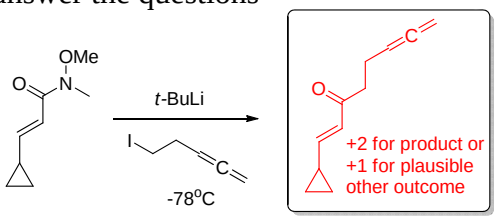
Institut für Chemie
und Biochemie

Modern Synthetic Methods
Exam #1

1.(organolithium; 8 pts)

a) Provide the product and answer the questions



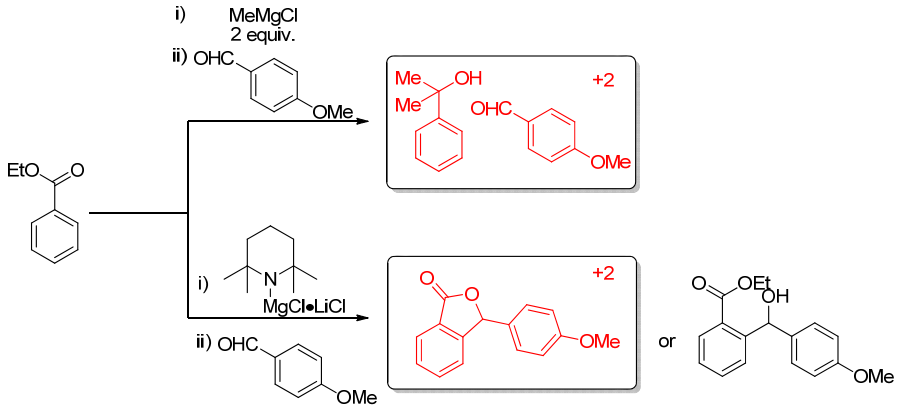
b) What type of organolithium preparation method is being used? This is an example of a lithium-halogen exchange. (+2 for correct response)

c) Describe how you would carry out the above reaction; specifically commenting on relative amounts of reagents and order of addition and why? Two equivalents of *t*-BuLi is required to (1) perform the exchange and (2) quench the equivalent of bromo-*t*-butane that is formed. The reaction should be carried out such that the lithium-halogen exchange is done first so that the exchange may take place before starting material is added. (+2)

d) What would the addition of HMPA do to the organolithium reagent and to the outcome of the reaction? Addition of 4eqs of HMPA is predicted to cause deaggregation of the organolithium species into a separated ion pair where four HMPAs coordinate each lithiuim cation. The addition of HMPA might change the reaction selectivity from 1,2-additon to 1,4 addition. (+2)

2. (organomagnesium; 8 pts)

a) Provide the products and answer the questions



b) What is the Barbier Reaction and how is it similar/different than a Grignard Reaction?

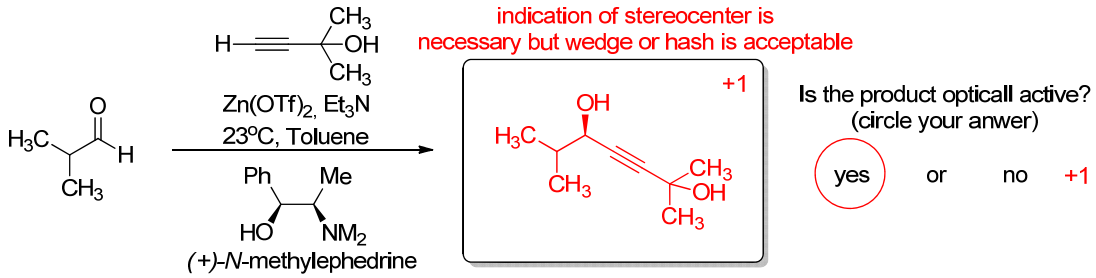
Barbier reaction combines Mg or other reducing metal with a carbonyl and alkyl (or aryl) halide to yield a Grignard-like addition product. The Grignard Reaction pre-forms an organomagnesium species by combining magnesium metal and an organic halide and then the electrophile is introduced (+2).

c) Describe two methods to activate magnesium metal to prepare Grignards.

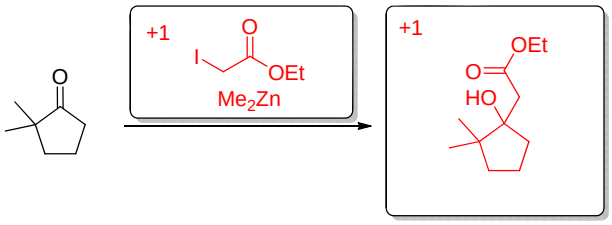
I2, Dibromoethane or diiodoethane, Rieke metal MgX2 + K -> Mg – any two of these (+2).

3. (organozinc; 6pts) Predict the products (and/or reagents):

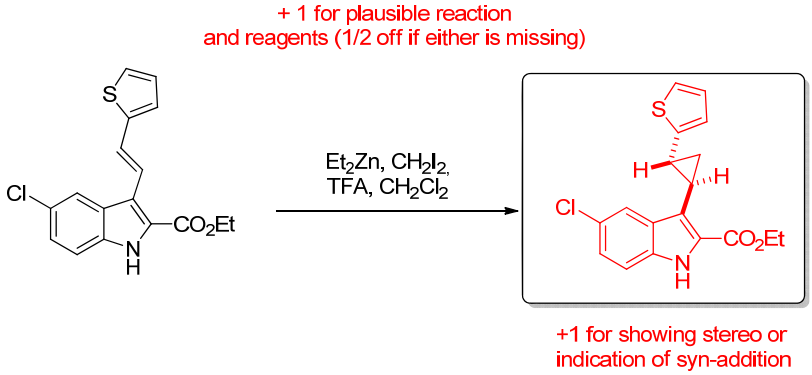
a) Carriera reaction .



b)Reformatsky reaction

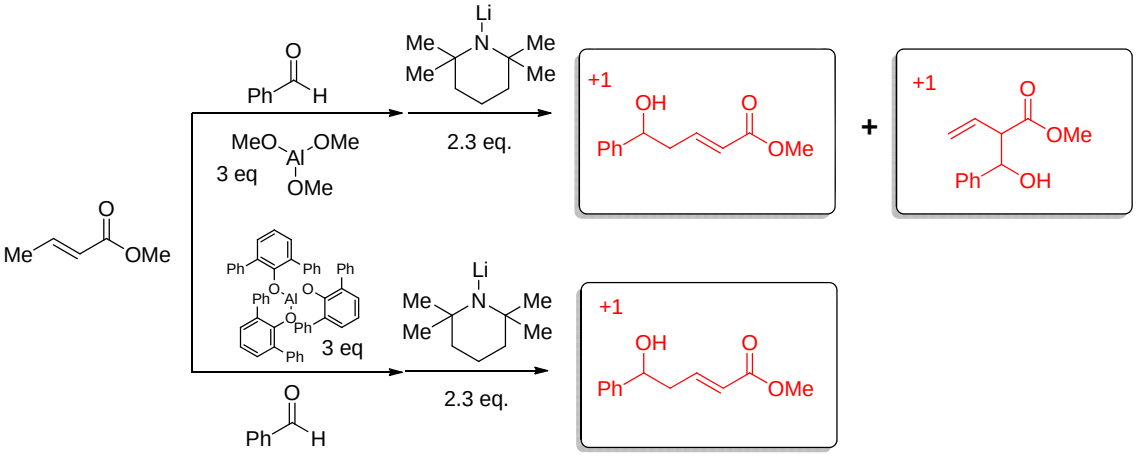


c) Simmons-Smith – Predict the product making sure to show relative stereochemistry:

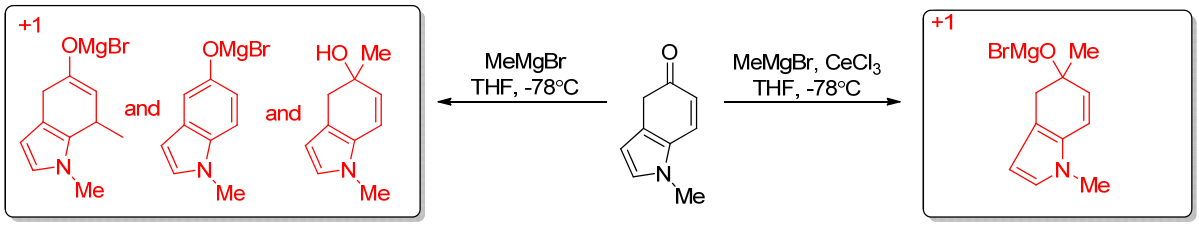


4.(organoaluminum/cerium; 5pts) Predict the product(s)

a)

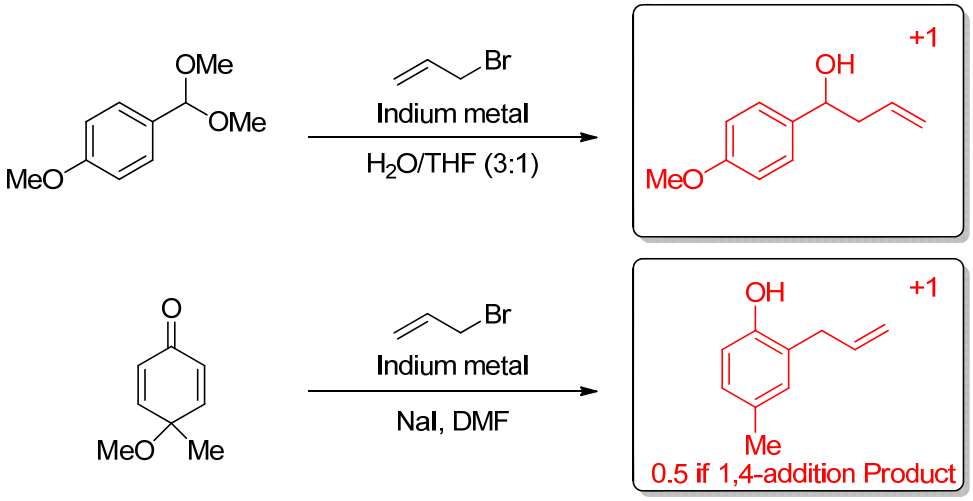


b) Predict the product(s)

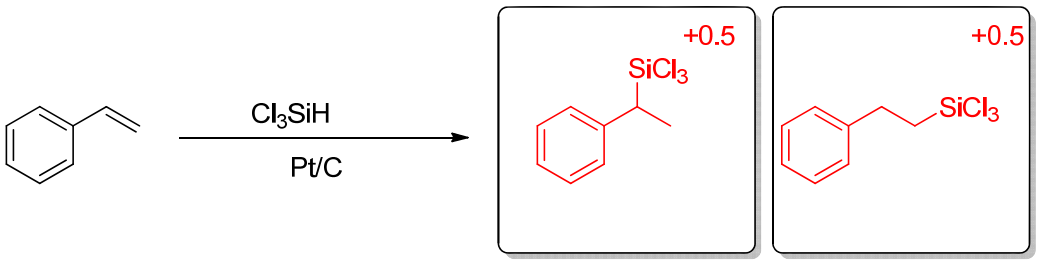


5. (organoindium/organosilicon; 5pts)

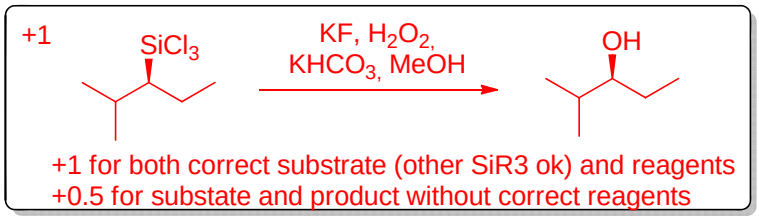
a) Predict the products



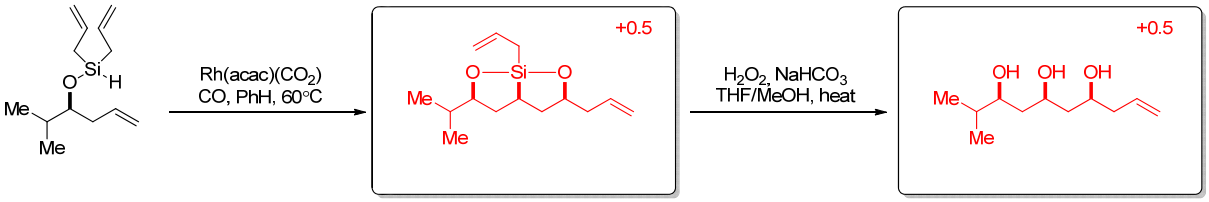
b) Predict the products



c) Draw an example of a Tamao Oxidation

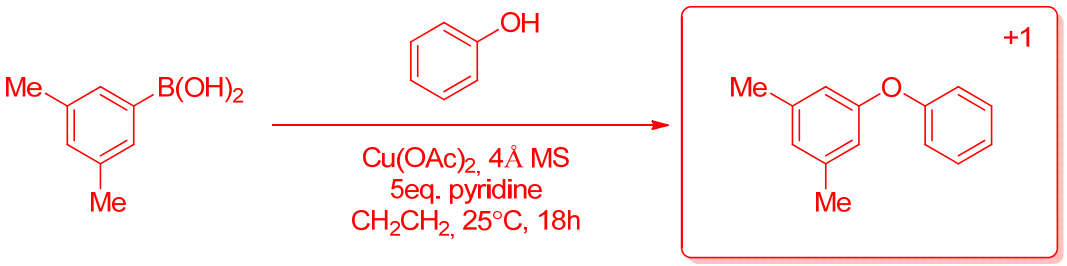


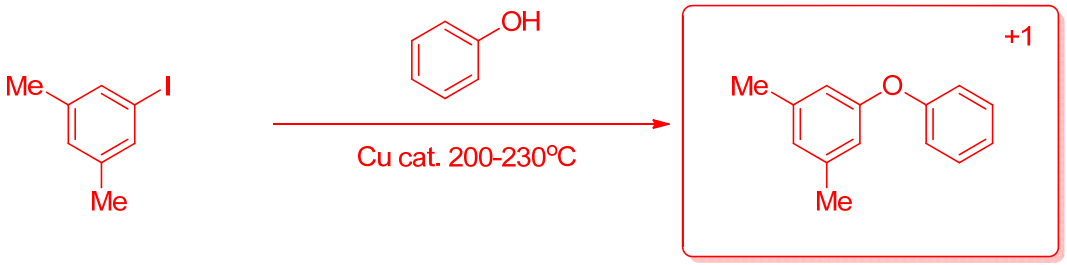
d) Predict the products



6. (Cu-stoichiometric; 6pts)

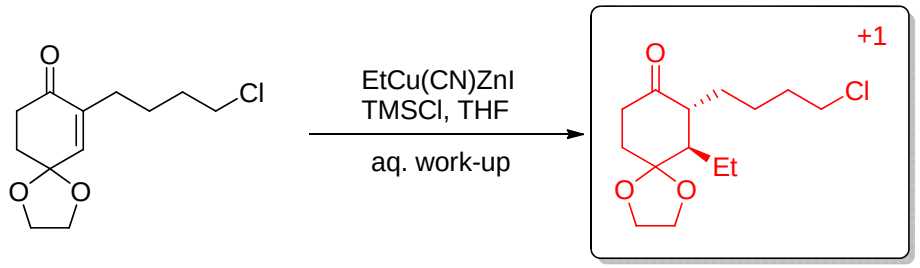
a) Give an example of a Chan-Lam coupling and an Ullmann coupling. What is the advantage and disadvantage of the Chan-Lam relative to the Ullmann coupling?

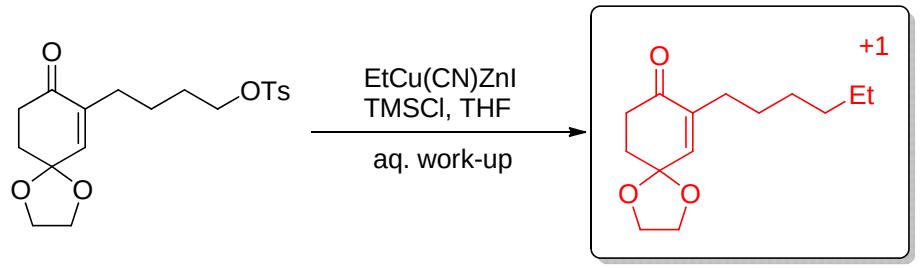




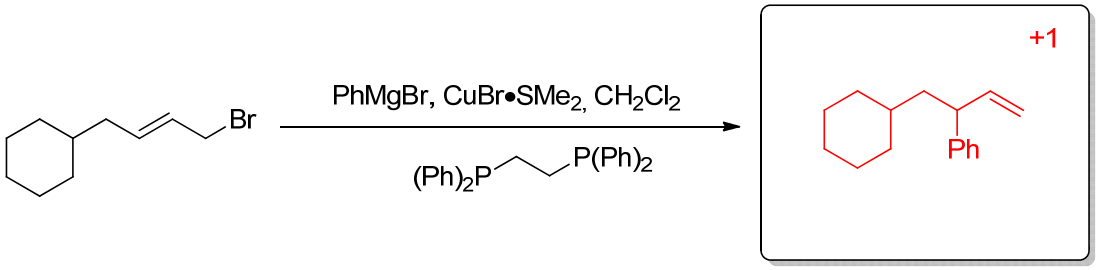
+1 The Chan-Lam couplings typically occur at much lower temperatures enabling the coupling of sensitive substrates. The disadvantage is that the reaction requires boronic acid substrates which require more steps to prepare compare to aryl halides.

b) Predict the products

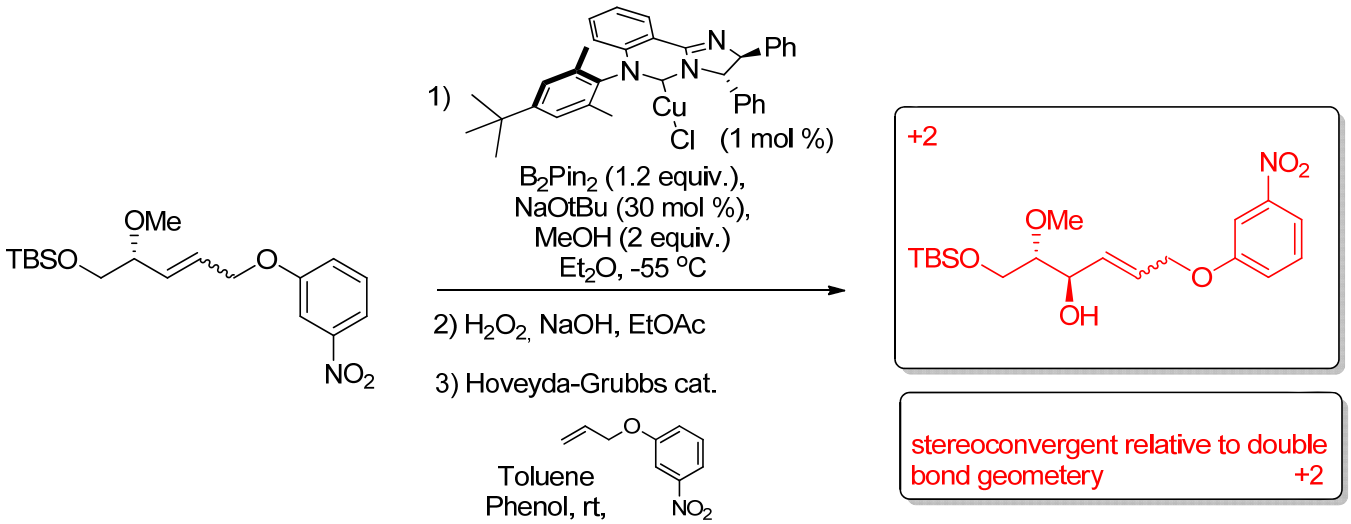




c) Predict the product

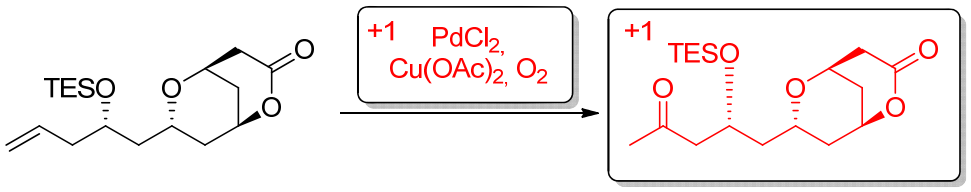


7. (Cu-catalytic; 4pts) Provide the product and what is unique about the stereochemical outcome

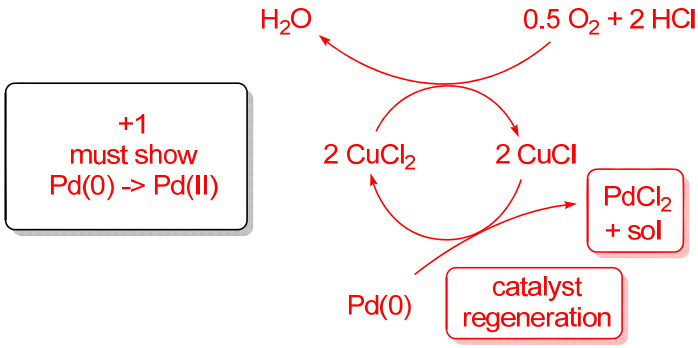


8.(Pd-non-cross-coupling; 6pts)

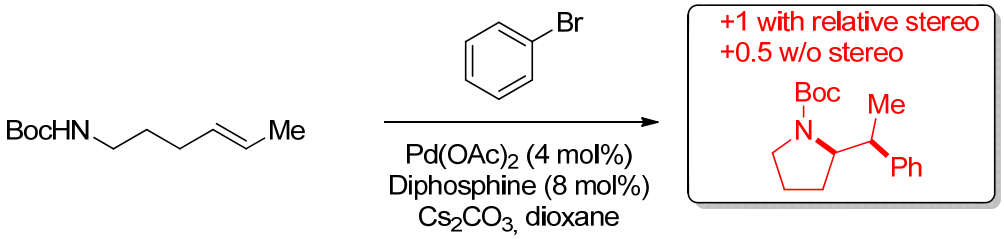
a) The following reaction is a Wacker Oxidation; provide the products and reagents;



b) Draw the portion of the Wacker catalytic cycle that involves the copper acetate and oxygen interacting with Pd.

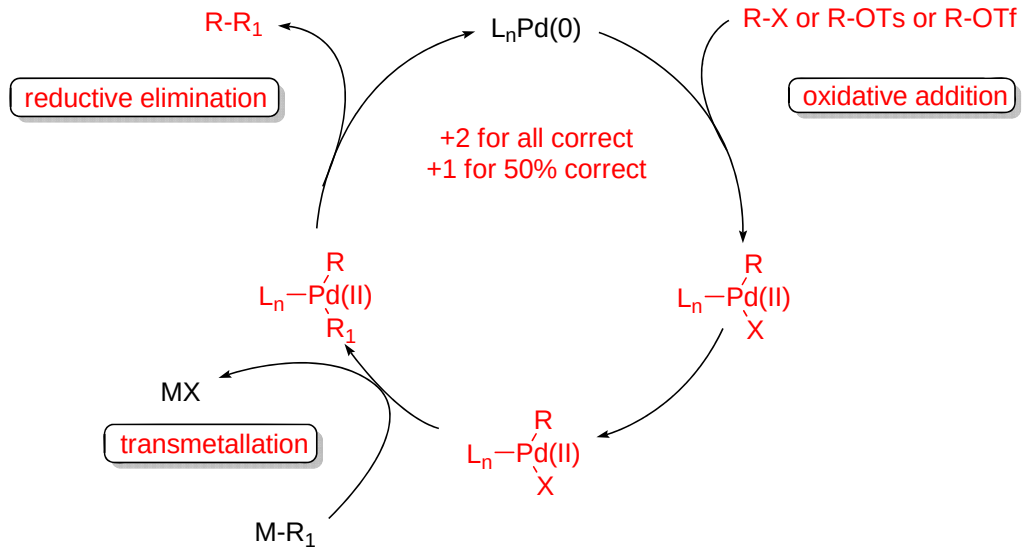


c) Predict the product – indicate relative stereochemistry

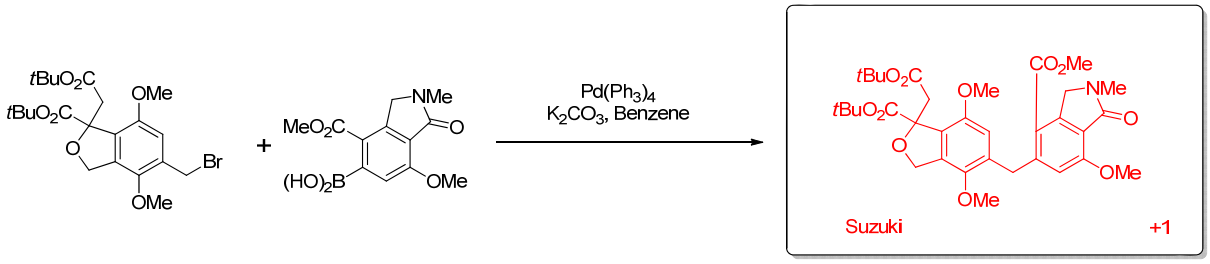


9. (Pd-cross-coupling; 6pts)

a) Fill-in the missing structures and descriptions (for the mechanistic steps)



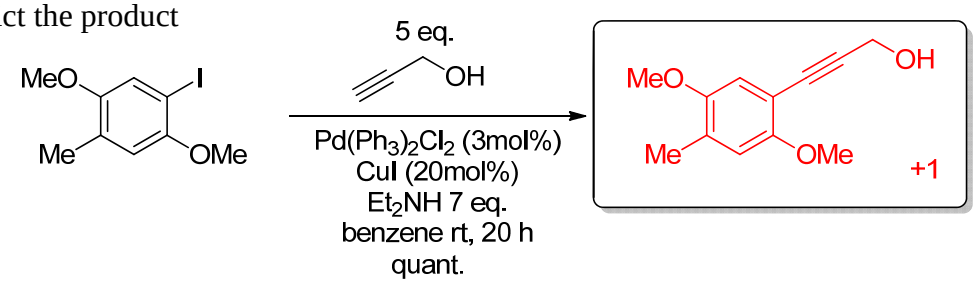
b) Predict the product



What function does the base provide?

