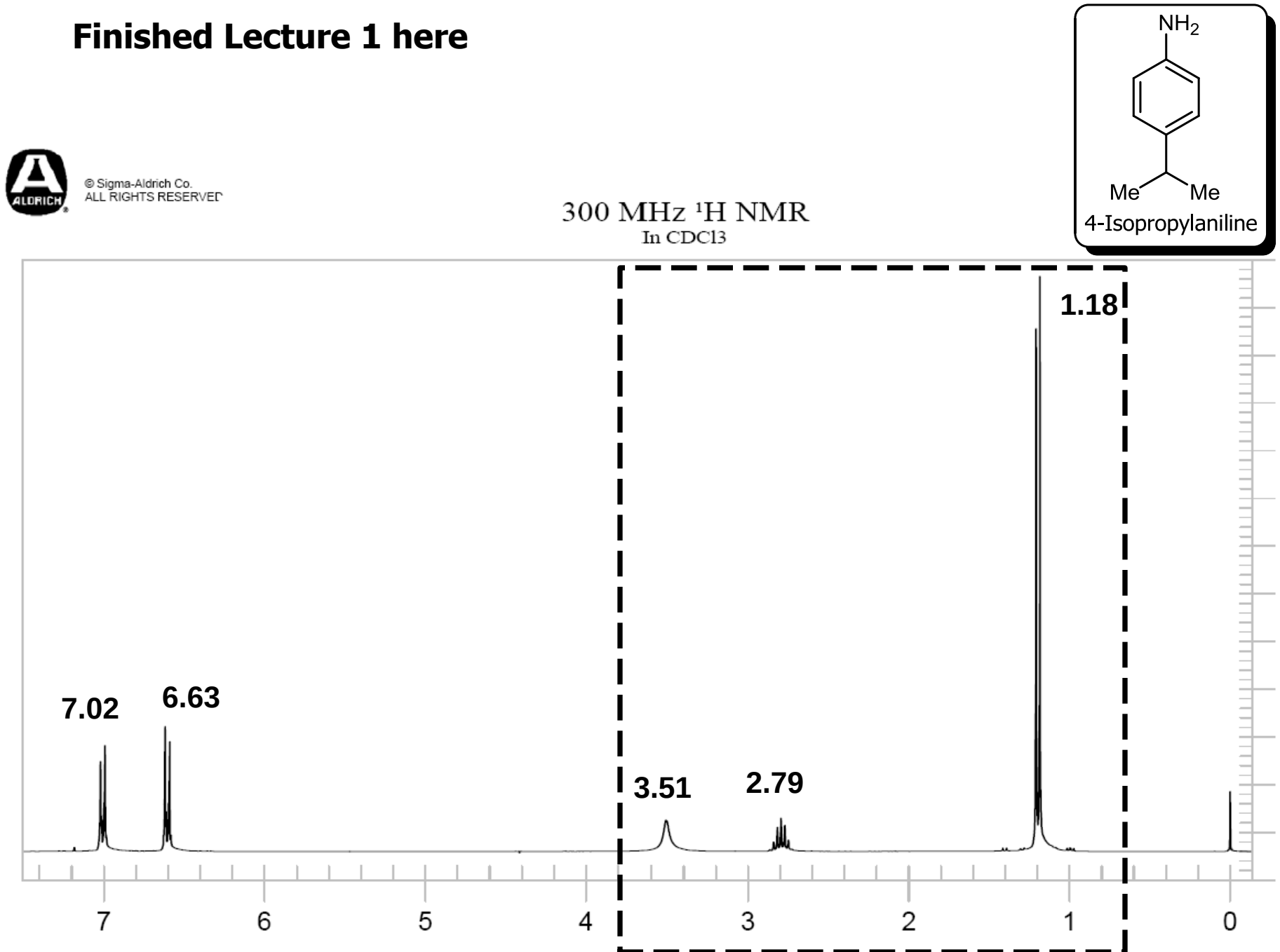
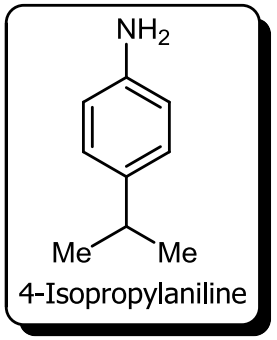
344 | Organic Chemistry Laboratory
Fall 2013

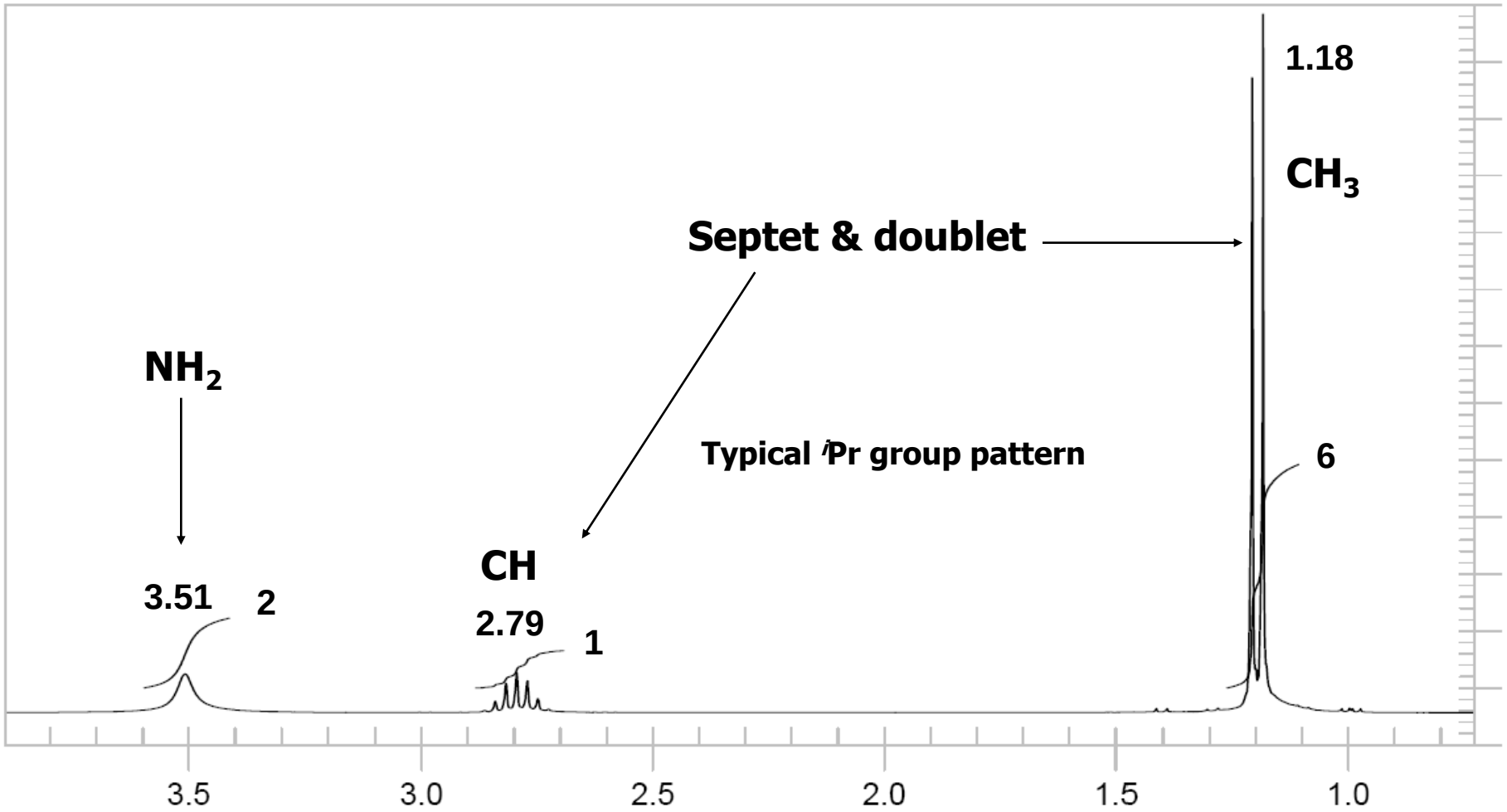
Lecture 2 More ^{1}H-NMR Spectroscopy
June 18 2013

Finished Lecture 1 here



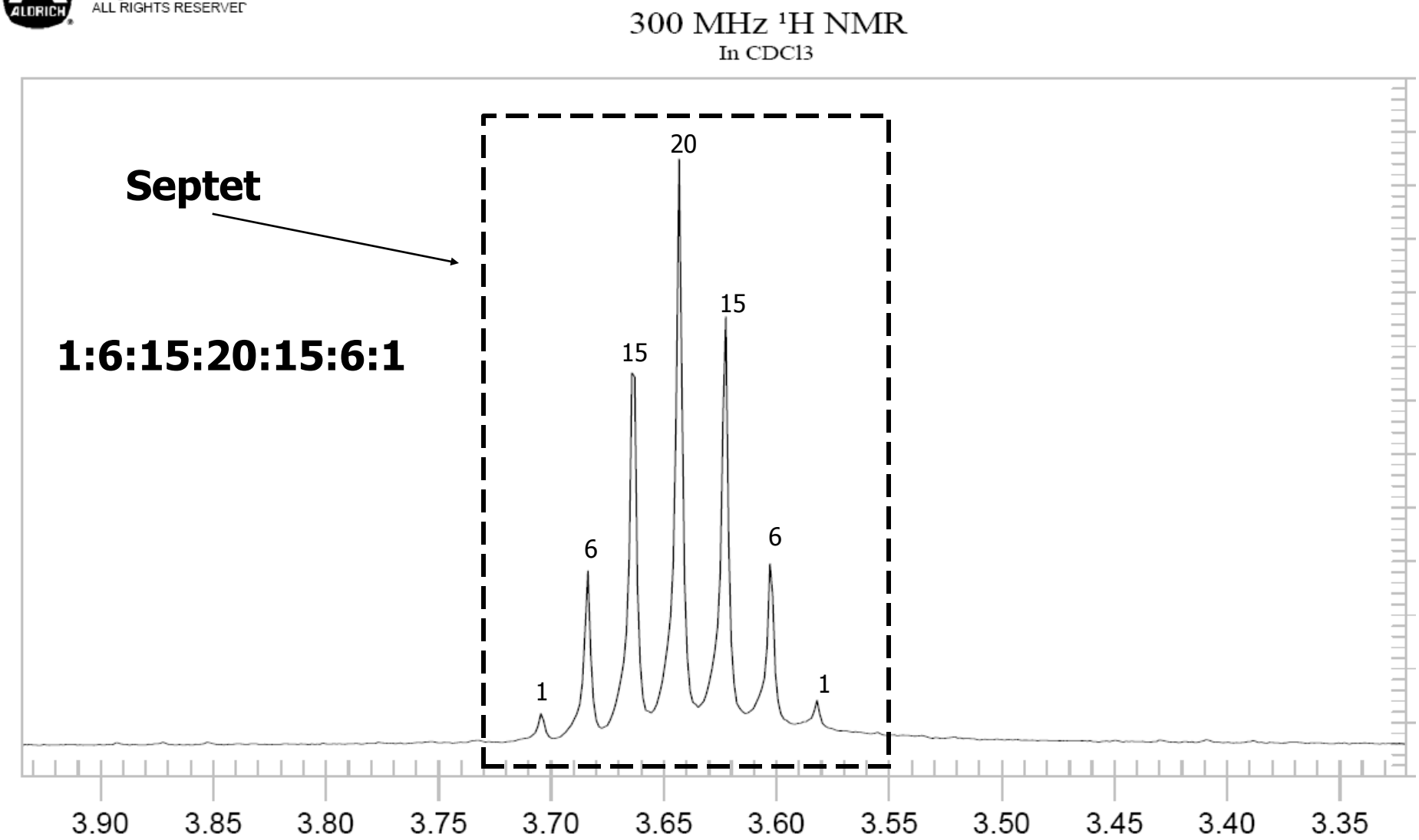


300 MHz ^{1}H NMR
In CDCl3



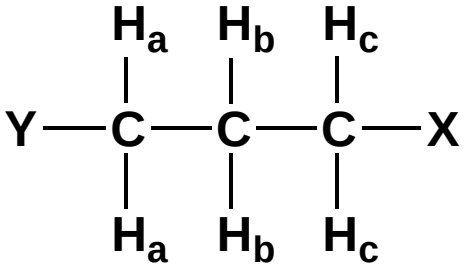
Coupling constant J (Hz) – indicates strength of coupling

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

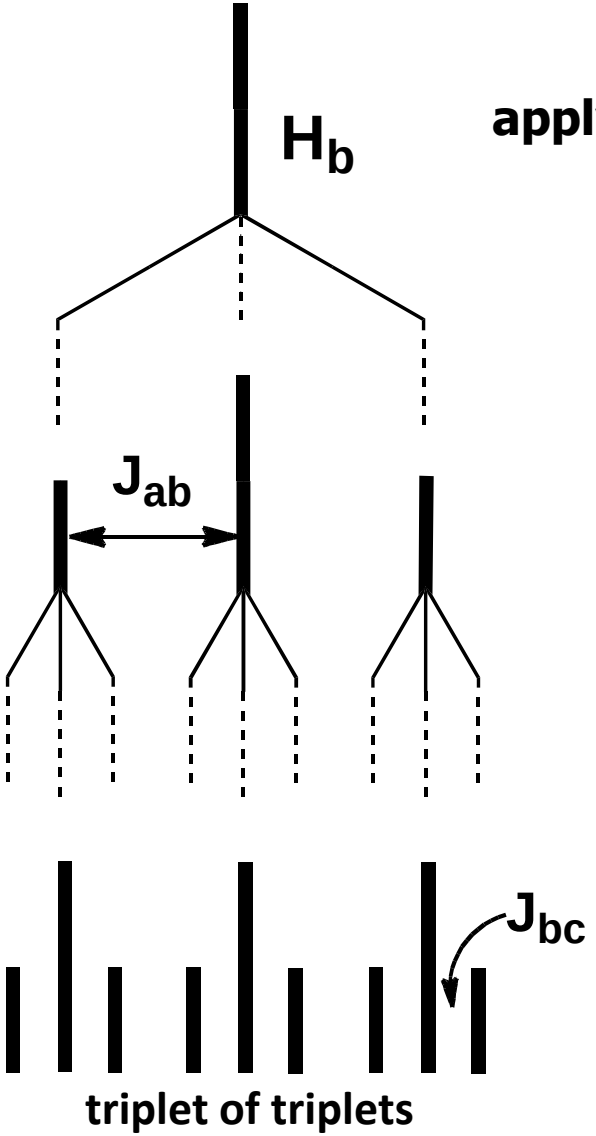


Derivation of splitting diagrams

1) Two different coupling constants in a simple alkyl chain (J_{ab} much larger than J_{bc})



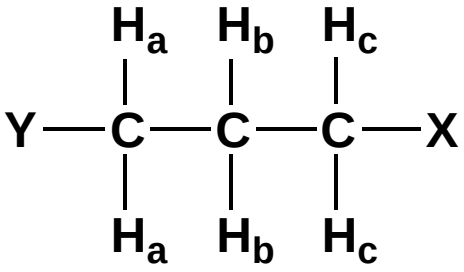
$J_{ab} > J_{bc}$



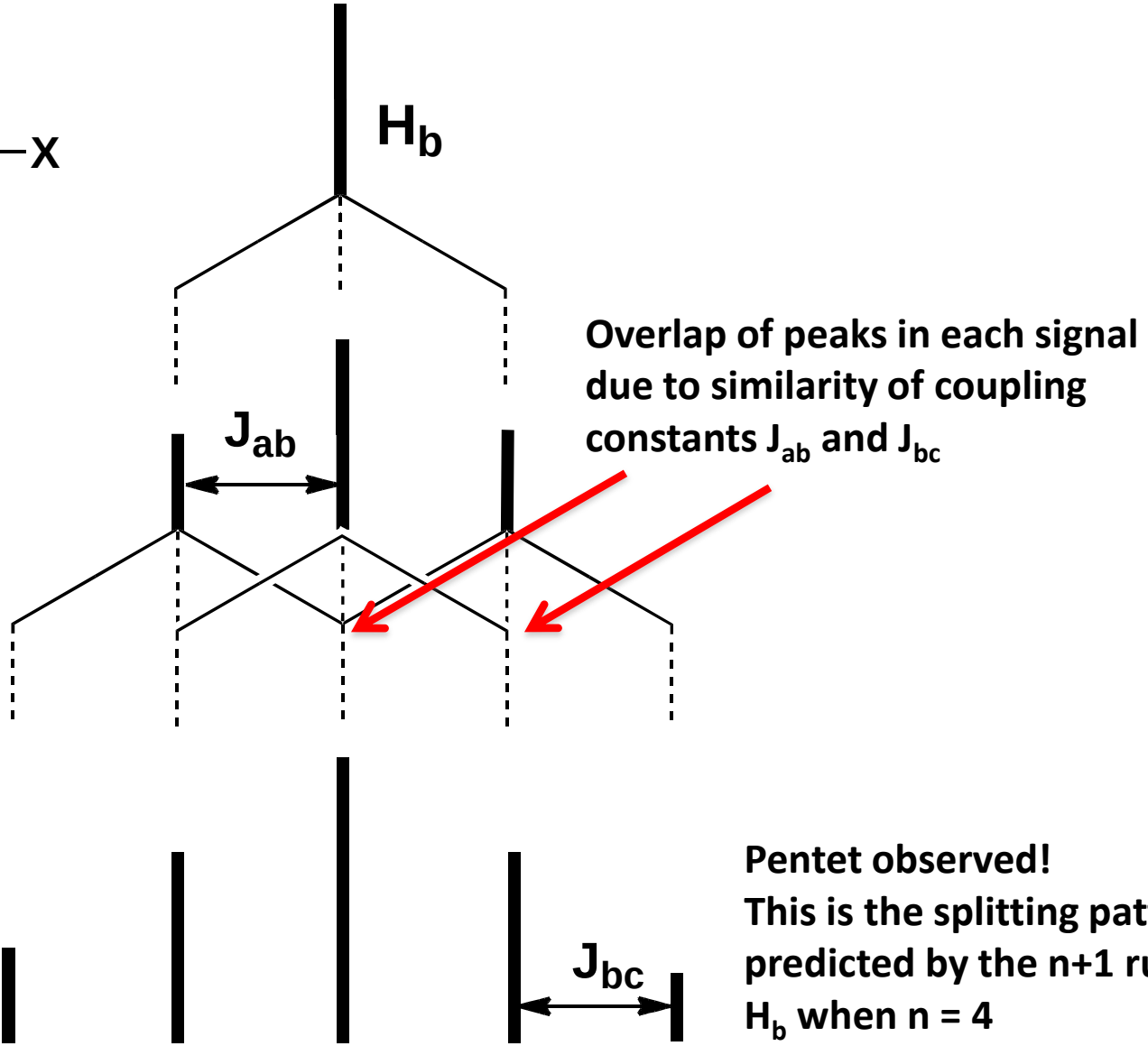
apply strongest coupling first!

Derivation of splitting diagrams

2) Two identical coupling constants in a simple alkyl chain (J_{ab} equal or almost equal to J_{bc})



$J_{ab} = J_{bc}$

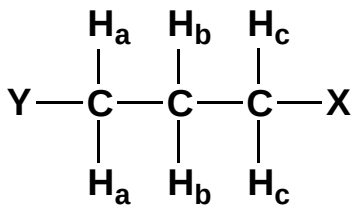


Overlap of peaks in each signal due to similarity of coupling constants J_{ab} and J_{bc}

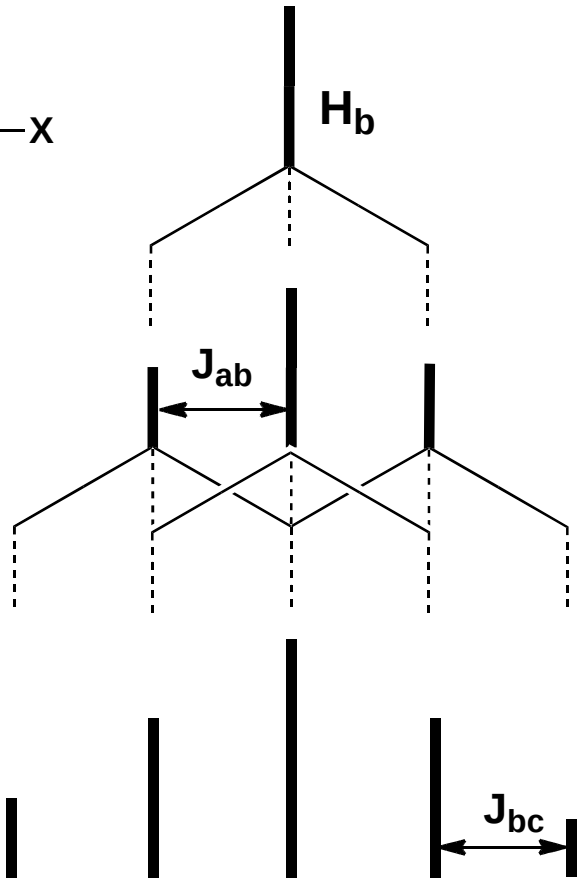
Pentet observed!
This is the splitting pattern predicted by the n+1 rule for H_b when n = 4

Derivation of splitting diagrams

2) Two identical coupling constants in a simple alkyl chain (J_{ab} equal or almost equal to J_{bc})



$J_{ab} = J_{bc}$



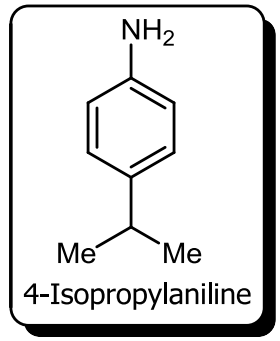
For H_b: n = 4

n + 1 = 5

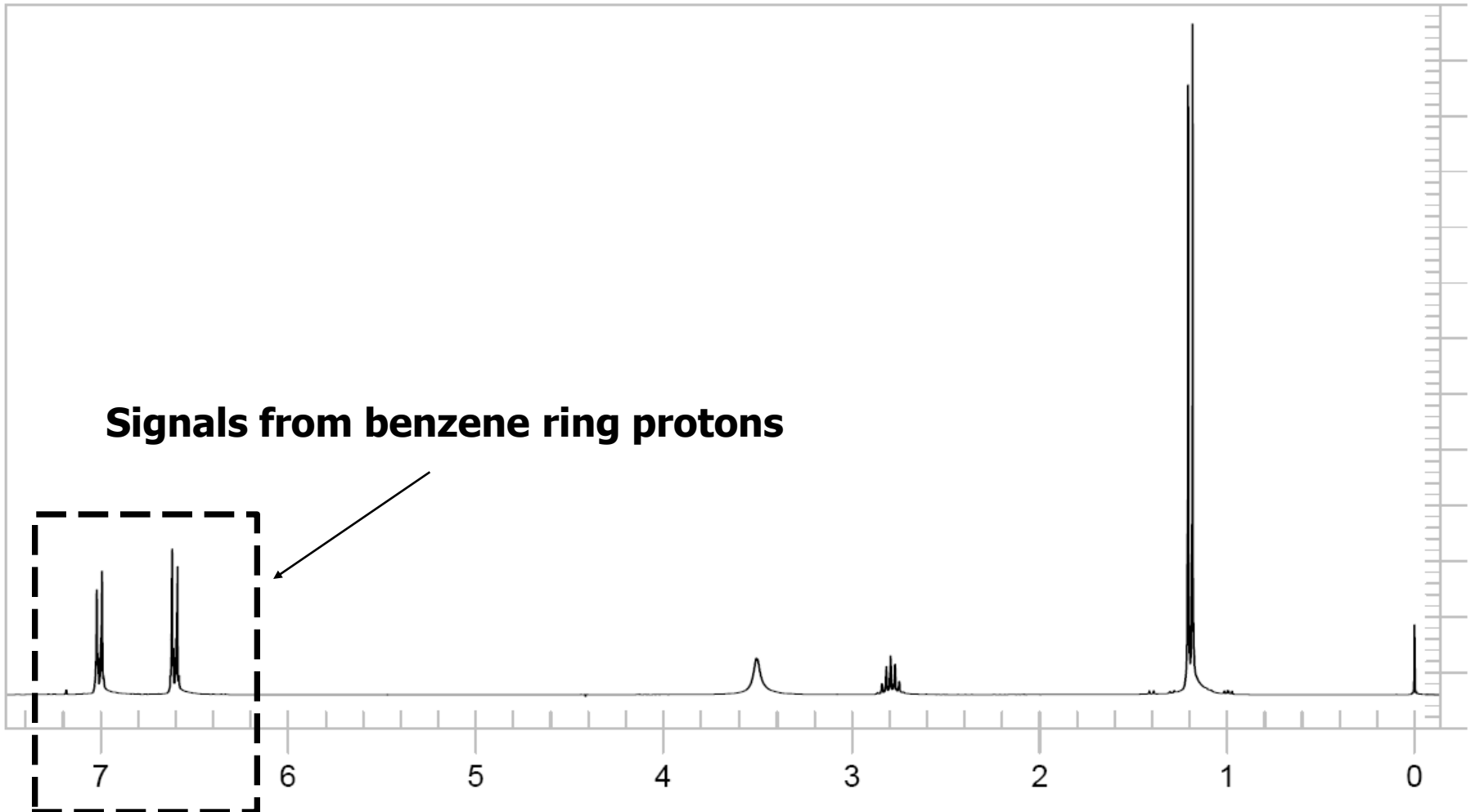
1:4:6:4:1 pentent

When coupling constants are equal, splitting results in n + 1 peaks (i.e. a "normal" splitting pattern)

