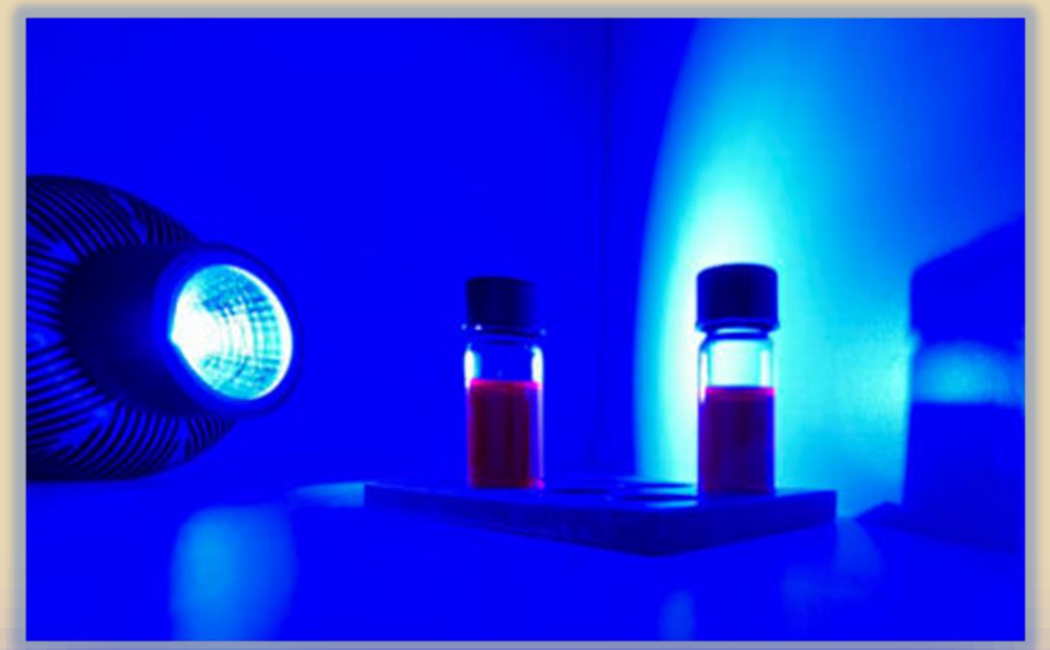
Photochemical Palladium by Visible Light

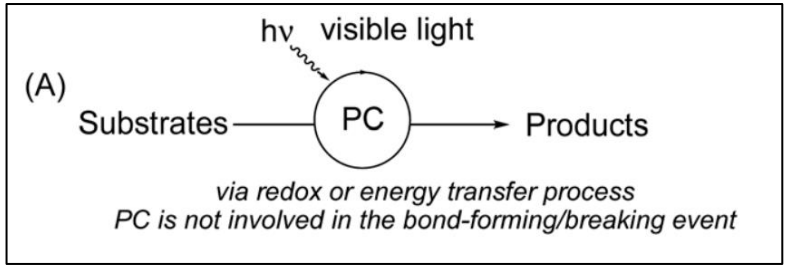
Jakub Sura

April 16th, 2024

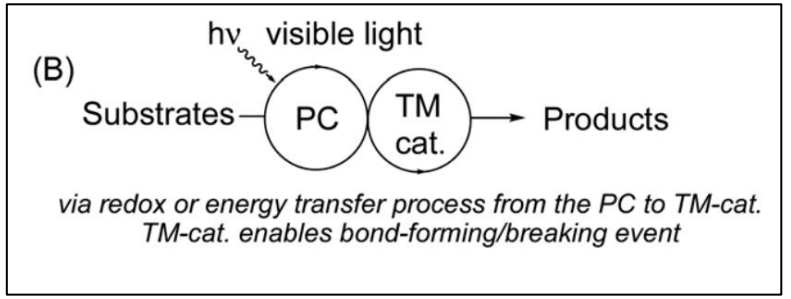


The categories of visible light-induced reactions

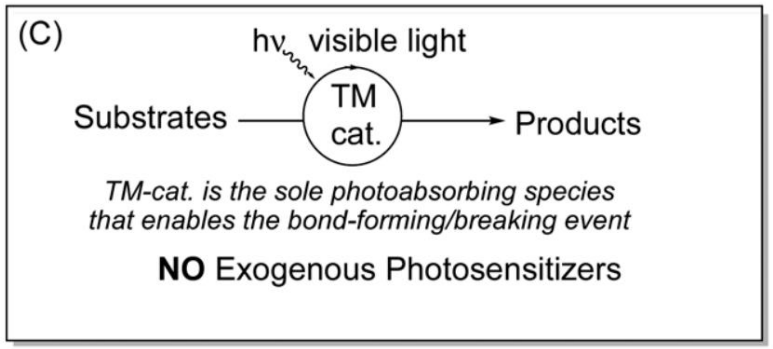
Type A: Photosensitization by a photocatalyst



Type B: Cooperative or dual photocatalysis



Type C: Transition metals serving as photocatalysts



ACS Catal. **2020**, *10*, 9170–9196.

Outline

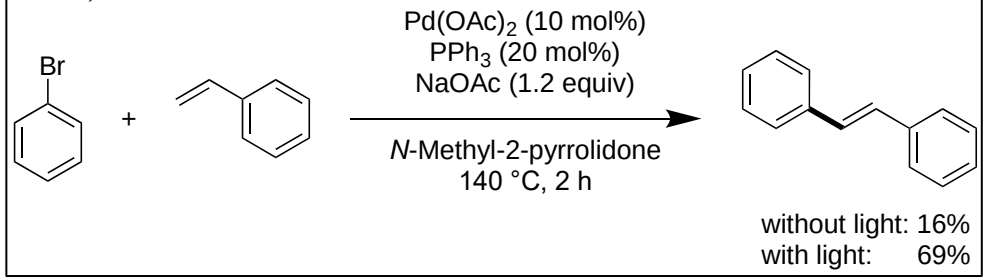
1. Initial reports and reactivities
2. Alkyl-Heck type reactivity
3. Carbonylation chemistry

Not discussed:

- Photoredox catalysis and cooperative photocatalysis
- Non-bond forming/breaking events
- Transition metals other than palladium
- Stoichiometric uses of metal

First report of photochemical palladium?

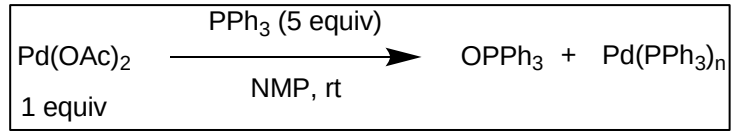
Köhler, 2010

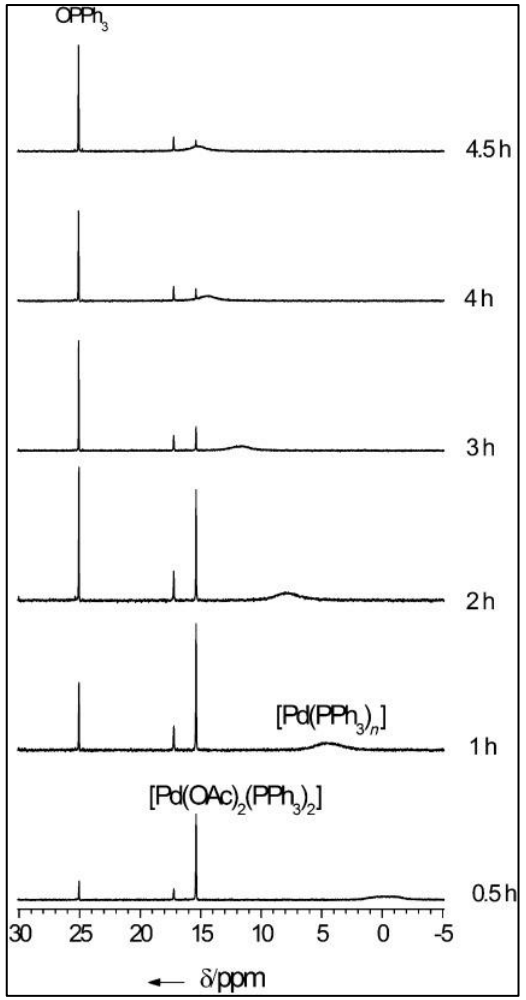


λ = 400 – 700 nm

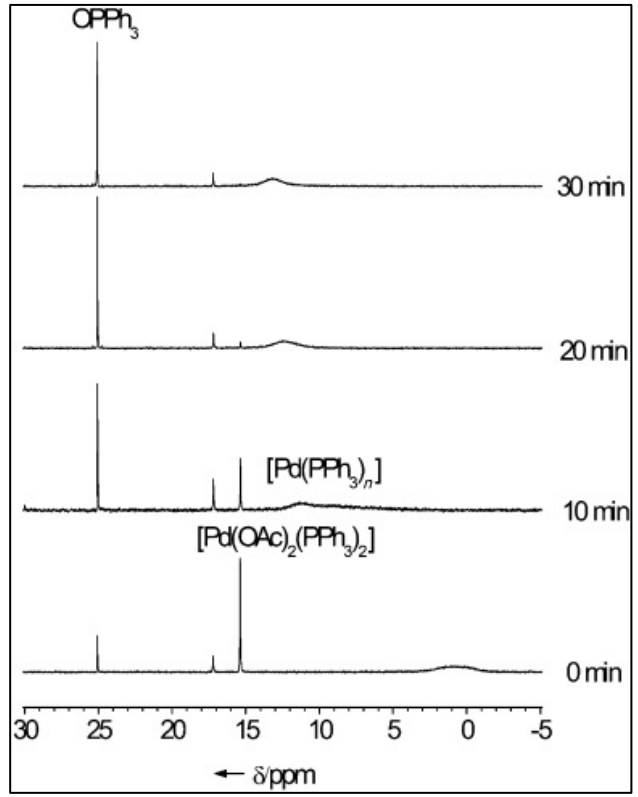
Conclusion:
Precatalyst activation is occurring faster under visible light irradiation.

^{31}P-NMR Experiments





Without irradiation



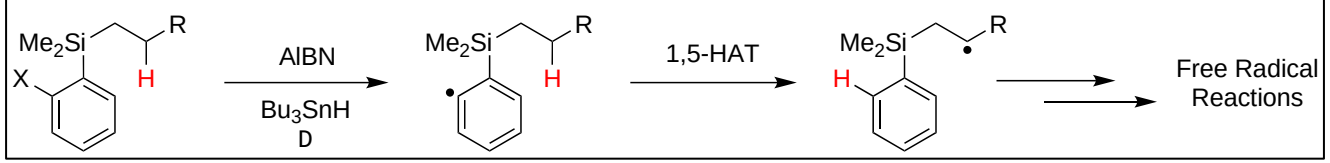
With irradiation

ChemCatChem, **2010,** *2*, 1467–1476.

The first report of photochemical palladium

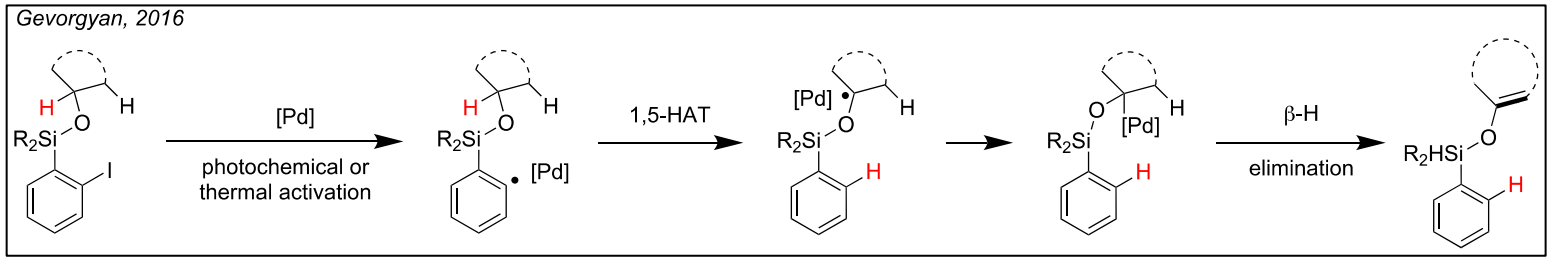
Gevorgyan envisioned a thermal or photochemical activation of aryl iodide in presence of Pd.

Curran, 1998

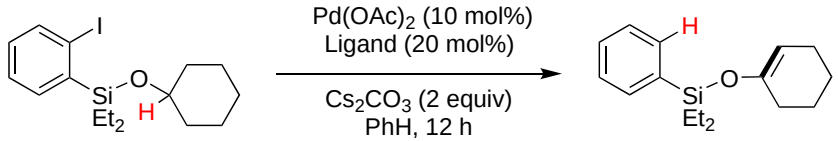


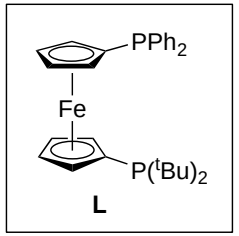
C-H functionalization of alcohols via 1,5-HAT

