344 Organic Chemistry Laboratory Spring 2013

Lecture 1 Introduction to ^{1}H-NMR Spectroscopy

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CHEM 344 Required Materials

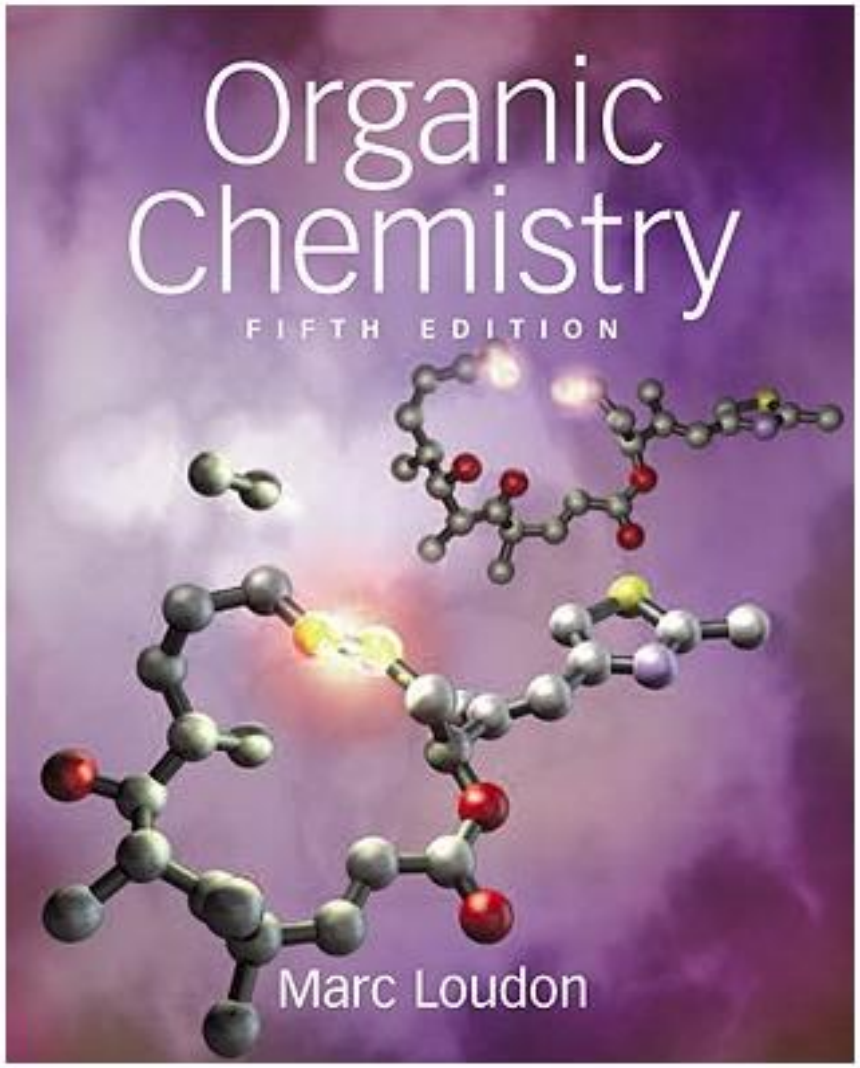
Spring 2013 Lab Manual
$30, Alpha Chi Sigma
all other manuals obsolete

Lab Notebook
Duplicate copy, spiral bound
$10-$15 bookstore or Alpha Chi Sigma

Lab Goggles
Not glasses
$8-$12 bookstore or Alpha Chi Sigma

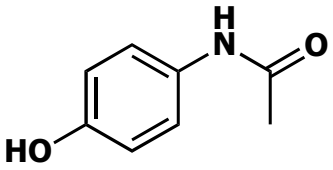
Recommended textbook

Loudon 5th Ed.

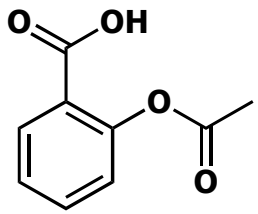


CHEM 343/345 notes

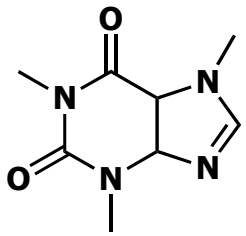
How do we **really** know the structure of these molecules?



