Chem 12B Midterm 3

Instructor: Richmond Sarpong
April 26th 2018
8:10–9:30 am, 100 Lewis

You have **80 minutes** to complete this exam. Please write your answers clearly only on the pages indicated *and be as detailed as possible*. Nothing written outside the numbered pages will be graded. There should be 9 total pages in this exam.

Name: KEY

UID: _____

GSI Name: _____

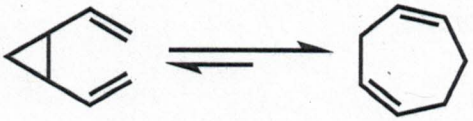
Question	Score
1	_____ (18 points)
2	_____ (12 points)
3	_____ (12 points)
4	_____ (15 points)
5	_____ (22 points)
6	_____ (9 points)
7	_____ (12 points)

Total _____*(100)*

Question 1 (18 points total):

(a) Classify the following transformations as either cycloadditions, electrocyclizations, cheletropic reactions, or sigmatropic rearrangements. (1 pt each)

(b) For each pericyclic reaction, provide a descriptor (e.g., [m+n] cycloaddition, [m,n] sigmatropic rearrangement, or nπ electrocyclization). (2 pts each)



a) Sigmatropic

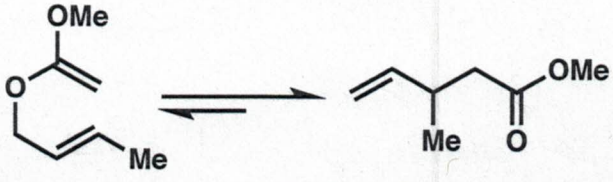
b) [3,3] sigmatropic / Cope

a) Cheletropic / chelotropic

b) [4+2] cycloaddn / retro cycloaddn

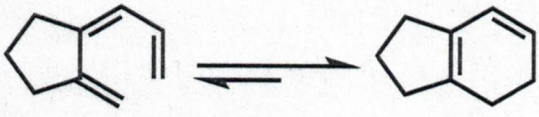
a) Cycloaddition

b) [4+2] cycloaddn / Diels-Alder



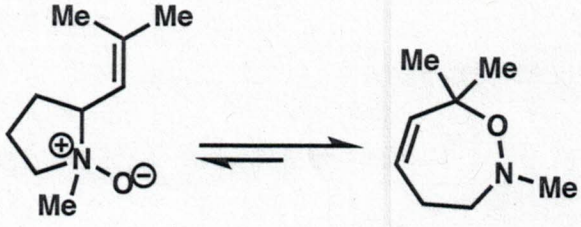
a) Sigmatropic

b) [3,3] sigmatropic / Claisen



a) Electrocyclization

b) 6 π e⁻



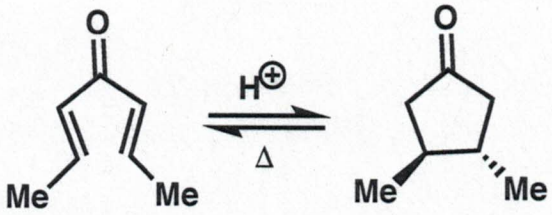
a) Sigmatropic

b) [2,3] Wittig

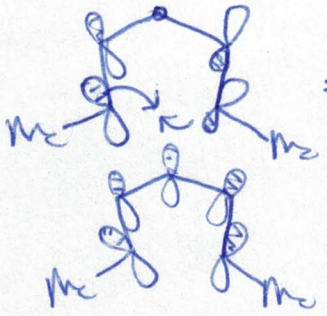
Sigmatropic

Question 2 (12 points):

(a) Provide a molecular orbital picture to rationalize the observed outcome of the following Nazarov transformation (6 pts).



MO picture +2

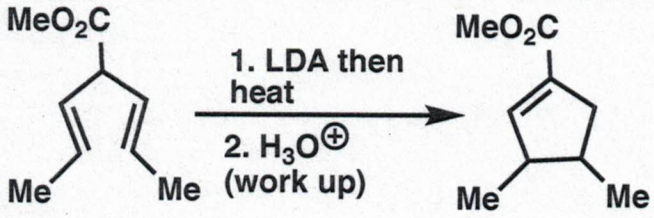


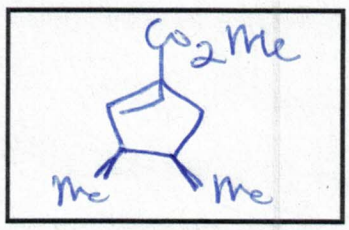
4t +2 consider this Homo

4t

Conrotatory closure +2

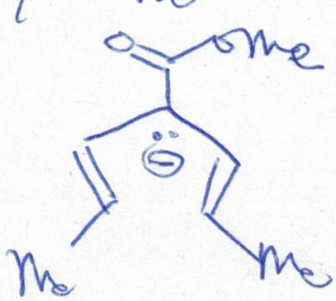
(b) Predict the stereochemistry of the following transformation (redraw in box) and provide a rationalization for your answer in three or less sentences (6 pts total)





