Lecture 6
Infrared spectroscopy

Chemical Shift additivity estimates

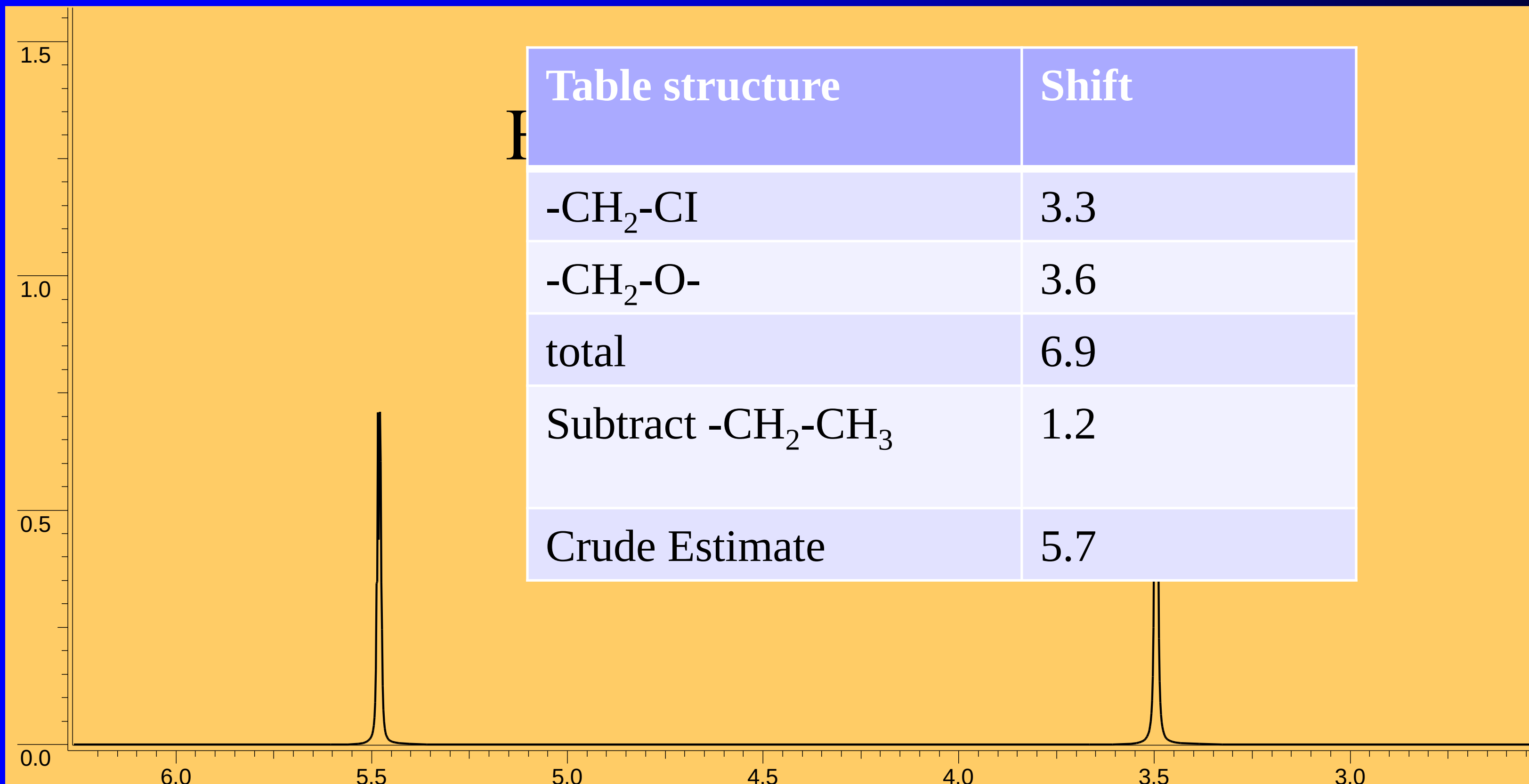


Table structure	Shift
$-CH_2-Cl$	3.3
$-CH_2-O-$	3.6
total	6.9
Subtract $-CH_2-CH_3$	1.2
Crude Estimate	5.7

Caution…..estimates only!!

