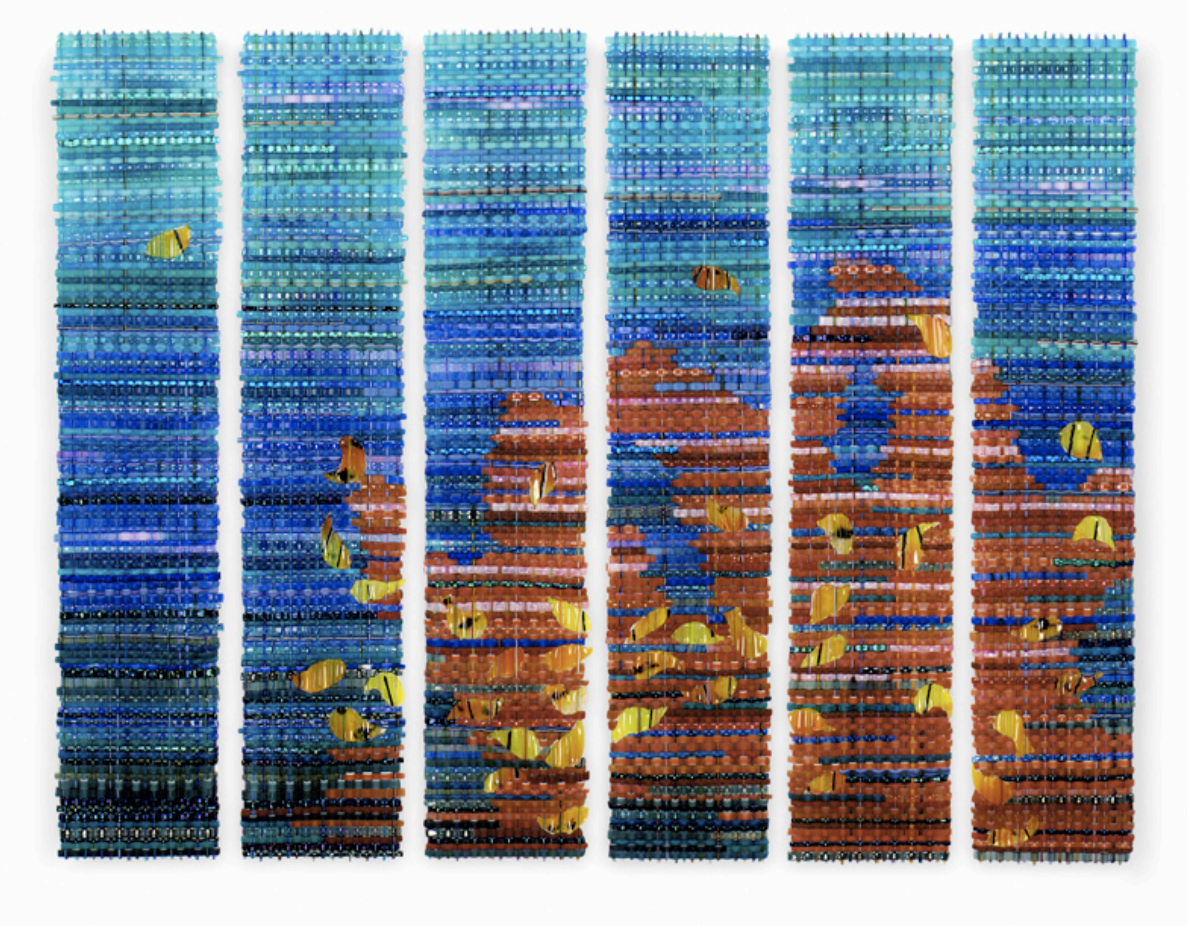
344 | Organic Chemistry Laboratory
Spring 2013

