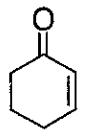
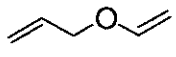
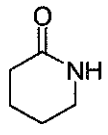
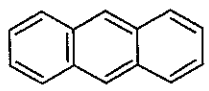
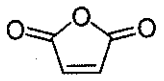
『有機化學』部份　總分50分

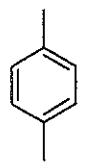
1. Give the expected major product with appropriate stereochemistry, if necessary. (2 pts each, 16 pts)

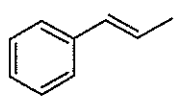
(1)  $\xrightarrow{Me_2CuLi}$

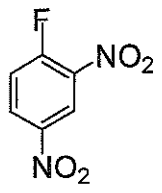
(2)  $\xrightarrow[\Delta]{}$

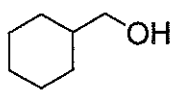
(3)  $\xrightarrow[2.\ H_2O]{1.\ LiAlH_4}$

(4)  $\xrightarrow[\Delta]{}$ 

(5)  $\xrightarrow[2.\ H_3O^+]{1.\ KMnO_4,\ ^-OH,\ \Delta}$

(6)  $\xrightarrow[RO\text{-}OR,\ \Delta]{HBr}$

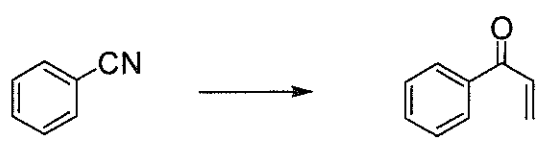
(7)  $\xrightarrow[\Delta]{NH_2NH_2}$

(8)  $\xrightarrow{\text{Jones reagent}}$

2. Suggest a reagents (or a series of reagents) that can be used to accomplish the following one transformation (3 pts each, 24 pts)

(1) 

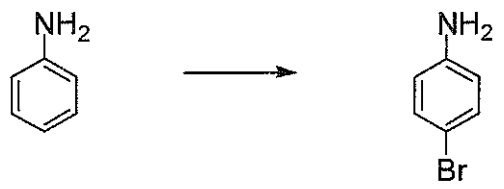
(2) 

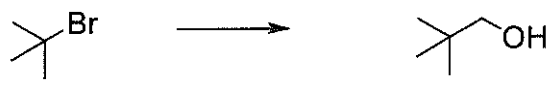
(3) 

(4) 

(5) 

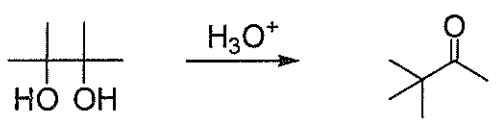
(6) 

(7) 

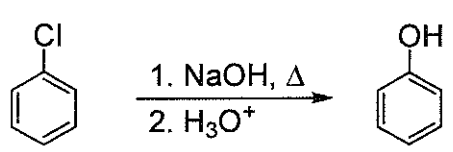
(8) 

3. Propose a mechanism for the following reactions. (3 pts each, 6 pts)

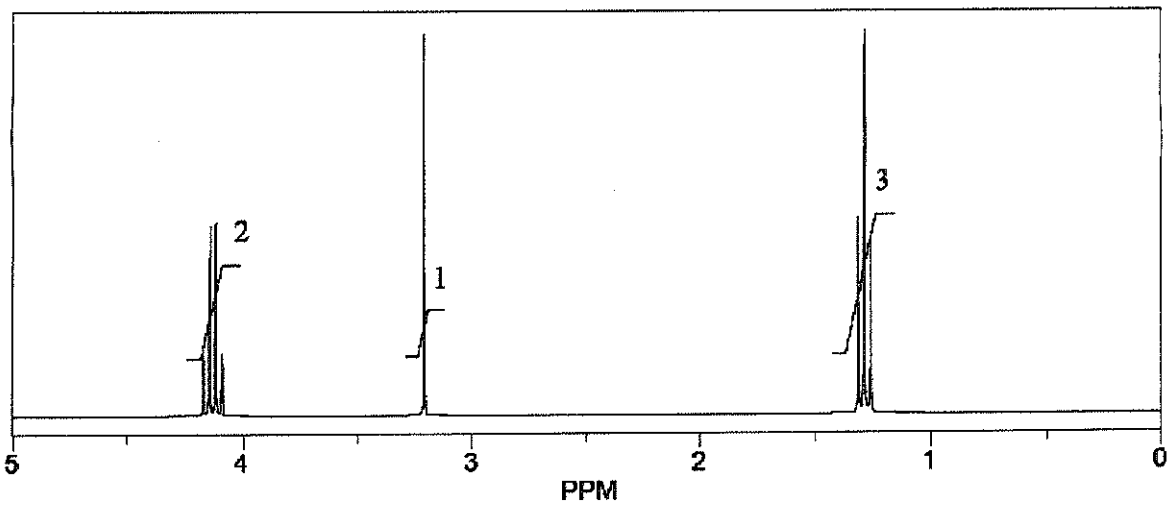
(1)



