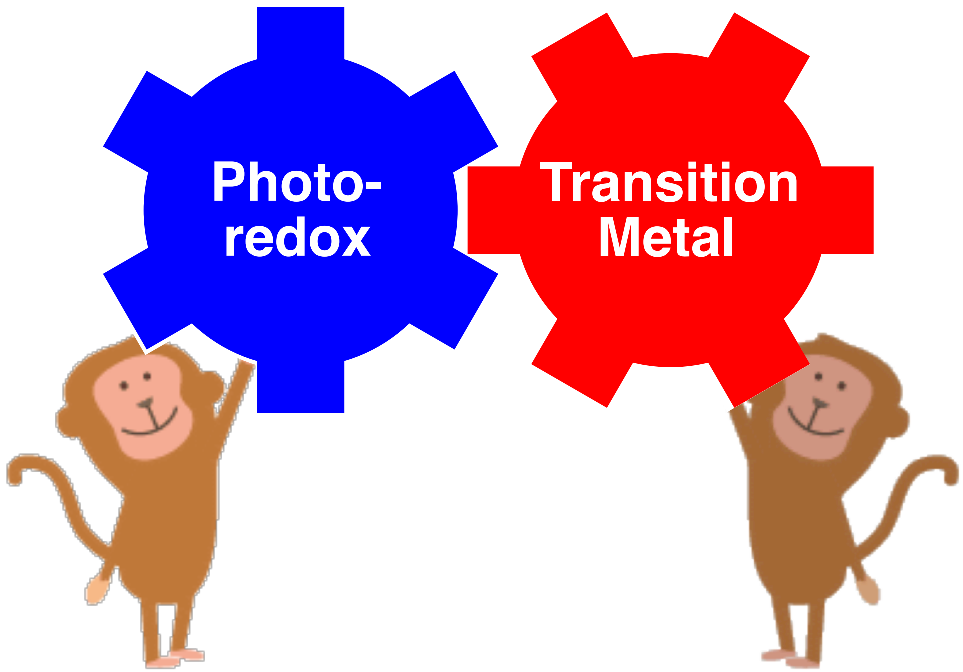
“Metallaphotoredox Catalysis”

(Including my work in Shū Kobayashi group from Oct. 2013 to Aug. 2015)



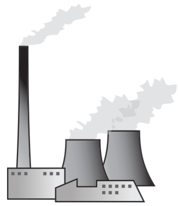
Tatsuhiro Tsukamoto

Literature Talk: Jan. 6th, 2016

the Dong group

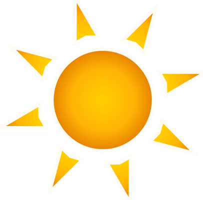
Contents

Visible Light as a Promising Energy Source



Fossil Fuels

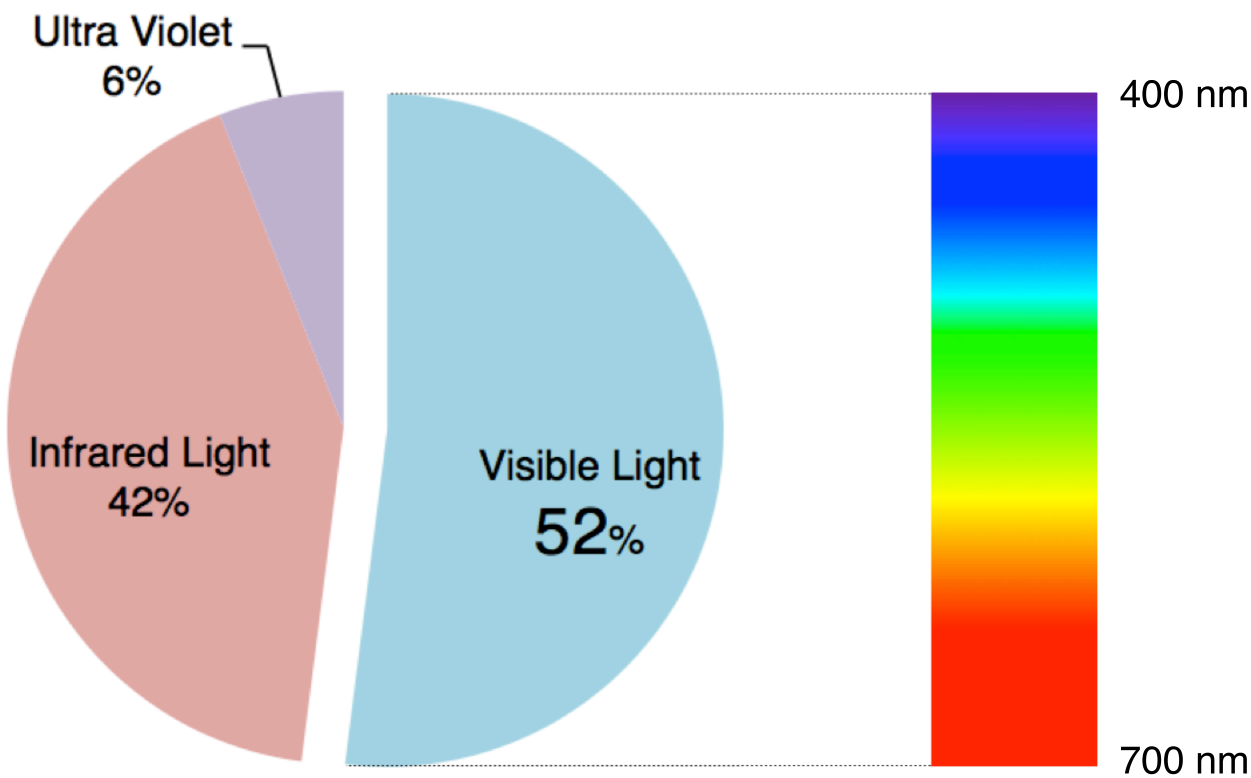
–is non-renewable, hazardous
–will be no longer available



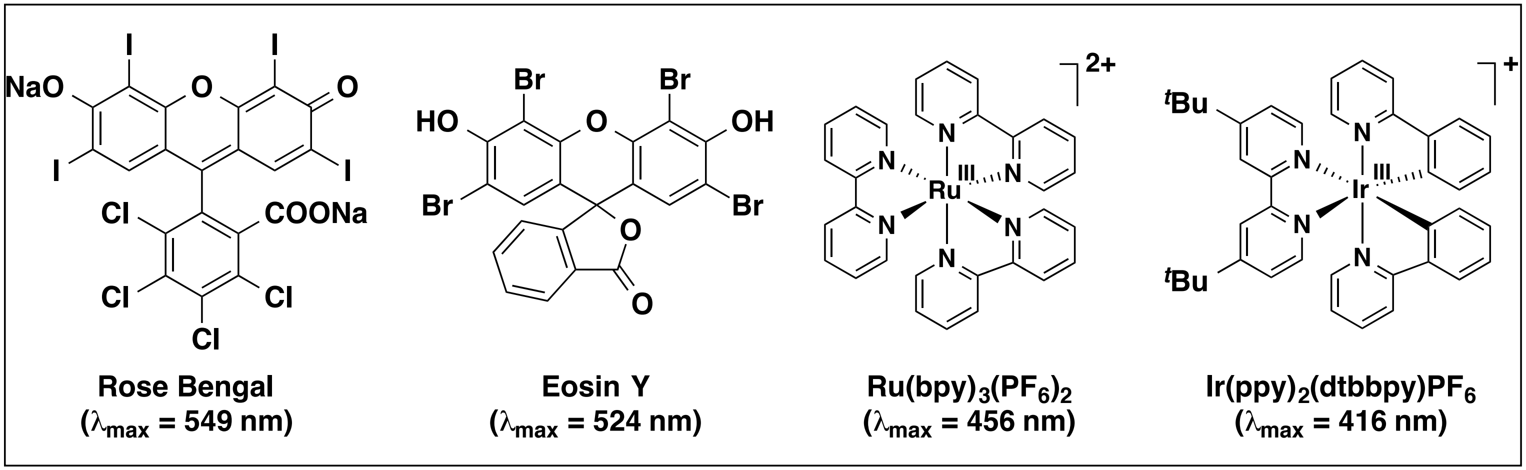
Sunlight

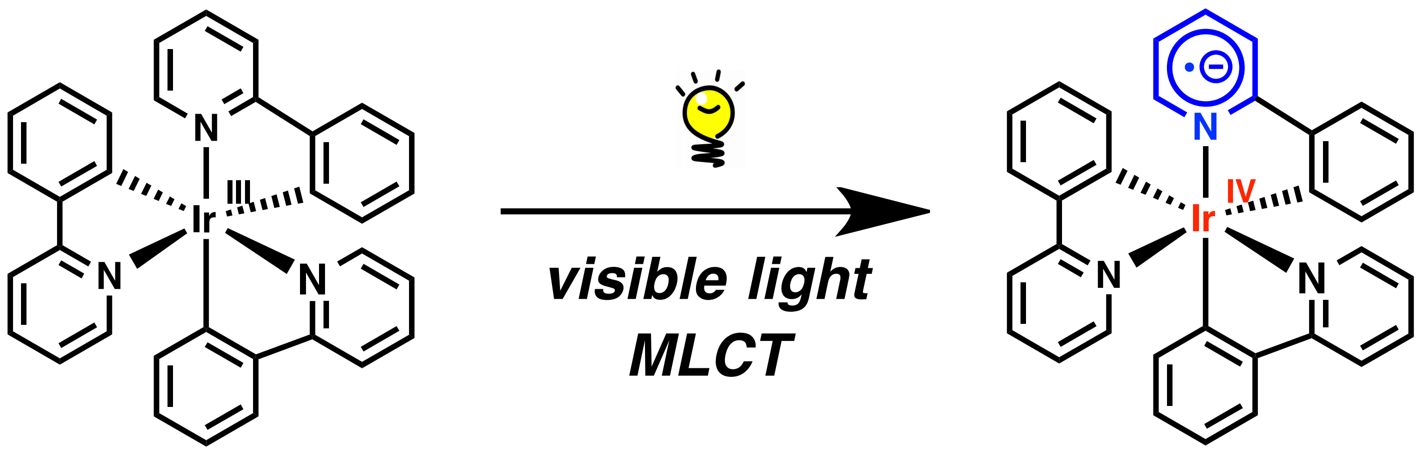
–nearly limitless energy

Solar Energy Distribution



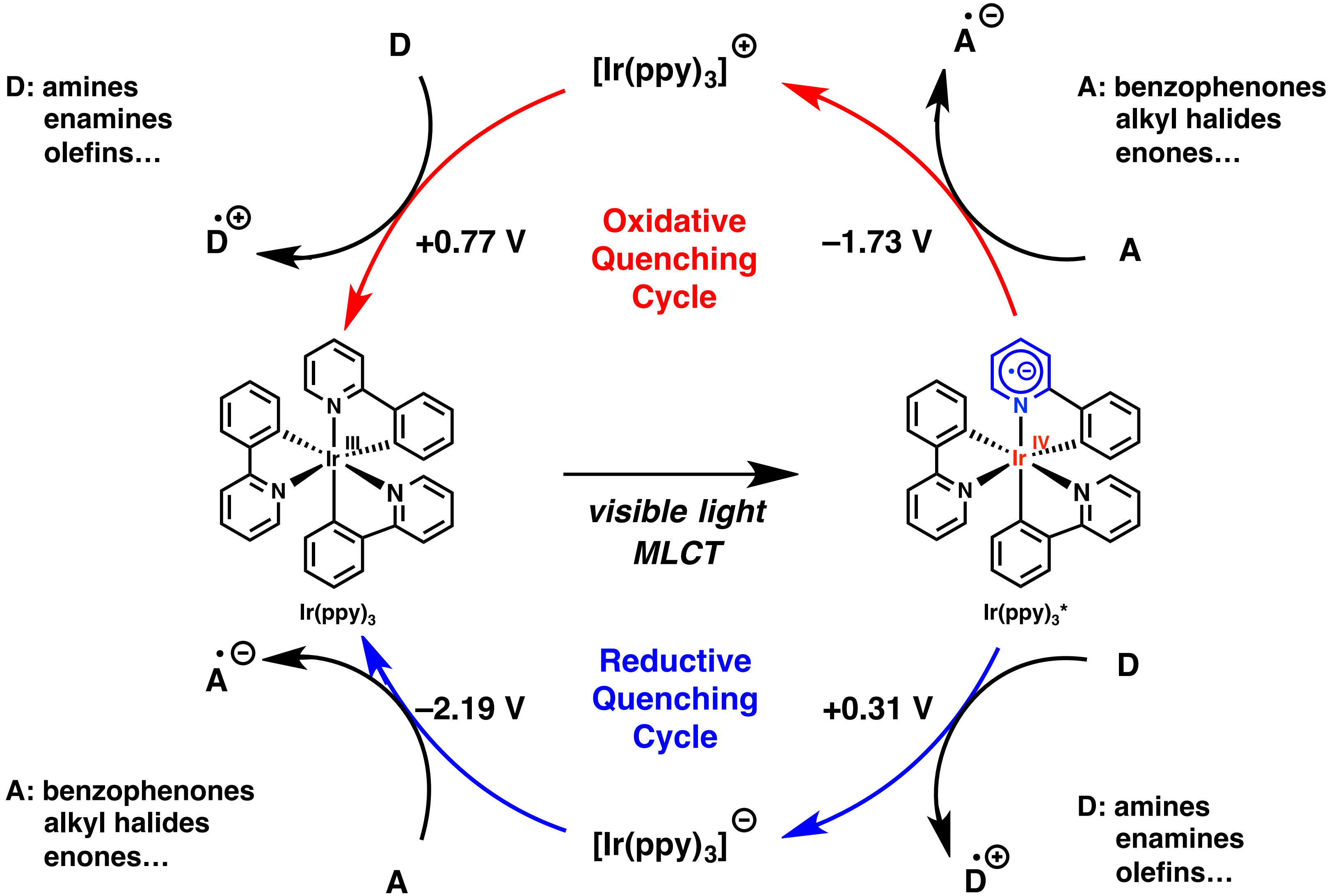
Photoredox Catalyst as Redox Mediator





❑ Irradiated photoredox catalyst works as both **oxidant** and **reductant**.

