Chemistry 233

Chapter 13

NMR Spectroscopy

<u>Methods for Structure Determination</u>

NMR Spectroscopy – Carbon-Hydrogen Framework

Infrared Spectroscopy – Functional Groups

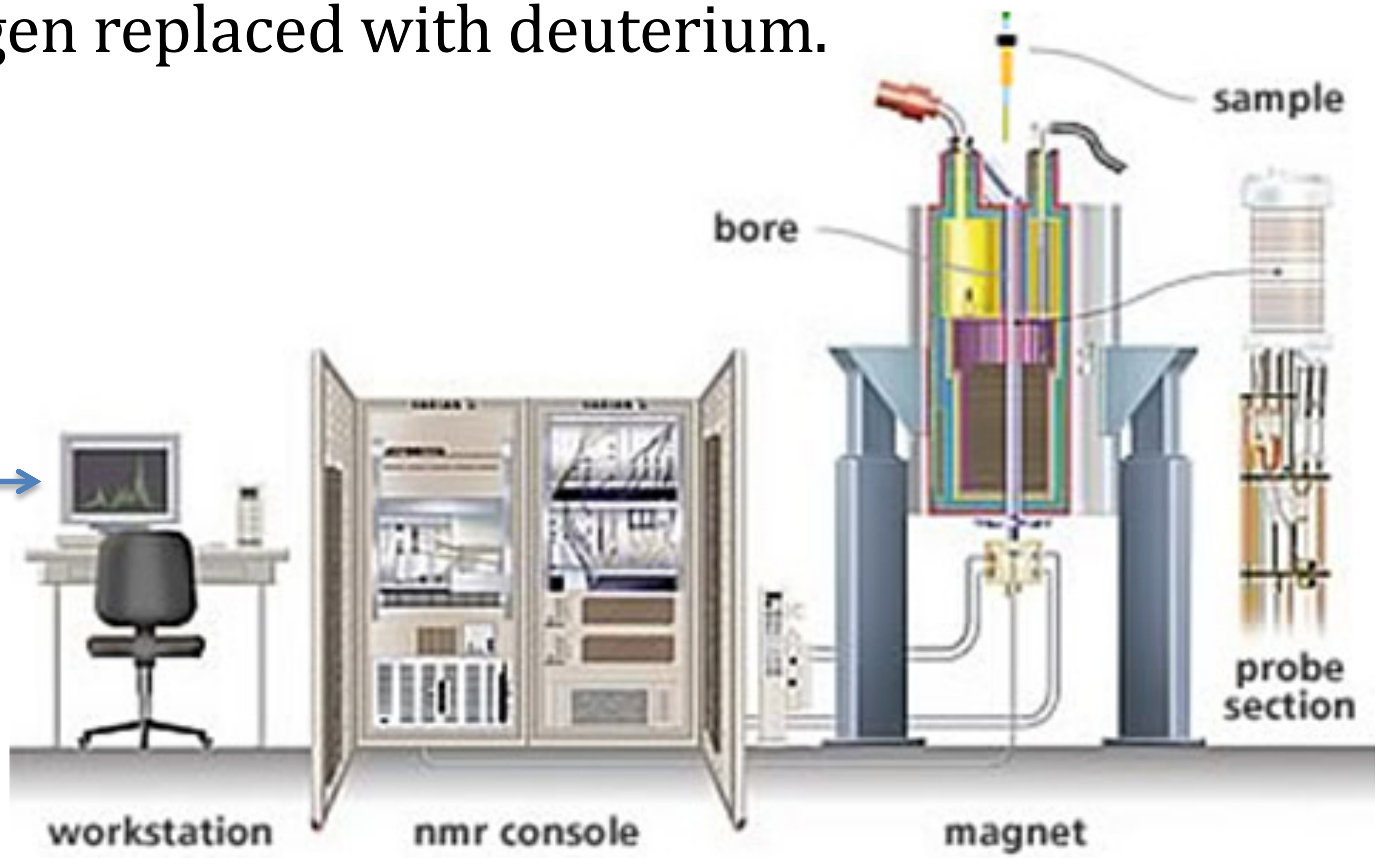
Mass Spectrometry – Molecular weight and formula

NMR Spectroscopy

NMR = Nuclear Magnetic Resonance
Resonance of certain nuclei (^{1}H, ^{13}C, and others) in the presence of a magnetic field.

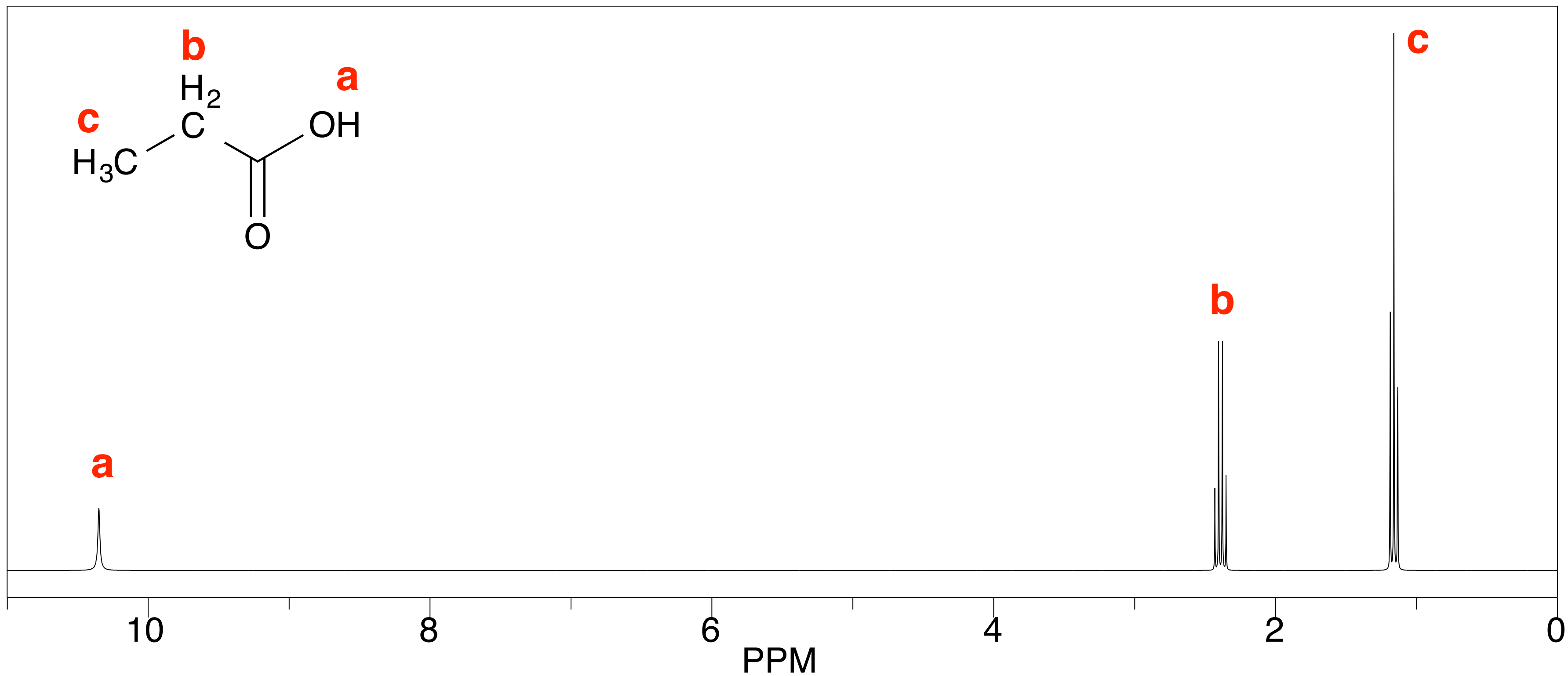
Sample is dissolved in an NMR solvent – A solvent that has had all the hydrogen replaced with deuterium.

