國立中山大學 109 學年度
碩士暨碩士專班招生考試試題

科目名稱：物理化學及分析化學【化學系碩士班】

物理化學 (50%)

R = 8.3145 J K^{-1} mol^{-1}
1 amu =1.660539040 × 10^{-27} kg
h = 6.626 × 10^{-34} J s

問答題

1. (14%) The $v = 0 \to 1$ vibrational band of ICl occurs at 382 cm^{-1}. Approximating this molecular vibration as a harmonic oscillator, answer following questions: (Atomic weights of I and Cl are 126.9 amu and 35.5 amu, respectively.)
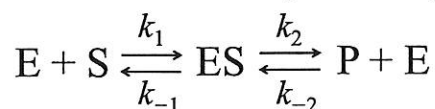(a) Calculate the zero point vibrational energy. (4%)
(b) Calculate the force constant of ICl. (4%)
(c) Calculate the ratio of the $v = 0$ and $v = 2$ populations at 200°C. (4%)
(d) Is the rotational constant, B, of ICl at $v = 1$ the same as that at $v = 0$? And explain why? ($B = \hbar^2/(2I)$, where I is moment inertia) (2%)

2. (15%) A reactant molecule S can be converted into its product P by an enzyme molecule E,

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} P + E$$

where k_1, k_{-1}, k_2 and k_{-2} are rate coefficients. The initial concentrations of E and S are [E]$_0$ and [S]$_0$, respectively. The initial concentrations of P and ES are zero.
(a) Write the rate expressions for [S], [E], [ES] and [P]. (Example: d[S]$/dt$ = ?) (4%)
(b) Prove [E] + [ES] = [E]$_0$. (4%)
(c) Assuming the steady-state approximation for ES, express [ES] in terms of [S], [P], [E]$_0$ and above rate coefficients. (4%)
(d) Continued from (c), prove that d[S]$/dt$ and d[P]$/dt$ is proportional to [E]$_0$. (3%)

3. (15%) Consider the dissociation reaction $H_2O(g) \to H_2(g) + 0.5O_2(g)$, the values of its standard reaction Gibbs energy ($\Delta_r G°$) are +135 kJ/mol at 2000 K and +118 kJ/mol at 2300K. Please answer following questions:
(a) Calculate the equilibrium constants at 2000 K and 2300 K. (5%)
(b) Calculate the reaction enthalpy of this reaction. (5%)
(c) Calculate the mole fraction of H_2, after the dissociation reaction of H_2O at 2300 K and 1 bar finishes. (5%)

4. (6%) Light incident on the surface of a metal causes electrons to be ejected. Answer following questions:
(a) Does the kinetic energy of ejected electrons depend on the frequency or intensity of light? And explain why? (2%)
(b) Does the number of electrons depend on the frequency or intensity of light? And explain why? (2%)
(c) The minimal energy required to remove an electron from a material is called work function. For elements Be, Mg and Ca, which one has the smallest work function? And which one has the largest work function? (2%)

分析化學(50%)

5. (11%) (a) Define: Buffer solution, describe its feature, significance and also possible application. (3%)
(b) Define buffer capacity, use one equation to express the term and explain the meaning for each parameter. (3%)
(c) Describe how you can prepare a buffer solution (1L) with a pH value of 4.5 from 0.9 M of acetic acid with sodium acetate. The K_a of the acetic acid is 1.75×10^{-5}. (5%)

6. (9%) Define the 3 different quantification methods in Analytical Chemistry that is listed below. Describe their principles in details and also give example of applications for how to use these quantification methods? Please also compare their advantages and limitations?
(a) External standard method (3%)
(b) Internal standard method (3%)
(c) Standard addition method (3%)

7. (10%) Calculate the molar solubility of $Ba(IO_3)_2$ in an aqueous solution while it is in the presence of 0.03 M of $Ba(NO_3)_2$ in the solution. $K_{sp} = 1.57 \times 10^{-9}$.

