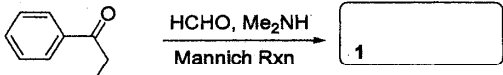
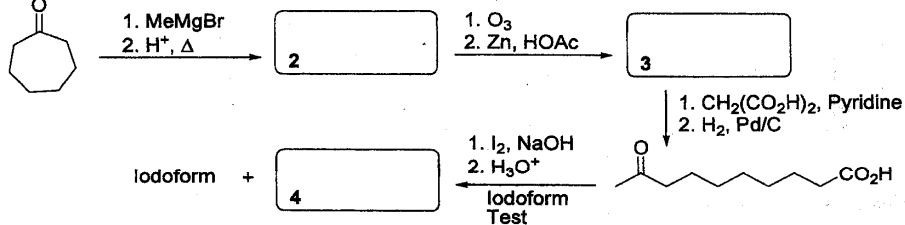


本節考題分兩部分：第一部分 有機化學 及 第二部分 無機化學

第一部分 有機化學 (共五十分；答案請依題號順序寫在答案卷上)

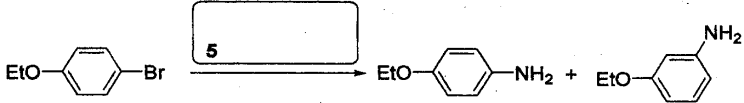
I. Complete the following syntheses. (2 points each, 30 points)

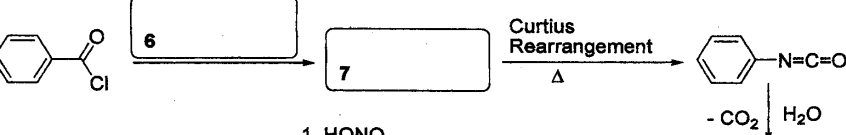
- 

1. CC(=O)c1ccccc1  $\xrightarrow[\text{Mannich Rxn}]{\text{HCHO, Me}_2\text{NH}}$  1
- 

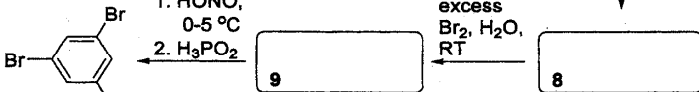
2. C1CCCCC1C=O  $\xrightarrow[2. \text{H}^+, \Delta]{1. \text{MeMgBr}}$  2  $\xrightarrow[2. \text{Zn, HOAc}]{1. \text{O}_3}$  3

3  $\xrightarrow[2. \text{H}_2, \text{Pd/C}]{1. \text{CH}_2(\text{CO}_2\text{H})_2, \text{Pyridine}}$  CCCCCCCC(=O)C(=O)O

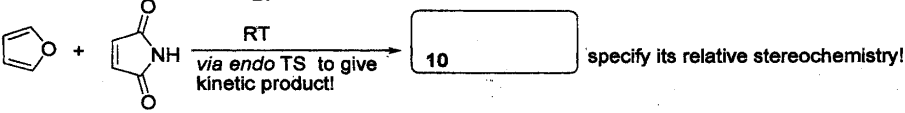
CCCCCCCC(=O)C(=O)O  $\xrightarrow[2. \text{H}_3\text{O}^+]{1. \text{I}_2, \text{NaOH}}$  Iodoform + 4
- 

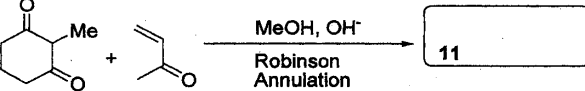
3. CCOC1=CC=C(Br)C=C1  $\xrightarrow{\text{5}}$  CCOC1=CC=C(N)C=C1 + CCOC1=CC=C(N)C=C1
- 

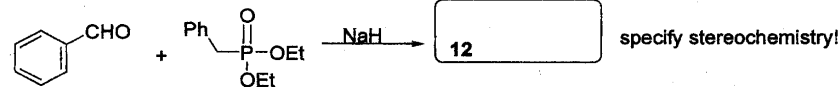
4. ClC(=O)c1ccccc1  $\xrightarrow{\text{6}}$  7  $\xrightarrow[\Delta]{\text{Curtius Rearrangement}}$  N=C=Oc1ccccc1


N=C=Oc1ccccc1  $\xrightarrow[-\text{CO}_2, \text{H}_2\text{O}]{} \text{8}$
- 

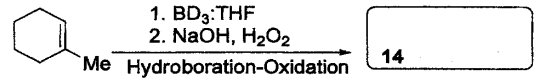
5. BrC1=CC(Br)=CC(Br)=C1  $\xrightarrow[2. \text{H}_3\text{PO}_2]{1. \text{HONO, 0-5 }^\circ\text{C}}$  9

