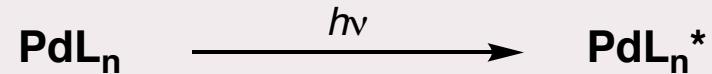


Photoexcited Palladium Catalysis



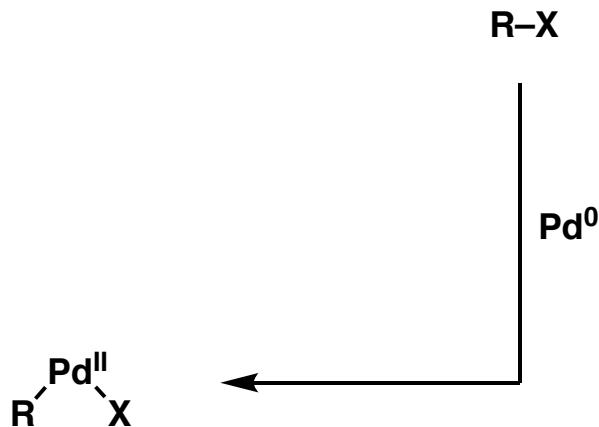
Nicholas A. Falcone
Literature Group Meeting
May 14th, 2021

Photoexcited Pd Complexes: An Emerging Platform for Novel Reactivity

R-X

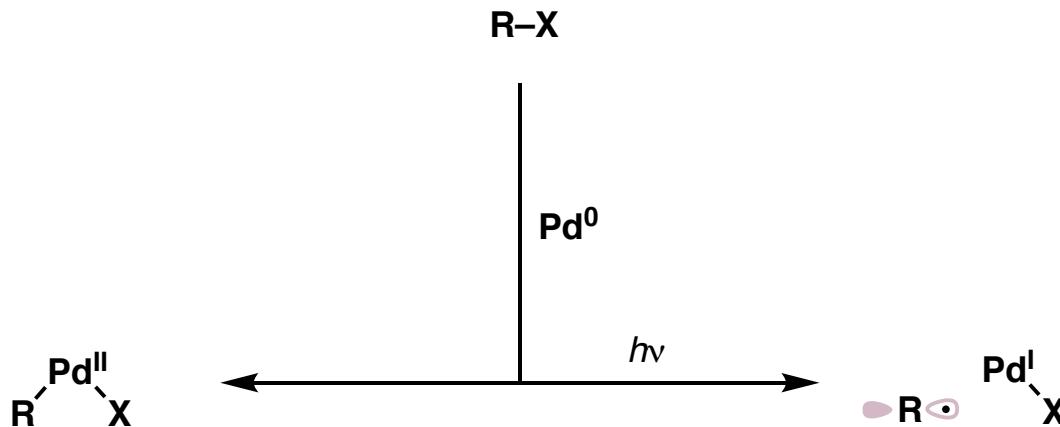
Pd⁰

Photoexcited Pd Complexes: An Emerging Platform for Novel Reactivity



- Two electron chemistry
- Pd⁰/Pd^{II} and Pd^{II}/Pd^{IV} cycles

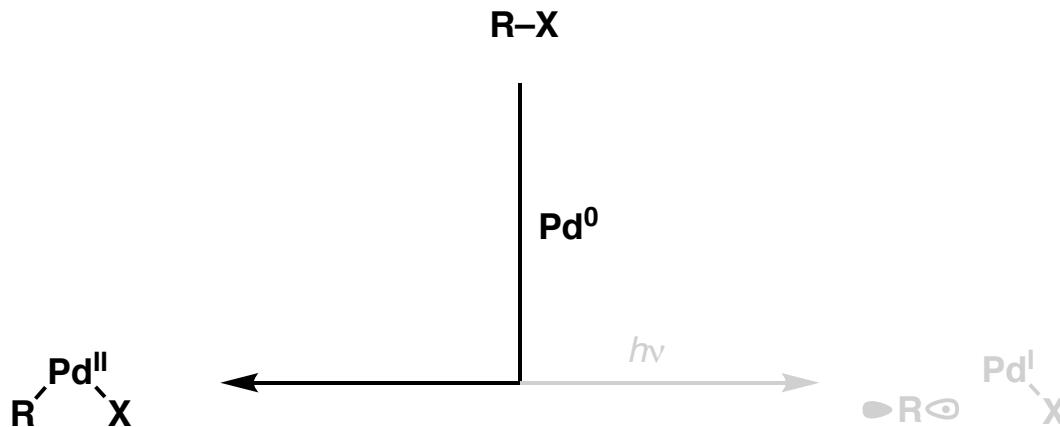
Photoexcited Pd Complexes: An Emerging Platform for Novel Reactivity



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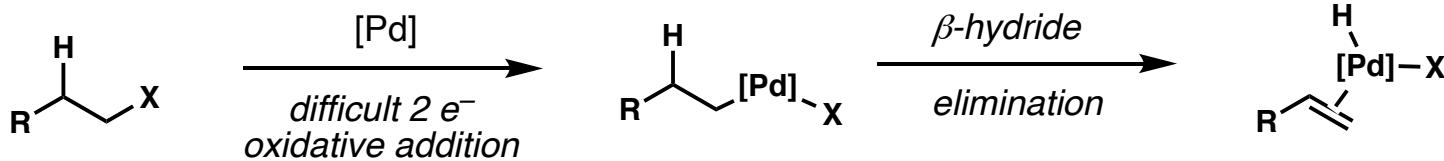
- One electron chemistry
- Hybrid Pd/radical species

Photoexcited Pd Complexes: An Emerging Platform for Novel Reactivity



- Two electron chemistry
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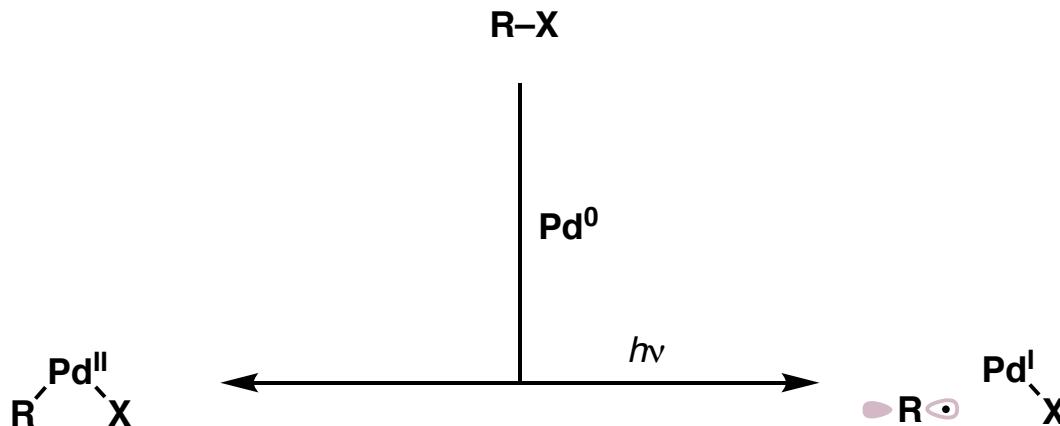


Shang, R.; Cheng, W.-M. ACS Catal. **2020**, 10, 9170.

Yu, D.-G. et al. Chem. Lett. **2019**, 48, 181.

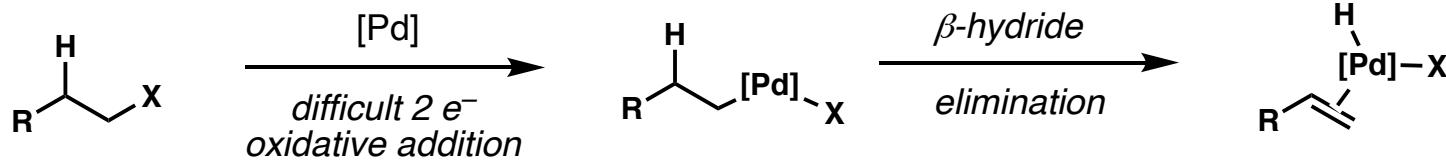
Gevorgyan, V. et al. Angew. Chem. Int. Ed. **2019**, 58, 11586.

Photoexcited Pd Complexes: An Emerging Platform for Novel Reactivity



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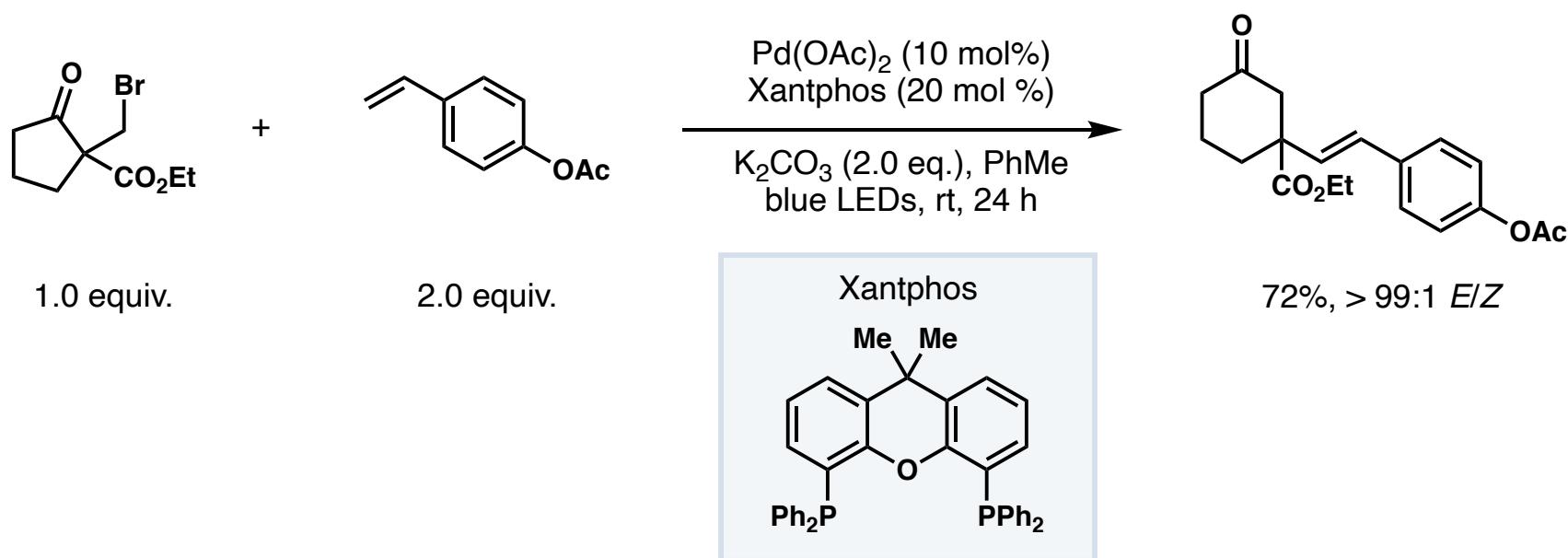
Shang, R.; Cheng, W.-M. ACS Catal. **2020**, 10, 9170.

