NMR SPECTROSCOPY

NMR Console with Computer

RF Signal Generator

Decoupler (^{1}H):

Amplifier

Frequency Generator
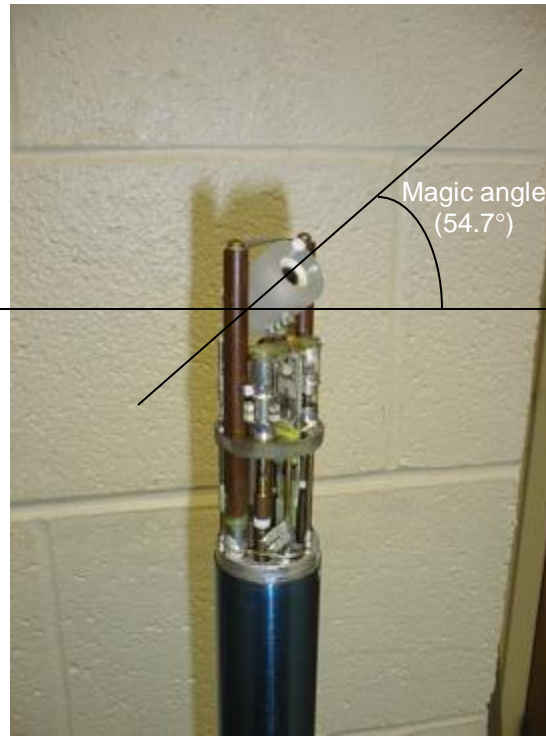
Transmitter:

Amplifier

Frequency Generator

Frequency Generators and Signal Amplifiers are required for each RF channel. This spectrometers have 2 channels, modern spectrometers can have up to 8 channels.
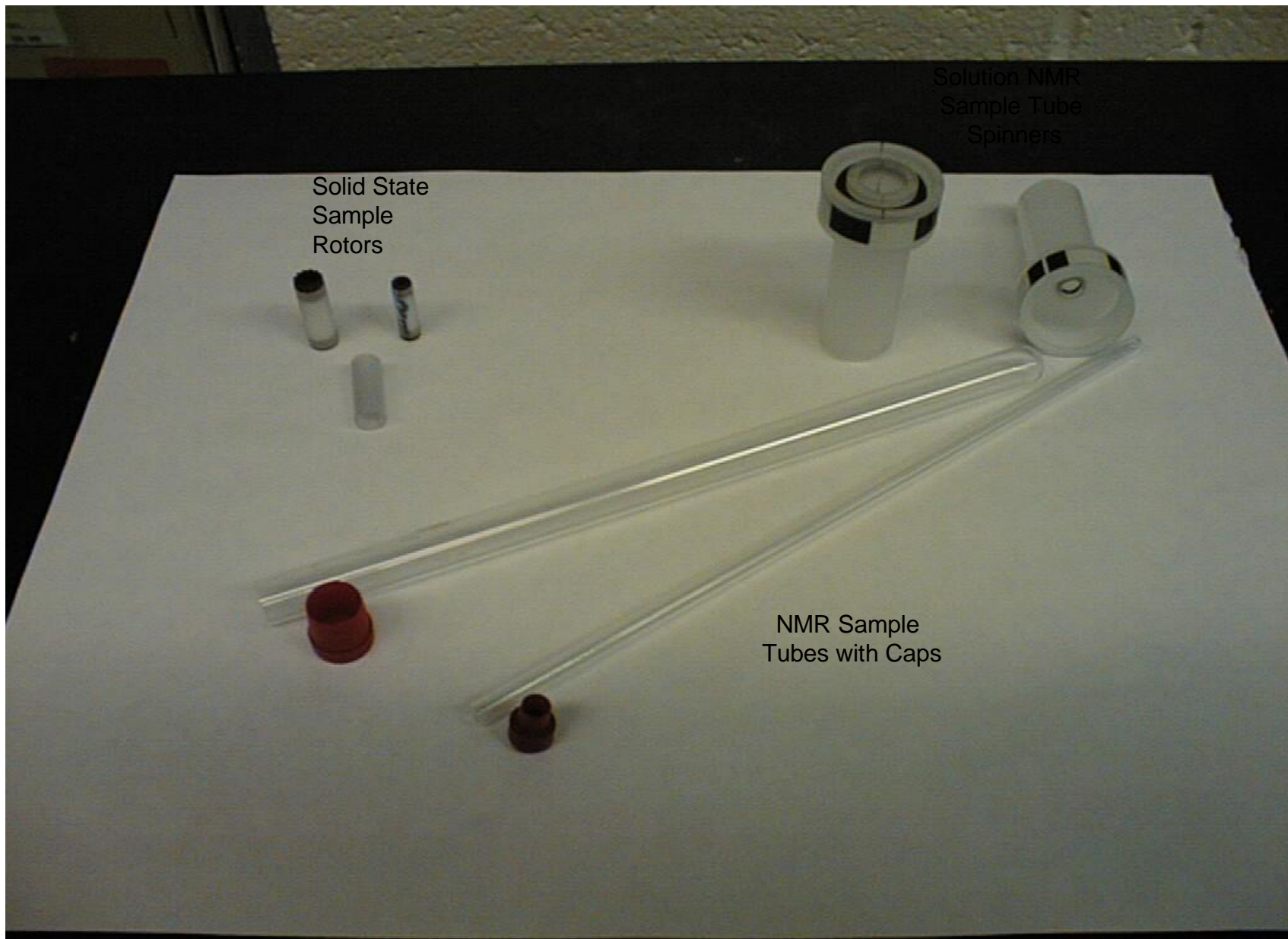
NMR Probes

Magic angle
(54.7°)

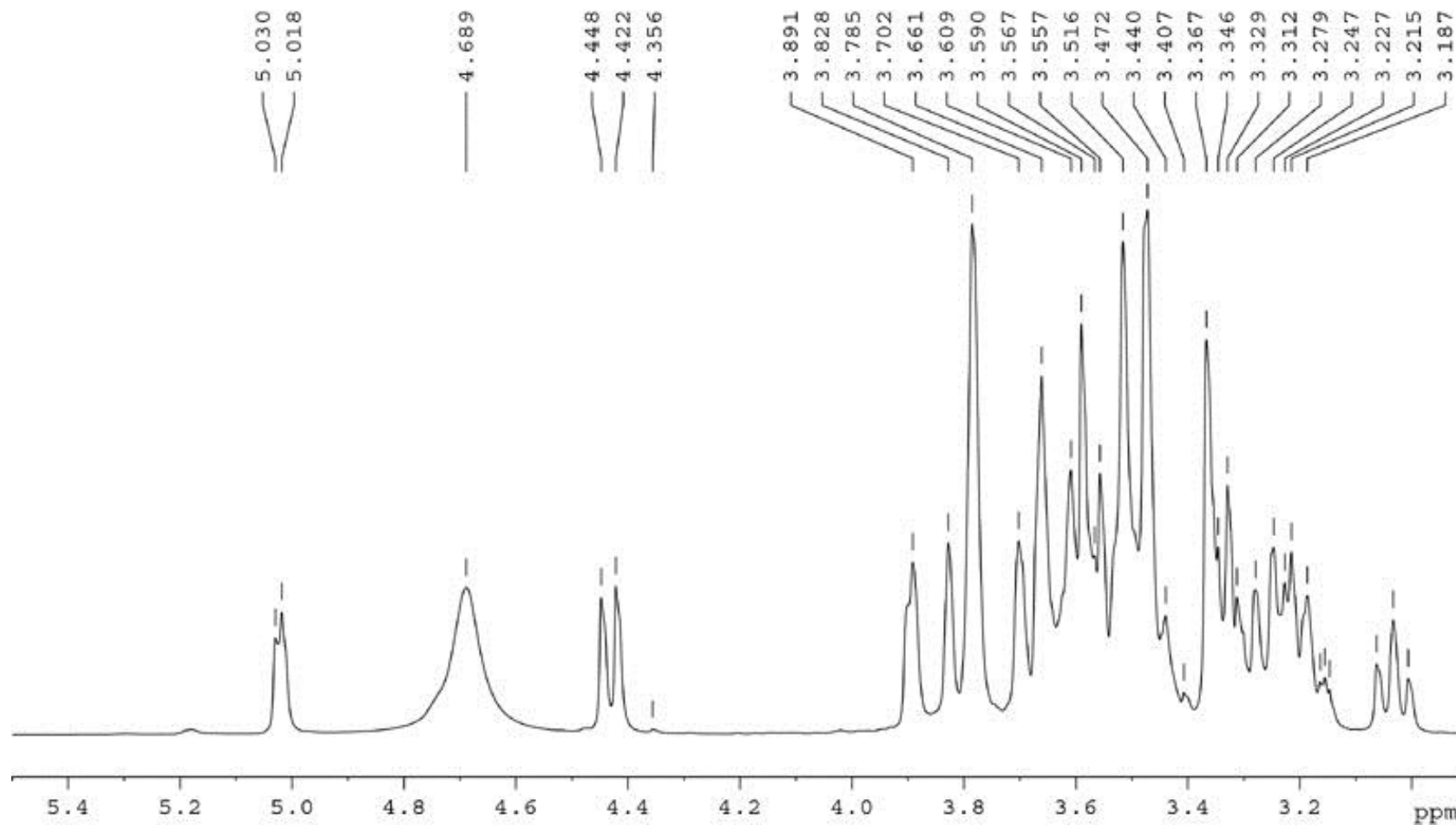Solids ←   Liquids

Solids

Liquids

Types of NMR Sample Holders

Solid State Sample Rotors

Solution NMR Sample Tube Spinners

NMR Sample Tubes with Caps
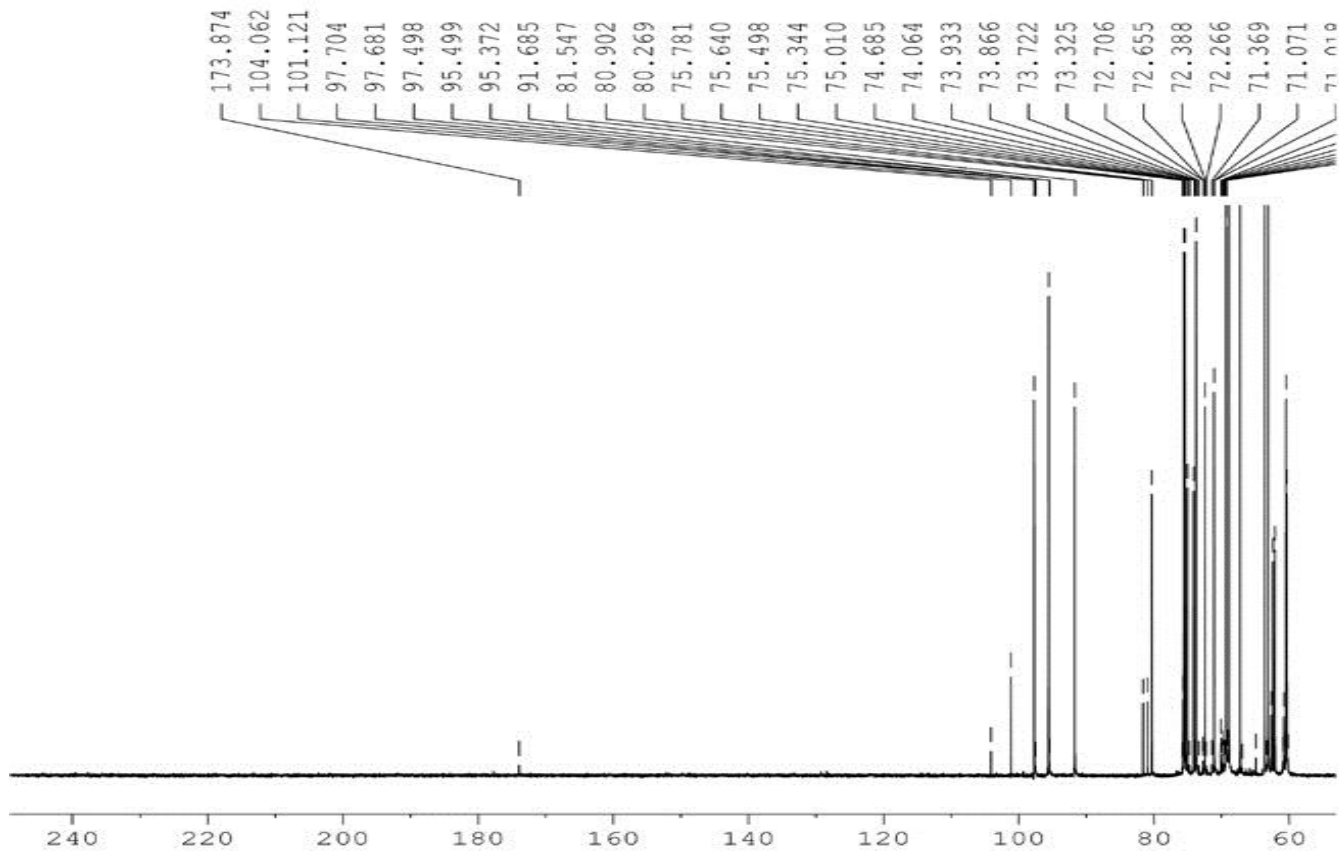
^{1}H Spectrum of Mountain Dew

^{13}C Spectrum
of Mountain Dew

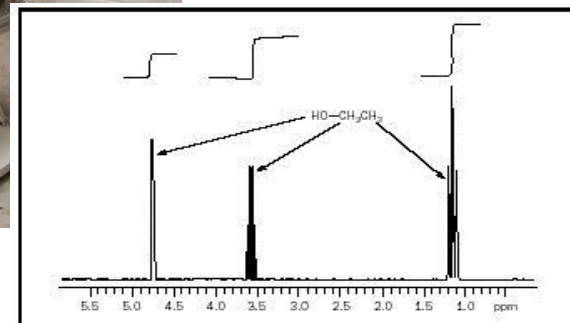# What is NMR?

NMR Stands for:

- N<small>UCLEAR</small>

- M<small>AGNETIC</small>

- R<small>ESONANCE</small>
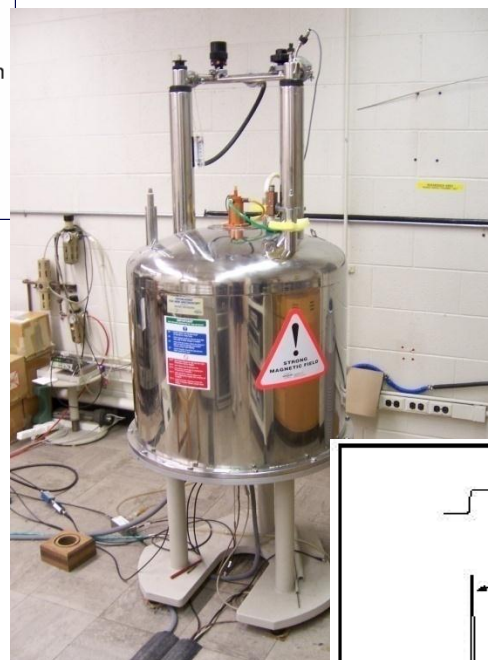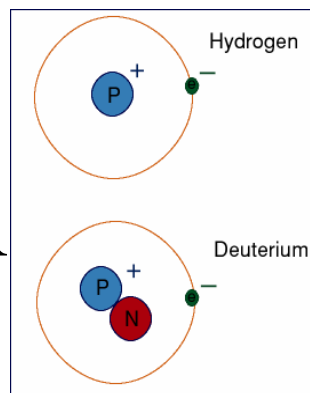
Spin States

- Nuclei with an odd mass, an odd number of protons, or both, are said to have spin angular momentum

- The number of allowed spin states is quantized, and is determined by its spin quantum number, I

- There are 2I+1 allowed spin states

Nuclei with I = 0 have only one spin state and are NMR inactive. These include ^{12}C and ^{16}O, two of the most common nuclei in organic compounds.

A spinning nucleus with a spin quantum number of ½ has 2 possible spin states.

2I+1 = 2 (1/2) + 1 = 2

The Most Interesting Elements (to us) All Have 2 Allowed Spin States

These are

- ^1H
- ^{13}C
- ^{19}F
- ^{31}P

Deuterium ^2H is spin active with I = 1!

