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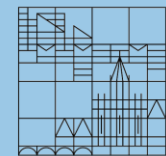
# Directed C-H Activation of Alkanes

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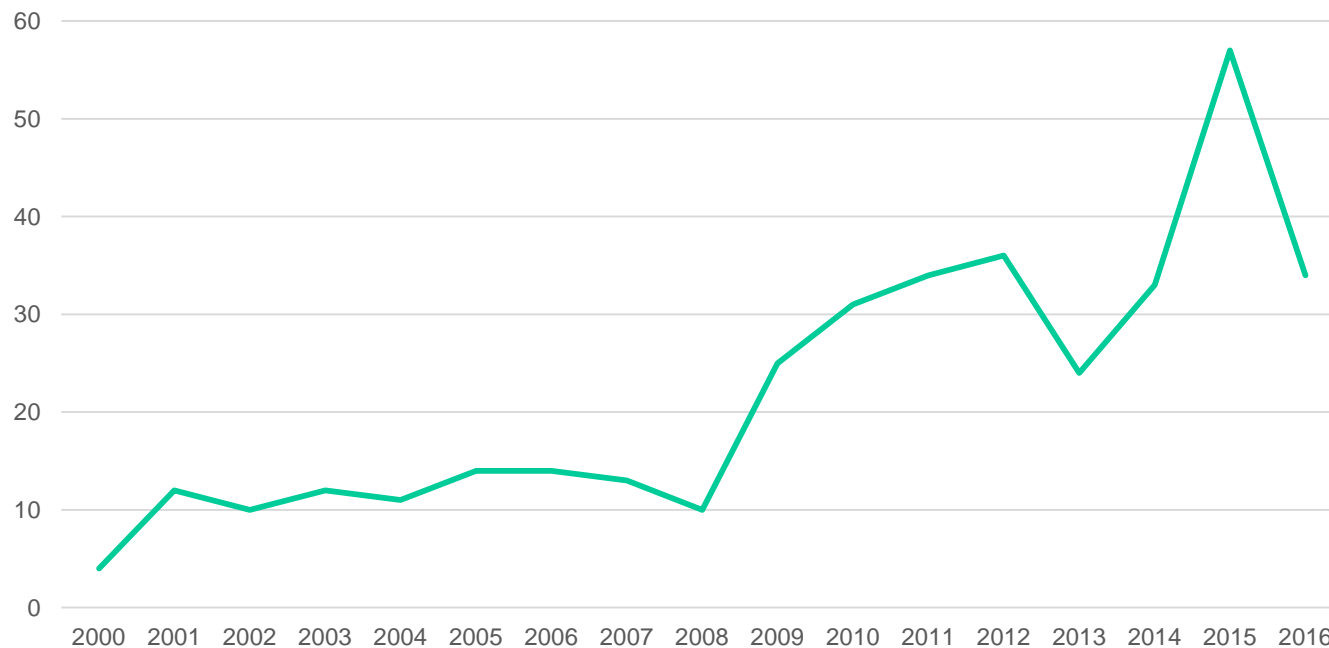
Work Group of Prof. Tanja Gaich

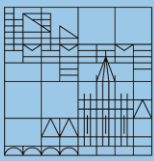
Konstantin Samarin

22.06.2016

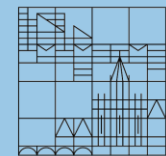


## Reviews about C-H activation





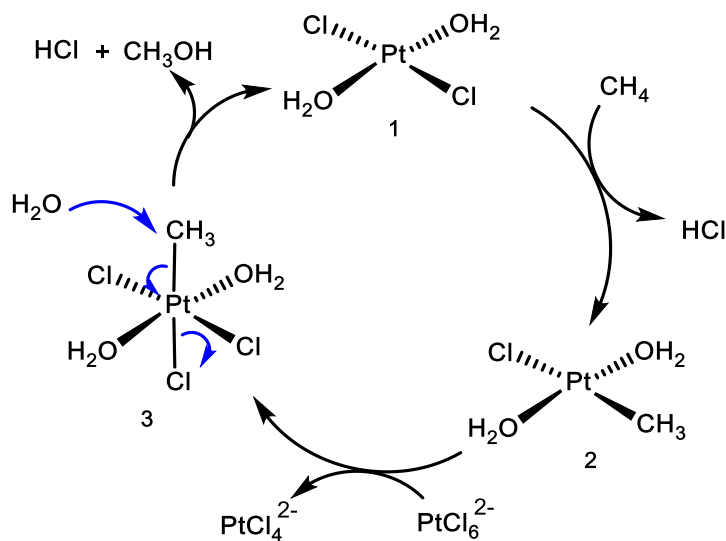
# Short historical perspective



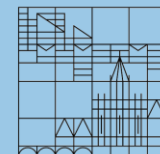
## Shilov process:



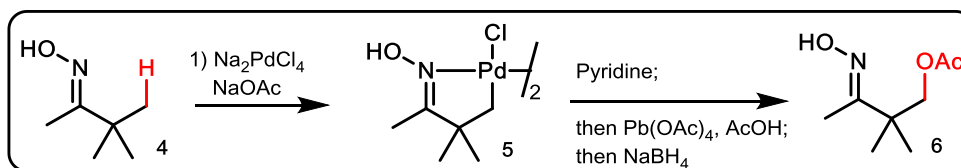
## Proposed mechanism:



Alexander E. Shilov

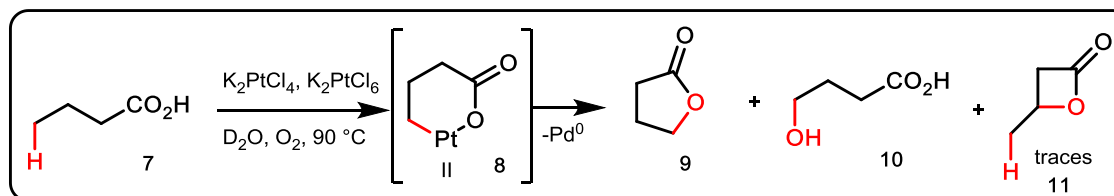


## 1,3-Oxime directed



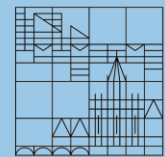
Jack Baldwin

## 1,4-Carboxylic acid directed

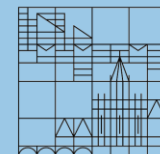


Ayusman Sen

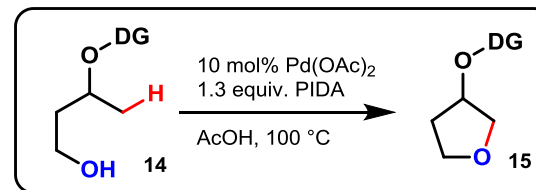
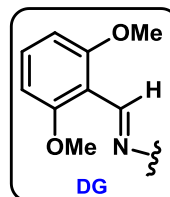
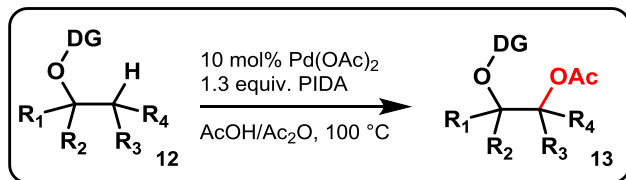
Shaw B.L., et al. *J. Chem. Soc., Chem. Commun.* **1978**, 1061;  
 Baldwin J.E., et al. *Tetrahedron* **1985**, *41*, 699;  
 Kao L.C. Sen A. *J. Chem. Soc., Chem. Comm.* **1991**, 1242.



