



Transition-Metal-Catalyzed C–H Functionalization for the Synthesis of Substituted Pyridines

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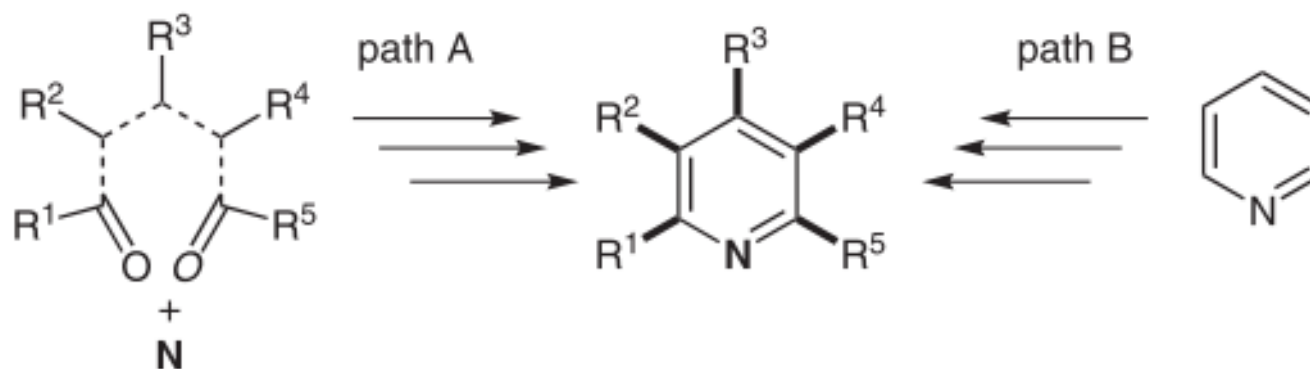
2013-11-25



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Background



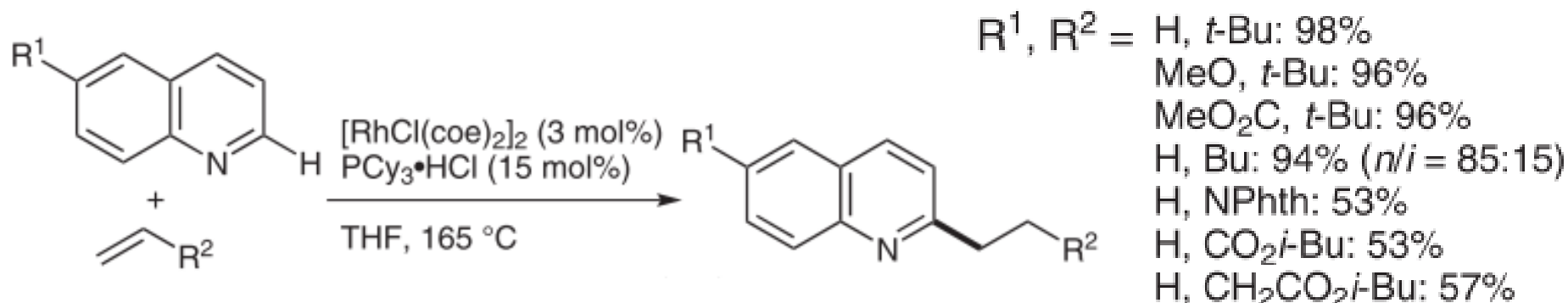
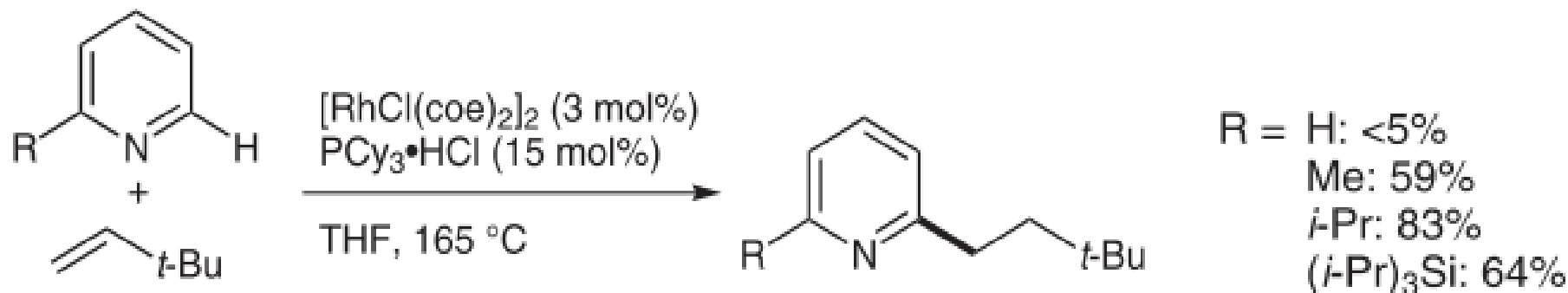
Challenge:

electron-poor;

N-bound coordination mode with metal centers.