Gevorgyan, 2016



Gevorgyan, 2016



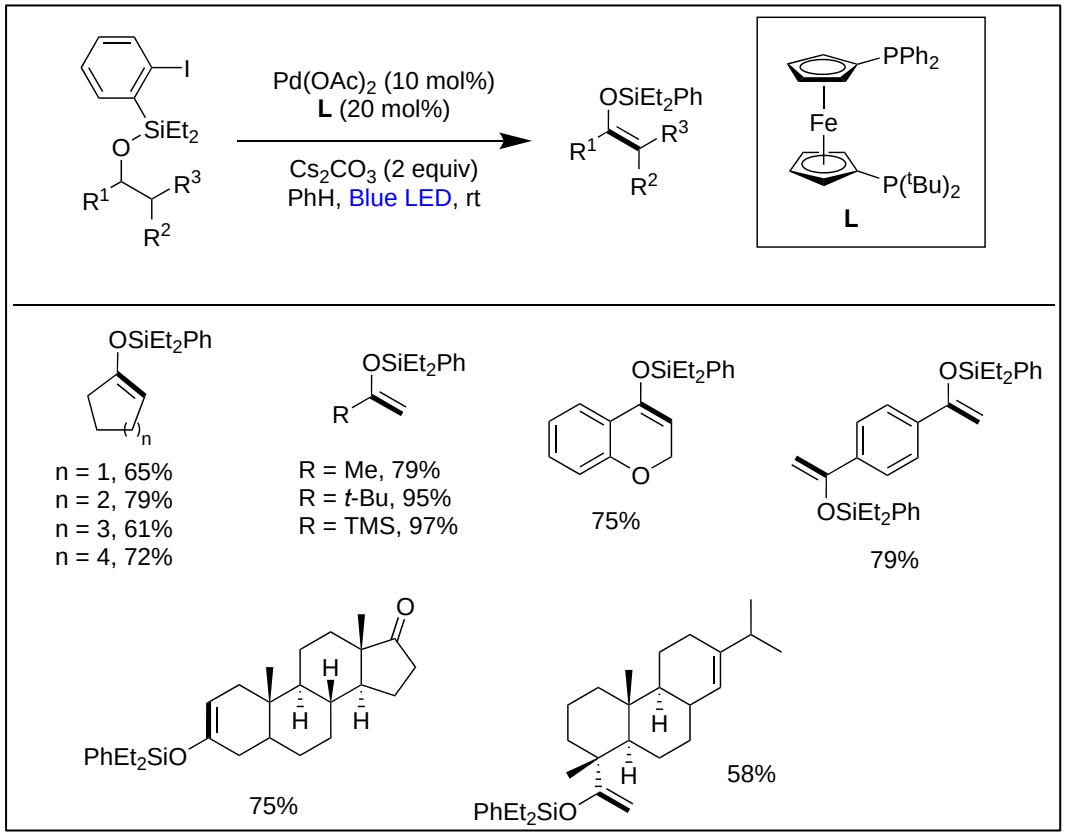


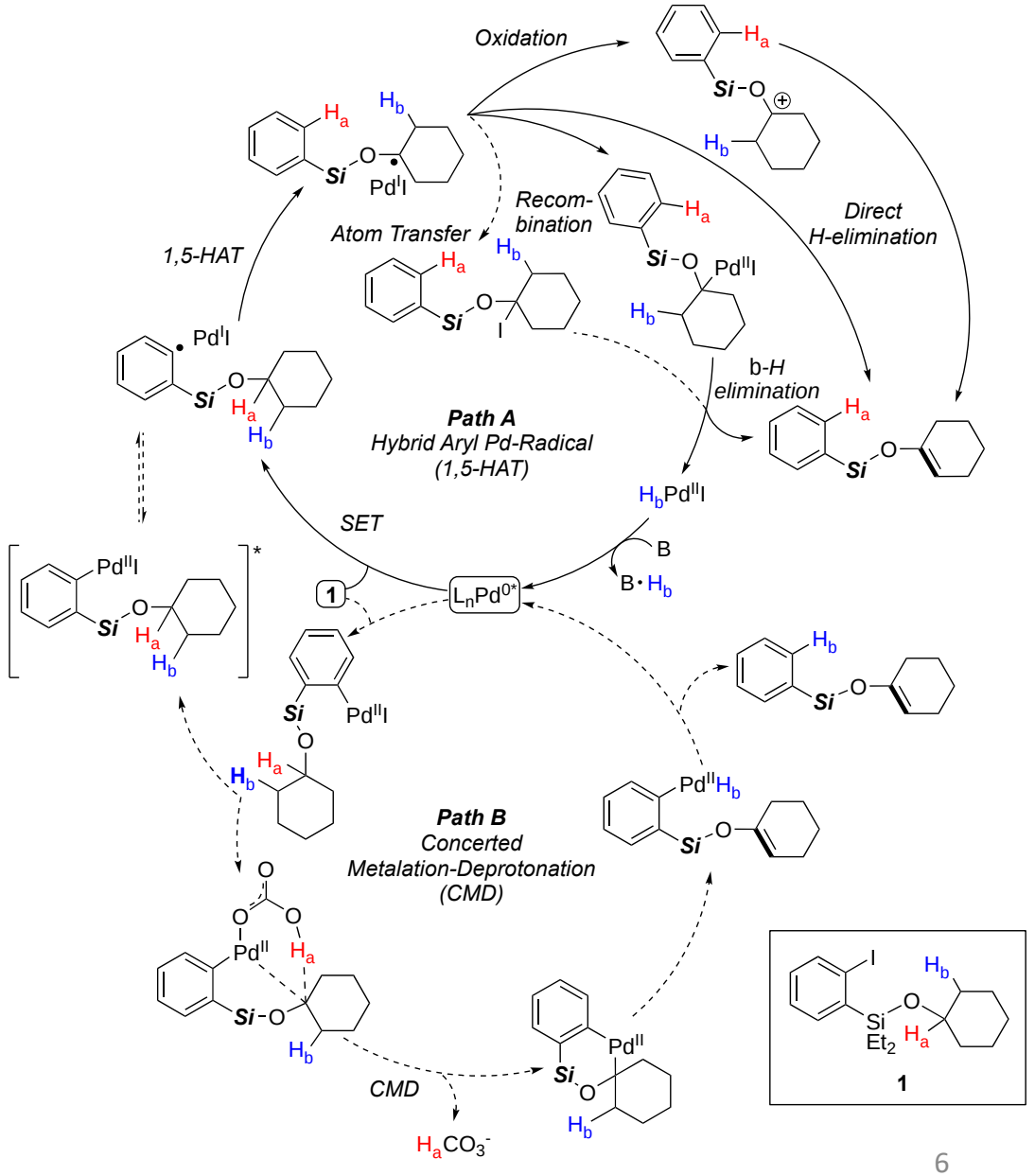
Entry	Ligand/Catalyst	Conditions	Yield, %
1	$Pd(PPh_3)_4$	120 °C	0
2	dppf	120°C	0
3	**L**	120°C	0
4	$Pd(PPh_3)_4$	rt, Blue LED	72
5	dppf	rt, Blue LED	67
6	**L**	rt, Blue LED	**79**

J. Am. Chem. Soc. **1988**, *110*, 5900; *J. Am. Chem. Soc.* **2016**, *138*, 6340–6343.

The first report of photochemical palladium

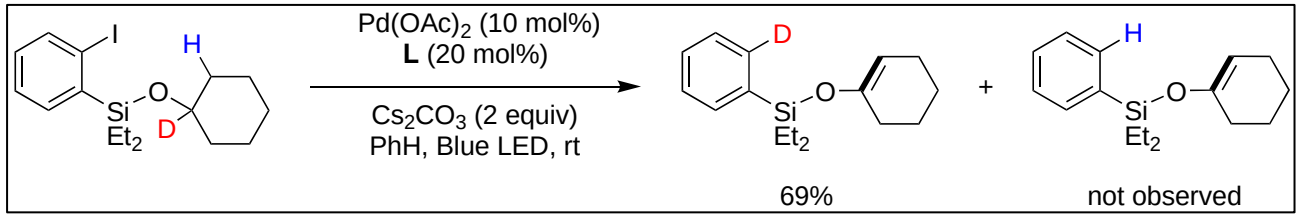
Substrate scope



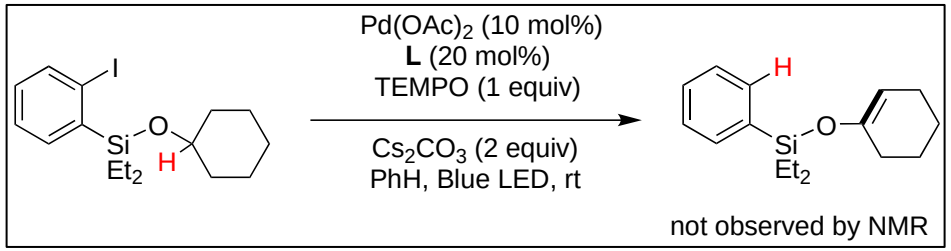


J. Am. Chem. Soc. **2016**, *138*, 6340–6343.

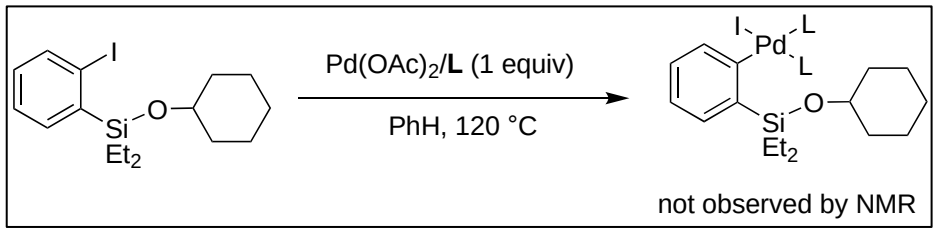
Mechanistic investigation



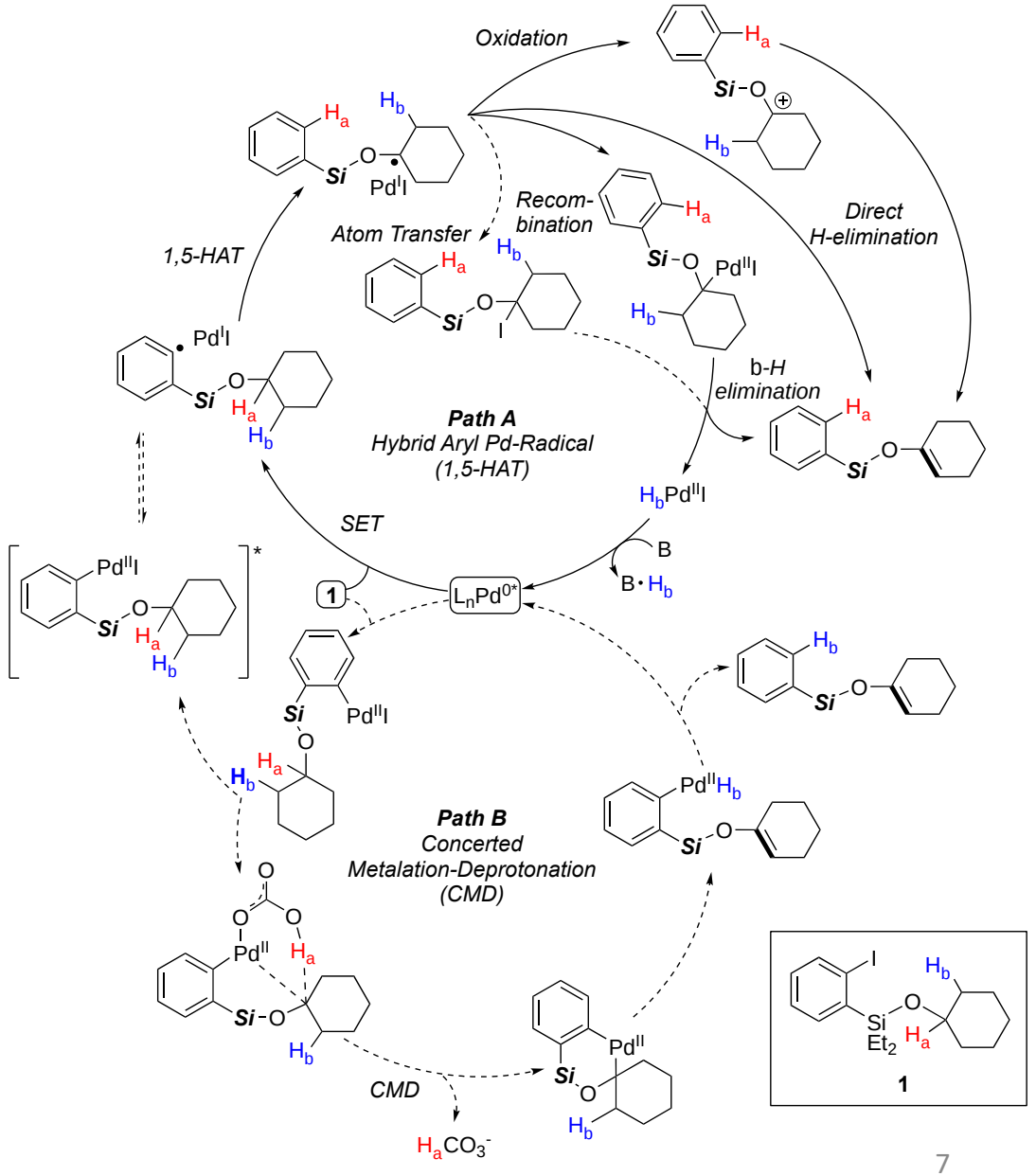
CMD pathway is not occurring



A radical pathway is occurring.



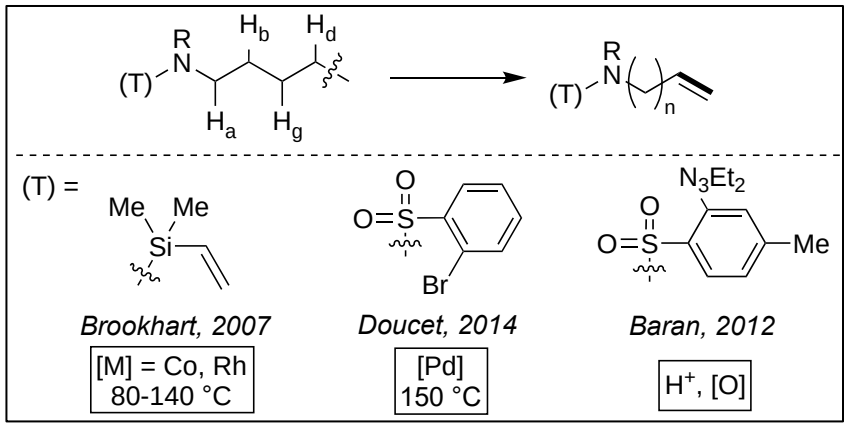
Oxidative addition is not occurring.



J. Am. Chem. Soc. **2016**, *138*, 6340–6343.

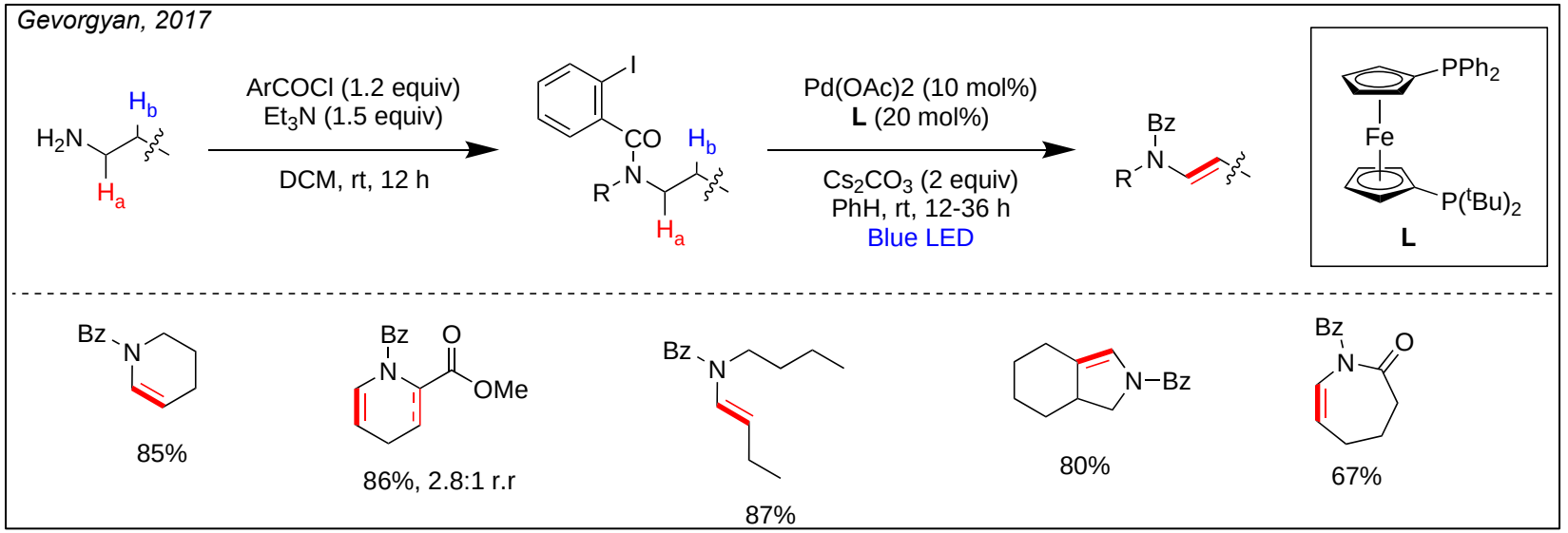
Desaturation of aliphatic amines

Past methods:



All methods had only moderate yields.
Brookhart and Doucet reported harsh conditions, while Baran reported low regiocontrol of deprotonation.

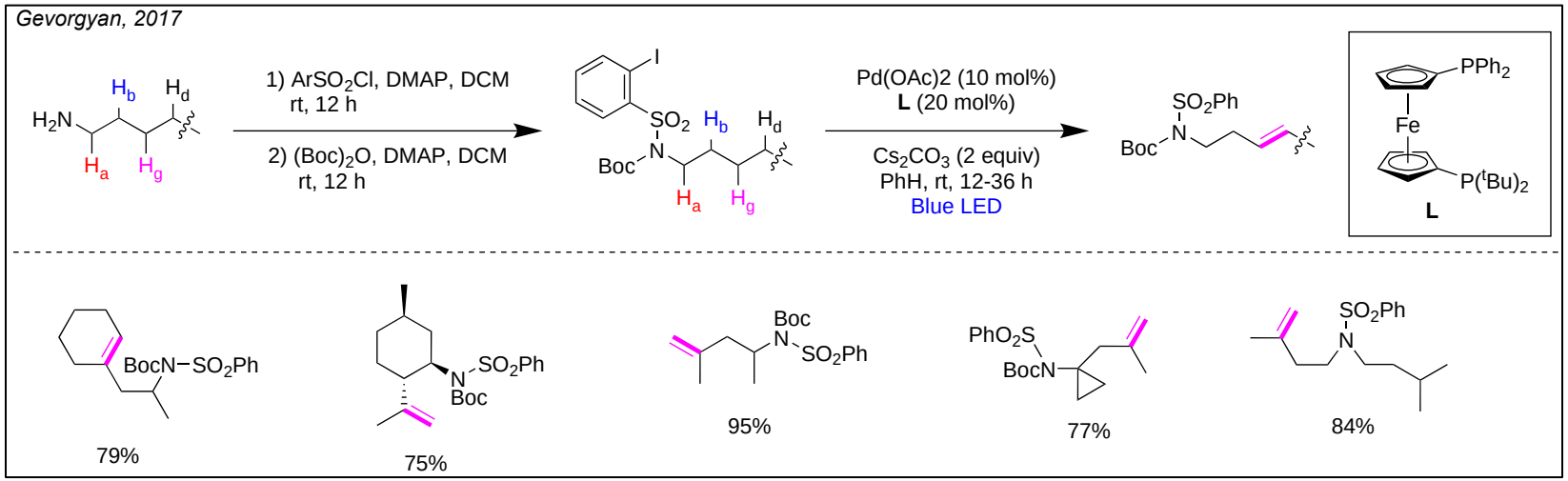
Hydrolytic stability of N-Si is lower compared to O-Si.