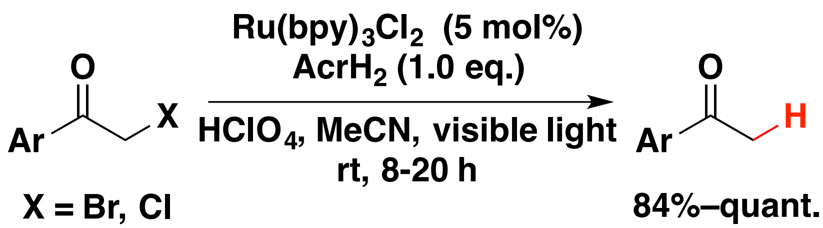
Visible Light Photoredox Catalysis

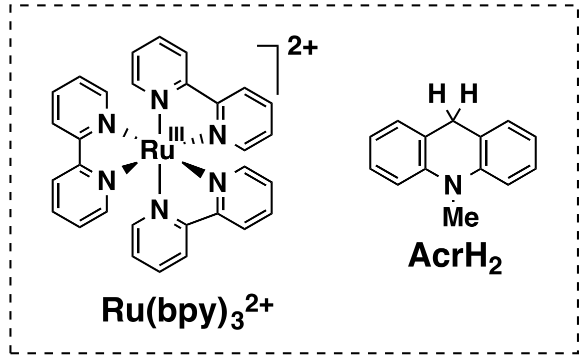


C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322.

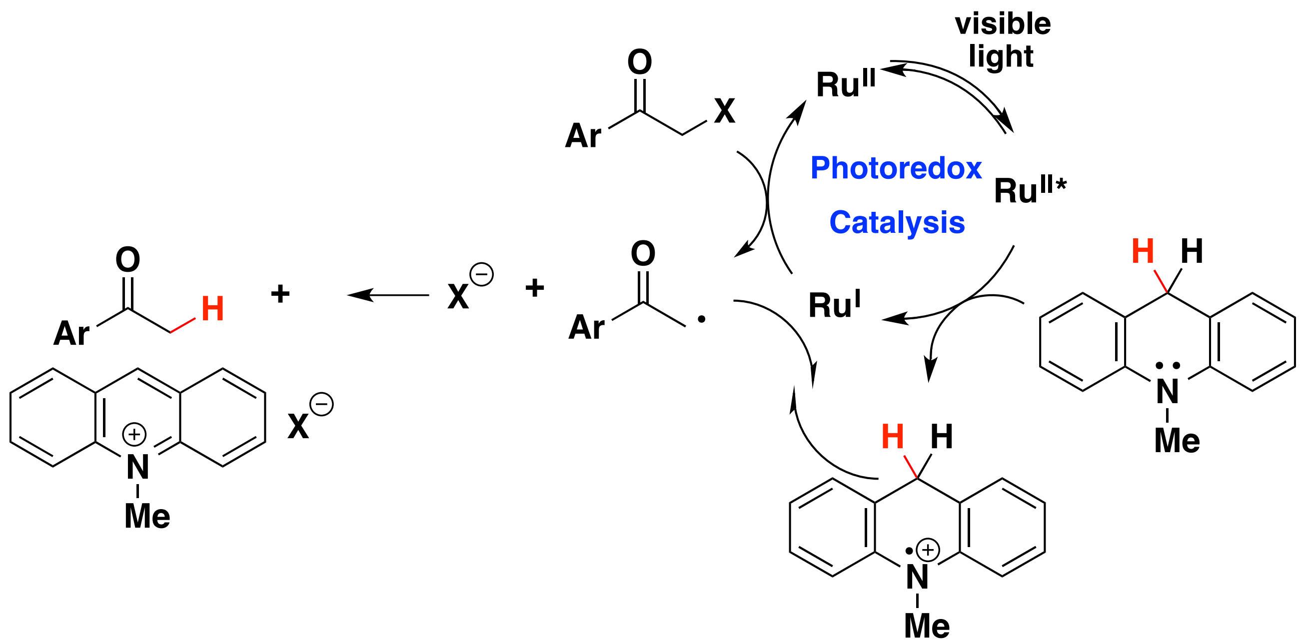
Photoredox Reactions

■ Reductive



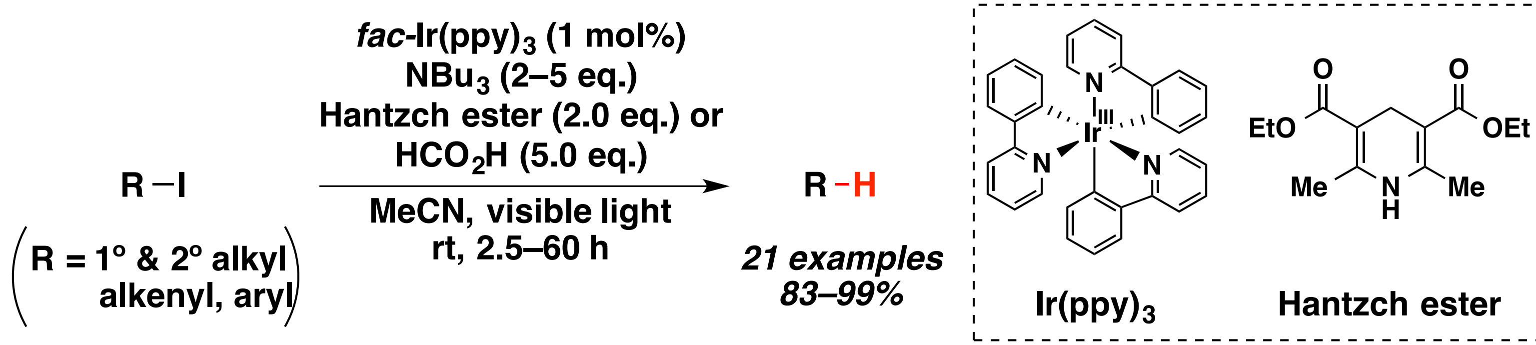


S. Fukuzumi, S. Mochizuki, T. Tanaka, *J. Phys. Chem*. **1990**, *94*, 722.

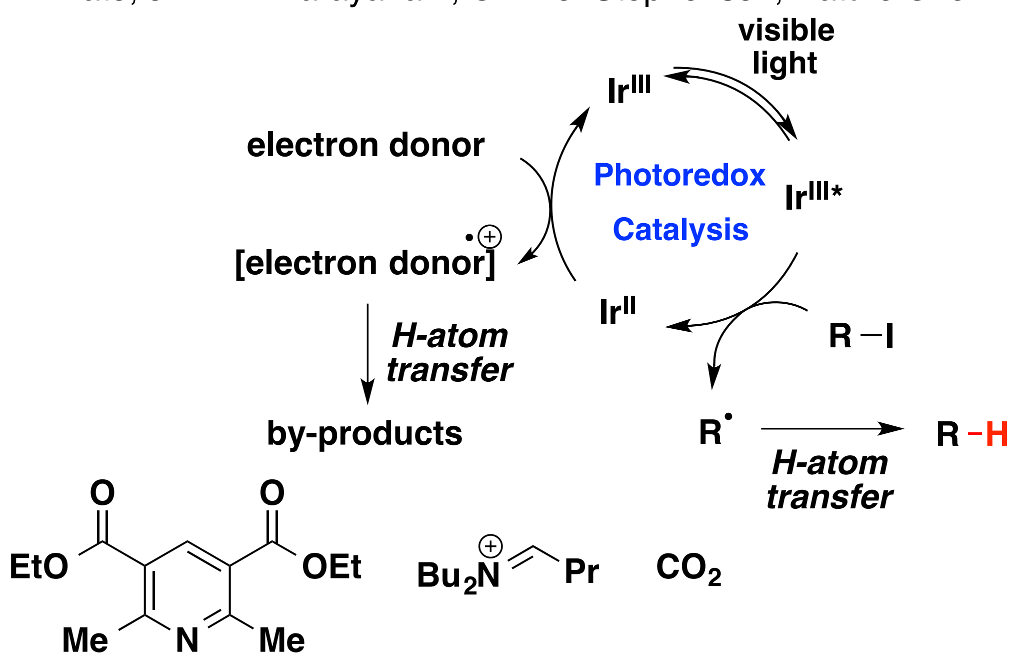


Photoredox Reactions

■ Reductive

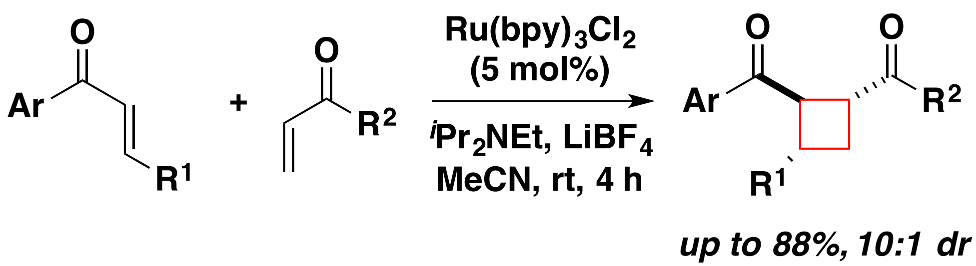


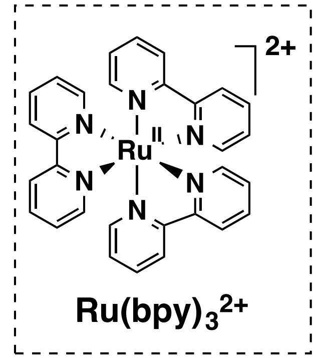
J. D. Nguyen, E. M. D'Amato, J. M. R. Narayanam, C. R. J. Stephenson, *Nature Chem*. **2012**, *4*, 854.