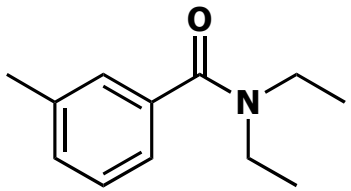
Acetaminophen



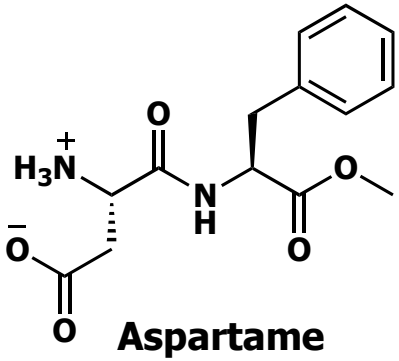
Acetylsalicylic acid



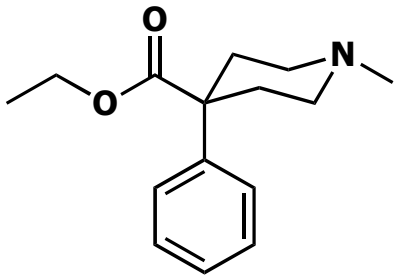
Caffeine



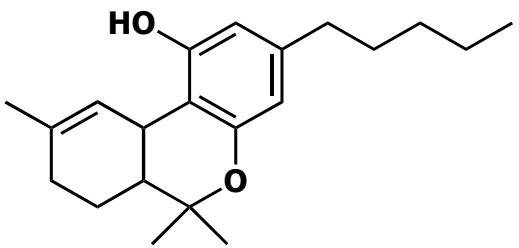
DEET



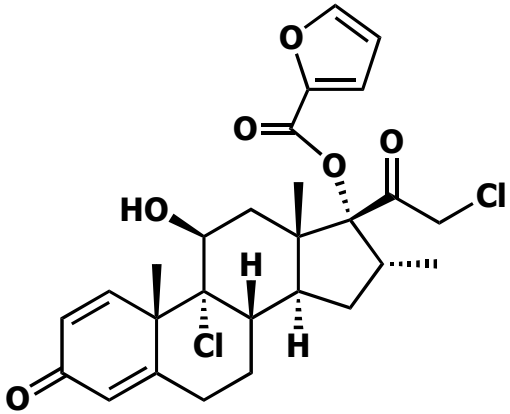
Aspartame



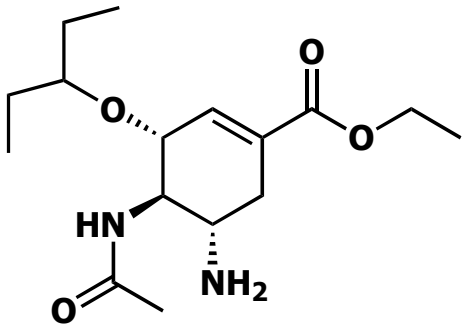
Demerol



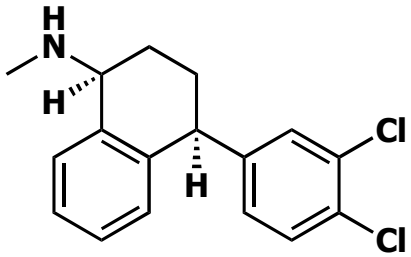
Δ^9-THC



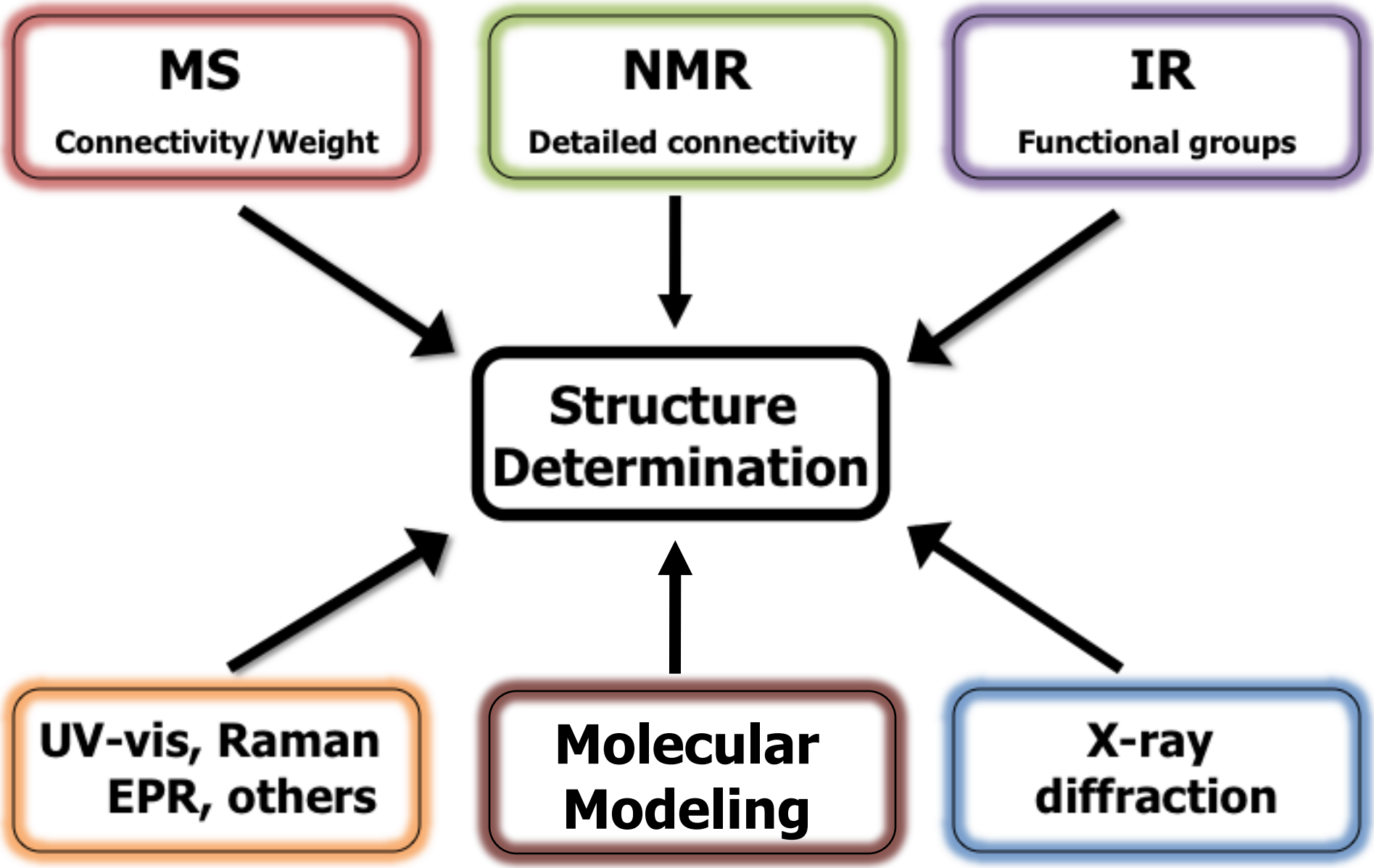
Nasonex



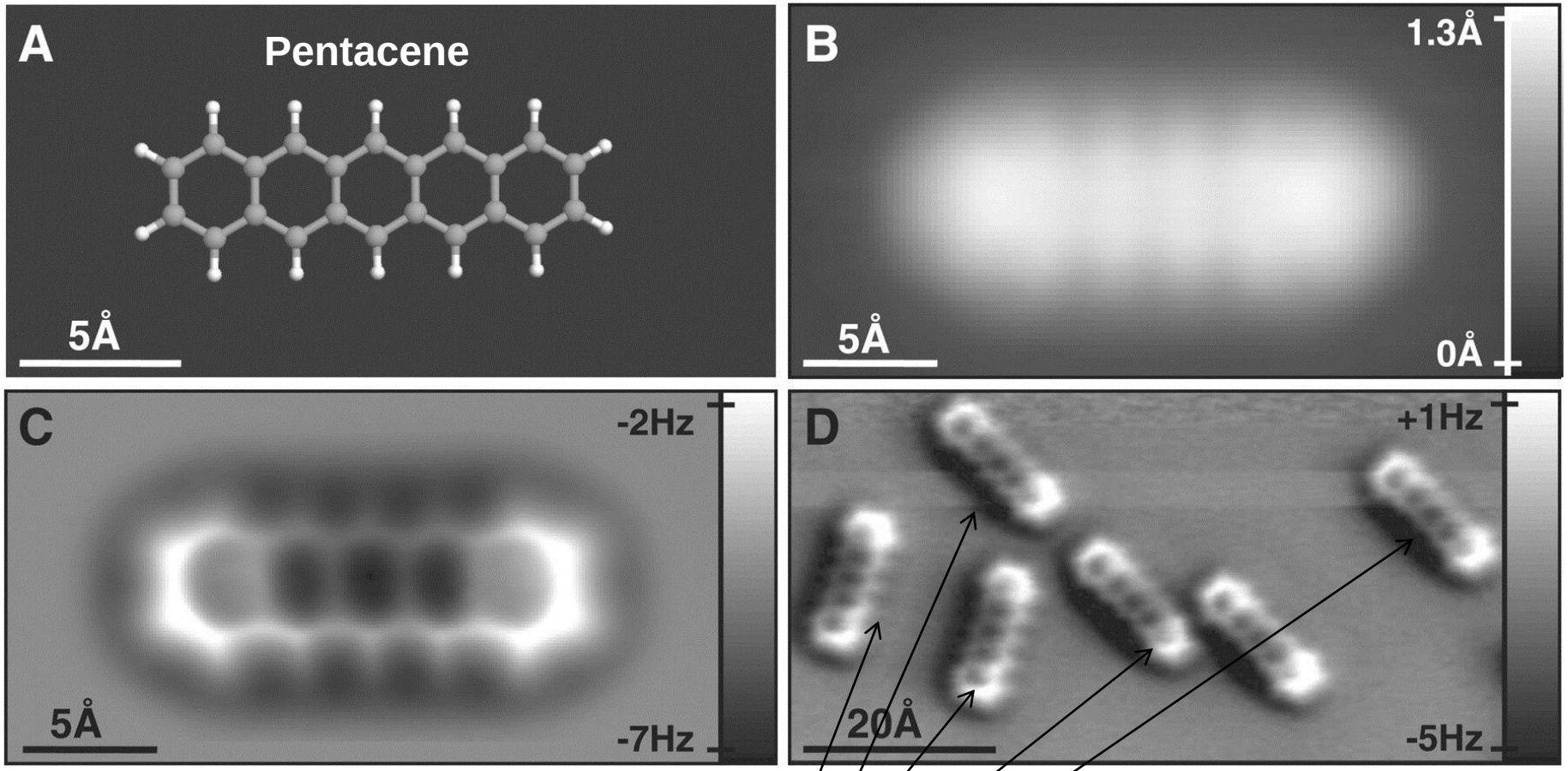
Tamiflu



Zoloft


MS
Connectivity/Weight
NMR
Detailed connectivity
IR
Functional groups
Structure Determination
UV-vis, Raman EPR, others
Molecular Modeling
X-ray diffraction

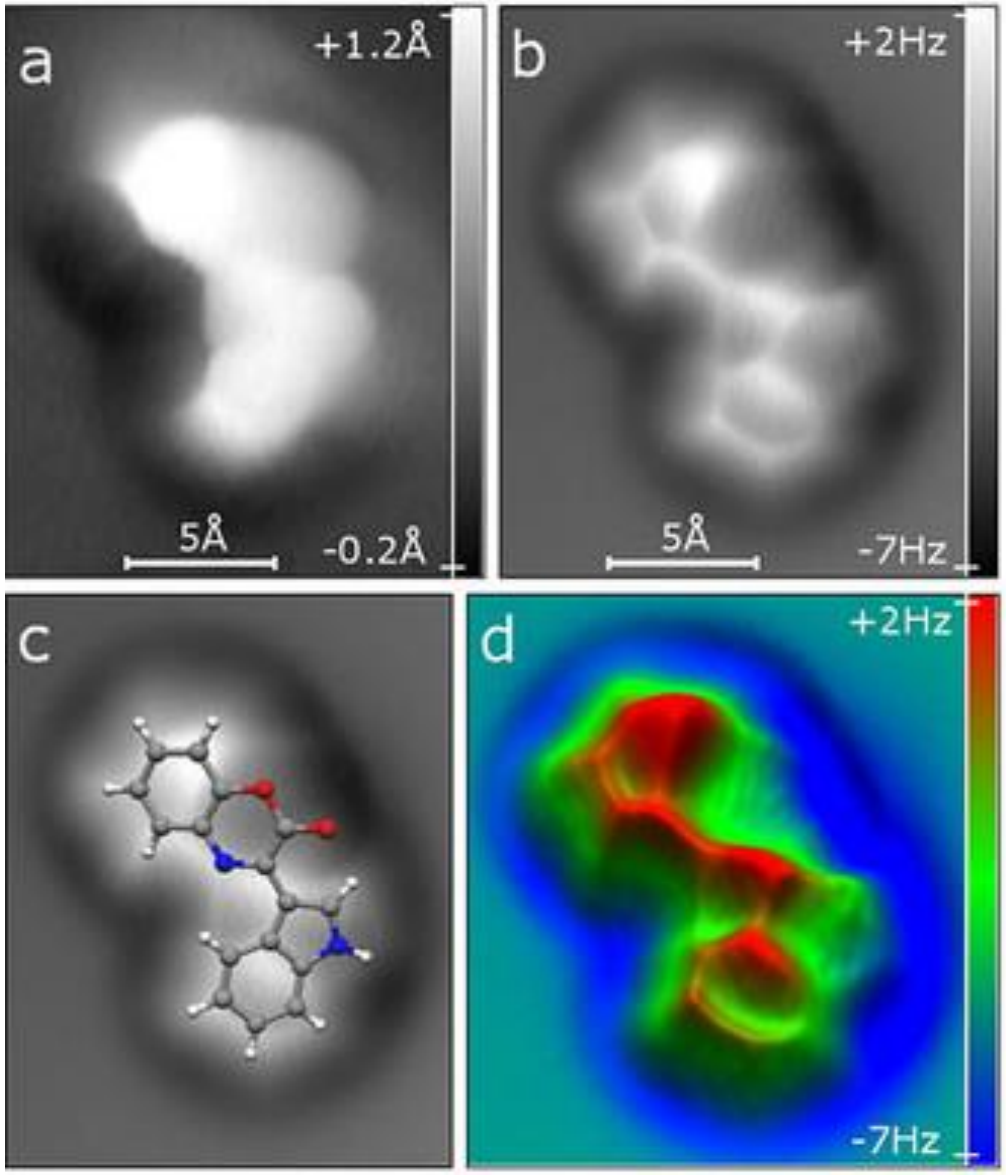
Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) first images of pentacene on a copper surface

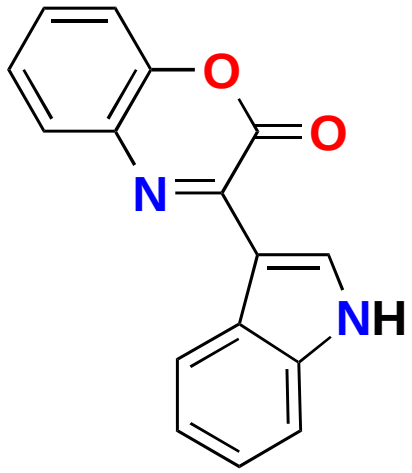


Can actually see the individual molecules of pentacene!

***Science* 2009, *325*, 1110 -1114.**

AFM imaging of cephalandole A





This is the current "frontier" method in structure determination

Neat…but way beyond what we need to know right now.

