

# Literature Report

---On the Interpretation of Deuterium Kinetic Isotope Effects in C-H Bond Functionalizations by Transition-Metal Complexes

Reporter: Pingping Duan

Advisors: Prof. Zhao

Dr. Hong

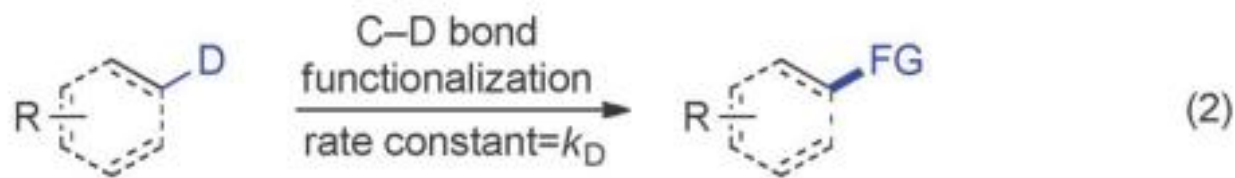
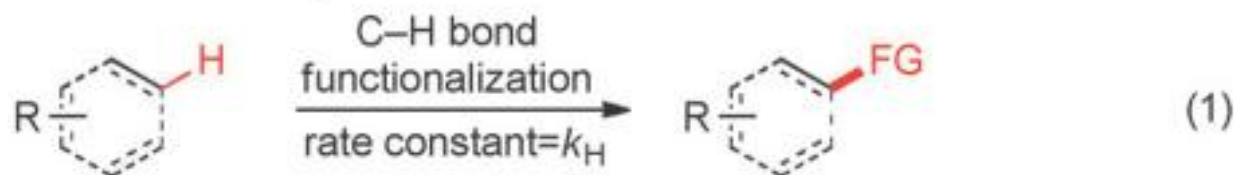
# Kinetic isotope effects (KIEs)

- Bonds are broken or formed at different stages of a reaction
- The properties of the transition state