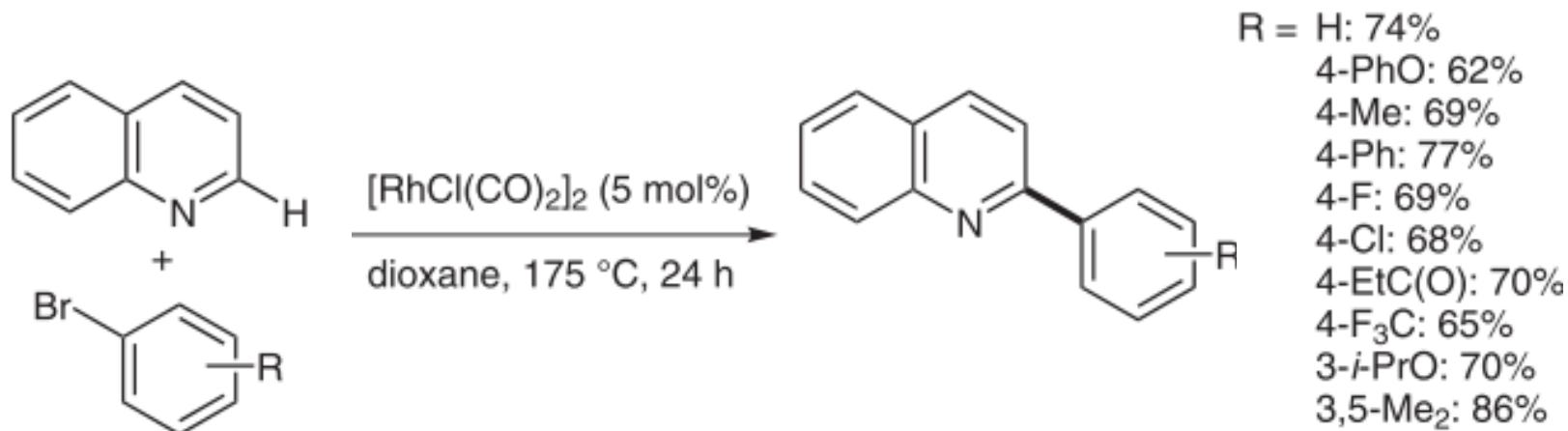
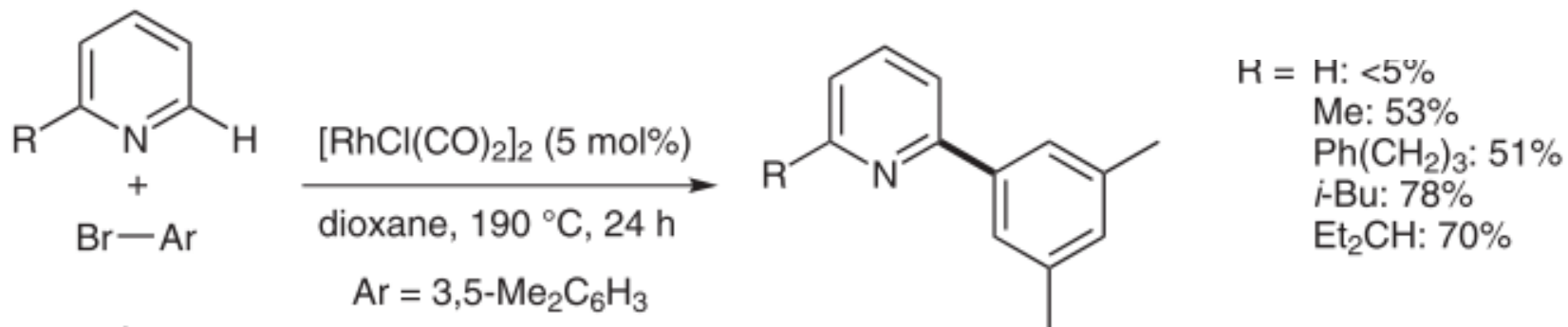
C2-Selective Functionalization