NMR spectrum is produced



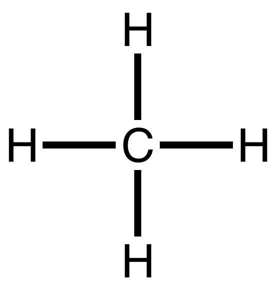
Sample ^{1}H (Proton) NMR

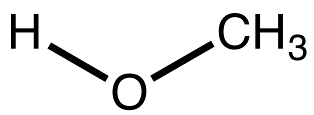
Each distinct type of hydrogen in the molecule produces a signal in the spectrum.



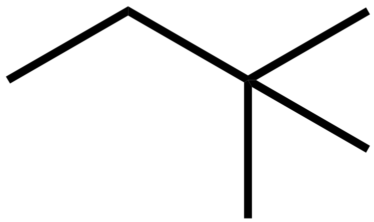
Chemically Equivalent/Distinct H

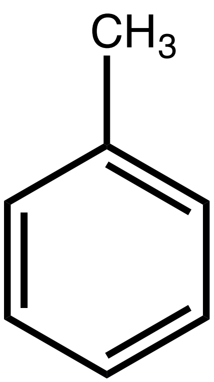
- Different types H in a molecule react differently -- consider the selectivity of radical halogenation.
- In proton (^{1}H) NMR, each distinct type of H gives rise to a signal.



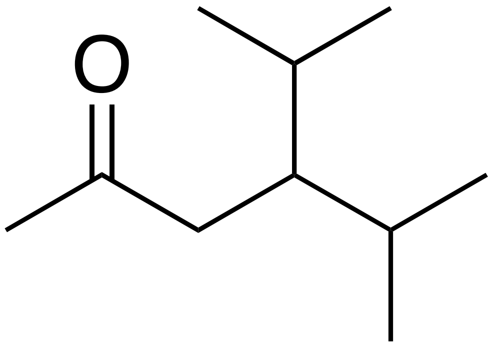


Chemically Equivalent/Distinct H





Question



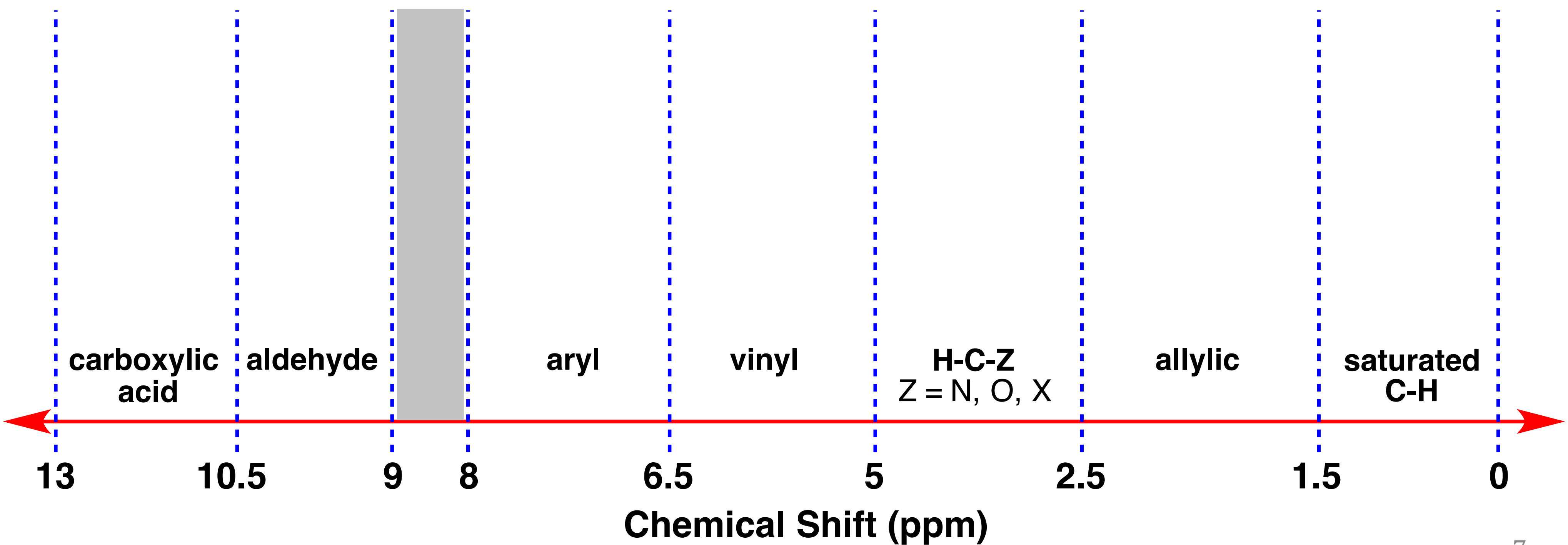
- How many distinct types of hydrogen are present in the molecule shown?

- How many distinct types of carbon are present in the molecule shown?

Chemical Shift

- Where between 0 and 13 ppm will the signals show up?
- Different H's live in different environments depending on its neighboring groups.