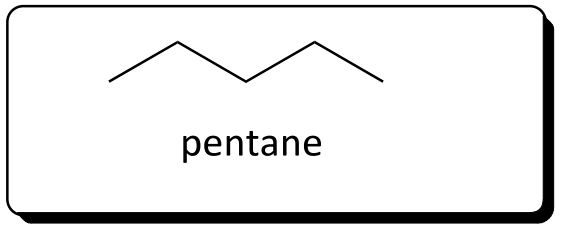


Lecture 4 Introduction to ^{13}C-NMR Spectroscopy

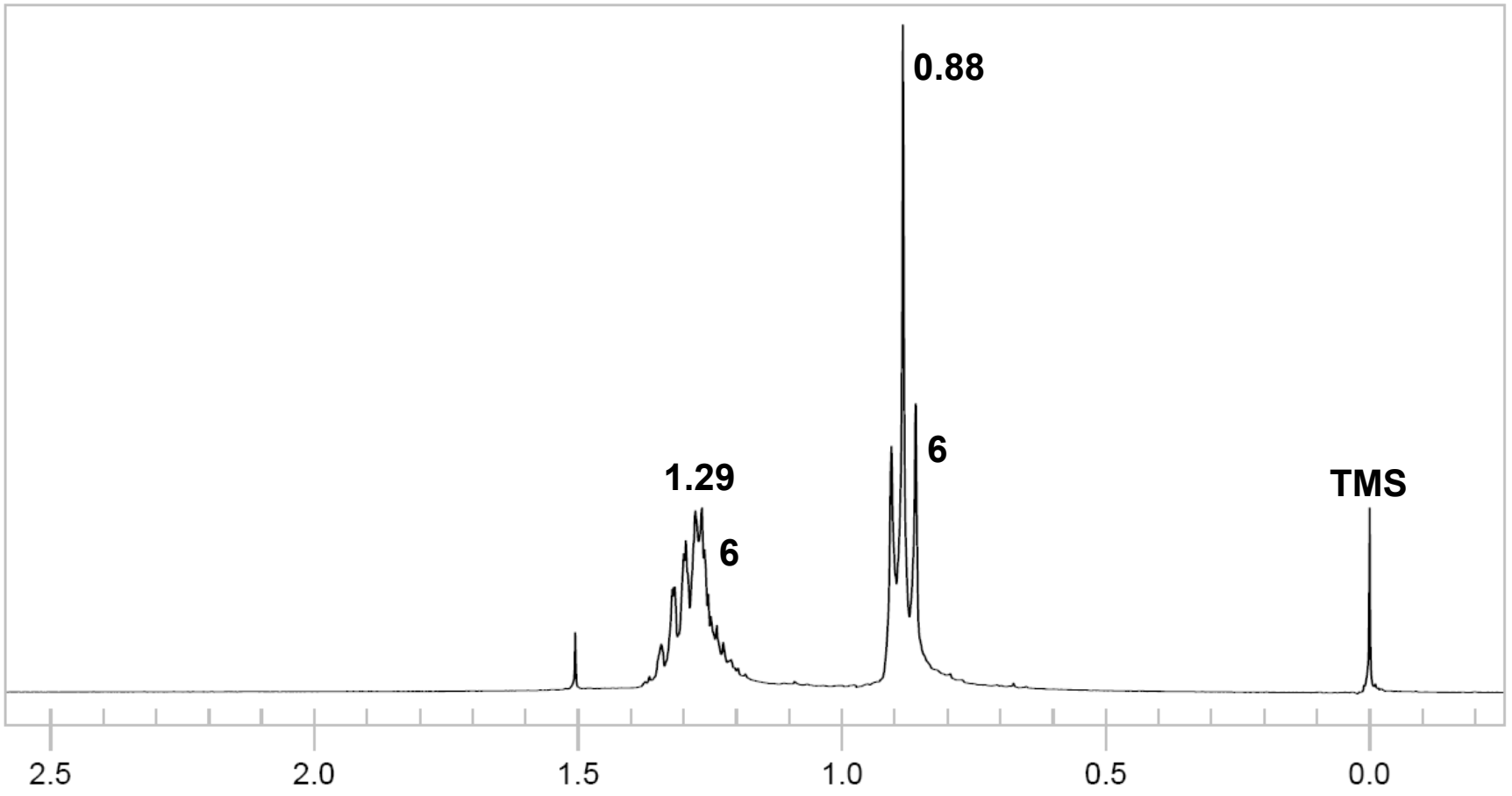
Nicholas J. Hill and Brian J. Esselman

^{1}H-NMR spectrum of pentane

looks odd…..not n+1

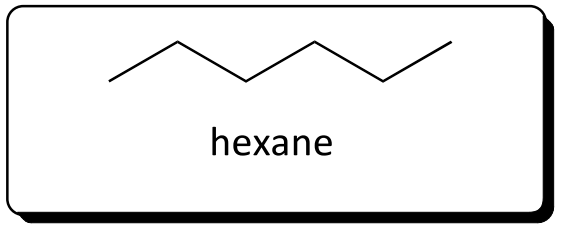


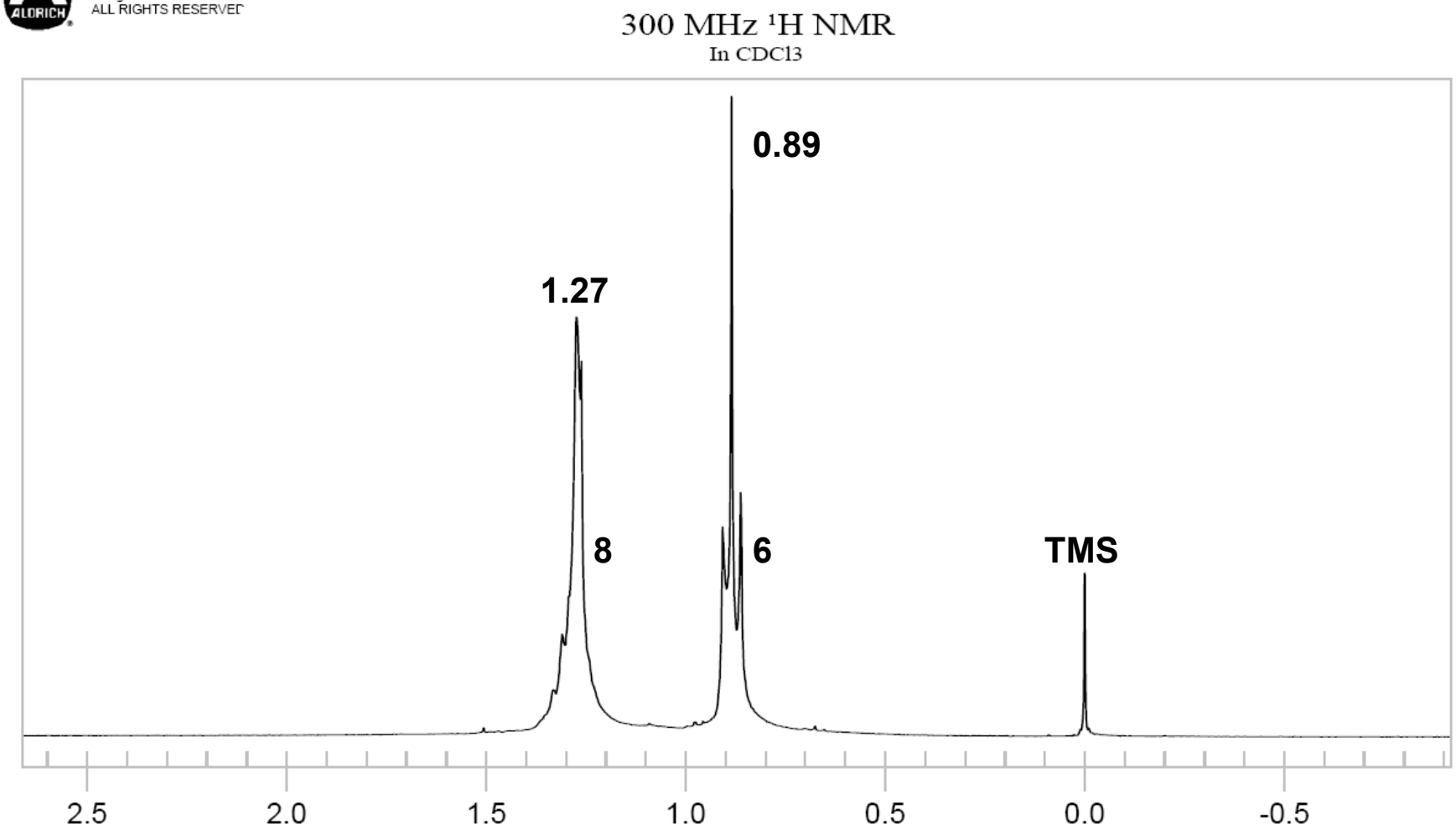
300 MHz ^{1}H NMR
In CDCl3



^{1}H-NMR spectrum of hexane

2nd order spectrum – difficult to interpret





^{13}C-NMR Spectroscopy

^{13}C is NMR active (I = ½), ^{12}C is NMR silent (I = 0)

The natural abundance of ^{13}C is ~1.1%

i.e. a molecule that contains 100 C atoms will contain just one ^{13}C nucleus

Good News
spectra are simple (no 2nd order effects)
shielding trends are same as for ^{1}H-NMR
can "count carbons"

