

Name:

**UNIVERSITY OF TORONTO
Faculty of Arts and Science**

**APRIL/MAY 2005 EXAMINATIONS
CHEMISTRY 249H**

DURATION = 3 HOURS

PRINT YOUR NAME AND STUDENT NUMBER
CLEARLY ON THE FIRST PAGE OF THE EXAM BOOKLET

NAME:

STUDENT NUMBER:

An abbreviation list, proton NMR and carbon NMR spectroscopic correlation tables are provided on pages 13, 14 and 15 respectively.

Allowed Aids: **Molecular Models**

Calculators and other electronic devices are not permitted in this examination

Credit will be given for partial answers

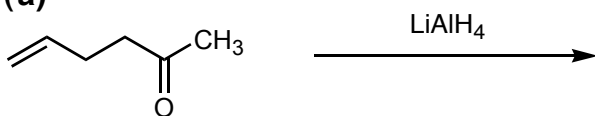
WAIT UNTIL YOU ARE TOLD TO BEGIN

Question 1	60	
Question 2	40	
Question 3	30	
Question 4	30	
Question 5	60	
Question 6	40	
Total	260	

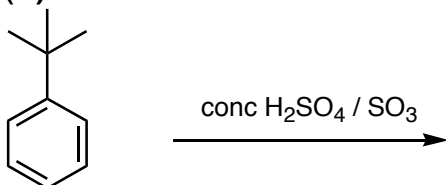
Name:

1. (60 marks) Draw the **final product** of the following reactions. You may assume standard aqueous work-up are used as required.

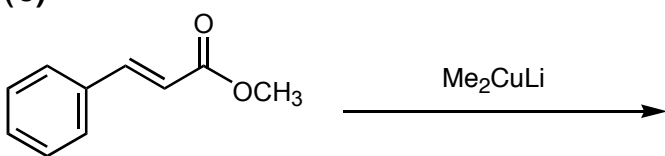
(a)



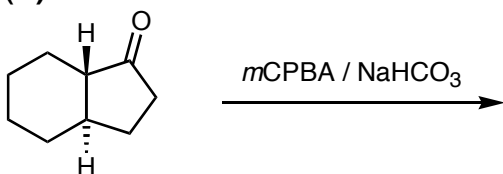
(b)



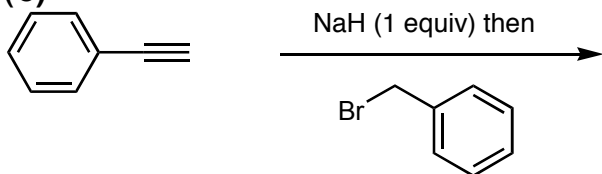
(c)



(d)

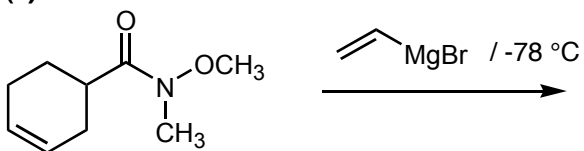


(e)

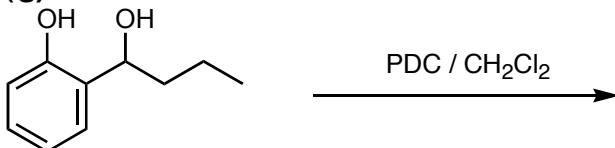


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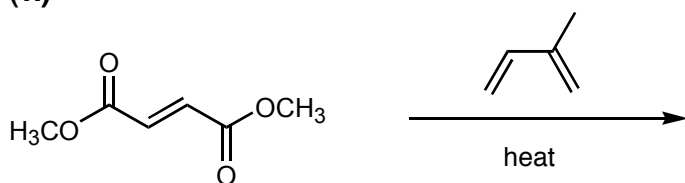
(f)



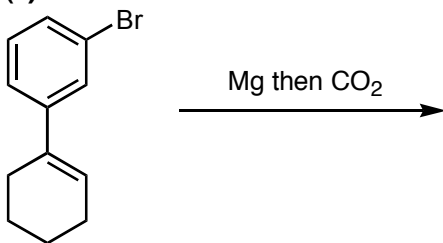
(g)