<u>Basic ^{1}H Chemical Shift Regions:</u>

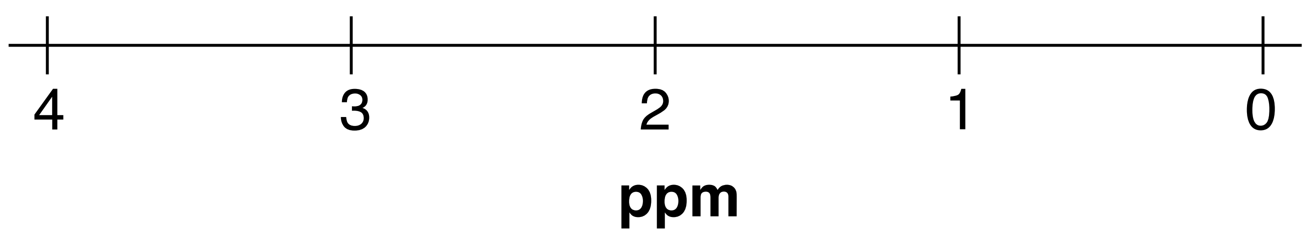


Integration (Peak Height)

The area under a signal is proportional to the number of hydrogen that the signal corresponds to.

Example:

$Cl-CH_2-CH_2-CH_3$

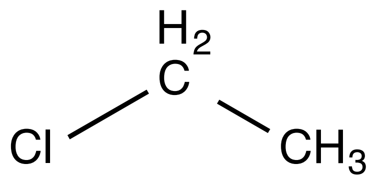


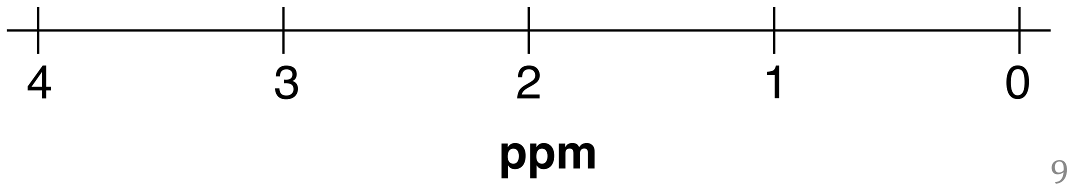
Coupling (Splitting of Signals)

The signal corresponding to a particular proton will split due to the protons on adjacent carbons.

Follows the n+1 rule where n = # of H's on adjacent C.

Example: Predict the ^{1}H NMR Spectrum for:

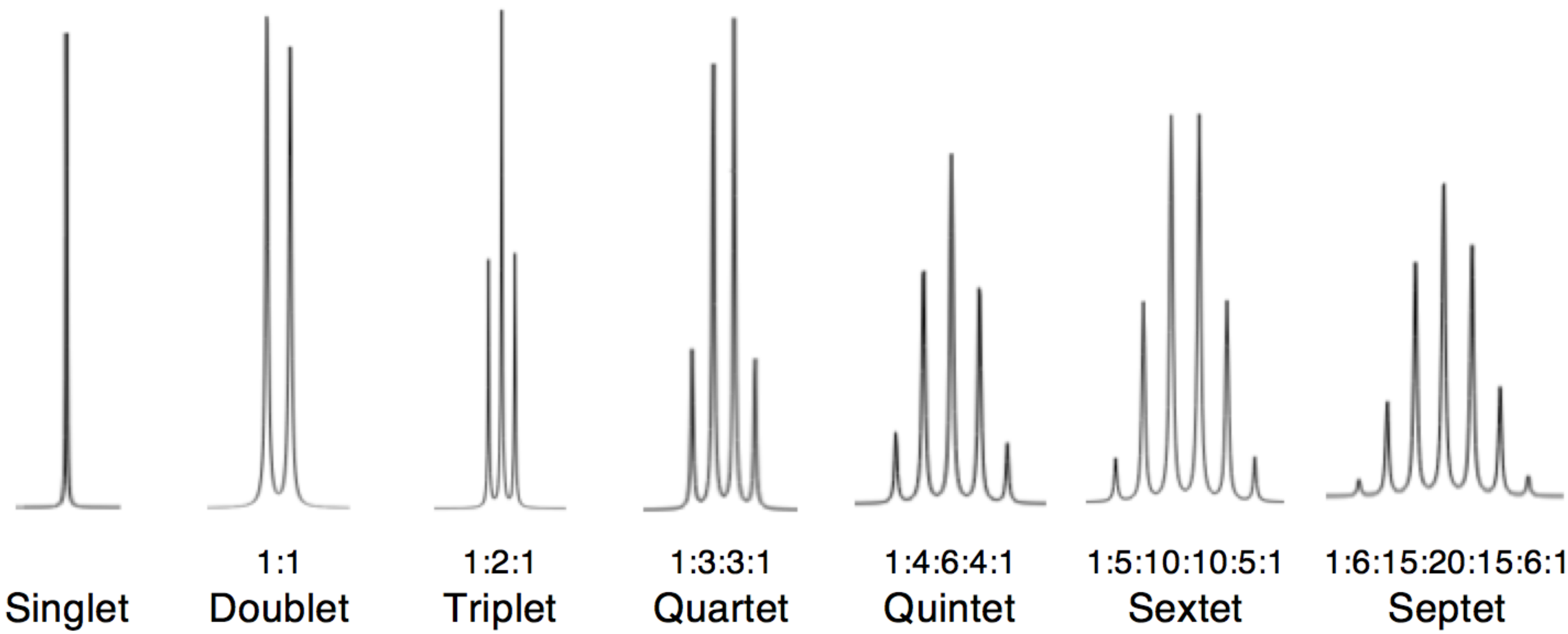




Common Multiplicities

# peaks	Multiplicity	Abbr.
1	singlet	s
2	doublet	d
3	triplet	t
4	quartet	q

# peaks	Multiplicity	Abbr.
5	quintet	quin
6	sextet	sex
7	septet	sep
>7	multiplet	m



Question

- Predict the splitting pattern for protons labeled a, b, and c, giving that for "a" first.

