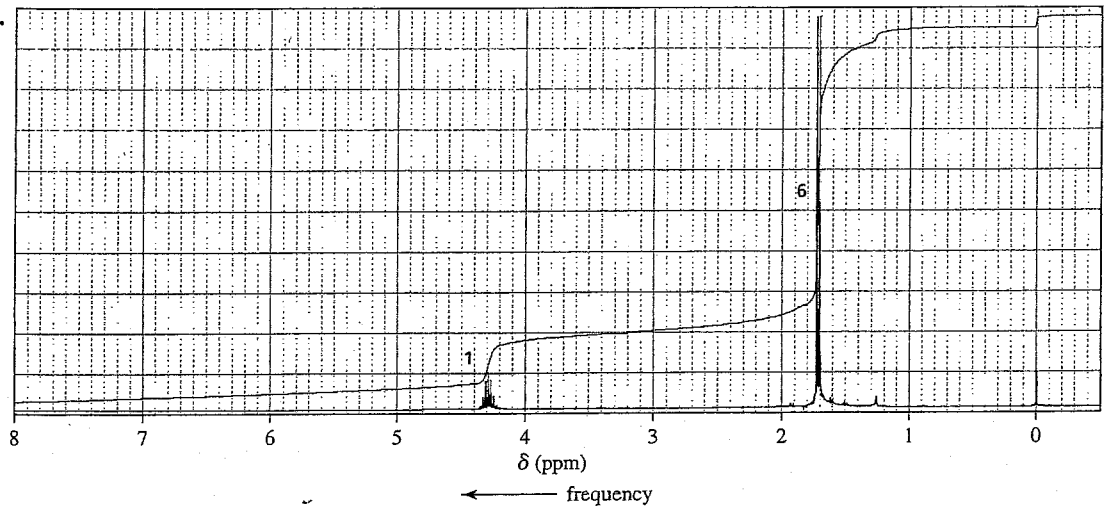
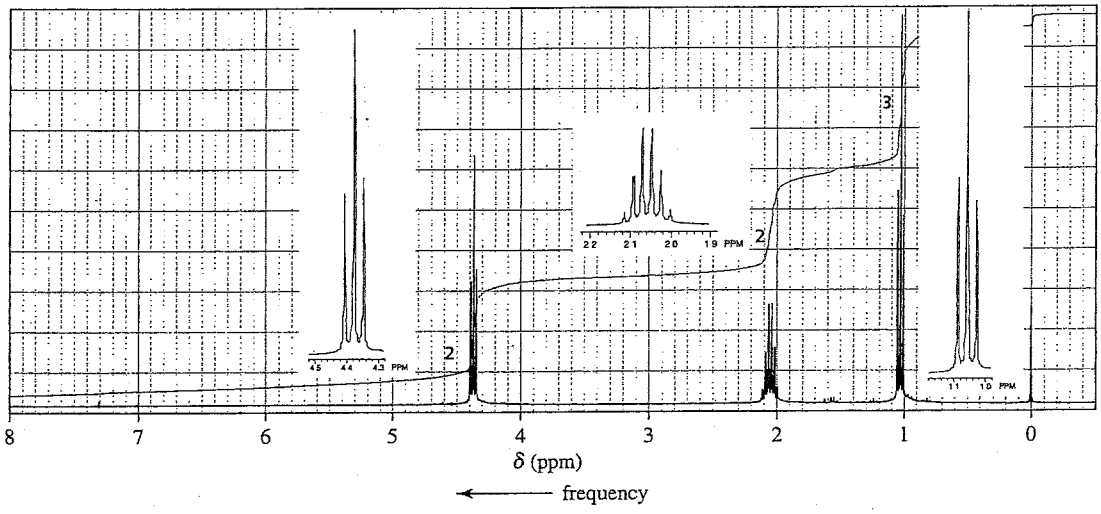
PUT ON WEB

a.



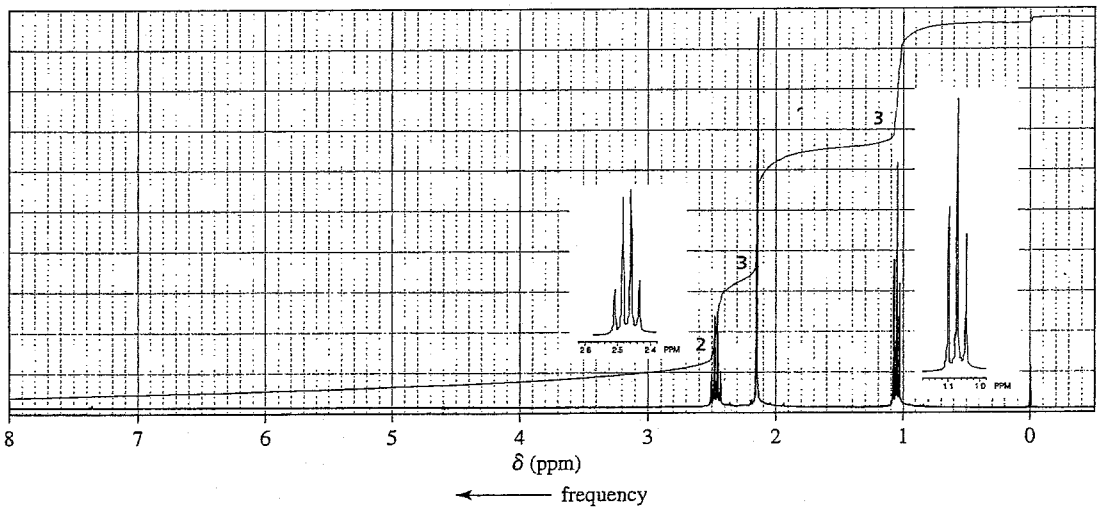
$C_6H_{14}O$

b.



$C_6H_{14}O$

c.



C_4H_8O

47. Determine the ratios of the chemically nonequivalent protons in a compound if the steps of the integration curves measure 40.5, 27, 13, and 118 mm, from left to right across the spectrum. Give the structure of a compound whose ^1H NMR spectrum would show these integrals in the observed order.

48. How could ^1H NMR distinguish between the compounds in each of the following pairs?

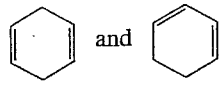
a. $CH_3CH_2CH_2OCH_3$ and $CH_3CH_2OCH_2CH_3$

b. $BrCH_2CH_2CH_2Br$ and $BrCH_2CH_2CH_2NO_2$

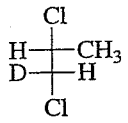
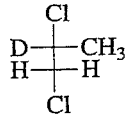
c. $CH_3CH(CH_3)CHCH_3$ and $CH_3C(CH_3)_2CH_2CH_3$

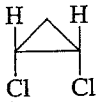
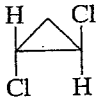
d. $CH_3C(CH_3)(CH_3O)C(=O)OCH_3$ and $CH_3C(CH_3)(OCH_3)CH_3$

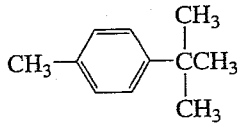
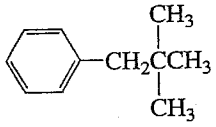
e. CH_3O–C$_6$H$_4$–CH_2CH_3 and CH_3–C$_6$H$_4$–OCH_2CH_3

f.  and

g. $CH_3CH(CH_3)Cl$ and $CH_3CD(CH_3)Cl$

h.  and 

i.  and 

j.  and 

49. Answer the following questions:

a. What is the relationship between chemical shift in ppm and operating frequency?

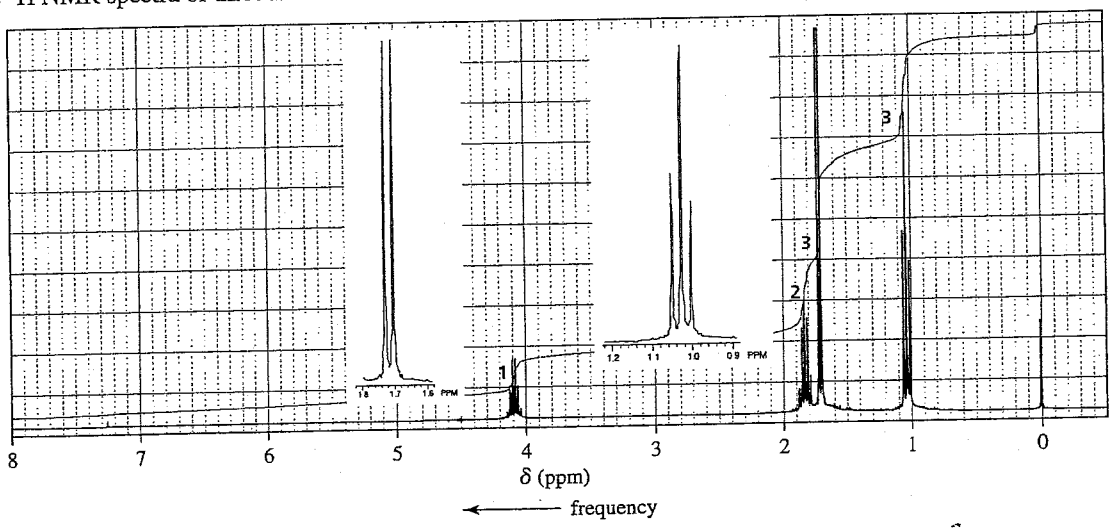
b. What is the relationship between chemical shift in hertz and operating frequency?

c. What is the relationship between coupling constant and operating frequency?

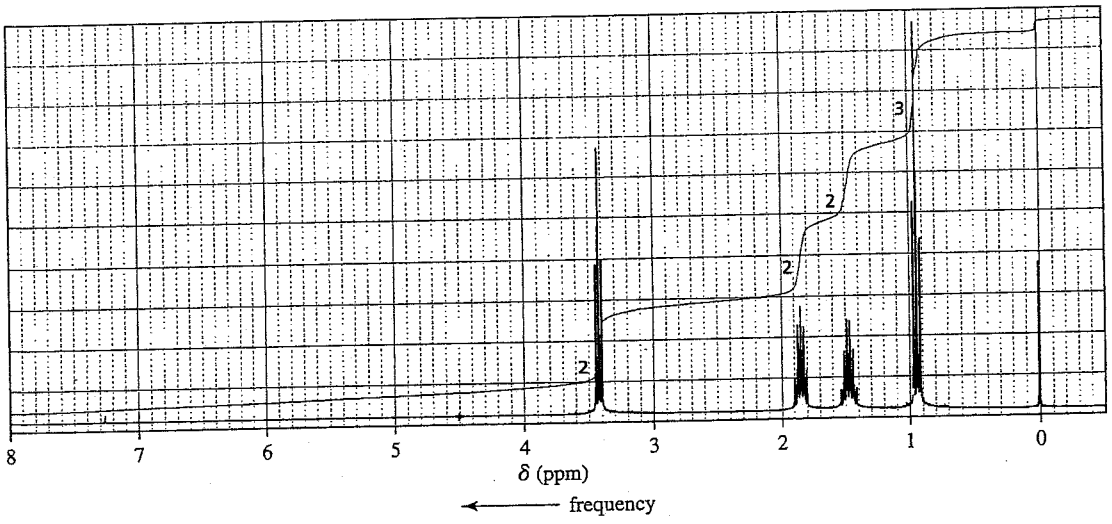
d. How does the operating frequency in NMR spectroscopy compare with the operating frequency in IR and UV/Vis spectroscopy?

50. The ^{1}H NMR spectra of three isomers with molecular formula C_4H_9Br are shown here. Which isomer produces which spectrum?