---alkylation



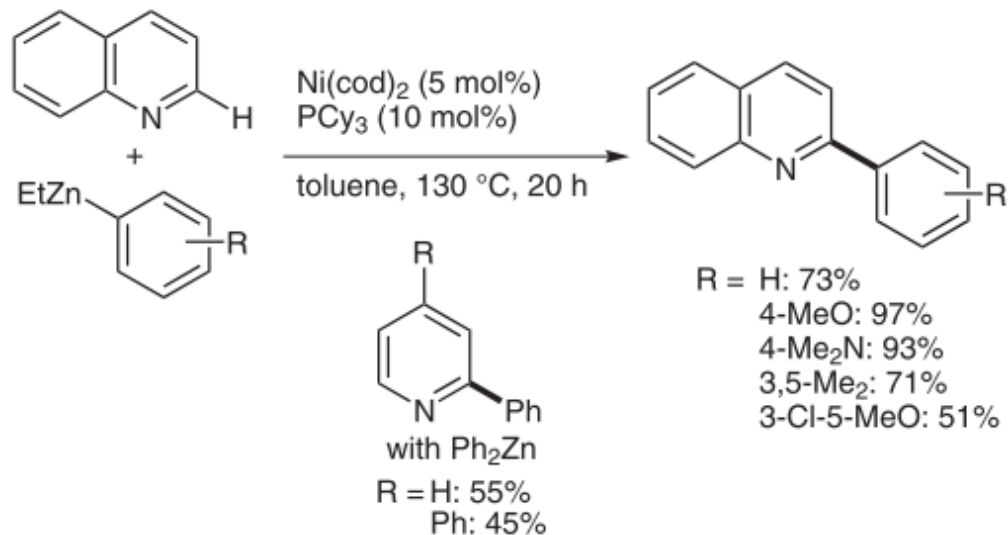


C2-Selective Functionalization ---arylation

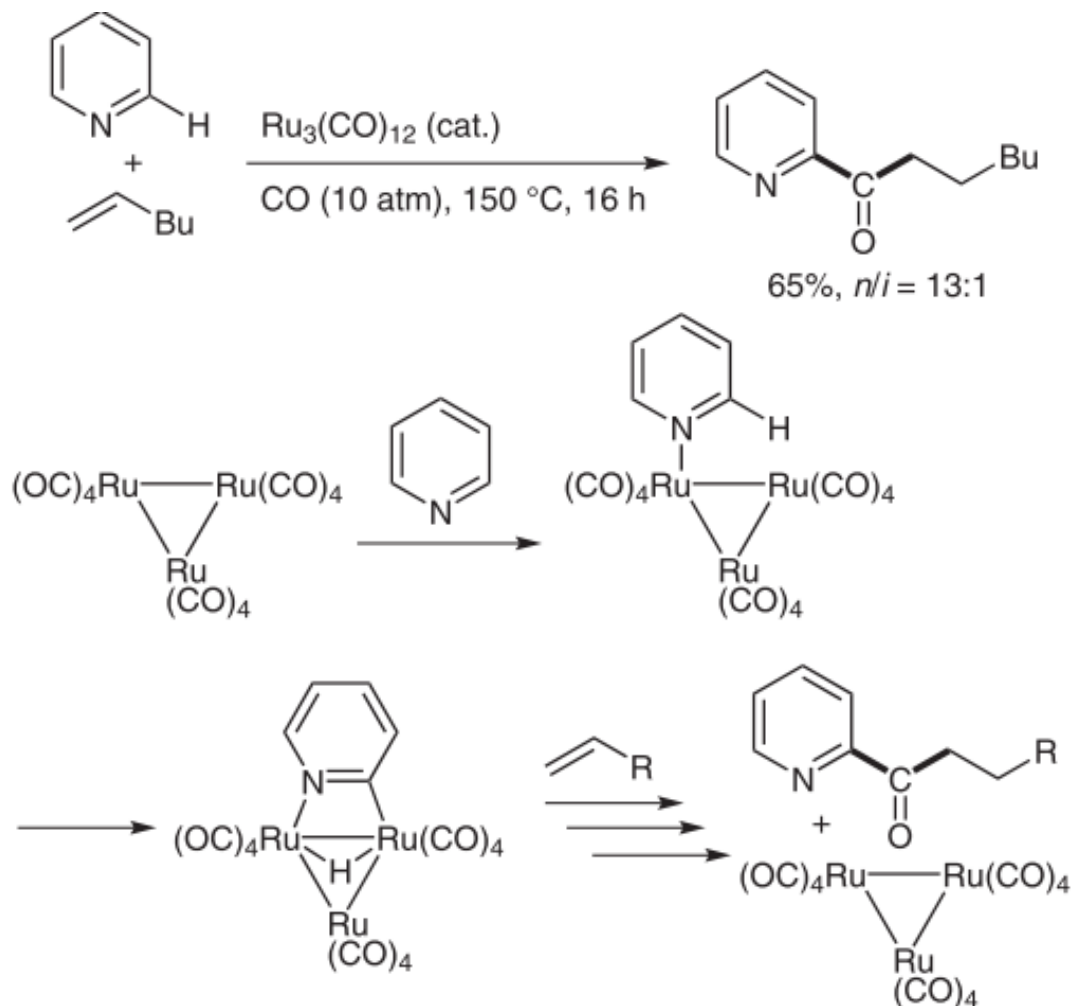


- a) Berman, A. M.; Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2008**, *130*, 14926.
b) Wiedemann, S. H.; Lewis, J. C.; Bergman, R. G.; Ellman, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 2452.

