Nuclear Magnetic Resonance Spectroscopy

The nuclei of interest are primarily hydrogen and carbon

^{1}H NMR also called PMR

^{13}C NMR also called CMR

The Basis of NMR

NMR is based on the absorption of radiowaves by certain atomic nuclei when the molecule is in a strong magnetic field.

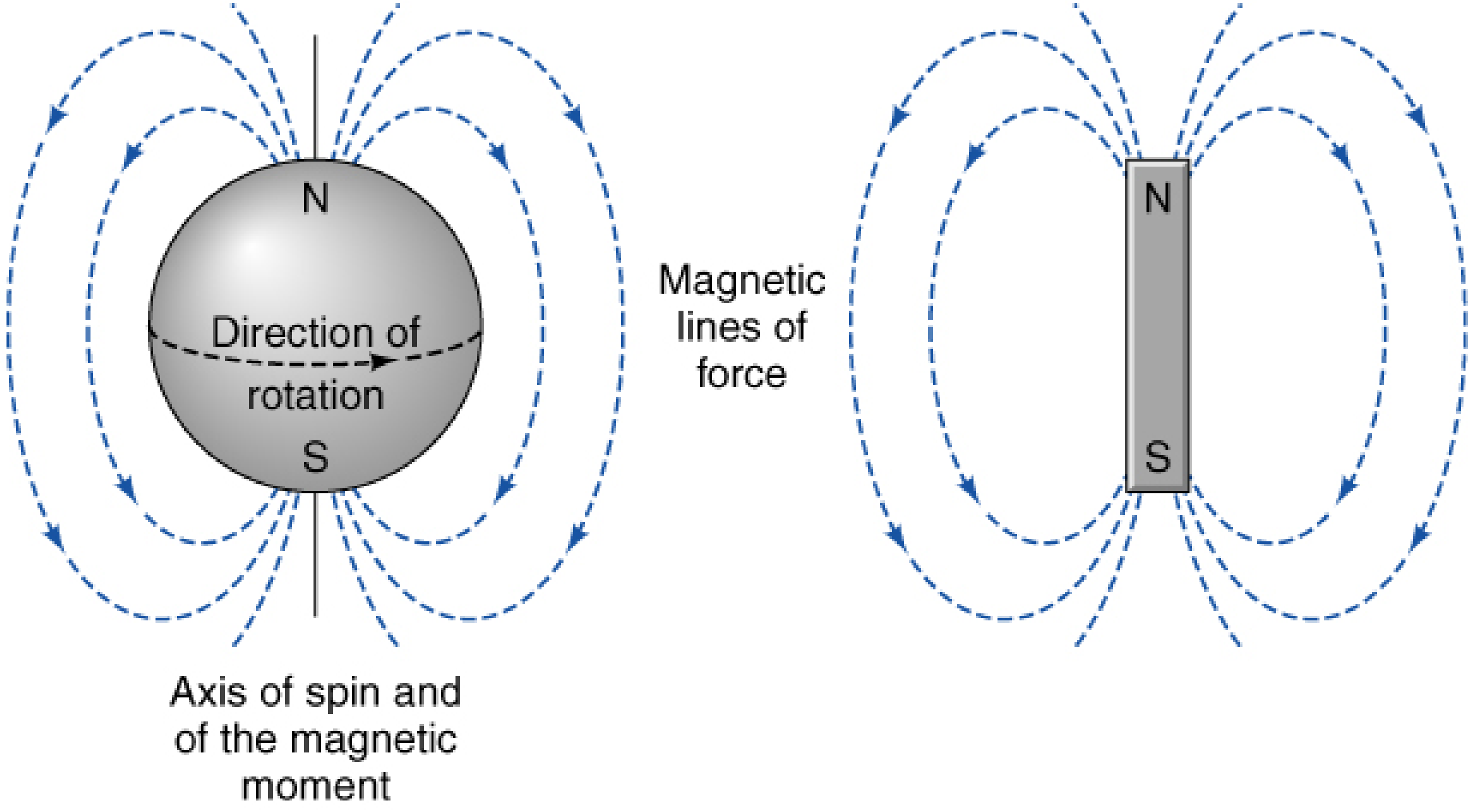
Previously, we learned that electrons have a spin quantum number
Atomic nuclei have spin states also
A non-zero spin is required for NMR

NMR Active and Non-active Nuclei

Nuclei with spin of +/- 1/2 include ^{1}H ^{13}C ^{15}N ^{19}F
These are called NMR active nuclei

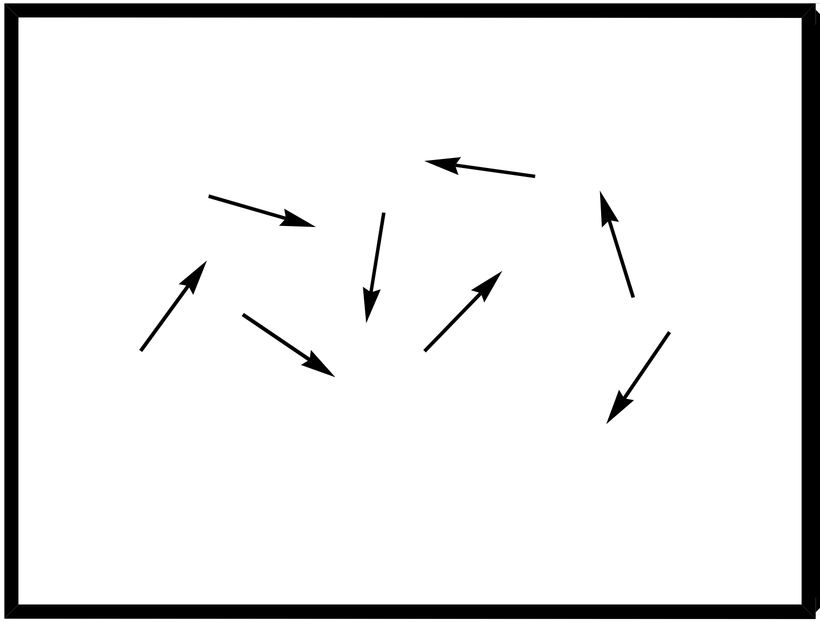
Some common isotopes have zero spin: ^{12}C and ^{16}O
These are called non-active NMR nuclei

Spinning proton resembles a tiny magnet

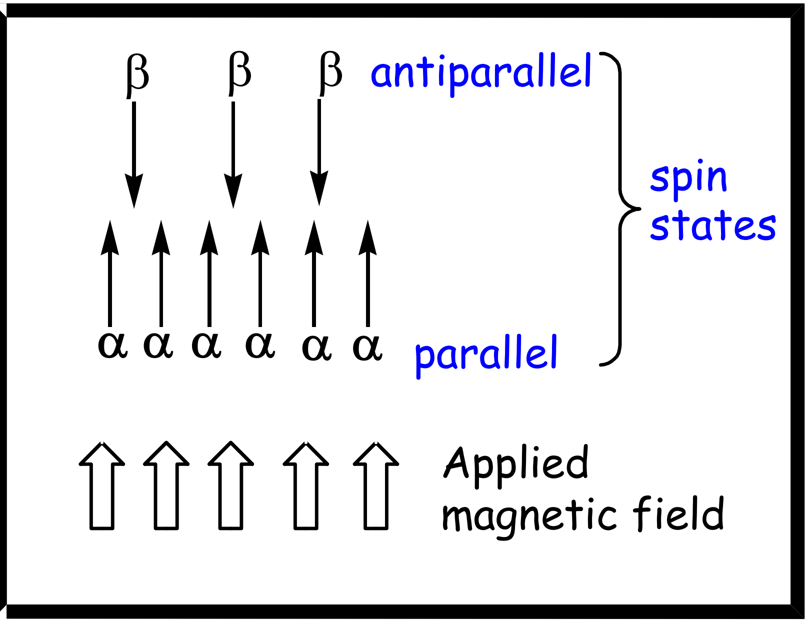


(*a*) (*b*)

Protons in a magnetic field

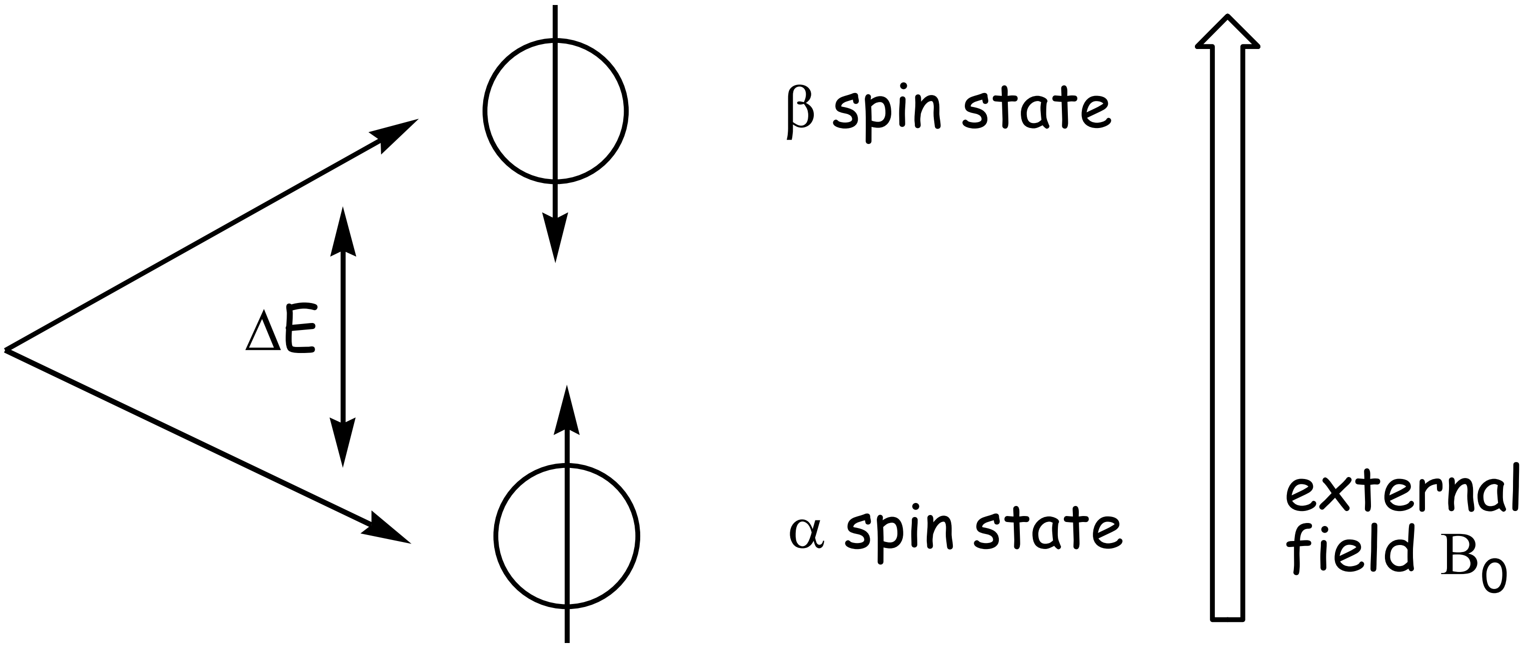


No Magnetic Field

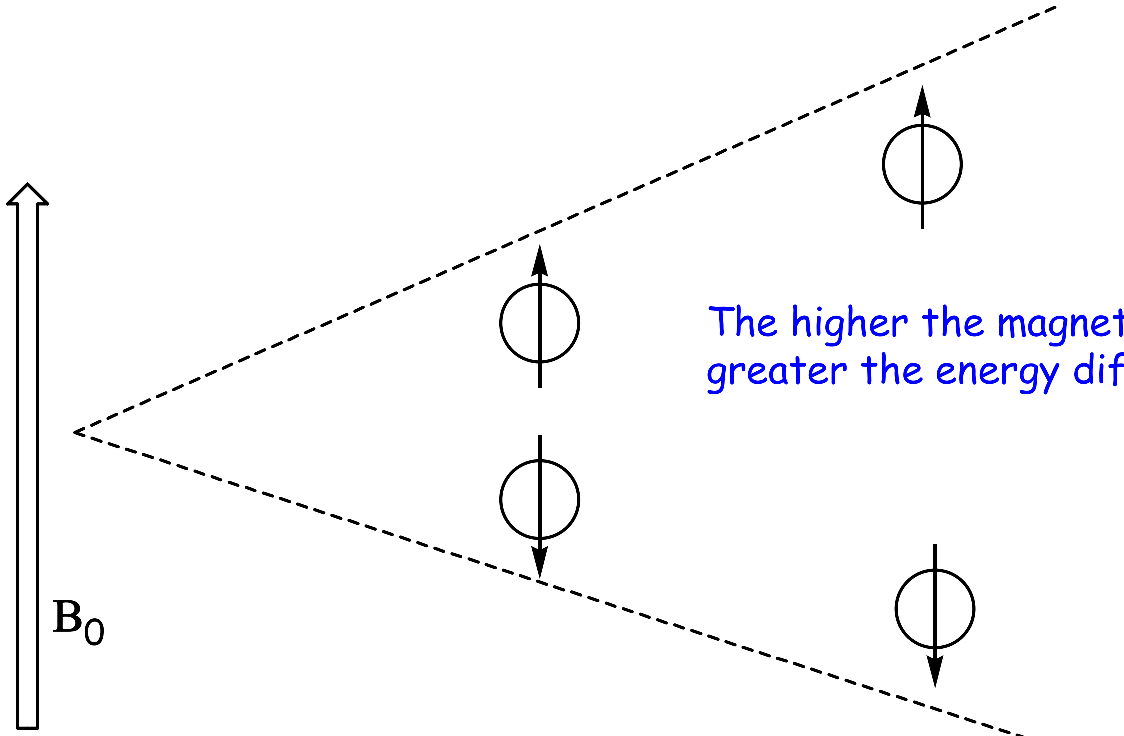


Applied Magnetic Field B_0

Absorption of energy causes nuclear "spin flip"



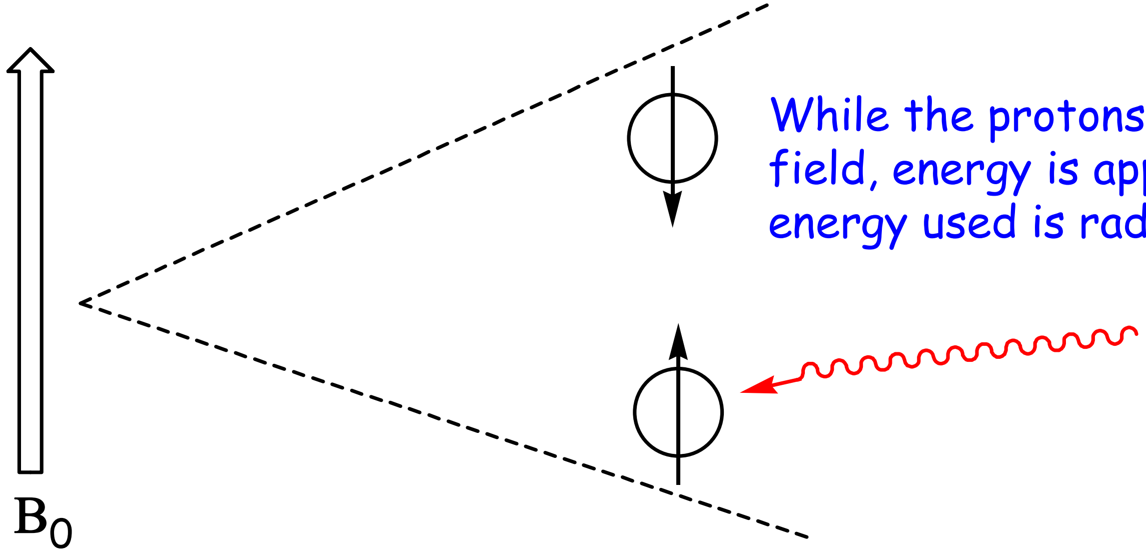
The size of the magnet determines energy difference between spin states



The higher the magnetic field strength, the greater the energy difference between spin states

The NMR Event- What Causes "Spin Flip"?