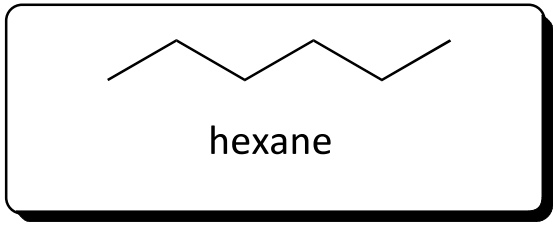
Loudon p. 622-629

Bad News
no coupling information about adjacent carbons
^{13}C data are more difficult to obtain than ^{1}H-data
(due to low abundance of ^{13}C isotope)

^{13}C-NMR spectrum

3 different types of carbon atom in hexane

1 x CH_3, 2 x CH_2 – expect 3 signals



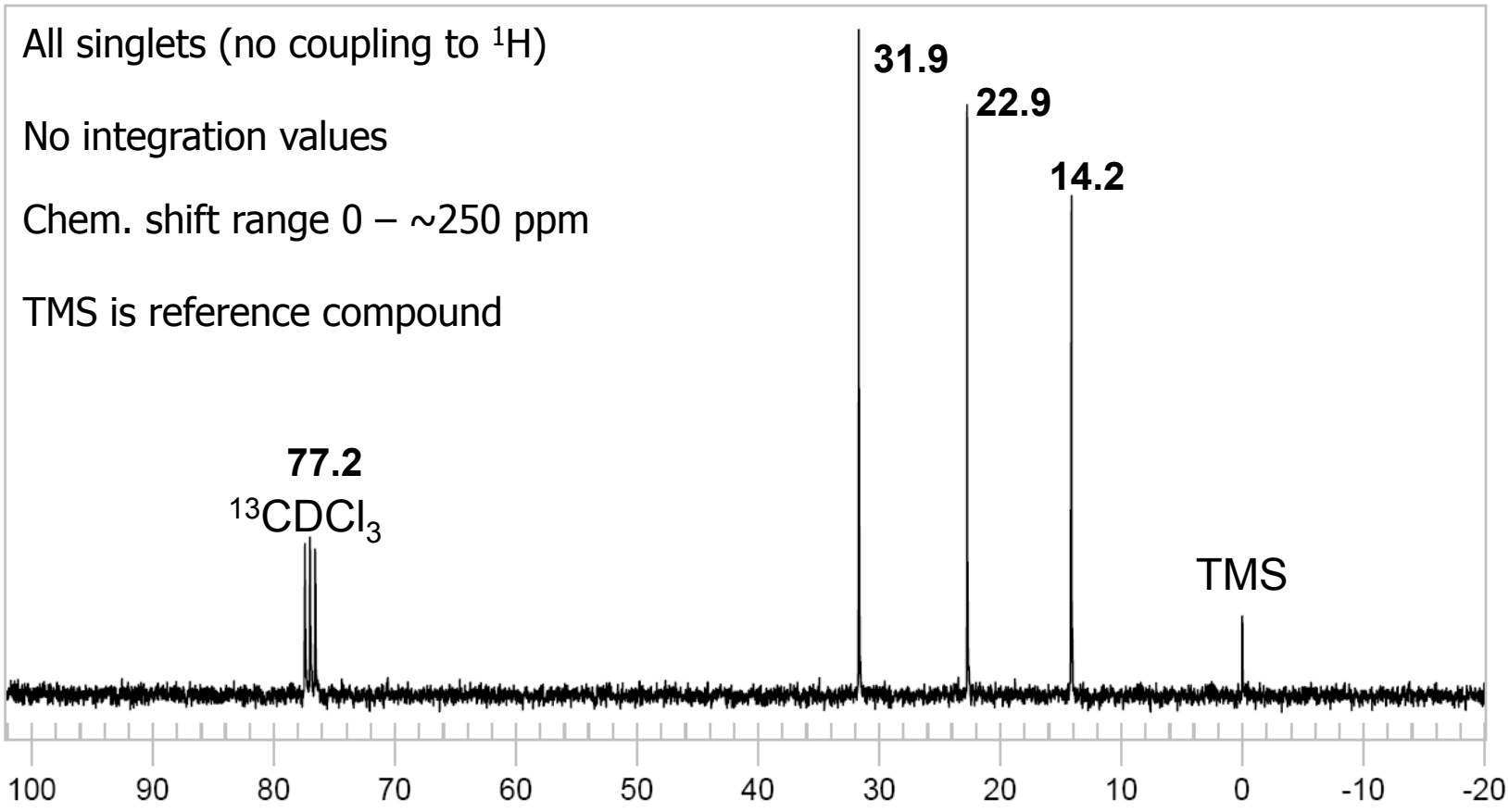
75 MHz ^{13}C NMR
In CDCl3

All singlets (no coupling to ^{1}H)

