

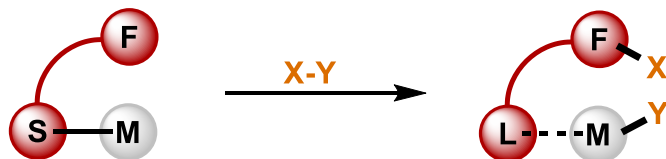
Catalytic Formation of nucleophilic Allylboranes by the Concept of Boron-Ligand Cooperation

Seminar talk presented by
Sebastian Ahles

July 3th, 2020

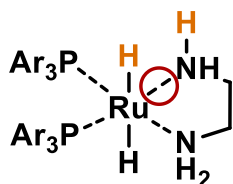
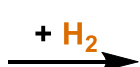
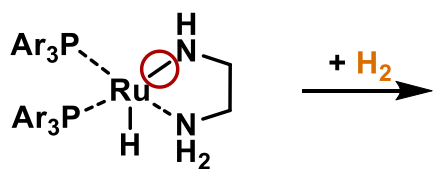
*Institute of Organic Chemistry
Justus-Liebig University Giessen*

Metal-Ligand Cooperation



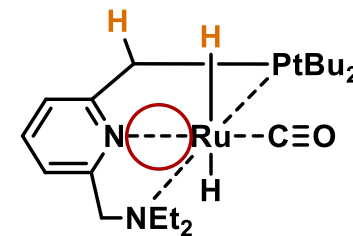
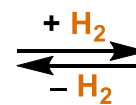
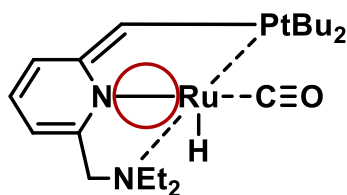
covalent bond

dative bond

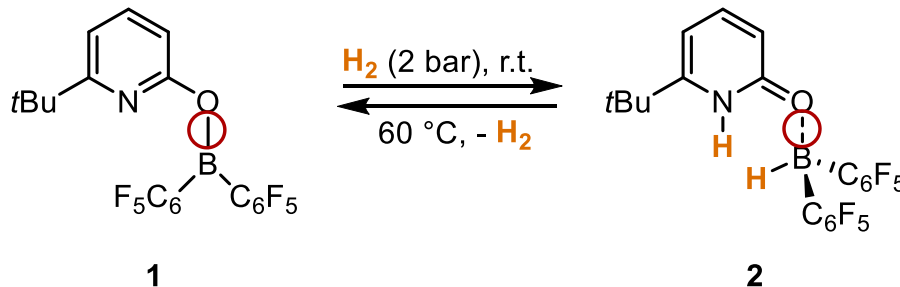


covalent bond

dative bond



Boron-Ligand Cooperation

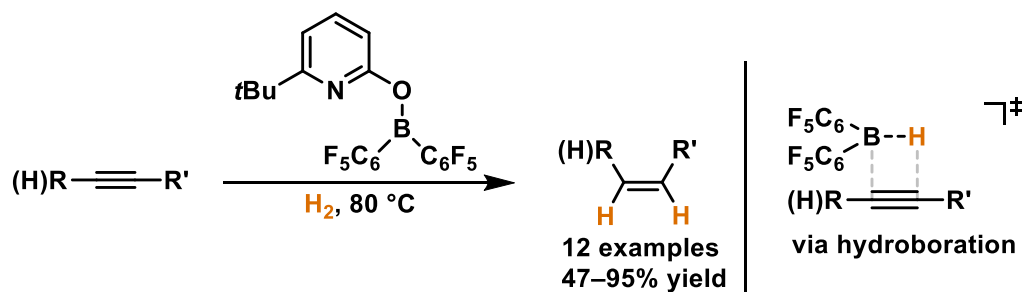
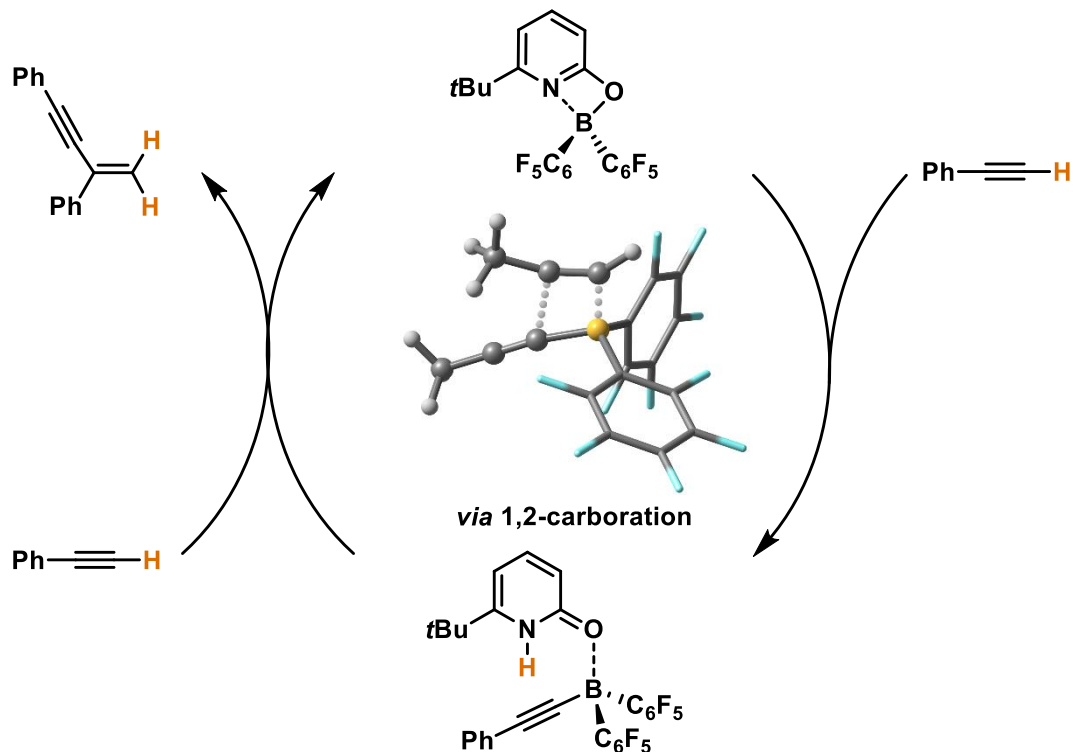