The combination of radio frequency and appled magnetic field causes the nuclei to "come into resonance"



While the protons are in the magnetic field, energy is applied to the sample; the energy used is radio frequency radiation

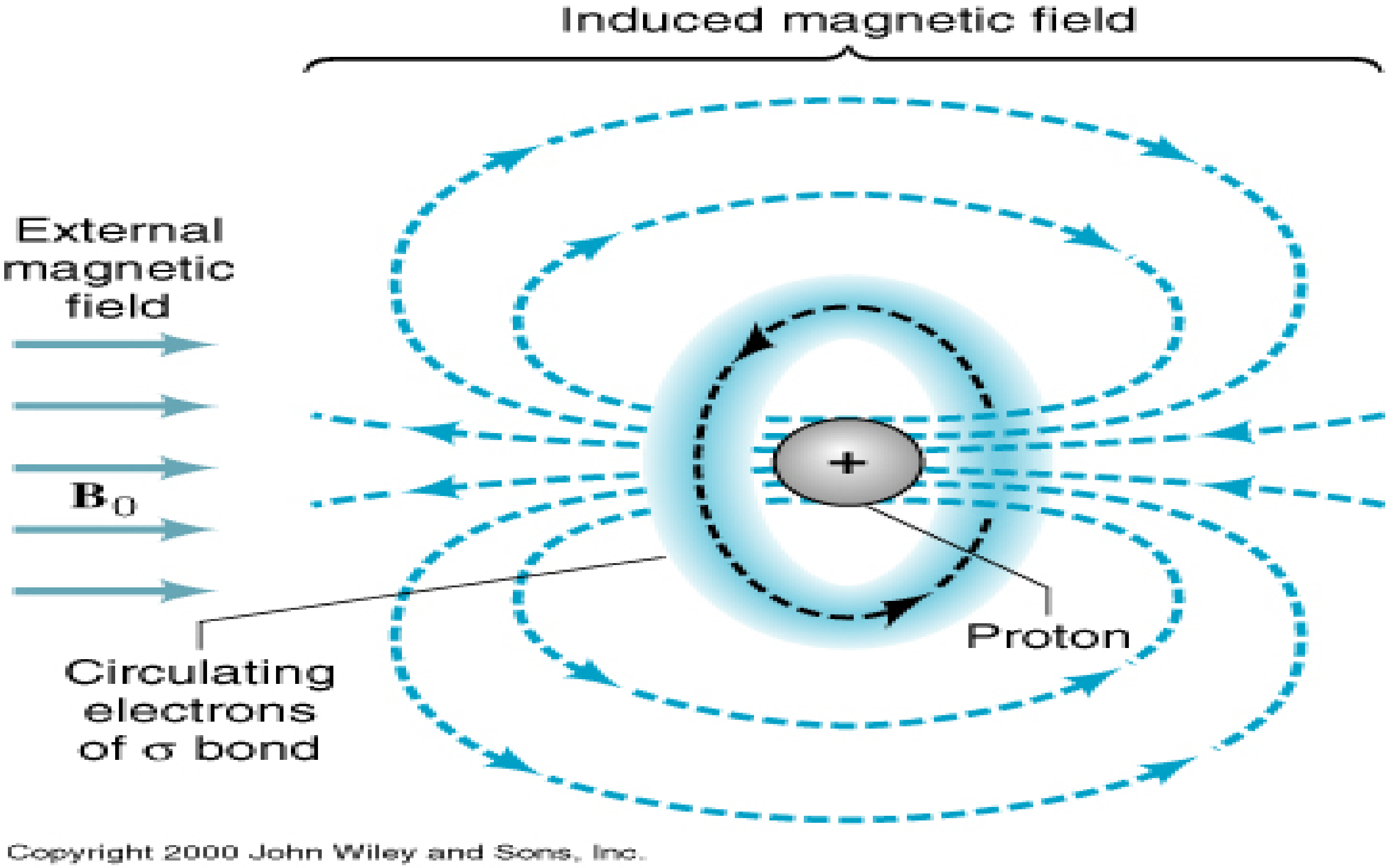
When the frequency of radiation exactly matches the energy gap between the spin states, the nucleus undergoes a "spin flip"

Magnetic Shielding by Electrons

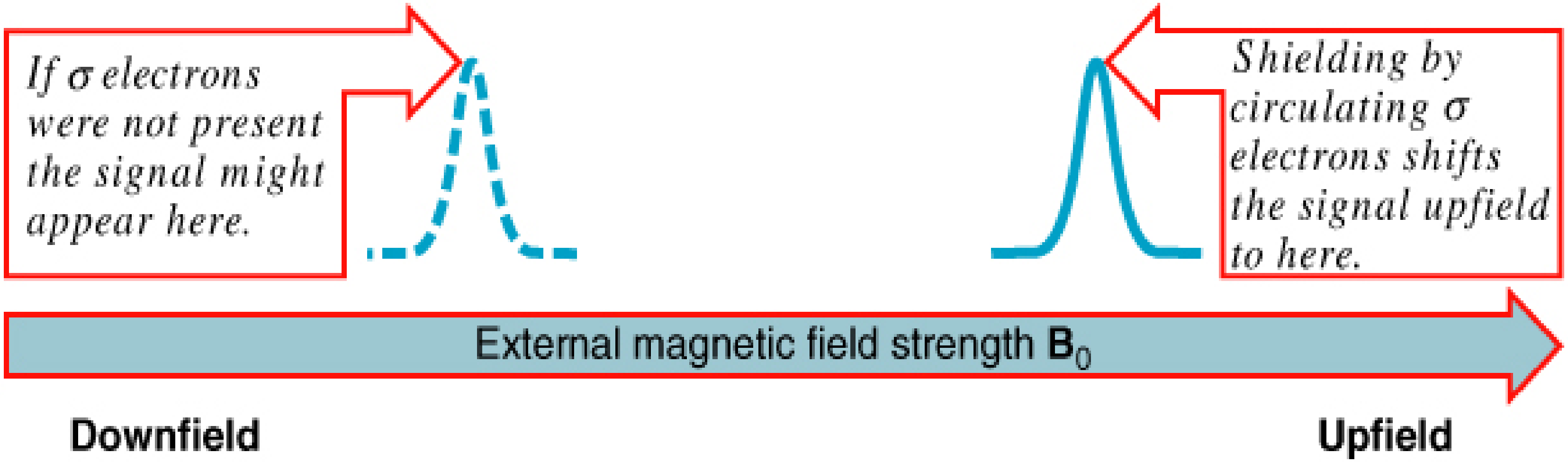
- The naked proton will come into resonance with a specific combination of radio energy and magnetic field strength.
- But real protons are surrounded by electrons
- Circulating electrons generate a small induced magnetic field that opposes the external magnetic field

$$(B_{\text{external}}) - (B_{\text{induced}}) = B_{\text{effective}}$$

Shielding of Proton due to Induced Magnetic Field



Chemical shift- position on the x-axis determined by shielding

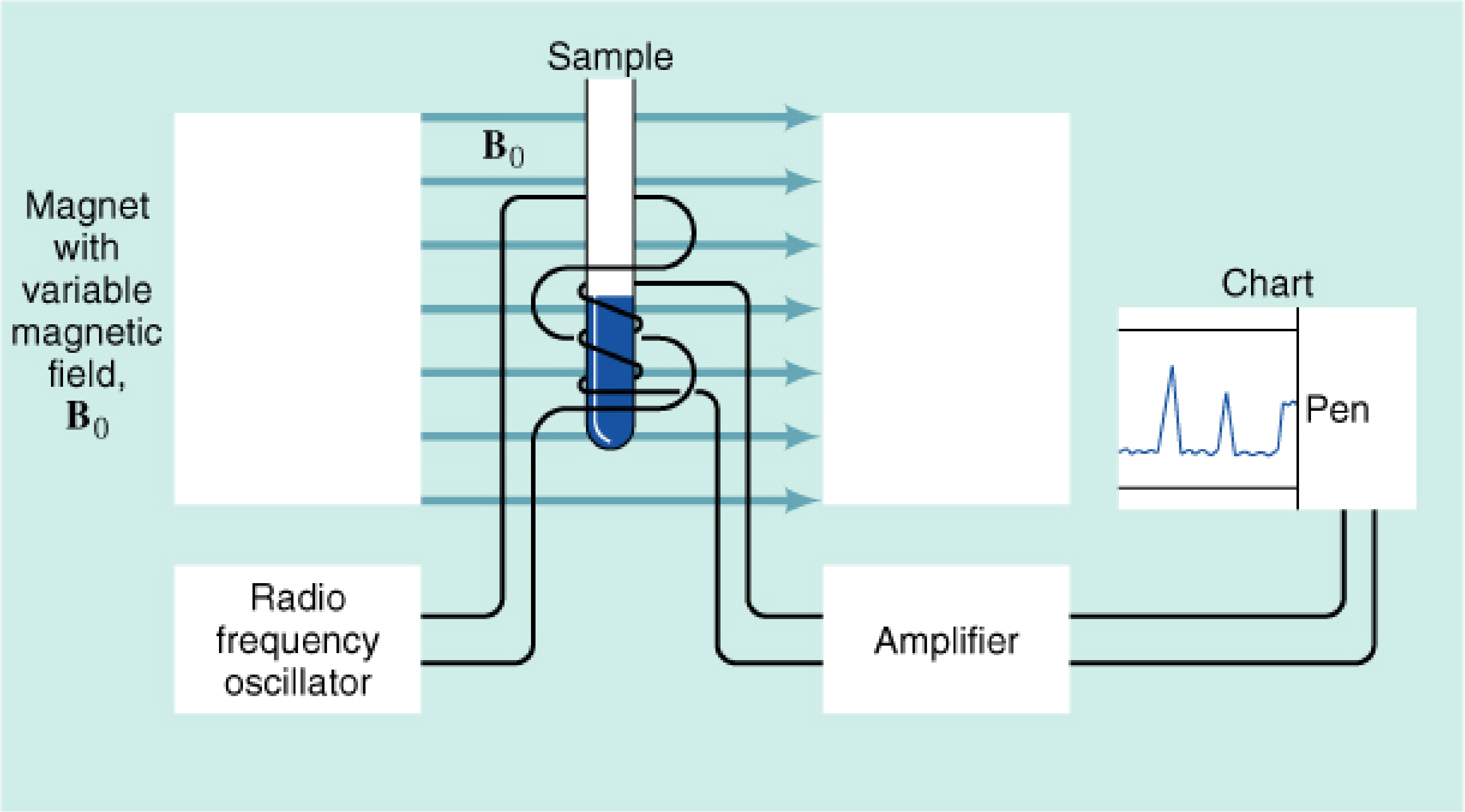


If σ electrons were not present the signal might appear here.

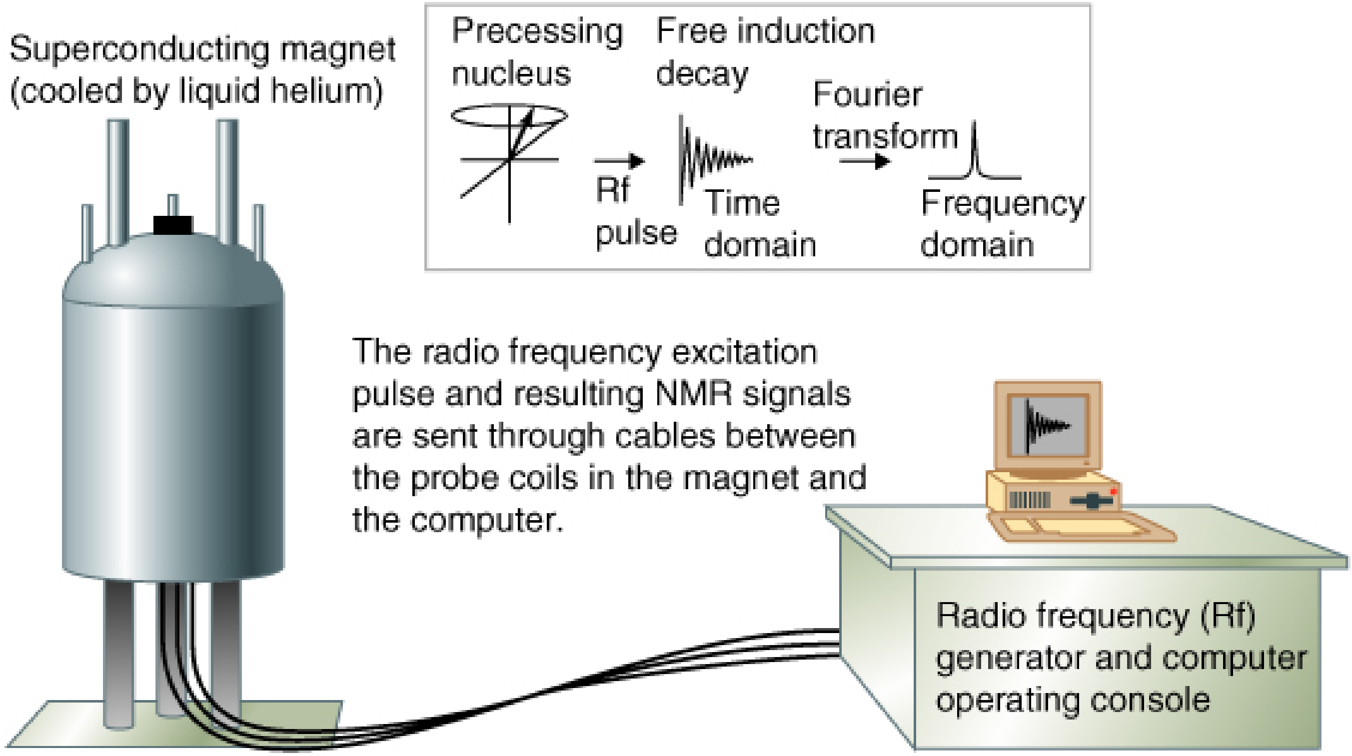
Shielding by circulating σ electrons shifts the signal upfield to here.

Figure 9.11 Shielding by σ electrons causes ^1H NMR absorptions to be shifted to higher external magnetic field strengths.

Field sweep NMR instrument



FT NMR Spectrometer



The radio frequency excitation pulse and resulting NMR signals are sent through cables between the probe coils in the magnet and the computer.

Sample tube spins within the probe coils in the hollow bore at the center of the magnet.

Fourier transformation of the signal from the time domain to the frequency domain occurs at the computer console.

NMR Information

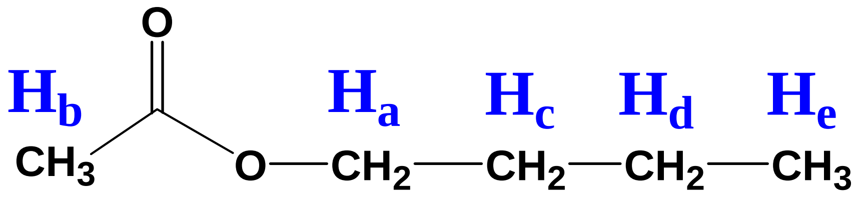
^{1}H NMR spectrum contains 3 pieces of information:

1. **Chemical shift- position of signal relative to TMS standard (zero ppm). Chemical shift determined by magnetic environment surrounding the proton.**

2. **Integration- the relative *ratio* of *non-equivalent* protons in each signal.**

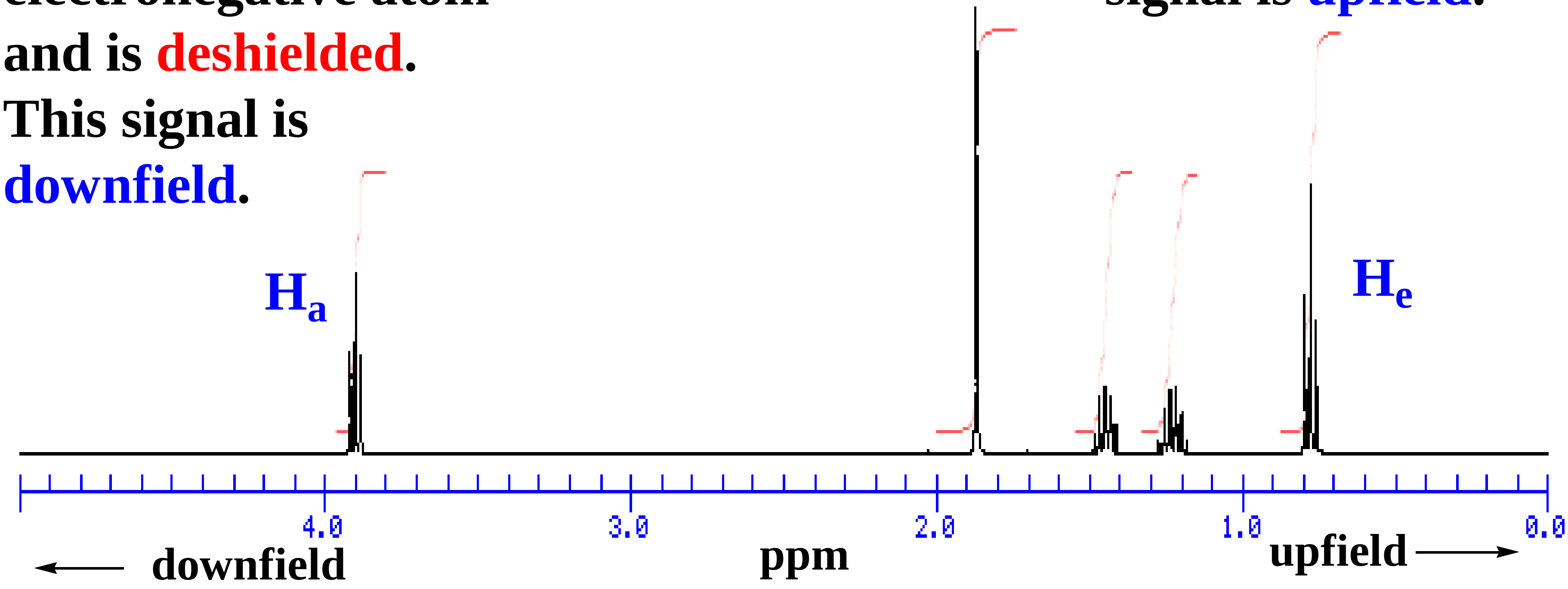
3. **Signal splitting- number of peaks in a signal is determined by the *n* + 1 rule.**

1. Chemical Shift



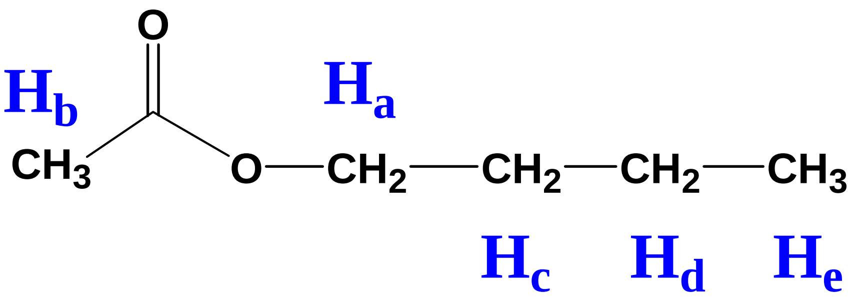
H_a is adjacent to electronegative atom and is deshielded. This signal is downfield.