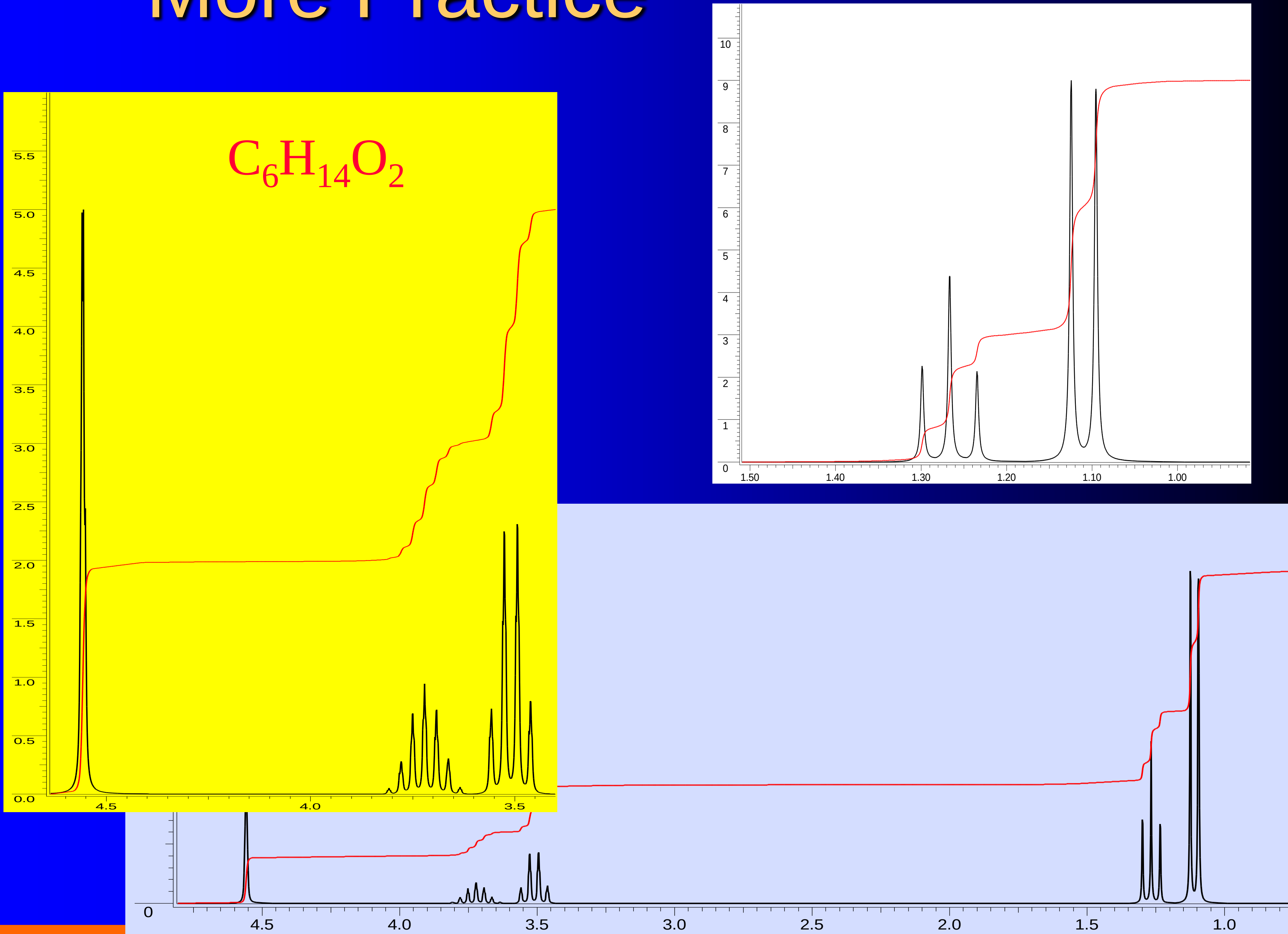
Chemical Shift - ^{1}H-NMR

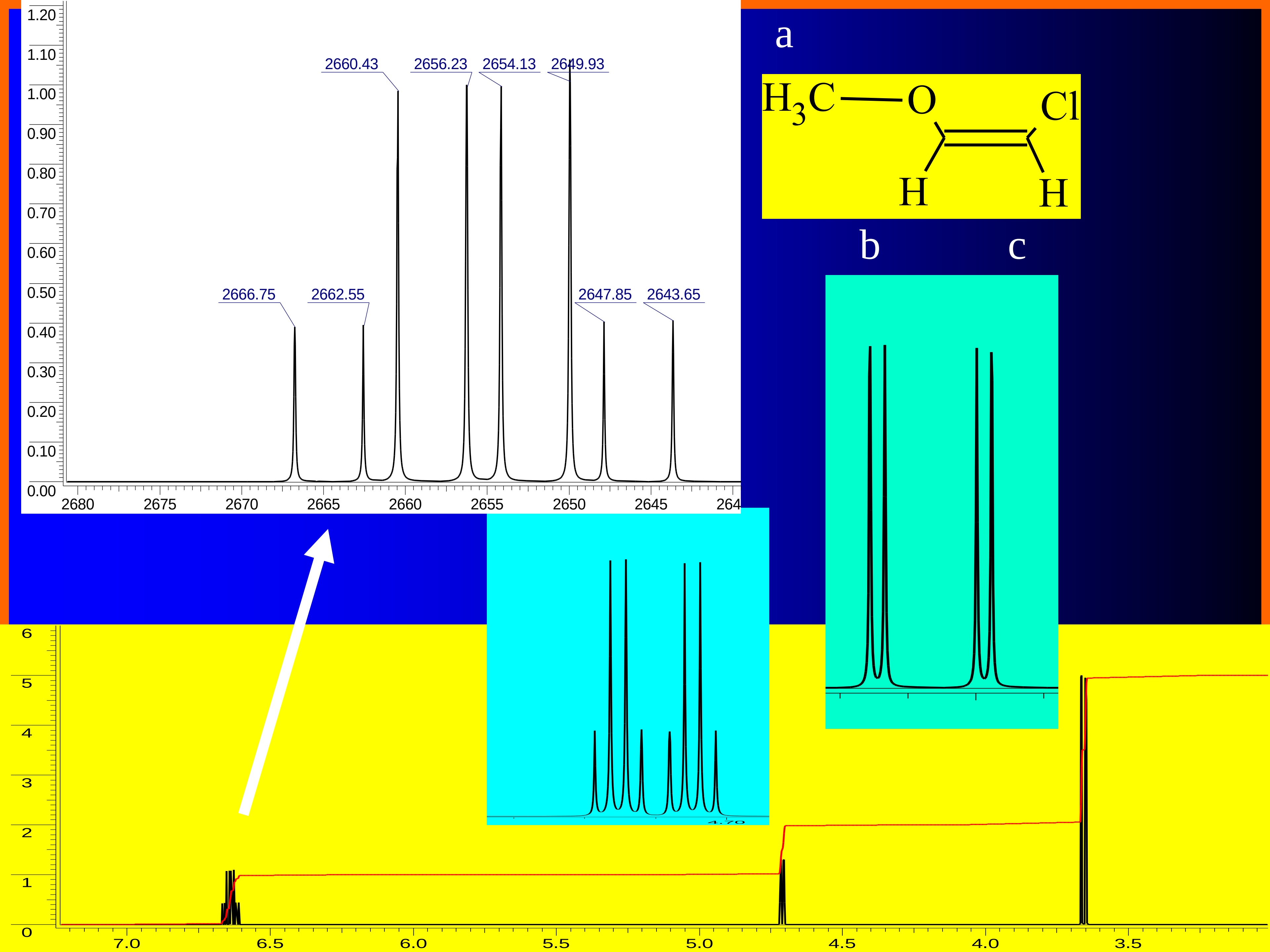
Type of H	δ	Type of H	δ
$(CH_3)_4Si$	0	ROH	0.5-6.0
RCH_3	0.9	RCH_2OR	3.3-4.0
RCH_2R	1.2-1.4	R_2NH	0.5-5.0
R_3CH	1.4-1.7	$RC(=O)CH_3$	2.1-2.3
$R_2C{=}CRCHR_2$	1.6-2.6	$RC(=O)CH_2R$	2.2-2.6
$RC{\equiv}CH$	2.0-3.0		
$ArCH_3$	2.2-2.5		
$ArCH_2R$	2.3-2.8		

Chemical Shift - ^{1}H-NMR

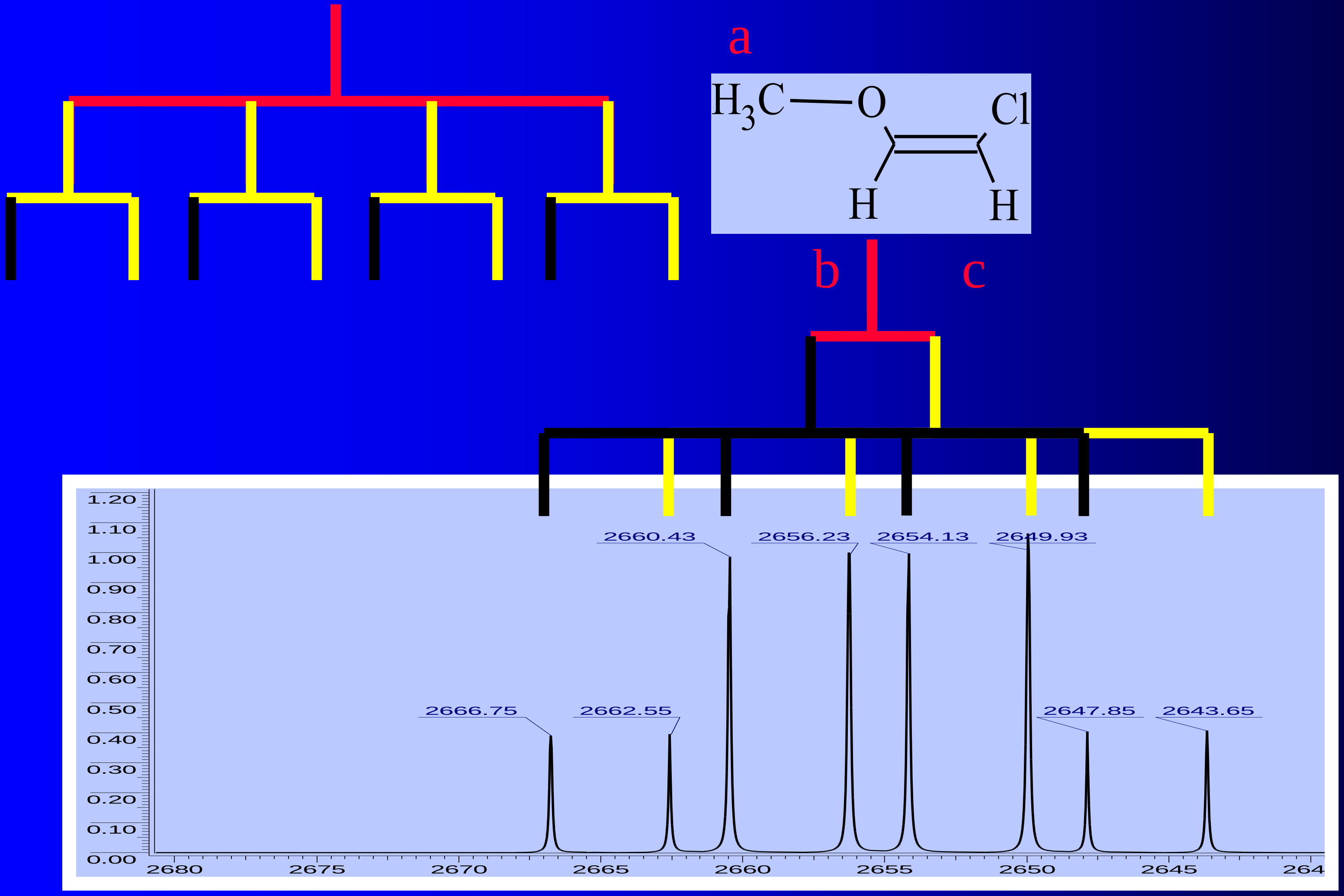
Type of H	δ	Type of H	δ
$RC(=O)OCH_3$	3.5-3.9	$R_2C{=}CH_2$	4.6-5.0
$RC(=O)OCH_2R$	4.1-4.7	$R_2C{=}CHR$	5.0-5.7
RCH_2I	3.1-3.3	ArH	6.5-8.5
RCH_2Br	3.4-3.6	$RC(=O)H$	9.5-10.1
RCH_2Cl	3.6-3.8	$RC(=O)OH$	10-13
RCH_2F	4.4-4.5		