No integration values

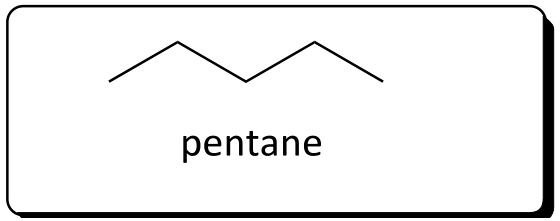
Chem. shift range 0 – ~250 ppm

TMS is reference compound



^{13}C-NMR spectrum

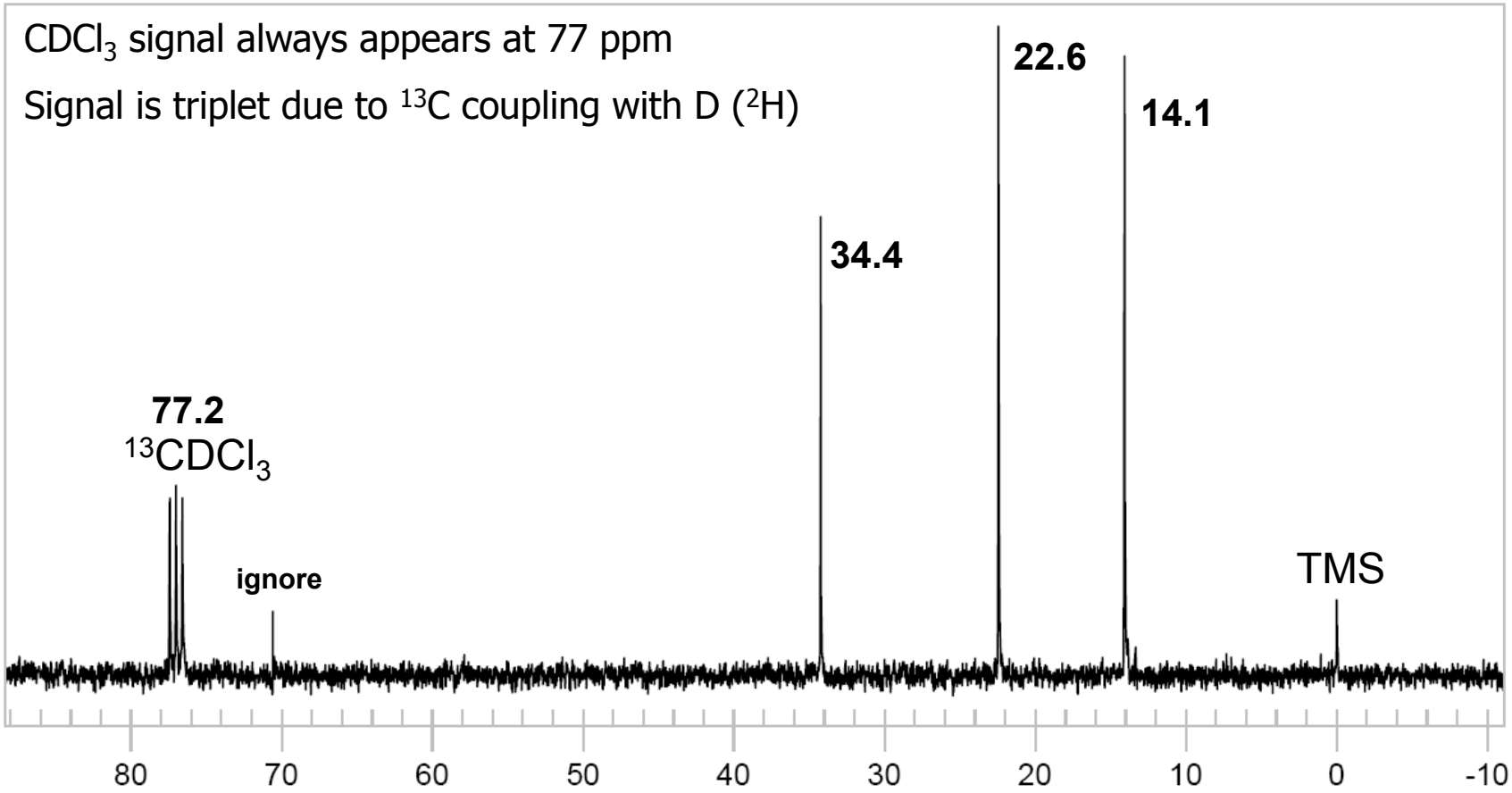
3 different types of carbon atom in pentane



75 MHz ^{13}C NMR
In CDCl3

$CDCl_3$ signal always appears at 77 ppm

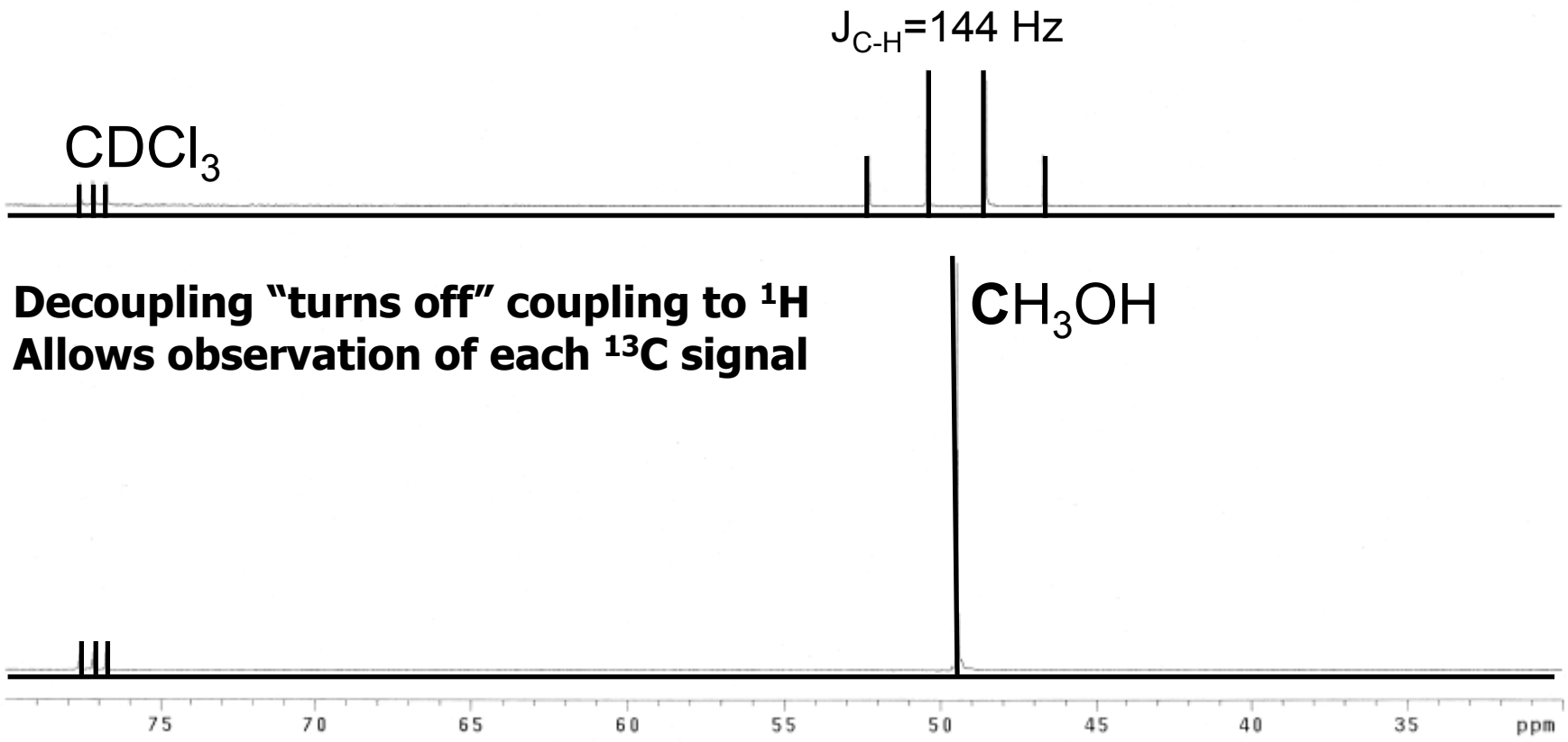
Signal is triplet due to ^{13}C coupling with D (^{2}H)



