

Name:

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

**APRIL/MAY 2007 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 14, 15 and 16 respectively.

Allowed Aids: **Molecular Models**

Calculators and other electronic devices are not permitted in this examination

Credit will be given for partial answers

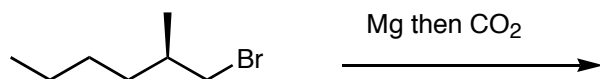
WAIT UNTIL YOU ARE TOLD TO BEGIN

Question 1	75	
Question 2	45	
Question 3	80	
Question 4	25	
Question 5	80	
Question 6	45	
Total	350	

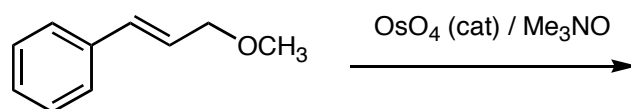
Name:

1. (75 marks) Draw the **final product** of the following reactions. In those cases where more than one-step is indicated, if you do not know the final product, partial credit will be given for intermediates. You may assume standard aqueous work-up steps are used as required.

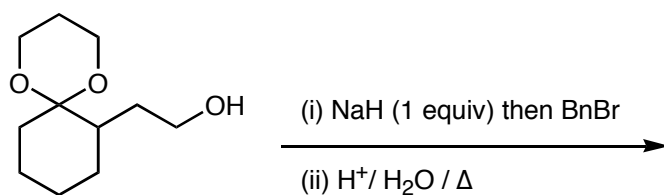
(a)



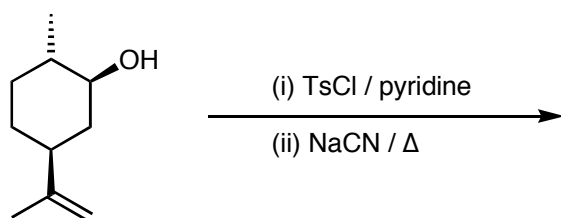
(b)



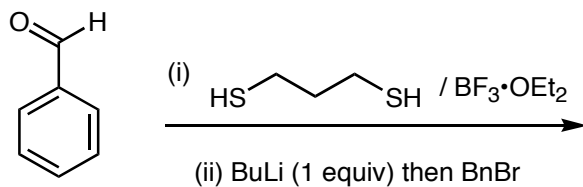
(c)



(d)

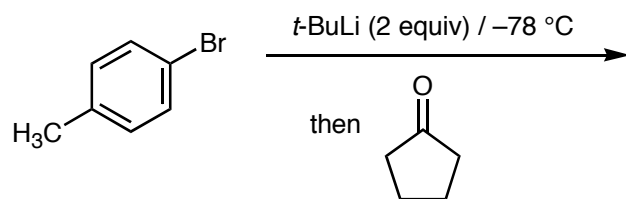


(e)

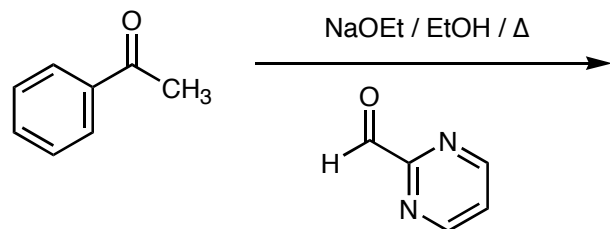


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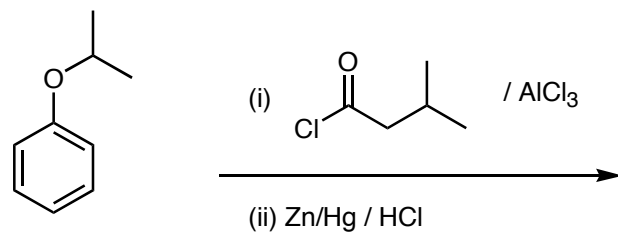
(f)



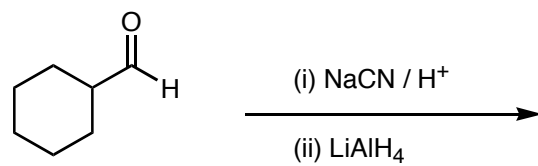
(g)



