

Name:

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

**APRIL/MAY 2006 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 15, 16 and 17 respectively.

Allowed Aids: **Molecular Models**

Calculators and other electronic devices are not permitted in this examination

Credit will be given for partial answers

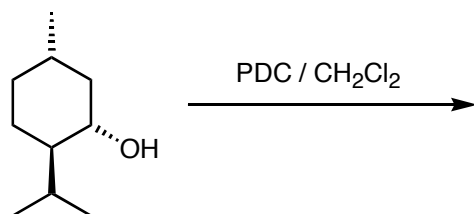
WAIT UNTIL YOU ARE TOLD TO BEGIN

| | | |
|--------------|------------|--|
| Question 1 | 60 | |
| Question 2 | 40 | |
| Question 3 | 80 | |
| Question 4 | 45 | |
| Question 5 | 35 | |
| Question 6 | 40 | |
| Total | 300 | |

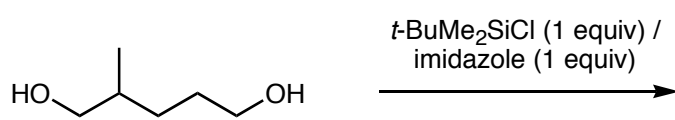
Name:

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

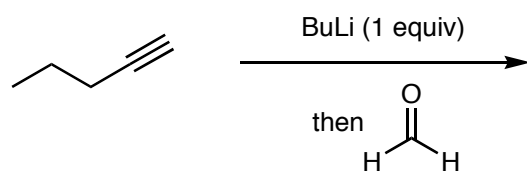
(a)



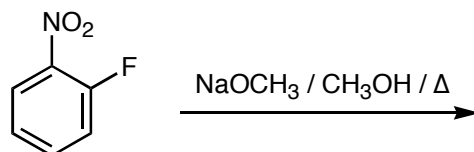
(b)



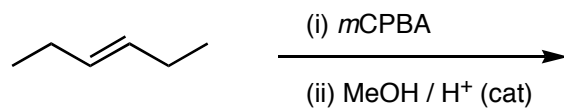
(c)



(d)

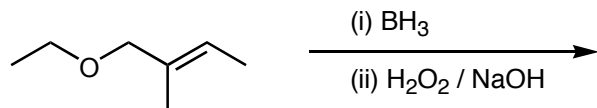


(e)

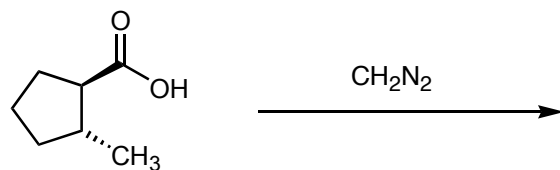


Name:

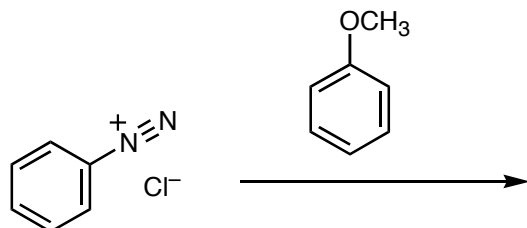
(f)



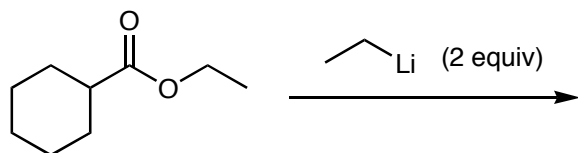
(g)



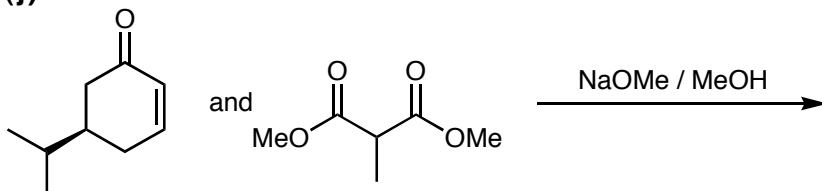
(h)



(i)