8. (10%) To date, there are many types of mass spectrometric instruments (mass analyzers) that have been developed. Please define the listed mass spectrometers below and also draw their instrumental designs, describe their working principles and also discuss their advantages and limitations for each type.
(a) Ion trap (2%)
(b) Time of flight (2%)
(c) Quadrupole (2%)
(d) Sector (2%)
(e) FTMS (Fourier Transform Mass Spectrometer) (2%)

9. (10%) In Analytical Chemistry, there are many terms that are significant. Please define all the following terms and also give detailed explanation for how to use these terms? Also, their significance must be explained.
(a) LOD (Limit of detection) (2%)
(b) Resolution (2%)
(c) Standard Deviation (please also write down the equation for this term and give meaning for each parameter in the equation (2%)
(d) Linear dynamic range (2%)
(e) CV(coefficient of variation) (2%)

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科目名稱：有機化學及無機化學【化學系碩士班】
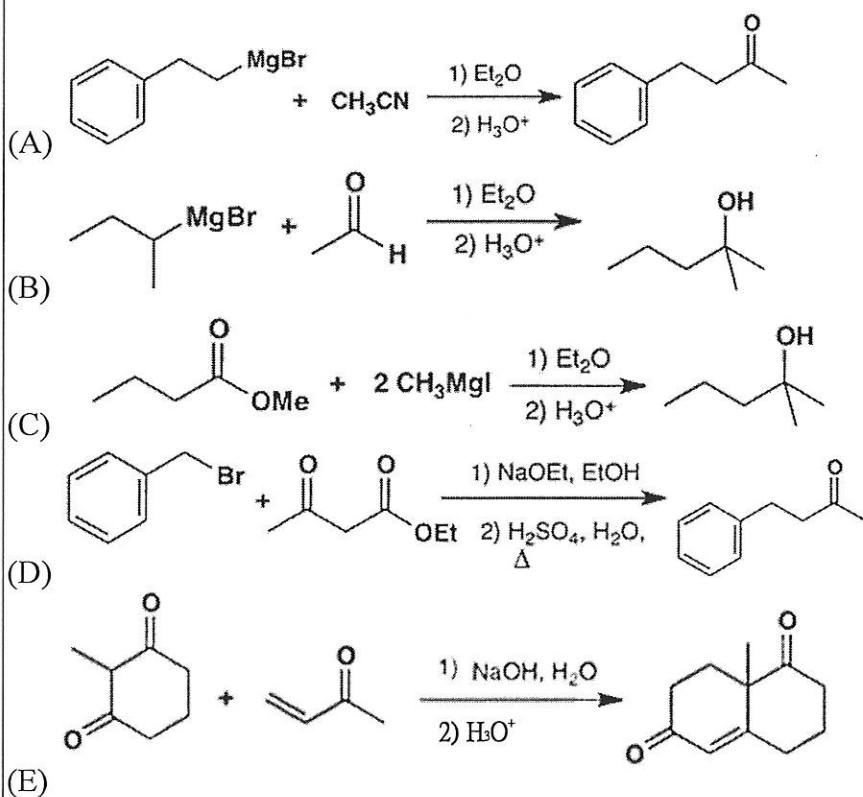
一、單選題（每題 3 分，總計 66 分）

