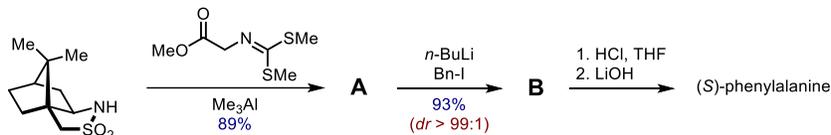


## Problem set #3

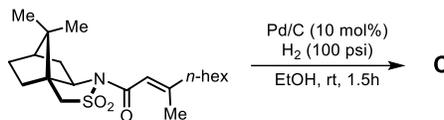
### Problem 1:

- The group of Oppolzer has extensively studied the stereoselectivity of reactions in the presence of chiral sulfamate auxiliaries. Four of these reactions are depicted below:

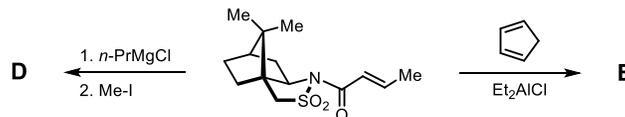
eq. 1



eq. 2



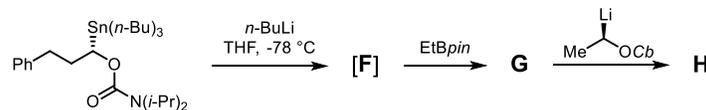
eq. 3



- Provide a model for the formation of (*S*)-phenylalanine depicted in eq. 1 and complete the sequence.
- Give the structure of compounds **C**, **D** and **E** with the right configuration, and explain their formation.

### Problem 2:

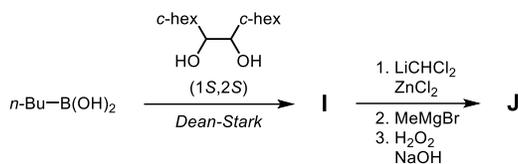
- Chiral carbenoid can be stored as configurationally stable organotin reagents. A metal-metal exchange reaction ( $\text{Li}/\text{Sn}$ ) is stereospecific and allows for the preparation of chiral organolithium reagents at low temperatures.



- Give intermediates and products **[F]**, **G** and **H** with the right stereochemistry, and explain their formation.

### Problem 3:

1. The condensation of 1,2-diols on a boronic acid gives the corresponding boronic ester **I**. Draw its structure with the right configuration.



2. Upon treatment of **I** under given conditions, compound **J** is obtained with high enantiomeric excess. Give its structure with the appropriate configuration.

### Problem 4:

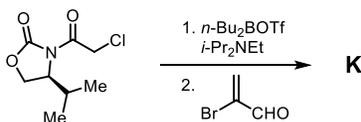
1. Consider the following molecules:



2. Estimate the structure of their favored conformations based on stereoelectronic effects.

### Problem 5:

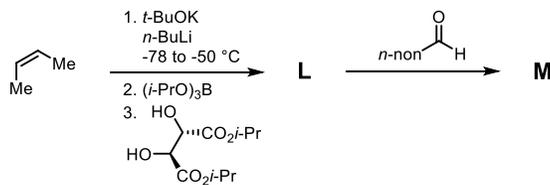
1. Chiral oxazolidinones are classical auxiliaries for asymmetric synthesis. Following conditions allow for the in situ formation of (*Z*)-boron enolates.



2. Give product **K** (major diastereoisomer) and explain the stereoselectivity of the reaction.

### Problem 6:

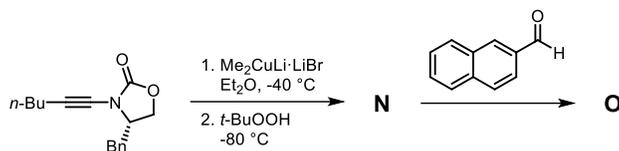
1. Chiral diols such as tartrate derivatives can be used in the formation of chiral allylboronate reagents for asymmetric allylation reactions, as in the sequence below.



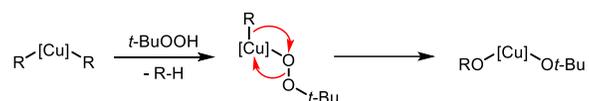
2. Give intermediate **L** and product **M** and explain their formation.

**Problem 7:**

1. In 2014, Marek described a sequence for the formation of quaternary stereocenters.



2. The use of TBHP allows for the in situ formation of enolates from organocopper species, as shown below:



3. Give intermediate **N** and product **O** with the right stereochemistry.

**Problem 8:**

Give the main product of the following reaction:

