

HONOUR SCHOOL OF NATURAL SCIENCE

Final Examination

ORGANIC CHEMISTRY OPTION I SAMPLE PAPER

Time: 2 hours

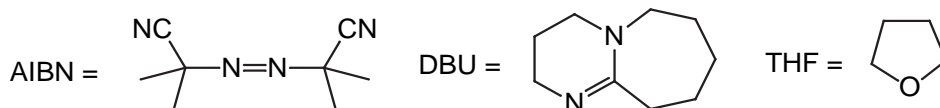
Candidates should answer *two* questions.

Please start each question in a new booklet.

The numbers in square brackets indicate the marks which examiners normally expect to assign to each part of the question.

The following abbreviations have been used:

Me = CH₃-; Et = CH₃CH₂-; *i*-Pr = (CH₃)₂CH-; Bu = CH₃CH₂CH₂CH₂-; *t*-Bu = (CH₃)₃C-;
Ph = C₆H₅-; Bn = C₆H₅CH₂-; Ac = CH₃CO-; Tf = CF₃SO₂-; Ts = 4-MeC₆H₄SO₂-;
Boc = *t*-BuOC(O)-; LDA = LiN*i*-Pr₂; D = deuterium; DEAD = EtO₂CN=NCO₂Et



Aqueous work-up procedures are implied throughout for separate numbered steps of syntheses, with concomitant protonation or deprotonation of charged intermediates. Assume reactions are carried out at room temperature unless otherwise indicated.

A wavy line(~~~~) indicates a mixture of stereoisomers.

Guide to Questions:

1. Asymmetric Synthesis
2. Synthesis
3. Organometallic Chemistry
4. Heteroatom chemistry
5. Materials Chemistry

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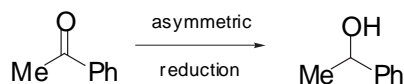
1. Answer *all* parts of this question.

All structures of chiral materials in this question refer to single enantiomers unless otherwise stated.

Part A

(a) With reference to any specific molecules of your choice, define the terms *enantiotopic*, *diastereotopic* and *prochiral*. [3]

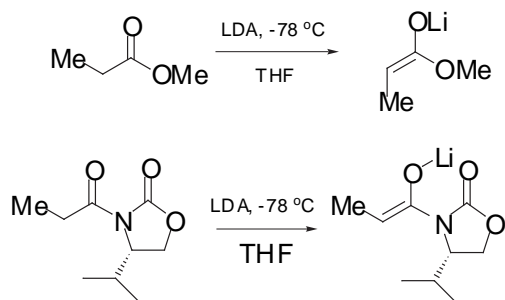
(b) (i) The following compound undergoes asymmetric reduction, whereby hydride is added preferentially to the *Si* face of the ketone. Draw the structure of the major reaction product. [3]



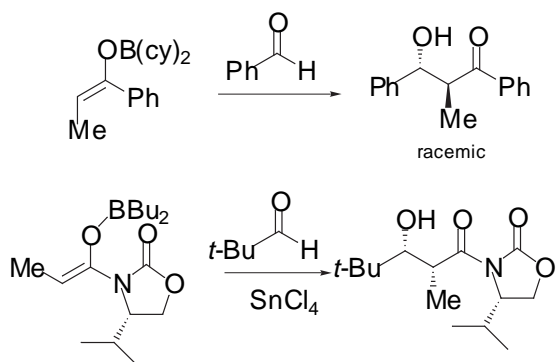
(ii) The determined specific rotation of the isolated reaction product is -0.415 , whereas the specific rotation of the pure single enantiomer is -0.439 under the same conditions. Calculate the e.e. (enantiomeric excess) for this reaction. [3]

Part B

(a) Explain the stereochemistry of the following two enolate forming reactions. [2 x 5]