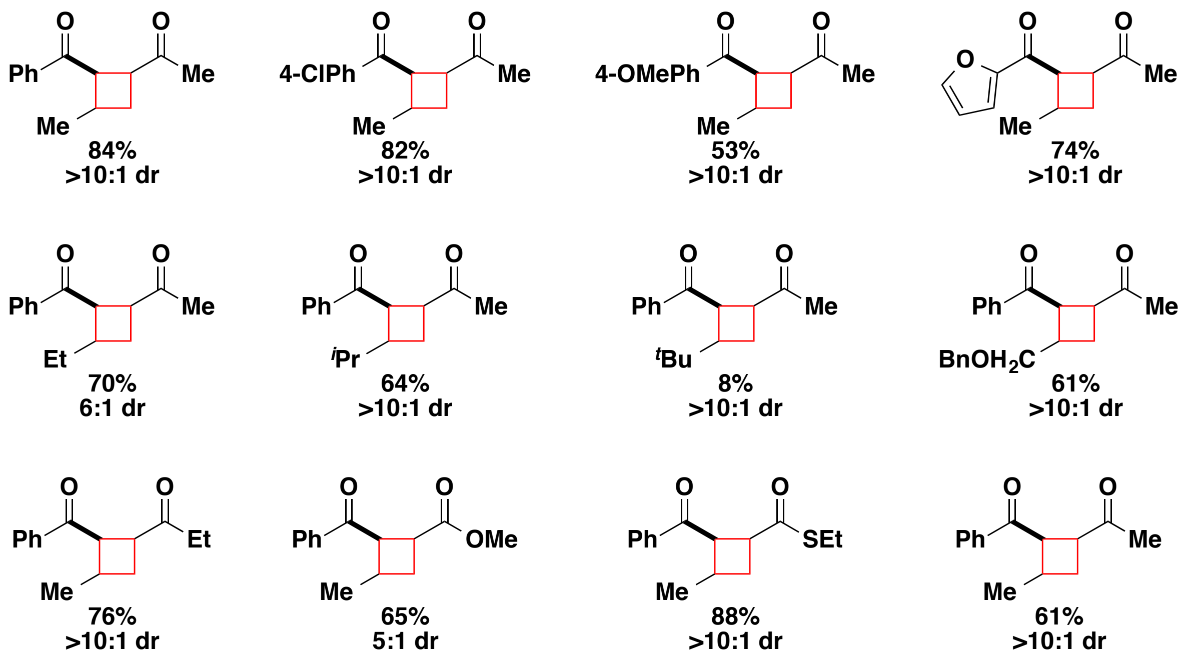
Photoredox Reactions

- Redox-neutral



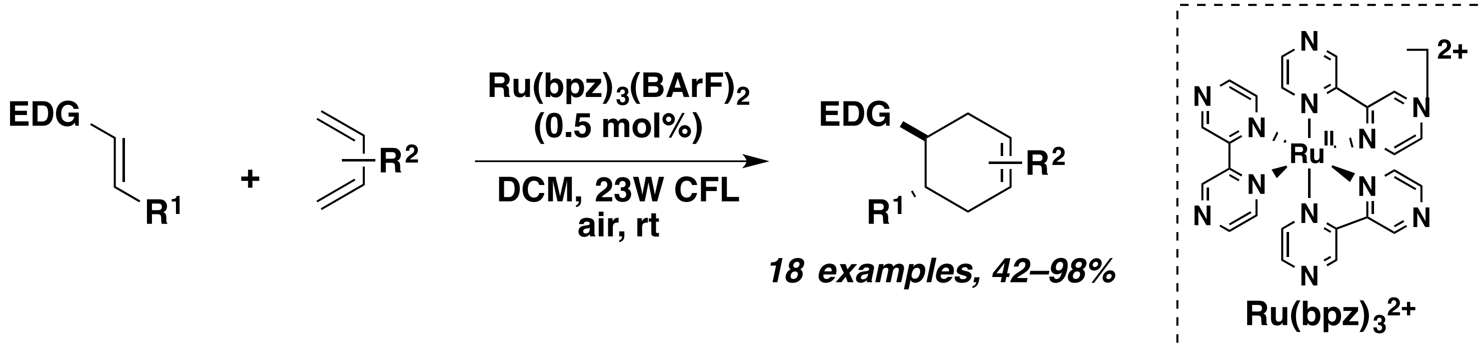


J. Du and T. P. Yoon, *J. Am. Chem. Soc.* **2009**, *131*, 14604.



Photoredox Reactions

■ Redox-neutral



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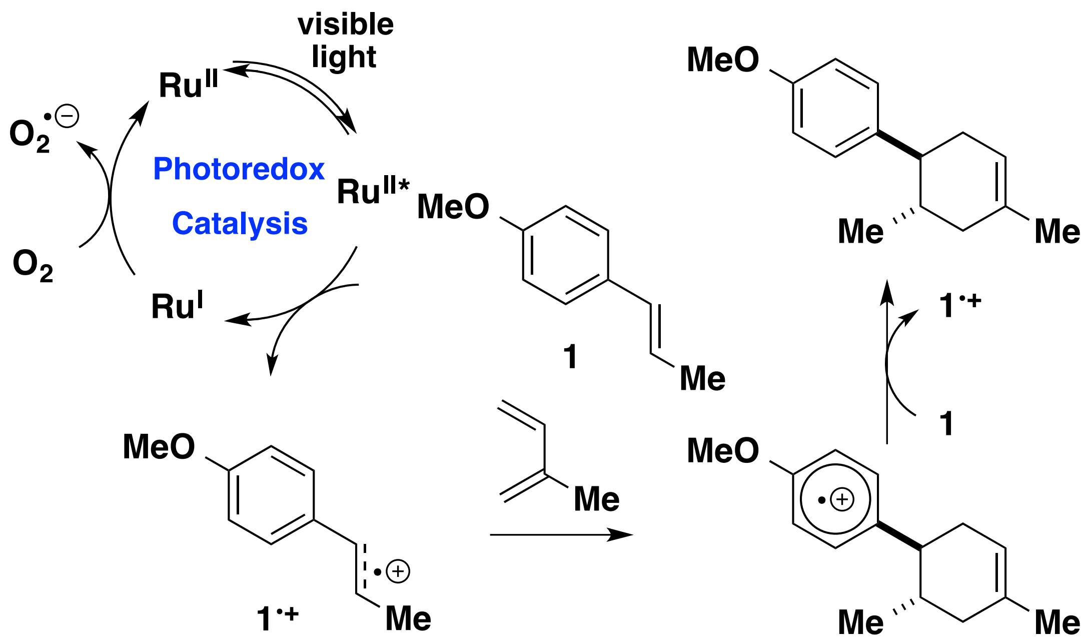
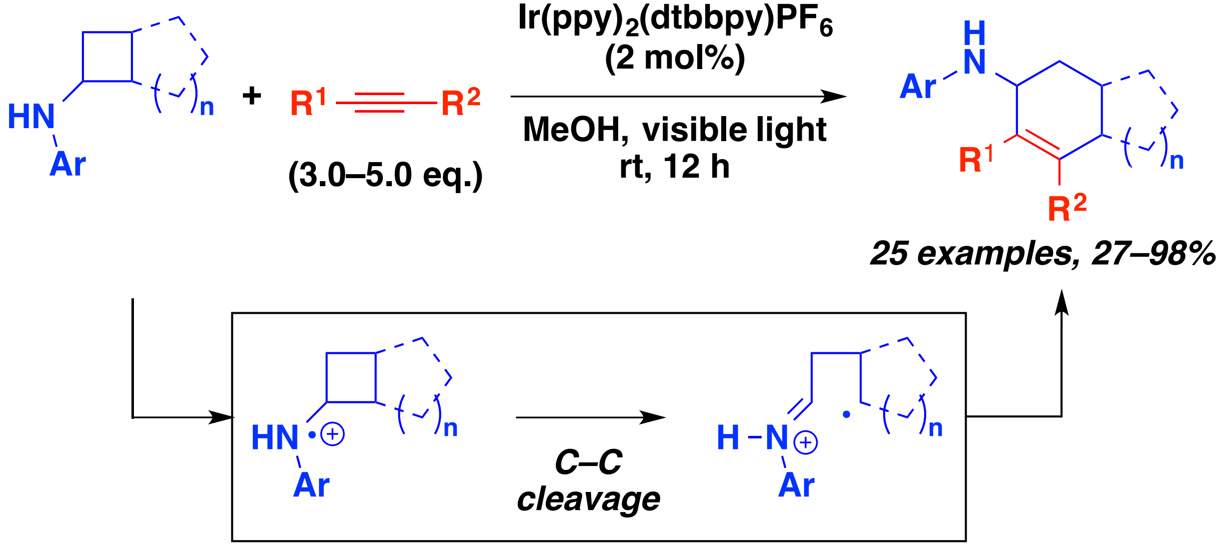
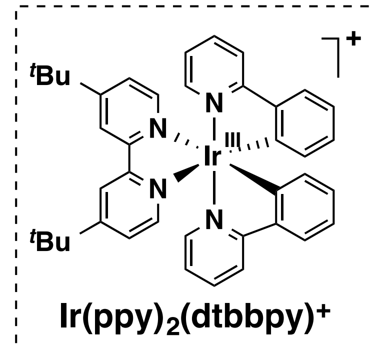


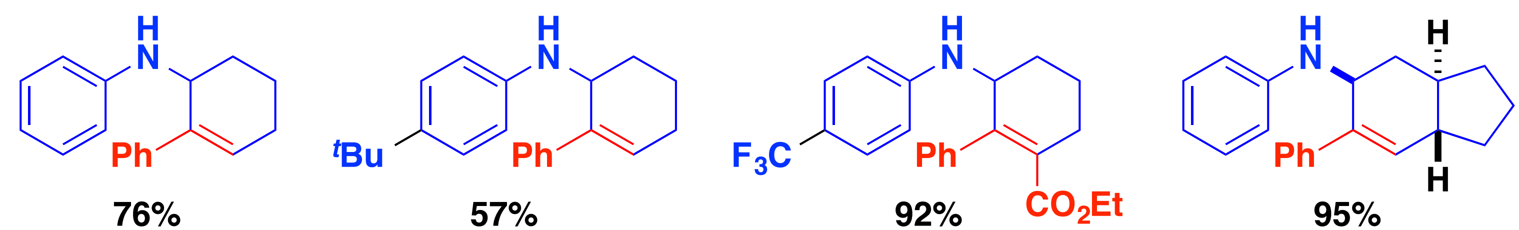
Photoredox Reactions

■ Redox-neutral



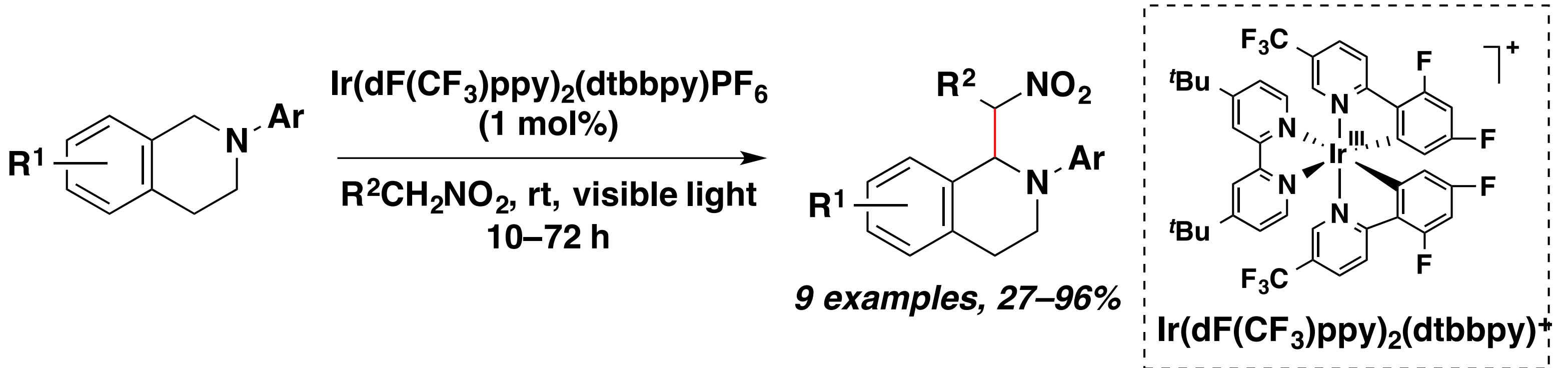


J. Wang, N. Zhang, *Angew. Chem. Int. Ed.* **2015**, *54,* 11424.

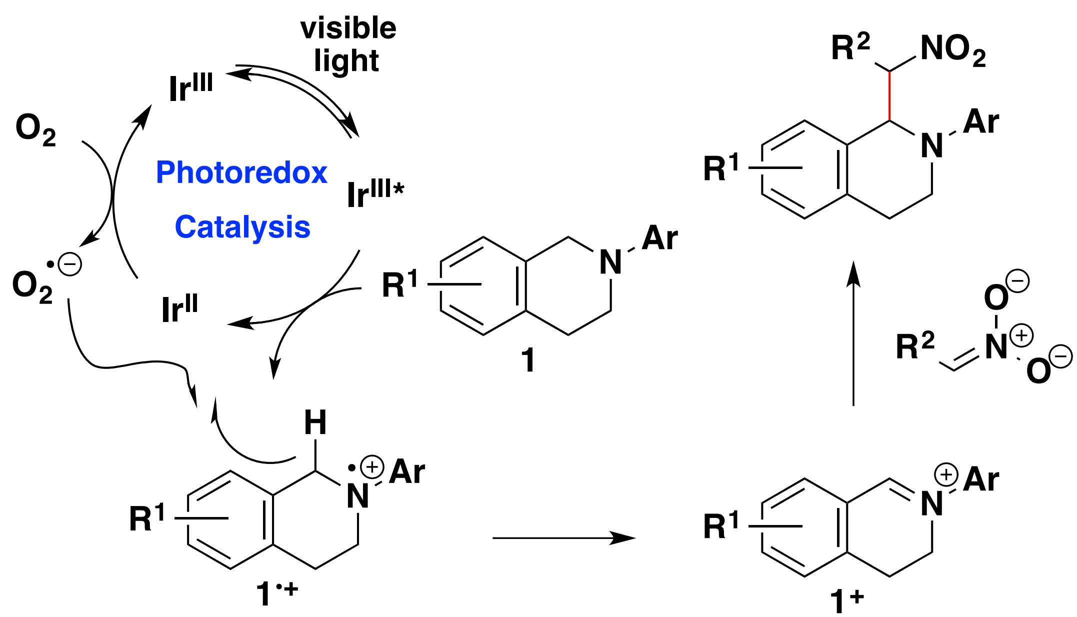


Photoredox Reactions

- **Oxidative**

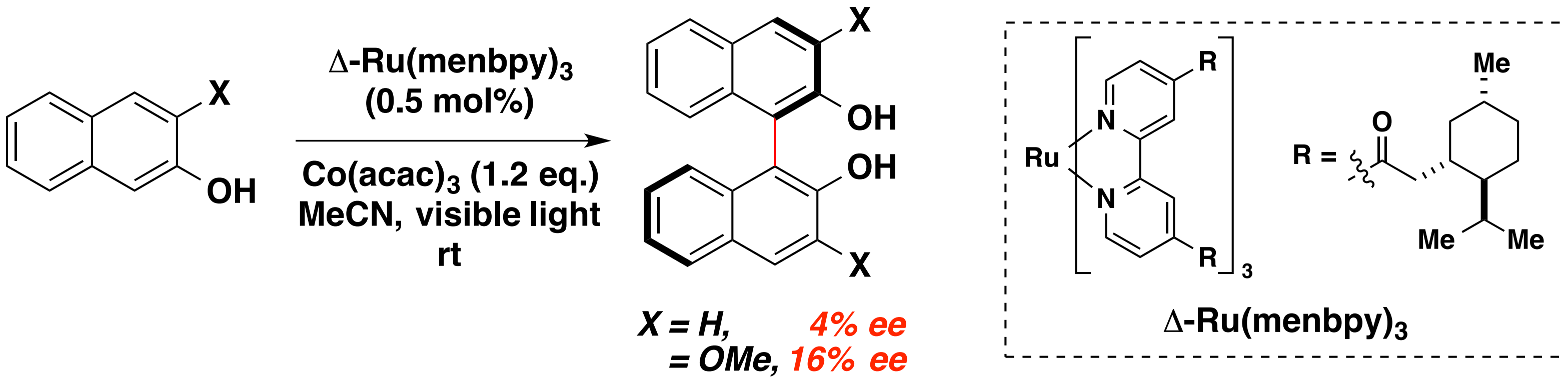


A. G. Condie, J. C. González-Gómez, C. R. J. Stephenson, *J. Am. Chem. Soc*. **2010**, *132*, 1464.

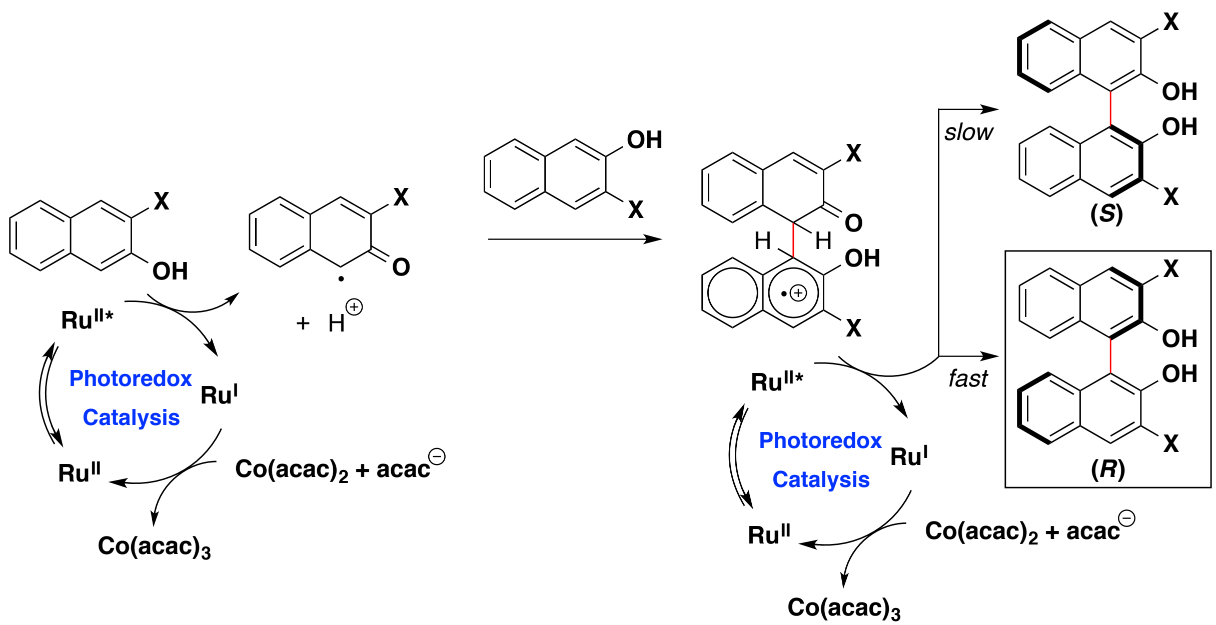


Photoredox Reactions

■ Oxidative

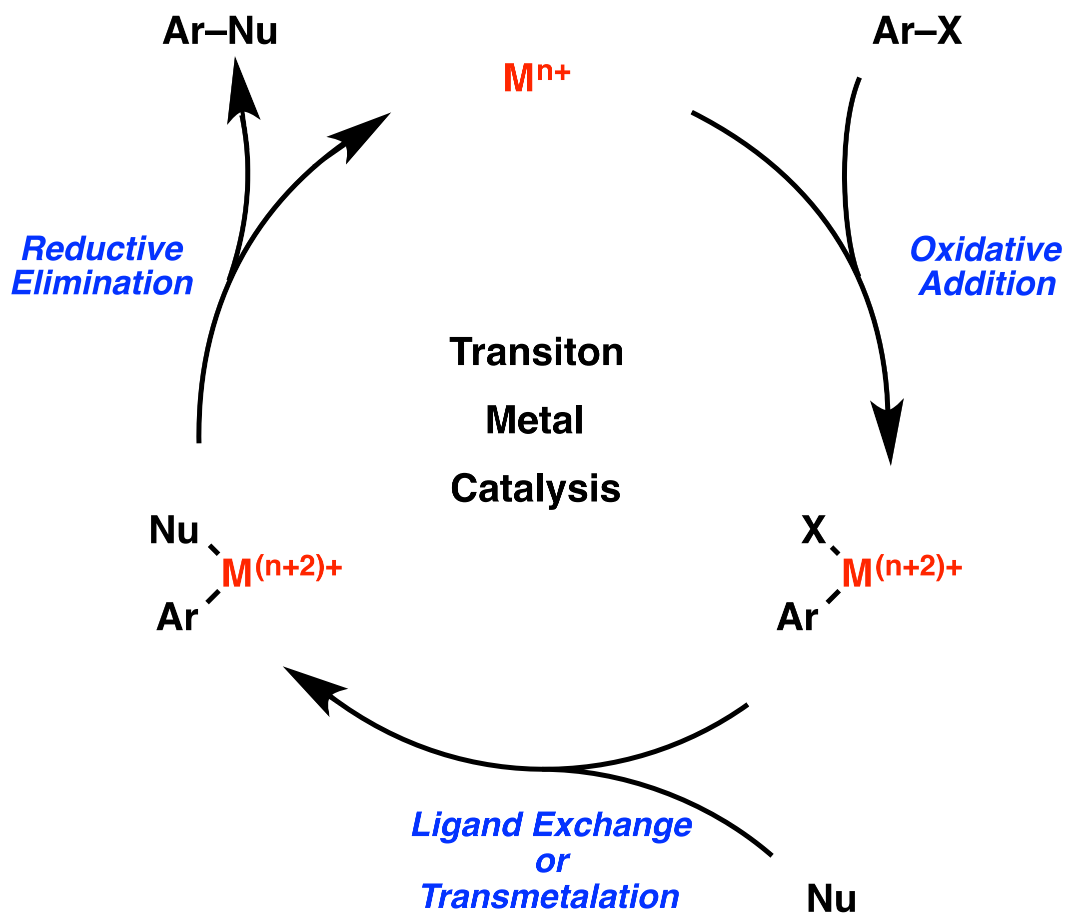


T. Hamada, H. Ishida, S. Usui, Y. Watanabe, K. Tsumura, K. Ohkubo, *J. Chem. Soc. Chem. Commun.* **1993**, 909.



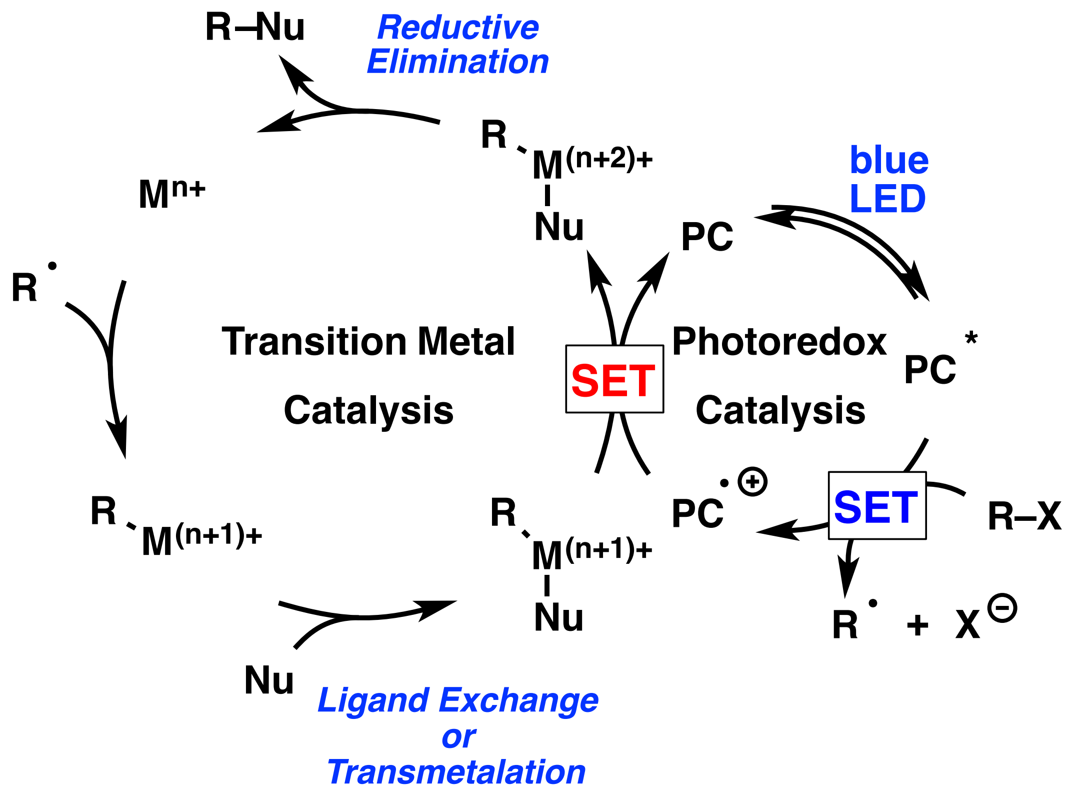
Contents

Transition Metal Catalysis and Photoredox Catalysis



- Two-electron redox pathway

"Metallaphotoredox Catalysis"



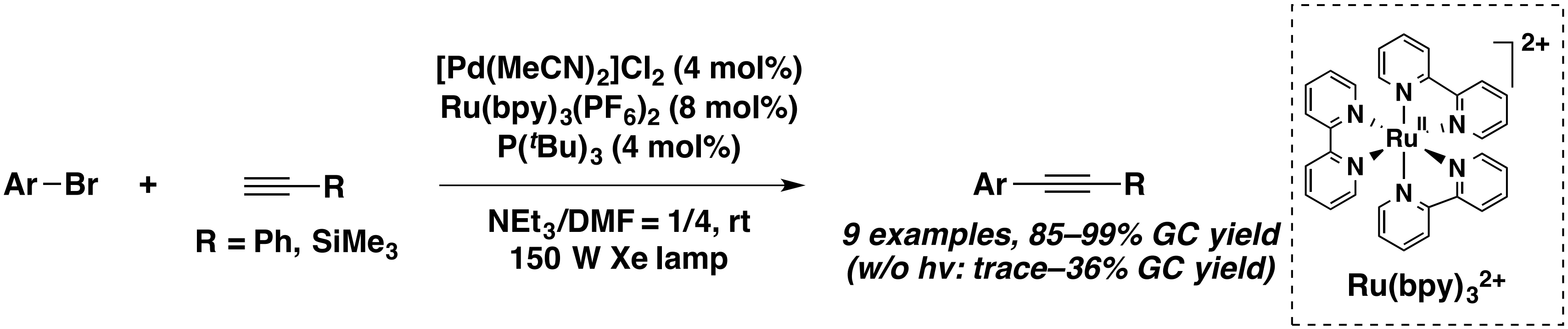
Mechanistic Concept from my previous work

(W.-J.Yoo, T. Tsukamoto, S. Kobayashi, *Org. Lett.* **2015**, *17*, 3640.**)**

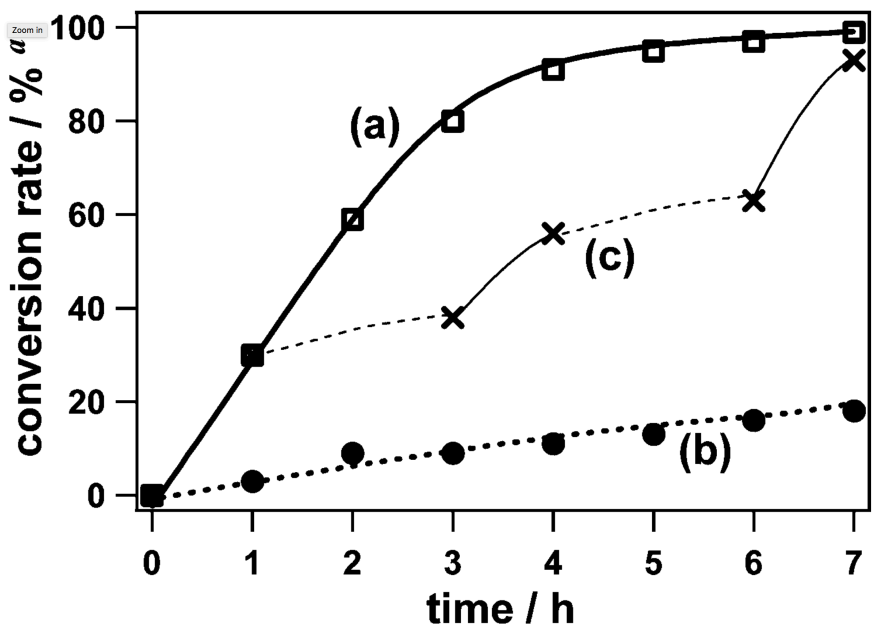
- **Single-electron oxidation of metal species**
- **Single-electron reduction of alkyl halide**

First example in “Metallaphotoredox Catalysis”

■ **Sonogashira coupling**



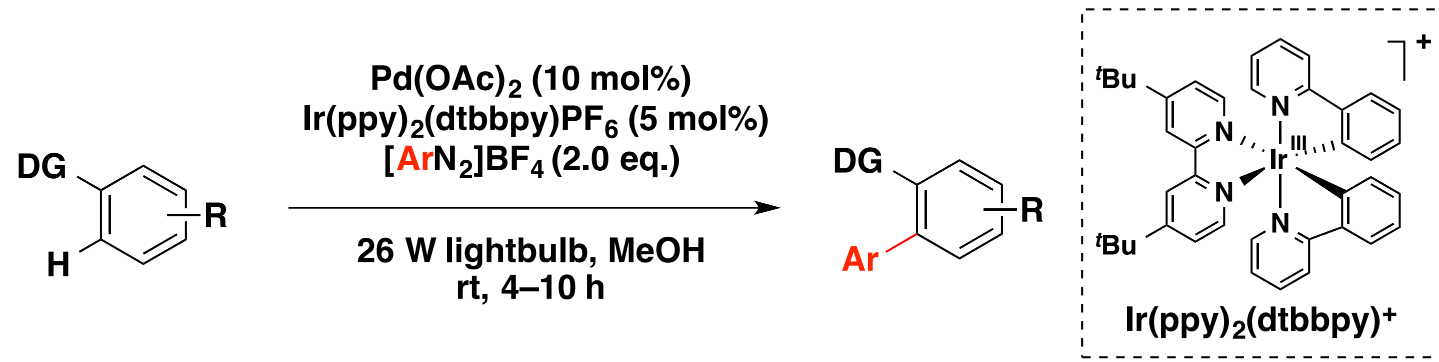
M. Osawa, H. Nagai, M. Akita, *Dalton Trans*. **2007**, 827.



