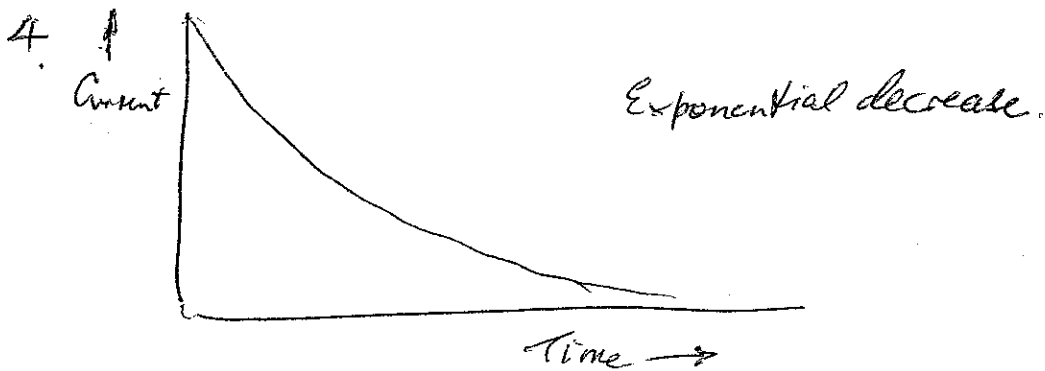


(7 each)

A. 1. Faraday is quantity of charge in a mole of electrons or (singly-charged) ions.

2. It is the quantitative connection between charge and amount of matter.

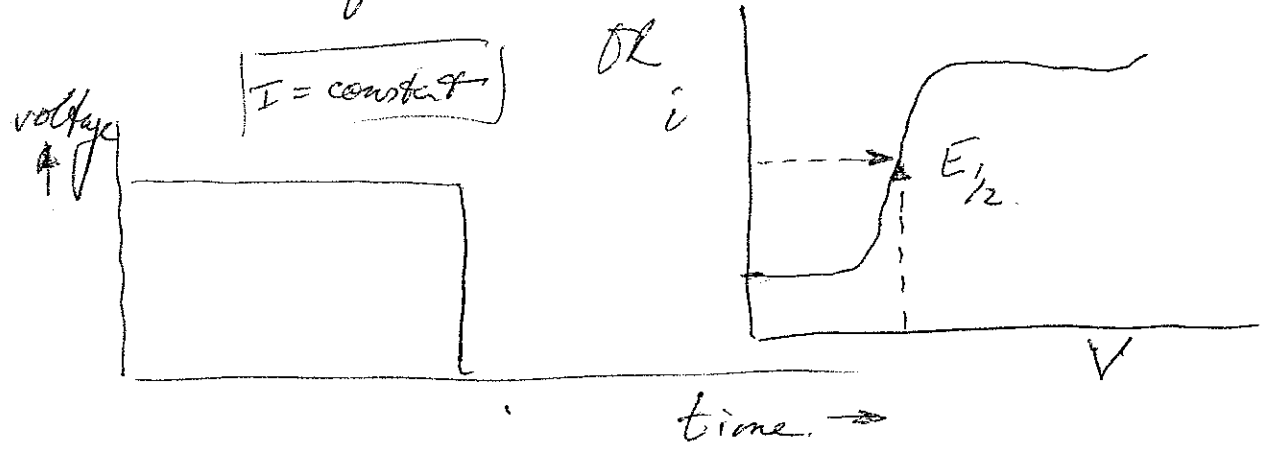
3. Set of electroanalytical measurements in which amount of charge is measured in order to make quantitative measurements on amounts of reagents involved in chemical rxns. Expt is done at fixed potential and current \times time is measured.



