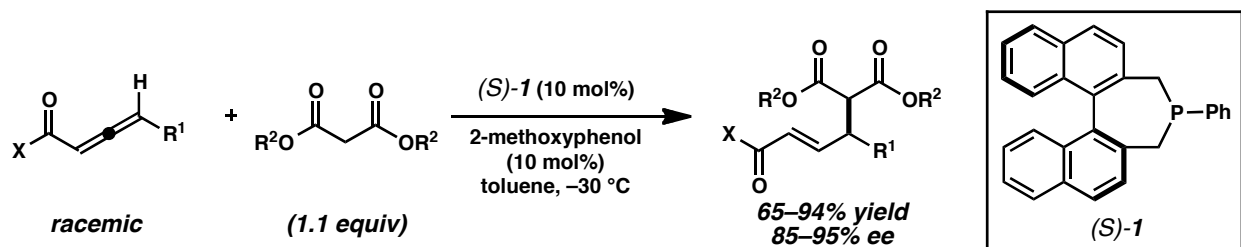
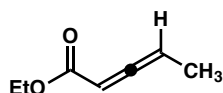


Attempt all questions. Each problem has multiple related parts. Read the entire question before you begin working. Present your answers **clearly** and **legibly** in the order that they appear below. Label each section according to the problem numbering. **(100 total points)**

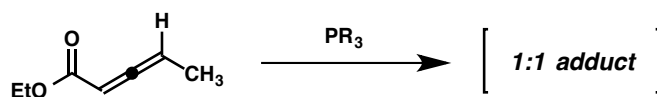
1. Consider the following transformation (*Proc. Natl. Acad. Sci. U.S.A.* **2010**, 107, 20652–20654):



A. Draw a molecular orbital picture that show the bonding in the  $\pi$ -system of the following compound. Clearly indicate the atomic orbitals that directly interact with one another in an ideal conformation. **(10 points)**



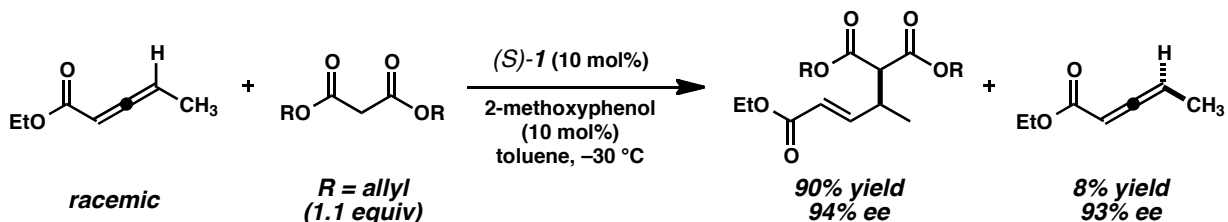
B. Based on your orbital picture and your understanding of orbital interactions, predict the location that a phosphine would likely interact with this compound. Propose a structure for the hypothetical adduct of the interaction. **(5 points)**



C. Briefly describe the considerations from part A that led to your conclusions in part B. **(3 points)**

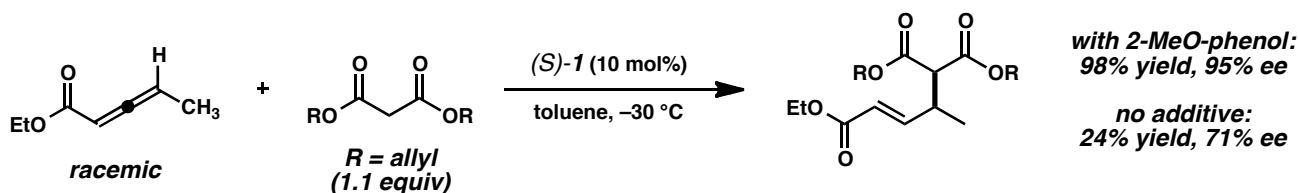
D. The following observations were made in the course of this study. Explain what each observation indicates about the mechanism of the reaction (e.g., what possibilities can be eliminated or what circumstances are required for the observation to be true). Be specific. **(5 points each, 25 points total)**

- (i) The enantiomeric excess (ee) of the product correlates linearly with the ee of catalyst **1**. (i.e., product ee  $\approx$  catalyst ee)
- (ii) The enantiomeric excess of the product is constant during the reaction.
- (iii) The rate law is first-order in catalyst and allene, and zero-order in malonate.
- (iv) The resting state of the catalyst during the reaction is phosphine **1** itself.
- (v) The following reaction was stopped prior to complete conversion of the allene and the remaining starting material was isolated and analyzed:



**(continued)**

- E. Draw a detailed arrow-pushing mechanism that is consistent with the data above. Indicate which steps are potentially reversible and which are irreversible.  
**(12 points)**
- F. What is the rate-determining step in the mechanism?  
**(10 points)**
- G. The phenolic additive increases both the rate and degree of enantioselectivity in the reaction (see below). Suggest a role for the phenol in your mechanism.  
**(6 points)**



2. Match the following named reaction to the appropriate reagent combination.  
**(4 points each, 20 points total)**

- |                        |   |
|------------------------|---|
| (i) Eschweiler–Clarke  | (a) $\text{PPh}_3$ , $\text{CBr}_4$ , $\text{Et}_3\text{N}$ ; $\text{EtMgBr}$                                 |
| (ii) Kulinkovich       | (b) $\text{CH}_2\text{O}$ (aq), $\text{HCO}_2\text{H}$  |
| (iii) Grieco–Sharpless | (c) $\text{NaH}$ , $\text{CS}_2$ ; $\text{CH}_3\text{I}$ ; 1-methylnaphthalene, $190\text{ }^\circ\text{C}$   |
| (iv) Corey–Fuchs       | (d) $2\text{-NO}_2\text{C}_6\text{H}_4\text{SeCN}$ , $\text{Bu}_3\text{P}$ , pyridine; $\text{H}_2\text{O}_2$ |
| (v) Chugaev            | (e) $\text{Ti}(\text{O}i\text{-Pr})_4$ , $\text{EtMgBr}$  |
3. Choose any three of the above named reaction/reagent combinations from question 2. Draw a scheme depicting an appropriate substrate and representing the chemical transformation for each of these three reactions. Be specific in your example (no R groups or abbreviations!).  
**(3 points each, 9 points total)**