More Practice

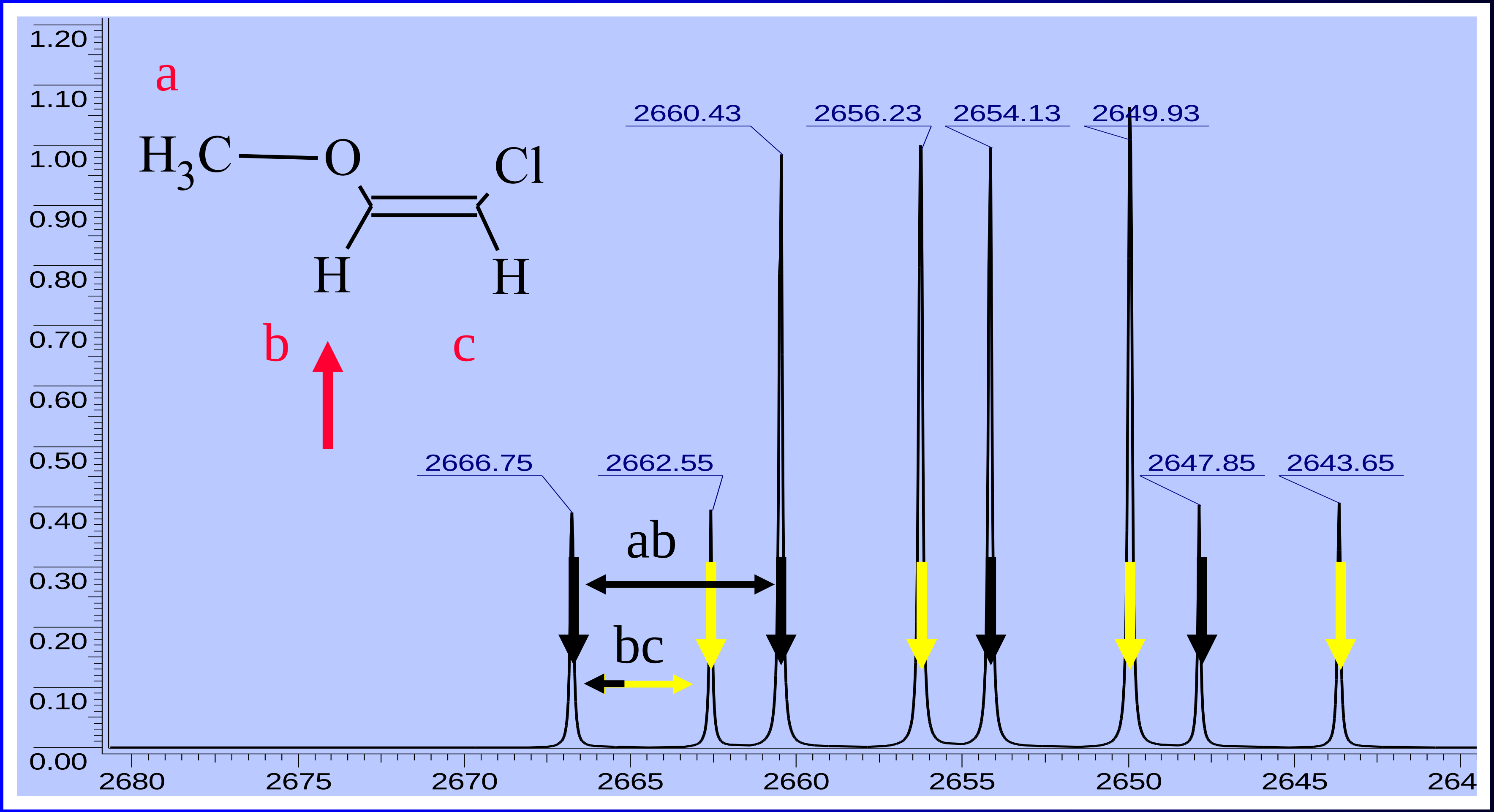



a
H3C
O
Cl
H
H
b
c
2666.75
2662.55
2660.43
2656.23
2654.13
2649.93
2647.85
2643.65
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
2680
2675
2670
2665
2660
2655
2650
2645
6
5
4
3
2
1
0
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

Whats with what??



Coupling Constants



Deuterium Oxide

- Heavy water is heavier than H_2O (duh?), having a density of 1.108 g/cm3. Heavy water ice will actually sink in light liquid water. The freezing and boiling points are also elevated somewhat, with heavy water freezing at 3.81° C (38.86° F) and boiling at 101.42° C (214.56° F) at standard atmospheric pressure.

- Heavy water toxicity manifests itself when about 50% of the water in the body has been replaced by D_2O. Prolonged heavy water consumption can cause death. The price is about $700 per kilogram.

D_2O in H_2O

D_2O ice in H_2O

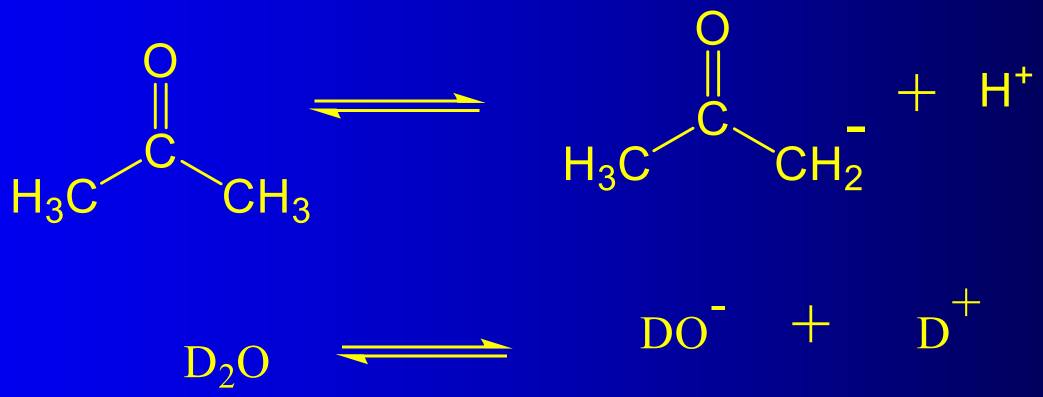
D_2O ice in D_2O

Deuterium Oxide vs Water

Property	D_2O (Heavy water)	H_2O (Light water)
Freezing point (°C)	3.82	0.0
Boiling point (°C)	101.4	100.0
Density at STP (g/mL)	1.1056	0.9982
Dynamic viscosity (at 20°C, mPa·s)	1.25	1.005
Heat of fusion (cal/mol)	1,515	1,436
pH (at 25°C)	7.41 (sometimes "pD")	7.00
Cost per kilogram	~$700.00	~$0.002 for tap ~$10.00 for Fiji!!?