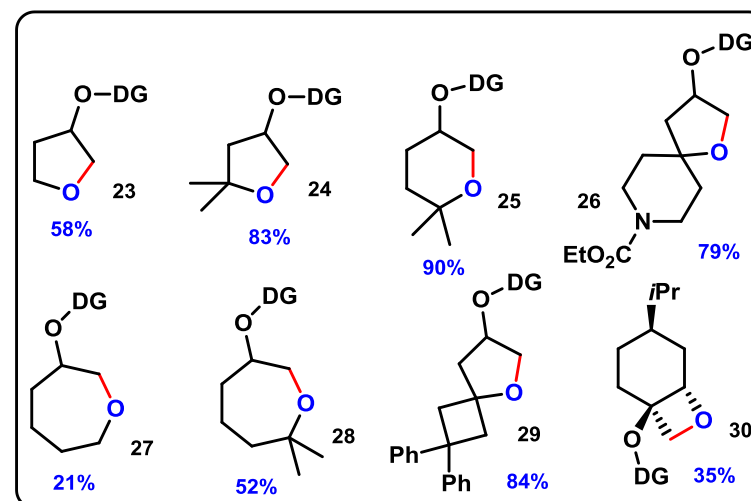
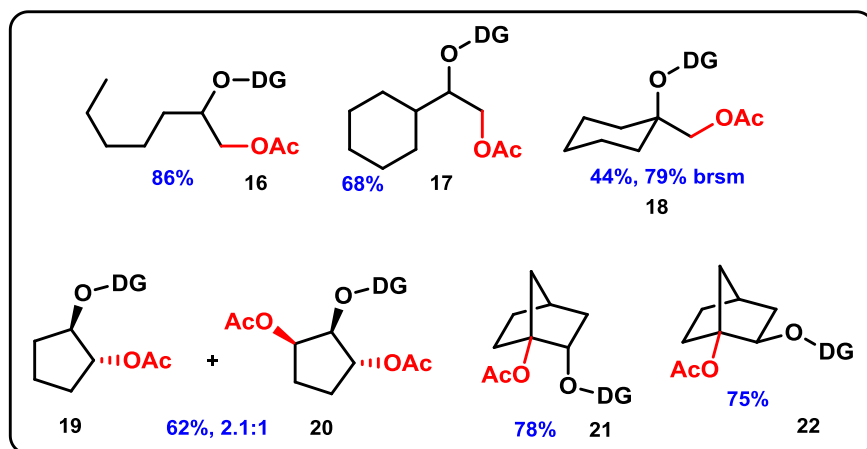
# Modern Pd-catalyzed C-H Activation

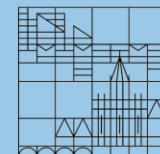


## Principal scheme:

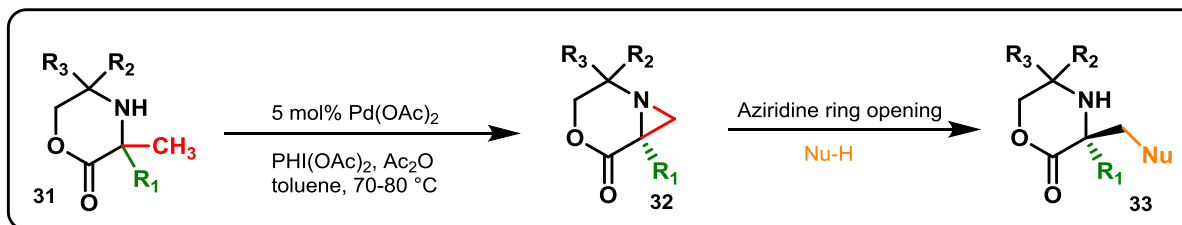


## Scope:

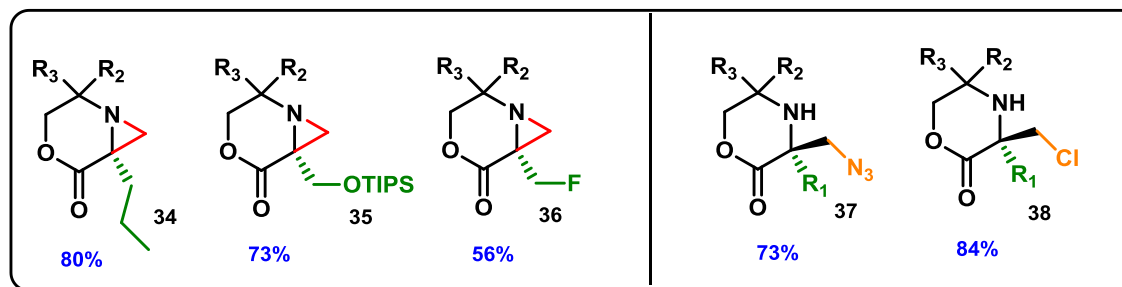




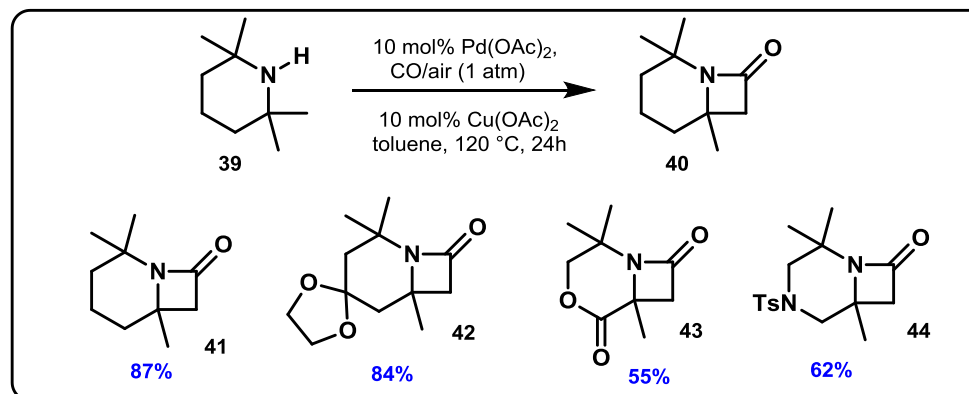
## Principal scheme:



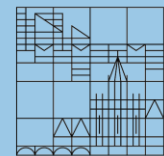
## Scope:



## Carbonylation Modification:

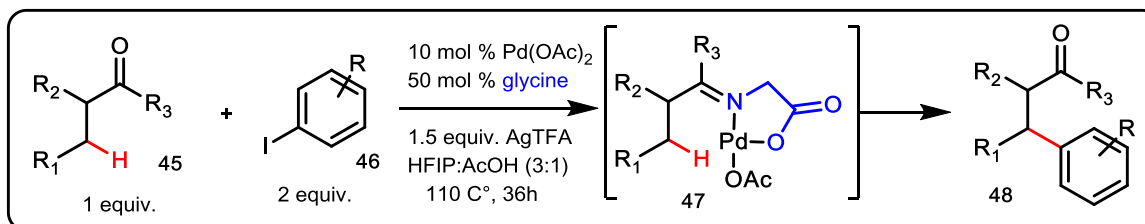




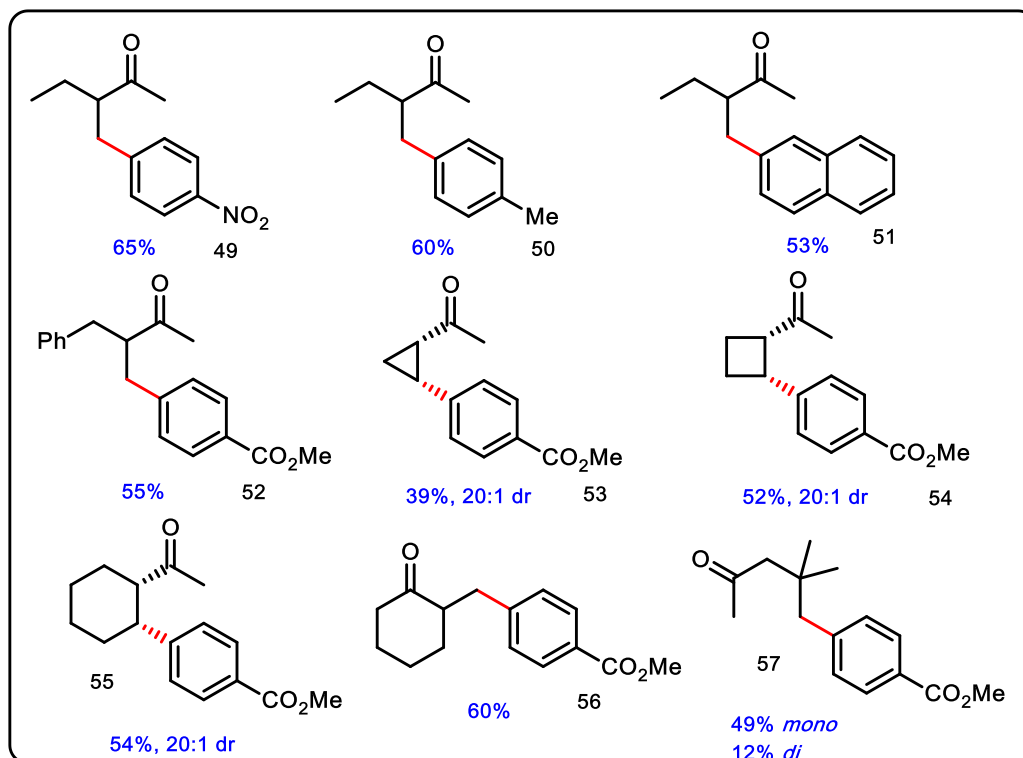


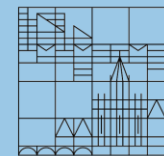
# Modern Pd-catalyzed C-H Activation

## Principal scheme:

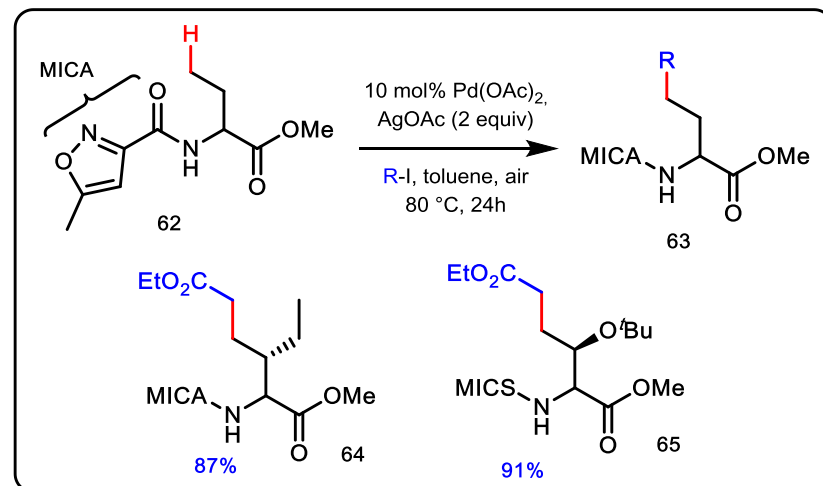
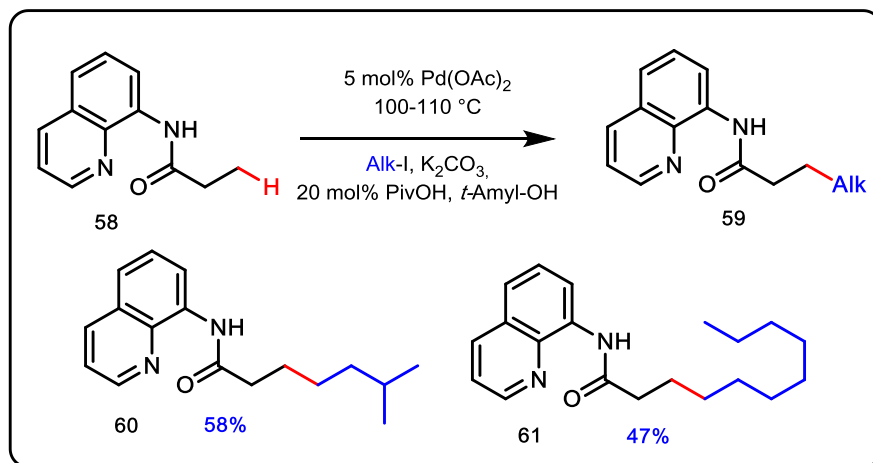


## Scope:



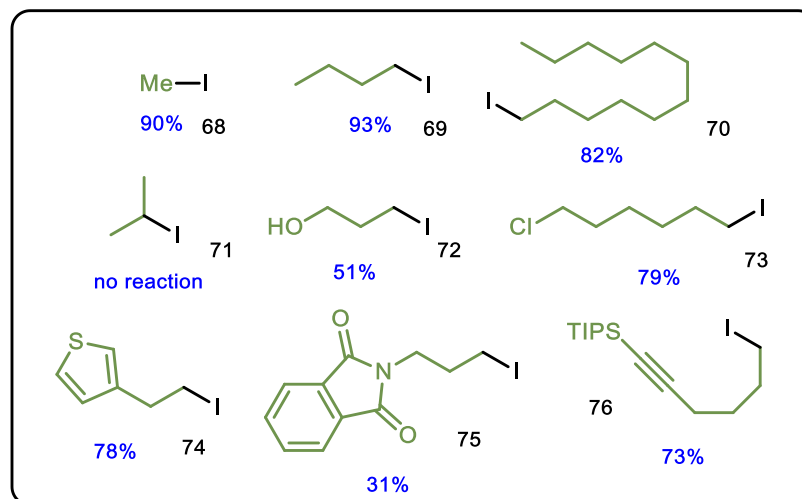
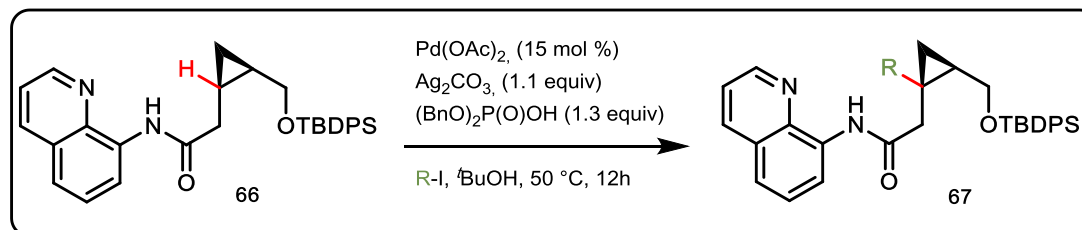