2 (1) + 1 = 3 spin states for deuterium

$$\mu(\text{nuclear magnetos}) = \gamma\hbar I$$

γ Is the gyromagnetic ratio (rad/G-s).

NMR properties of nuclei of interest in polymers

Isotope	Natural abundance	Resonance frequency (MHz) for field of 10 KG (1 T)	Relative sensitivity for equal number of nuclei at constant H_0	Magnetic moment (units of nuclear nuclear magnetons)	Spin I in multiples of $\hbar$
^{1}H	99.9844	42.577	1.000	2.79270	1/2
^{2}H (D)	0.0156	6.536	0.00964	0.85738	1
^{13}C	1.108	10.705	0.0159	0.70216	1/2
^{14}N	99.635	3.067	0.00101	0.40357	1
^{15}N	0.365	4.315	0.00104	−0.28304	1/2
^{17}O	0.037	5.772	0.0291	−1.8930	5/2
^{19}F	100.0	40.055	0.834	2.6273	1/2
^{29}Si	4.70	8.460	0.0785	−0.55477	1/2
^{31}P	100.0	17.235	0.0664	1.1305	1/2
^{35}Cl	75.4	4.172	0.00471	0.82089	3/2
^{37}Cl	24.6	3.472	0.00272	0.68329	3/2

- The spinning of the nuclei causes them to behave like magnets.

- These nuclear magnets are influenced by other magnetic fields. These other magnetic fields may be externally applied or they can be generated by other nearby nuclei or electrons in the molecule.

- Externally applied magnetic fields may result from the magnet that the sample is placed in or from irradiation by radio frequency light.

In an Applied Magnetic Field

•Nuclei with 2 allowed spin states can align either <u>with</u> or <u>against</u> the field, with slight excess of nuclei aligned with the field

The nuclei precess about an axis parallel to the applied magnetic field, with a frequency called the Larmor Frequency (ω).

Applied magnetic field

Precessional orbit

Spinning nucleus
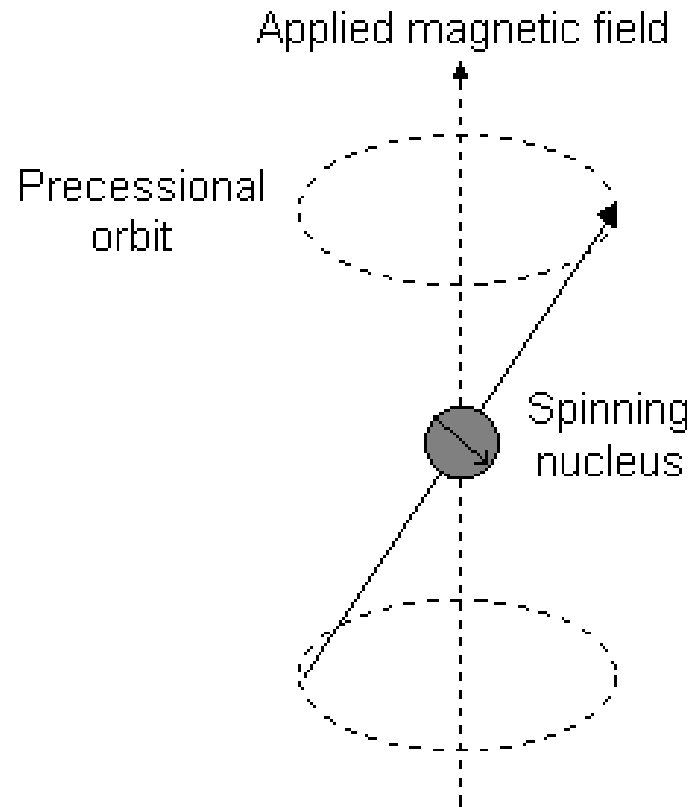
$$\omega_0 \,(\text{rad/s}) = \gamma H_0$$

or in MHz

$$\nu_0 \,(\text{MHz}) = \left(\frac{\gamma}{2\pi}\right) H_0$$

In an applied magnetic field the spin states have different energies and therefore different populations.

___ less populated

___ $I = -1/2$ equally populated

more populated ___ ___ $I = -1/2$

$I = +1/2$ ___ $I = +1/2$

$\uparrow\uparrow\uparrow$ $\Delta E(MHz) = \gamma\hbar H_0$

H_0
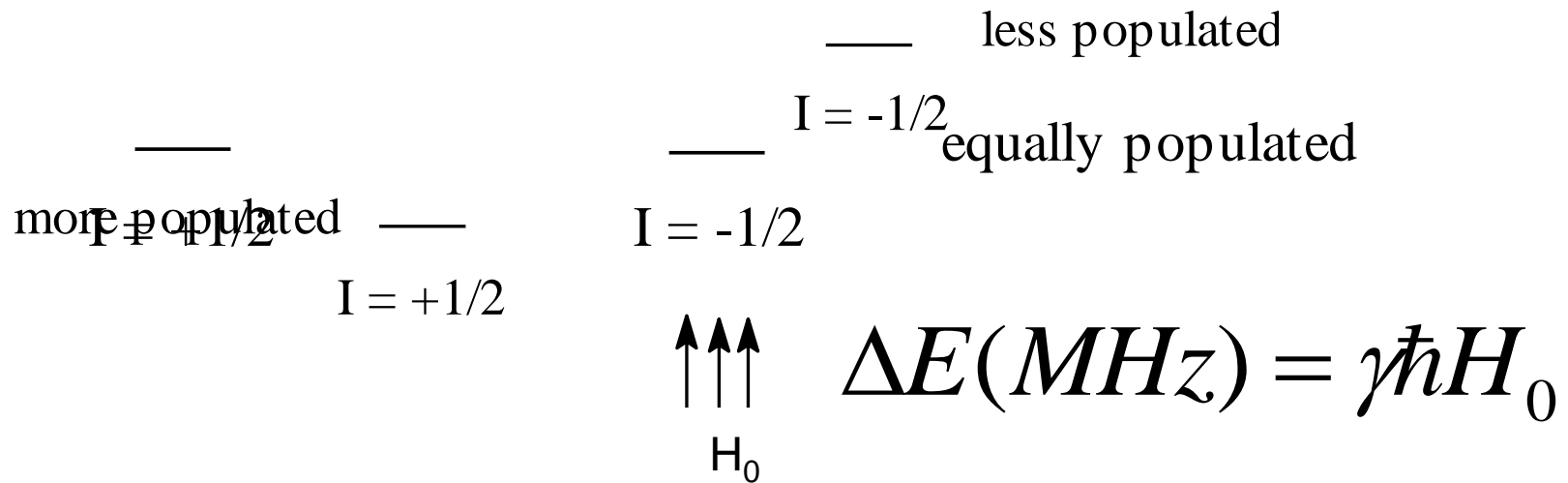
Transitions may occur between these energy states which allows NMR signals to be observed. The greater the difference in population, the stronger the NMR signal.

Larmor Frequency is Proportional to the Applied Magnetic Field

Applied magnetic field

Precessional orbit

Spinning nucleus

Applied magnetic field

Precessional orbit

Spinning nucleus
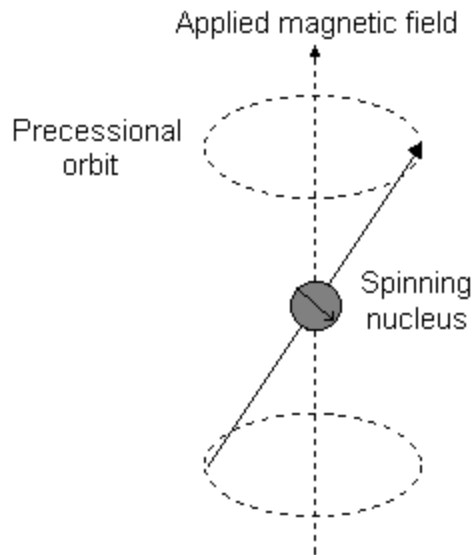
Slow precession in small magnetic field
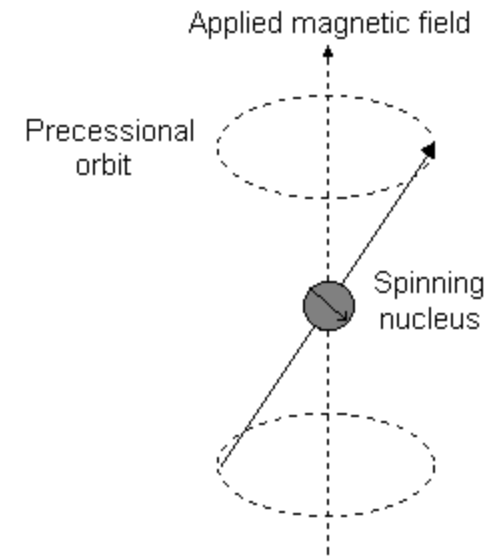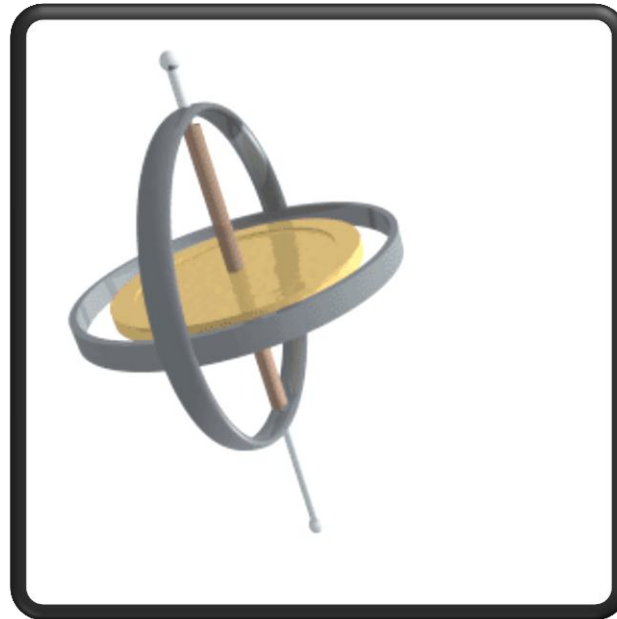
Faster precession in larger magnetic field

The difference in energy between the 2 spin states is proportional to the Larmor frequency
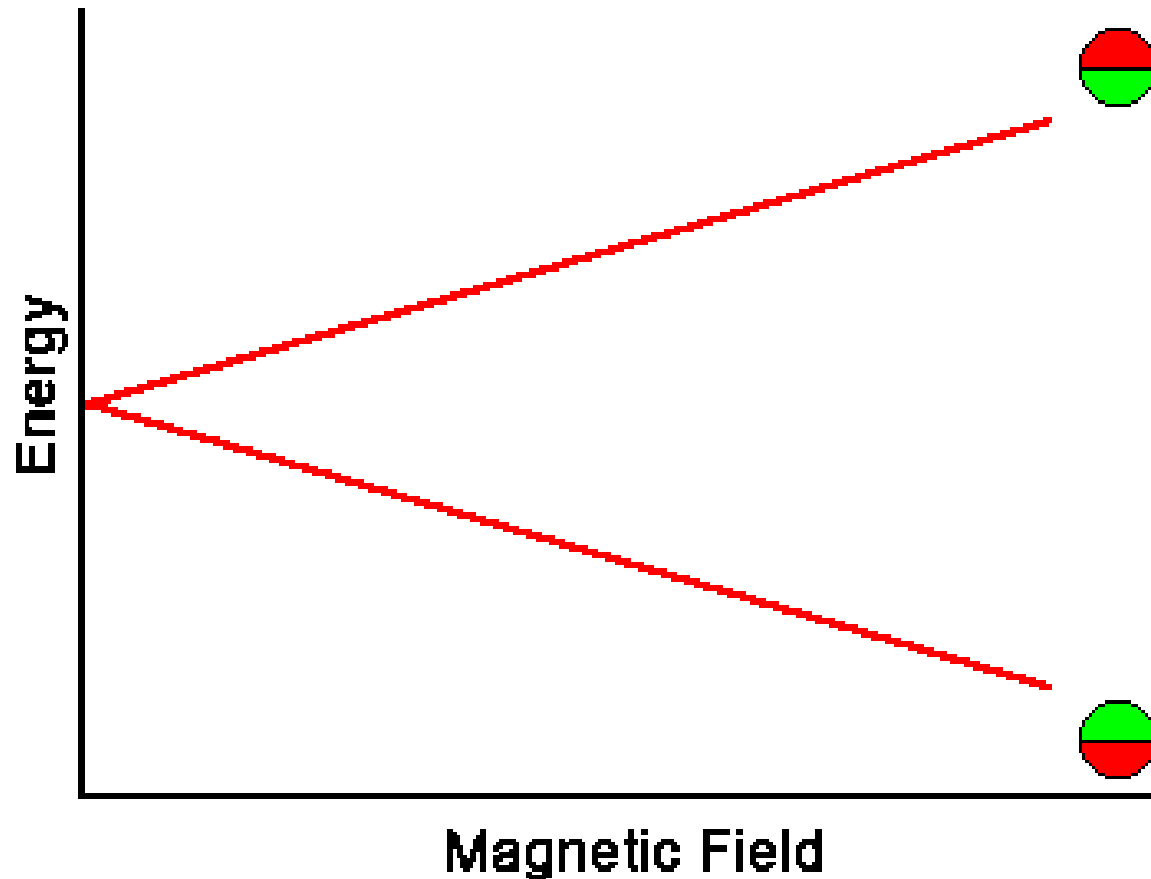
RF Energy Can Be Absorbed

•Precessing nuclei generates an oscillating electric field of the same frequency

•RF energy with the same frequency as the Larmor frequency can be applied to the system and absorbed by the nuclei
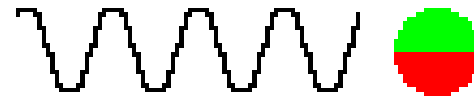
Chemical Shifts in NMR

- The nuclei not only interact with the magnetic field but also with the surronding nuclei and their electrons.

- The results has important implications for the study of molecules by NMR.

Why chemical shift?

$$H_{effe} = H_0 - H_{loc}$$

And now:

$$\Delta E(MHz) = \gamma \hbar H_{effe}$$

And not:

$$\Delta E(MHz) = \gamma \hbar H_0$$

$$\nu \, (\text{MHz}) = \left(\frac{\gamma}{2\pi} \right) H_{effe}$$

H_{loc} is the sum of all the magnetic filed exerted by any local magnets such as electrons, other nuclei, bonds etc.

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Chemical Shift

- We define the relative position of absorption in the NMR spectrum the **<u>chemical shift</u>**. It is a unitless number (actually a ratio, in which the units cancel), but we assign 'units' of ppm or δ (Greek letter delta) units.

- For ^{1}H, the usual scale of NMR spectra is 0 to 10 (or 12) ppm (or δ).

- The usual ^{13}C scale goes from 0 to about 220 ppm.

- The zero point is defined as the position of absorption of a standard, tetramethylsilane (TMS):

- This standard has only one type of C and only one type of H.