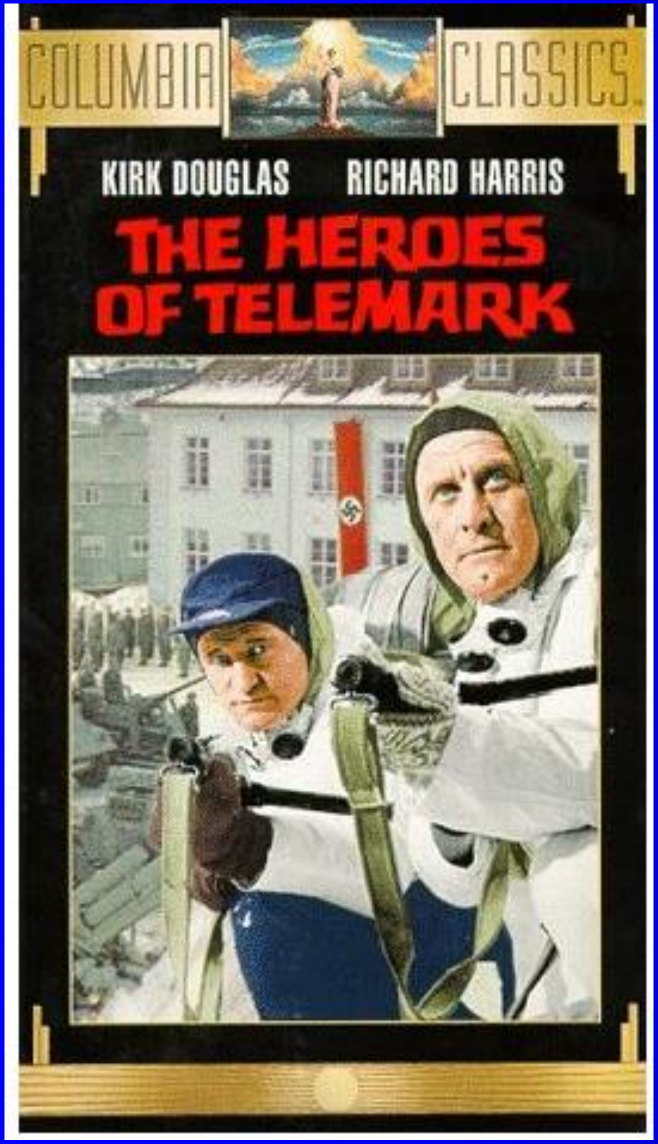
Chemical Exchange

- Hydrogens on electronegative atoms such as Oxygen and Nitrogen
  - Undergo rapid "exchange" and often give only a relatively broad singlet due to "averaging"
  - These hydrogens also exchange (equilibrate) with Deuterium in D_2O and "disappear" from the spectrum



Common ^{1}H-nmr Solvents

- $DCCl_3$
- CCl_4
- $(CD_3)_2SO$
- D_2O
- C_6D_6

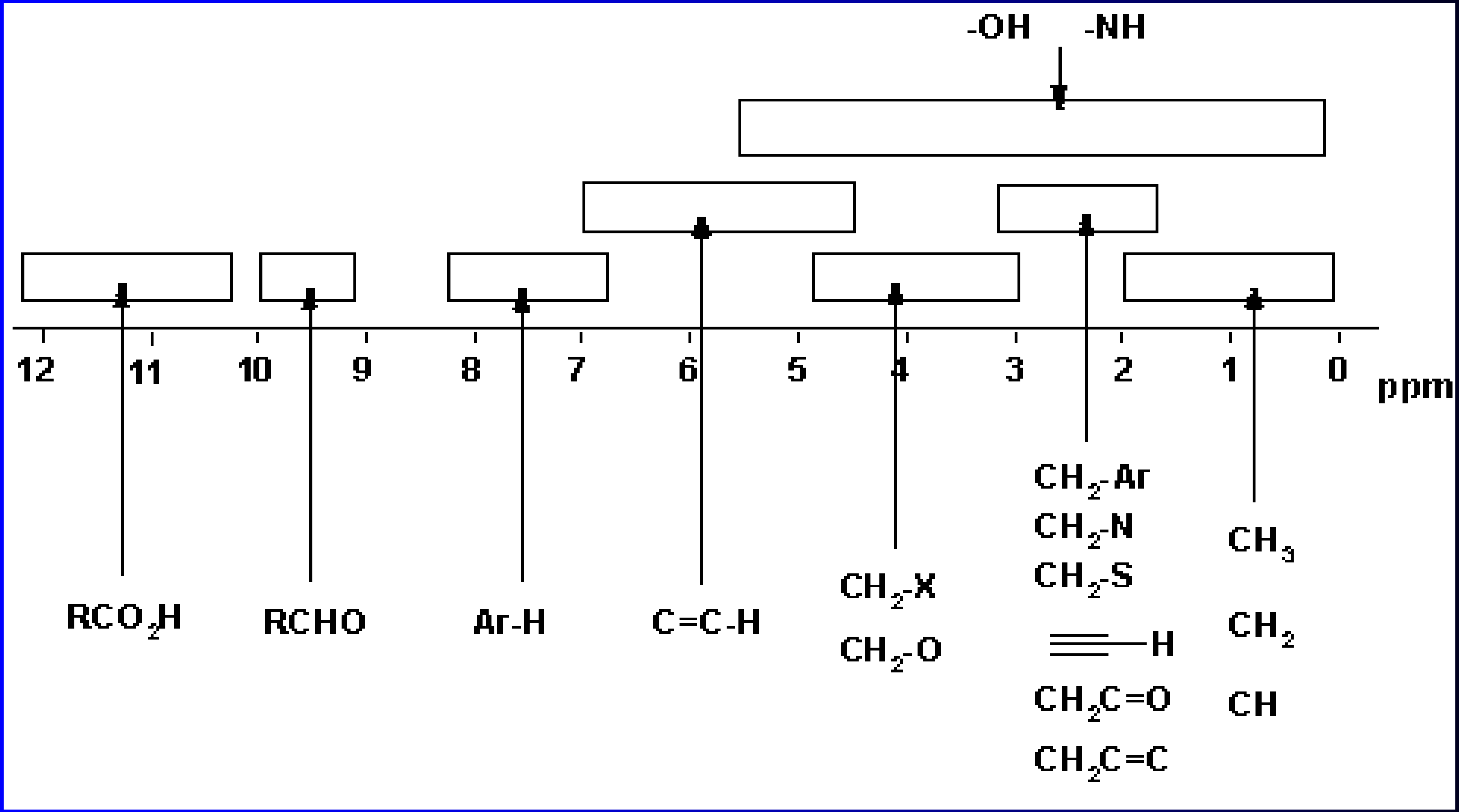


http://www.imdb.com/title/tt0059263/

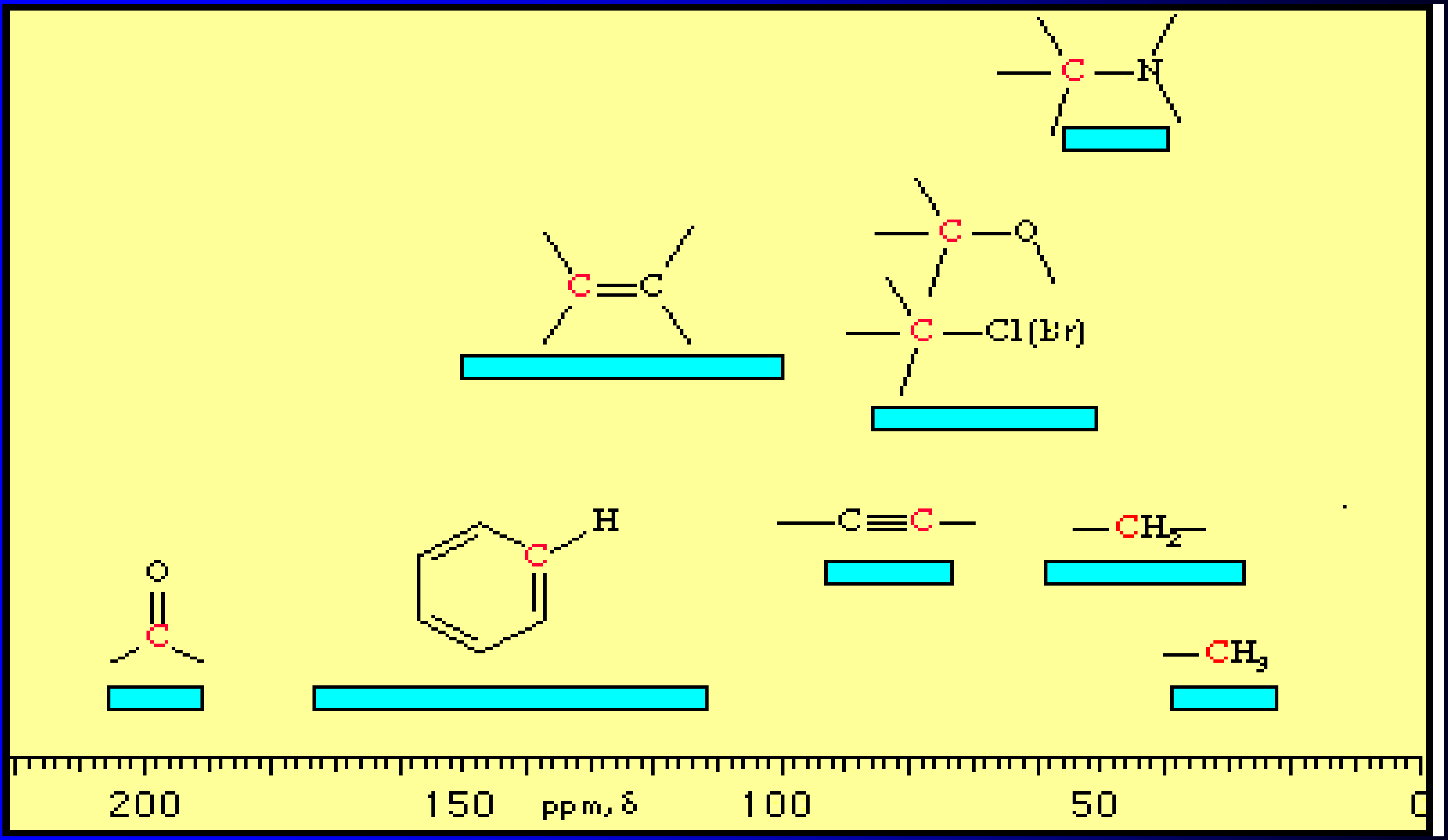
http://www.telegraph.co.uk/news/7664351/A-new-mission-for-the-hero-of-Telemark.html