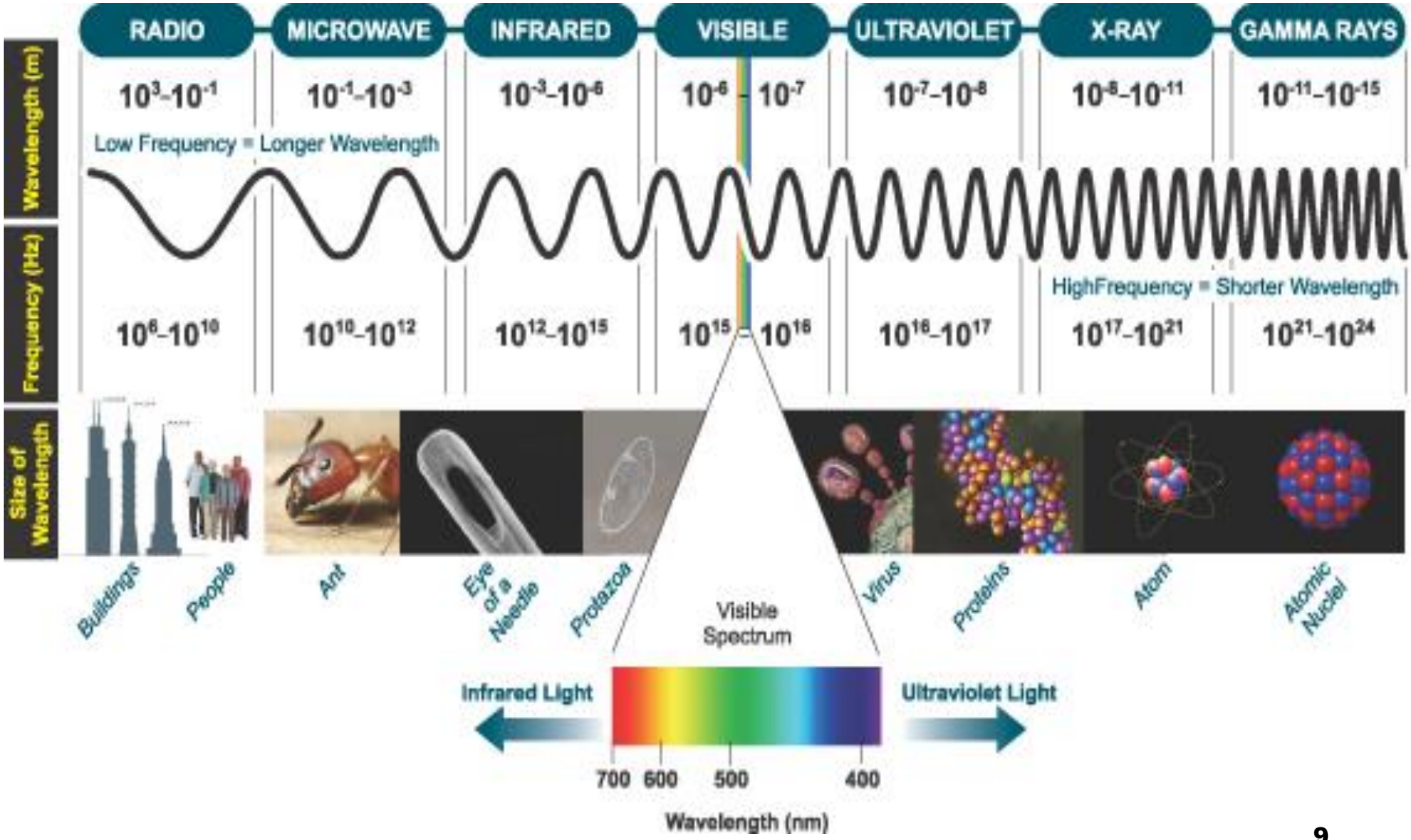
***Nature Chem.* 2010, *2*, 821-825.**

nature chemistry

Spectroscopy = using electromagnetic radiation to give info on molecular structure

E = hν E = energy (kJ/mol)

ν = frequency (Hz), h = Planck constant



Background & theory: Loudon, p. 536-538

Nuclear Magnetic Resonance

Spin ½ nuclei **^{1}H, ^{13}C**
NMR active, easy to do, widely used

Spin 1 nuclei **^{2}H (D), ^{14}N**
NMR active but not widely used

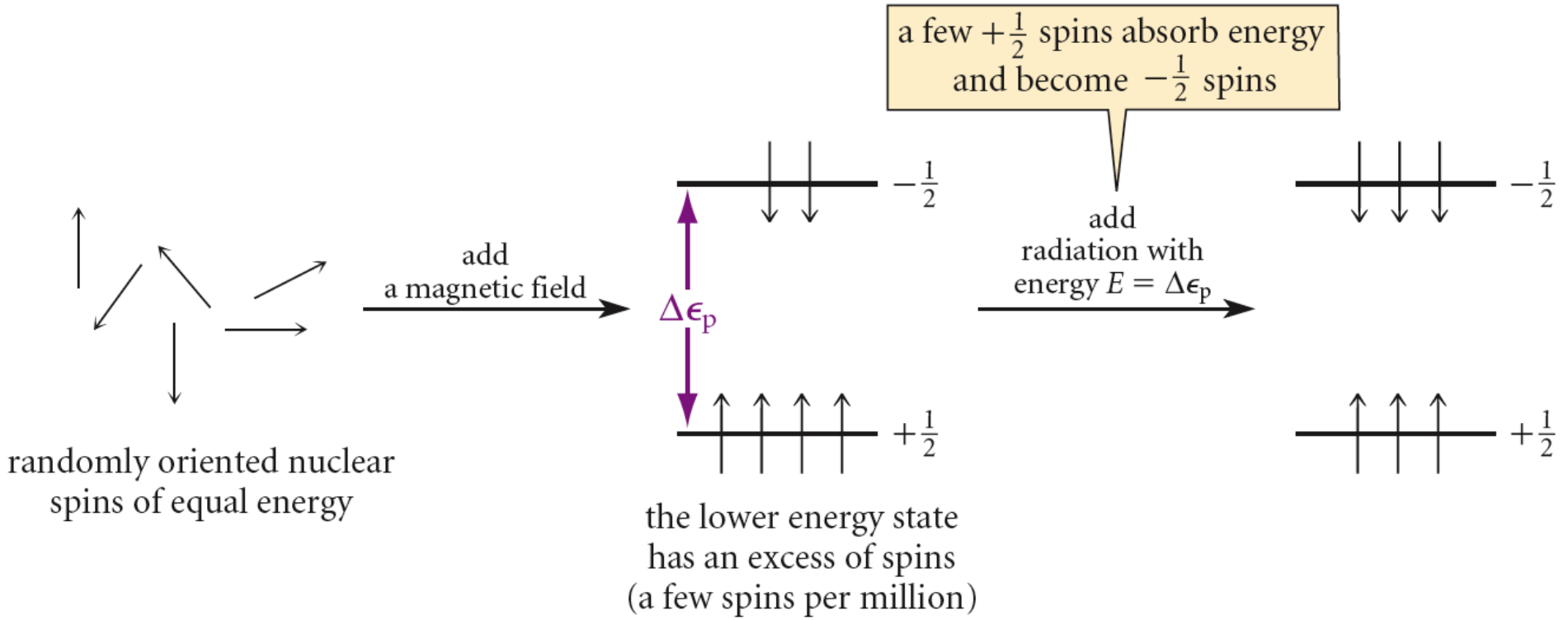
Spin 0 nuclei **^{12}C, ^{16}O, ^{32}S**
NMR silent

Background & theory: Loudon, p. 578-636

Nuclear Magnetic Resonance (NMR)

Spin ½ nuclei ^{1}H, ^{13}C

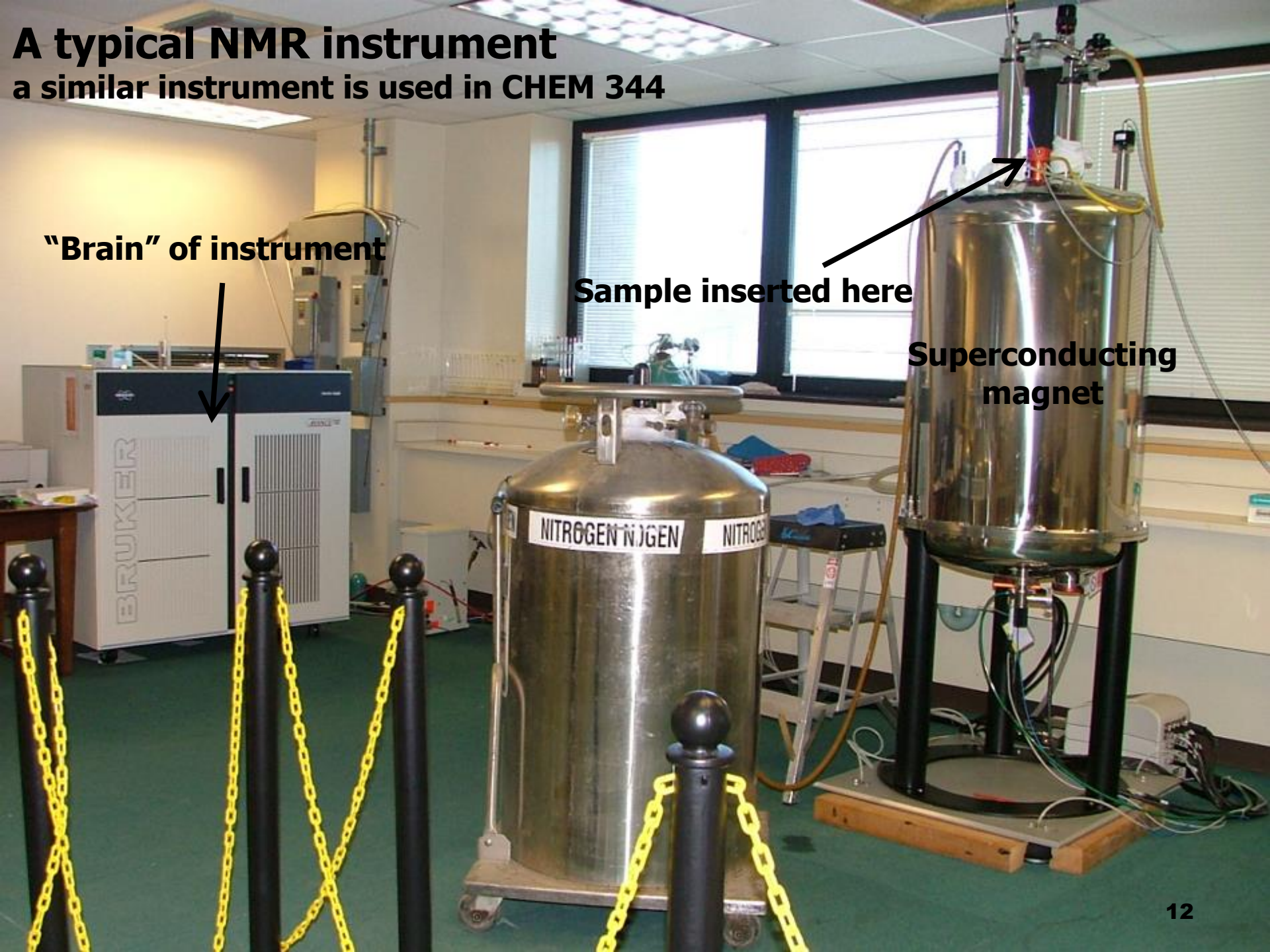
$^{1}H/^{13}C$ nucleus behaves like a bar magnet