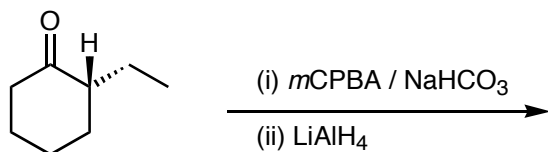
(h)



(i)

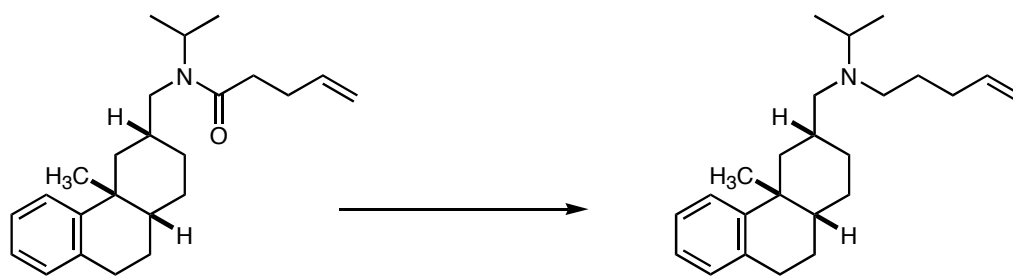
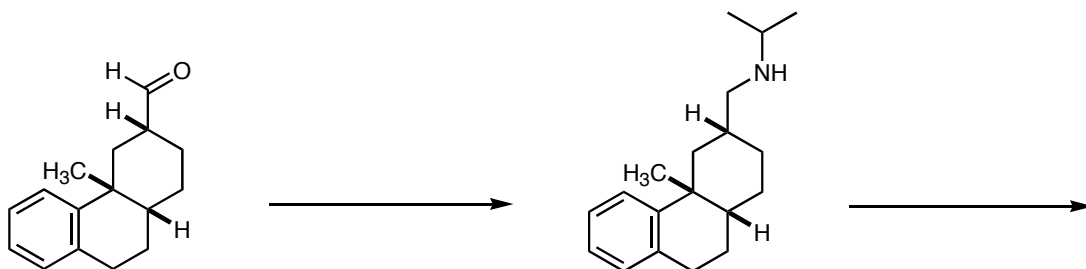
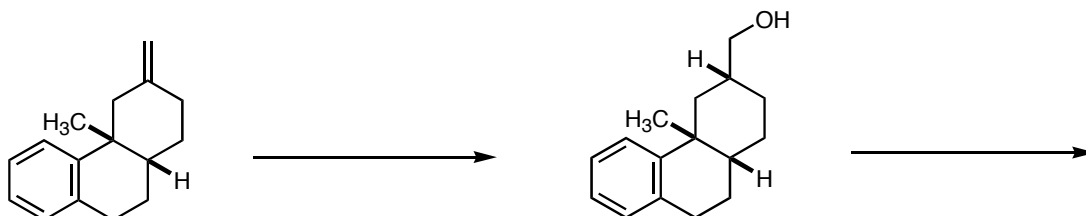
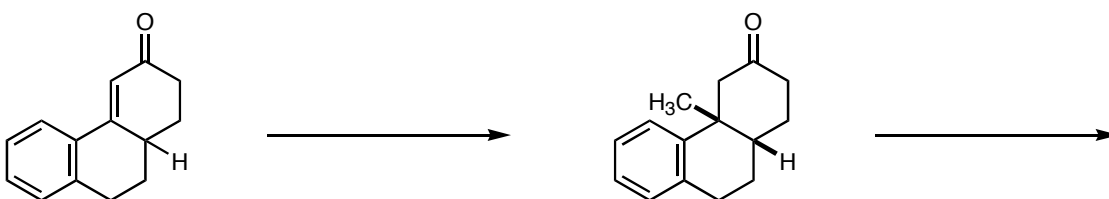
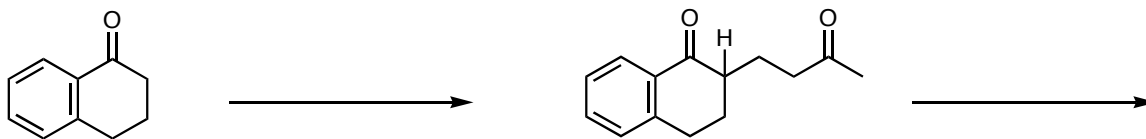


