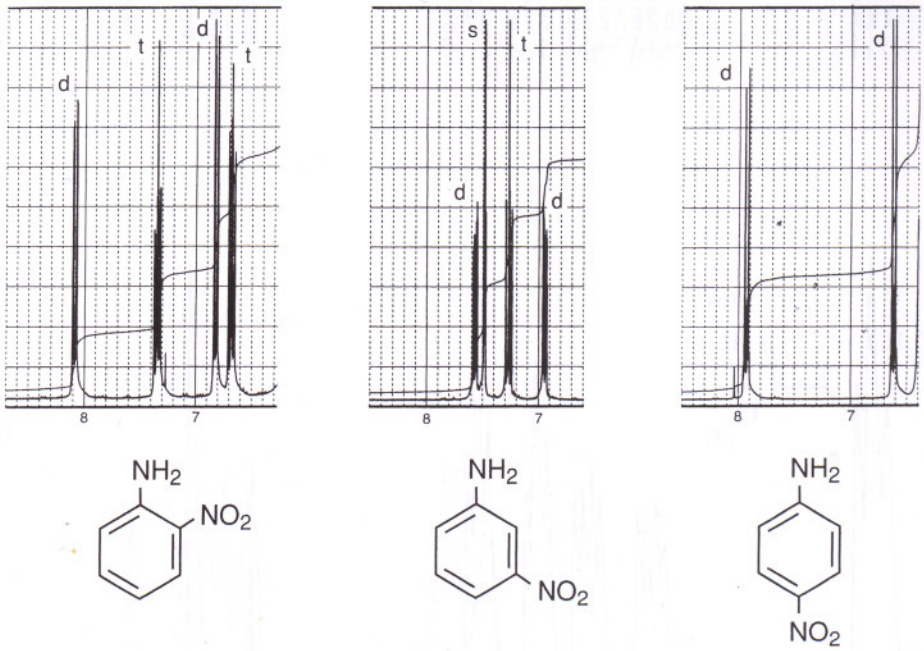


FIGURE 5.48 The 300-MHz ^{1}H NMR spectra of the aromatic-ring portions of 2-, 3-, and 4-nitroaniline.

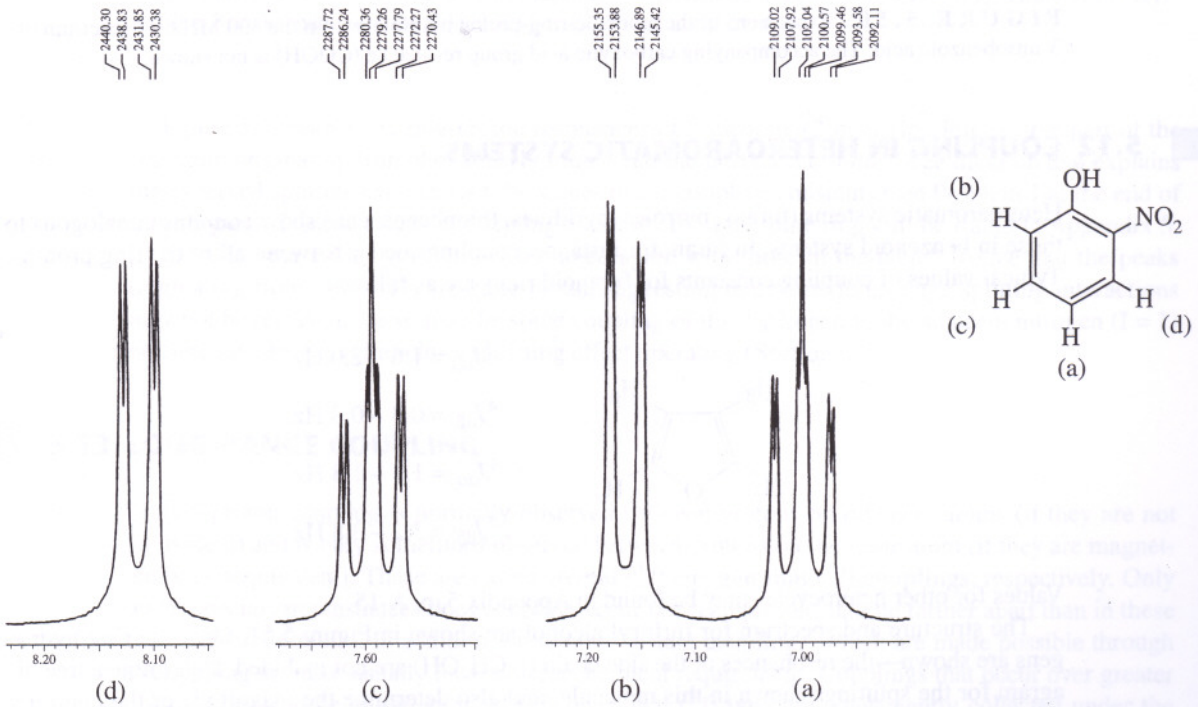


FIGURE 5.49 Expansions of the aromatic-ring-proton multiplets from the 300 MHz ^{1}H spectrum of