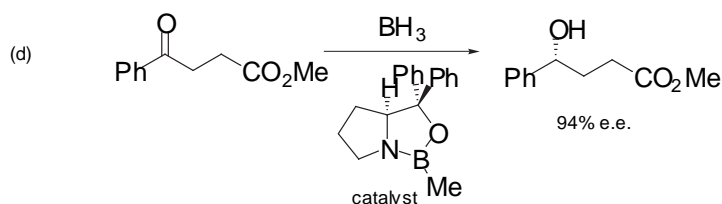
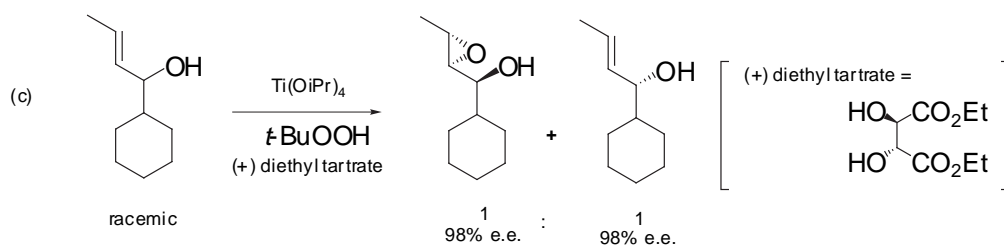
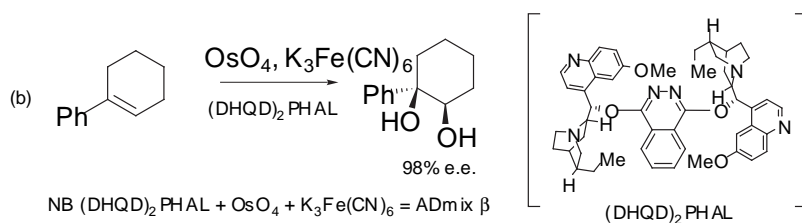
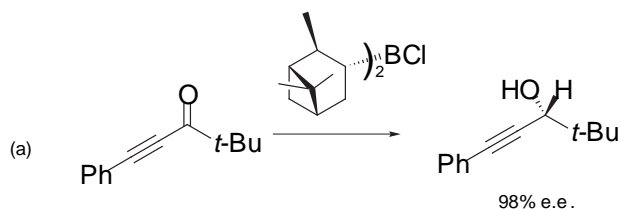
(b) Explain the stereochemical outcome of the two following aldol reactions. [2 x 5]



Part C

Explain *three* of the following reactions involving asymmetric oxidation or reduction. Your answer should include an explanation of how the absolute configuration of the product is derived, either by reference to an approximate transition structure of the reaction, or by detailing a mnemonic where appropriate.

[3 x 7]