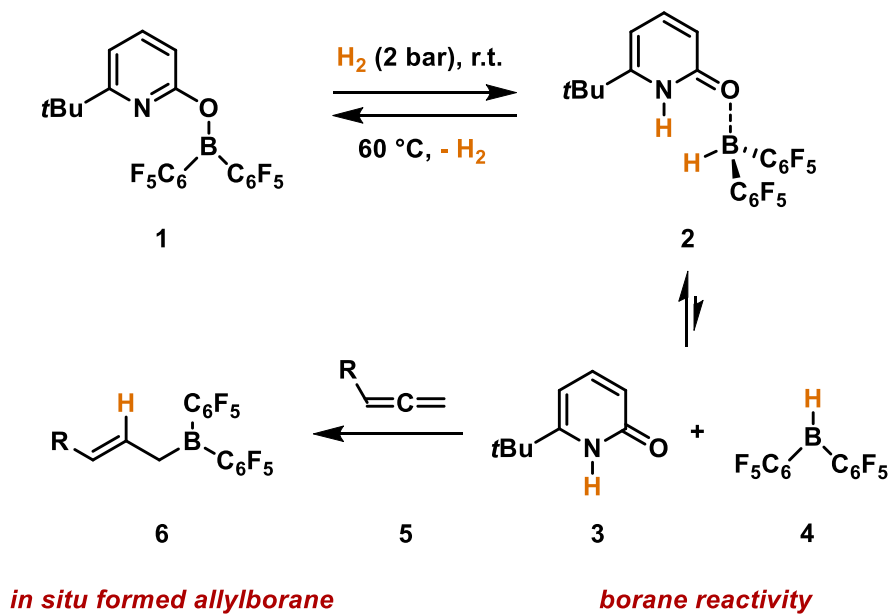
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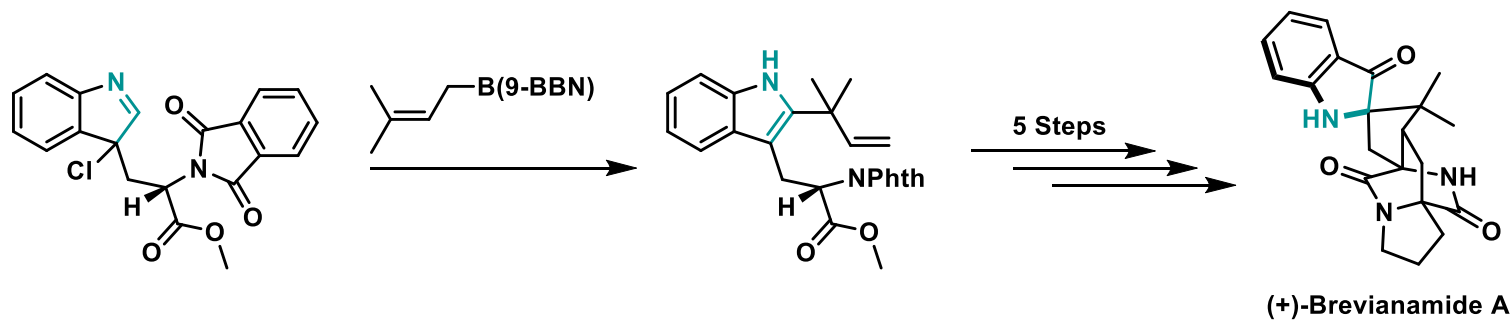
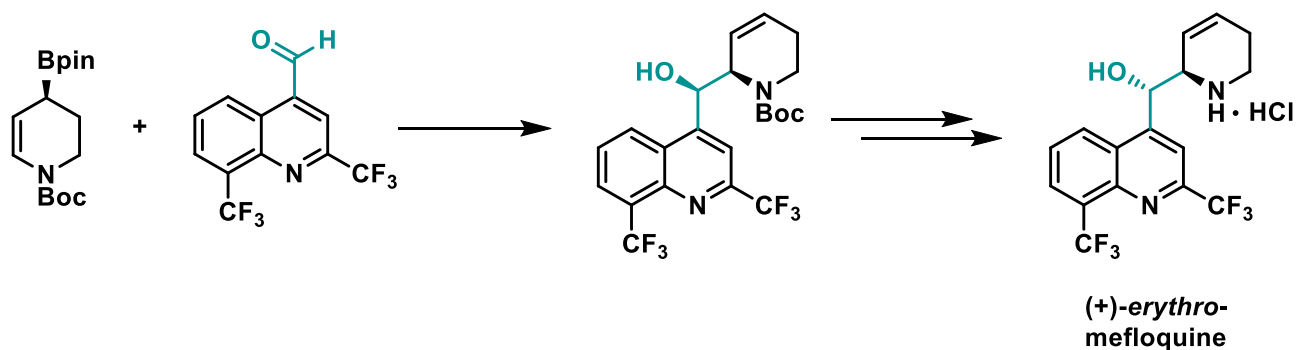
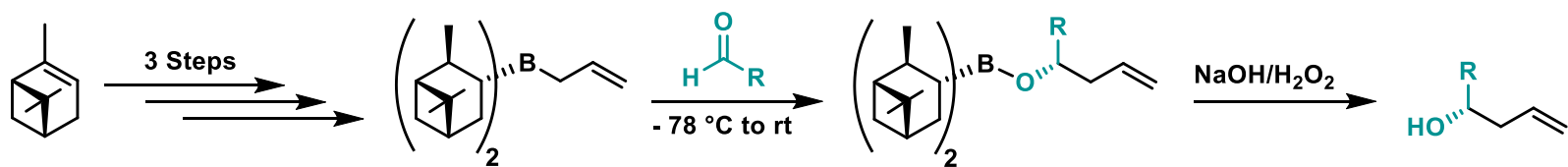
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Boron-Ligand Cooperation