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3$$

Chemical Shifts

Proton Chemical Shift (δ) vs. Electronegativity

CH_3-F

CH_3-O

CH_3-N

CH_3-C

CH_3-Si

CH_3-H

H Chemical Shift
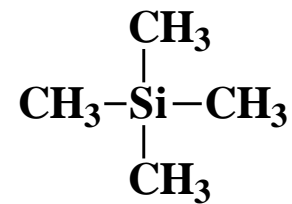
Electronegativity
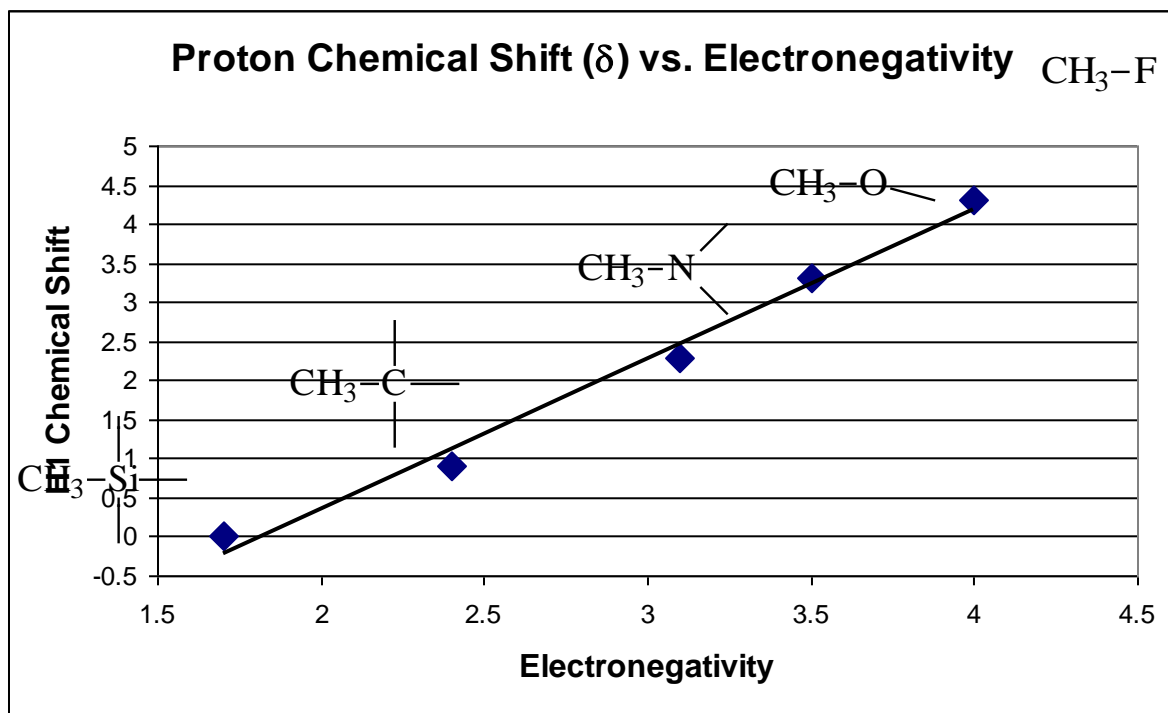
Chemical Shifts

- Both ^1H and ^{13}C Chemical shifts are related to three major factors:

  - The hybridization (of carbon)

  - Presence of electronegative atoms or electron attracting groups

  - The degree of substitution (1º, 2º or 3º).   These latter effects are most important in ^{13}C NMR, and in that context are usually called 'steric' effects.

- Now we'll turn our attention to ^1H NMR spectra

  (they are more complex, but provide more structural information)

Unit of chemical shift, δ

$$\delta = \frac{\text{distance from TMS in Hz}}{\text{spectrometer frequency in MHz}} \, ppm$$

^{1}H Chemical Shifts
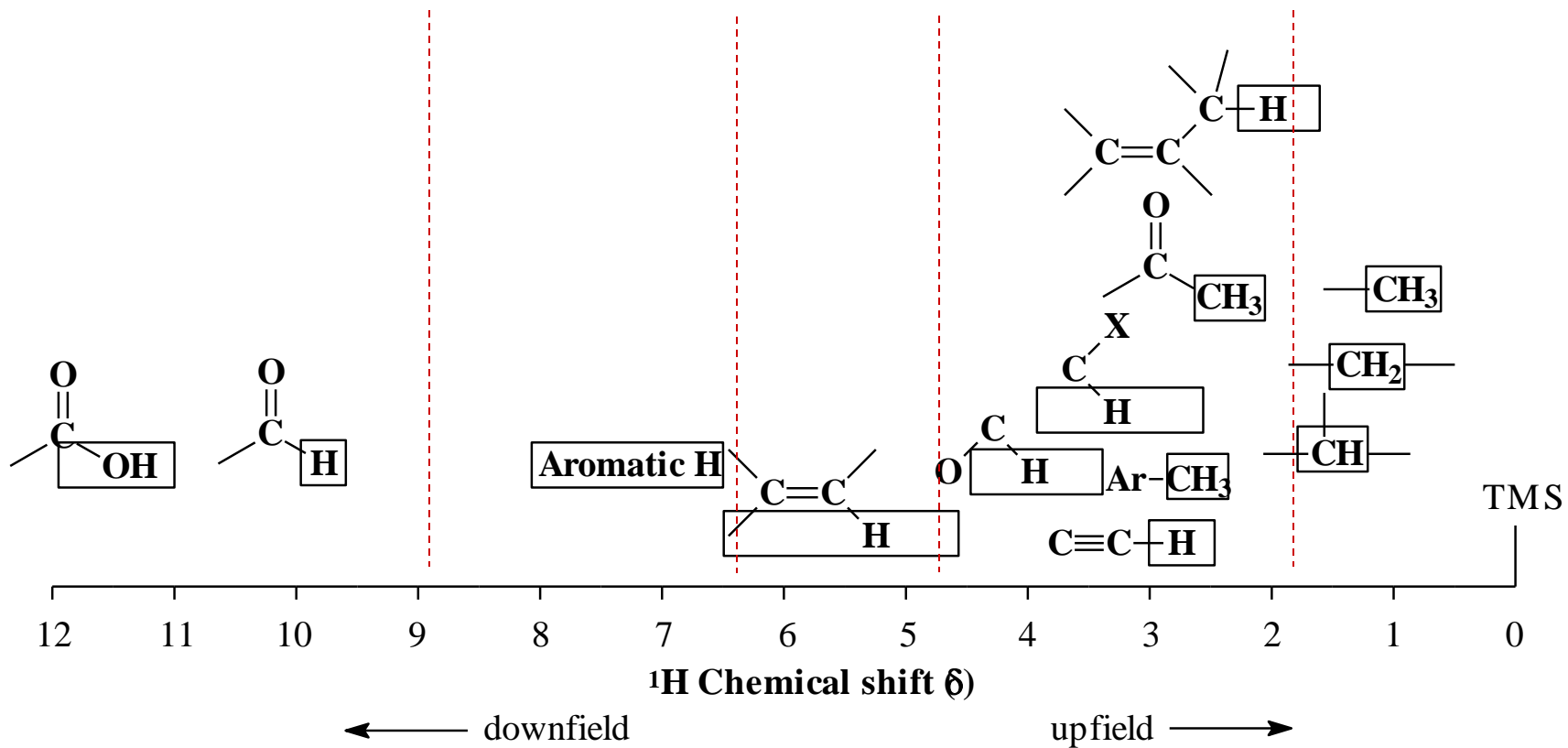
Classification of Protons

- To interpret or predict NMR spectra, one must first be able to classify proton (or carbon) environments.

- Easiest to classify are those that are <u>unrelated</u>, or <u>different</u>. Replacement of each of those one at a time with some group (G) in separate models creates **constitutional isomers**.

$$CH_3CH_2CH_2CH_3: \qquad CH_3CH_2\overset{\overset{\displaystyle G}{|}}{C}HCH_3 \qquad CH_3CH_2CH_2\overset{\overset{\displaystyle G}{|}}{C}H_2$$
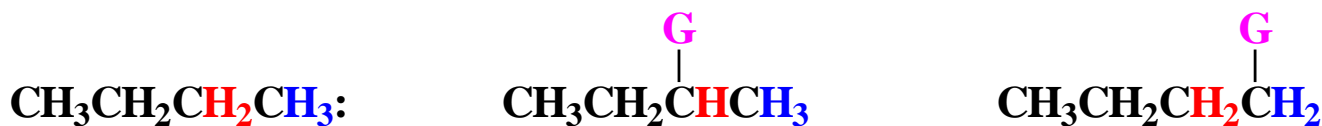
These protons have **different chemical shifts.** This classification is usually the most obvious.

Classification of Protons

- **Homotopic** hydrogens are those that upon replacement one at a time with some group (**G**) in separate models creates **identical structures.**

$CH_3CH_2CH_2CH_3$: $CH_3CH_2CH_2C$ **G** **H** **H** $CH_3CH_2CH_2C$ **H** **G** **H** $CH_3CH_2CH_2C$ **H** **H** **G**
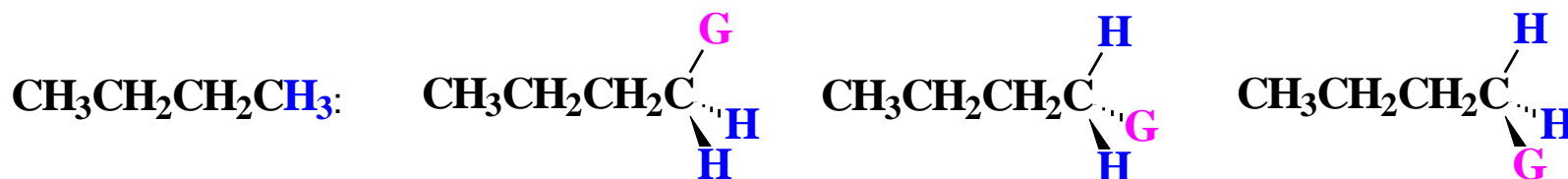
Homotopic protons have **the same chemical shifts.** We sometimes call them identical. Methyl hydrogens will always be in this category (because of free rotation around the bond to the methyl carbon). Molecular symmetry can also make protons homotopic.

Classification of Protons

- If replacement of one hydrogen at a time in separate models creates <u>enantiomers</u>, the hydrogens are **enantiotopic**.

CH$_3$CH$_2$C**H$_2$**CH$_3$:
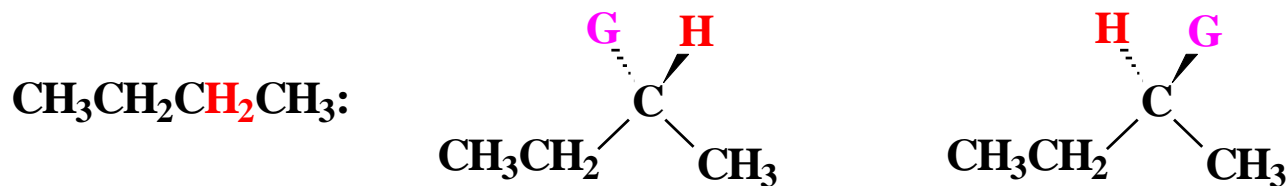
Enantiotopic protons have **the <u>same</u> chemical shifts.**

Classification of Protons

- If replacement of hydrogens in separate models creates <u>diastereomers</u>, the hydrogens are **diastereotopic**.
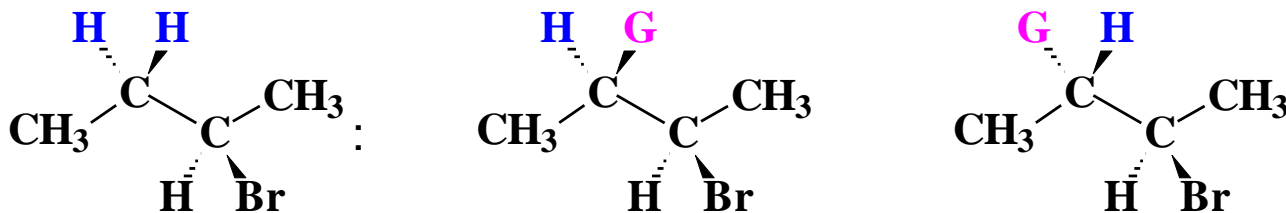
Diastereotopic protons have **different chemical shifts.** Usually, in order to have diastereotopic protons, there has to be a stereocenter somewhere in the molecule. However, cis-trans alkene stereoisomers may also have diastereotopic protons.

^{1}H NMR Problems

- How many unique proton environments are there in:

$$CH_3CH_2Br \qquad = \qquad CH_3CH_2Br \qquad \textbf{2 environments}$$

$$CH_3OCH_2CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle |}{C}}HCH_3 \qquad = \qquad CH_3OCH_2CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle |}{C}}HCH_3 \qquad \textbf{5 environments}$$

4 environments

33
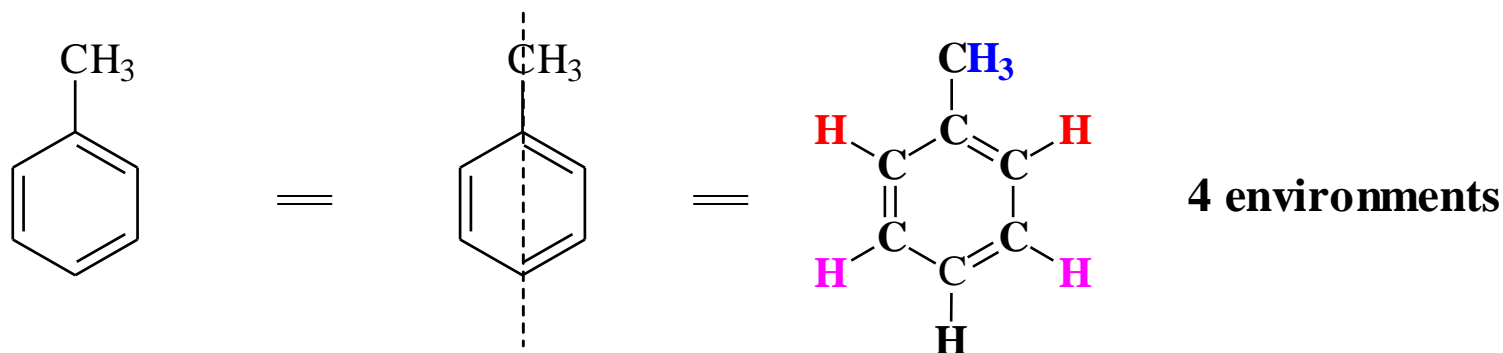
^{1}H NMR Problems
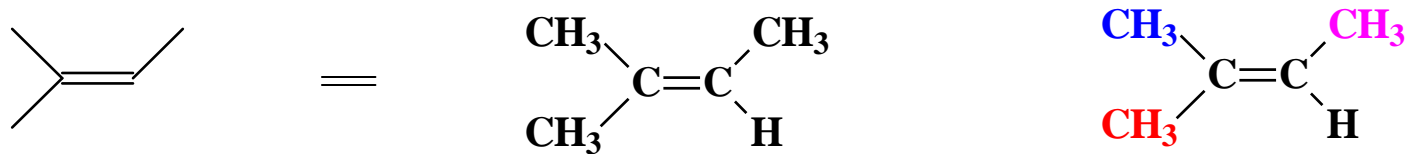
4 environments
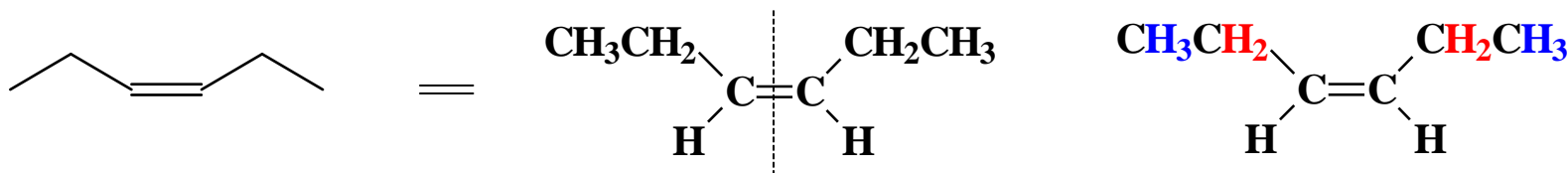
3 environments

Symmetry Simplifies Spectra!!!