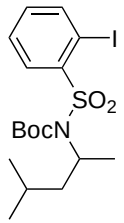


J. Am. Chem. Soc. **2007**, *129*, 14544; *Adv. Synth. Catal.* **2014**, *356*, 119; *Nat. Chem.* **2012**, *4*, 629; *J. Am. Chem. Soc.* **2018**, *140*, 2465–2468.

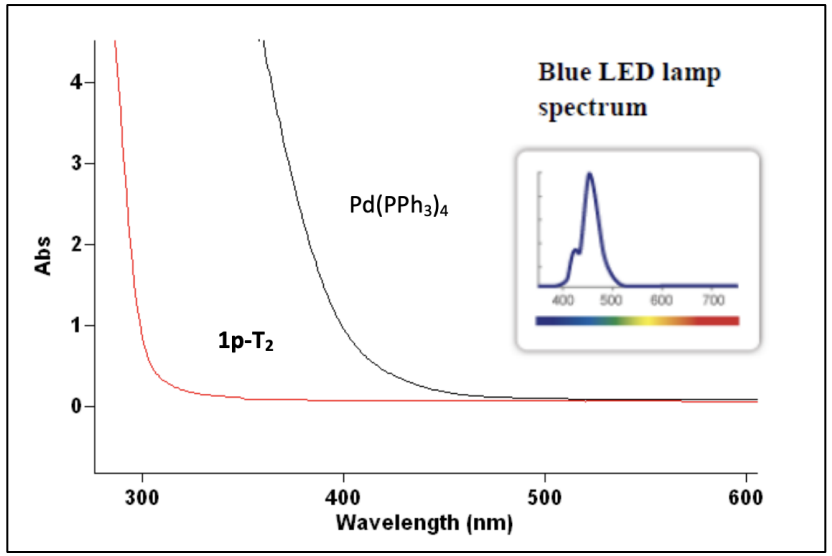
Desaturation of aliphatic amines

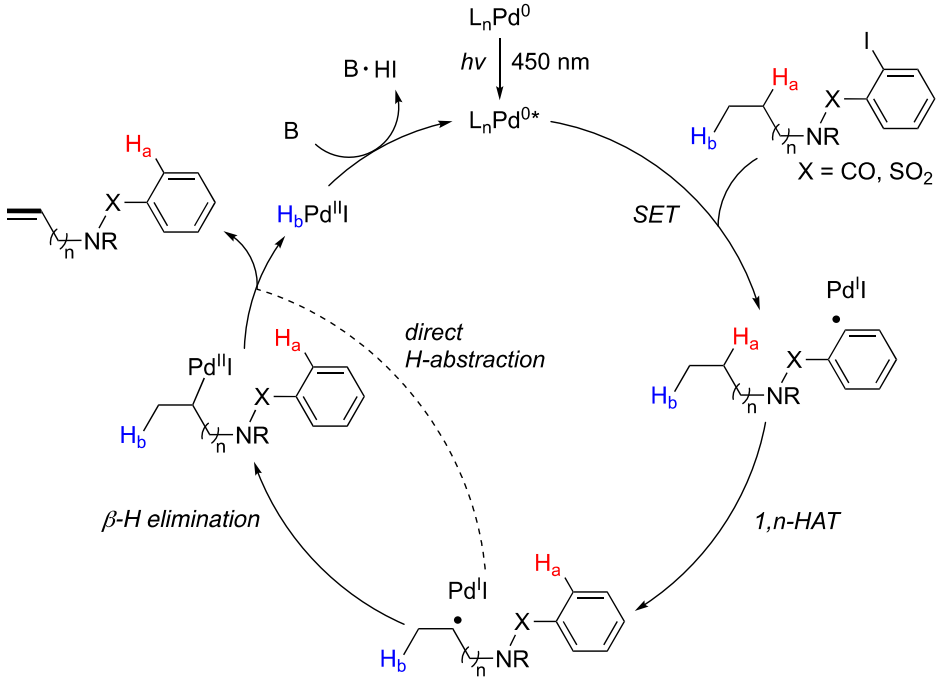
Use of sulfonyl for 1,7-HAT is precedented from *Baran, 2012.*





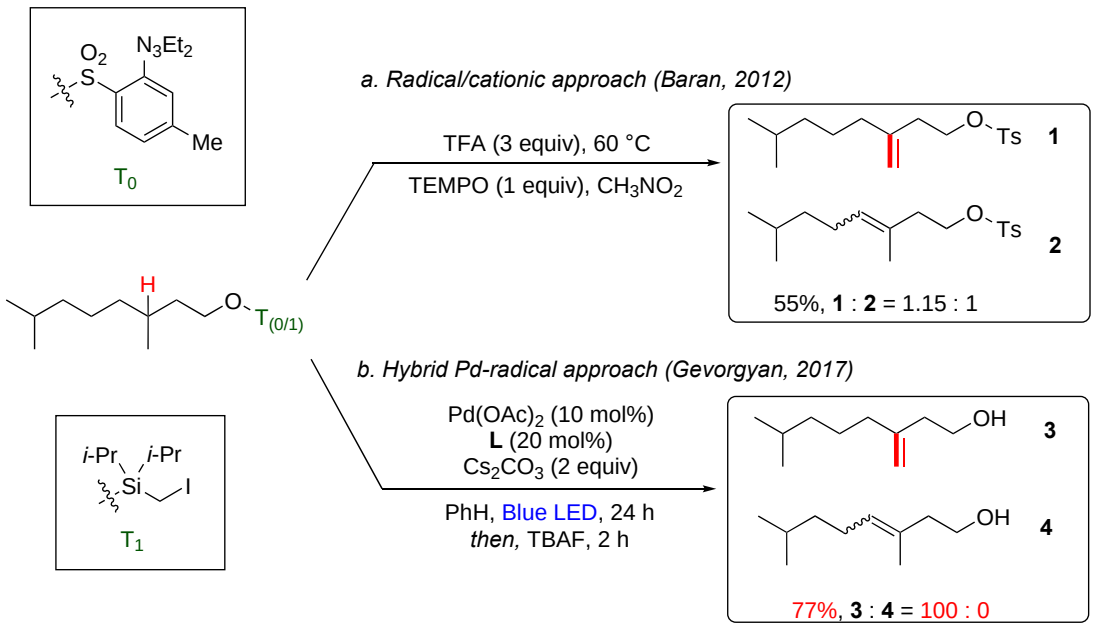
1p-T_2





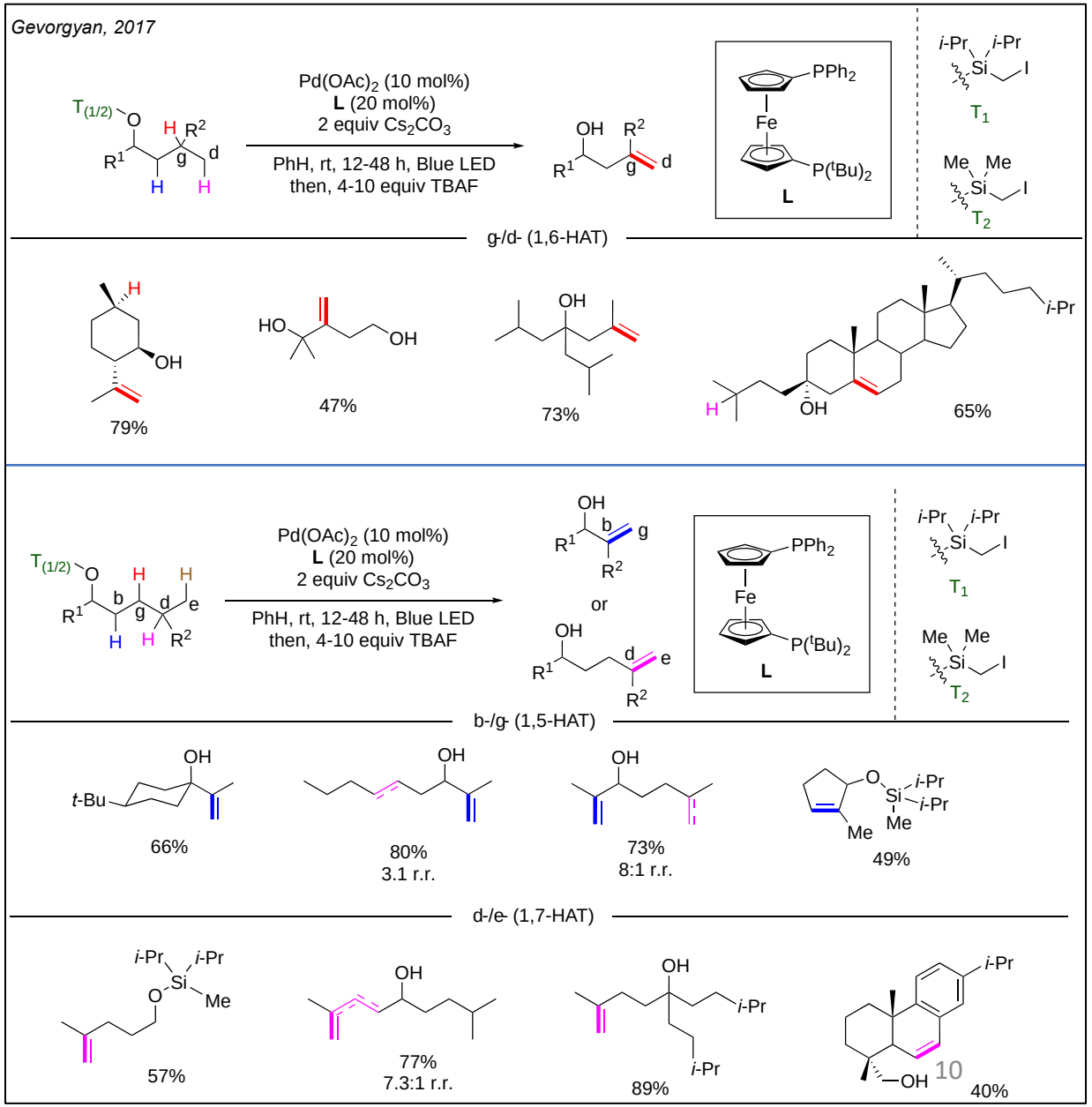
Nat. Chem. **2012**, *4*, 629; *J. Am. Chem. Soc.* **2018**, *140*, 2465–2468.

Desaturation of aliphatic alcohols



Gevorgyan shows higher degrees of regiocontrol.

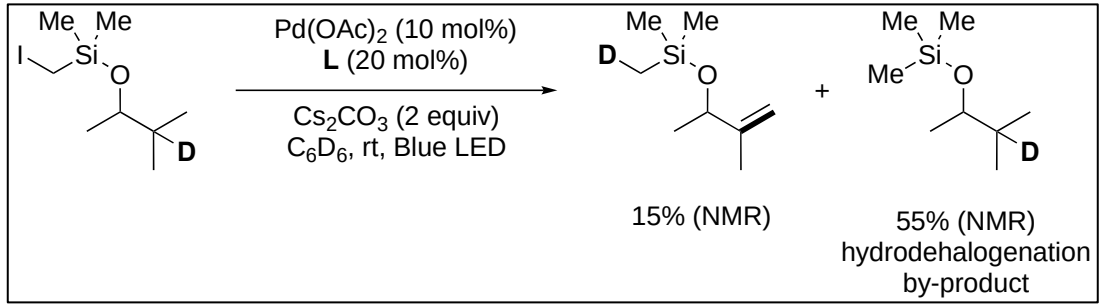
For ease of installation, tether T_2 was used on bulkier secondary alcohols.



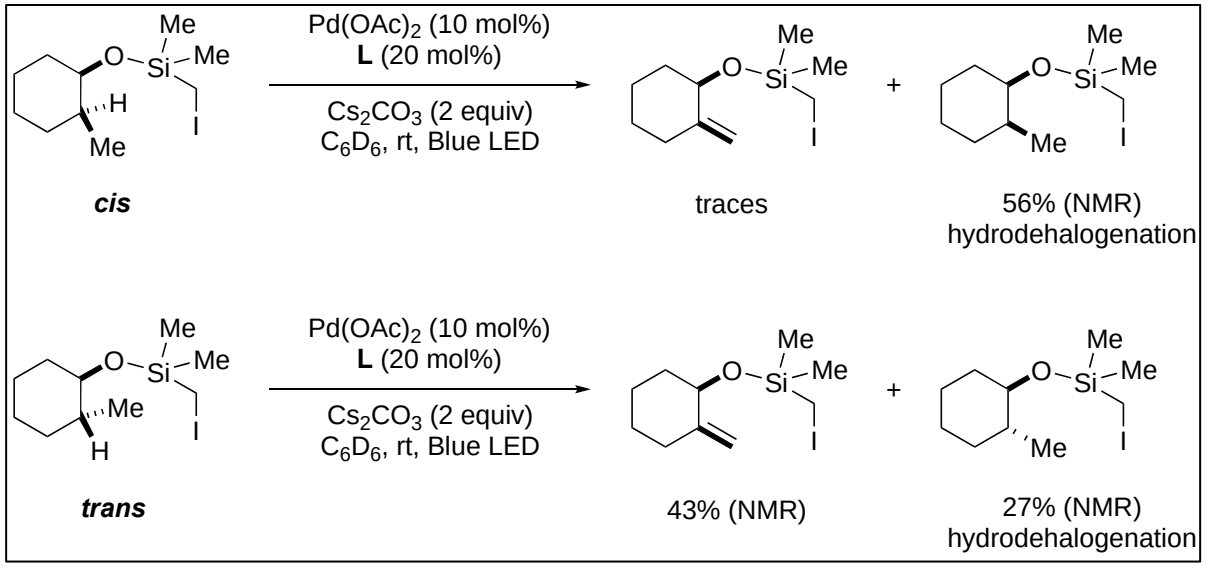
Nat. Chem. **2012**, *4*, 629**;** *J. Am. Chem. Soc.* **2017**, *139*, 14857-14860.