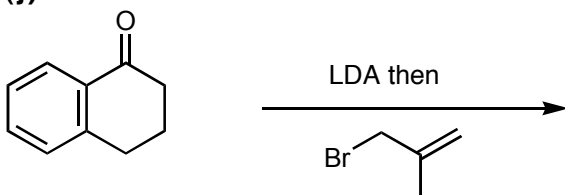
(h)



(i)

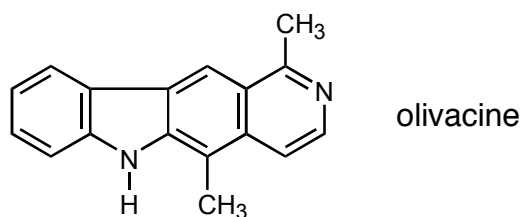


(j)

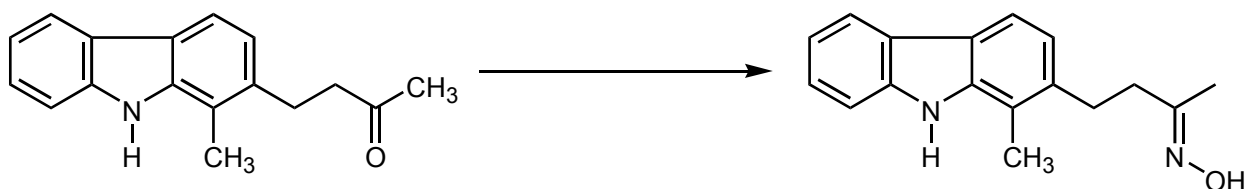
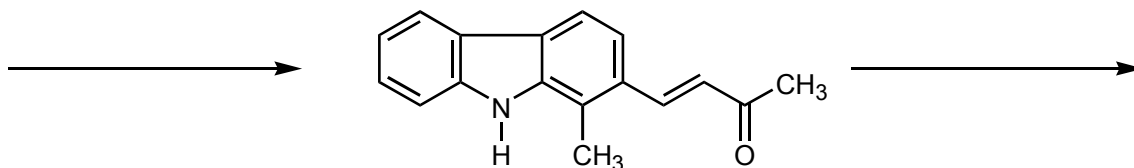
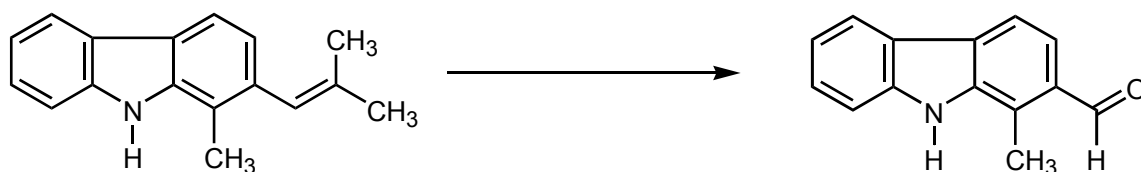


Name:

2. (40 marks) The alkaloid olivacine and related compounds show high cytotoxicity toward a variety of human cancer cells, in part due to their topoisomerase II activity. Answer the following questions about the synthesis of olivacine and its properties.

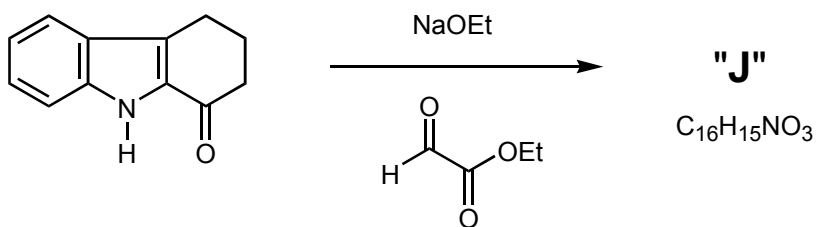


(a) Suggest reagents to complete the following four steps used in Wenkert's synthetic sequence to olivacine. You do not need to specify the aqueous "work-up" steps in your answers.