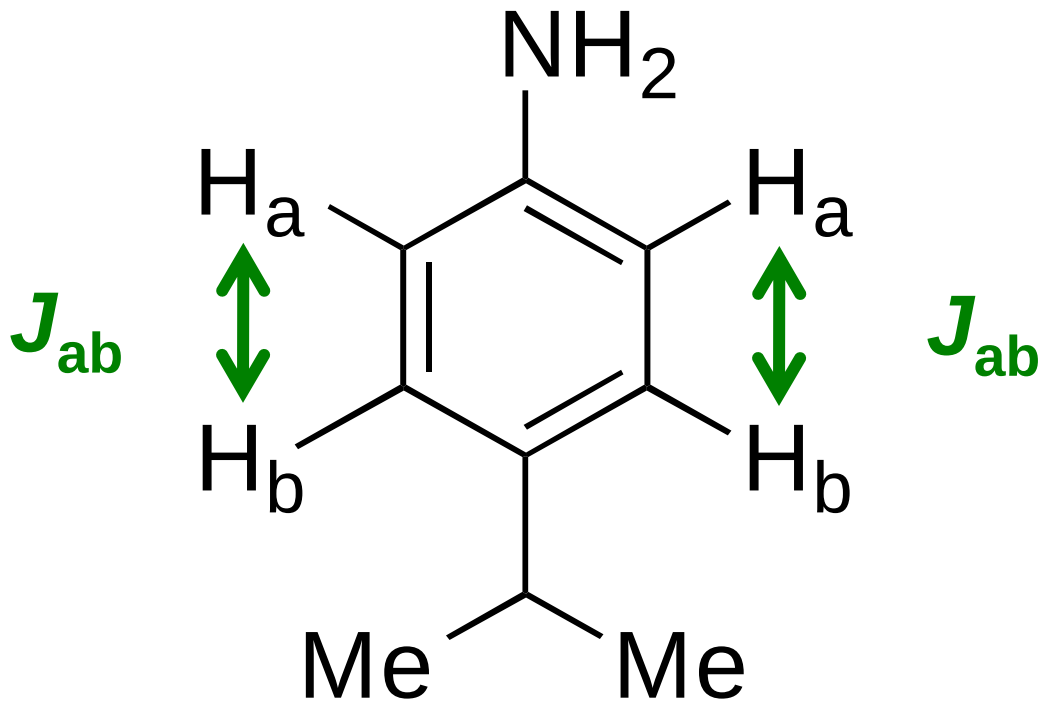
THIS IS THE MOST COMMON CASE FOR A SIMPLE ALKYL GROUP



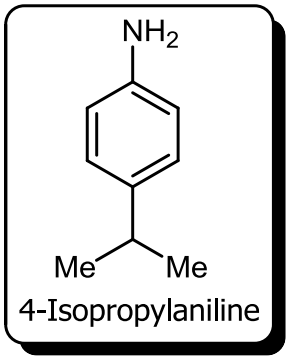
300 MHz ^{1}H NMR
In CDCl3



Coupling constants in aromatic systems



$J_{ab} = J_{ortho}$ = 6 – 12 Hz



300 MHz ^{1}H NMR
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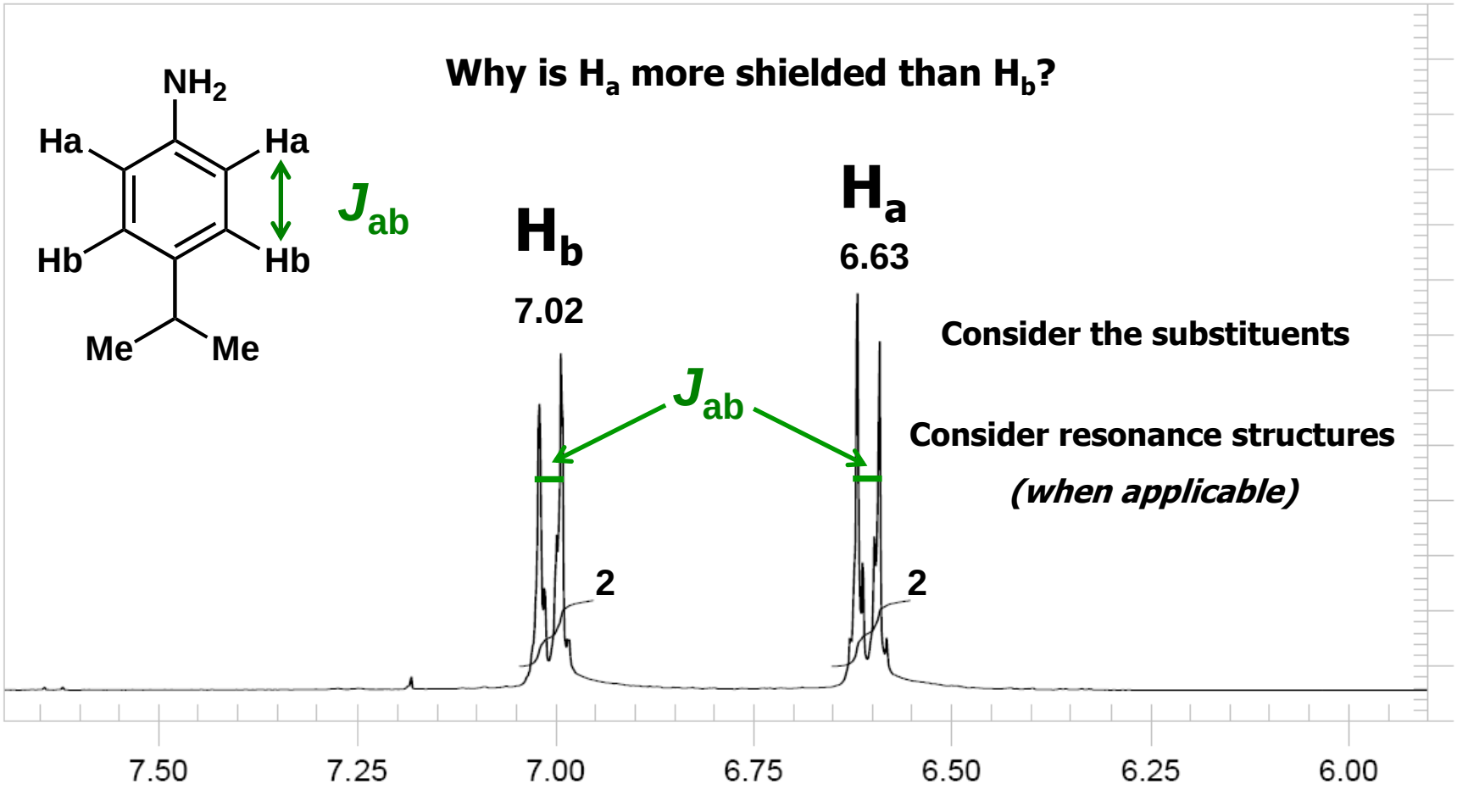
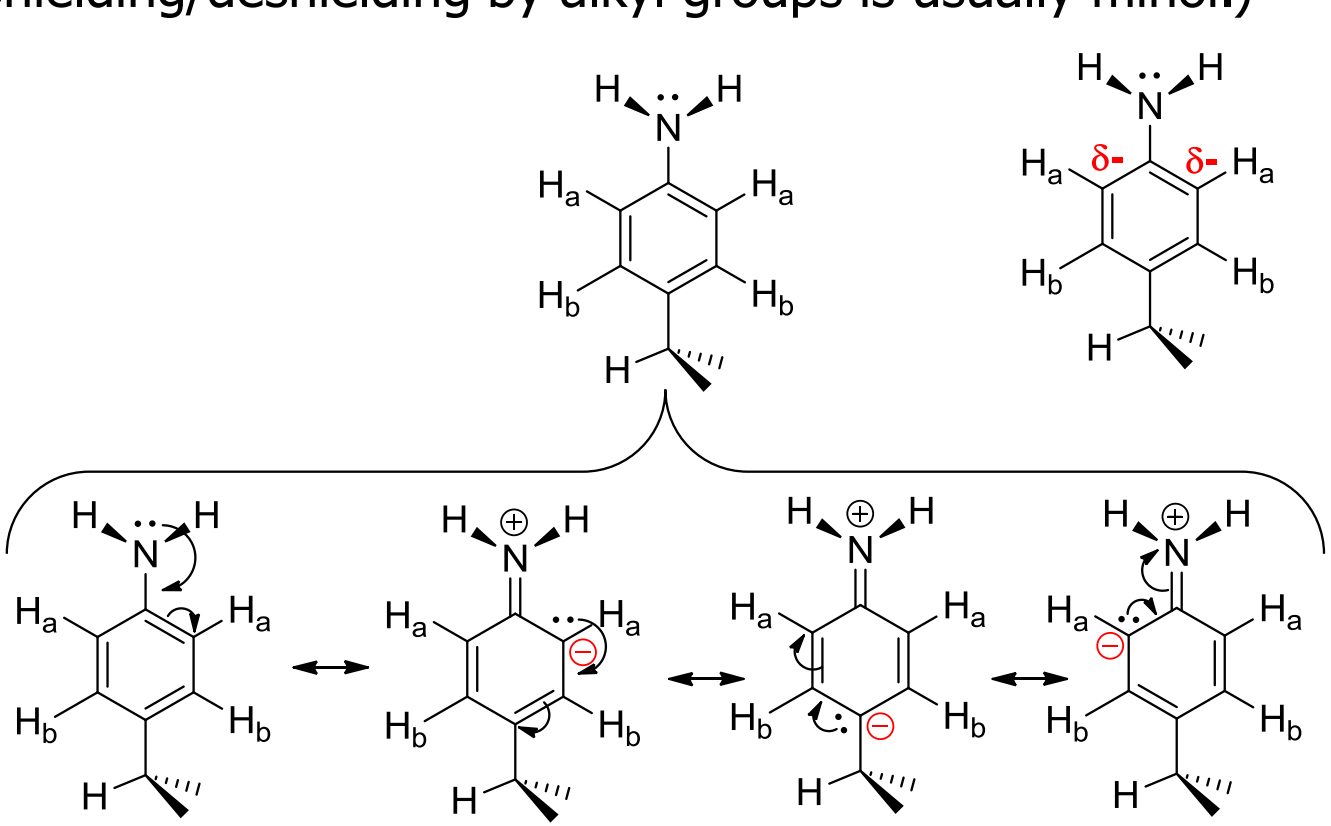
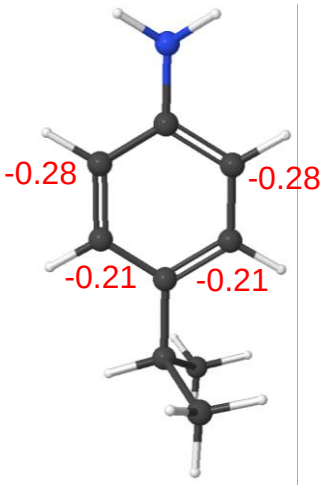


H_a shielded relative to H_b which can be rationalized by resonance effects.
(Shielding/deshielding by alkyl groups is usually minor.)