acetone

$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_3$$
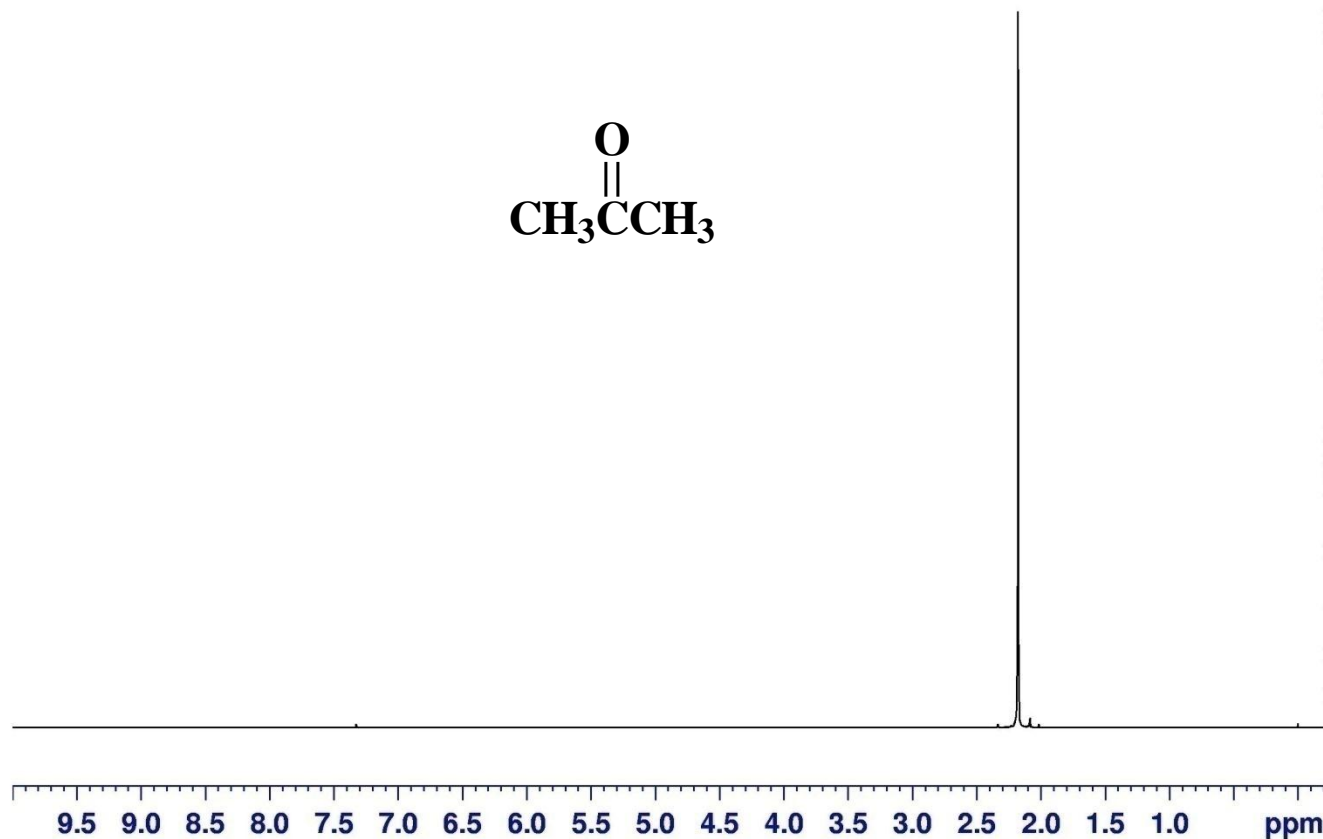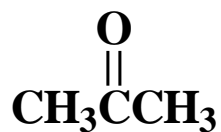
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FIDRES   0.079473 Hz
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RG   64
DW   96.000 usec
DE   6.00 usec
TE   690.7 K
D1   1.00000000 sec
TD0   1

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PL1   -6.00 dB
SFO1   400.1324008 MHz

F2 - Processing parameters
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SF   400.1299813 MHz
WDW   EM
SSB   0
LB   0.50 Hz
GB   0
PC   0.50

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0   ppm

35

methyl acetate

—OCH$_3$ CH$_3$—

$$\underset{\displaystyle \text{CH}_3\text{COCH}_3}{\overset{\displaystyle \overset{\text{O}}{\|}}{}}$$
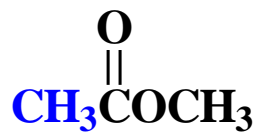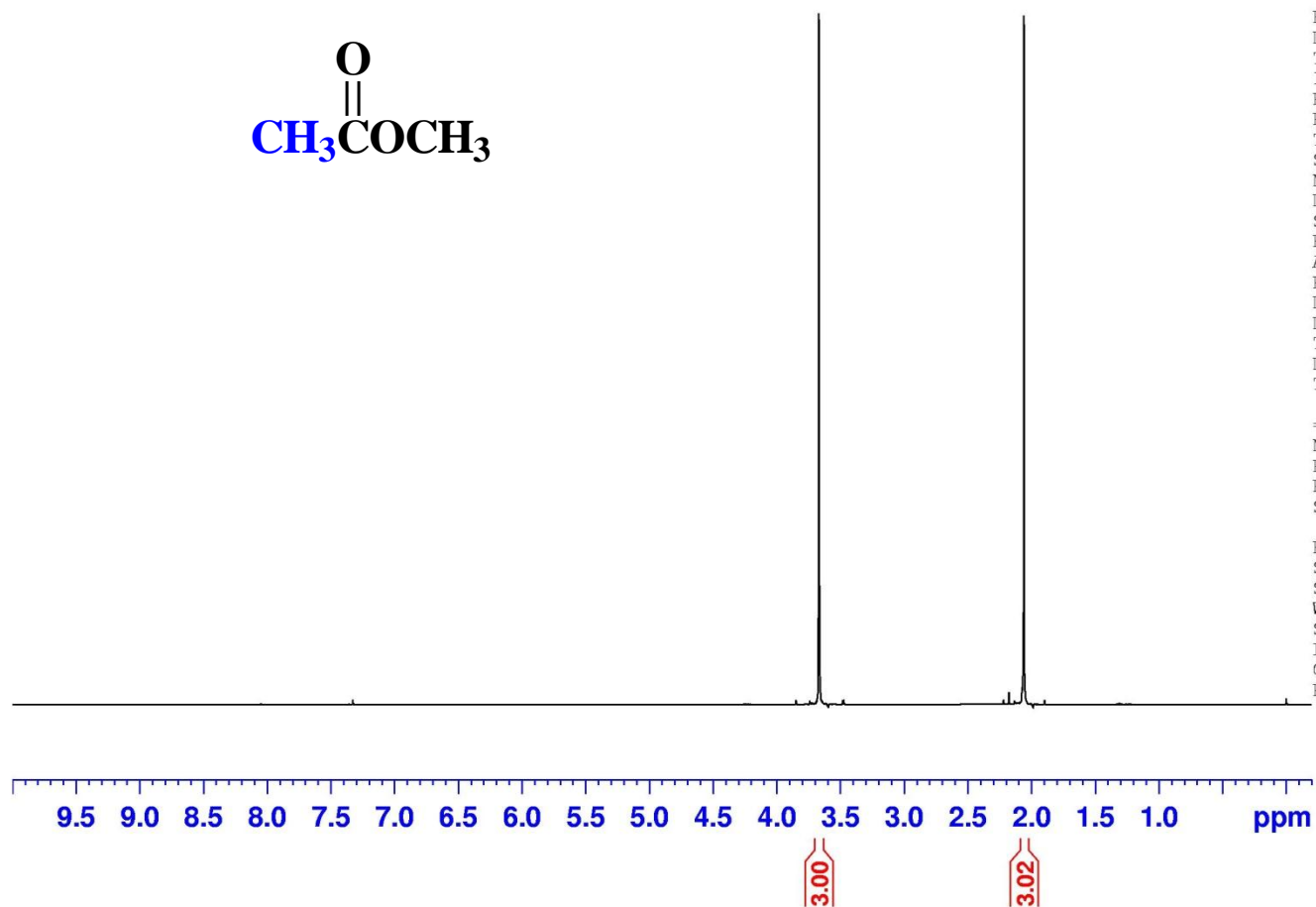
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DE   6.00 usec
TE   690.7 K
D1   1.00000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   1H
P1   7.50 usec
PL1   -6.00 dB
SFO1   400.1324008 MHz

F2 - Processing parameters
SI   32768
SF   400.1299813 MHz
WDW   EM
SSB   0
LB   0.50 Hz
GB   0
PC   0.50

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0   ppm

3.00   3.02

36

Spin-spin splitting (Coupling)

- Proton NMR spectra are not typically as simple as CMR (^{13}C NMR) spectra, which usually give a single peak for each different carbon atom in the structure.

- Proton NMR spectra are often much more complex.

- Because of its nuclear spin, each proton exerts a slight effect on the localized magnetic field experienced by its neighboring proton(s).

- The spin state (↑ or ↓) of any one proton is independent of any other proton.

- The energies of protons of different spin states are so nearly equal that there is close to a 50:50 chance for each proton to be up (or down).

Spin-spin splitting (Coupling)

- The spin states of the neighboring protons (those on the adjacent carbon) exert a small influence on the magnetic field, and therefore on the chemical shift of a given proton.

- The result is that proton signals in the NMR spectrum are typically split into multiplets. This phenomenon is called coupling; the consequence is signal splitting.

- The type of multiplet (doublet, triplet, quartet, etc.) depends on the number of protons on the next carbon.

The n+1 rule

- The <u>multiplicity</u> of a proton or a group of protons is given   by the <u>n+1 rule</u>, where n = the number of protons on the <u>adjacent (adjoining)</u> carbon atom (or atoms)

<u>n</u>	<u>n+1</u>	<u>multiplet name (abbrev)</u>	<u>intensity pattern</u>
1	2	**d**oublet (d)	1 : 1
2	3	**t**riplet (t)	1 : 2 : 1
3	4	**q**uartet (q)	1 : 3 : 3 : 1
4	5	quintet/pentet -	1 : 4 : 6 : 4 : 1
5	6	sextet -	1 : 5 : 10 : 10 : 5 : 1
6	7	septet/heptet -	1 : 6 : 15 : 20 : 15 : 5 : 1

Multiplets

- Consider the ethyl group in chloroethane CH_3CH_2Cl.

- The methyl protons experience a magnetic field that is somewhat influenced by the chlorine on the adjacent carbon, but is also affected slightly by the nuclear spin states of the <u>adjacent</u> methylene (CH_2) protons.

- The two CH_2 protons can have the following   possible combination of spins:

  magnetic field $\longrightarrow$

    two spin up (1 way)
    one up and one down (2)
    two spin down (1)

$$↓↑$$

$$↑↑ \quad ↑↓ \quad ↓↓$$
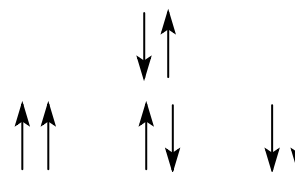
1 : 2 : 1

- This results in a **1:2:1 triplet** for the <u>methyl group</u>

Multiplets

- The magnetic field experienced by the CH_2 protons in chloroethane (CH_3CH_2Cl) is mainly influenced by the electronegative chlorine.

- However, it is slightly perturbed by the spin states of the three methyl (CH_3) protons on the adjoining carbon

- They have four possible combinations of spins:

  Three spin up (1 way)

  Two up and one down (3)

  Two down and one up (3)

  Three spin down (1)

  $↓↑↑$ $↑↓↓$

  $↑↓↑$ $↓↑↓$

  $↑↑↑$ $↑↑↓$ $↓↓↑$ $↓↓↓$
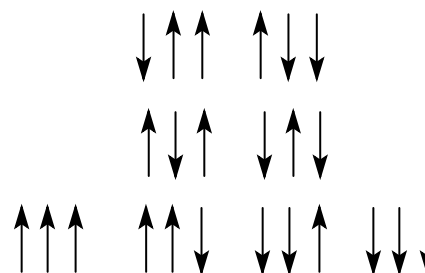
  1 : 3 : 3 : 1

- As a result, the <u>CH_2 group</u> appears as a **1:3:3:1 quartet**.

Spectrum of chloroethane

- Putting the multiplets together gives the predicted spectrum.

- The pattern of a **downfield quartet** and an **upfield triplet** is typical of the presence of an <u>ethyl group</u> in the molecular structure.

- Note that the triplet is larger than quartet. That is because are 3 protons giving rise triplet, and only 2 protons rise to the quartet.

- The <u>integrated signal areas</u> are in a 3:2 ratio.

CH₃

—CH₂—

the
there
TMS
to the

giving

CH₃CH₂Cl

4   3   2   1   0
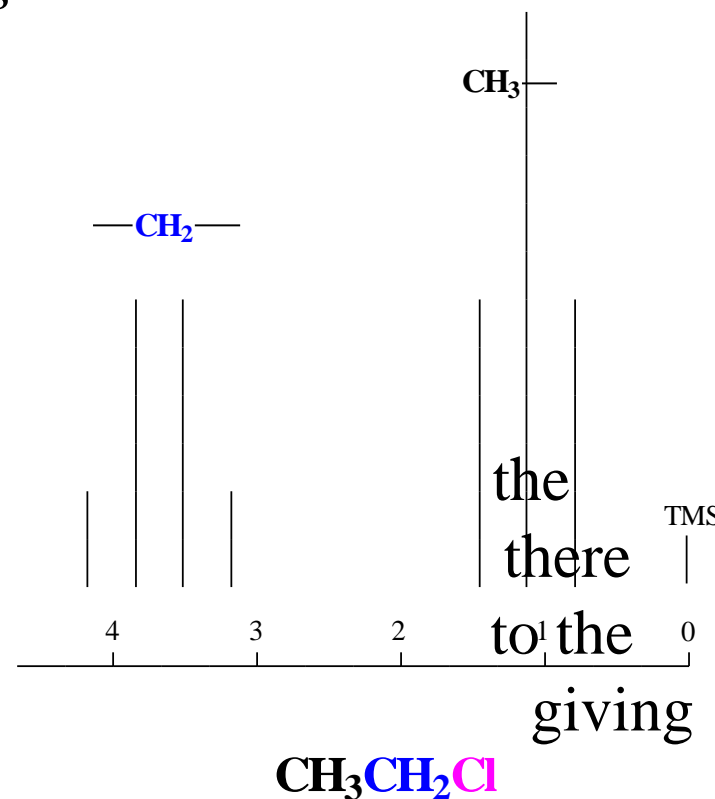
^{1}H NMR Problems

- Predict the splitting patterns (multiplets) for each proton environment in the following:

CH$_3$CHBr$_2$

CH$_3$OCH$_2$CH$_2$Br

ClCH$_2$CH$_2$CH$_2$Cl

$$\begin{array}{cc} \text{O} & \text{CH}_3 \\ \| & | \\ \end{array}$$
CH$_3$CH$_2$COCHCH$_3$

singlet

singlet

doublet

doublet

triplet

triplet

triplet

triplet

quartet

quartet

quintet

septet

43
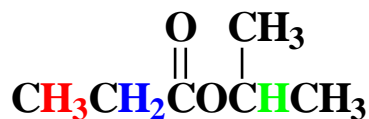
The Integral

- Integration is performed to determine the <u>relative number</u> of protons in a given environment.

- The number is set at 1, 2 or 3 for a given peak, then the areas of the other signals are reported relative to that one.