(2)



4. What is the structure of the compound in the following ^1H NMR spectrum with the molecular formula $C_7H_{12}O_4$? The ^{13}C NMR spectrum shows peaks at 14.1, 40.8, 61.0 and 166.8 ppm. Relative integration is shown. (4 pts)



科目：無機化學

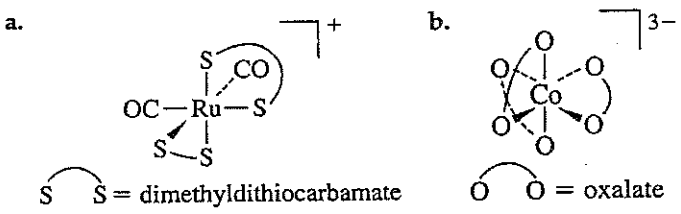
1. Please assign the point groups. (6 points)
a. SF_4 _____ b. B_3H_8 _____ c. d_{x2-y2} _____.

2. Determine the number of IR-active C-O stretching vibrations for (a) *cis*-$FeCl_2(CO)_4$ and (b) *trans*-$FeCl_2(CO)_4$; Character Table is shown in the next page. (6 points)

3. Please order the bond angles for (a) PF_3, PCl_3, and PBr_3 and (b) H_2O, H_2S, and H_2Se. (4 points)

4. Determine the hybrid-orbital type of the central atom in PF_5 and $[PtCl_4]^{2-}$ (a square-planar ion); Character Table is shown in the next page. (6 points)

5. Assign absolute configurations (Λ or Δ) to the following: (4 points)



6. Determine the ground terms for high- and low-spin d^4 configurations in O_h symmetry. (4 points)

7. (a) The complexes $[Co(NH_3)_5X]^{2+}$ (X = Cl, Br, I) have charge transfer to metal bands. Which of these complexes would you expect to have the lowest-energy charge-transfer band ? Why ? (b) For the isoelectronic series $[V(CO)_6]^-$, $Cr(CO)_6$, and $[Mn(CO)_6]^+$ would you expect the energy of metal to ligand charge-transfer bands to increase or decrease with increasing charge on the metal ? Why ? (5 points)

8. (a) Account for the following trend in IR frequencies:
$[Cr(CN)_5(NO)]^{4-}$ $\nu(NO) = 1515\ cm^{-1}$
$[Mn(CN)_5(NO)]^{3-}$ $\nu(NO) = 1725\ cm^{-1}$
$[Fe(CN)_5(NO)]^{2-}$ $\nu(NO) = 1939\ cm^{-1}$
(b) The ion $[RuCl(NO)_2(PPh_3)_2]^+$ has N-O stretching bands at 1687 and 1845 cm^{-1}. The CO stretching bands of dicarbonyl complexes typically are much closer in energy. Explain. (4 points)

9. Determine the unknown quantity: (6 points)
(a) $[(\eta^5\text{-}C_5H_5)W(CO)_x]_2$ (has a W-W single bond)
(b) $Br(CO)_yRe{=}C(OCH_3)_2$
(c) $[(CO)_3Ni\text{-}Co(CO)_3]^z$

10. The compound $Fe(CO)_4I_2$ reacts with cyanide in methanol solution to form complex **A**, which has intense IR bands at 2096 and 2121 cm^{-1} and less intense bands at 2140 and 2162 cm^{-1}. Reaction of **A** with additional cyanide yields **B**. Ion **B** also has two pairs of infrared bands, a more intense pair at 1967 and

2022 cm^{-1} and a less intense pair at 2080 and 2106 cm^{-1}. Neither **A** nor **B** contains iodine. Propose structures of **A** and **B**. (5 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)