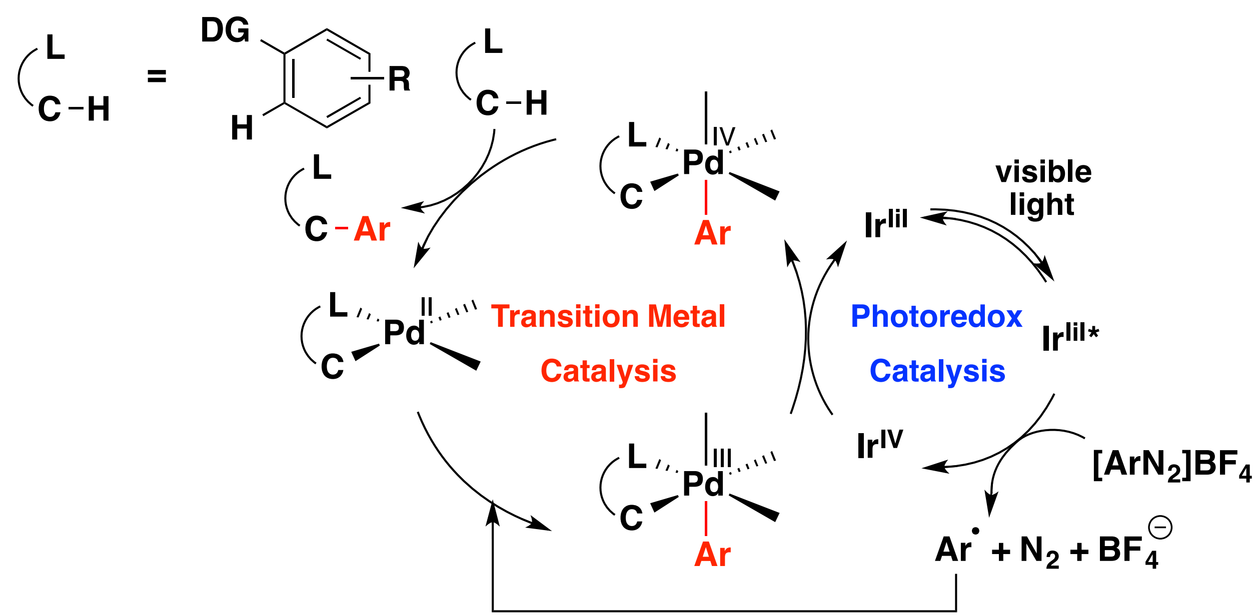
(a): Under light irradiation
(b): Dark (dash line)
(c): On and off

“Metallaphotoredox Catalysis” –Palladium–

■ **Directed C–H activation**

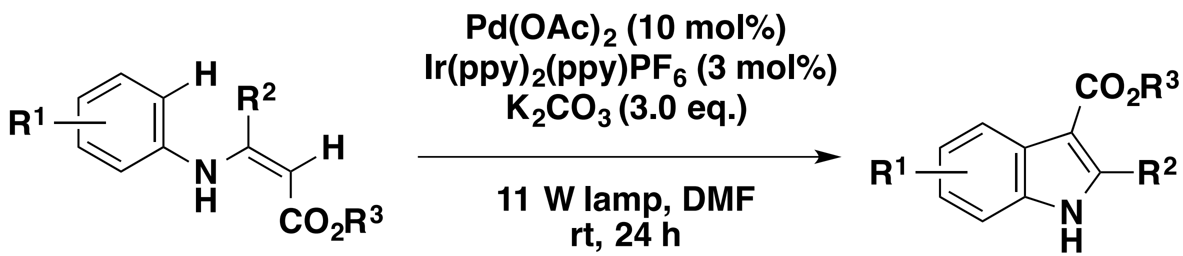


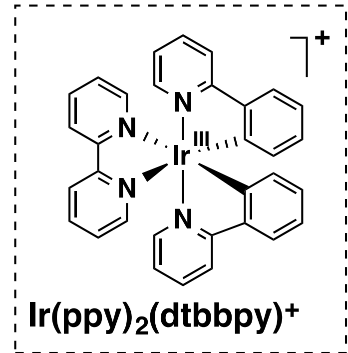
D. Kalyani, K. B. McMurtrey, S. R. Newfeldt, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18566.



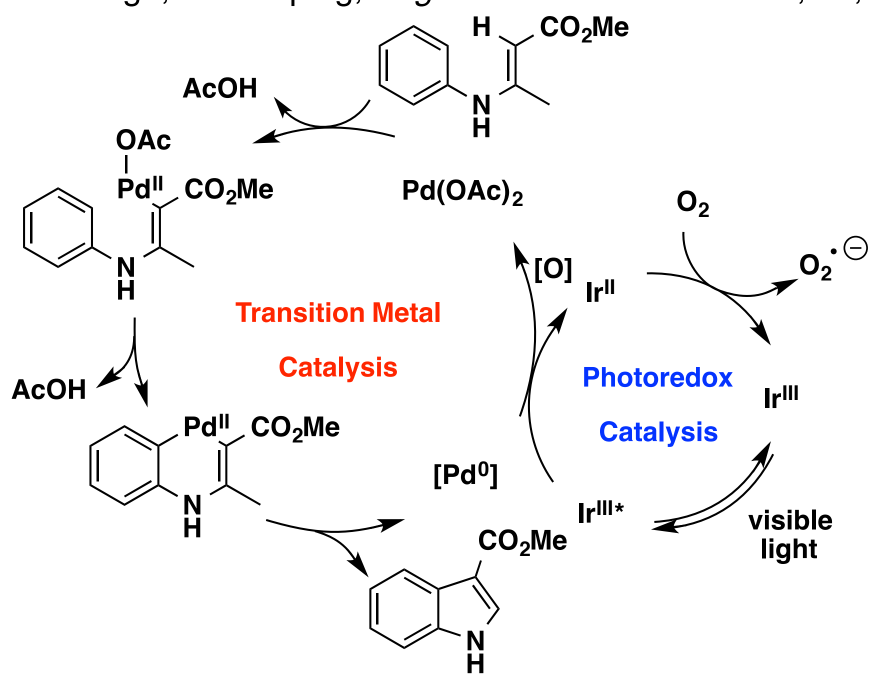
"Metallaphotoredox Catalysis" –Palladium–

■ Cross Dehydrogenative Coupling



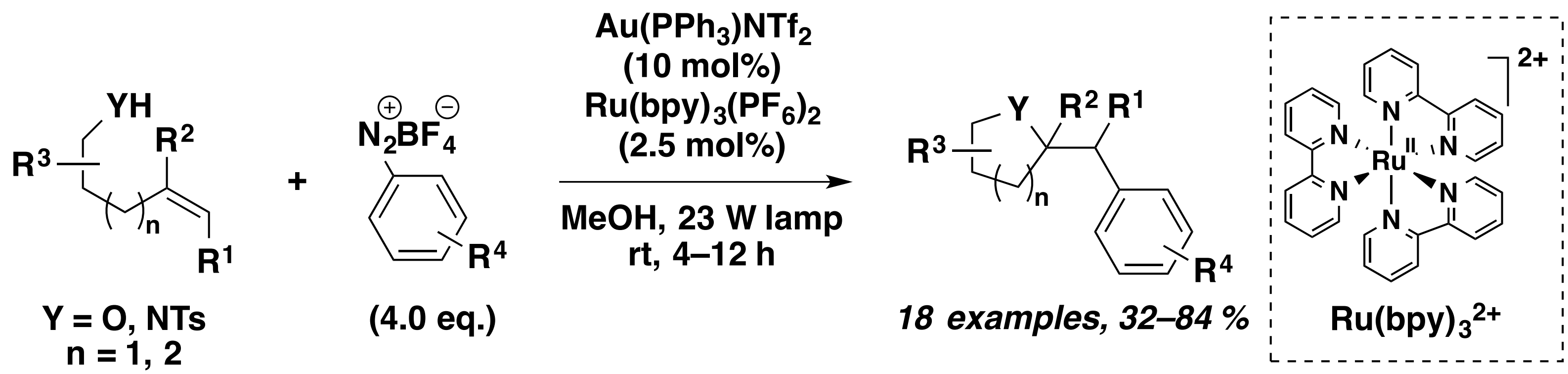


J. Zoller, D. C. Fabry, M. A. Ronge, M. Rueping, *Angew. Chem. Int. Ed.* **2014**, *53*, 13264.

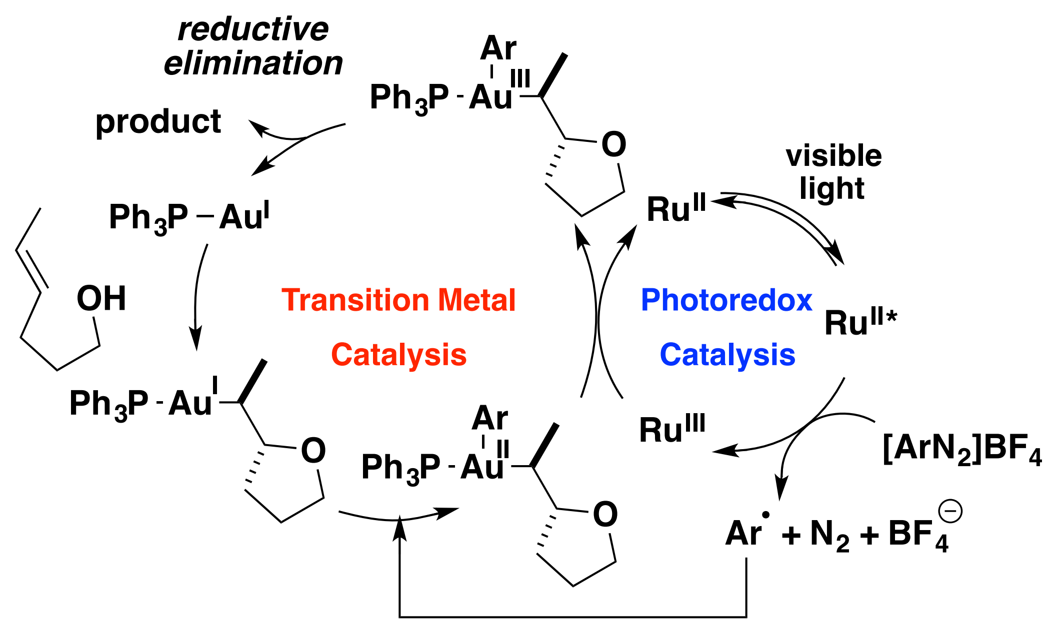


"Metallaphotoredox Catalysis" −Gold−

■ **Redox-neutral Cyclization**

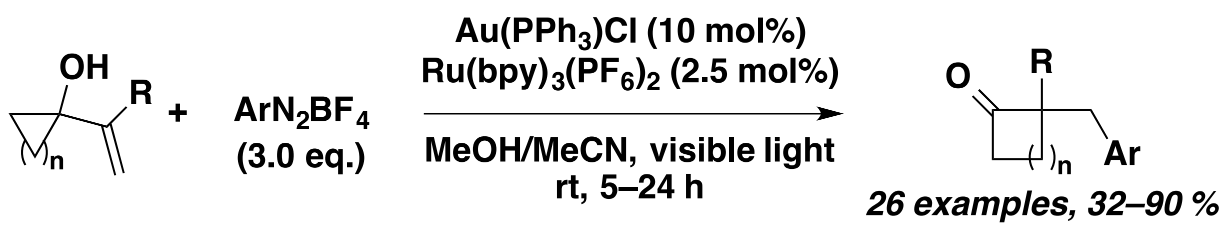


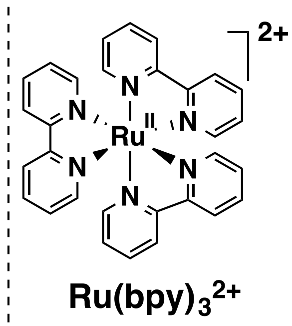
B. Sahoo, M. N. Hopkinson, F. Glorius, *J. Am. Chem. Soc.* **2013**, 1*35*, 5505.