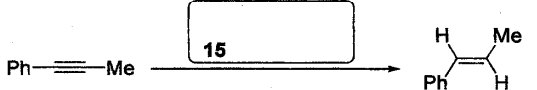
9  $\xrightarrow[\text{RT}]{\text{excess Br}_2, \text{H}_2\text{O}}$  8
- 

6. C1=CC=COC1 + O=C1NC(=O)C=C1  $\xrightarrow[\text{via endo TS to give kinetic product!}]{\text{RT}}$  10 specify its relative stereochemistry!
- 

7. CC1CCCCC1=O + CC=CC=O  $\xrightarrow[\text{Robinson Annulation}]{\text{MeOH, OH}^-}$  11
- 

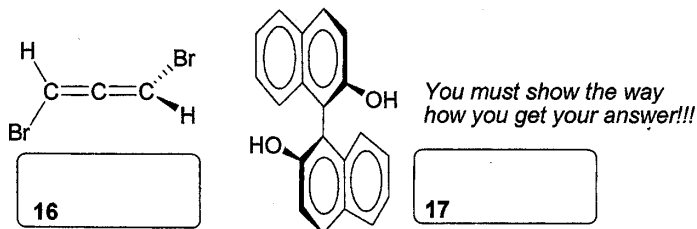
8. O=Cc1ccccc1 + CCOP(=O)(OCC)Cc1ccccc1  $\xrightarrow{\text{NaH}}$  12 specify stereochemistry!
- 

9. CCC=C  $\xrightarrow{\text{HBr, cat. ROOR}}$  13
- 

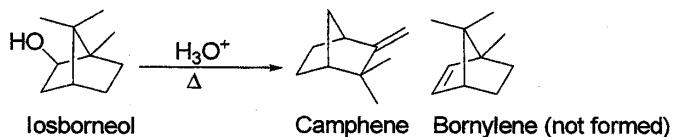
10. CC1=CCCCC1  $\xrightarrow[2. \text{NaOH, H}_2\text{O}_2]{1. \text{BD}_3:\text{THF}}$  14
- 

11. CC#Cc1ccccc1  $\xrightarrow{\text{15}}$  C/C=C/c1ccccc1

II. Give (*R*) and (*S*) designations for the following chiral compounds. (4 points)



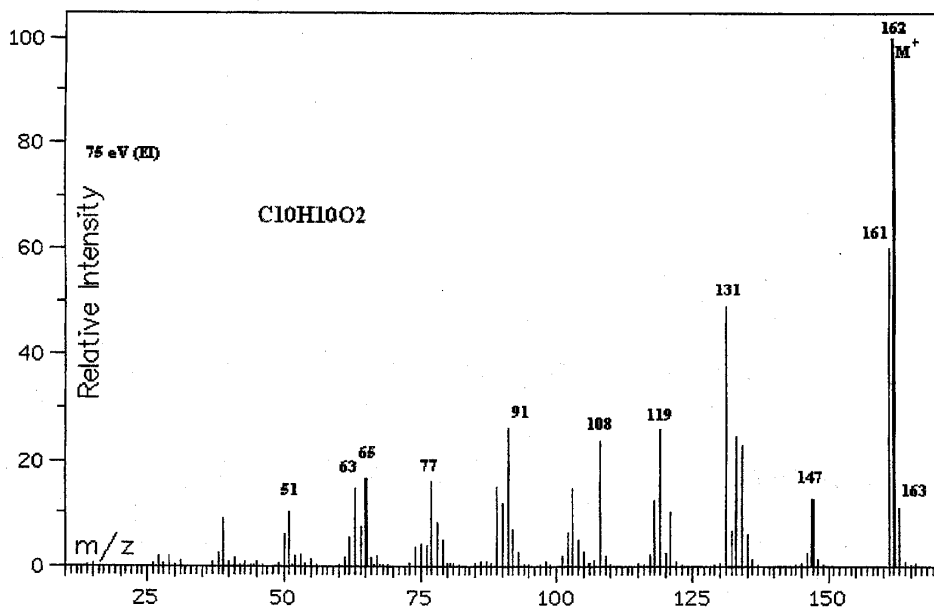
III. When isoborneol heated with 9 M H<sub>2</sub>SO<sub>4</sub>, the product is camphene and not bornylene. Please write a step-by-step mechanism showing how camphene is formed. (5 points)

