

CHEM202

Organic Chemistry

Nick Green

nick.green@otago.ac.nz, 3n11

Module 1: Spectroscopy and Characterisation

Lecture 9: ^{13}C NMR Spectroscopy

^{13}C NMR

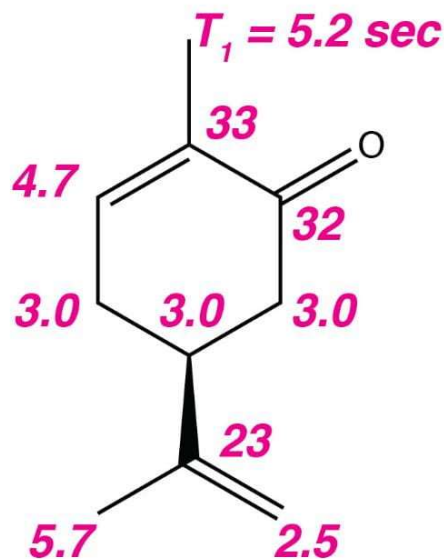
^{13}C - spin 1/2 nuclei, low sensitivity compared to ^1H (1.76×10^{-4} , see prev. Table of NMR active isotopes) due to;

- low natural abundance, 1.11 %
- inherent low sensitivity ie $\gamma_{\text{H}}/\gamma_{\text{C}} = 4$
- ^{13}C nuclei can have long relaxation times

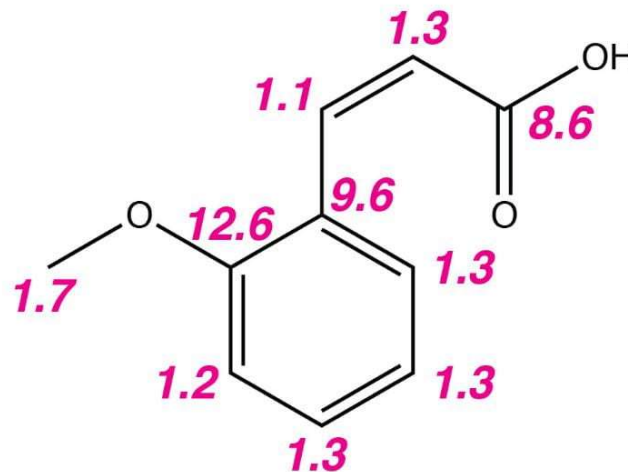
^{13}C NMR relaxation

Example Compounds and ^{13}C T_1 s

S-carvone

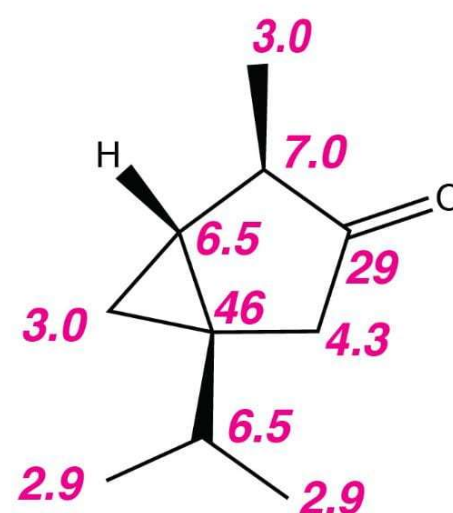


cis-2-methoxycinnamic acid



Range: 1.1 - 46 sec

(-)- α -thujone

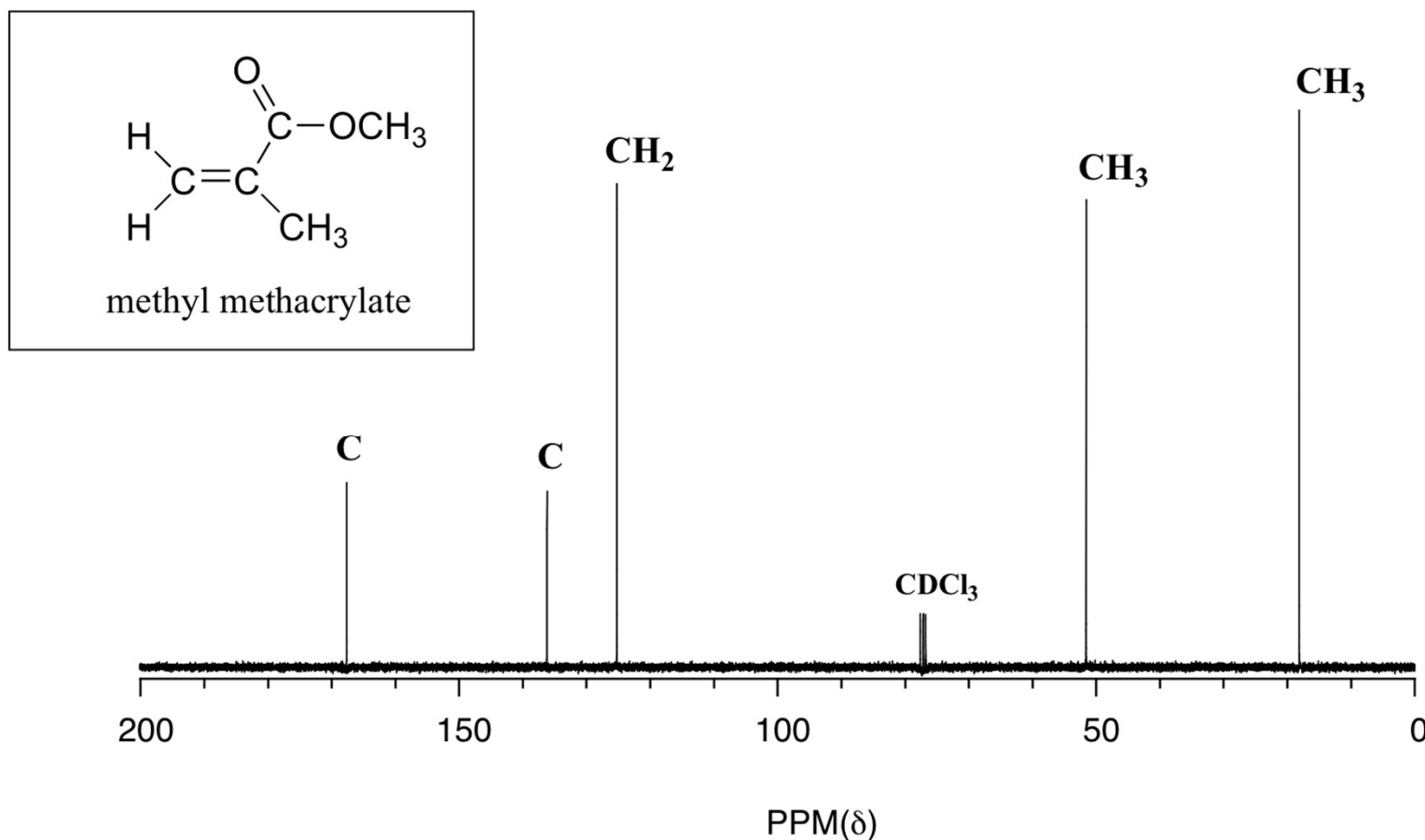


What do the long relaxation time carbons have in common?