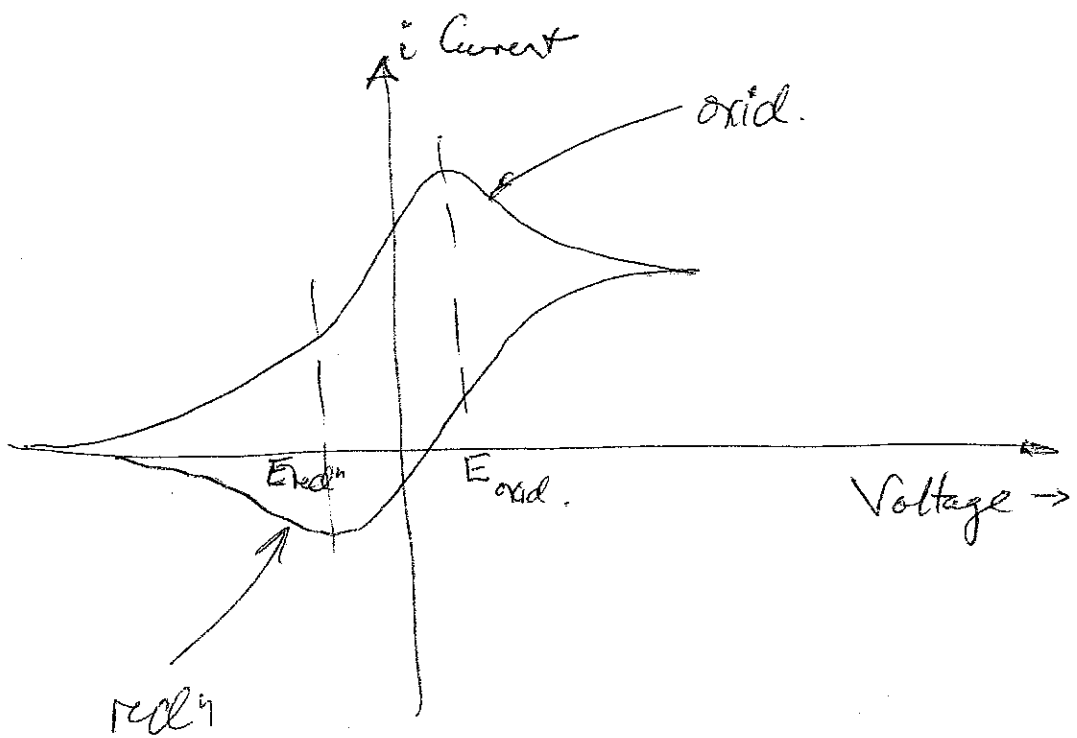
5.

An experiment in which a scan is followed, usually at constant current
example Karl-Fischer titration to determine water.
Only meas. of time is needed for quant. analysis.

6.



7.



$$1. H = A + \frac{B}{u} + C_s u + C_m u$$

Height Equivalent Plate (H)

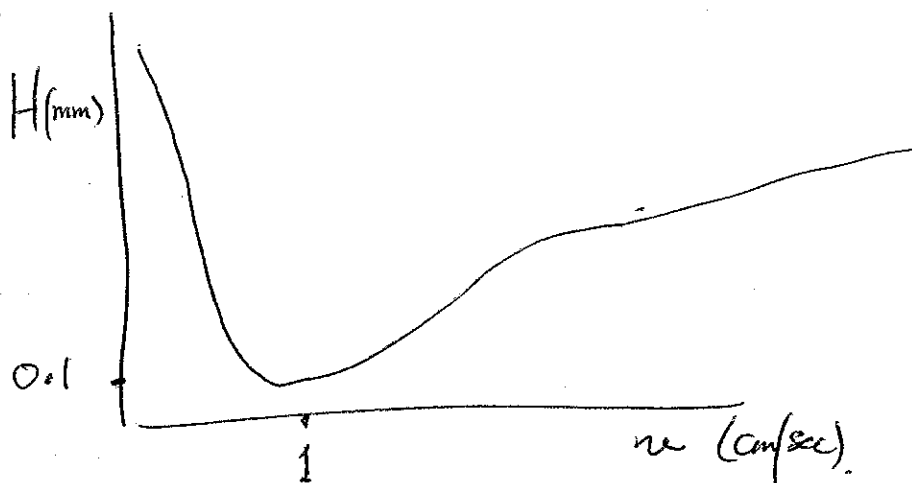
A indep. of mobile phase velocity (u)

B inverse, C_s, C_m prop^l to u

B represents mass transfer in mobile ph.

$C_m + C_s$ " " " between mobile stationary & within stationary.

2.