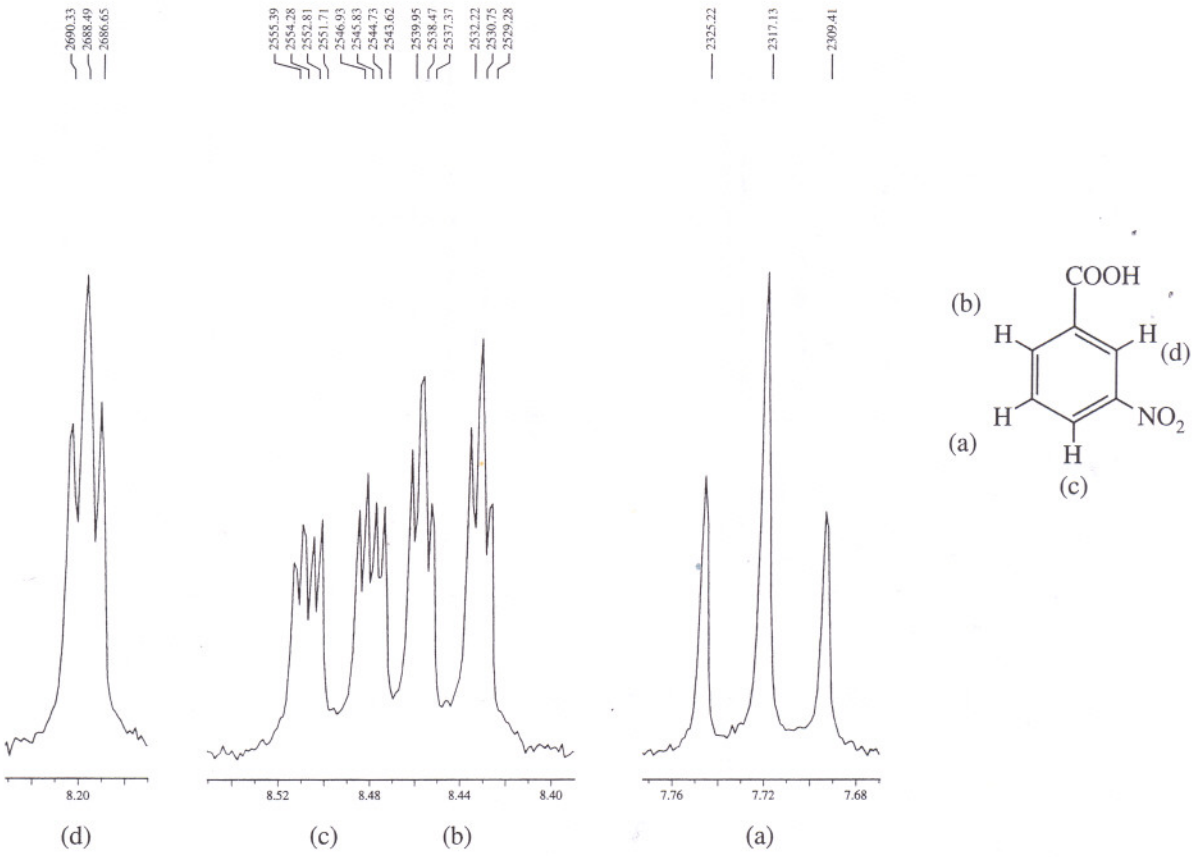
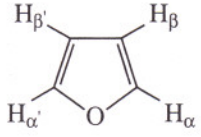


FIGURE 5.50 Expansions of the aromatic-ring-proton multiplets from the 300 MHz ^{1}H spectrum of 3-nitrobenzoic acid. The accompanying carboxylic acid group resonance (COOH) is not shown.

5.12 COUPLING IN HETEROAROMATIC SYSTEMS

Heteroaromatic systems (furans, pyrroles, pyridines, thiophenes, etc.) show couplings analogous to those in benzenoid systems. In furan, for instance, couplings occur between all of the ring protons. Typical values of coupling constants for furanoid rings are as follows.