H_e is shielded. This signal is upfield.

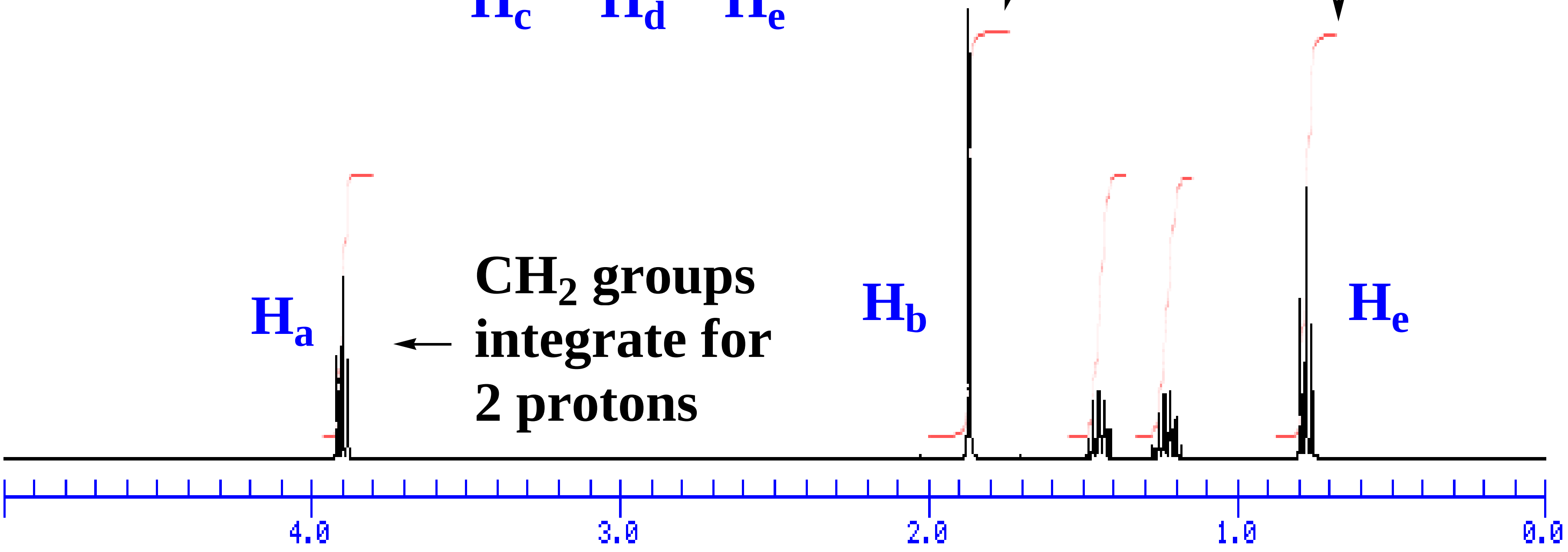


2. Integration of Peaks

The red curves represent the peak areas (integration)



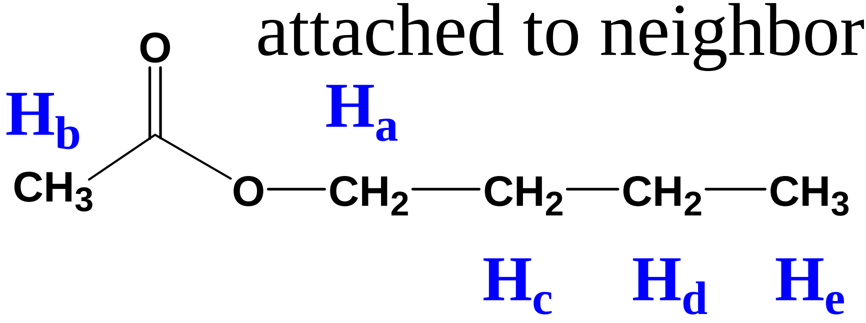
methyl groups integrate for 3 protons

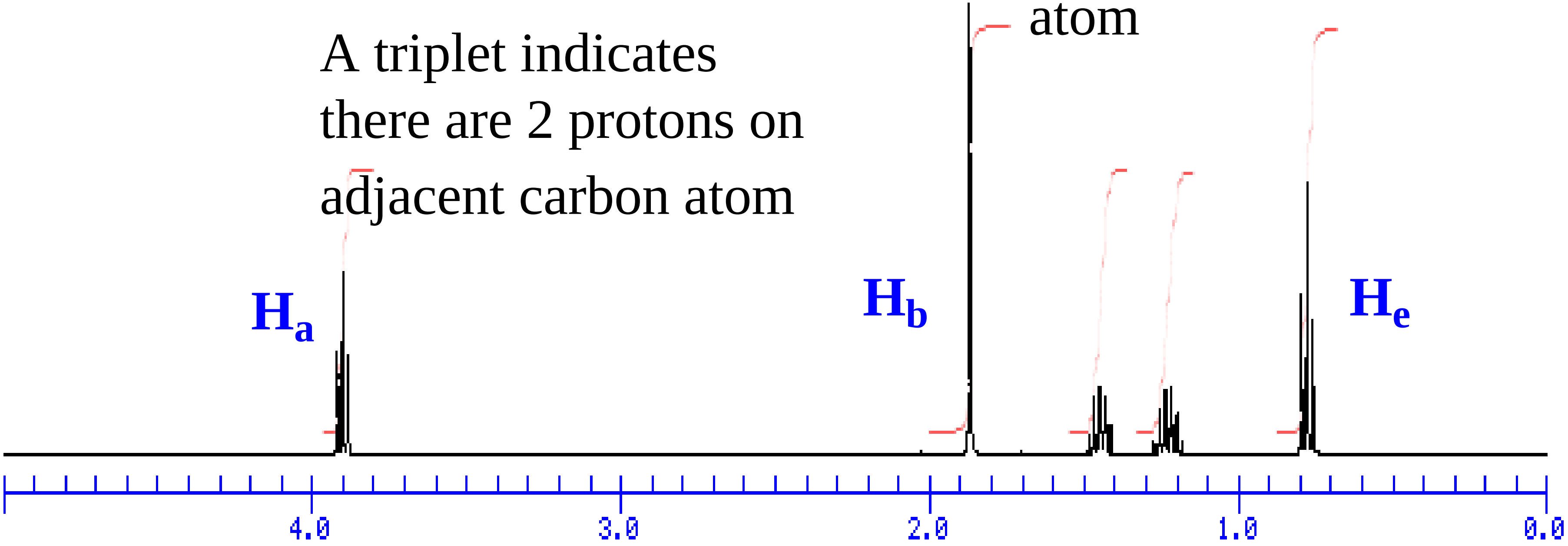


CH_2 groups integrate for 2 protons

3. Peak Splitting

The (n+1) rule indicates the number of protons attached to neighboring carbon atoms





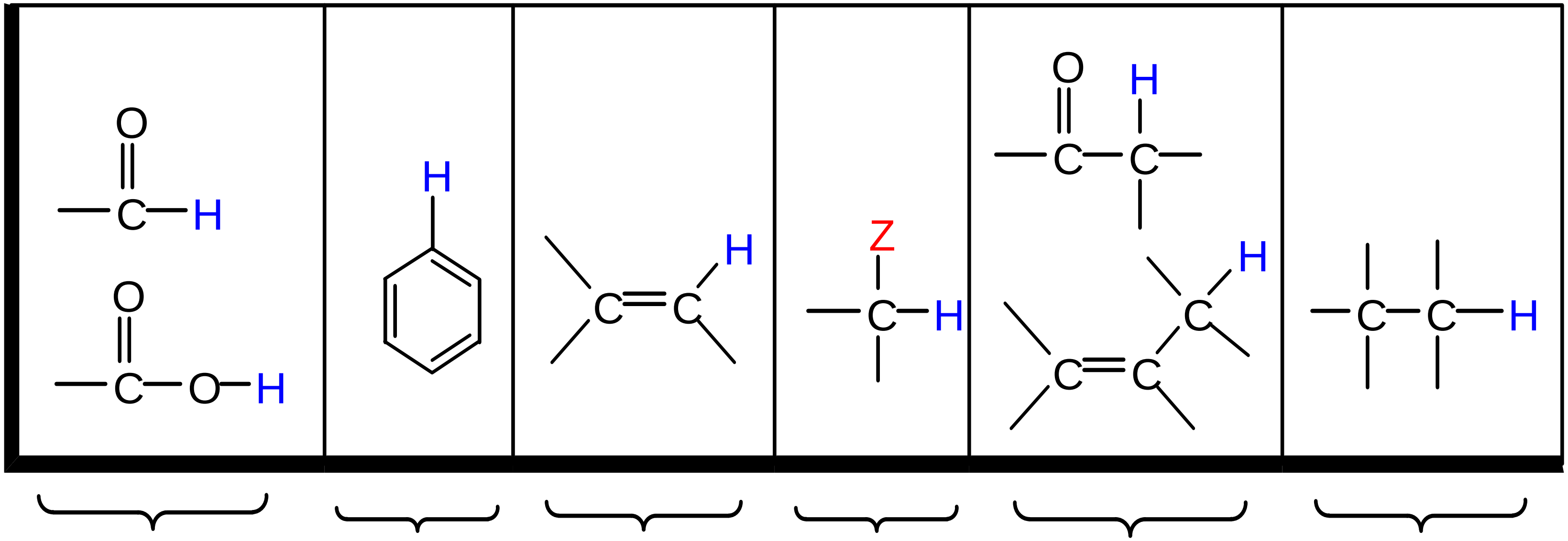
A singlet indicates there are no protons on adjacent carbon atom

A triplet indicates there are 2 protons on adjacent carbon atom

Chemical Shift

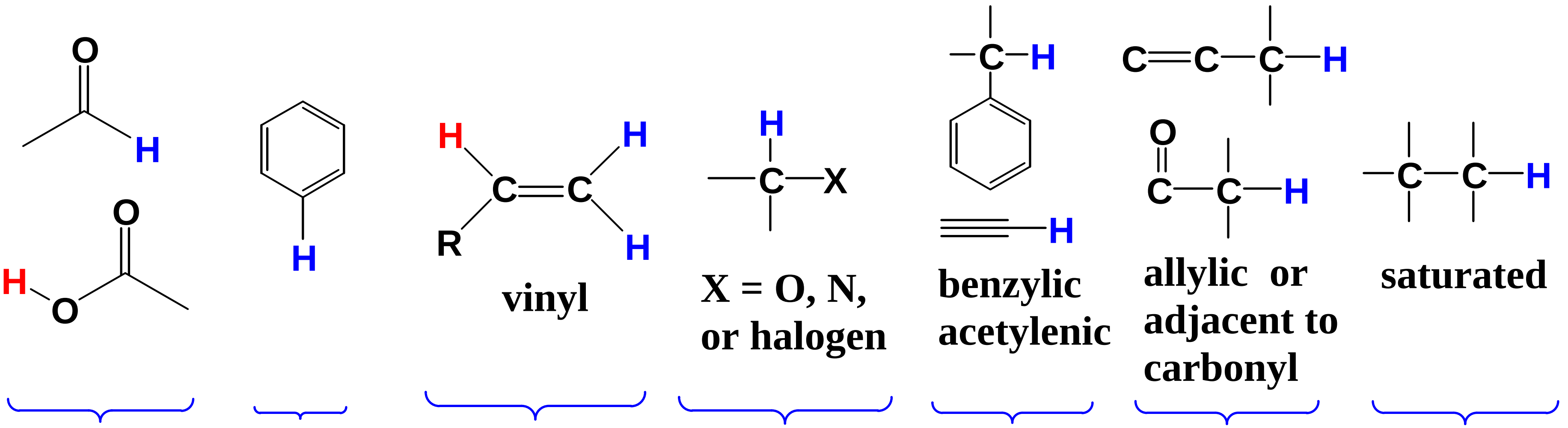
6 regions of NMR spectrum

Z = O, N



aldehydes acids	aromatic	vinyl	halogen	allylic	saturated
12 - 9.0	8.0 - 6.5	6.5 - 4.5	4.5 - 2.5	2.5 - 1.5	1.5 - 0

Table of Chemical Shifts

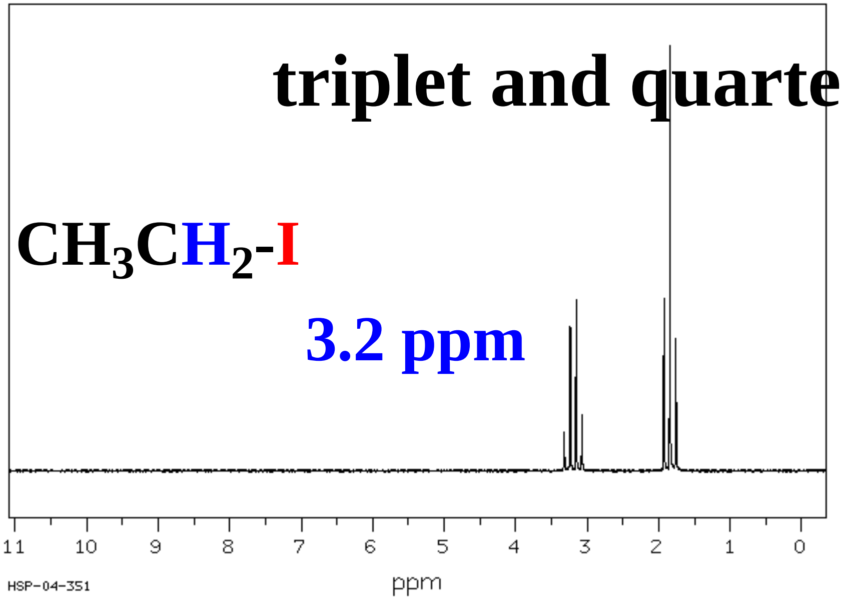


	13 - 9.0	H 13 - 10 H 10.5 - 9.5
	8.5 - 6.5	
vinyl	6.5 - 4.5	H 6.0 - 5.0 H 5.5 - 4.5
X = O, N, or halogen	5.0 - 2.5	F >Cl >Br >I O 4.0 - 3.0 N 3.0 - 2.0
benzylic acetylenic	3.0 - 2.5	
allylic or adjacent to carbonyl	2.5 - 2.0	
saturated	1.5 - 0	$3^{o} > 2^{o} > 1^{o}$