Yu, D.-G. et al. Chem. Lett. **2019**, 48, 181.

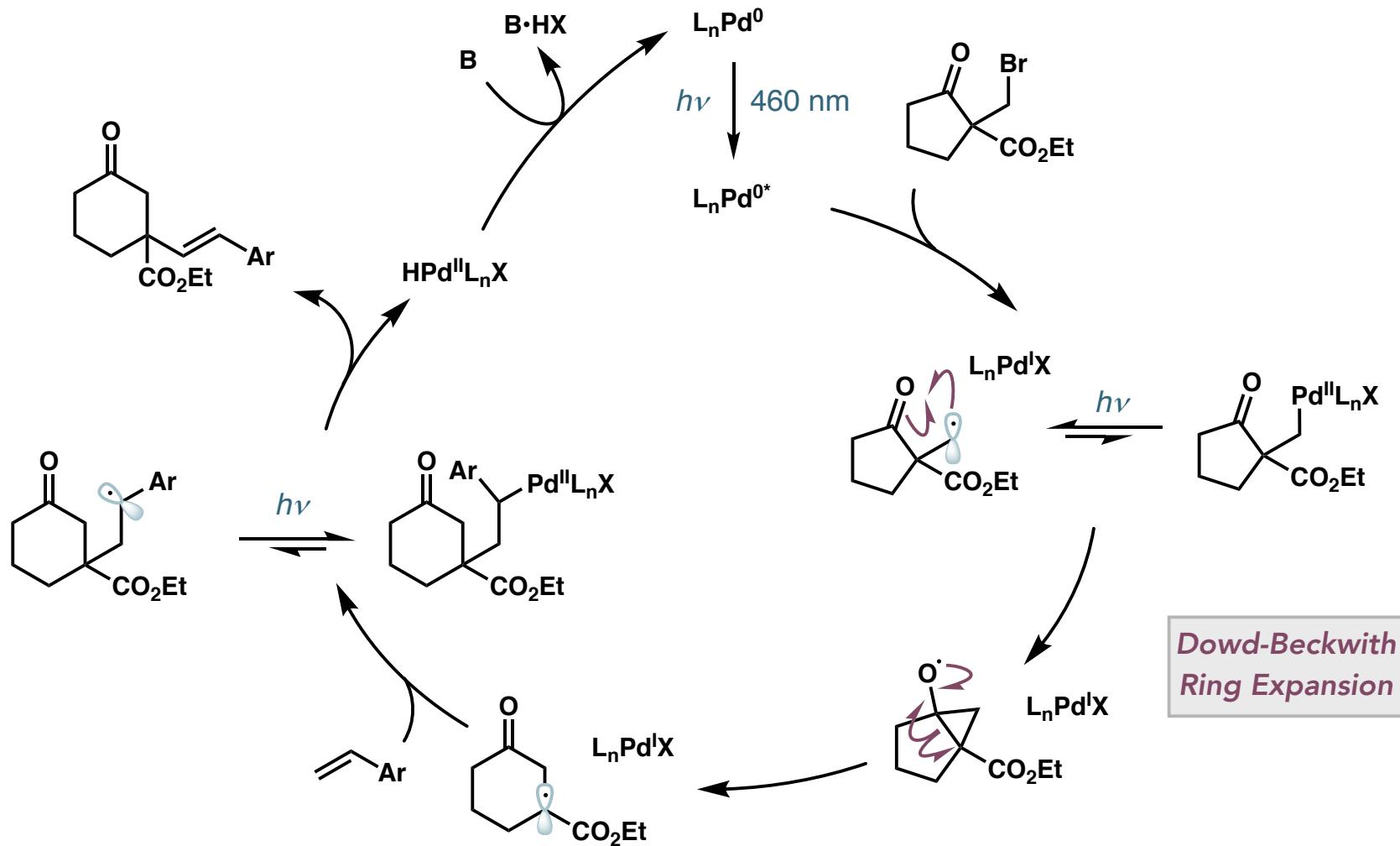
Gevorgyan, V. et al. Angew. Chem. Int. Ed. **2019**, 58, 11586.

Remember this Problem?

(1) Propose a mechanism and provide the name of the reaction.

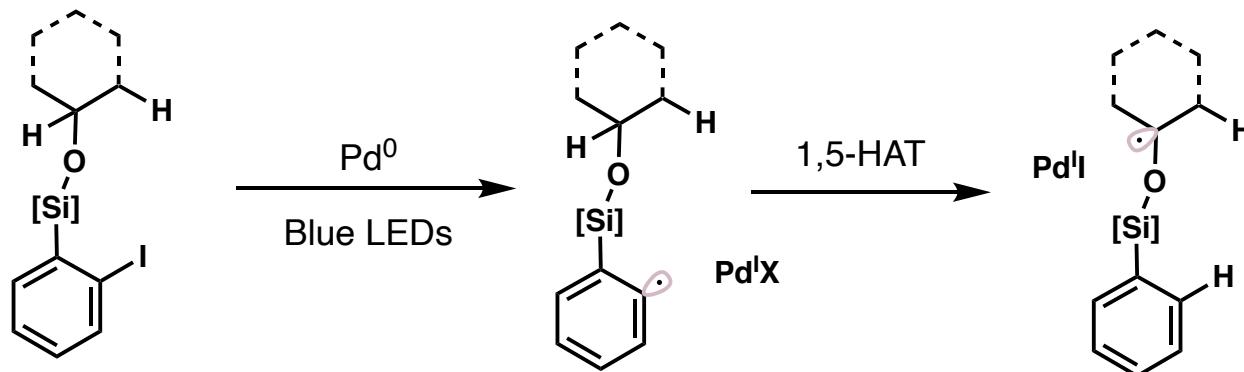


Pd-catalyzed Dowd-Beckwith/C–C Bond Formation Cascade

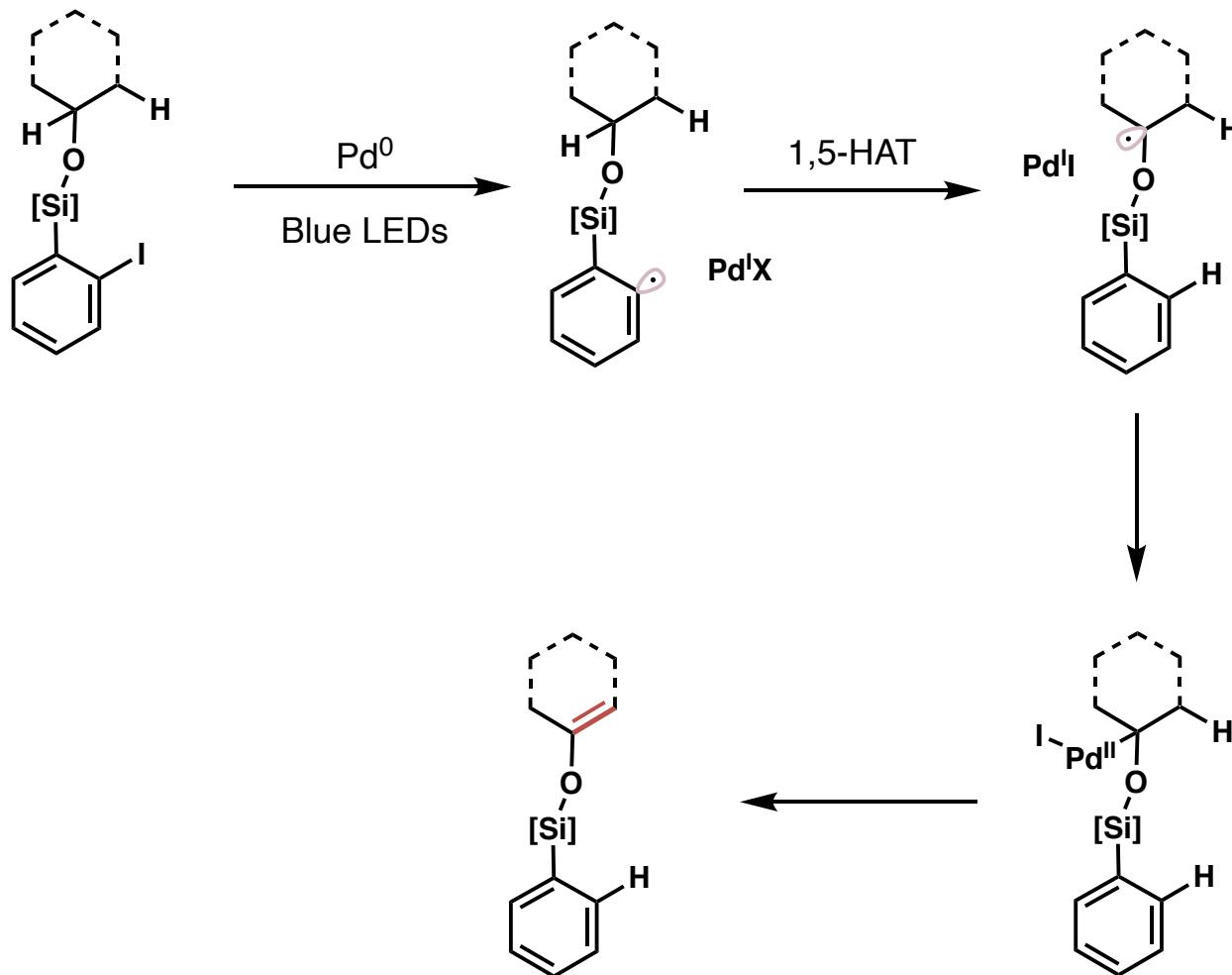


Dowd-Beckwith
Ring Expansion

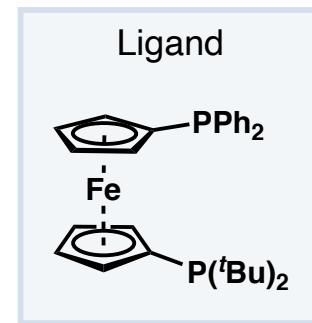
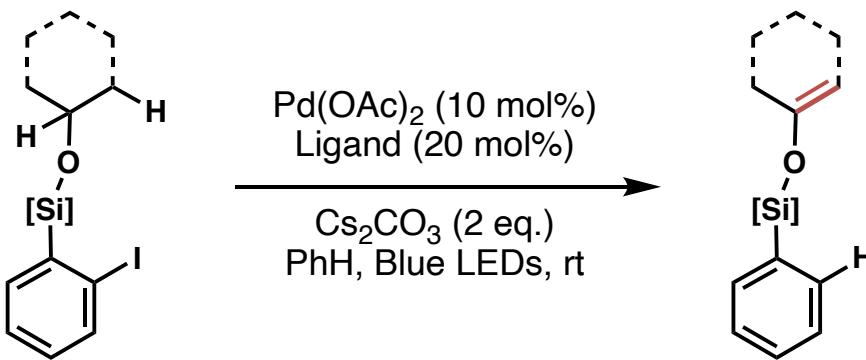
Oxidation of Silyl Ethers to Silyl Enol Ethers