Investigating 1,n-HAT

Isotope labeling

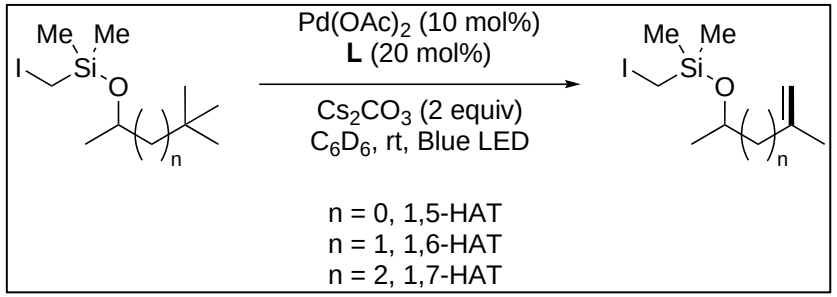


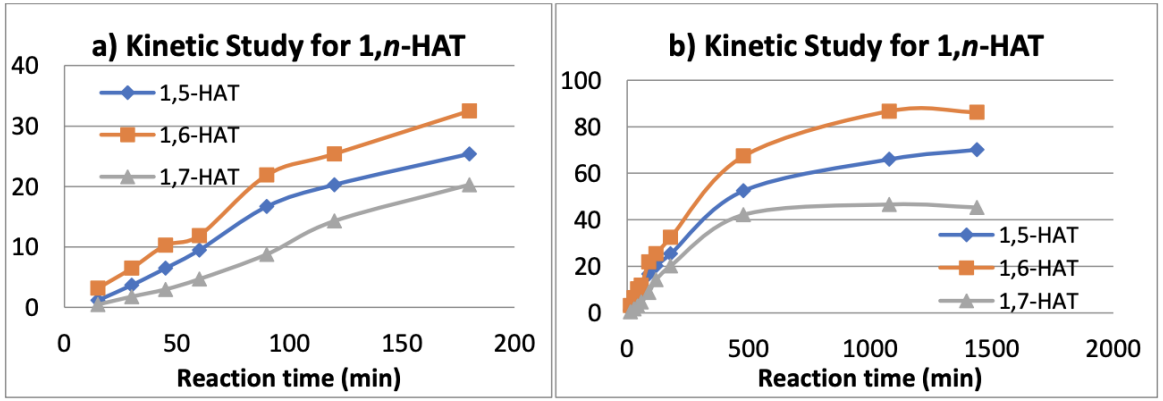
Stereoselectivity for HAT



J. Am. Chem. Soc. **2017**, *139*, 14857-14860.

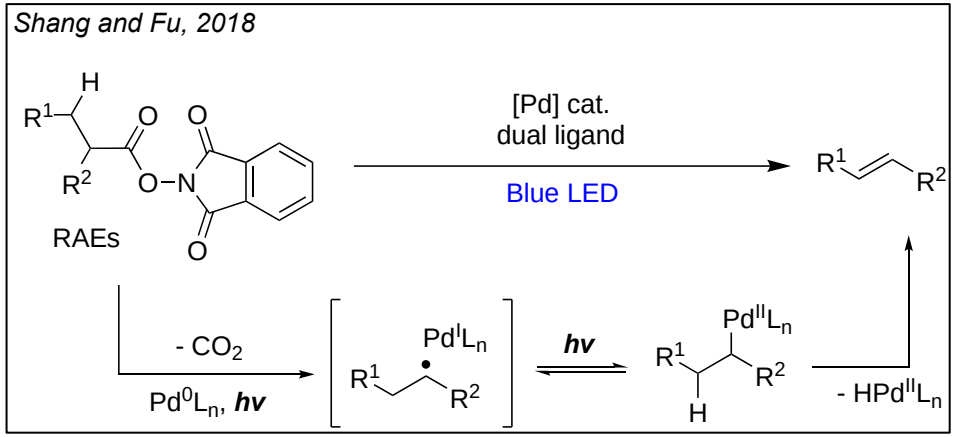
Kinetic Studies





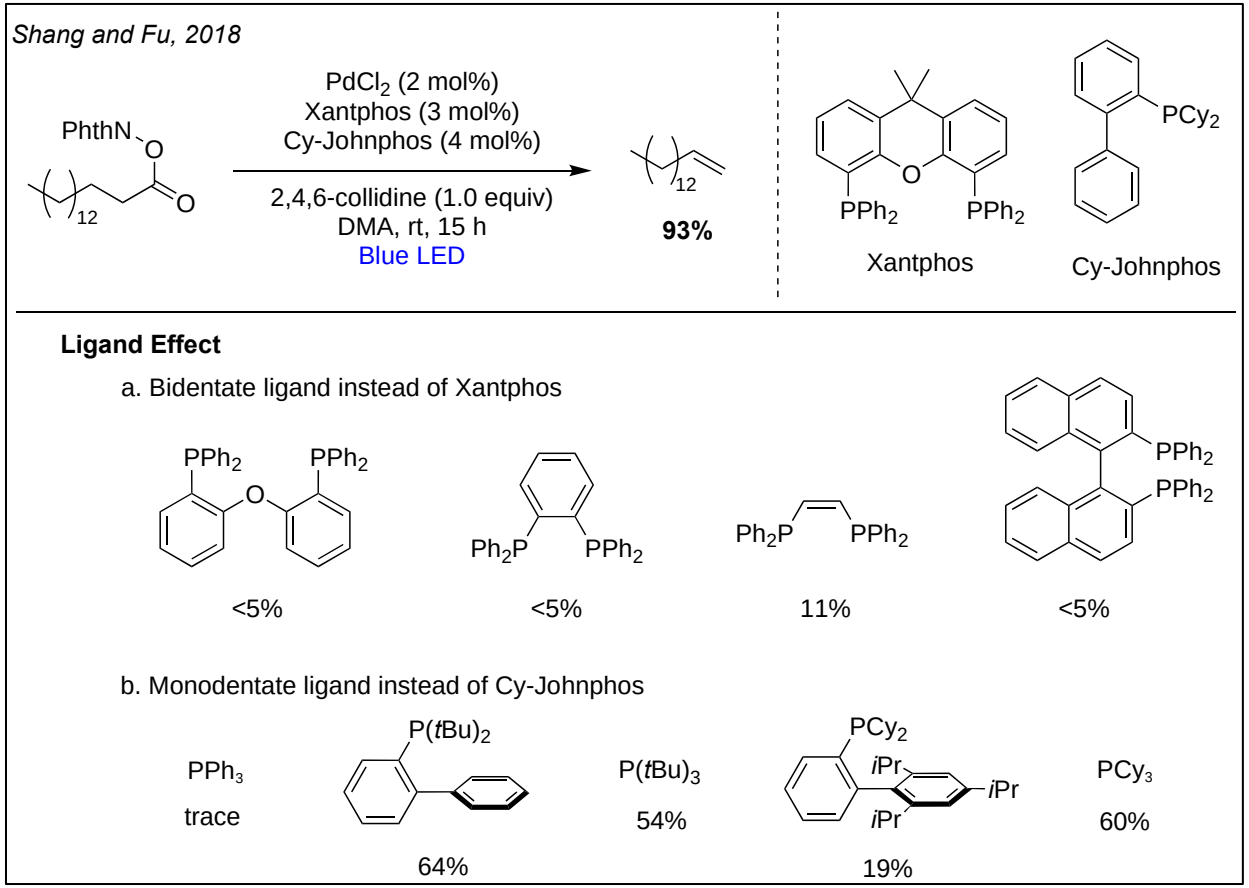
1,6-HAT > 1,5-HAT > 1,7 HAT

Decarboxylative desaturation of aliphatic RAEs



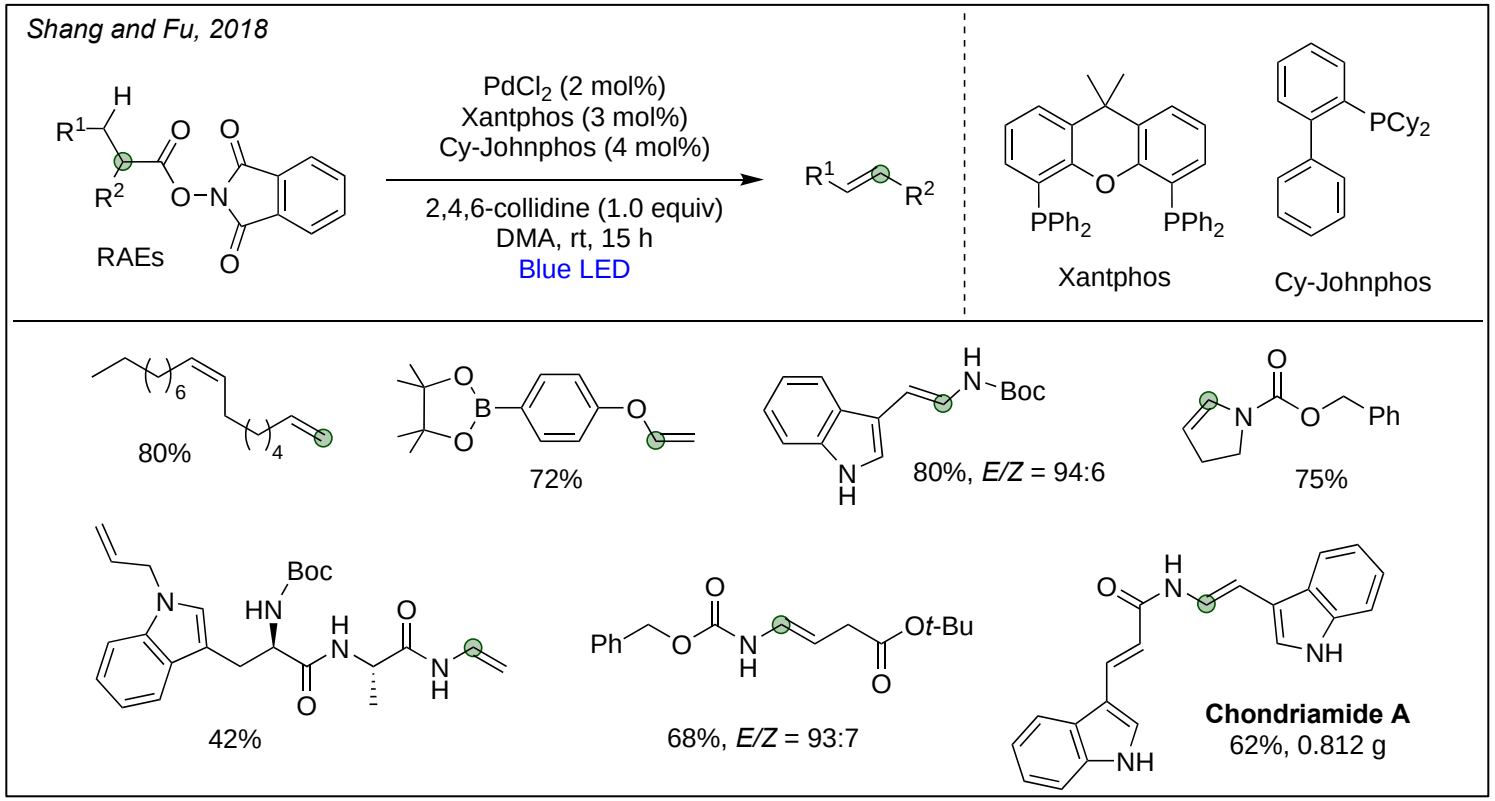
The bite angle and backbone structure of the bidentate ligand affects the outcome of the reaction significantly.

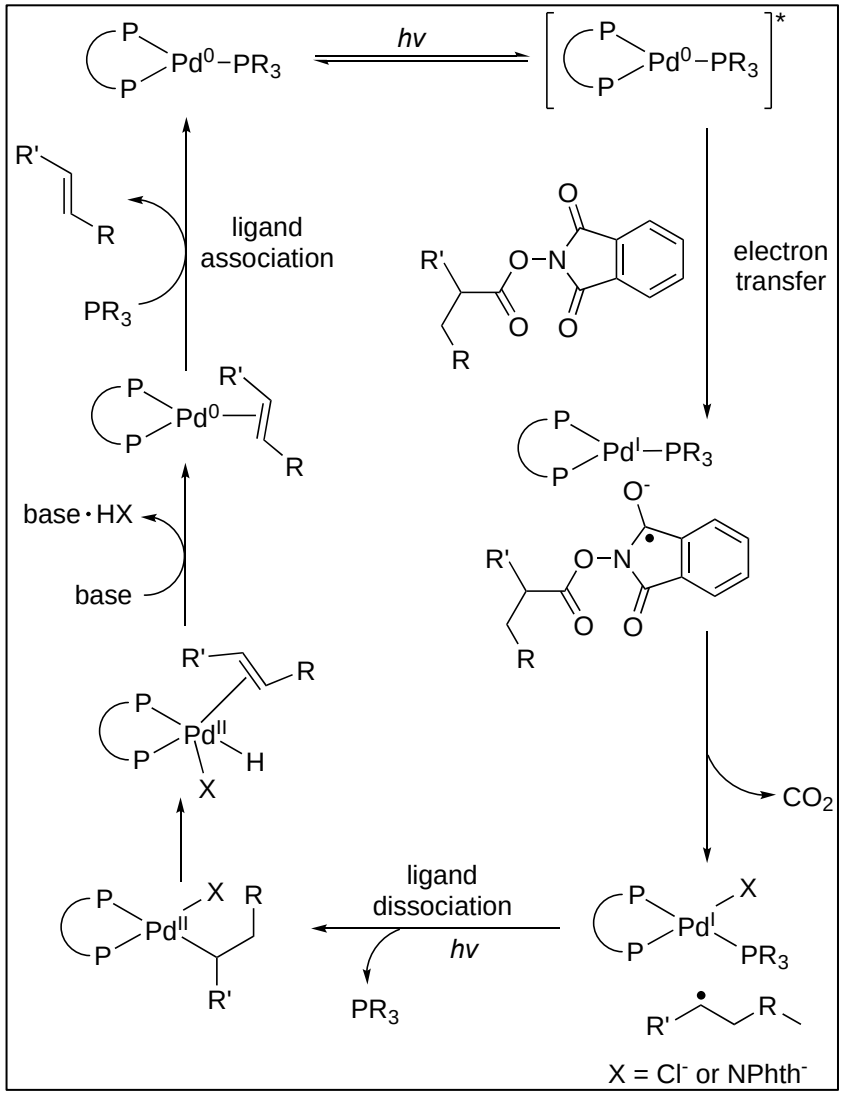
The cone angle and the steric bulk of the monodentate phosphine ligands control the reactivity



Nat. Commun. **2018**, *9*, 5215.

Decarboxylative desaturation of aliphatic RAEs



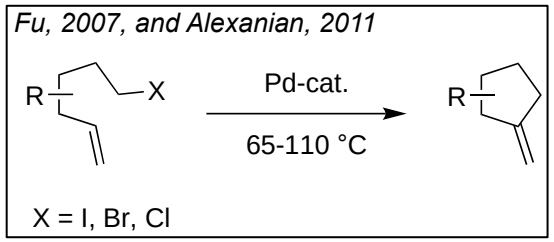


Nat. Commun. **2018**, *9*, 5215.

Alkyl Heck type reactions

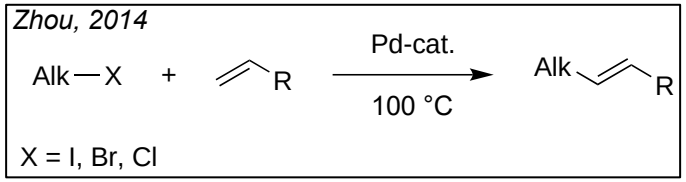
Intramolecular Heck

Fu, 2007, and Alexanian, 2011



Intermolecular Heck

Zhou, 2014

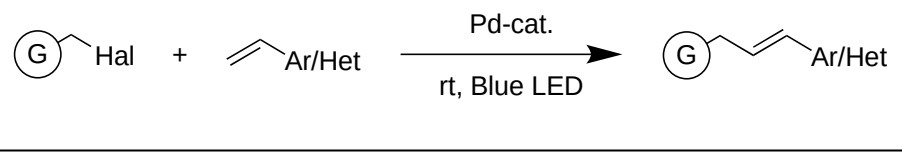


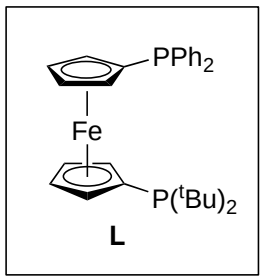
Plagued by slow rates of oxidative addition.

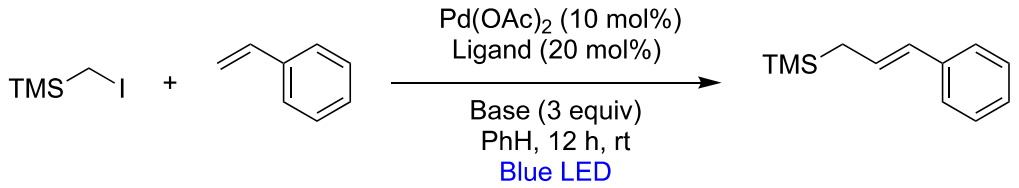
Harsh conditions required.

α-heteroatom-substituted alkyl electrophiles have not been used.