$^3J_{\alpha\beta} = 1.6 - 2.0$ Hz

$^4J_{\alpha\beta'} = 0.3 - 0.8$ Hz

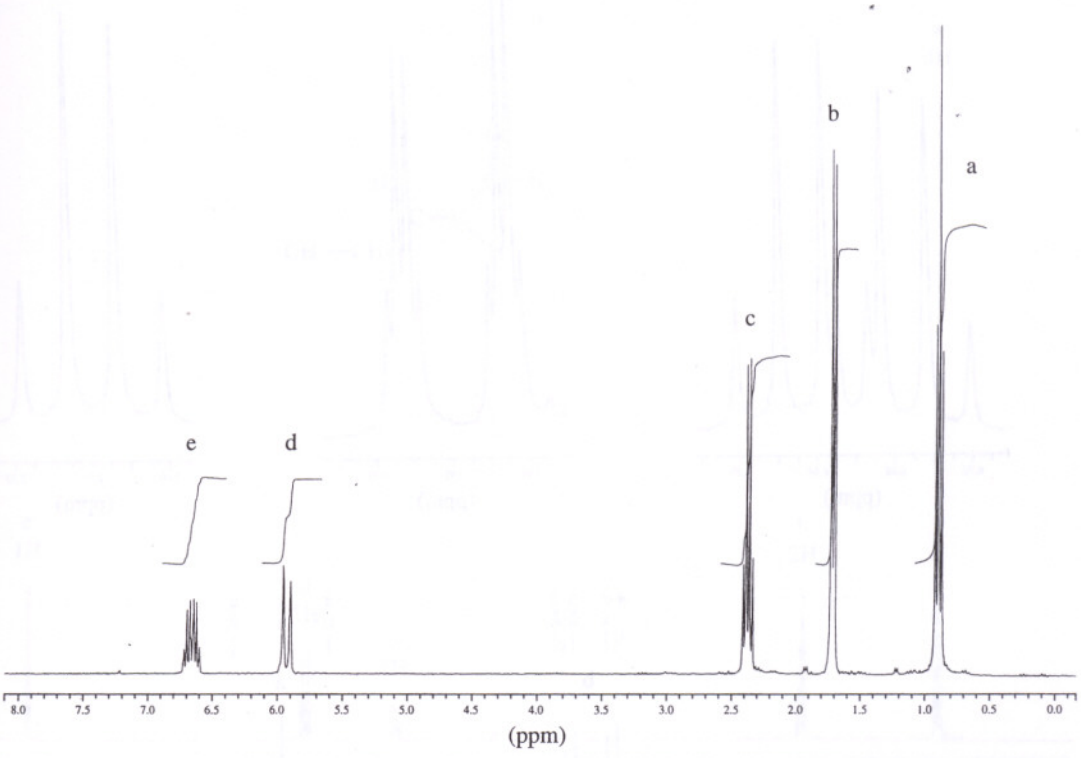
$^4J_{\alpha\alpha'} = 1.3 - 1.8$ Hz

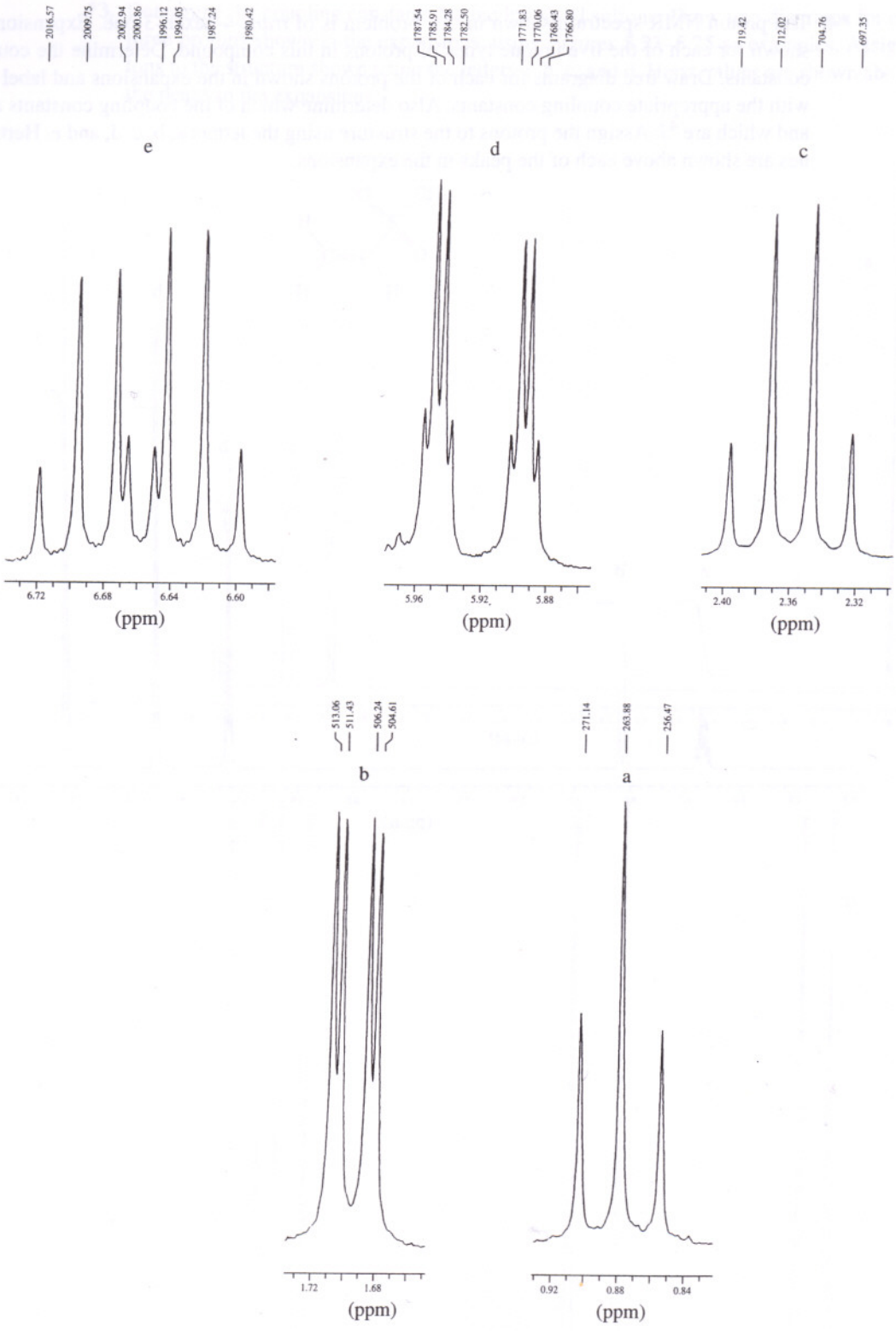
$^3J_{\beta\beta'} = 3.2 - 3.8$ Hz

Values for other heterocycles may be found in Appendix 5, p. A-15.

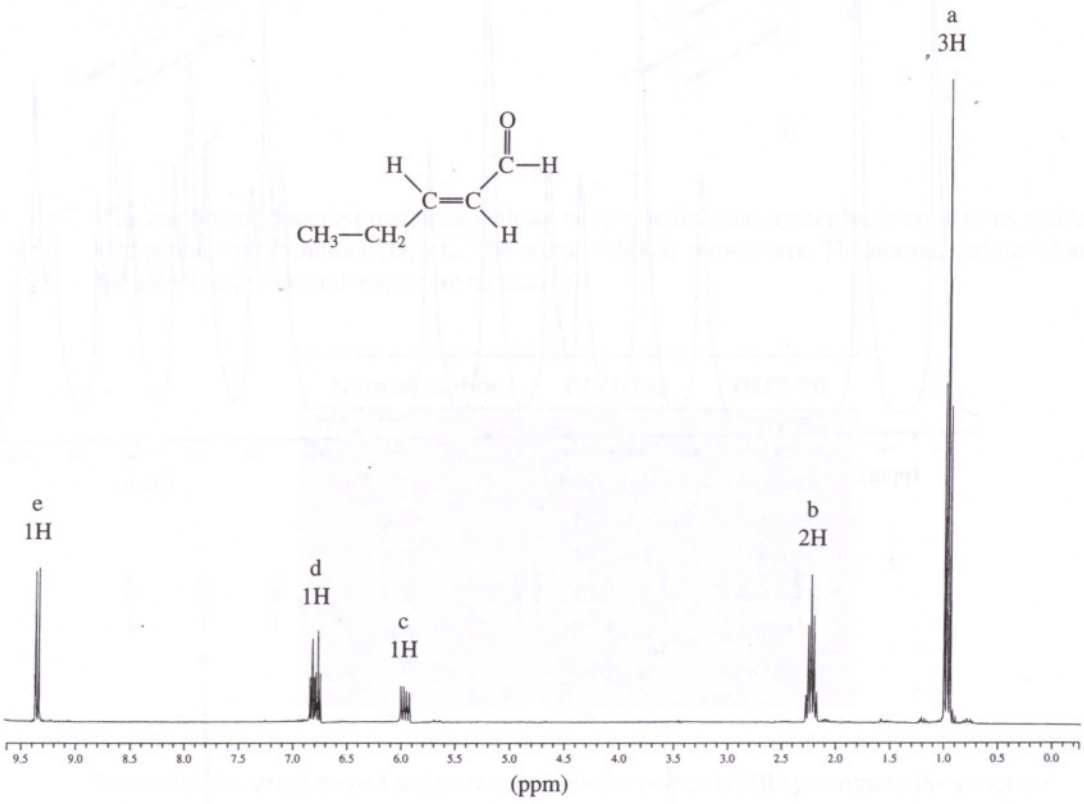
The structure and spectrum for furfuryl alcohol are shown in Figure 5.51. Only the ring hydrogens are shown—the resonances of the side chain ($-CH_2OH$) are not included. Determine a tree diagram for the splittings shown in this molecule, and also determine the magnitude of the coupling constants (see Problem 1 at the end of this chapter). Notice that proton H_a not only shows coupling to the other two ring hydrogens (H_b and H_c), but appears to have small unresolved *cis*-allylic inter-