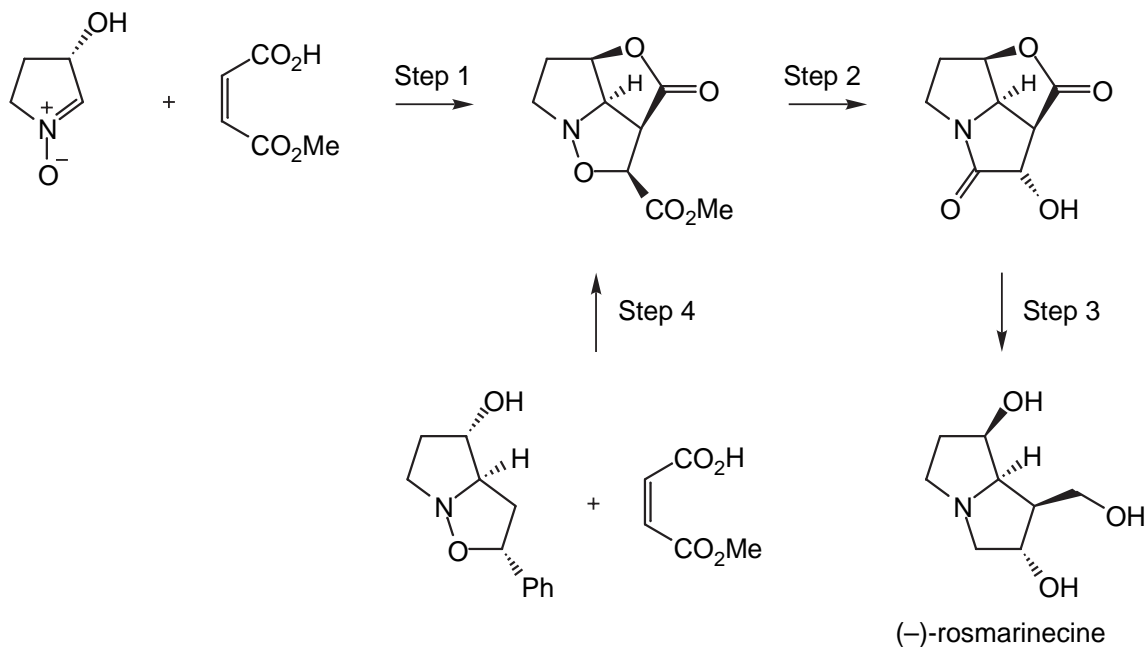


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2. Answer *both* parts **A** and **B** of this question.

Each step may require more than one synthetic transformation.

Part A



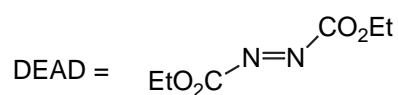
Reagents for selected stages:

Step 1 Ph_3P , DEAD.

Step 2 H_2 , $\text{Pd}(\text{OH})_2$ (cat.).

Step 4 (i) Ph_3P , DEAD

(ii) *o*-dichlorobenzene, reflux

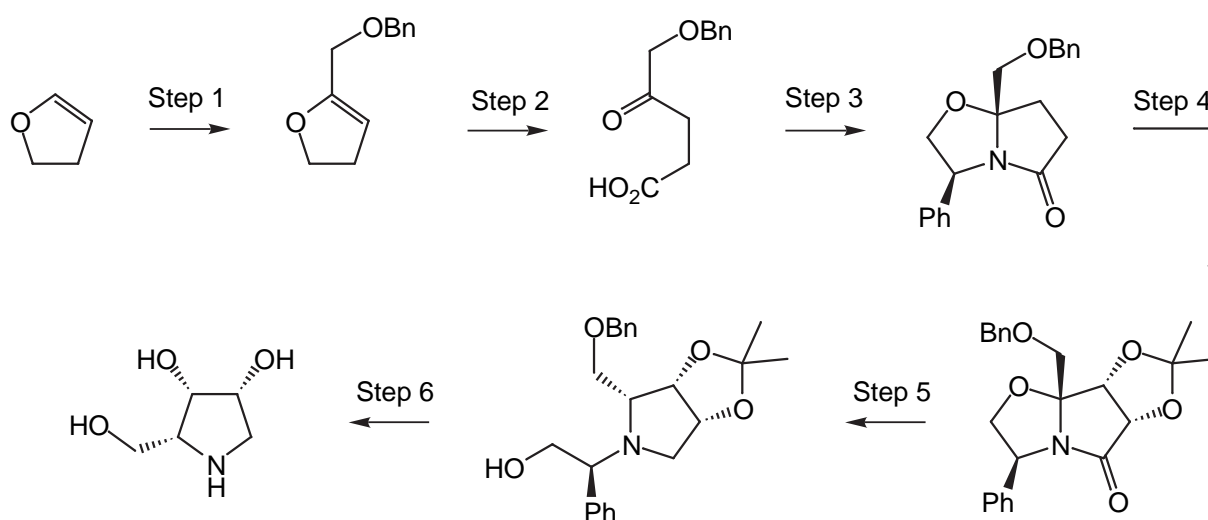


(a) Explain the chemistry in Step 1 and Step 4. [12]

(b) Suggest a mechanism for Step 2. [6]