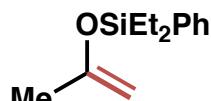
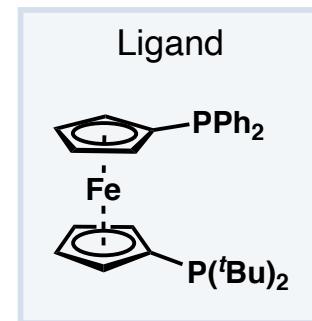
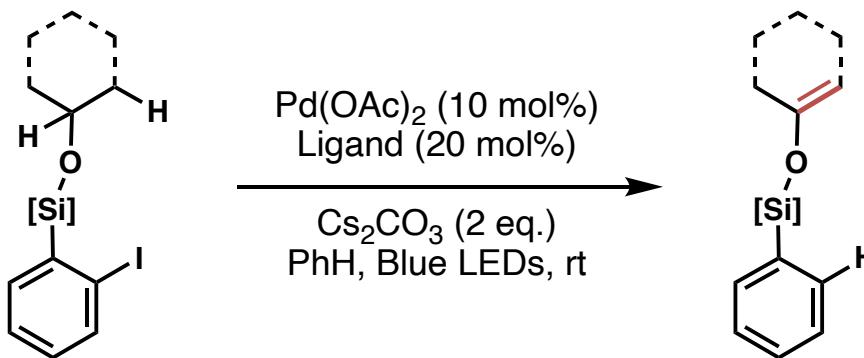
Oxidation of Silyl Ethers to Silyl Enol Ethers



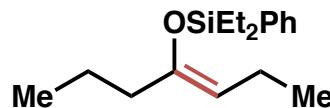
Oxidation of Silyl Ethers to Silyl Enol Ethers



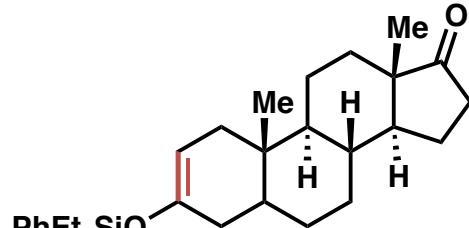
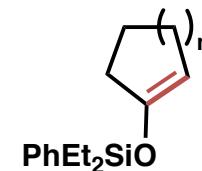
Oxidation of Silyl Ethers to Silyl Enol Ethers



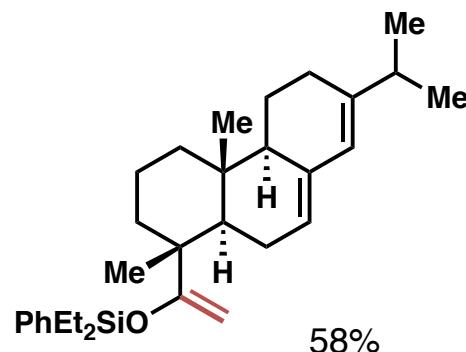
95%



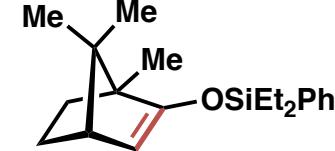
61%
Z:E = 3:1



75%

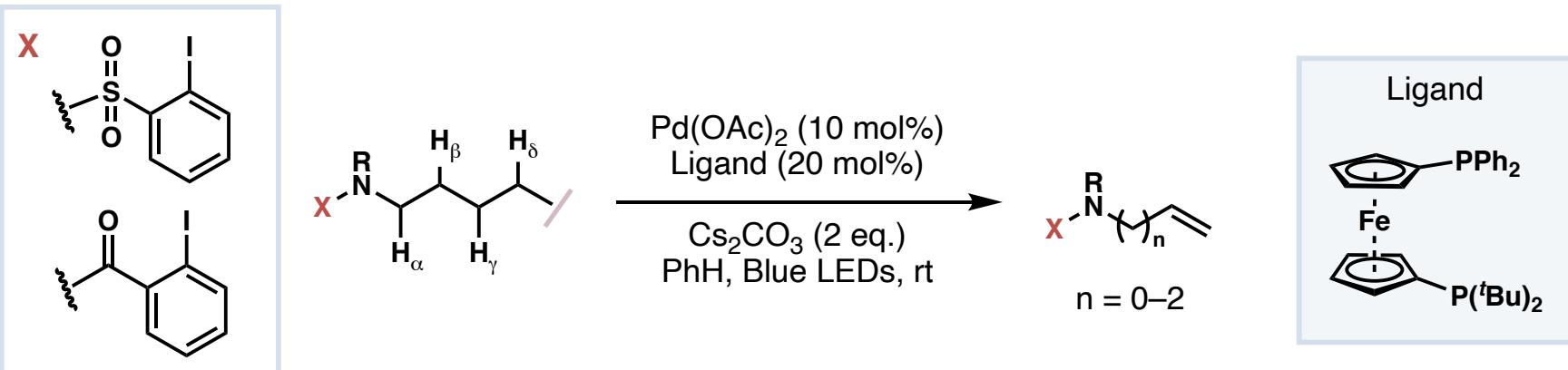


58%

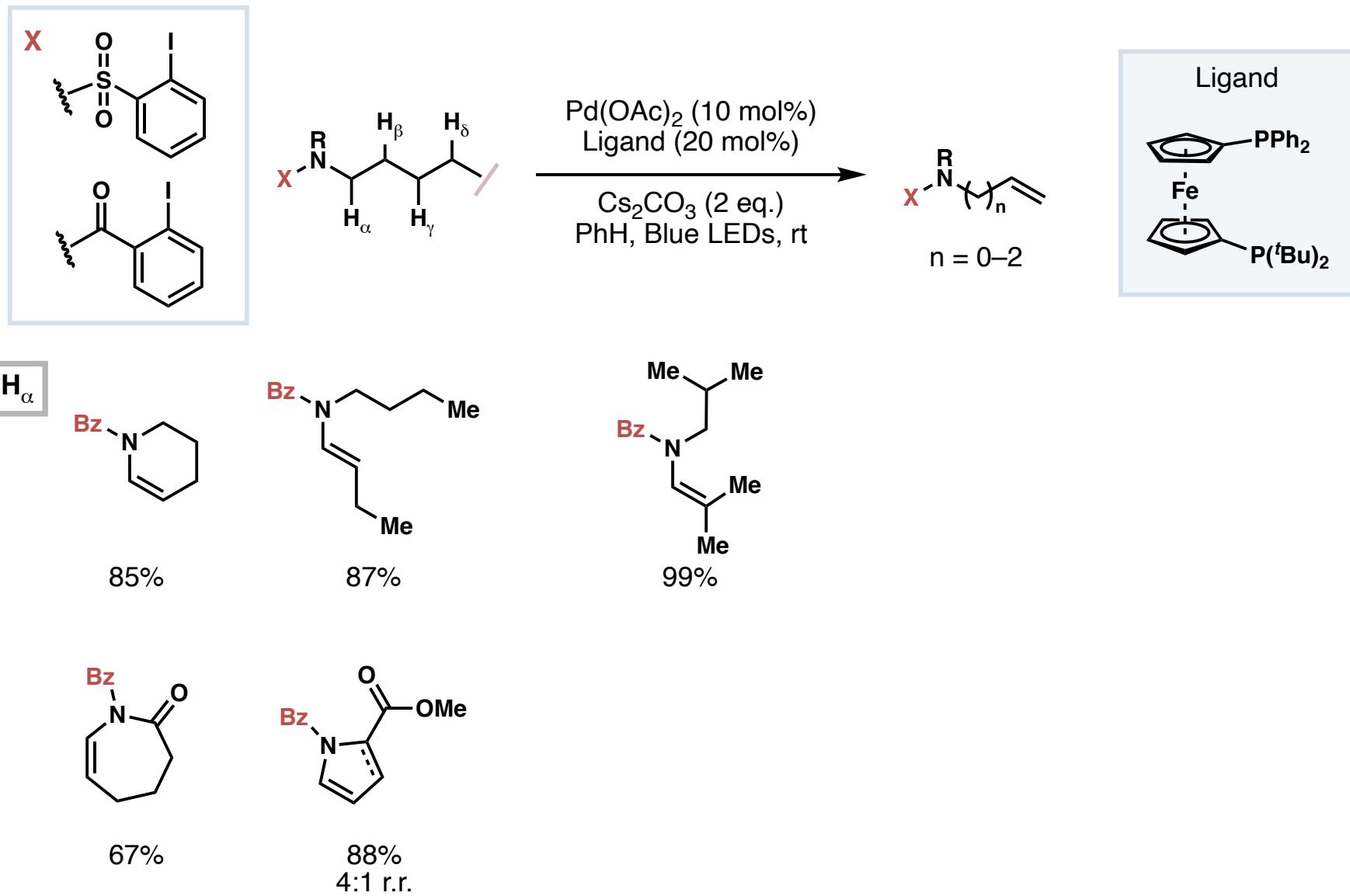


40% (85% brsm)