$$\mathrm{Cl{-}C\overset{a}{H}_2{-}C\overset{b}{H}_2{-}O{-}C\overset{c}{H}_3}$$

A. doublet, doublet, singlet

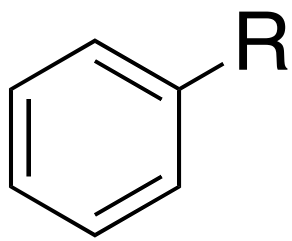
B. multiplet, triplet, singlet

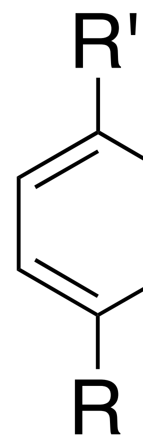
C. triplet, multiplet, triplet

D. triplet, triplet, singlet

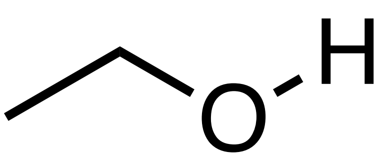
E. all singlets

Splitting in Aromatic Rings

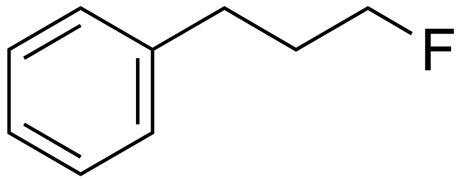


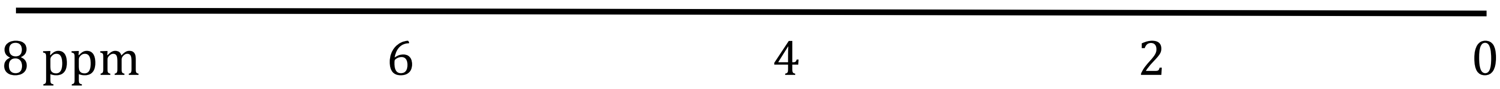


Typically no coupling through heteroatoms



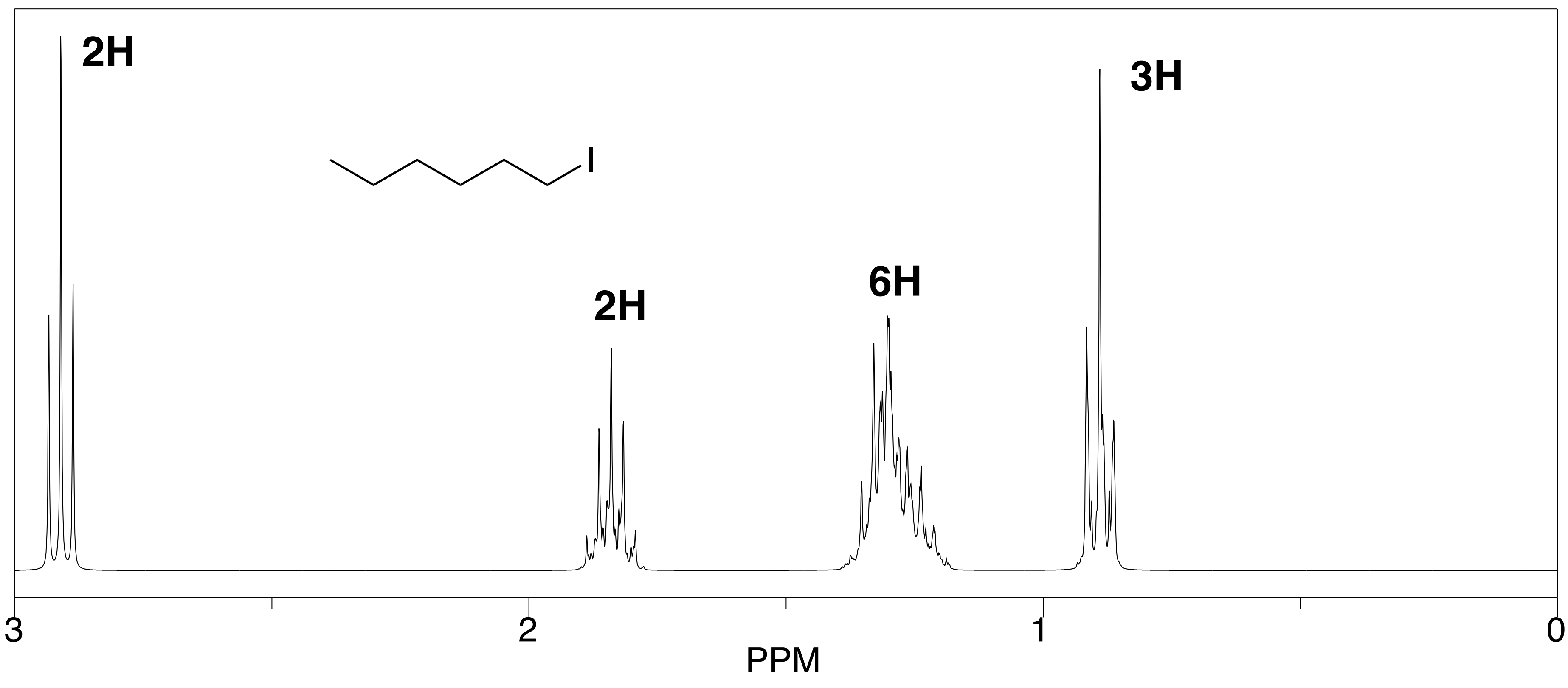
Example



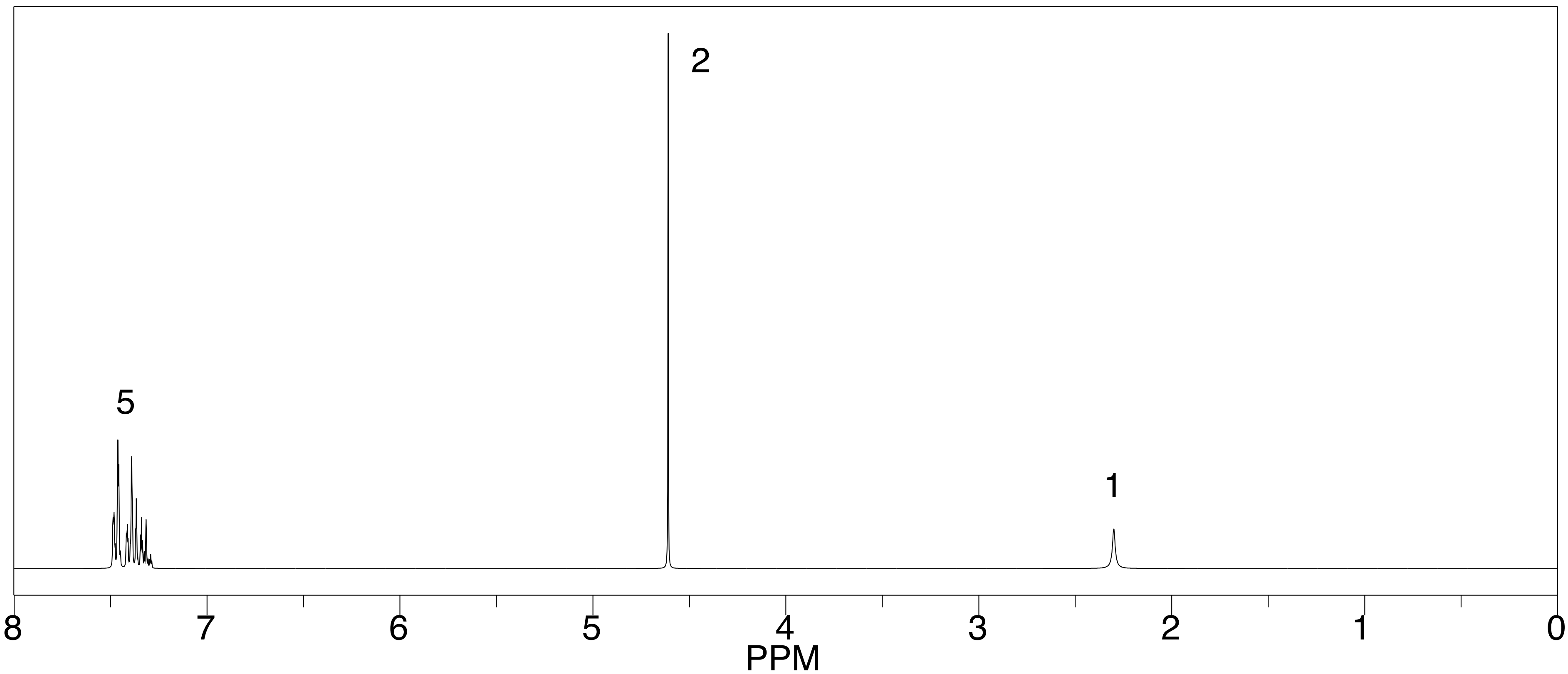


Overlapping Signals

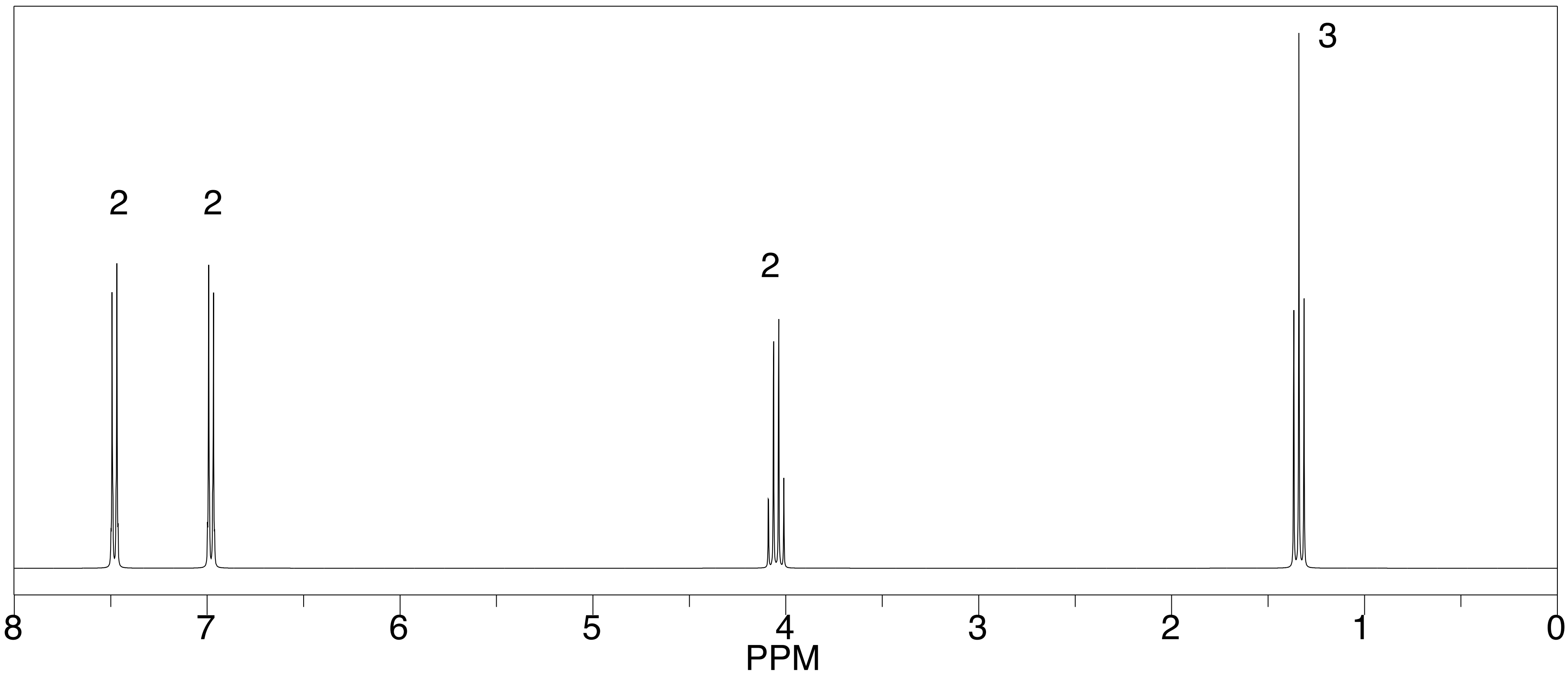
Protons that are chemically distinct, yet have similar chemical environments can potentially overlap creating a multiplet.