1. Which of the following will **not** be the major product for the following reactions below?
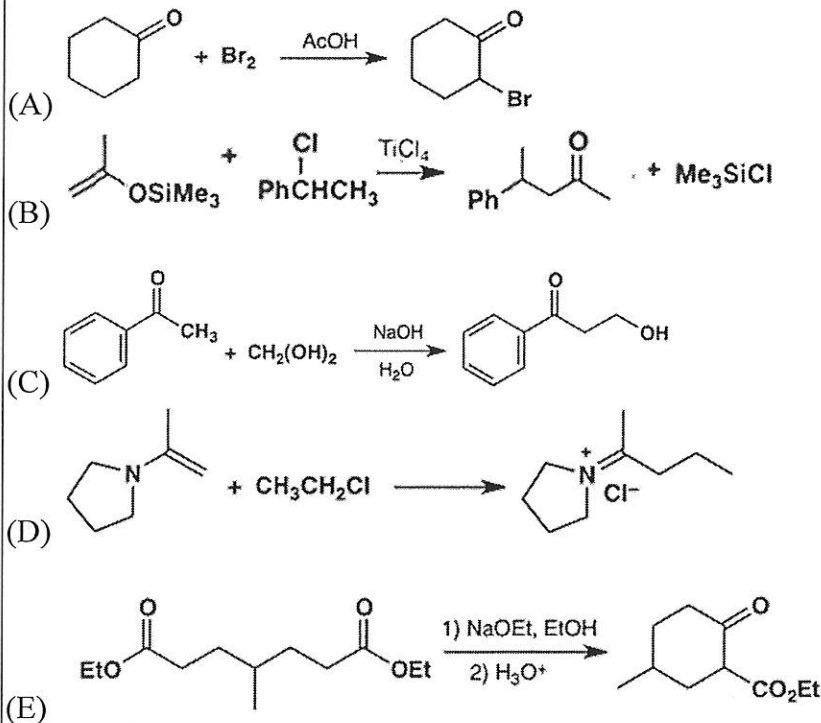
2. Which reaction will **not** give the desire product ?
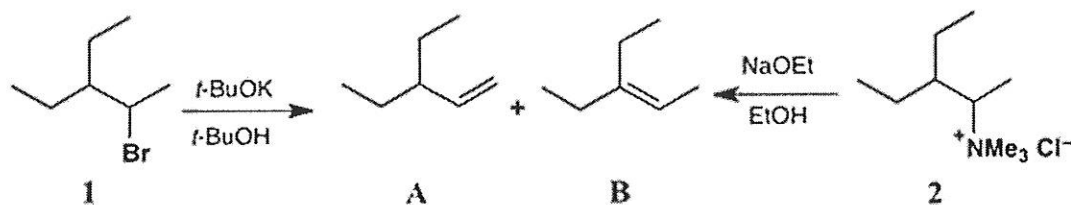
3. Which reaction conditions are **not** appropriate for the following transformation?

(A) Zn (Hg) / HCl　　　　　　(B) H$_2$NNH$_2$ / NaOH　　　　(C) NaNH$_2$, NH$_3$

(D) HSCH$_2$CH$_2$CH$_2$SH / H$^+$, then H$_2$ / Ni　　　(E) 1, NaBH4; 2. TsCl,　3. LiAlH4

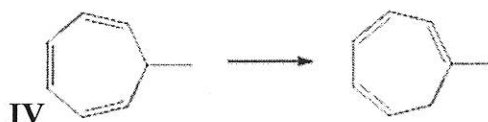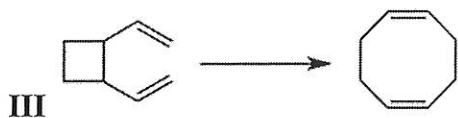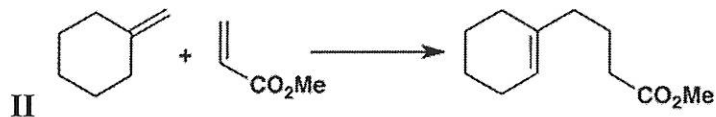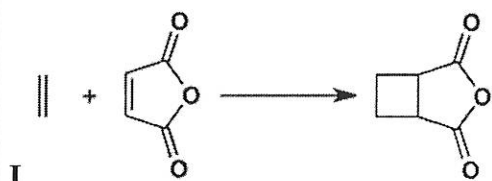4. Which of the following statements best indicates the most probable outcome?

(A) **1** and **2** give **A** as major product　　　(B) **1** and **2** give **B** as major product

(C) **1** give **A** and **2** give **B**　　　(D) **1** give **B** and **2** give **A**　　　(E) **1** and **2** give **A** and **B** complex mixture