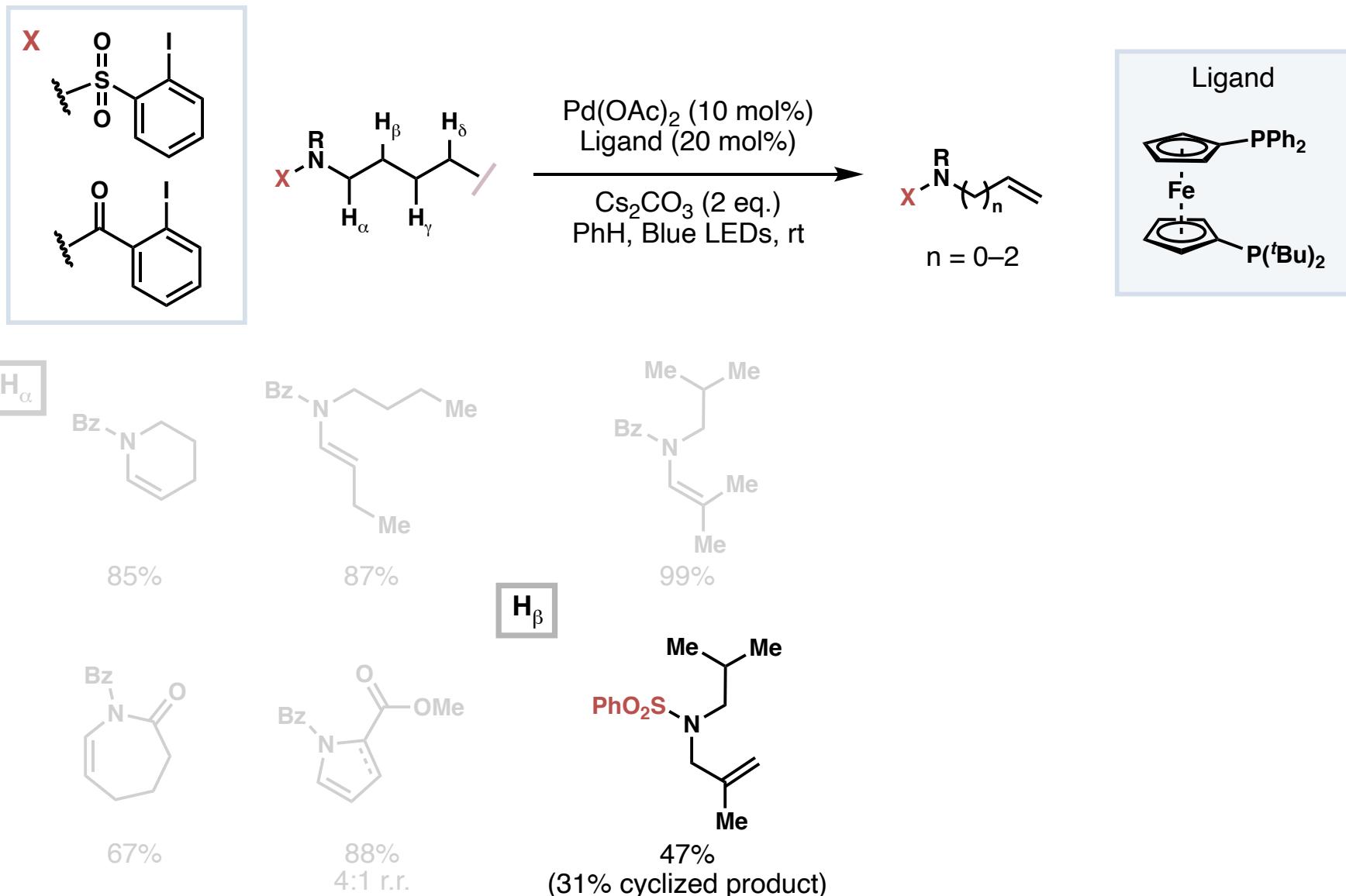
Application to Amine Desaturation



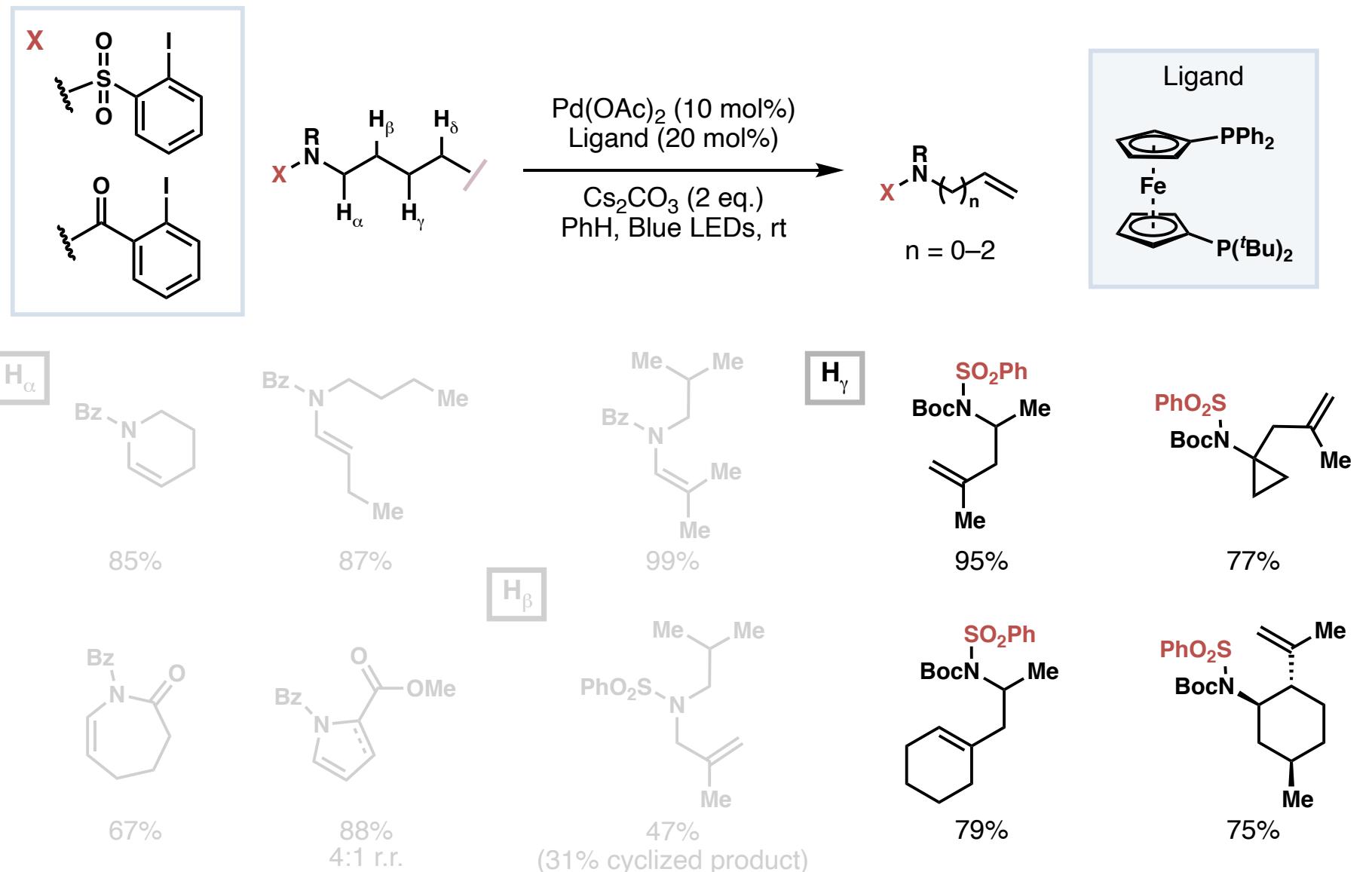
Application to Amine Desaturation



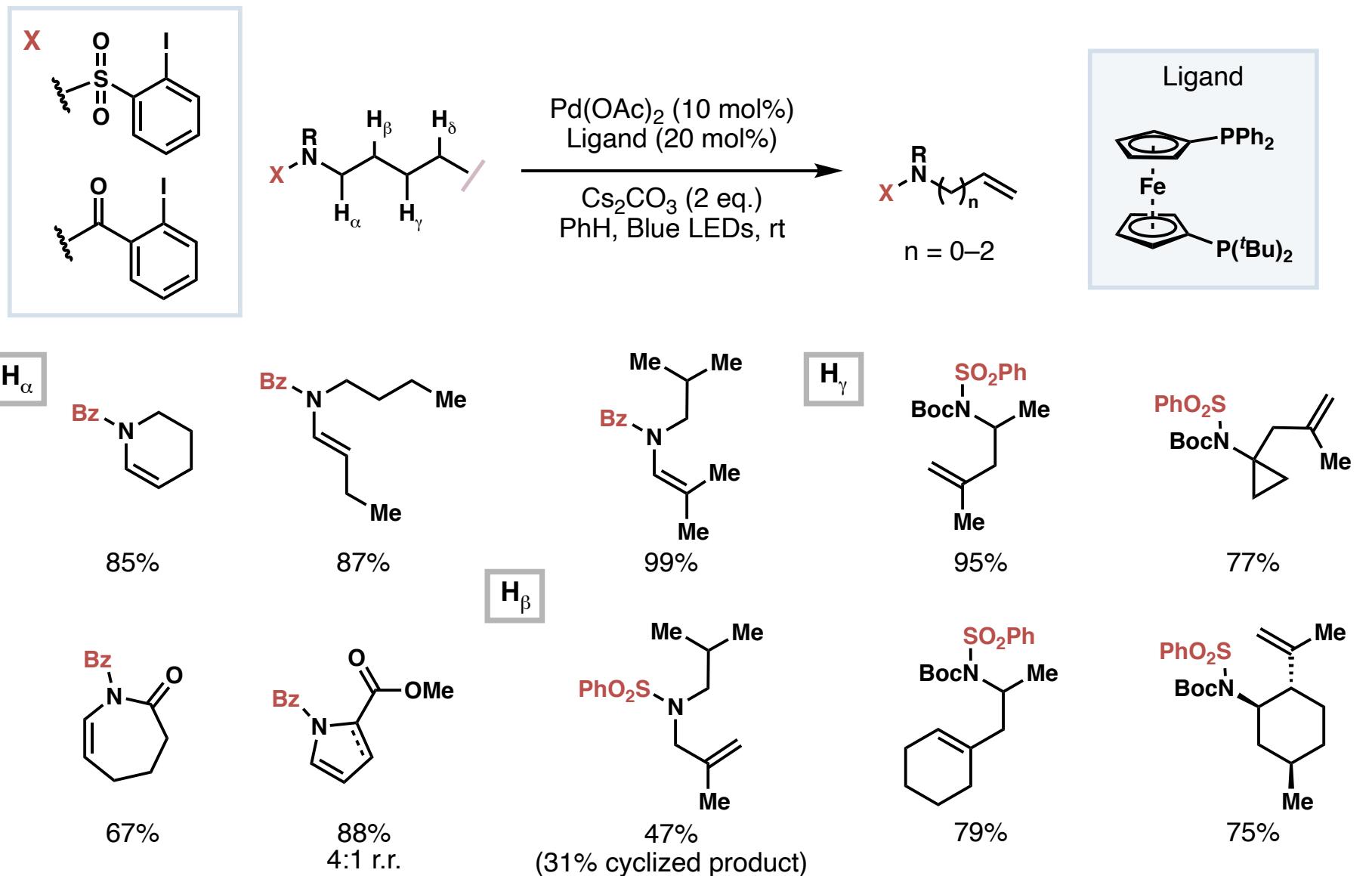
Application to Amine Desaturation



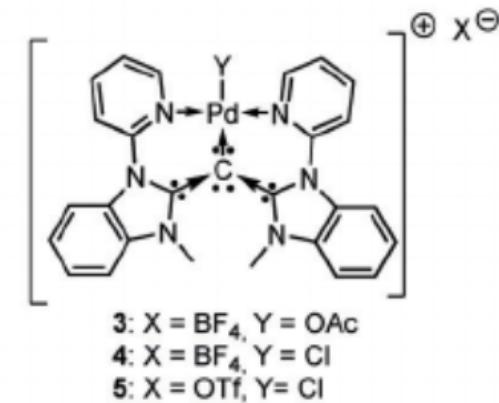
