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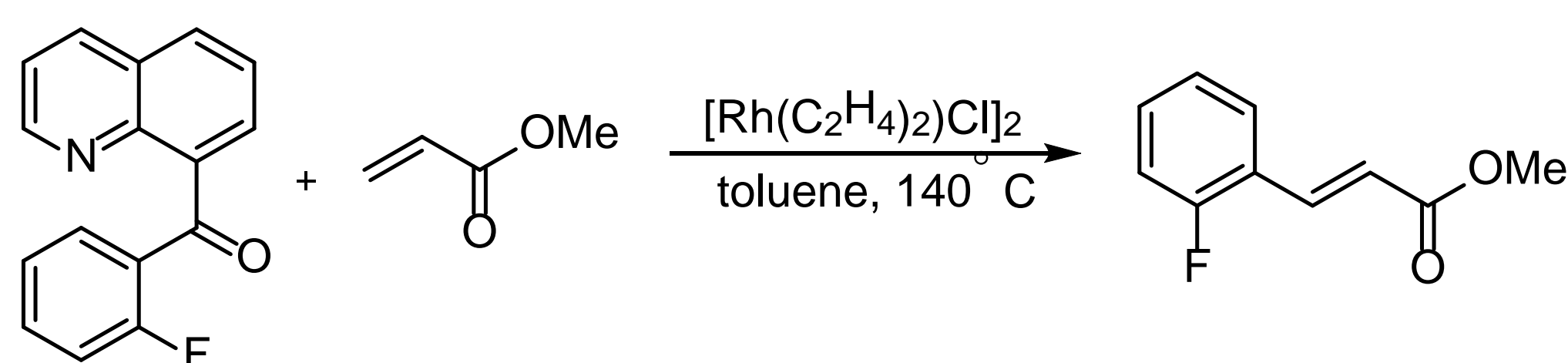
Carbon-Carbon Single Bond Activation Used for Coupling with Michael Acceptors

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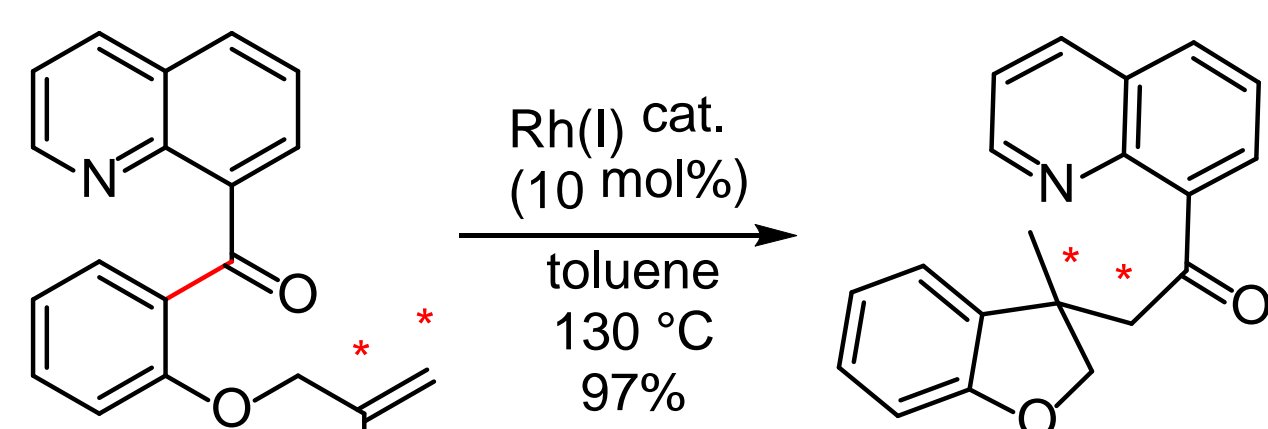
Abstract

Carbon-carbon single bond activation and functionalization occurs in a quinolinylyl ketone structure through rhodium catalyzed carbon-carbon bond activation and subsequent insertion of a Michael acceptor, primarily methyl acrylate and N,N-dimethylacrylamide. A variety of quinolinylyl ketones and Michael acceptors are seen to undergo conversion catalytically, forming a disubstituted alkene coupling product. A broad scope of quinolinylyl ketones and Michael acceptors have been used to investigate the mechanism for the reaction.



Background

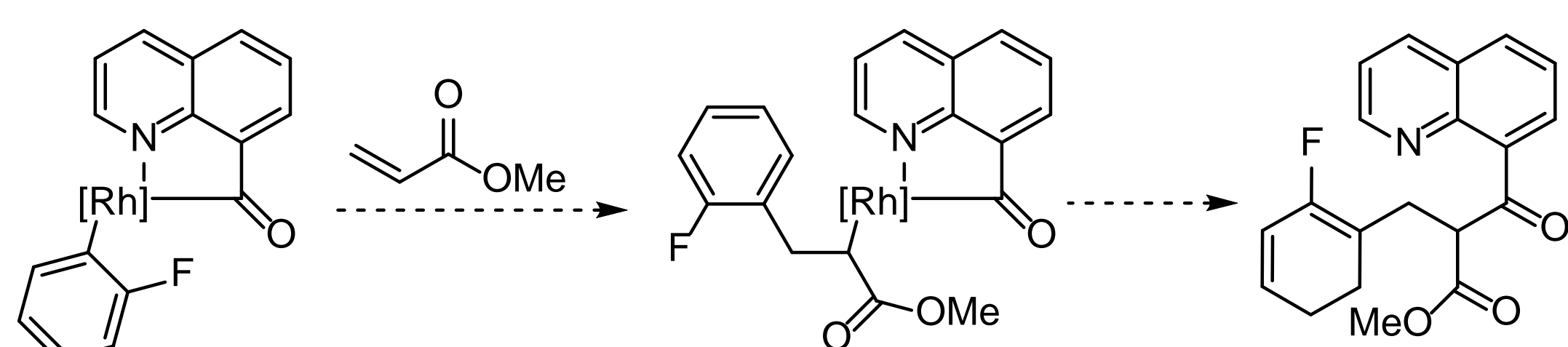
Dreis, Douglas, and coworkers first reported the intramolecular reaction of a quinolinylyl ketone and a rhodium catalyst, allowing carbon-carbon single bond activation and the insertion of the alkene in that bond. This provided potential for carbon-carbon single bond activation to become a method for synthesis.



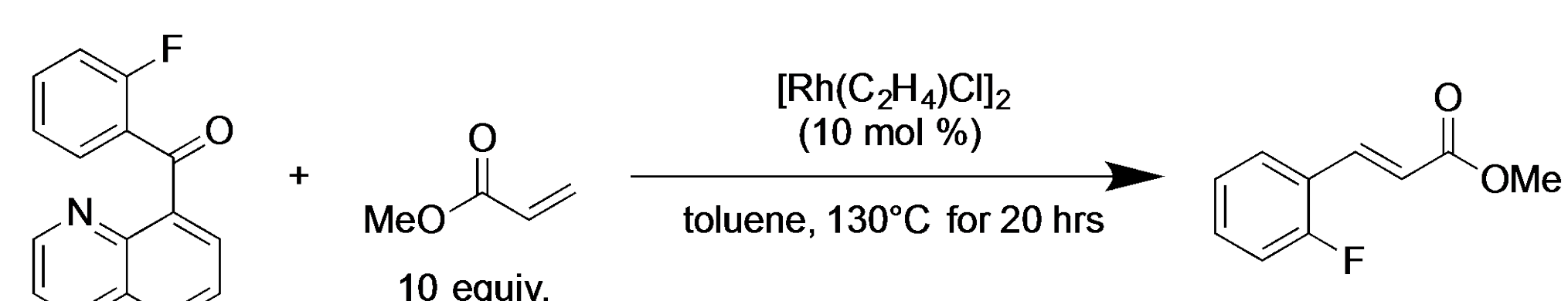
Dreis, A. M.; Douglas, C.J.; *J. Am. Chem. Soc.* 2009, 131, 412

Based upon further analysis, previous Johnson group members hypothesized that an ortho-fluoro substituted quinolinylyl ketone would allow for a stable intermediate that would enable interception with an intermolecular alkene.

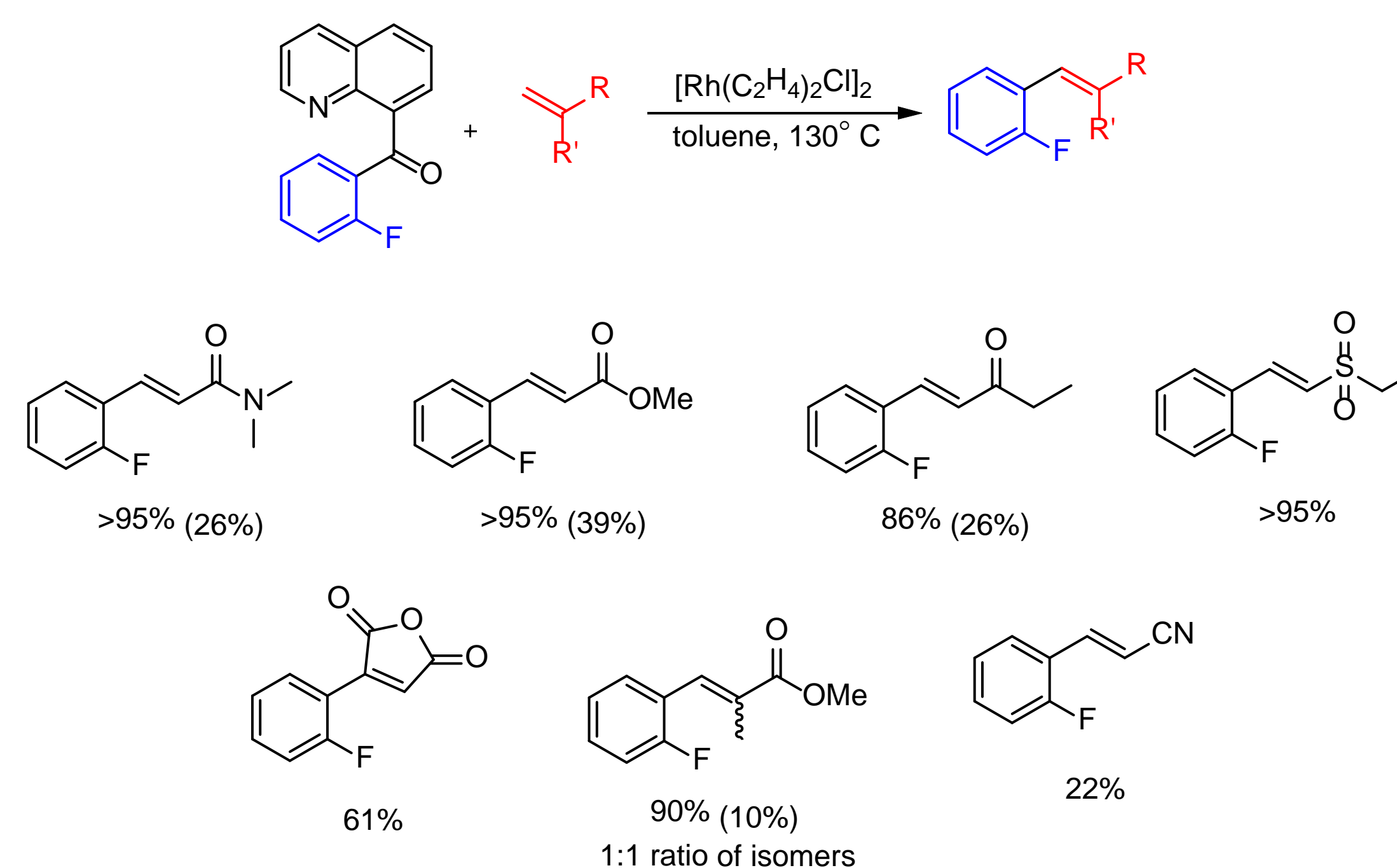
Hypothesis:



When conducted, however, an unexpected product formed from carbon-carbon single bond activation and an oxidative nucleophilic addition to Michael acceptors. It was assumed this reaction followed a mechanism similar to intramolecular carboacylation.

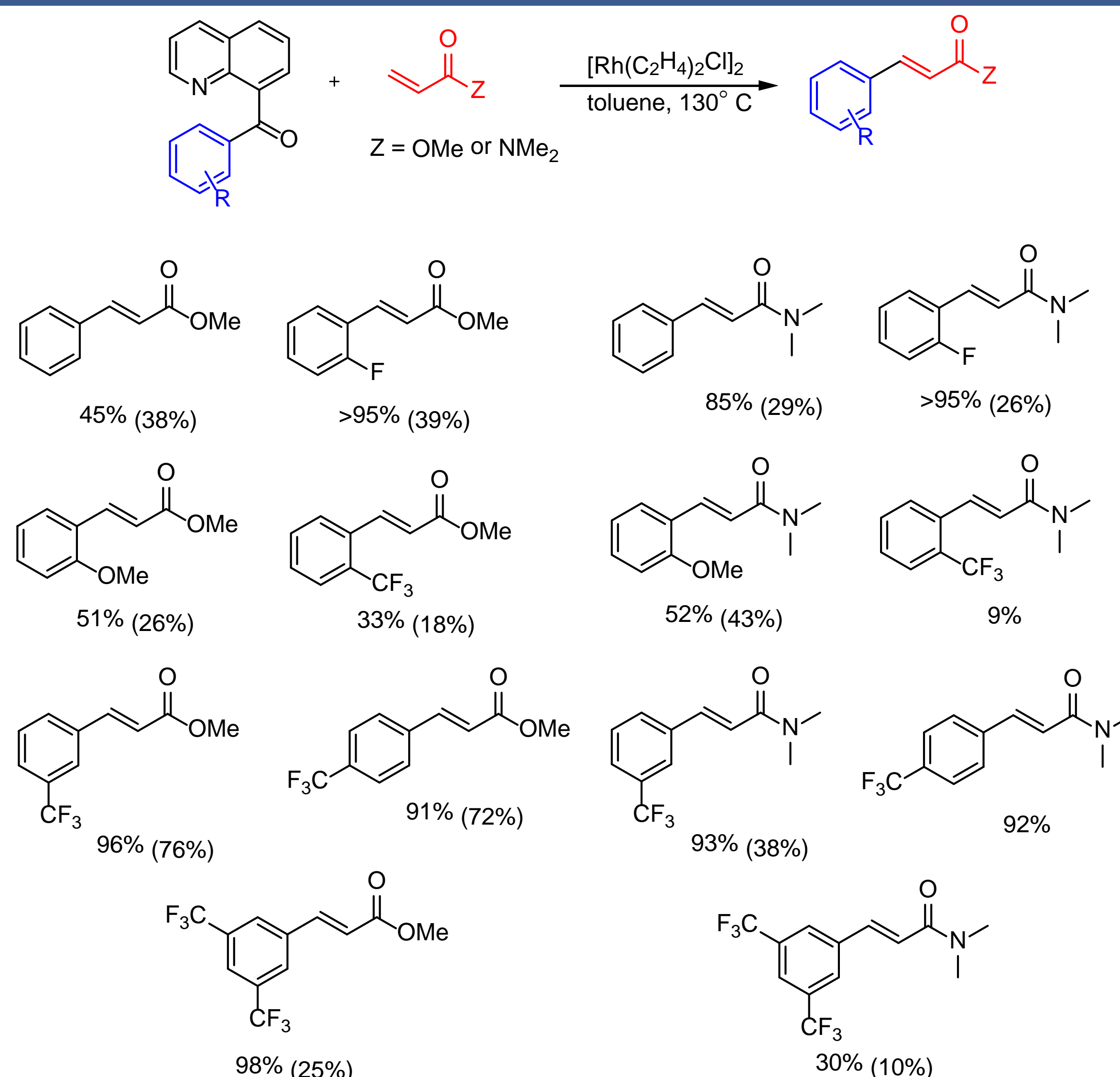


Scope of Michael Acceptors



*Isolated yields in parentheses. Challenges in isolation primarily due to the excess of alkene present. All reactions were run under nitrogen.

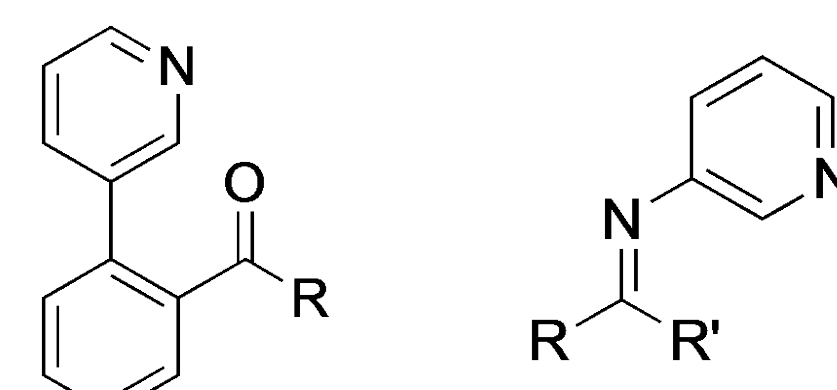
Scope of Quinolinylyl Ketones



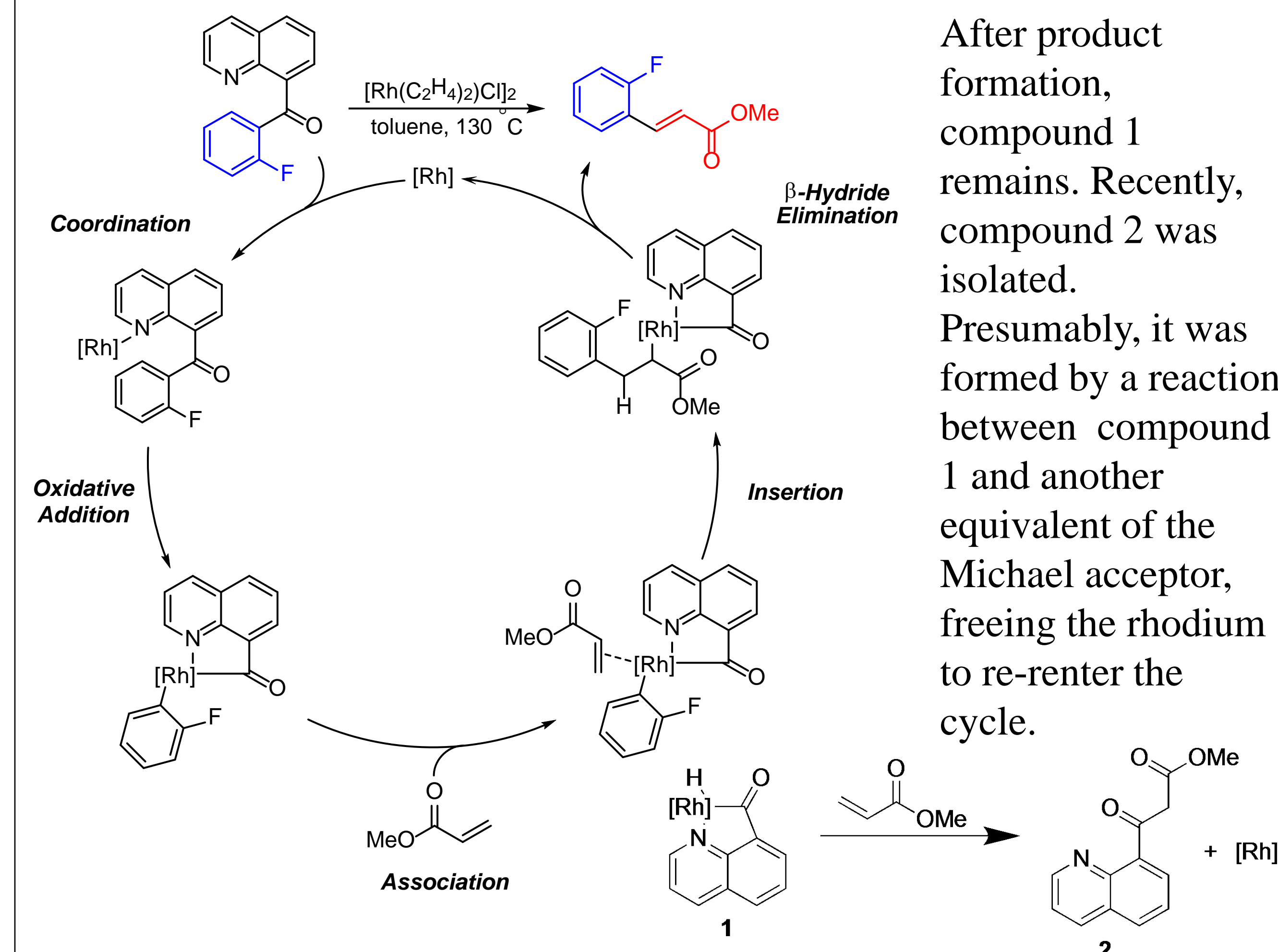
*Isolated yields in parentheses. Challenges in isolation primarily due to the excess of alkene present. All reactions were run under nitrogen.

Future Work

Future projects include setting up more competition reactions with different quinolinylyl ketones and Michael acceptors, and finding viable directing groups to replace quinolinylyl ketones.

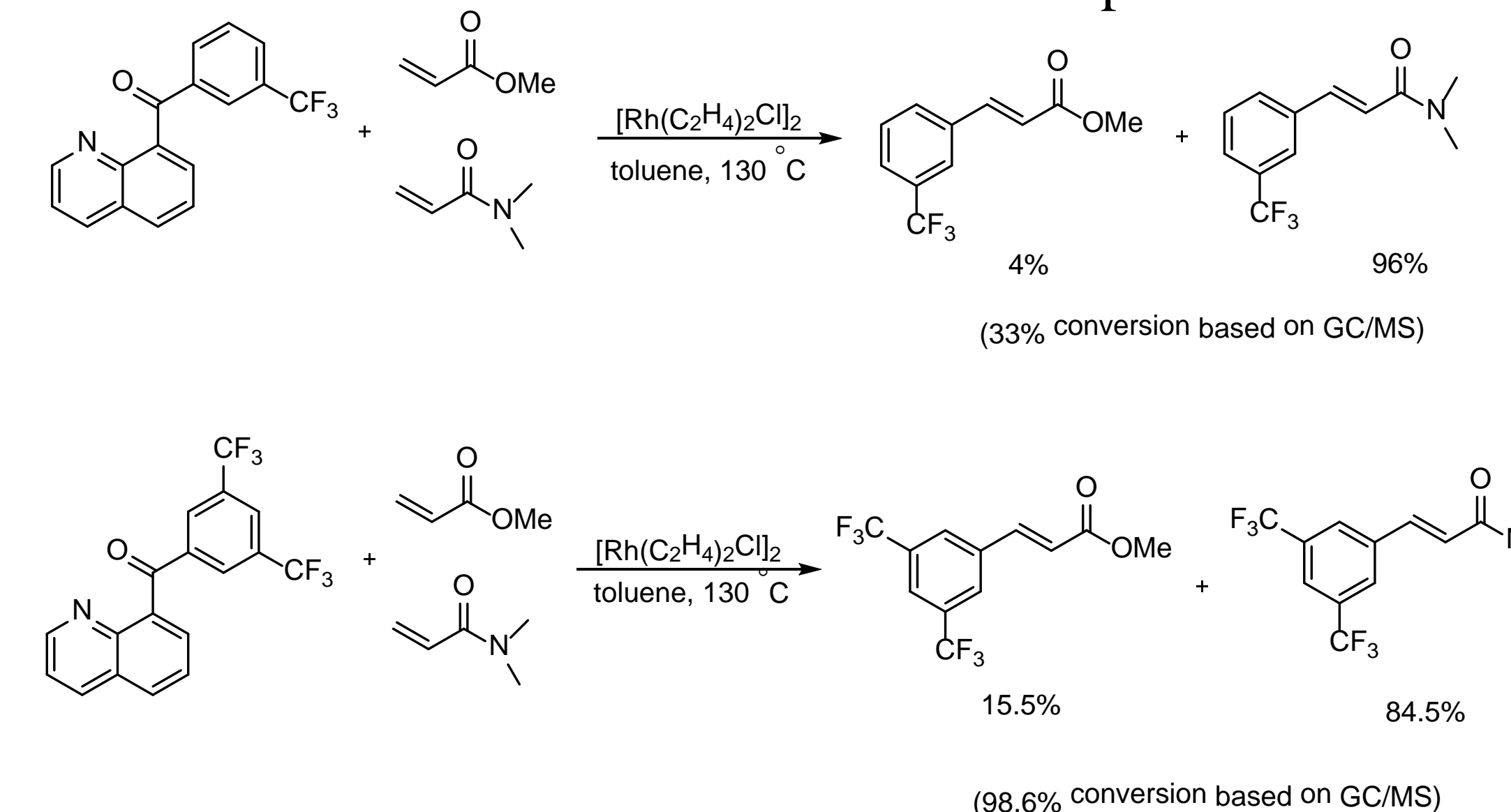


Proposed Catalytic Cycle



Competition Reactions

Competition reactions were performed to further investigate the reaction's mechanism. Preliminary results suggested that the rate determining step for the reaction is the reaction with a Michael acceptor.



Based on the above reactions, N,N dimethyl acrylamide is favored over methyl acrylate.

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