- The <u>integral</u> should be rounded to the nearest whole number; after all, there is either 1, or 2, or 3 protons in a certain environment, never a decimal fraction.

ethyl acetate
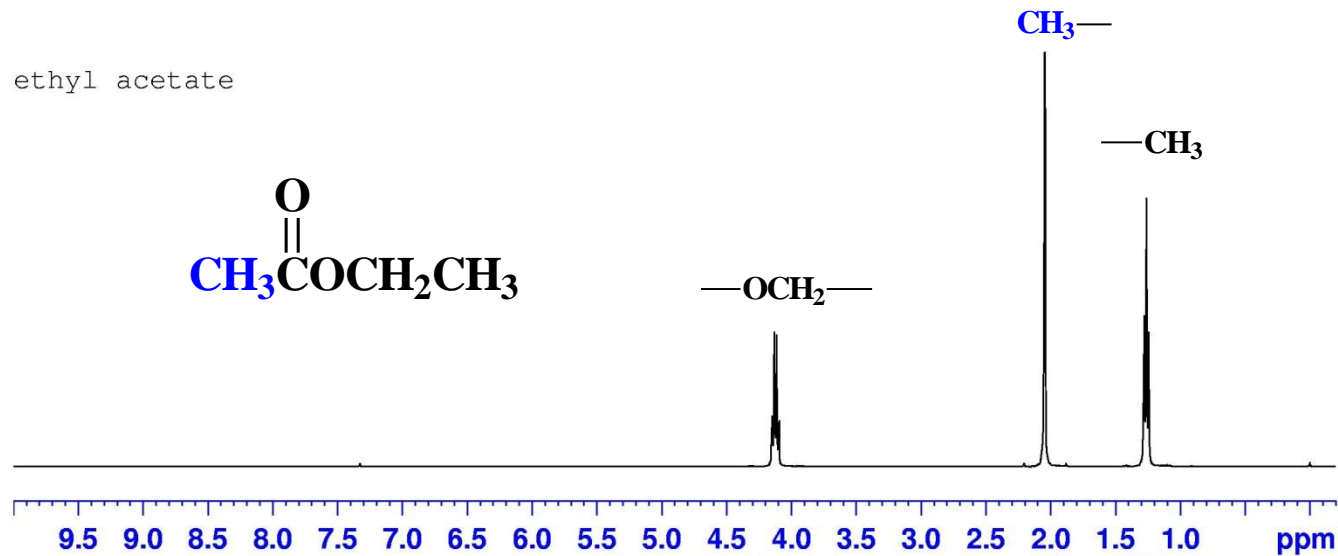
CH_3—

—CH_3

O
‖
$CH_3COCH_2CH_3$

—OCH_2—

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

1.95   3.00   2.94

(2H)   (3H) (3H)

CH_3—

—CH_3

—OCH_2—

4.0   3.5   3.0   2.5   2.0   1.5   ppm

1.952   3.000   2.944

45

ethyl propanoate

CH_3 CH_3

$$\underset{CH_3CH_2}{}\overset{O}{\underset{\|}{C}}\,OCH_2CH_3$$

—OCH₂—   —CH₂—

Current Data Parameters
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FIDRES   0.079473 Hz
AQ   6.2915058 sec
RG   35.9
DW   96.000 usec
DE   6.00 usec
TE   690.6 K
D1   1.00000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   1H
P1   7.50 usec
PL1   -6.00 dB
SFO1   400.1324008 MHz

F2 - Processing parameters
SI   32768
SF   400.1299890 MHz
WDW   EM
SSB   0
LB   0.10 Hz
GB
PC

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0   ppm

1.99   1.99   3.01 3.00

—CH₃   CH₃—

—OCH₂—   —CH₂—

4.0   3.5   3.0   2.5   2.0   1.5   ppm

1.991   1.990   3.014 3.000

46

ethyl butanoate

$$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OCH_2CH_3$$

OCH$_2$

CH$_2$

CH$_2$

CH$_3$

CH$_3$

1663.24
1656.08
1648.95
1641.82

918.40
910.98
903.57

711.77
681.16
673.72
666.25
658.82
651.43
644.09

510.55
503.40
496.25

387.78
380.42
372.96

1.97   1.99   1.98   3.01   3.00

4.0   3.5   3.0   2.5   2.0   1.5   1.0   ppm
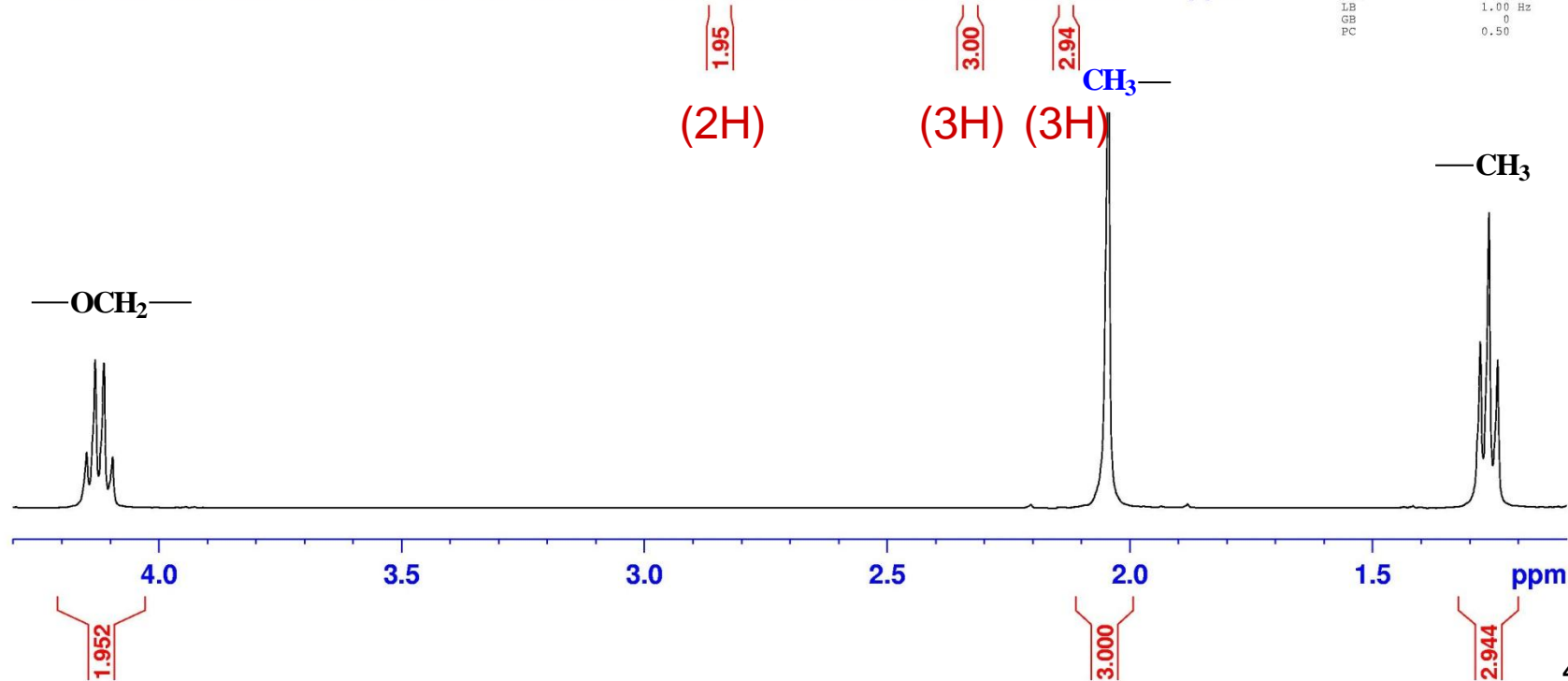
Current Data Parameters
NAME   512unknownJ
EXPNO   1
PROCNO   1

F2 - Acquisition Parame
Date_   20060222
Time   13.16
INSTRUM   spect
PROBHD   5 mm Multinucl
PULPROG   zg30
TD   65536
SOLVENT   CDCl3
NS   16
DS   2
SWH   8250.825
FIDRES   0.125898
AQ   3.9715316
RG   57
DW   60.600
DE   6.00
TE   690.1
D1   1.00000000
TD0   1

======== CHANNEL f1 ===
NUC1   1H
P1   7.50
PL1   -6.00
SFO1   400.1320563

F2 - Processing paramet
SI   32768
SF   400.1299982
WDW   EM
SSB   0
LB   0.30
GB   0
PC   1.00

47

2-butanone

CH₃—

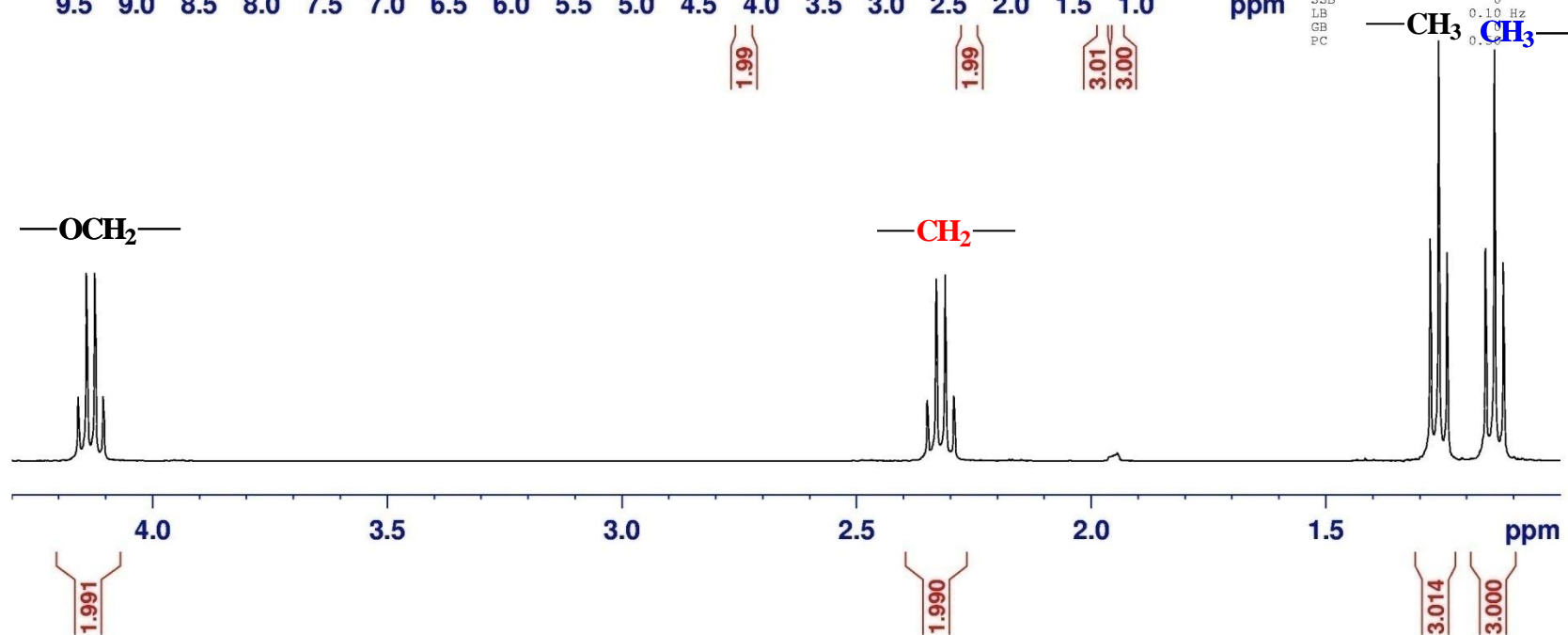—CH₃

$$O$$

$$CH_3CCH_2CH_3$$
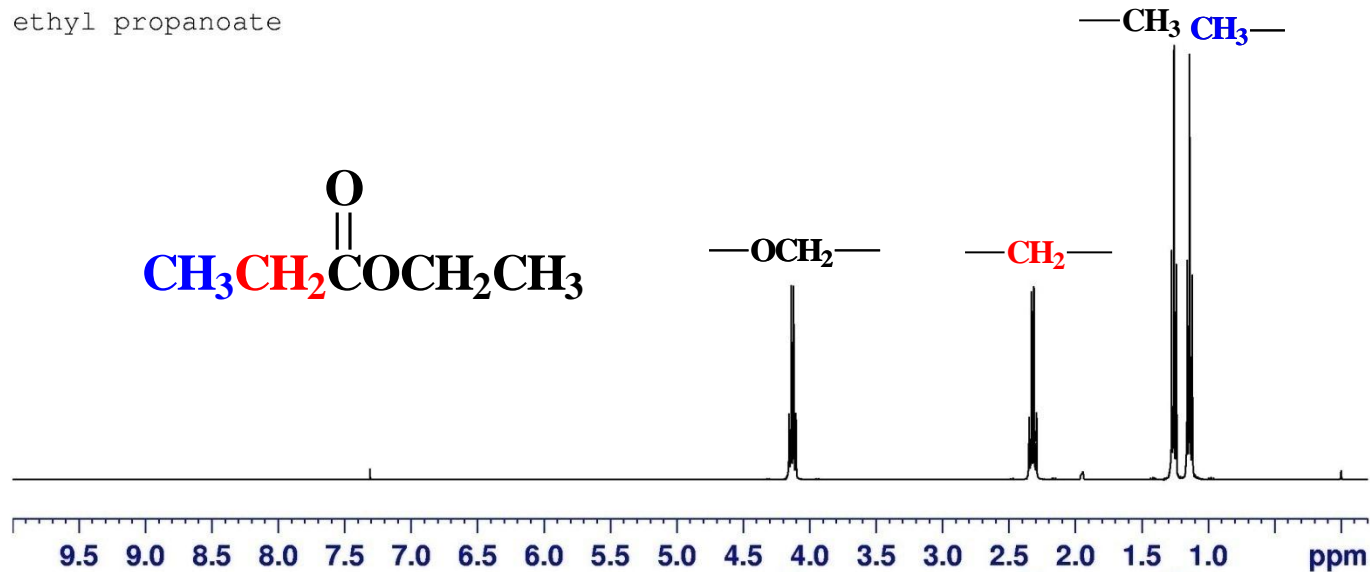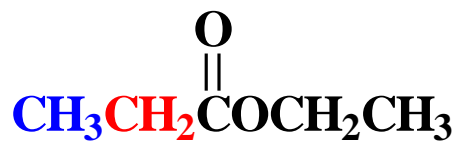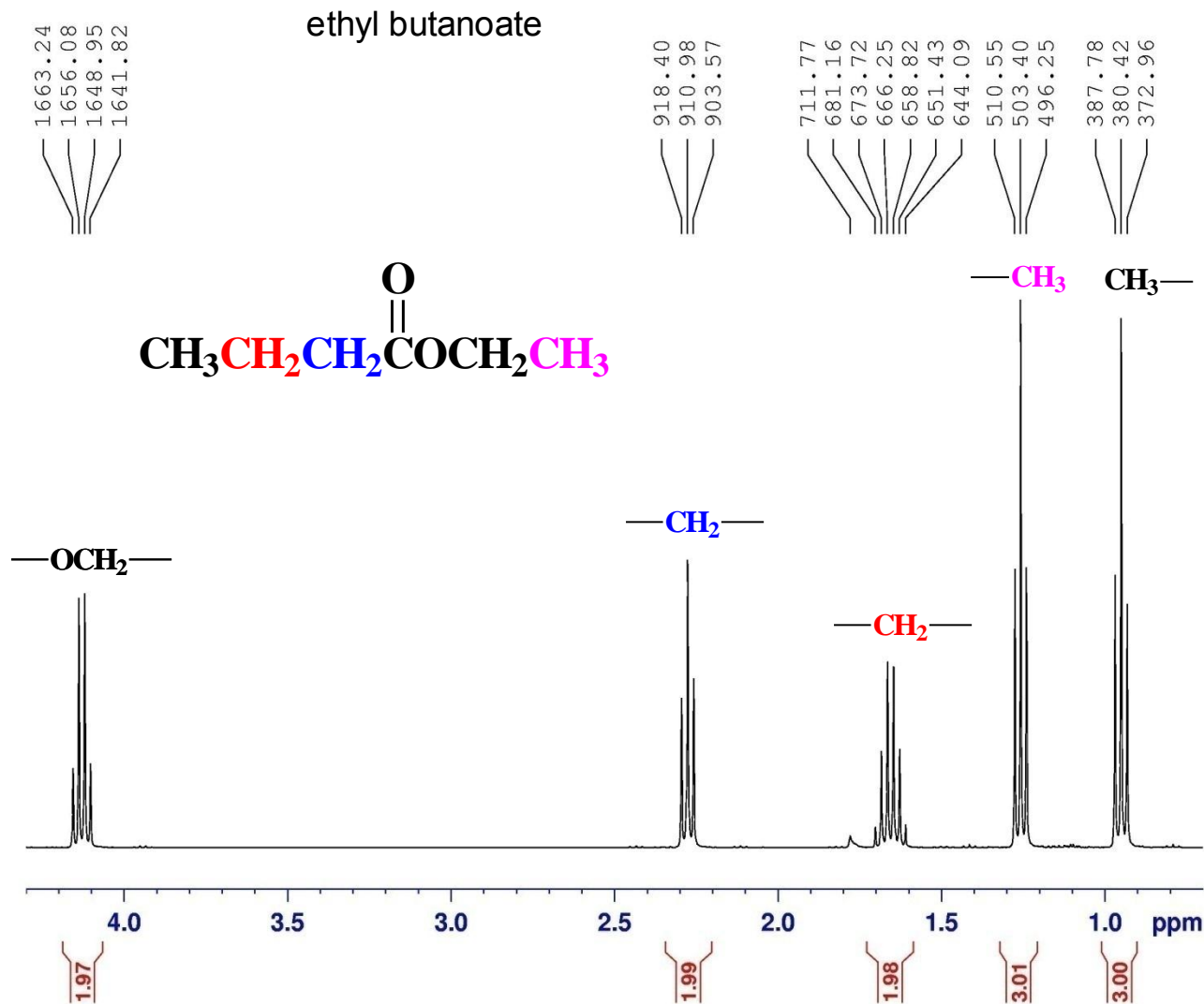
—CH₂—