***4.** The proton NMR spectrum shown in this problem is of *trans*-4-hexen-3-one. Expansions are shown for each of the five unique types of protons in this compound. Determine the coupling constants. Draw tree diagrams for each of the protons shown in the expansions and label them with the appropriate coupling constants. Also determine which of the coupling constants are ^3J and which are ^4J. Assign the protons to the structure using the letters a, b, c, d, and e. Hertz values are shown above each of the peaks in the expansions.

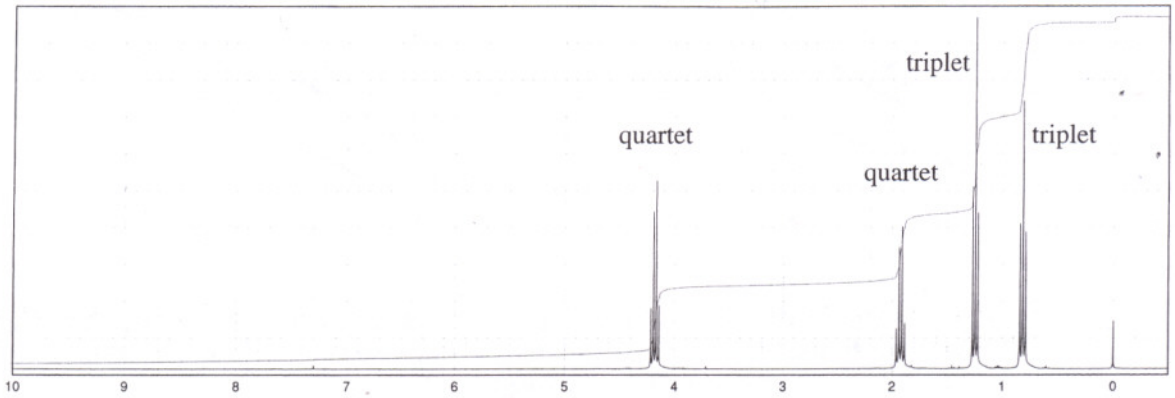


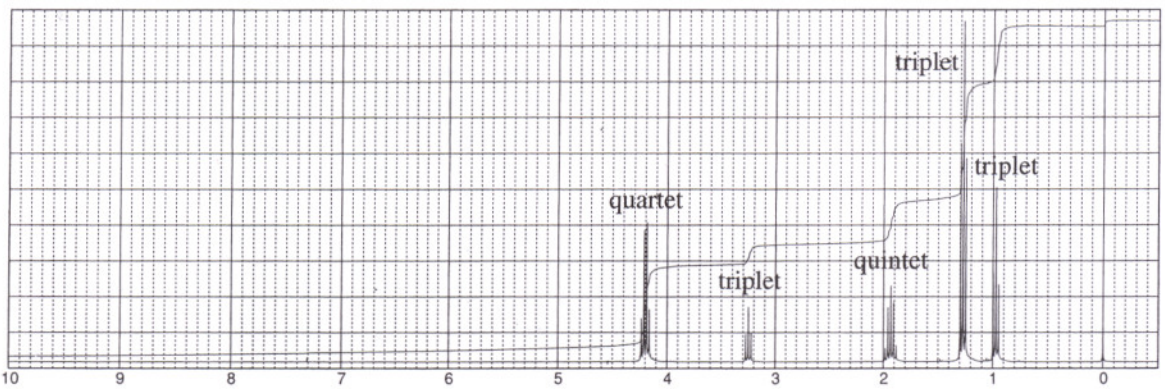

2016.57
2009.75
2002.94
2000.86
1996.12
1994.05
1987.24
1980.42
e
6.72
6.68
6.64
6.60
(ppm)
1787.54
1785.91
1784.28
1782.50
1771.83
1770.06
1768.43
1766.80
d
5.96
5.92
5.88
(ppm)
719.42
712.02
704.76
697.35
c
2.40
2.36
2.32
(ppm)
513.06
511.43
506.24
504.61
b
1.72
1.68
(ppm)
271.14
263.88
256.47
a
0.92
0.88
0.84
(ppm)

***5.** The proton NMR spectrum shown in this problem is of *trans*-2-pentenal. Expansions are shown for each of the five unique types of protons in this compound. Determine the coupling constants. Draw tree diagrams for each of the protons shown in the expansions and label them with the appropriate coupling constants. Also determine which of the coupling constants are ^3J and which are ^4J. Assign the protons to the structure using the letters a, b, c, d, and e. Hertz values are shown above each of the peaks in the expansions.