The base is necessary in the Suzuki reaction to activate the boronic acid by forming an anion ate complex. The ate complex formation is necessary for the transmetallation step. +1

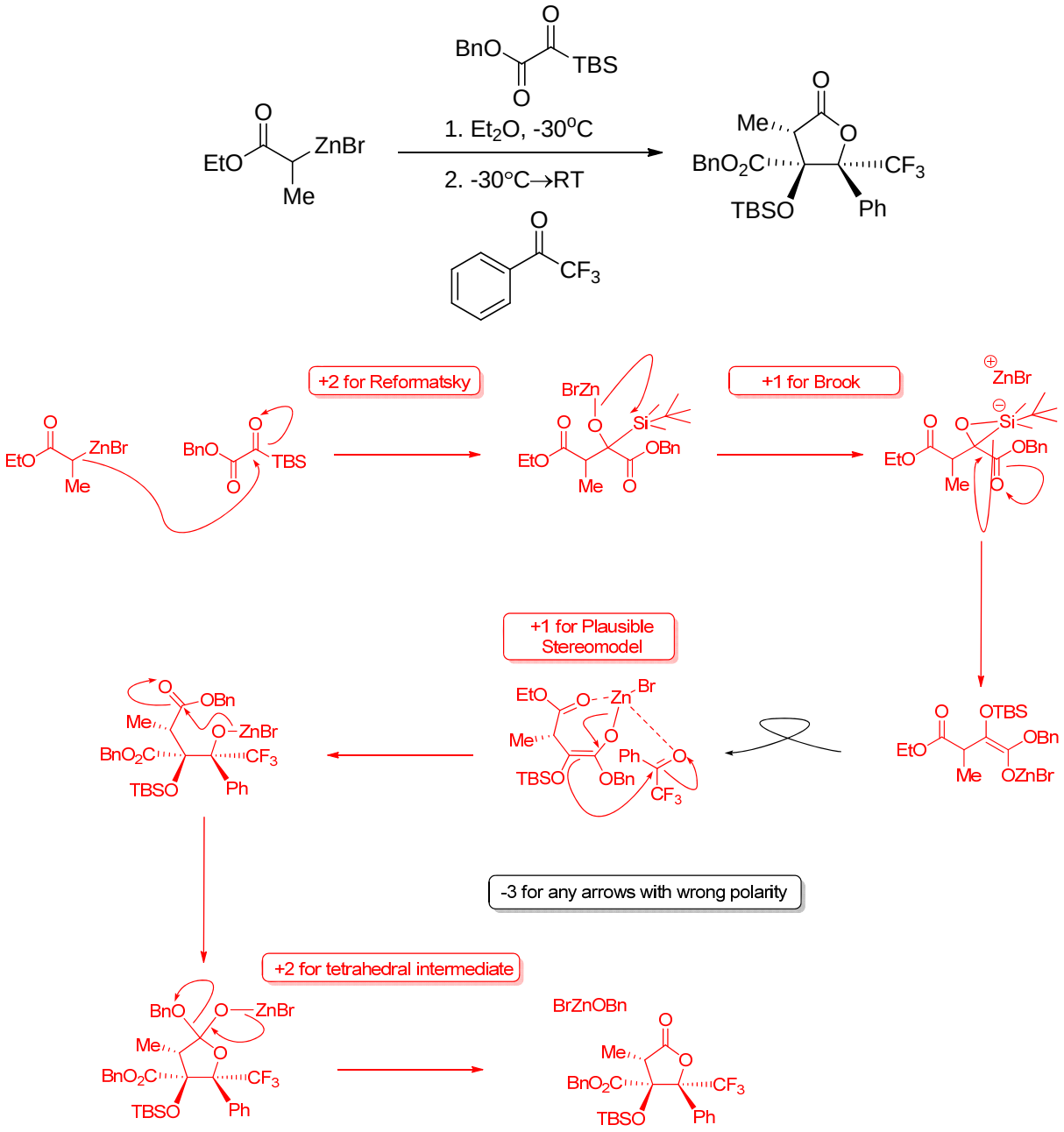
c) Predict the product



What function does the CuI salt provide?

The copper salt is necessary to provide a Cu-acetylide that can undergo transmetallation. +1

10.(Mechanism Question; 6pts) Provide an arrow pushing mechanism for the following reaction.



Extra Credit (+1): Assuming the stereochemistry of the product is correct which allyl group is transferred to obtain the product. Circle your answer.