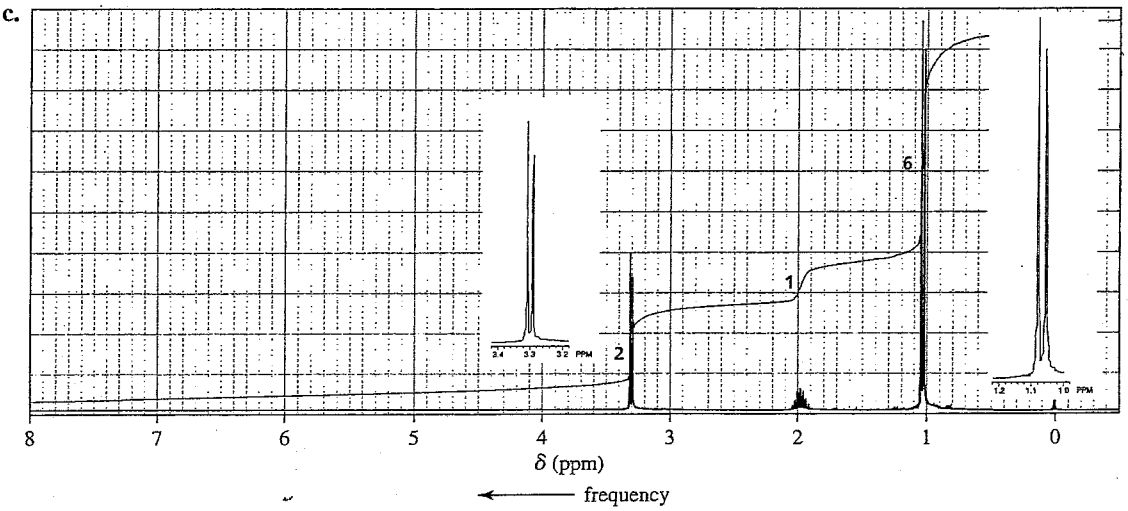
a.



b.



c.



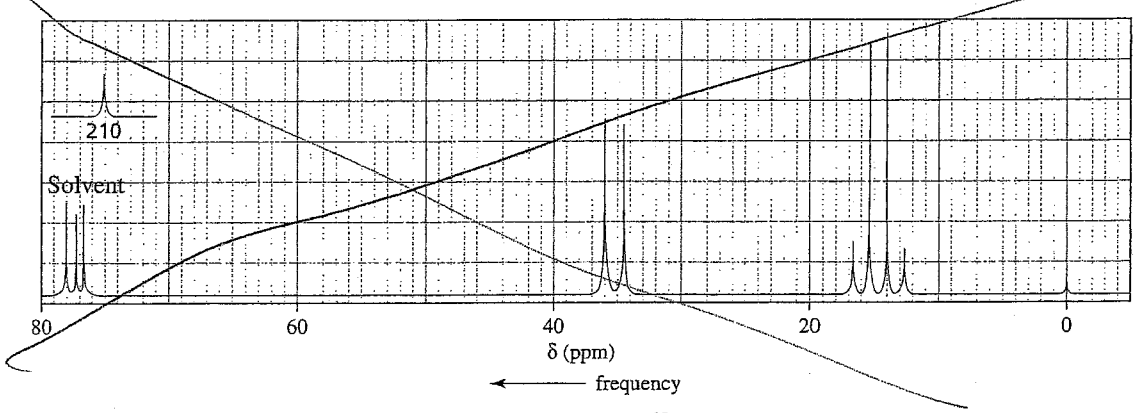
51. Identify each of the following compounds from the ^{1}H NMR data and molecular formula. The number of hydrogens responsible for each signal is shown in parentheses.

a. $C_4H_8Br_2$ 1.97 ppm (6) singlet
3.89 ppm (2) singlet

b. C_8H_9Br 2.01 ppm (3) doublet
5.14 ppm (1) quartet
7.35 ppm (5) broad singlet

c. $C_5H_{10}O_2$ 1.15 ppm (3) triplet
1.25 ppm (3) triplet
2.33 ppm (2) quartet
4.13 ppm (2) quartet

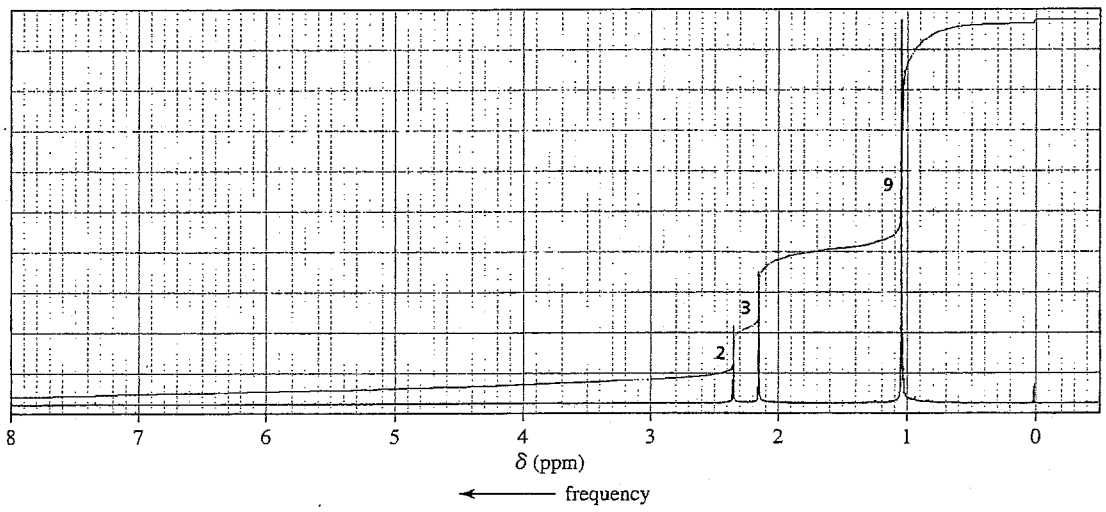
52. Identify the compound with molecular formula $C_7H_{14}O$ that gives the following proton-coupled ^{13}C NMR spectrum:



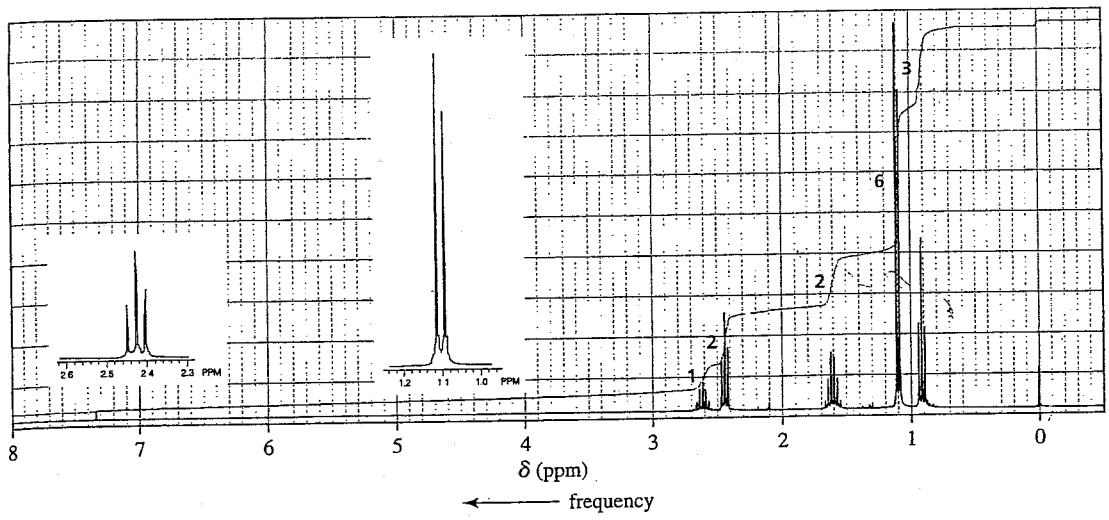
53. Compound A, with molecular formula C_4H_9Cl, shows two signals in its ^{13}C NMR spectrum. Compound B, an isomer of compound A, shows four signals, and in the proton-coupled mode, the signal farthest downfield is a doublet. Identify compounds A and B.

54. The ^{1}H NMR spectra of three isomers with molecular formula $C_7H_{14}O$ are shown here. Which isomer produces which spectrum?

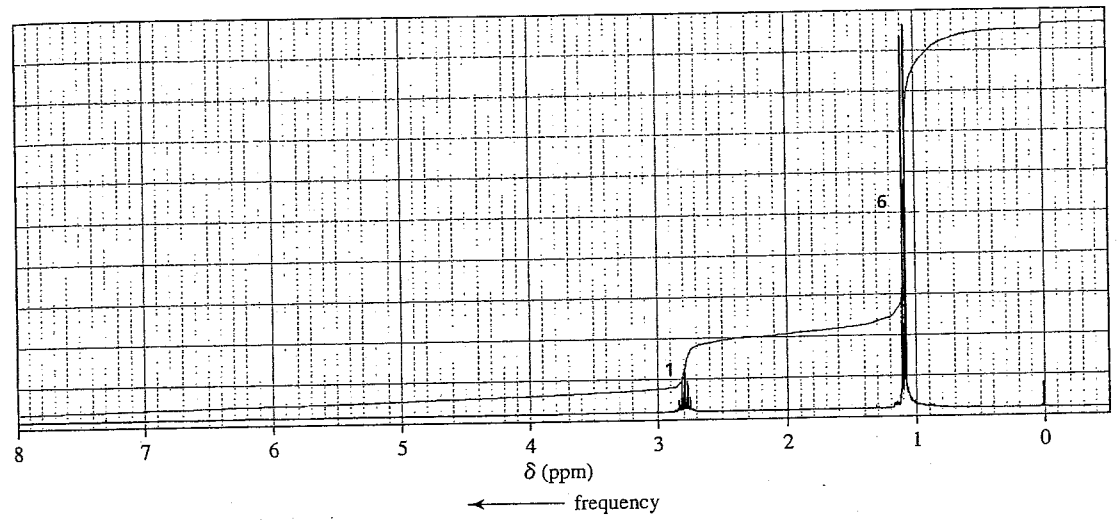
a.



b.



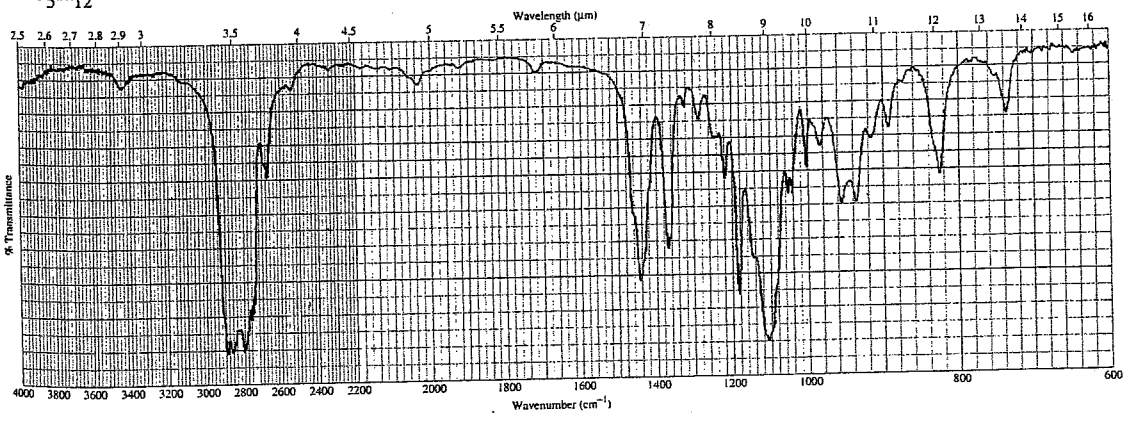
c.