5. Which of the following reactions will **not** give rise to racemic mixture or chiral product?
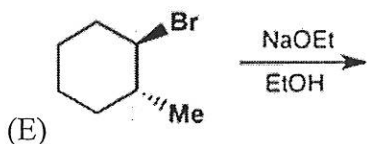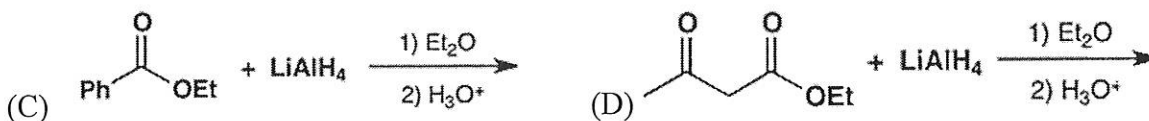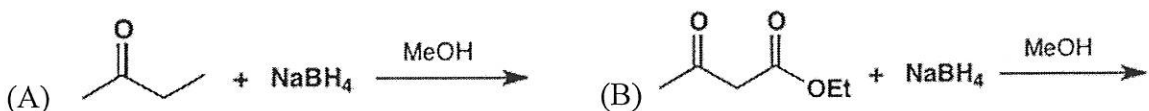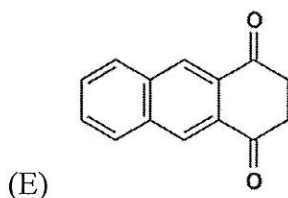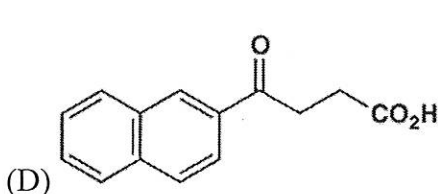
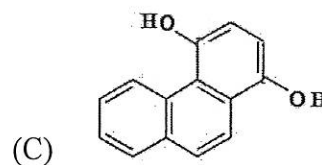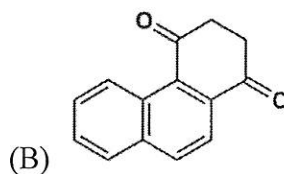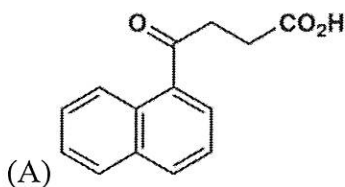6. Which of the following reactions is thermally allowed?

(A) I, II　　　　(B) II, III　　　　(C) III, IV　　　　(D) II, III, IV　　　　(E) IV

7. Which is the **most** probable main product of the following reaction?
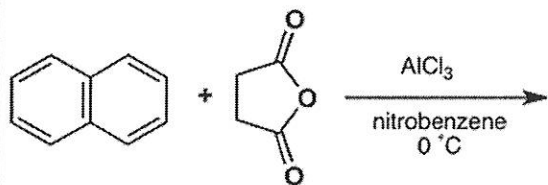
8. Which is the main product of the following reaction?
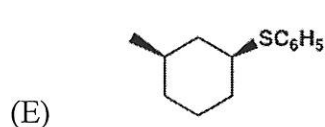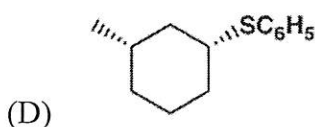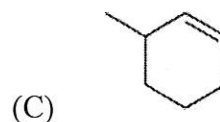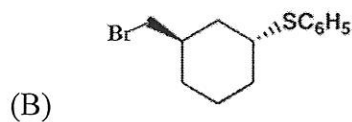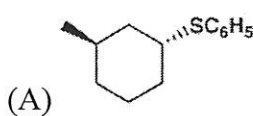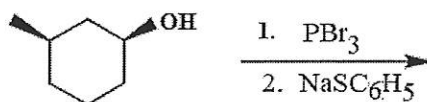
9. In which of the following reaction give the **incorrect** desire product?

(A)

(B)

(C)

(D)