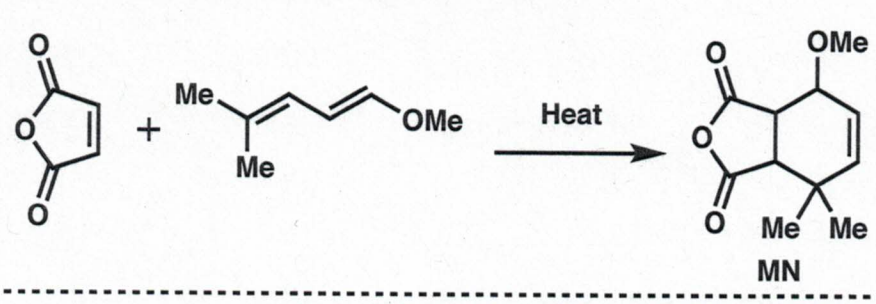
2pts

Rationalization (4 pts): Dis rotatory +2 closure because 6 π e⁻ +2 system

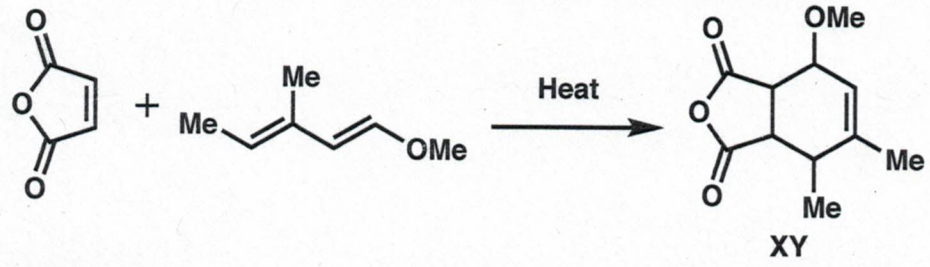


Question 3 (12 points total):

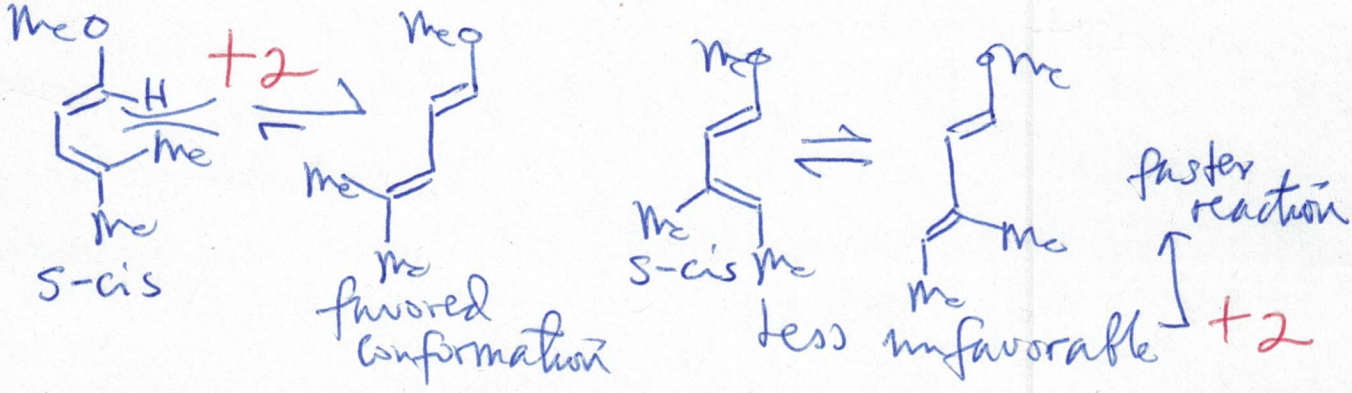
(a) Provide rationalization for the observed differences in the relative rate of reaction (K_{rel}) for the following reactions in three sentences or less. (4 pts).