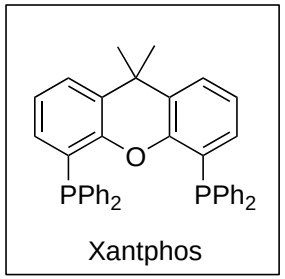
Gevorgyan, 2017





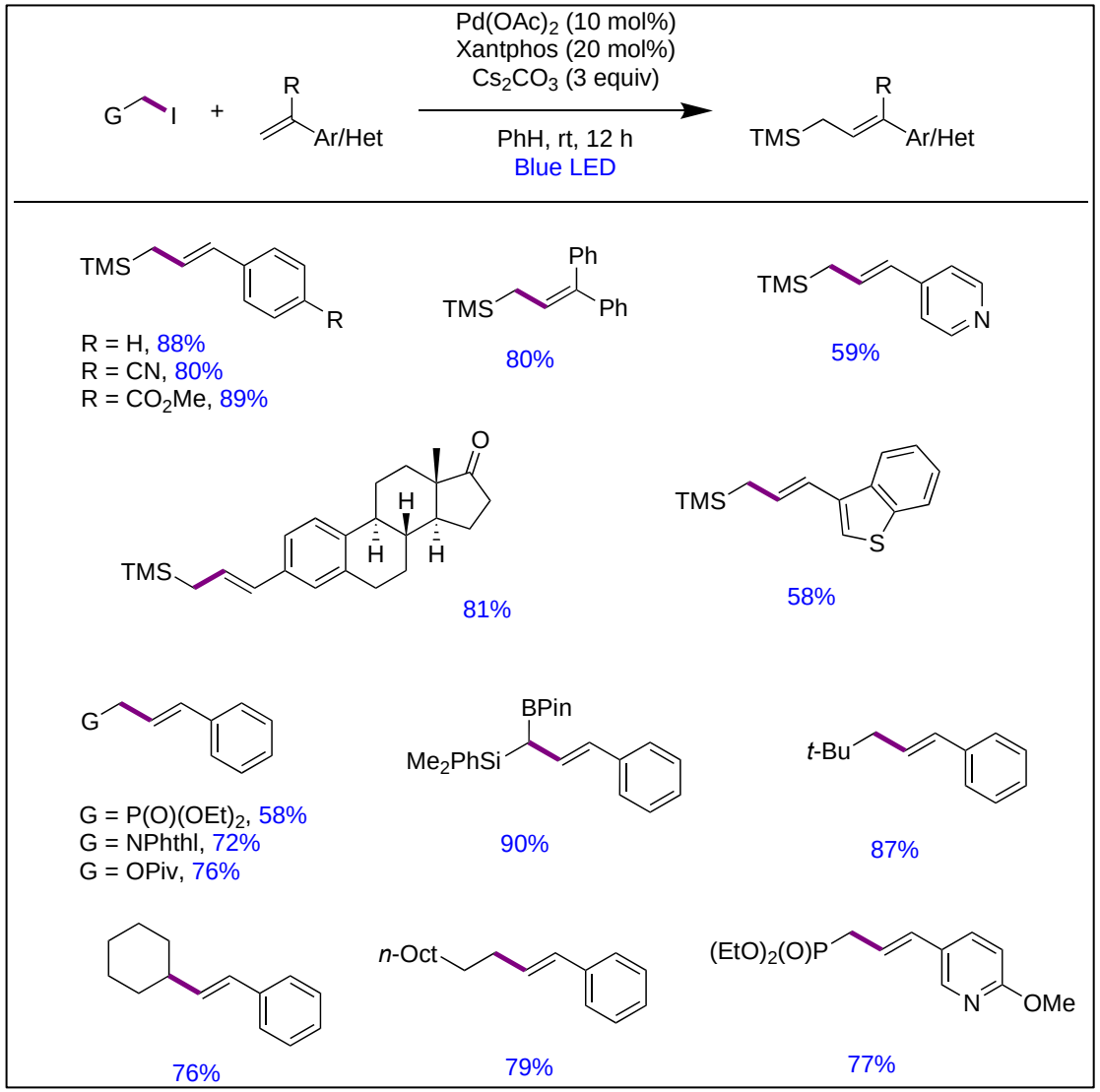


Entry	Ligand	Base	Yield, % (E:Z)
1	**L**	Cs_2CO_3	trace
2	**L**	*i*Pr_2NEt	trace
3	Xantphos	Cs_2CO_3	85 (49:1)
4	Xantphos	100 °C, no light, Cs_2CO_3	0

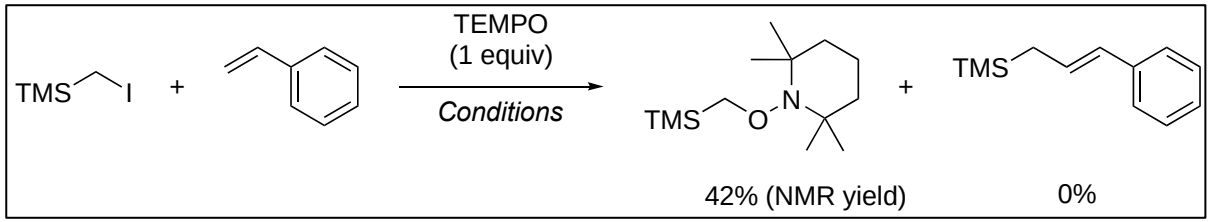


J. Am. Chem. Soc. **2007**, *129*, 11340–11341; *J. Am. Chem. Soc.* **2011**, *133*, 20146–20148; *Angew. Chem. Int. Ed*. **2014**, *53*; 6650; *Angew. Chem. Int. Ed*. **2017**, *56*, 14212–14216.

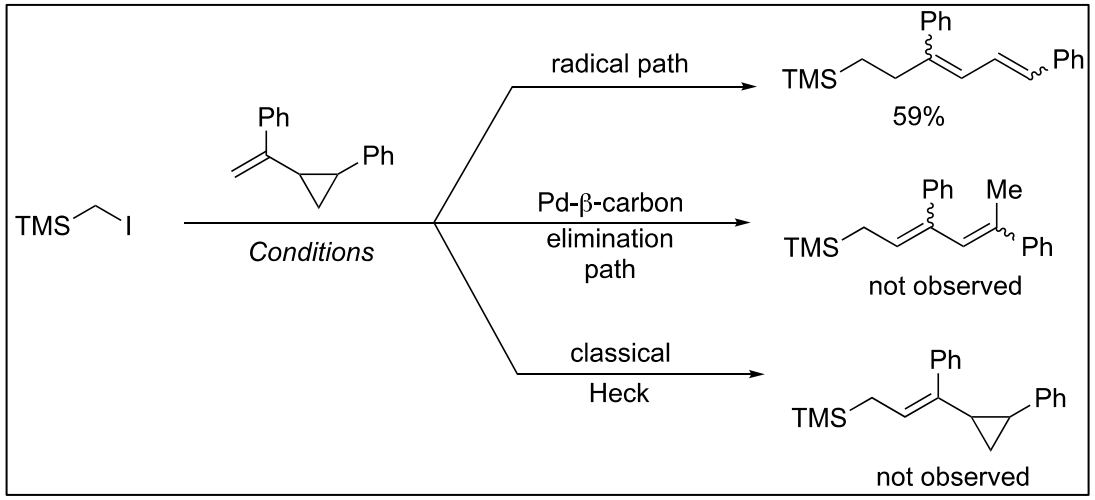
First photochemical [Pd]-catalyzed alkyl-Heck reaction



Radical trapping

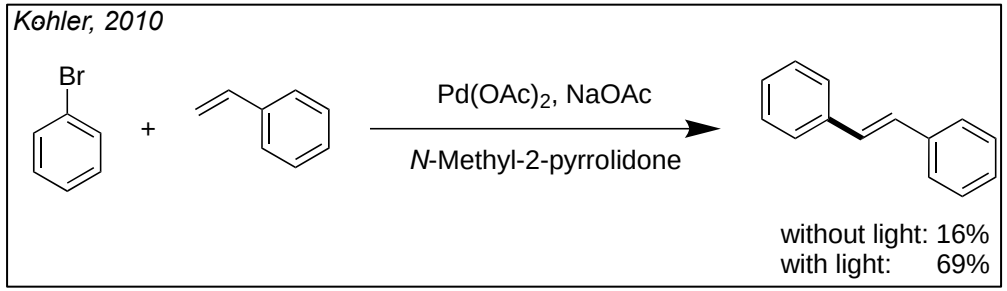


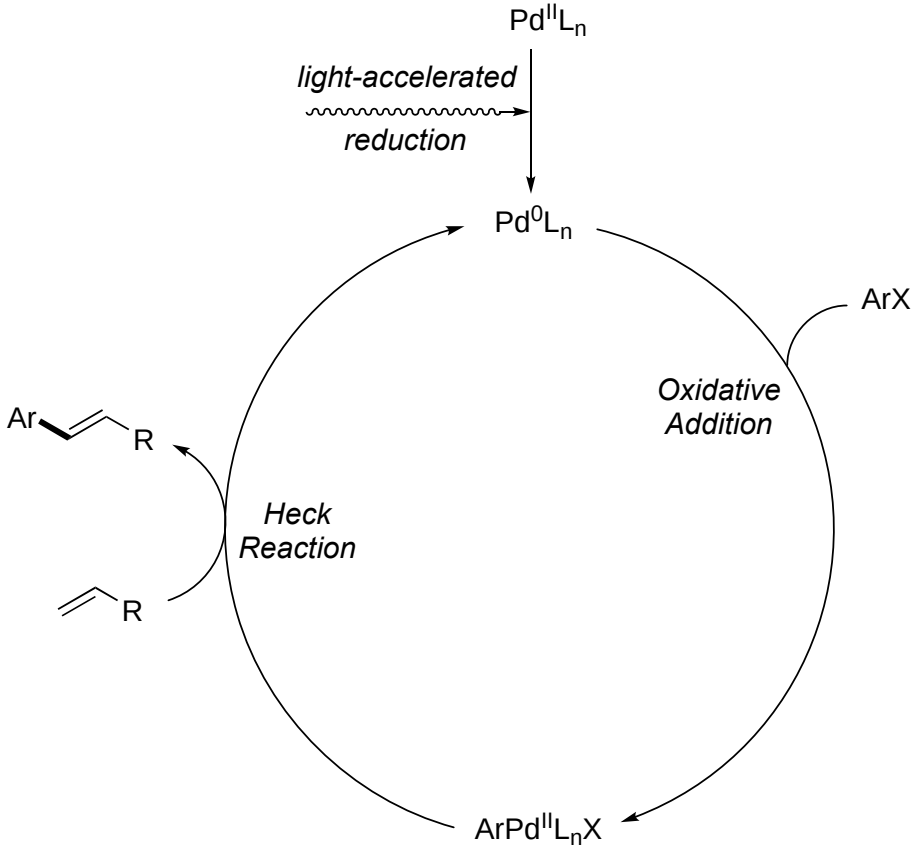
Radical clock work

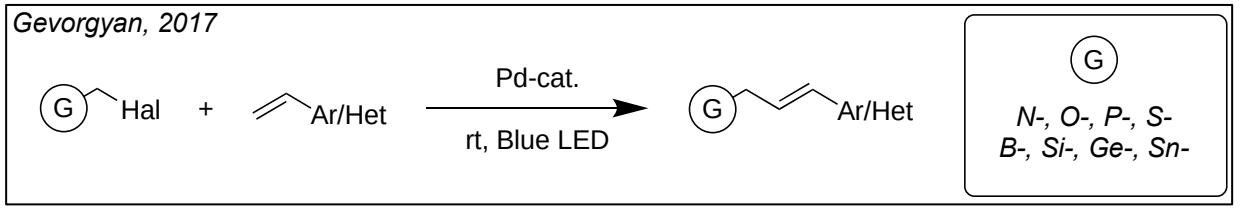


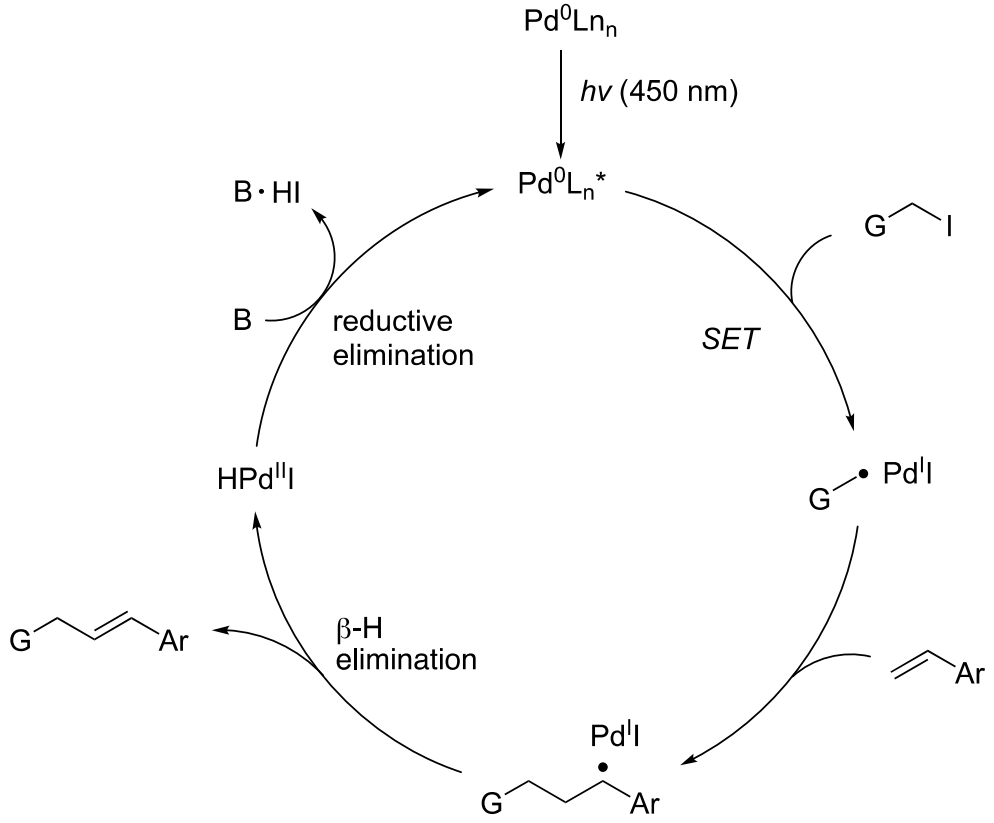
Angew. Chem. Int. Ed. **2017**, *56*, 14212–14216.

First photochemical [Pd] catalyzed Heck reaction





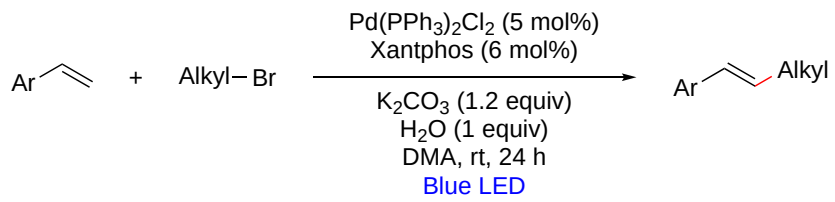


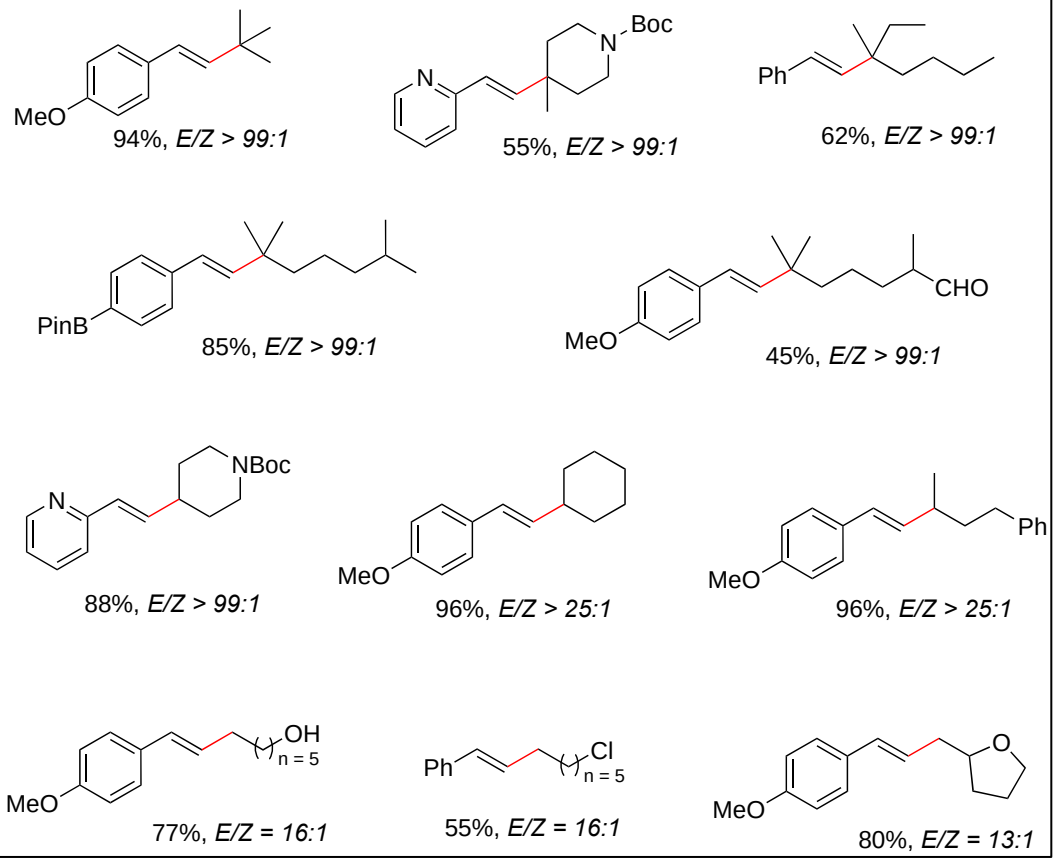


ChemCatChem, **2010,** *2*, 1467–1476*; Angew. Chem. Int. Ed*. **2017**, *56*, 14212–14216.

