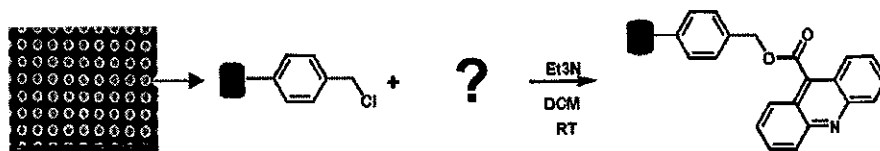


**Qualifying Examination (Organic chemistry)** spring 2009

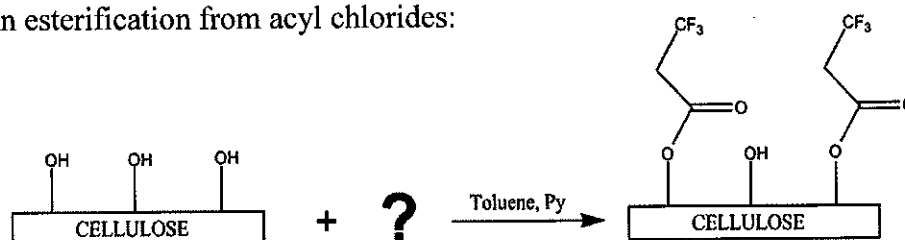
1. Some organic reactions can be used to modify the surface of inorganic materials. Please **write down the reactants** which are not given in the following reactions and **draw the reaction mechanisms**. (20%)

(1) A substitution reaction:



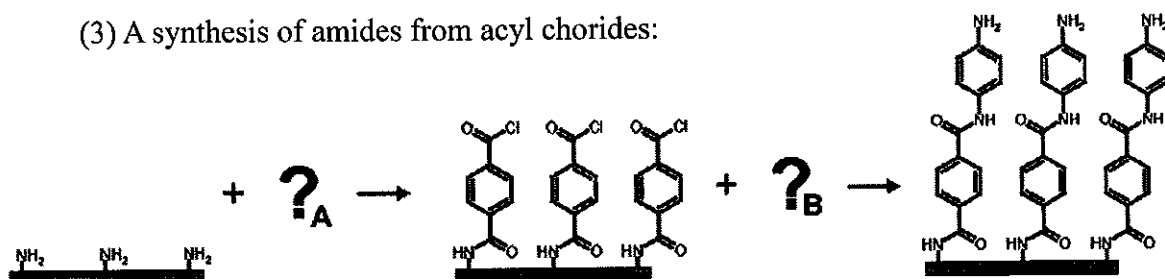
*Langmuir* **2006**, *22*, 5520-5524.

(2) An esterification from acyl chlorides:



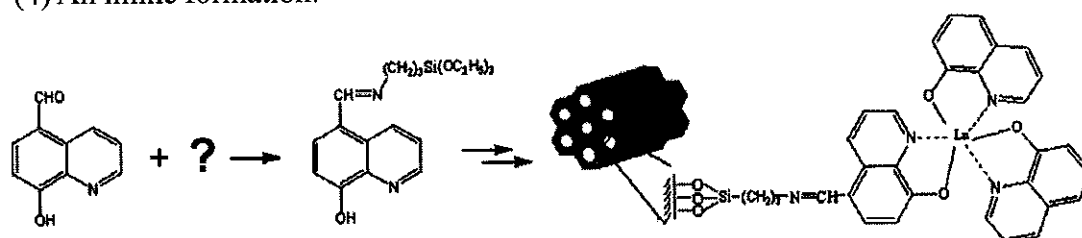
*Langmuir* **2007**, *23*, 10801-10806.

(3) A synthesis of amides from acyl chlorides:



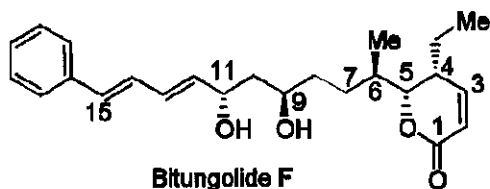
*Langmuir* **2008**, *24*, 2081-2089.

(4) An imine formation:



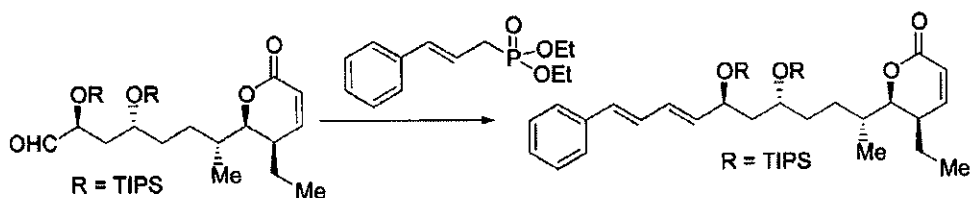
*Langmuir* **2008**, *24*, 5500-5507.