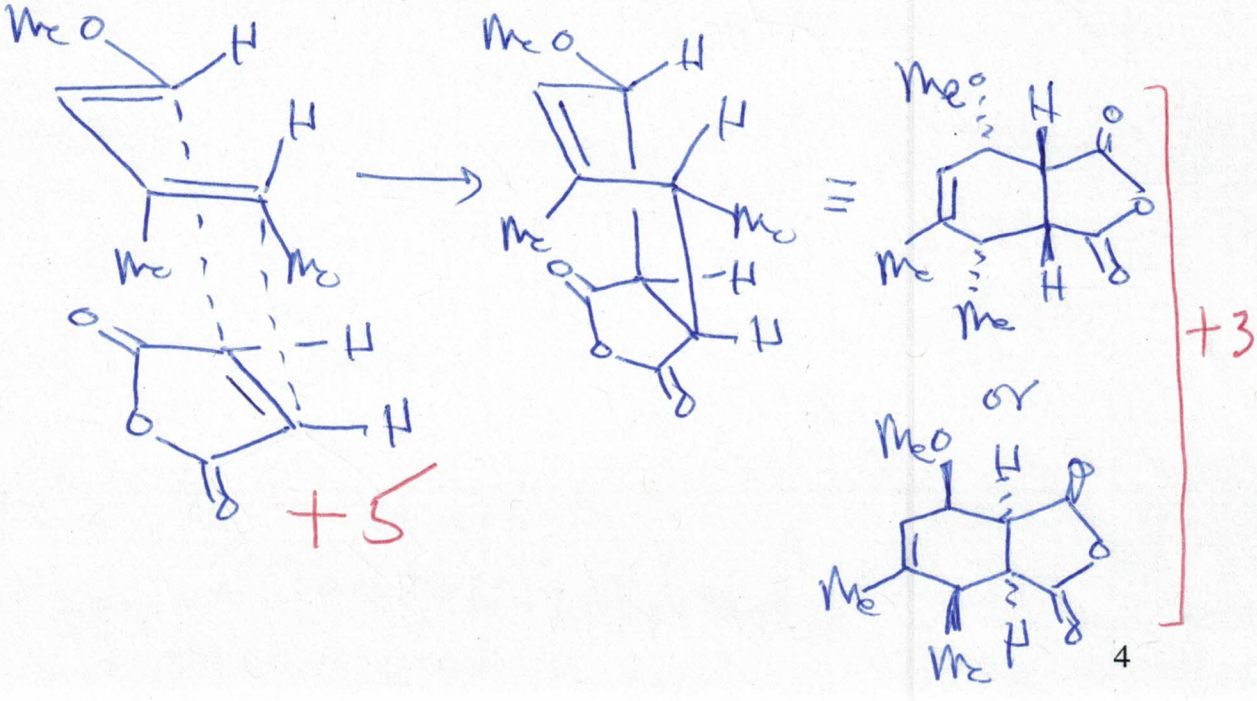
K_{rel} = 1



K_{rel} = 10^3



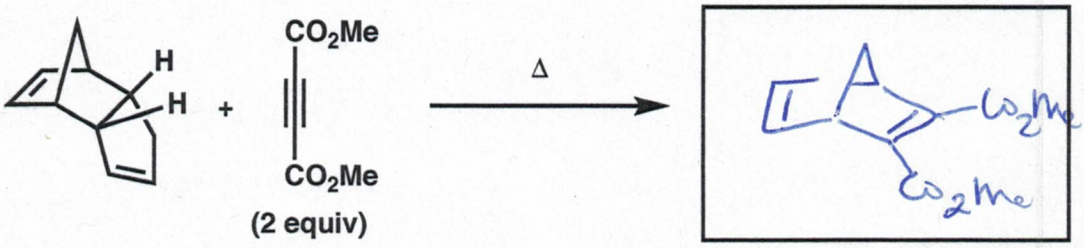
(b) Knowing that the reactions above proceed through an *endo* transition state, redraw **XY** showing the relative stereochemistry of all four stereocenters (3 pts) and provide a conformational drawing of the presumed transition state to rationalize your answer (5 pts).



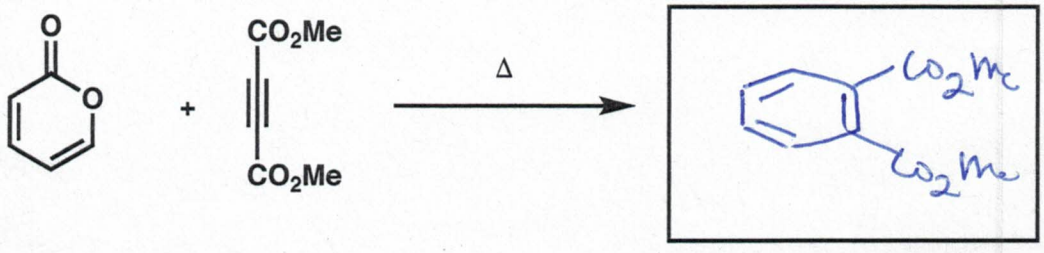
Question 4 (15 Points total):

Provide the products of the following reactions knowing that they involve several steps including a Diels-Alder cycloaddition. Unless indicated, each reactant is 1 equiv (3 pts each).