# Three types of KIE experiments

## --- Experiment A

A) KIE determined from two parallel reactions

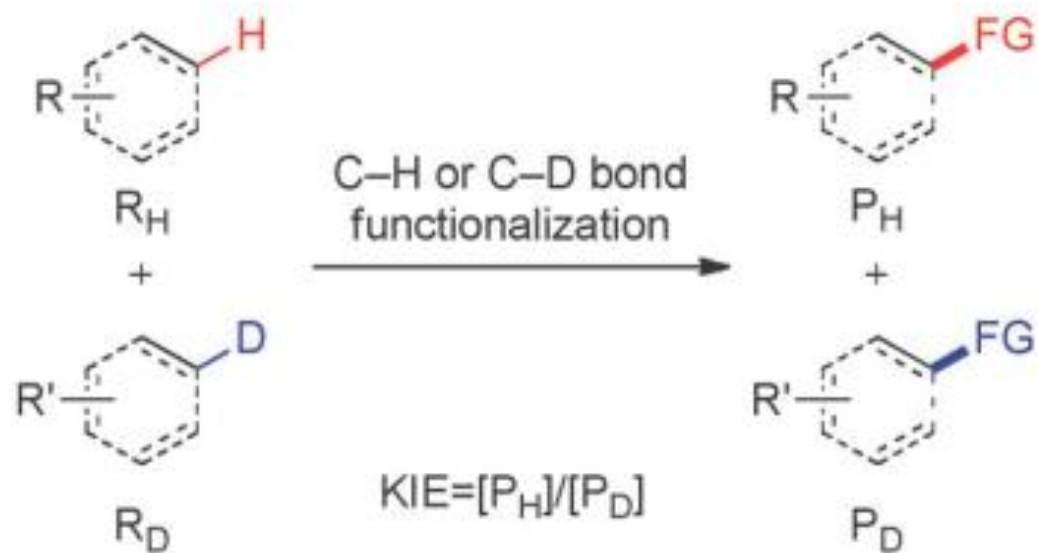


$$\text{KIE} = k_{\text{H}}/k_{\text{D}}$$

# Three types of KIE experiments

## --- Experiment B

B) KIE determined from an intermolecular competition

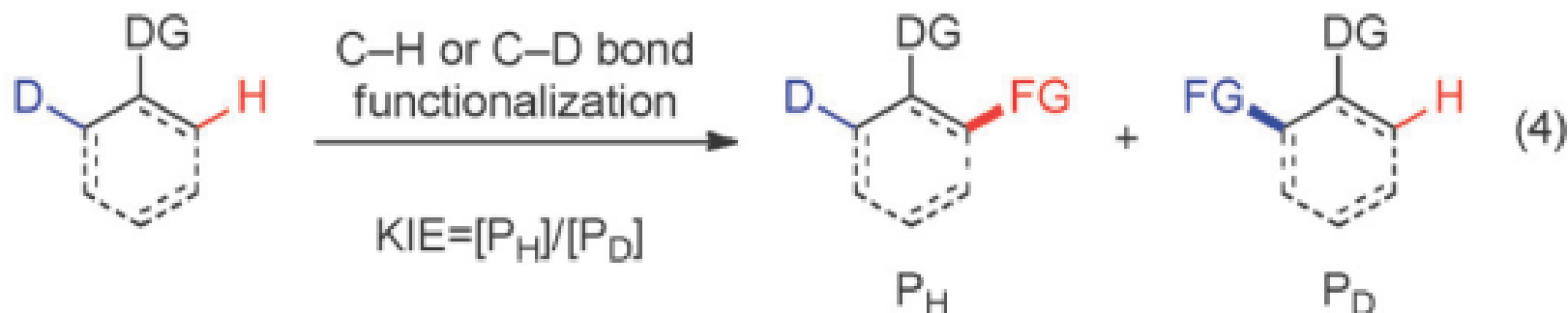


(3)