Current Data Parameters
NAME   psnmr9
EXPNO   1
PROCNO   1

F2 - Acquisition Parameters
Date_   20070616
Time   11.32
INSTRUM   spect
PROBHD   5 mm Multinucl
PULPROG   zg30
TD   65536
SOLVENT   CDCl3
NS   16
DS   2
SWH   5208.333 Hz
FIDRES   0.079473 Hz
AQ   6.2915058 sec
RG   35.9
DW   96.000 usec
DE   6.00 usec
TE   690.8 K
D1   1.00000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   1H
P1   7.50 usec
PL1   -6.00 dB
SFO1   400.1324008 MHz

F2 - Processing parameters
SI   32768
SF   400.1299687 MHz
WDW   EM
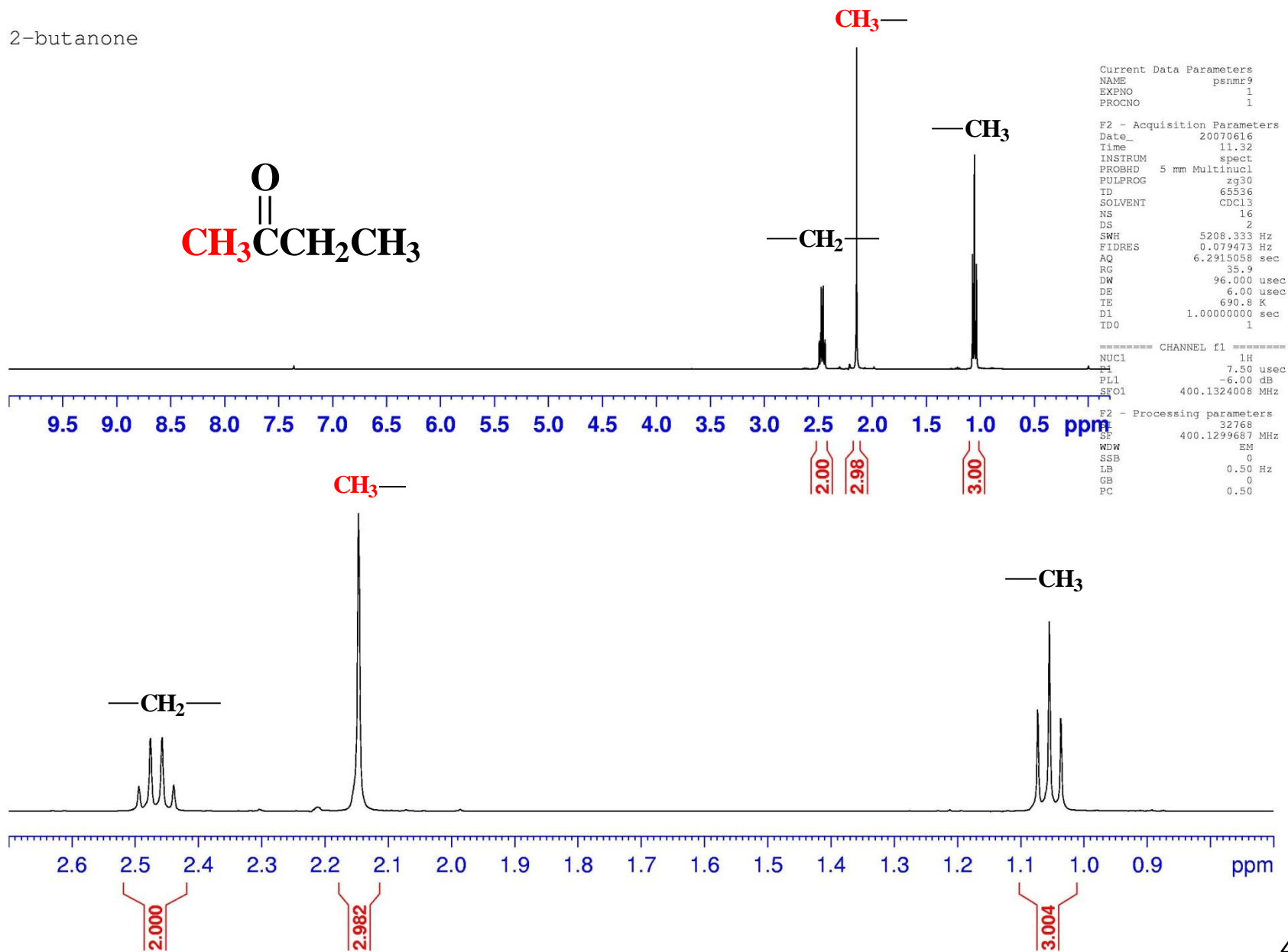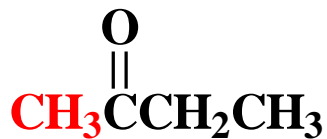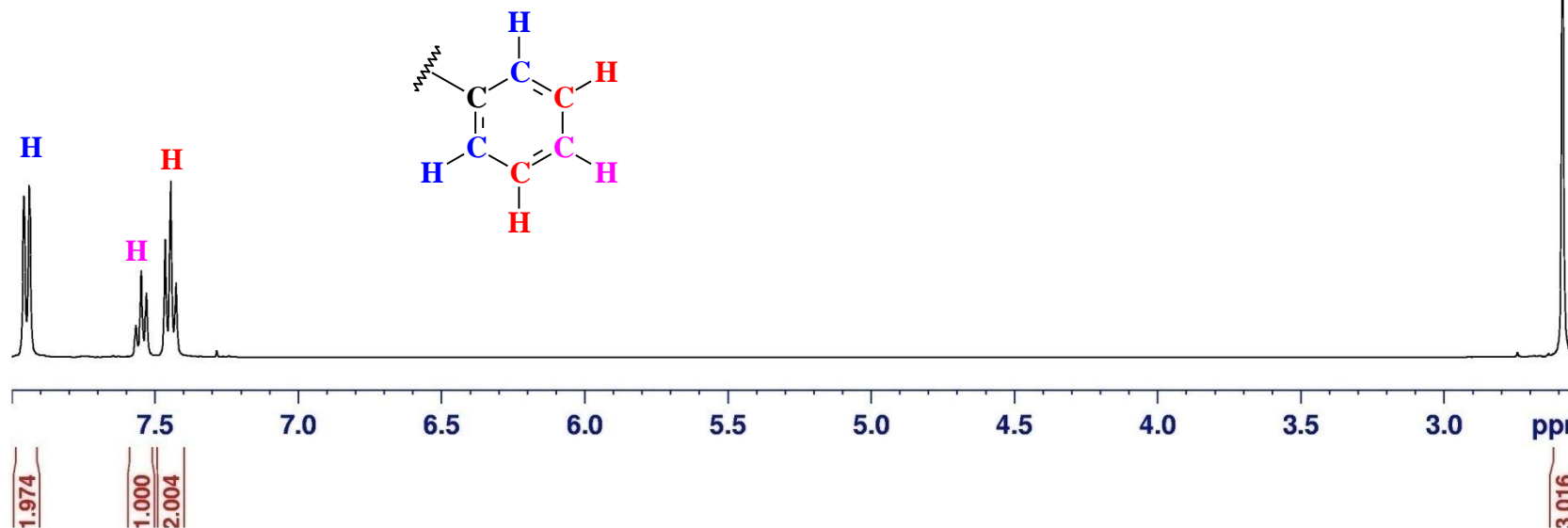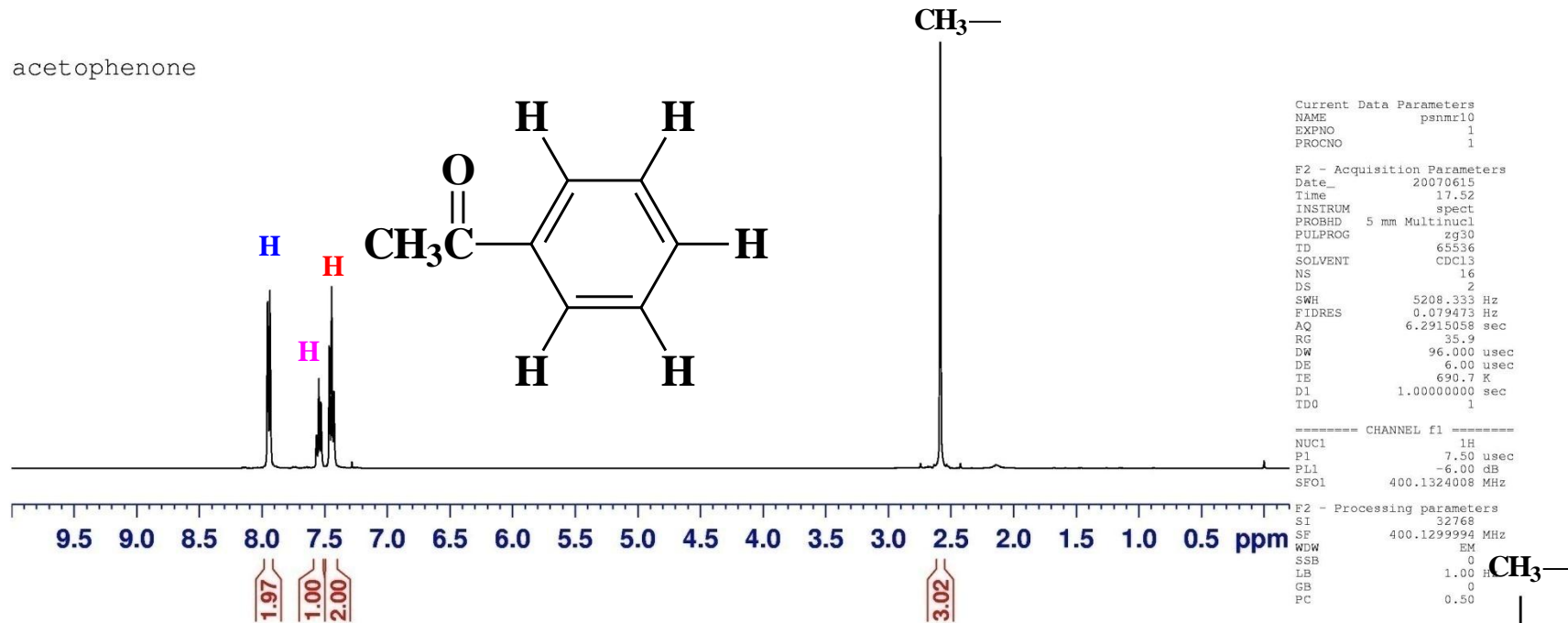SSB   0
LB   0.50 Hz
GB   0
PC   0.50

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

2.00 2.98   3.00

CH₃—

—CH₃

—CH₂—

2.6   2.5   2.4   2.3   2.2   2.1   2.0   1.9   1.8   1.7   1.6   1.5   1.4   1.3   1.2   1.1   1.0   0.9   ppm

2.000   2.982   3.004

48

acetophenone

CH₃—

49

1-butanol

$CH_3CH_2CH_2CH_2OH$

51

1-pentanol

$CH_3CH_2CH_2CH_2CH_2OH$

—CH_2—O

CH_2 and CH_3

—CH_2—

—CH_2—

—CH_2—

—OH

Current Data Parameters
NAME   psnmr13
EXPNO   1
PROCNO   1

F2 — Acquisition Parameters
Date_   20070616
Time   13.52
INSTRUM   spect
PROBHD   5 mm Multinucl
PULPROG   zg30
TD   65536
SOLVENT   CDCl3
NS   16
DS   2
SWH   5208.333 Hz
FIDRES   0.079473 Hz
AQ   6.2915058 sec
RG   35.9
DW   96.000 usec
DE   6.00 usec
TE   690.8 K
D1   1.00000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   1H
P1   7.50 usec
PL1   -6.00 dB
SFO1   400.1324008 MHz