(a)



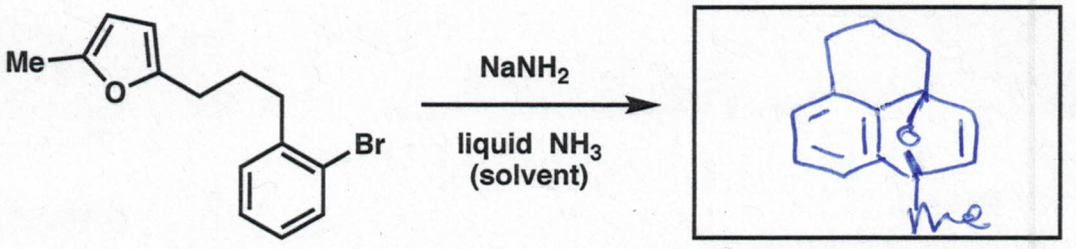
(b)



+ byproduct (gas)

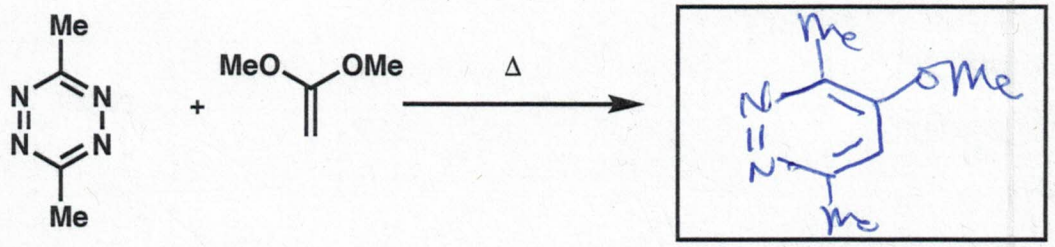
$CO_2(g)$

(c)



via benzyne

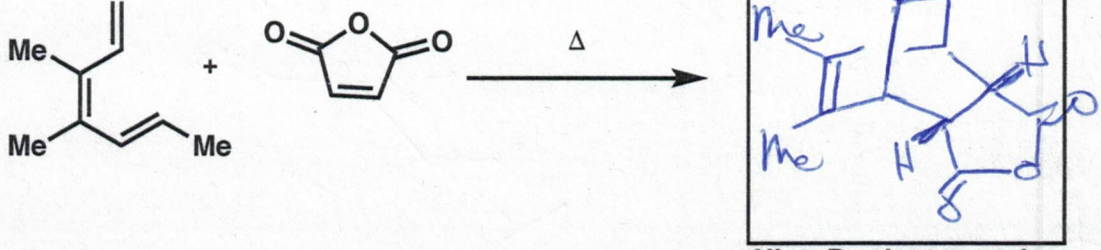
(d)



+ byproduct (gas)

+ MeOH

(e)