3. Change flow rate but this is assumed in #2
Change loading — decrease it.
Decrease No. of plates.

4. Capacity factor $k' = \frac{t_R - t_m}{t_m}$

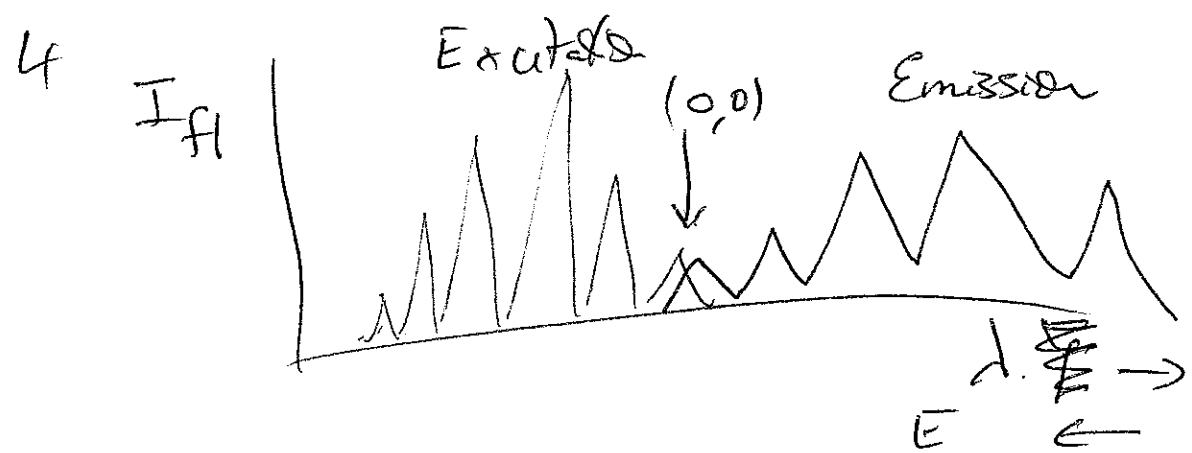
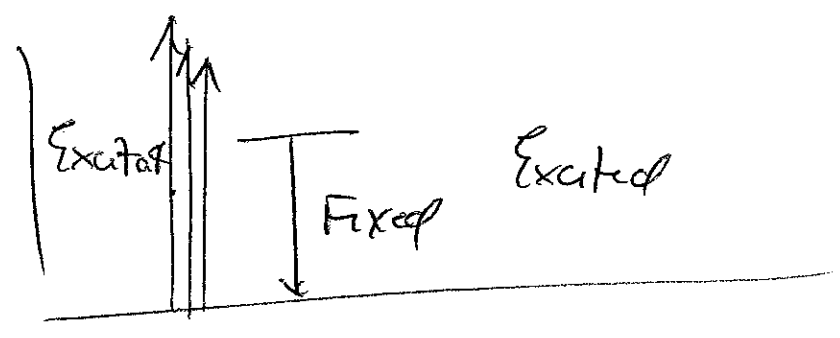
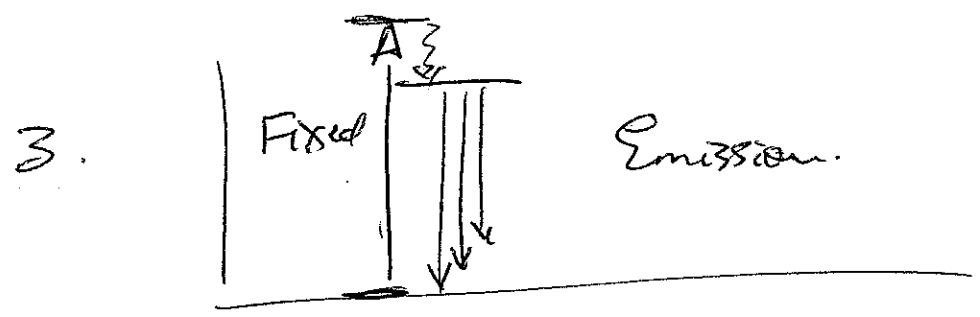
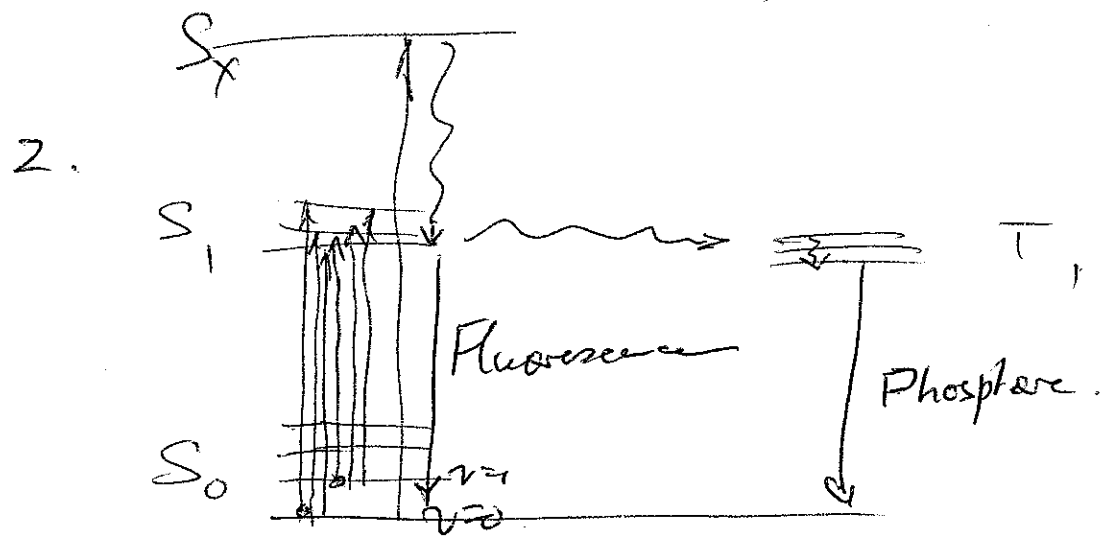
retention time of mobile & stationary phases.