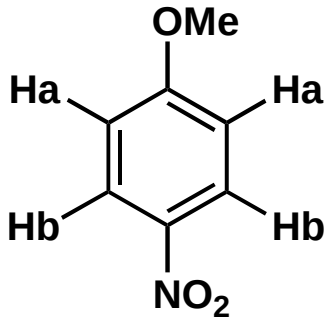


NBO charges
B3LYP/6-31G(d)

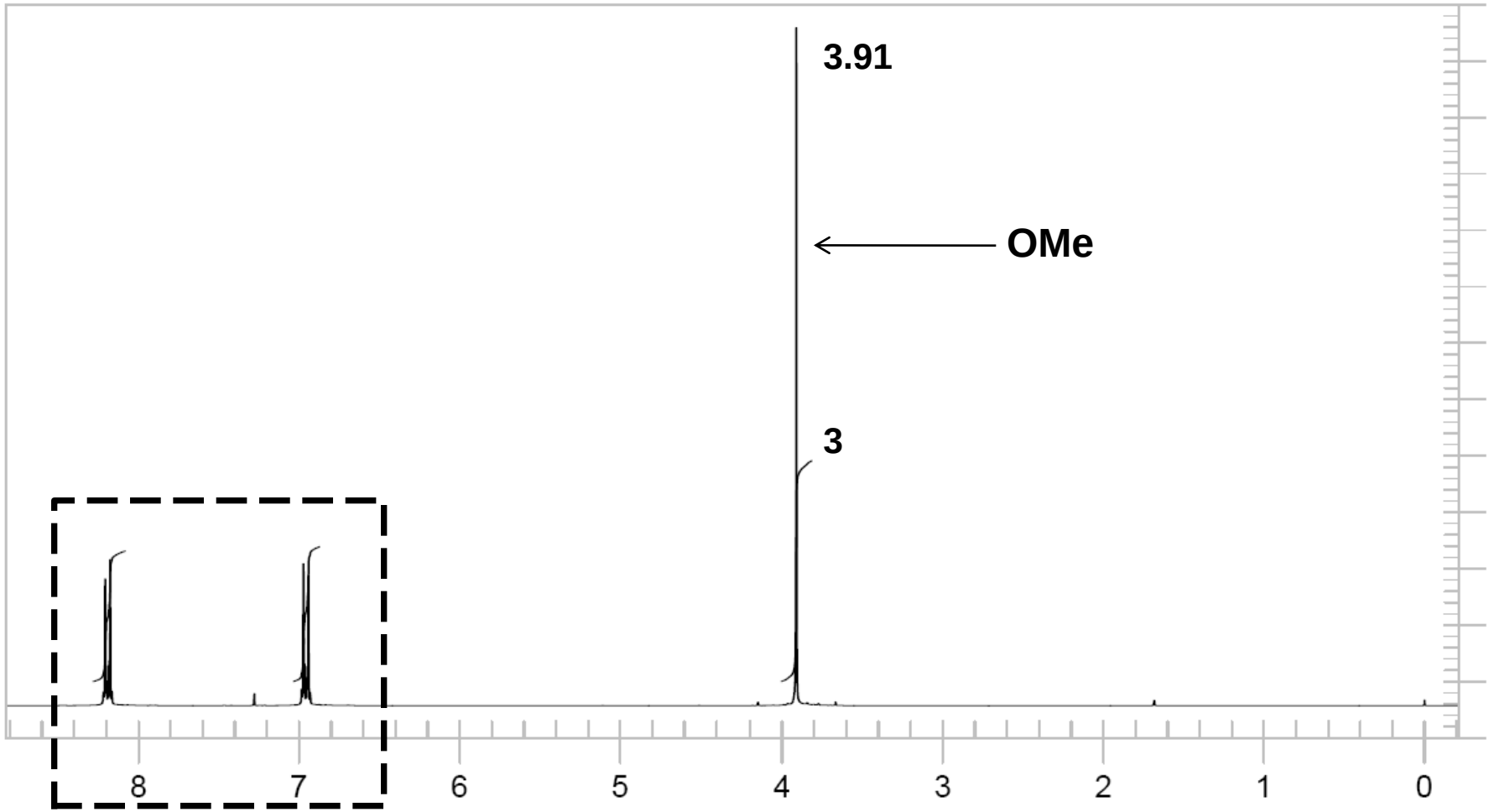
-NH_2, -NR_2, -OMe, -OH, etc. are common electron-donating groups.

Electron-donating groups increase e^- density at the *o* and *p* C-atoms.

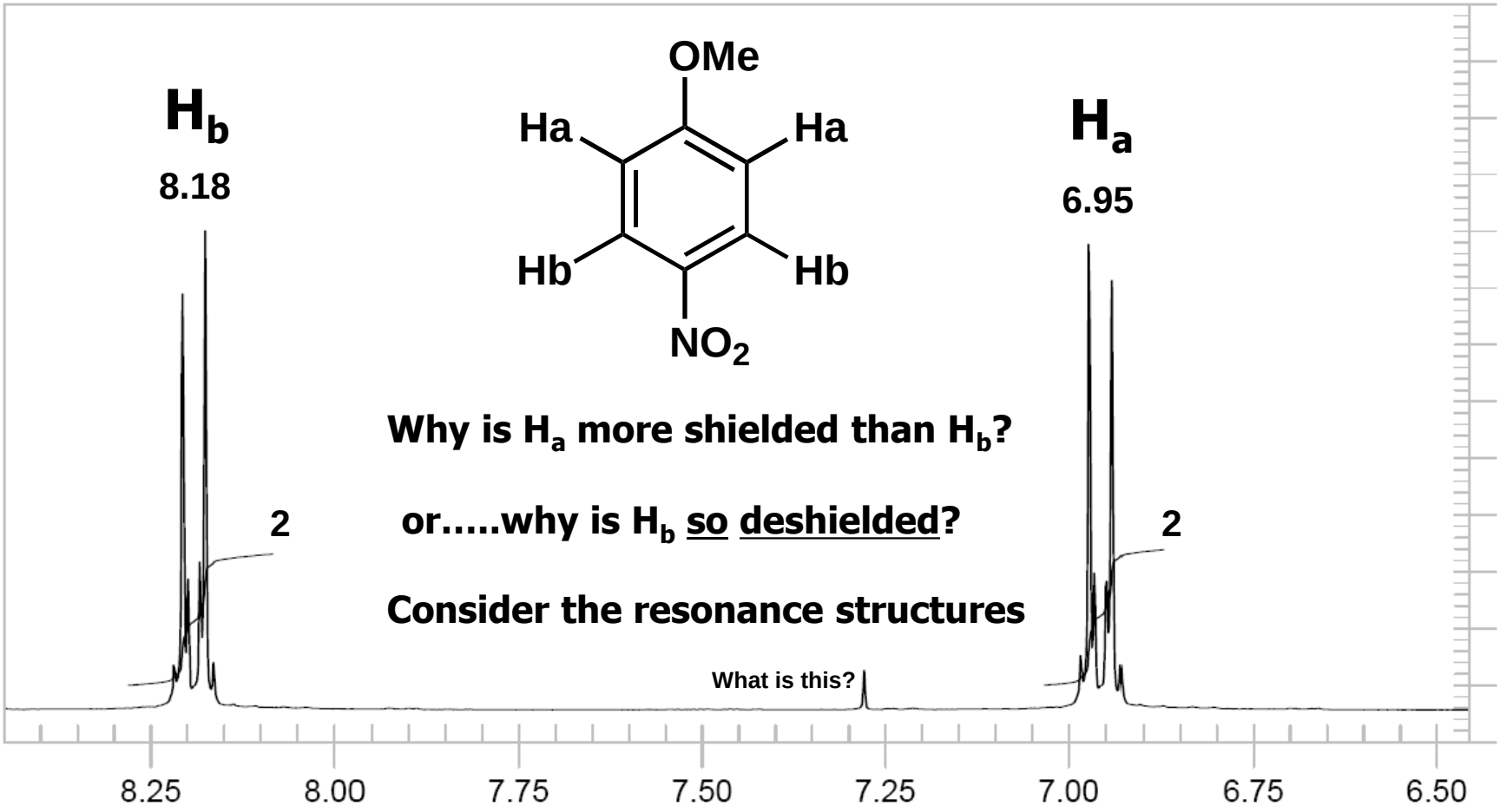
This shields the H-atoms at those positions relative to benzene H-atoms.



300 MHz ^{1}H NMR
In CDCl3



300 MHz ^{1}H NMR
In CDCl3



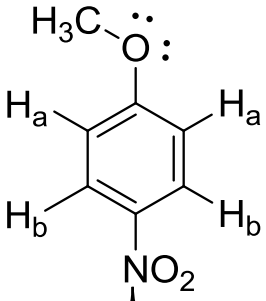
Why is H_a more shielded than H_b?

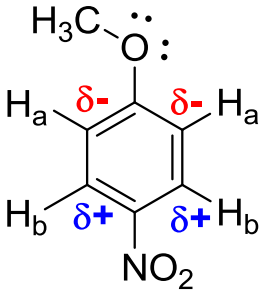
or…..why is H_b so deshielded?

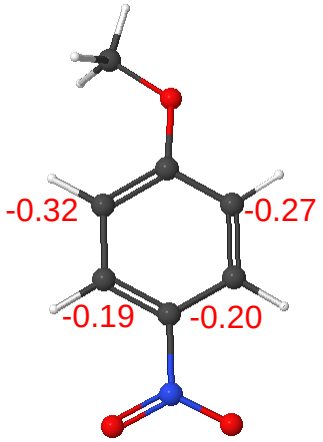
Consider the resonance structures

H_b deshielded relative to H_a which can be rationalized by resonance effects.

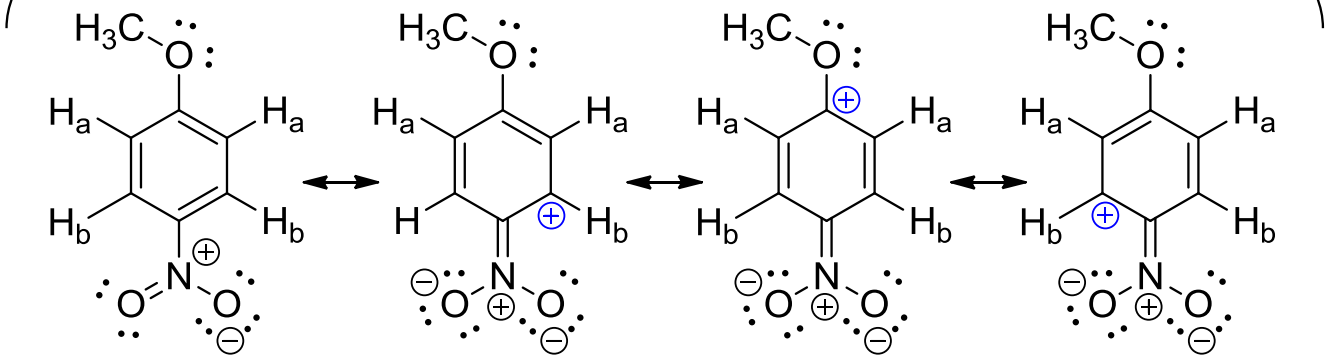
Recall, $-OCH_3$ is electron-donating which helps shield the H_a atoms.







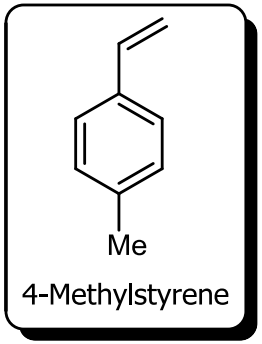
NBO charges
B3LYP/6-31G(d)



$-NO_2$, $-NR_3^+$, $-CF_3$, $-CO_2R$ etc. are common electron-withdrawing groups.

Electron-withdrawing groups reduce e^- density at the *o* and *p* C-atoms.

This deshields the H-atoms at those positions relative to benzene H-atoms.



