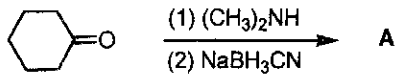
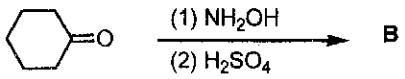
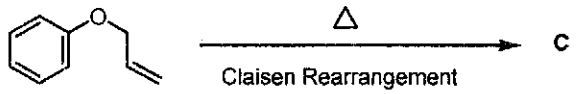
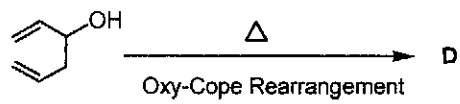
『有機化學』部份　總分 50 分

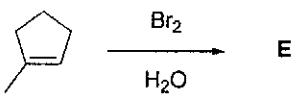
1. **(10 points, 2 points each)** Predict the major product of each step in the following reactions:



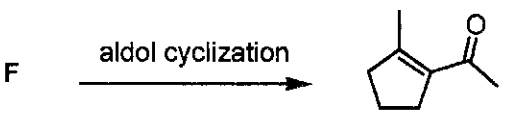


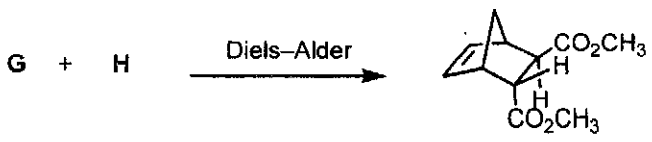






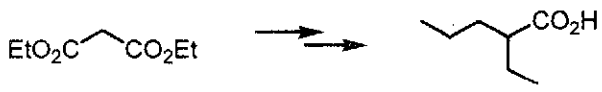
2. **(4 points, 2 points each)** Predict the starting compound(s)for the following reactions:



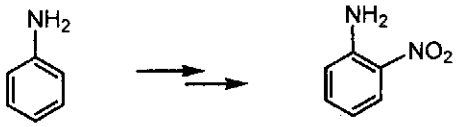


3. **(8 points, 2 points each)** Outline all steps in a synthesis of the following compounds.

(a)

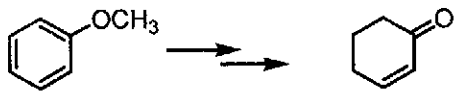


(b)



(c)

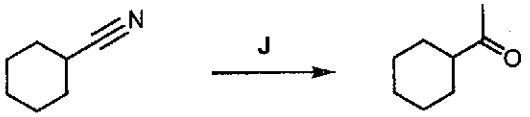
(d)



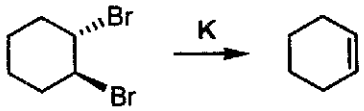
4. **(6 points. 2 points each)** Suggest a reagents (or a series of reagents) that can be used to accomplish the following transformation:

(a)

(b)

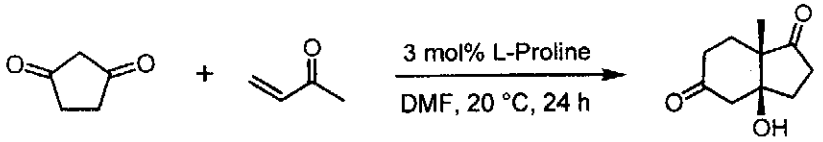


(c)

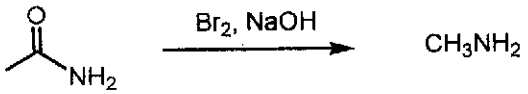


5. **(14 points, 2 point each)** Please provide the reasonable mechanism for the following reactions:

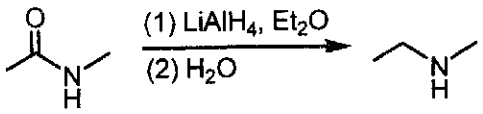
(a)



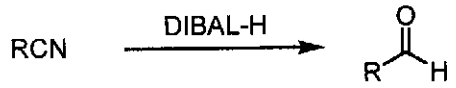
(b)