Attachment to protons allows more rapid relaxation (nOe)

Quaternary carbons usually have the longest relaxation times.

Integration is rarely useful on a ^{13}C spectrum



Carbon peaks are usually measured as narrow singlets so their **intensity is a proxy for their integral**

Peaks with long relaxation times will not receive a full 90 degree pulse upon repeated excitation, unless the delay between experiments is extended.

The integral/intensity thus varies considerably and cannot normally be used in the same way as in ^1H NMR.

Features of ^{13}C NMR Spectra

Differences to ^1H spectra

- the chemical shift range is much wider, δ 0-230 ppm
- no homo-nuclear, ^{13}C - ^{13}C , coupling is observed. This is a consequence of the **low natural abundance** of ^{13}C nuclei
ie it is very unlikely to find two neighbouring ^{13}C nuclei.
- hetero-nuclear, ^{13}C - ^1H , coupling is observed and yields the number of H's attached to each C ie the carbon type: methyl, methylene, methine or quaternary carbon.
- Whether a carbon is C, CH, CH₂ or CH₃ is often referred to as its **multiplicity**.
- the spectrum can be obtained with **hetero-nuclear decoupling** ie all the ^{13}C signals will appear as singlet, irrespective of C-H coupling. Referred to as broad band decoupling, helps with sensitivity (why?)

C-H coupling

Works the same as proton coupling, but now we consider one bond (C-H) coupling.

$^1J_{\text{C-H}}$ ranges between 120 – 250 Hz

Varies strongly with hybridisation,

e.g. $\text{sp}^3 = 125 \text{ Hz}$, $\text{sp}^2 = 155 \text{ Hz}$, $\text{sp} = 250 \text{ Hz}$

Also affected by substituents

e.g. $\text{F}-^{13}\text{C}-\text{H}$; $^1J_{\text{C-H}} = 150 \text{ Hz}$

e.g. $\text{alkyl}-^{13}\text{C}-\text{H}$; $^1J_{\text{C-H}} = 125 \text{ Hz}$

Decreases with distance, $^2J_{\text{C-H}} \sim -10 - 20 \text{ Hz}$

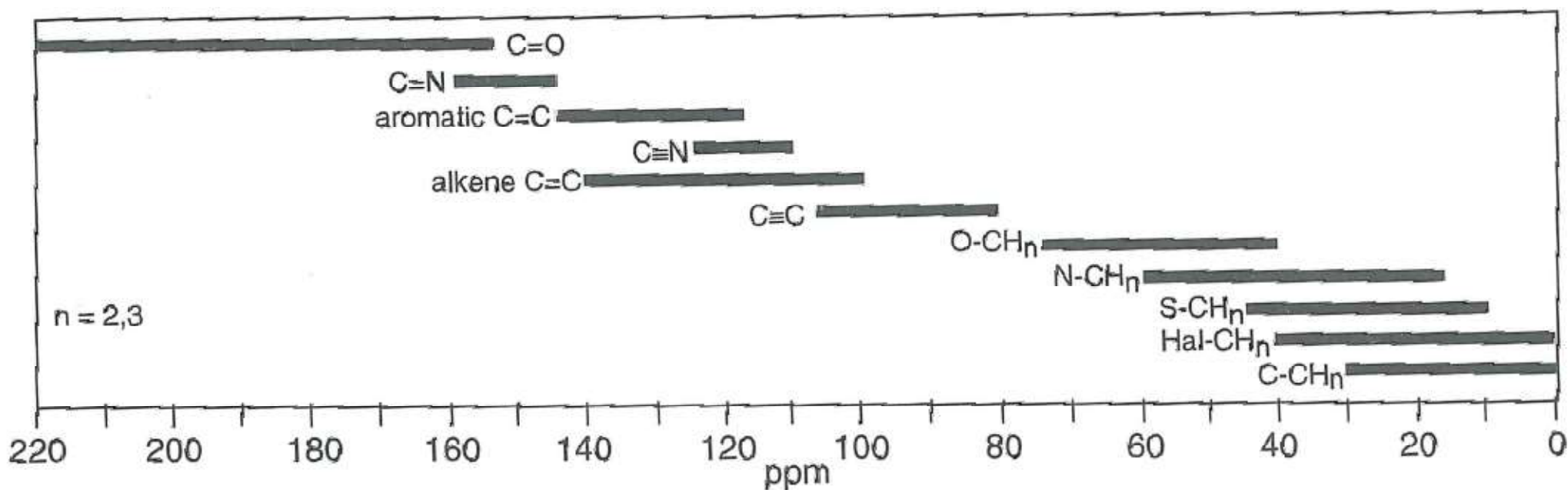
$^3J_{\text{C-H}}$ for unsaturated systems $\sim 5 - 15 \text{ Hz}$

Most ^{13}C spectra are broadband decoupled, so you won't see these splittings!

Similarities to ^1H spectra

- The number of signals from the proton decoupled spectrum gives the number of different carbon environments.
- The chemical shift gives information on the hybridisation of the carbon and the chemical environment.
- The factors that influenced the chemical shift of ^1H also affect the δ of ^{13}C eg shielding and deshielding effects.