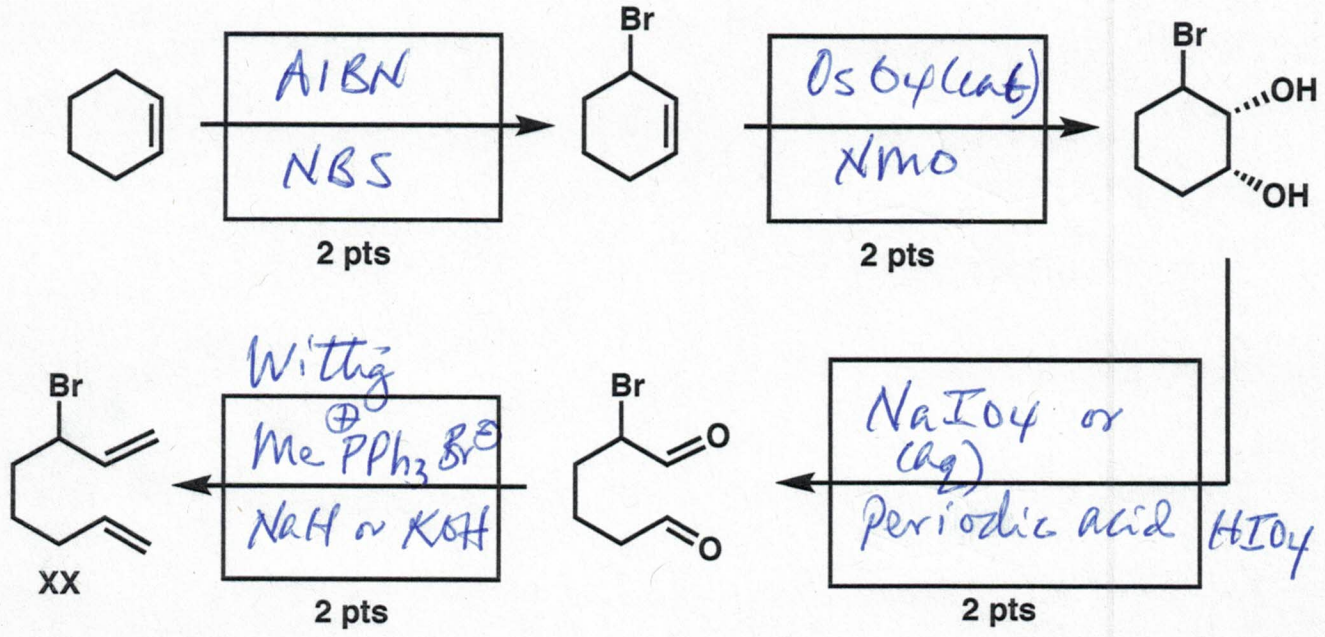


partial credit for connectivity

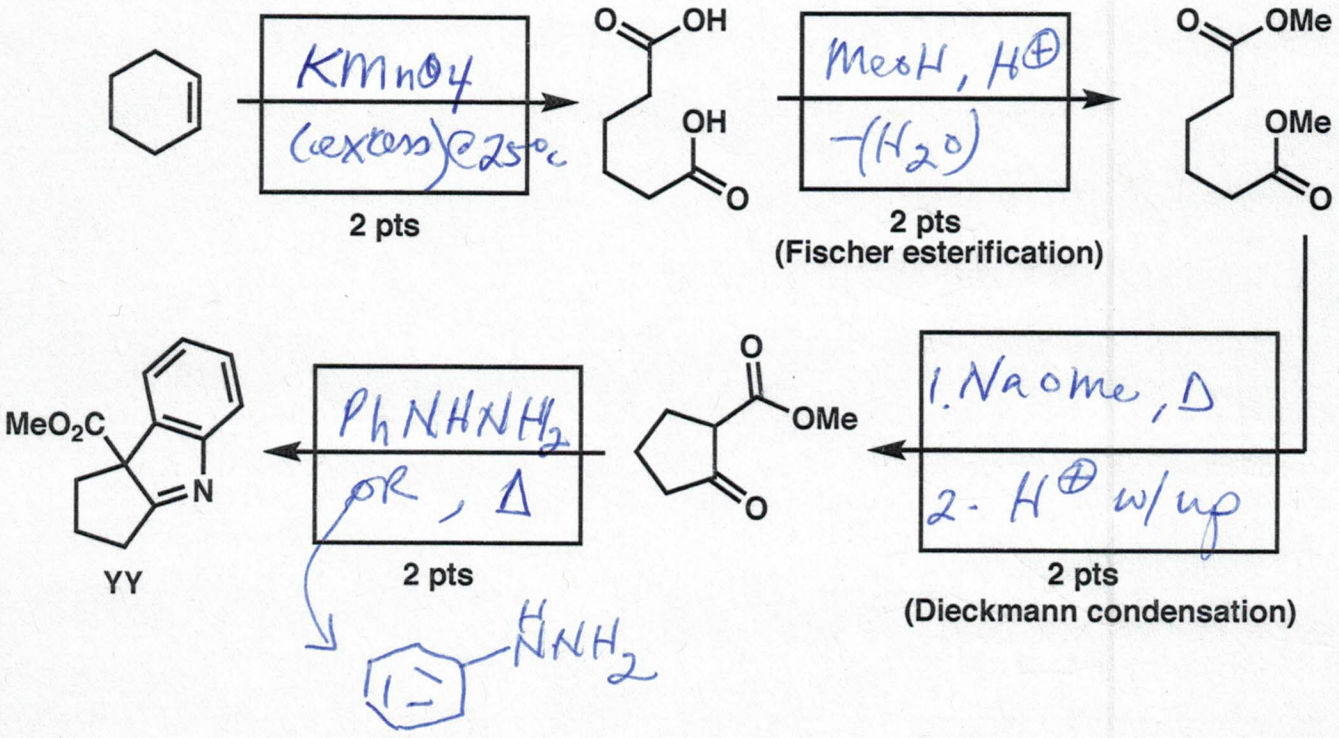
Hint: Product contains a 2.2.2 bicycle

Question 5 (22 points):

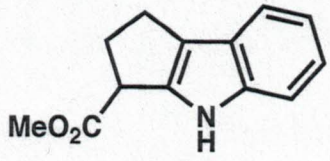
(a) Fill in the following boxes for the transformation of cyclohexene to bromodiene **XX**.