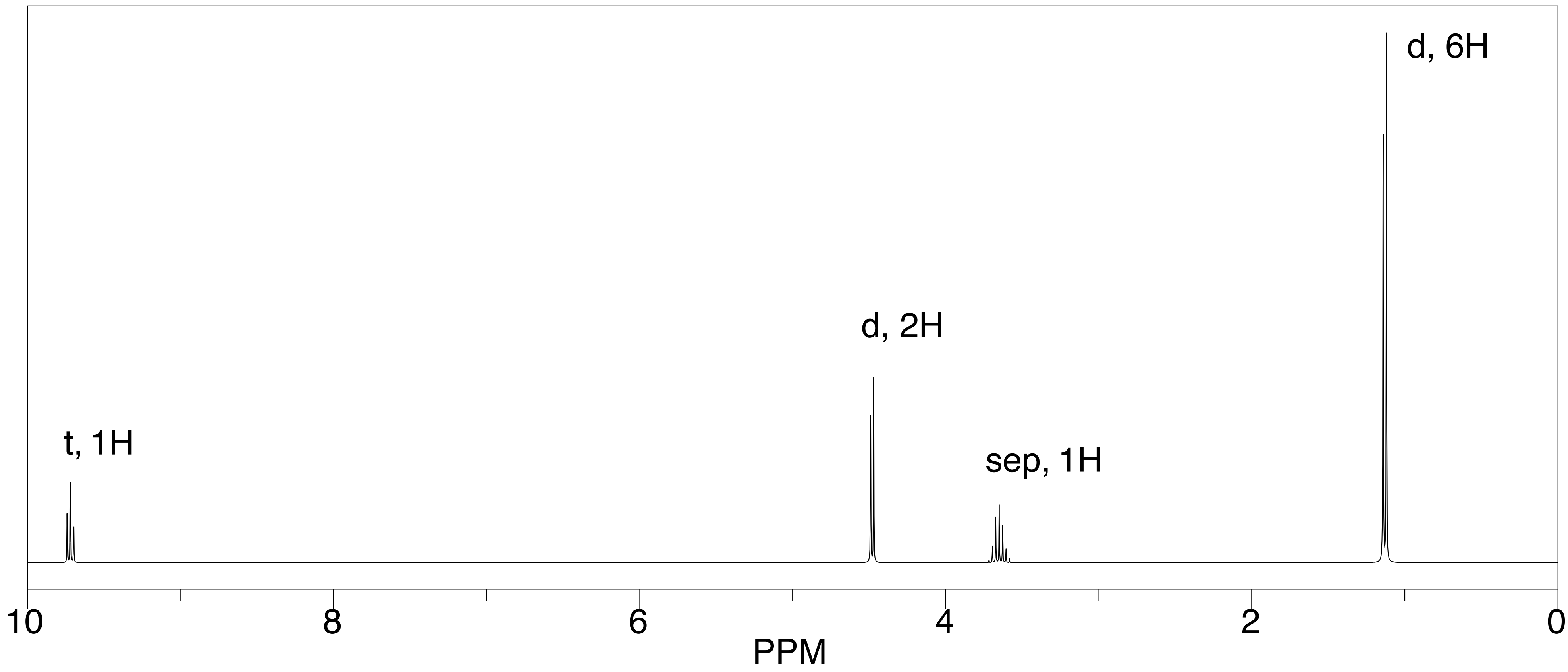
Example 1 – C_7H_8O



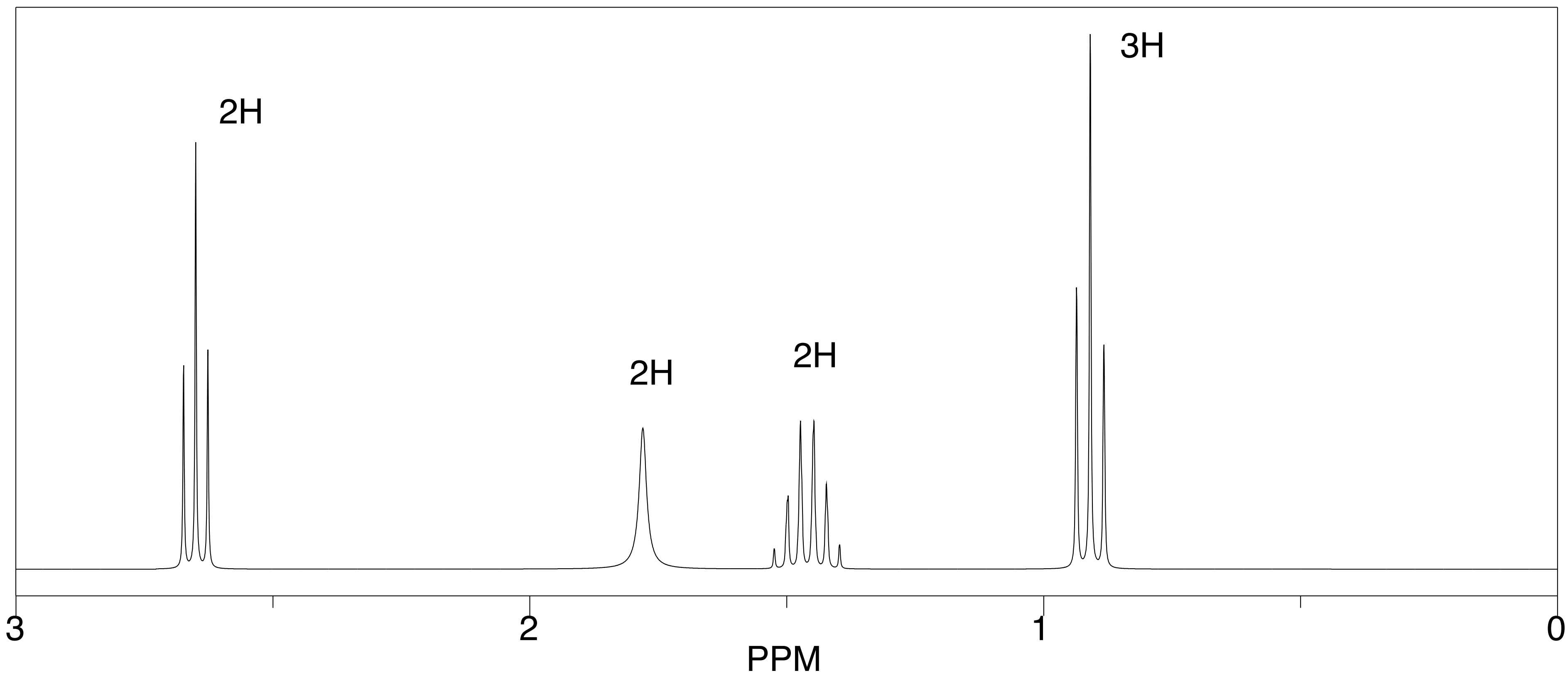
Example 2 – C_8H_9BrO



Example 3 – $C_5H_{10}O_2$

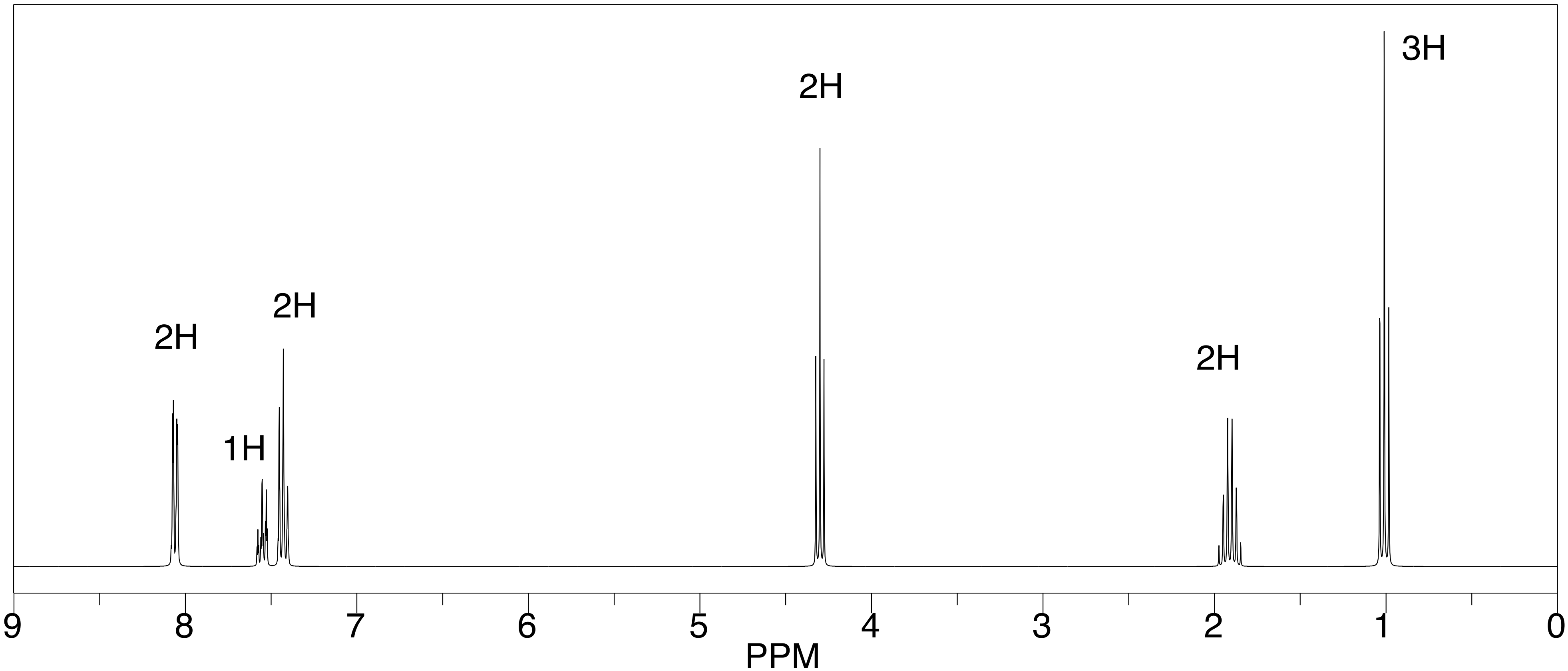