^{13}C-NMR spectrum of methanol

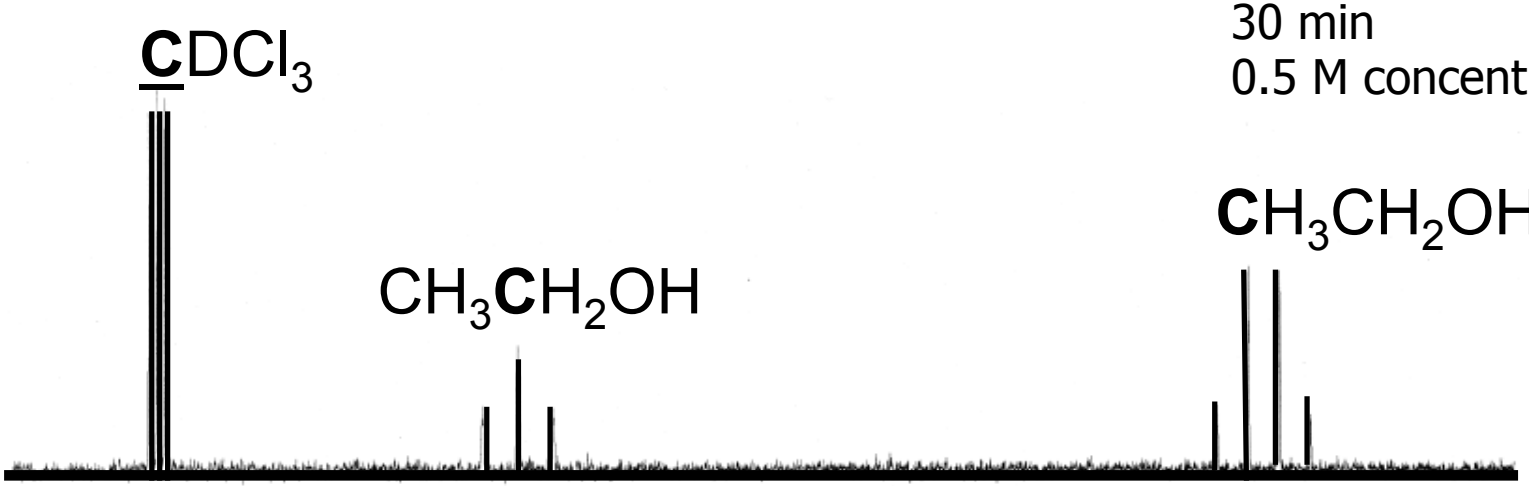
512 scans
30 min
10 M concentration

^{1}H is > 99% abundant, so it couples with the ^{13}C it is attached to (1 bond 100-180 Hz)