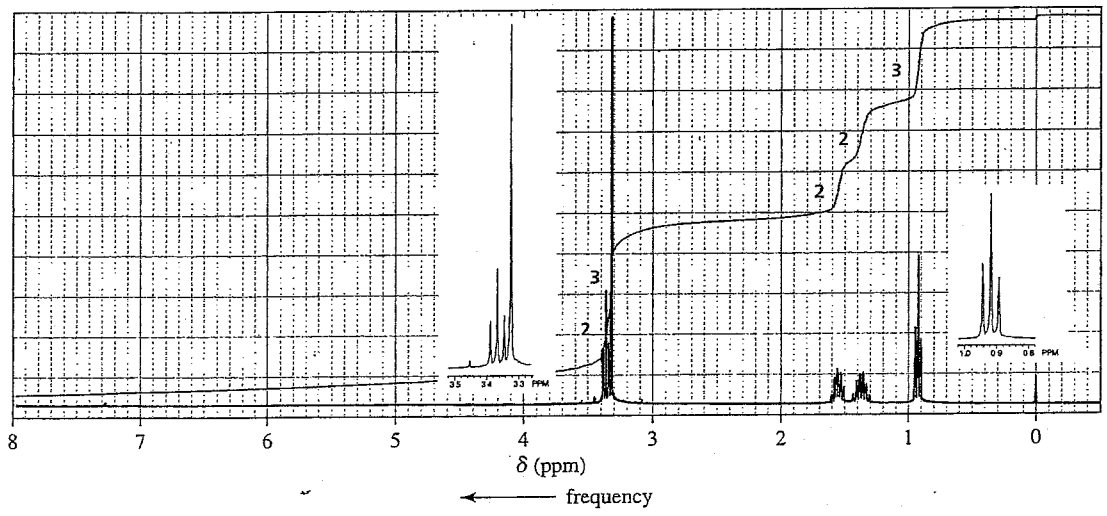


55. Would it be better to use ^{1}H NMR or ^{13}C NMR to distinguish between 1-butene, *cis*-2-butene, and 2-methylpropene? Explain your answer.

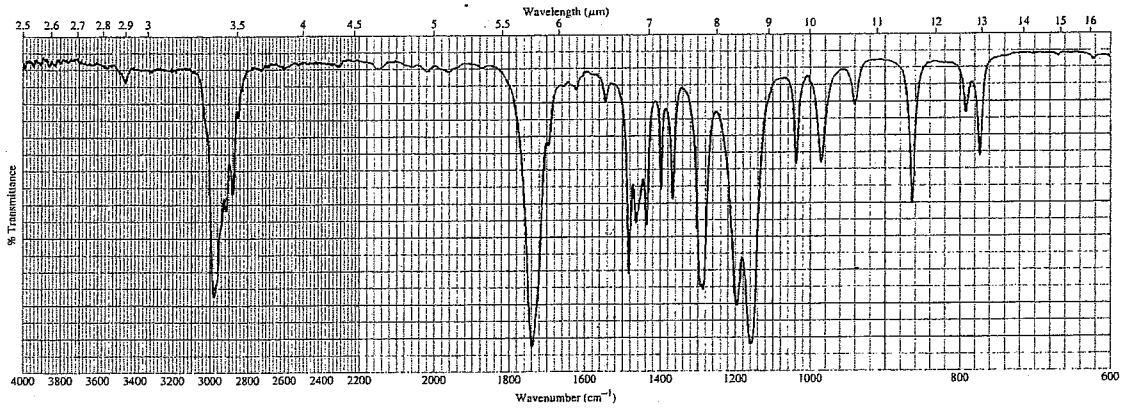
56. Determine the structure of each of the following unknown compounds based on its molecular formula and its IR and ^{1}H NMR spectra.

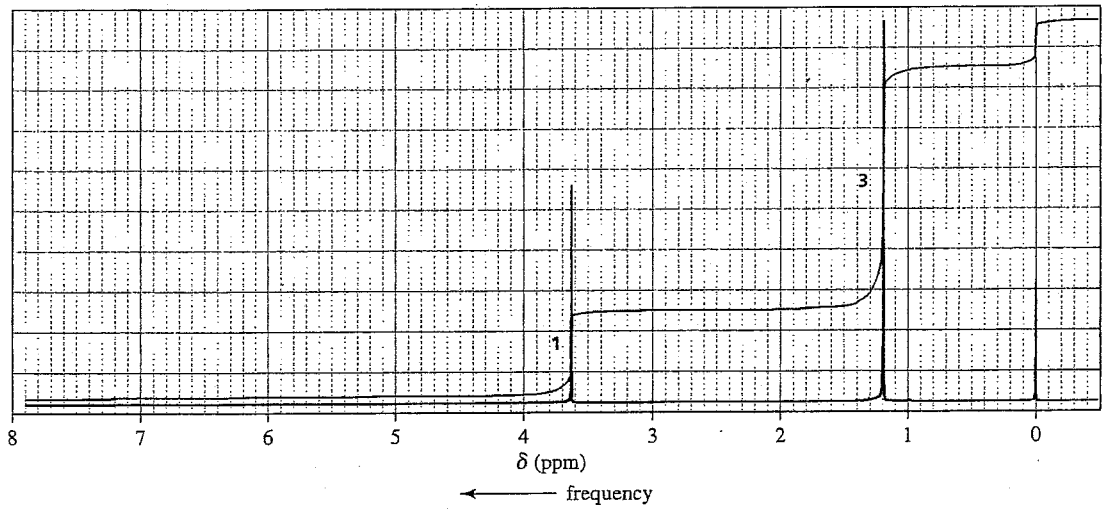
a. $C_5H_{12}O$



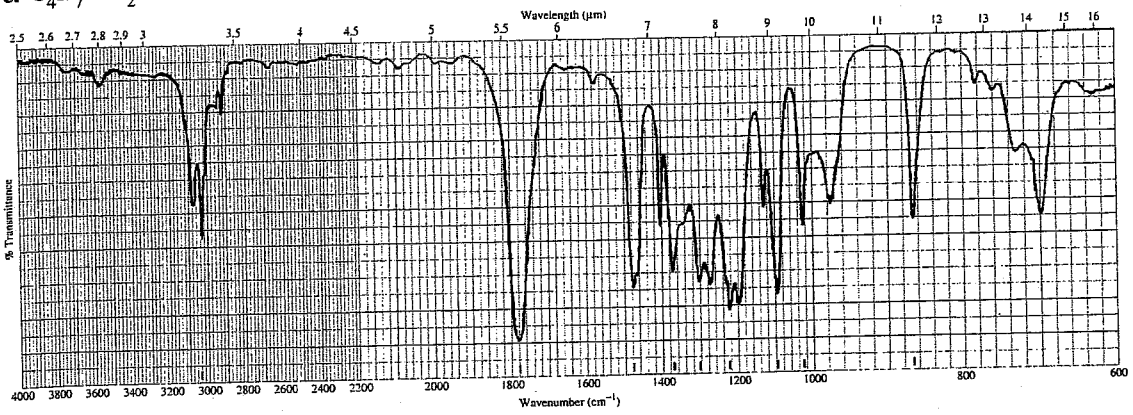

3
2
2
3
2
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency

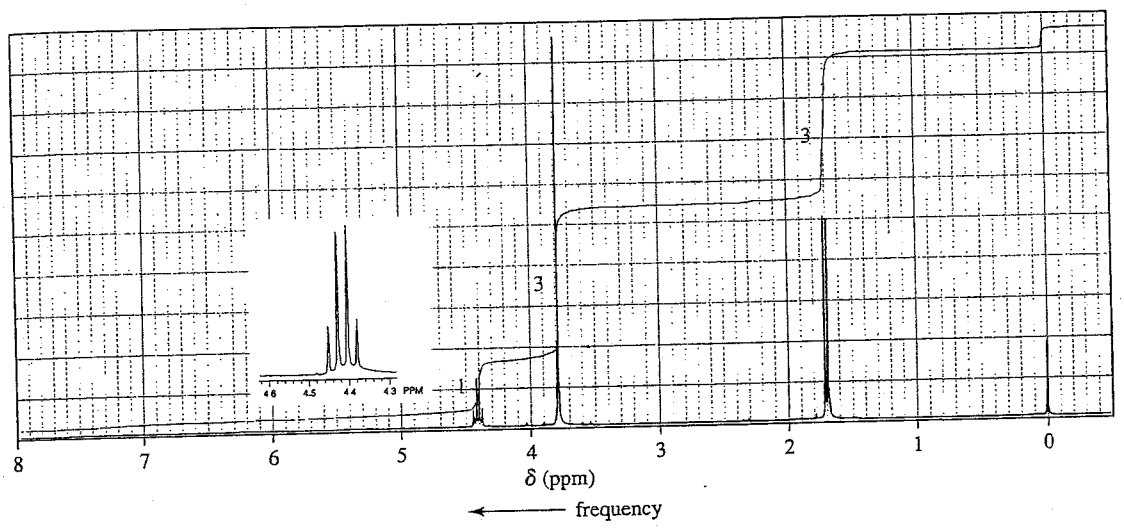
b. $C_6H_{12}O_2$


Wavelength (μm)
% Transmittance
Wavenumber (cm⁻¹)