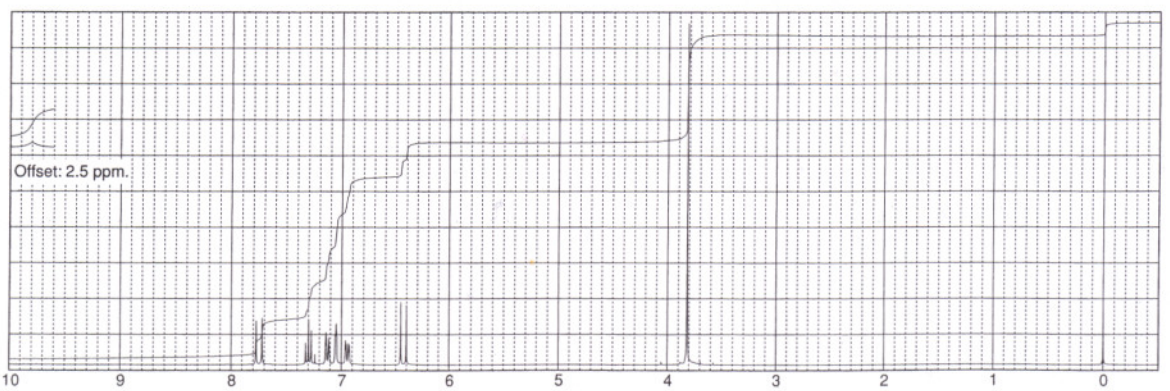


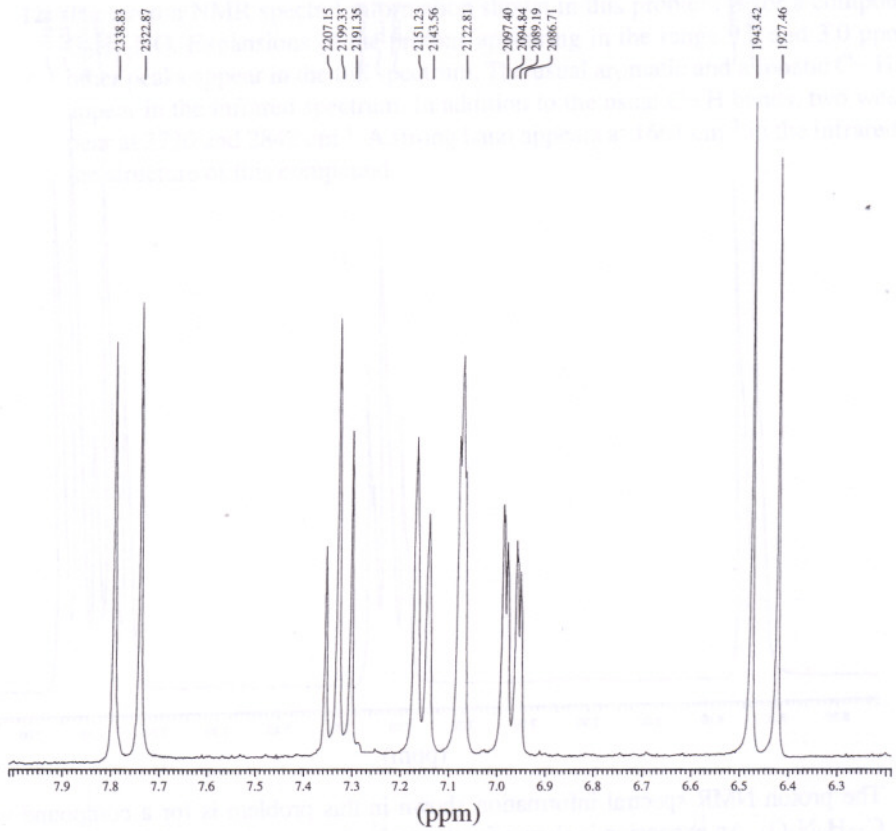
8. Diethyl malonate can be monoalkylated and dialkylated with bromoethane. The proton NMR spectra are provided for each of these alkylated products. Interpret each spectrum and assign an appropriate structure to each spectrum.