(j)



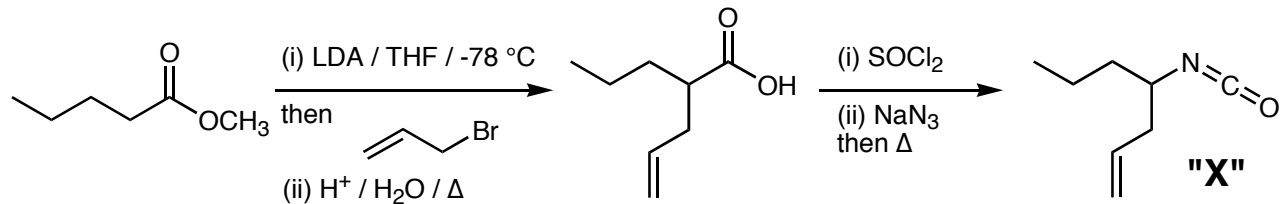
Name:

2. (45 marks) Suggest reagents (and catalysts where necessary) to accomplish each of the transformations shown below. It is not necessary to draw mechanisms for your reactions. You do not need to specify the aqueous "work-up" steps in your answers.



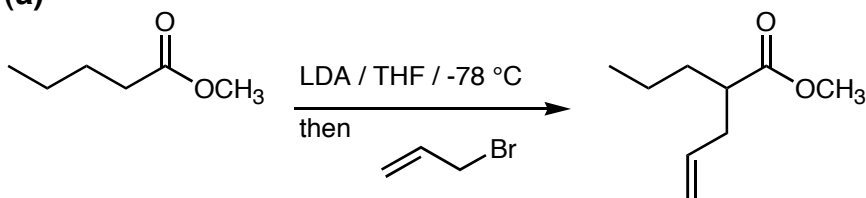
Name:

3. (80 marks) Consider the following four-step synthesis of the isocyanate "X".

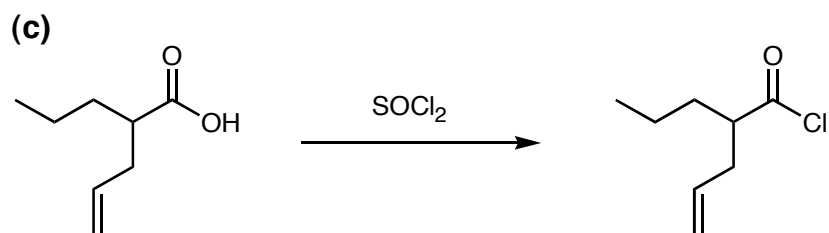
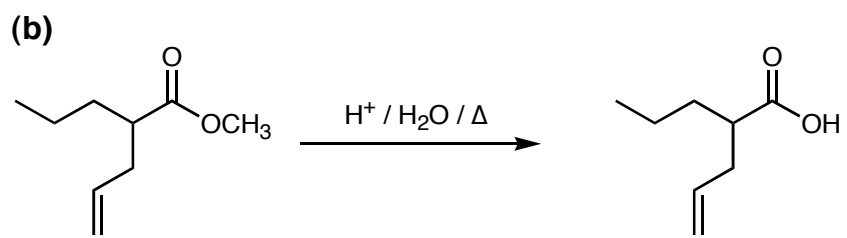


Propose full mechanisms for each of the four transformations, indicating electron flow with "curved arrows" *and* including *all* intermediates.

(a)

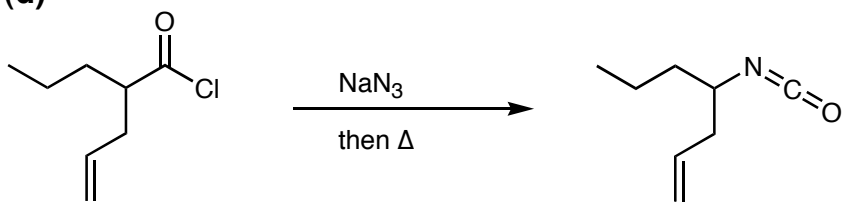


Name:



Name:

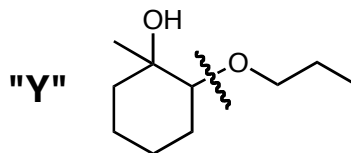
(d)



(e) Organic reactions are often named after their discoverers/inventors. What is the name of the transformation shown in part (d) above?