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(b) The first step of Wenkert's synthesis used the following condensation reaction.

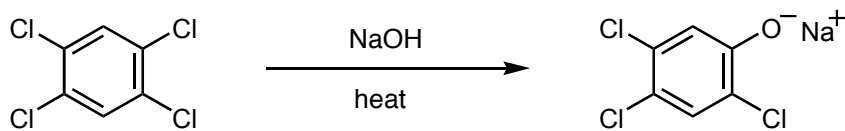


Draw the structure of product "J" and give the name of this reaction.

(c) Under mildly acidic conditions olivacine exists in a protonated form. Which one of the two nitrogen atoms in olivacine is protonated? Give a brief explanation for your answer.

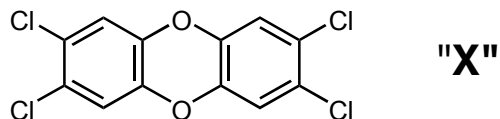
Name:

3. (30 marks) One of the reactions used in the synthesis of the herbicidal agent '2,4,5-T' is shown below.



(a) Write a full mechanism for this reaction indicating electron flow with "curly arrows" and including all intermediates.

(b) One of the side-products of the reaction shown above is the molecule "X" shown below. What is the "trivial" name of this molecule and what characteristics made it "newsworthy" in 2004?

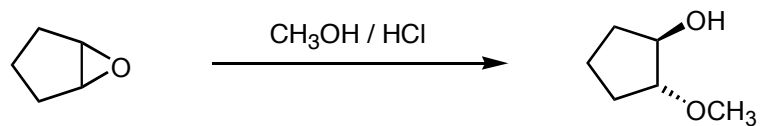


(c) How many peaks would you expect to see in the ^{13}C NMR of "X"?

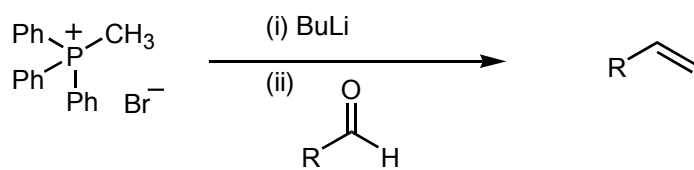
Name:

4. (30 marks) Propose mechanisms for the following transformations, indicating electron flow with "curly arrows" and including all intermediates.

(a)



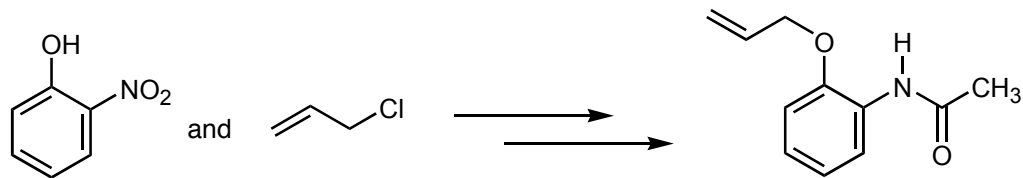
(b)



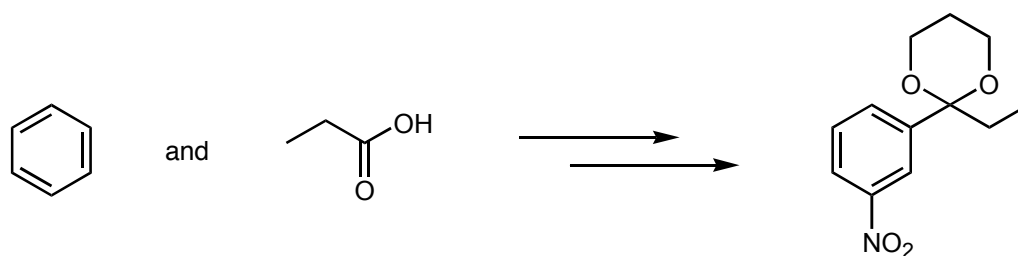
Name:

5. (60 marks) Propose efficient syntheses of the following compounds from the starting materials indicated, and any other chemical reagents / precursors that are necessary. In each case more than one step is required. Indicate the products after each step of your proposed syntheses.