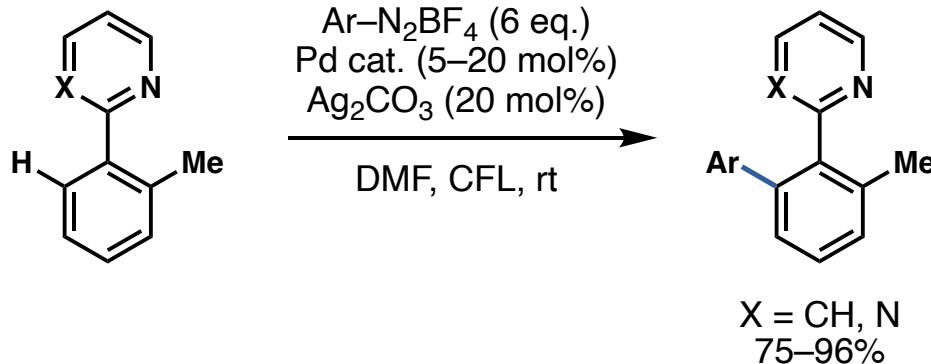
Application to Amine Desaturation



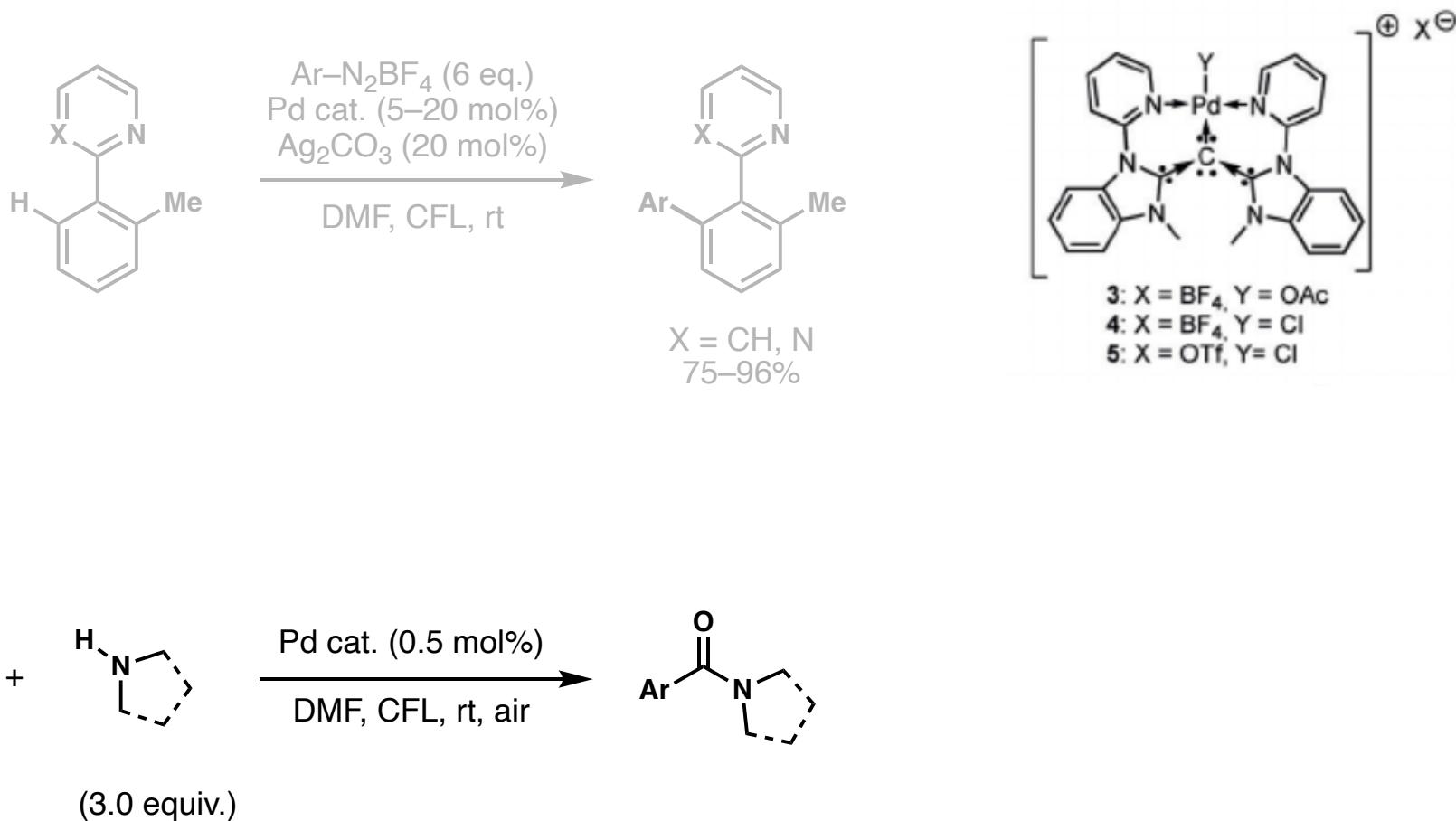
Application to Amine Desaturation



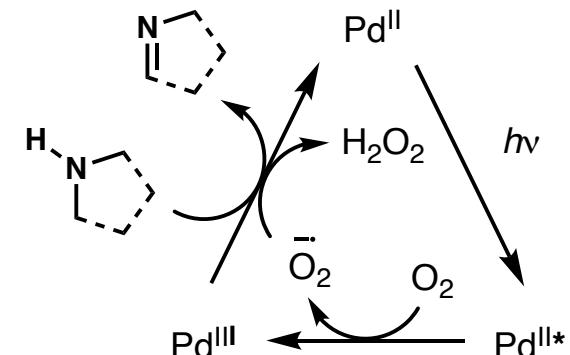
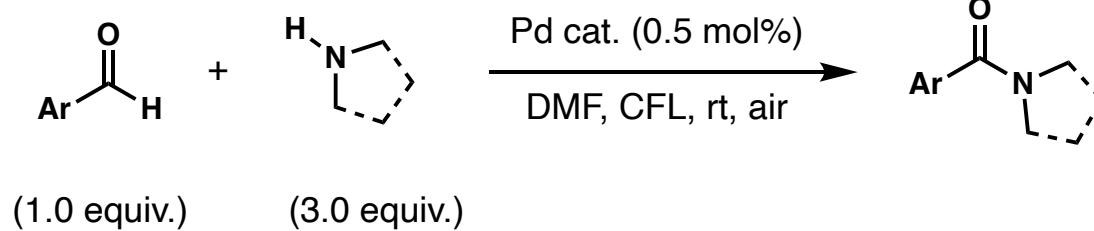
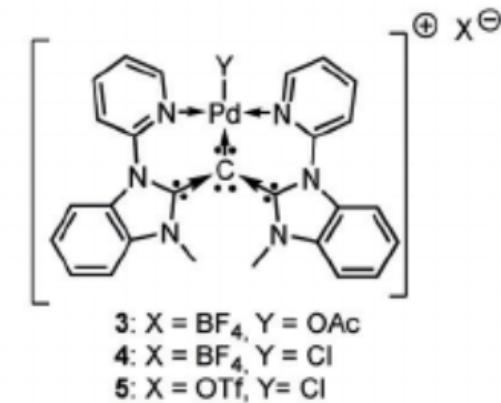
Ong's Carbodicarbene Complexes