^{13}C chemical shift range

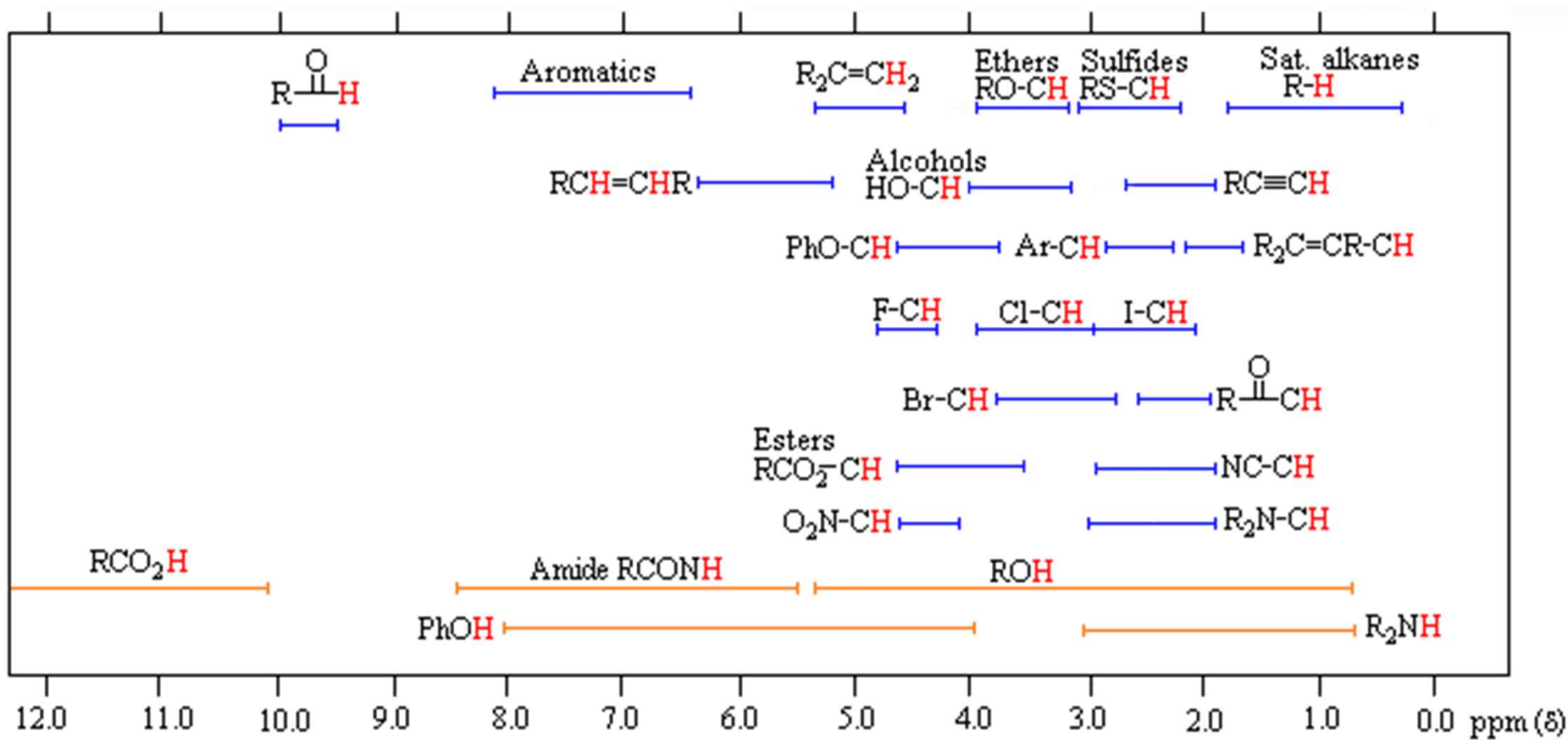


Typical ^{13}C shift ranges for various chemical environments.

^{13}C chemical shift range

similar relative positions to ^1H

(^1H chemical shift)

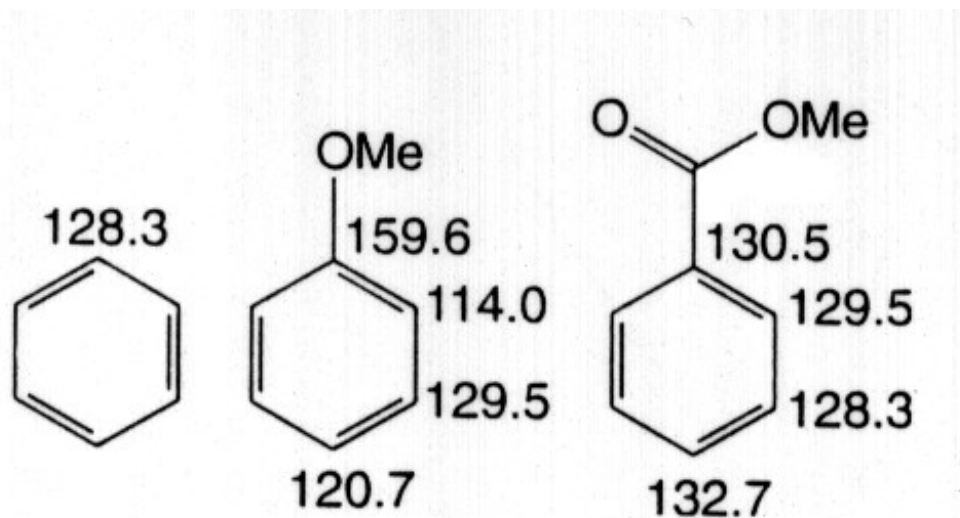


Inductive Effects

XC ¹ H ₂ C ² H ₂ C ³ H ₃			
X	C ¹ H ₂	C ² H ₂	C ³ H ₃
Et	34	22	14
HOOC	36	18	14
SH	27	27	13
NH ₂	44	27	11
Phe	39	25	15
Br	36	26	13
Cl	47	26	12
OH	64	26	10
NO ₂	77	21	11

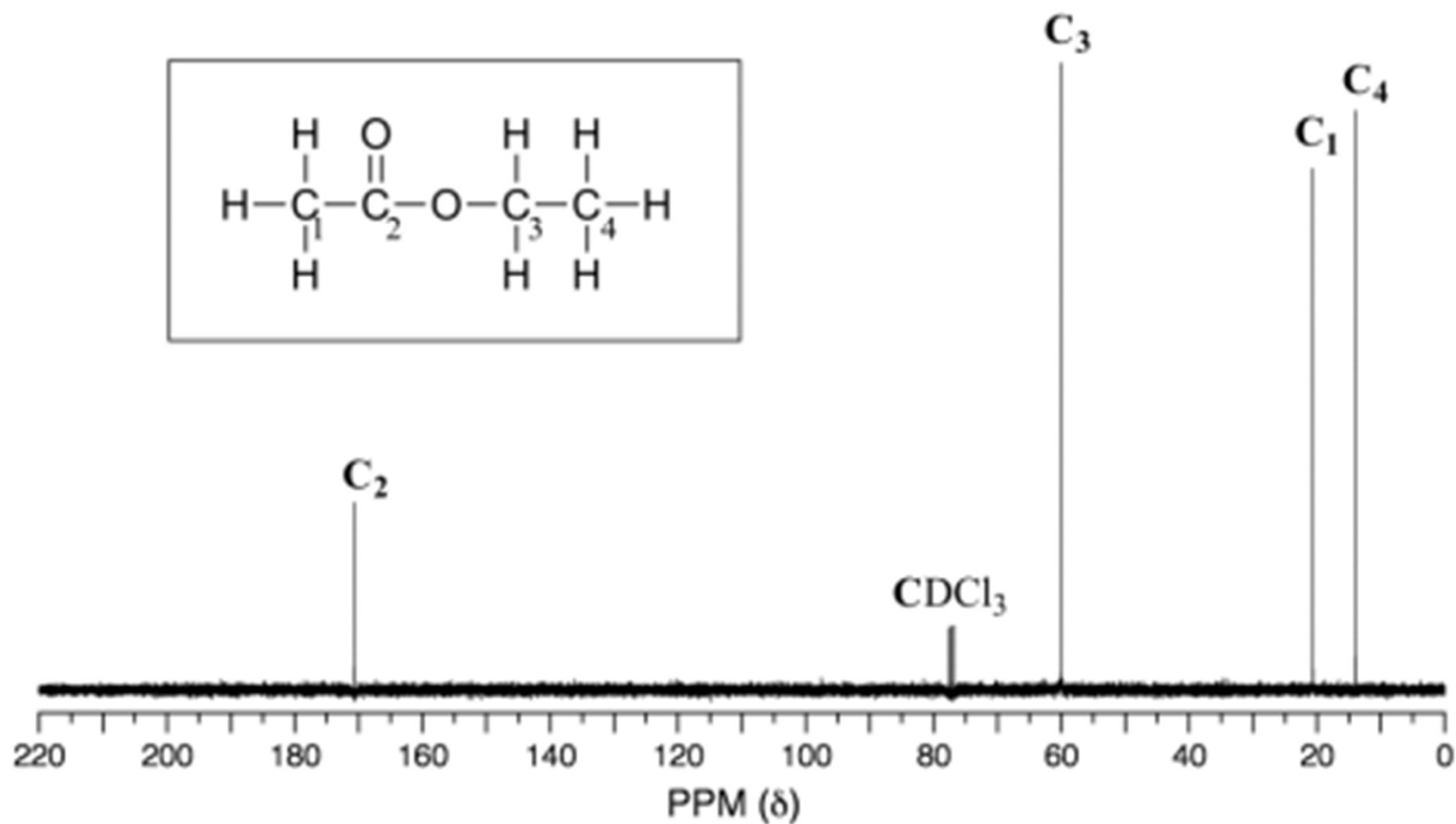
The influence of
electronegative substituents on ¹³C
chemical shifts