Vemork Hydroelectric Plant

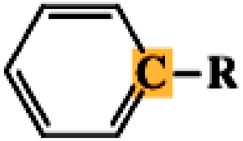
^1H Chemical Shifts



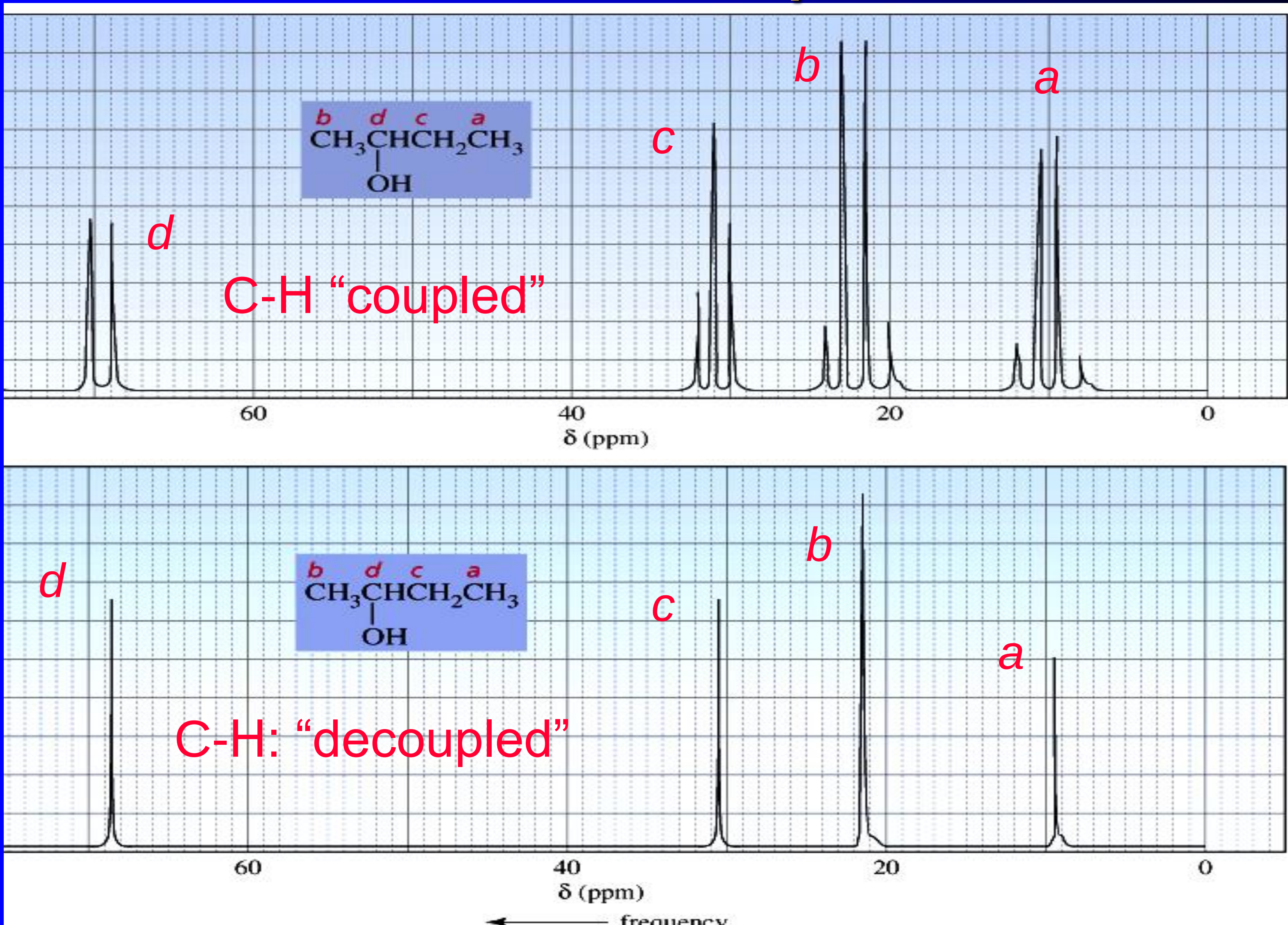
^{13}C Chemical Shifts



^{13}C-NMR chemical shifts

Type of Carbon	Chemical Shift (δ)	Type of Carbon	Chemical Shift (δ)
RCH_3	0–40		110–160
RCH_2R	15–55		
R_3CH	20–60		
RCH_2I	0–40	RC(=O)OR	160–180
RCH_2Br	25–65		
RCH_2Cl	35–80	$RC(=O)NR_2$	165–180
R_3COH	40–80		
R_3COR	40–80	RC(=O)OH	175–185
RC≡CR	65–85		
$R_2C{=}CR_2$	100–150	RC(=O)H, RC(=O)R	180–210