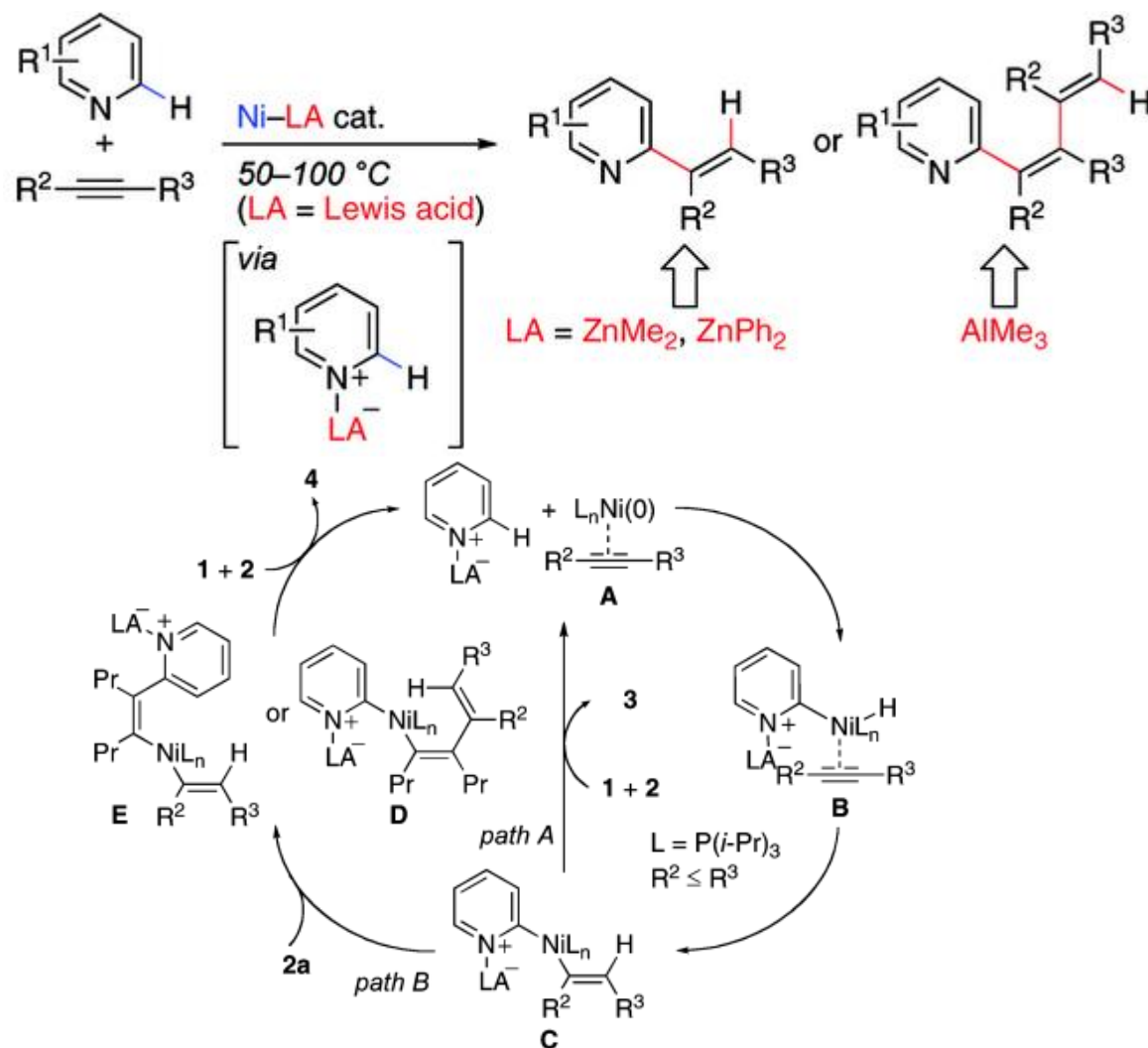
C2-Selective Functionalization ---arylation