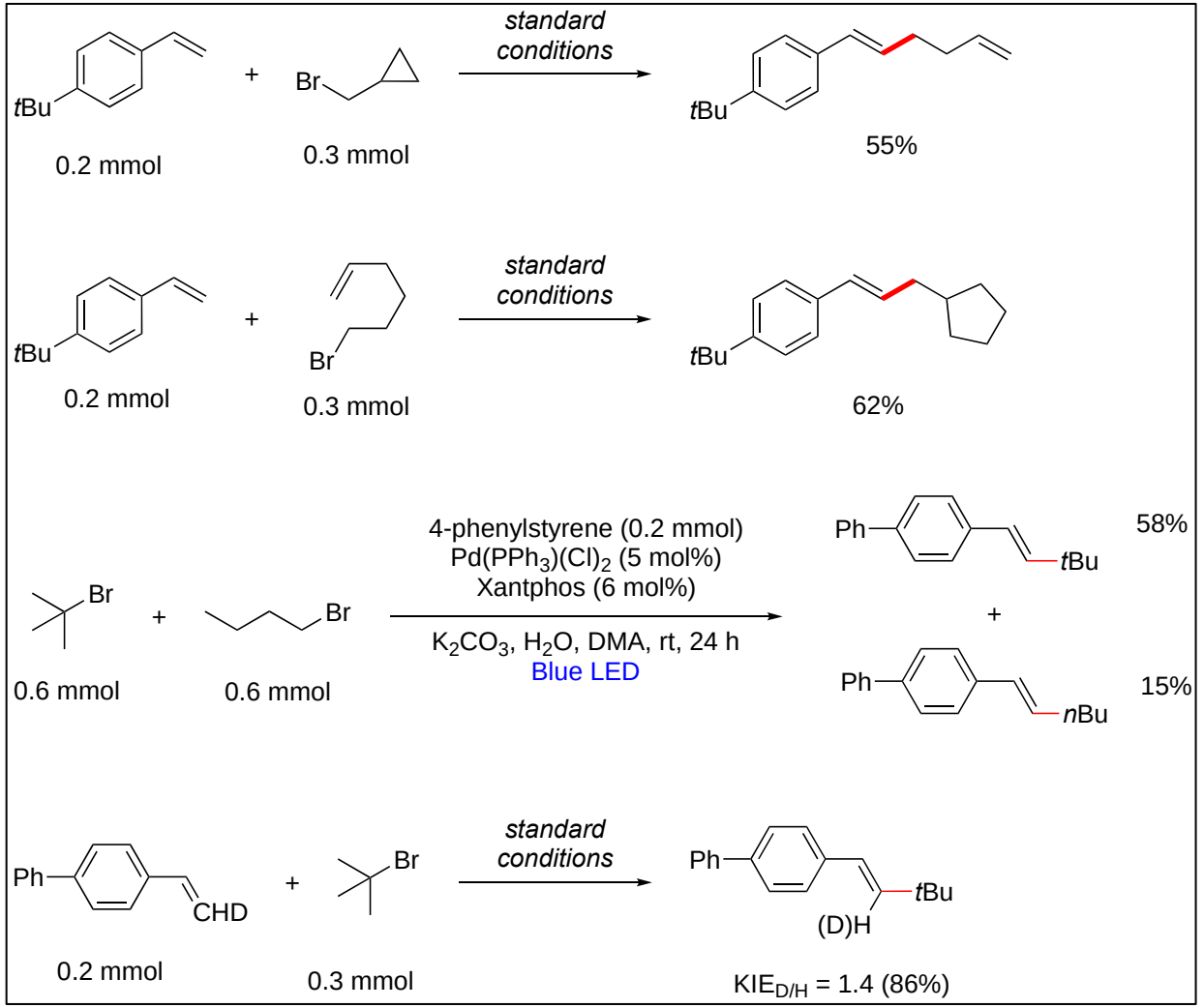
Alkyl-Heck with unactivated halides

Shang and Fu, 2017



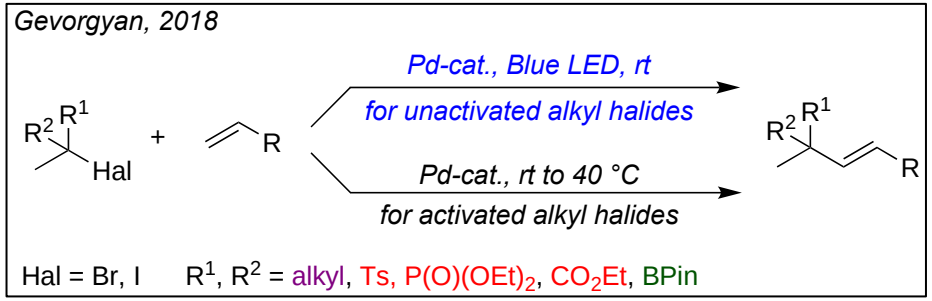


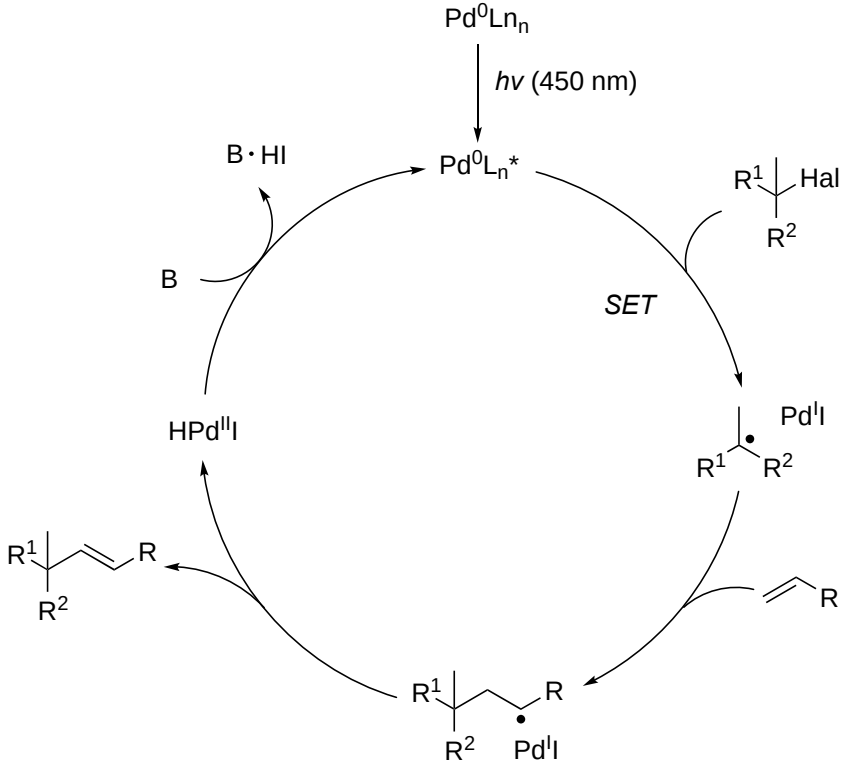
Mechanistic studies



J. Am. Chem. Soc. **2017**, *139*, 18307–18312.

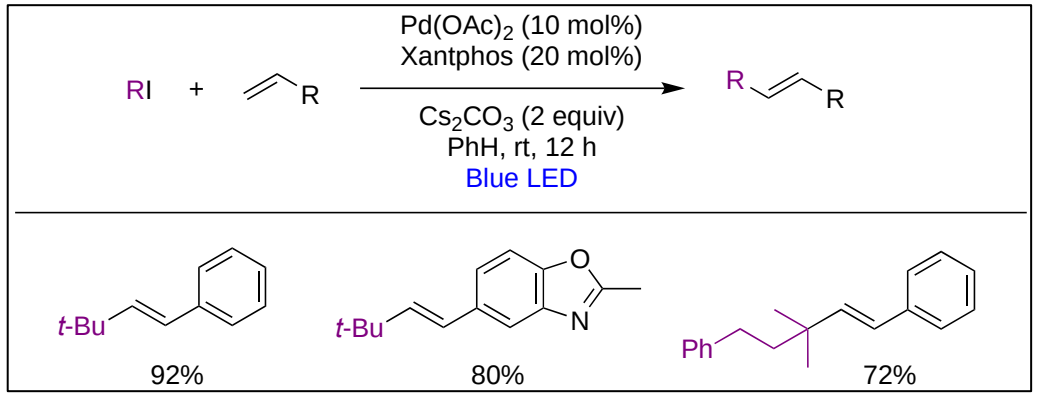
More alkyl Heck reactivity



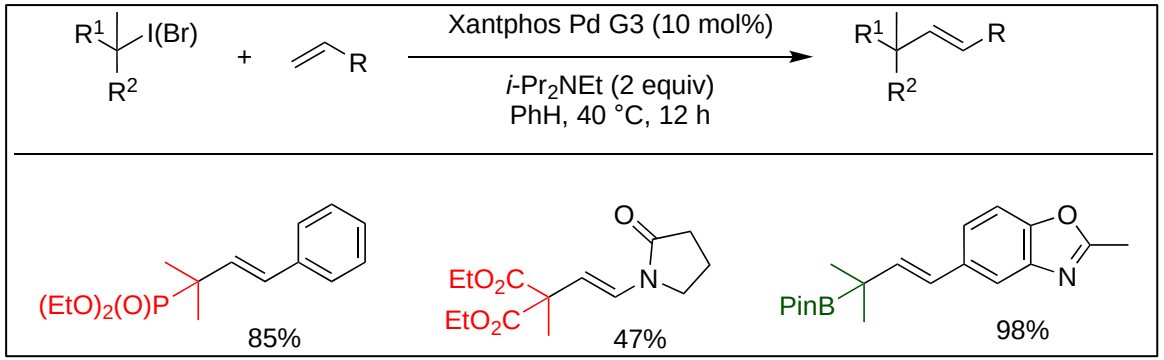


Org. Lett. **2018**, *20*, 357 –360.

Unactivated tertiary halides

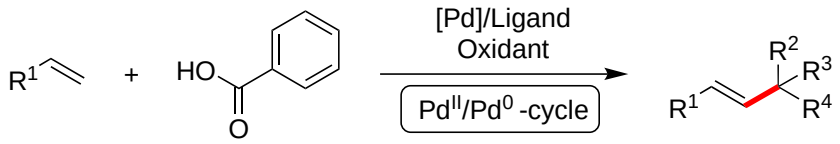


Activated tertiary halides

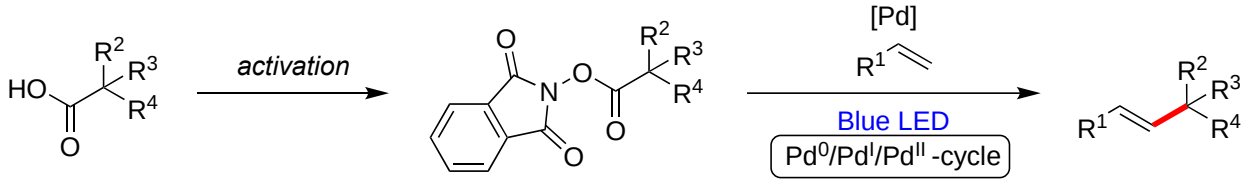


Decarboxylative Heck-type reaction

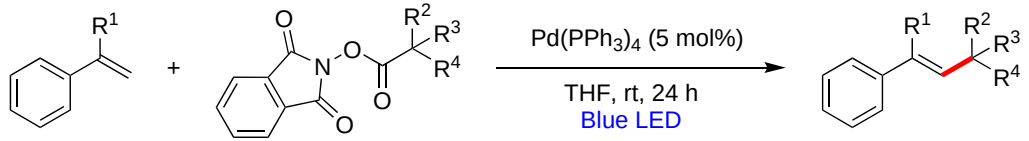
Decarboxylative Heck-type coupling of aryl carboxylic acids

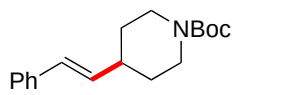


Decarboxylative Heck-type coupling of aliphatic carboxylic acids

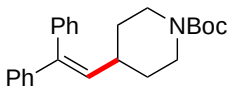


Glorius, 2018

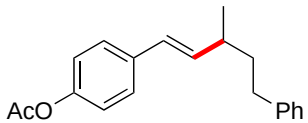




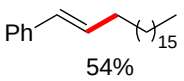
86%
(91% with 6 mol% Xantphos)



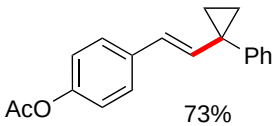
68%



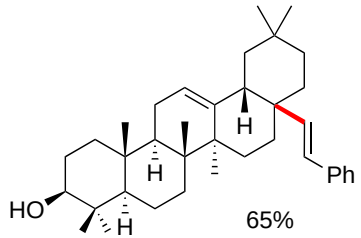
23%
(62% with Xantphos)



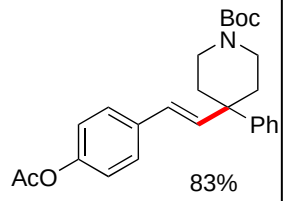
54%



73%



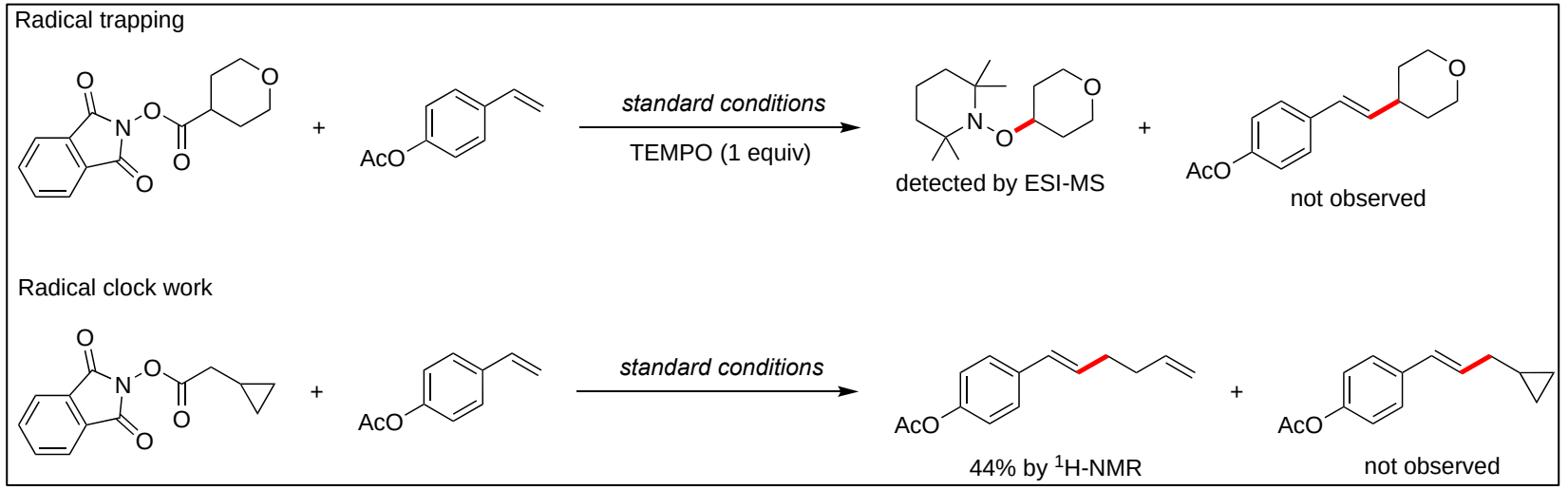
65%



83%

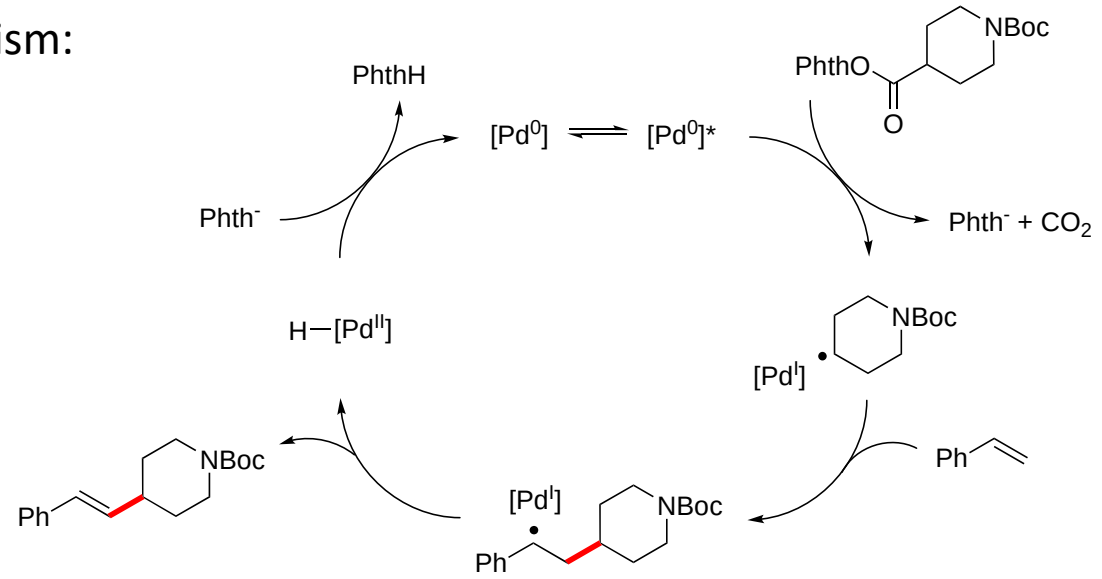
Chem. Eur. J. **2018**, *24*, 4552 –4555.