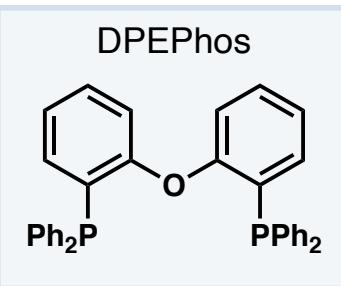
Ong's Carbodicarbene Complexes



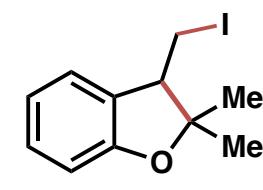
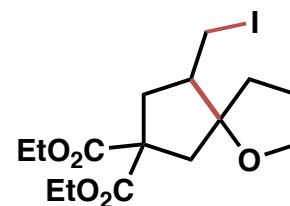
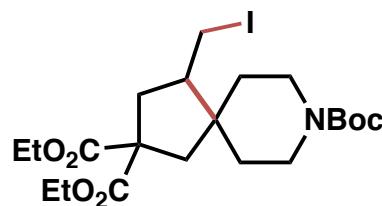
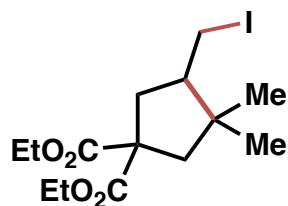
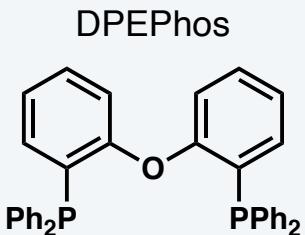
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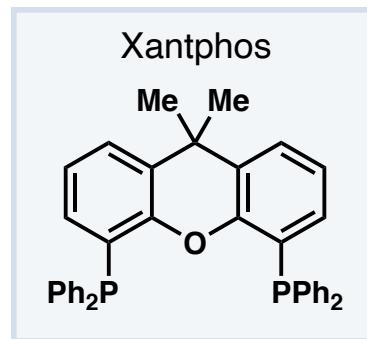
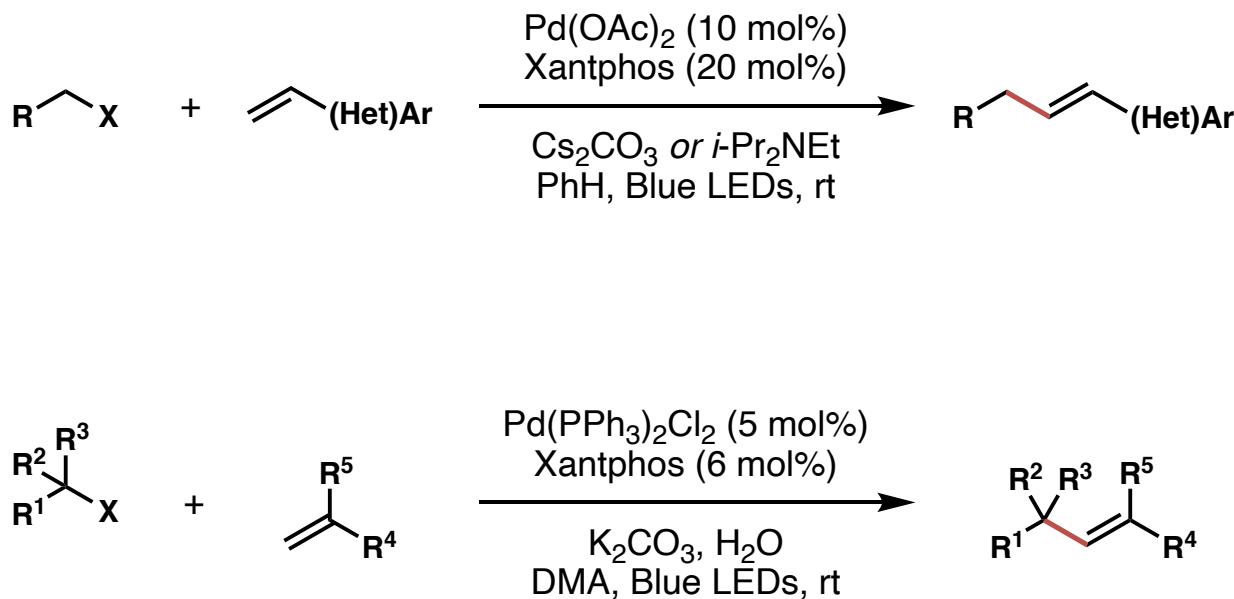
Atom-Transfer Radical Cyclization



Atom-Transfer Radical Cyclization



Alkyl-Heck Reactions

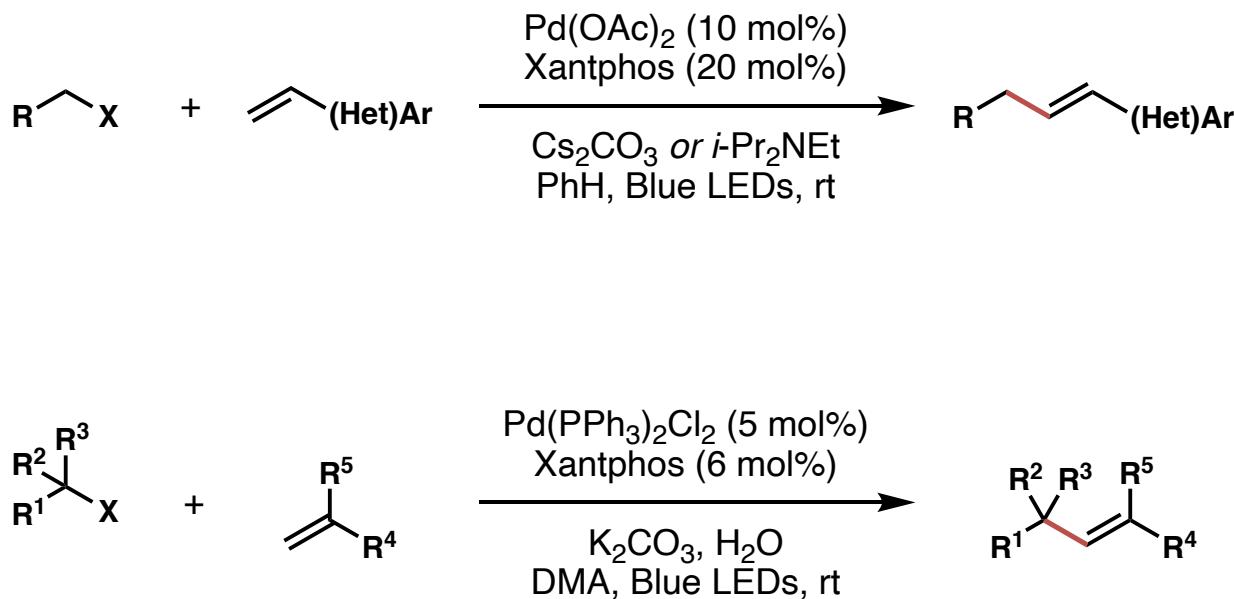


Gevorgyan, V. et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 14212.

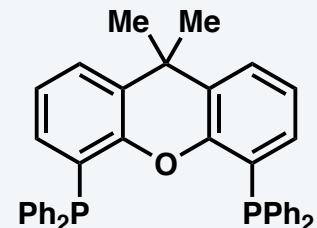
Gevorgyan, V. et al. *Org. Lett.* **2018**, *20*, 357.

Fu, Y. et al. *J. Am. Chem. Soc.* **2017**, *139*, 18307.

Alkyl-Heck Reactions

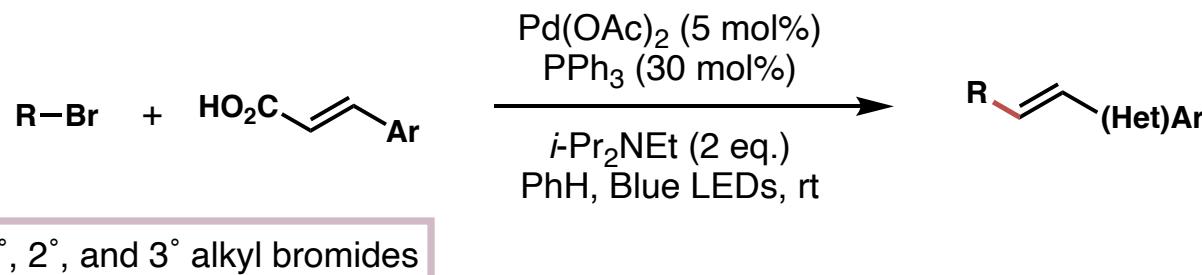


Xantphos

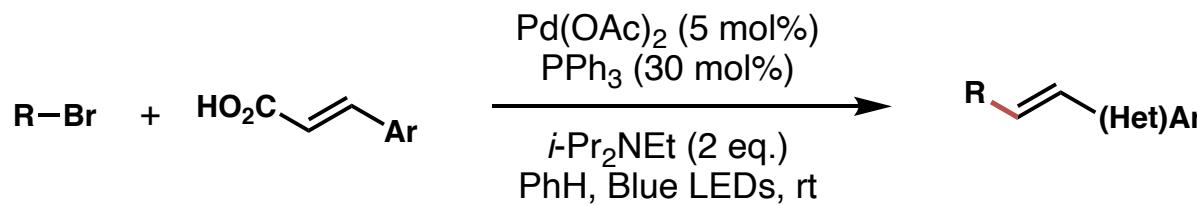


- Room temperature alkyl-Heck reaction
- 1°, 2°, and 3° alkyl halides (X = Br, I)
- Pd⁰/Pd^I/Pd^{II} catalysis

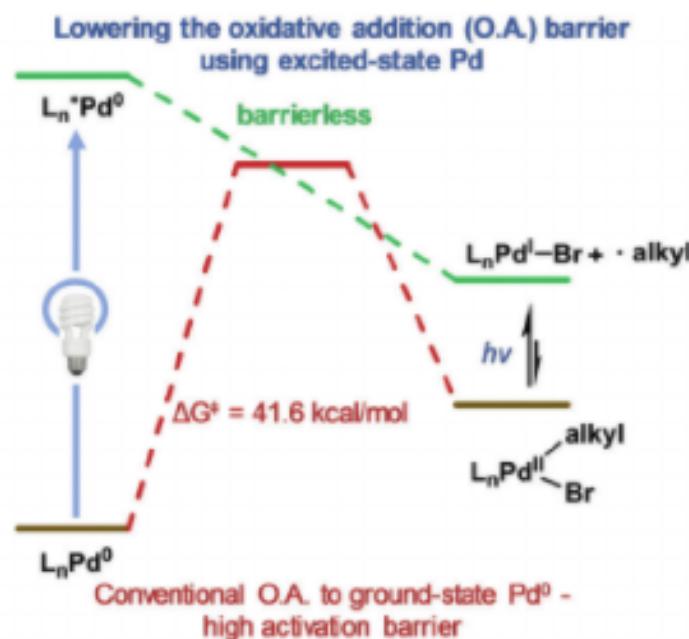
Decarboxylative Coupling



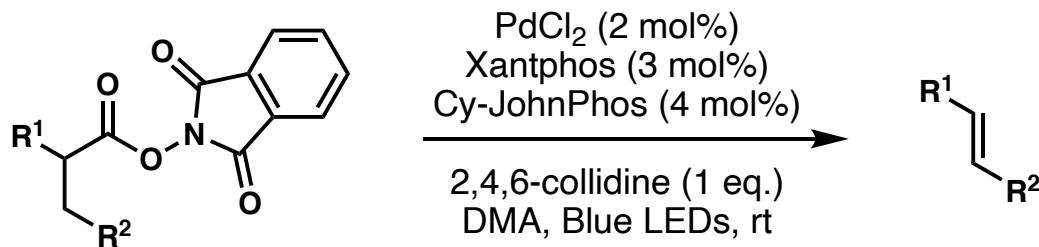
Decarboxylative Coupling



1°, 2°, and 3° alkyl bromides

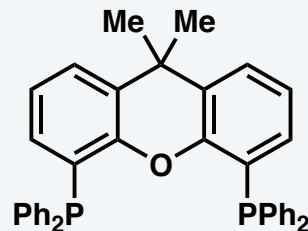


Decarboxylative Desaturation of Redox-Active Esters

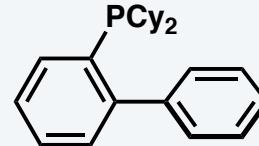


- Terminal and internal olefins
- Cyclic alkenes, enol ethers, enamines
 - Broad FG tolerance