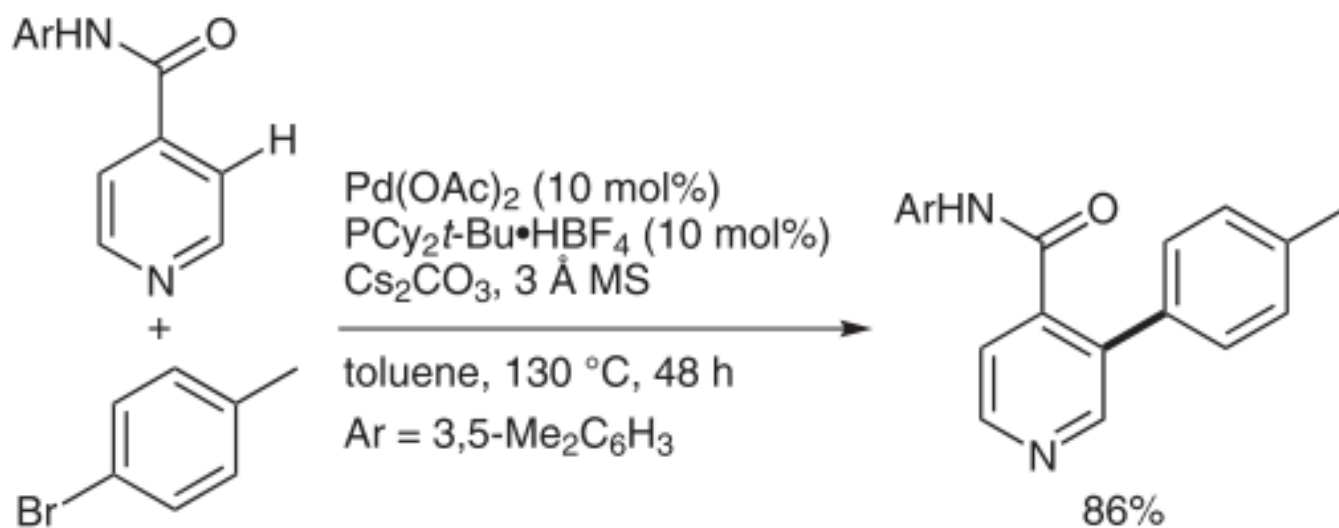
C2-Selective Functionalization ---acylation



C2-Selective Functionalization ---alkenylation

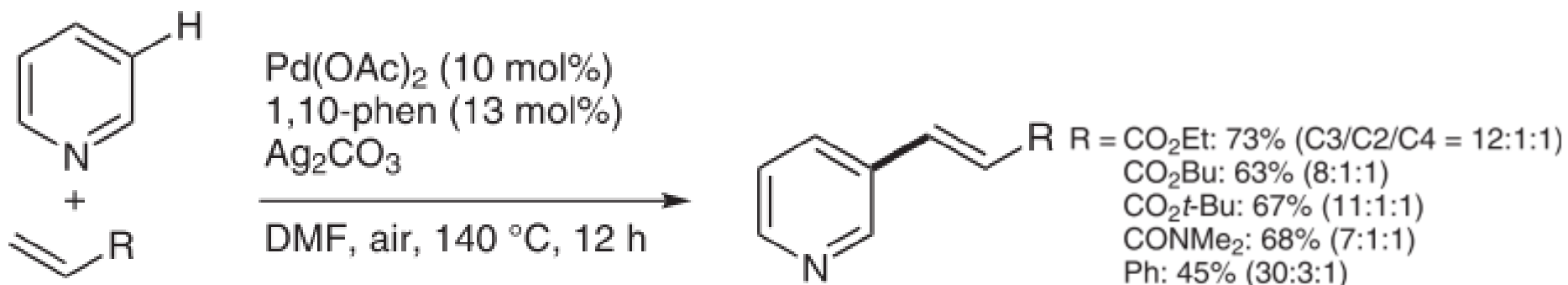
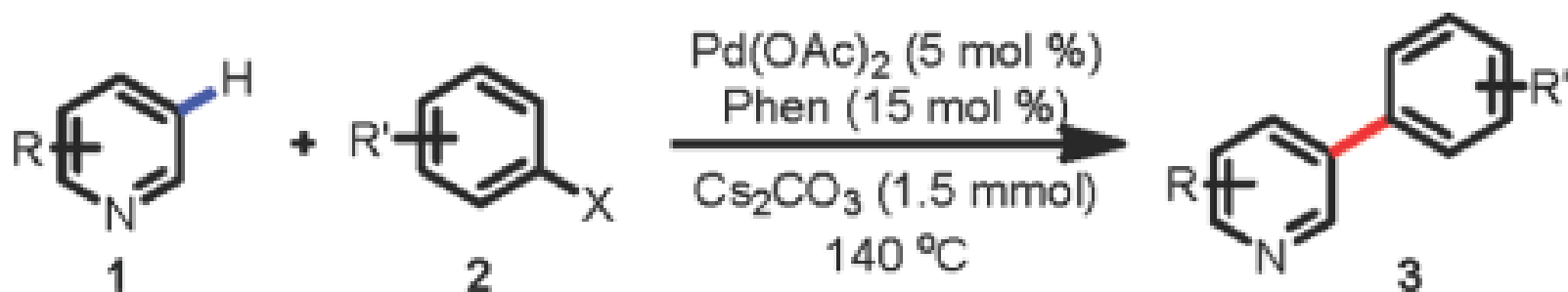