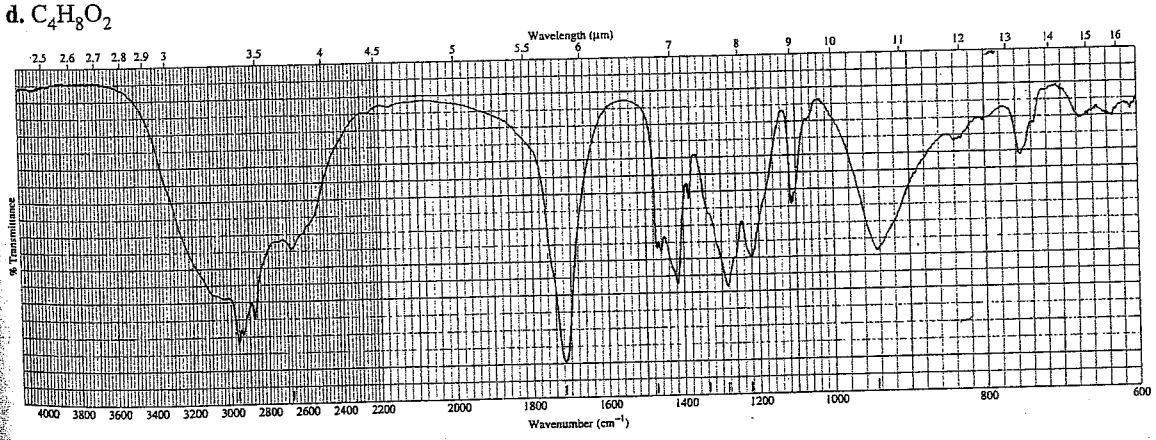

3
1
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency

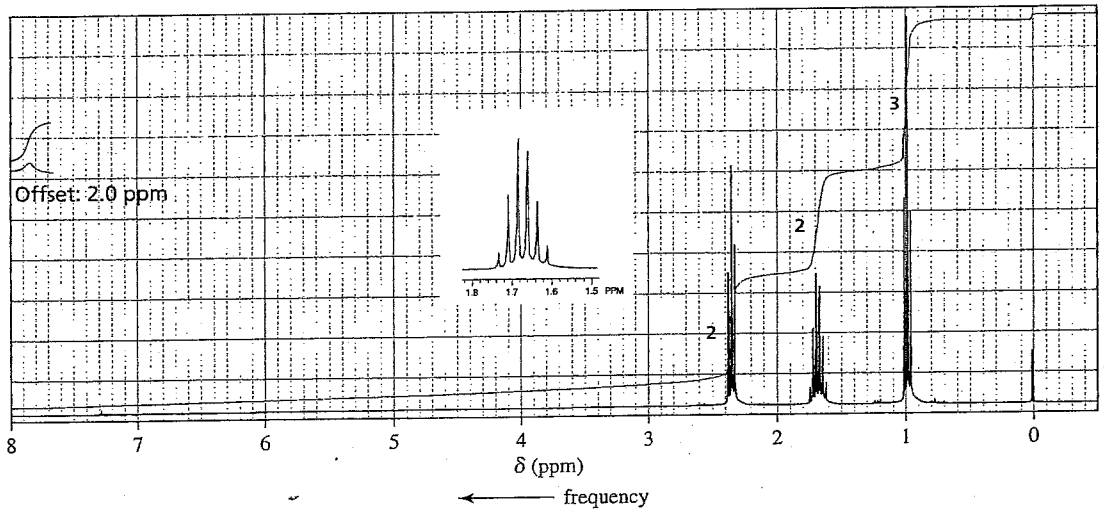
c. $C_4H_7ClO_2$





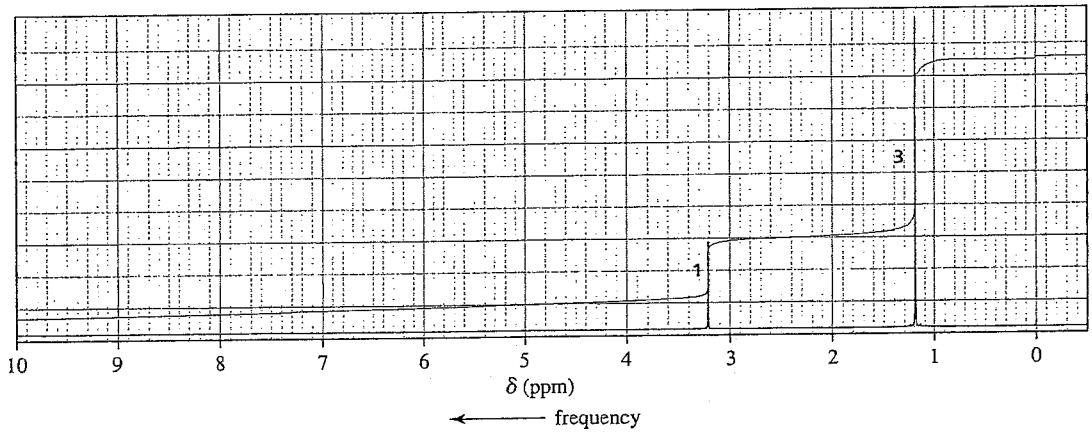
d. $C_4H_8O_2$





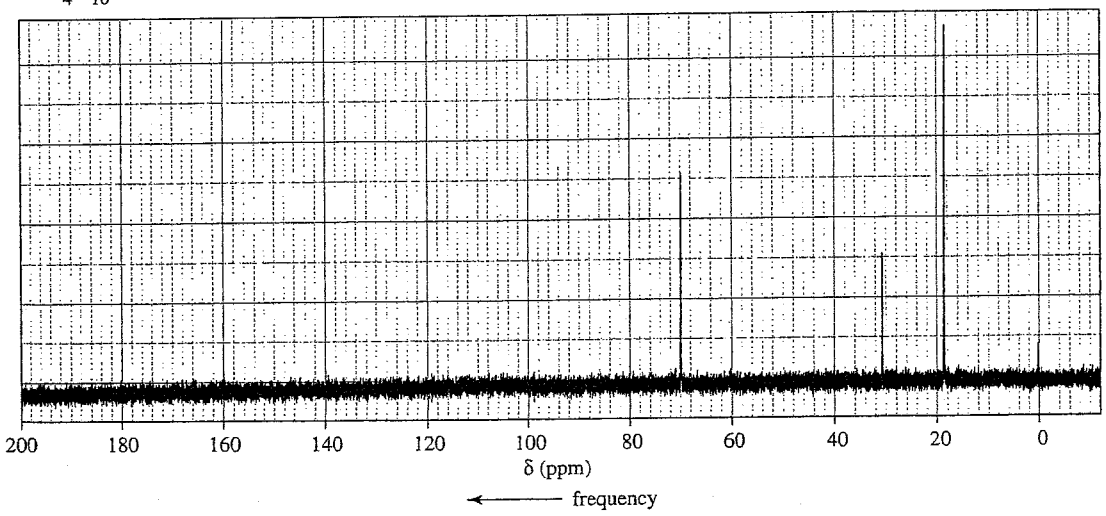
57. There are four esters with molecular formula $C_4H_8O_2$. How could they be distinguished by ^1H NMR?

58. An alkyl halide reacts with an alkoxide ion to form a compound whose ^1H NMR spectrum is shown here. Identify the alkyl halide and the alkoxide ion. (*Hint:* See Section 9.9.)

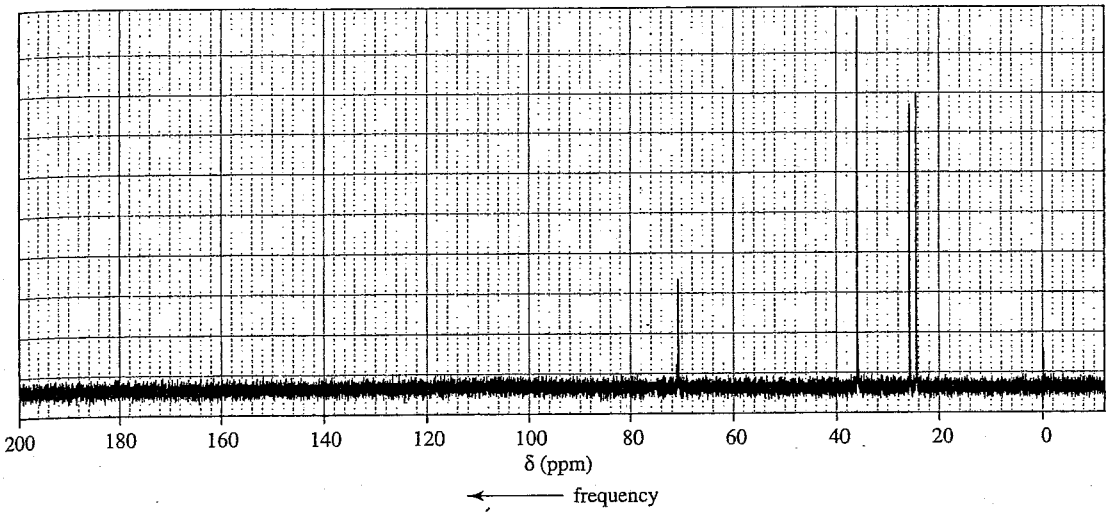


59. Determine the structure of each of the following compounds based on its molecular formula and its ^{13}C NMR spectrum:

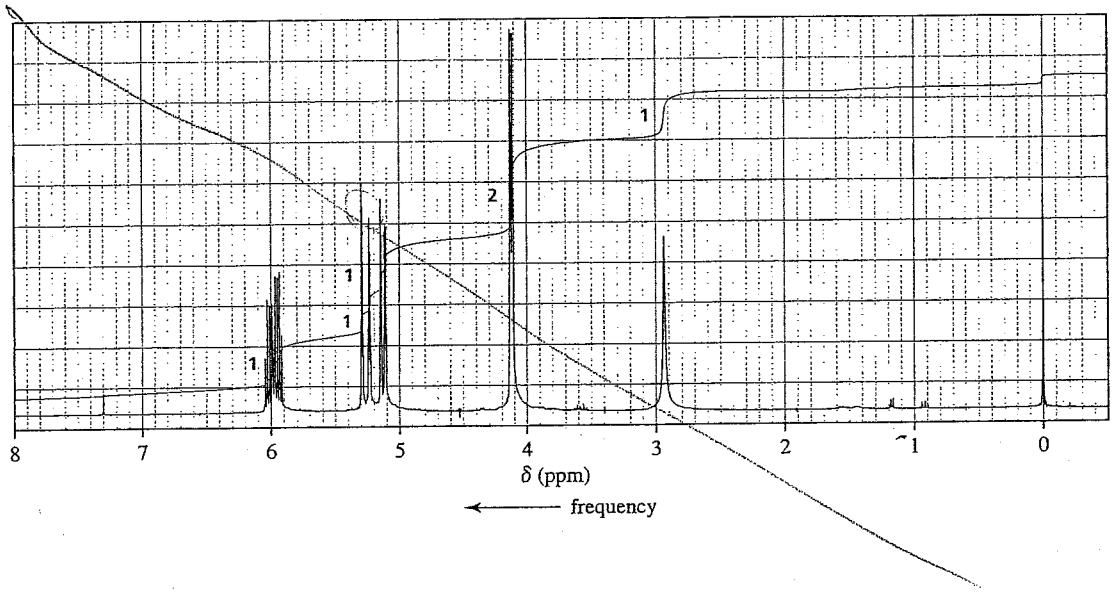
a. $C_4H_{10}O$



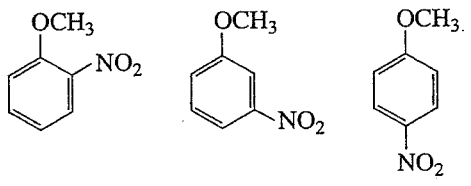
b. $C_6H_{12}O$



60. The ^1H NMR spectrum of 2-propen-1-ol is shown here. Indicate the protons in the molecule that give rise to each of the signals in the spectrum.

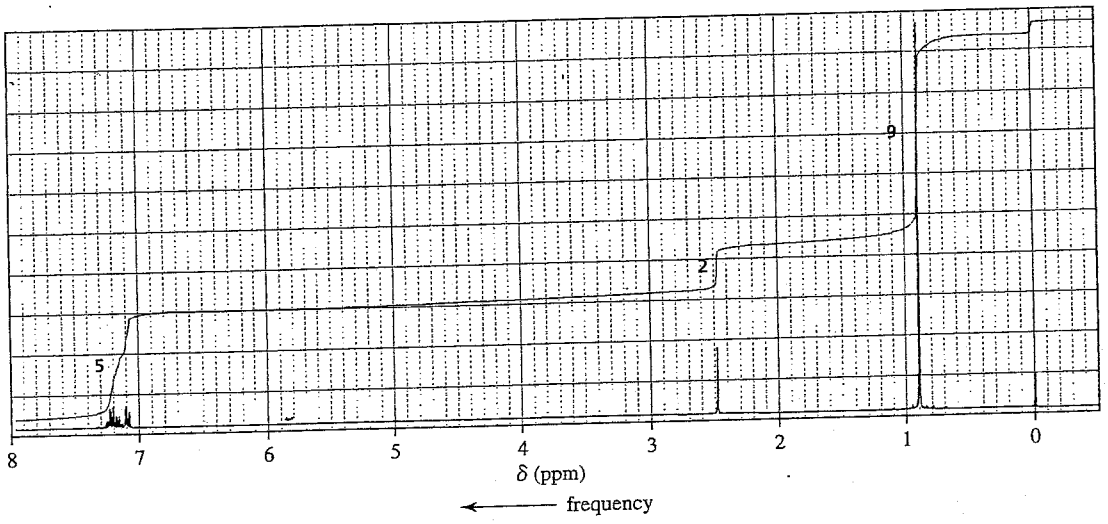


61. How could the signals in the 6.5 to 8.1-ppm region of their ^1H NMR spectra distinguish between the following compounds?