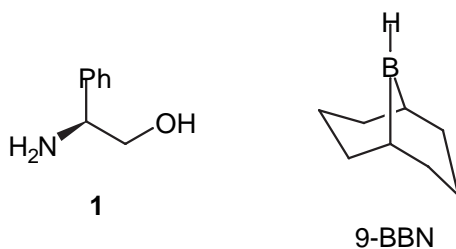
(c) Suggest a reagent for Step 3 and provide a mechanism. [7]

Part B



Reagents for selected stages:

- | | |
|--------|--|
| Step 1 | <i>t</i> -BuLi then BnOCH ₂ Cl. |
| Step 2 | Jones' reagent (aq. H ₂ SO ₄ , CrO ₃ , Me ₂ CO). |
| Step 3 | (<i>S</i>)-phenylglycinol 1 , heat |
| Step 5 | Excess 9-BBN |



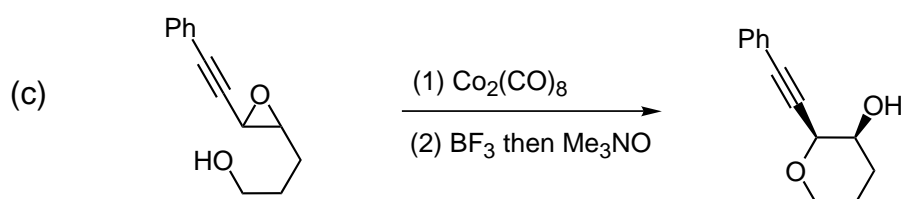
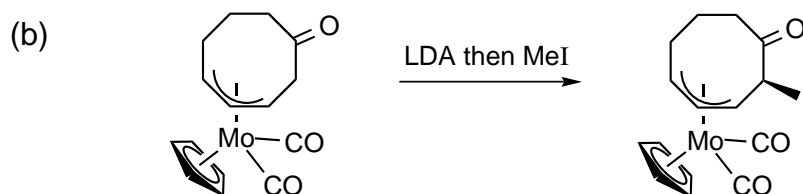
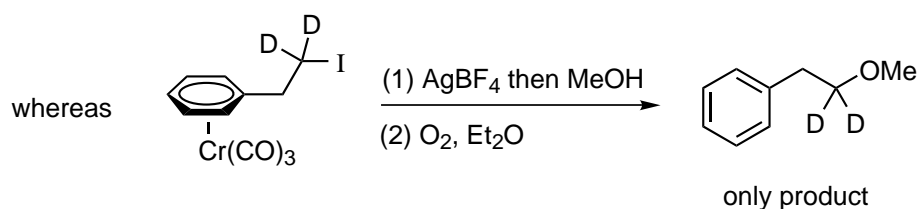
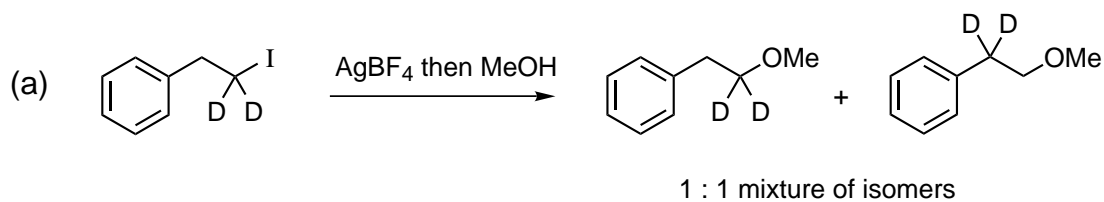
- (a) Explain the chemistry in Steps 1, 2 and 3. [12]
- (b) Suggest reagents for Steps 4 and 6. [6]
- (c) Provide a mechanism for Step 5 and explain the stereochemical outcome. [7]