(a)

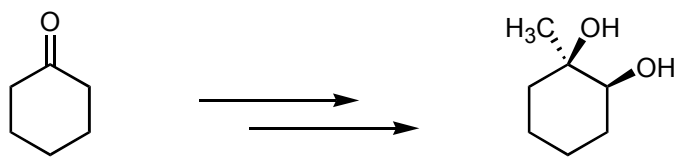


(b)

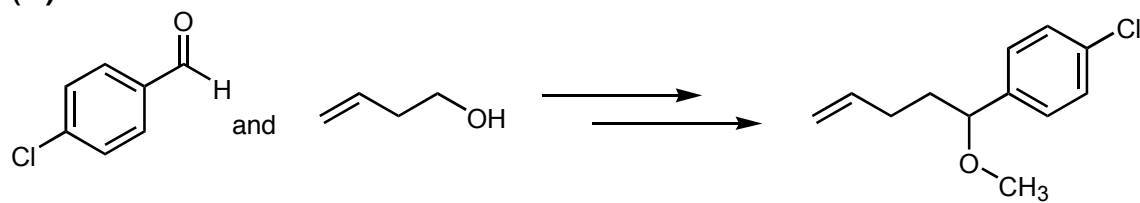


Name:

(c)



(d)



Name:

6. (40 marks) Deduce the structure of the compounds **A** and **B**, using the spectral data provided on the following pages.