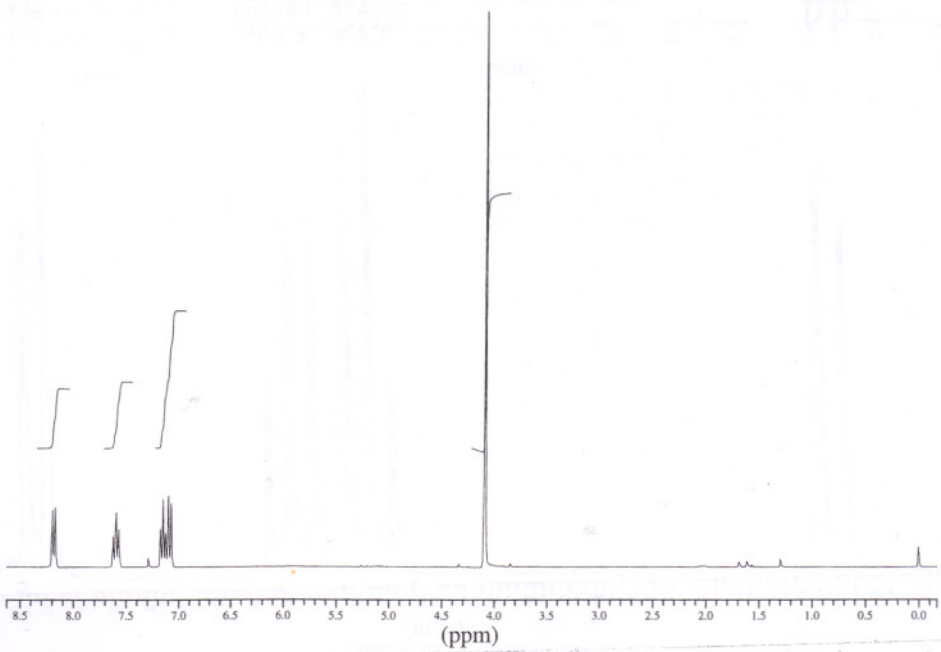


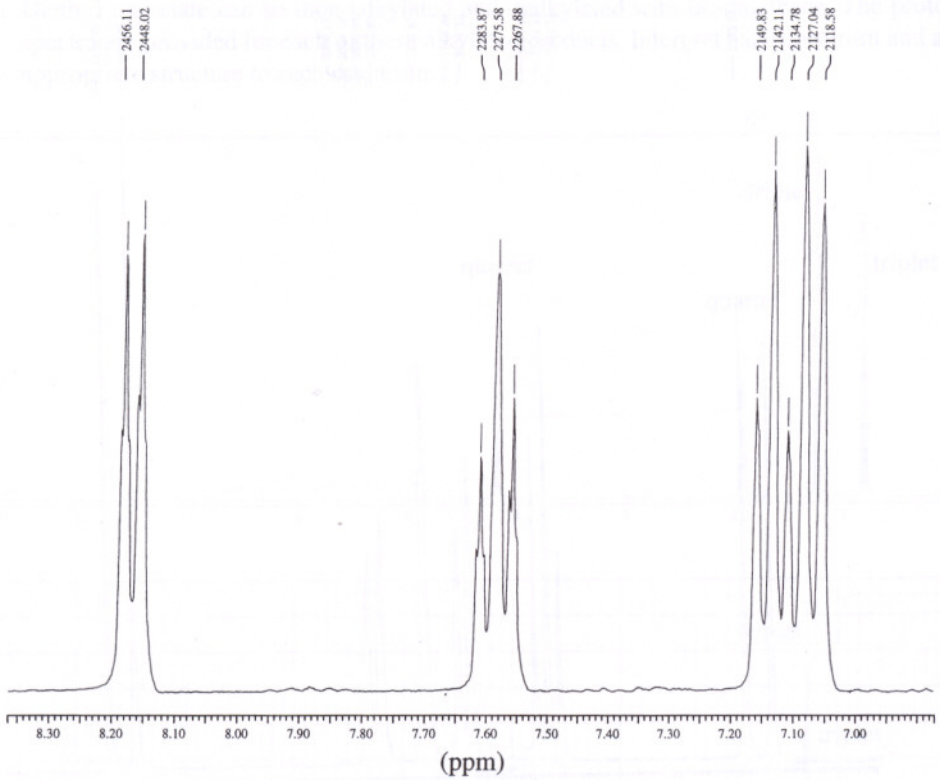
9. The proton NMR spectral information shown in this problem is for a compound with formula $C_{10}H_{10}O_3$. A disubstituted aromatic ring is present in this compound. Expansions are shown for each of the unique protons. Determine the J values and draw the structure of this compound. The doublets at 6.45 and 7.78 ppm provide an important piece of information. Likewise, the broad peak at about 12.3 ppm provides information on one of the functional groups present in this compound. Assign each of the peaks in the spectrum.



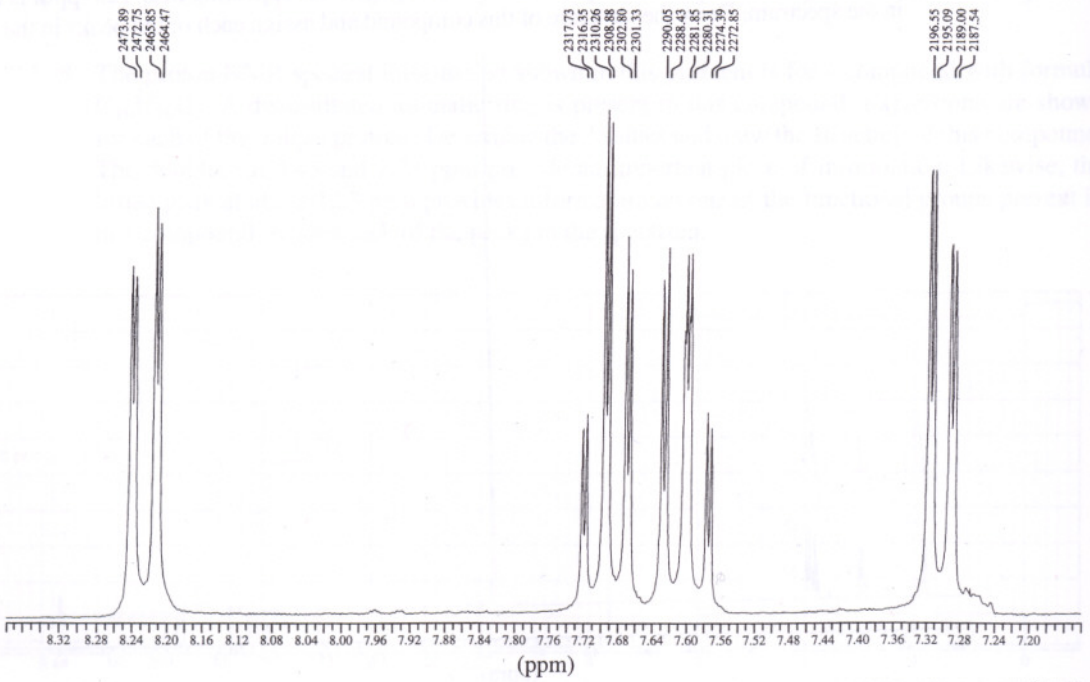


10. The proton NMR spectral information shown in this problem is for a compound with formula $C_8H_8O_3$. An expansion is shown for the region between 8.2 and 7.0 ppm. Analyze this region to determine the structure of this compound. A broad peak (1H) appearing near 12.0 ppm is not shown in the spectrum. Draw the structure of this compound and assign each of the peaks in the spectrum.