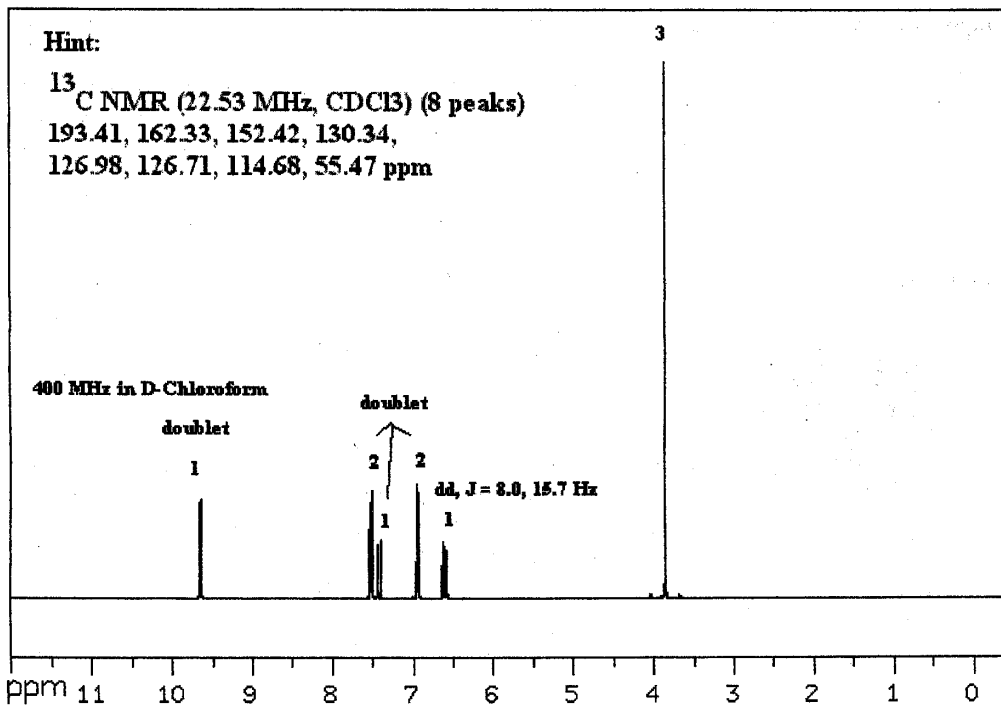
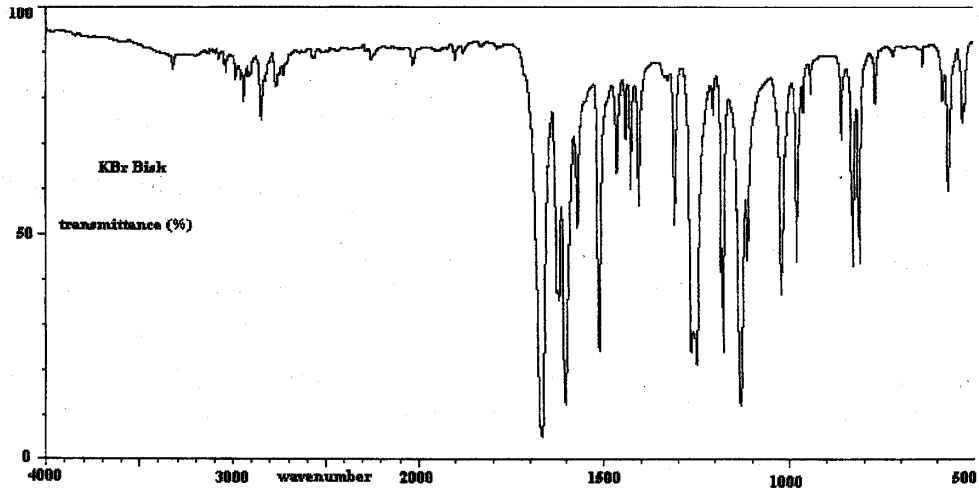


IV. Please explain the following glossary briefly. (6 points)

- (a) Hammond-Leffler Postulate:
- (b) Hückel's Rule:
- (c) Atropisomerism:

V. Propose a structure for the compound (C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>) whose spectra are shown below. (5 points) Please show "index of the hydrogen deficiency" of this compound and the way how you get the answer.