Decarboxylative Heck-type reaction



This radical clock experiment proves the formation of an alkyl radical derived from *N*-hydroxyphthalimide ester after decarboxylation.

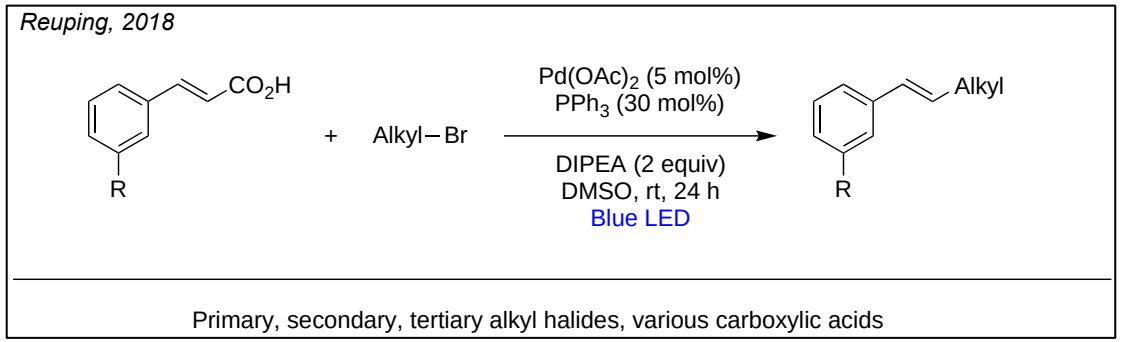
Mechanism:



Chem. Eur. J. **2018**, *24*, 4552 –4555.

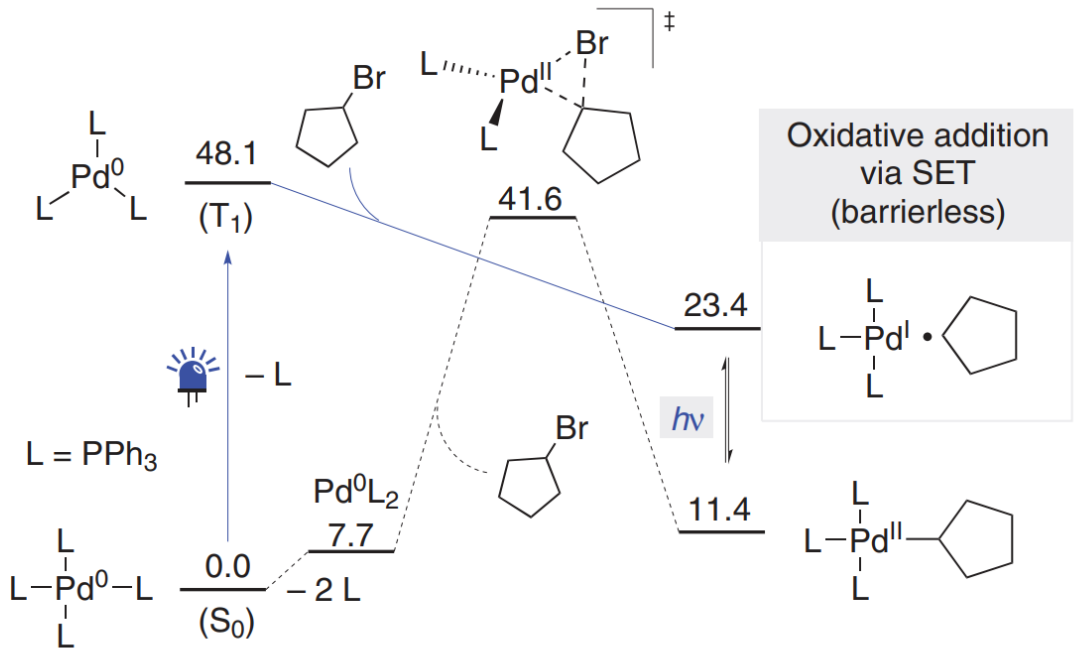
Investigating alkyl-Heck reaction

Reuping, 2018

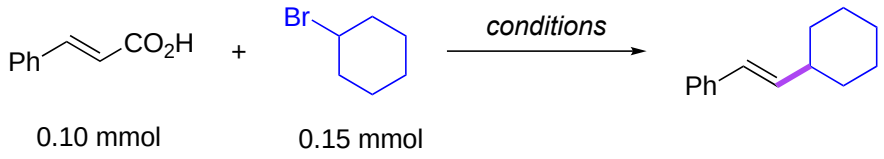


Primary, secondary, tertiary alkyl halides, various carboxylic acids

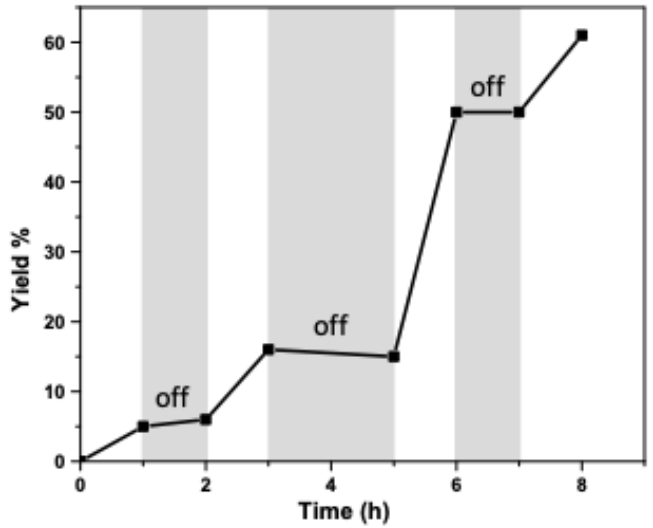
Cavallo and Rueping (2019)



Free energies in solution (in kcal/mol) at the M06(SMD)/SDD/Def2-TZVP//PBE0/SDD/Def2-SVP level



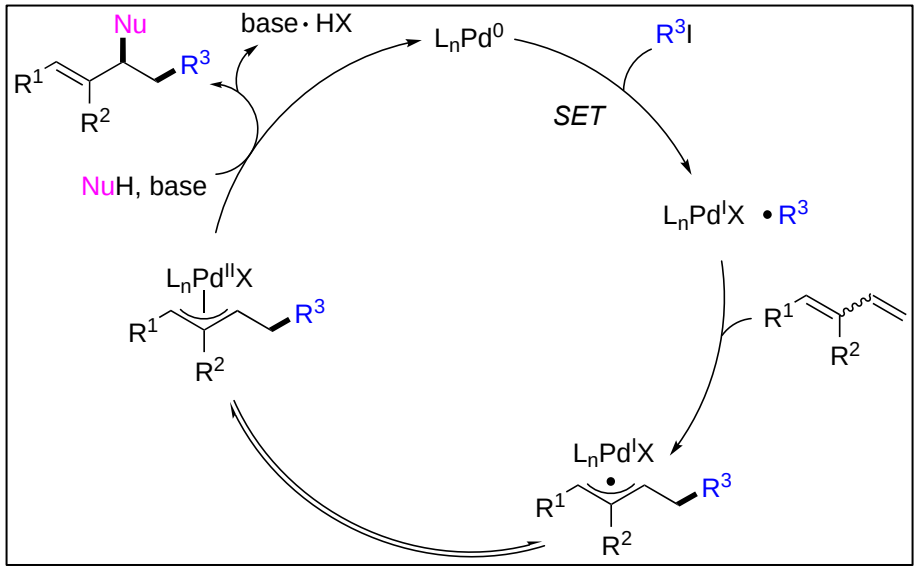
light was swithched off during the 'off' periods



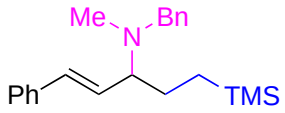
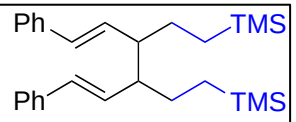
Angew. Chem. Int. Ed. **2019**, *58*, 3412 –3416

1,2-Aminoalkylation

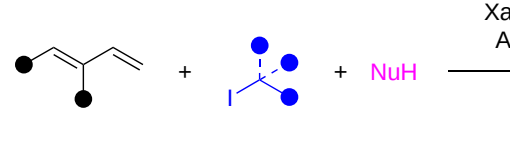
Proposed Mechanism

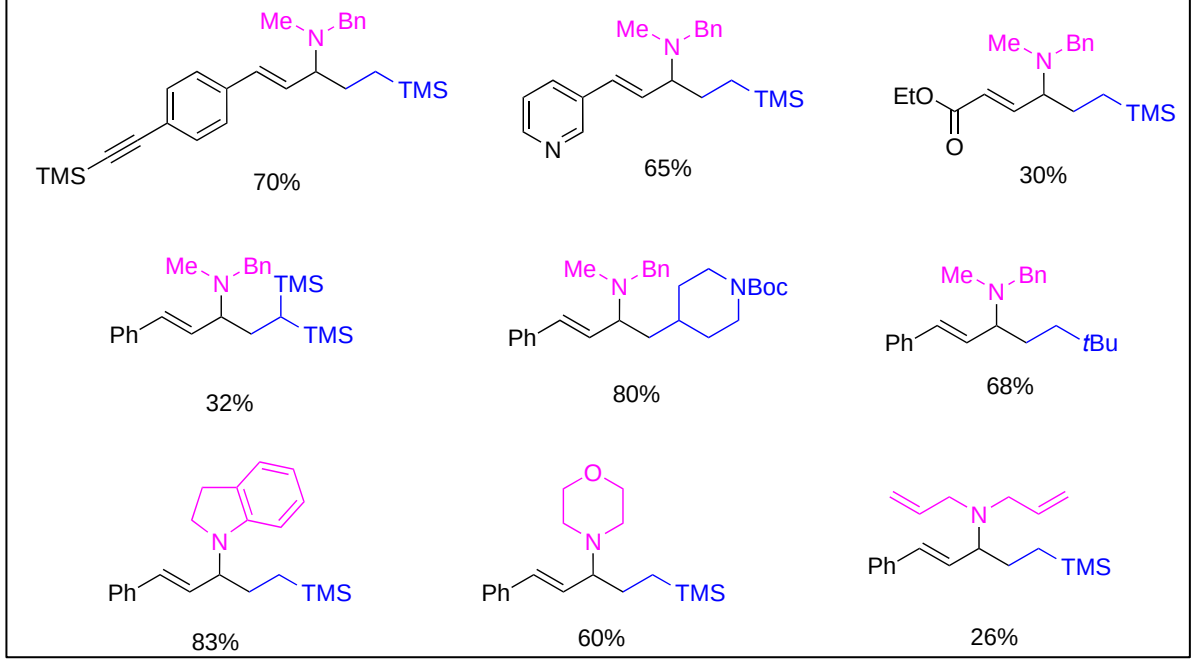


Dimer effect

		
w/ AnNTf2	89%	trace
w/o AgNTF2	44%	34%

Gervorgyan, 2020



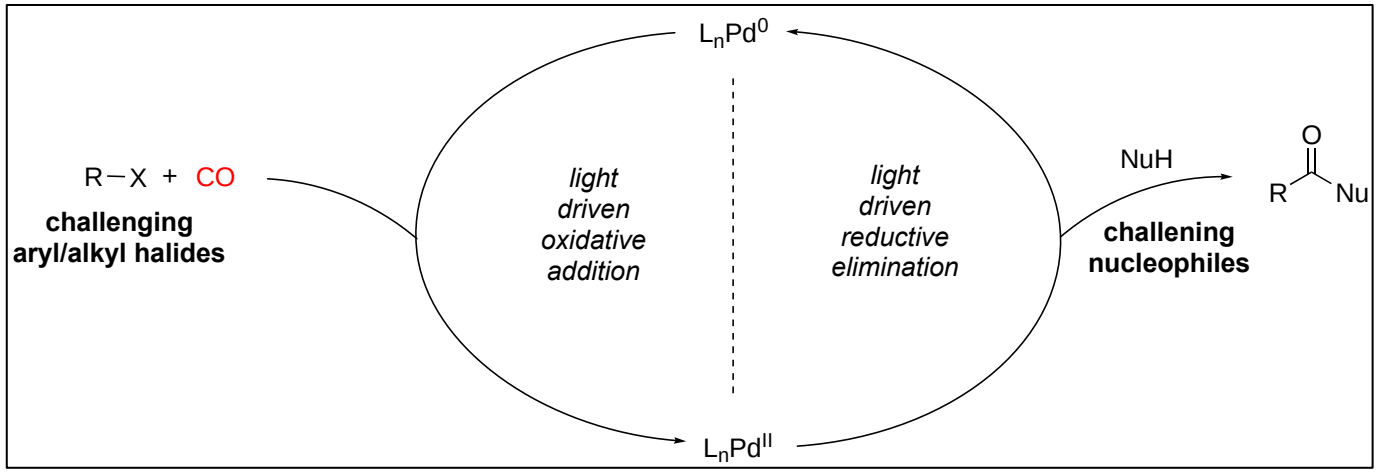


J. Am. Chem. Soc. **2020**, *142*, 9932–993.

Carbonylation chemistry

Oxidative Addition

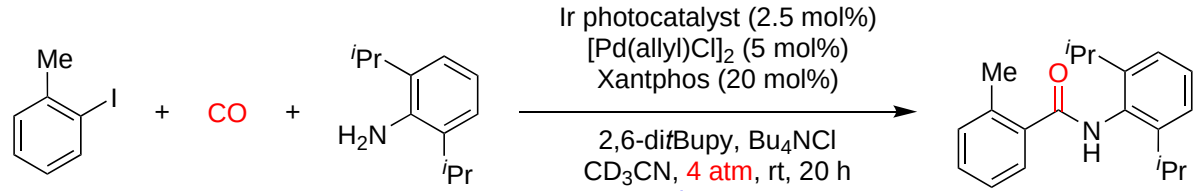
Typically favored by:
- electron rich complexes
- unsaturated metals
- weak R – X bond