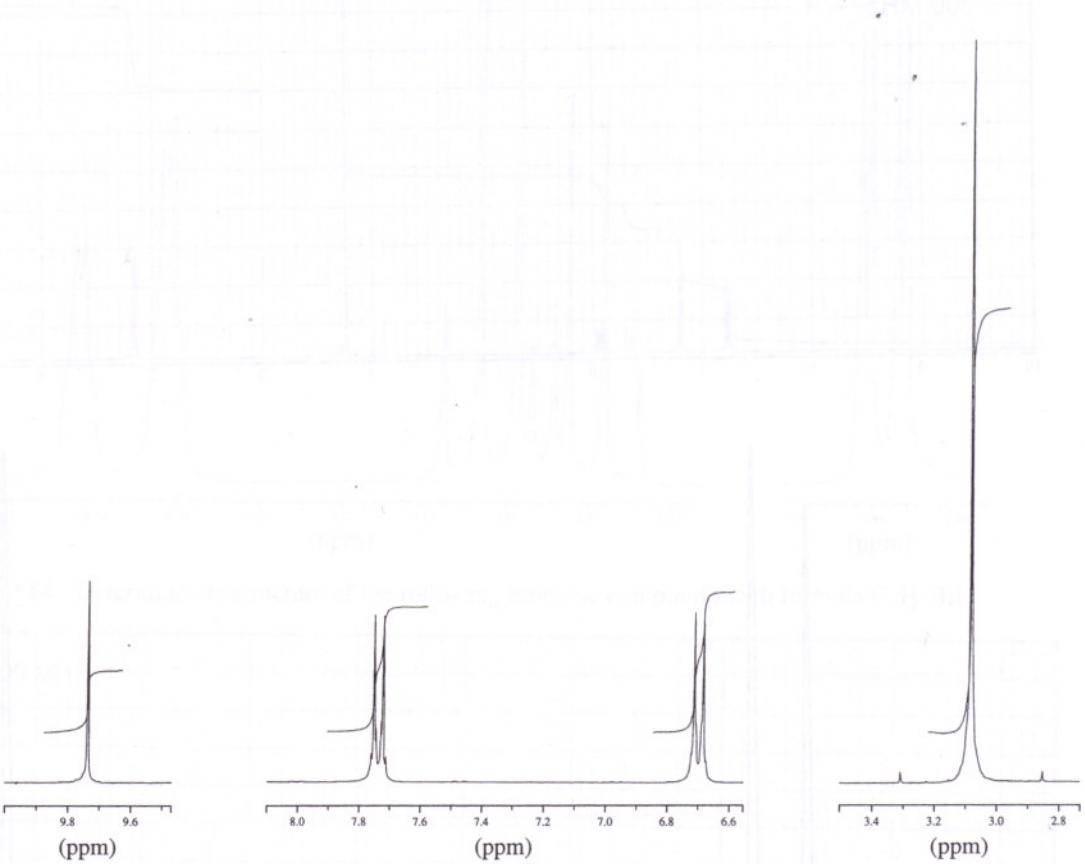




11. The proton NMR spectral information shown in this problem is for a compound with formula $C_{12}H_8N_2O_4$. An expansion is shown for the region between 8.3 and 7.2 ppm. No other peaks appear in the spectrum. Analyze this region to determine the structure of this compound. Strong bands appear at 1352 and 1522 cm^{-1} in the infrared spectrum. Draw the structure of this compound.

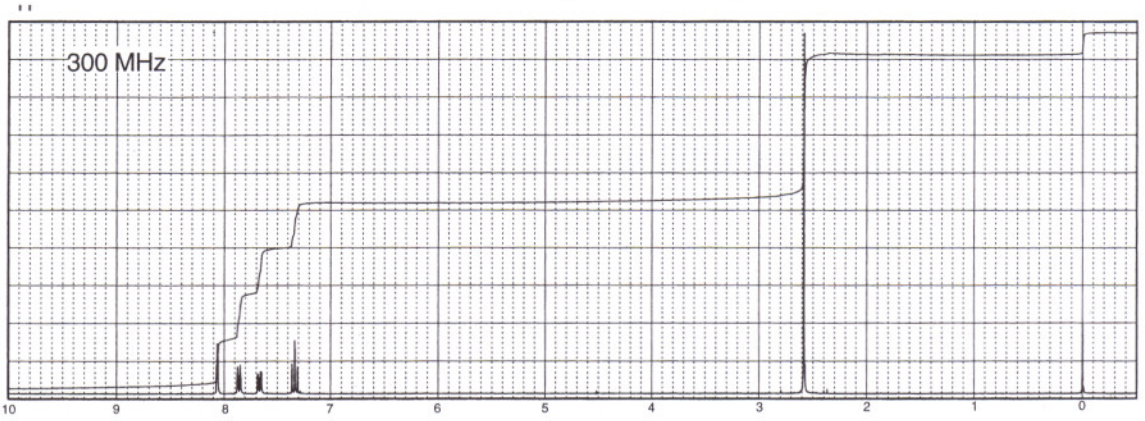


12. The proton NMR spectral information shown in this problem is for a compound with formula $C_9H_{11}NO$. Expansions of the protons appearing in the range 9.8 and 3.0 ppm are shown. No other peaks appear in the full spectrum. The usual aromatic and aliphatic C−H stretching bands appear in the infrared spectrum. In addition to the usual C−H bands, two weak bands also appear at 2720 and 2842 cm^{-1}. A strong band appears at 1661 cm^{-1} in the infrared spectrum. Draw the structure of this compound.

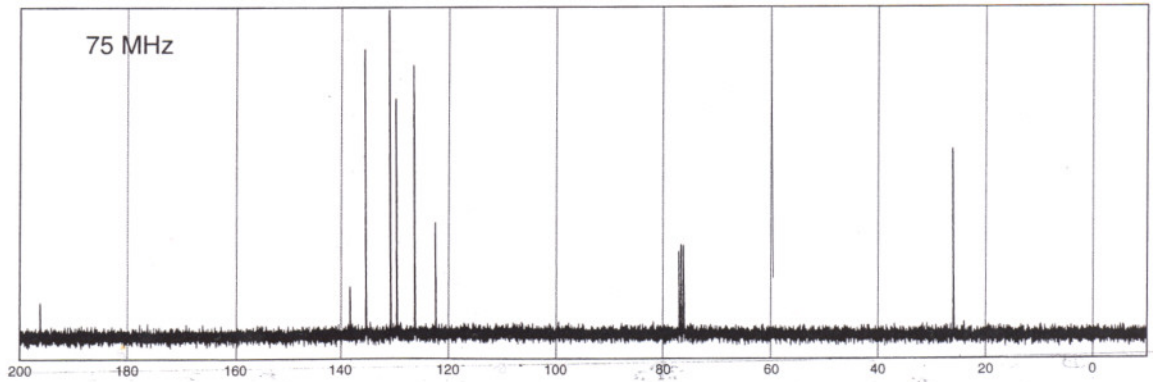


(ppm) (ppm)