## Coupling with alkyl iodides



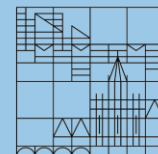


## Coupling with alkyl iodides

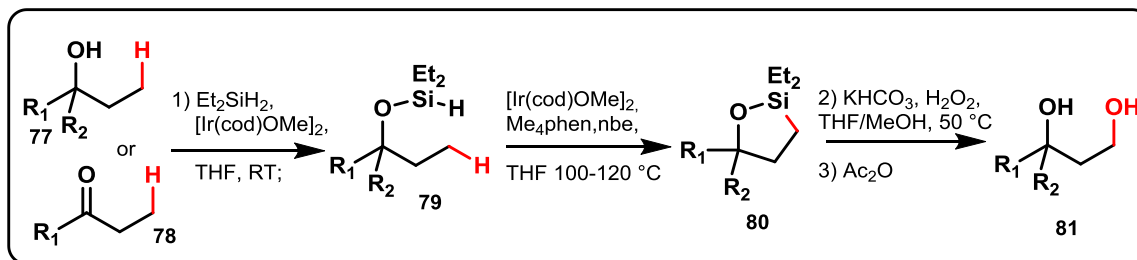




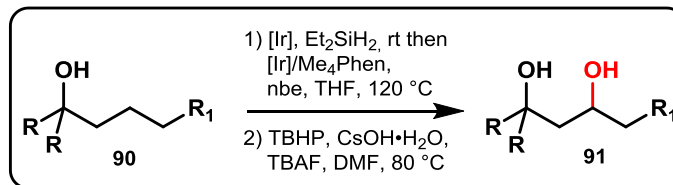
# Ir-catalyzed C-H Activation



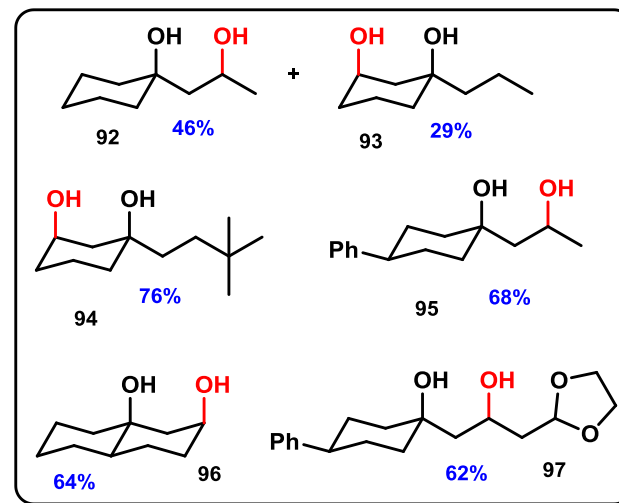
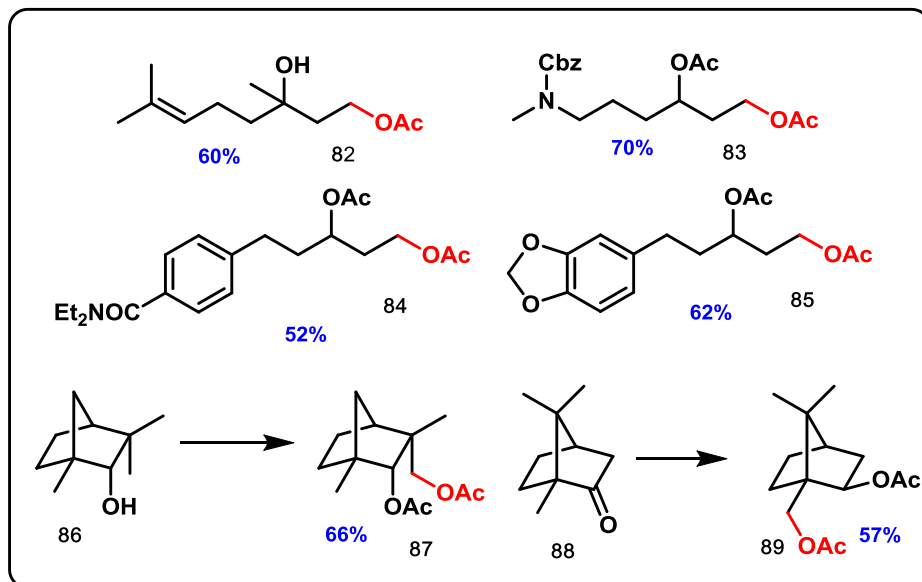
## C-H activation at CH<sub>3</sub>:



## C-H activation at CH<sub>2</sub>:

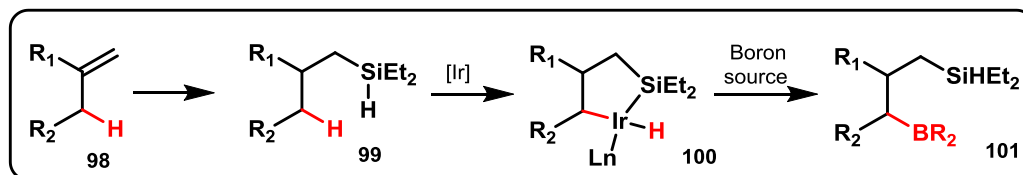


## Scope:

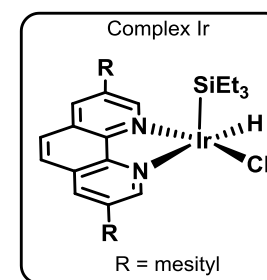
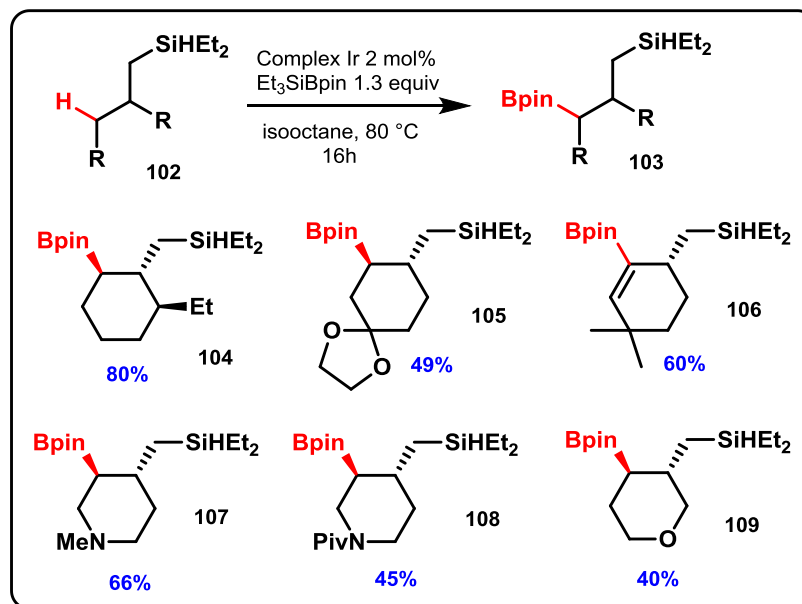