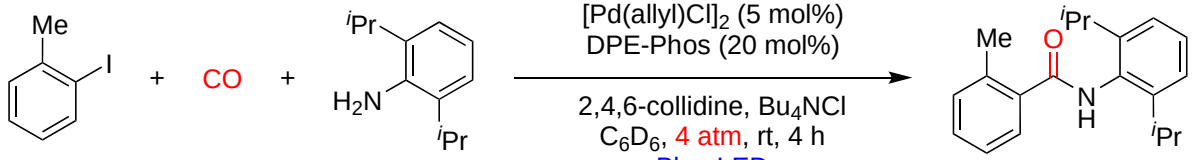
Reductive Elimination

Typically favored by:
- electron poor complexes
- strong encumbrance

Arndsten, 2020



34%
No [Ir]: 30%

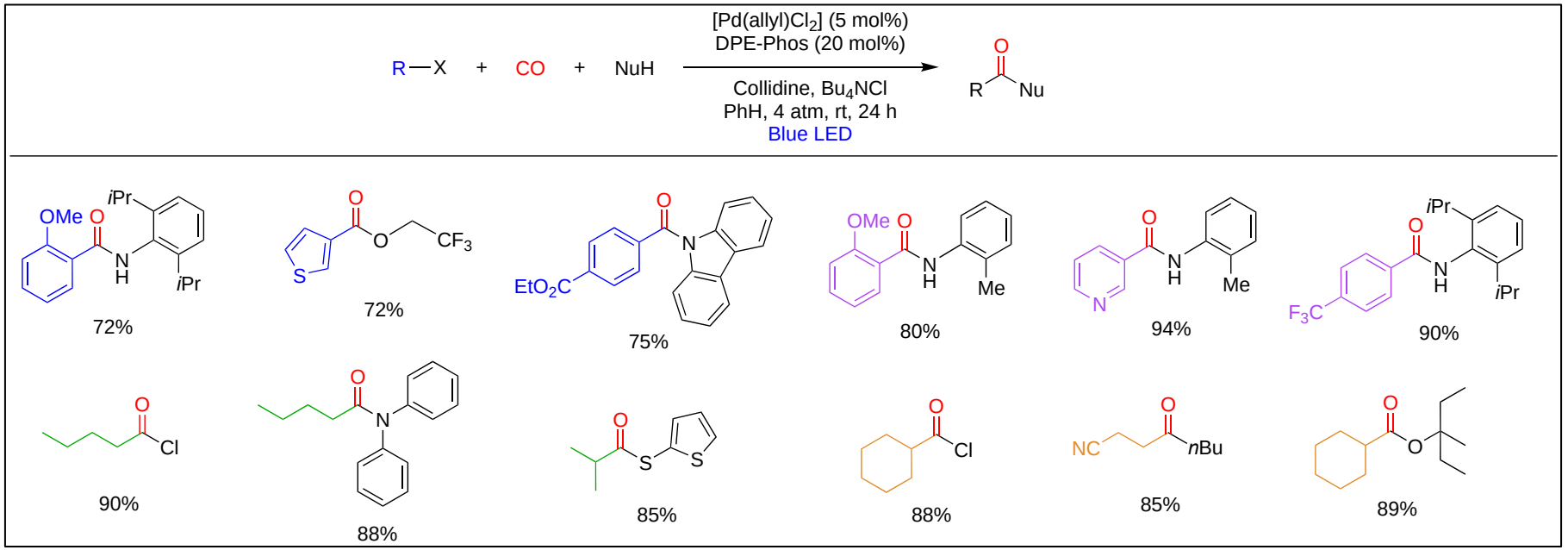


99%

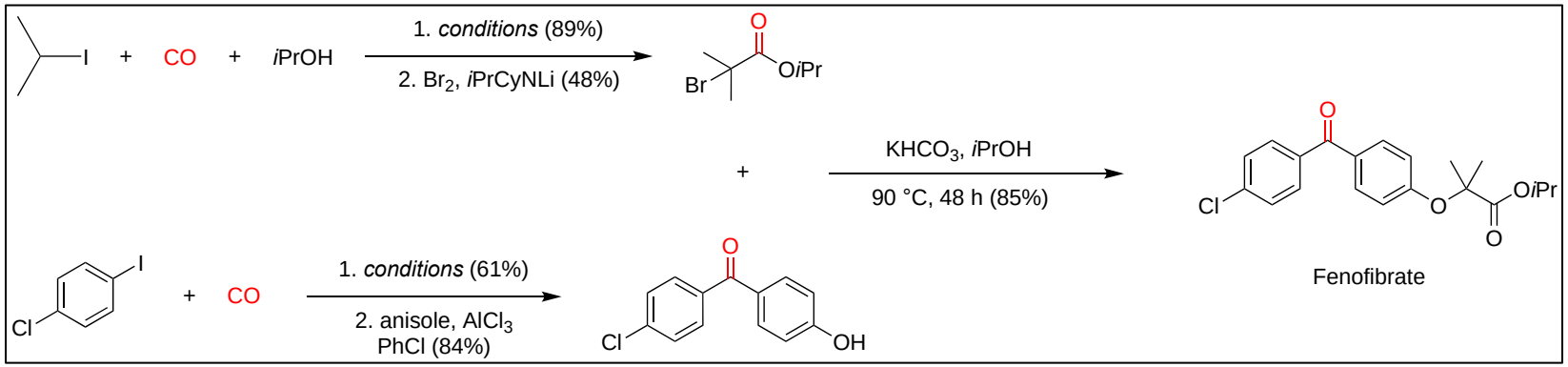
Initial studies showed that cooperative photocatalysis was not necessary for this transformation.

Science **2020**, *368*, 318–323.

Carbonylation chemistry



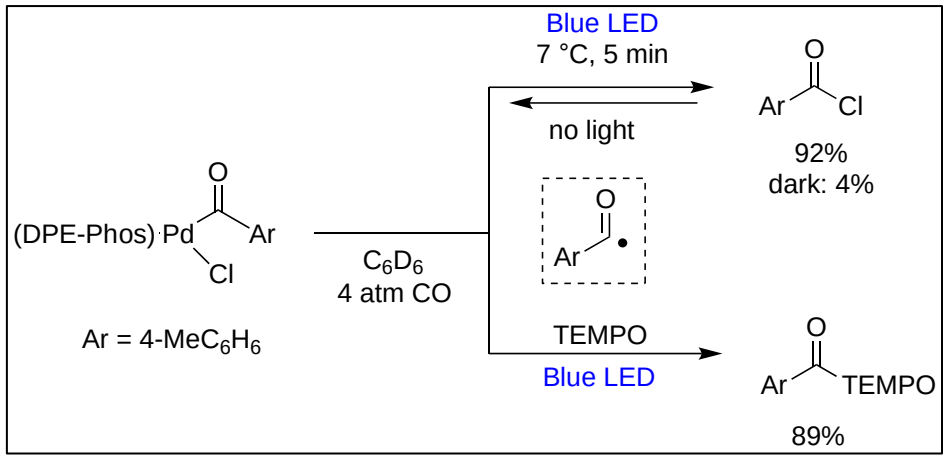
Targeted Synthesis



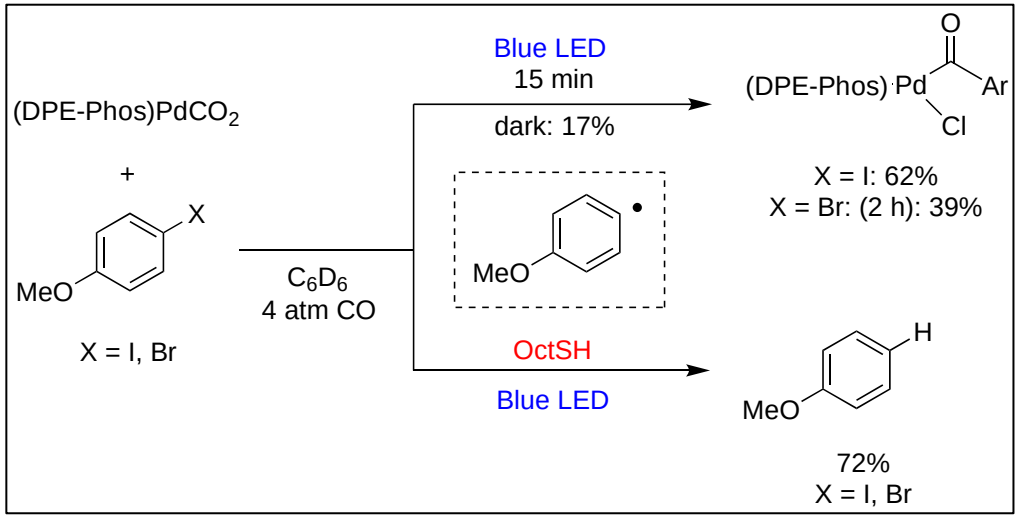
Science **2020**, *368*, 318–323.

Carbonylation chemistry

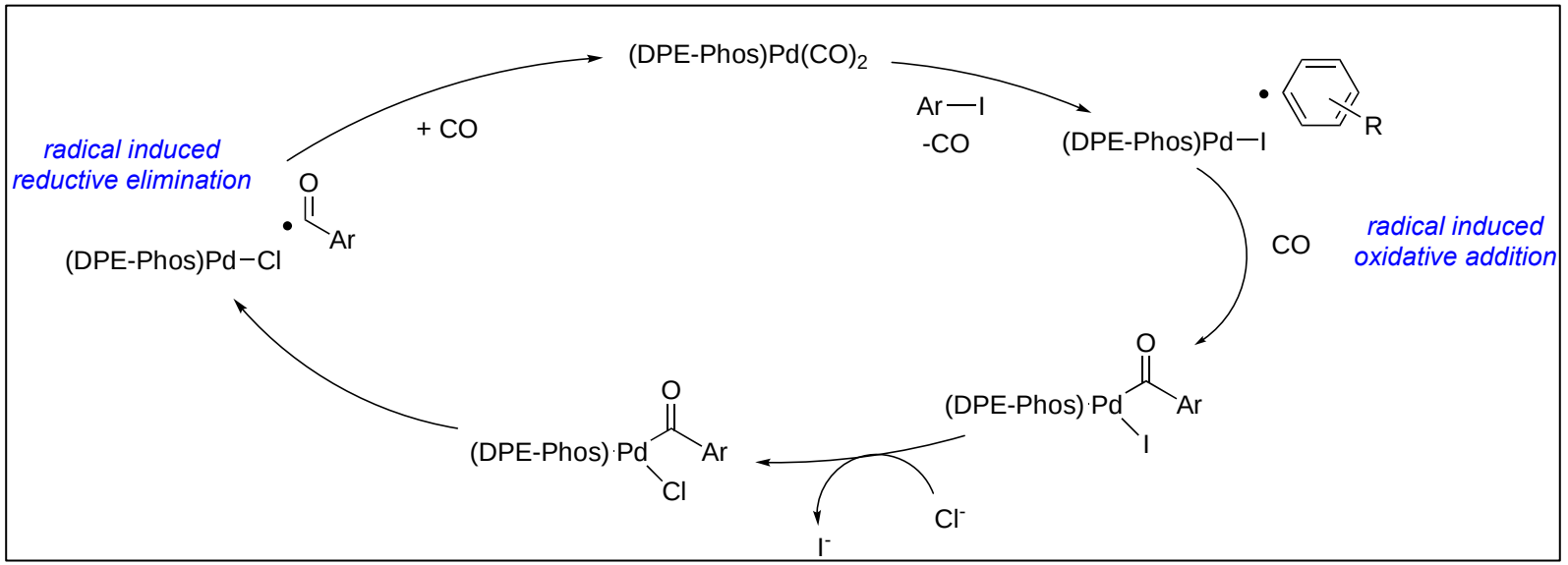
Visible light in reductive elimination



Visible light in oxidative addition



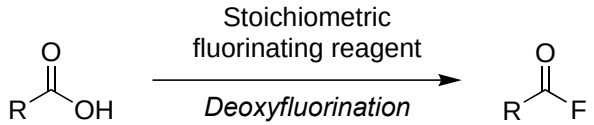
Mechanistic Hypothesis:



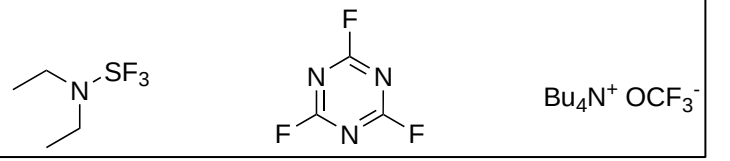
Science **2020**, *368*, 318–323.

Carbonylation chemistry

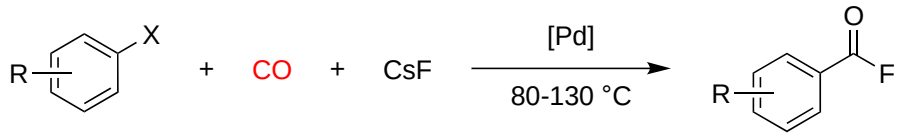
Typical methods for acyl fluoride synthesis



Fluorinating reagents:



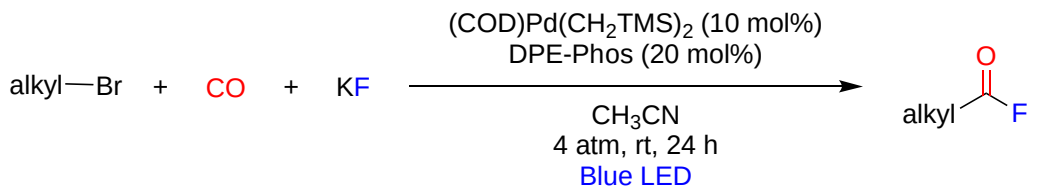
Tanaka, 1987

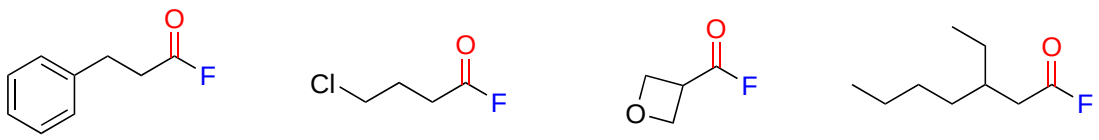


only aromatic products

Corrosive reagents and functional group incompatible.

Arndsten, 2022



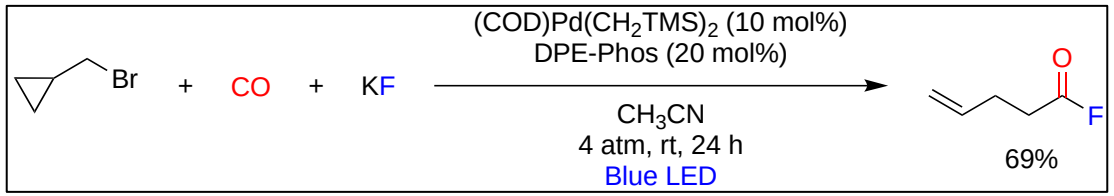


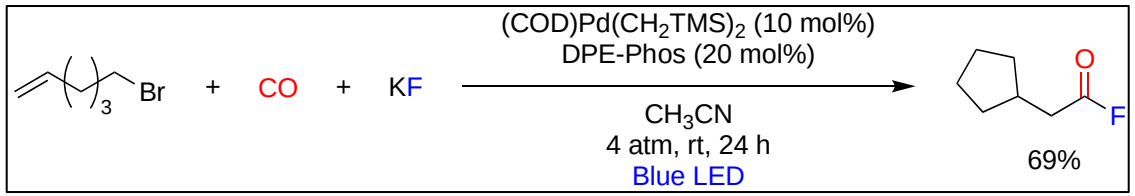
75% 89% 92% 73%

J. Organomet. Chem. **1987**, *334*, 205– 211; *J. Am. Chem. Soc.* **2022**, *144*, 9413–9420.

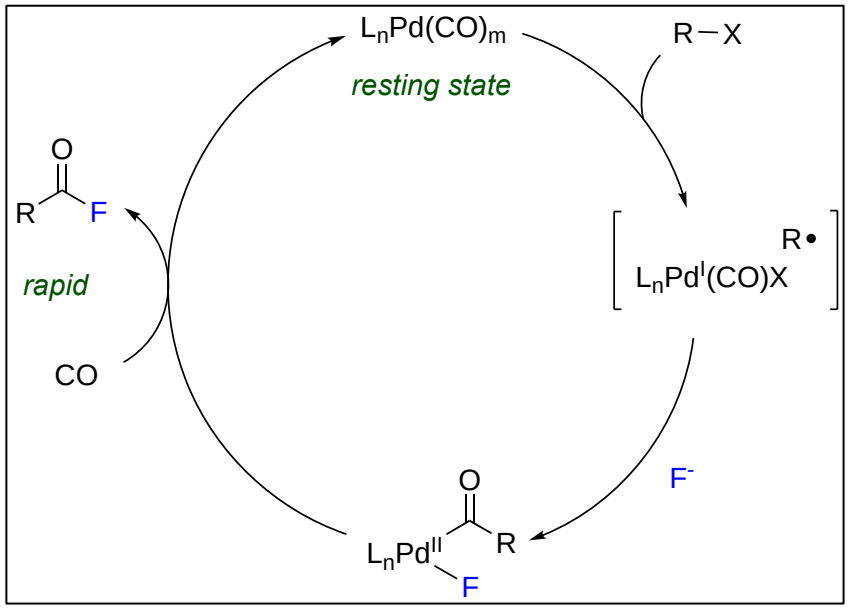
Carbonylation chemistry

Radical clock experiments





^{1}H- and ^{31}P-NMR analyses show that $L_nPd(CO)_m$ is the major catalyst resting state.



CO appears to stabilize photoactive species upon reductive elimination.

J. Am. Chem. Soc. **2022**, *144*, 9413–9420.

Conclusion and Outlook

- **Conclusion:**
  - Visible light-mediated palladium catalysis is an effective strategy for accelerating elementary steps
  - Due to the formation of aryl/allyl/alkyl hybrid Pd radical species, deleterious pathways, such as B-H hydride elimination, can be avoided.
  - This chemistry is uniquely effective at performing reactions where ground state palladium catalysis often fails.
- **Outlook:**
  - Although computation studies have implicated a aryl/allyl/alkyl hybrid Pd radical species, there is no direct evidence of such an intermediate.
  - Demonstration of *unique* reactivity.
  - Pd(0)/Pd(II) cycles have been investigated the most; what about Pd(II)/Pd(IV)?

Reviews followed

Palladium Catalysis

International Edition: DOI: 10.1002/anie.201813523
German Edition: DOI: 10.1002/ange.201813523

Catalysis with Palladium Complexes Photoexcited by Visible Light

*Padon Chuentragool[†], Daria Kurandina[†], and Vladimir Gevorgyan**

Photochemistry

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doi.org/10.1002/anie.202311972

Recent Advances in Visible Light Induced Palladium Catalysis

*Sumon Sarkar, Kelvin Pak Shing Cheung, and Vladimir Gevorgyan**

Light-Driven Palladium-Radical Hybrid Species: Mechanistic Aspects and Recent Examples

Guilherme A. M. Jardim*
Juliana A. Dantas
Amanda A. Barboza
Márcio W. Paixão*
Marco A. B. Ferreira*

Angew. Chem. Int. Ed. **2019**, *58*, 11586; *Angew. Chem. Int. Ed*. **2024**, *63*, e202311972; *Synthesis* **2022**, *54*, 4629-4645.

Questions?