3. Answer **both** parts **A** and **B** of this question.

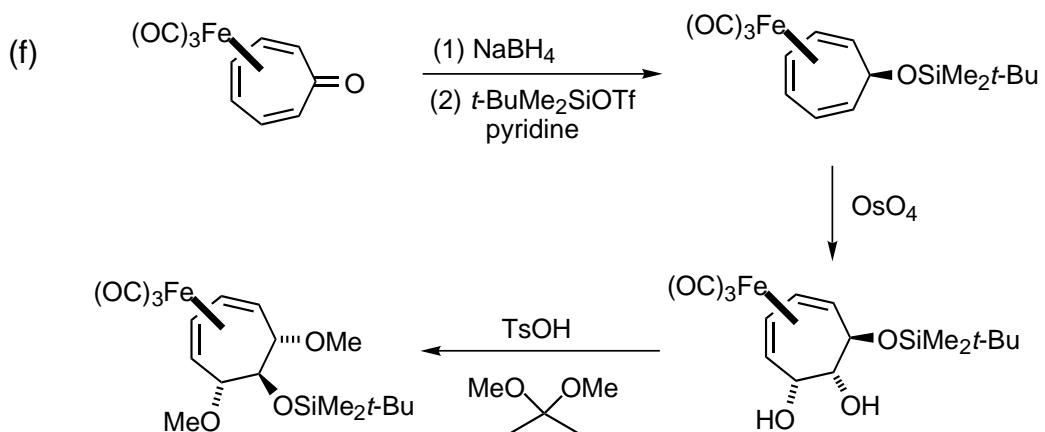
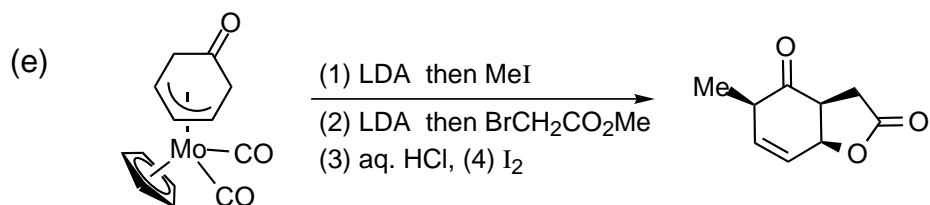
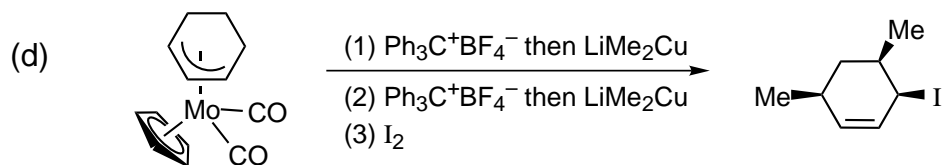
A) Discuss the changes in reactivity that occur on complexation of arenes to chromium tricarbonyl. Consider both arene and benzylic reactivities. [11]

B) By comparison with the reactivity of arene chromium tricarbonyl complexes suggest mechanisms for *all* of the following reactions commenting on the regioselectivities and stereoselectivities.

[6 x 6.5]