C3-Selective Functionalization ---arylation



C3-Selective Functionalization

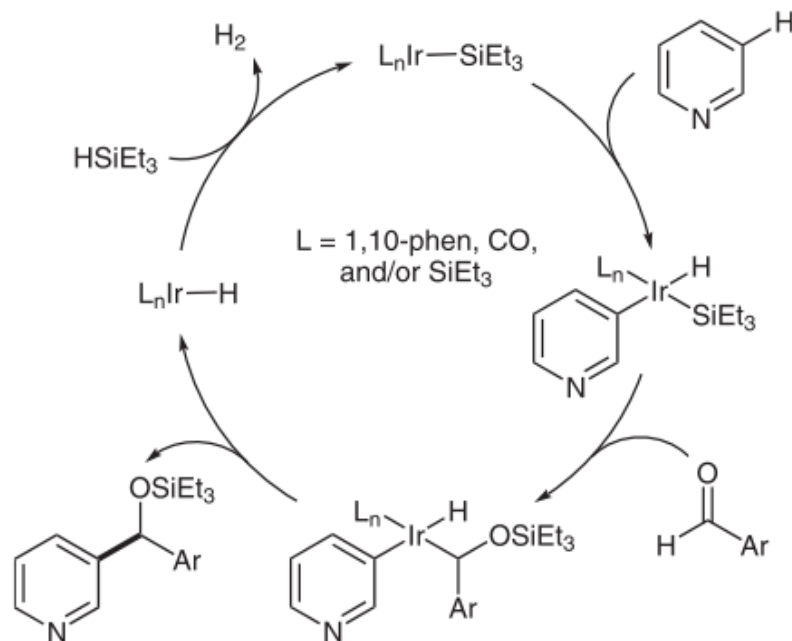
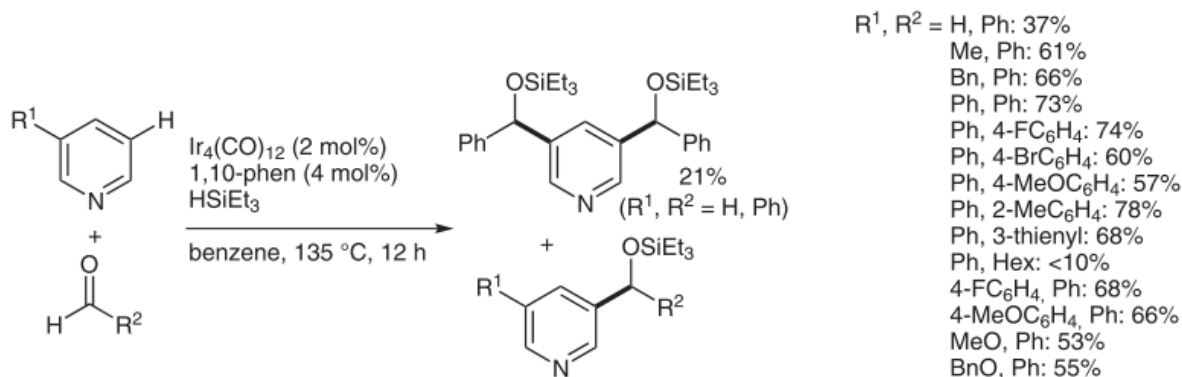
---arylation and alkenylation



- a) Ye, M.-C ; Gao, G.-L.; Edmunds, A. J. F.; Worthington, P. A.; Morris, J. A.; Yu, J.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 19090.
b) Ye, M.; Gao, G.-L.; Yu, J.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 6964.

