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Rhodium-Catalyzed Carbon-Carbon Bond Activation and Functionalization Using Imine Reactions

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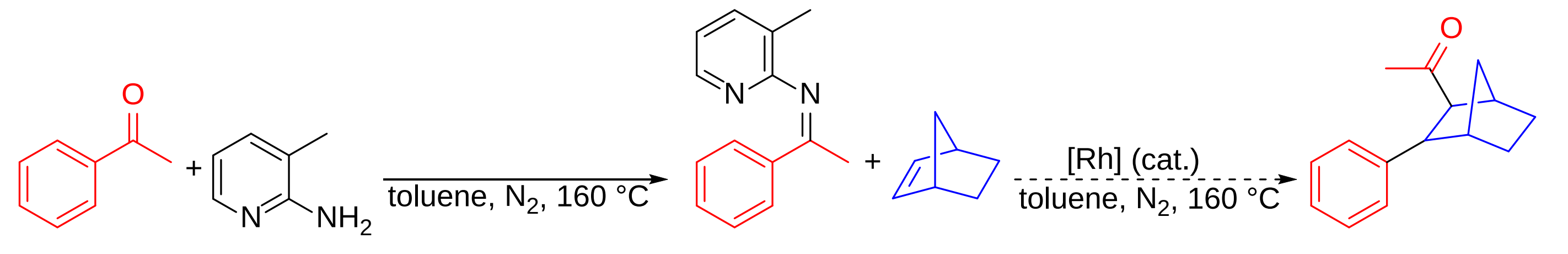
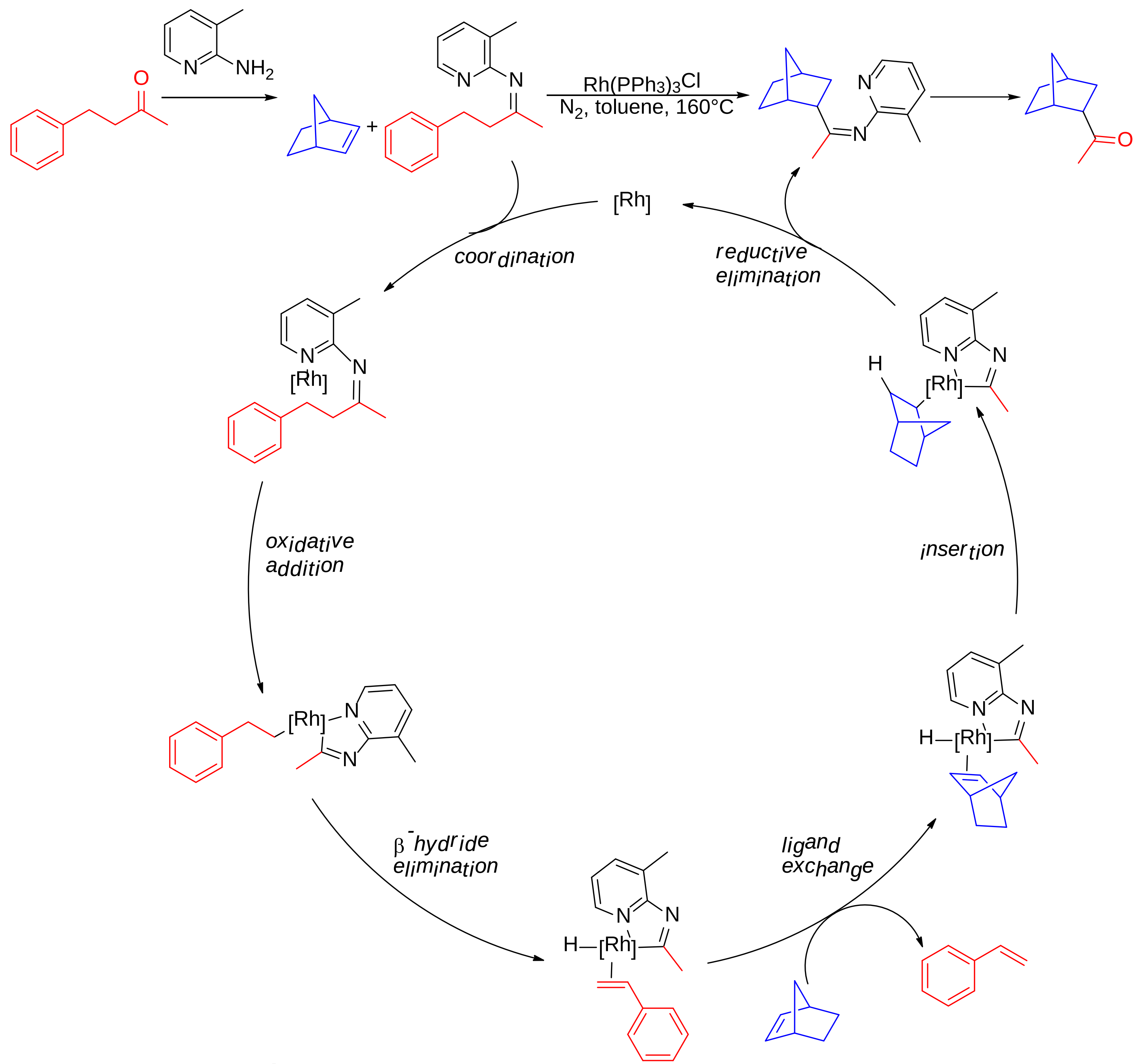
Abstract