Mesomeric effects



The influence of mesomeric effects on ^{13}C chemical shifts

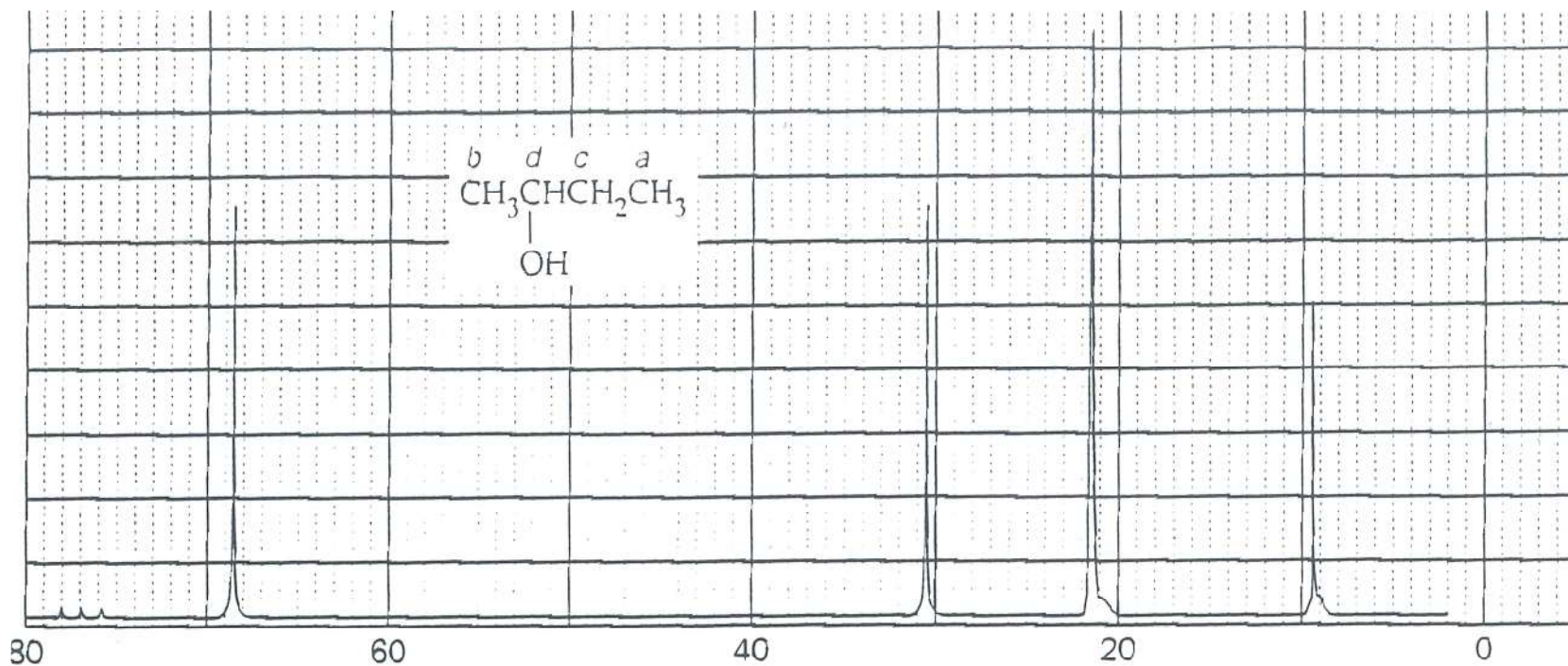
Example ^{13}C spectrum (H-decoupled)