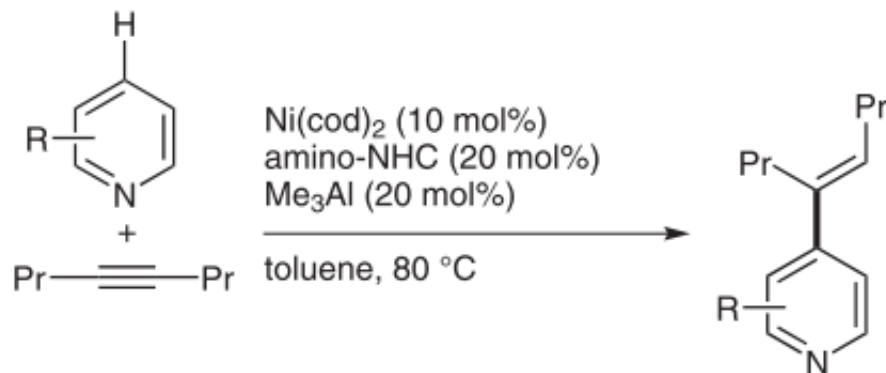
C3-Selective Functionalization

---alkylation

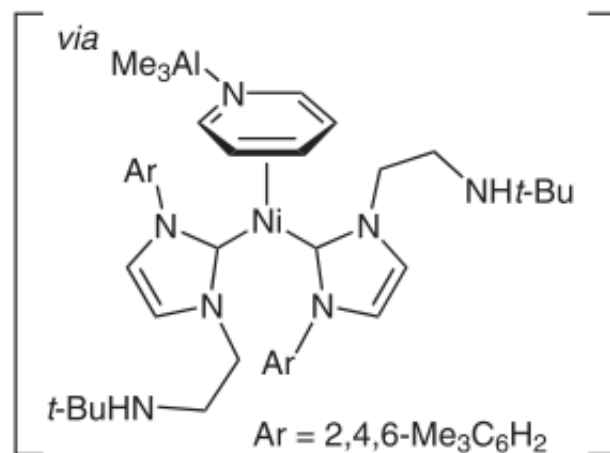


C4-Selective Functionalization

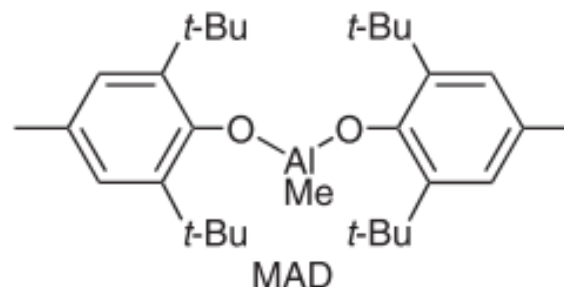
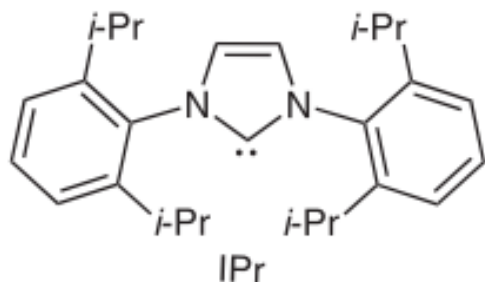
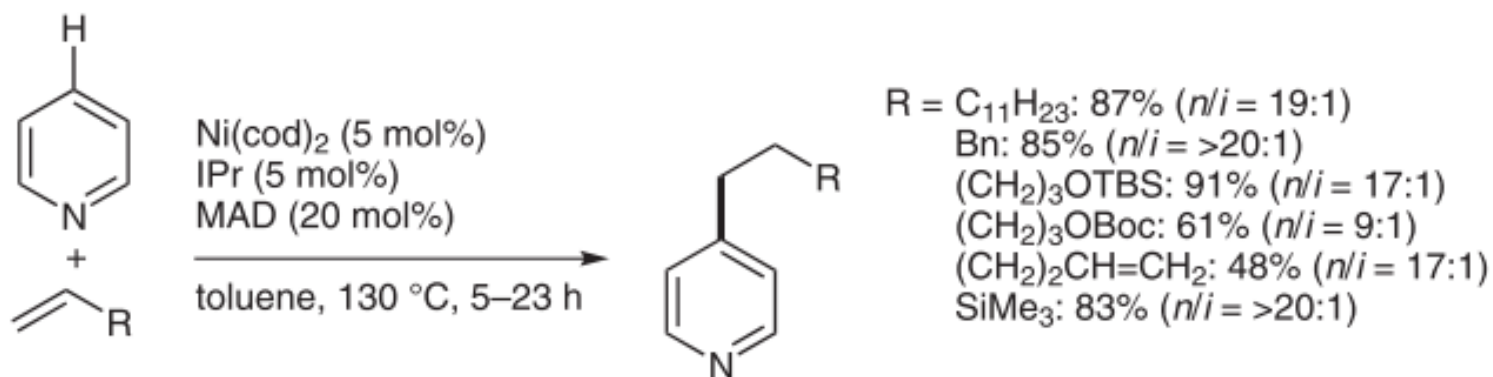
---alkenylation