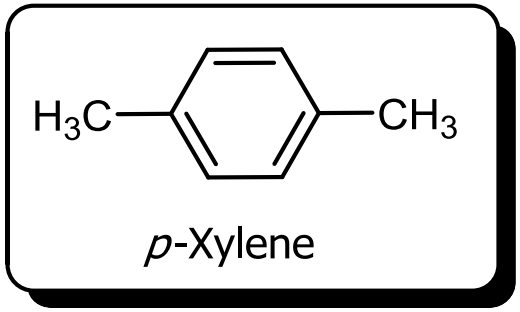
Background & theory: Loudon, p. 578-636

A typical NMR instrument

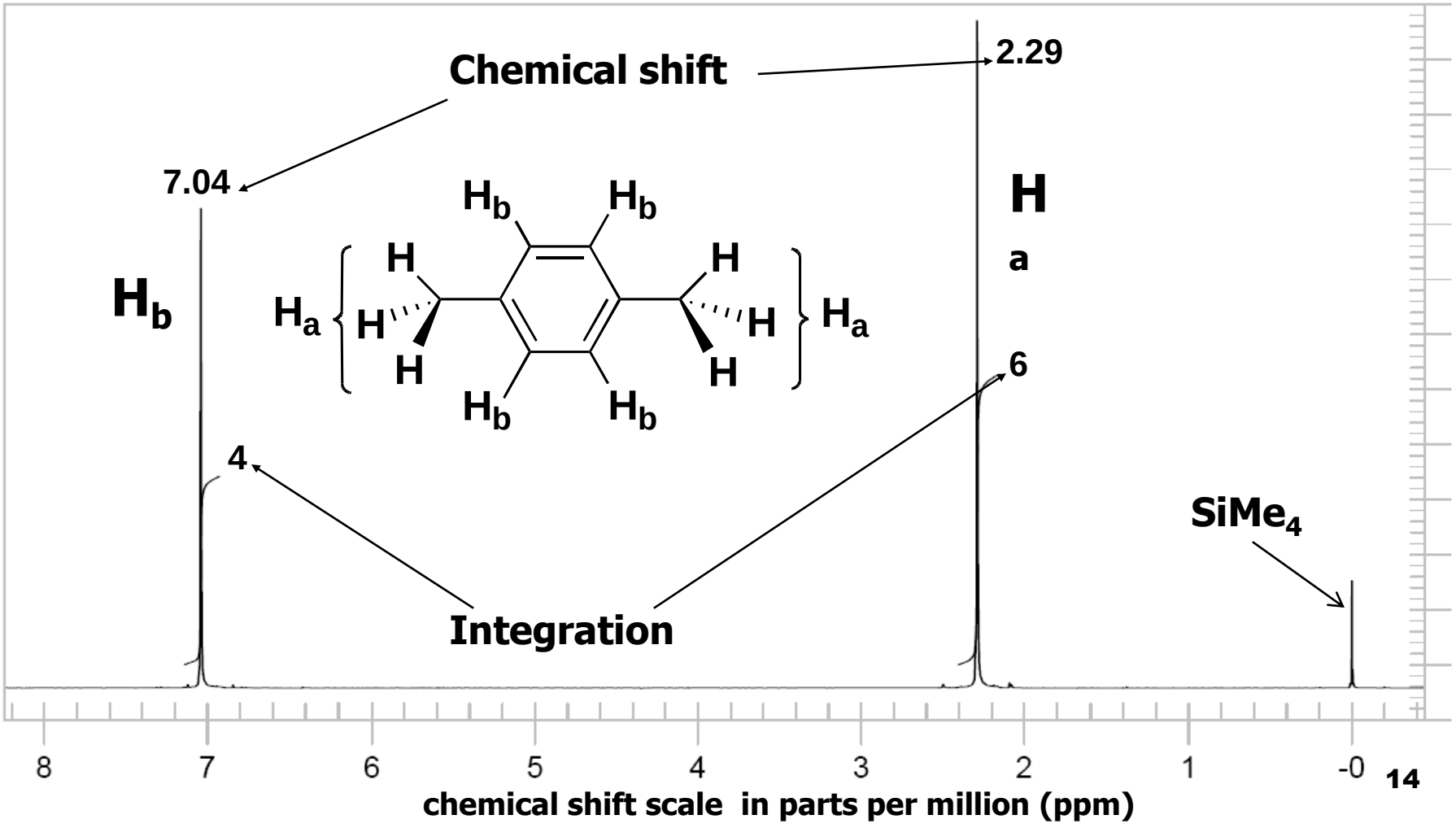
a similar instrument is used in CHEM 344

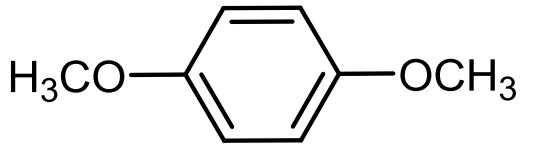


A more powerful (and expensive) NMR instrument



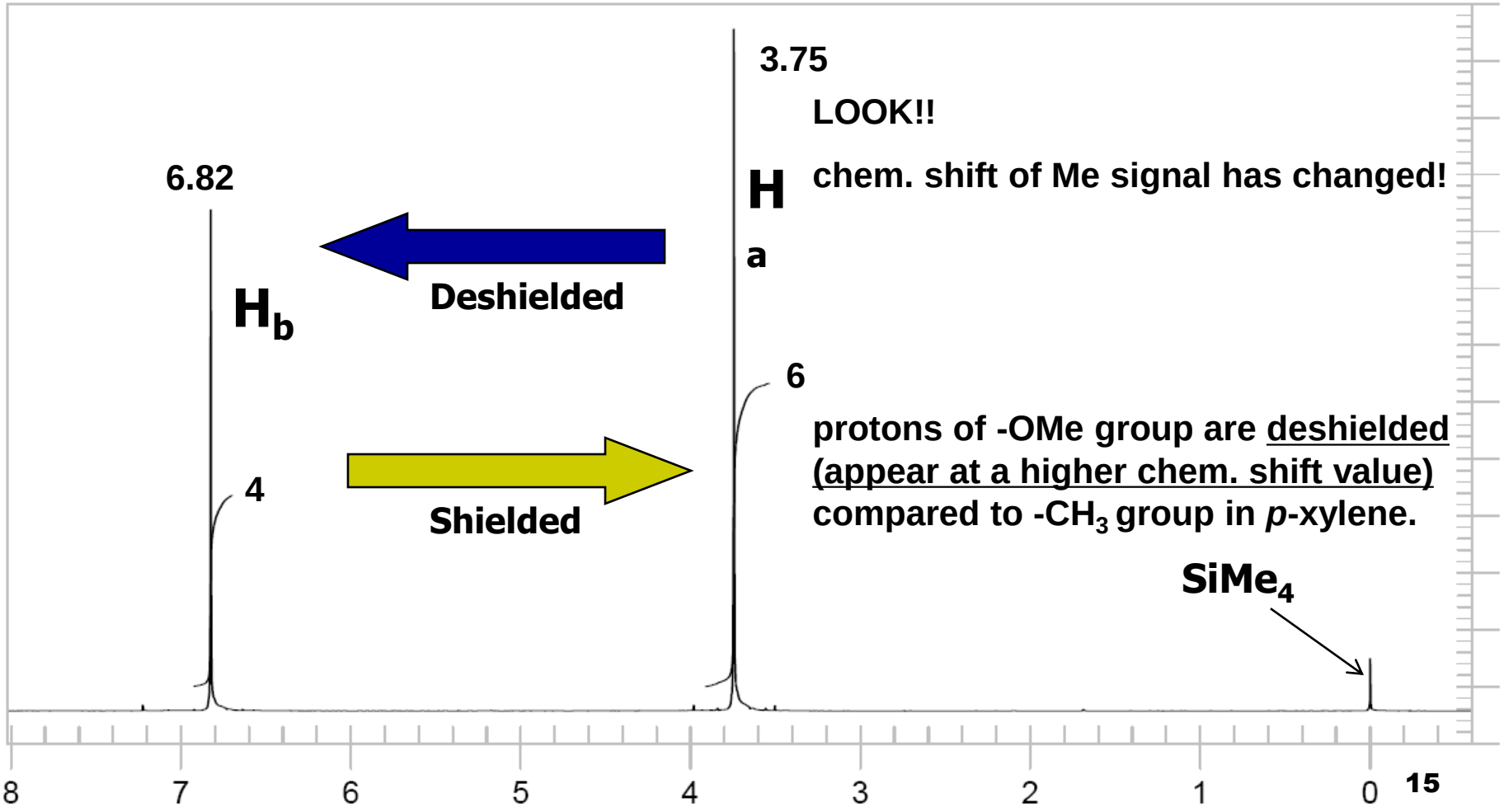
300 MHz ^{1}H NMR
In CDCl3

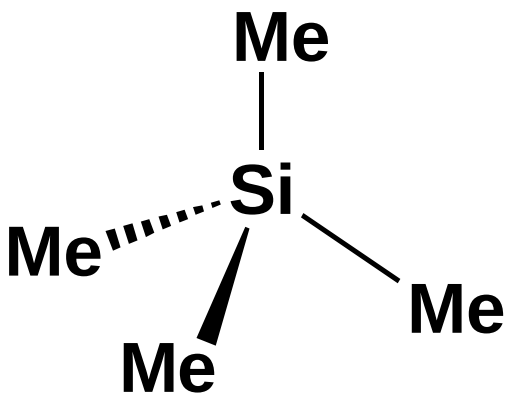




1,4-Dimethoxybenzene

300 MHz ^{1}H NMR
In CDCl3





$SiMe_4$ = TMS = Tetramethylsilane

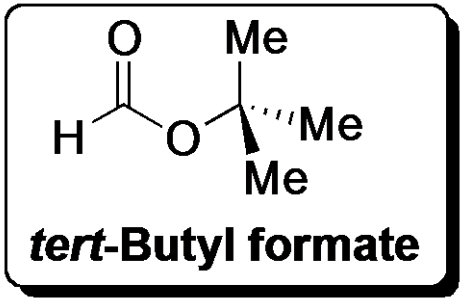
0.00 ppm reference compound

Why TMS?