Name:

4. (25 marks) Consider the compound "Y" shown below. A bond-disconnection for this compound is indicated by the wavy line.



(a) Draw an appropriate pair of donor and acceptor 'synthons' that relate to this disconnection.

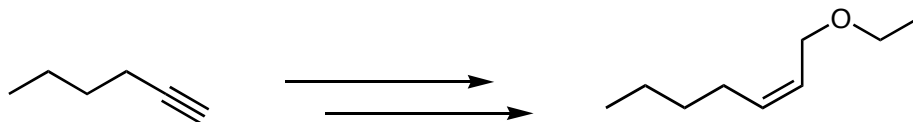
(b) Suggest reagents equivalent to the pair of 'synthons' you have chosen, and show how you would synthesize "Y" from simple reagents.

(c) Draw the relative stereochemistry of the product "Y" that you would expect to obtain in your synthesis.

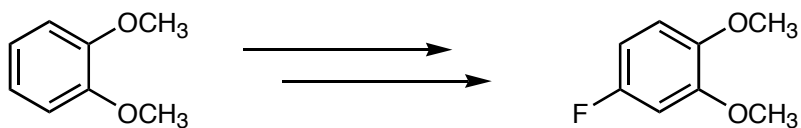
Name:

5. (80 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)

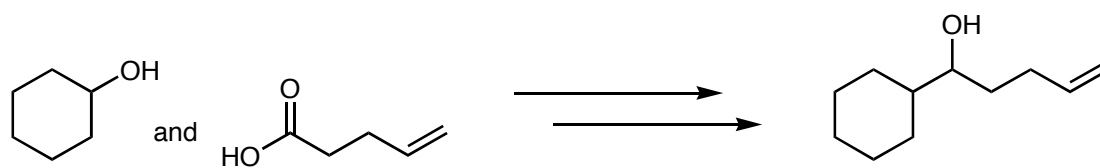


(b)

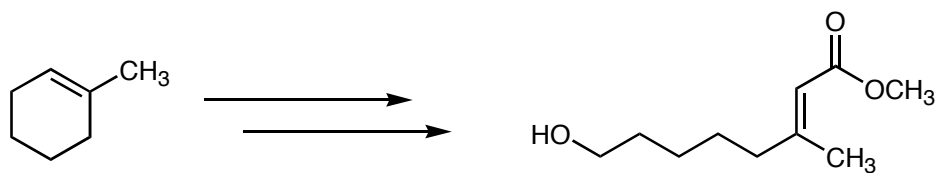


Name:

(c)



(d)



Name:

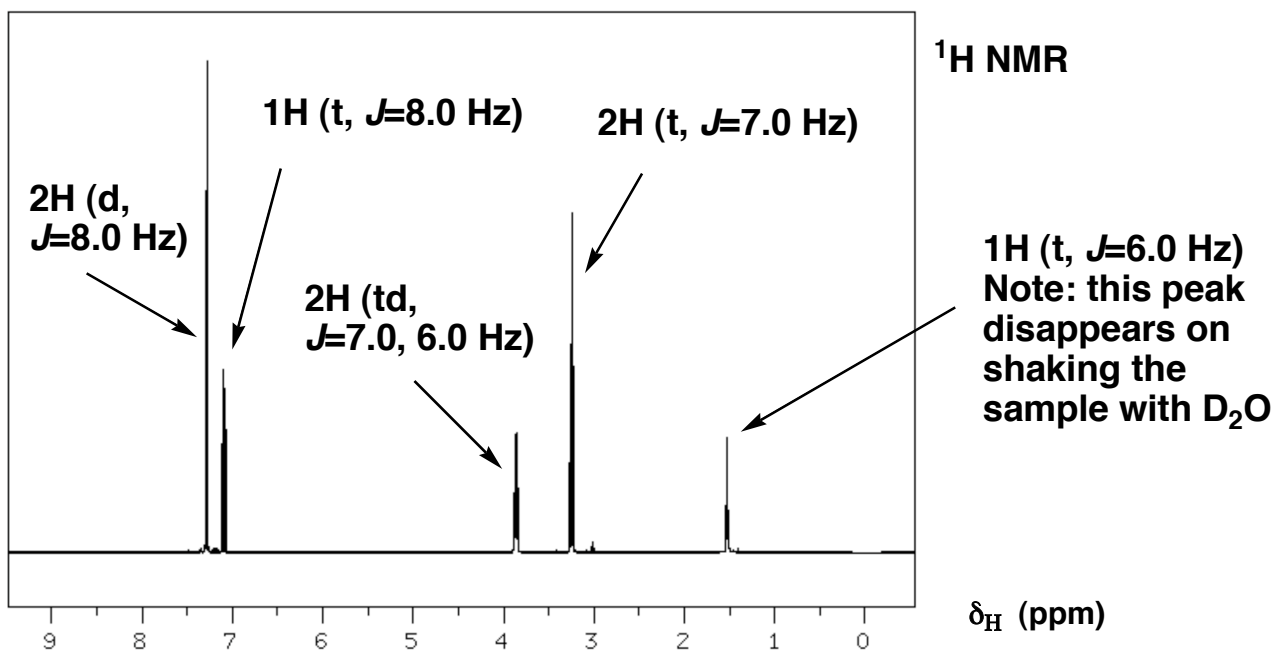
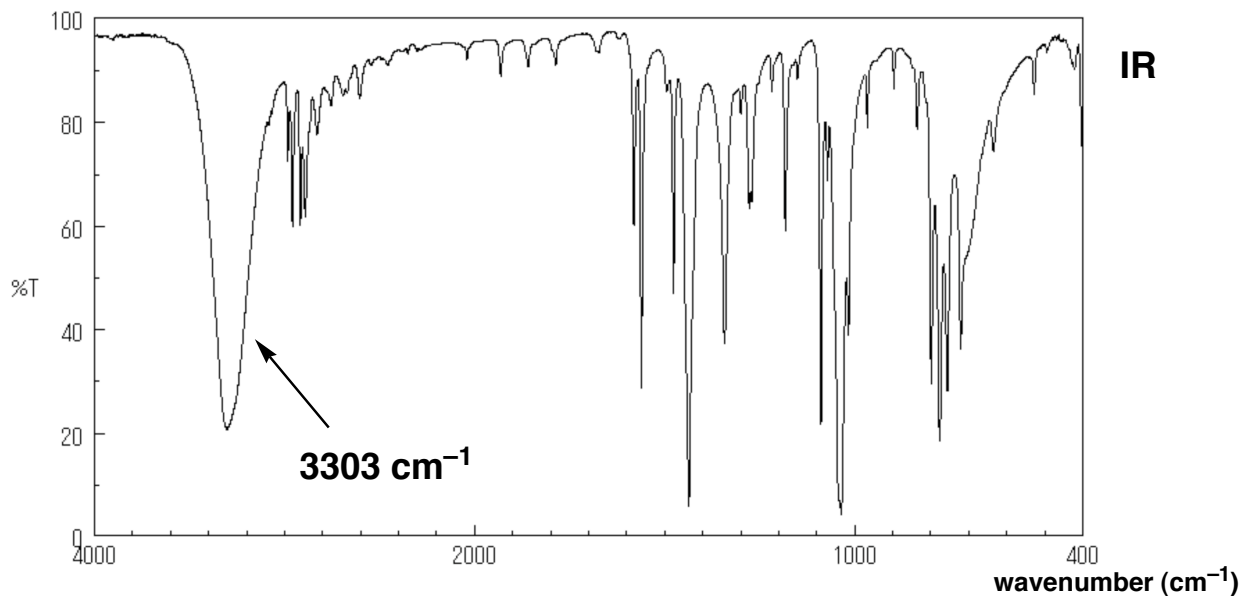
6. (45 marks) Deduce the structure of the compounds **A** and **B**, using the spectral data provided on the following pages.