# Three types of KIE experiments

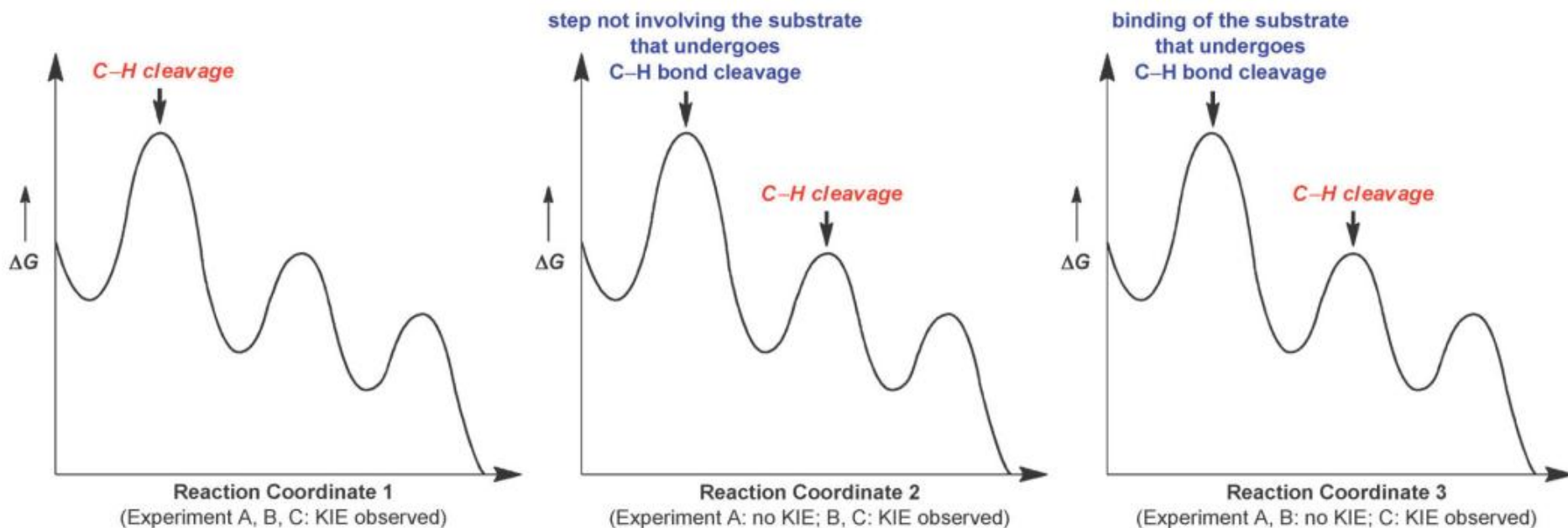
## --- Experiment C

C) KIE determined from an intramolecular competition



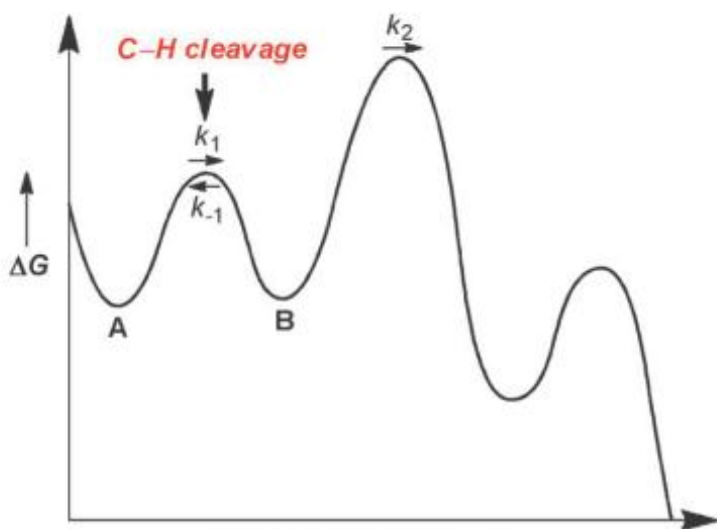
# Representative mechanistic scenarios

---1-3