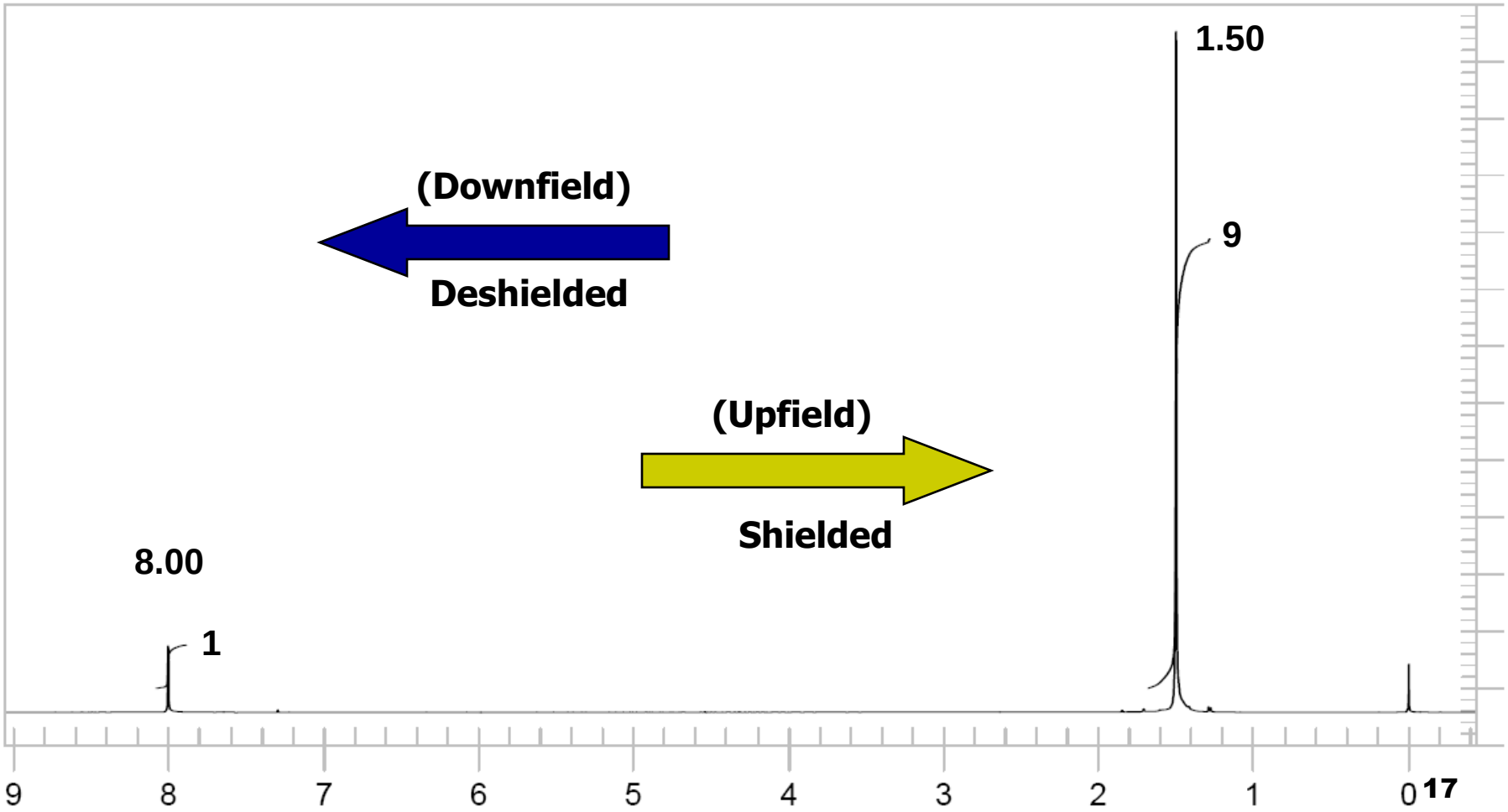
- chemically inert (won't react with most molecules)
- volatile (easily removed)
- cheap
- signal is unsplit and "out of the way"