The activation and functionalization of carbon-carbon single bonds has proven difficult to achieve using traditional organic methods. Previous Johnson Lab projects have explored the use of rhodium catalysts to permit the selective activation and functionalization of carbon-carbon bonds in ketones. However, these reactions have required a nearby nitrogen atom, presumably to coordinate with the rhodium. Herein, we explore a new type of reaction in which the coordinating nitrogen is provided by reversible imine formation from a ketone and a primary amine. Efforts towards making this reaction more generalizable are currently underway.



Background

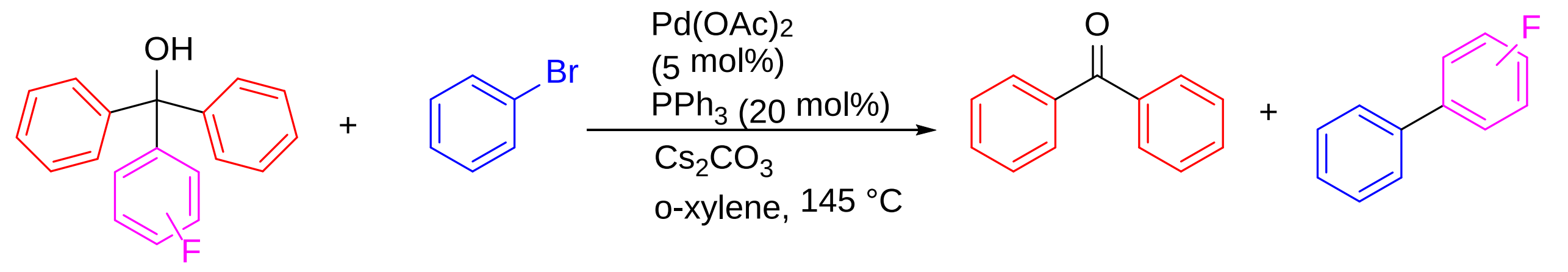
Previous Johnson Lab members examined the Jun rhodium-catalyzed carbon-carbon bond activation reaction, which utilizes a reversible imine reaction to provide a nitrogen-containing directing group. This reaction is one of very few examples of reactions which achieve carbon-carbon bond activation of an unstrained bond. In addition, this reaction is potentially very generalizable – because the directing group is reversibly added, neither the substrate nor the desired product needs to contain a directing group near the ketone. This reaction is thought to proceed through the following mechanism.



