

Halogen Magnesium Exchange

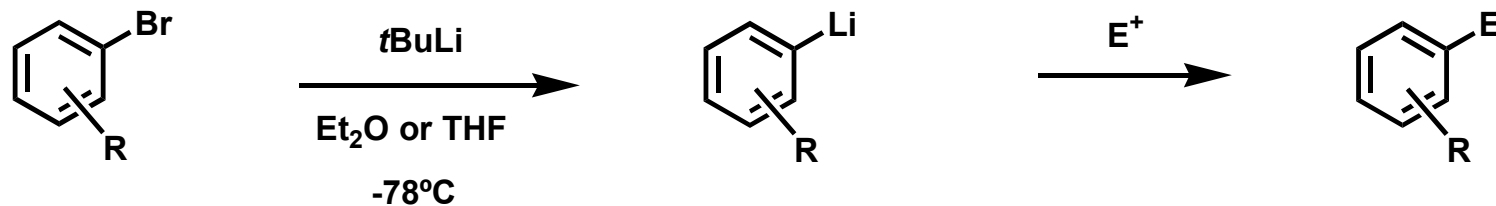
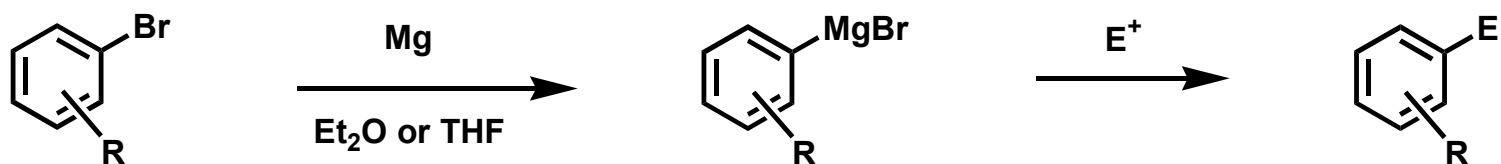


Günther Scheid

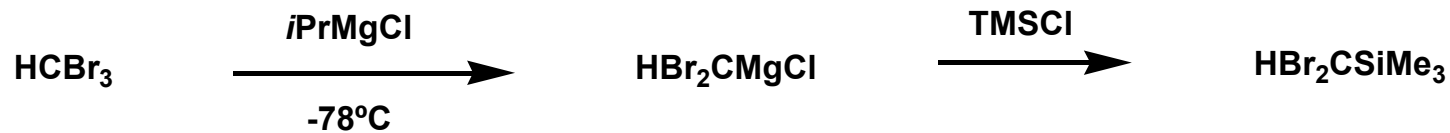
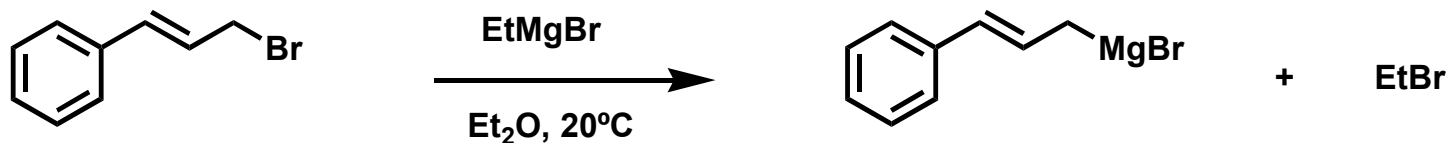
Supergroupmeeting Princeton 04/21/2004

Why?

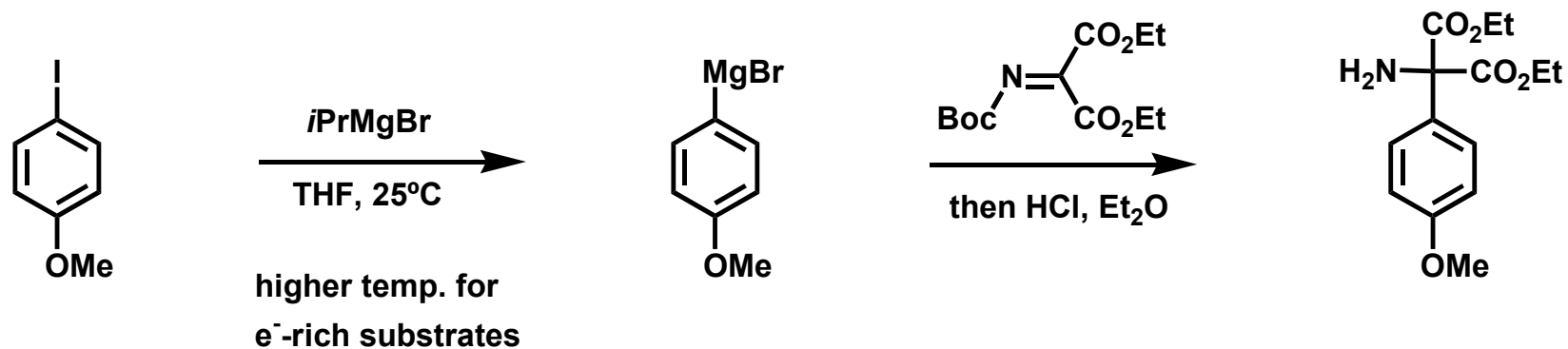
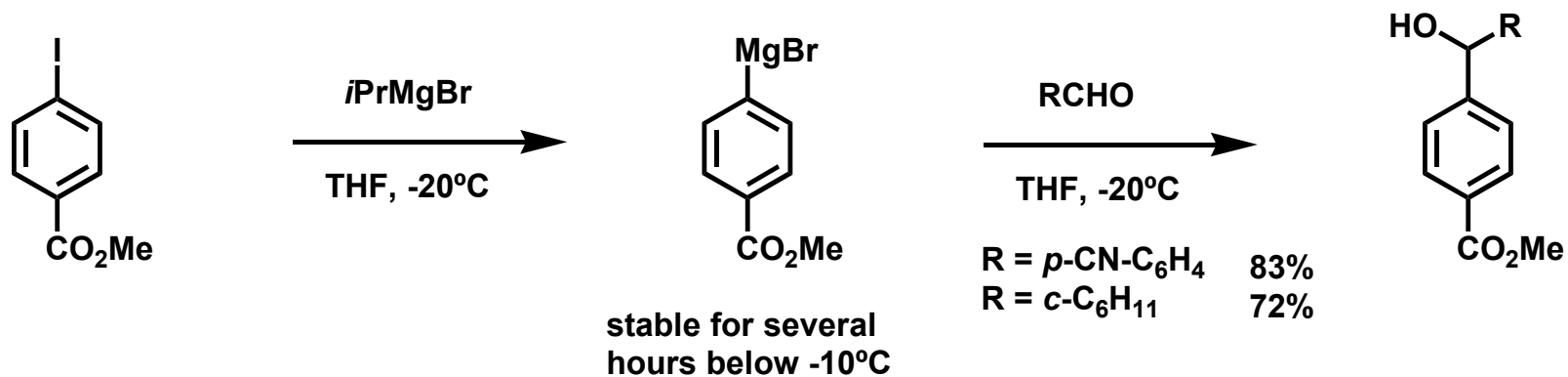
Why? ... or what is wrong with...