<u>Don't assign the TMS signal as part of your molecule!</u>

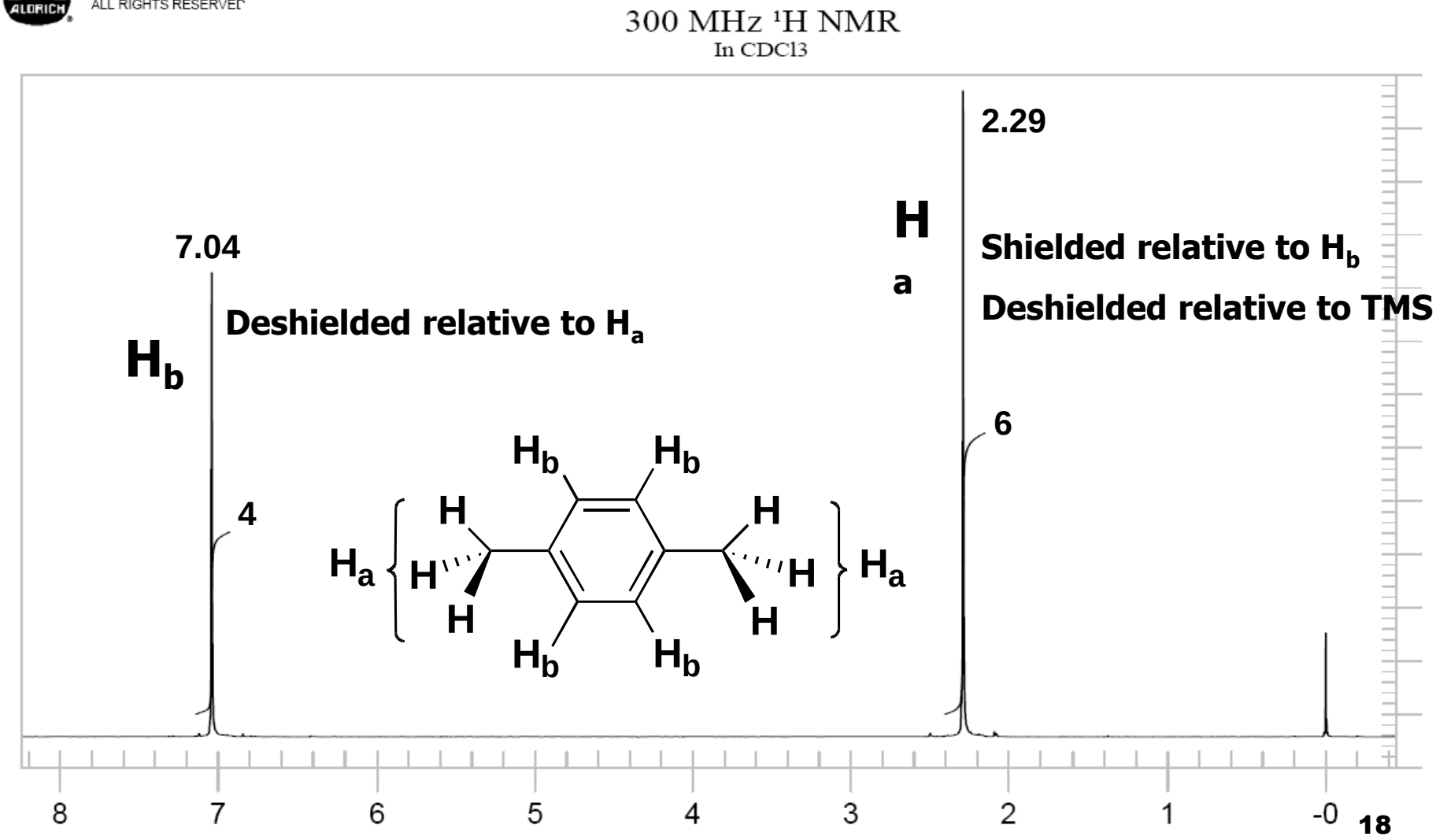
300 MHz ^{1}H NMR
In CDCl3



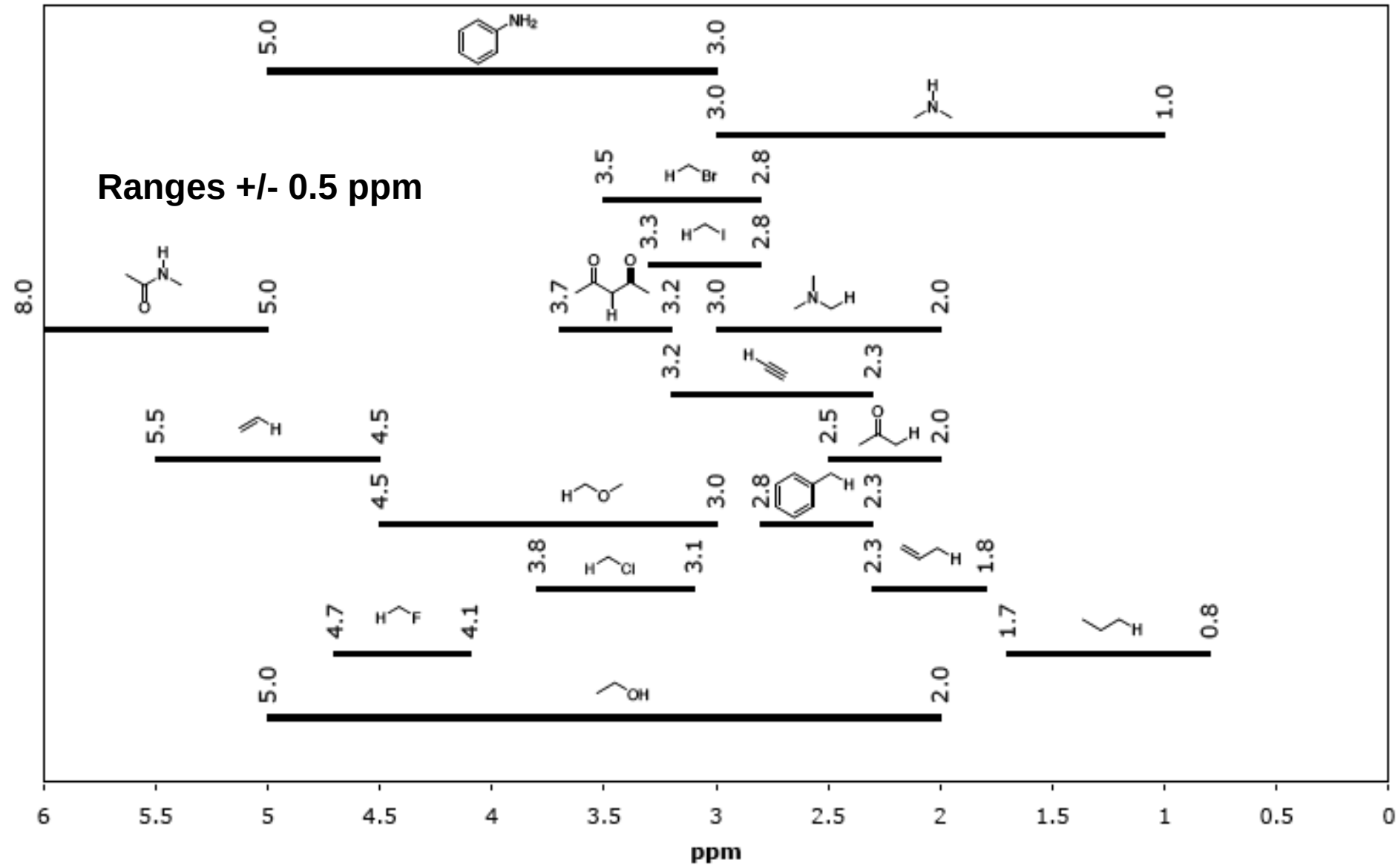
***tert*-Butyl formate**



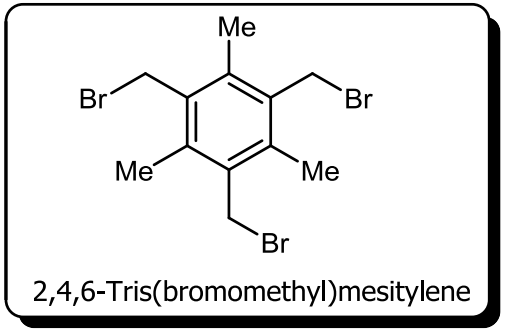
Shielding/deshielding is a relative term



^{1}H-NMR Chemical Shift Table



Confirm that the spectrum makes sense…..



2,4,6-Tris(bromomethyl)mesitylene

300 MHz ^{1}H NMR
In CDCl3

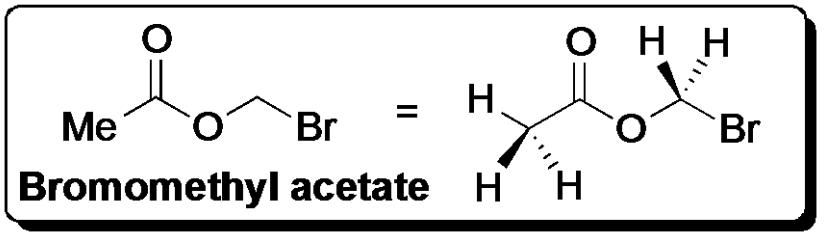
Deuterated chloroform ($CDCl_3$) used as solvent

Deuterium (D, ^{2}H) is "silent" in ^{1}H freq. range

$CDCl_3$ always contains <0.1% $CHCl_3$

Signal @ 7.27 ppm

Reporting ^{1}H-NMR data



300 MHz ^{1}H NMR
In CDCl3

Standard notation for reporting NMR data

[chemical shift, (multiplicity, integration)]

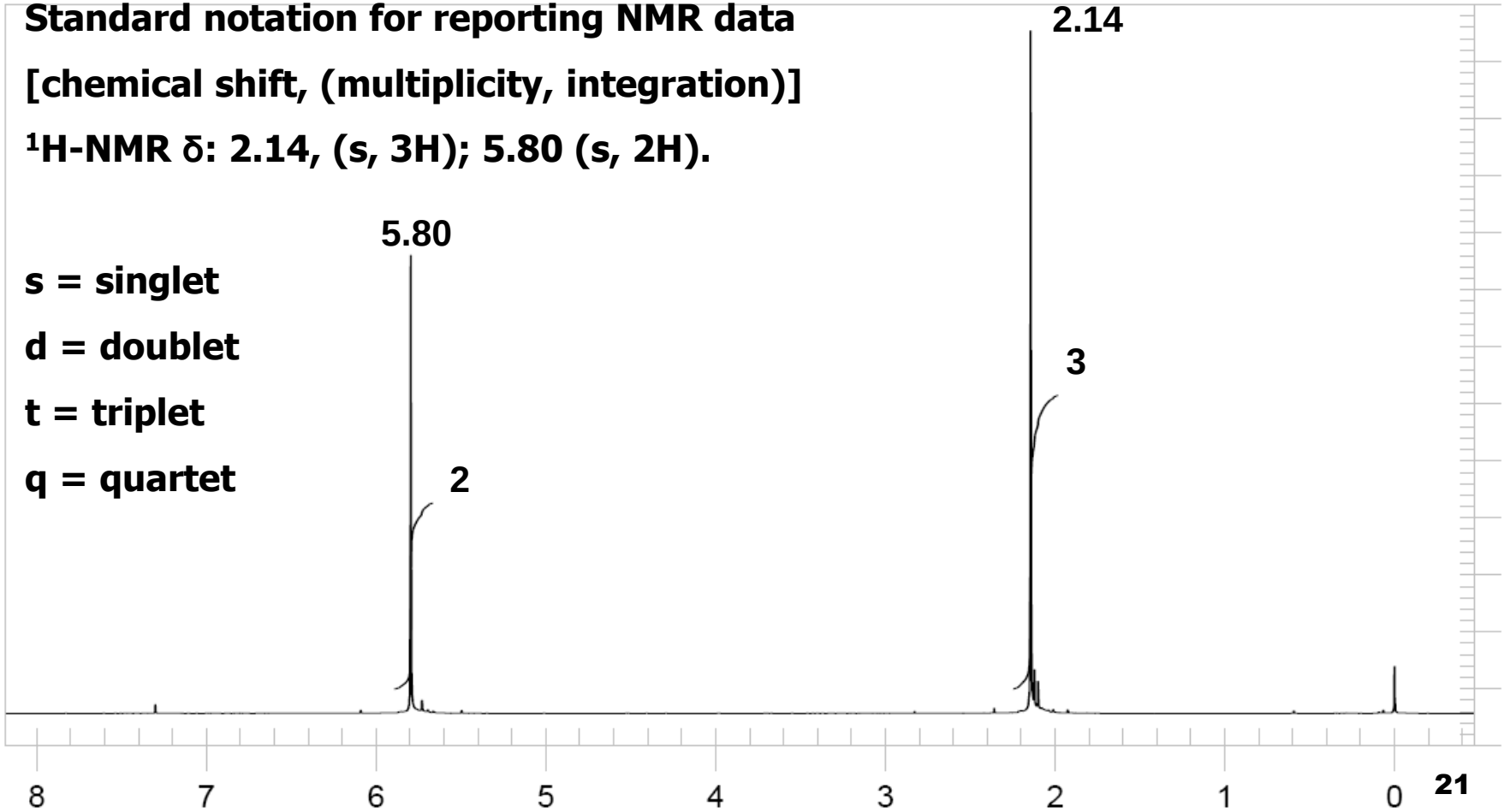
^{1}H-NMR δ: 2.14, (s, 3H); 5.80 (s, 2H).