Jun, C.H.; Lee, H. *J. Am. Chem. Soc.* **1999,** *121*, 880

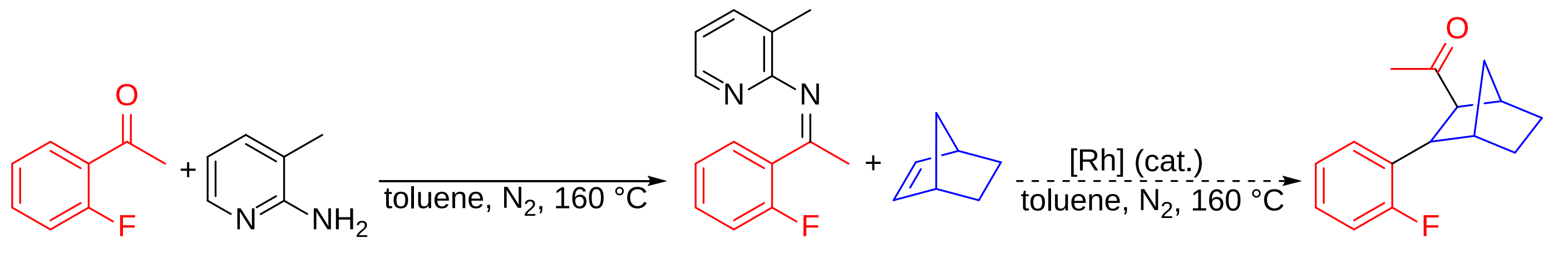
Approach

Previous Johnson group research involving palladium-catalyzed β-aryl elimination demonstrated that fluorinated aryl rings formed more stable intermediates in carbon-carbon bond activation reactions, resulting in an increase in activation.



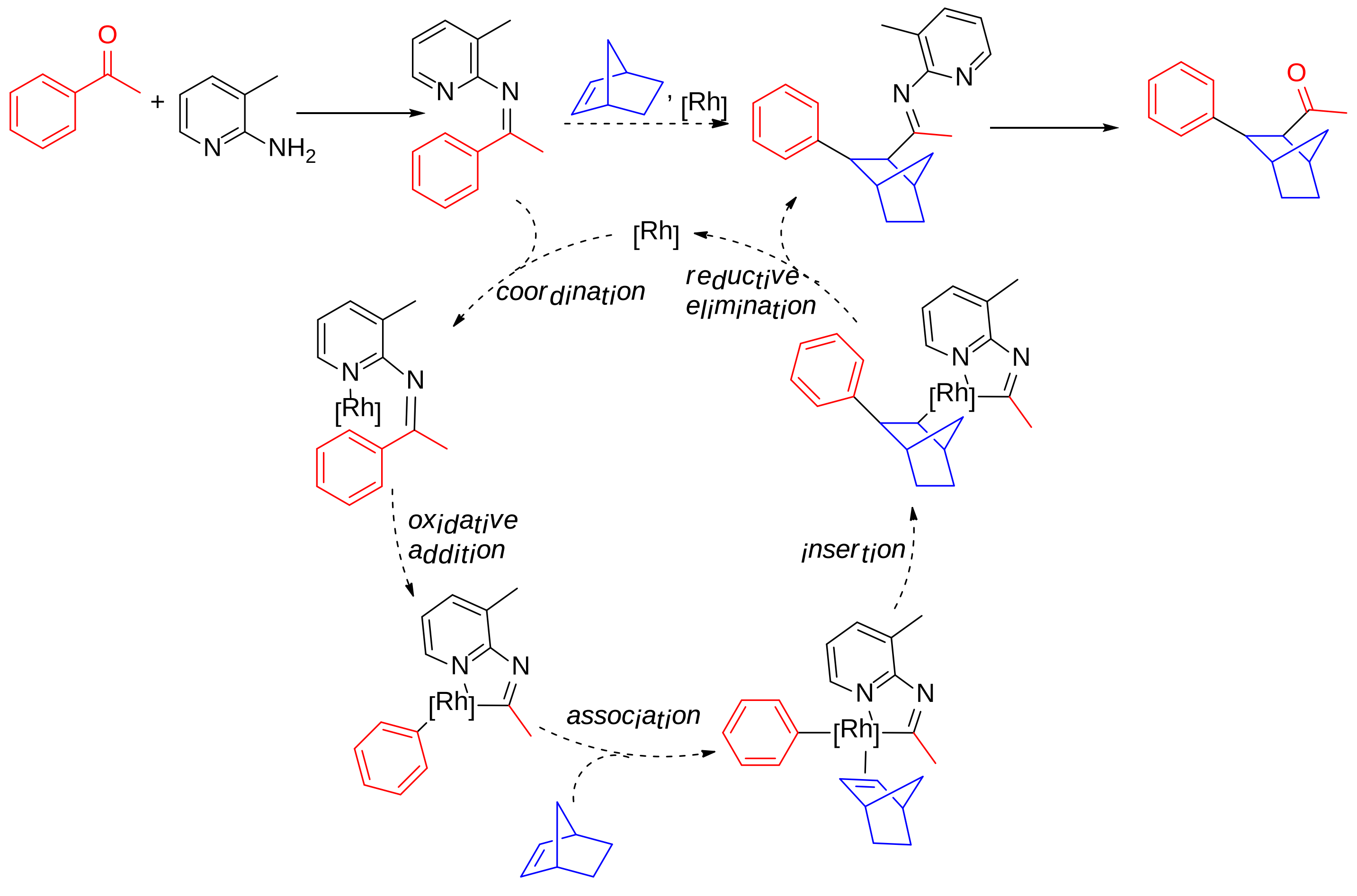
Bour, J. R.; Green, J. C.; Winton, V. J.; Johnson, J. B. *J. Org. Chem.* **2013,** *78*, 1665