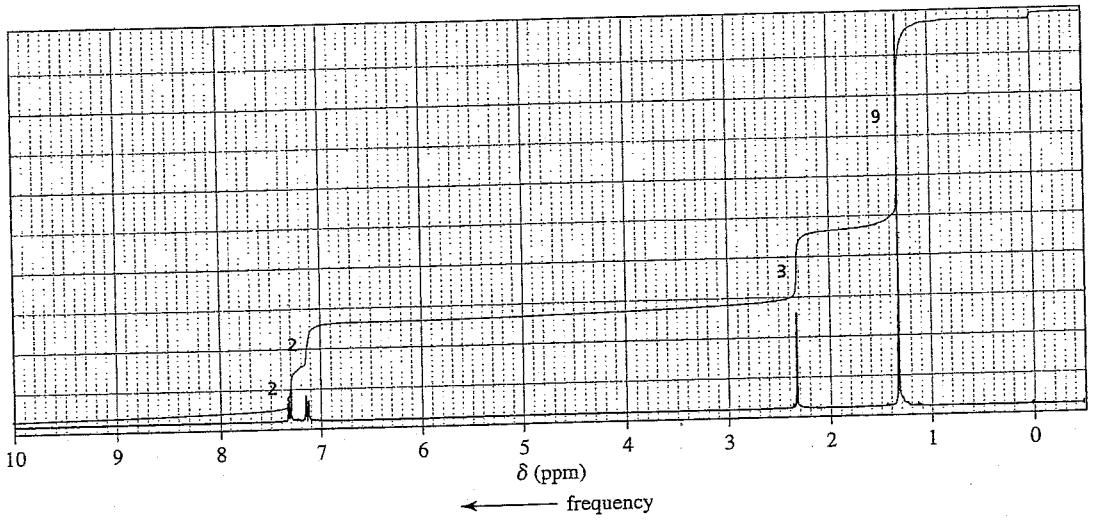


62. The ^{1}H NMR spectra of two compounds, each with molecular formula $C_{11}H_{16}$, are shown here. Identify the compounds.

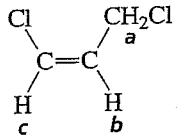
a.



b.



63. Draw a splitting diagram for the H_b proton if $J_{bc} = 10$ and $J_{ba} = 5$.

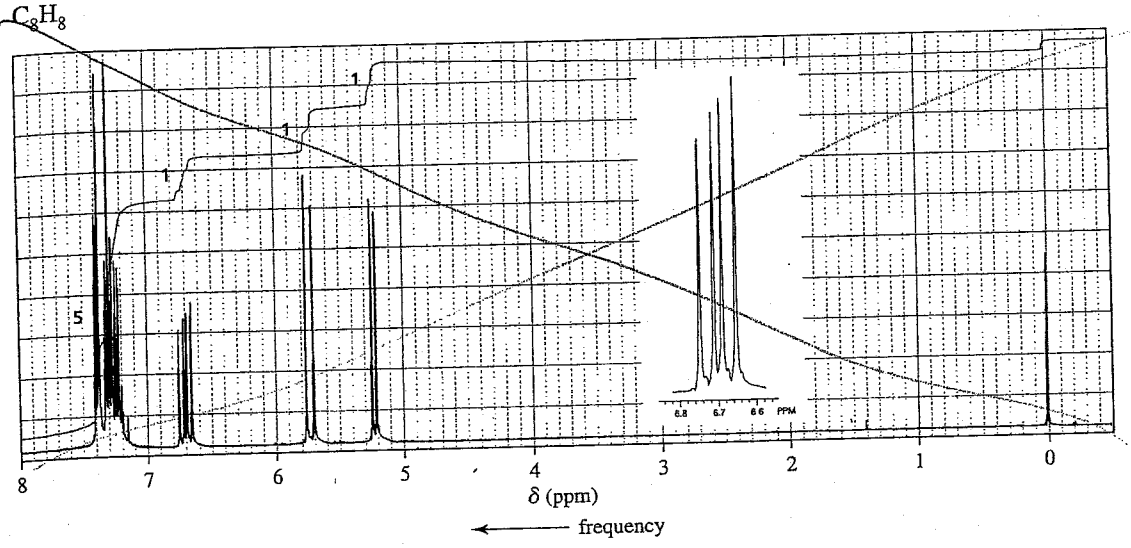


64. Sketch the following spectra that would be obtained for 2-chloroethanol:
- **a.** the ^{1}H NMR spectrum for a dry sample of the alcohol.
- **b.** the ^{1}H NMR spectrum for a sample of the alcohol that contains a trace amount of acid.
- **c.** the ^{13}C NMR spectrum.
- **d.** the proton-coupled ^{13}C NMR spectrum.
- **e.** the four parts of a DEPT ^{13}C NMR spectrum.

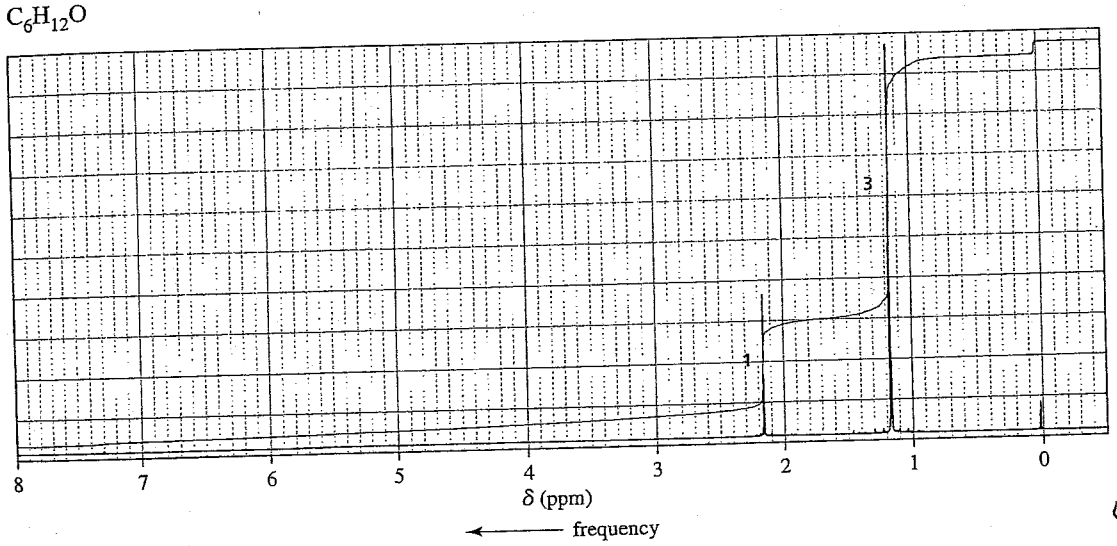
65. How could ^{1}H NMR be used to prove that the addition of HBr to propene follows the rule that says that the electrophile adds to the sp^2 carbon bonded to the greater number of hydrogens?