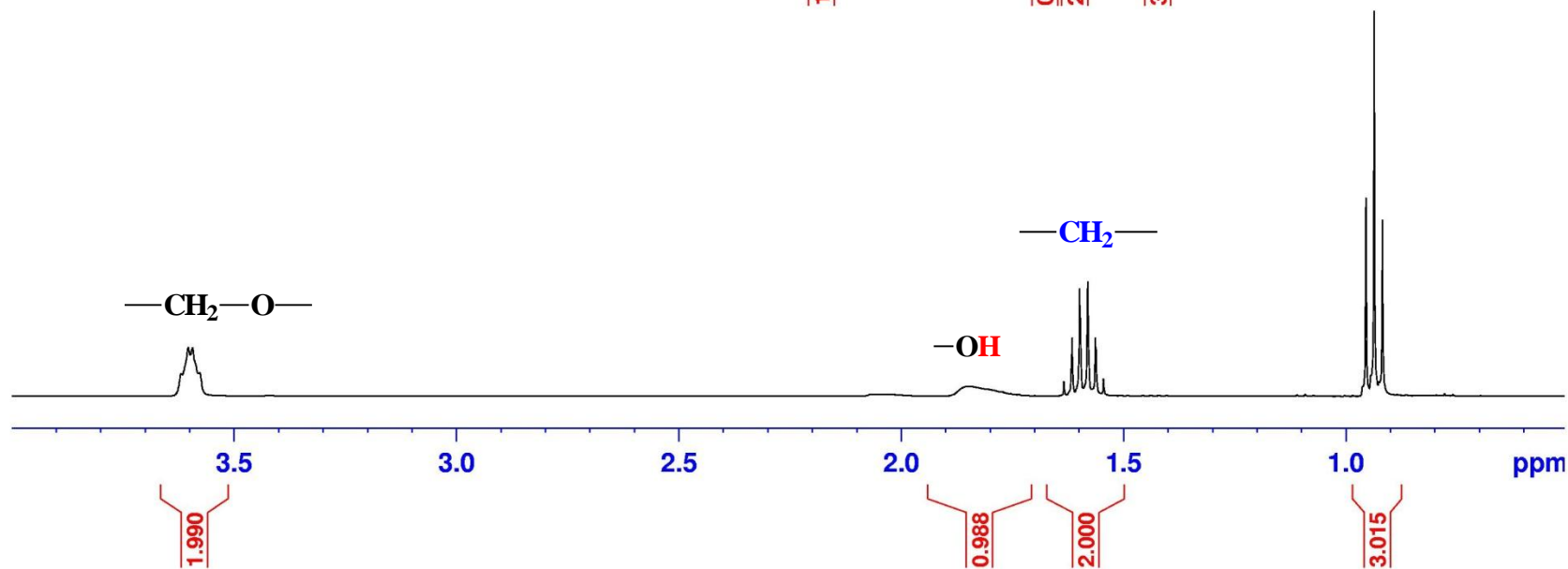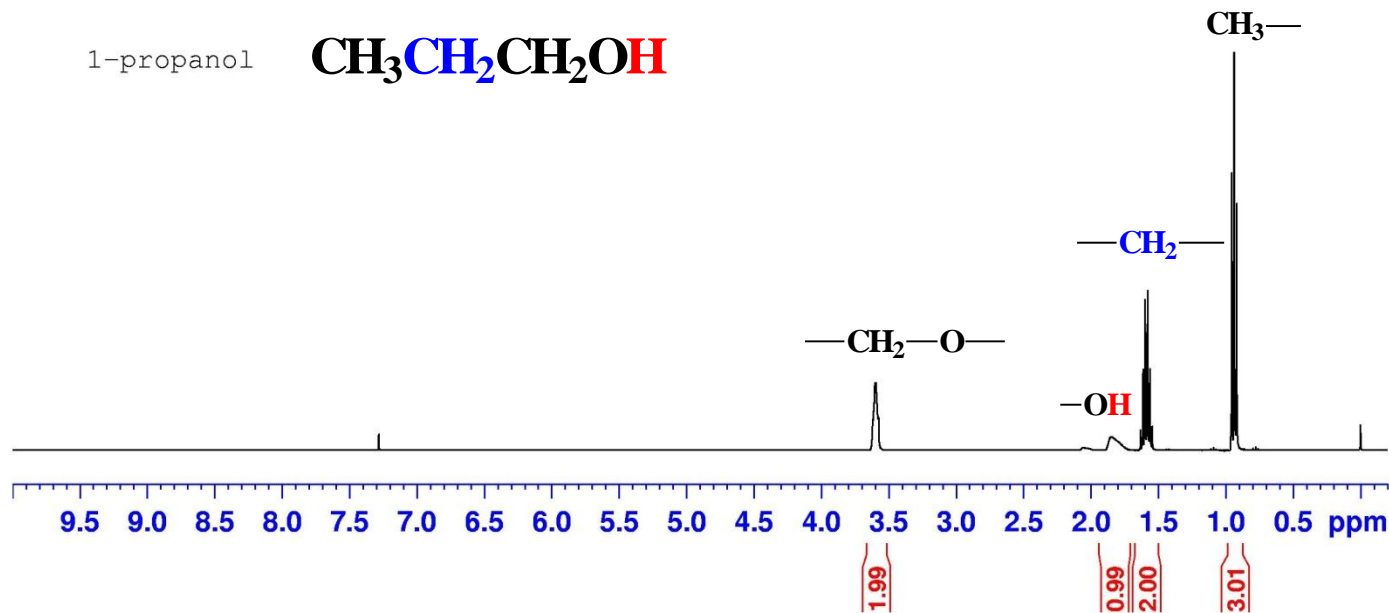F2 — Processing parameters
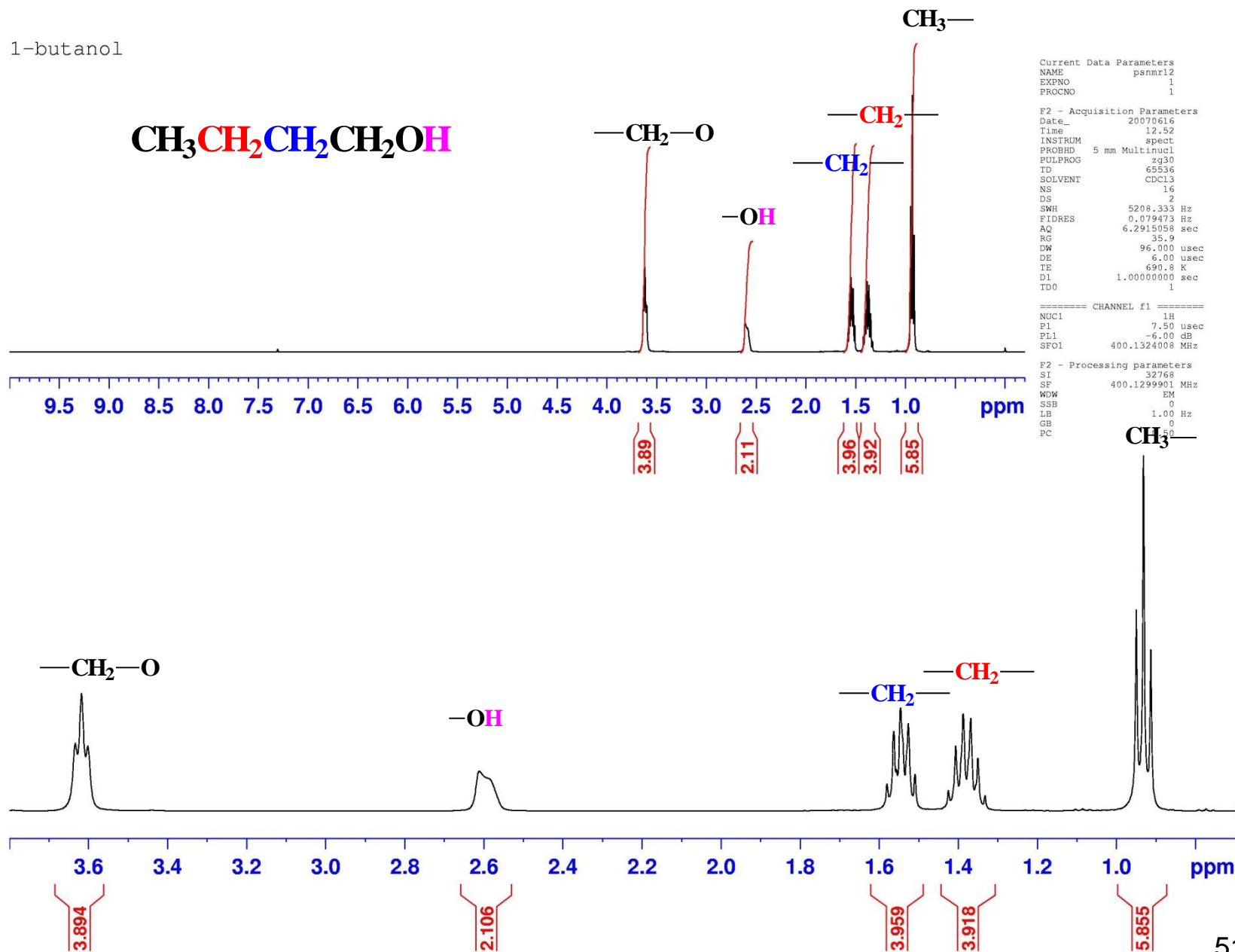SI   32768
SF   400.1299963 MHz
WDW   EM
SSB   0
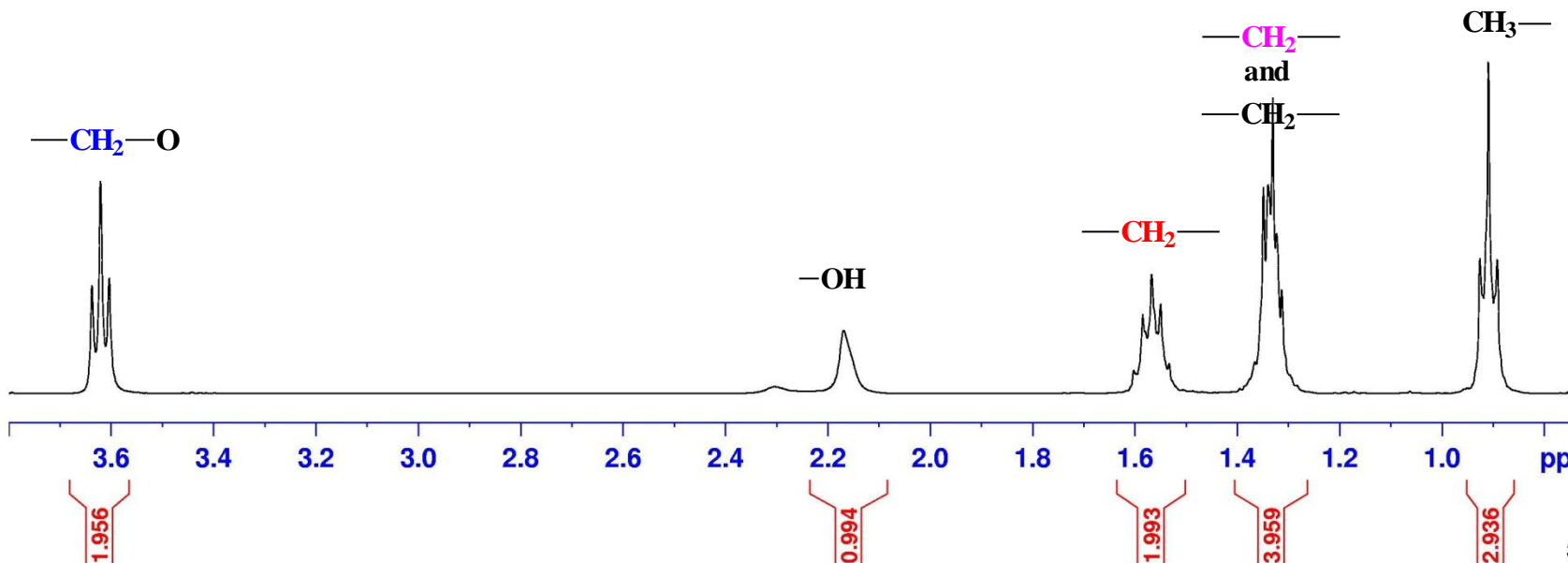LB   0.50 Hz
GB   0
PC   0.50

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

1.96   0.99   1.99 3.96   2.94

—CH_2—O

CH_2 and CH_2

CH_3

—CH_2—

—OH

3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 pp

1.956   0.994   1.993   3.959   2.936

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1-methylcyclohexene

CH₃

H

H

CH₃

H

H

H

H

other Hs

H
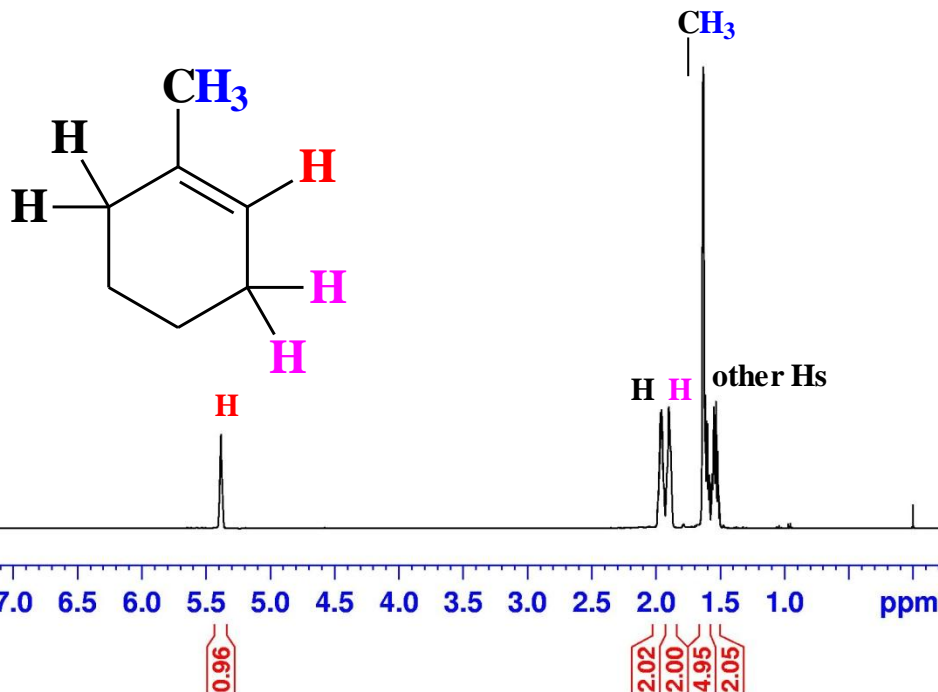
Current Data Parameters
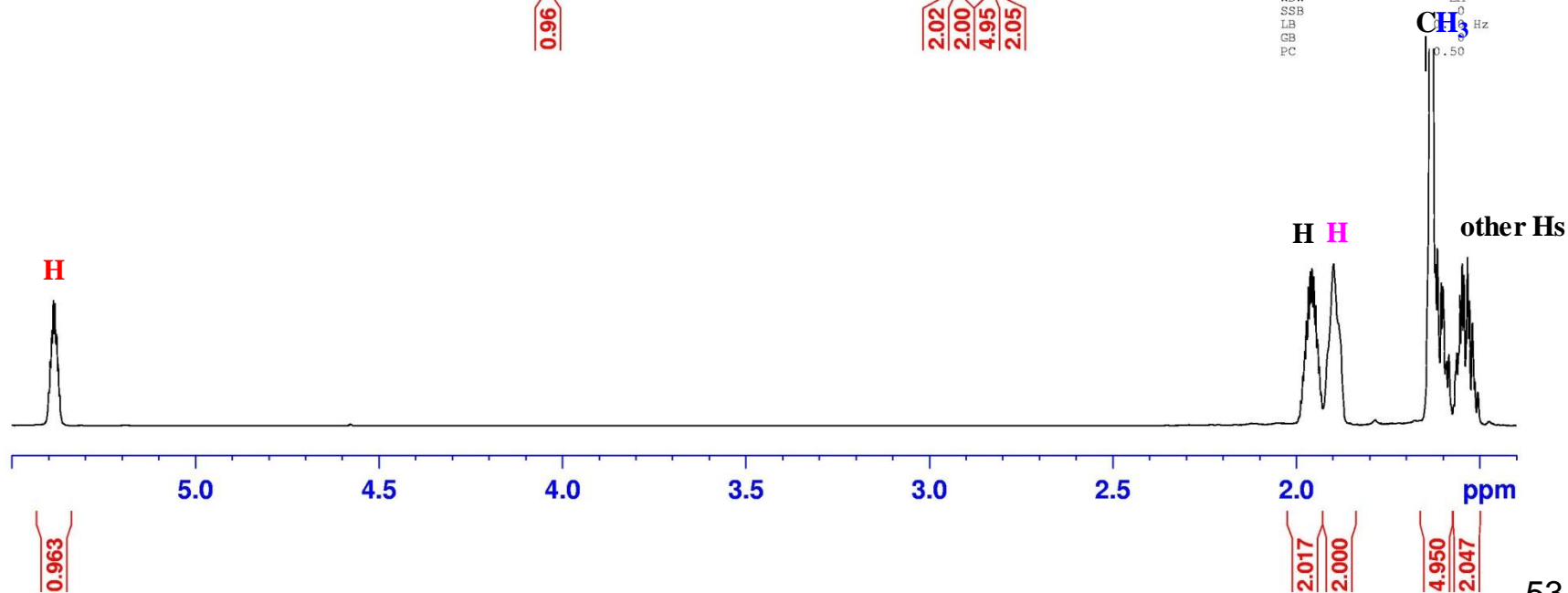NAME   psnmr15
EXPNO   1
PROCNO   1

F2 - Acquisition Parameters
Date_   20070616
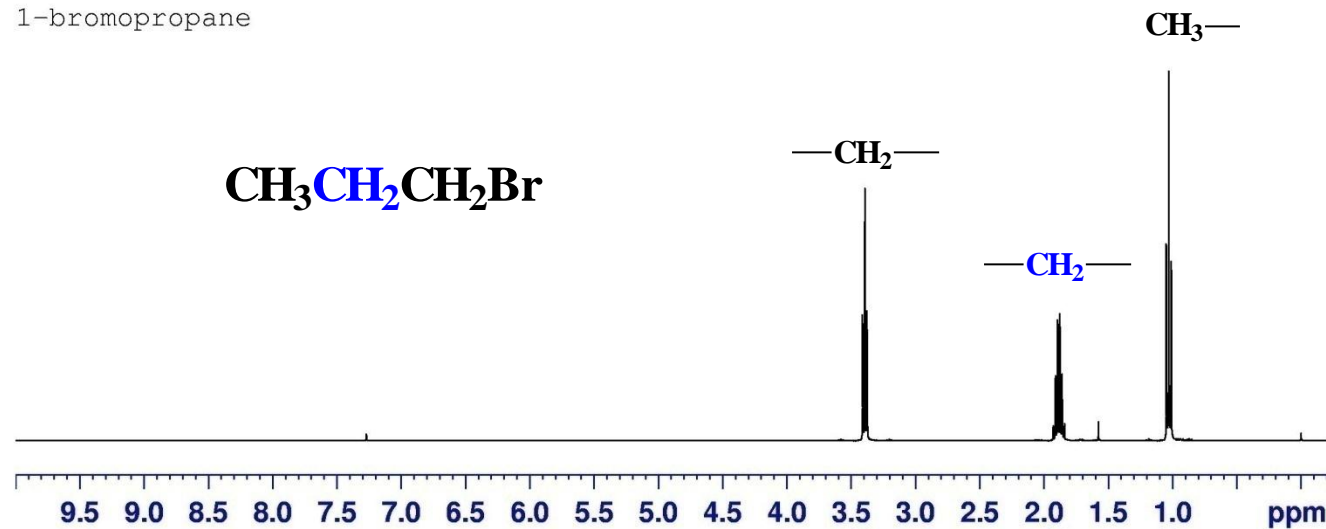Time   18.25
INSTRUM   spect
PROBHD   5 mm Multinucl
PULPROG   zg30
TD   65536
SOLVENT   CDCl3
NS   16
DS   2
SWH   5208.333 Hz
FIDRES   0.079473 Hz
AQ   6.2915058 sec
RG   35.9
DW   96.000 usec
DE   6.00 usec
TE   690.9 K
D1   1.00000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   1H
P1   7.50 usec
PL1   -6.00 dB
SFO1   400.1324008 MHz