2. Stereochemistry is very important to the drug action. The structure below is **bitungolide F** which was isolated from an Indonesian sponge, *Theonella cf. swinhoei* and showed interesting biological activities. Please **assign the R or S configurations** for carbons 4, 5, 6, 9, and 11. (10%)



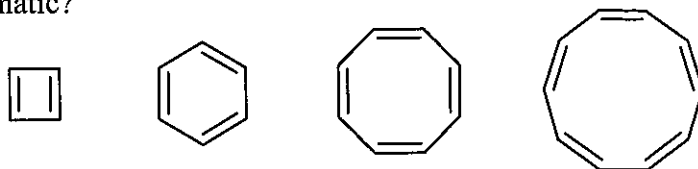
*J. Org. Chem.* **2008**, 73, 1582-1585

3. One of the synthetic steps to synthesize **bitungolide F** is Horner-Wadsworth-Emmons reaction (the figure below), which is a variation of the Wittig reaction. The Wittig reaction is a useful tool to construct a double bond in organic synthesis. Please **give a simple example of the Wittig reaction and write the mechanism**. (10%)



*J. Org. Chem.* **2008**, 73, 1582-1585

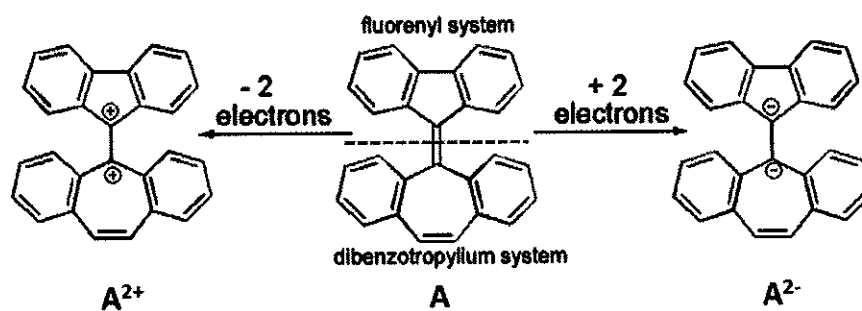
4. Huckel's rule describes the aromaticity of cyclic organic compounds which have continuously overlapping p orbitals. (10%)
- (1) Please **explain Huckel's rule** and use it to **predict the aromaticity** of the following compounds. Which of them are aromatic? Which of them are antiaromatic?



- (2) Tetrabenzo[5.7]fulvalene(A), consists of fluorenyl and dibenzotropylium systems, can be oxidized to dication( $A^{2+}$ ) and reduced to dianion( $A^{2-}$ ). In both of the two charged forms ( $A^{2+}$  and  $A^{2-}$ ), the charges will be stabilized respectively by the fluorenyl and dibenzotropylium systems. (see the figure on next page)

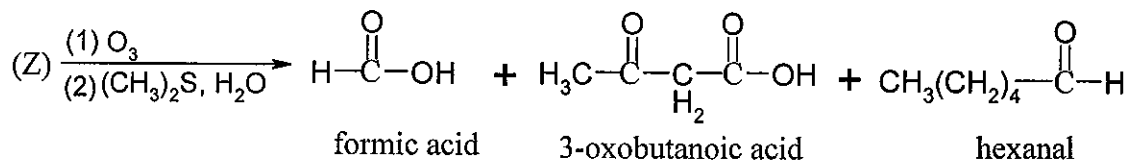
Please **point out the aromaticity** (aromatic or antiaromatic) of each part of the compounds:

1.  $A^{2+}$  fluorenyl systems
2.  $A^{2+}$  dibenzotropylium systems
3.  $A^{2-}$  fluorenyl systems
4.  $A^{2-}$  dibenzotropylium systems



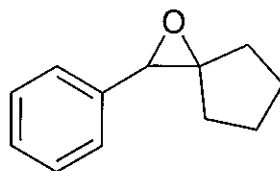
*J. Am. Chem. Soc.* **2008**, *130*, 14883–14890.

5. When compound (Z) is treated with ozone, followed by dimethyl sulfide and washing with water, the products are formic acid, 3-oxobutanoic acid, and hexanal.

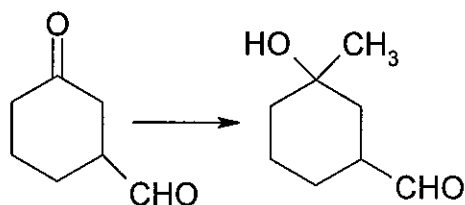


Propose a structure for compound (Z). What uncertainty is there in the structure you have proposed? ( 10% )

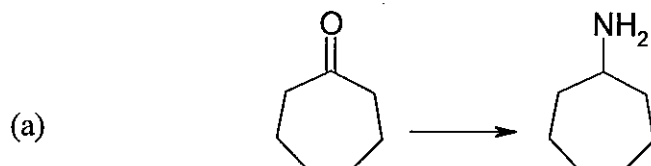
6. Show how you would synthesize the following compound from any starting materials containing no more than six carbon atoms. ( 10% )



7. Show how you would accomplish the following syntheses. You may use whatever additional reagents you need. ( 10% )



8. Using any necessary reagents, show how you would accomplish the following syntheses. ( 20% )



(b)