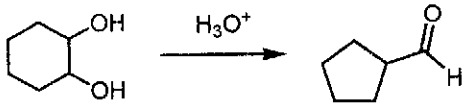
(c)



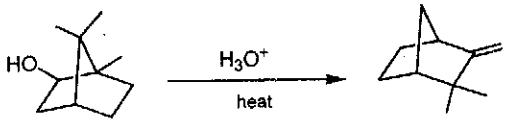
(d)



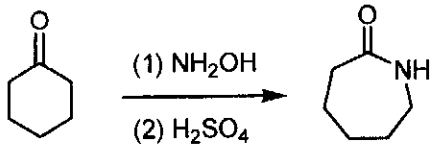
(e)



(f)



(g)



6. **(4 point)** Phenyl bromide is unreactive in either S_N2 or S_N1 reactions. Please draw the structure and provide explanations for this behavior.

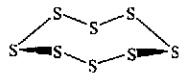
7. **(4 point)** Compound **L** has the molecular formula $C_4H_8O_2$. The broad-band-decoupled ^{13}C spectrum is shown as following: ^{13}C NMR ($CDCl_3$): δ 170.3 (C), 61.0 (CH_2), 20.7 (CH_3), 14.1 (CH_3). The ^1H NMR spectra shown as following: 1H NMR ($CDCl_3$): δ 4.12 (q), 2.01 (s), 1.30 (t). Propose the structure for **L**.

『無機化學』部分　總分 50 分

1. Explain the trend for HBr (mp = -86 °C), $HBr{\cdot}H_2O$ (mp = -4 °C), and $HBr{\cdot}4H_2O$ (mp = -56.8 °C). (5 points)

2. A nitrogen atom with three p electrons could have three unpaired electrons (high-spin), or one unpaired electron only (low-spin). Find the Coulombic and exchange energies for the atom. Which arrangement would be lower in energy ? (5 points)

3. Please assign the point group.
(a) Cyclohexane (chair form), (b) Cyclohexane (boat form), (c) S_8 (puckered ring), (d) 69. (6 points)



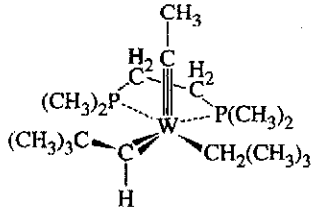
4. Determine the number of IR-active C-O stretching vibrations for (a) *fac*-$[Mo(CO)_3(NCCH_3)_3]$ and (b) *mer*-$[Mo(CO)_3(NCCH_3)_3]$. (6 points)

5. Analysis of ClF_3 gives the reducible representation (Γ):
(a) What is Γ ?
(b) Reduce Γ to its irreducible representations.
(c) Classify the irreducible representations into translational, rotational, and vibrational modes.
(d) Which vibrational modes are infrared active ? (6 points)

6. Given rational accounts for the following observations :
(a) The formation constant for the addition of a third molecule of en to Cu^{2+} is much lower than for Ni^{2+},
(b) Tetrahedral complexes are much more common for Co^{2+} than for Ni^{2+},
(c) Ligands such as CO and phosphines tend to stabilize the low oxidation states of the transition metals.
(6 points)

7. Please order the M-C distances for complexes $(\eta^5\text{-}C_5H_5)_2M$ (M = Fe, Co, Ni). (4 points)

8. Electron count. (a) $(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)Fe(PPh_3)$, (b) $(CO)_3Fe(\mu\text{-}CO)_3Fe(CO)_3$ (has a single metal-metal bond), (c) $ReO_3(H)$, (d) (6 points)



9. Please depict the electronic transition in the $I_2{\cdot}D$ (D : donor) adduct (I_2 : LUMO - $9\sigma_u^*(5p)$; HOMO - $4\pi_g^*(5p)$) and indicate the donor-acceptor and charge-transfer transitions and also predict the energy order of the donor-acceptor transition for I_2 in hexane (a), methanol (b) and aqueous KI (c). (6 points)

D_{nh} GROUPS

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	$(x^2 - y^2, xy)$
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		$x^2 - y^2$
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

C_{nv} GROUPS

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	−1	R_z	
E	2	−1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)