(ppm)

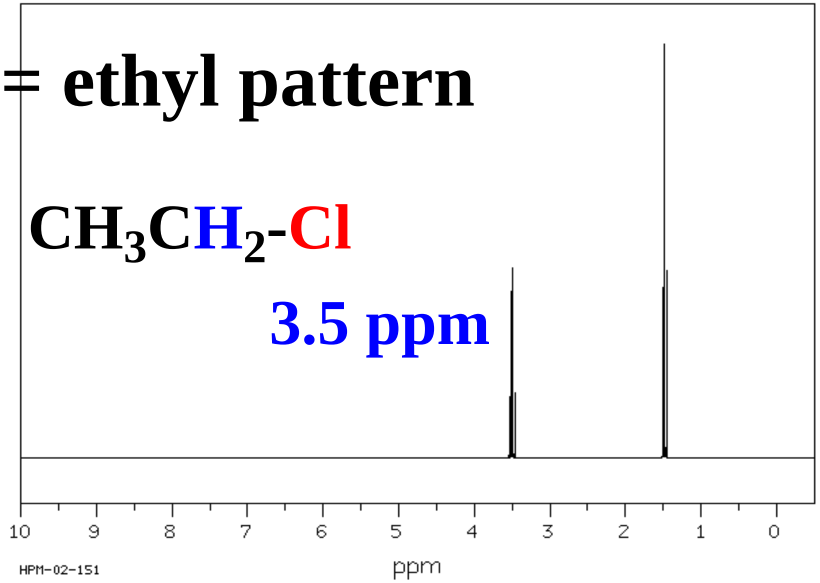
Chemical Shift due to electron withdrawing effect

triplet and quartet = ethyl pattern



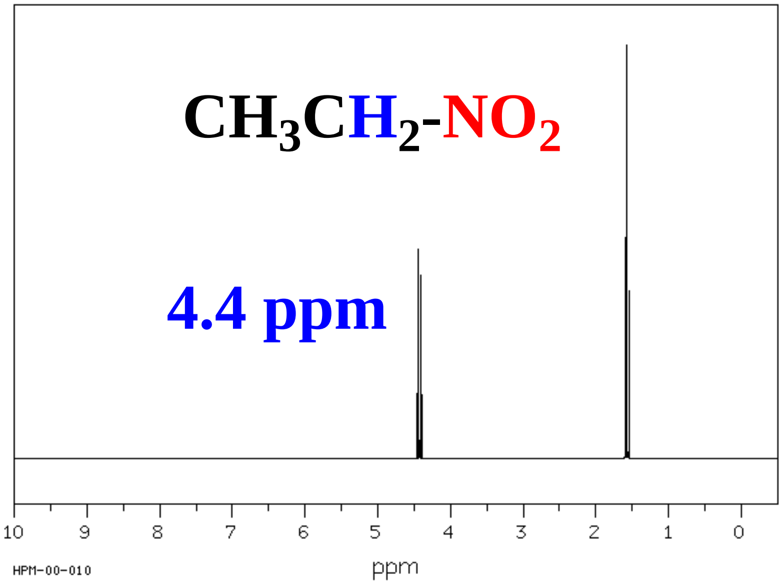
CH_3CH_2-I

3.2 ppm



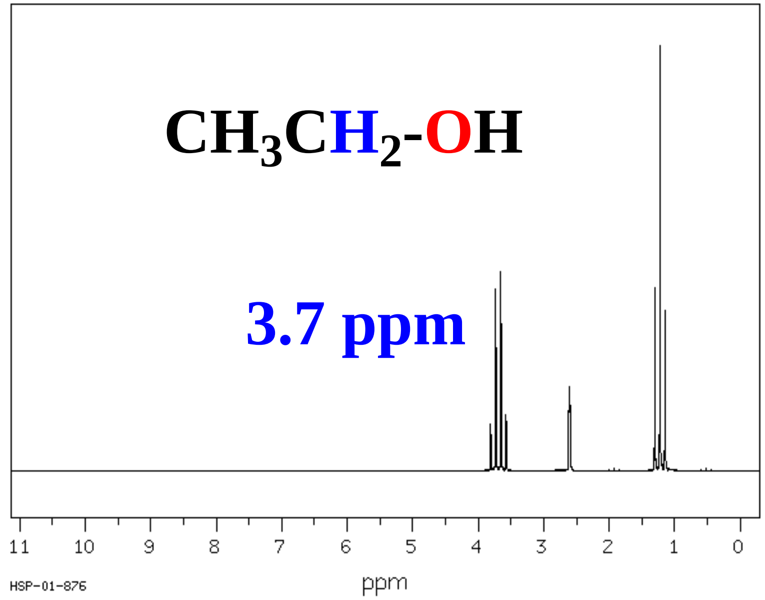
CH_3CH_2-Cl

3.5 ppm



CH_3CH_2-NO_2

4.4 ppm

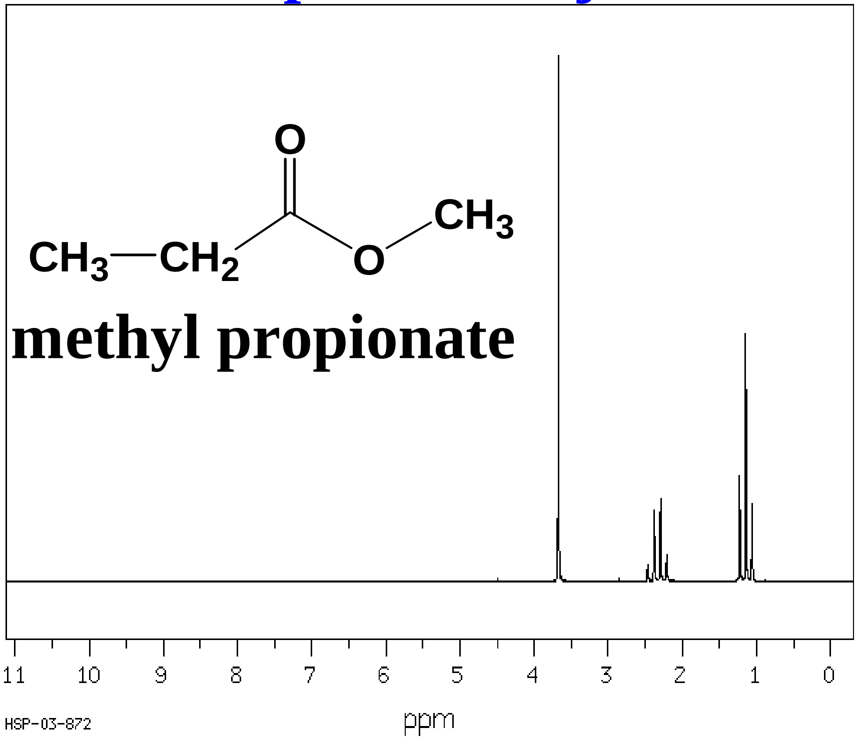


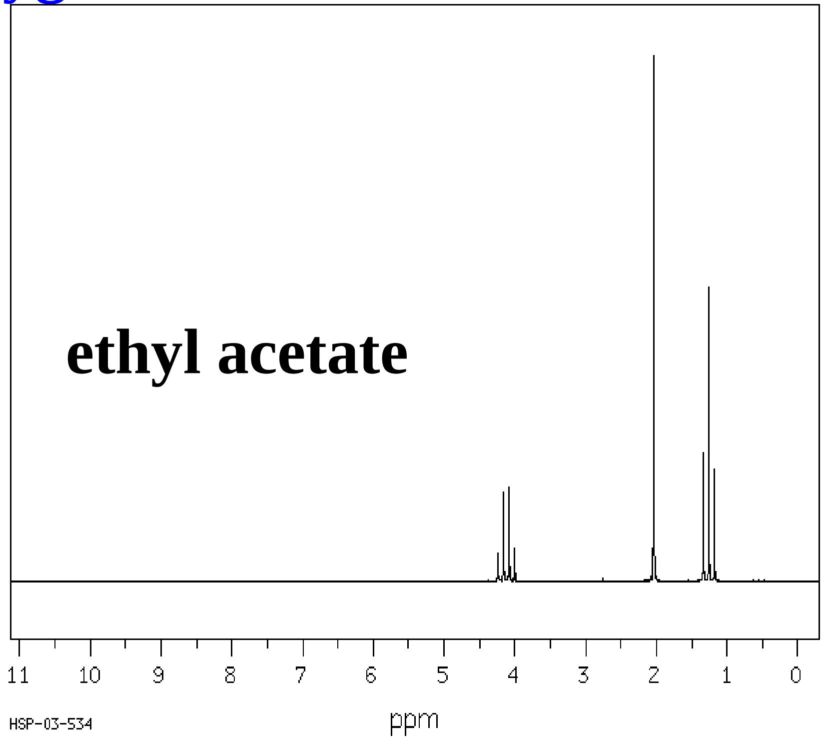
CH_3CH_2-OH

3.7 ppm

Chemical Shift for two Isomeric Esters: $C_4H_8O_2$

protons adjacent to oxygen are downfield



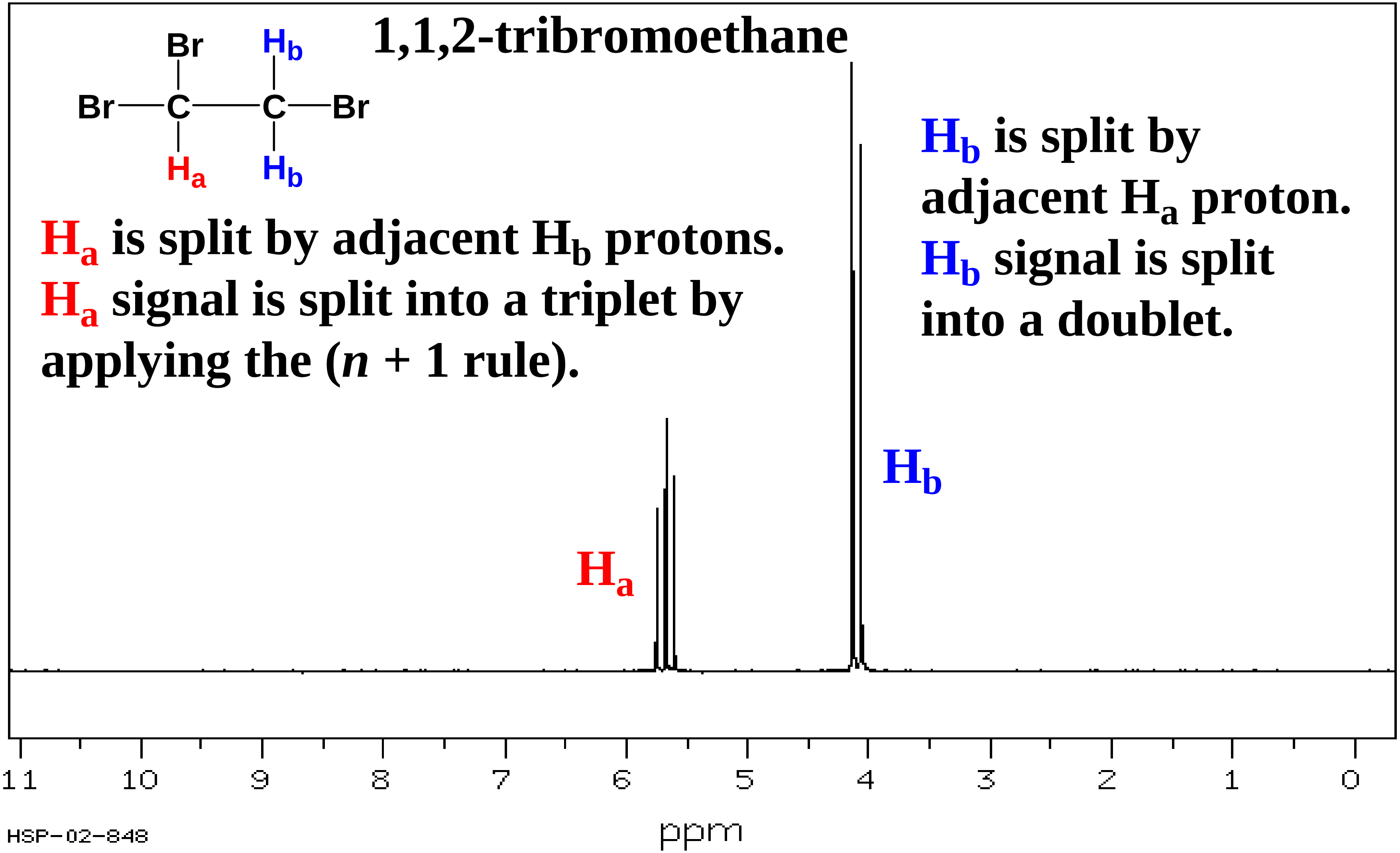


The signals for both spectra are the same: a singlet, triplet & quartet.

Splitting Patterns: n+1 Rule

- A signal is split into multiple peaks by adjacent protons
- The signal is split into n+1 peaks, where n = the number of *equivalent* adjacent protons

Splitting Pattern for 1,1,2-tribromoethane



H_a is split by adjacent H_b protons. H_a signal is split into a triplet by applying the (*n* + 1 rule).

H_b is split by adjacent H_a proton. H_b signal is split into a doublet.

Splitting Pattern for 1,1,2-trichloroethane

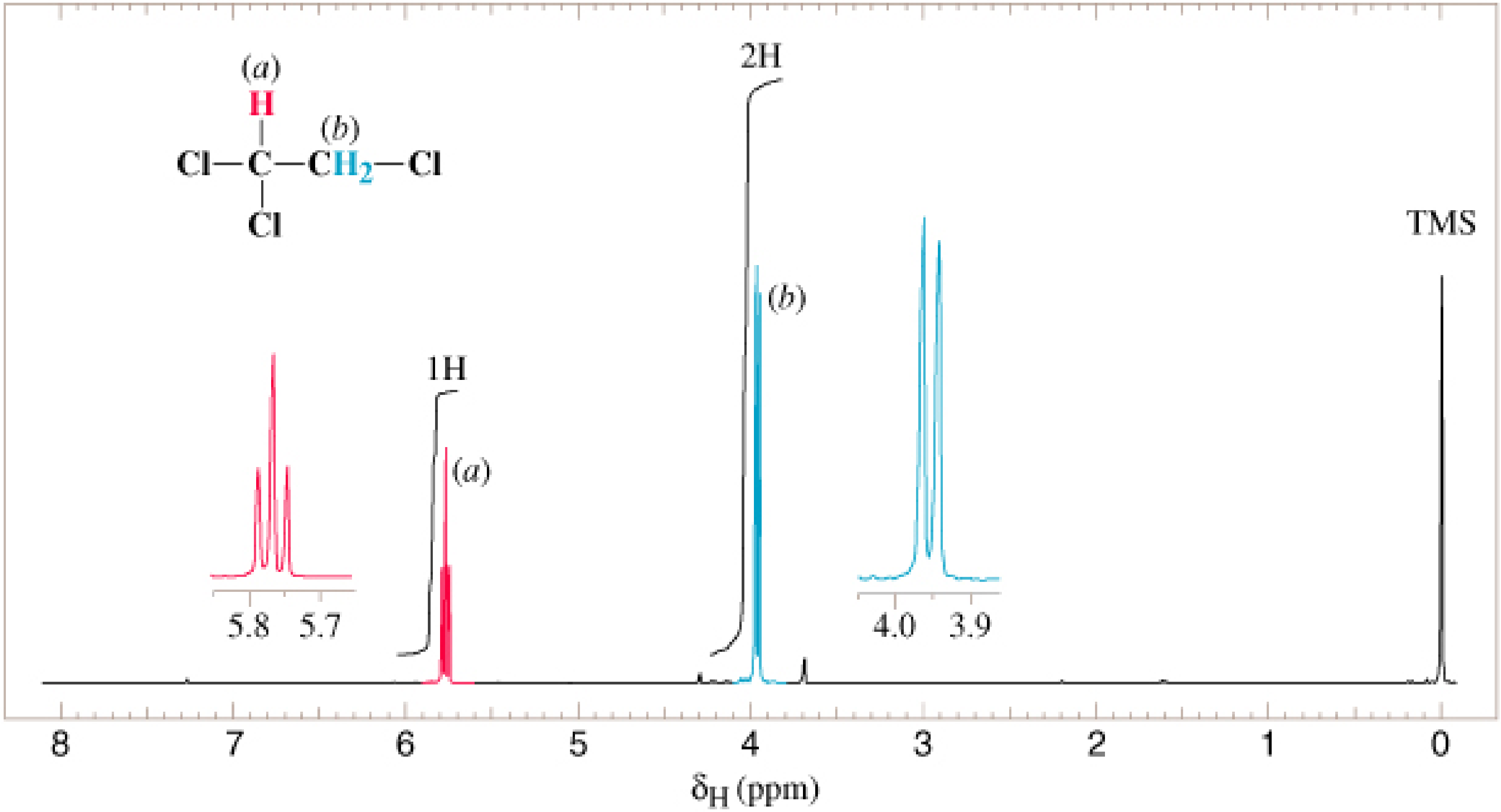
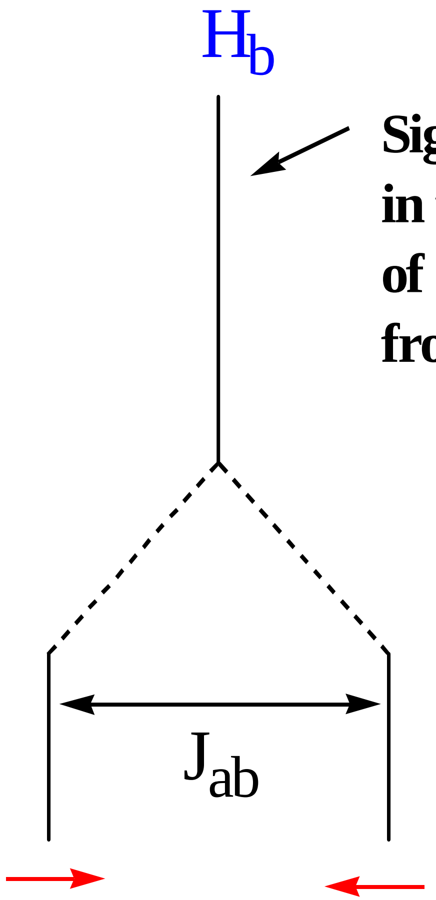
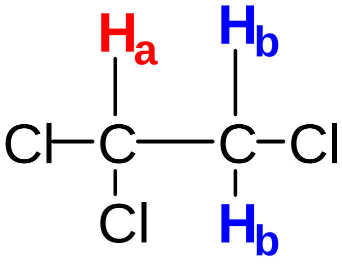


Figure 9.6 The 300 MHz ^{1}H NMR spectrum of 1,1,2-trichloroethane. Expansions of the signals are shown in the offset plots.