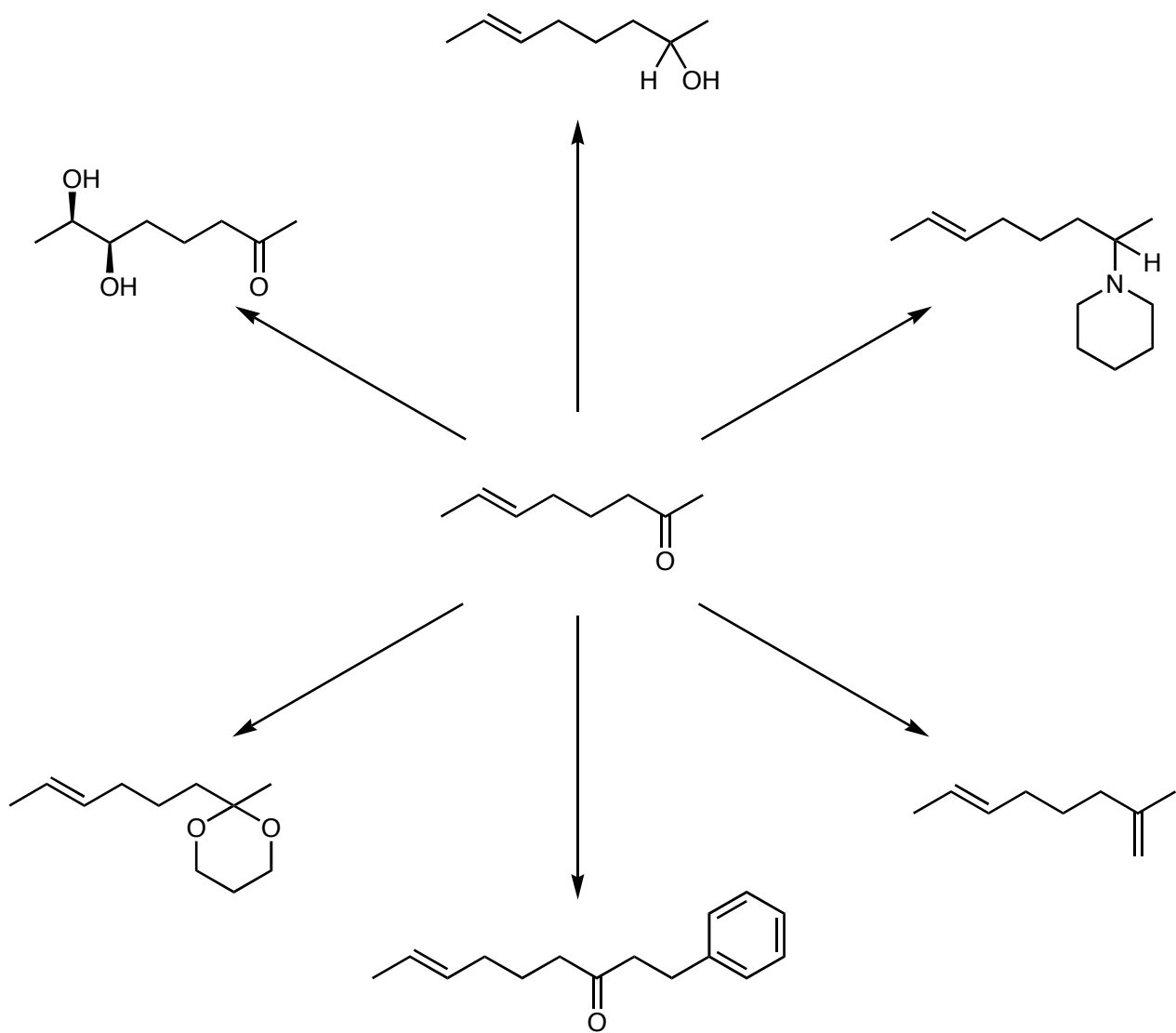


(j)

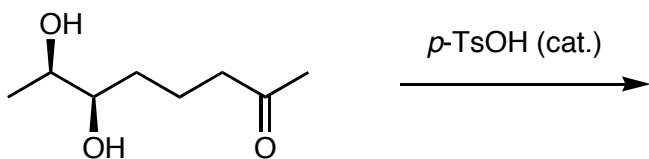


Name:

2. (40 marks) (a) Suggest reagents (and catalysts where necessary) to accomplish the transformations shown below. You do not need to specify the aqueous "work-up" steps in your answers.