(E)
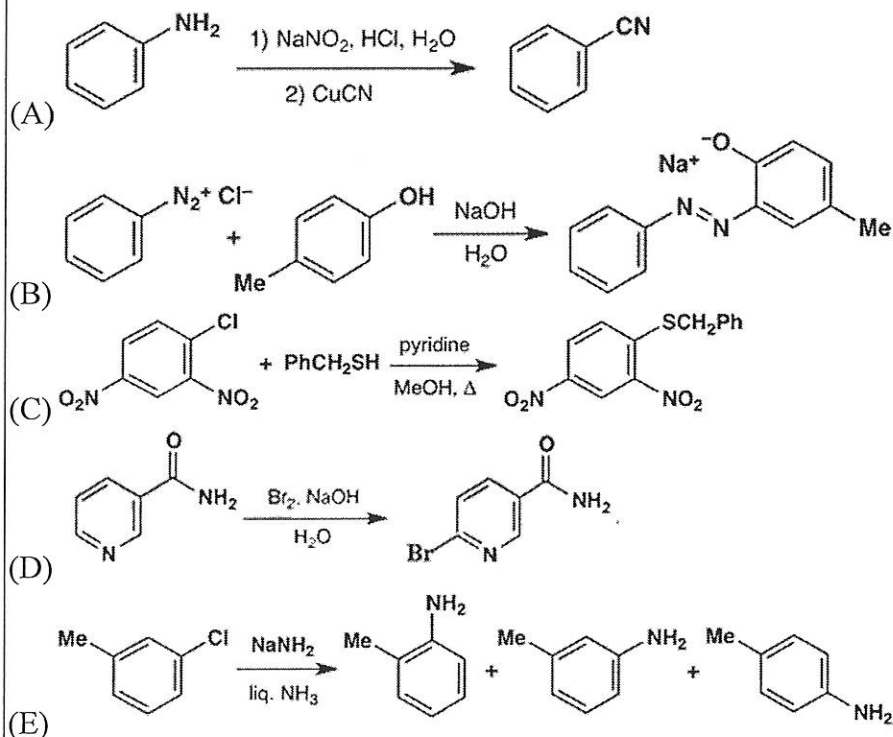
10. Below is a propose synthesis of compound X. Which step would **not** work.
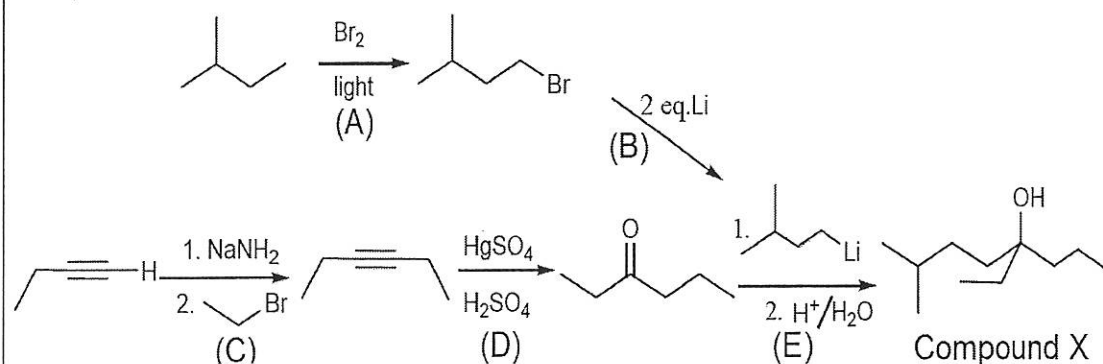
11. Which of the following Newman projections represents *meso*-2,3-dibromobutane?