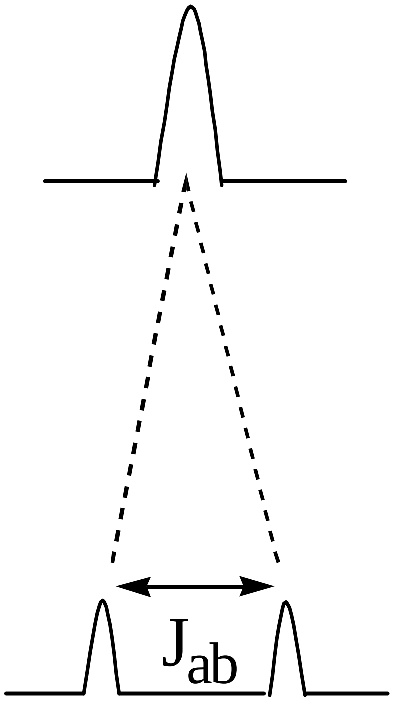
Signal Splitting from one adjacent proton



Signal from H_b in the absence of splitting from H_a



magnetic moments of H_a split the signal into two peaks of equal intensity; signal is split into a 1:1 doublet



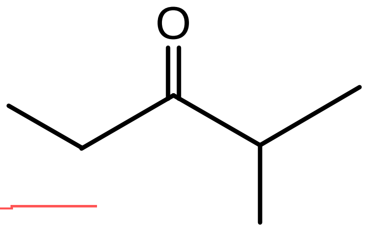
two magnetic orientations of H_a

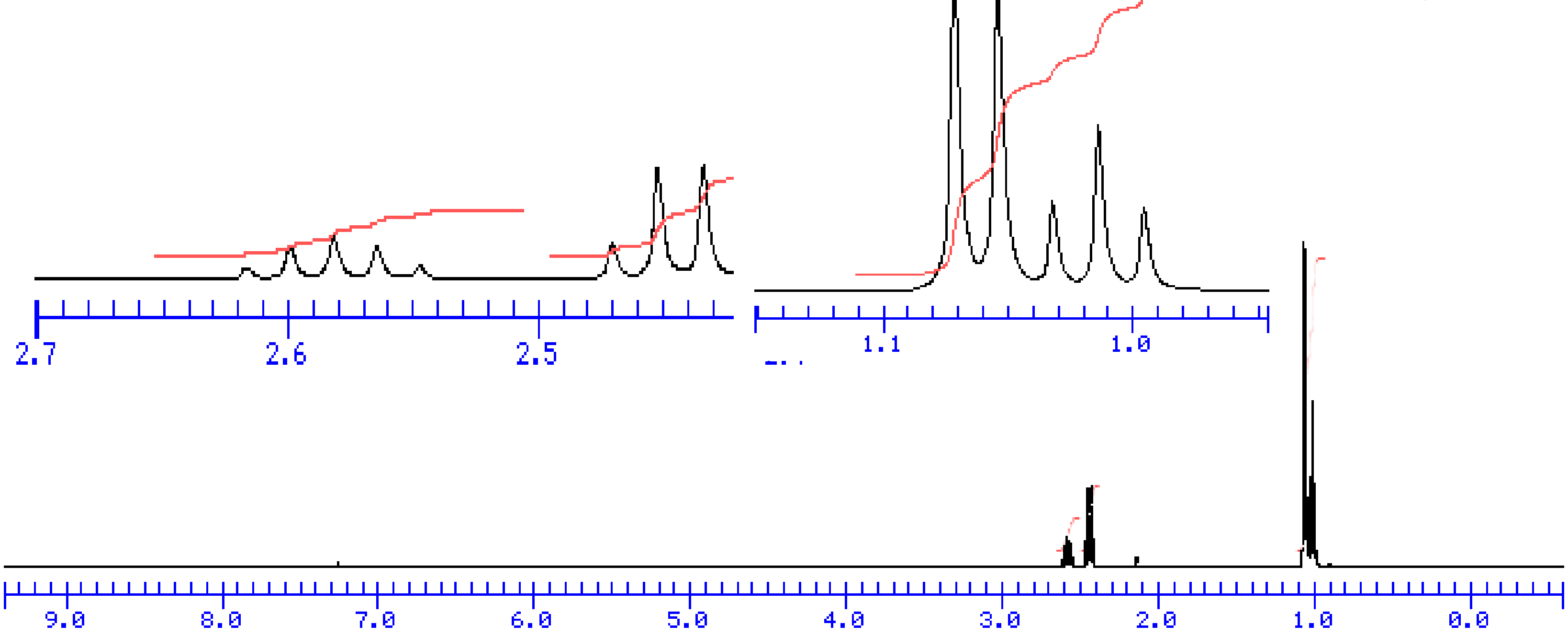
applied field β_0

Splitting pattern for ethyl isopropyl ketone

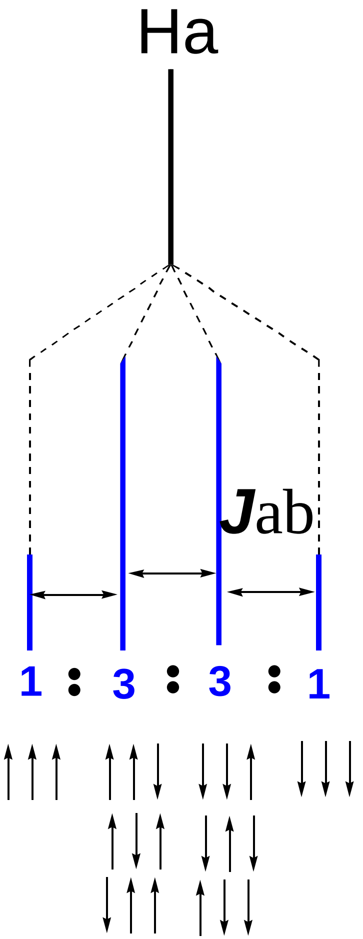
$C_6H_{12}O$

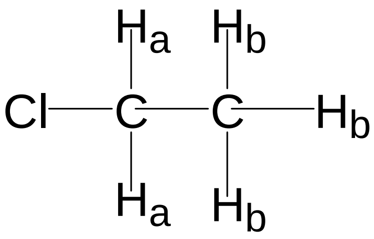
2-methyl-3-pentanone

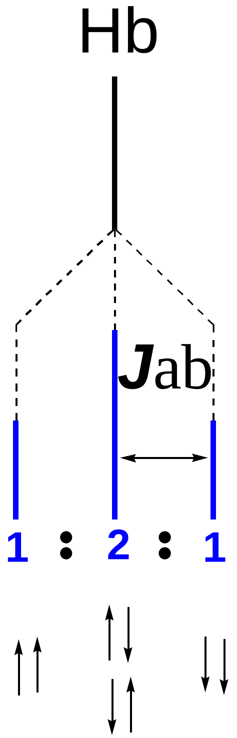




Splitting Pattern for Ethyl Group



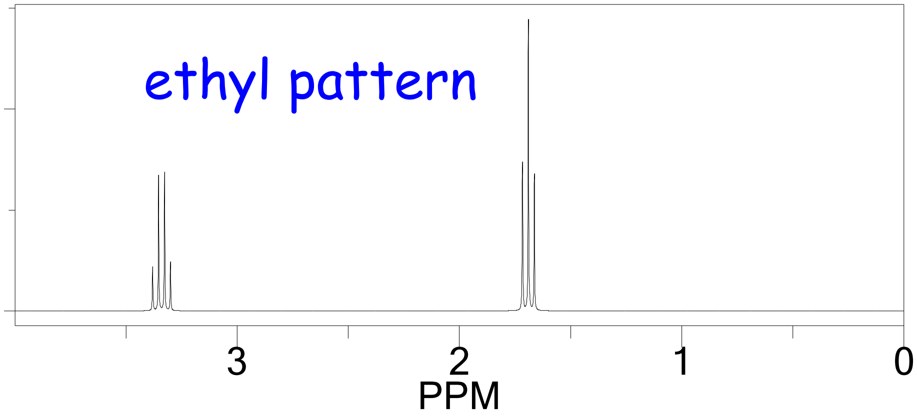


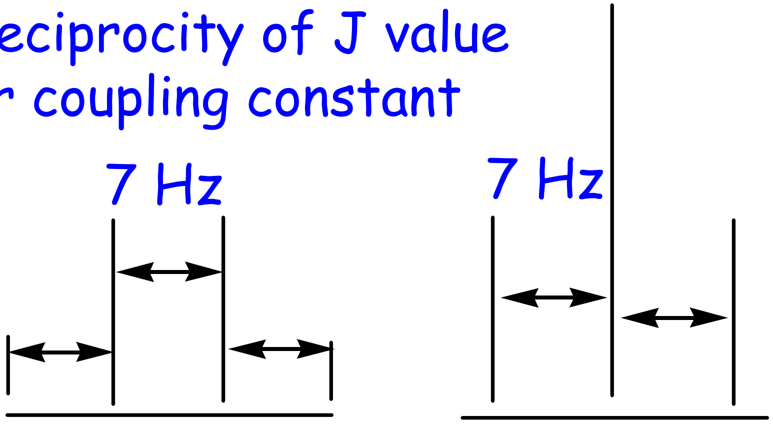


Reciprocity of Coupling Constants

- The distance between peaks of a multiplet are called coupling constants or *J values*

$Br{-}CH_2{-}CH_3$





Reciprocity of J value or coupling constant

Pascal’s Triangle

1 singlet
1 1 doublet
1 2 1 triplet
1 3 3 1 quartet
1 4 6 4 1
1 5 10 10 5 1
1 6 15 20 15 6 1

Intensities of the lines in a multiplet can be determined using Pascal's triangle.

NMR spectrum of *p*-xylene (no signal splitting)

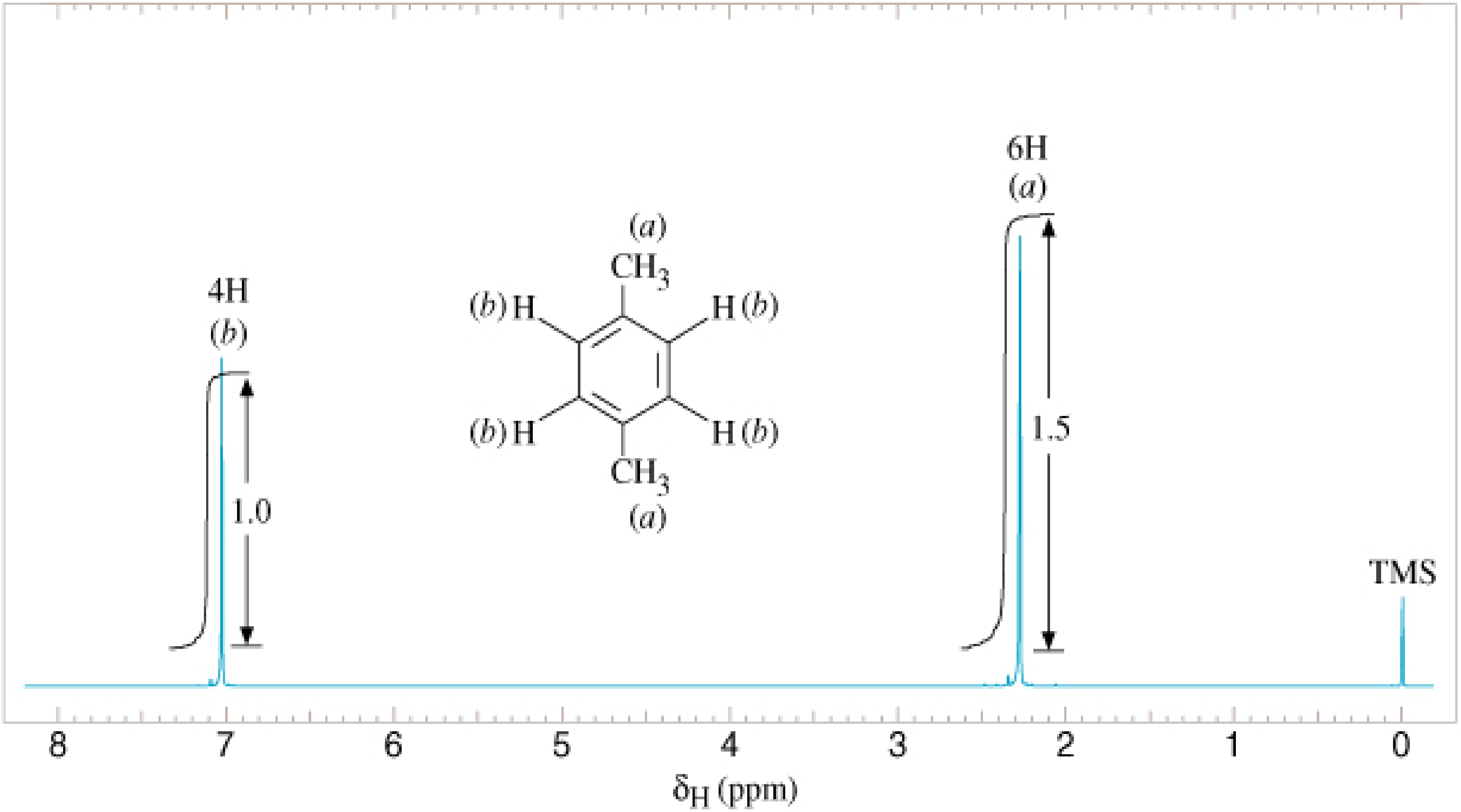


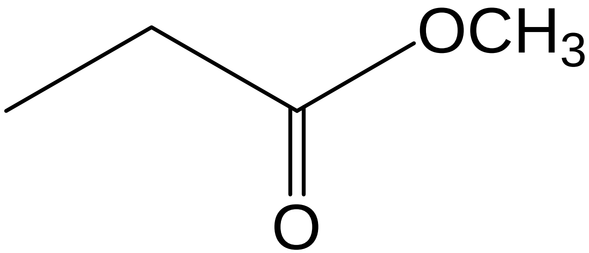
Figure 9.5 The 300 MHz ^{1}H NMR spectrum of 1,4-dimethylbenzene.