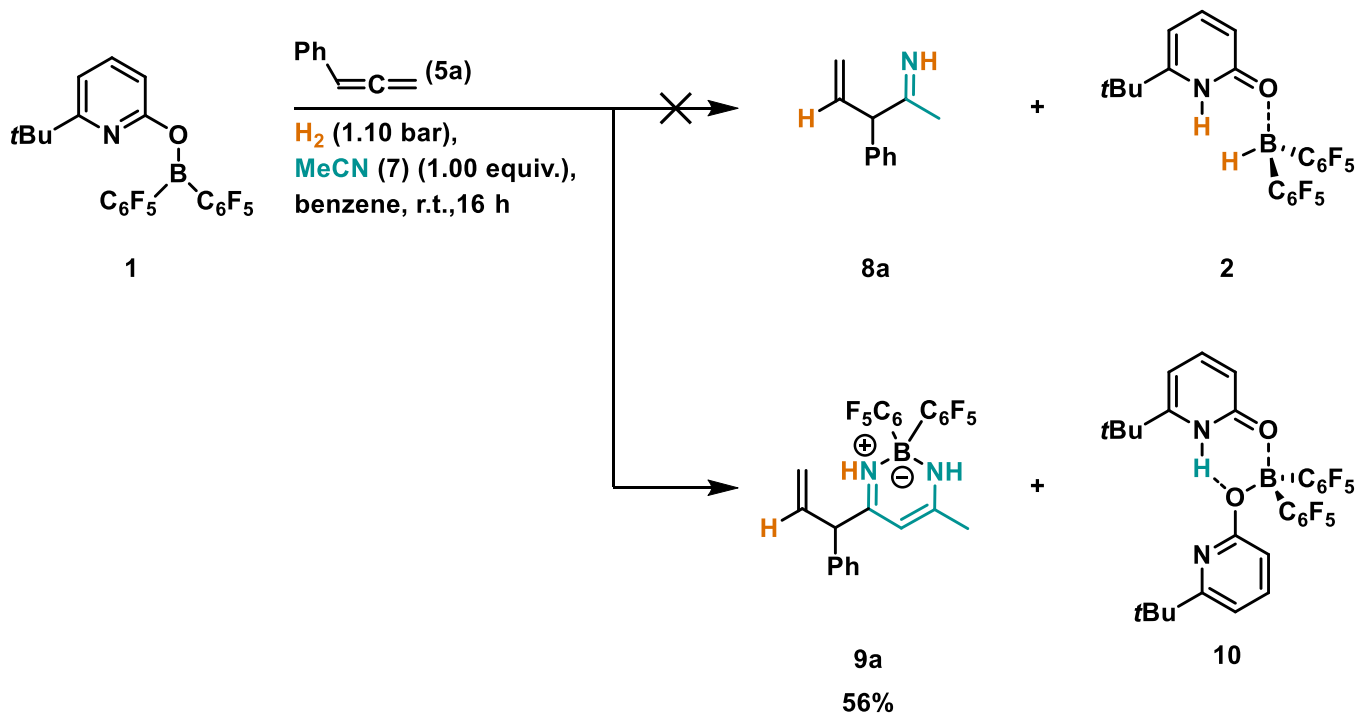
Applications of Allylboranes



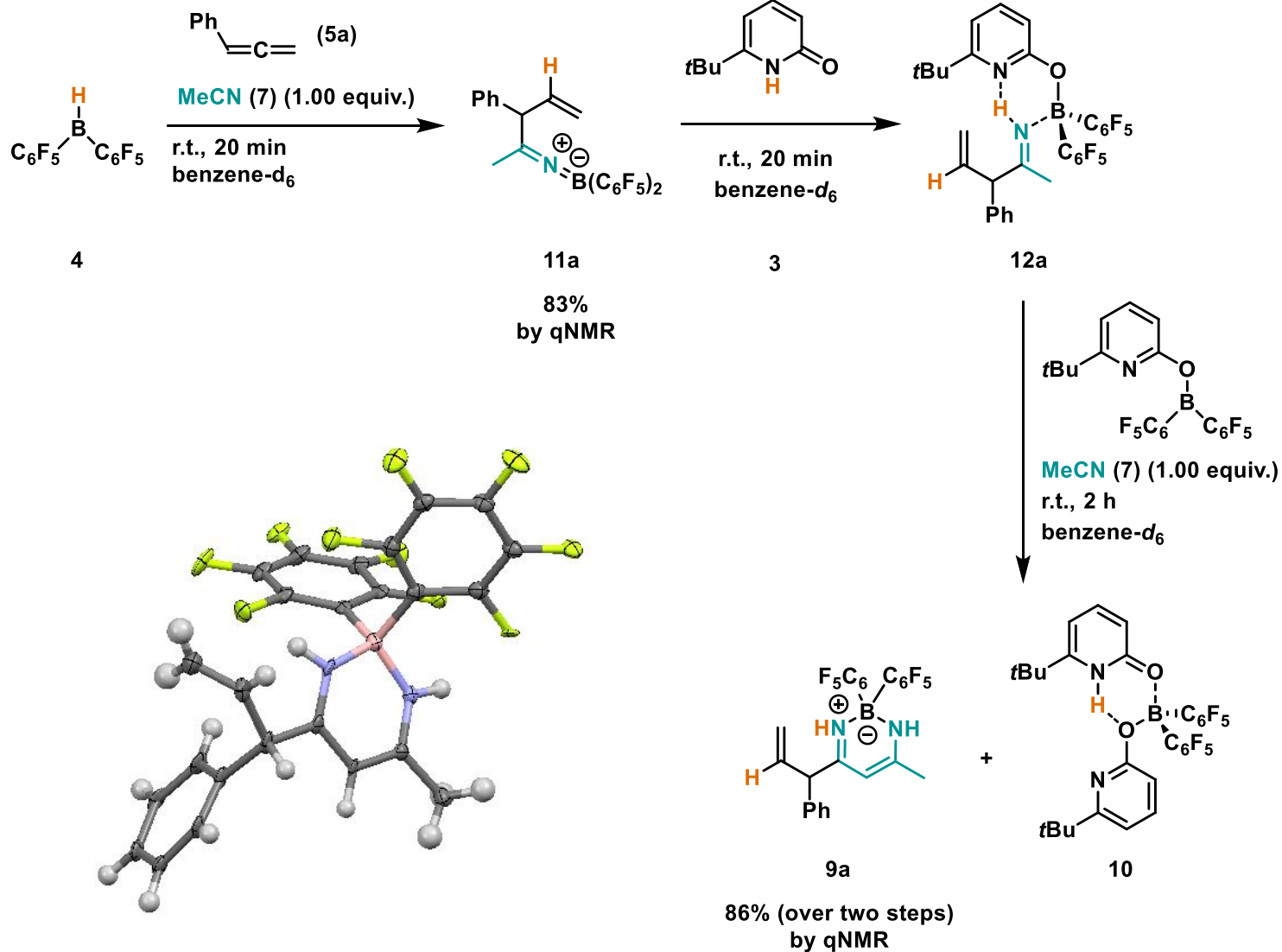