300 MHz ^{1}H NMR

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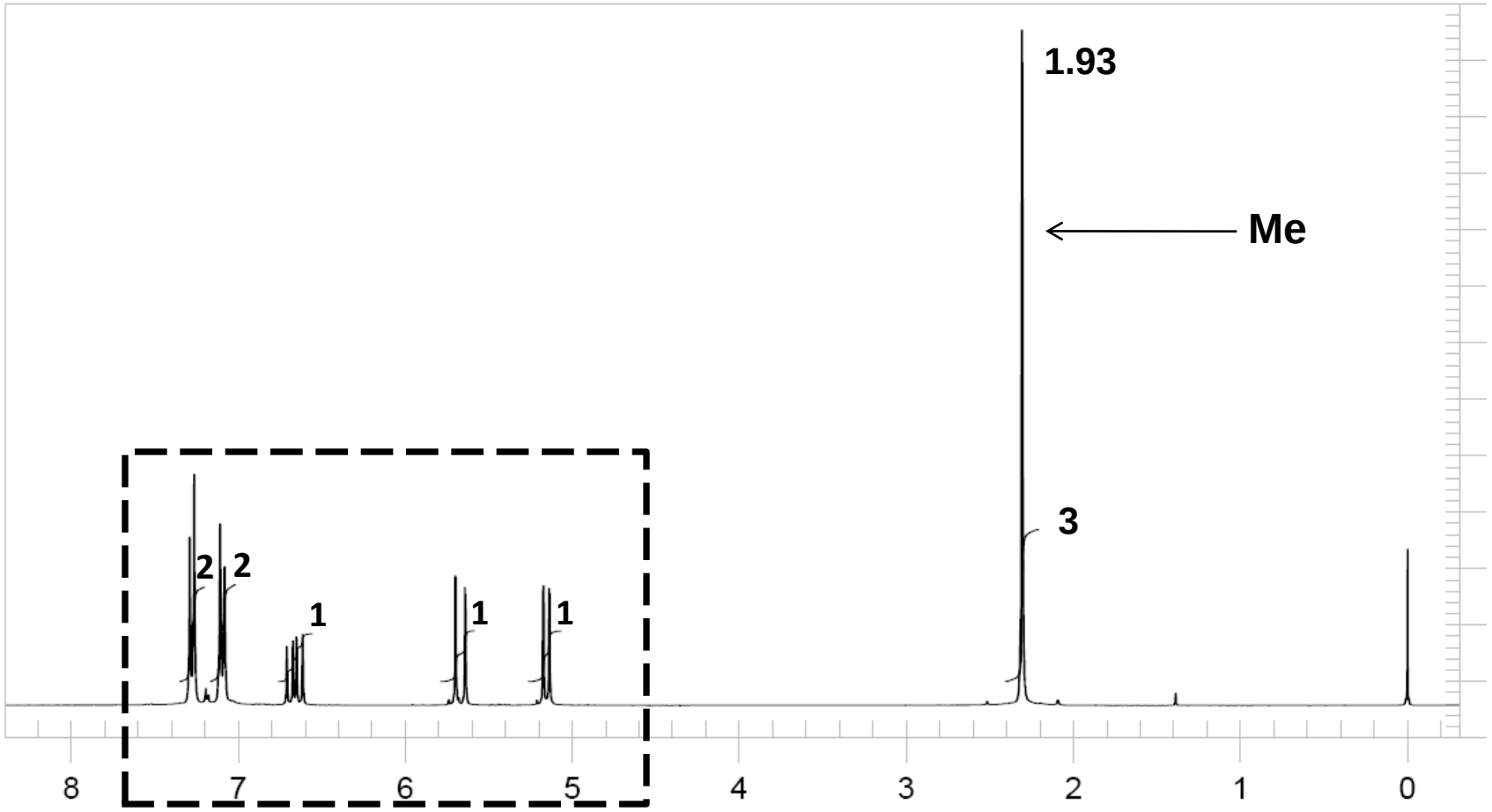
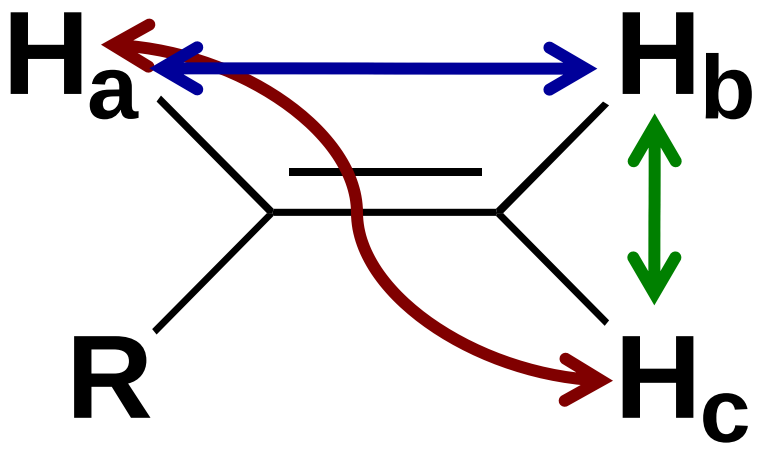


Coupling constants in alkene systems

$J_{ab} = J_{cis} = 6 – 12$ Hz



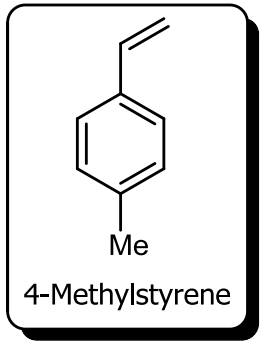
$J_{bc} = J_{gem} = 1 – 3$ Hz

$J_{ac} = J_{trans} = 12 – 18$ Hz

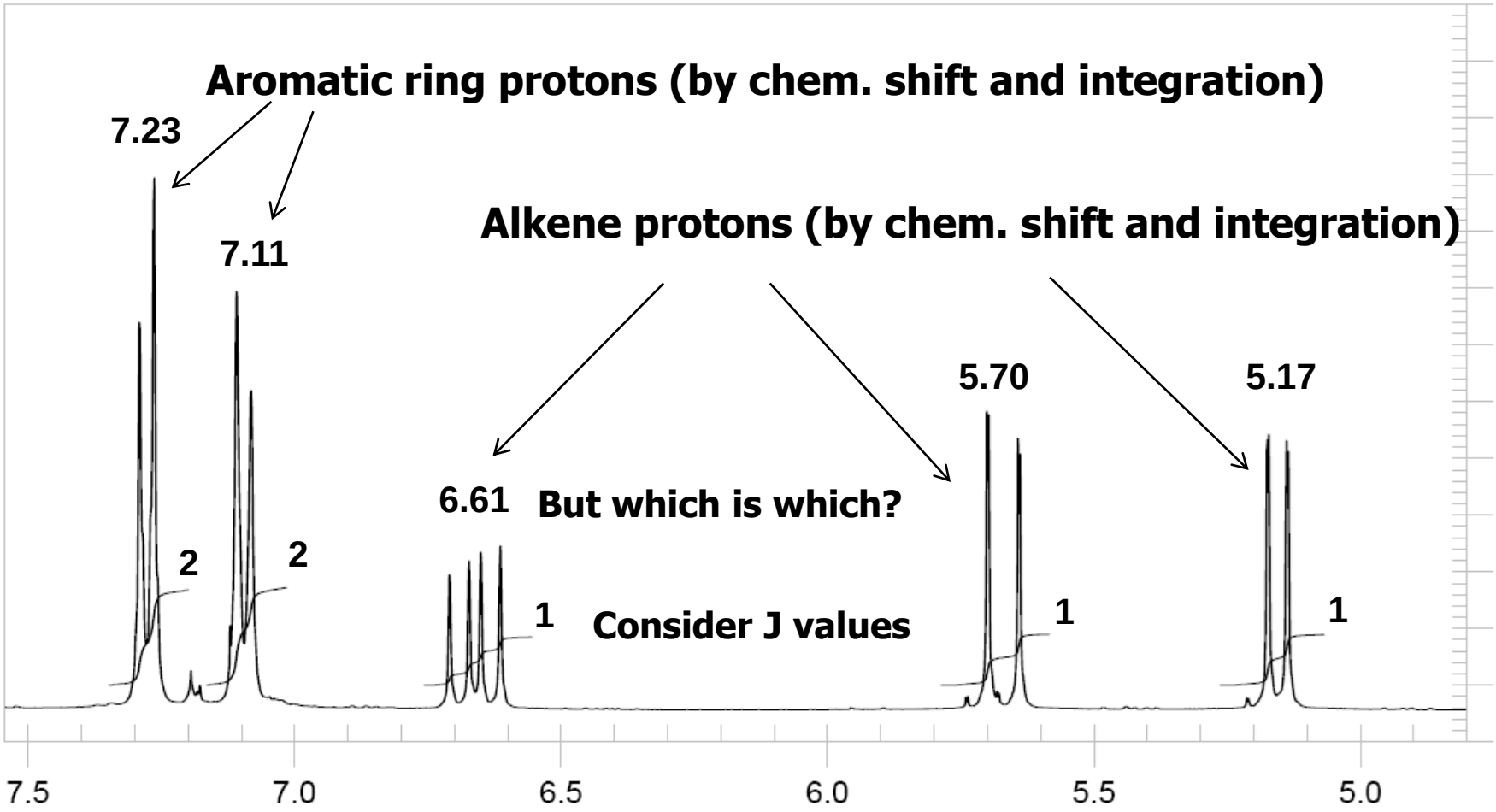
$$J_{trans} > J_{cis} > J_{gem}$$

H_a is trans to H_c

H_a is cis to H_b



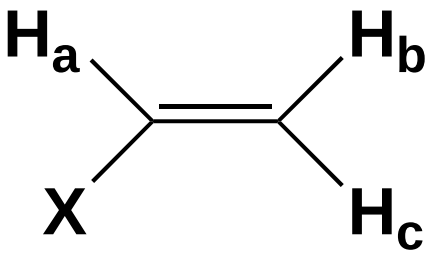
300 MHz ^{1}H NMR
In CDCl3



Derivation of splitting diagrams

3) Splitting in alkene systems ($J_{ac} > J_{ab}$)

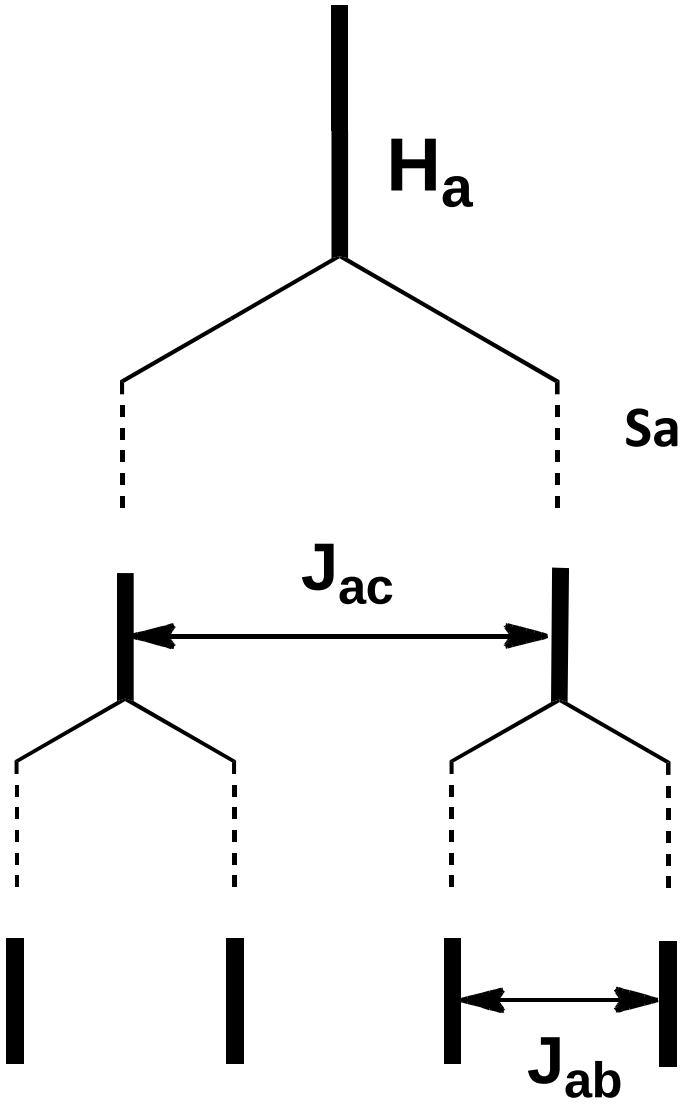
apply strongest coupling first!