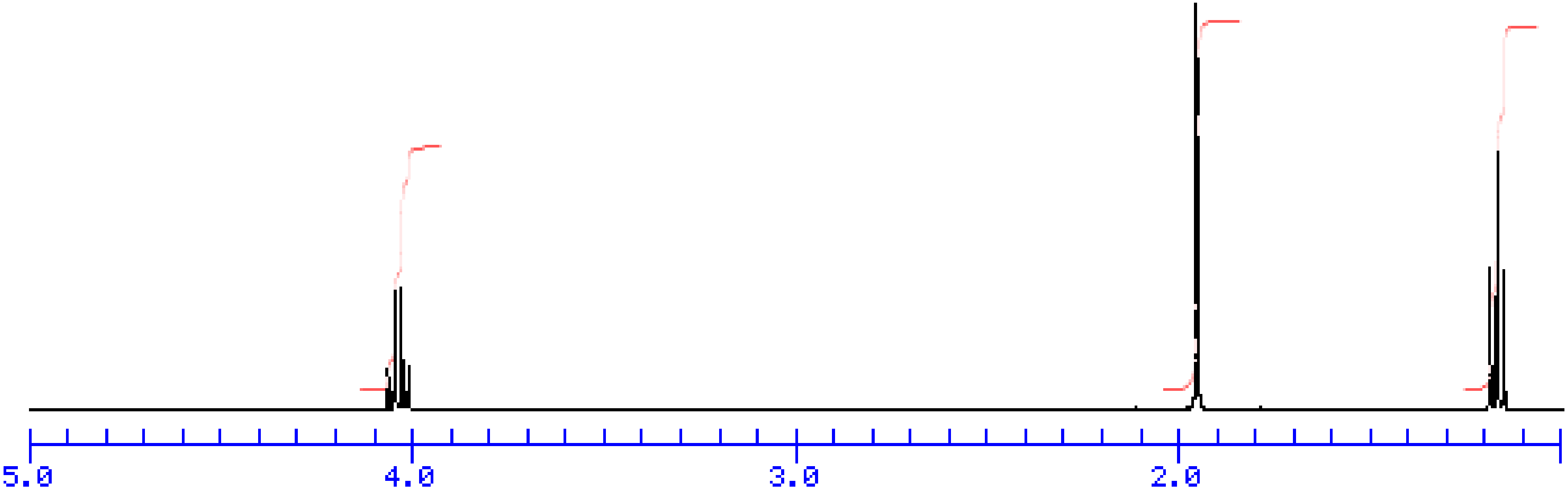
Interpreting Spectra

- Look for diagnostic chemical shifts
- Look for relative ratios (integration)
- Analyze splitting patterns
- Consult Tables of chemical shifts and Tables of coupling constants (*J* values)