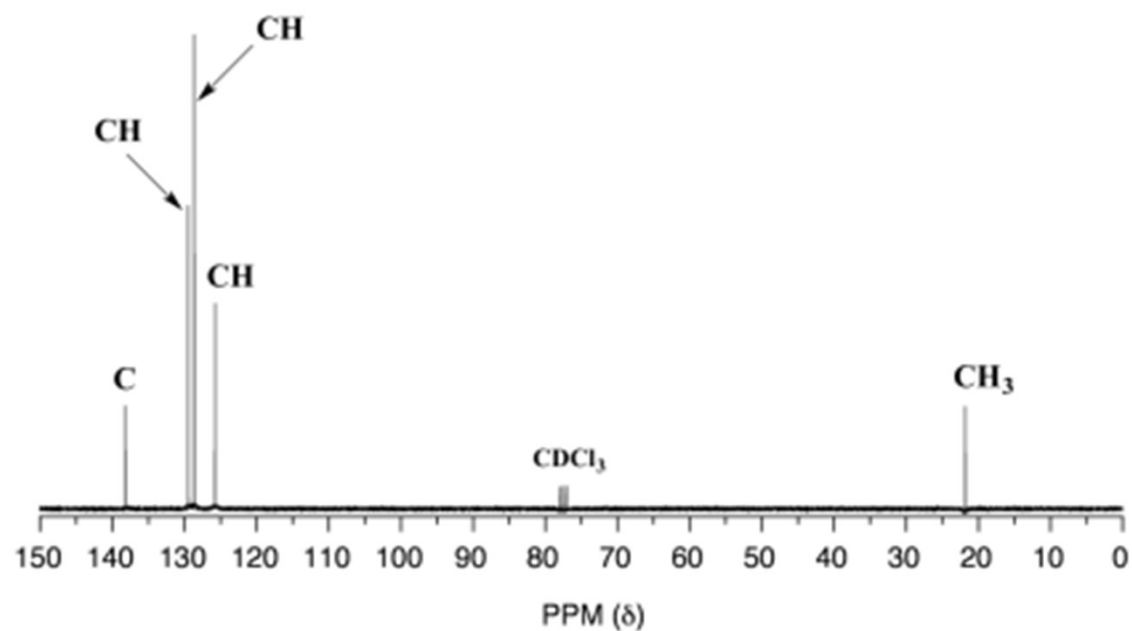
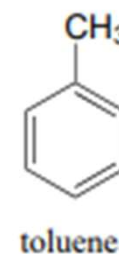
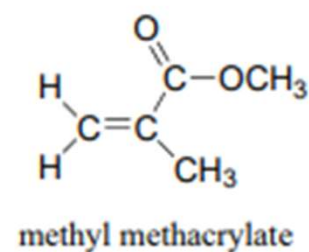
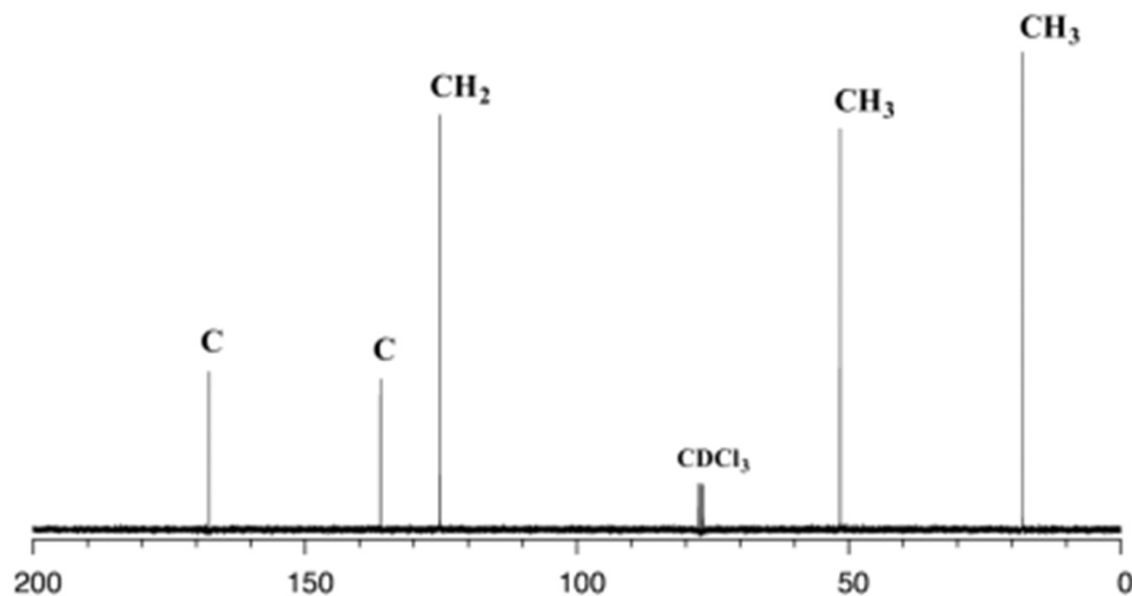
Bonus question:

- Why does CDCl_3 appear as a triplet in H-decoupled ^{13}C spectra?
- *Hint: Deuterium is not affected by broadband H decoupling*

Broad band decoupled ^{13}C $\{^1\text{H}\}$

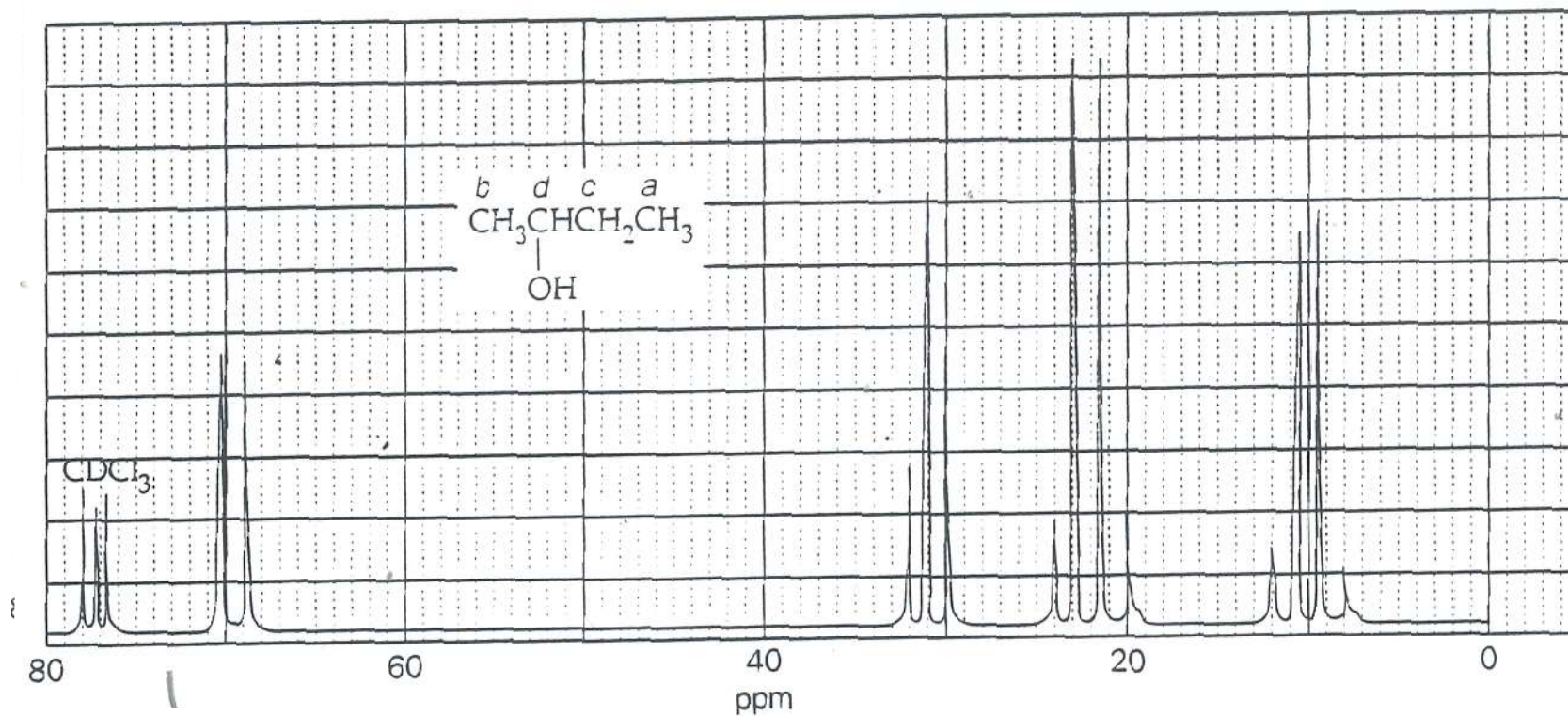


Which is which?