(a) **COMPOUND A:**

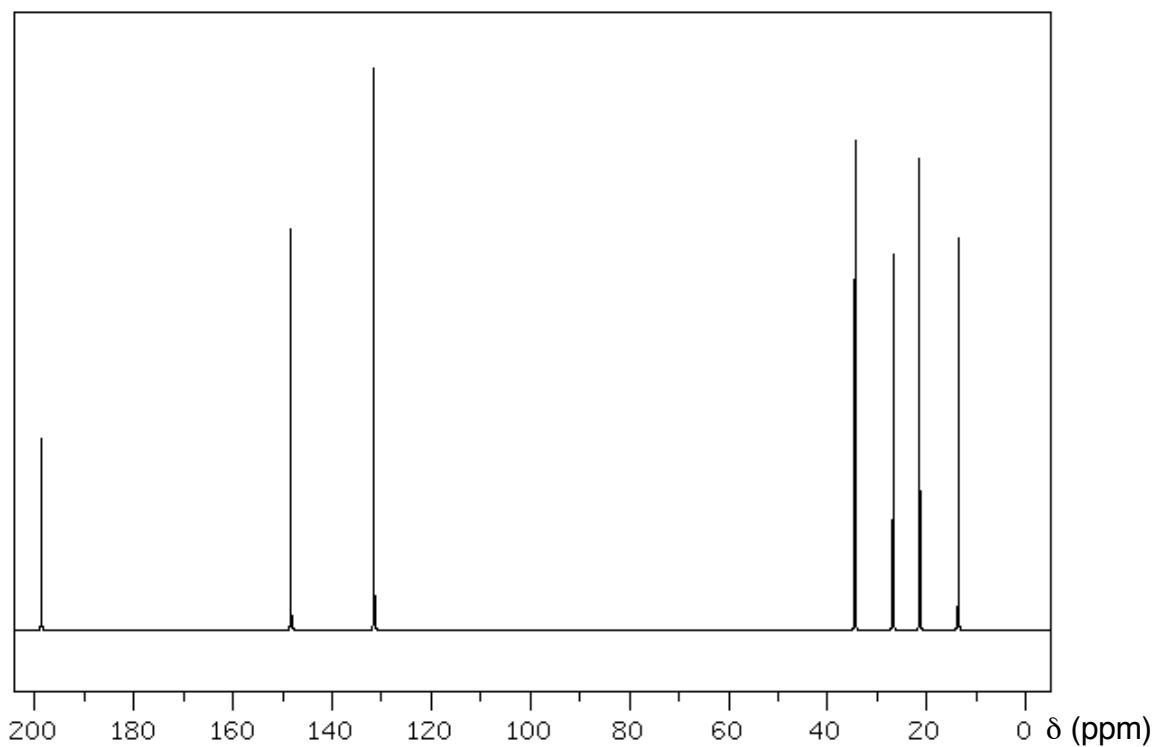
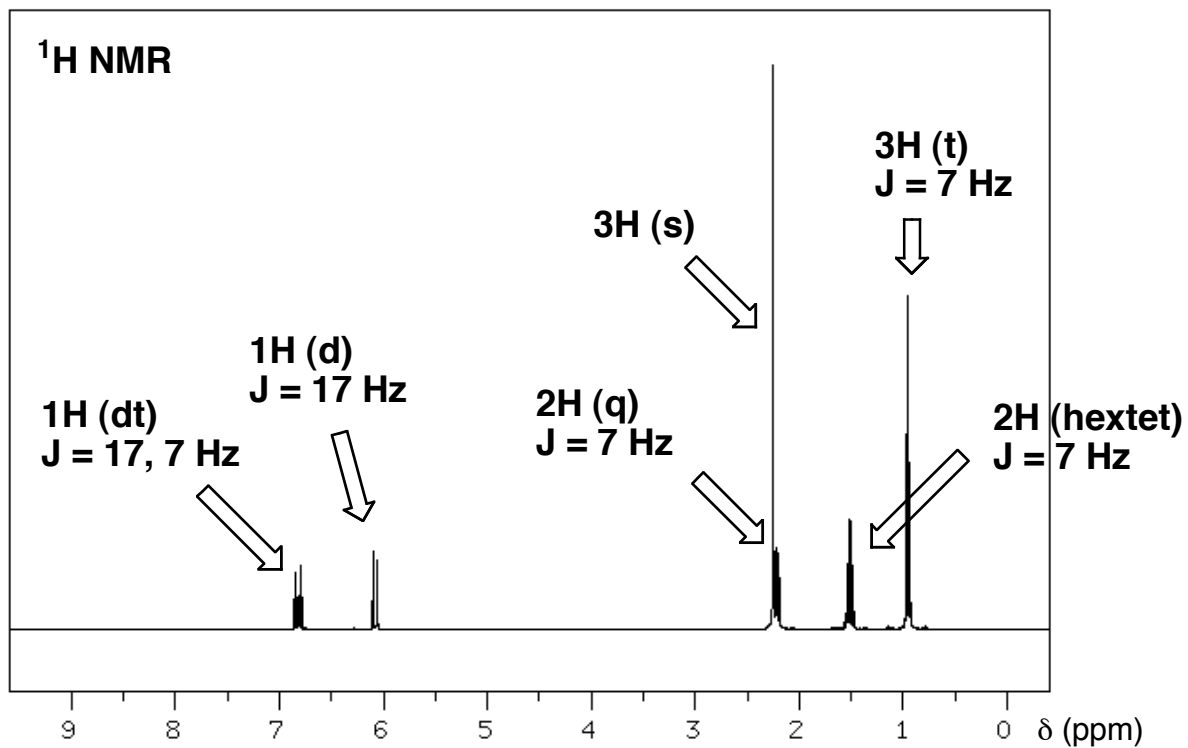
(b) **COMPOUND B:**

Name:

COMPOUND A:

Molecular Formula: $C_7H_{12}O$

IR Spectra ($\nu\text{ cm}^{-1}$): strong peak at 1674

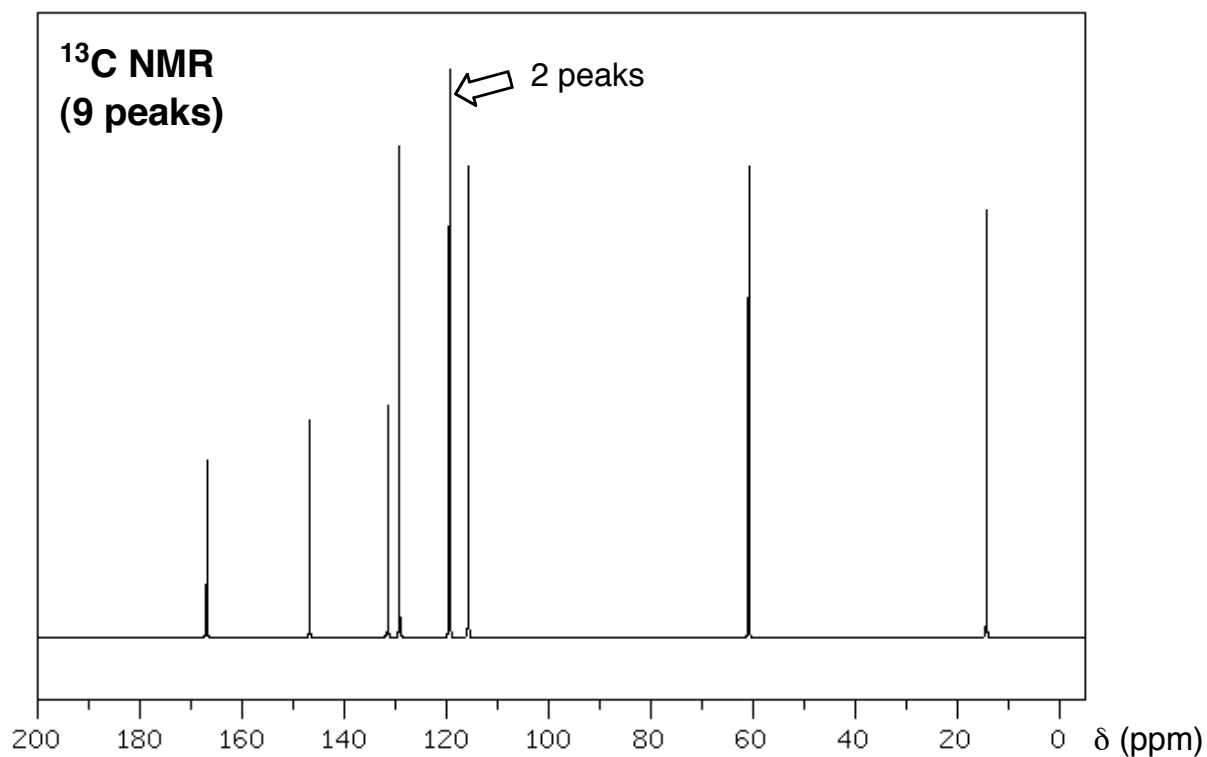
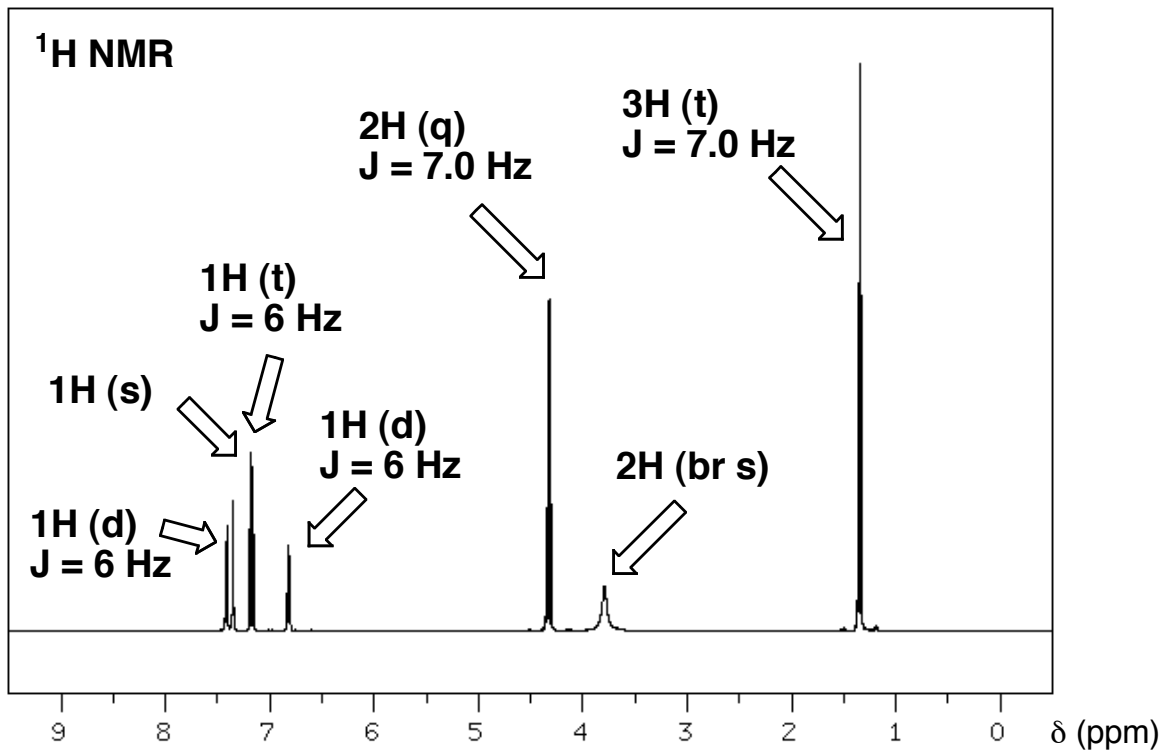


