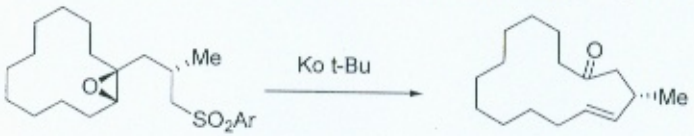
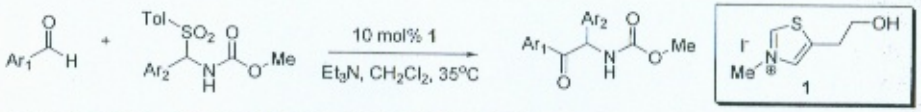
1. Fishi and Branca have reported the annulation reaction sequence shown below.



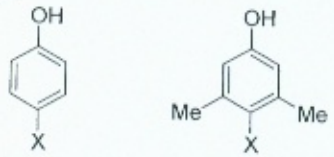
Provide a detailed mechanism for this transformation in the space below.
(*Helv. Chim. Acta.* **1976**, *59*, 2443) (8 pts)

2. The reaction illustrated below was reported by Murry and co-worker from the Merck Process Group. Provide a mechanism for this transformation in the space below.



(*J. Am. Chem. Soc.* **2001**, *123*, 9696-9697) (9pts)

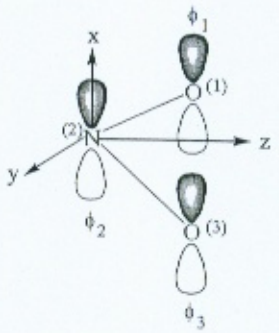
3. The acidity of **1a** and **2a** are almost the same but **1b** is stronger than **2b**. Why? (8 pts)



1a X=CN
1b X=NO_2

2a X=CN
2b X=NO_2

(1) For the three p_x orbitals (ϕ_1, ϕ_2 and ϕ_3) of nitrite ion as plotted below, (十五分)

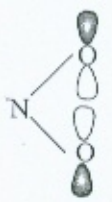


(a) Obtain the total representations and symmetry symbols using the following C_{2v} character table

C_{2V}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1
Γ				

(b) Using SALC (symmetry adapted linear combination) method to obtain three wave functions which represent the 3 MO of this ion. The projection operator is $\hat{P} = \frac{\ell}{h}\sum_R X_R \hat{R}$.

(c) Assign properly the three wavefunctions to the 3 MO structures as presented below

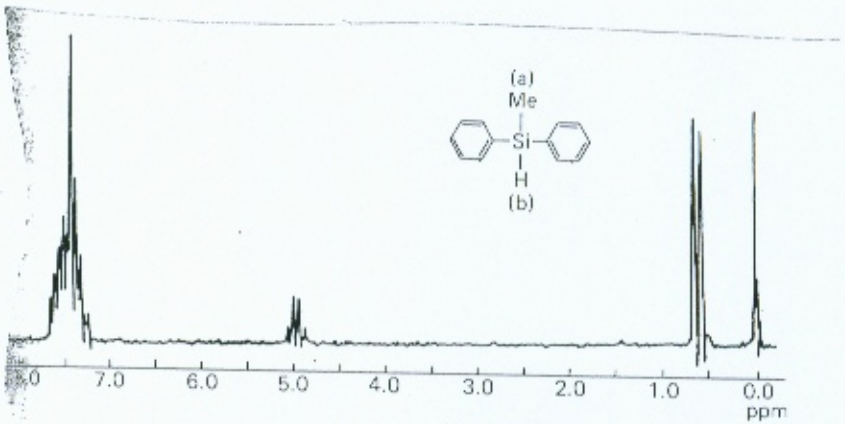


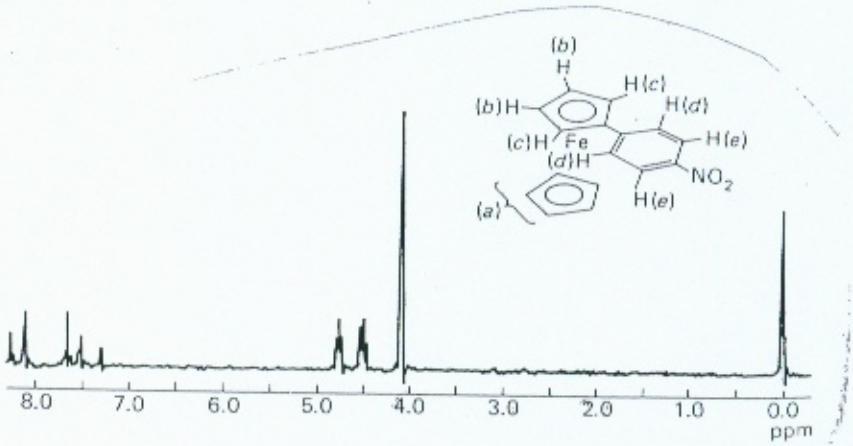
$\psi_1 = ?$

$\psi_2 = ?$

$\psi_3 = ?$

(2) Given the following ^1H nmr spectra & molecular structure, assign all peaks: (十分)


(a)
Me
Si
H
(b)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm


(b)
H
H(c)
(b)H
H(d)
(c)H
Fe
H(e)
(d)H
NO2
(a)
H(e)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

1. Consider the following sequential reaction scheme:

$$A \xrightarrow{k_A} I \xrightarrow{k_I} P$$

Assuming that only reactant A is present at $t = 0$, what is the expected time dependence of [P] using the steady-state approximation? (7%)

2. Assume that a particle is confined to a box of length a, and that the ground state wave function is $\psi(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$.

a) What is the probability of finding the particle in the central third of the box? (4%)

b) Is this state an eigenfunction of the position operator? (4%)

c) Calculate the average value of the position $\langle x \rangle$ that would be obtained for a large number of measurements. (4%)

Hint: You will use the standard integral

$$\int \sin^2 bx dx = \frac{1}{2}x - \frac{1}{4b}\sin 2bx \quad \text{and} \quad \int x(\sin bx)^2 dx = \frac{x^2}{4} - \frac{\cos 2bx}{8b^2} - \frac{x \sin 2bx}{4b}$$

3. Please describe three laws of thermodynamics in your words. (6%)

1.(10 pt) Define: a) DSC b) EI c) HPLC d) COSY e) ICP

2.(5 pt) What is a guard column in partition chromatography?

3.(5 pt) How do multichannel diode-array and double-beam of UV differ?

4.(5pt) How will $\triangle E$ for an isolate ^{13}C nucleus compare with that of a ^{1}H nucleus?