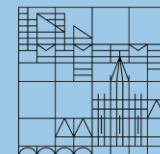


## Borylation scheme:

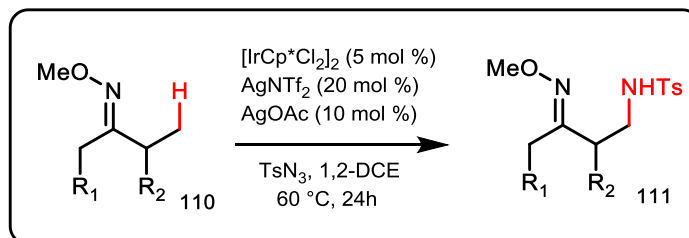


## Scope:

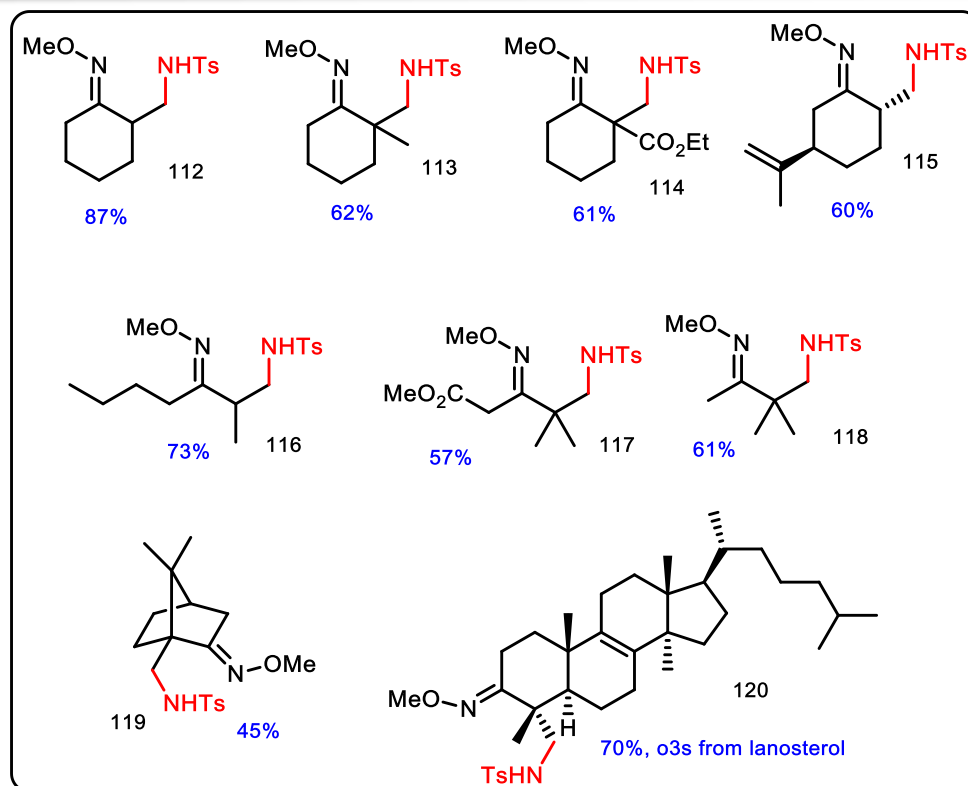


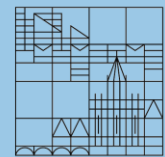


## Principal scheme:



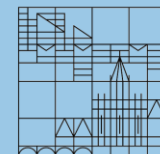
## Scope:



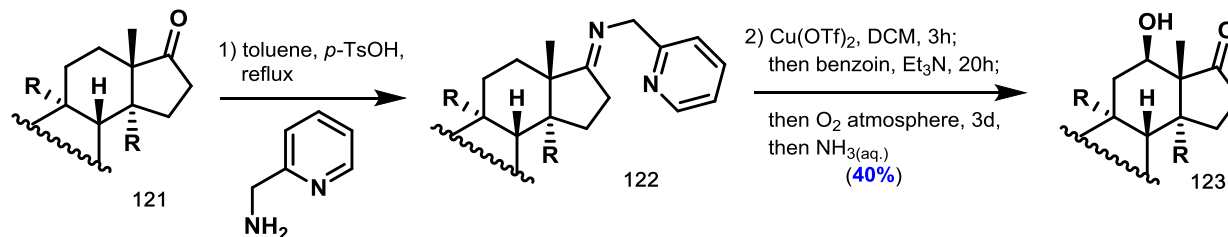


# Cu-catalyzed C-H Activation

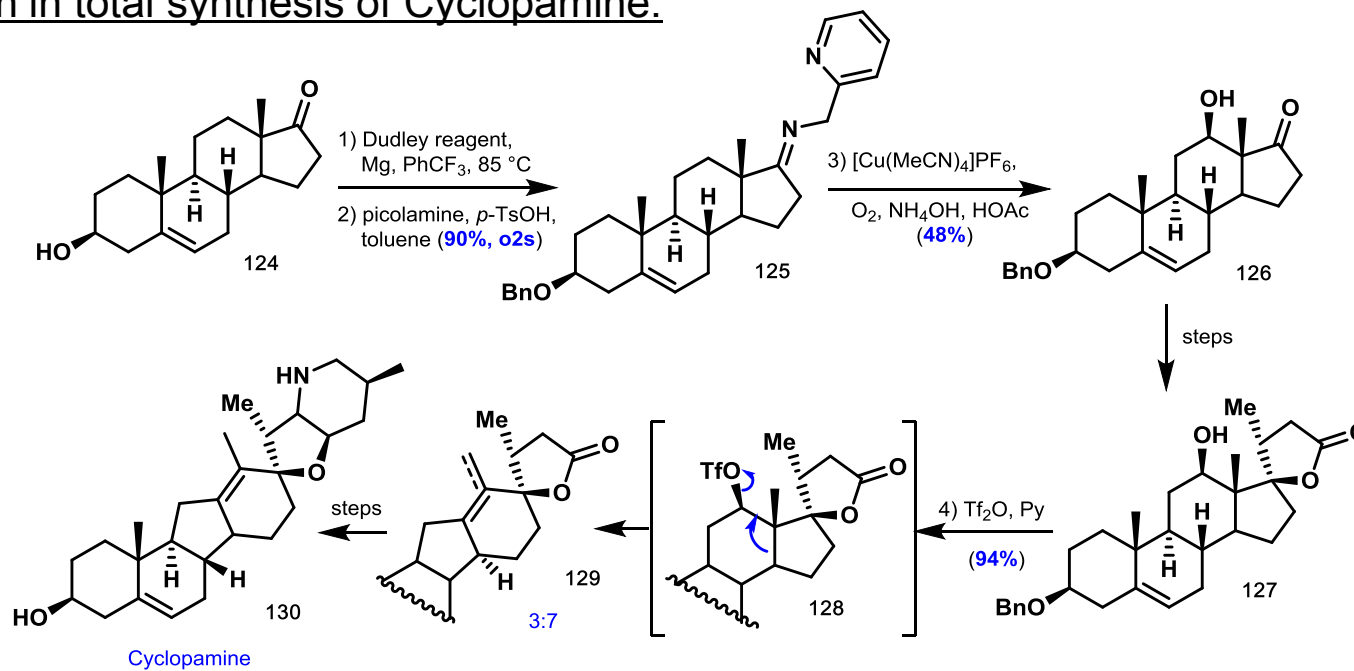


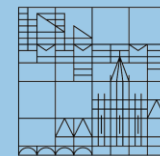


## Schönecker methodology:

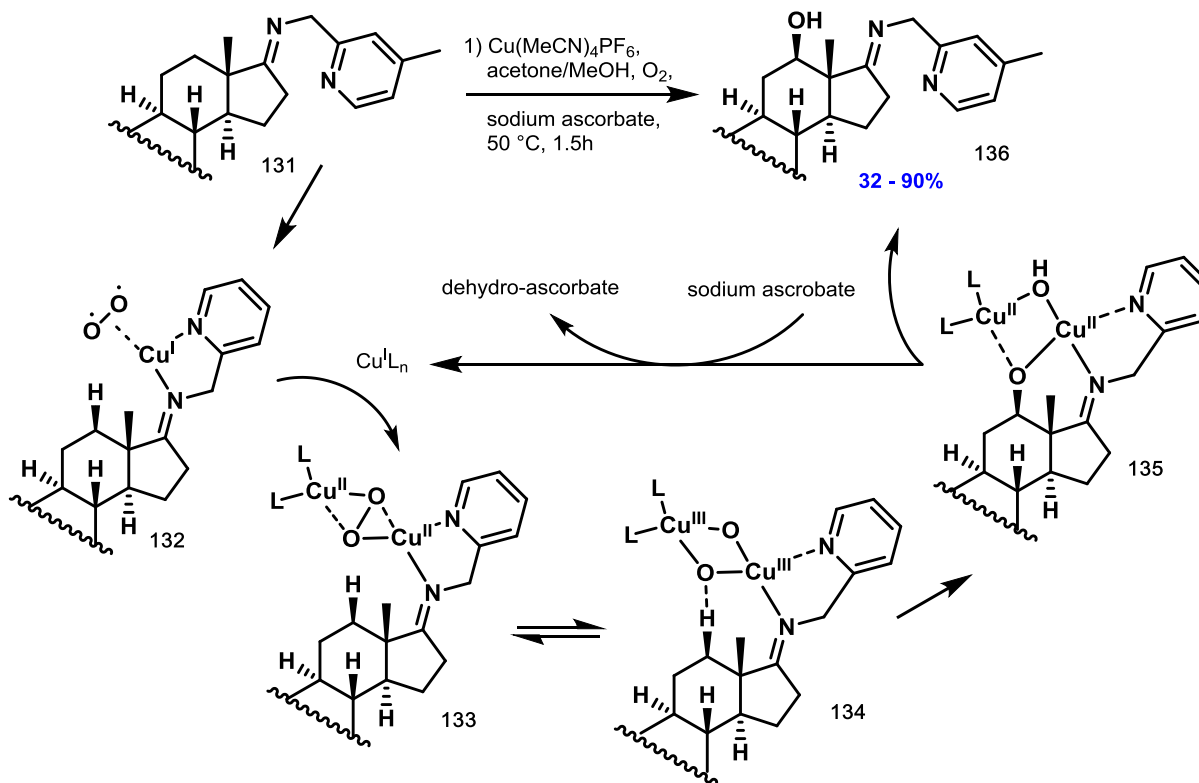


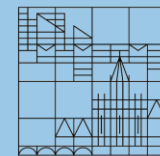
## Application in total synthesis of Cyclopamine:



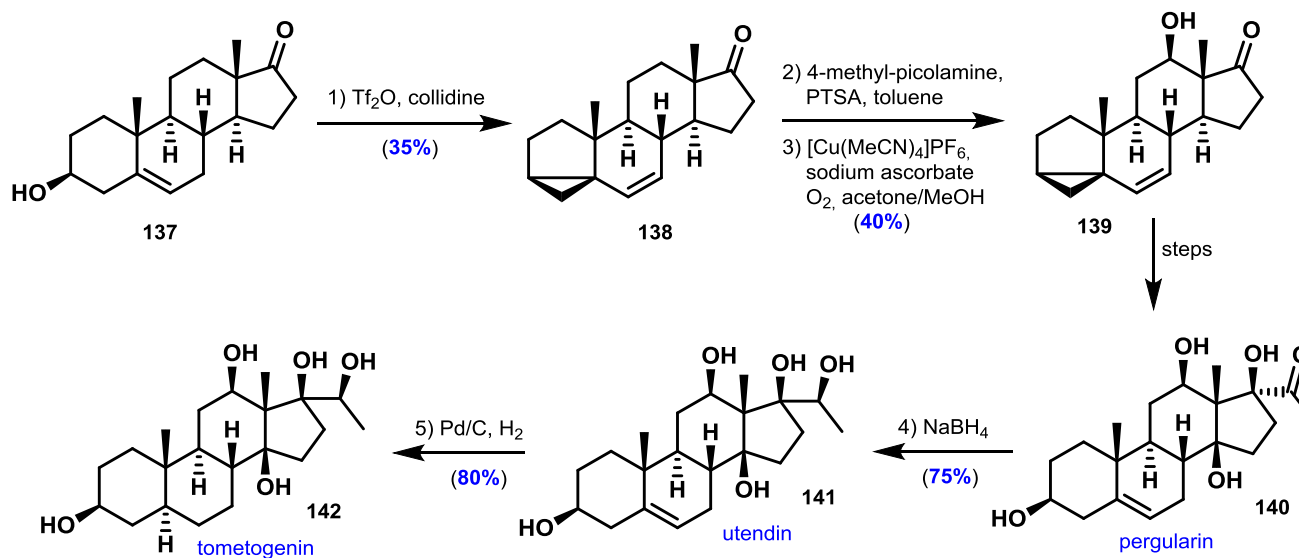


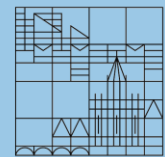
## Baran optimized protocol and proposed mechanism:





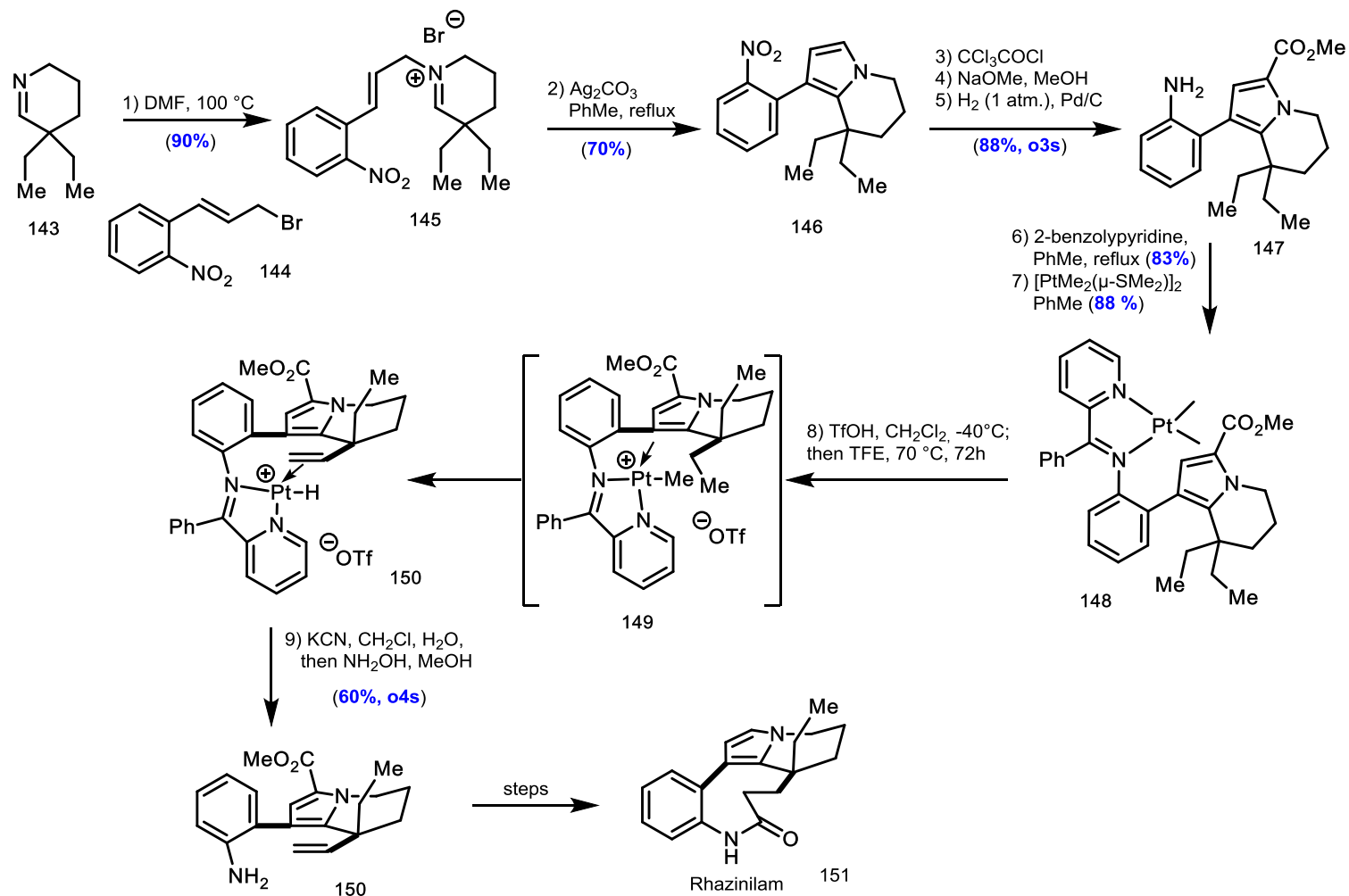
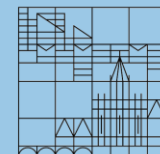
## Application in total synthesis:



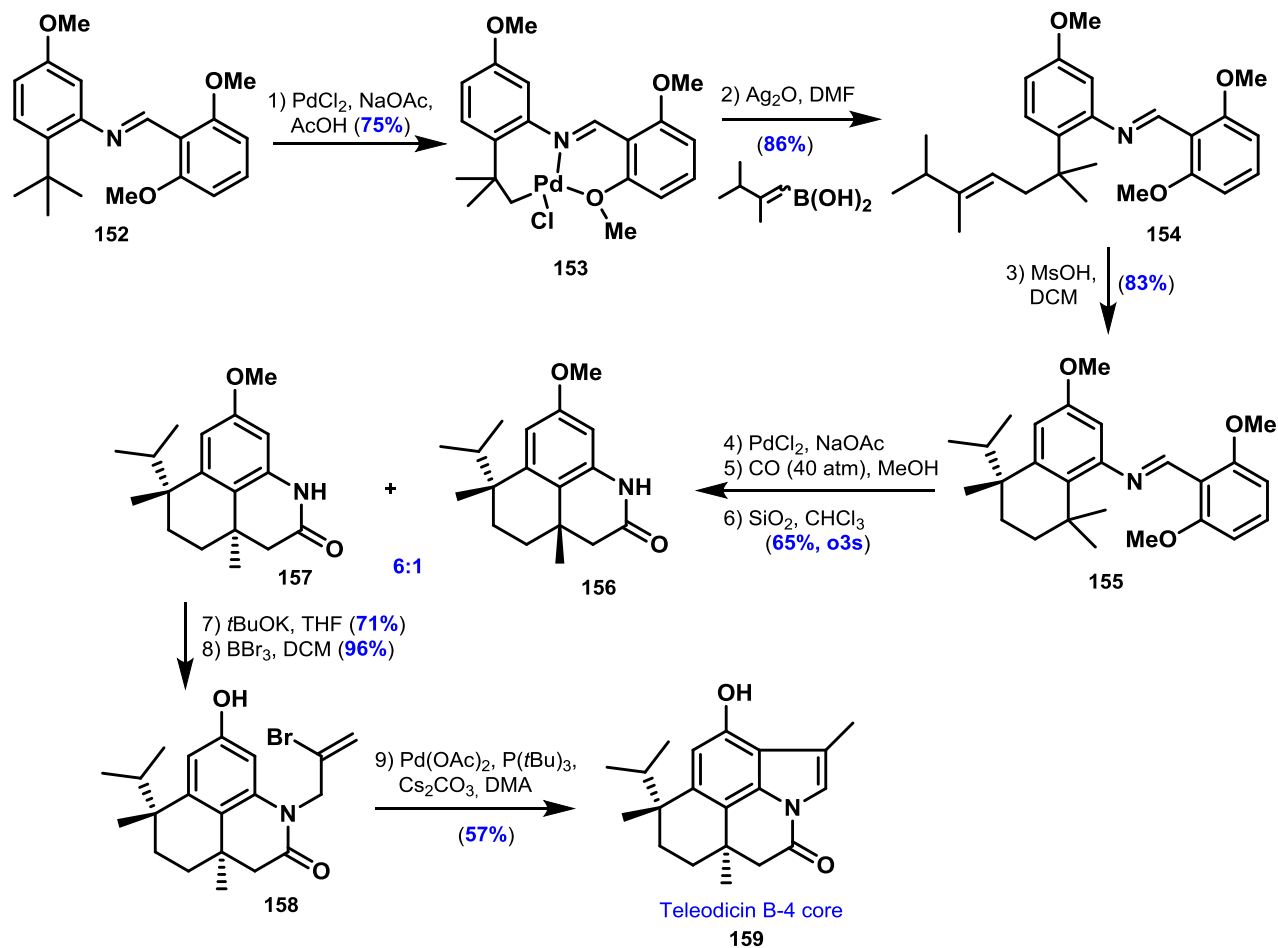
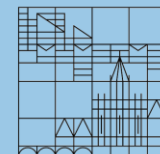


# Remarkable Applications in Total Synthesis

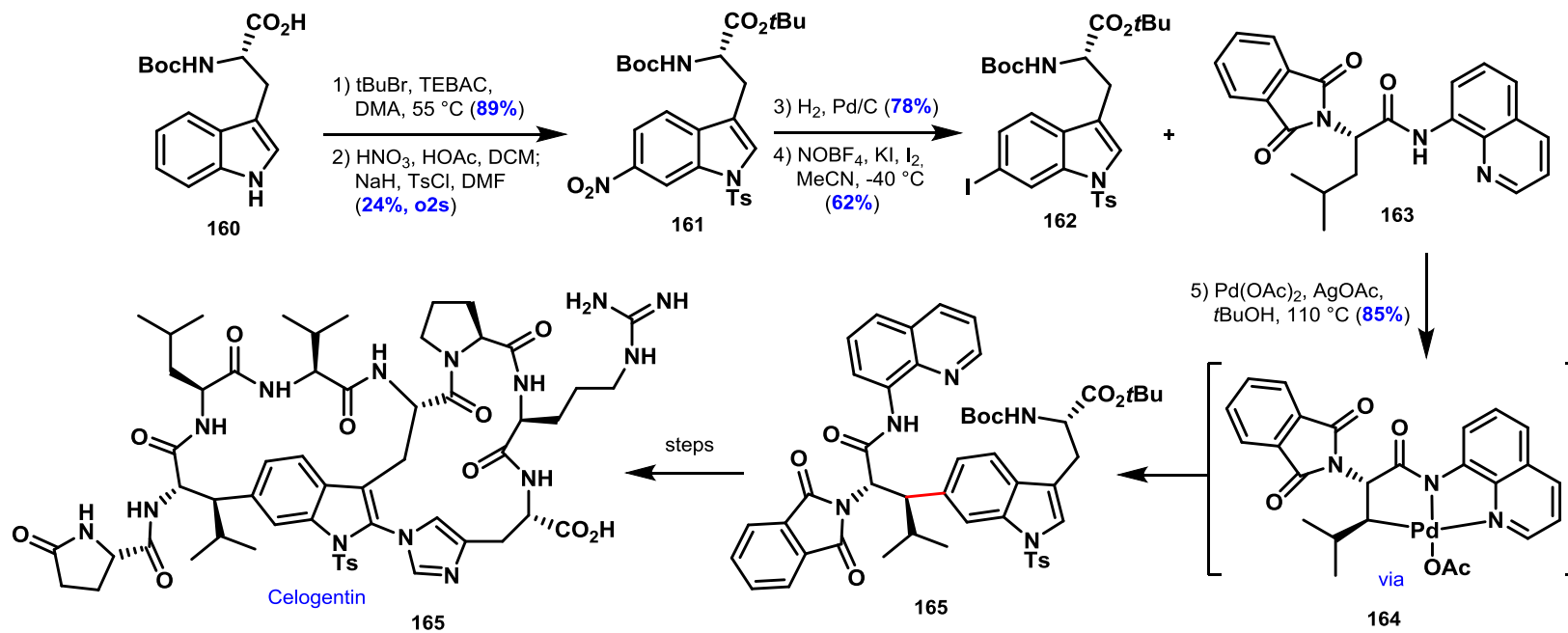
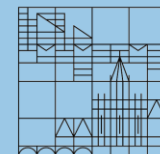
# Total Synthesis of the Rhazinilam