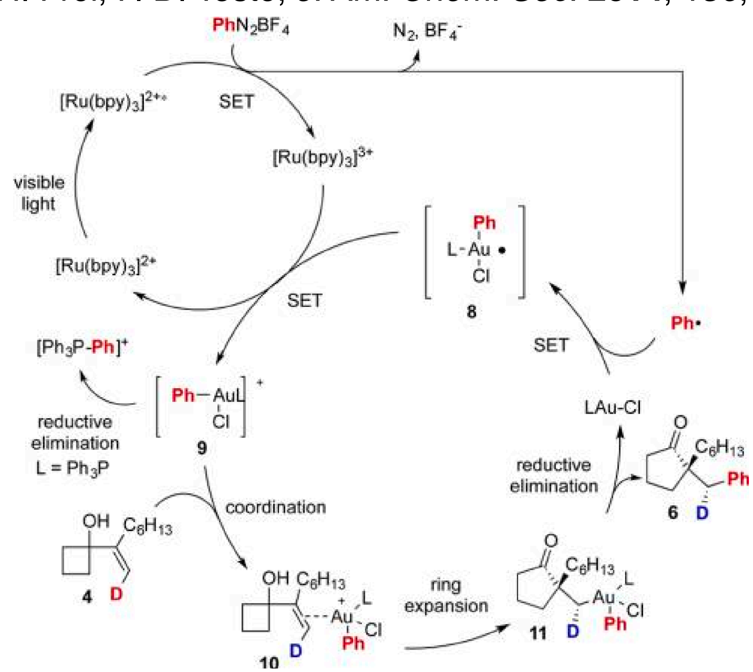
"Metallaphotoredox Catalysis" −Gold−

- Redox-neutral Ring expansion



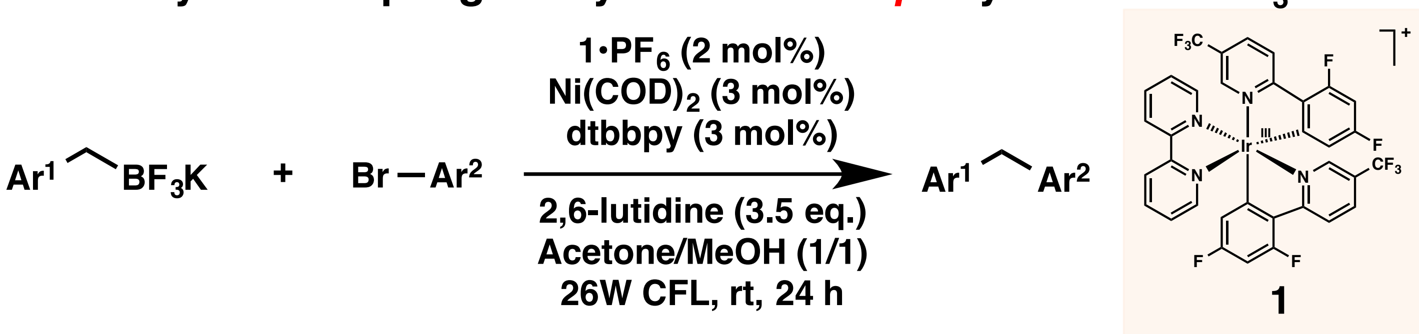


X.-Z. Shu, M. Zhang, Y. He, H. Frei, F. D. Toste, *J. Am. Chem. Soc.* **2014**, 1*36*, 5844.

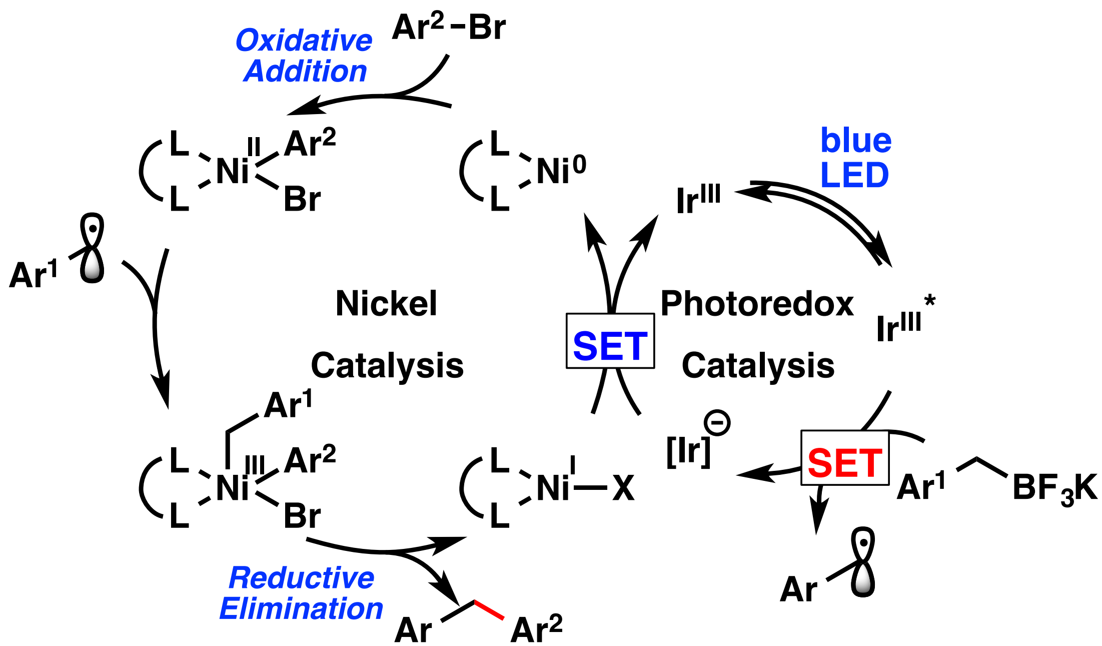


"Metallaphotoredox Catalysis" –Nickel–

■ **Suzuki–Miyaura coupling of aryl halide and *sp³*-hybridized RBF_3K**



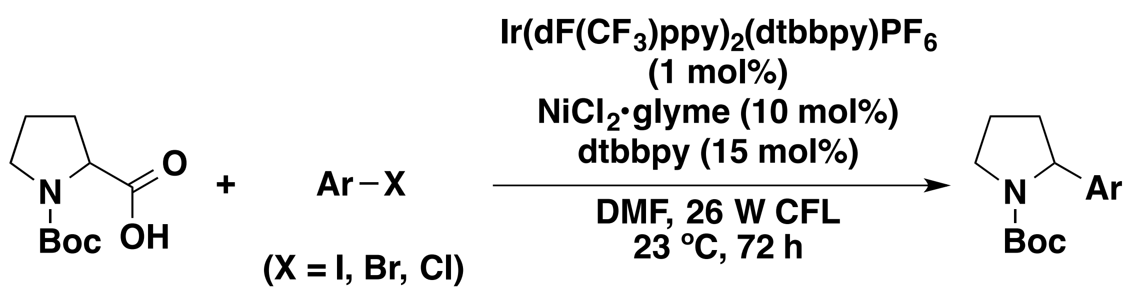
J. C. Tellis, D. N. Primer, G. A. Molander, *Science* **2014**, *345*, 433.

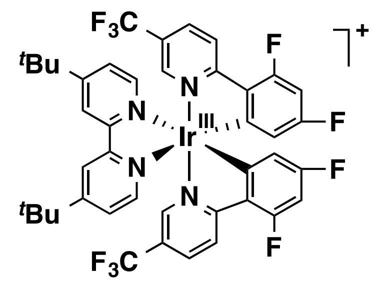


☐ **Driven by the one-electron oxidation of organic molecule.**

“Metallaphotoredox Catalysis” –Nickel–

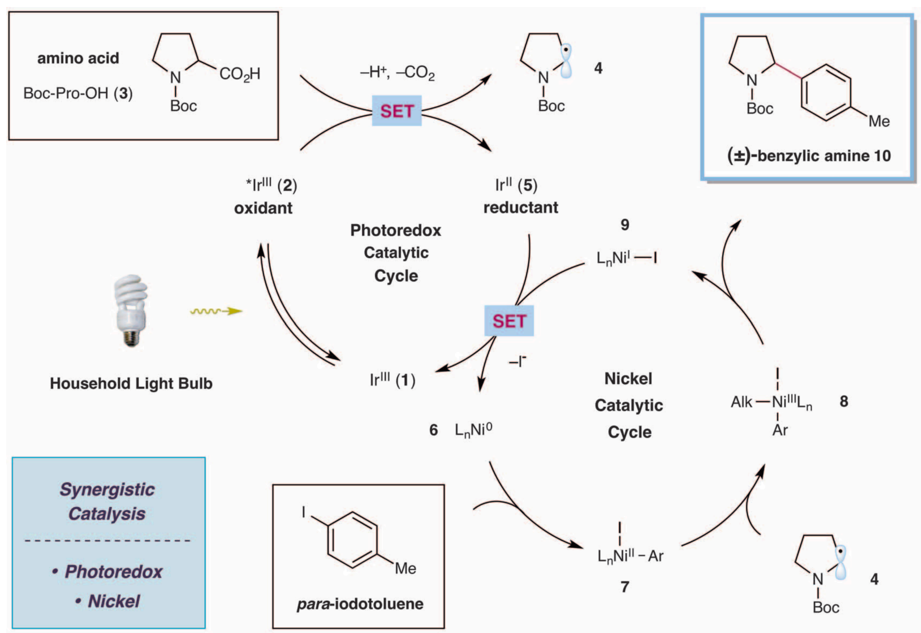
■ **Decarboxylative coupling of α-amino acids and aryl halides**





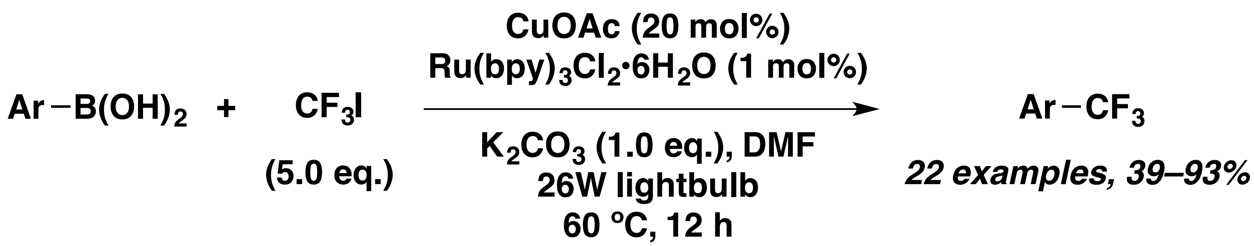
$Ir(dF(CF_3)ppy)_2(dtbbpy)^+$

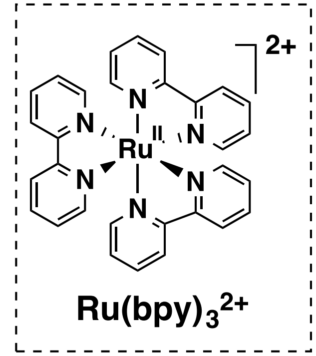
Z. Zuo, D. T. Ahneman, L. Chu, J. A. Terrett, A. G. Doyle, D. W. C. MacMillan, *Science* **2014**, *345*, 437.