Example 4 – C_3H_9N

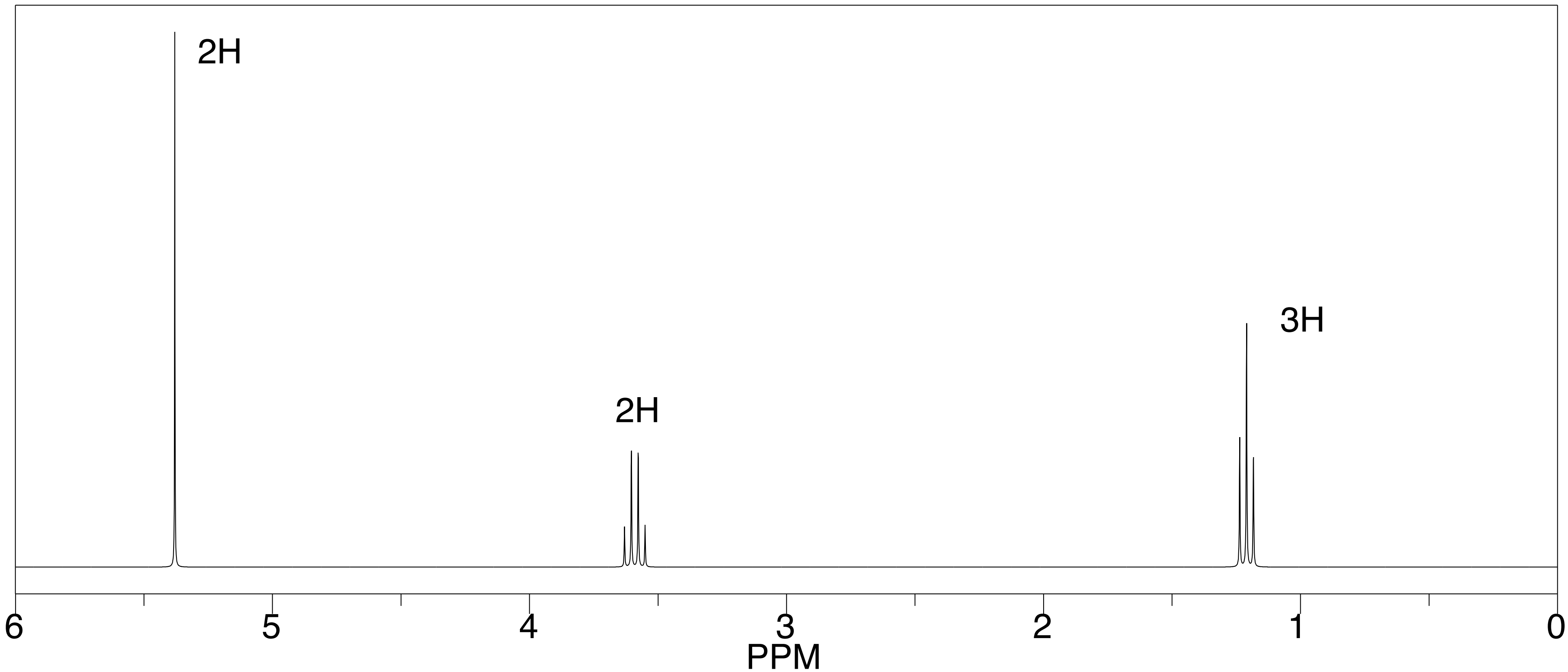


Example 5 – $C_{10}H_{12}O_2$

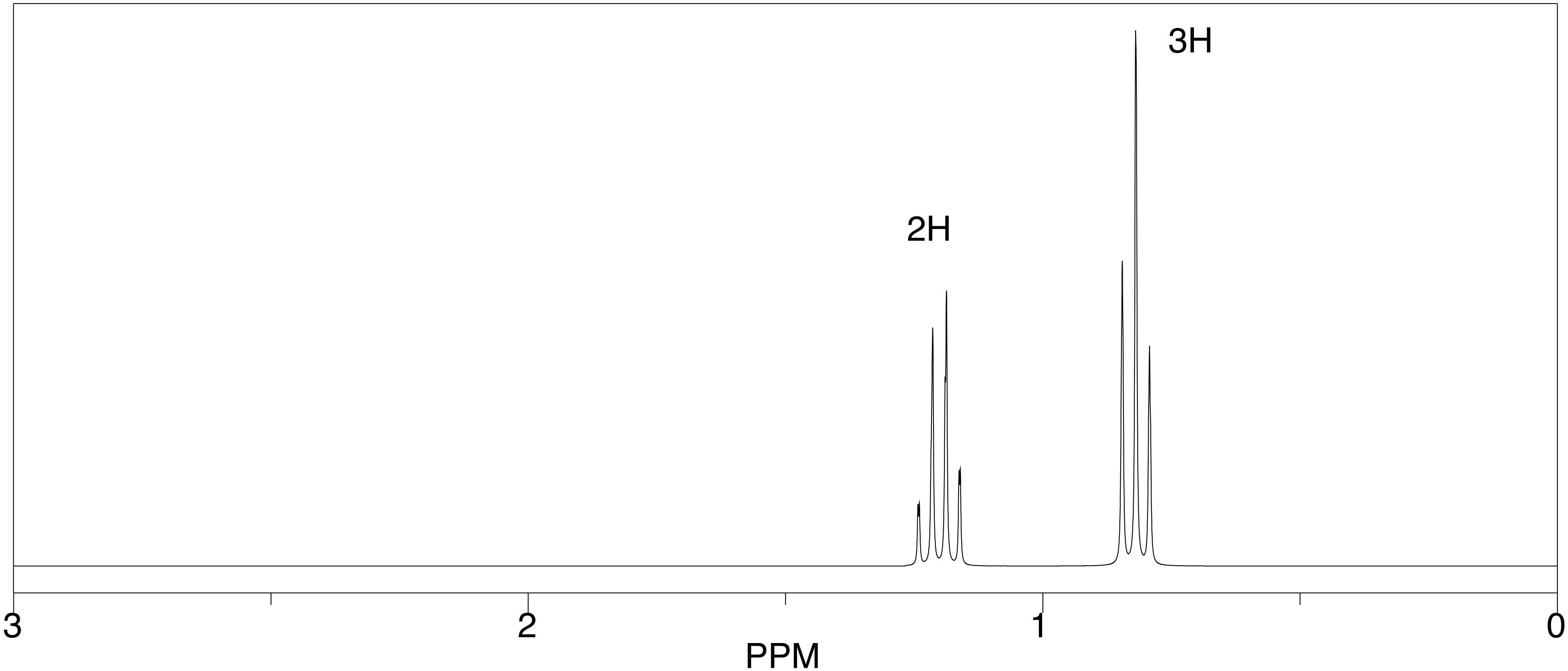
IR Data: 1720, 1610, 1505, 1210, 1010 cm^{-1}



Example 6 – C_3H_7BrO

