

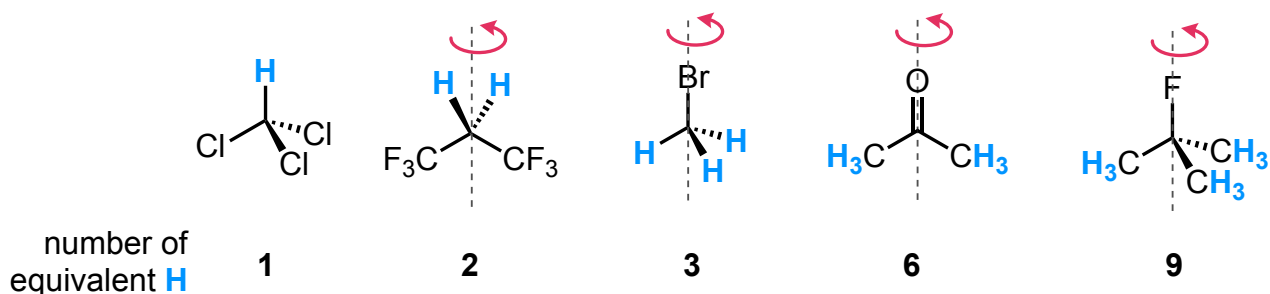
¹H NMR Spectroscopy

NMR spectroscopy is the most powerful and broadly applicable technique available for determining the structure of organic molecules. This can be achieved by considering the (1) number of signals, (2) chemical shift, (3) integration, and (4) splitting patterns in a spectrum.

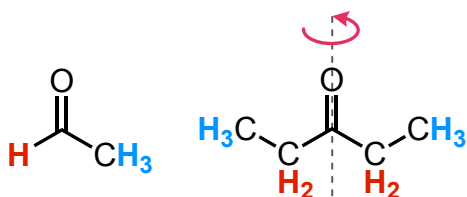
1. Number of Signals

The number of signals corresponds to the number of protons that are in unique chemical environment. Multiple protons are considered to be in the same electronic environment (chemically equivalent) if they can be interchanged through a symmetry operation, such as *rotation* or *reflection*, or if they have fast bond rotation.

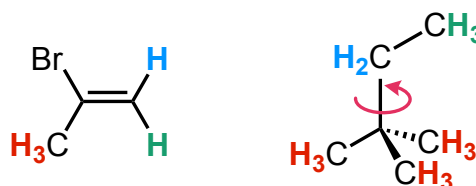
Example molecules with 1 signal



Example molecules with 2 signals



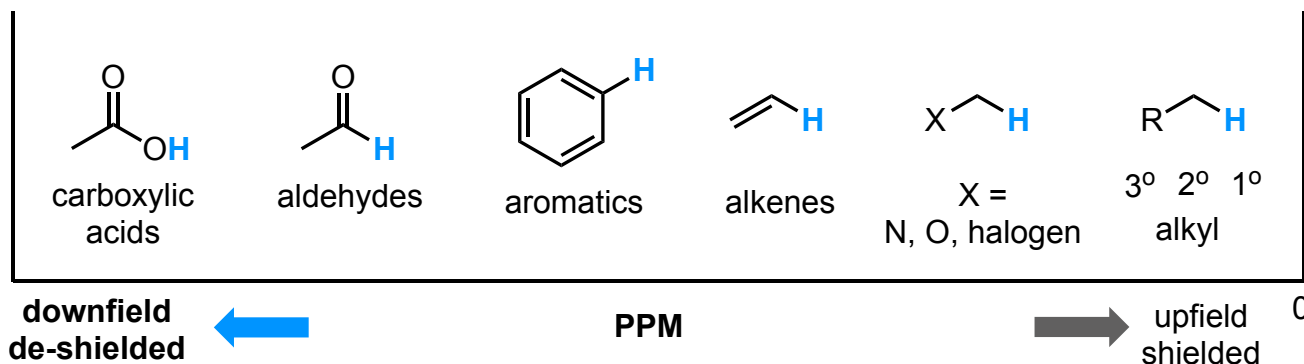
Example molecules with 3 signals



2. Chemical Shift

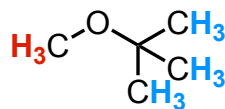
The **primary factors** that impact the chemical shift of a proton are (A) **proximity to a π system** and (B) **inductive effects**. Both cause nearby protons to be **deshielded**, producing a signal at a higher chemical shift (**downfield**).