^{13}C NMR Spectra



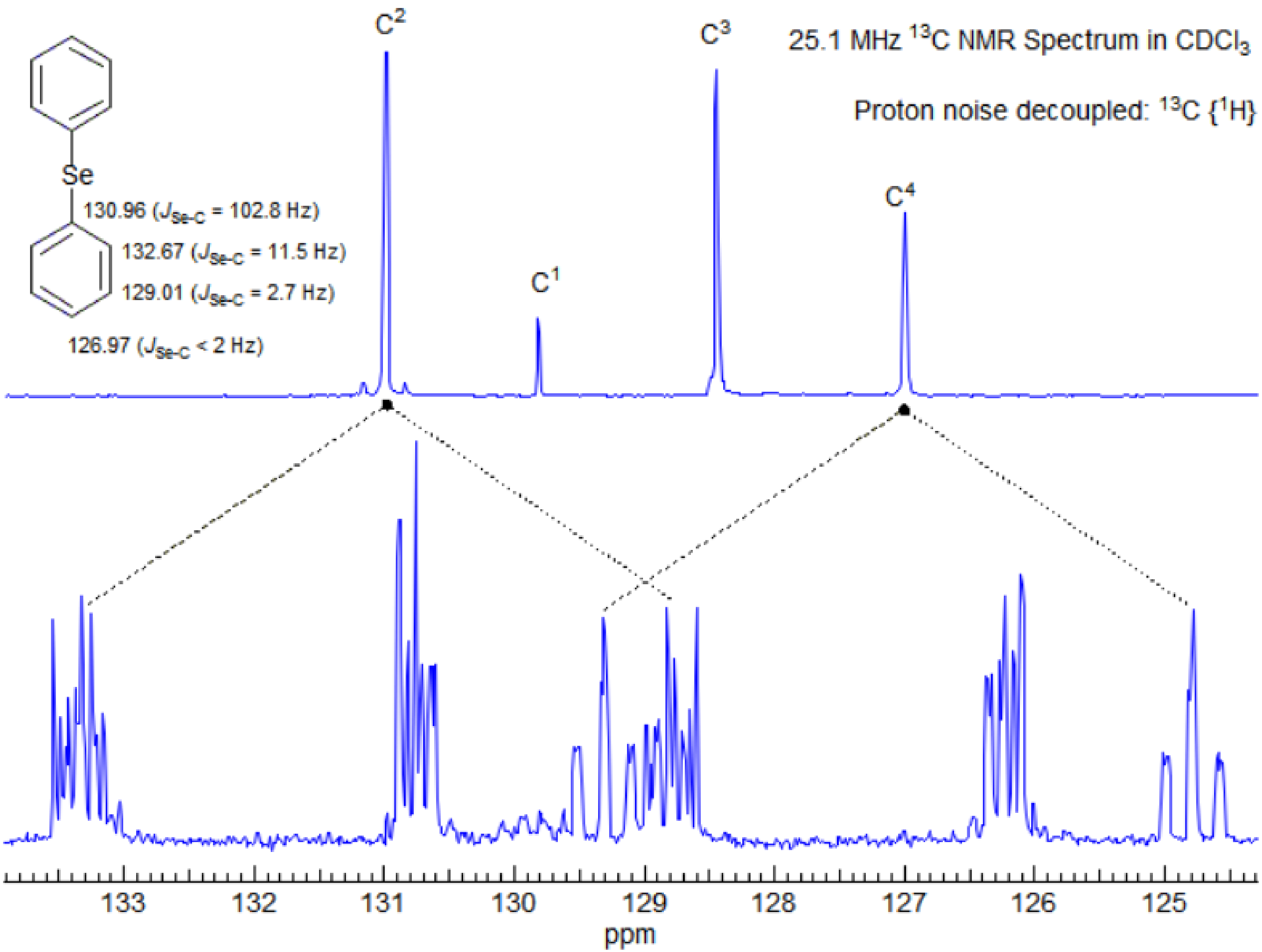
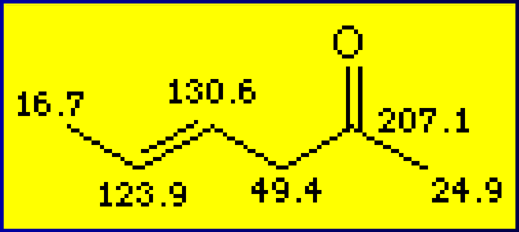
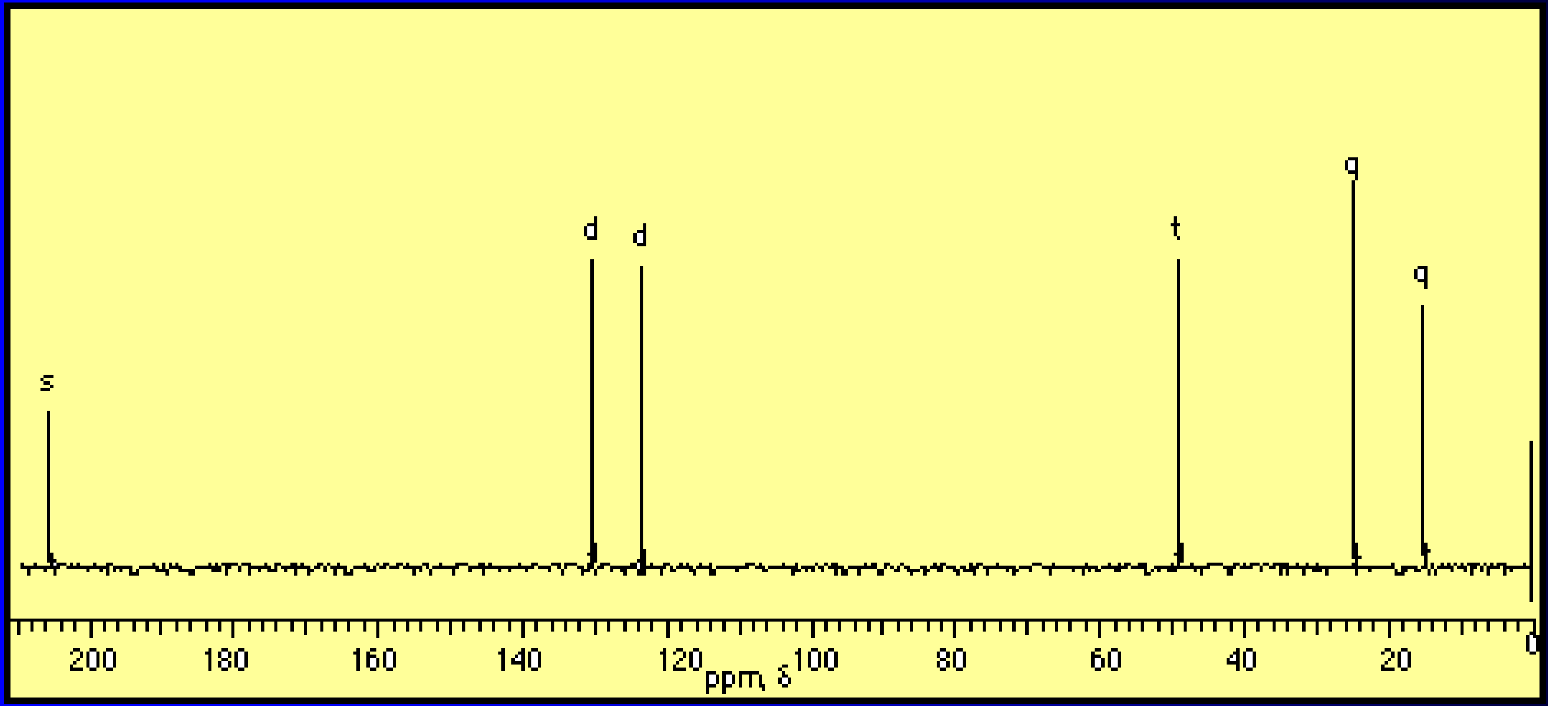


Figure 6-1.2. 25 MHz ^{13}C NMR spectrum of diphenyl selenide in $CDCl_3$.