66. Identify each of the following compounds from its molecular formula and its ^{1}H NMR spectrum.

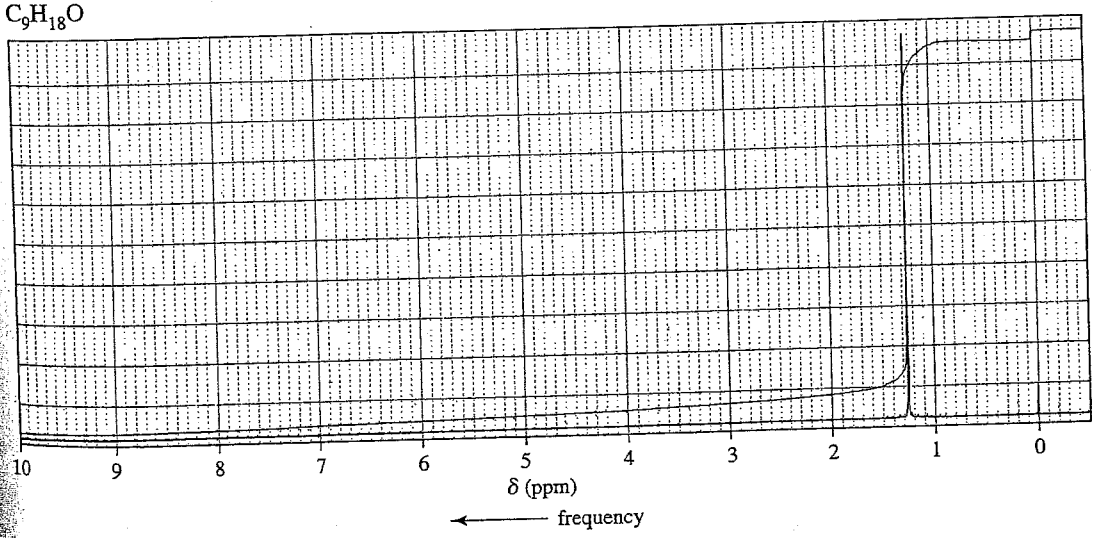
a. C_8H_8



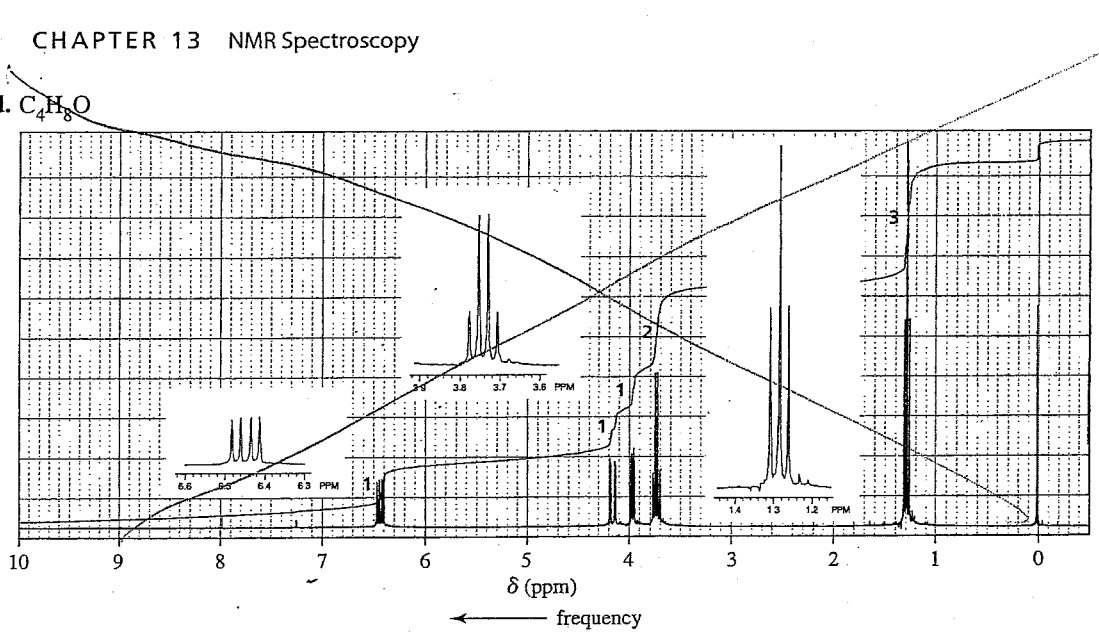
b. $C_6H_{12}O$



c. $C_9H_{18}O$



d. C_4H_8O

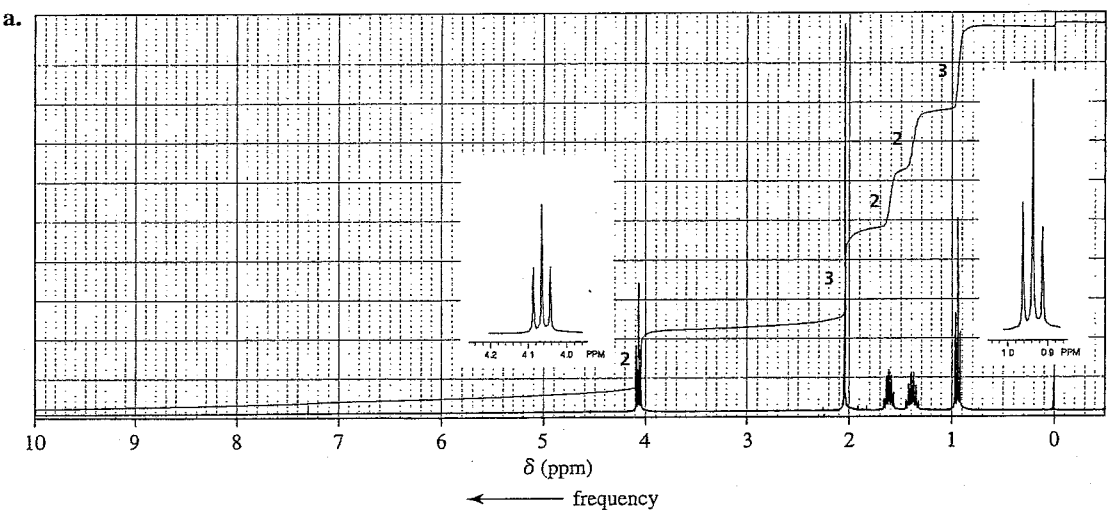


67. Dr. N. M. Arr was called in to help analyze the ^{1}H NMR spectrum of a mixture of compounds known to contain only C, H, and Br. The mixture showed two singlets—one at 1.8 ppm and the other at 2.7 ppm—with relative integrals of 1 : 6, respectively. Dr. Arr determined that the spectrum was that of a mixture of bromomethane and 2-bromo-2-methylpropane. What was the ratio of bromomethane to 2-bromo-2-methylpropane in the mixture?

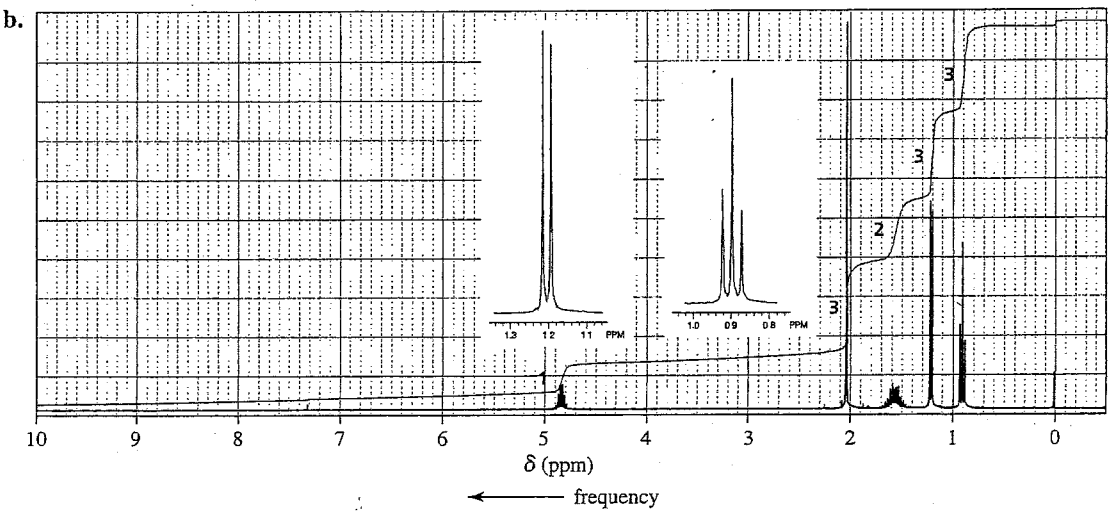
68. Calculate the amount of energy (in calories) required to flip an ^{1}H nucleus in an NMR spectrometer that operates at 60 MHz.

69. The following ^{1}H NMR spectra are for four compounds each with molecular formula $C_6H_{12}O_2$. Identify the compounds.

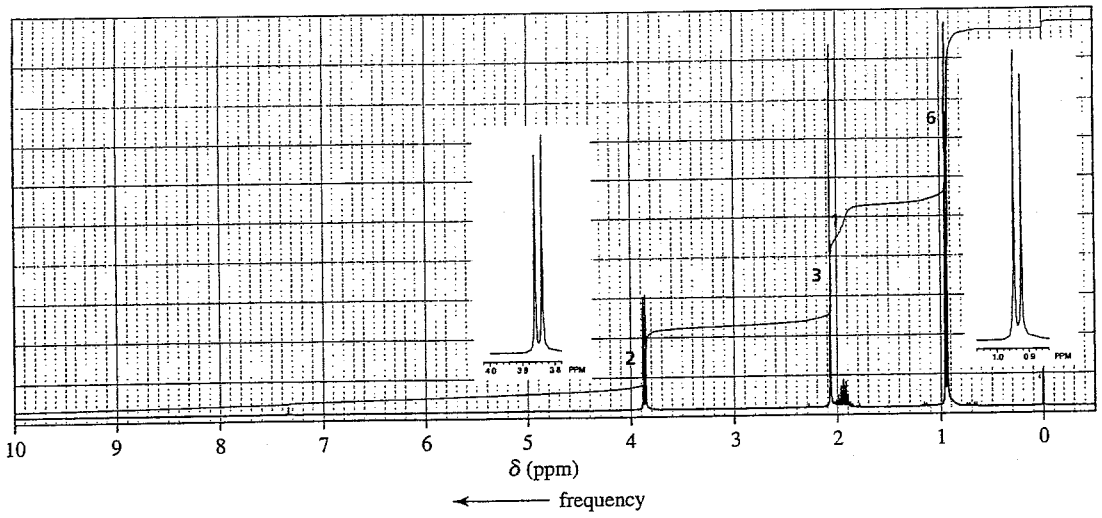
a.



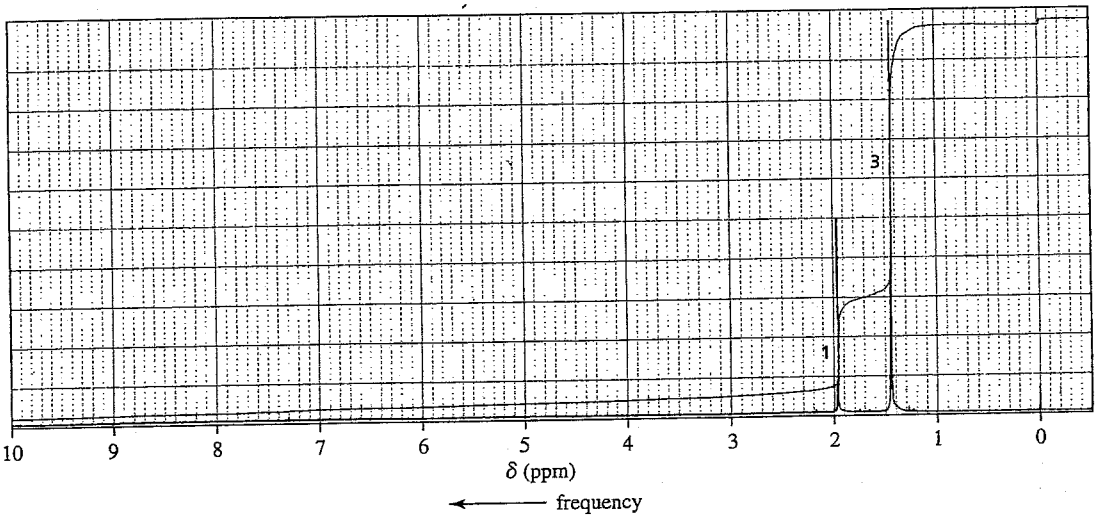
b.



c.



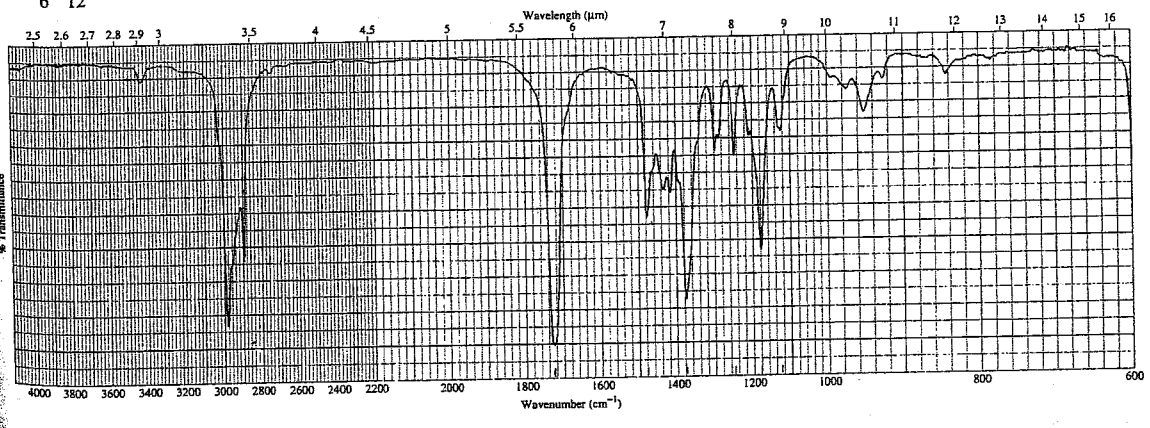
d.

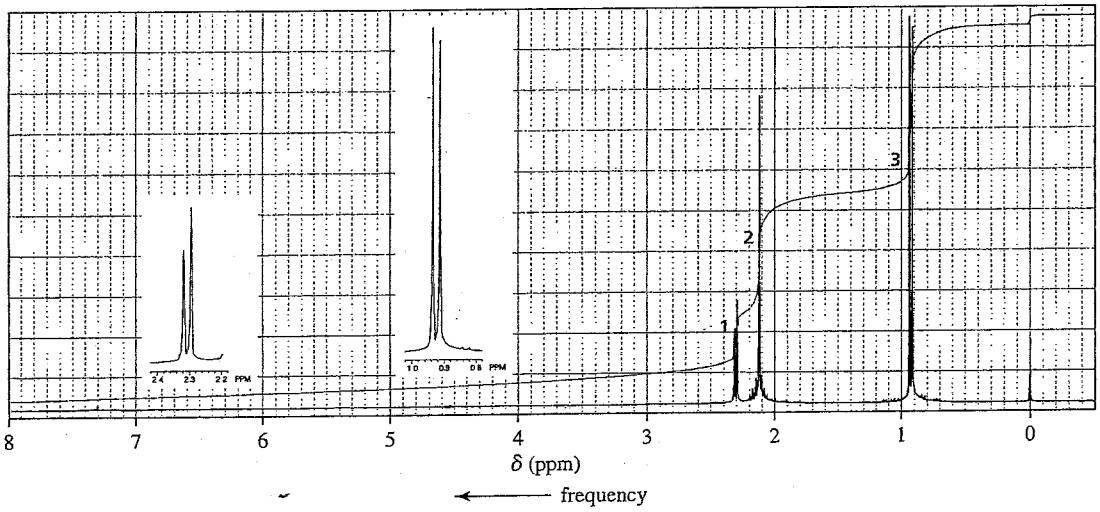


70. When compound A ($C_5H_{12}O$) is treated with HBr, it forms compound B ($C_5H_{11}Br$). The ^1H NMR spectrum of compound A has one singlet (1), two doublets (3, 6), and two multiplets (both 1). (The relative areas of the signals are indicated in parentheses.) The ^1H NMR spectrum of compound B has a singlet (6), a triplet (3), and a quartet (2). Identify compounds A and B.