Question 3 continues on the next page

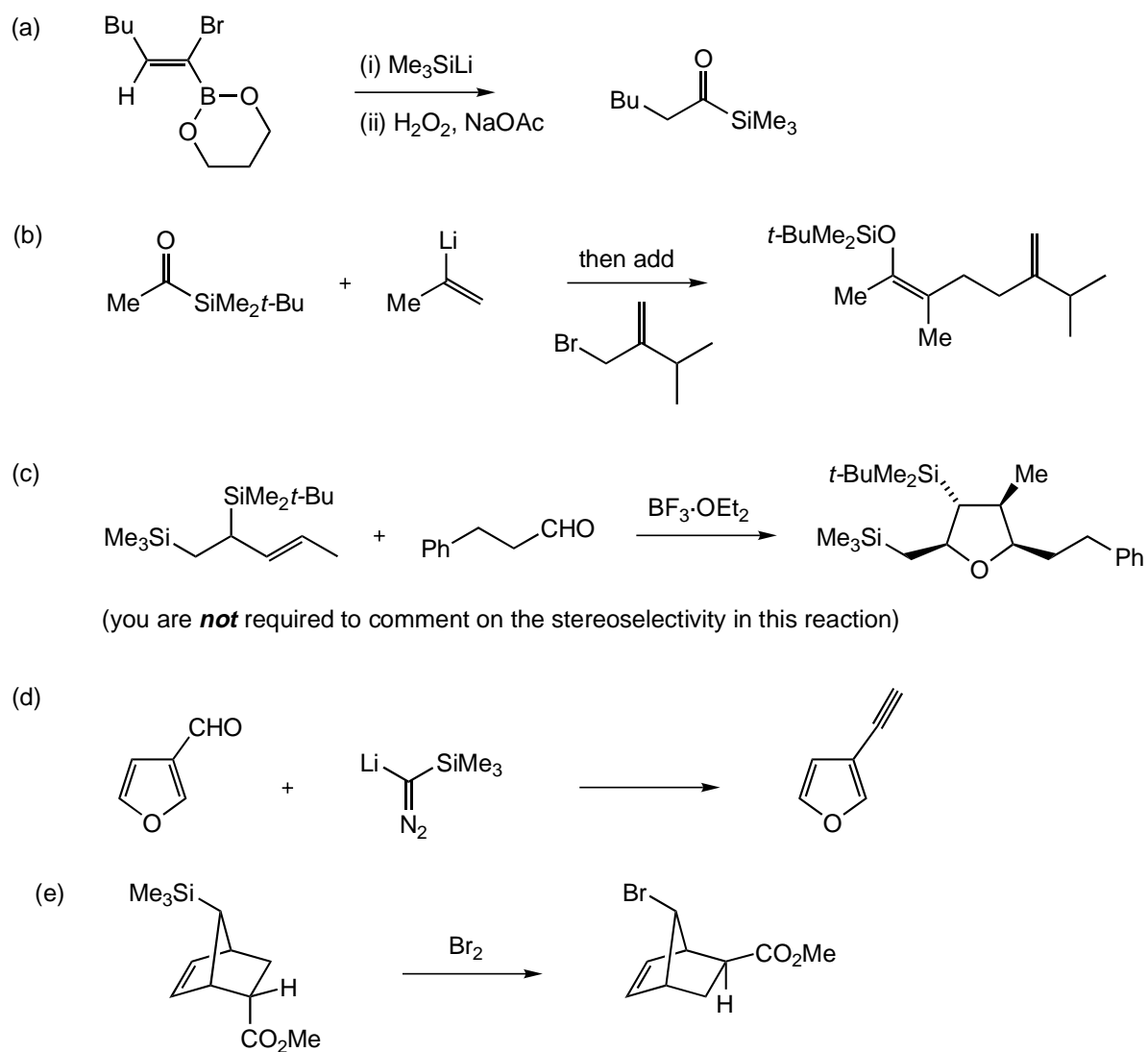


4. Answer *both* Part A and B of this question.

Part A

Provide a mechanistic explanation of *four* of the following reactions of silicon-containing compounds.

[4 × 6¹/₄]



Question continues on the next page

Part B

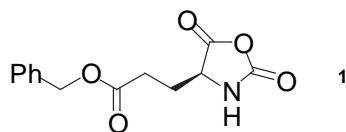
Outline the preparation of organoselenium compounds and their use in organic synthesis. Illustrate your answer with specific examples of your own choice.

[25]

5. Answer *any three* of Parts **A**, **B**, **C** and **D** of this question.

Part A

When compound **1** is treated with a trace of butylamine it polymerises.