Greater k' means better but slows sep.

$Res = \frac{\sqrt{N}}{4} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{1 + k'_B}{k'_B} \right)$ — Res depends on capacity factor # plates & selectivity

1. $I_F = I_0 \epsilon c l \phi$

Annotations:
 I_0 : Initial I
 ϵ : molar absorptivity
 c : conc
 l : path length
 ϕ : quantum yield



No Biochemistry crib available

August 25, 2007

Written by Professor Hrycyna

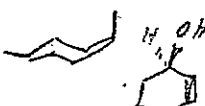

No Inorganic crib available

August 25, 2007

Written by Professor Robinson

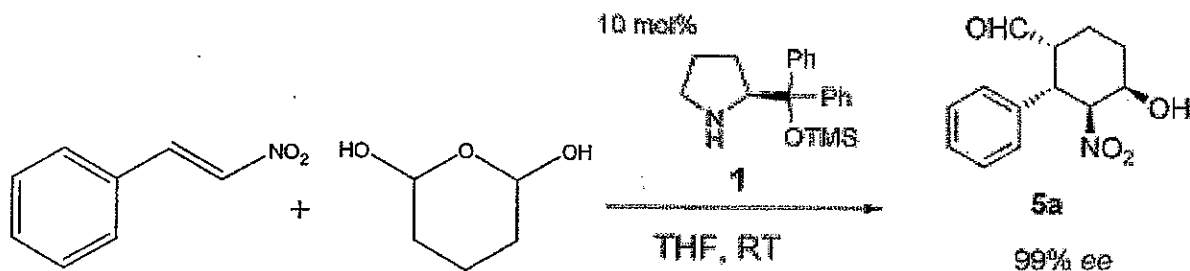
ORGANIC CUME (Aug 2007)
(3 pages)

1. (24 pts) Provide the following information. An order of magnitude estimate will receive half credit.

- (a) The diameter of a benzene ring. $2 \times (1.4 + 1.1 + 0.7) = 6.4 \text{ \AA}$
- (b) The bond dissociation energy of the weakest bond in propene. π bond 80 kcal/mol/e
- (c) The boiling point of diethyl ether. 34°
- (d) The ^{13}C NMR spectrum of CD_2Cl_2 . $\delta 54$
- (e) The most stable conformation of cis-1,4-dimethylcyclohexane. 
- (f) The structure of R-cyclohexenol 
- (g) The activation energy for the chair to chair inversion of cyclohexane and its rate at 25°C . 10.6 kcal/mol 10^5 s^{-1}
- (h) The pK_a values and isoelectric point of phenylalanine. pK_a 1.8, 9.2 $\text{pI} = 5.5$