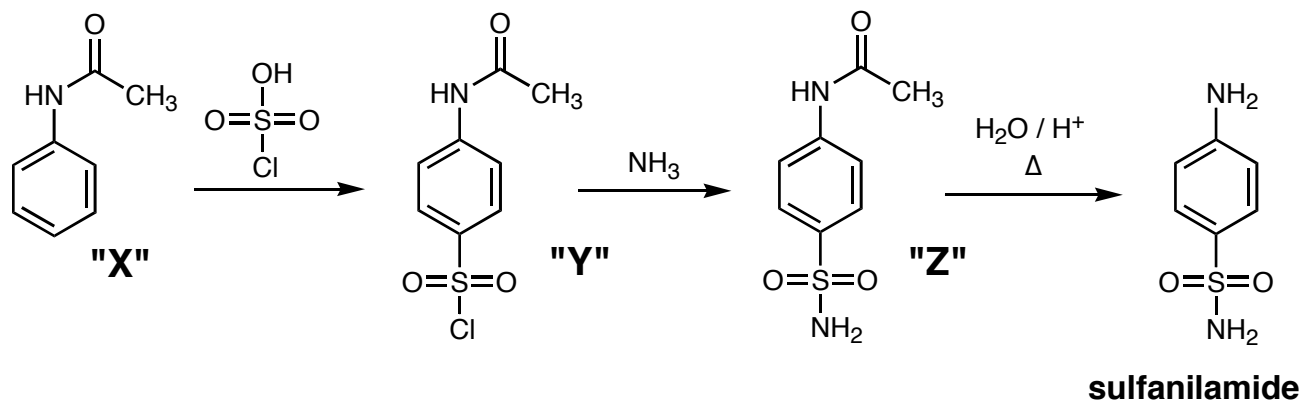


(b) Draw the product of the following reaction, which has a molecular formulae $C_8H_{14}O_2$.

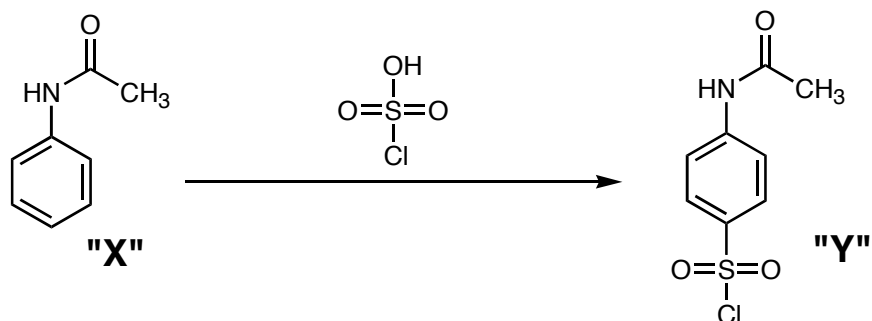


Name:

3. (80 marks). Sulfanilamide is an antibiotic drug that was developed during the late 1930's, and was used as a treatment during World War II, saving many lives. Sulfanilamide is synthesized in a three-step approach from "X" (acetanilide) (shown below). Answer the following questions about the synthesis of sulfanilamide.



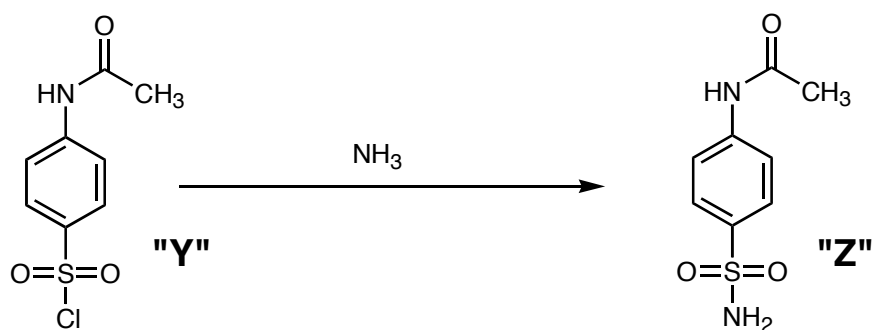
(a) Suggest a plausible mechanism for the first step of the synthesis ("X" to "Y"). Your answer should be a full mechanism indicating electron flow with "curved arrows" and including all intermediates.



Name:

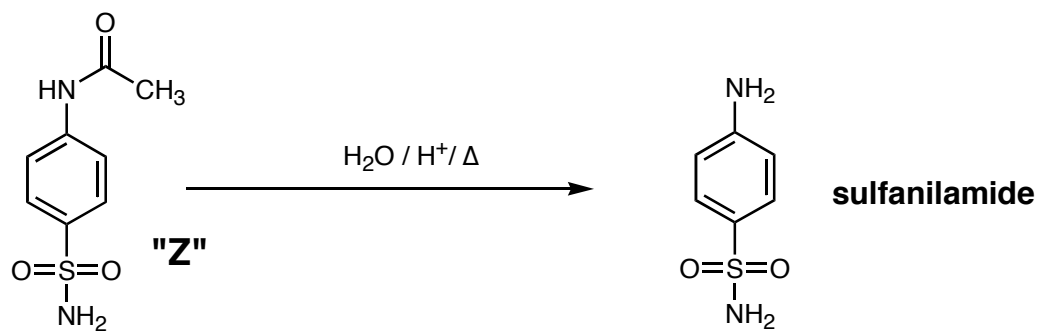
(b) Why does this reaction ("X" to "Y") lead to the para substituted product?