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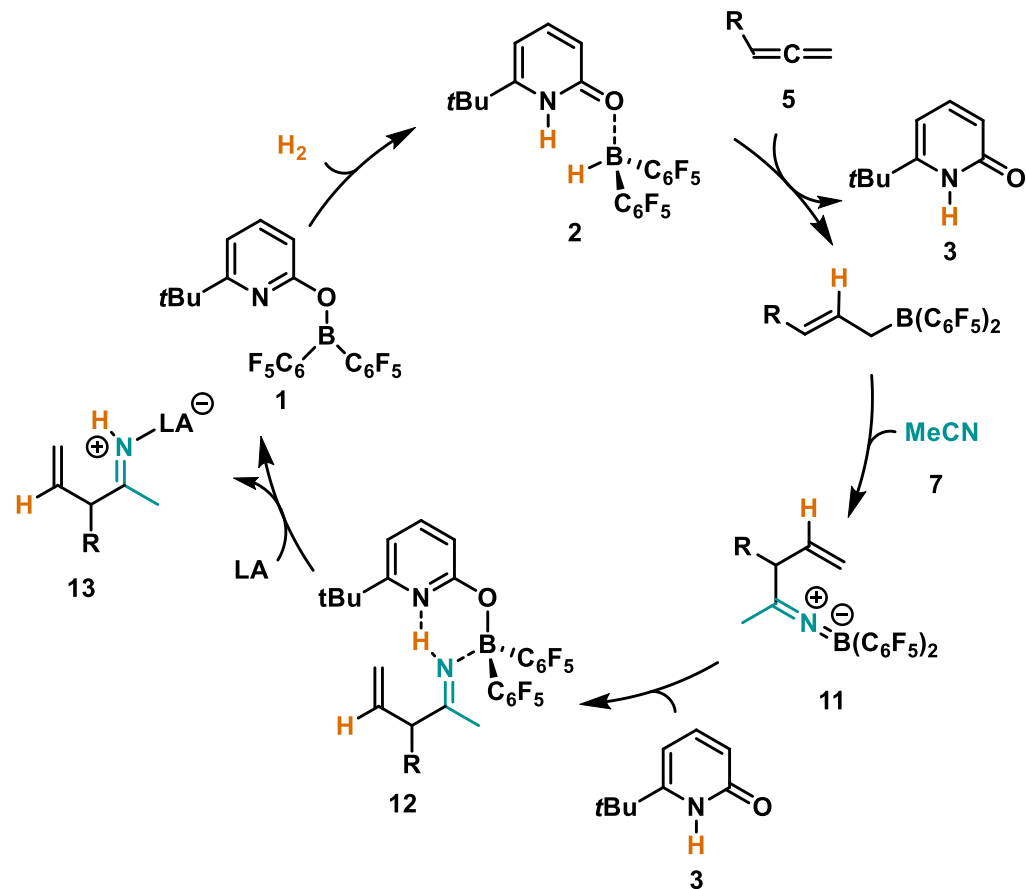