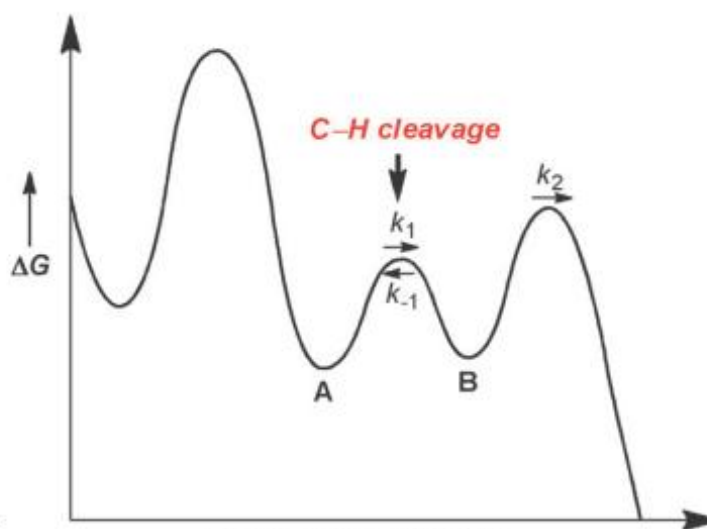


# Representative mechanistic scenarios

---4-5

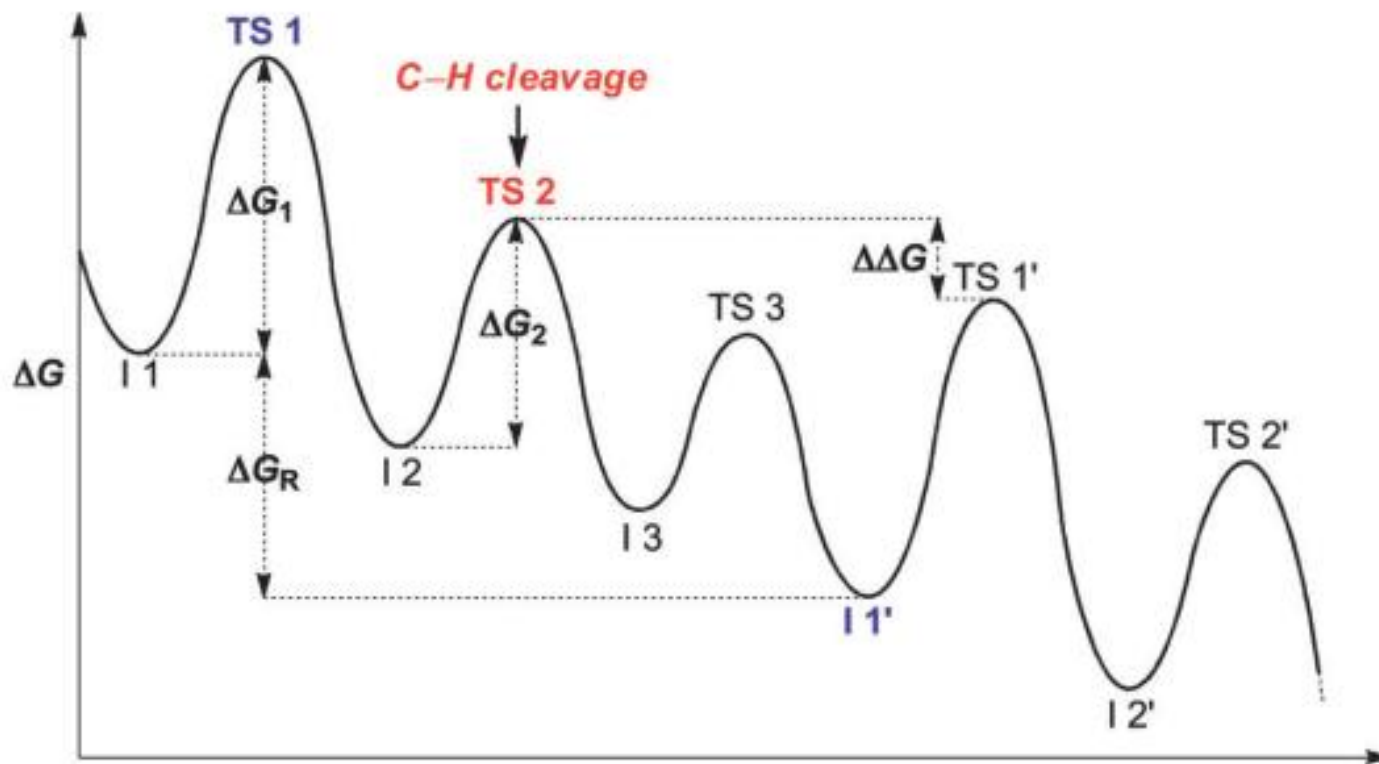


Reaction Coordinate 4  
(Experiment A, B, C: potential KIE)