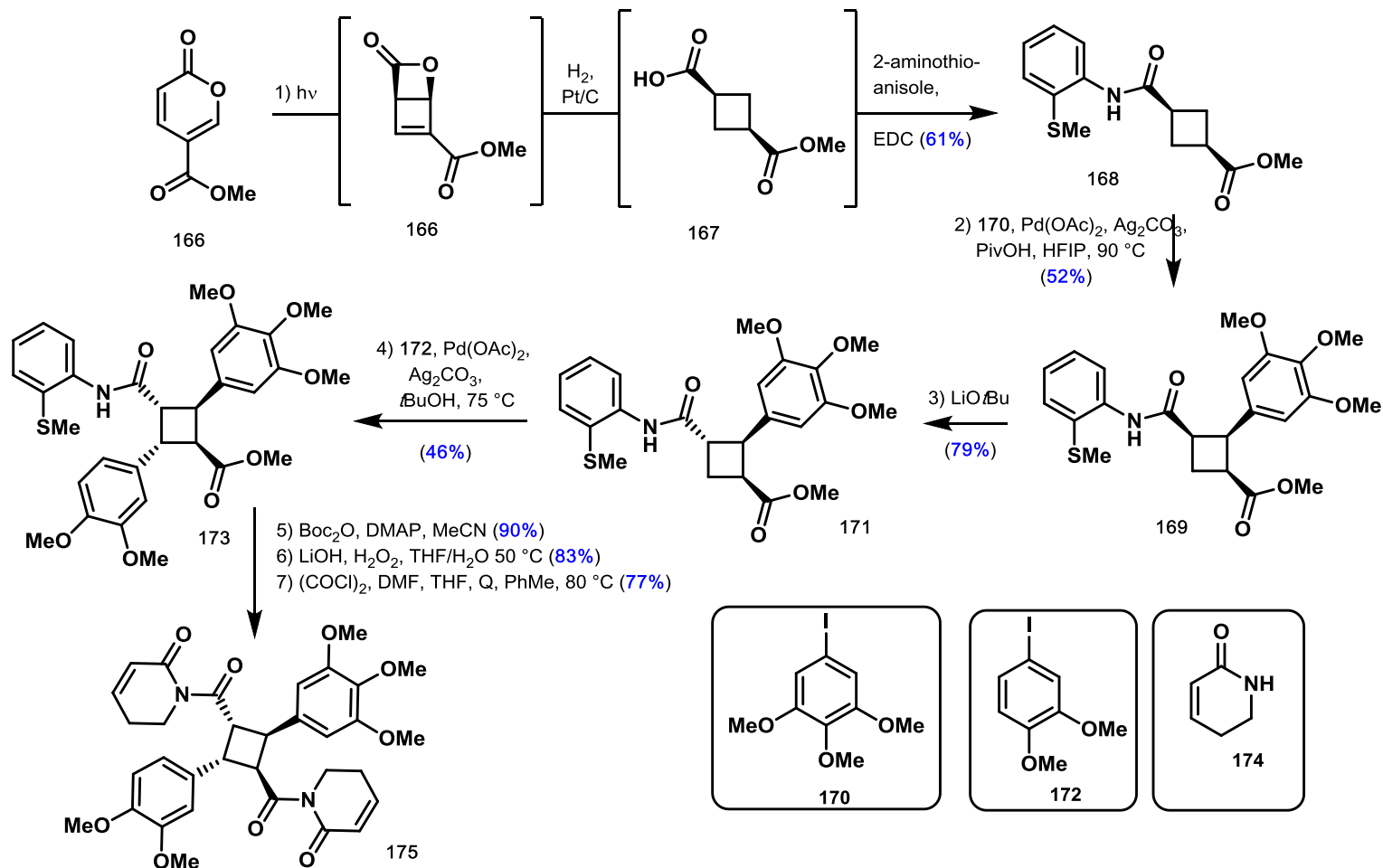
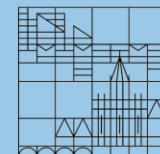
# Synthesis of teleodacin B-4 core



# Total Synthesis of Celogentin C

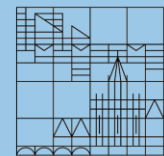


# Total Synthesis of piperaborenine B

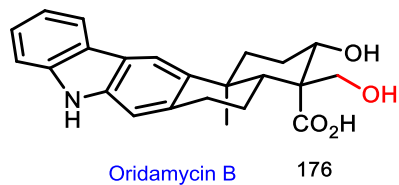


piperaborenine B

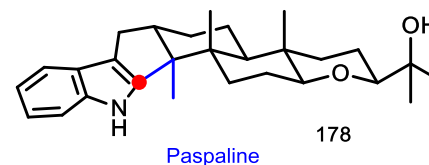




Li A., et al. *Nature communications* 2015, 6, 6096.  
Trotta A.H. *Org. Lett.* 2015, 17, 3358.

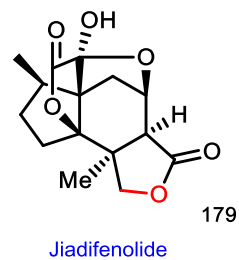
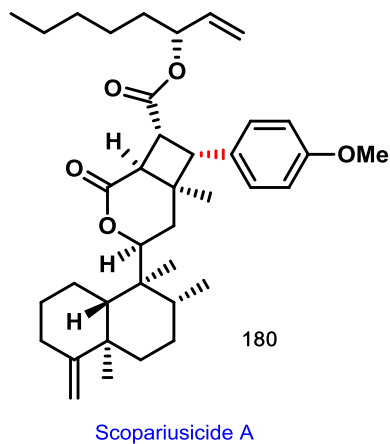


Sharpe R.J., Johnson J.S. *J. Am. Chem. Soc.* 2015, 137, 4968.  
Sharpe R.J., Johnson J.S. *J. Org. Chem.* 2015, 80, 9470.

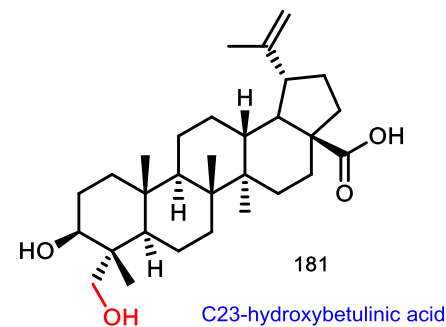


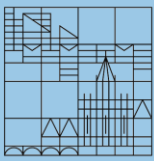
Sorenson E.J., et al. *Angew. Chem., Int. Ed.* 2014, 53, 5332.

Sun H.-D., et al. *Org. Lett.* 2015, 17, 6062.



Baran P.S. et al. *Angew. Chem.* 2014, 126, 12287





Thank You For Your Attention