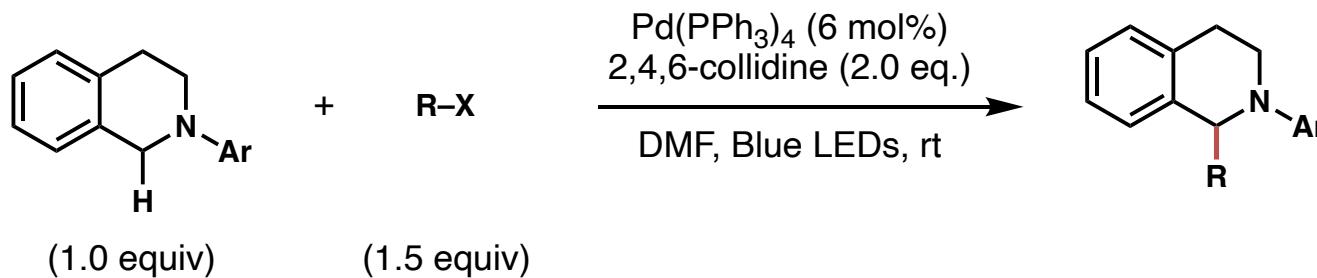
Xantphos



Cy-JohnPhos



C–H Functionalization with Alkyl Halides

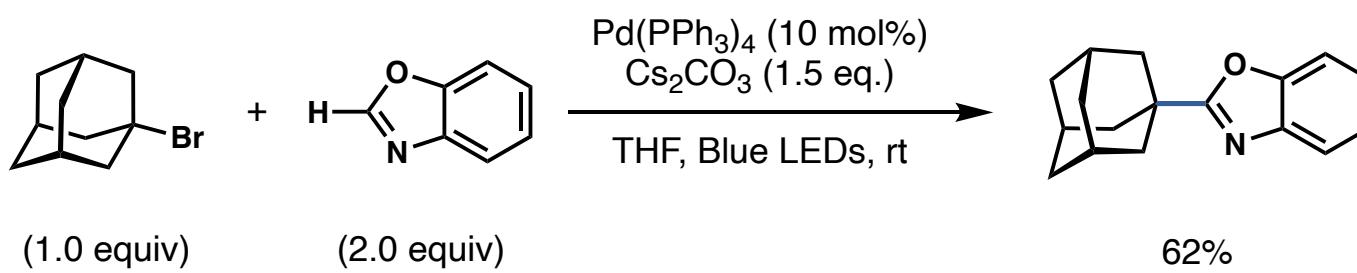
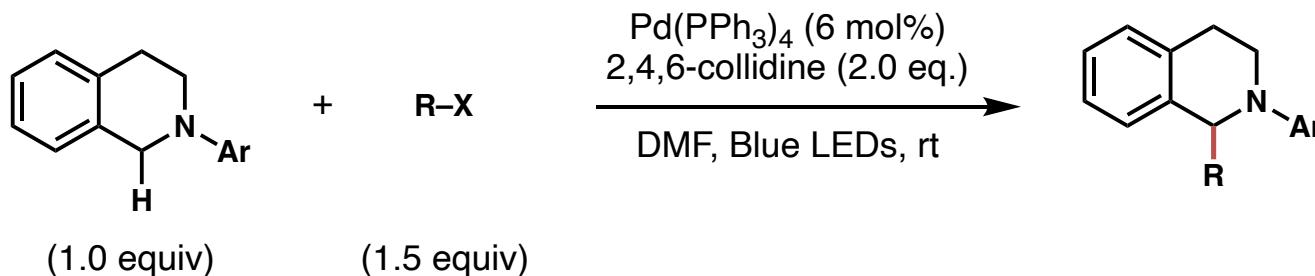


Yu, D.-G. et al. *Angew. Chem. Int. Ed.* **2017**, *56*, 15683.

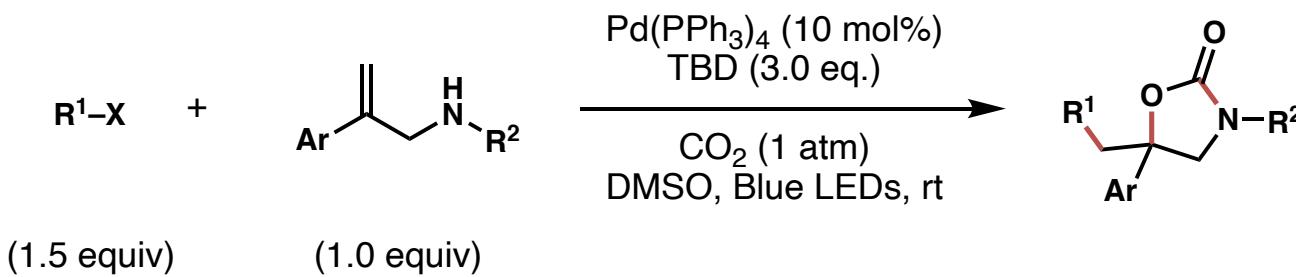
Zhou, S. et al. *Angew. Chem. Int. Ed.* **2018**, *57*, 15889.

Fu, Y. et al. *Synthesis* **2018**, *50*, 2908.

C–H Functionalization with Alkyl Halides

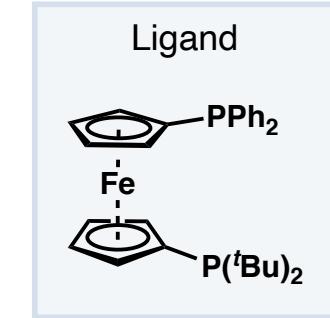
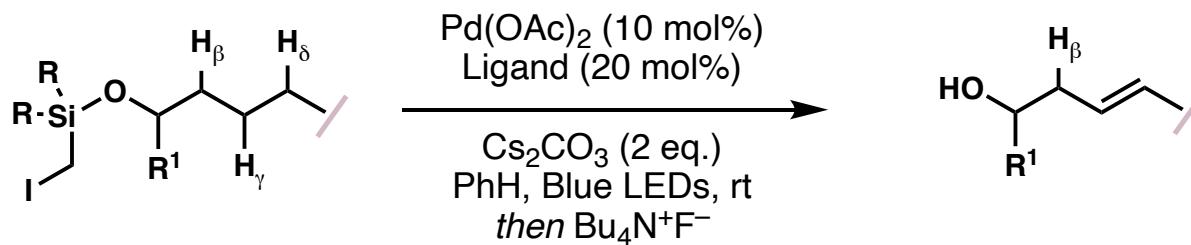


Oxy-alkylation of Allylamines

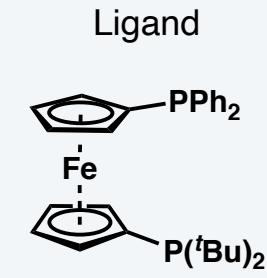
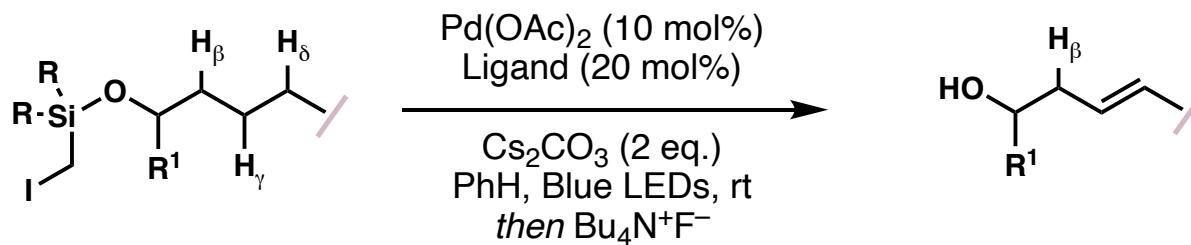


- 1,1-disubstituted alkenes
- 1°, 2°, and 3° R-X (X = Br, I)

Remote Functionalization of Alcohols

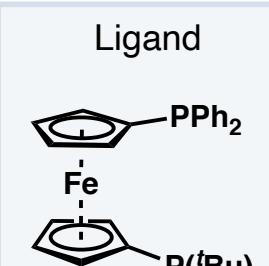
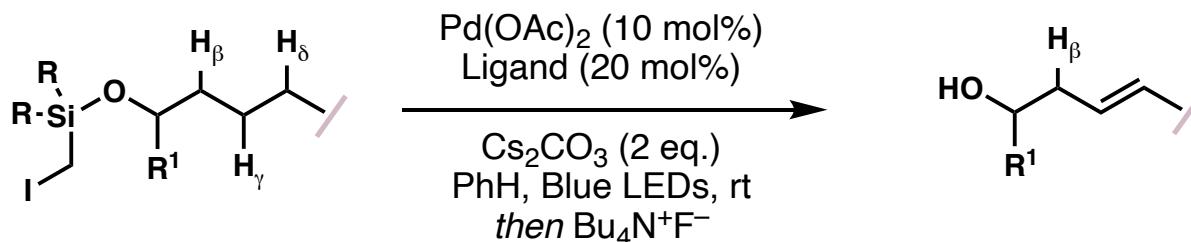


Remote Functionalization of Alcohols



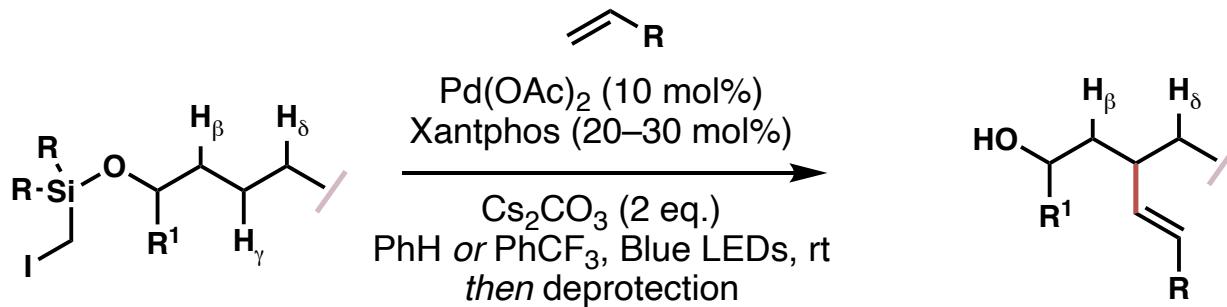
1,6-HAT is kinetically preferred in this setting