Name:

COMPOUND B:

Molecular Formula: $C_9H_{11}NO_2$

IR Spectra ($\nu\text{ cm}^{-1}$): strong peaks at 3374, 1708



Name:

Abbreviations:

Bu = Butyl ($-C_4H_9$)

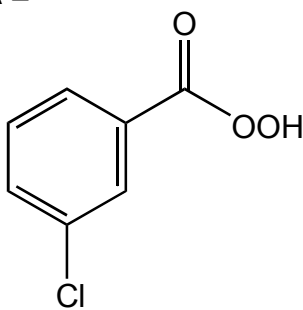
equiv = equivalents

Et = Ethyl ($-C_2H_5$)

IR (ν) = Infra red signal (cm^{-1})

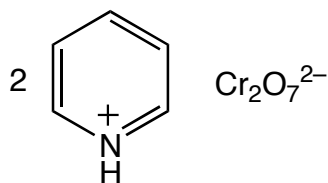
LDA = lithium diisopropylamide ($Li^+ \ ^-N(CH(CH_3)_2)$)

*m*CPBA =



Me = methyl ($-CH_3$)

PDC = pyridinium dichromate

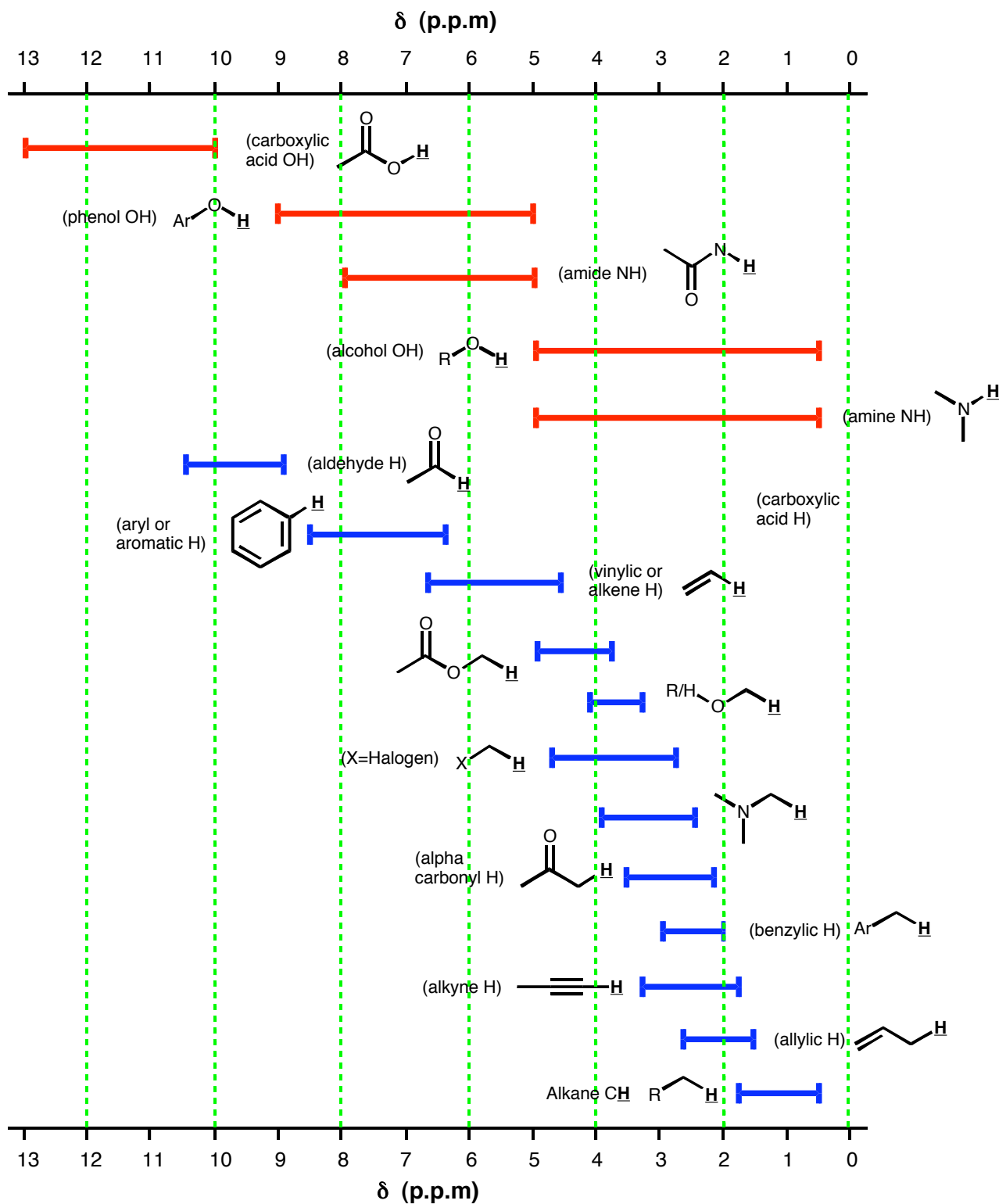


Ph = phenyl ($-C_6H_5$)

R = Alkyl