Selective Formation of β -Diketimate Borane Complex

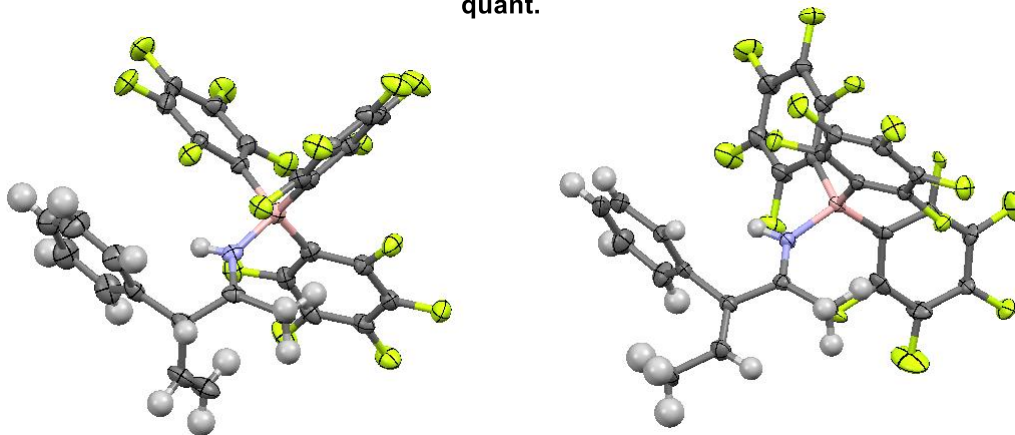
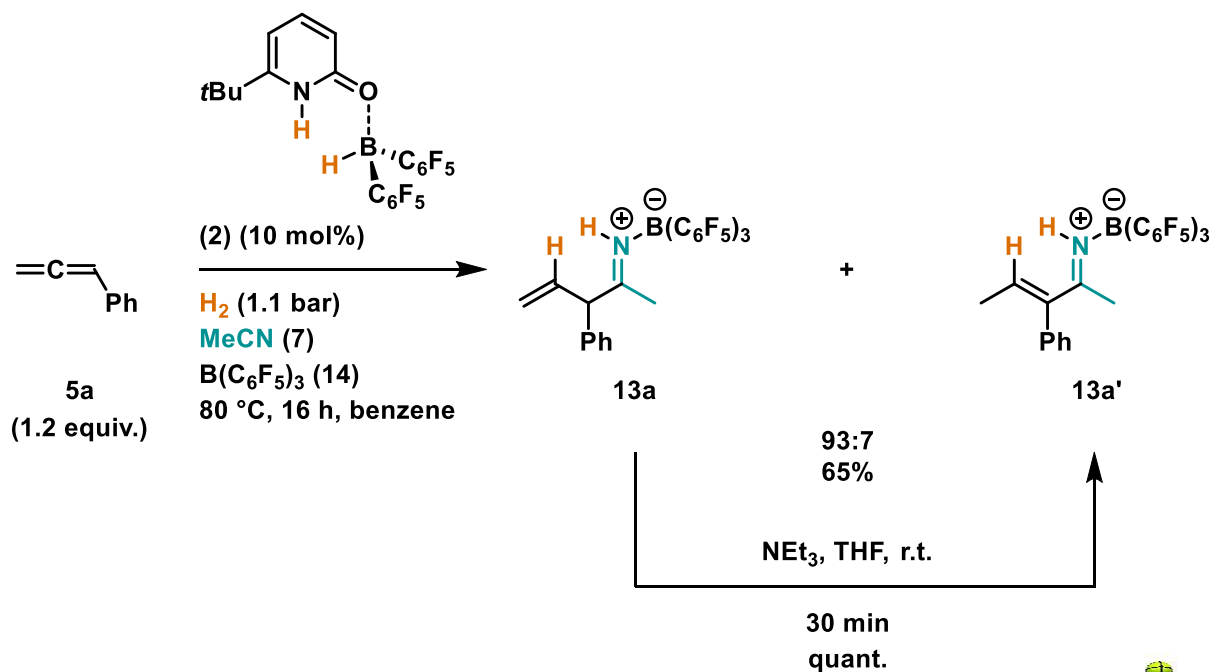


Reaction conditions: 0.03 mmol scale; 0.4 mL $\text{benzene-}d_6$; 1,3,5-trimethoxybenzene was used as internal standard for qNMR analysis
Molecular structure of **9a** derived from SCXRD (50% probability ellipsoids).

Proposed Catalytic Cycle

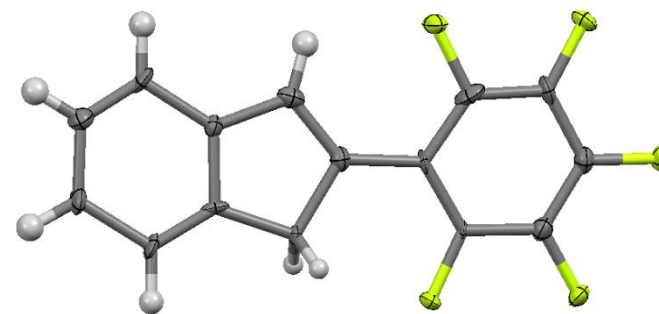
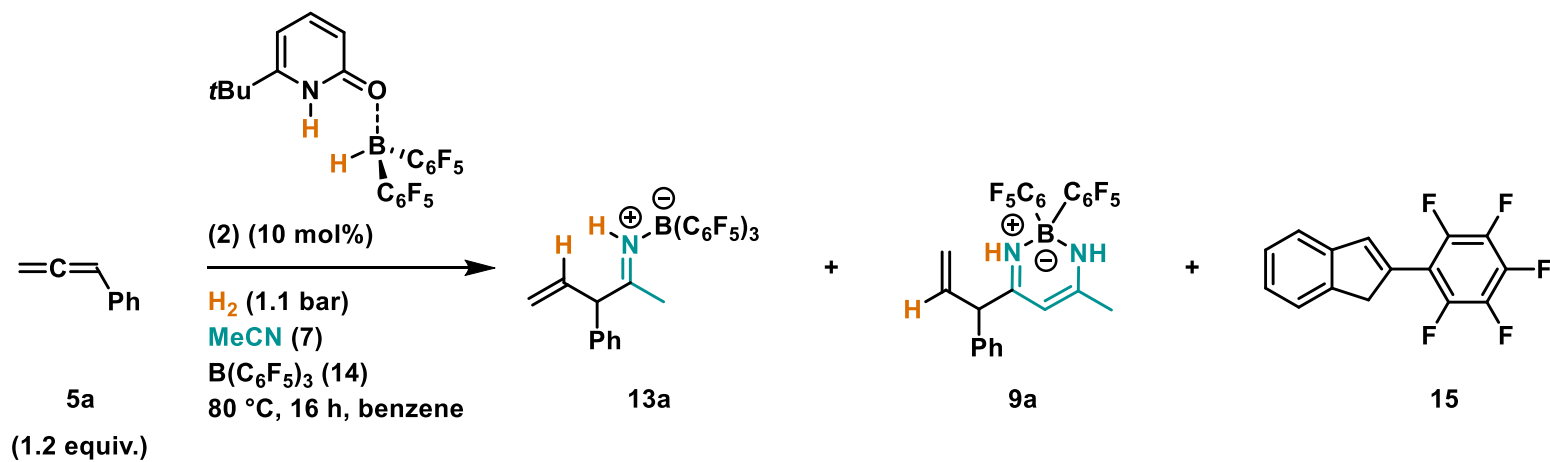