Remote Functionalization of Alcohols



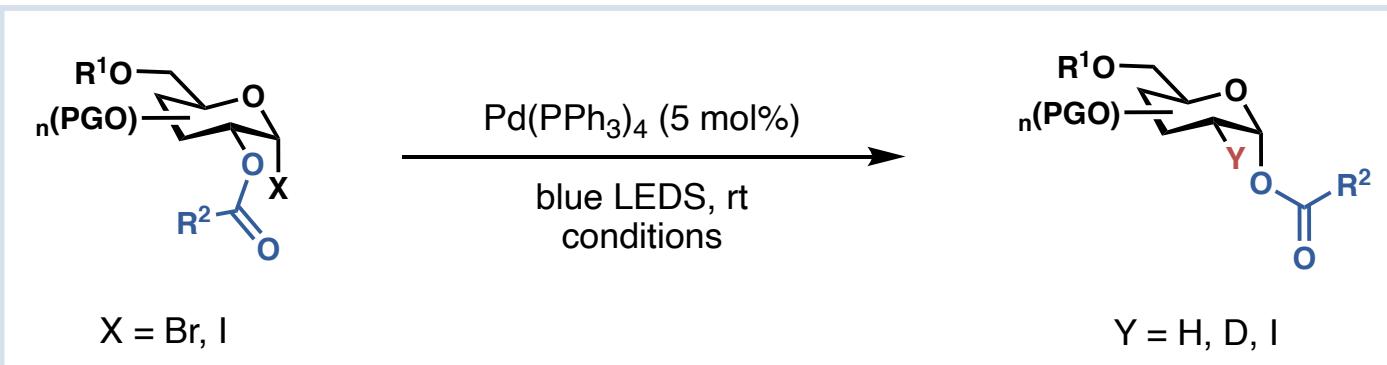
1,6-HAT is kinetically preferred in this setting

Radical Relay Heck Reaction

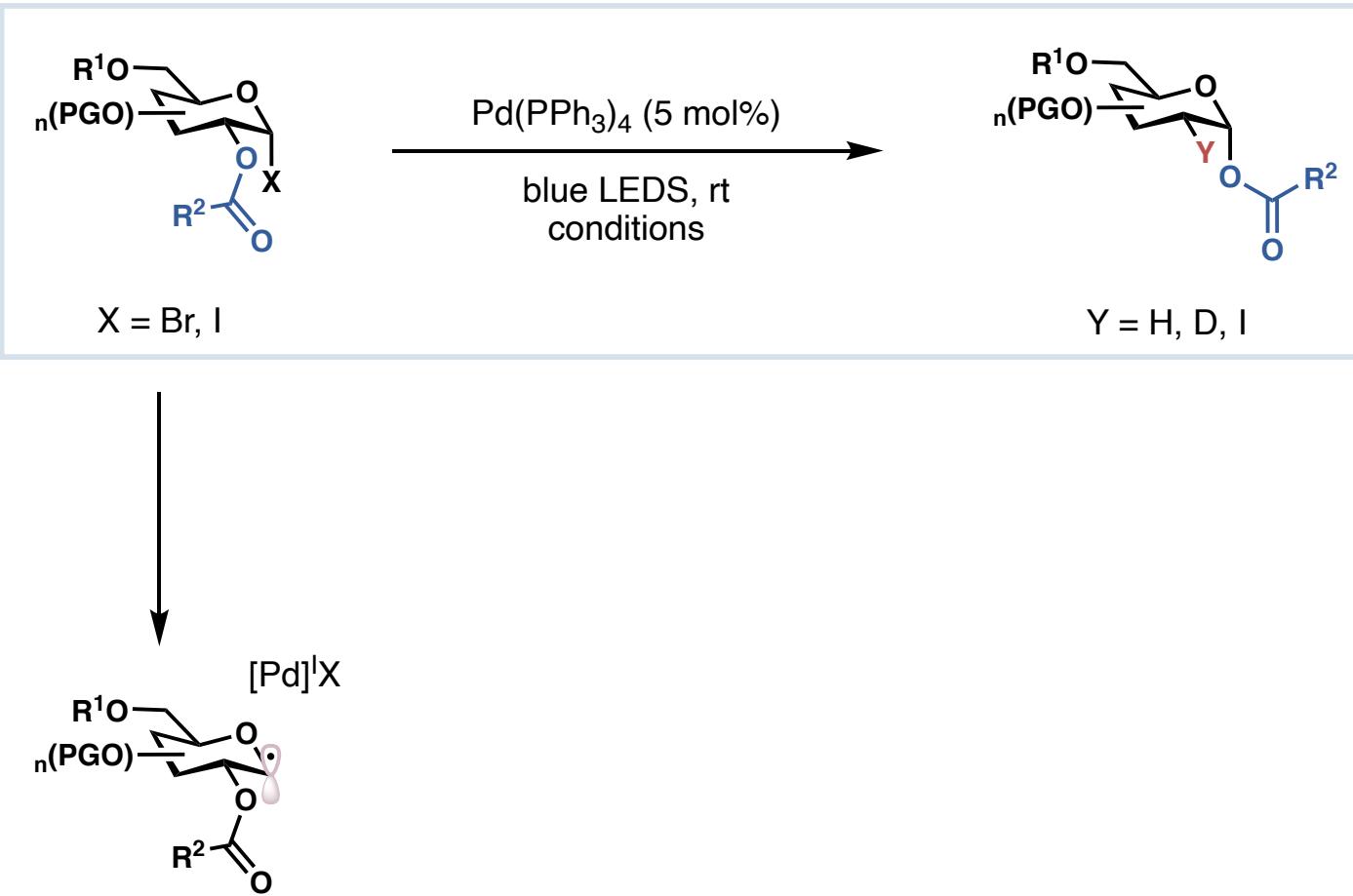


Can also achieve β- and δ-functionalization

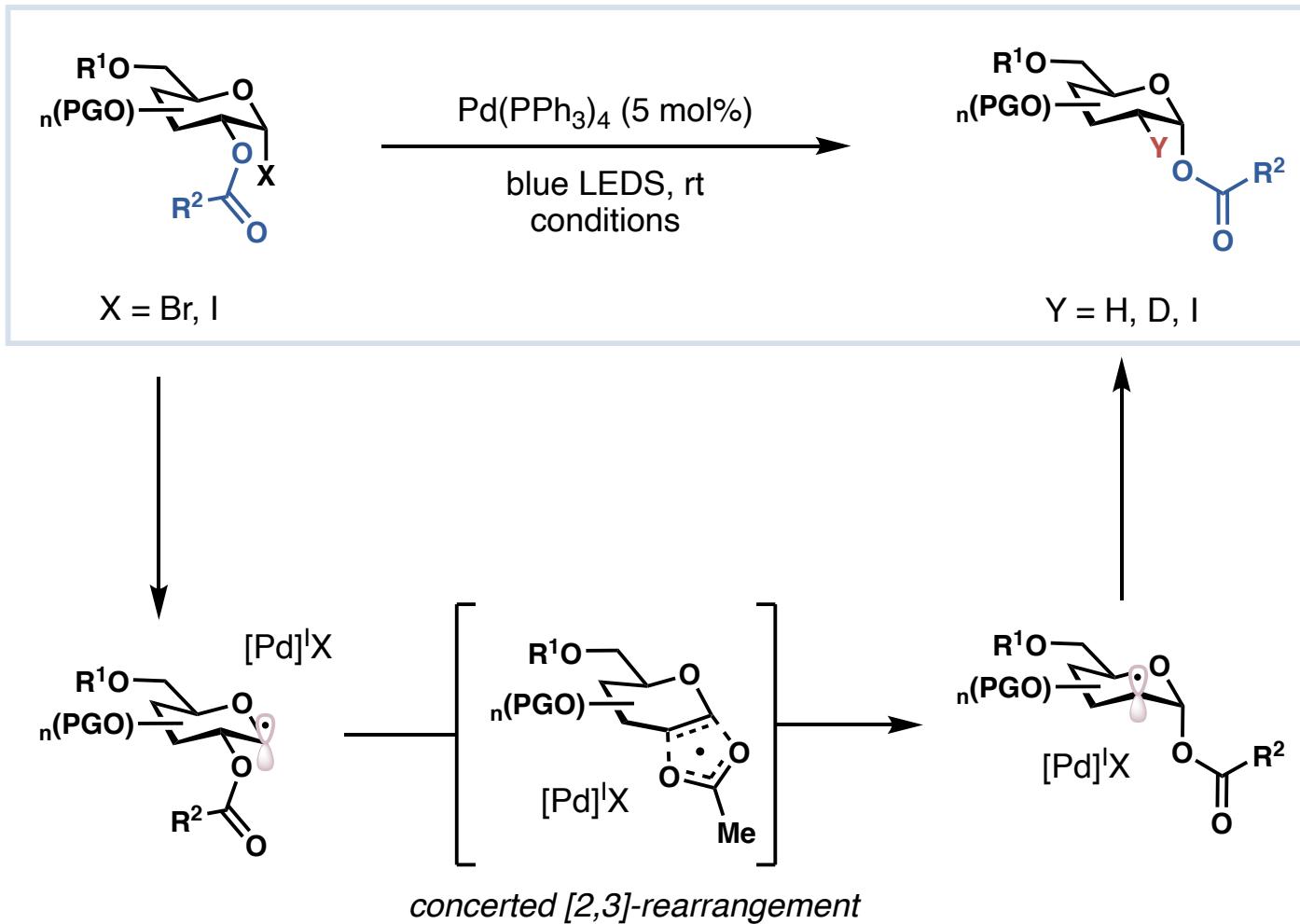
Selective C2 Functionalization of Sugars



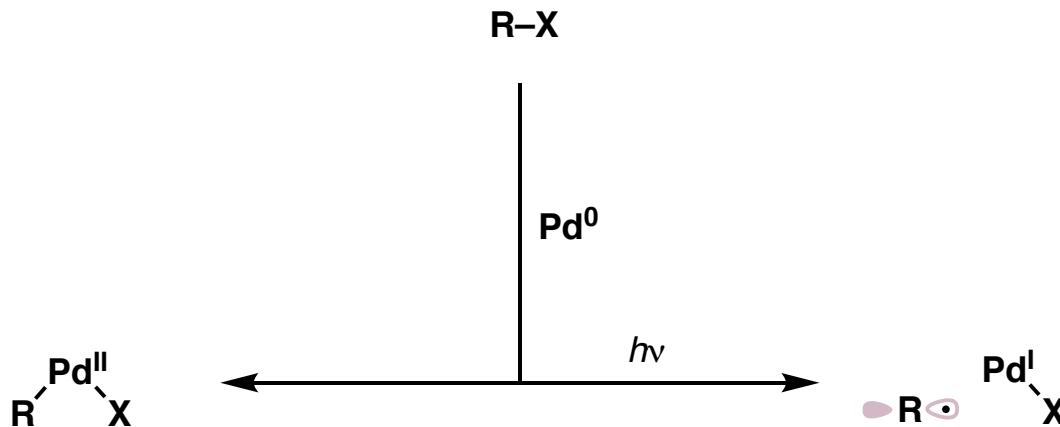
Selective C2 Functionalization of Sugars



Selective C2 Functionalization of Sugars



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