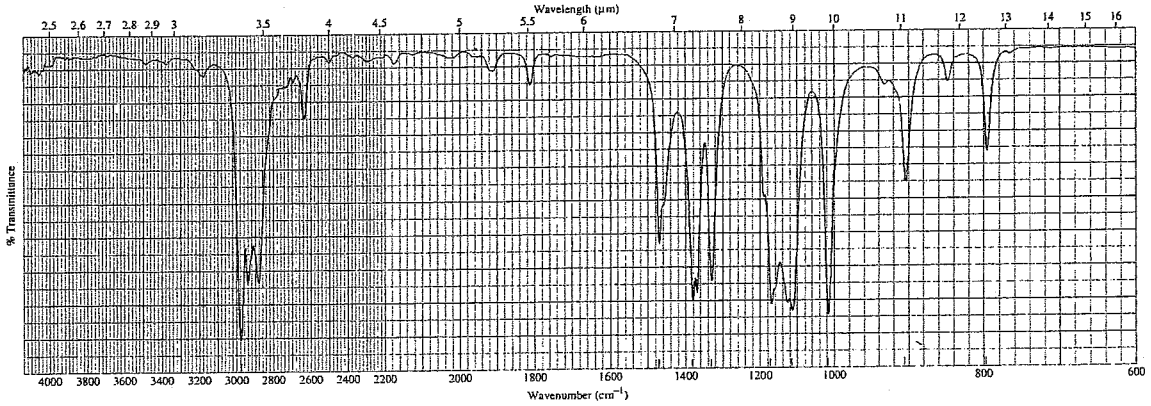
71. Determine the structure of each of the following compounds, based on its molecular formula and its IR and ^1H NMR spectra.

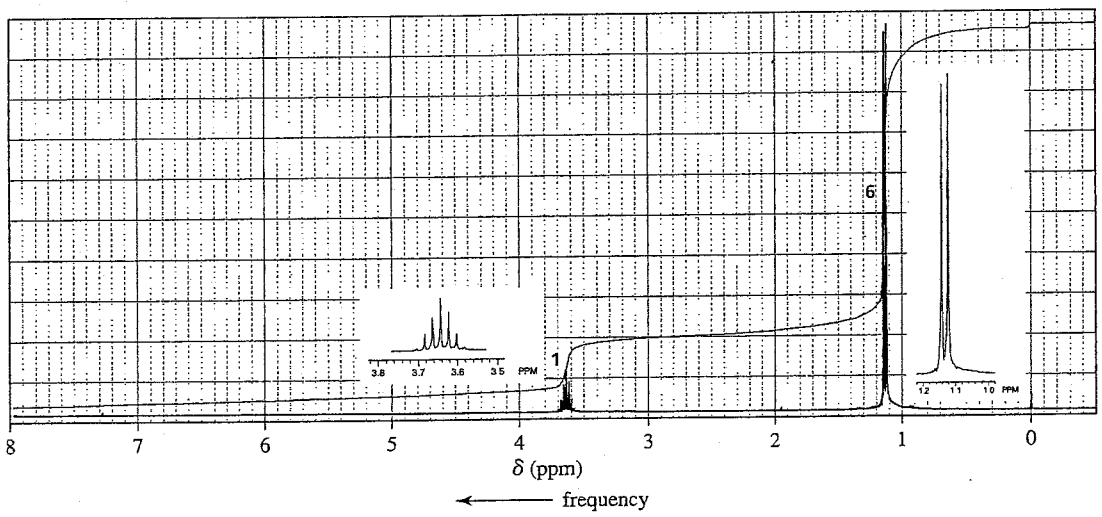
a. $C_6H_{12}O$



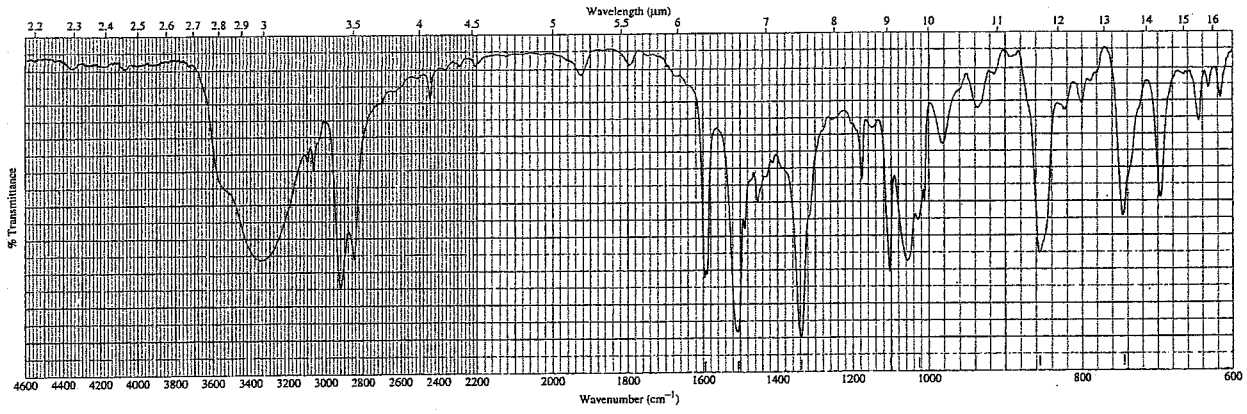

1
2
3
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency

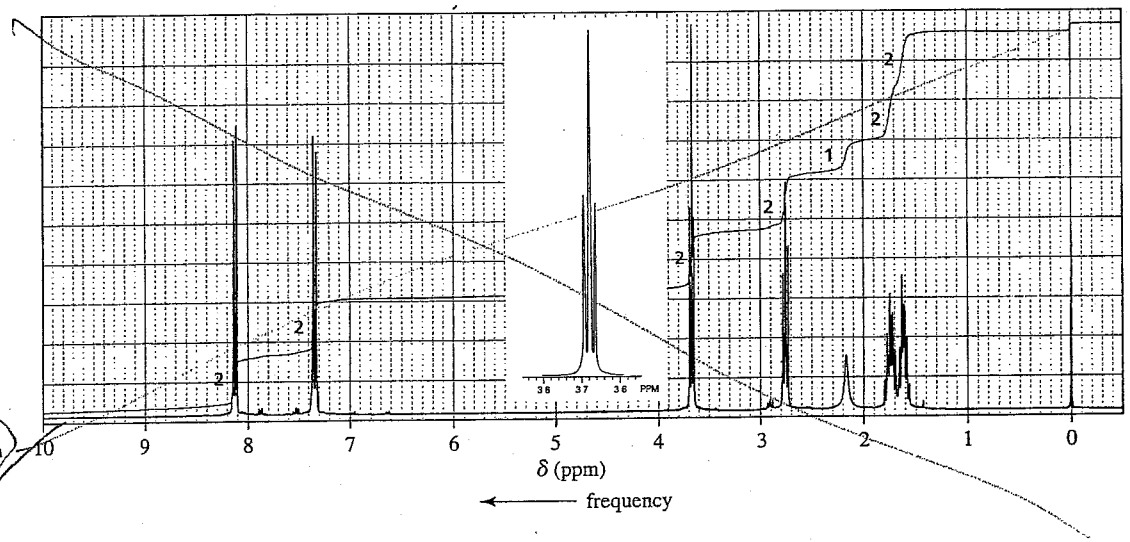
b. $C_6H_{14}O$


Wavelength (μm)
% Transmittance
Wavenumber (cm⁻¹)