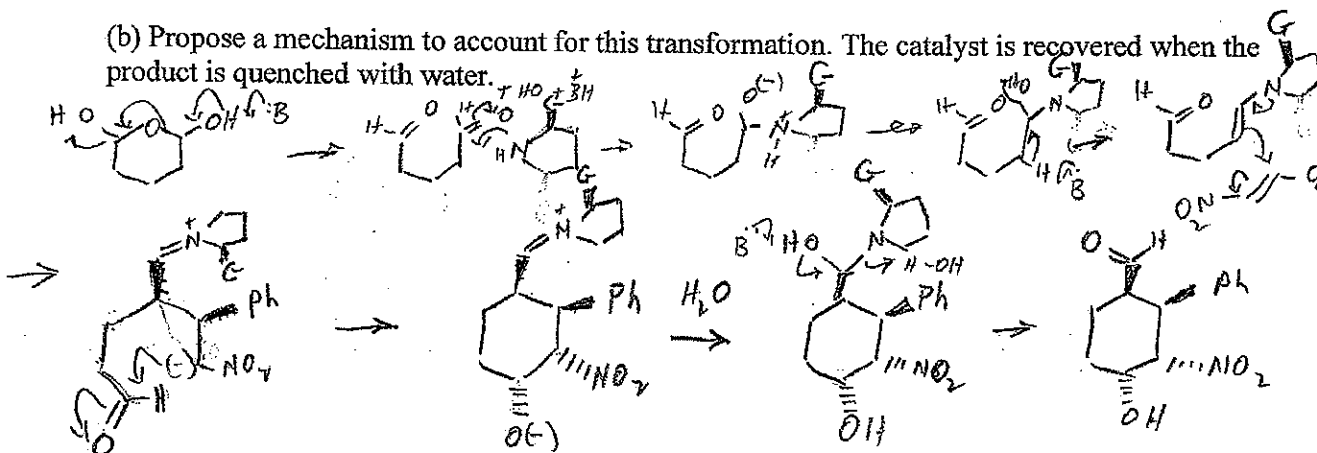
2. (25 pts) Hayashi and coworkers (*Angew Chem* 46, 4922-4925, 2007) reported

Diphenylprolinol Silyl Ether as a Catalyst in an Enantioselective, Catalytic, Tandem Michael/Henry Reaction for the Control of Four Stereocenters**



(a) The first step involves the condensation between the catalyst and the product of the dehydration of the starting diol. Give the structure of this intermediate.

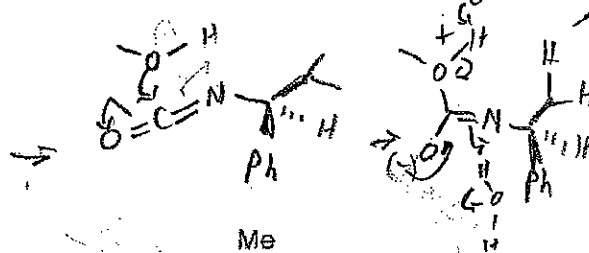
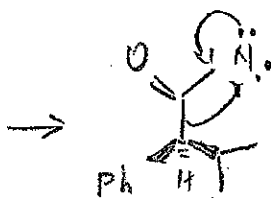
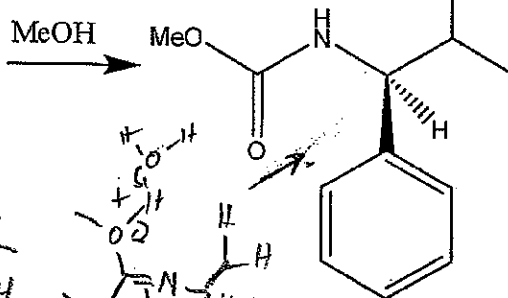
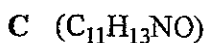
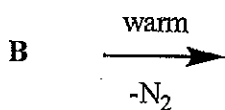
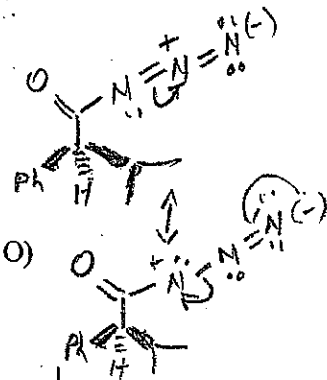
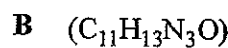
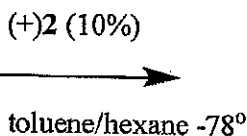
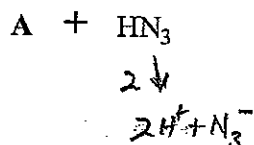
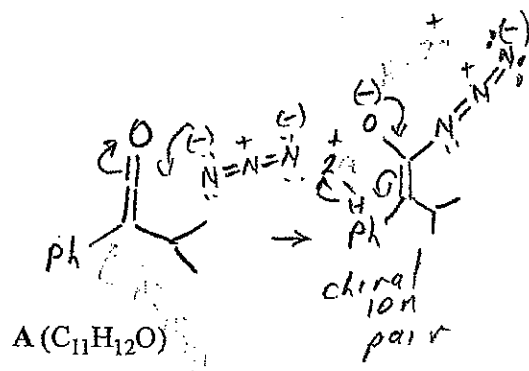
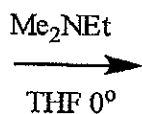
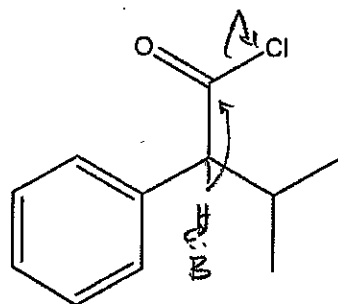
(b) Propose a mechanism to account for this transformation. The catalyst is recovered when the product is quenched with water.