(c) Suggest a plausible mechanism for the second step of the synthesis ("Y" to "Z"). Your answer should be a full mechanism indicating electron flow with "curved arrows" and including all intermediates.



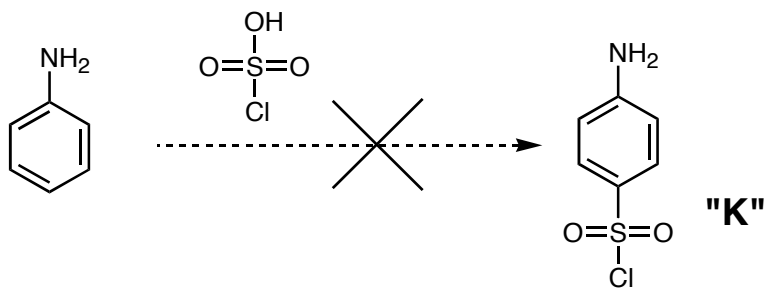
Name:

(d) Draw a mechanism for the final step of the synthesis ("Z" to sulfanilamide). Your answer should be a full mechanism indicating electron flow with "curved arrows" and including all intermediates.

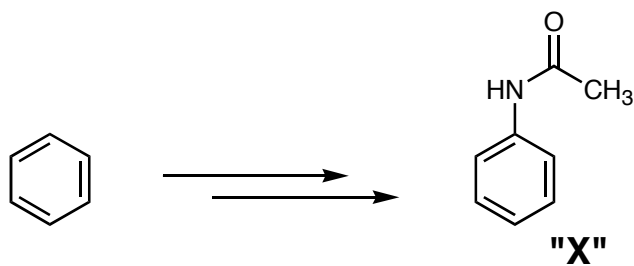


Name:

(e) Suggest one reason why it is not possible to directly convert aniline to the intermediate "K", as shown below?

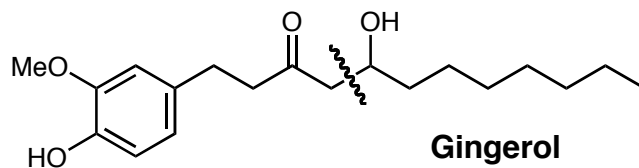


(f) How can the precursor molecule "X" be synthesized from benzene?



Name:

4. (45 marks) The natural product *gingerol* is one of the active constituents of a ginger roots. A carbon-carbon disconnection for *gingerol* is given below (wavy line).

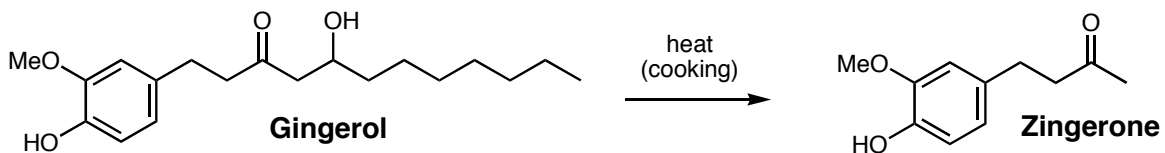


(a) Draw BOTH pairs of synthons that relate to this disconnection.

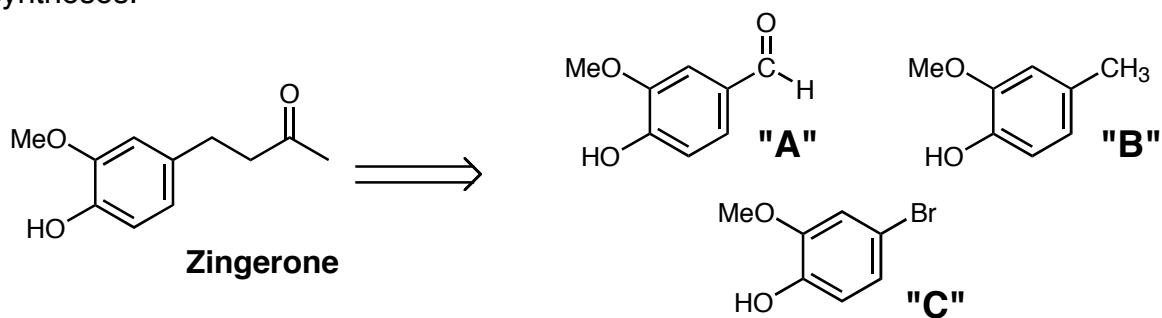
(b) One of these pairs constitutes a more "natural" disconnection than the other. Which is more appropriate? Suggest reagents equivalent to the pair of synthons you have chosen, and the reaction conditions that you would use to synthesize *gingerol*.