s = singlet

d = doublet

t = triplet

q = quartet

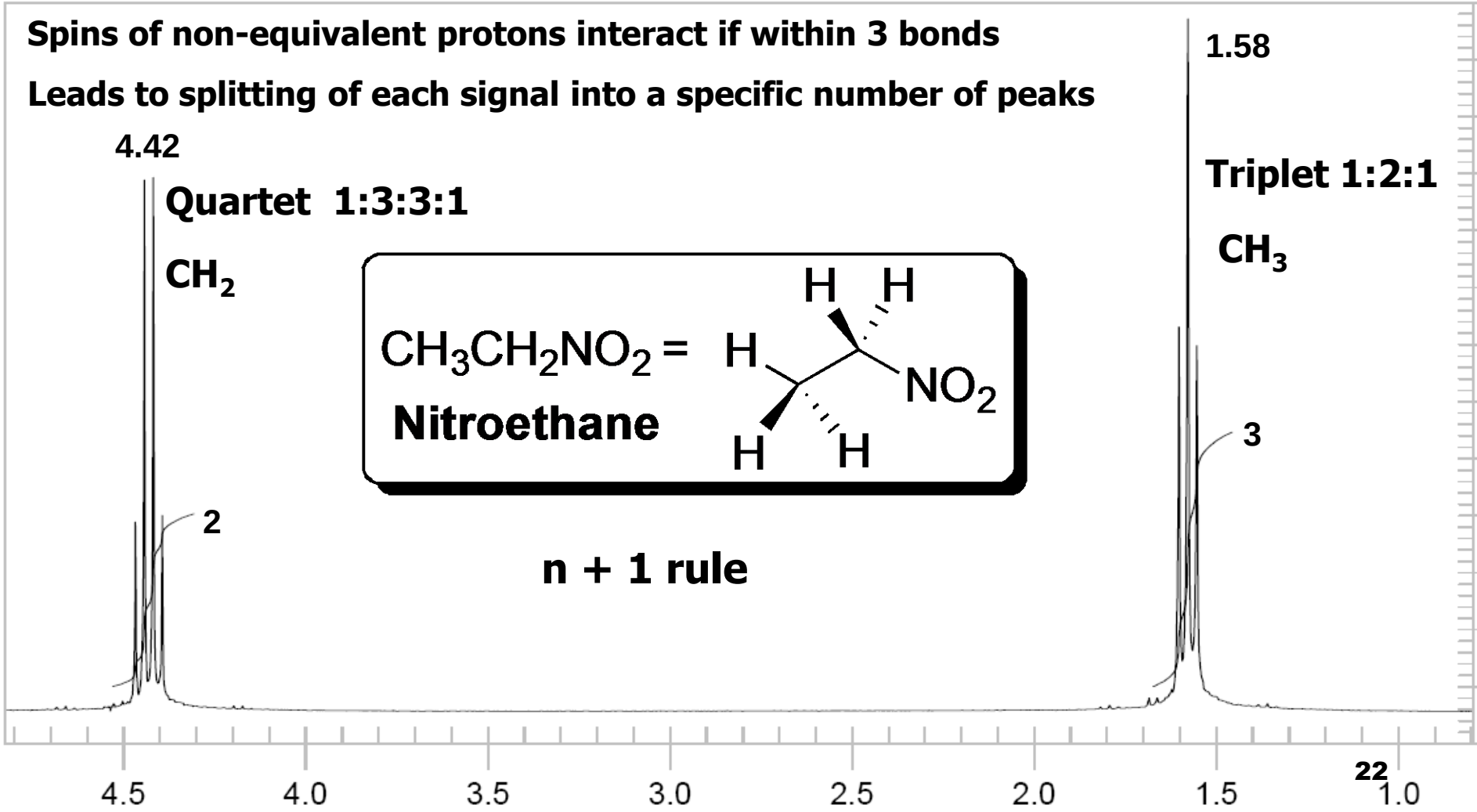


Spin-spin splitting

300 MHz ^{1}H NMR
In CDCl3

Spins of non-equivalent protons interact if within 3 bonds

Leads to splitting of each signal into a specific number of peaks



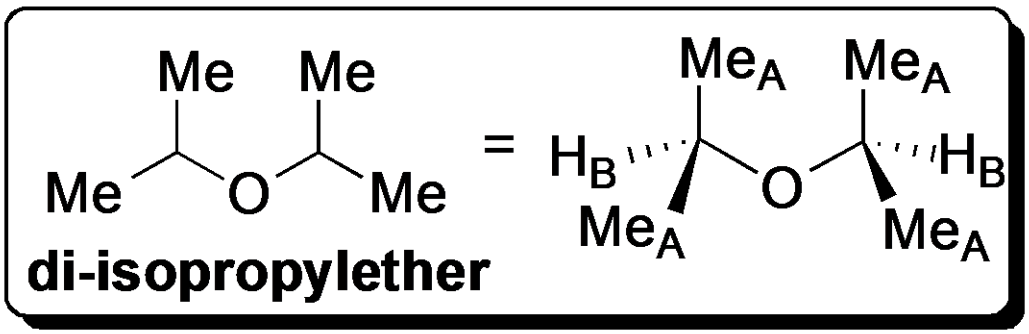
Spin-spin splitting (coupling)

- Splitting arises from the effect that one set of protons has on neighboring protons
- For a given proton, identify the number (n) of neighboring non-equivalent protons (on *adjacent* carbons)
- The resonance for this proton will then appear as n+1 lines
- Splitting is always mutual i.e. if H_a splits H_b, then H_b must split H_a (H_a and H_b are then said to be **coupled)**
- Splitting is <u>not</u> observed between equivalent protons

Background & theory: Loudon, p. 595-603

300 MHz ^{1}H NMR

In CDCl3



di-isopropylether

1:1 Doublet

Me protons (H_A)

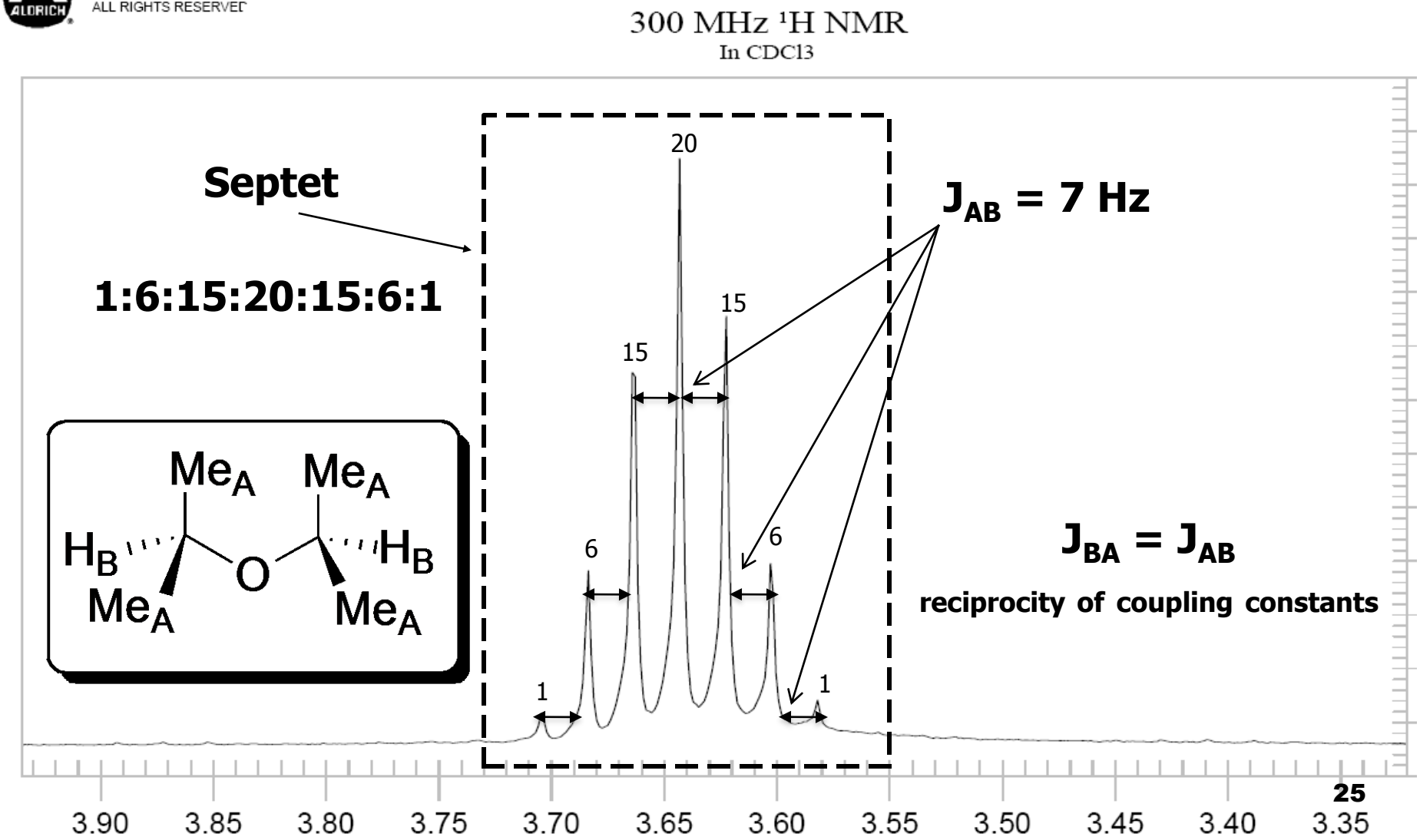
n = 1, n+1 =2

Me_2C<u>H</u> protons (H_B)