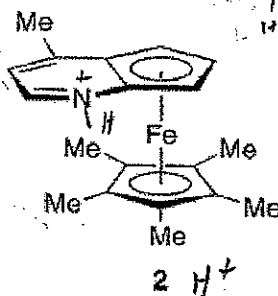
3. (25 pts) Fu and coworkers (*Angew Chem* 46, 4367-4369, 2007) have reported the following sequence of reactions.

(a) Propose structures for the unknowns A - C.

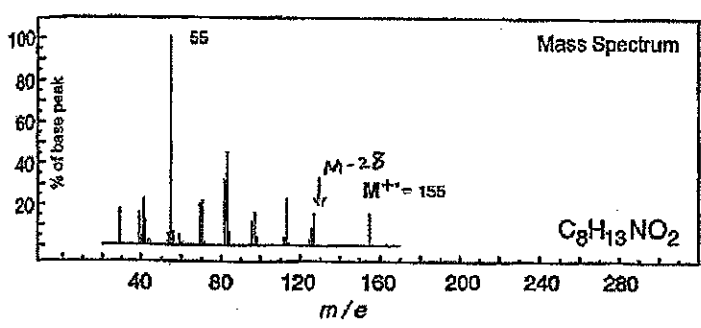
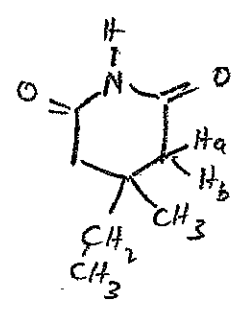
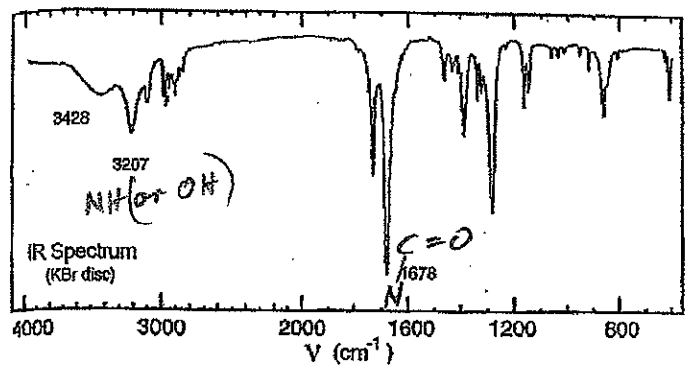
(b) Propose plausible mechanisms for each transformation.



