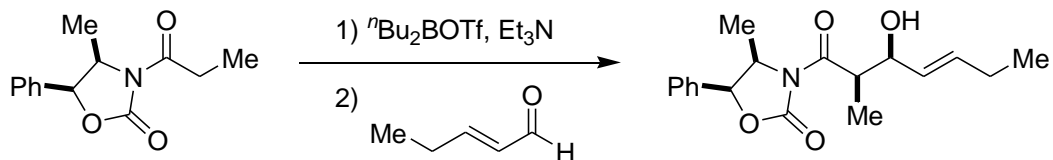


Problem Set No. 8 (26.6.2012)

1. In their total synthesis of cytovaricin, Evans et al. used a diastereoselective aldol reaction.
- a) Explain the observed diastereoselectivity by providing a representation of the product-forming transition state.

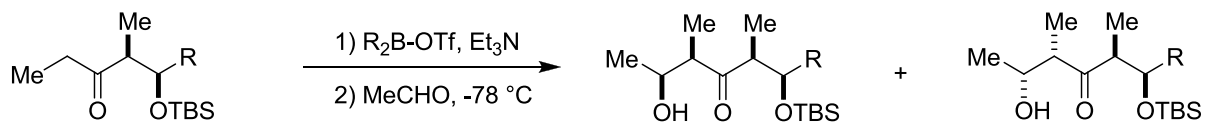


- b) Suggest a pathway for the synthesis of the starting material!

- c) Convert the aldol product into the corresponding carboxylic acid!

- d) Which product do you expect, if the starting material is treated with LDA and subsequently with allyl iodide!

2. Analyse the stereochemical outcome of this aldol reaction. Explain why the three boron reagents lead to differences in selectivity.

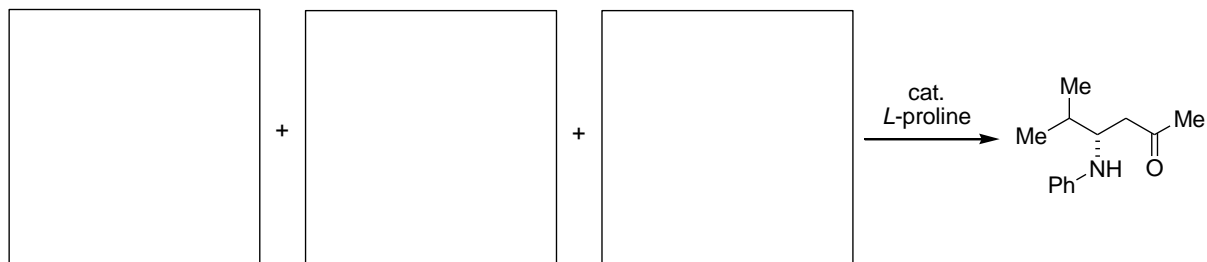


**R<sub>2</sub>B-OTf**

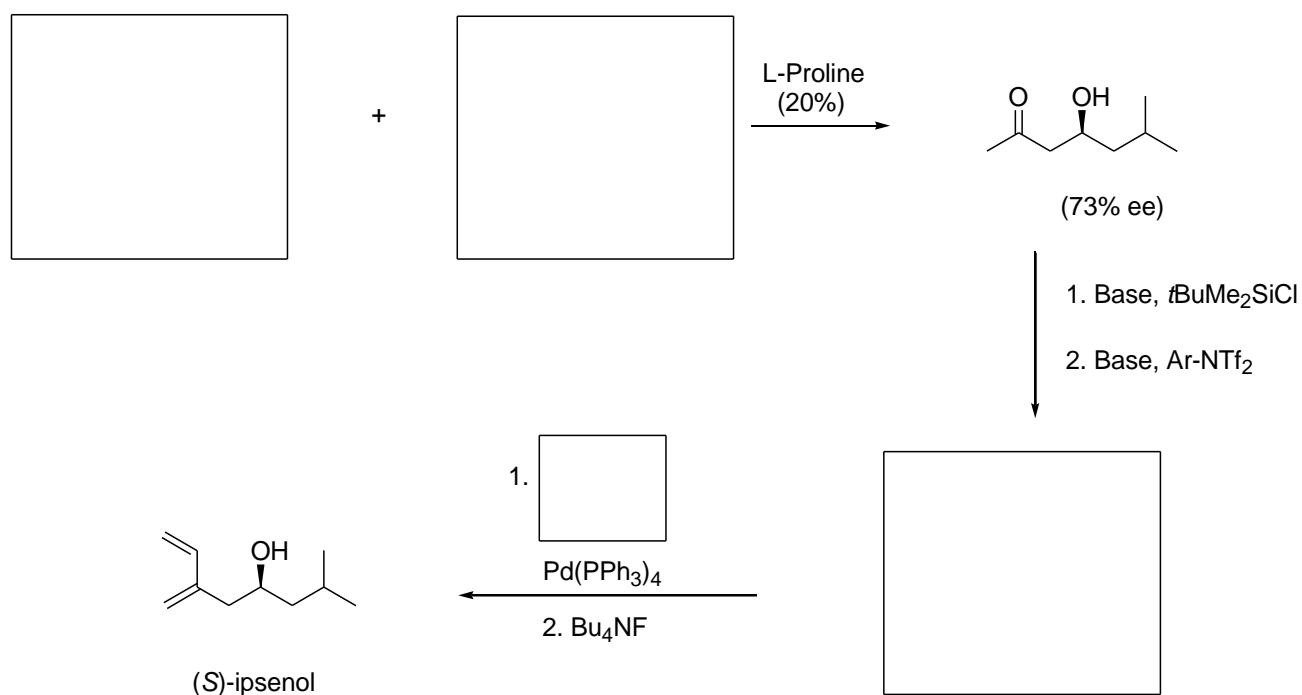
9-BBN-OTf	92	:	8
(+)-(IpC) <sub>2</sub> BOTf	98	:	2
(-)-(IpC) <sub>2</sub> BOTf	75	:	25

3. The following reactions involve organocatalysis.

a) Provide suitable starting materials and key intermediates for the following synthesis of a chiral secondary amine. Draw the transition state of this Mannich reaction!



b) The natural product ipsenol has been prepared in an enantio-enriched form as shown below. Supplement the equations (no mechanism), but draw the transition state explaining the outcome of the first step!



c) The reaction of an aldehyde and diethyl azodicarboxylate in the presence of L-proline also occurs in an enantioselective fashion. Supplement the equations! Give the transition state for the reaction.