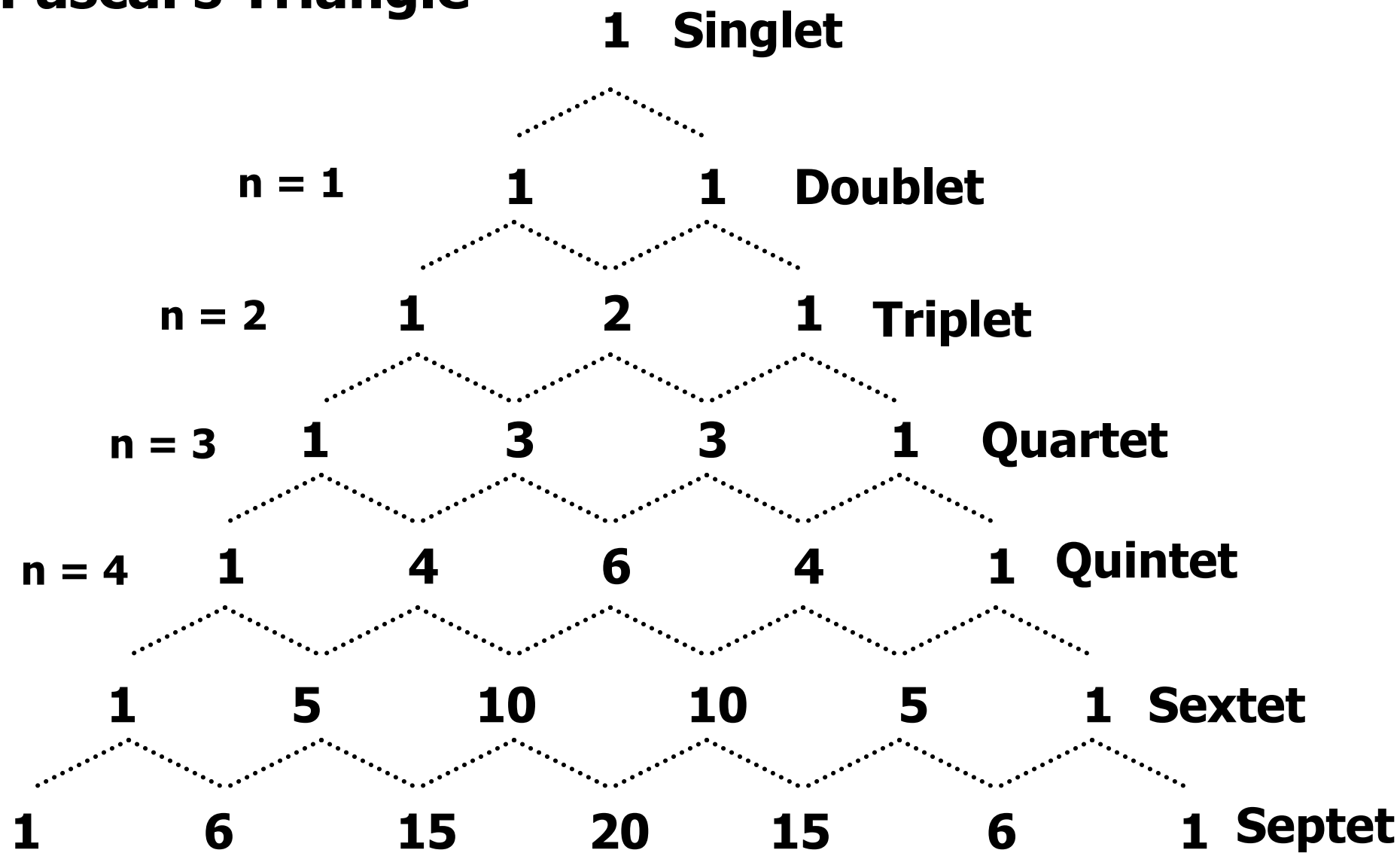
n = 6, n+1 =7, septet

Coupling constant J (Hz) – indicates strength of coupling

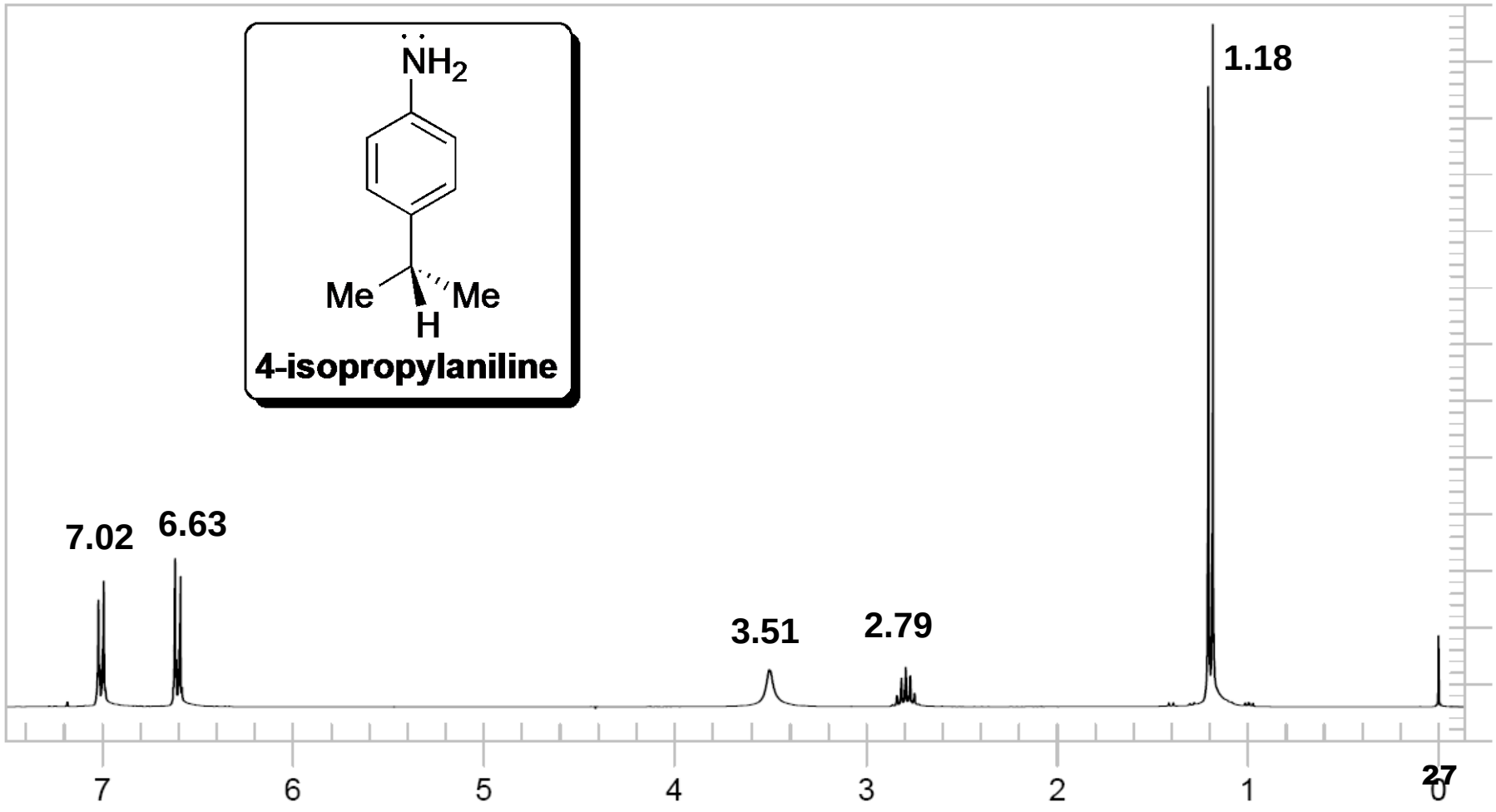
J ~ 7 Hz for alkyl (sp^3) systems

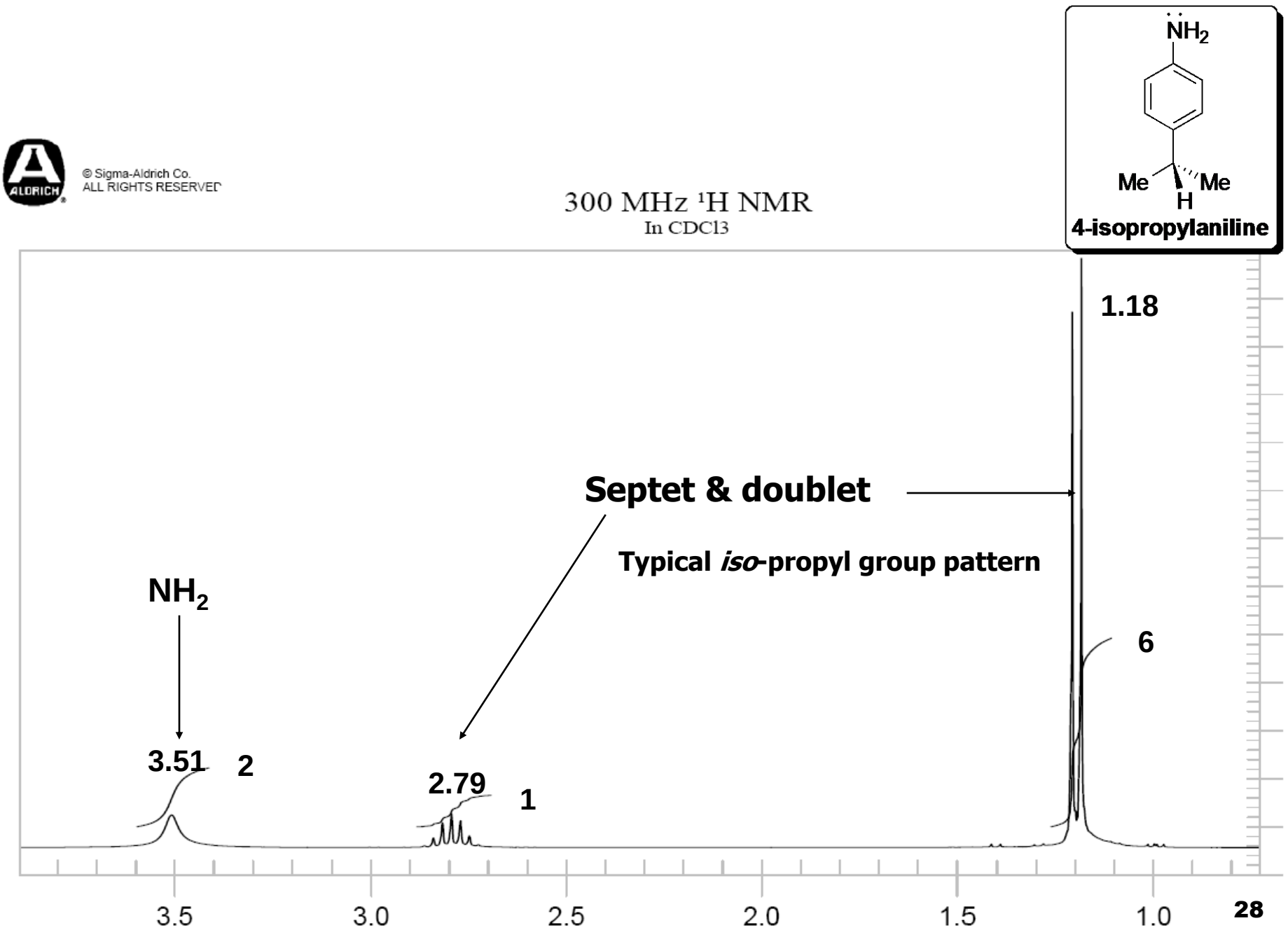


Pascal's Triangle



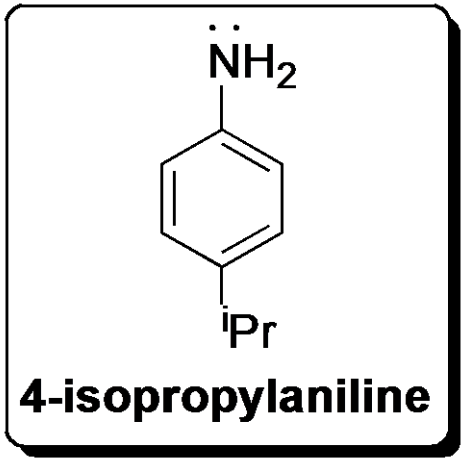
300 MHz ^{1}H NMR
In CDCl3





300 MHz ^{1}H NMR

In CDCl3



4-isopropylaniline

"Organic Elements"	
Me = $-CH_3$	Methyl
Et = $-CH_2CH_3$	Ethyl
Pr = $-CH_2CH_2CH_3$	Propyl
^{i}Pr = $-CHMe_2$	*iso*-Propyl
^{t}Bu = $-CMe_3$	*tert*-Butyl
Ph = $-C_6H_5$	Phenyl