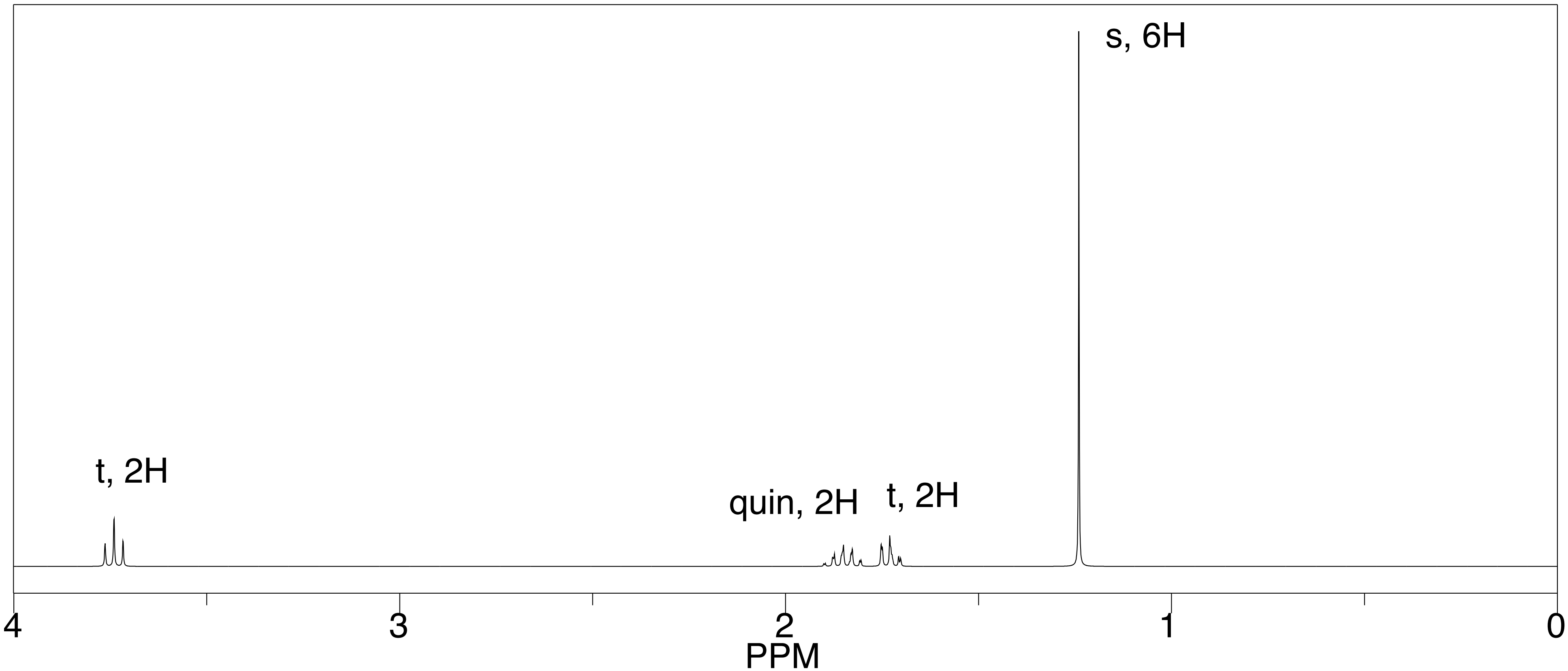


Example 7 – C_9H_{20}



Example 8 – $C_6H_{12}O$

No IR stretches in the 1600-1700 cm^{-1} region



Example 9 – $C_6H_{10}O_2$

IR Data: 3100 (broad, strong); 1730, 1650 cm^{-1}