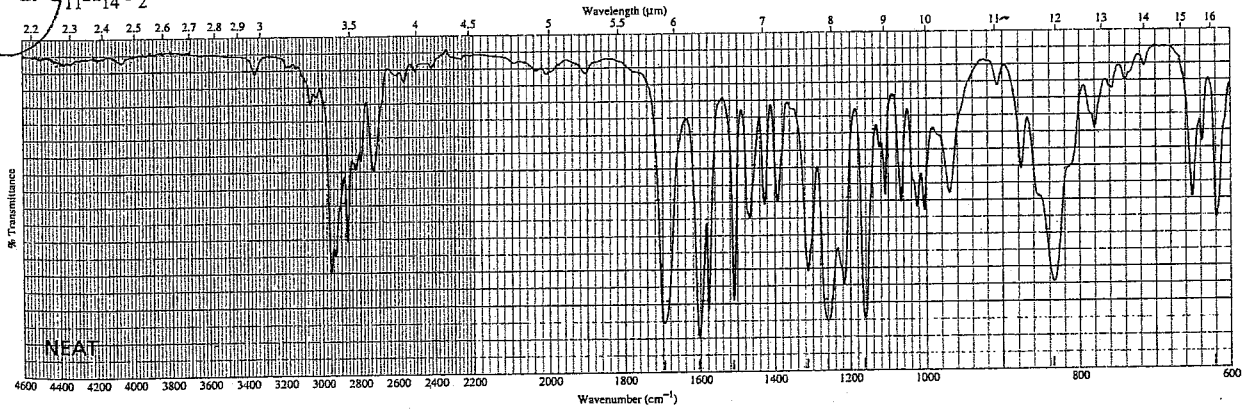

6
1
8
7
6
5
4
3
2
1
0
δ (ppm)
frequency

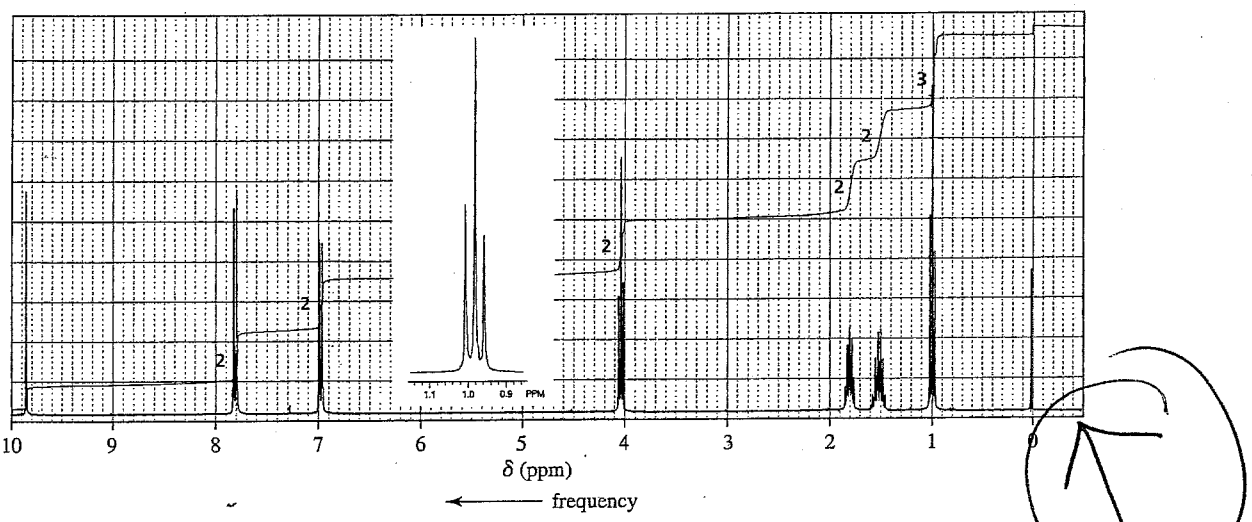
c. $C_{10}H_{13}NO_3$





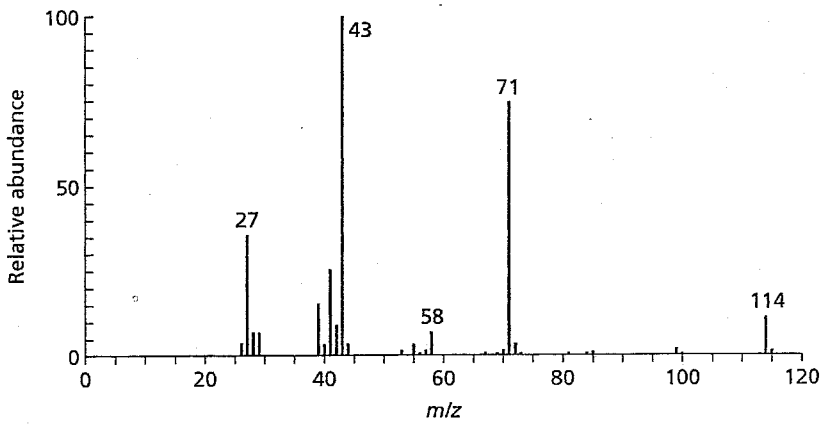
d. $C_{11}H_{14}O_2$

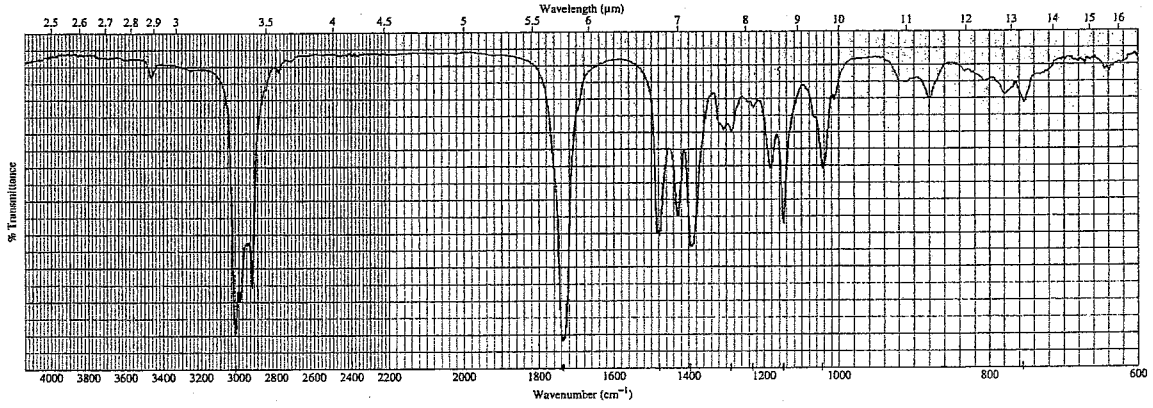


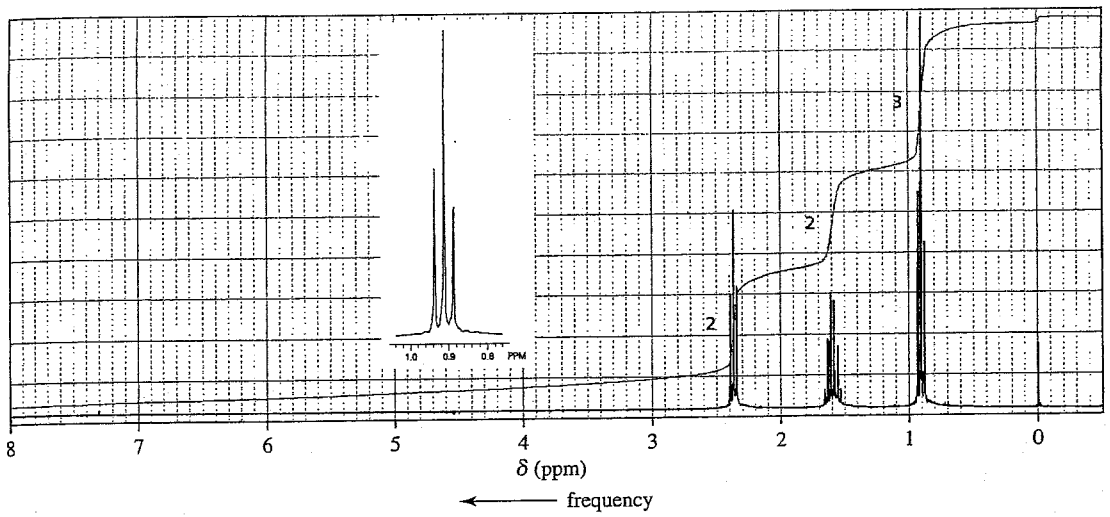


72. Determine the structure of each of the following compounds, based on its mass, IR, and ^{1}H NMR spectra.

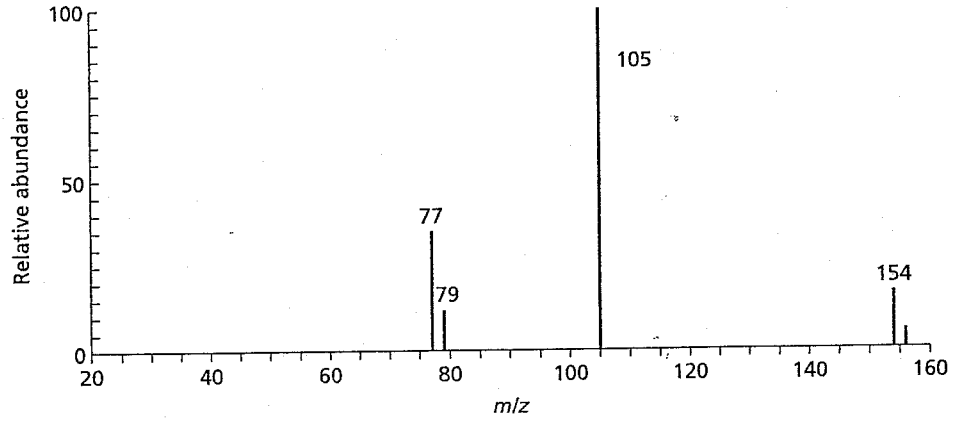
a.

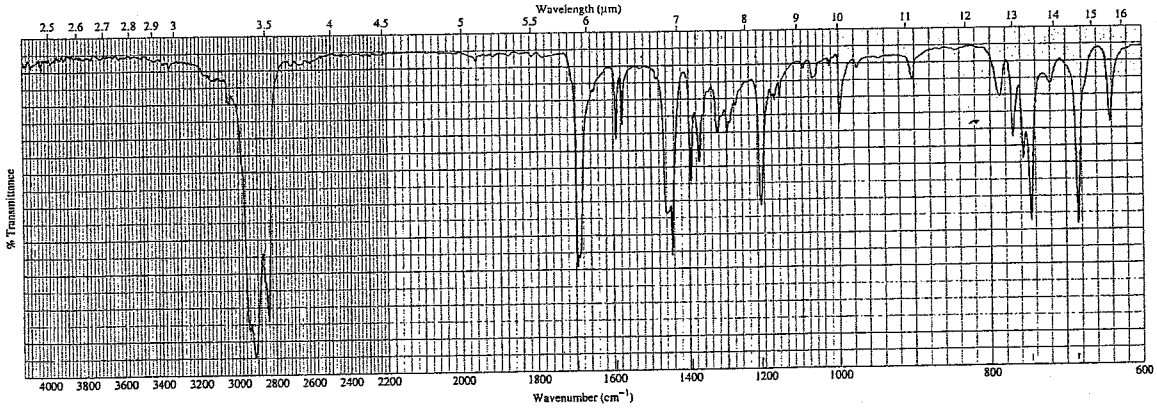


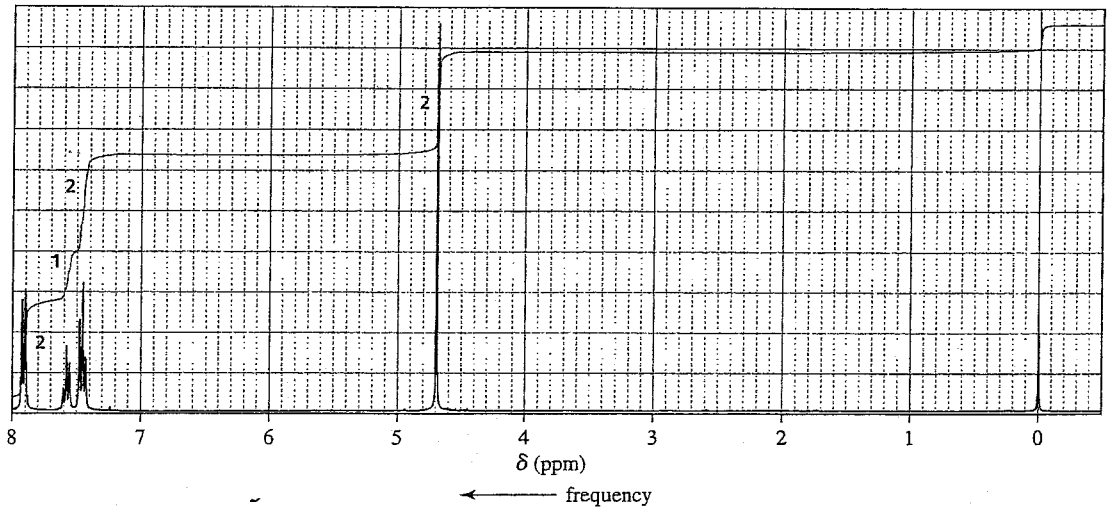



3
2
2
1.0 0.9 0.8 PPM
8 7 6 5 4 3 2 1 0
δ (ppm)
frequency

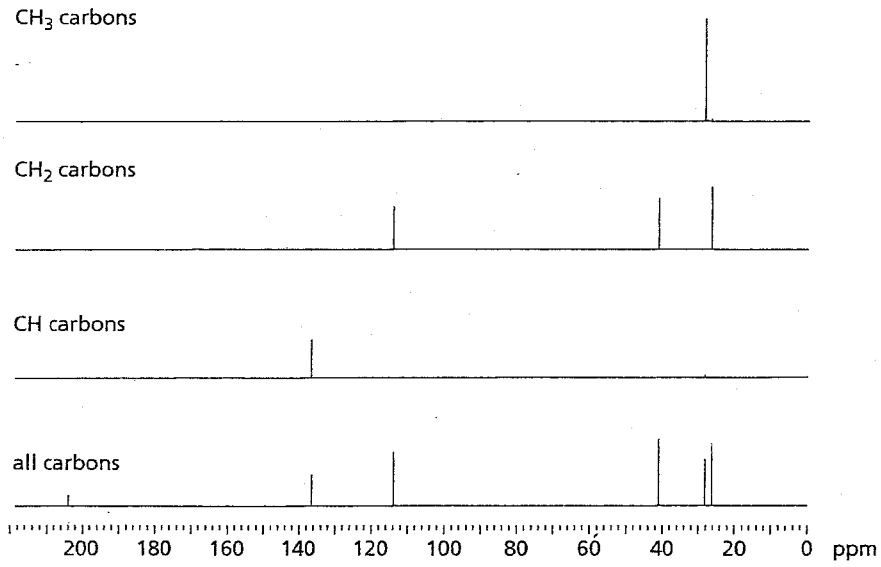
b.


100
50
0
Relative abundance
105
77
79
154
20 40 60 80 100 120 140 160
m/z


Wavelength (μm)
2.5 2.6 2.7 2.8 2.9 3 3.5 4 4.5 5 5.5 6 7 8 9 10 11 12 13 14 15 16
% Transmittance
4000 3800 3600 3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600
Wavenumber (cm⁻¹)



73. Identify the compound with molecular formula $C_6H_{10}O$ that is responsible for the following DEPT ^{13}C NMR spectrum:



74. Identify the compound with molecular formula C_6H_{14} that is responsible for the following ^1H NMR spectrum: