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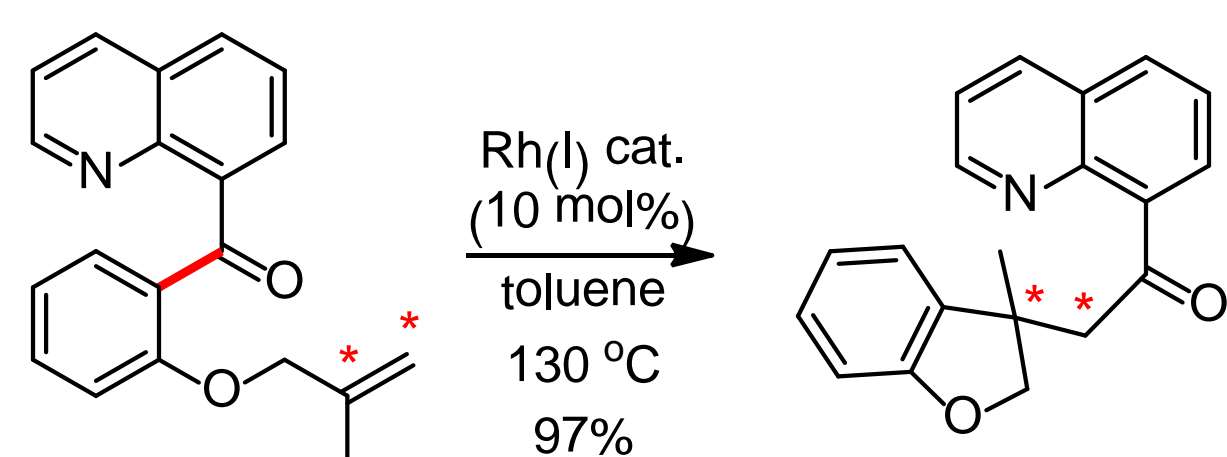
# Carbon-Carbon Single Bond Activation for Nucleophilic Addition to Michael Acceptors

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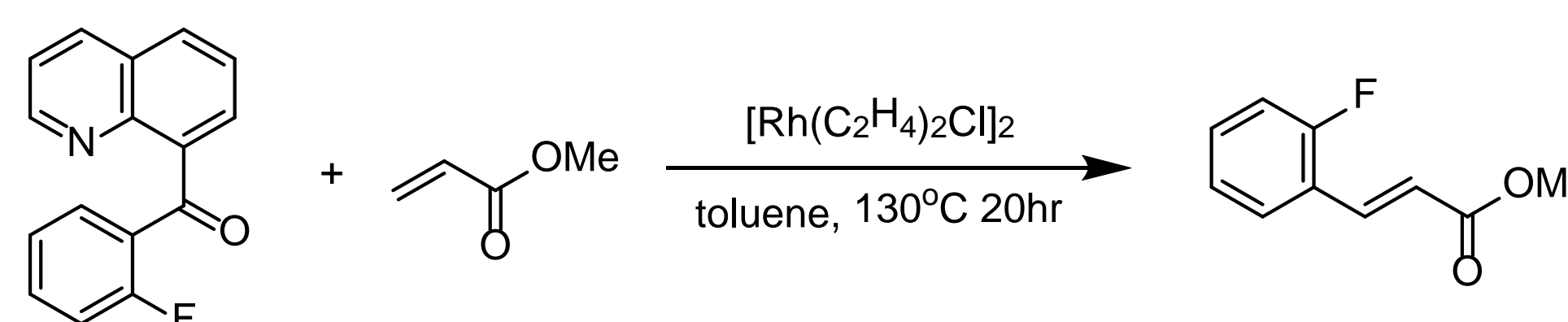
## Background- Alkene Insertion Carboacylation

The reaction of a quinolinyl ketone with a rhodium catalyst results in the activation of a carbon-carbon single bond and the insertion of the alkene into this activated bond. This reaction was first reported by Douglas and coworkers (Dreis, A. M.; Douglas, C. J. *J. Am. Chem. Soc.* 2009, 131, 412) and has been analyzed in depth by past Johnson group members with mechanistic and kinetic studies.

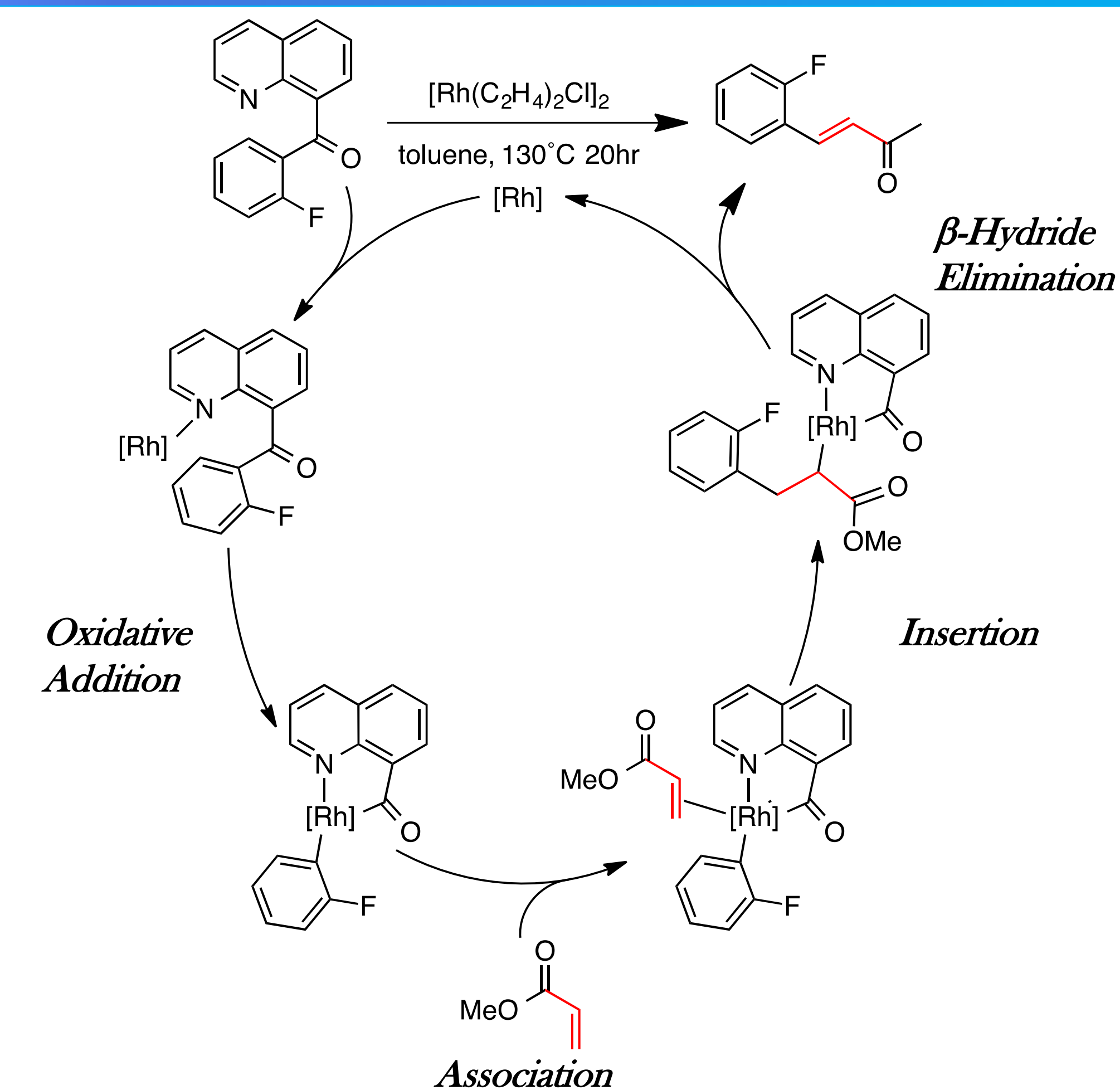


## Intermolecular Reaction

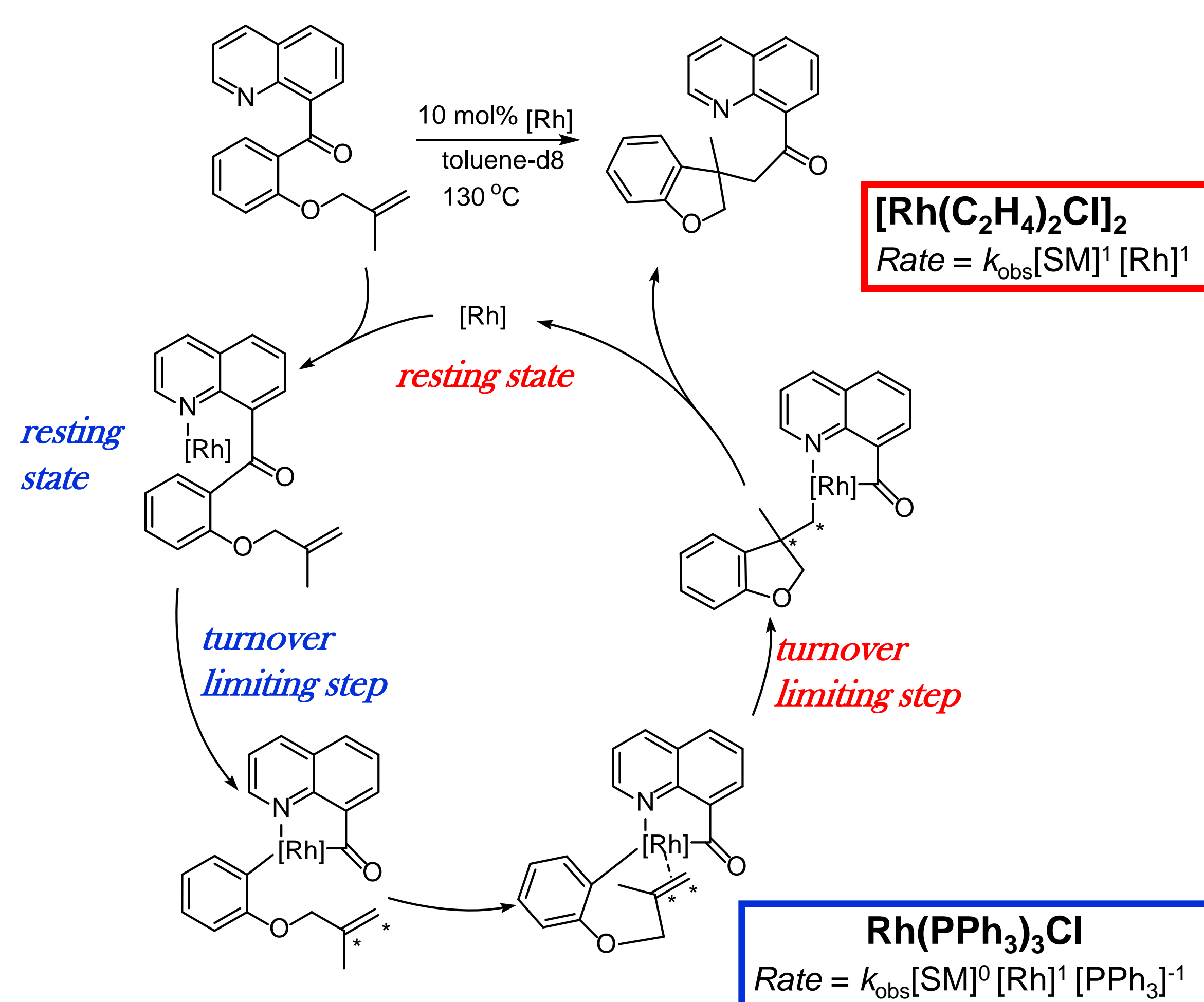
In attempts to make the alkene insertion successful with intermolecular conditions an unexpected product was formed involving the carbon-carbon single bond activation and nucleophilic addition to these Michael acceptors. This reaction is observed with ortho-substitution on the quinolinyl ketone. Ortho-substituted fluorine was used based on prior Johnson group research involving carbon-carbon bond activation using palladium catalysis (Bour, et. al. *J. Org. Chem.* 2013, 78, 1665).



## Proposed Catalytic Cycle

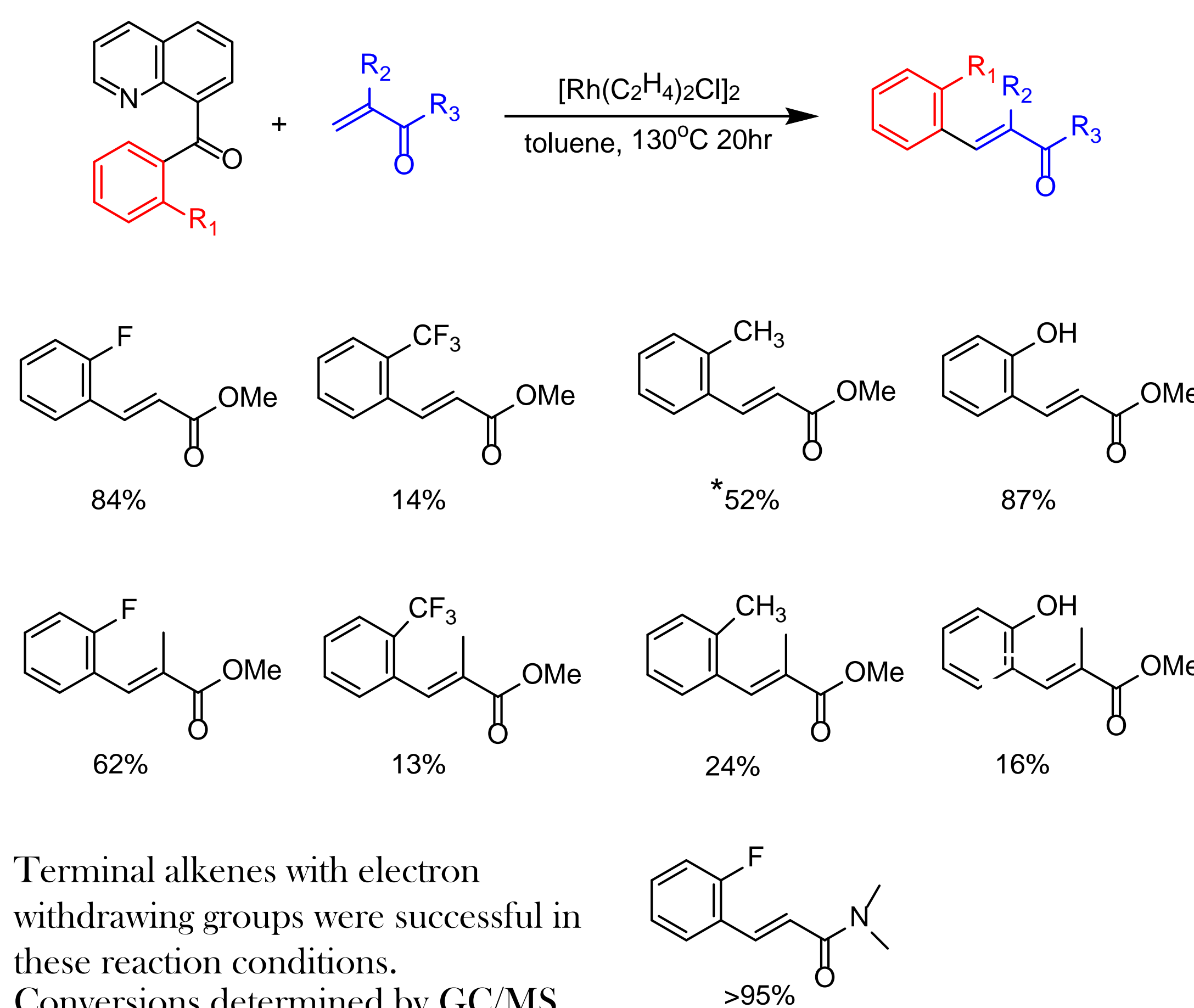


## Catalytic Cycle of Carboacylation



Rathbun, C. M.; Johnson, J. B. *J. Am. Chem. Soc.* 2011, 133, 2031  
Lutz, Rathbun, Stevenson, Powell, Boman, Baxter, Zona, Johnson, *J. Am. Chem. Soc.* 2012, 134, 715

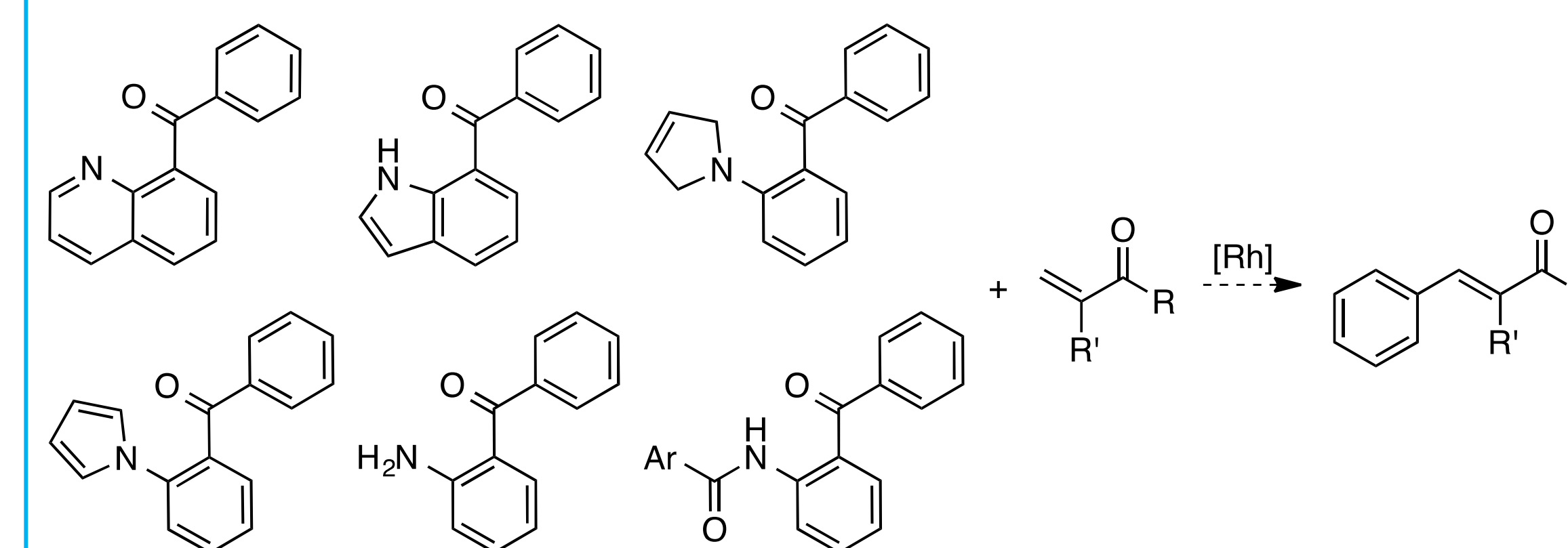
## Reaction Scope



- Terminal alkenes with electron withdrawing groups were successful in these reaction conditions.
- Conversions determined by GC/MS

\* Reaction run for 46 hours

## Future Research



- Work toward synthesizing the intermolecular carboacylation product
- Change conditions leading to optimization of both the carboacylation and nucleophilic addition reactions
- Expand alkene scope and work toward alkyne insertion