Catalytic Formation of Allylimine Borane Complex



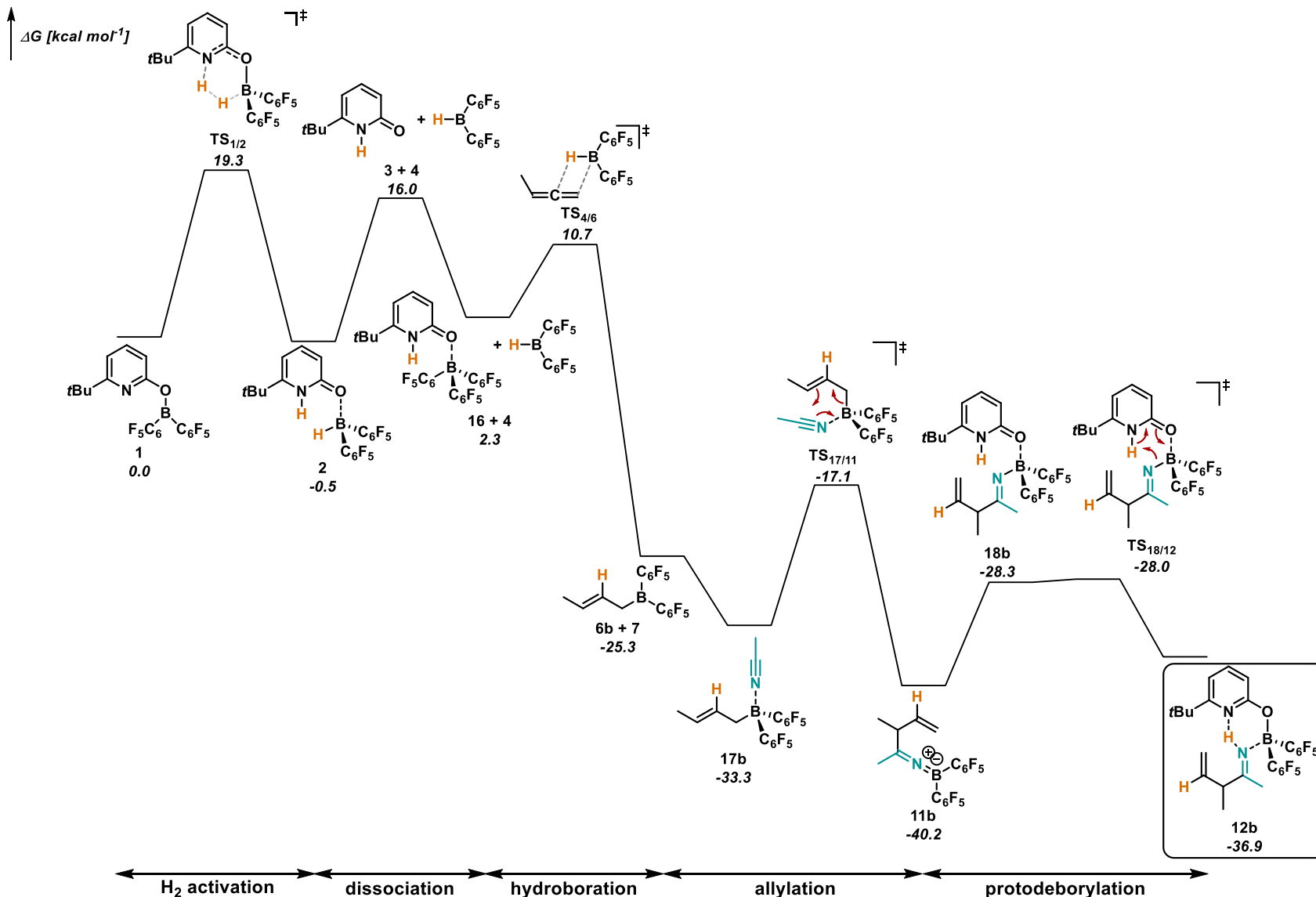
Reaction conditions: 0.36 mmol Phenylallene (**5a**); 0.30 mmol Acetonitril (**7**); 0.30 mmol $\text{B}(\text{C}_6\text{F}_5)_3$ (**14**); 0.03 mmol 6-tBu-Pyridone (**3**); 0.033 mmol $\text{HB}(\text{C}_6\text{F}_5)_3$ (**4**); 6.00 mL benzene; 1.10 bar H_2 ; 100 mL Flask with Yong-Valve
Molecular structure of **13a** and **13a'** are derived from SCXRD (50% probability ellipsoids).

Observed Side Products



Possible intermediate of **15**: X. Tao; C. G. Daniliuc; K. Soloviova; C. A. Strassert; G. Erker, *Chem. Commun.*, **2019**, 55, 10166–10169.