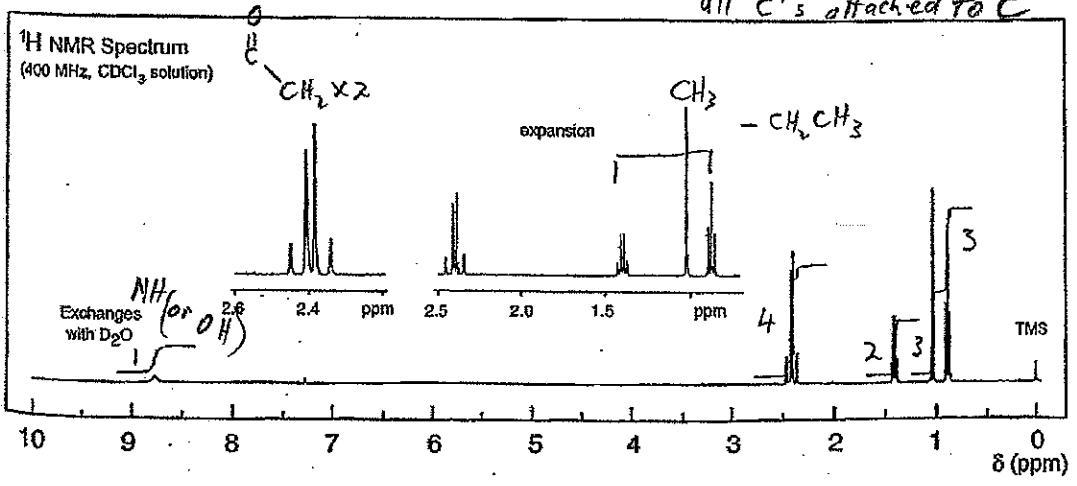
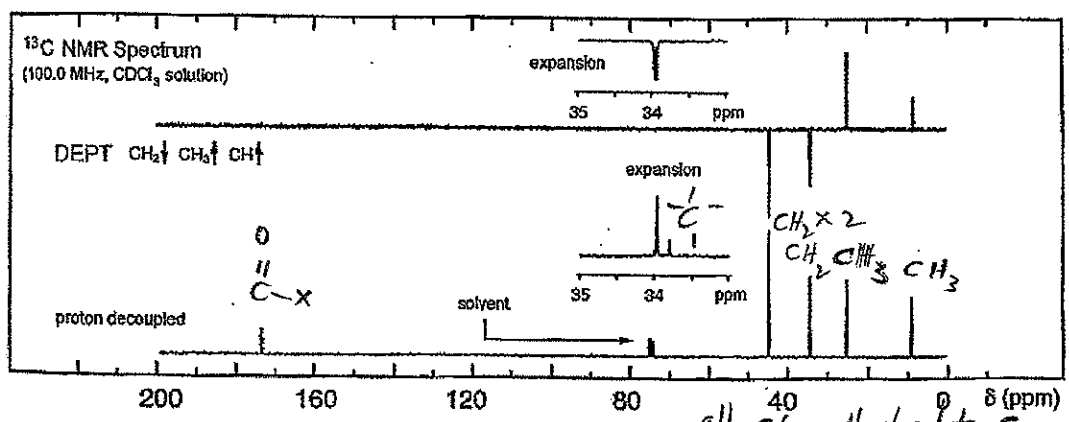
93% yield 96%ee



4. (26 pts) Determine the structure of the compound whose spectra are shown below. Briefly show your reasoning. Partial credit given for partial structures.



UV Spectrum
 λ_{max} 230 nm (log₁₀ ε 3.6) pH 11
 λ_{max} 230 nm (log₁₀ ε 4.4) pH 13
 solvent: water
 3 unsaturation



P. Chem, Course Aug. 2007

1) $q = \sum_i g_i e^{-\beta \epsilon_i}$ where $\beta = 1/kT$

2) $q = \#$ of thermally populated states (if $\epsilon_0 = 0$)

3) $P(\epsilon_i) = \frac{e^{-\beta \epsilon_i}}{q}$

4) $P(\epsilon_i) = \frac{g_i e^{-\beta \epsilon_i}}{q}$

5) $q^E \approx 1$, $q^V \approx 1$, $q^R \approx 50$, $q^T \approx 10^{33}$
because $\Delta \epsilon \gg kT$, $\nu \approx 2000 \text{ cm}^{-1}$, $\theta_R \approx 3 \text{ K}$, $\approx \frac{V}{\Lambda^3}$, $\Lambda \sim 10^{-11} \text{ m}$
(note: $\frac{kT}{hc} \sim 200 \text{ cm}^{-1}$)
 $q \approx \frac{T}{2\theta_R}$
 $\theta_V \approx 3000 \text{ K}$

6) $Q = \frac{q^n}{n!}$

7) $A = -kT \ln Q$

8) $S = -\left(\frac{\partial A}{\partial T}\right)_{V,n} = k \ln Q + kT \frac{\partial \ln Q}{\partial T}$