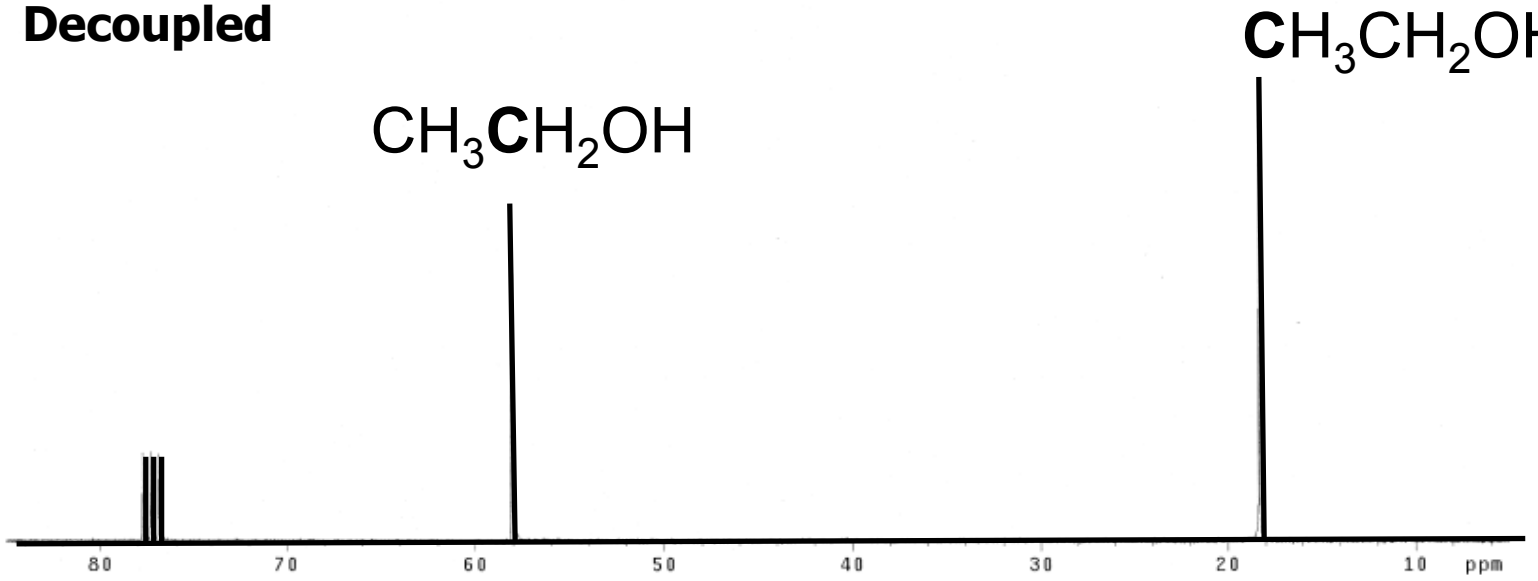


^{13}C-NMR spectrum of ethanol

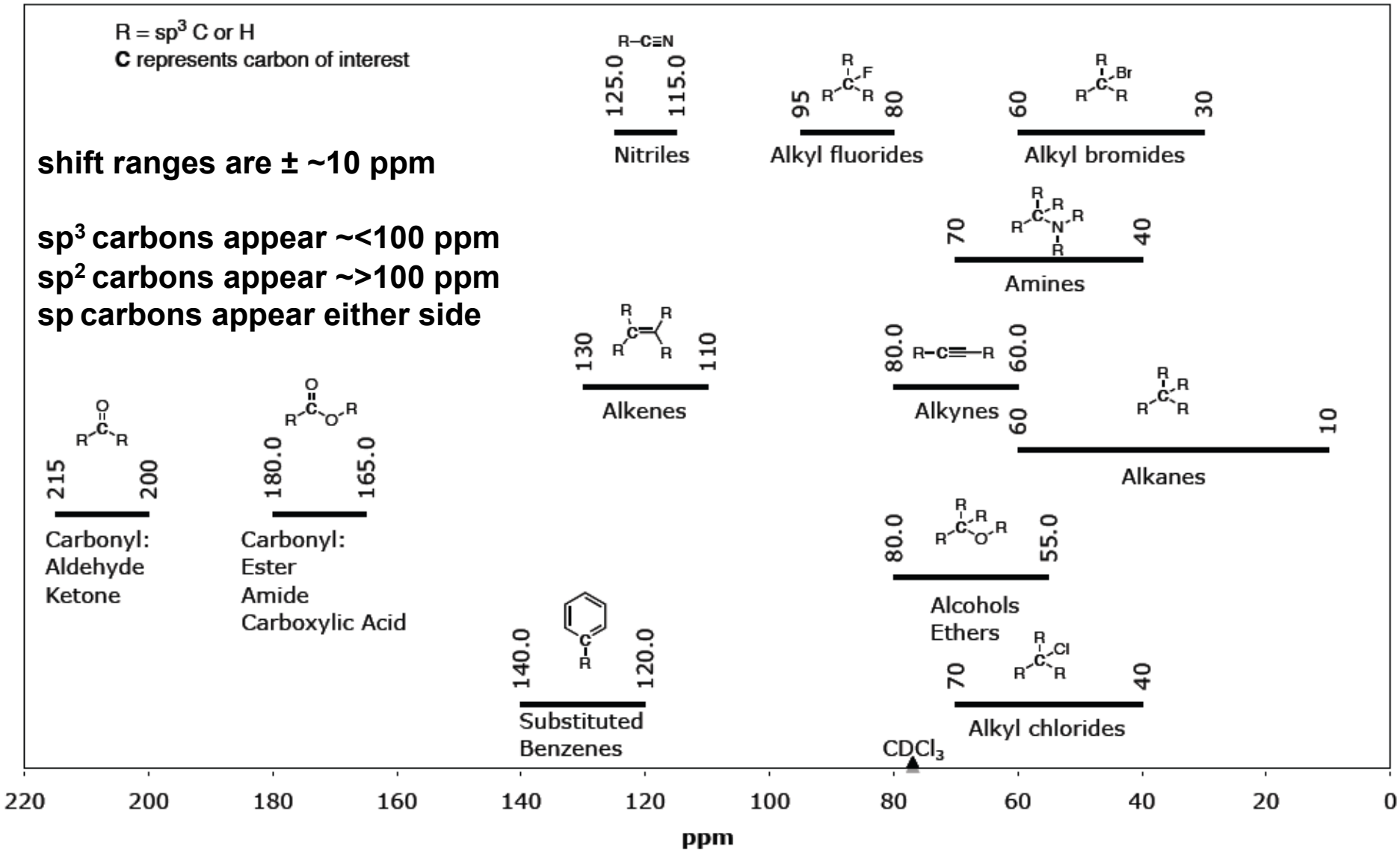
512 scans
30 min
0.5 M concentration



Decoupled

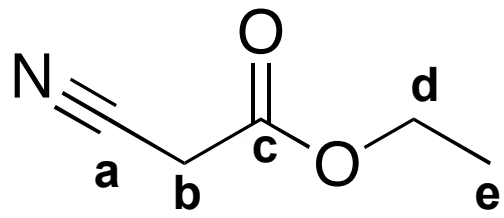


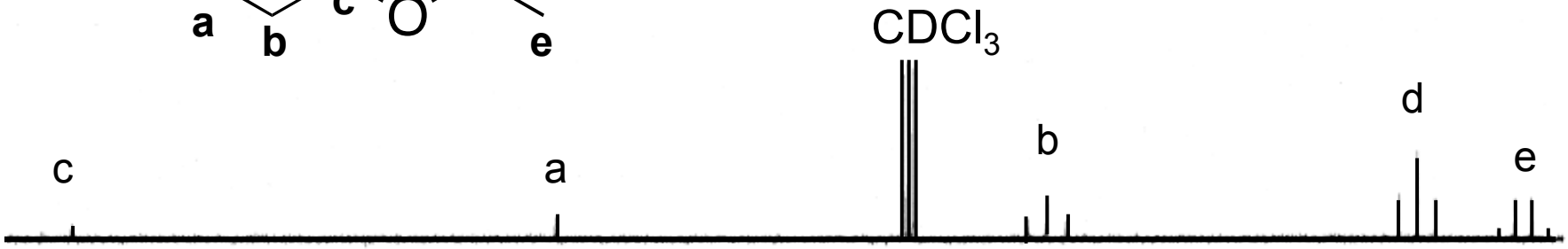
^{13}C-NMR Chemical Shift Table



Effects of decoupling: Ethyl cyanoacetate

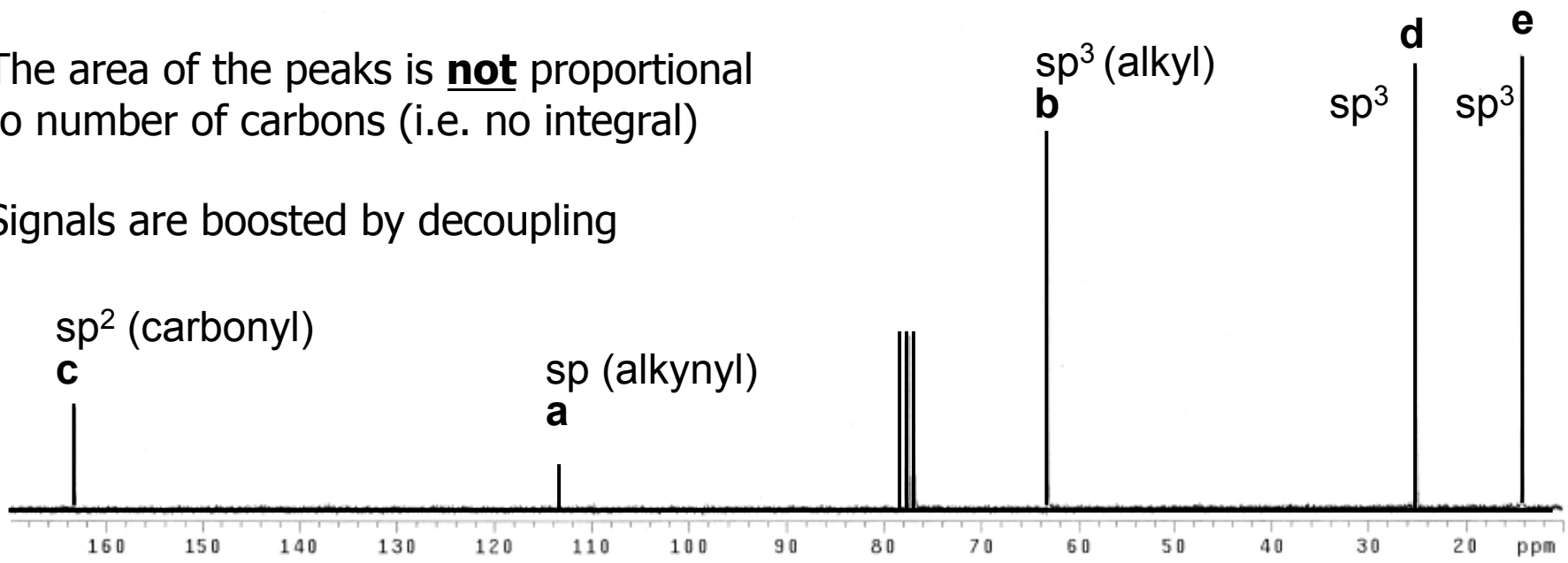
512 scans
30 min
0.35 M concentration





The area of the peaks is **not** proportional to number of carbons (i.e. no integral)