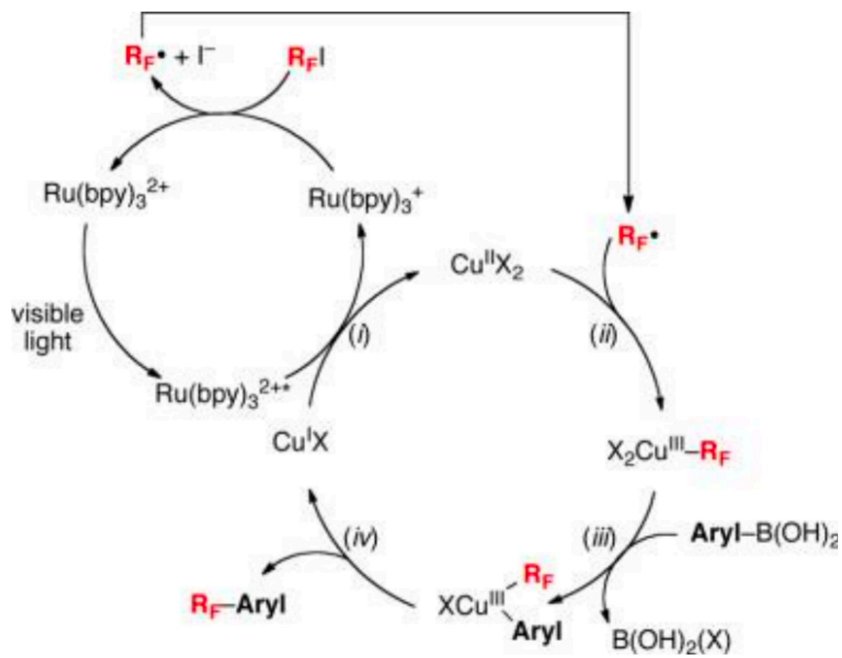
“Metallaphotoredox Catalysis” −Copper−

■ **Trifluoromethylation**





Y. Ye, M. S. Sanford, *J. Am. Chem. Soc.* **2012**, *134*, 9034.



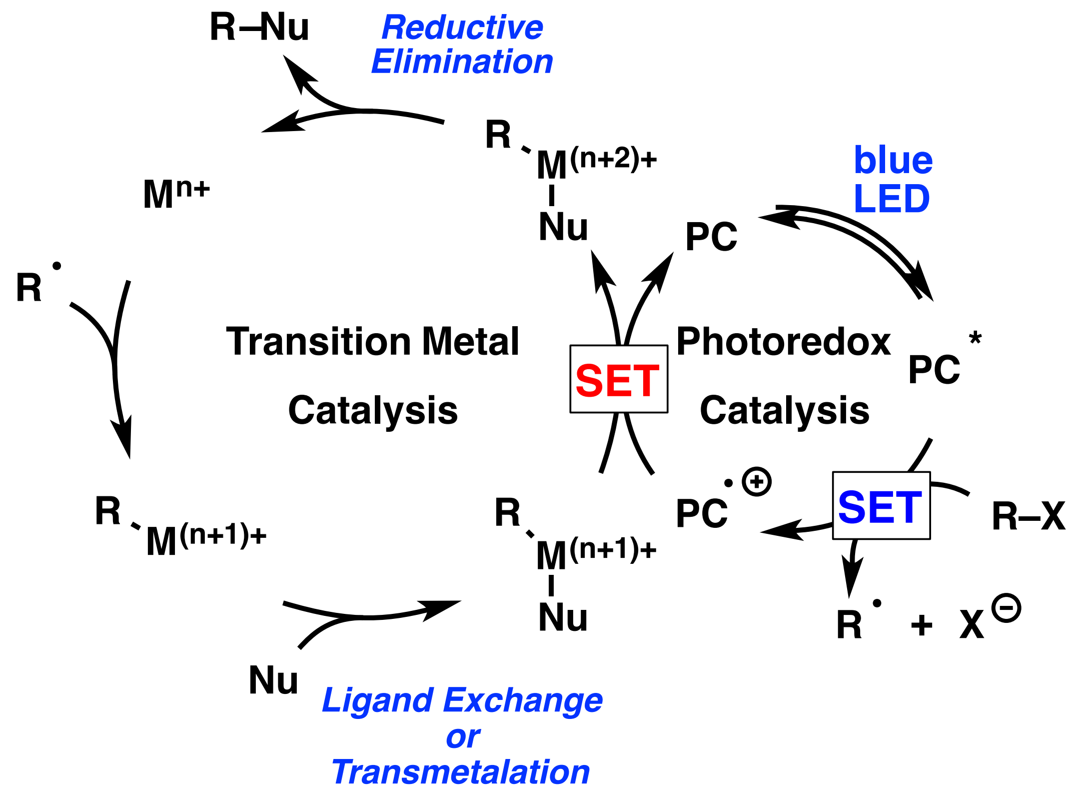
Contents

1. Visible Light Photoredox Catalysis (PC)

2. PC + Transition Metal Catalysis (Ni, Pd, Pt, Cu)

3. **My Previous Work (PC + Cu)**

“Metallaphotoredox Catalysis”



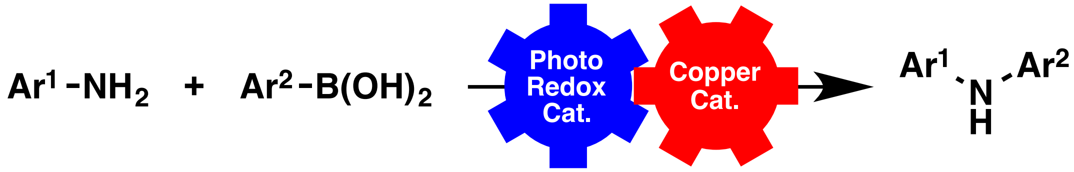
Mechanistic Concept from my previous work

(W.-J.Yoo, T. Tsukamoto, S. Kobayashi, *Org. Lett.* **2015**, *17*, 3640.**)**

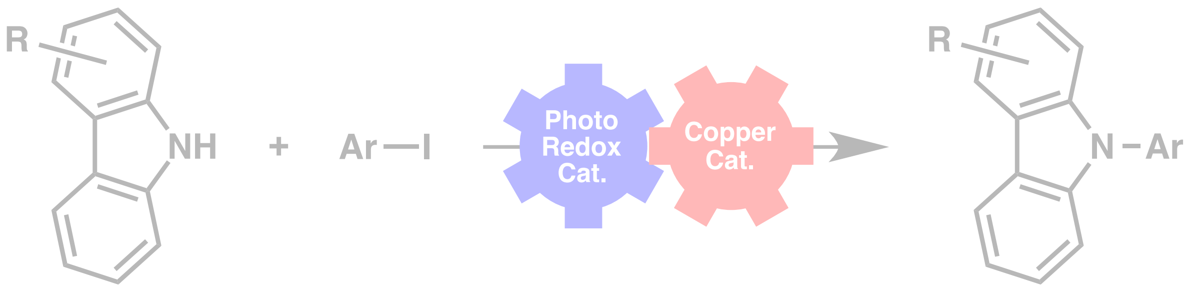
- ☐ **Single-electron oxidation of metal species**
- ☐ **Single-electron reduction of alkyl halide**

Topics

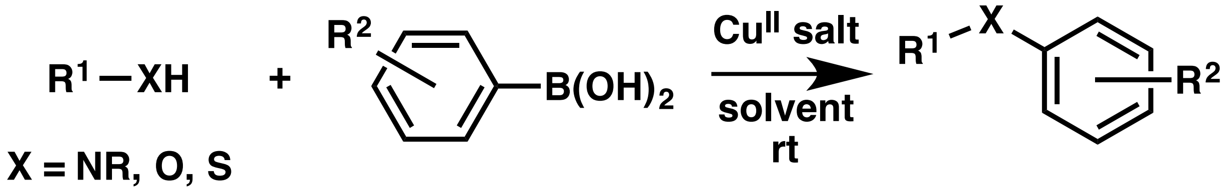
1. Visible-Light-Mediated Chan–Lam Coupling Reaction



2. Visible-Light-Mediated C–N Ullmann-type Coupling Reaction

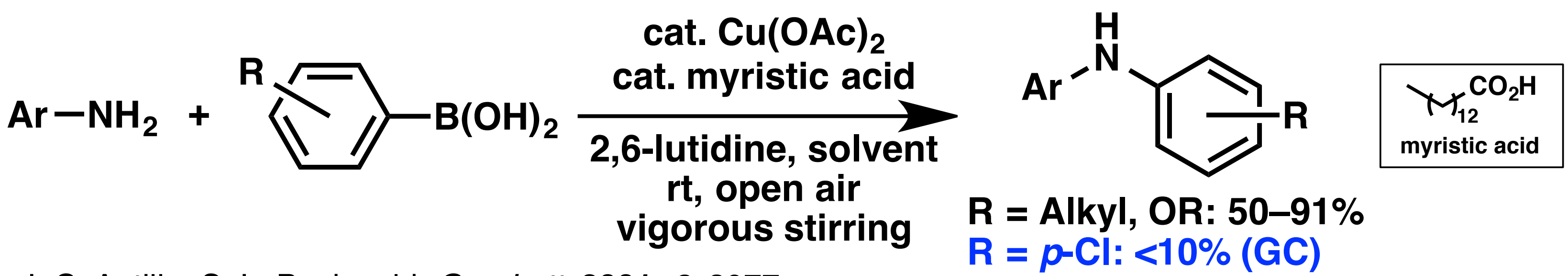


Chan-Lam Coupling Reactions (1)



D. M. T. Chan, K. L. Monaco, R.-P. Wang, M. P. Winters, *Tetrahedron Lett*. **1998**, *39*, 2933.
D. A. Evans, J. L. Katz, T. R. West, *Tetrahedron Lett*. **1998**, *39*, 2937.
P. Y. S. Lam, C. G. Clark, S. Saubern, J. Adams, M. P. Winters, D. M. T. Chan, A. Combs, *Tetrahedron Lett*. **1998**, *39*, 2933.

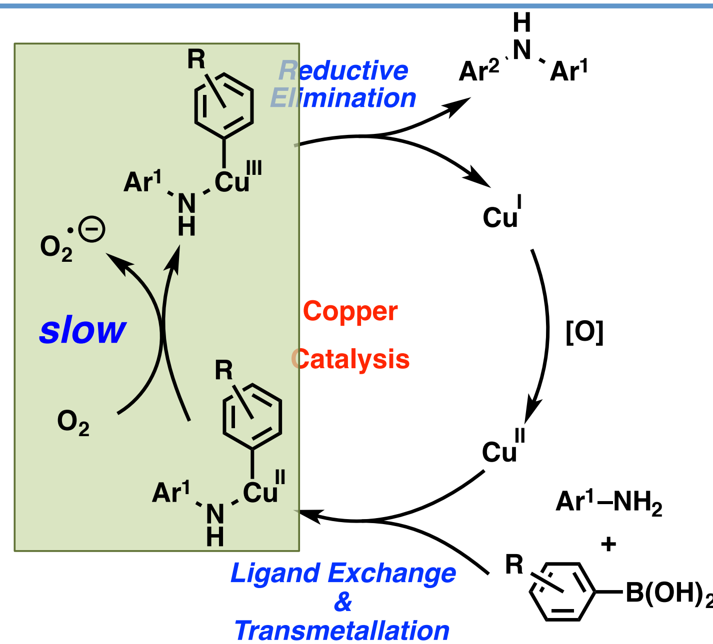
- **Stoichiometric Cu^{II} salt**

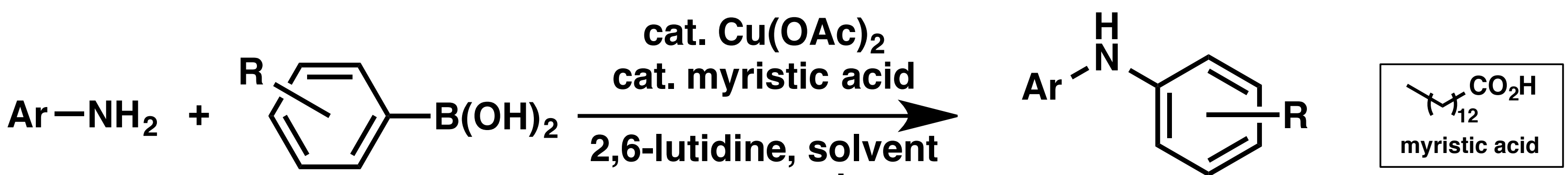


J. C. Antilla, S. L. Buchwald. *Org. Lett*. **2001**, *3*, 2077.

- **Catalytic amount of Cu^{II} species**
- **Limited substrate scope**

Chan-Lam Coupling Reactions (1)





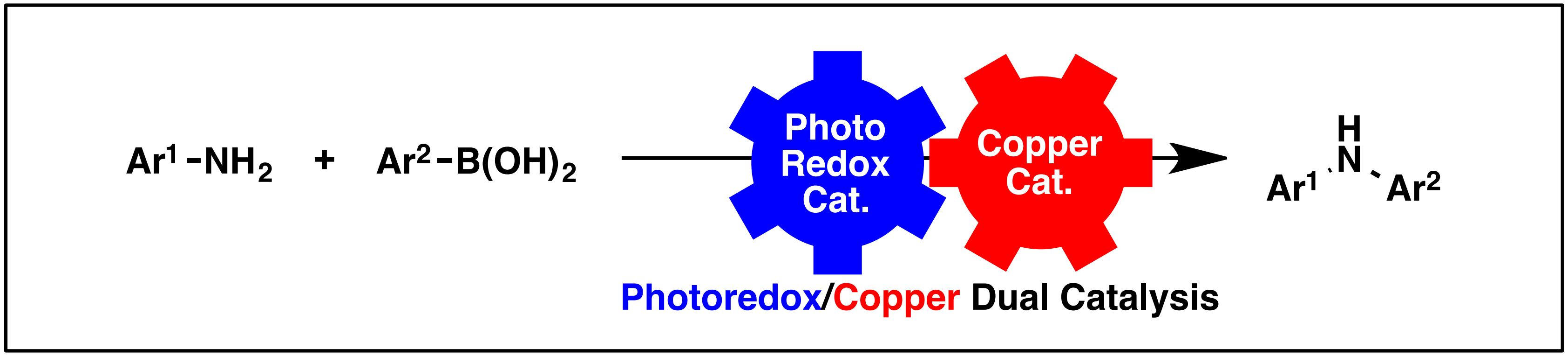
R = Alkyl, OR: 50–91%

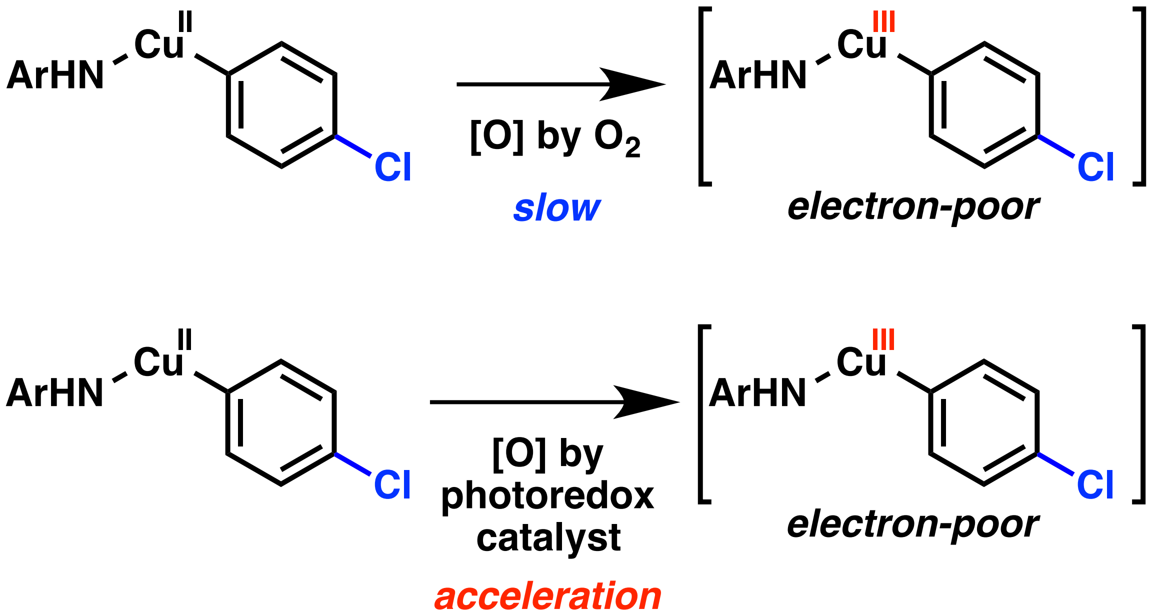
R = *p*-Cl: <10% (GC)