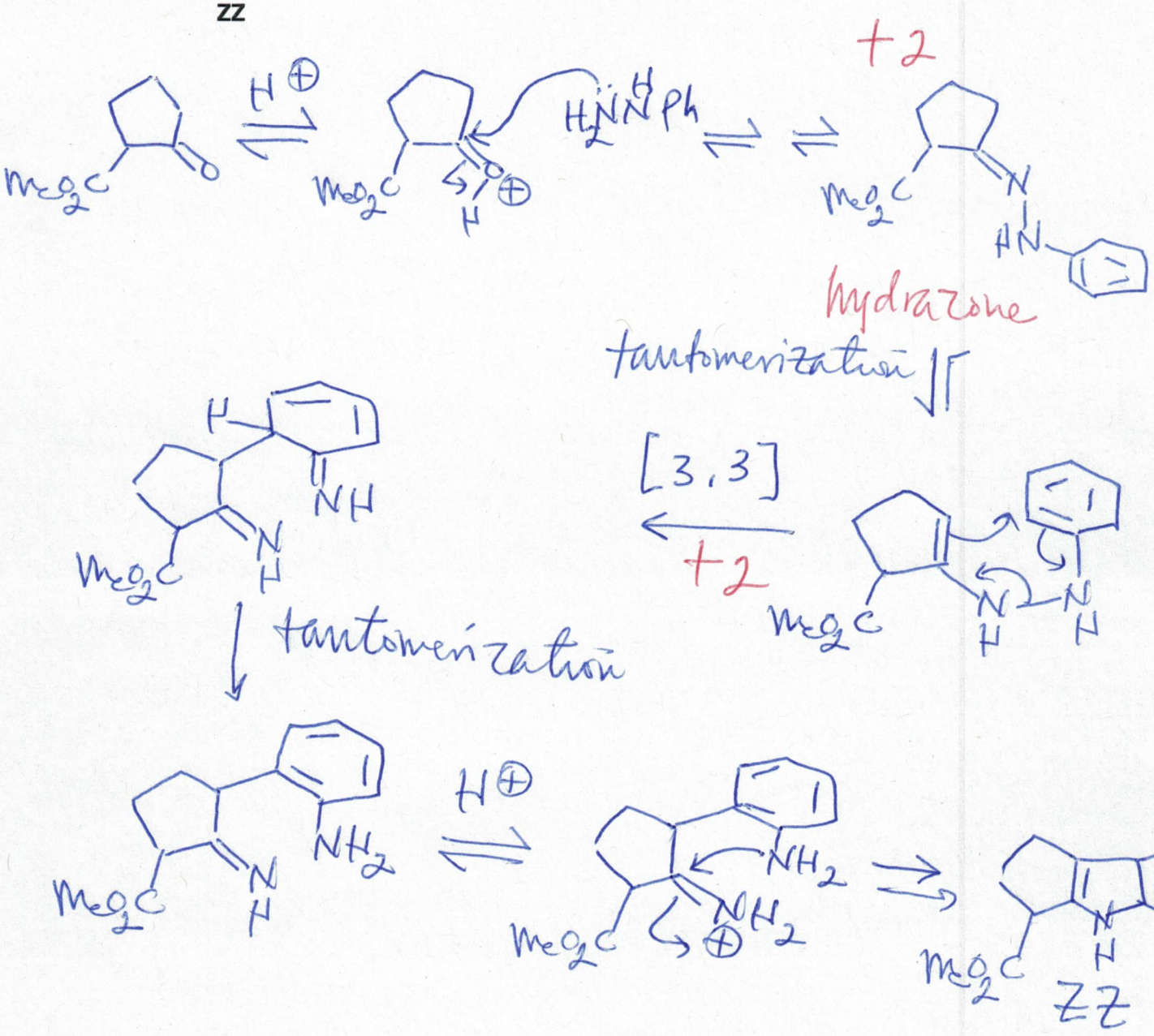
(b) Provide conditions that lead to **YY** from cyclohexene (2 pts each).



(c) **ZZ** forms as the minor product of the Fischer indolization type reaction that leads to **YY** in 5(b). Provide a mechanism for the formation of **ZZ** from the β-ketoester precursor shown in 5(b) (6 pts).