Name:

Proton Chemical Shifts

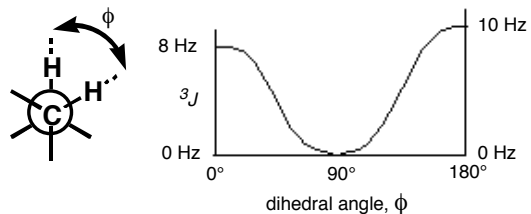
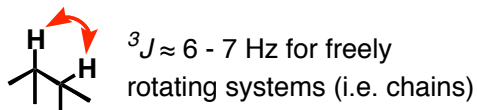


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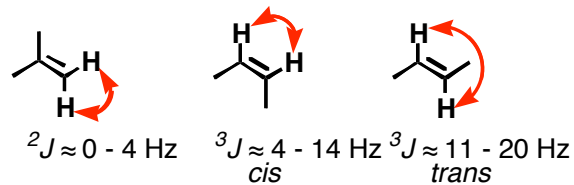
Abbreviations for proton multiplicities: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Higher multiplicities are given in full i.e. pentet, hextet, heptet, etc.

Coupling Constants (J values)

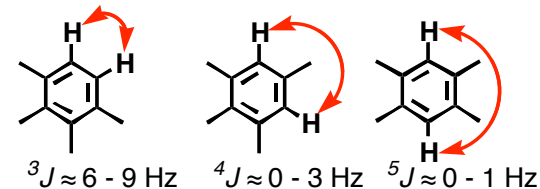
Aliphatic Protons:



Alkene Protons:



Aromatic Protons:



^{13}C Chemical Shifts