Signals are boosted by decoupling



Effects of decoupling: Ethyl cyanoacetate

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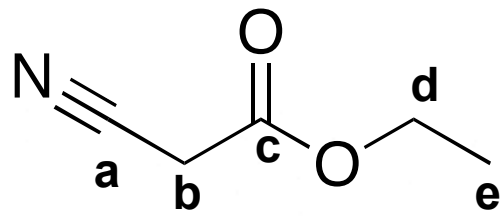
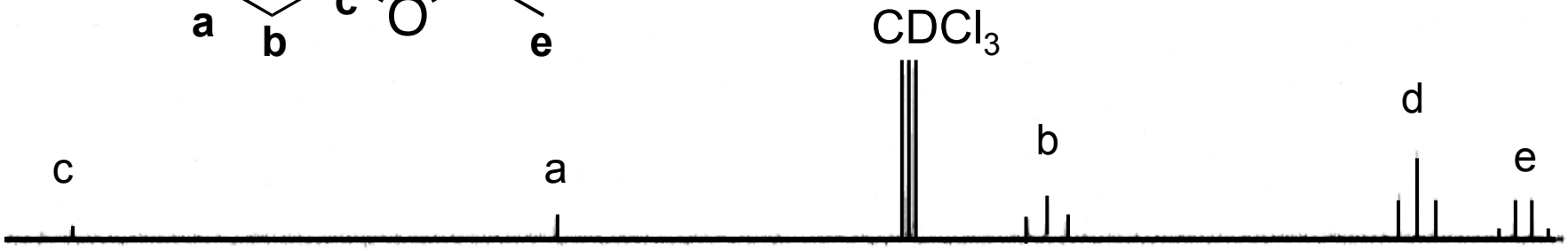
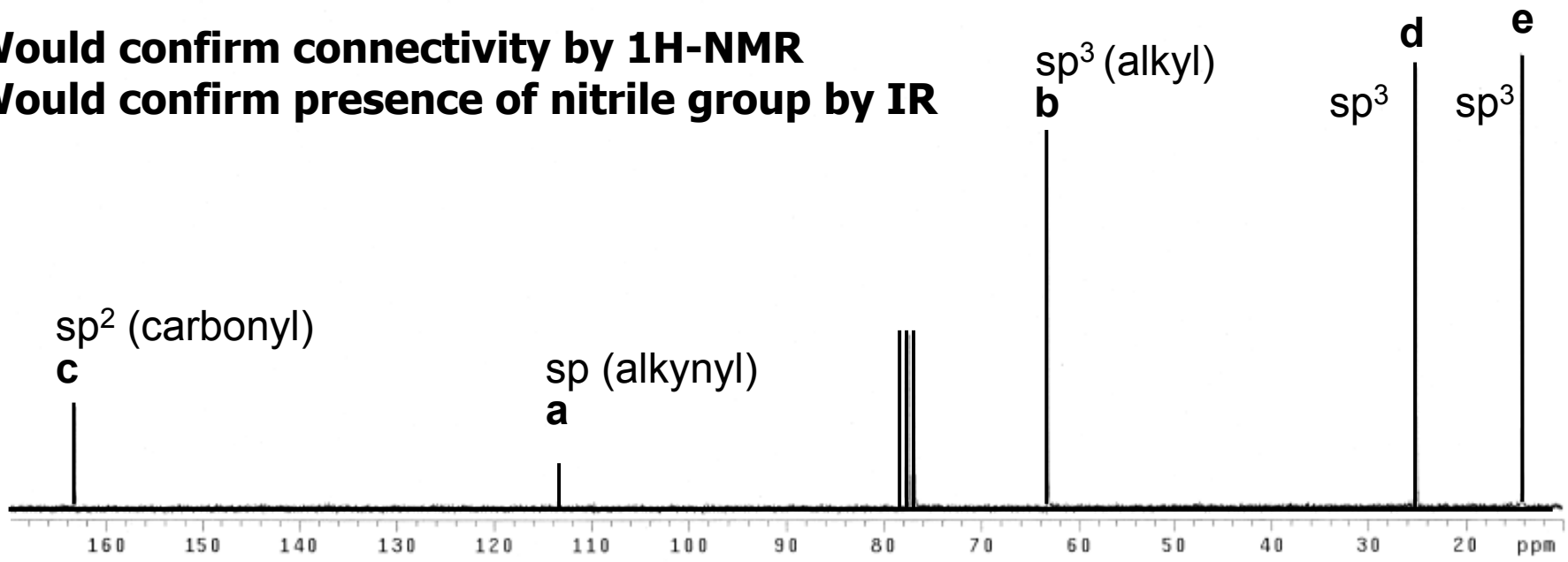
30 min
0.35 M concentration

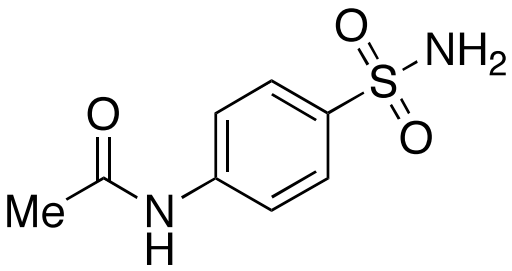




Would confirm connectivity by 1H-NMR
Would confirm presence of nitrile group by IR