Name:

(c) Cooking fresh ginger transforms *gingerol* into *zingerone*. Suggest a reaction process that would be capable of this degradation?



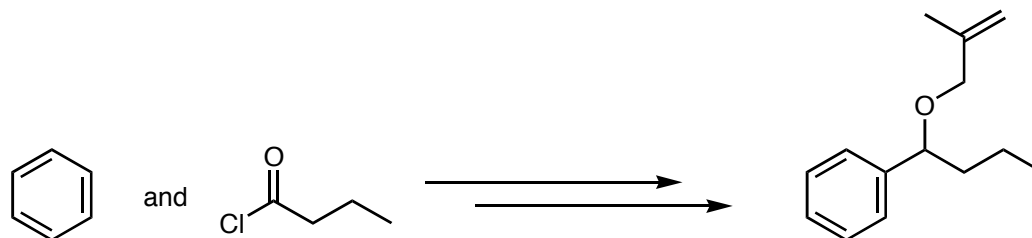
(d) Propose a synthesis of *zingerone* from **one** of the starting materials indicated ("A", "B" or "C"). You may use any other chemical reagents / precursors that are necessary. More than one step is required. Indicate the products after each step of your proposed syntheses.



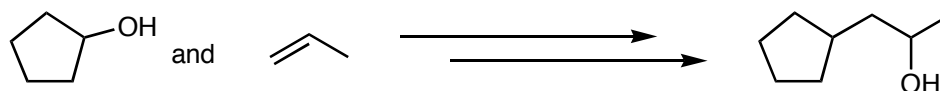
Name:

5. (35 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:

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

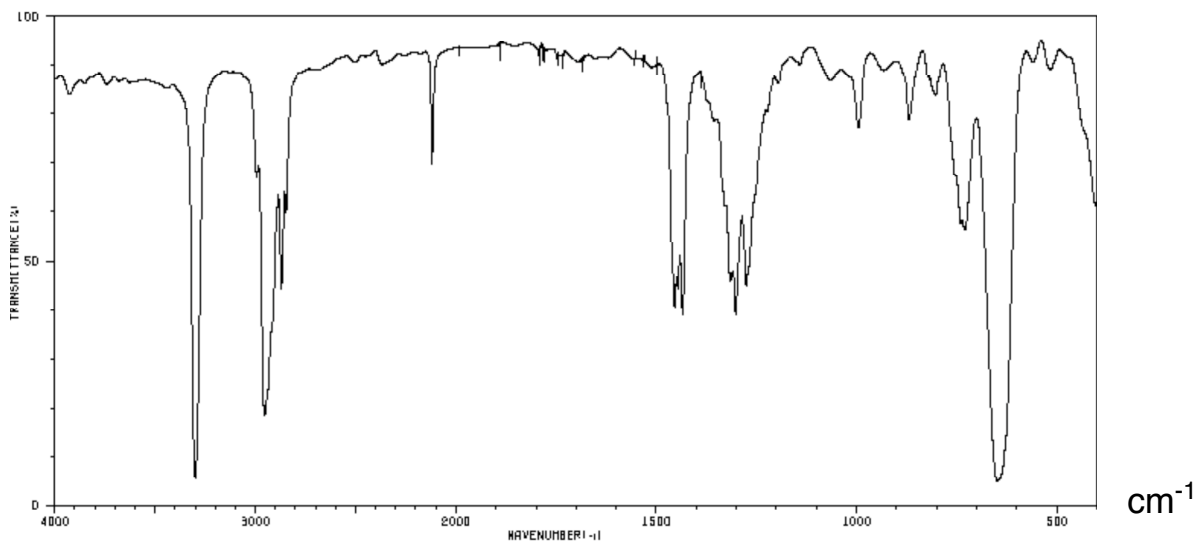
(a) **COMPOUND A:**

(b) **COMPOUND B:**

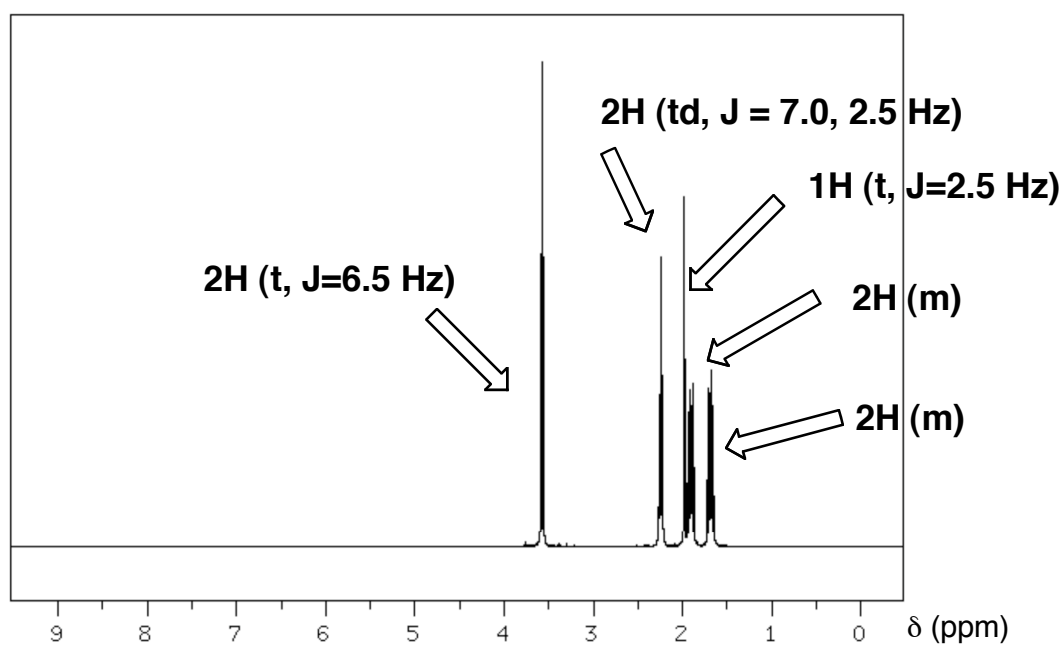
Name:

COMPOUND A:

Molecular Formula: C_6H_9Cl



1H NMR



^{13}C / DEPT NMR δ (ppm) =

- 83.7 (C)
- 68.9 (CH)
- 44.5 (CH_2)
- 31.4 (CH_2)
- 25.6 (CH_2)
- 17.7 (CH_2)

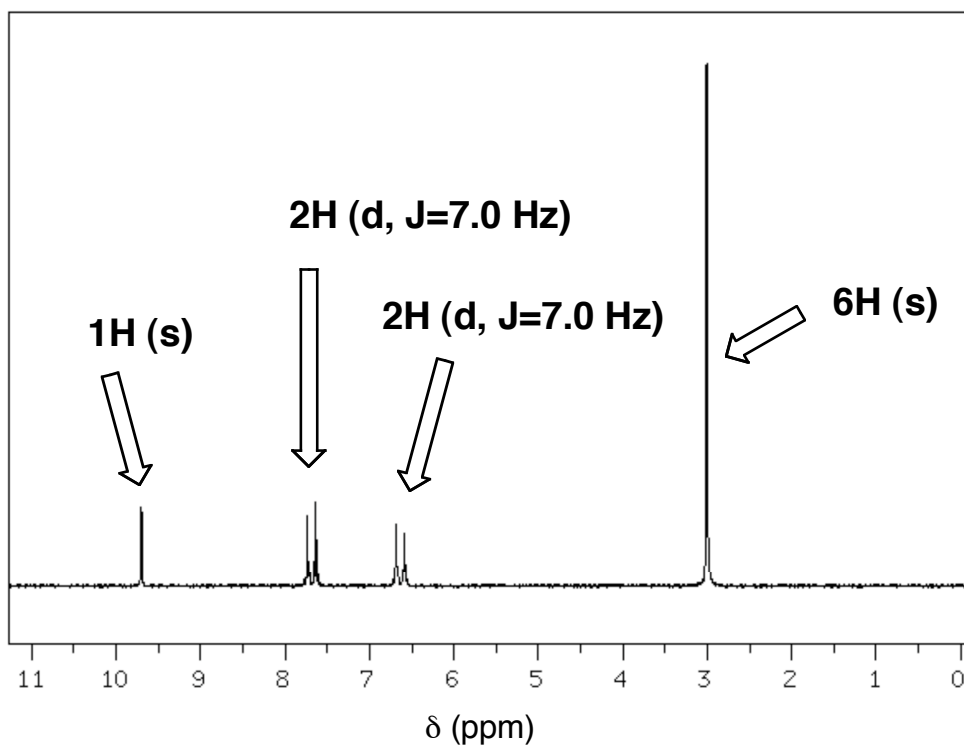
Name:

COMPOUND B:

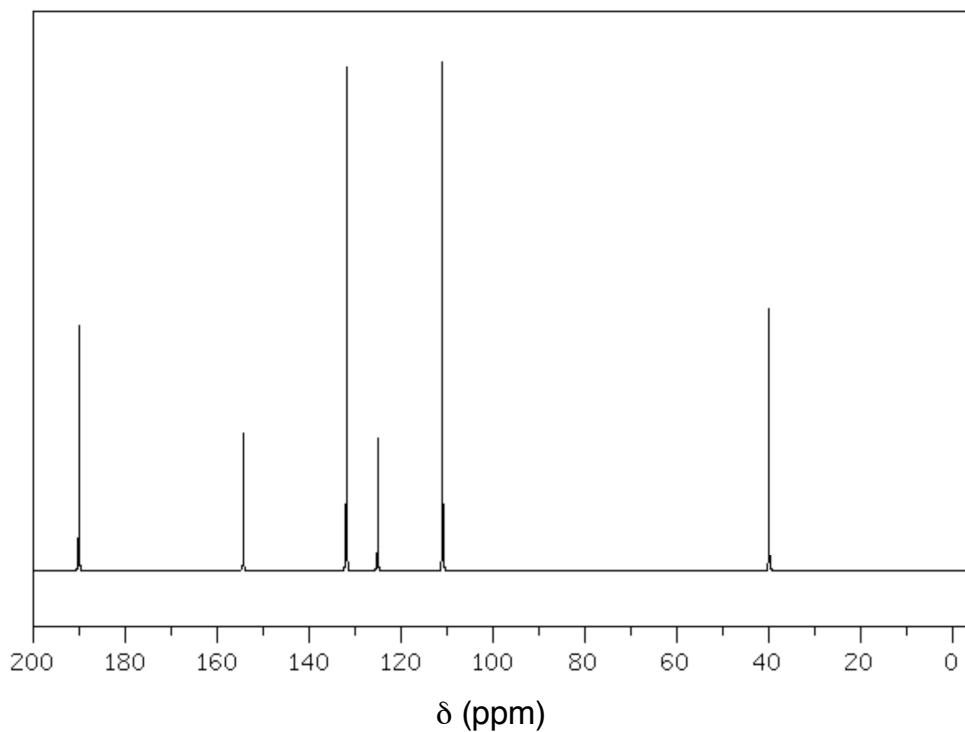
Molecular Formula: $C_9H_{11}NO$

IR = 1694, 1602 cm^{-1}

1H NMR



^{13}C NMR



Name:

Abbreviations:

Bu = Butyl ($-C_4H_9$)

cat = catalytic

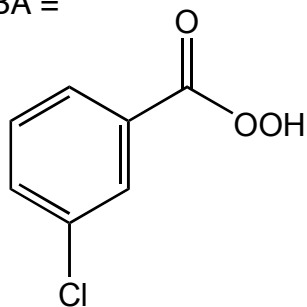
δ (ppm) = chemical shift (parts per million)

Δ = heat

equiv = equivalents

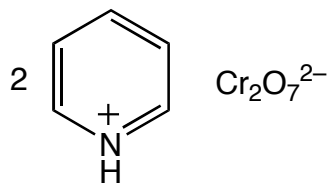
IR (ν) = Infra red signal (cm^{-1})

*m*CPBA =

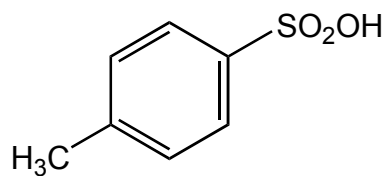


Me = methyl ($-CH_3$)