(a) **COMPOUND A:**

(b) **COMPOUND B:**

Name:

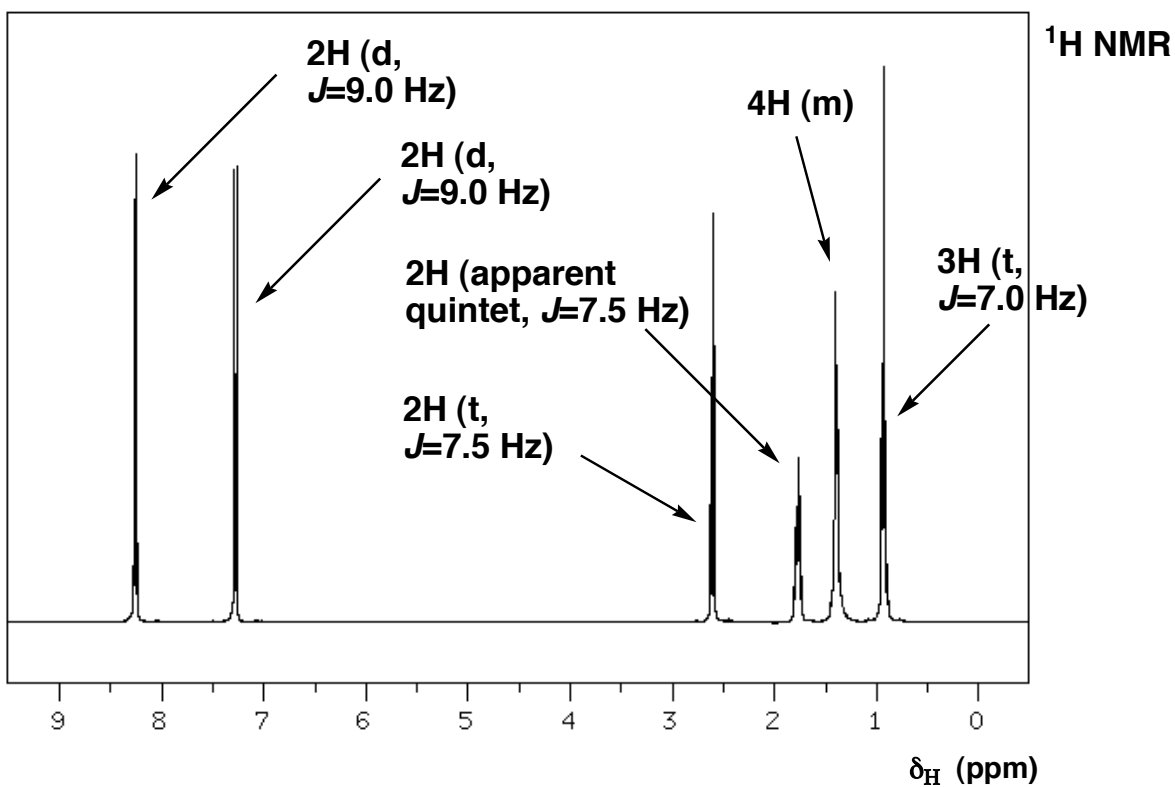
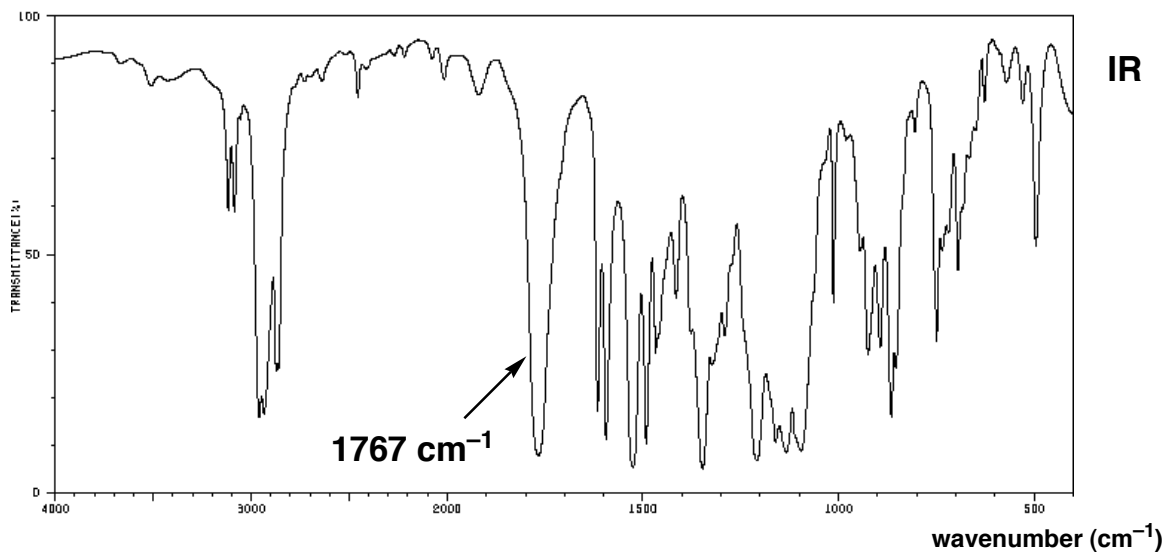
COMPOUND A: Molecular Formula $C_8H_8Cl_2O$