^{13}C-nmr Spectroscopy

- Each nonequivalent ^{13}C gives a different, resolved signal





The DEPT Experiment

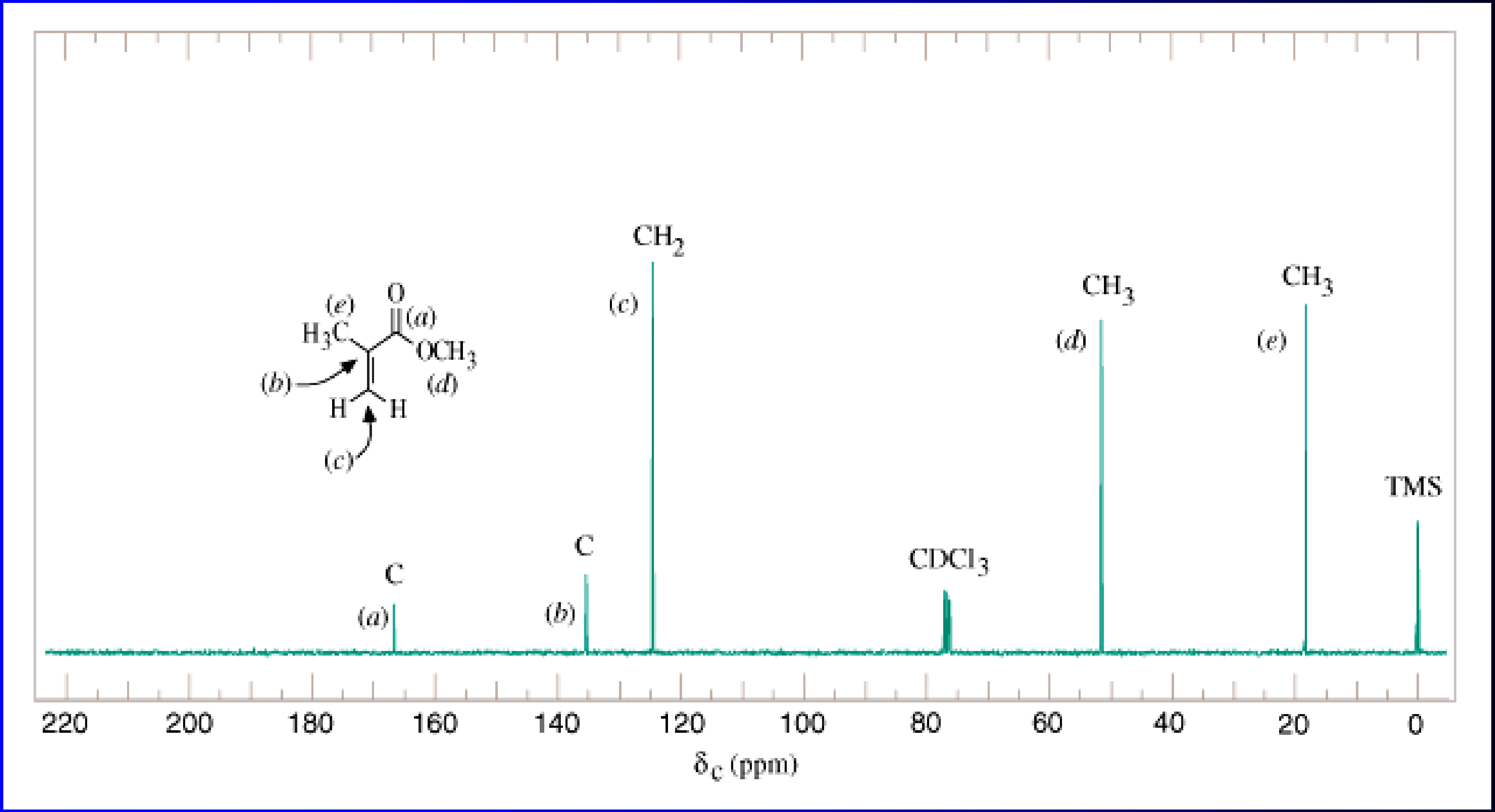
- In the hydrogen-decoupled mode, information on spin-spin coupling between ^{13}C and attached hydrogens is lost
- Distortionless Enhancement by Polarization Transfer (DEPT) is an NMR technique for determining whether ^{13}C signals are from CH_3, CH_2, CH, or quaternary carbons
- DEPT is an instrumental trick that provides the means to acquire this information

The DEPT method

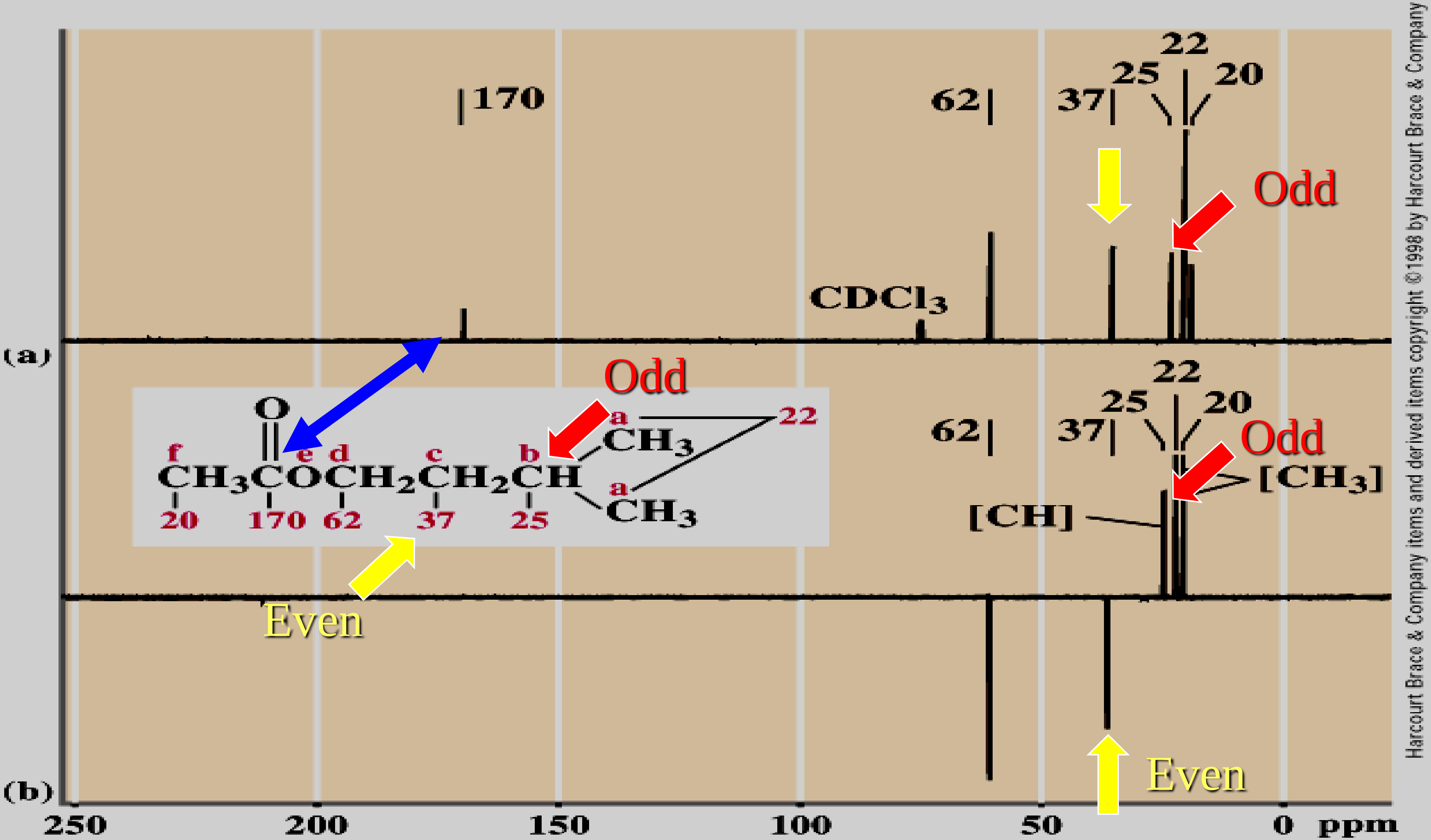
- DEPT uses a complex series of pulses in both the ^1H and ^{13}C ranges, with the result that CH_3, CH_2, and CH signals exhibit different phases;
  - signals for CH_3 and CH carbons are recorded as positive signals *(odd numbers of H)*
  - signals for CH_2 carbons are recorded as negative signals *(even numbers of H)*
  - quaternary carbons give no signals in the DEPT method *(zero H)*