Potential energy surface Part 1

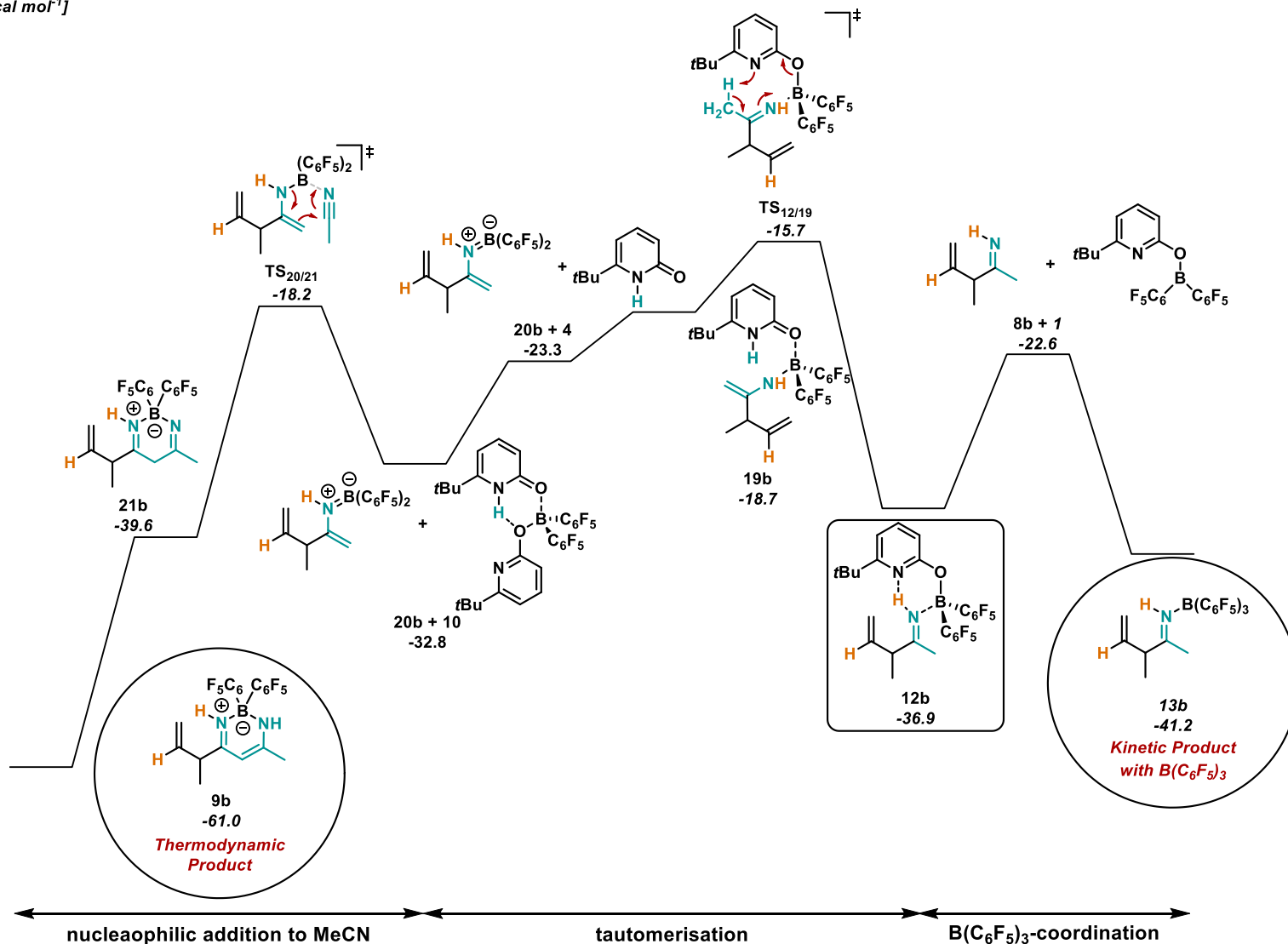


revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c. The SMD model for benzene was used to implicitly account for solvent effects.
 Molecules, which are not part of the respective step are omitted for clarity

Potential energy surface Part 2

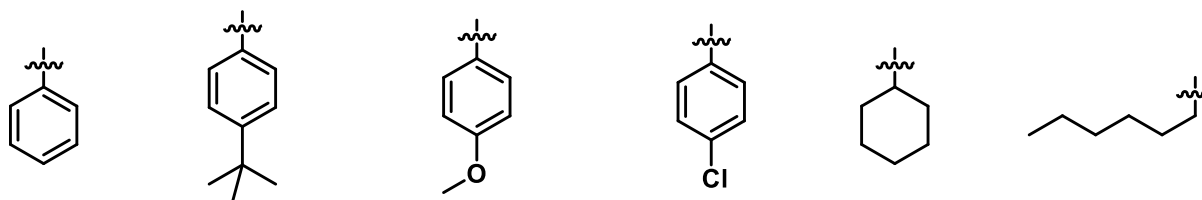
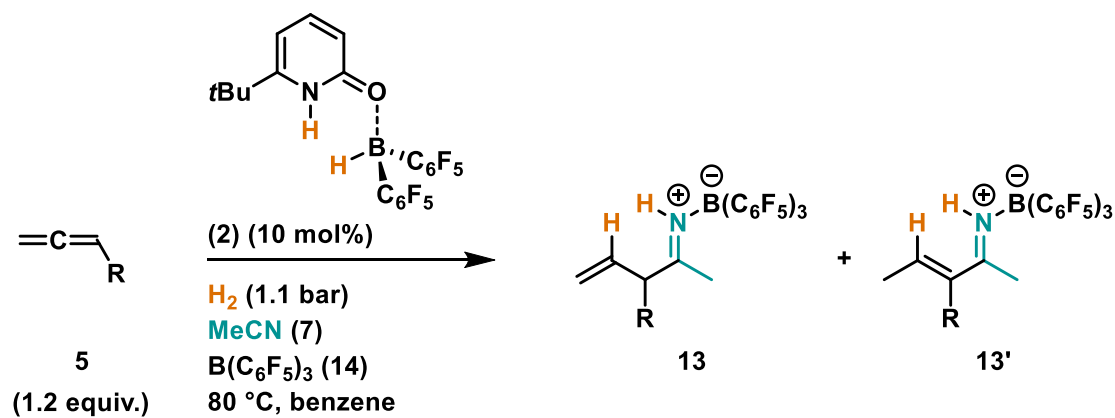


↑ ΔG [kcal mol⁻¹]



revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c. The SMD model for benzene was used to implicitly account for solvent effects. Molecules, which are not part of the respective step are omitted for clarity

