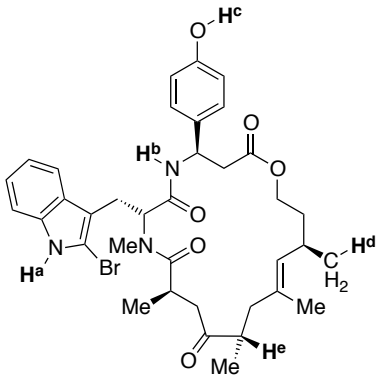
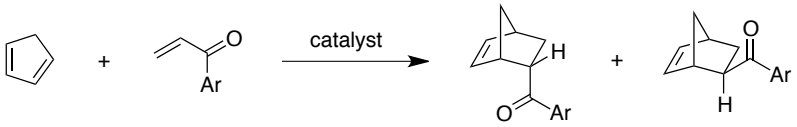
1. (10 points) Number the following protons in (+)-jasplakinolide from 1 to 5 in terms of acidity, where 1 is the most acidic proton and 5 is the least acidic proton.



2. (15 points) Using frontier molecular orbital theory, explain the difference in diastereoselectivity for following two [4+2] cycloaddition reactions. Be sure that your answer includes a detailed analysis the transition states that lead to each product.

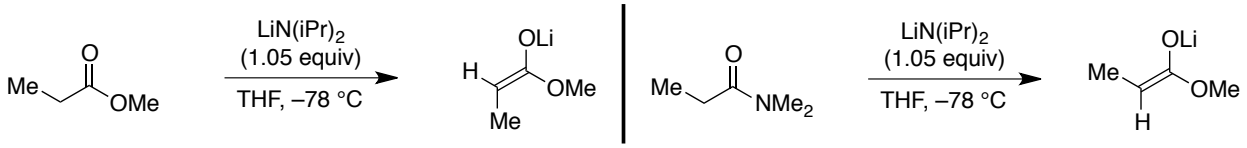


catalyst	d.r.
Me_3Al	99 : 1
ATPH	18 : 82

ATPH = Al(O-2,3,5-*i*-$Pr_3C_6H_2)_3$

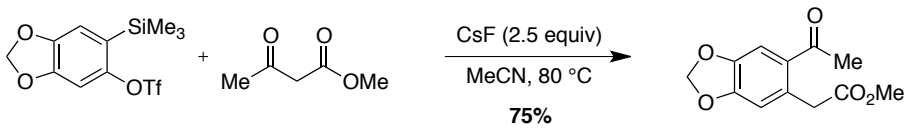
Maruoka, K.; Imoto, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 12115.

3. (15 points) Provide the transition state that leads to the enolate isomer for each of the following deprotonations.



Ireland, R. E.; Wipf, P.; Armstrong, J. D. *J. Org. Chem.* **1991**, *56*, 650.

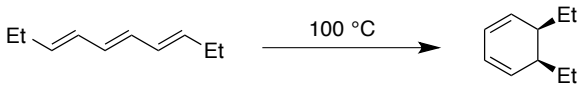
4. (10 points) Provide a reasonable mechanism for the reaction below.



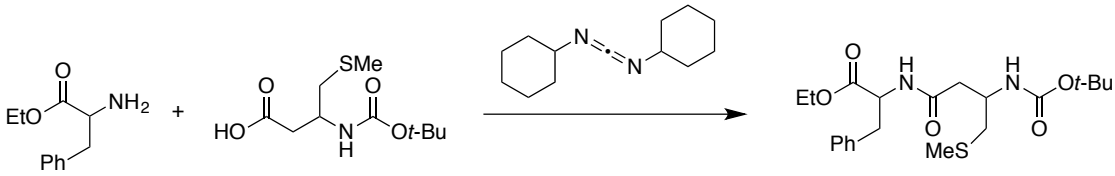
Tambar, U. K.; Stoltz, B. M. *J. Am. Chem. Soc.* **2005**, *127*, 5340.

6. (10 points) For the reaction given below provide: a) an electron-pushing mechanism; b) the transition

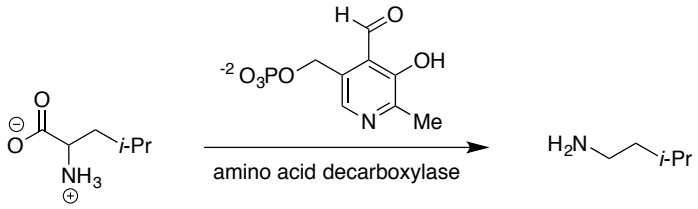
state for the transformation; c) the frontier molecular orbital interaction that forms the new sigma bond.



8. (10 points) Provide a reasonable mechanism for the DCC coupling reaction given below.



9. (10 points) Provide a reasonable mechanism for the PLP co-factor mediated amino acid decarboxylation illustrated below.



10. (20 points) a) Illustrate a three unit single strand of DNA with the follow nucleotide base pairs: guanine, thymine, and adenine. b) Separately, illustrate the hydrogen-bonding between adenine and thymine, and cytosine and guanine that is responsible for the ladder structure of DNA. Note: The nucleotide base pairs are illustrated below for your reference but you are required to know, which ones are capable of hydrogen-bonding and, which ones are present in DNA.