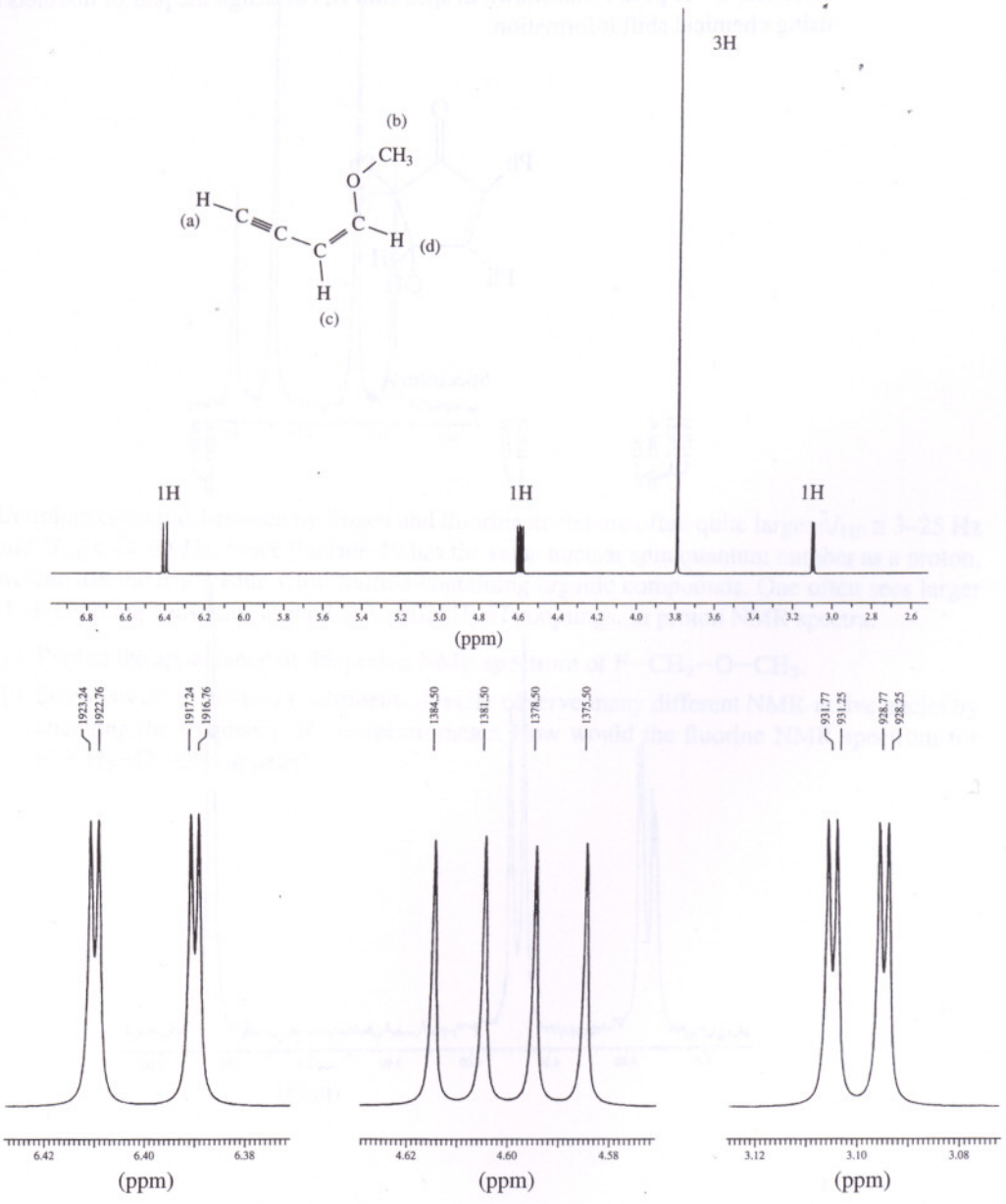
***14.** Determine the structure of the following aromatic compound with formula C_8H_7BrO.

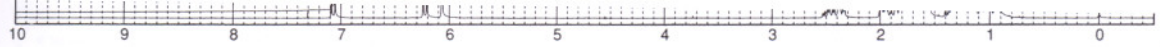


^{13}C



20. The spectrum shown in this problem is of 1-methoxy-1-buten-3-yne. Expansions are shown for each proton. Determine the coupling constants for each of the protons and draw tree diagrams for each. The interesting part of this problem is the presence of significant long-range coupling constants. There are ^3J, ^4J, and ^5J couplings in this compound. Be sure to include all of them in your tree diagram (graphical analysis).





***30.** Calculate the chemical shifts for the indicated protons, using Table 1 in Appendix 6.

(a) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (b) $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3$

(c) $Cl-CH_2-\overset{\overset{O}{\|}}{C}-O-CH_3$ (d) $CH_3-CH_2-CH_2-C\equiv C-H$

(e) $CH_3-CH_2-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-H$ (f) $CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2-O-H$

***31.** Calculate the chemical shifts for the vinyl protons, using Table 2 in Appendix 6.

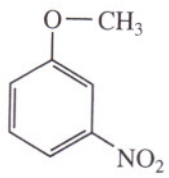
(a) $H-C(H)=C(CH_3)-\overset{\overset{O}{\|}}{C}-O-CH_3$ (b) $CH_3-C(H)=C(H)-\overset{\overset{O}{\|}}{C}-O-CH_3$

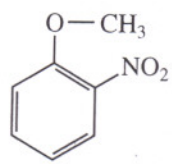
(c) $H-C(H)=C(C_6H_5)-H$ (d) $C_6H_5-C(H)=C(H)-\overset{\overset{O}{\|}}{C}-CH_3$

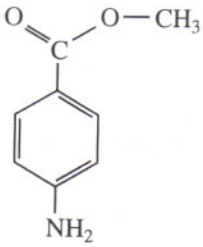
(e) $H-C(CH_3)=C(CH_2-OH)-H$ (f) $CH_3-C(CH_3)=C(H)-\overset{\overset{O}{\|}}{C}-CH_3$

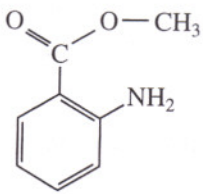
*32. Calculate the chemical shifts for the aromatic protons, using Table 3 in Appendix 6.

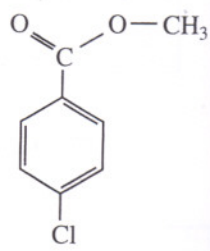
(a) 

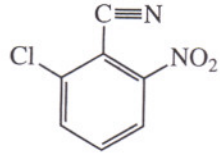
(b) 

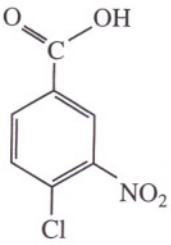
(c) 

(d) 

(e) 

(f) 

(g) 

(h) 

(i)