^{13}C NMR / DEPT NMR δ_C (ppm) =	135.9	C
	134.3	C
	128.3	CH
	128.2	CH
	61.0	CH_2
	34.6	CH_2

Name:

COMPOUND B: Molecular Formula $C_{12}H_{15}NO_4$



^{13}C NMR / DEPT NMR δ_C (ppm):

171.4	C	34.3	CH_2
155.6	C	31.2	CH_2
145.3	C	24.5	CH_2
125.2	CH	22.3	CH_2
122.5	CH	13.9	CH_3

Name:

Abbreviations:

Bn = benzyl ($-\text{CH}_2\text{Ph}$)

t-Bu = *tert*-butyl ($-\text{C}(\text{CH}_3)_3$)

cat = catalytic quantity

δ = chemical shift (ppm)

Δ = heat

DEPT = distortionless enhancement by polarization enhancement spectra

equiv = equivalents

Et = ethyl ($-\text{CH}_2\text{CH}_3$)

IR (ν) = Infra red signal (cm^{-1})

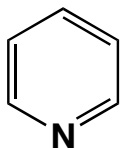
LDA = lithium diisopropylamide ($\text{Li}^+ \text{ } ^-\text{N}(\text{CH}(\text{CH}_3)_2)$)

Me = methyl ($-\text{CH}_3$)

NMR = nuclear magnetic resonance

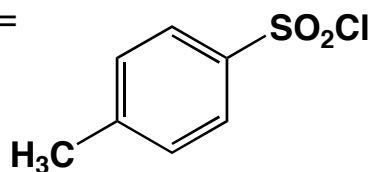
Ph = phenyl ($-\text{C}_6\text{H}_5$)