F2 - Processing parameters
SI   32768
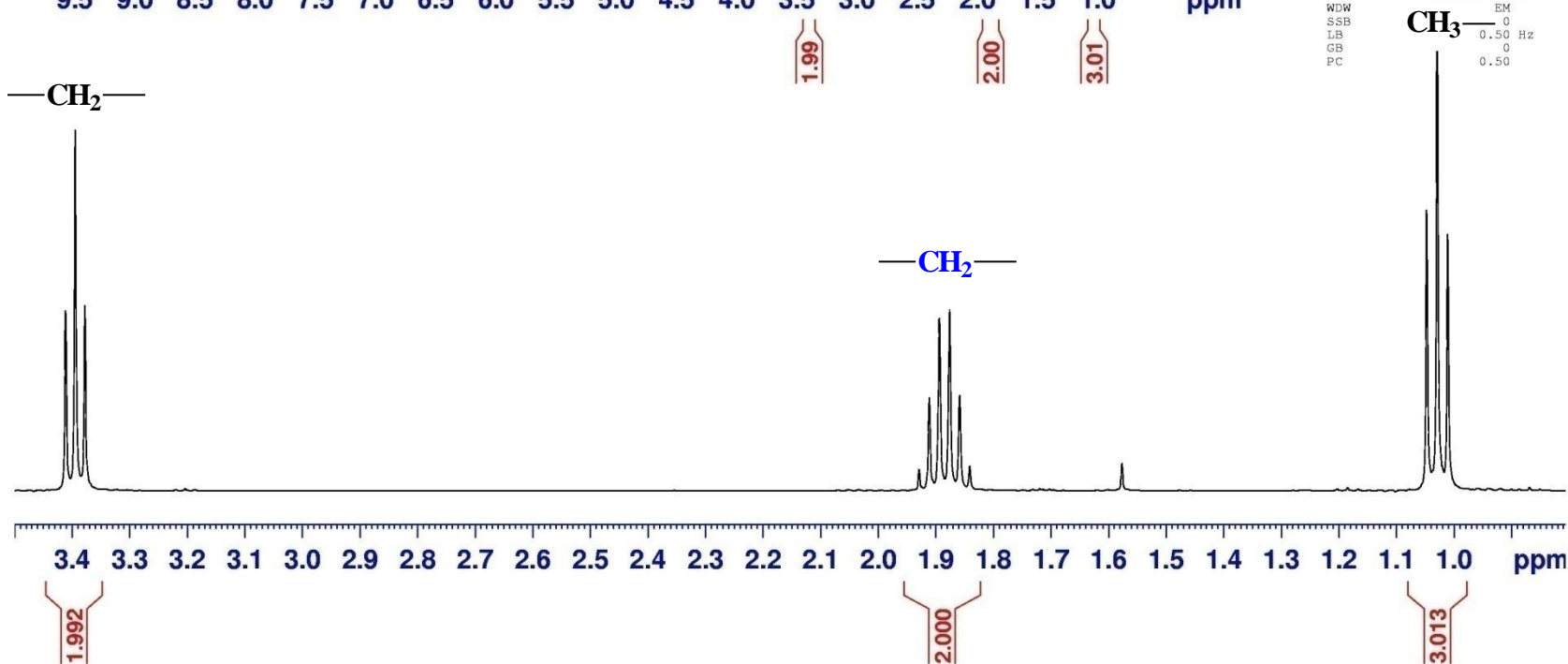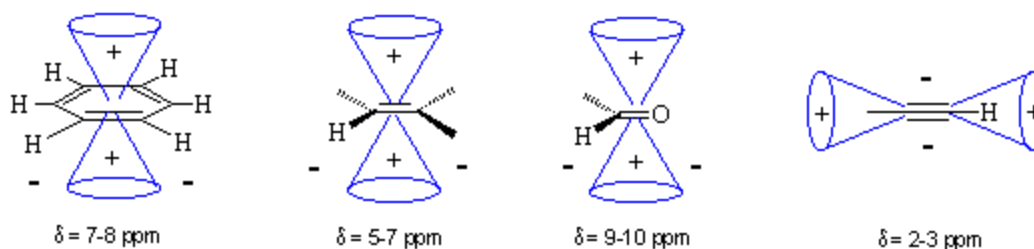SF   400.1300114 MHz
WDW   EM
SSB   0
LB   Hz
GB   0
PC   0.50

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0   ppm

0.96   2.02 2.00 4.95 2.05

CH₃

H H   other Hs

H

5.0   4.5   4.0   3.5   3.0   2.5   2.0   ppm

0.963   2.017 2.000   4.950 2.047

53

1-bromopropane

$CH_3CH_2CH_2Br$

—CH_2—

CH_3—

—CH_2—

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0   ppm

1.99   2.00   3.01

—CH_2—

—CH_2—

CH_3—

3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0   ppm

1.992   2.000   3.013

54

Magnetic Anisotropy

- Magnetic anisotropy means that there is a "non-uniform magnetic field". Electrons in p systems (*e.g.* aromatics, alkenes, alkynes, carbonyls *etc.*) interact with the applied field which induces a magnetic field that causes the anisotropy. As a result, the nearby protons will experience 3 fields: the applied field, the shielding field of the valence electrons and the field due to the p system. Depending on the position of the proton in this third field, it can be either shielded (smaller δ) or deshielded (larger δ), which implies that the energy required for, and the frequency of the absorption will change.

Magnetic Anisotropy

Field lines oppose the applied field creating a
reduced field in this region (equivalent to shielding)

Anisotropic induced magnetic field lines
due to the induced circulation of the pi
electrons in benzene

Field lines aligned with applied field creating a
larger field in this region (equivalent to deshielding)

Applied
Magnetic
Field

$\delta = 7\text{-}8$ ppm $\qquad$ $\delta = 5\text{-}7$ ppm $\qquad$ $\delta = 9\text{-}10$ ppm $\qquad$ $\delta = 2\text{-}3$ ppm
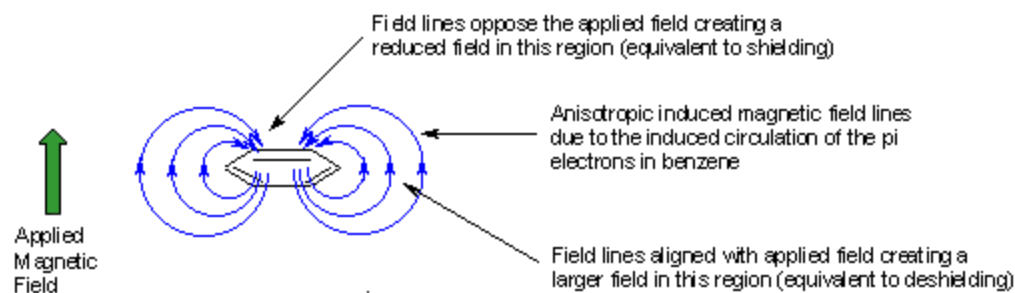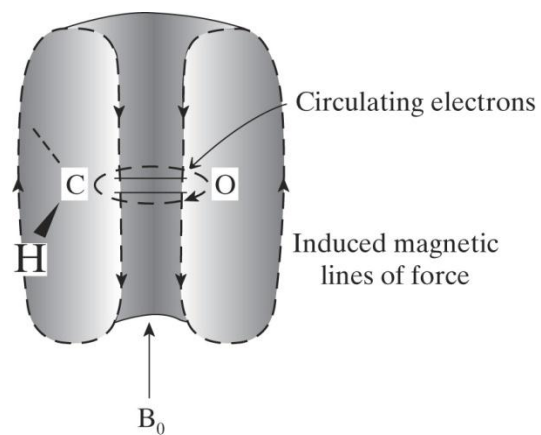
Schematic diagram of shielding cones for common pi systems.
The + denotes shielding areas and - denotes deshielding areas.
Remember shielding lowers the chemical shift, δ and
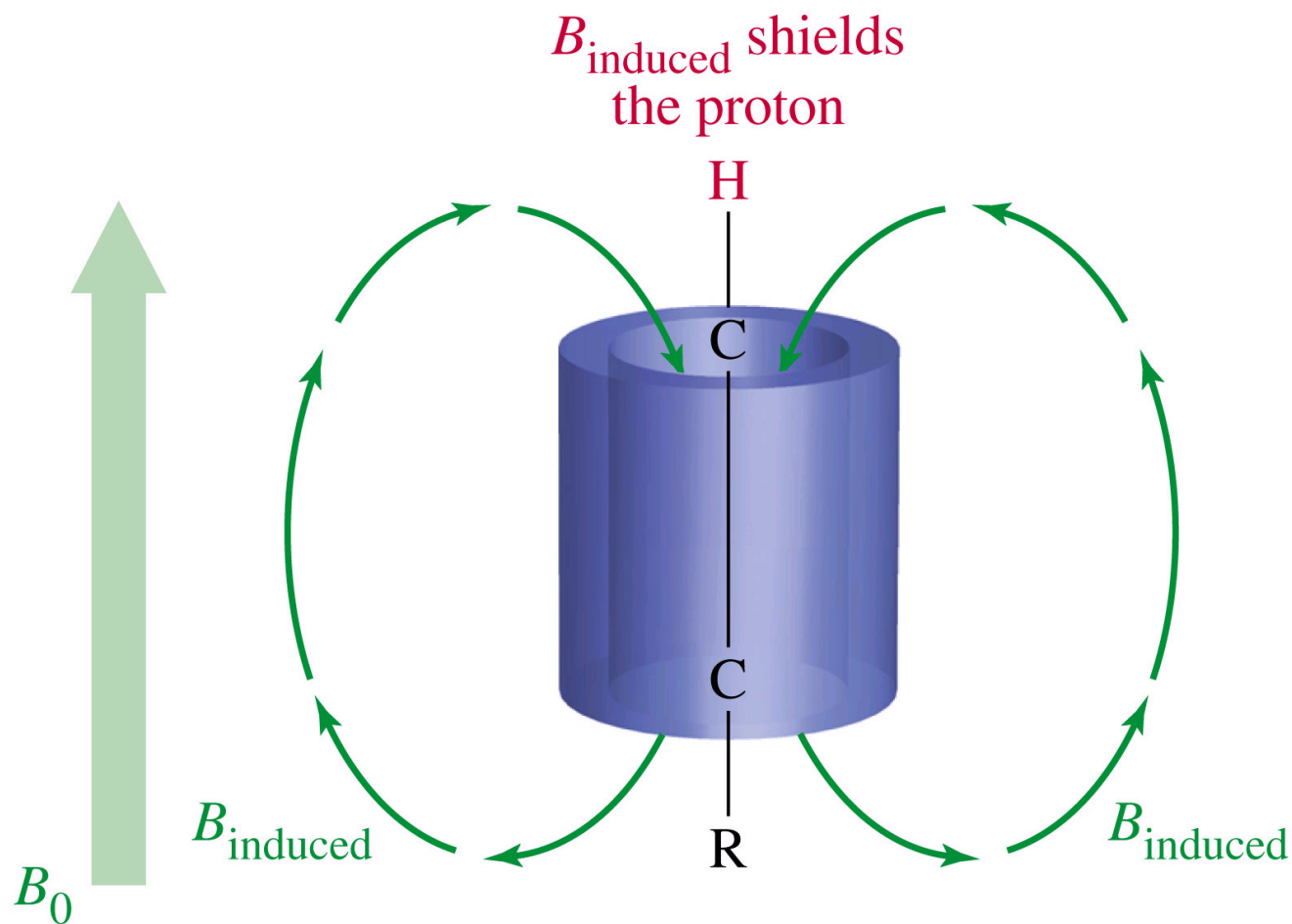deshielding increases δ. Typical H δ values are also shown.

Benzene Deshielding
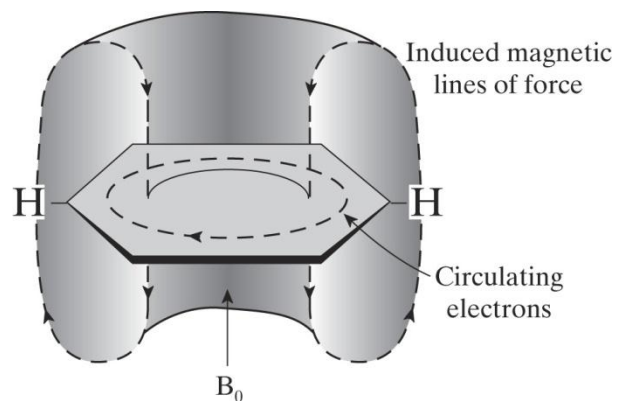
Carbonyl Deshielding

Alkyne Shielding

$B_{induced}$ shields the proton

H

$B_{induced}$

B_0

$B_{induced}$

Electronegativity and chemical shift

- Since the field experienced by the proton defines the energy difference between the two spin states, the frequency and hence the chemical shift, δ /ppm, will change depending on the electron density around the proton. Electronegative groups attached to the C-H system decrease the electron density around the protons, and there is less shielding (*i.e.* deshielding) so the chemical shift increases.

- This is reflected by the plot shown in the graph to the left which is based on the data shown below.
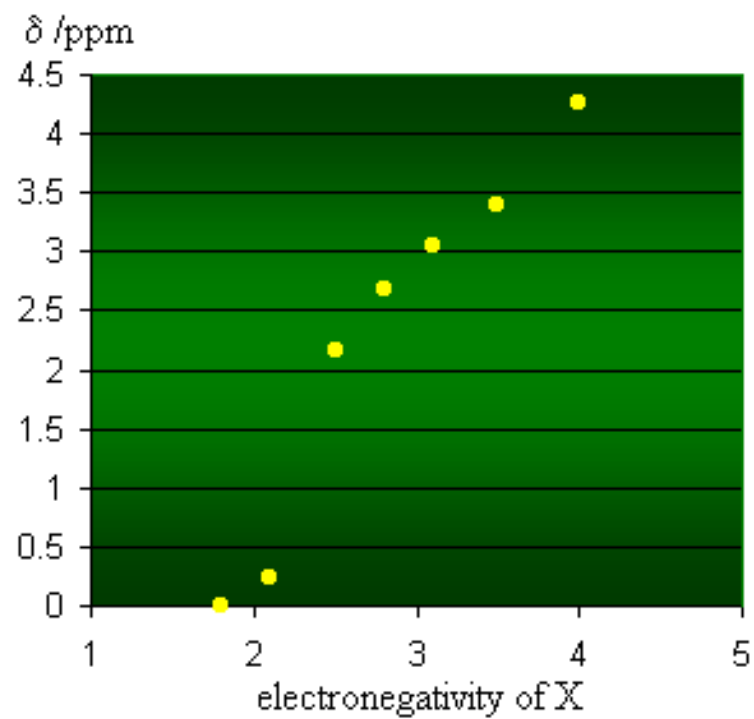
Compound, CH3X	CH$_3$F	CH$_3$OH	CH$_3$Cl	CH$_3$Br	CH$_3$I	CH$_4$	(CH$_3$)$_4$Si
X	F	O	Cl	Br	I	H	Si
Electronegativity of X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift, δ / ppm	4.26	3.4	3.05	2.68	2.16	0.23	0

These effects are cumulative, so the presence of more electronegative groups produce more deshielding and therefore, larger chemical shifts.

Compound	CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$
δ / ppm	0.23	3.05	5.30	7.27

These inductive effects at not just felt by the immediately adjacent protons as the disruption of electron density has an influence further down the chain. However, the effect does fade rapidly as you move away from the electronegative group. As an example, look at the chemical shifts for part of a primary bromide

H signal	$-CH_2-CH_2-CH_2Br$
δ / ppm	1.25 1.69 3.30