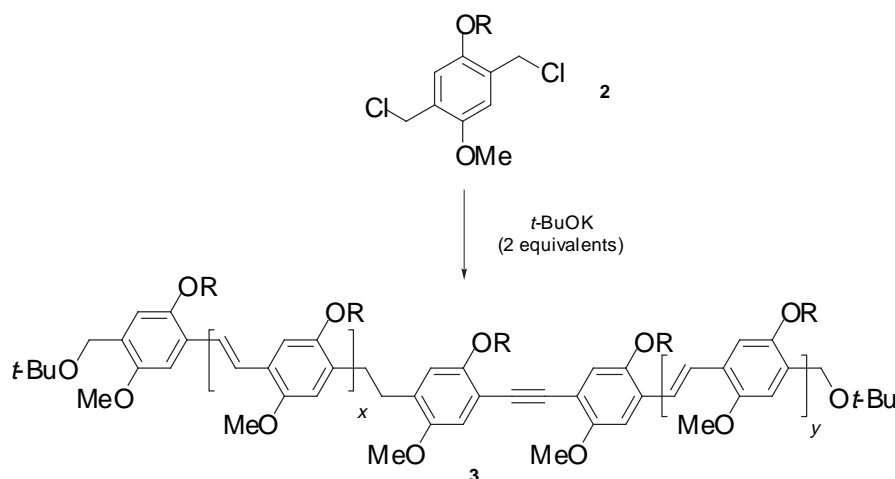


(a) Write a mechanism for this reaction and predict the structure of the product. [7]

(b) Concentrated solutions of this polymer are coloured, even in unpolarised light, and have a birefringent Schlieren texture when viewed with a polarising microscope. Explain these observations and suggest how a material of this type can be used to make a thermometer (e.g. for measuring the temperature of a baby's bath). [10]

Part B

The reaction of compound **2** with two equivalents of potassium *t*-butoxide forms a soluble high molecular weight poly(*p*-phenylenevinylene) derivative **3** with some Ar-C≡C-Ar and ArCH₂CH₂Ar defects and ether end groups as shown below (R = long alkyl side-chain).

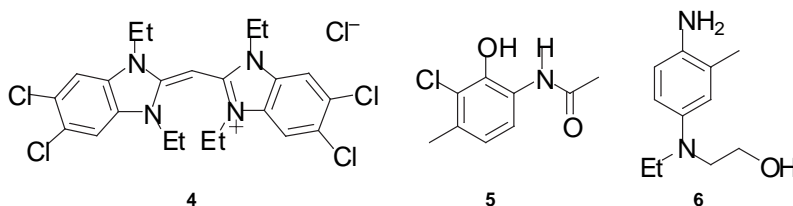


a) Suggest a likely mechanism for this reaction and account for the formation of the specified defects and end groups. [9]

b) A light emitting diode can be made by sandwiching a thin layer of polymer **3** between a calcium cathode and an indium-tin oxide transparent anode. How does this work? [8]

Part C

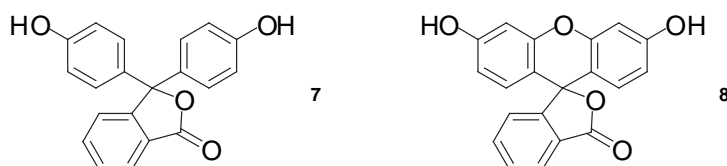
One layer of a colour photographic film consists of a silver chloride colloid, sensitizer **4** and coupler **5** in gelatine. When this layer is treated with developer **6**, areas which have been exposed to blue light become blue, whereas the unexposed areas remain colourless.



- (a) Suggest a likely structure for the compound giving rise to this blue colour and explain how it is formed. [9]
- (b) Explain how a film consisting of several layers containing different components can produce a realistic colour image when the whole film is treated with the same developer. [8]

Part D

Compound **7** is used as a pH indicator.



- (a) How could you synthesise **7** from simple starting materials containing just one arene ring. Write a mechanism for the reaction. [5]
- (b) Explain why **7** becomes coloured under basic conditions (pH > 9) and why it becomes colourless again in more concentrated alkali (around pH 12). Both colour changes are reversible with pH. [6]
- (c) Compound **8** is closely related to **7**, but its properties differ in two respects:
- Compound **8** is coloured over a wider pH range (pH > 6 to pH 12).
 - The coloured form of **8** is strongly fluorescent, whereas that of **7** is not.
- Explain how these differences are related to the molecular structures.
- (Note that both **7** and **8** are colourless in the forms drawn above.) [6]