Pyridine =



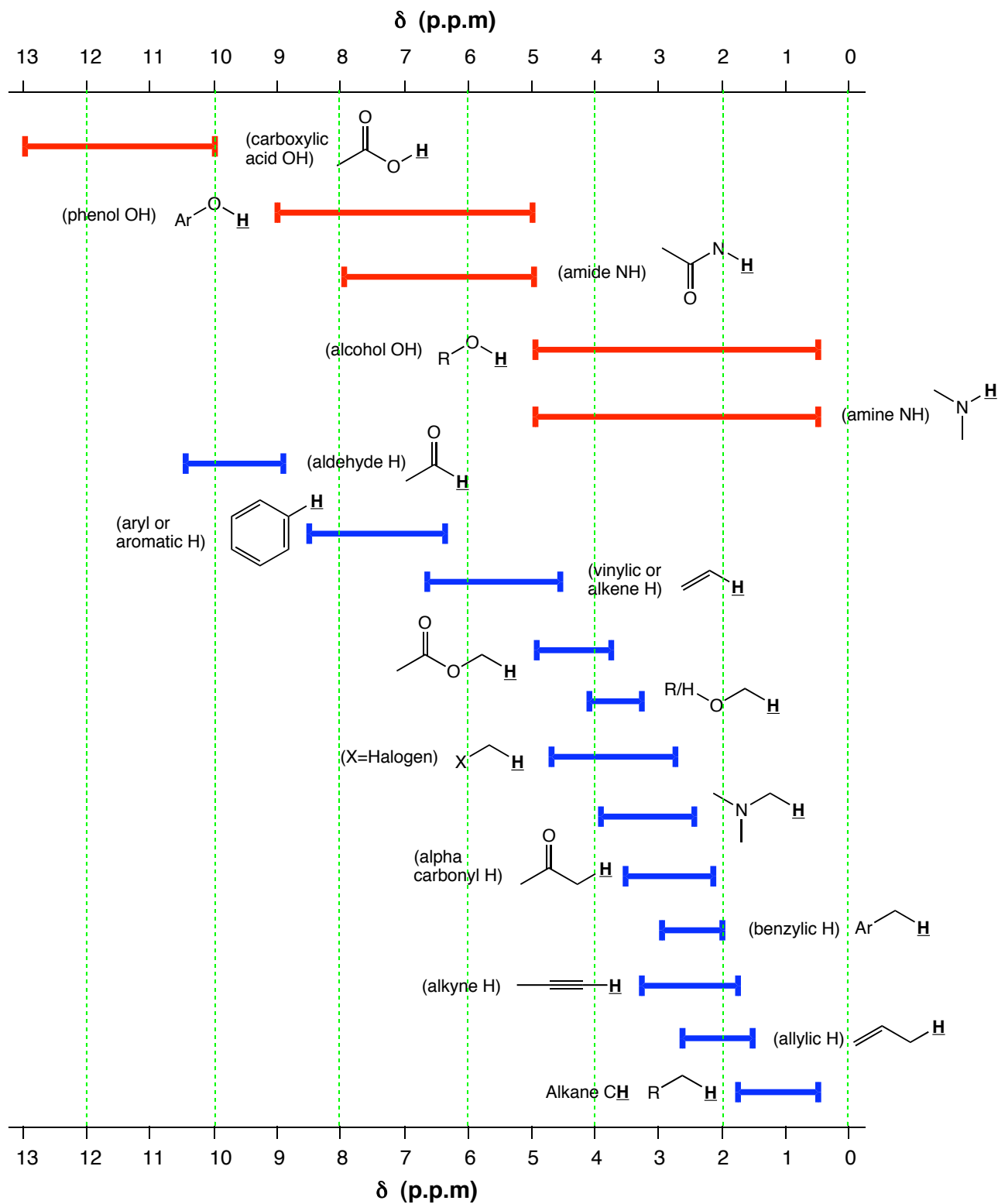
THF = tetrahydrofuran

TsCl =



Name:

Proton Chemical Shifts

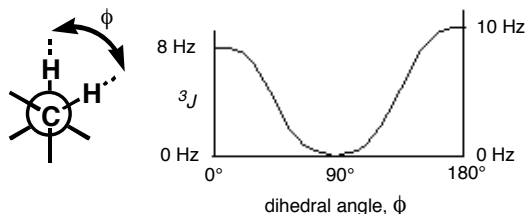
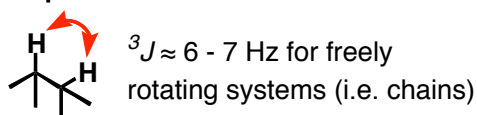


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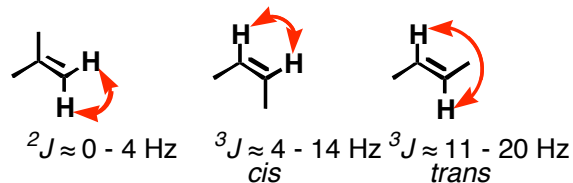
Abbreviations for proton multiplicities: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Higher multiplicities are given in full i.e. quintet, sextet, septet, etc.

Coupling Constants (J values)

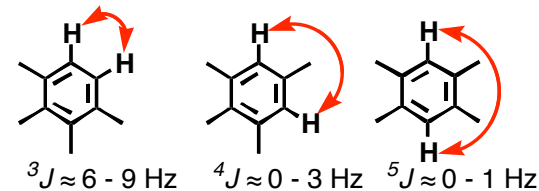
Aliphatic Protons:



Alkene Protons:



Aromatic Protons:



^{13}C Chemical Shifts