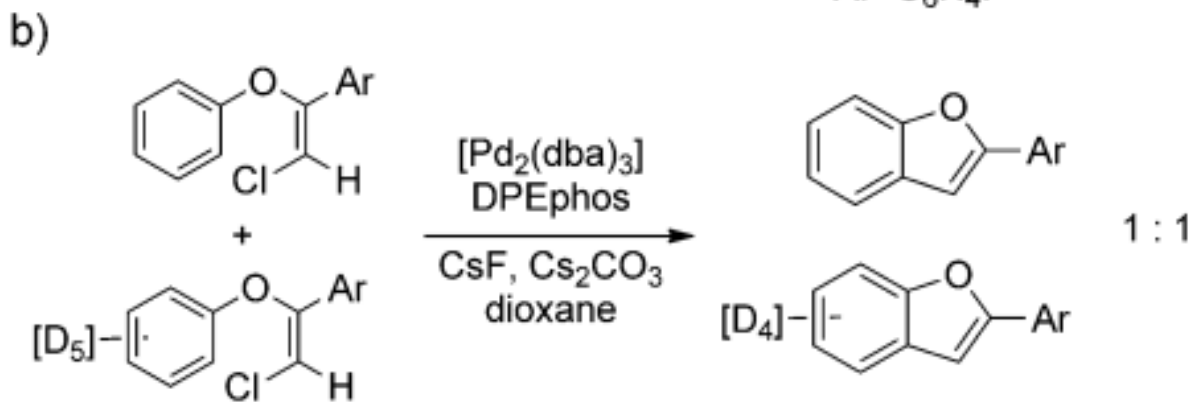
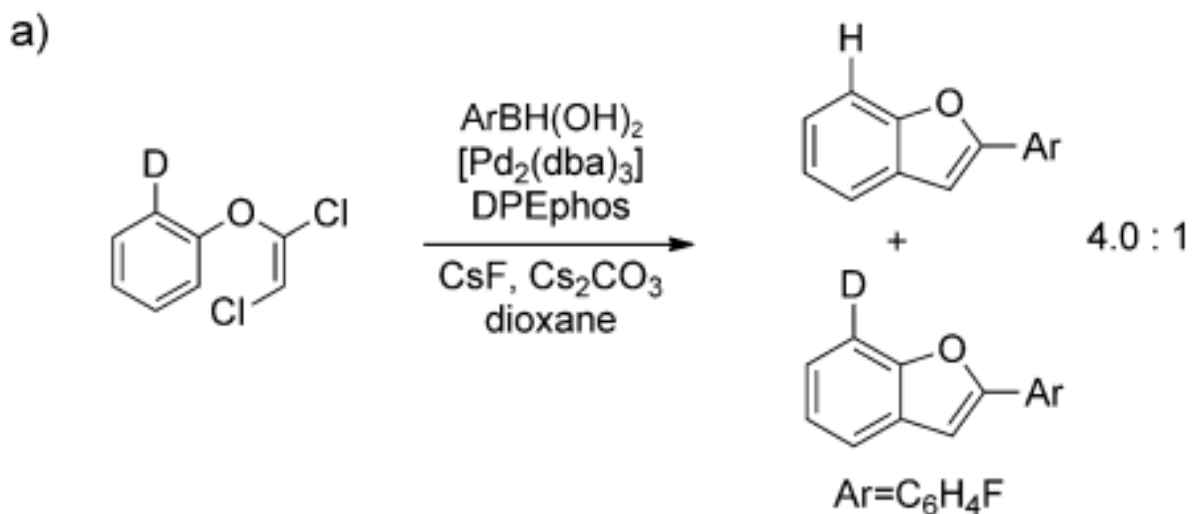
Reaction Coordinate 5  
(Experiment A: no KIE; B, C: potential KIE)