How has the multiplicity of the peaks in these spectra been determined??

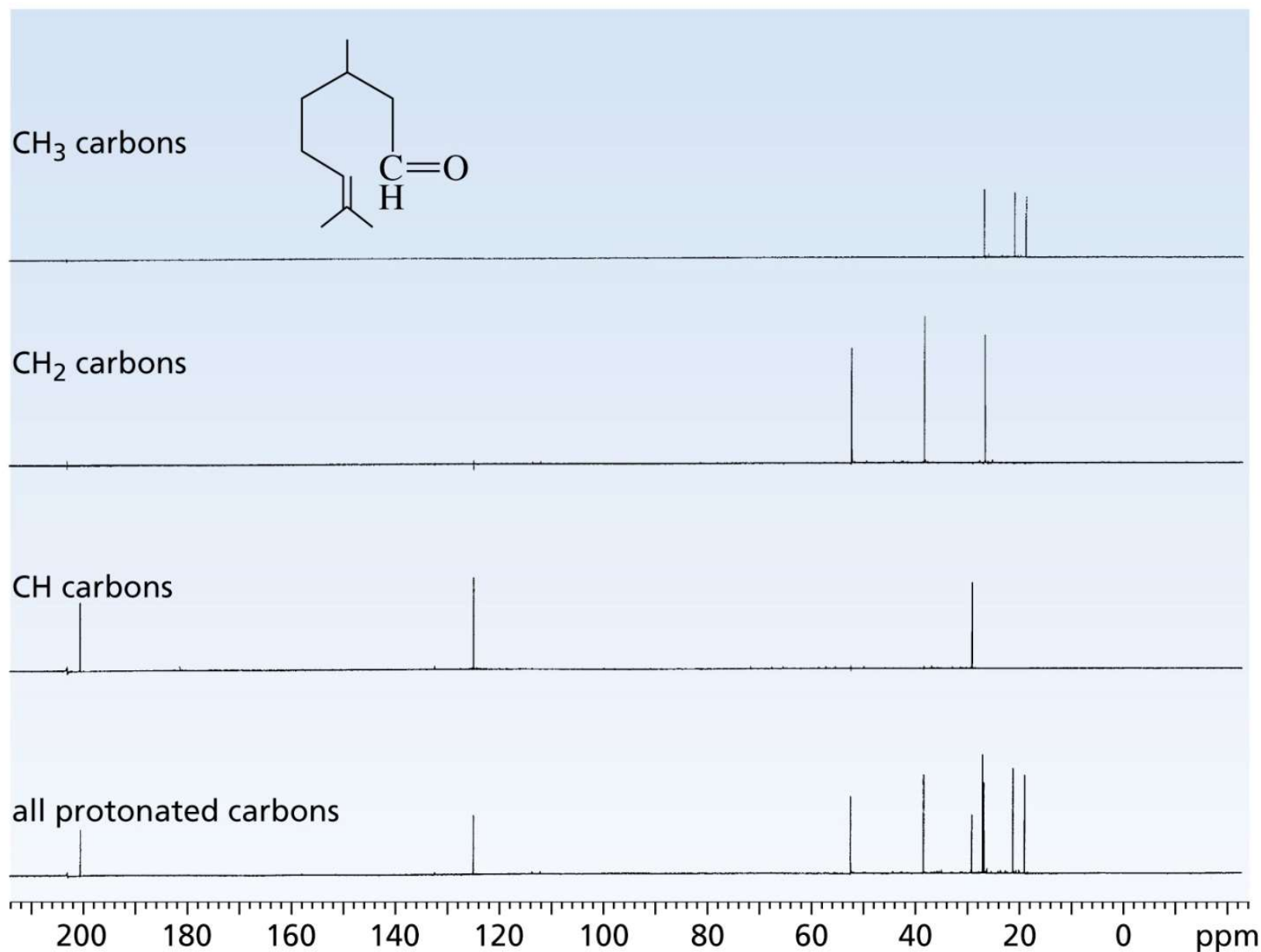
Single frequency off resonance decoupling (SFORD)



DEPT (**D**istortionless **E**nhancement by **P**olarisation **T**ransfer) and **APT** (**A**ttached **P**roton **T**est) experiments

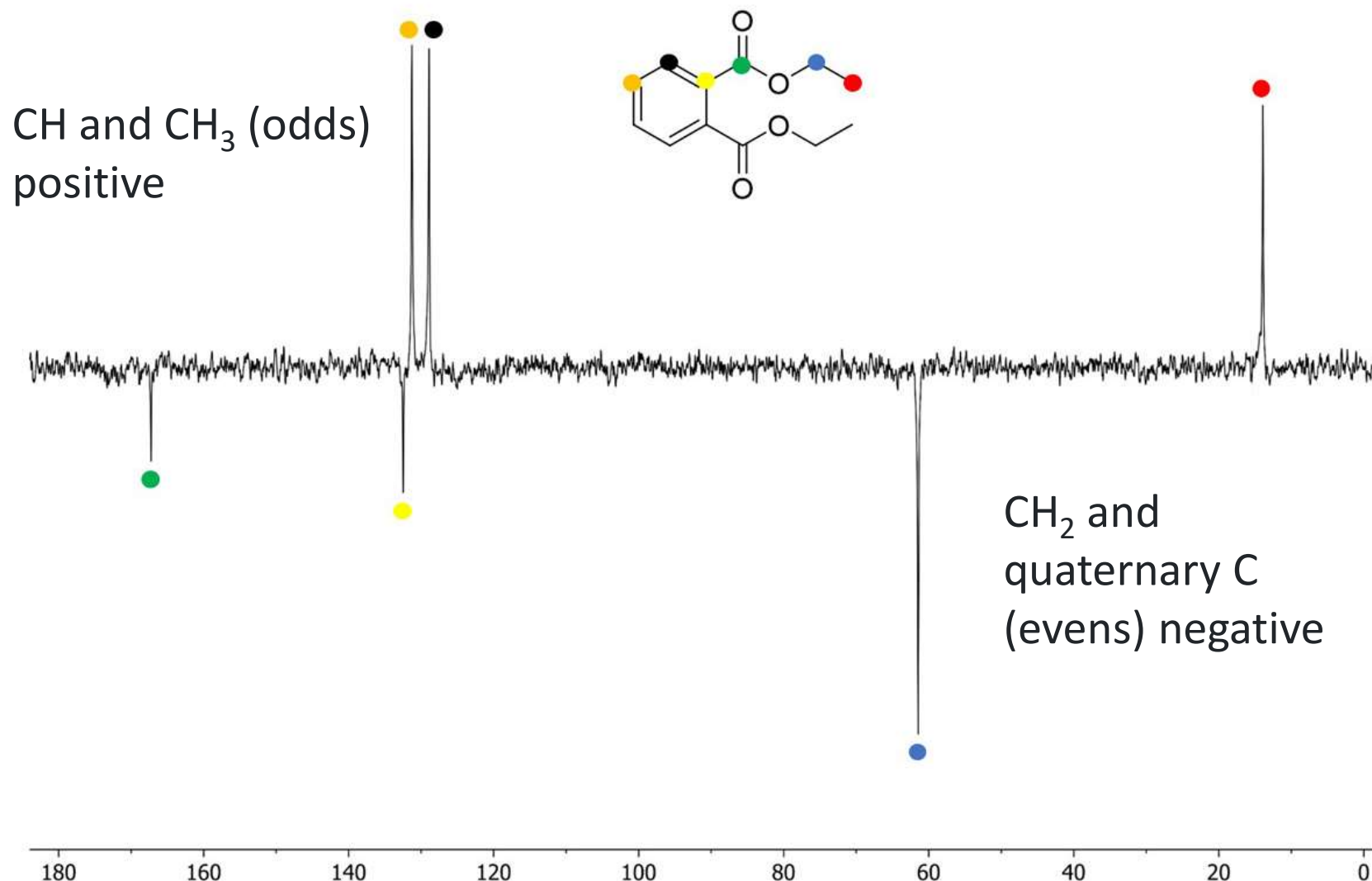
- Either of these two experiments can be used to detect protonated carbons and determine carbon-type *ie* methyl, methylene or methine (**carbon multiplicity**)
- Energy (polarisation) is transferred from one nuclei (^1H) to the other (^{13}C)
- The degree of transfer is dependent on experimental constraints and the carbon-type and impacts significantly on the relative intensity (and phase) of the carbon signals