(A) **I**　　(B) **II**　　(C) **III**　　(D) **IV**　　(E) **I** and **IV**

12. Which structure shown below is consistent with the following NMR spectrum?

A. (HO-C(=O)-CH₂-CH₂-CH₃ drawn)

B. (CH₃-C(=O)-O-CH₂-CH₃ drawn)

C. (H-C(=O)-O-CH(CH₃)₂ drawn)

D. (CH₃-C(=O)-CH₂-O-CH₃ drawn)

E. (tetrahydrofuran-2-yl-methanol with OH drawn)
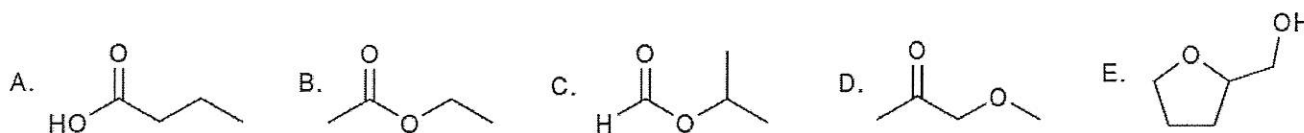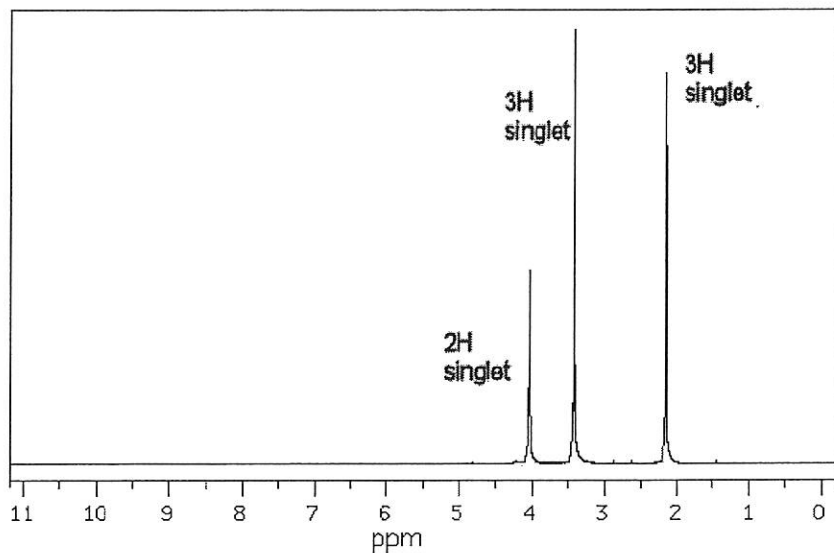
13. What are the effective nuclear charge Z^* on a 5f, 6d, and 7s in a uranium atom?
   (A) 14.3, 2.0, 3.0　　　　　　　(B) 15.3, 3.0, 2.0
   (C) 12.3, 2.0, 2.0　　　　　　　(D) 13.3, 3.0, 3.0

14. The reaction A → B + C is known to be zero order in A with a rate constant of 4.8×10^{-2} mol/L · s at 25 °C. An experiment was run at 25°C where $[A]_0 = 2.0M$. What is the concentration of B after 4.0 s ?
   (A) 1.8 M　　　　(B) $5.5 \times 10^{-1} M$　　　　(C) $1.1 \times 10^{-1} M$　　　　(D) $1.9 \times 10^{-1} M$

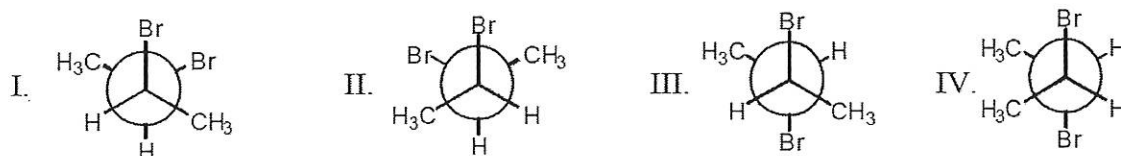15. For As_2P_2, what are the irreducible representations for experimentally observed Raman bands ?

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

   (A) $3A1+A2+B1+B2$　　　　　　(B) $2A1+2A2+B1+B2$　　　　　(C) $2A1+A2+2B1+B2$
   (D) $A1+A2+B1+3B2$

試題請隨卷繳回，請留意背面是否有題

16. What is SALC of b_{2u} molecular orbital consisted of four p orbitals in cyclobutadiene ?

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)	

(A) $\chi_1+\chi_2+\chi_3+\chi_4$ (B) $\chi_1+\chi_2-\chi_3-\chi_4$ (C) $\chi_1-\chi_2+\chi_3-\chi_4$ (D) $\chi_1-\chi_2-\chi_3-\chi_4$

17. What is the enthalpy of formation of MgO, which crystallizes in the NaCl lattice (use the Born–Haber cycle to calculate). Use these data in the calculation: O_2 bond energy = 494 kJ/mol; $\Delta H_{sub}(Mg)$ = 37 kJ/mol. Second ionization energy of Mg = 1451 kJ/mol; second electron affinity of O = -744 kJ/mol.
(A) 2352 kJ mol^{-1} (B) -3934 kJ mol^{-1} (C) -1341 kJ mol^{-1} (D) 1341 kJ mol^{-1}

18. The half-life of ^{14}C is 5730 years. A sample taken for radiocarbon dating was found to contain 56 percent of its original ^{14}C. What was the age of the sample? (Radioactive decay of ^{14}C follows first-order kinetics.)?
(A) 2.2×10^3 (B) 3.1×10^2 (C) 4.8×10^3 (D) 1.1×10^4

19. Which of the following is the free ion terms of d^2 configuration?
(A) $^3G, {}^1F, {}^1D, {}^3P, {}^1S$ (B) $^1G, {}^3F, {}^1D, {}^3P, {}^1S$ (C) $^3G, {}^1F, {}^1D, {}^1P, {}^3S$
(D) $^1G, {}^1F, {}^1D, {}^3P, {}^3S$