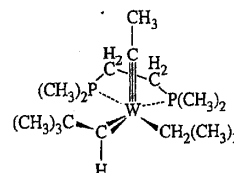




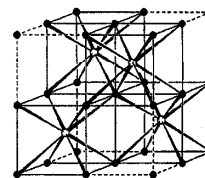
第二部分 無機化學

VI. 單選題，共 7 題，每題 2 分，答錯不倒扣。

1. What is the electron count for the complex shown on the right?  
 (A) 14, (B) 15, (C) 16, (D) 17, (E) 18.



2. Using the diagram of unit cells shown on the right, count the numbers of atoms at each type of position (corner, edge, face, internal) and each atom's fraction in the unit cell to determine the formulas ( $M_mX_x$ ) of the compounds represented. Open circles represent cations and closed circles represent anions.  
 (A)  $M_2X$ , (B)  $MX$ , (C)  $MX_2$ , (D)  $M_2X_3$ , (E)  $MX_3$ .



3. Which has the least solubility?  
 (A)  $LiF_{(s)}$ , (B)  $LiI_{(s)}$ , (C)  $AgF_{(s)}$ , (D)  $AgI_{(s)}$ , (E) all are the same.

4. About  $[Re(CO)_3(PCy_3)_2]$  [ $PCy_3$  = tri(cyclohexyl)phosphine] and  $[(CO)_5Re-Re(CO)_5]$ , which is not correct?

- (A)  $[Re(CO)_3(PCy_3)_2]$  does not obey 18 electron rule,
- (B)  $[(CO)_5Re-Re(CO)_5]_2$  obeys 18 electron rule,
- (C)  $[Re(CO)_3(PCy_3)_2]$  is paramagnetic,
- (D)  $[(CO)_5Re-Re(CO)_5]$  is paramagnetic,
- (E) there is a formal metal—metal (single) bond in  $[(CO)_5Re-Re(CO)_5]$ .

5. The orbital splitting ( $\Delta_o = 10 Dq$ , O : octahedral field), please calculate the CFSE (crystal field stabilization energy) of high-spin  $d^4$  ion,

- (A) -4, (B) -6, (C) -8, (D) -10, (E) -12 Dq.

6.  $[Ir(NCS)(NH_3)_5]^{2+}$  and  $[[Ir(SCN)(NH_3)_5]^{2+}$  belong to :

- (A) hydrate isomerism, (B) coordination isomerism, (C) linkage isomerism, (D) ionization isomerism, (E) geometrical isomerism.

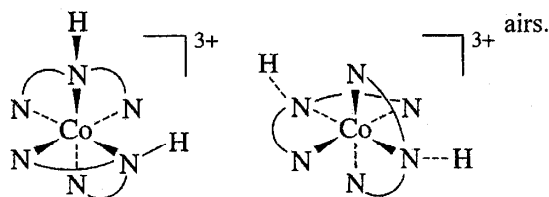
7. Please order the spectrochemical series : (1)  $NH_3$ , (2)  $CO$ , (3)  $OH^-$ , (4)  $H_2O$ .

- (A) (1)>(2)>(3)>(4), (B) (2)>(1)>(3)>(4), (C) (2)>(1)>(4)>(3), (D) (2)>(3)>(4)>(1), (E) (2)>(3)>(1)>(4).

VII. 非選擇題，共 6 題，每題 6 分。

1. (a)  $Cr(CO)_5PF_3$ ,  $Cr(CO)_5PCl_3$ , and  $Cr(CO)_5PBr_3$ , which would you expect to have the shortest C-O bond?  
 (b)  $[Cr(CO)_6]$ ,  $[V(CO)_6]^-$ , and  $[Mn(CO)_6]^+$ , which has the lowest stretching frequency?

2. Identify the  $\Delta$  and  $\lambda$  chirality of the rings for (a) and (b)



3. The microstates for  $d^2$  and its reduction to free-ion terms.

(a) (b)

4. Please explain :

- (a) The Lanthanide contraction.

(b) Spin pairing is much more common for 2<sup>nd</sup> and 3<sup>rd</sup> row transition metal complexes than for the 1<sup>st</sup> row series. Why?

5. Tetrahedral complexes often absorb more strongly than octahedral complexes of the same metal in the same oxidation state. Why? Vibronic coupling often provides a way to relax the Laporte selection rule. Why?

6. Give the point groups of the following compounds : (a) C<sub>6</sub>H<sub>6</sub>F<sub>2</sub>Cl<sub>2</sub>Br<sub>2</sub> (on the right)

(b) Cyclohexane (boat form) \_\_\_\_\_, (c) H<sub>3</sub>O<sup>+</sup> \_\_\_\_\_, (d) Diborane (B<sub>2</sub>H<sub>6</sub>) \_\_\_\_\_.