DEPT carbon-13 NMR spectrum of citronellal.



CH and CH₃ positive while CH₂ and quaternary C are negative

APT provides the same information based on phase (positive or negative)



CH and CH₃ positive while CH₂ and quaternary C are negative

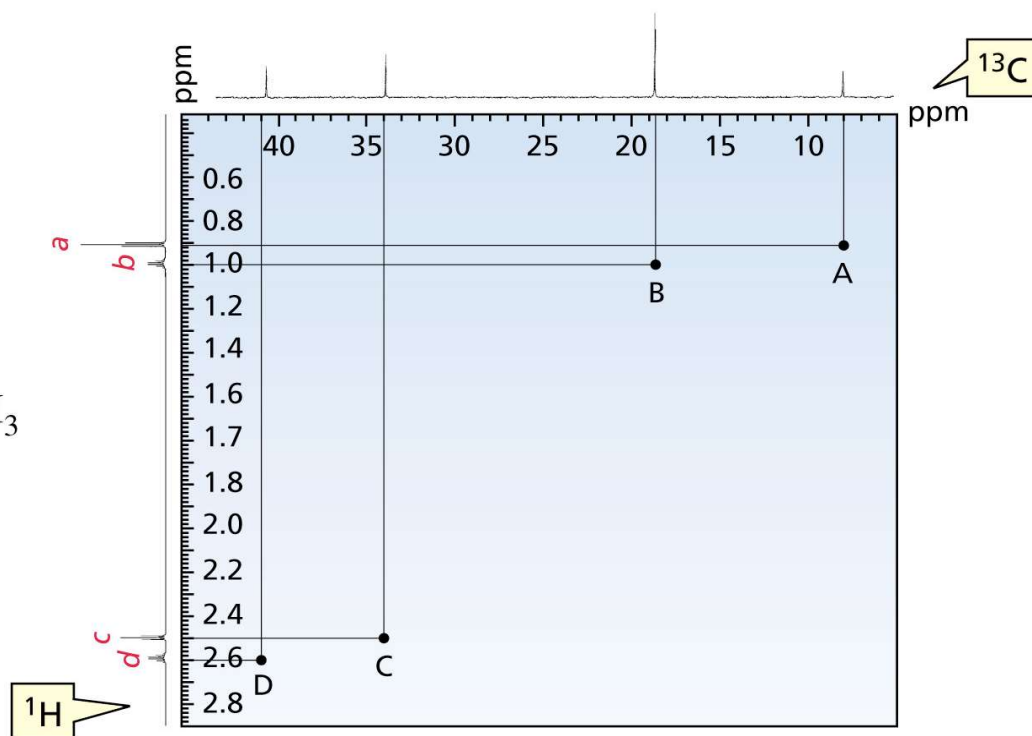
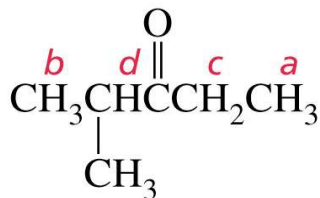
HETCOR (Heteronuclear correlation spectroscopy)

- Spectrum is a 2D plot of ^1H frequency vs ^{13}C frequency (cf COSY)
- HSQC correlates proton signals to the carbon to which the protons are attached (specific to one-bond C-H coupling)
- By checking cross peaks for every carbon signal, we can assign carbon multiplicity

**HSQC spectrum of
2-methyl-3-
pentanone.**

**Heteronuclear
Single
Quantum
Coherence**

(Single = 1 bond)