methyl propionate

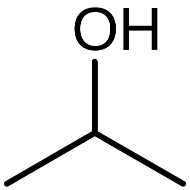
$C_4H_8O_2$

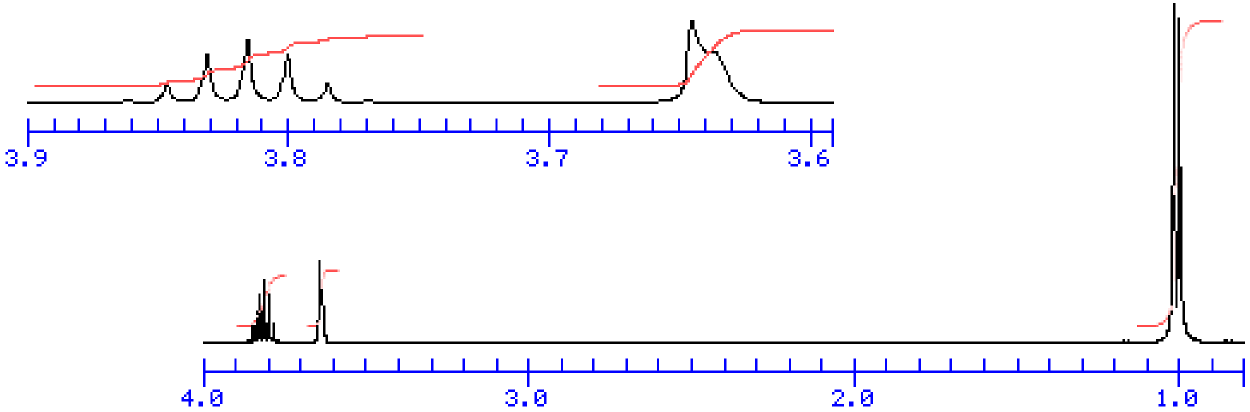




isopropanol

C_3H_8O

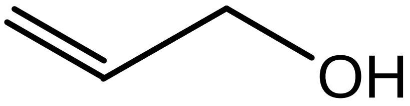


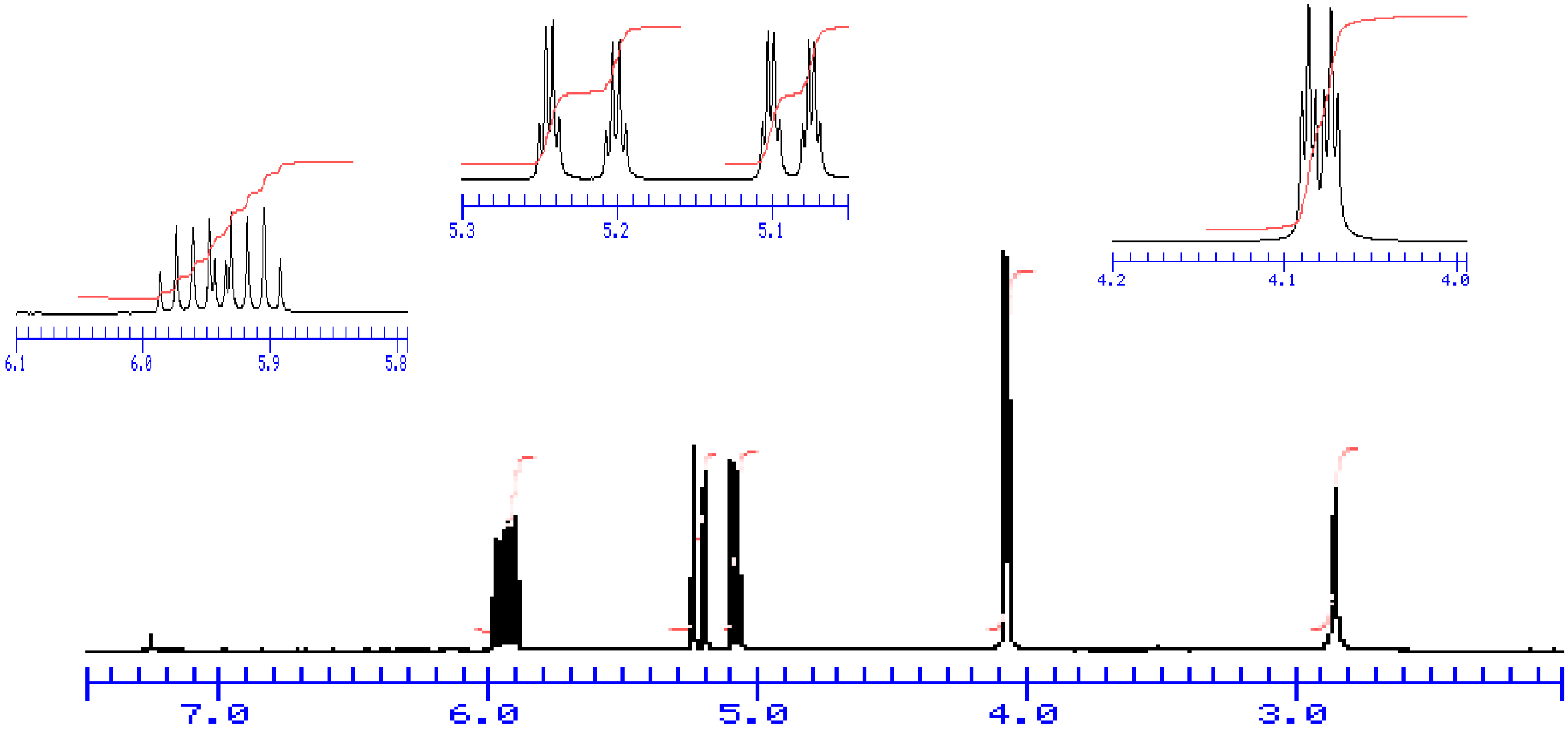


Long-Range Coupling: allyl alcohol

C_3H_6O

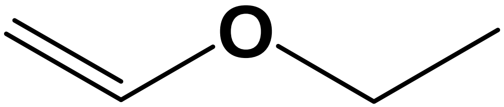
2-propenol

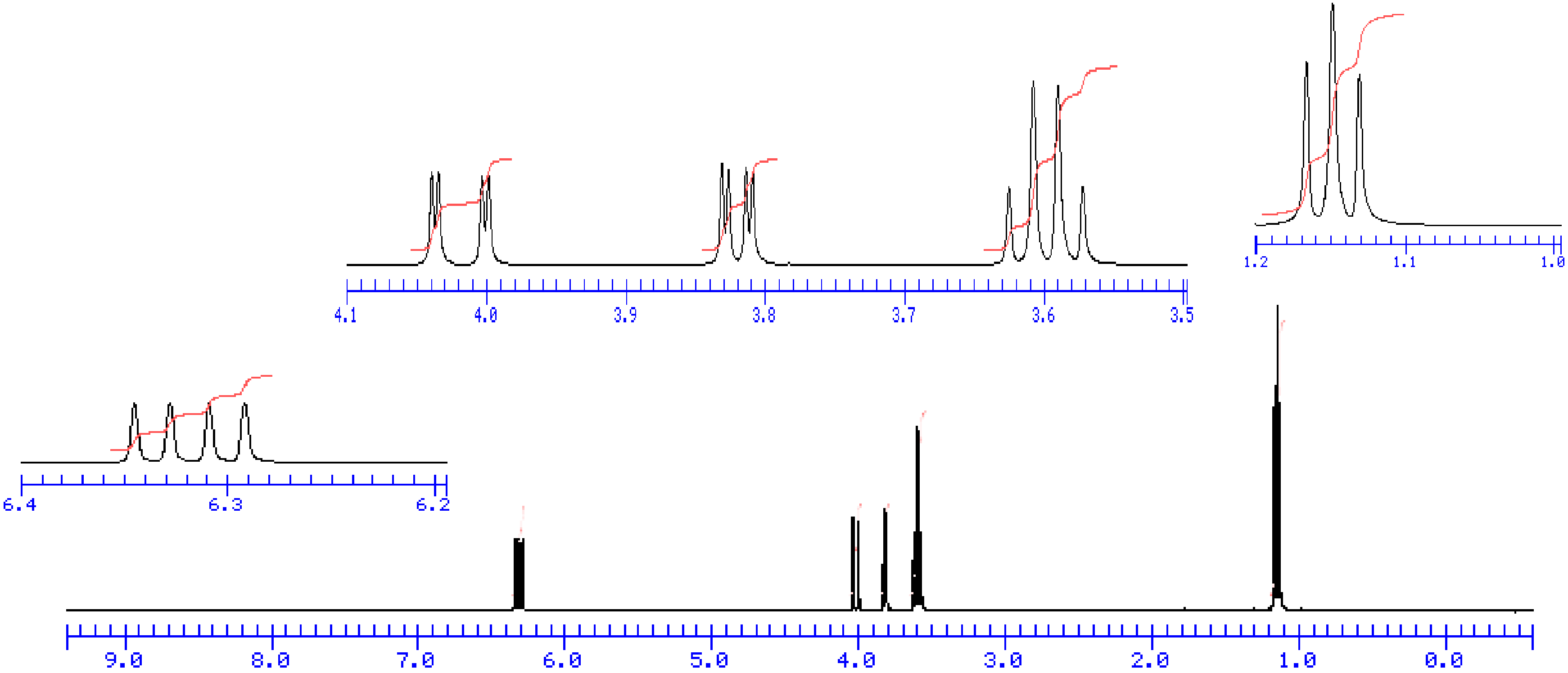




ethyl vinyl ether

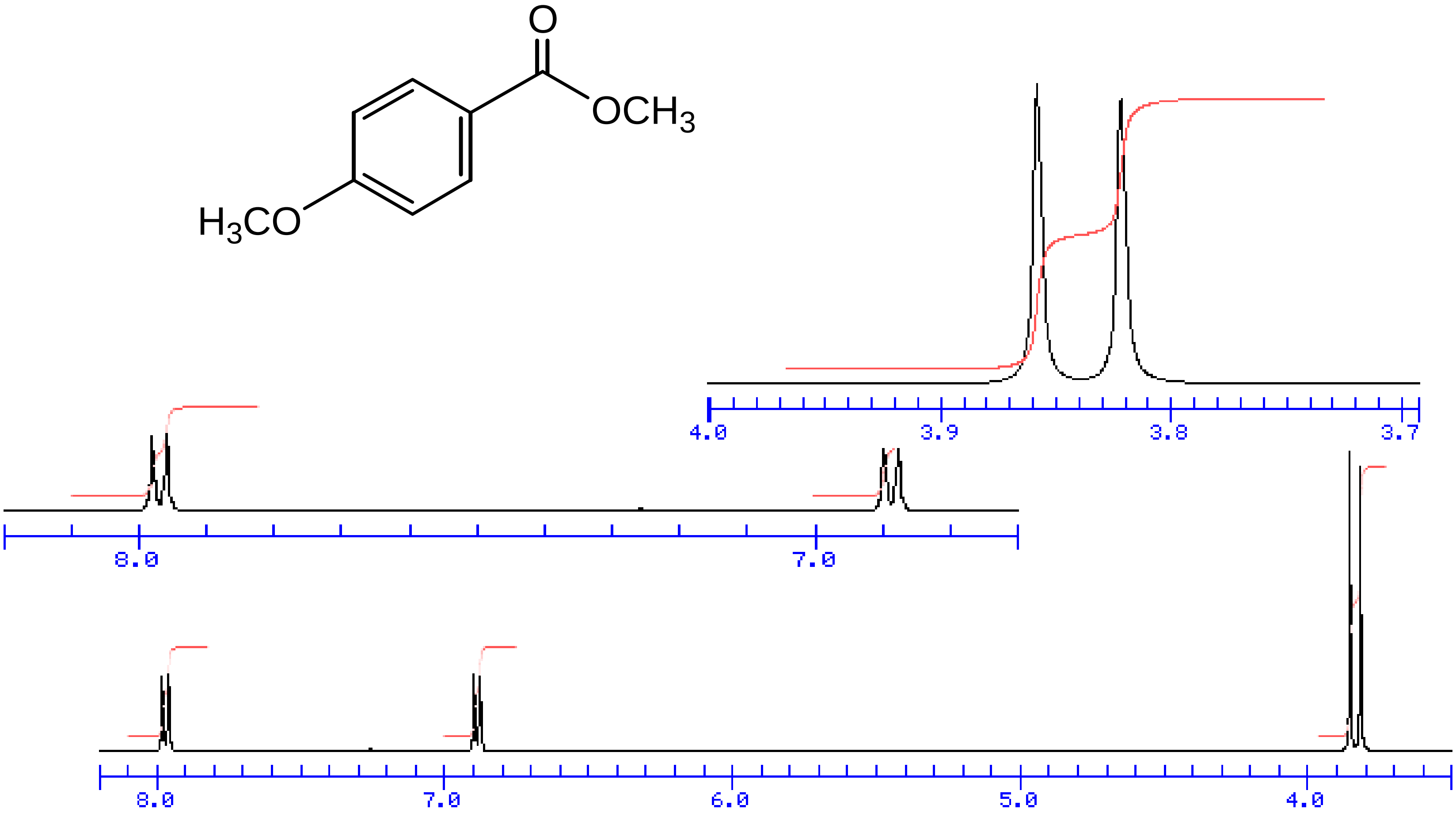
C_4H_8O



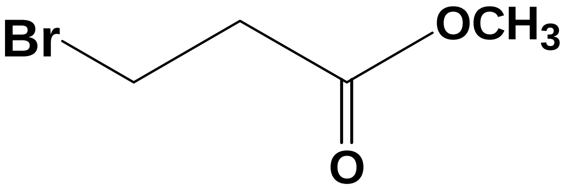


$C_9H_{10}O_3$

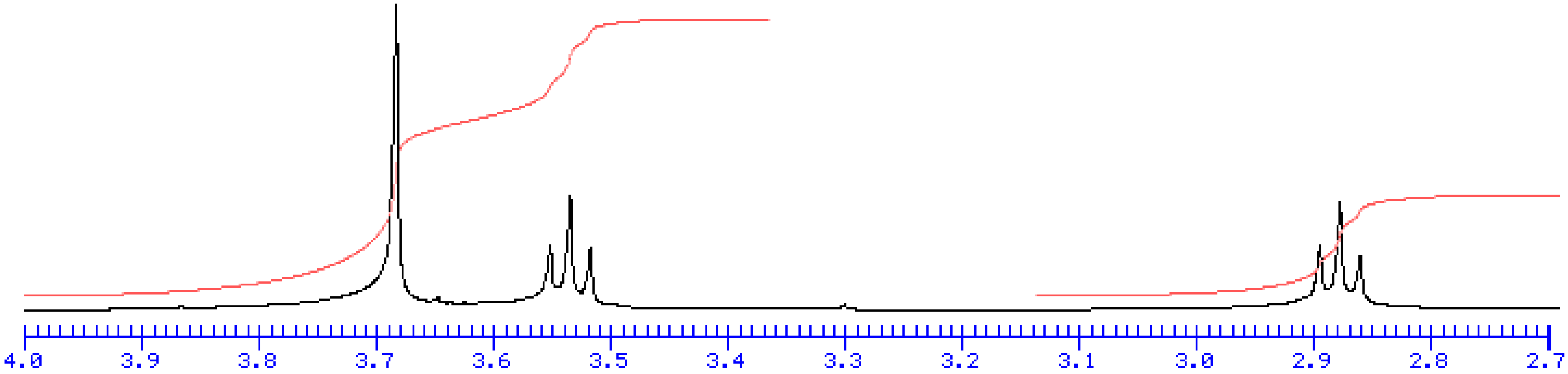
methyl-4-methoxybenzoate



$C_4H_7O_2Br$

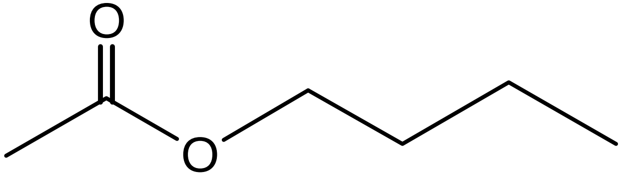


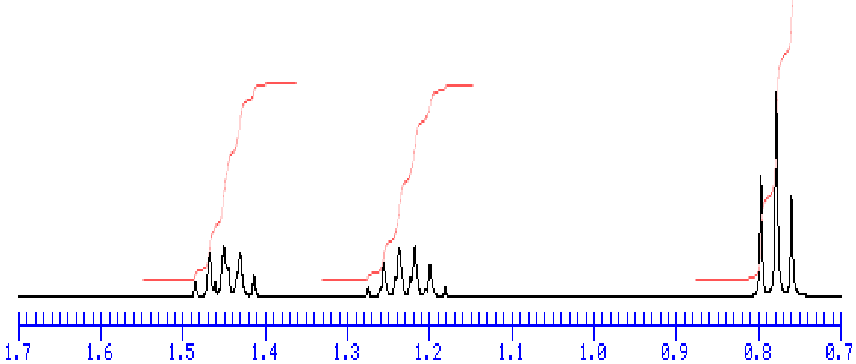
methyl-3-bromopropionate

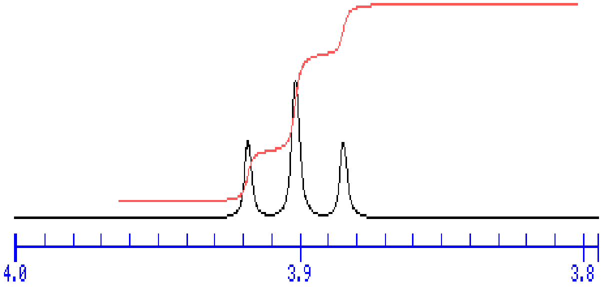


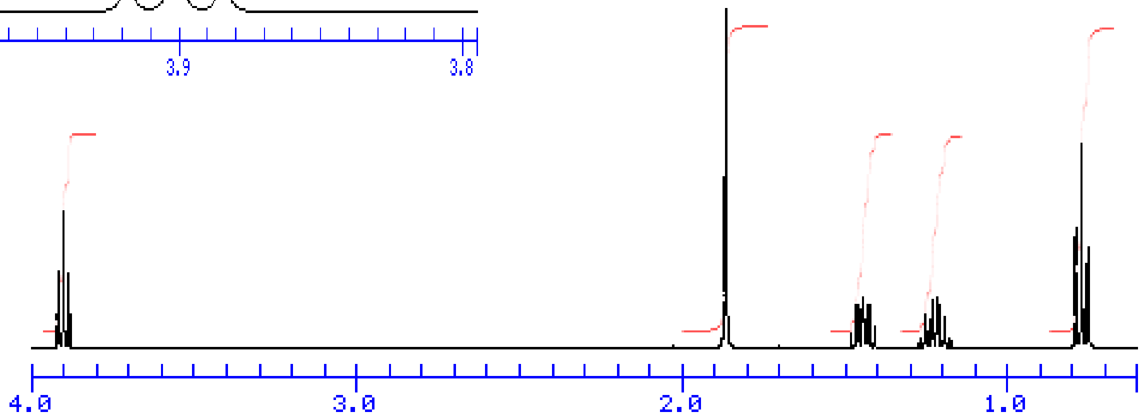
$C_6H_{12}O_2$

butyl acetate

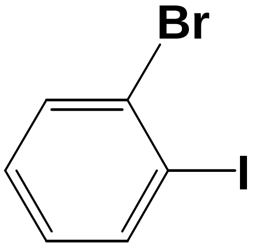




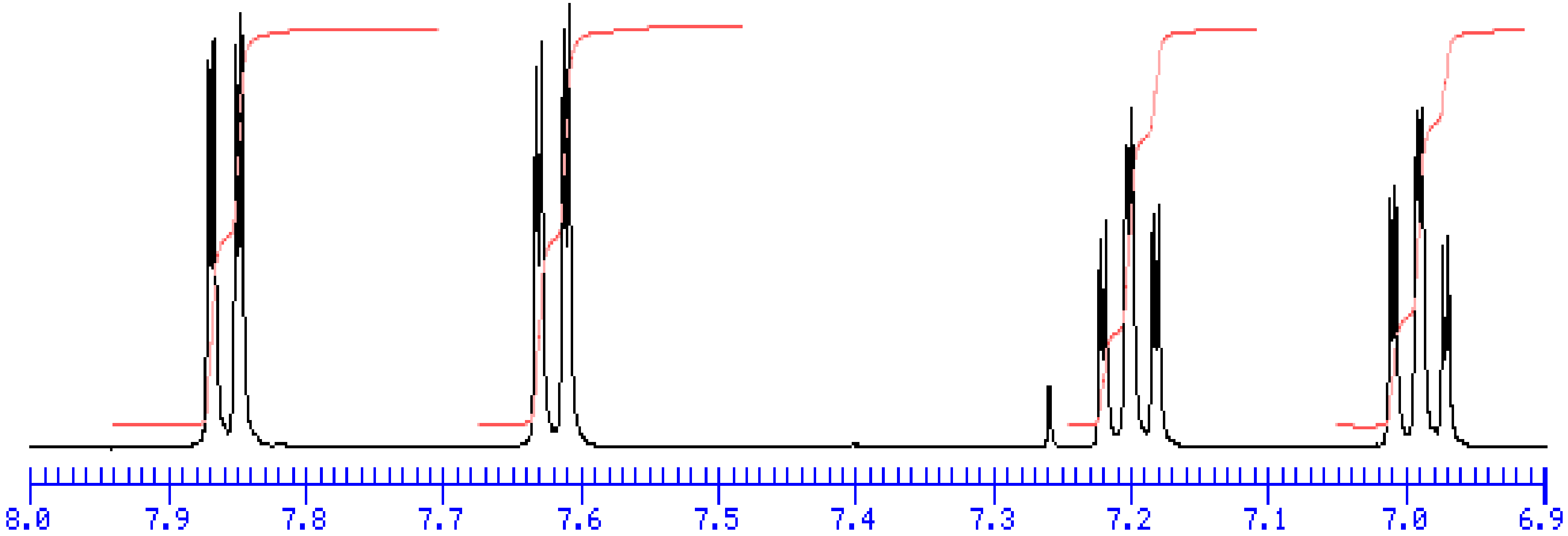




C_6H_4BrI

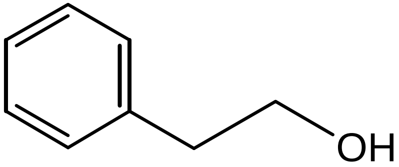


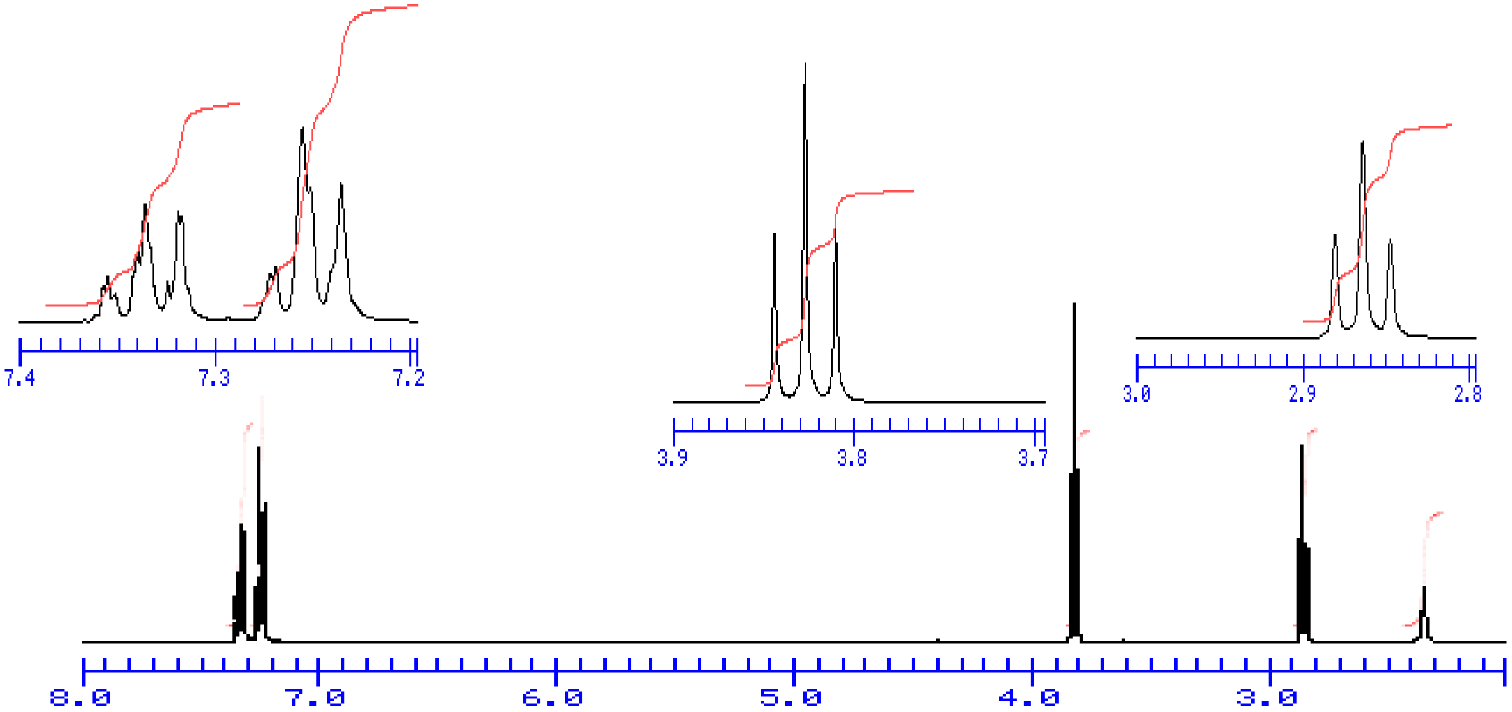