R = H: 85% (C4/C3 = 3:1)
 2-Me: 56% (C4 only)
 3-Me: 85% (C4/C5 = 2.5:1)
 4-Me: 34% (C3 only)
 2-Ph: 19% (C4/C3 = 1.3:1)
 3-Ph: 71% (C4/C5 = 1:1)
 2-MeO: 49% (C4 only)
 3-MeO: 89% (C4 only)

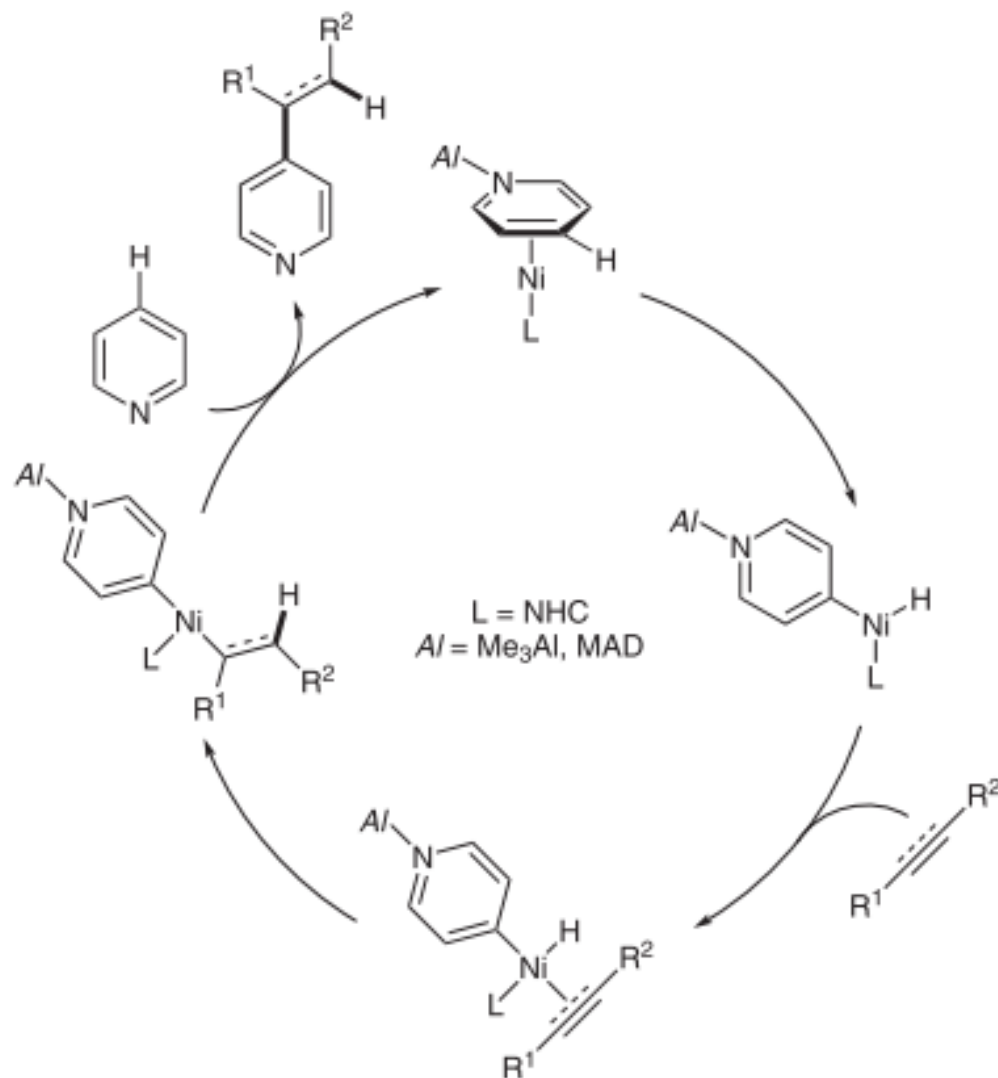


C4-Selective Functionalization ---alkylation



C4-Selective Functionalization

---alkenylation and alkylation





Summary

- *Construct carbon–carbon bonds on pyridine*
 - *alkylation, alkenylation, arylation, acylation*
 - *selectively at C2, C3 or C4*

- *Construct carbon–oxygen and carbon–nitrogen bonds*



Thanks for Your Attentions!