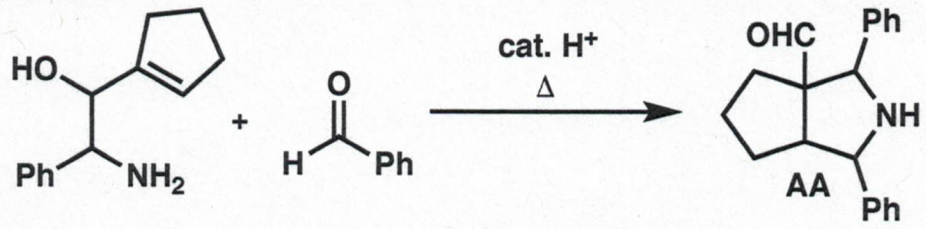
ZZ

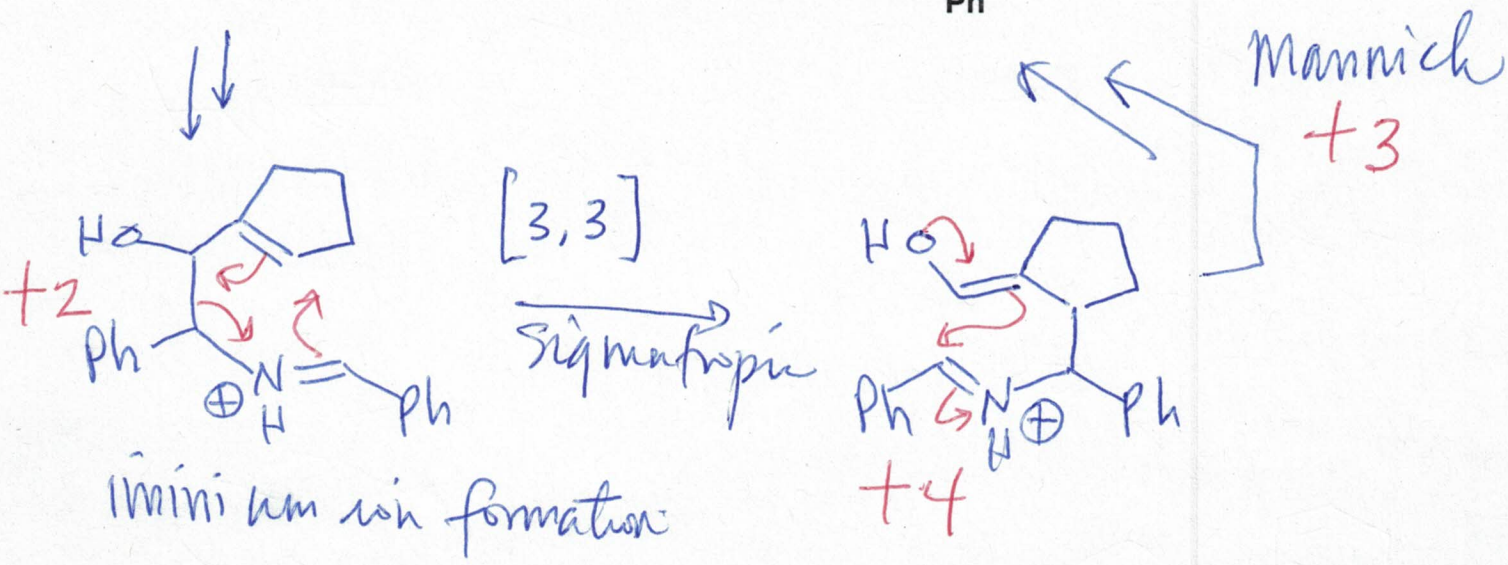


* Do not penalize for lack of reversible arrows

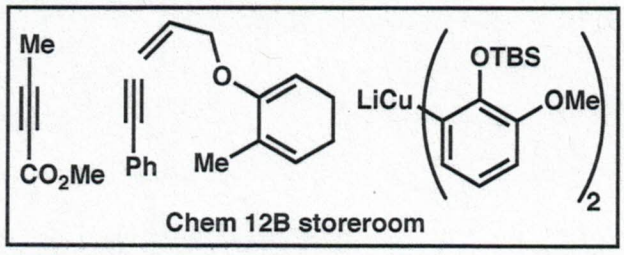
Question 6 (9 pts)

Provide a mechanism for the following conversion to **AA** knowing that it involves an aza-Cope Mannich reaction.