Shown below are approximate chemical shifts for protons in a variety of functional group. **Note:** Due to primarily hydrogen-bonding, O—H and N—H signals are observed over a wide range of shifts.



3. Integration of Peaks

The integration, or **the area under each signal**, corresponds to the **number of protons of that type**. Let's consider **MTBE**, shown below.

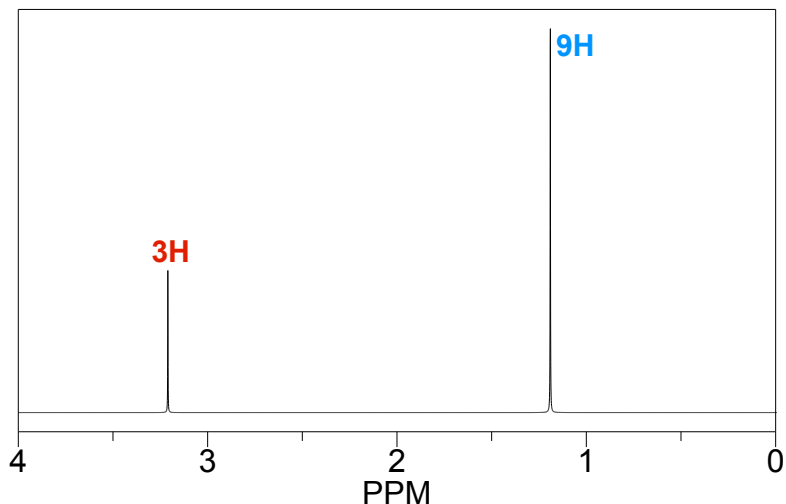


MTBE

Has **two unique protons** = 2 signals

Integration of peaks: 3 H 9 H

Note: NMR will provide the simplest form of the ratio. In this case, it would read as **1 : 3**



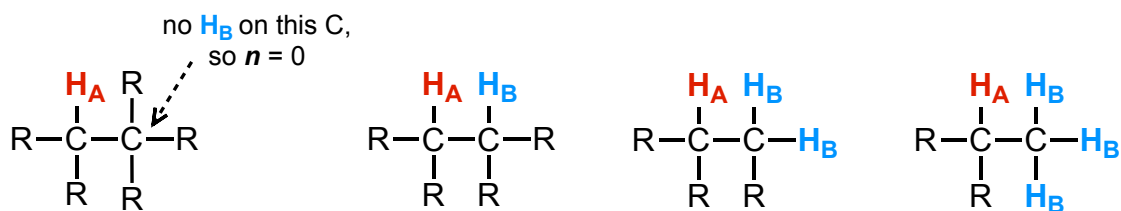
4. Splitting Patterns

The splitting patterns, also referred to as multiplicity, references the *shape or number of peaks* portrayed by signal - a singlet has one, a doublet has two, etc...

The splitting pattern observed for a signal often follows the **$n + 1$ rule**, where **n** is the number of non-equivalent protons up to three bonds away.

Ultimately, the **n** value **can be determined by looking at the number of non-equivalent protons on any neighboring carbon atom**.

For example, **H_A** below will split on any **H_B**'s and the signal for **H_A** may appear as a singlet, doublet, triplet, etc... depending on the number of **H_B**.



Splitting formula $n + 1$

0 + 1 = 1

1 + 1 = 2

2 + 1 = 3

3 + 1 = 4

Splitting of **H_A**

singlet

doublet

triplet

quartet

For the shapes of these peaks, see Ch 13.6 of your textbook

Note: O-H and N-H are exceptions to this "n+1 rule" and will usually produce broad singlets.