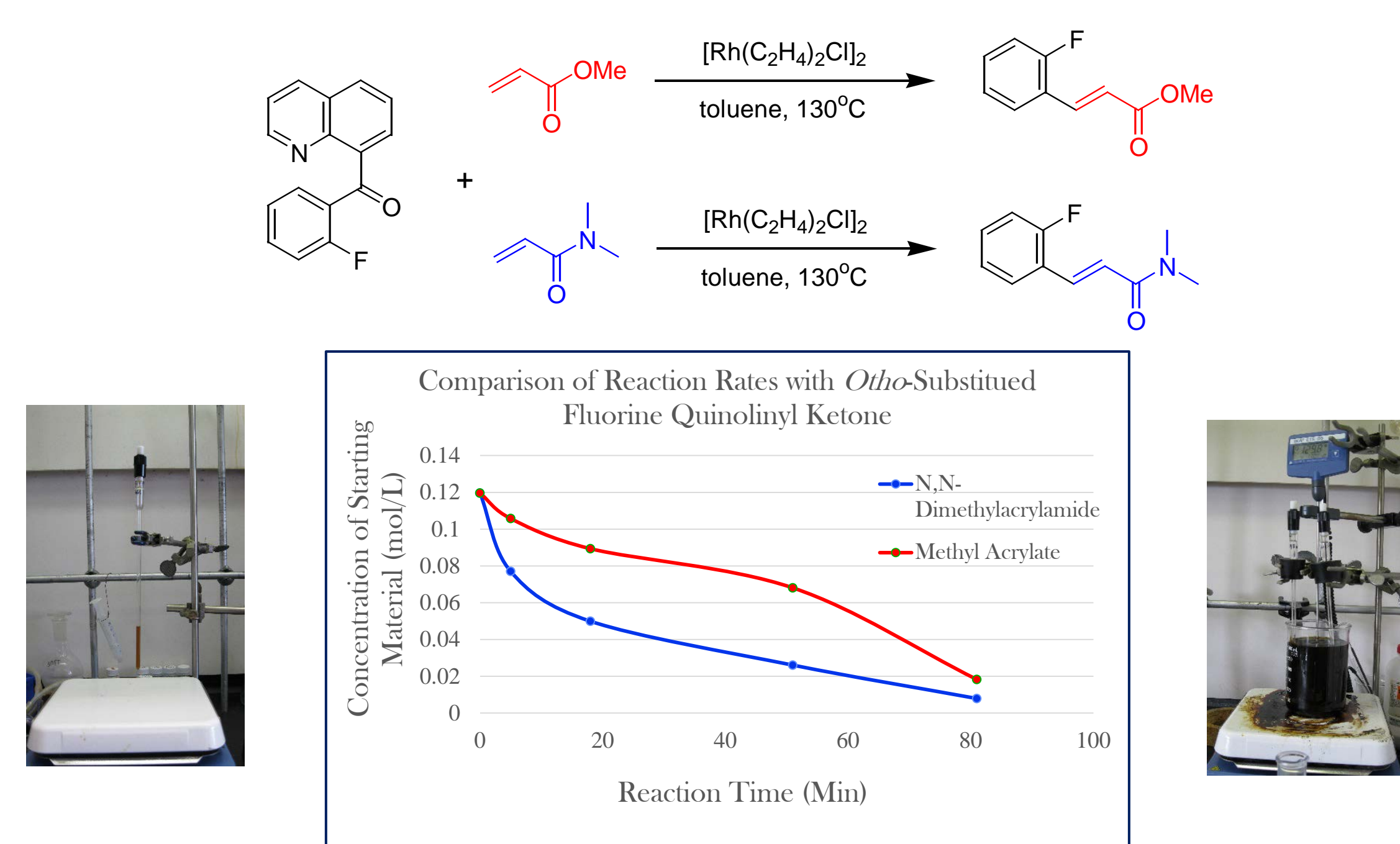
## Kinetic Studies

The reaction occurs with several rhodium(I) catalysts and proceeds at varying rates. Research was done to see how different Rh(I) catalysts affected the rate of the reaction, specifically the initial rate of the reaction. The initial rate was determined from the first 15% of the reaction. A table of results is shown below.

| Rh(I) Catalyst  | Initial Rate (M • s <sup>-1</sup> ) | k <sub>obs</sub> (s <sup>-1</sup> )* |
|---|-------------------------------------|--------------------------------------|
| Rh(COD) <sub>2</sub> OTf  | 6.52 * 10 <sup>-5</sup>             | 3.022 * 10 <sup>-3</sup>             |
| [Rh(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> Cl] <sub>2</sub> | 8.39 * 10 <sup>-5</sup>             | 2.214 * 10 <sup>-3</sup>             |
| RhCl(PPh <sub>3</sub> ) <sub>3</sub>                              | 1.80 * 10 <sup>-5</sup>             | 8.322 * 10 <sup>-4</sup>             |
| Rh(nbd) <sub>2</sub> BF <sub>4</sub>                              | 5.47 * 10 <sup>-6</sup>             | 2.813 * 10 <sup>-4</sup>             |
| Rh(CO) <sub>2</sub> acac  | 6.50 * 10 <sup>-6</sup>             | 1.817 * 10 <sup>-4</sup>             |
| [Rh(COD)Cl] <sub>2</sub>  | 2.05 * 10 <sup>-6</sup>             | 5.233 * 10 <sup>-5</sup>             |
| Rh(acac)(COD)   | 6.57 * 10 <sup>-7</sup>             | 2.333 * 10 <sup>-5</sup>             |

\* Calculated from (initial rate/[Rh])

## Preliminary <sup>1</sup>H NMR Kinetic Study



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