Based on these findings, we hypothesized that reacting an ortho-fluoro substituted phenyl ketone with a primary amine with a nitrogen directing group that would produce a relatively stable intermediate upon activation, which might allow carbon-carbon bond activation to occur. Since this substrate cannot follow the same pathway as the Jun reaction due to the lack of adjacent protons, we anticipate that insertion of the alkene followed by reductive elimination can be achieved instead.



Hypothesized Catalytic Cycle

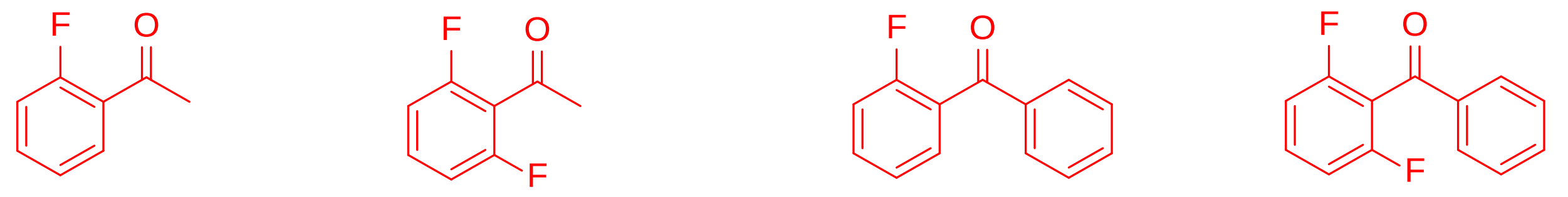
We hypothesize that a reversible imine reaction could be used to allow other types of organometallic carbon-carbon bond activation without β-hydride elimination, such as insertion of an alkene followed by reductive elimination.



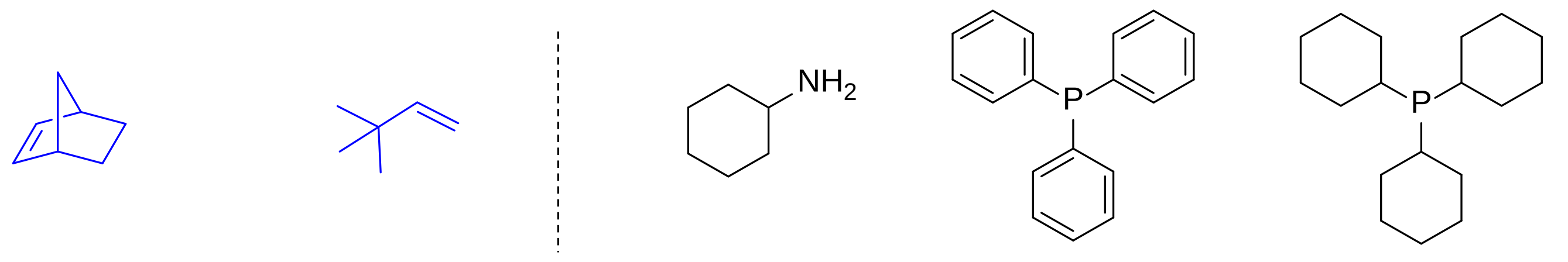
Variables

- Catalyst:
  - Rh(PPh$_3$)$_3$Cl
  - [Rh(C$_2$H$_4$)$_2$Cl]$_2$
  - [Rh(COD)Cl]$_2$
  - [Rh(NBD)$_2$]$^+$BF$_4^-$
  - Rh(CO)$_2$Cp*
  - Rh(acac)(COD)
  - Rh(acac)(CO)$_2$
  - [Rh(COD)$_2$]$^+$BF$_4^-$
  - [Rh(COD)(dippf)]$^+$BF$_4^-$
- Amine:

- Ketone:



- Alkene:
- Other Compounds:



Future Work

- Continue to try different combinations of starting materials and catalysts
- Explore a wider variety of amines and ketones
- Introduce transmetallating agents

Acknowledgements

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