^{1}H-NMR spectrum of Acetamidobenzenesulfonamide



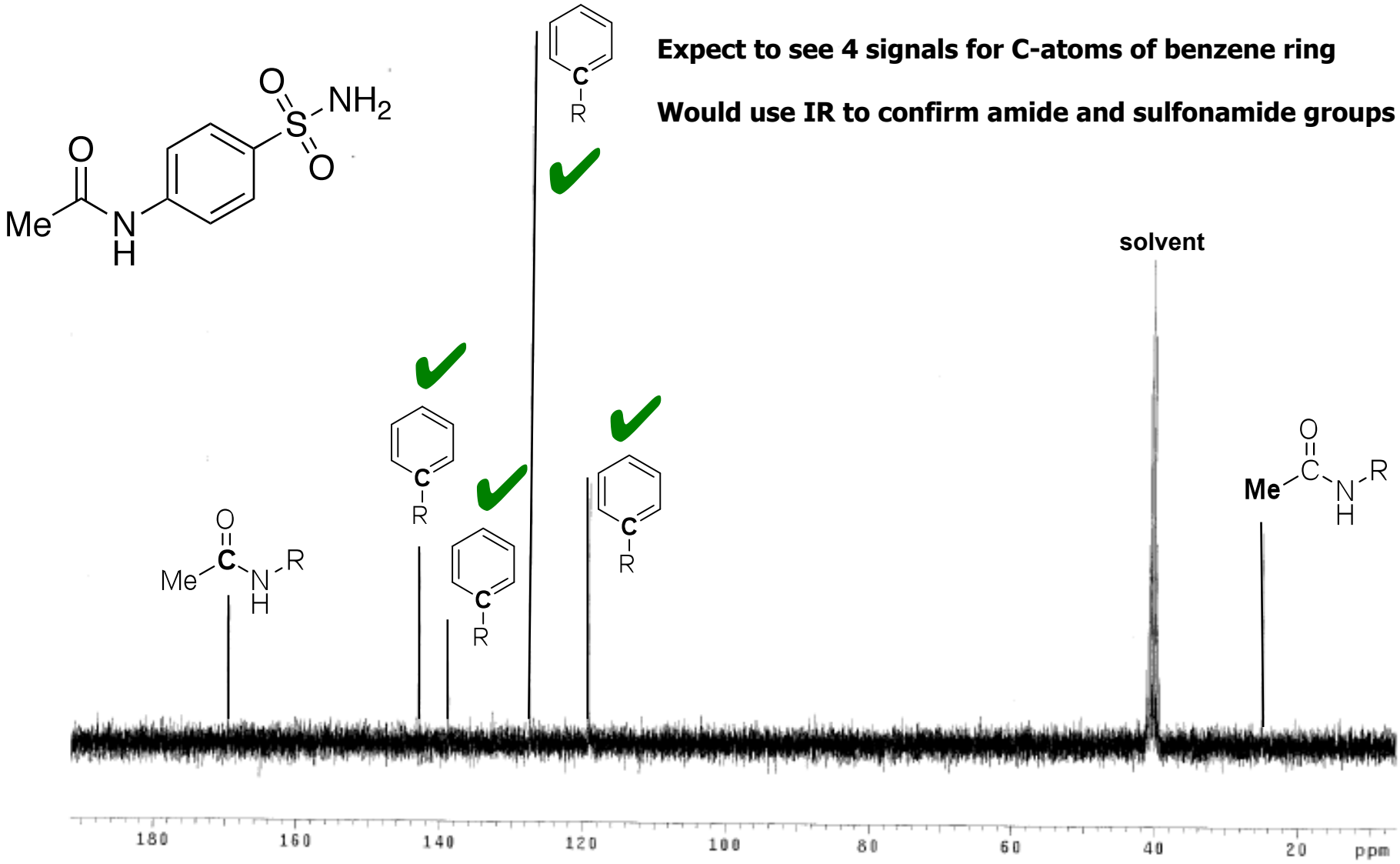
Functional group signals look OK

Signal for aromatic protons a little odd…expect two doublets

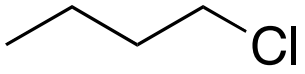
Need to confirm structure via ^{13}C-NMR

(Think about why we don't see two doublets)

^{13}C-NMR spectrum of Acetamidobenzenesulfonamide



Counting Carbons – practice!



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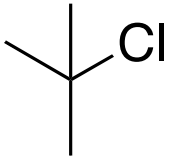

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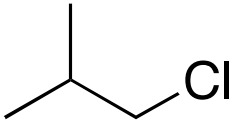

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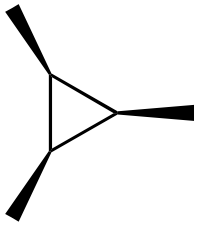

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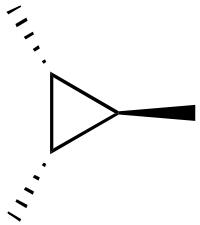

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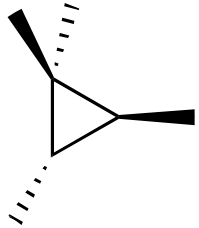

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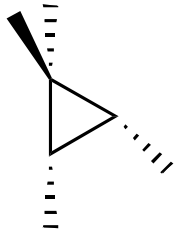

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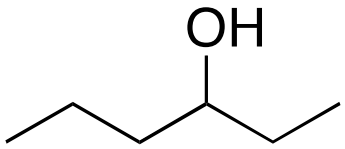

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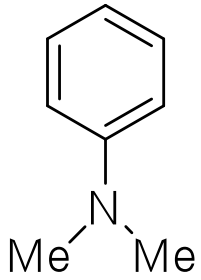

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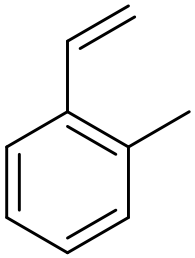

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think about equivalence and symmetry

Safety in CHEM 344

No eating, drinking, smoking, chewing, sipping, etc.
Nothing ingested in the lab, EVER.

Wear goggles at ALL TIMES
Safety specs are not acceptable

Wear shoes that cover all of the foot
Toe to hell - avoid exposed skin

Wear something old
Don't wear anything you care about

Wear plastic disposable gloves when handling ALL chemicals
Discard the gloves off whenever you leave lab!
Put on a fresh pair when you re-enter

Be aware of lab surroundings
Know where the fire extinguishers, eye wash station, shower are located
If in doubt, ask TA

Advice for success in CHEM 344

Plan ahead
Don't wait until 10 min before lab begins to read the procedure or write your pre-lab.

Understand what you need to do in lab
Is it a 2-day lab? Do you need to reflux the reaction? Come prepared.

Think about what you are doing in lab while you are doing it!
Why do you need to reflux/cool/add acid/add base/extract/distill?

Know exactly what you need to do for the lab report
Typically NMR and/or GC-MS, post-lab questions (including computational modeling).

Plan ahead (again)
Know when each lab report is due (entire schedule is printed in the lab manual)
Look at the spectra and questions at least 24 hrs before report is due