PDC = pyridinium dichromate

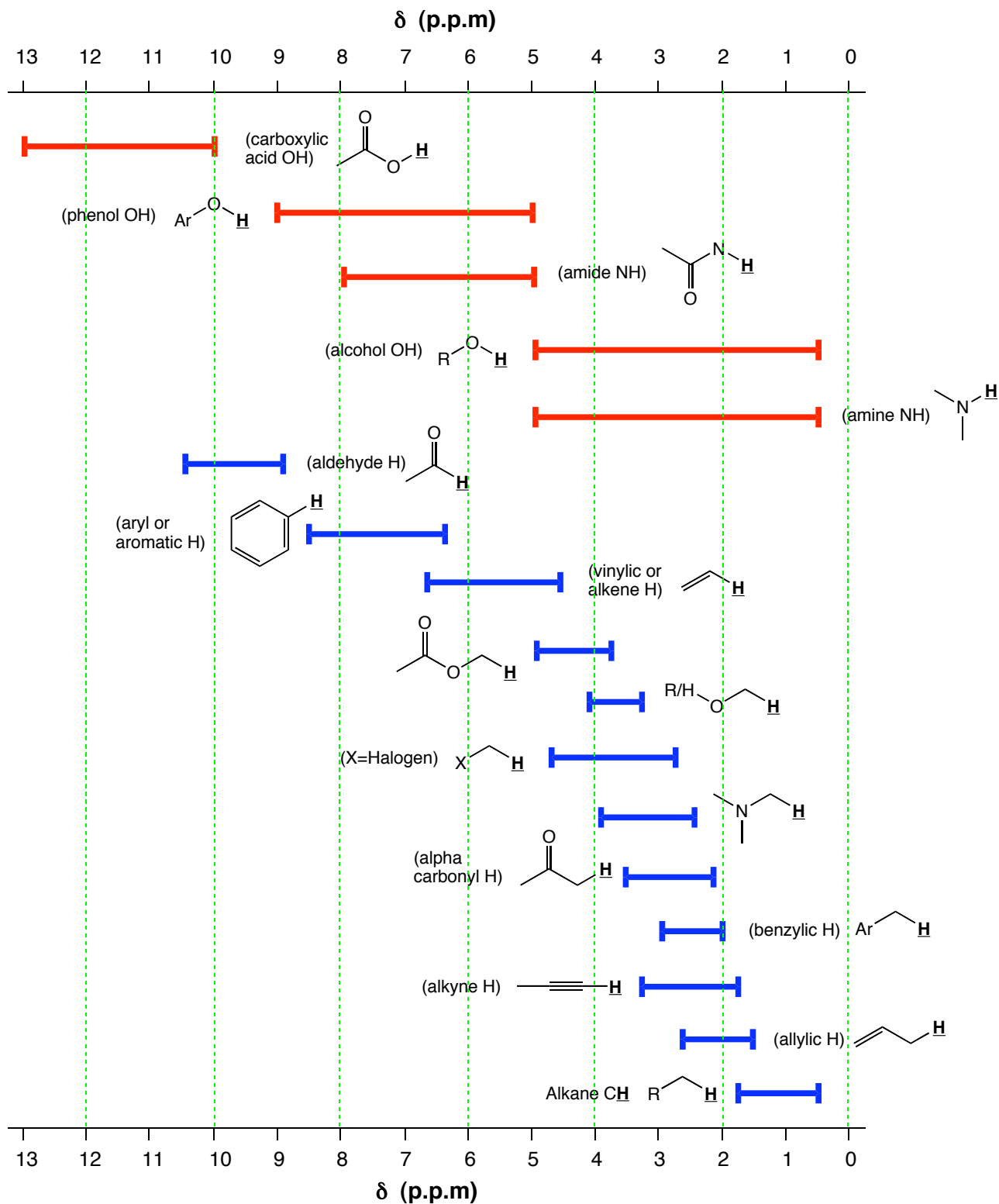


p-TsOH = para-toluenesulfonic acid



Name:

Proton Chemical Shifts

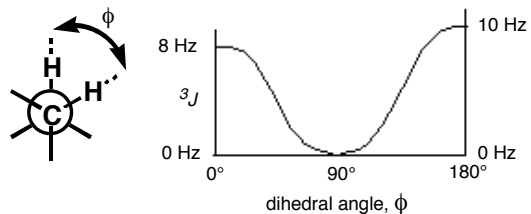
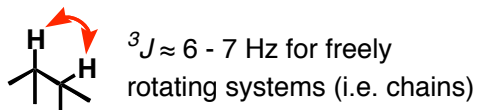


Name:

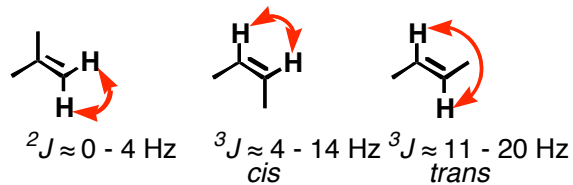
Abbreviations for proton multiplicities: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Higher multiplicities are given in full i.e. quintet, sextet, septet, etc.

Coupling Constants (J values)

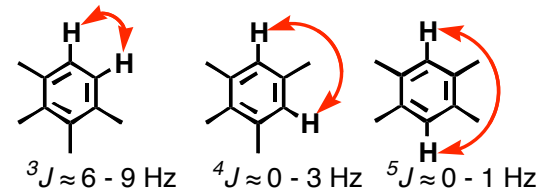
Aliphatic Protons:



Alkene Protons:



Aromatic Protons:



^{13}C Chemical Shifts