# A catalytic cycle with a fast, irreversible C-H bond cleavage step

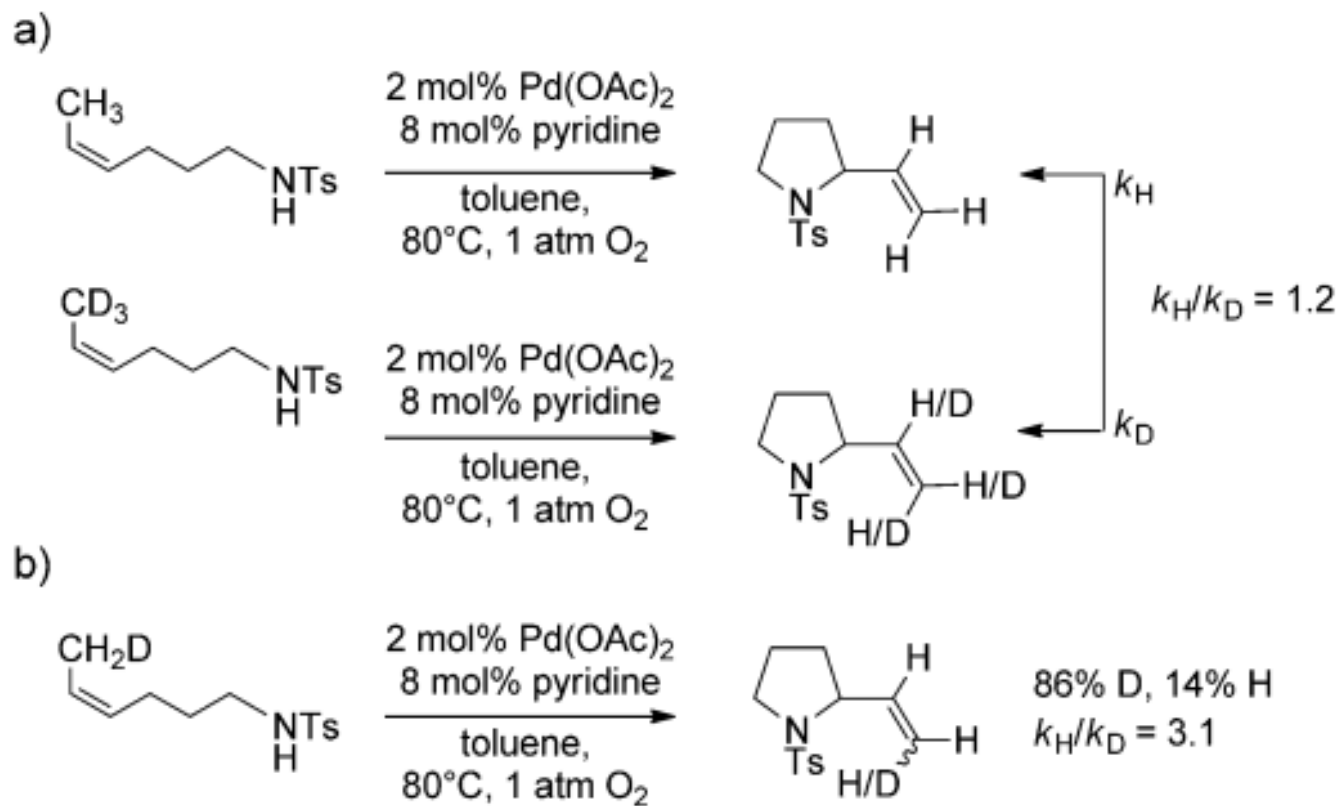




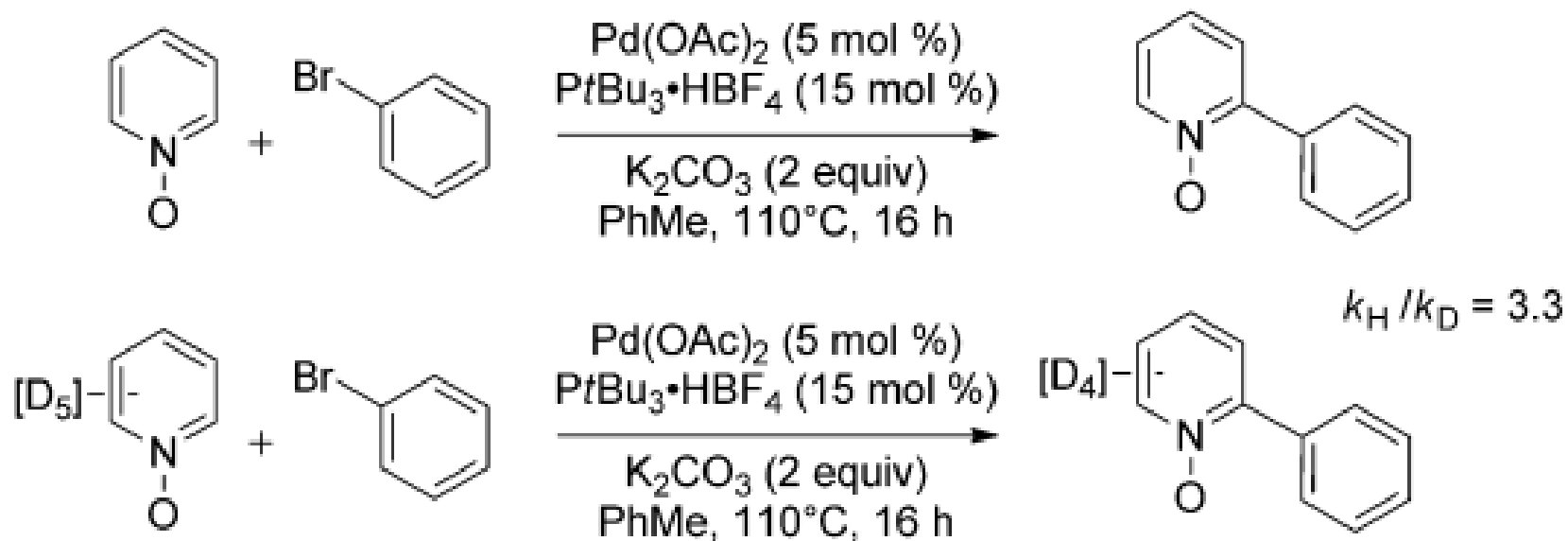
# A comparison of intramolecular versus intermolecular KIE values



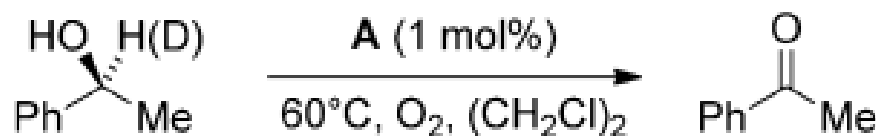
# A comparison of intramolecular versus intermolecular KIE values



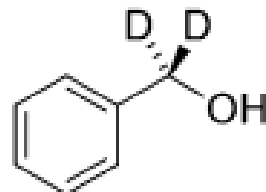
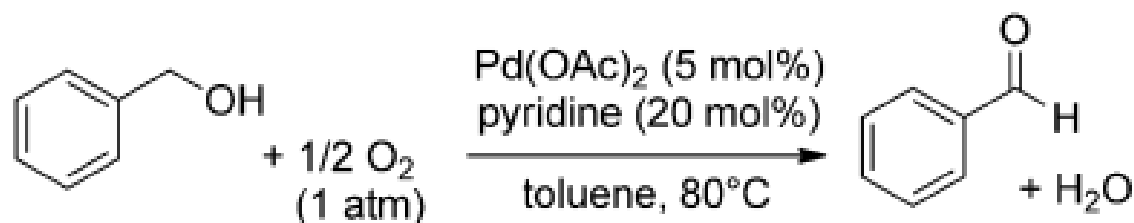
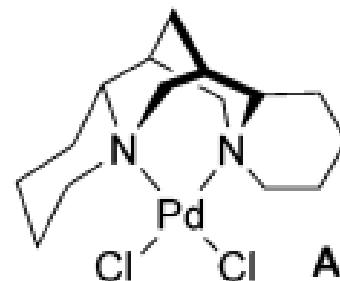
# KIE measurement from two parallel reactions



# KIE measurements at different reactant concentrations



(-)-sparteine	$k_H/k_D$
4 mol%	$1.04 \pm 0.06$
50 mol%	$1.31 \pm 0.04$



KIE: 1.3 at [alcohol] = 0.10 M  
1.8 at [alcohol] = 1.0 M

# Conclusion

- Specifically, the authors have shown that the KIE experiment that allows one to conclude that CH bond cleavage occurs during the rate-determining step of a reaction is the measurement of the rates or rate constants of two independent reactions with two substrates, one containing a C-H bond and one containing a C-D bond.

**Thank You!**