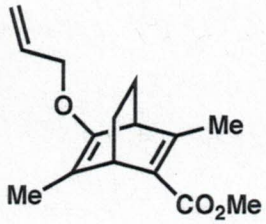




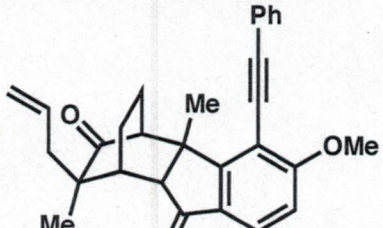
Question 7 (12 points):
Propose a synthesis of **FF** using the materials in the Chem 12B stockroom as well as any other materials six carbons or less that you deem necessary. Hint: 2.2.2 bicycle **DD** is an intermediate in the synthesis.



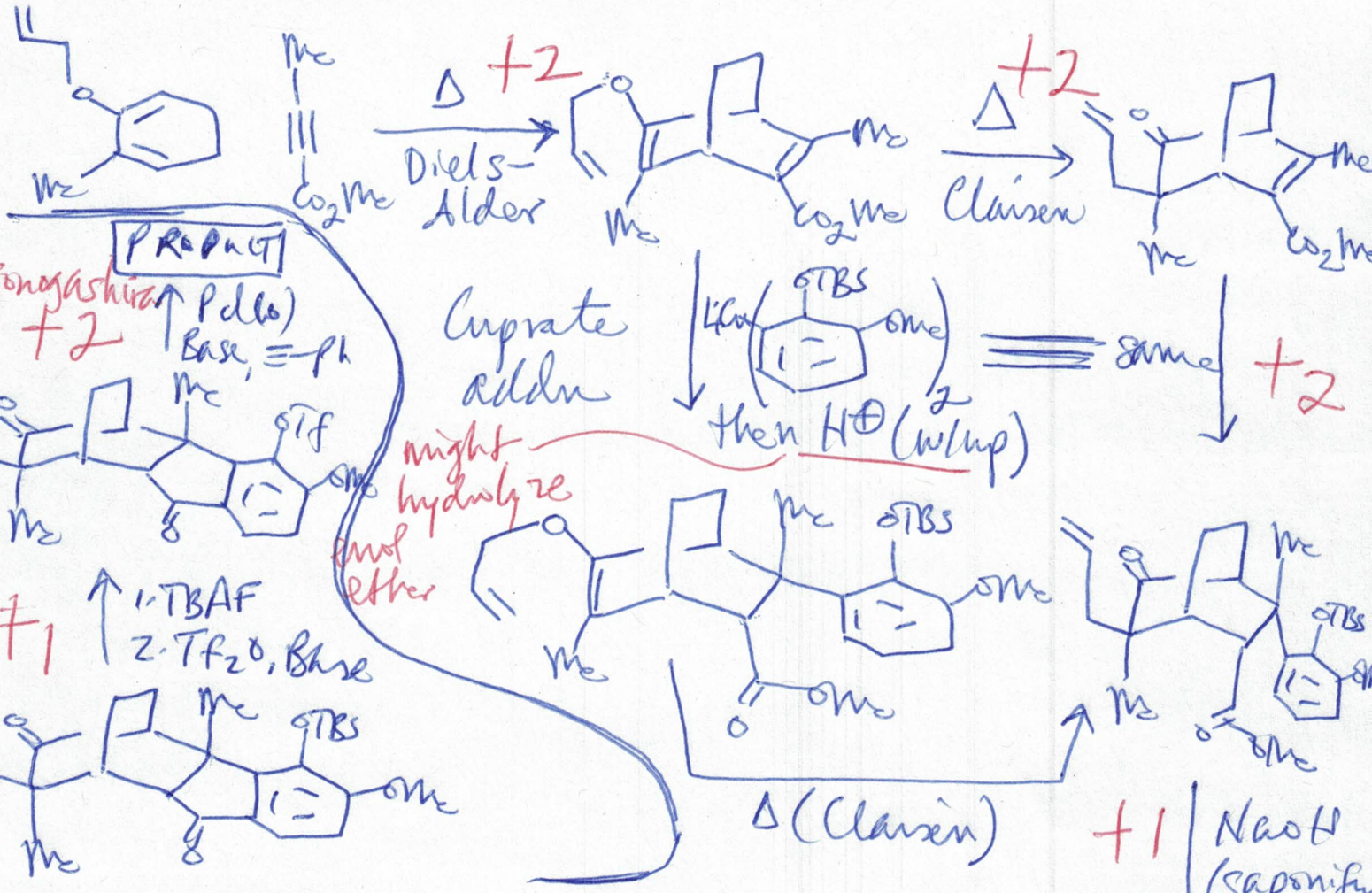
Chem 12B storeroom



DD



FF



The End