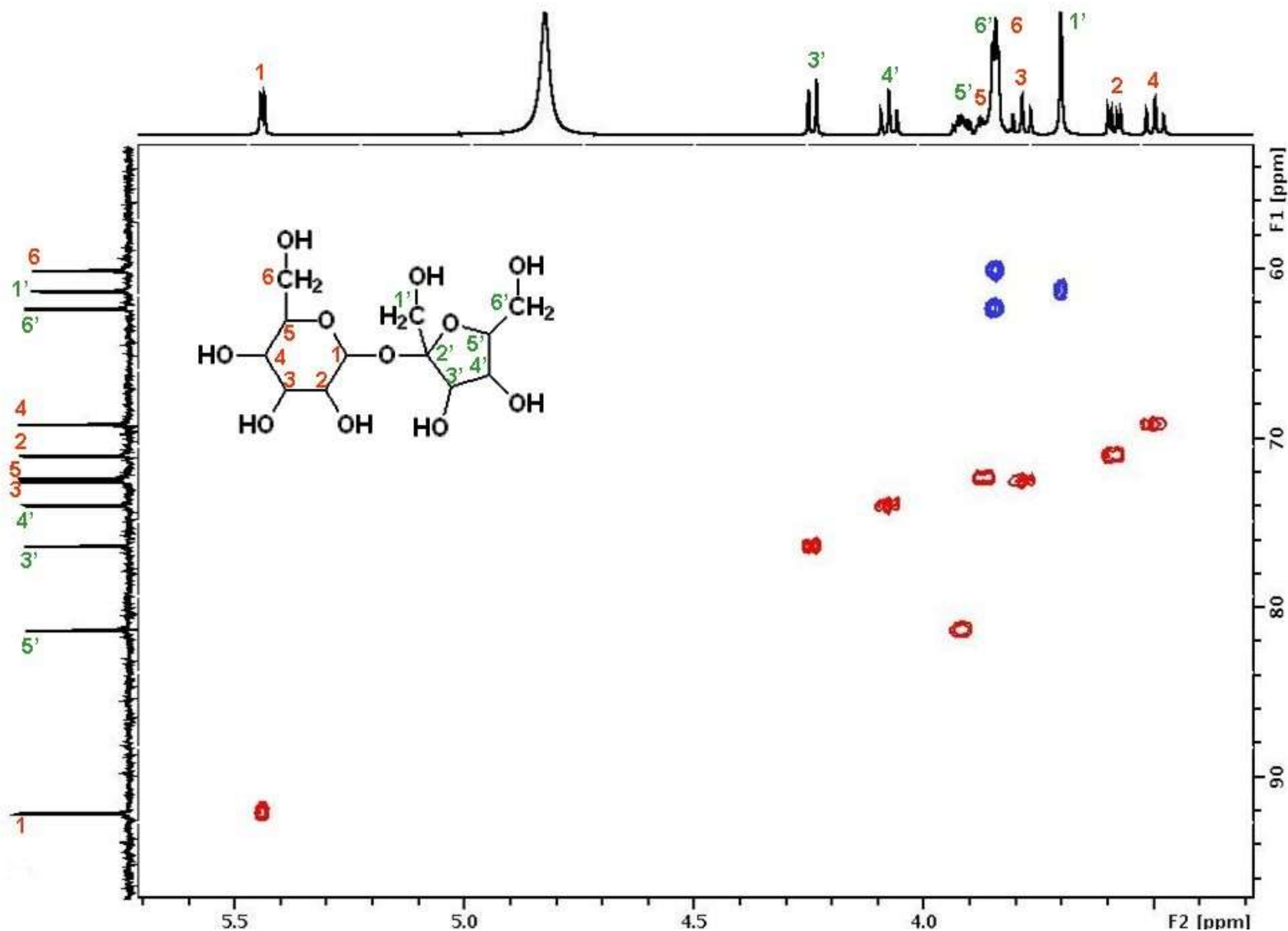


HSQC is powerful

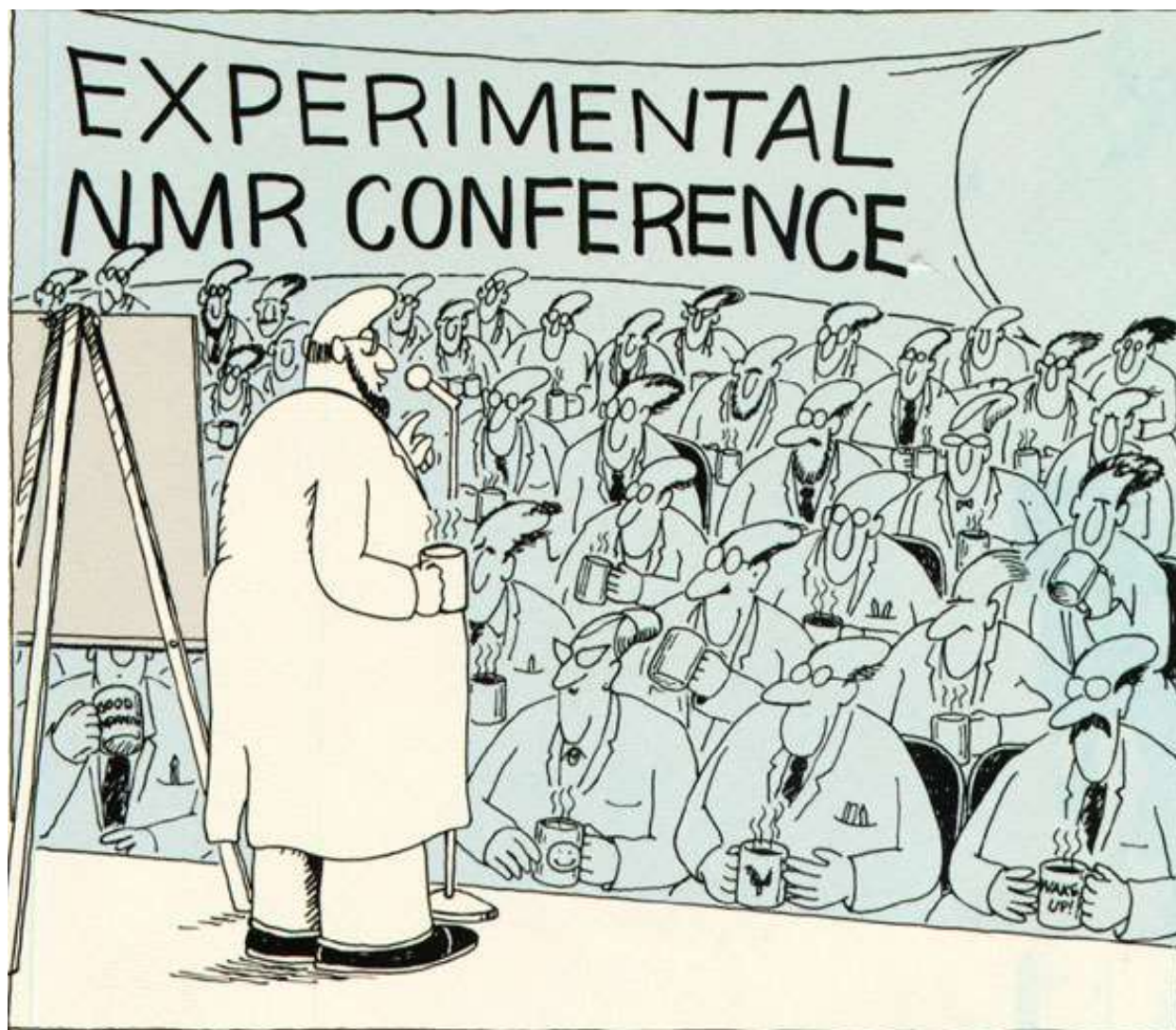
The APT or DEPT would help deconvolute ^{13}C spectrum

But HSQC also gives us the (mutual) information about the ^1H signals

Blue = CH_2 , Red = CH/CH_3 , quaternary signals have no cross peak



End of Module!



"Therefore, we can draw the conclusion that long-term exposure to high magnetic fields has no known harmful physical effect."

Use the websites

NMR tutorial next week

Practical NMR experience will also come from labs