OPEN ?? 😊

Broadband decoupled ^{13}C nmr spectrum

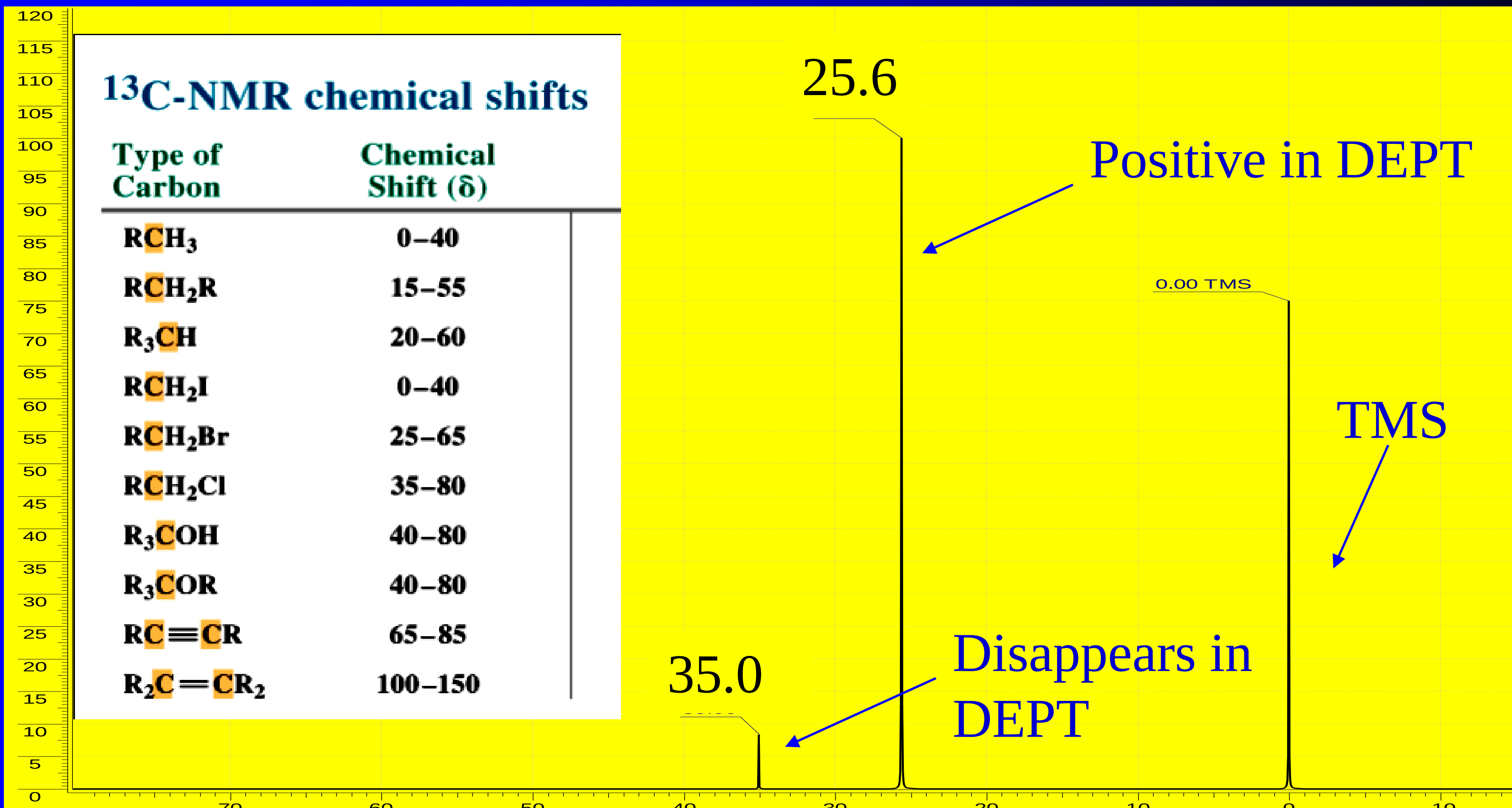


^{13}C-NMR (a) and DEPT (b) spectra of isopentyl acetate



An Unknown ☺

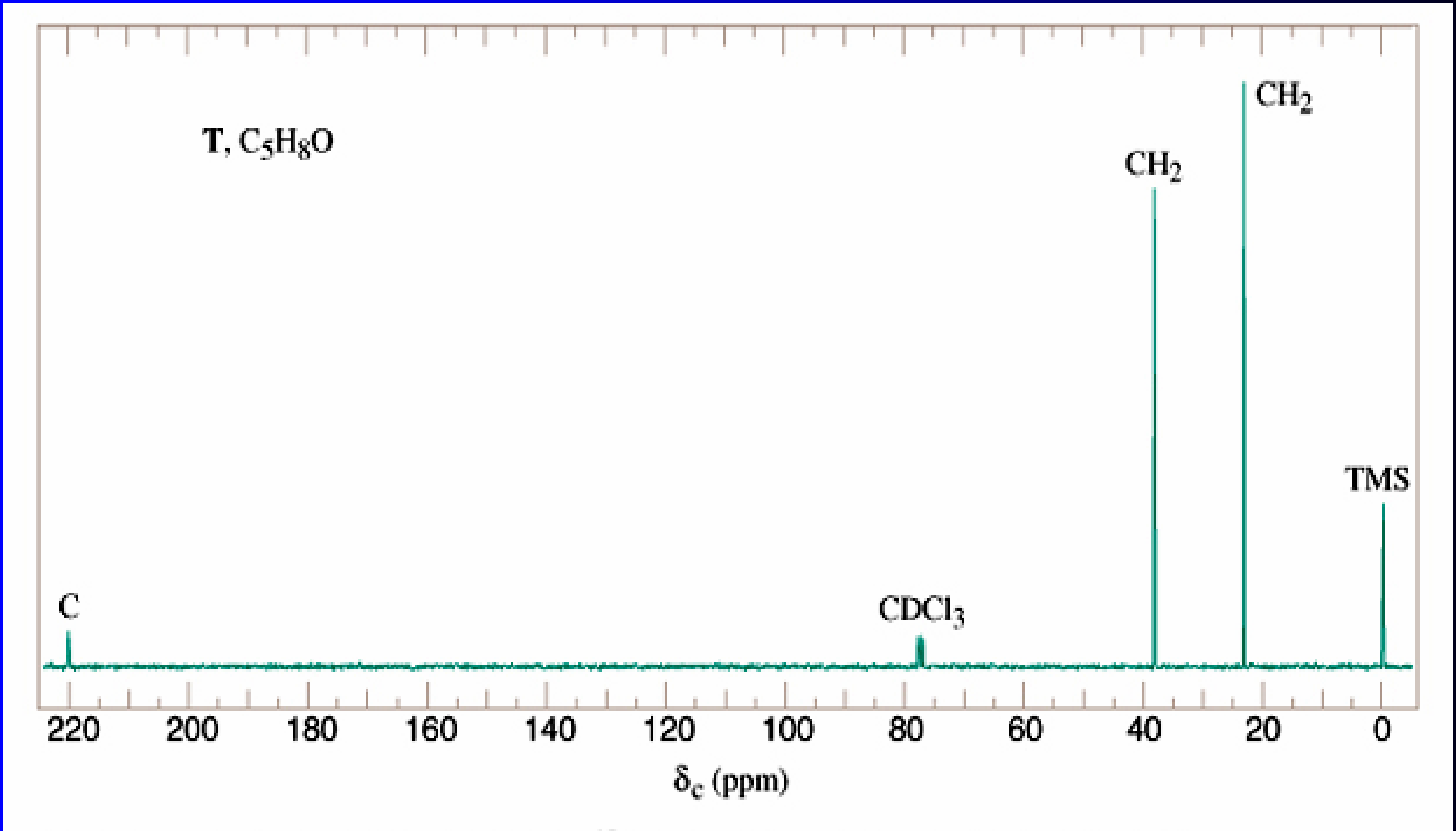
Empirical formula C_4H_9, MW =114



^{13}C-NMR chemical shifts

Type of Carbon	Chemical Shift (δ)
RCH_3	0–40
RCH_2R	15–55
R_3CH	20–60
RCH_2I	0–40
RCH_2Br	25–65
RCH_2Cl	35–80
R_3COH	40–80
R_3COR	40–80
$RC{\equiv}CR$	65–85
$R_2C{=}CR_2$	100–150

Whatzit??



T, C5H8O
CH2
CH2
TMS
C
CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
δc (ppm)

^{13}C-NMR Spectroscopy review

- Each nonequivalent ^{13}C gives a different signal
- Low abundance means weak signals
- C-C splitting is insignificant
- C-H splitting is big and complex so it is “turned off” by “decoupling”
- Range of Chemical Shifts is large compared to H
- Some Coupling info can be recovered by DEPT
- Integrals of ^{13}C spectra are not useful except under very special circumstances
- Mnemonic device…. OPEN???

Practice Problems

https://edisciplinas.usp.br/pluginfile.php/255042/mod_resource/content/2/OC307-Solving_NMR.pdf

https://www.khanacademy.org/science/organic-chemistry/spectroscopy-jay/proton-nmr/v/proton-nmr-practice-2

https://www.khanacademy.org/science/organic-chemistry/spectroscopy-jay/proton-nmr/v/proton-nmr-practice-3

http://pnorris.people.ysu.edu/index_files/page0016.html

http://orgchemboulder.com/Spectroscopy/Problems/index.shtml