$J_{ac} = J_{trans}$

$J_{ab} = J_{cis}$

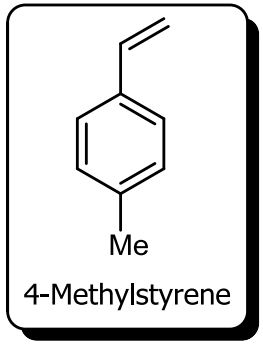
$J_{trans} > J_{cis}$



Same concept as example 1)

Doublet of doublets

Hb-Hc geminal coupling not shown



300 MHz ^{1}H NMR
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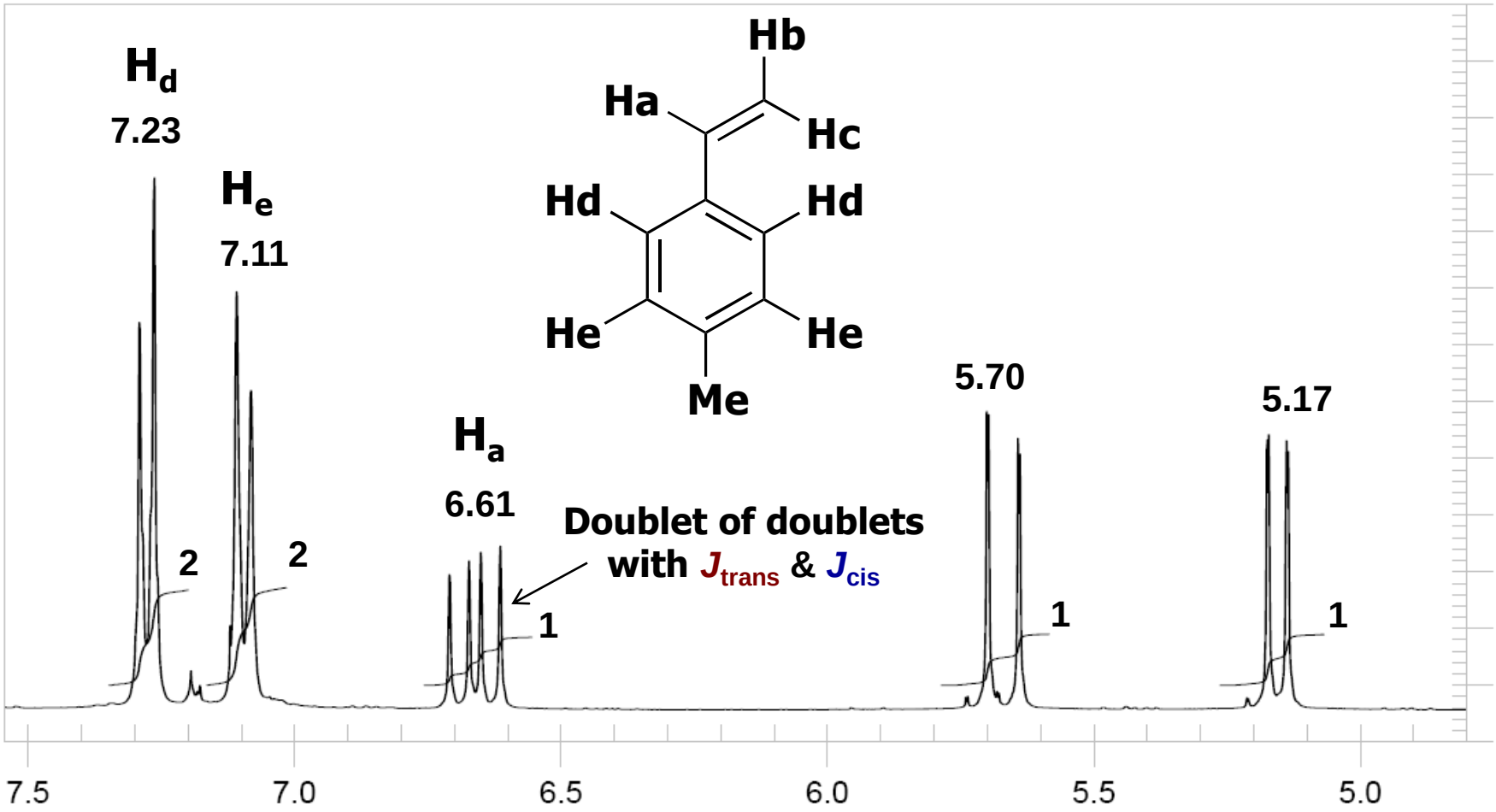

300 MHz ^{1}H NMR

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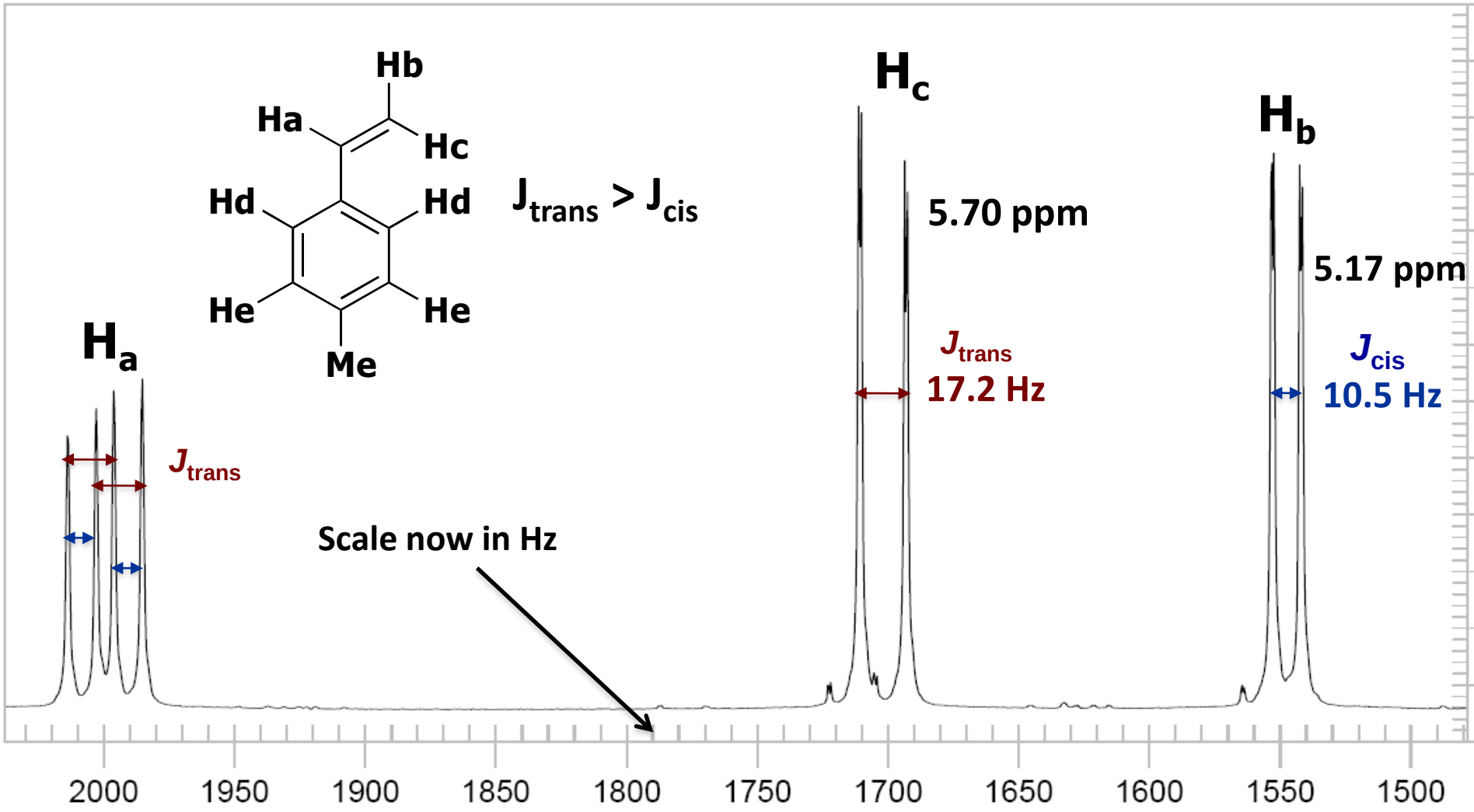
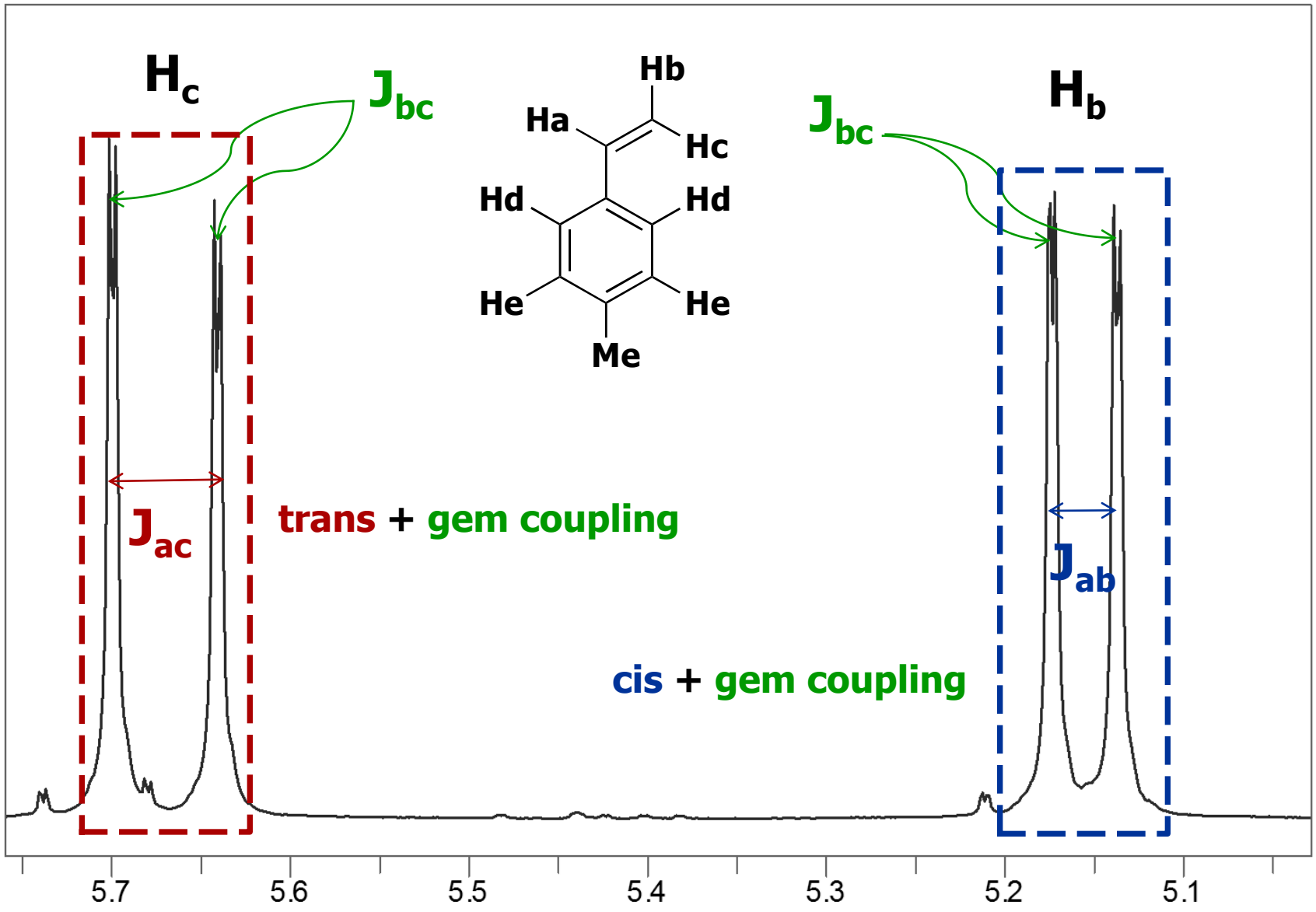
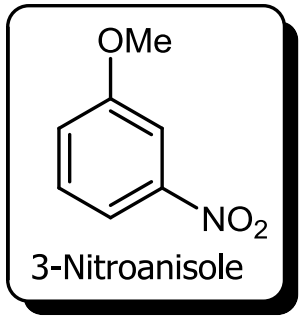
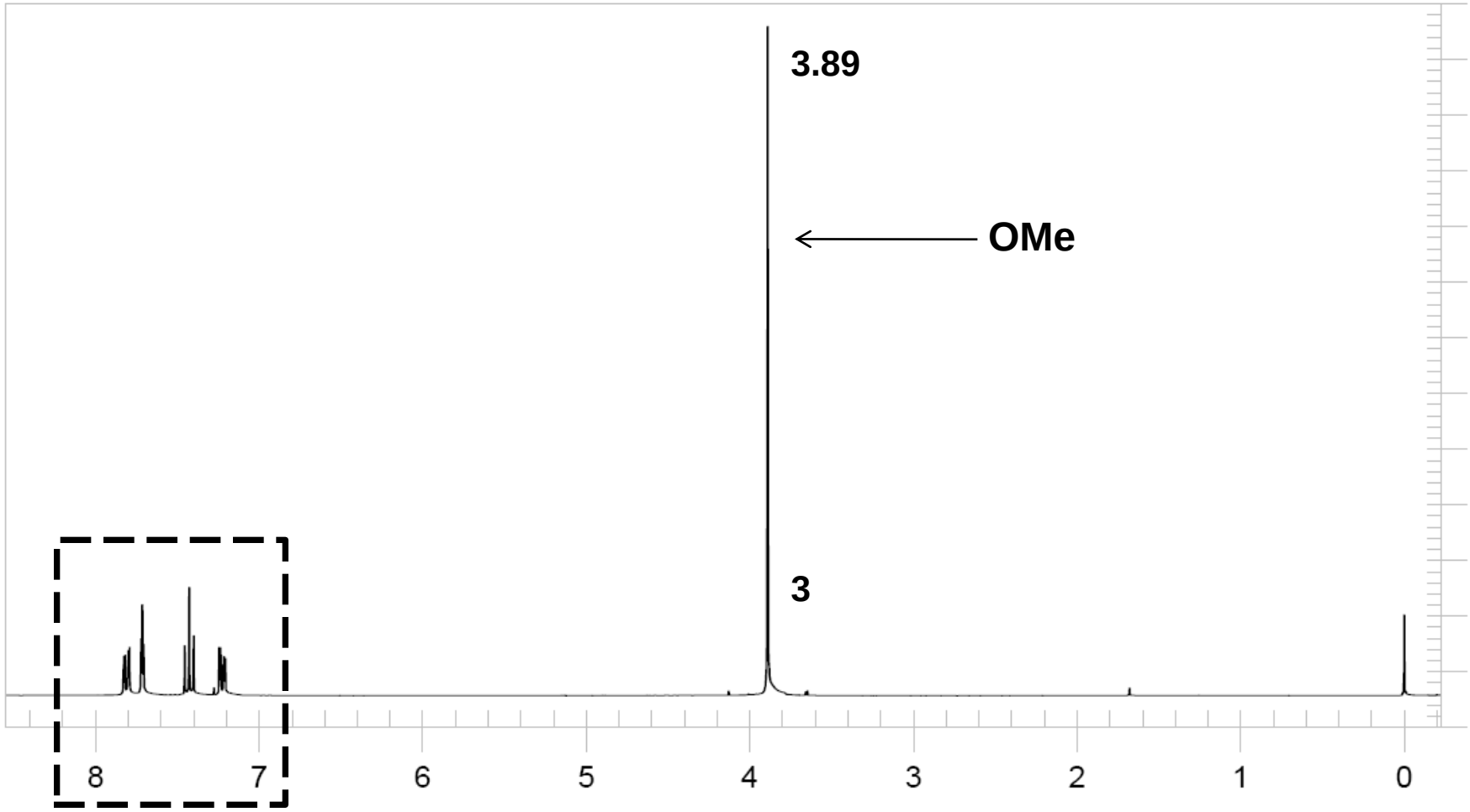