20. Which is the correct splitting pattern of d orbitals for $[CuCl_5]^{3-}$ energetically?
(A) $d_{xz} = d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$ (B) $d_{xz} = d_{yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$
(C) $d_{xz} = d_{yz} < d_{x^2-y^2} = d_{xy} < d_{z^2}$ (D) $d_{xy} = d_{x^2-y^2} < d_{xz} = d_{yz} < d_{z^2}$

21. The ^{14}N and ^{15}N derivatives of TpOs(NS)Cl$_2$ [Tp = hydrotris(1-pyrazolyl)borate, a tridentate ligand] have been prepared. The ^{14}N derivative has a nitrogen–sulfur stretch at 1284 cm^{-1}. Predict the N—S stretch for the ^{15}N derivative.
(A) 1314 cm^{-1} (B) 1254 cm^{-1} (C) 1224 cm^{-1} (D) 1194 cm^{-1}

22. Which of the following step is NOT included in the hydroformylation (oxo) process?
(A) β elimination   (B) Addition of CO
(C) Alkyl migration   (D) 1,2-insertion

二、(每題 2 分，總計 10 分)

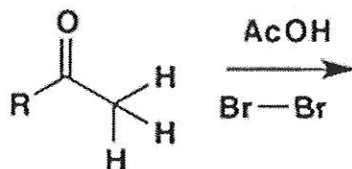Please give the product for the reaction below, illustrating the stereochemistry of the product when necessary.

1.
1. Ph_3P
2. nBuLi, THF
3.

2.
CH_3CH_2OH
HCl

3.
PCC
1. EtMgBr
2. H_3O^+
$Na_2Cr_2O_7$
H_2SO_4, H_2O

4.
Δ

5.
Δ
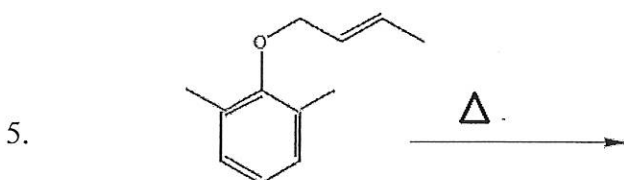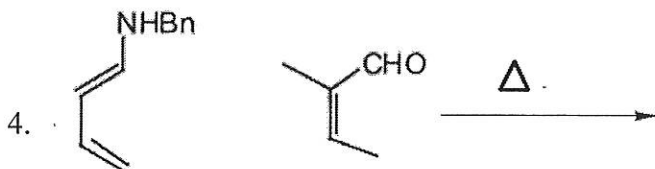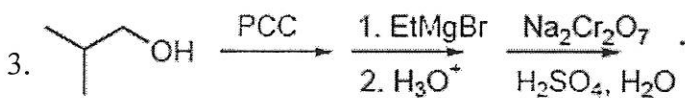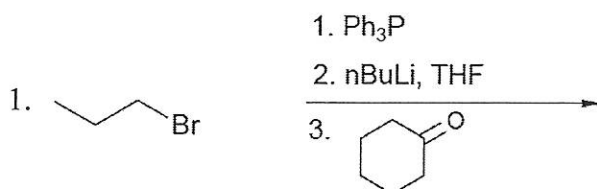
三、(每題 4 分，總計 4 分)

1. Shows a mechanism for the α-bromination of a methyl ketone with bromine in acetic acid. (Include all the lone-pair of electrons)

AcOH
Br—Br

四、(每題 10 分，總計 20 分)

1. Please give the step-by-step reaction mechanism of water gas shift reaction using $Ru(bpy)_2Cl_2$ as a homogeneous catalyst.

2. (a) Please construct the molecular orbital diagram of CO step by step with orbital contour for each. molecular orbital (Potential Energy of C(2s): -19.43; C(2p): -10.66; O(2s): -32.38; O(2p): -15.85; H(1s): -13.61 eV)

(b) Briefly explain the information provided by its photoelectron spectrum of CO including the. meaning of fine structure of photoelectron spectrum in terms of bonding and antibonding characters as well as the difference of the intensity in terms of overlapping of vibrational wavefunction