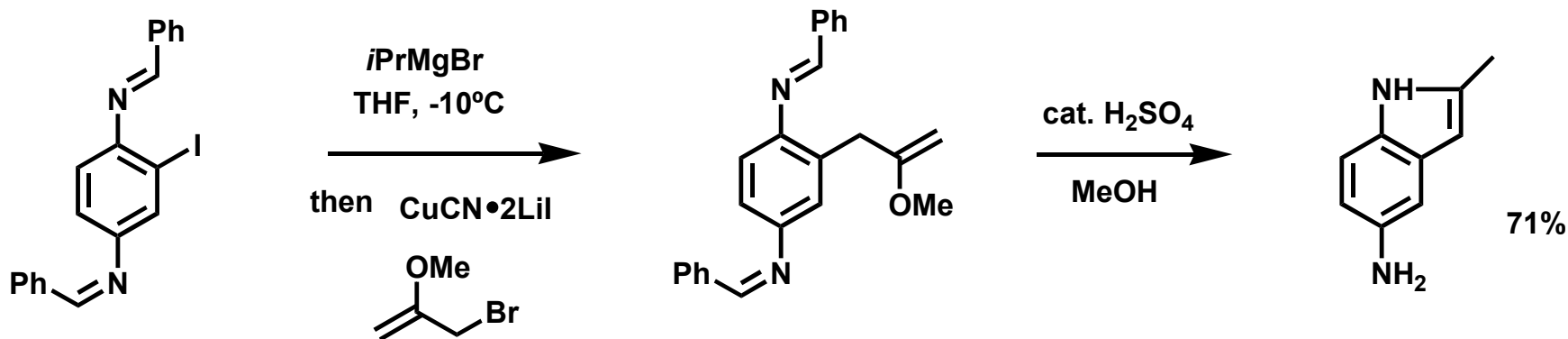
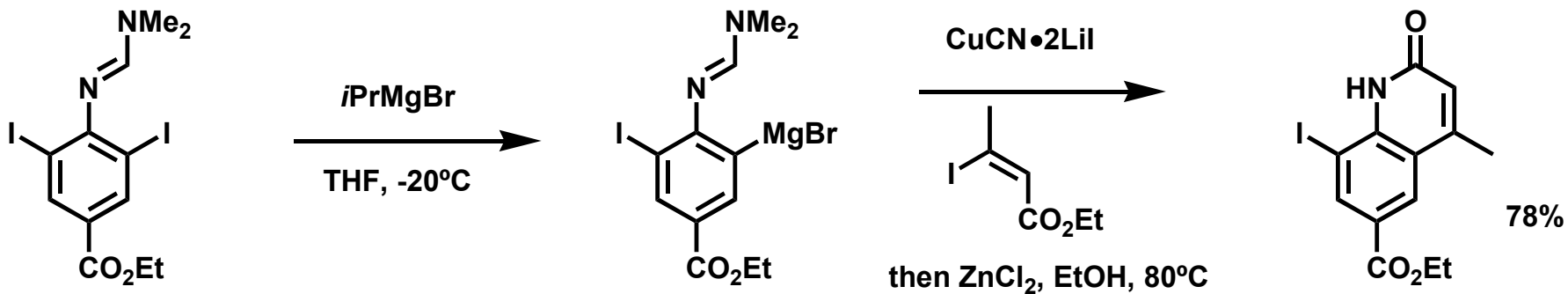
Two Early Examples



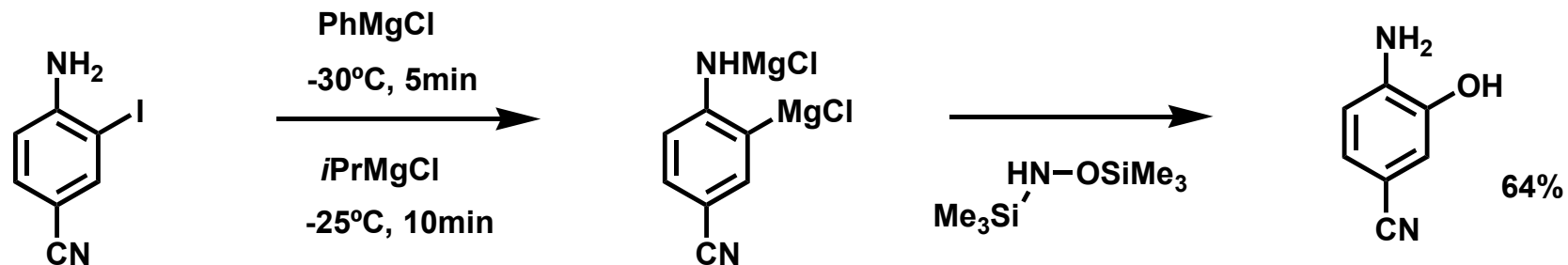
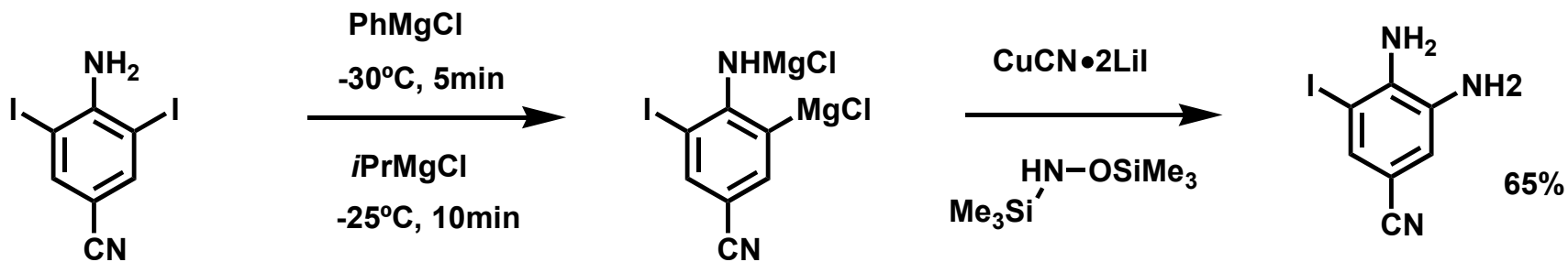
Functionalized Aryl Reagents I



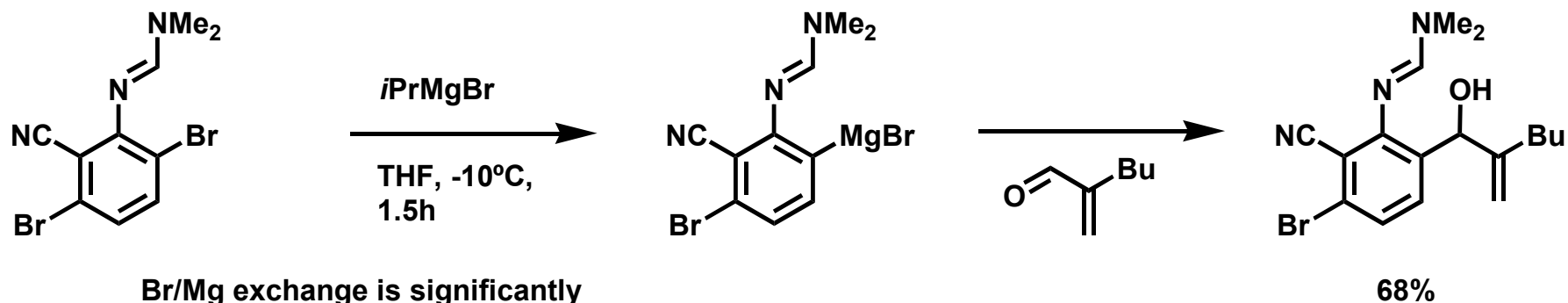
Functionalized Aryl Reagents II



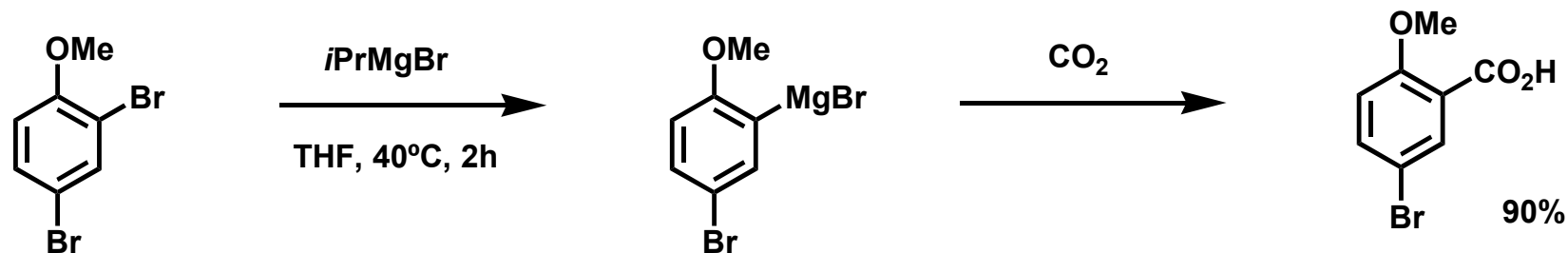
Functionalized Aryl Reagents III - free amines



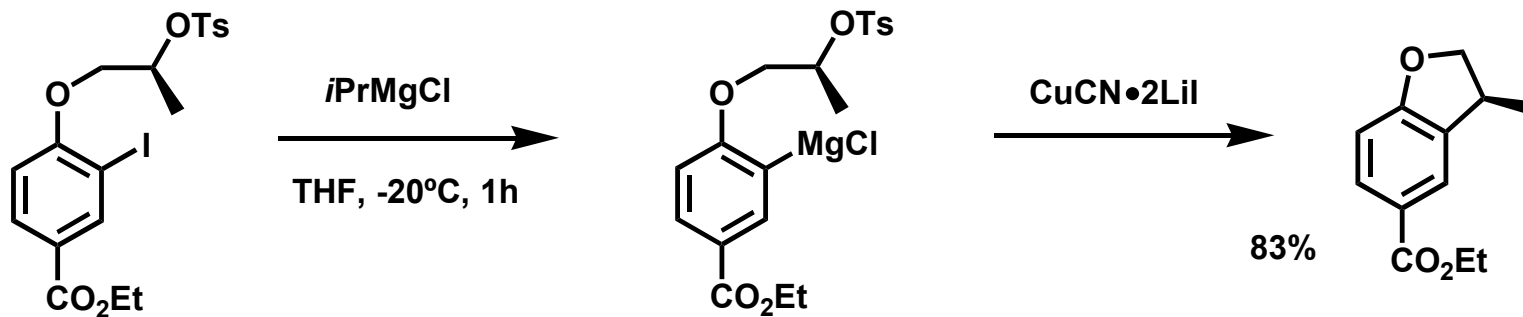
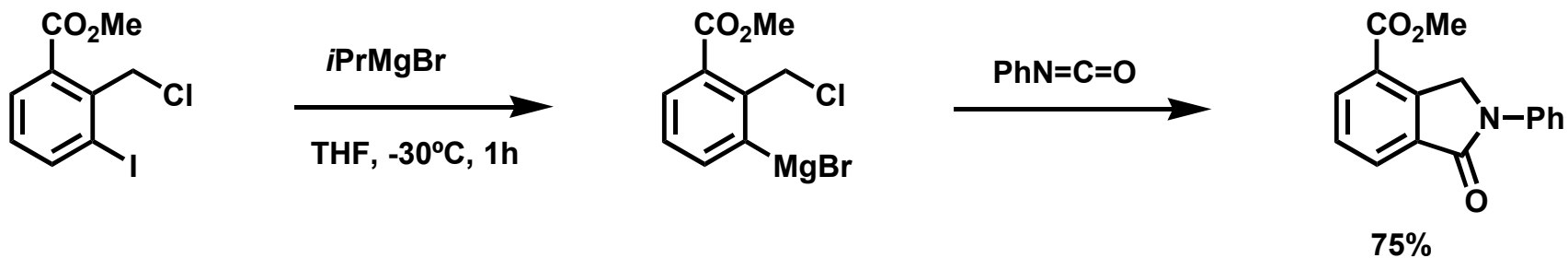
Functionalized Aryl Reagents IV - directing groups ⁸



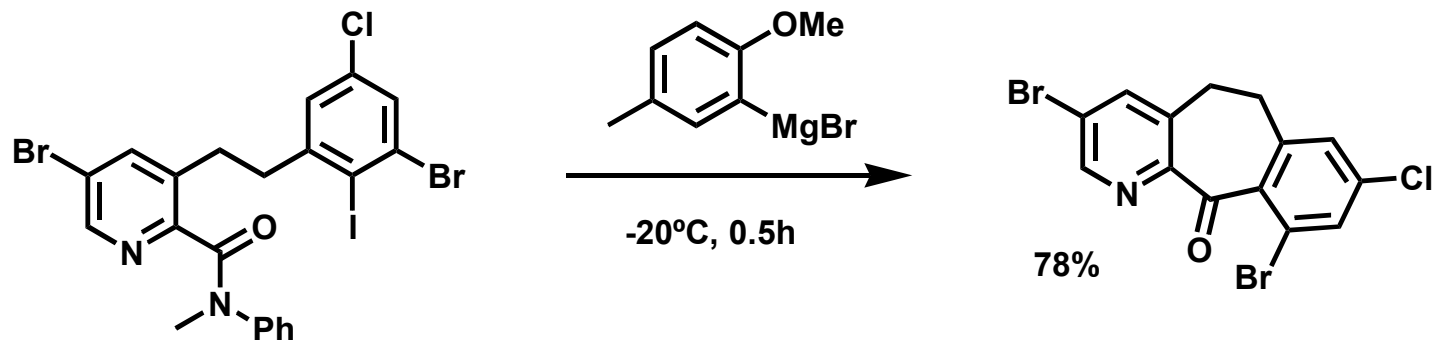
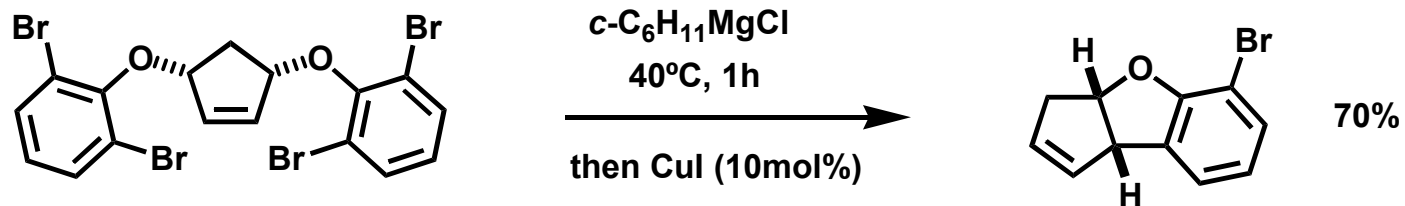
Br/Mg exchange is significantly slower than I/Mg exchange!!!



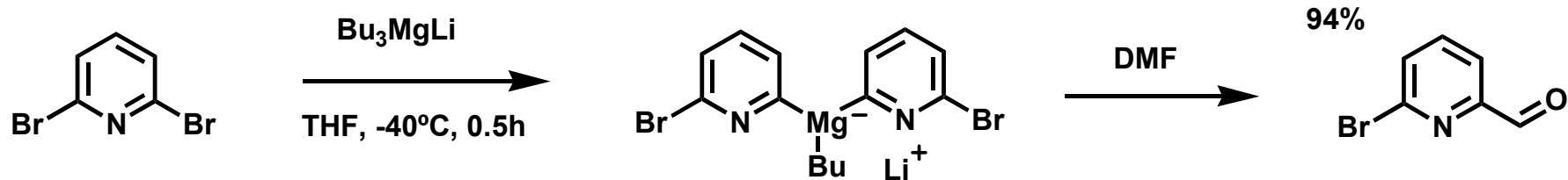
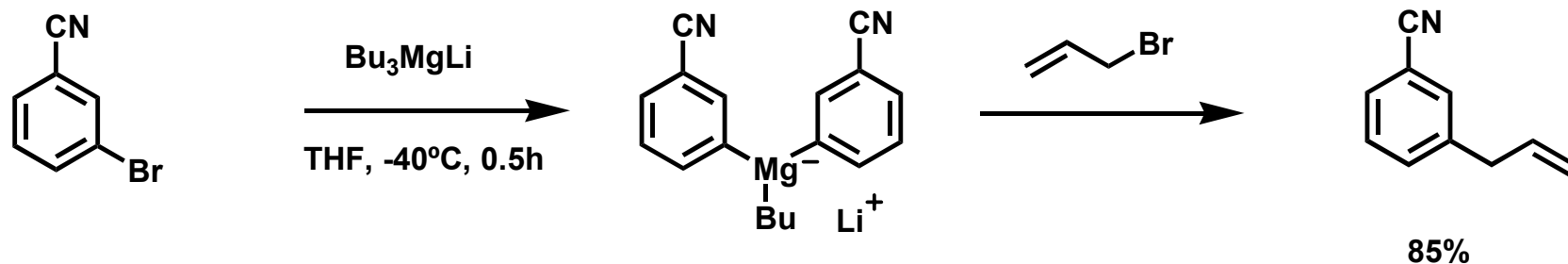
Functionalized Aryl Reagents V



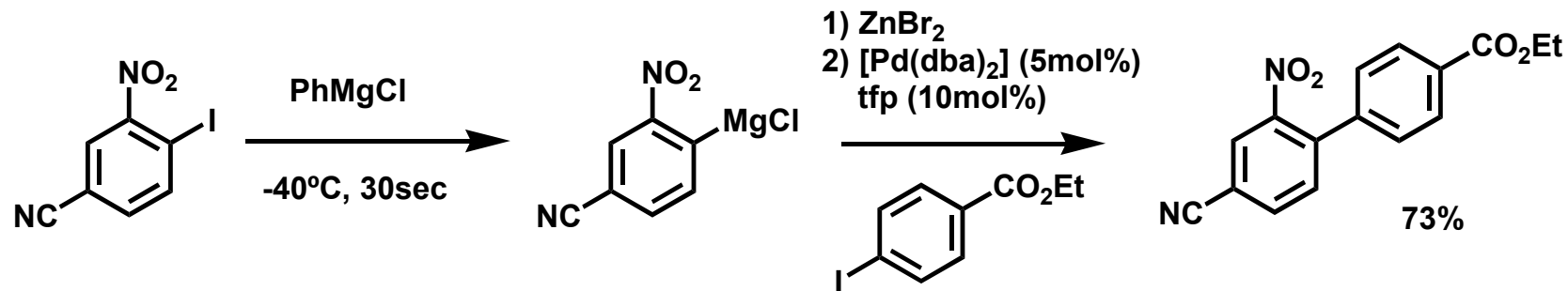
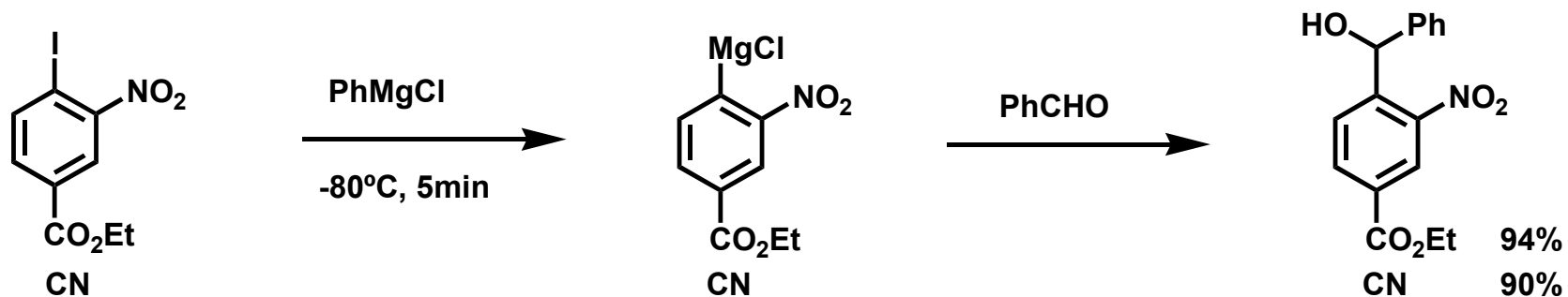
Functionalized Aryl Reagents VI - cyclizations



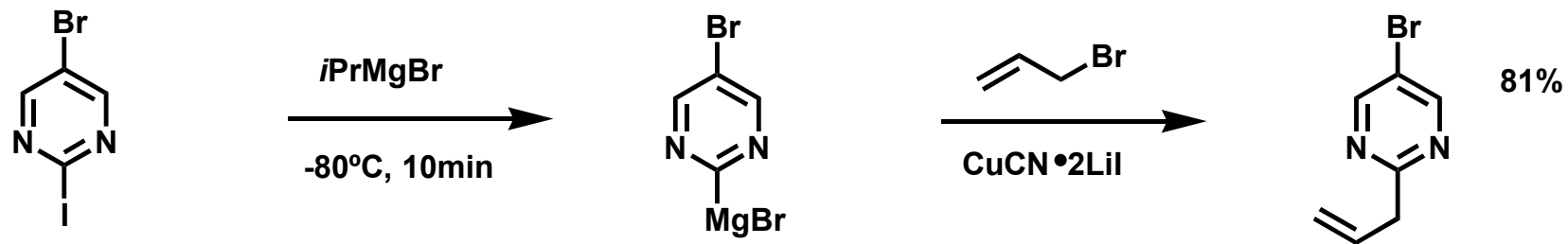
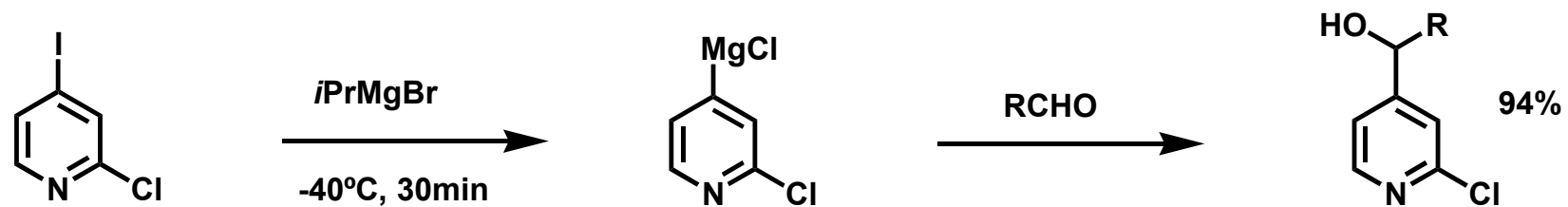
Functionalized Aryl Reagents VII - Magnesiates



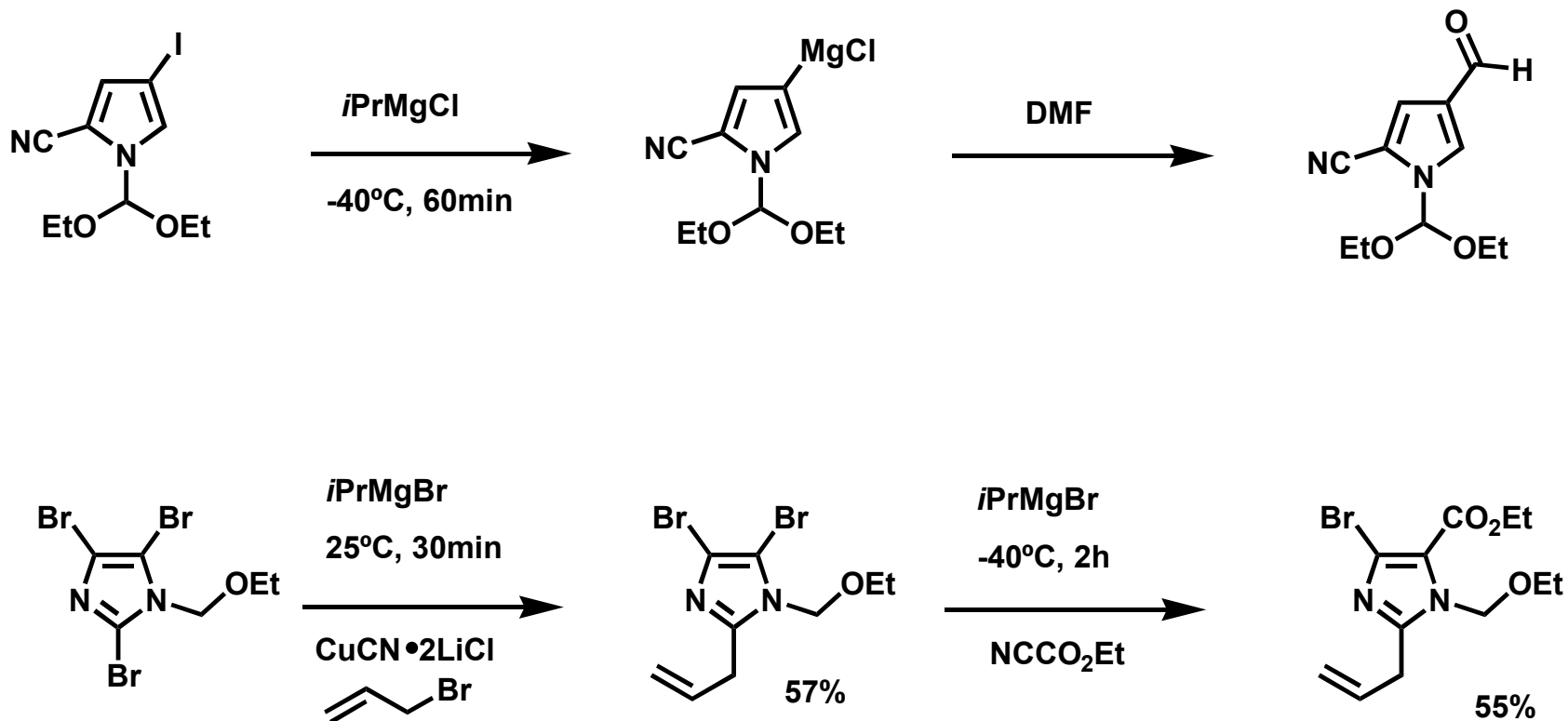
Functionalized Aryl Reagents VIII - Nitroarenes



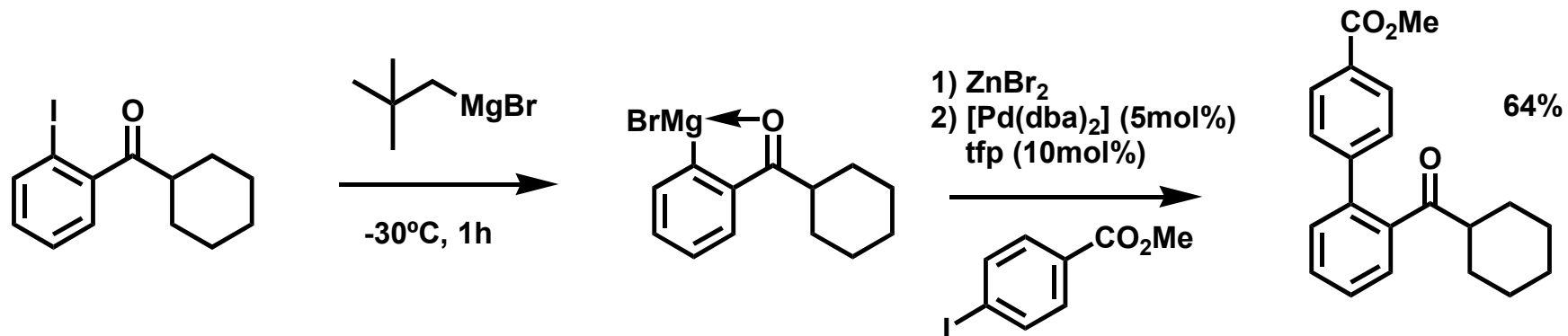
Heteroaryl Reagents I



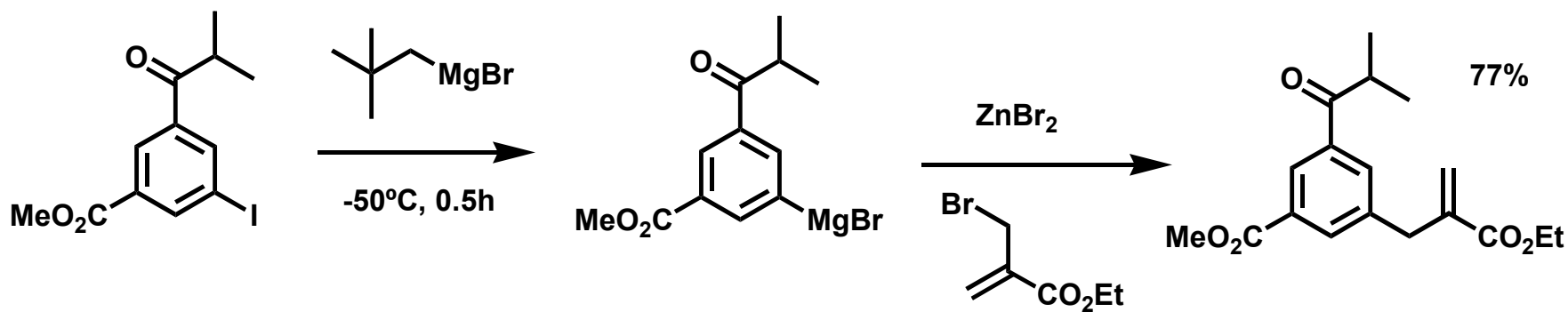
Heteroaryl Reagents II



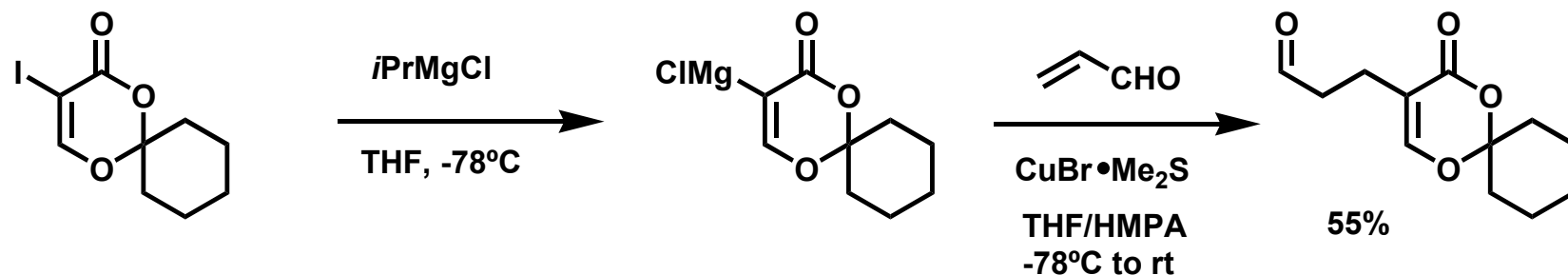
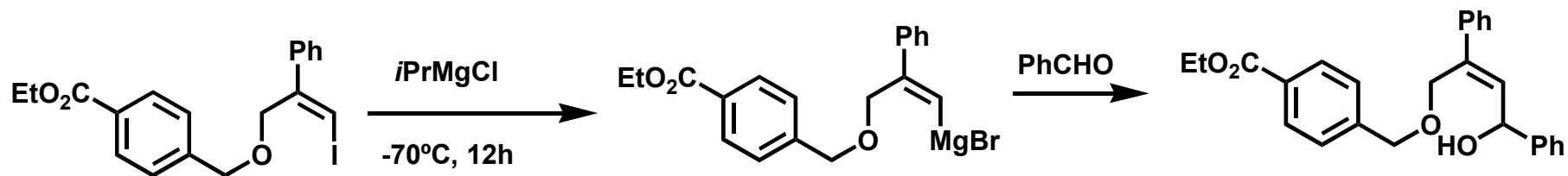
Functional Group Tolerance



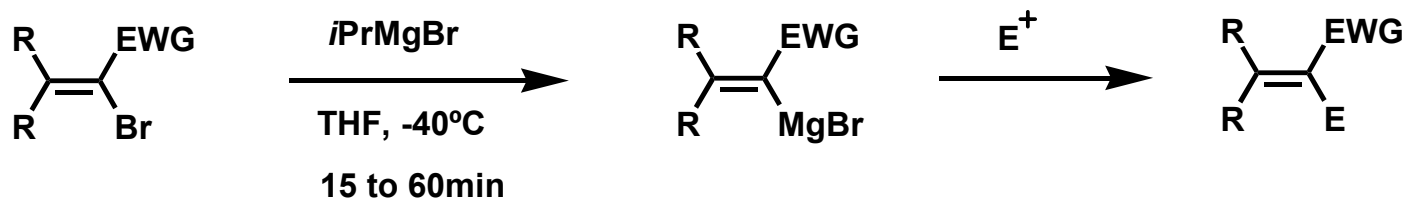
no hydride transfer reduction with neopentylmagnesium bromide!!!



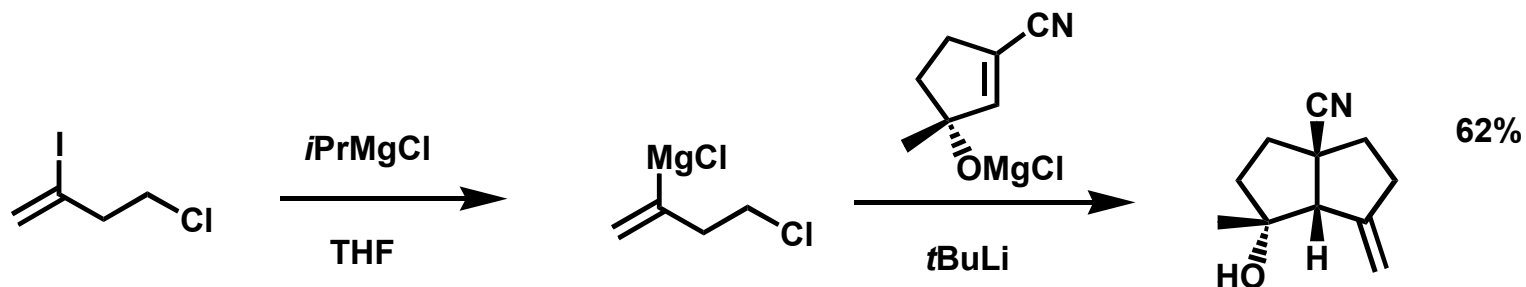
Alkenyl Magnesium Reagents I



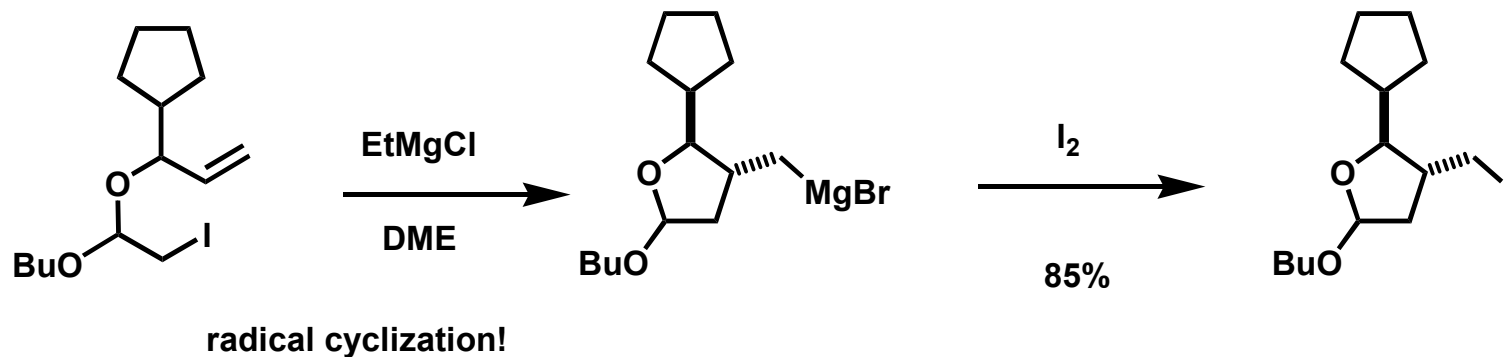
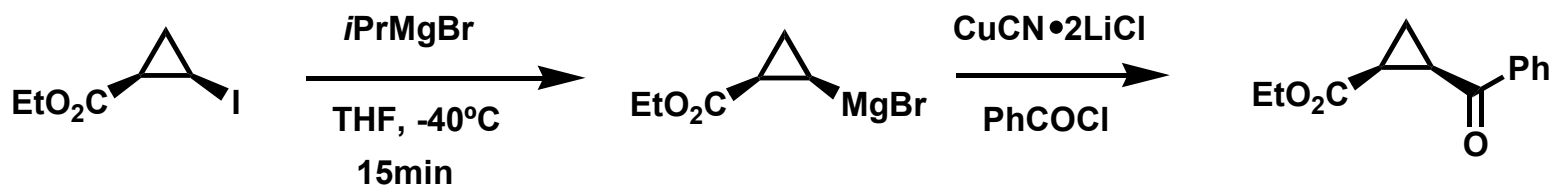
Alkenyl Magnesium Reagents II



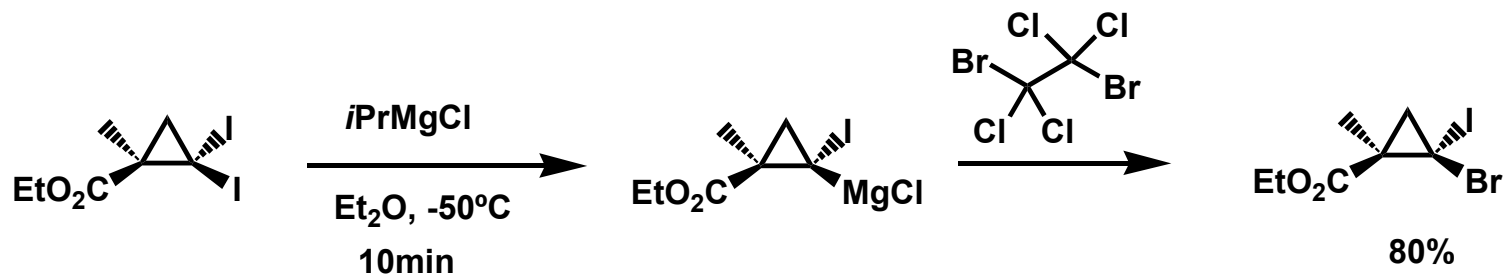
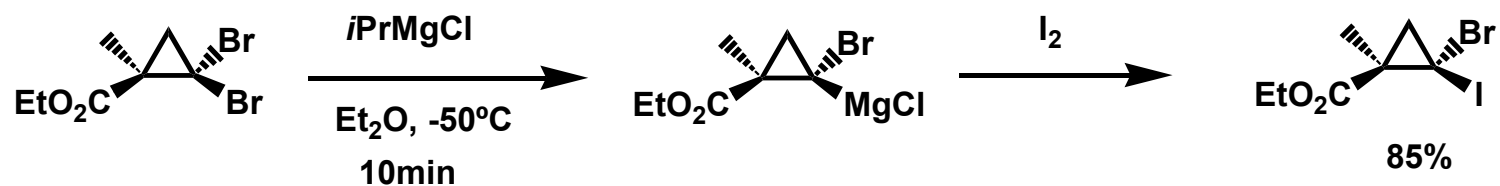
EWG = CN, SO₂Ph, CO₂*t*Bu, CONEt₂



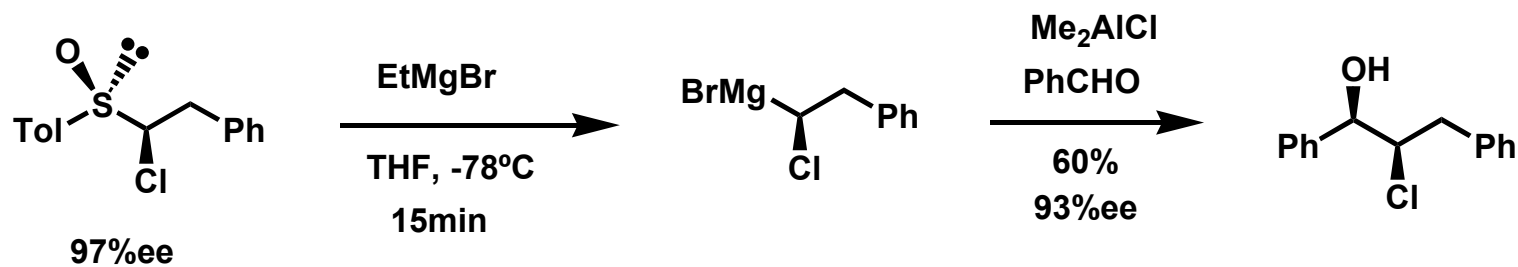
Alkyl Grignard Reagents and Carbenoids I



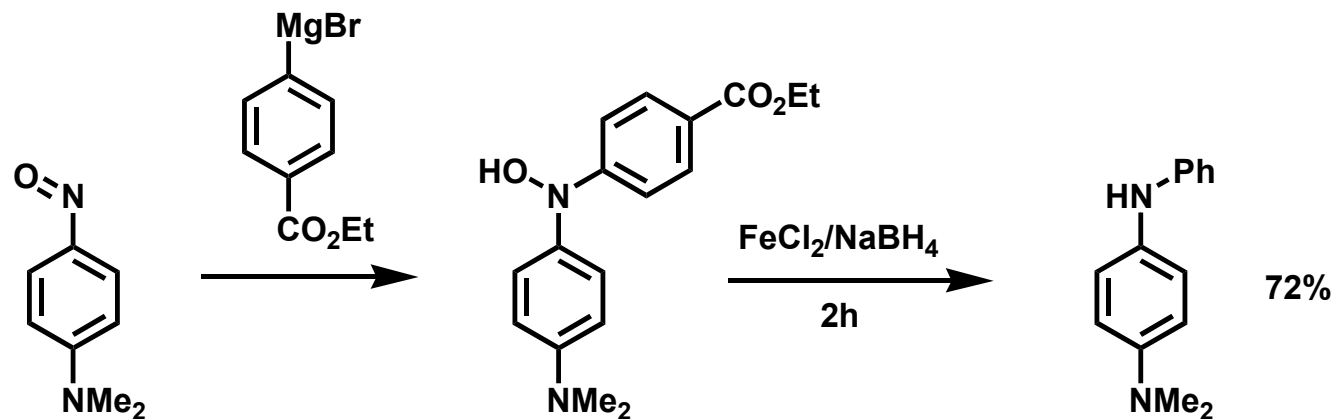
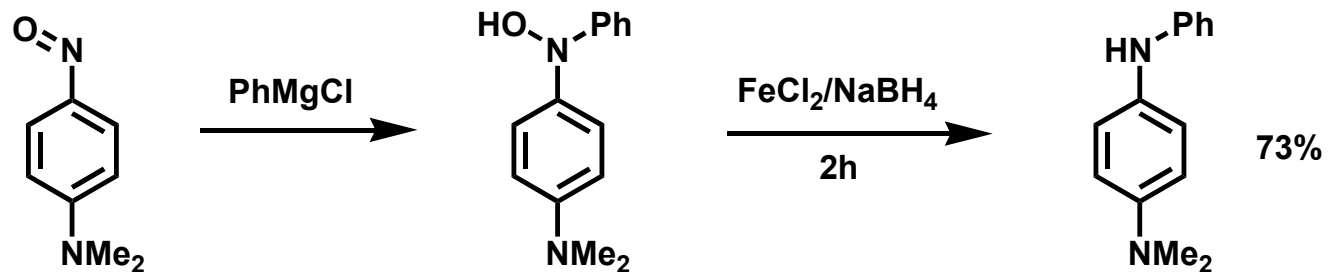
Alkyl Grignard Reagents and Carbenoids II



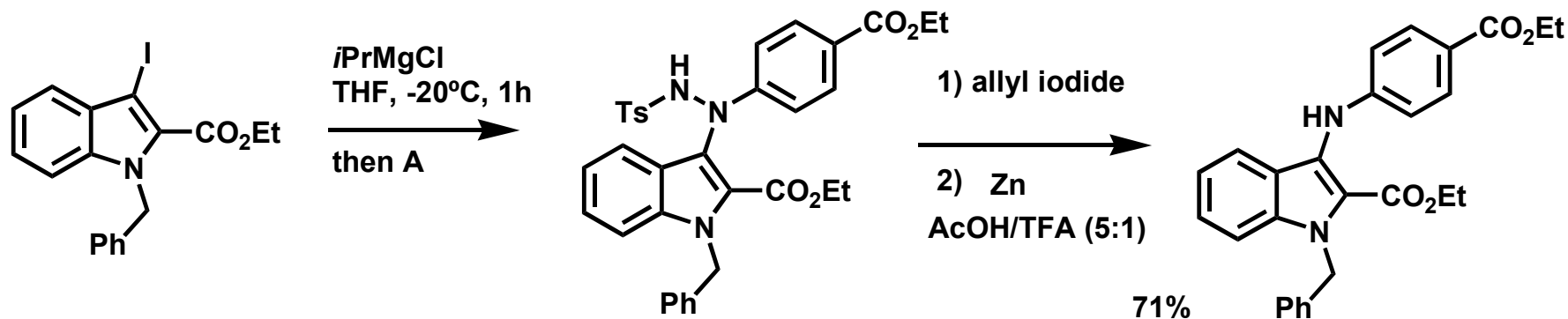
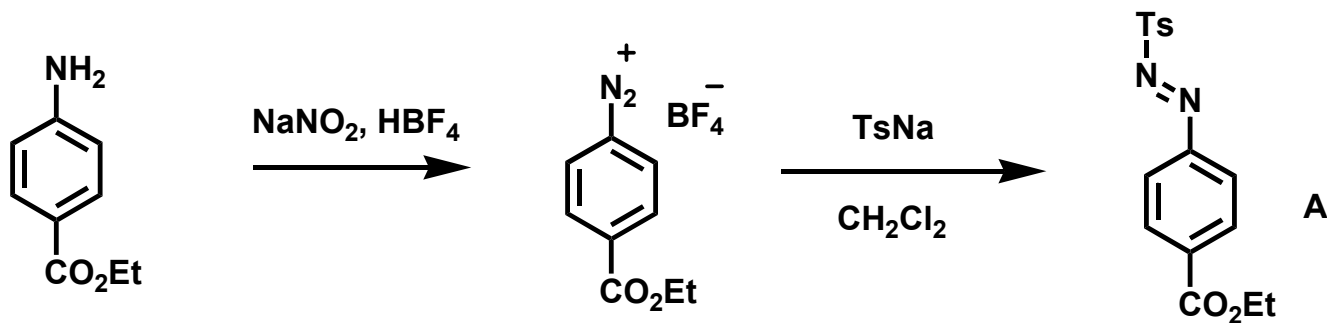
Alkyl Grignard Reagents and Carbenoids III



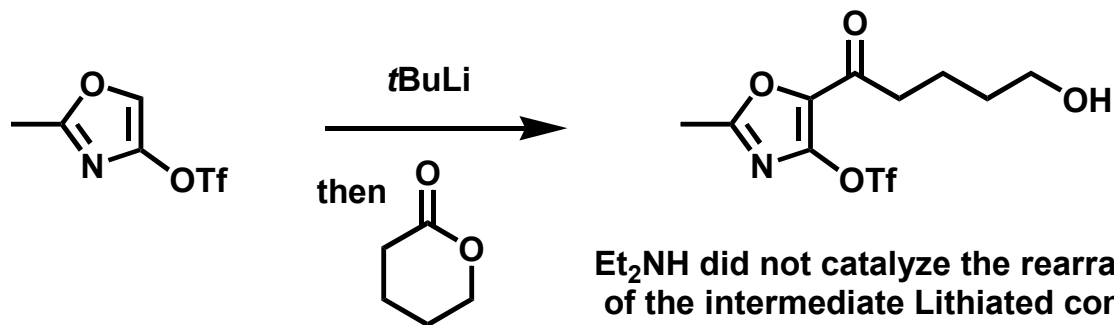
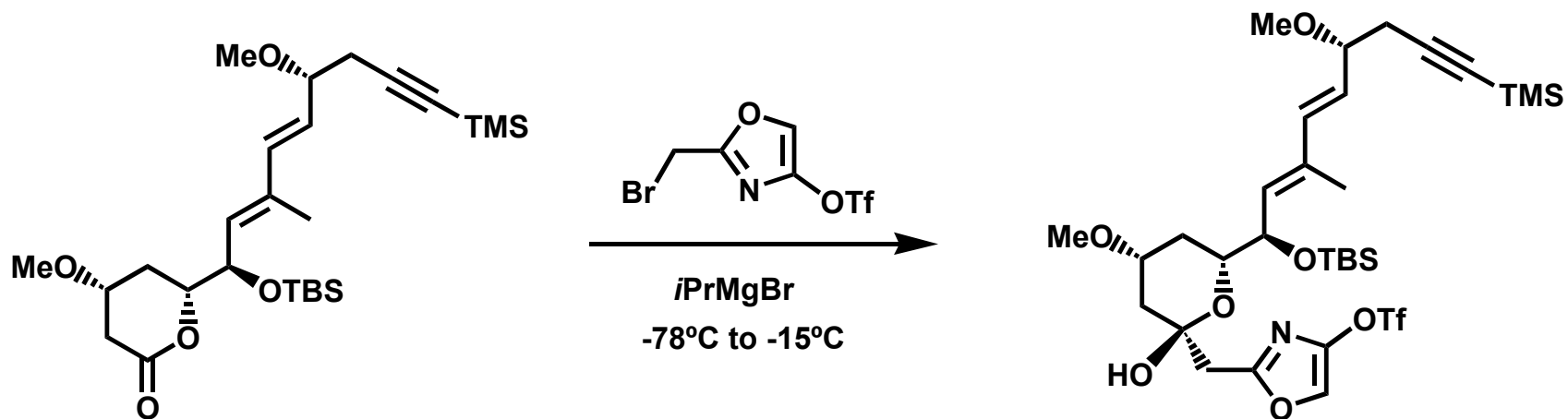
Bisaryl Amine Synthesis without Pd



Bisaryl Amine Synthesis without Pd

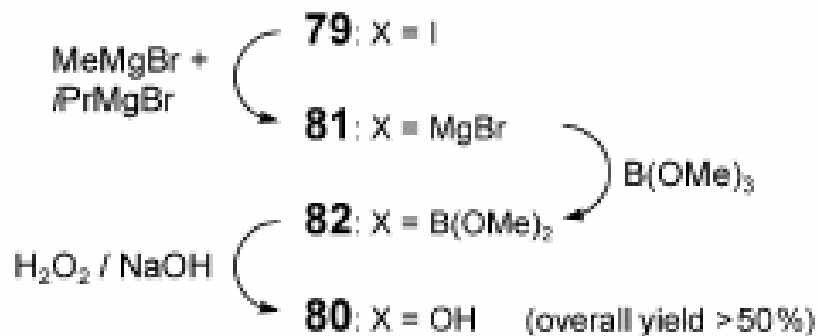
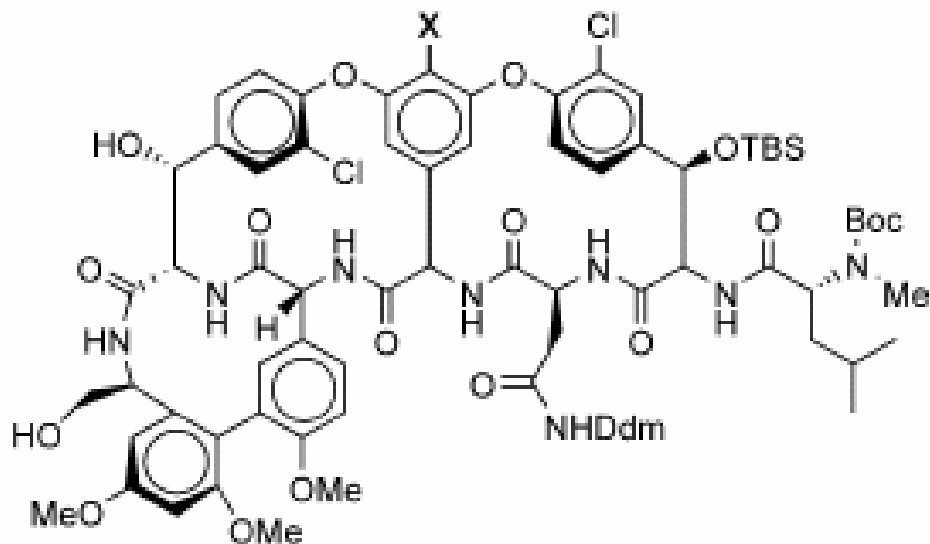


Total Synthesis (“complex”) Substrates I



Et_2NH did not catalyze the rearrangement of the intermediate Lithiated compound

Total Synthesis (“complex”) Substrates II

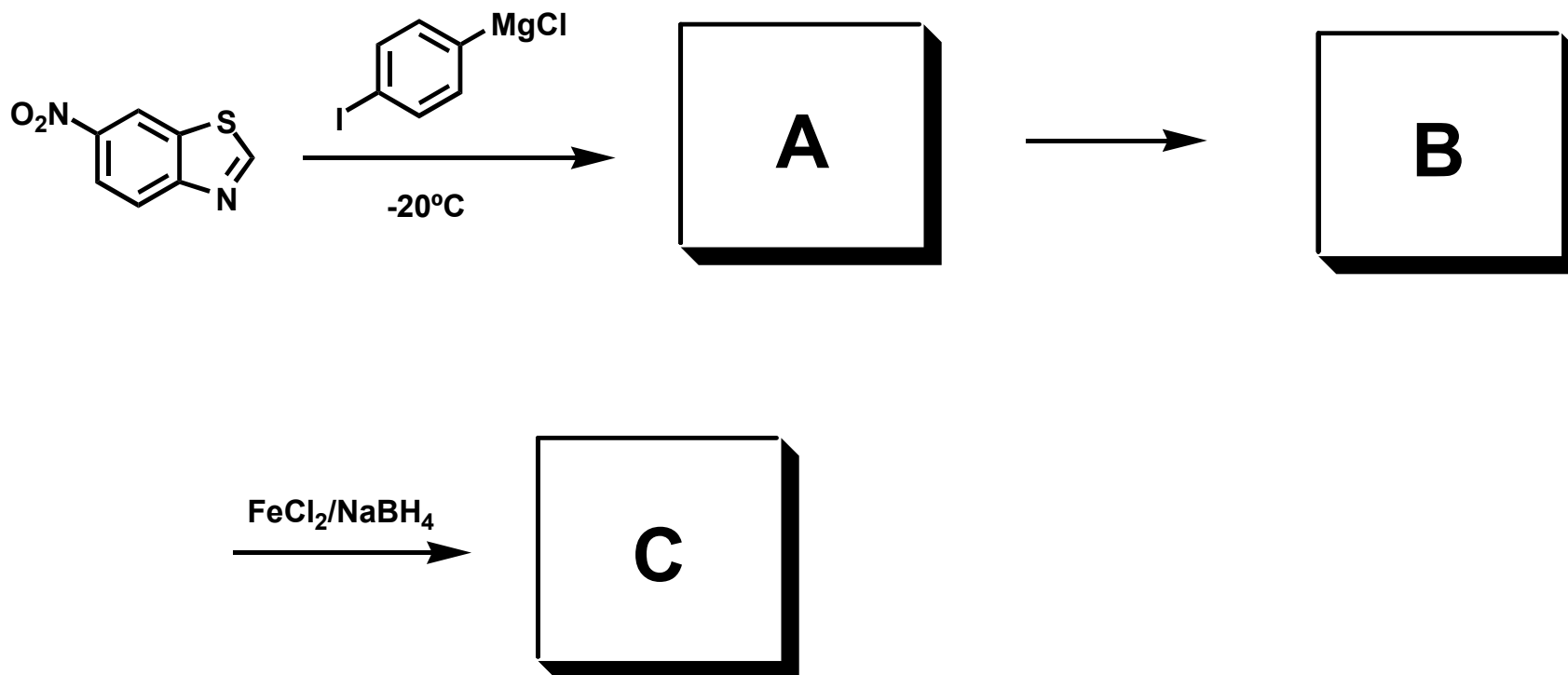


Summary

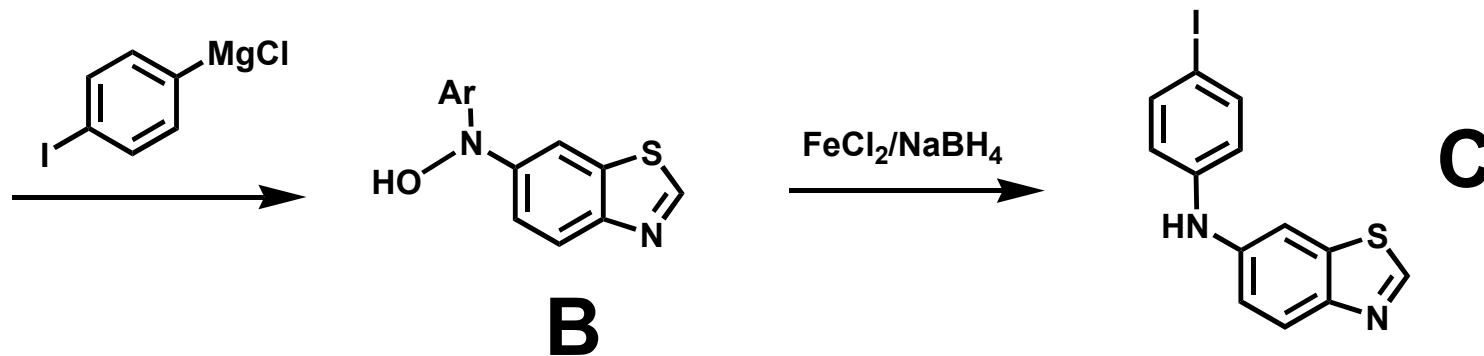
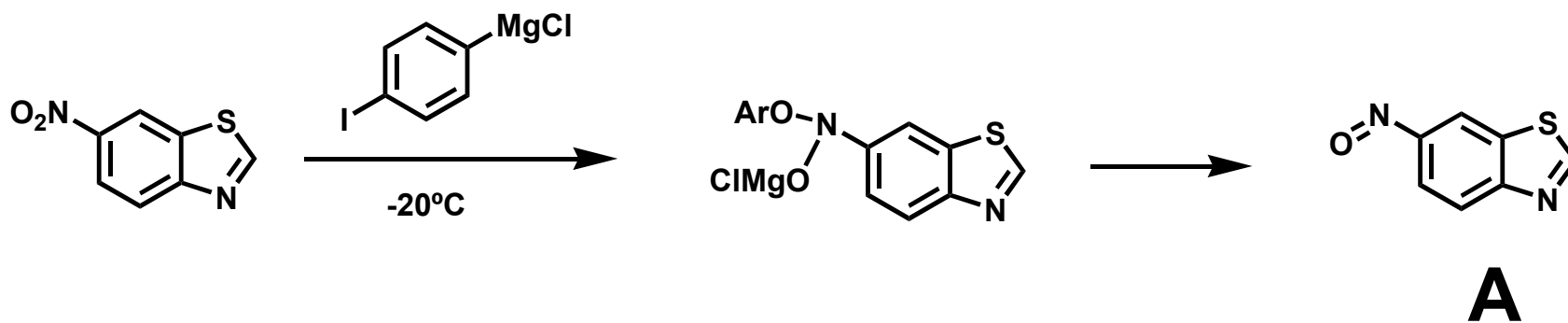
Halogen Magnesium exchange allows the Synthesis of organomagnesium reagents with many more functional groups than previously thought.

The mild reaction conditions are the key for assuring high functional group tolerance.

Problem



Problem



Problem