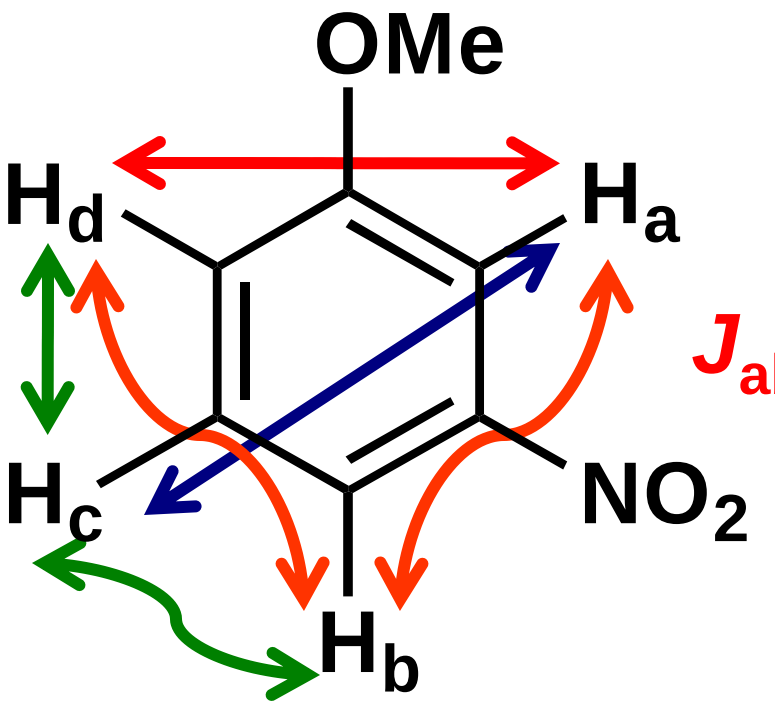




300 MHz ^{1}H NMR
In CDCl3



Coupling constants in aromatic systems



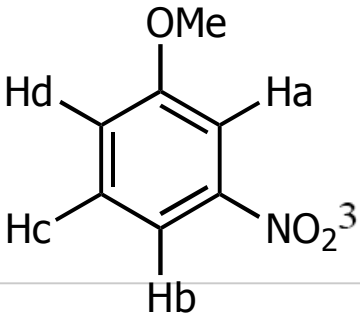
$J_{ab} \approx J_{ad} \approx J_{bd} = J_{meta}$ = 1-3 Hz

$J_{ac} = J_{para}$ = 0 - 1 Hz

$J_{ortho} > J_{meta} > J_{para}$

$J_{bc} \approx J_{cd} = J_{ortho}$ = 6 – 12 Hz

Write down the relationships between the protons!



300 MHz ^{1}H NMR
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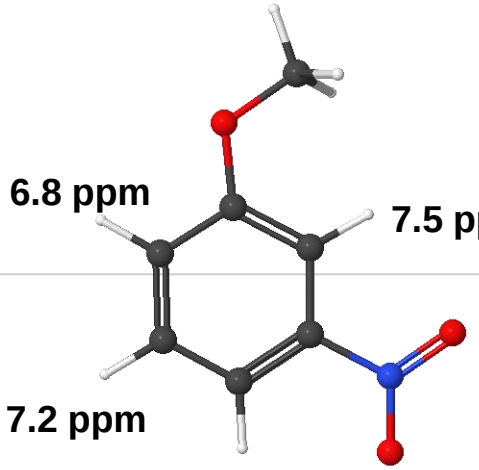
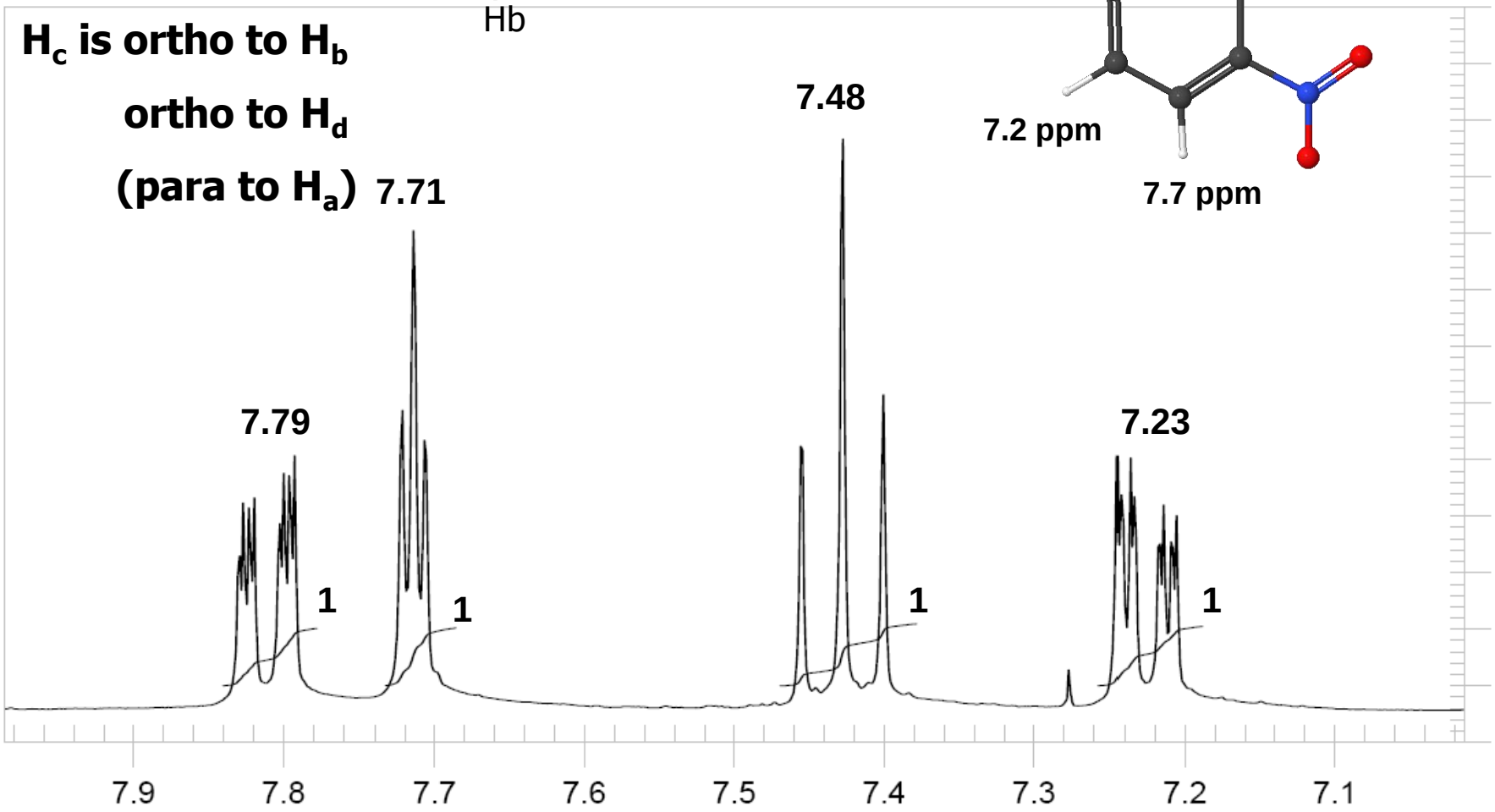


H_c is ortho to H_b

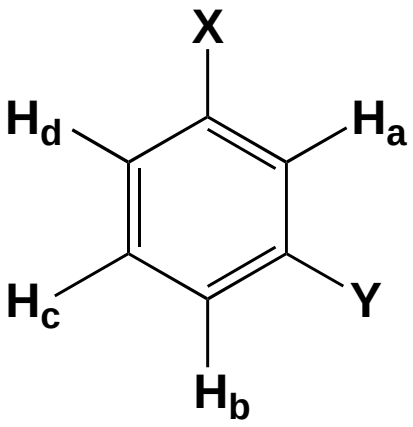
ortho to H_d

(para to H_a)



Derivation of splitting diagrams

4) Splitting in aromatic systems ($J_{cb} = J_{cd}$)



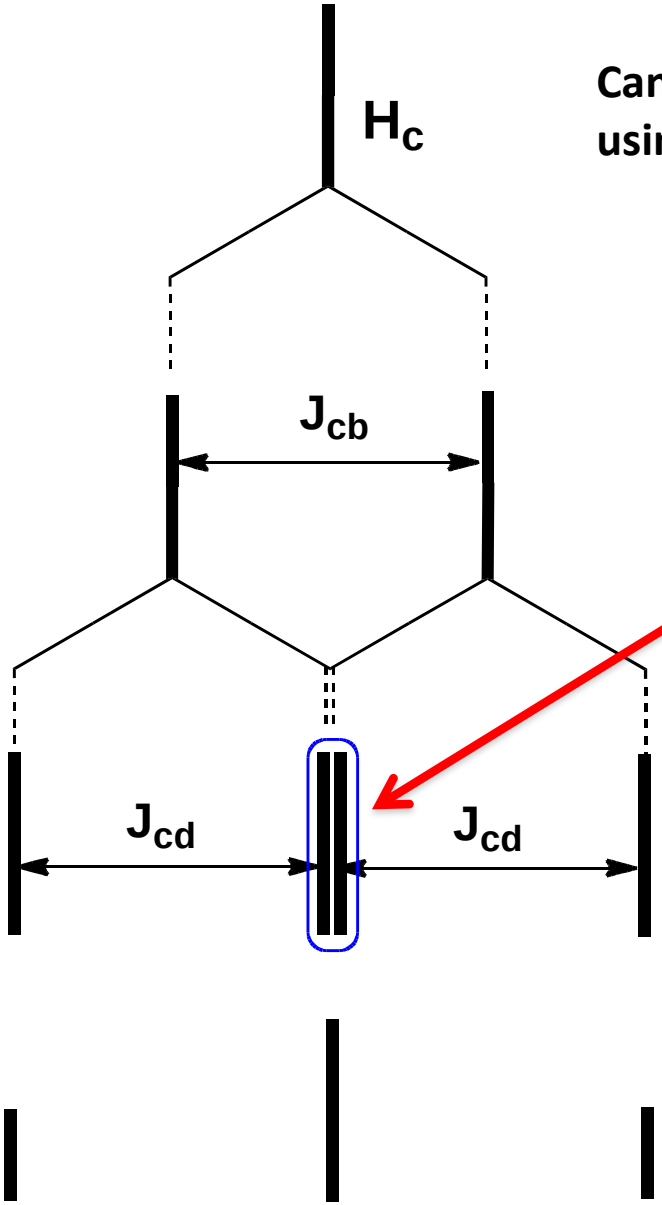
$J_{cb} = J_{ortho}$

$J_{cd} = J_{ortho}$

H_c is ortho to H_b

ortho to H_d

(para to H_a)