1-bromo-2-iodobenzene



$C_8H_{10}O$

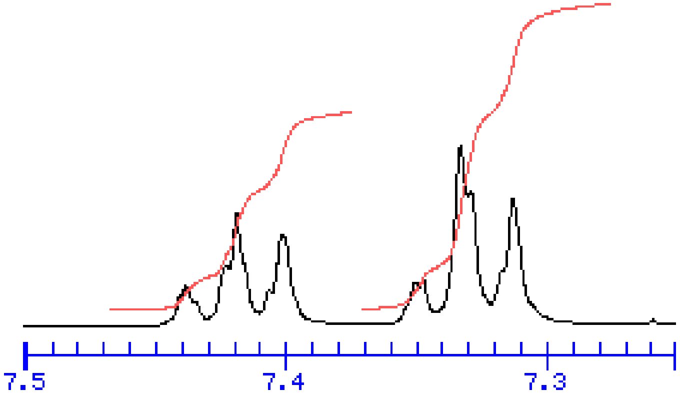
2-phenyl ethanol



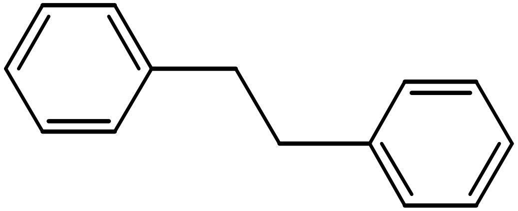


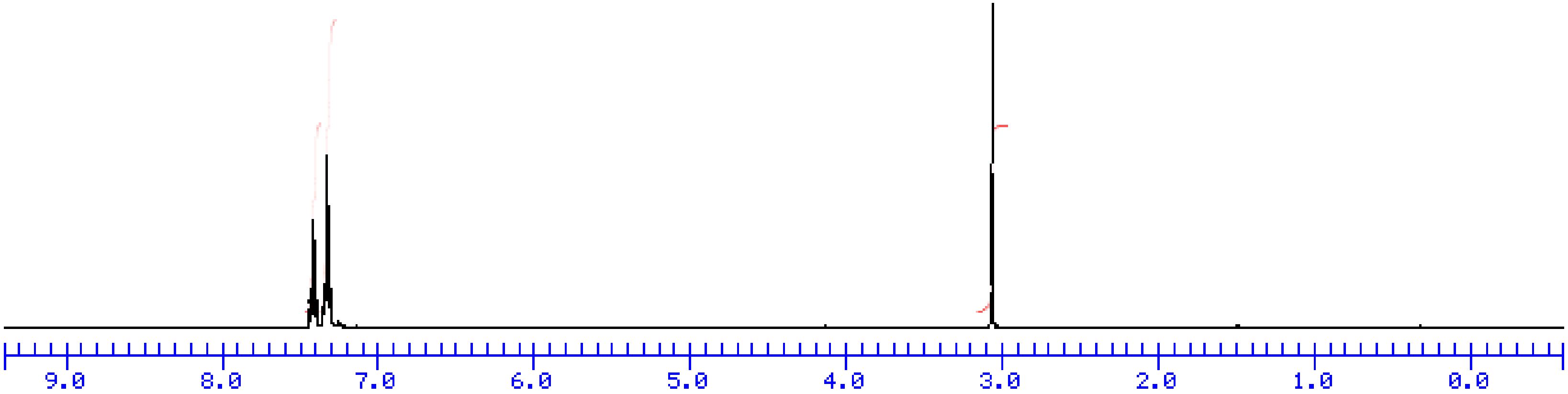
More complex spectra to follow…

$C_{14}H_{14}$



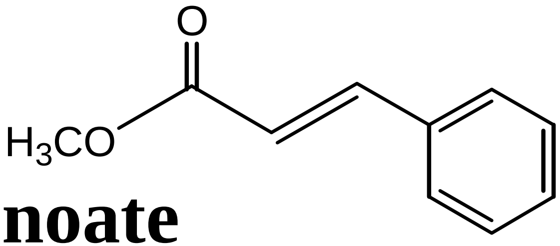
1,2-diphenylethane

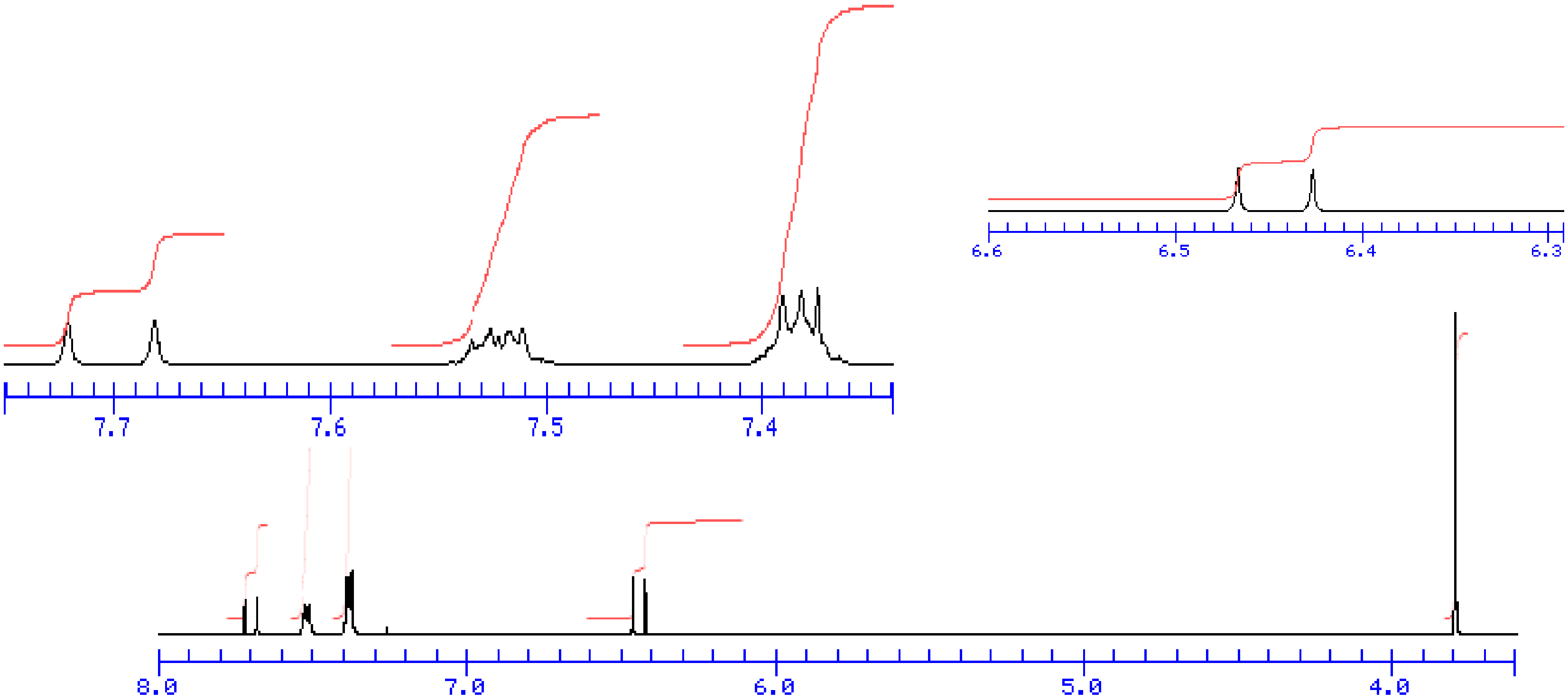




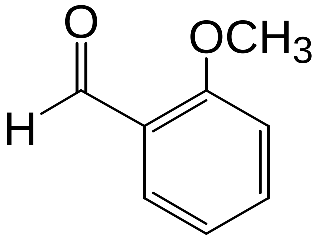
$C_{10}H_{10}O_2$

methyl cinnamate
methyl-3-phenylpropenoate

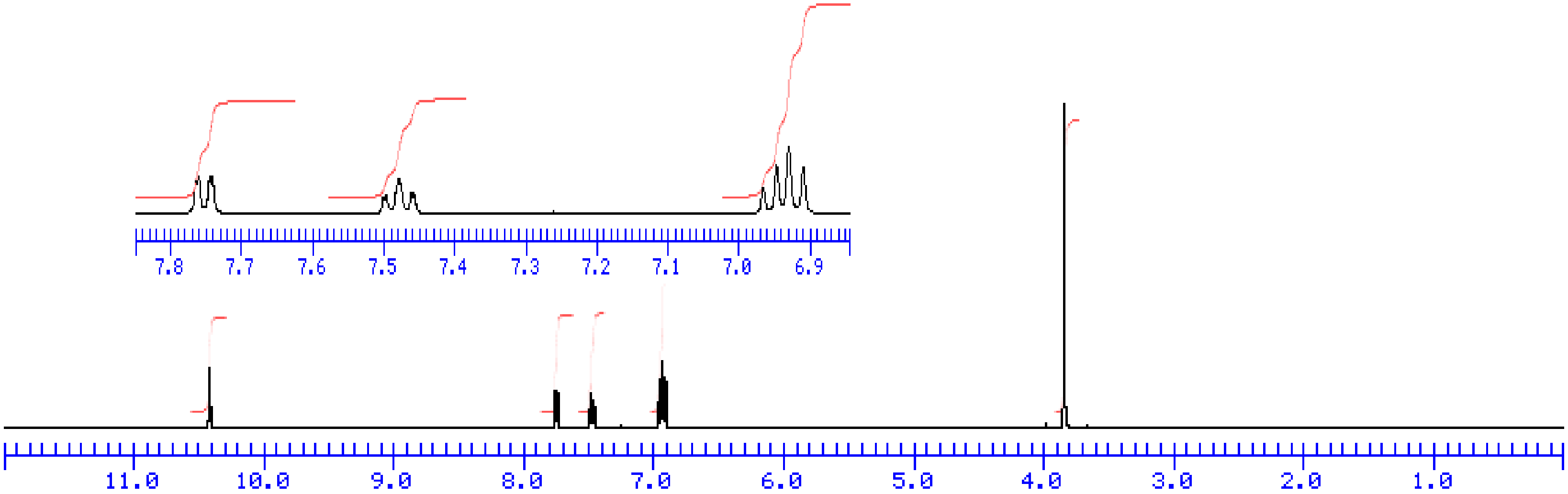




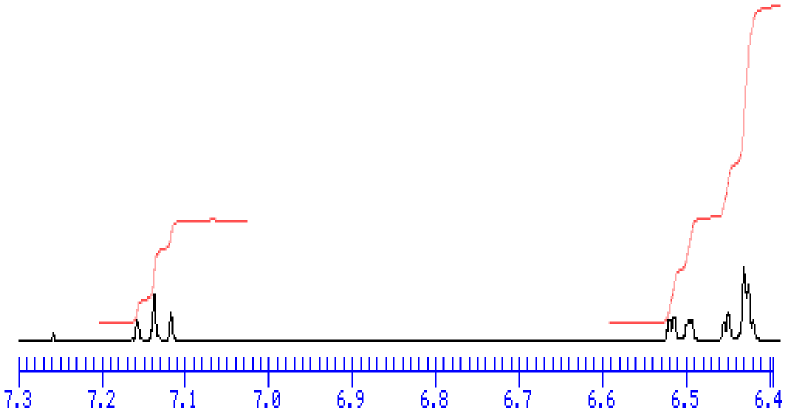
$C_8H_8O_2$



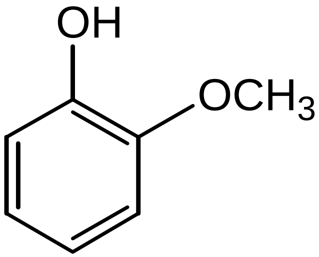
2-methoxybenzaldehyde
o-anisaldehyde

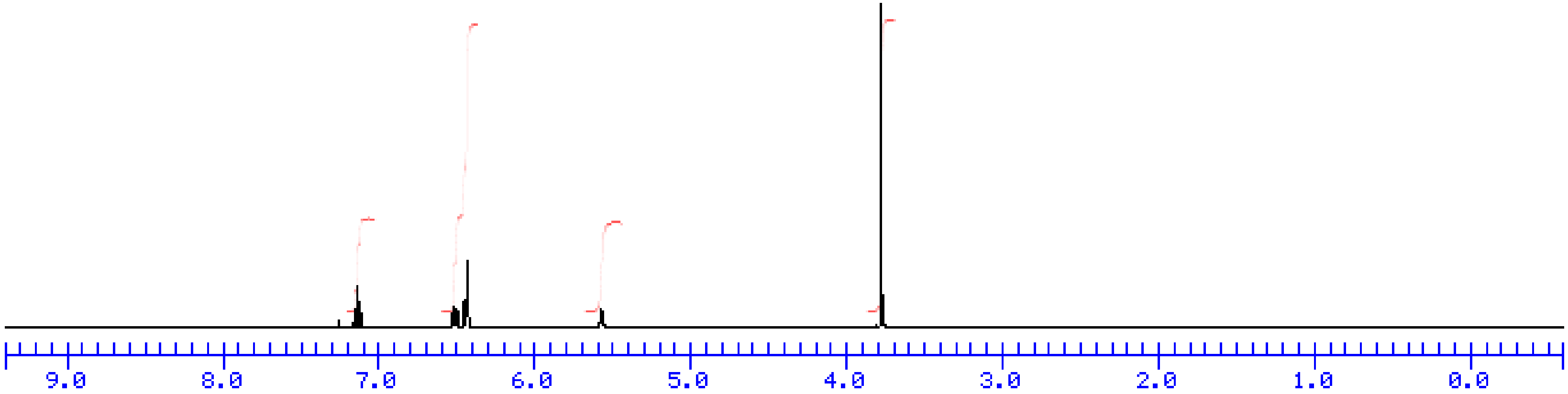


$C_7H_8O_2$



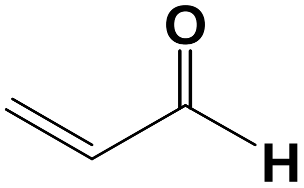
3-methoxyphenol

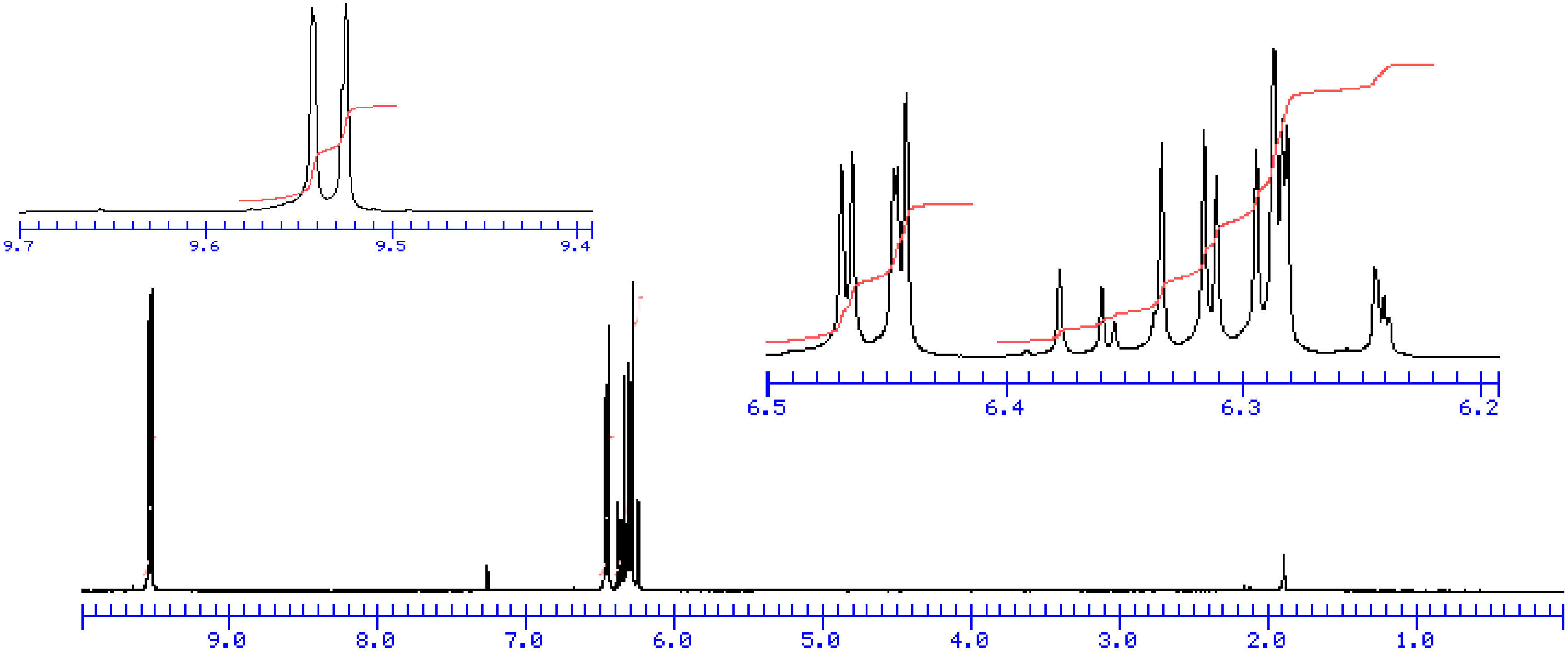




C_3H_4O

propenal
acrolein

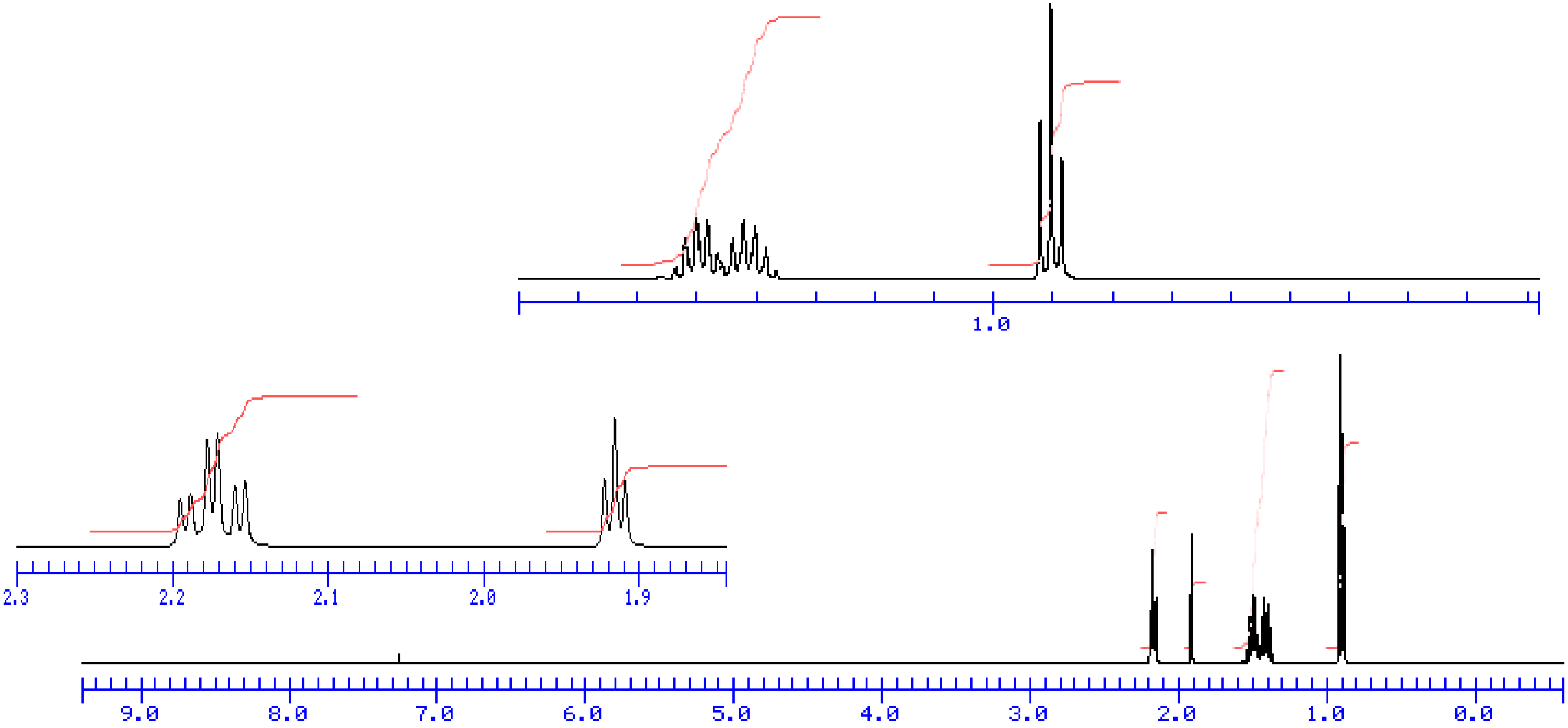




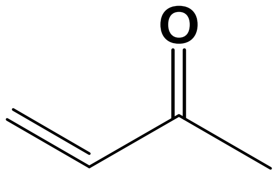
C_6H_{10}

$H-C\equiv C-CH_2-CH_2-CH_2-CH_3$

1-hexyne



C_4H_6O



methyl vinyl ketone