Substrate Scope

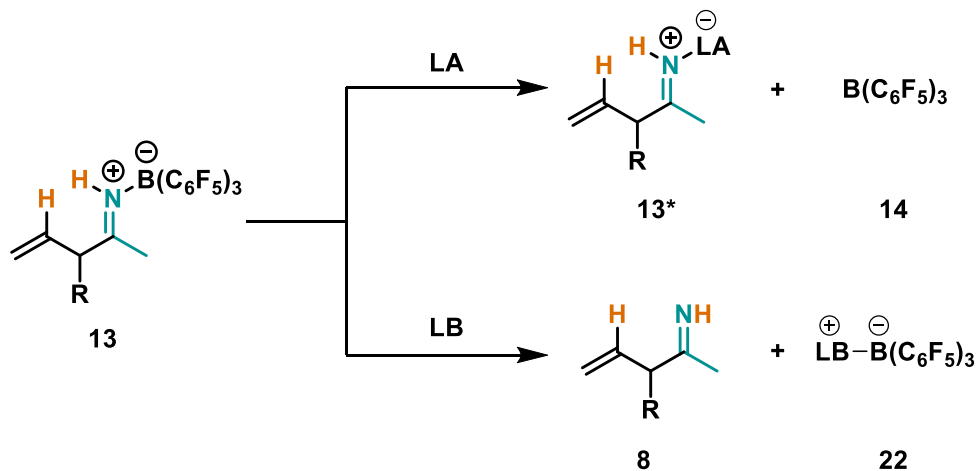


Reaction time:	16 h	16 h	16 h	3 d	5 d	5 d
Ratio:	13a / 13a'	13c / 13c'	13d	13e / 13e'	13f	13g
Yield:	93:7 65%	9:1 40%	<10% (qNMR)	3:2 66%	72%	51%

Reaction conditions: 0.36 mmol Allene; 0.30 mmol Acetonitril; 0.30 mmol $\text{B}(\text{C}_6\text{F}_5)_3$; 0.03 mmol 6-tBu-Pyridone; 0.033 mmol $\text{HB}(\text{C}_6\text{F}_5)_3$; 6.00 mL benzene; 1.10 bar H_2 ; 100 mL Flask with Yong-Valve

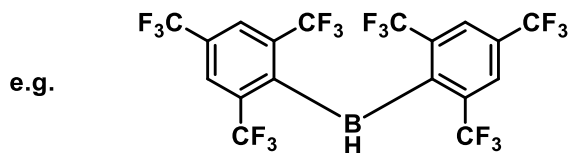


“Deprotection” of imine / Regeneration of $B(C_6F_5)_3$



Further Investigation of Substrate Scope

Investigation of Piers Borane Derivatives

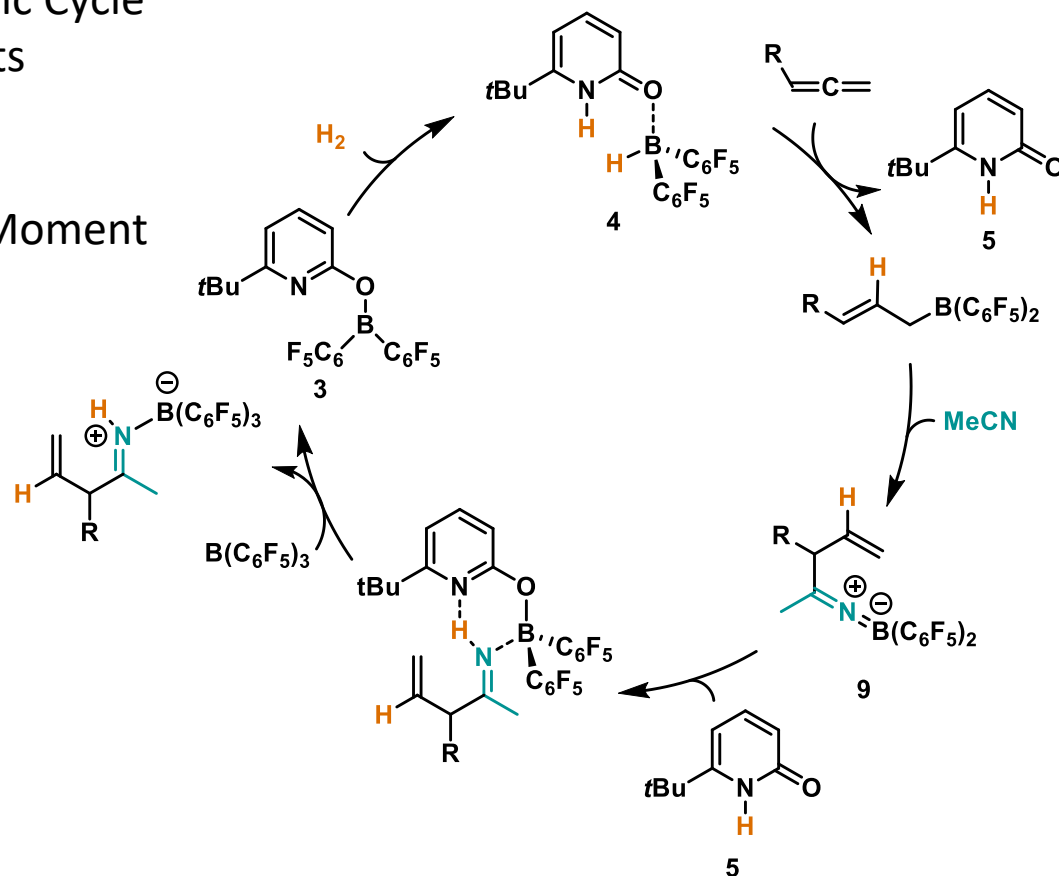




First Catalytic Formation Allylboranes

Complete Investigation of Catalytic Cycle
by Computations and Experiments

Imitated Substrate Scope at the Moment



Acknowledgement



Urs

Max and Arthur

Tizian, Jama and Felix

AG Schreiner, AG Wegner, AG Göttlich