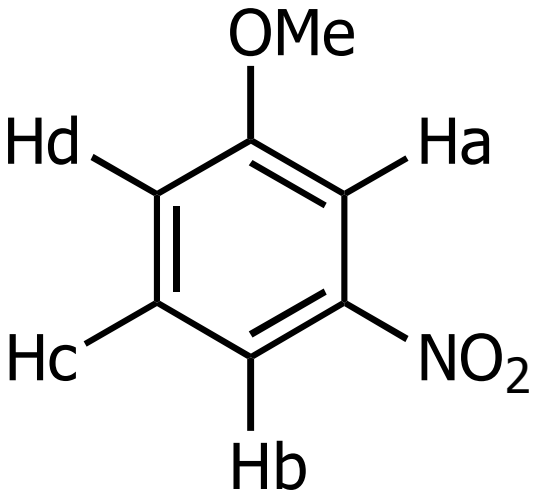
Can also apply to H_a, just draw diagram using meta coupling constants

Overlap of peaks in each signal due to similarity of coupling constants J_{cb} and J_{cd}

Same concept as example 2)

Doublet of doublets but…….. central peaks overlap to give <u>appearance</u> of 1:2:1 triplet *<u>(ITS NOT A REAL TRIPLET!!!)</u>*

Ha-Hc *para* coupling not shown



As practice, draw the splitting diagrams for H_b and H_d

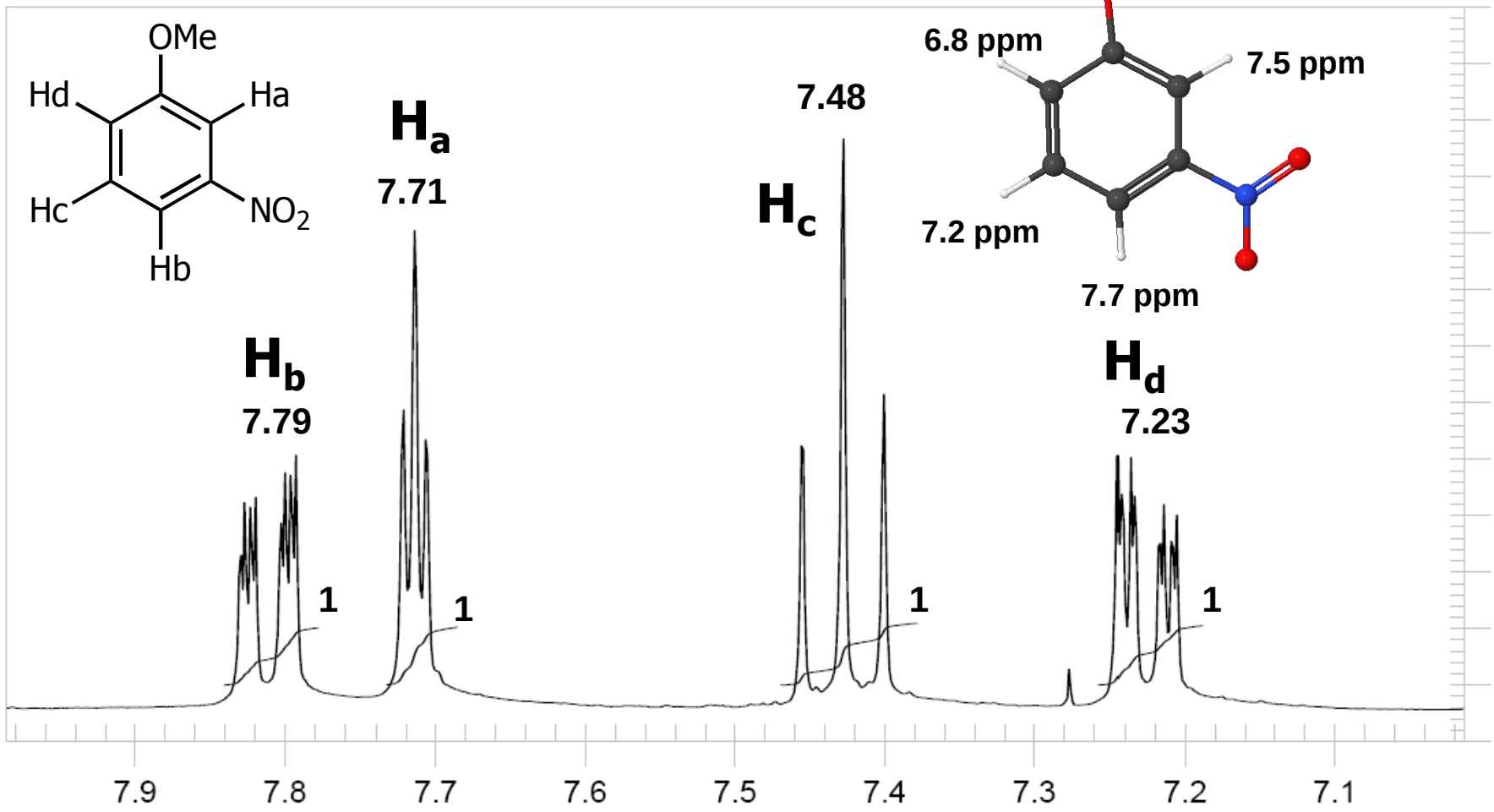
- list relationships of each proton

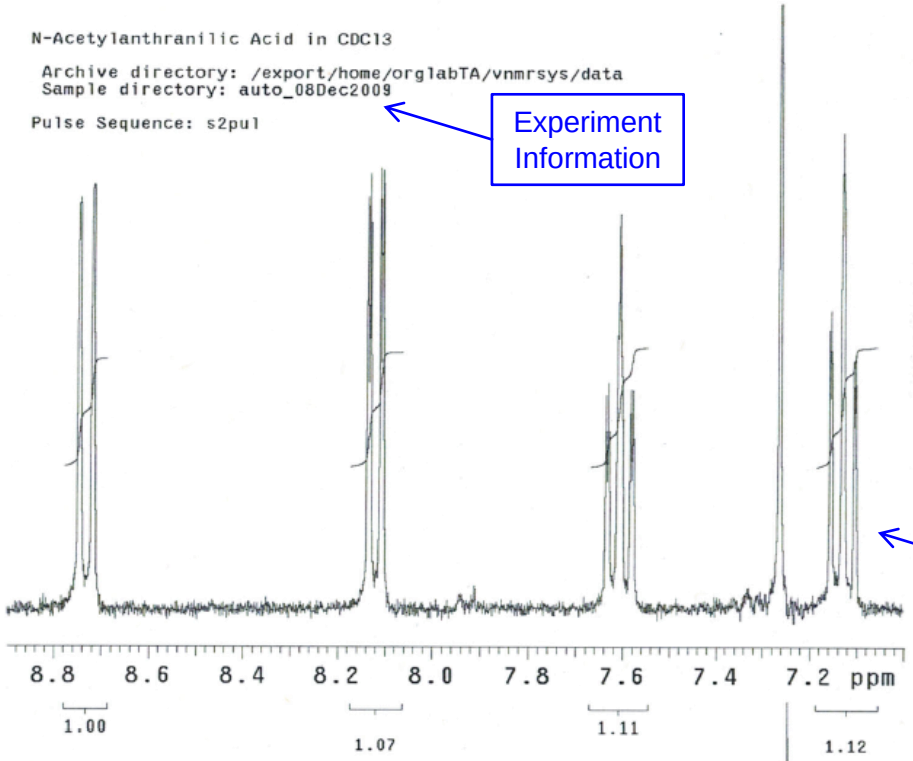
- apply n+1 rule to these relationships

- factor in the coupling constants

H_b is most deshielded (proximity to NO_2 group)

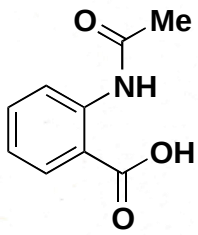
H_d is most shielded (proximity to OMe group)



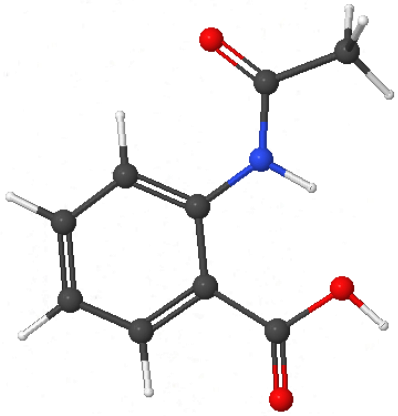


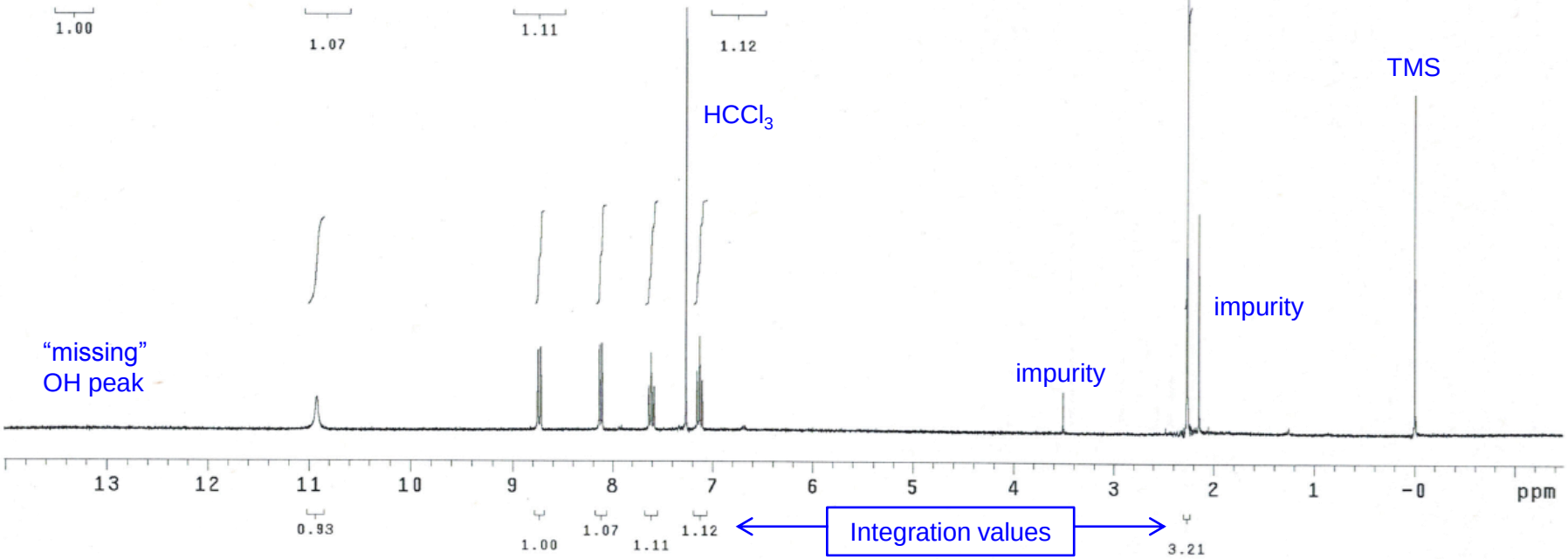
Experiment Information

Inset Spectrum 7.0 - 8.9 ppm



***N*-Acetylanthranillic acid**





Integration values

Strategy and Tactics for solving NMR spectra

How many different types of H-atoms?
Indicated by how many groups of signals

What types of H-atoms?
Indicated by the chemical shift of each signal

How many H-atoms of each type are there?
Indicated by the integration of the signal for each group

What is the connectivity of the molecule?
Indicated by the splitting pattern and coupling constant of each signal

What other evidence do you have?
Use GC-MS, ^{13}C-NMR, IR, melting point etc. as complimentary information

Practice and Ask Questions!