J. C. Antilla, S. L. Buchwald. *Org. Lett.* **2001**, *3*, 2077.

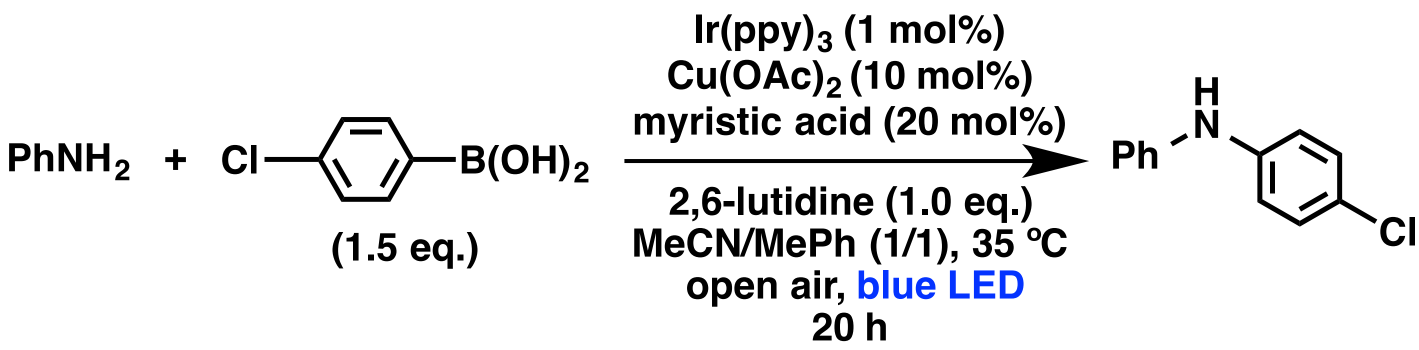
- Catalytic amount of Cu^{II} species
- Limited substrate scope

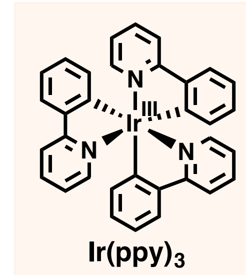
Chan-Lam Coupling Reactions (2)

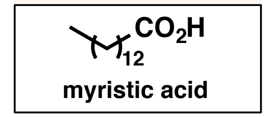




Control Experiments







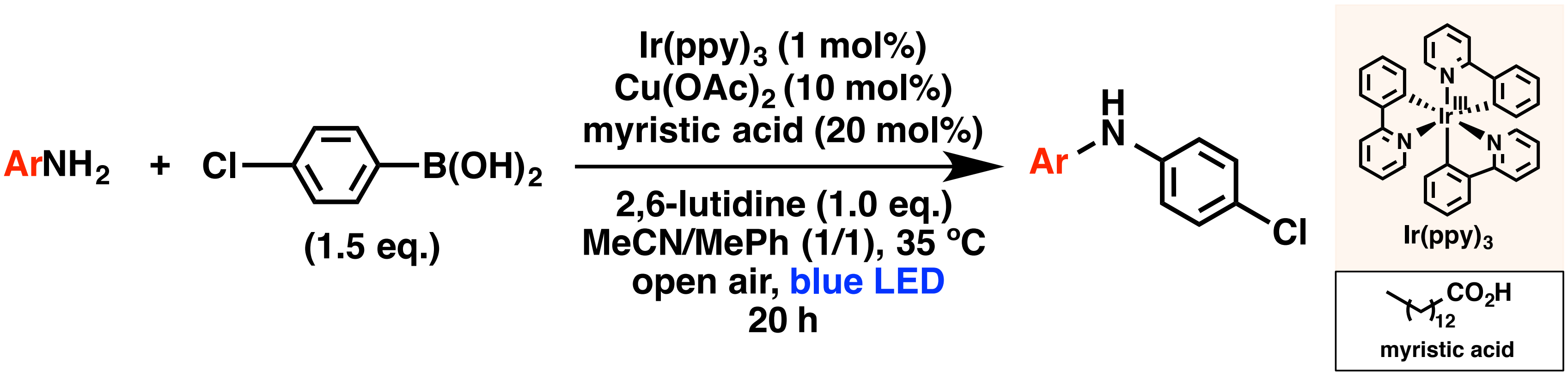
Screened conditions

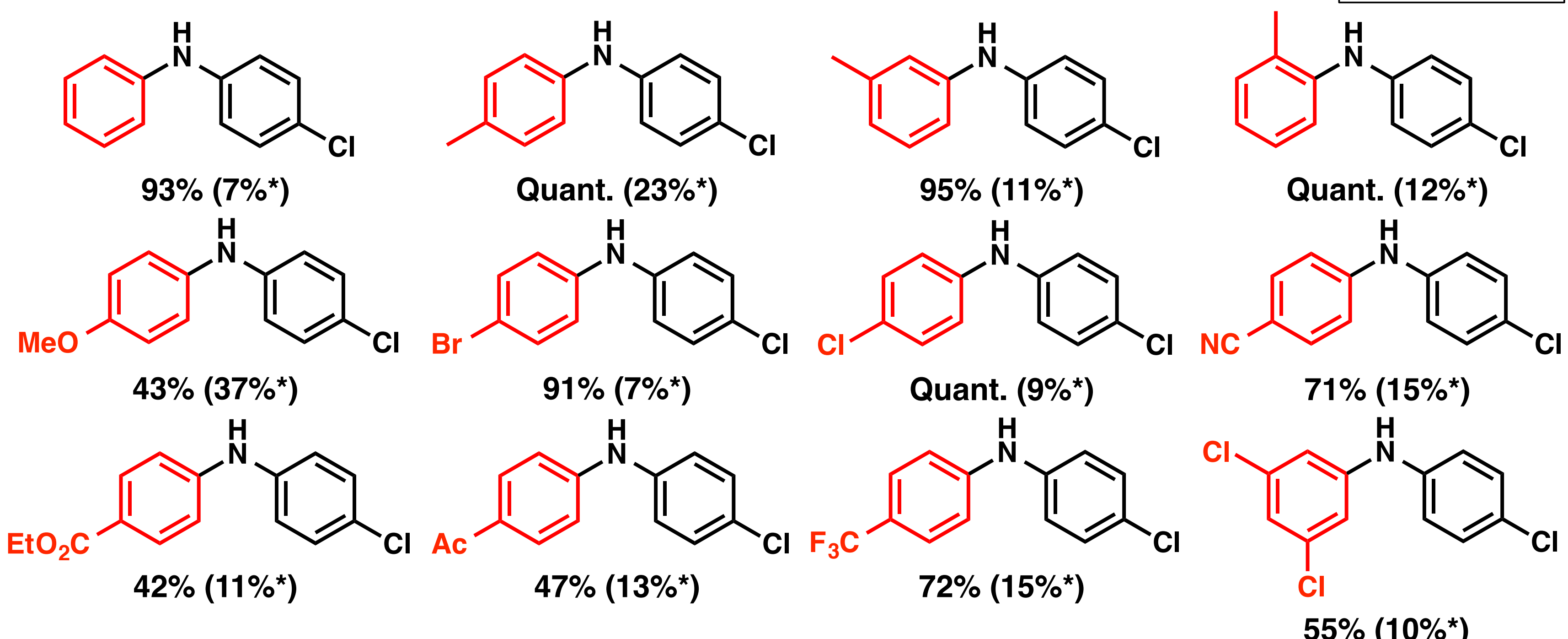
- ☐ Visible light photoredox catalysts
- ☐ Transition metal catalysts
- ☐ Solvents

entry	$Ir(ppy)_3$	blue LED	$Cu(OAc)_2$ & myristic acid	yield [%][a]
1	✔	✔	×	0
2	×	×	✔	7
3	✔	✔	✔	>95

[a] Determined by ^{1}H-NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

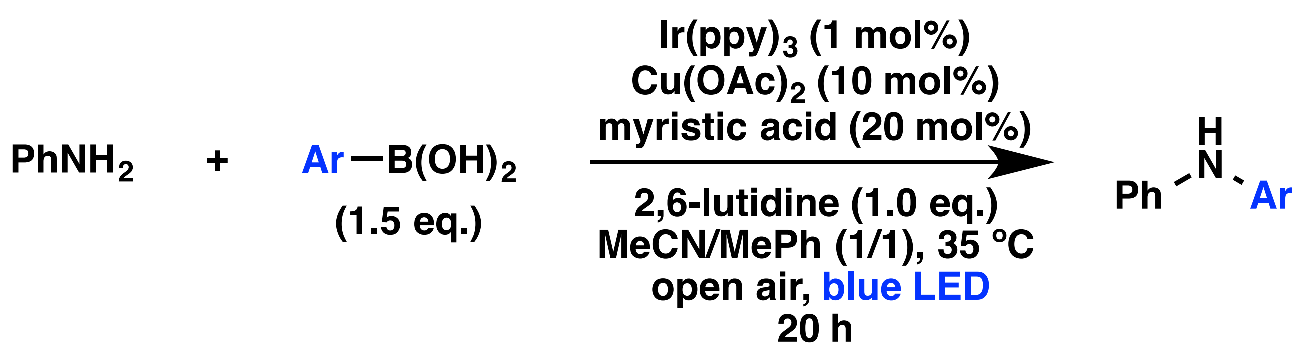
Substrate Scope (1)

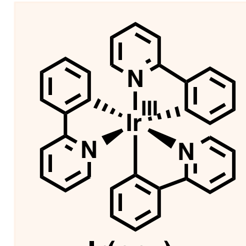




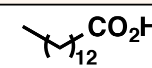
*in the absence of $Ir(ppy)_3$ and blue LED irradiation.

Substrate Scope (2)

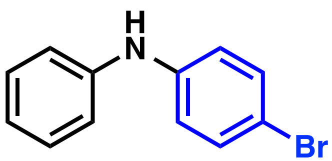




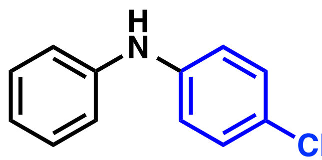
Ir(ppy)3



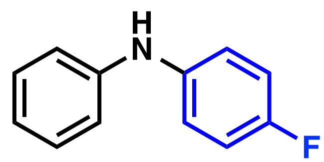
myristic acid



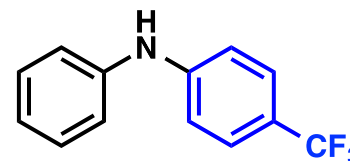
89% (12%*)



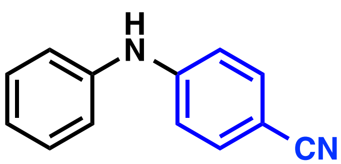
93% (7%*)



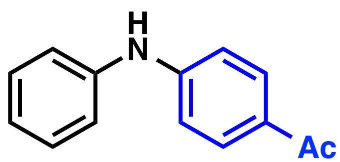
79% (12%*)



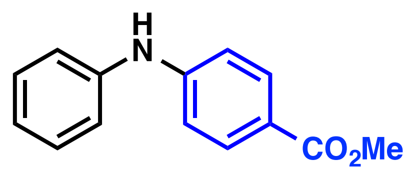
85% (19%*)



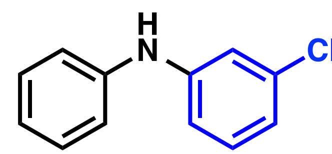
43% (5%*)



47% (18%*)



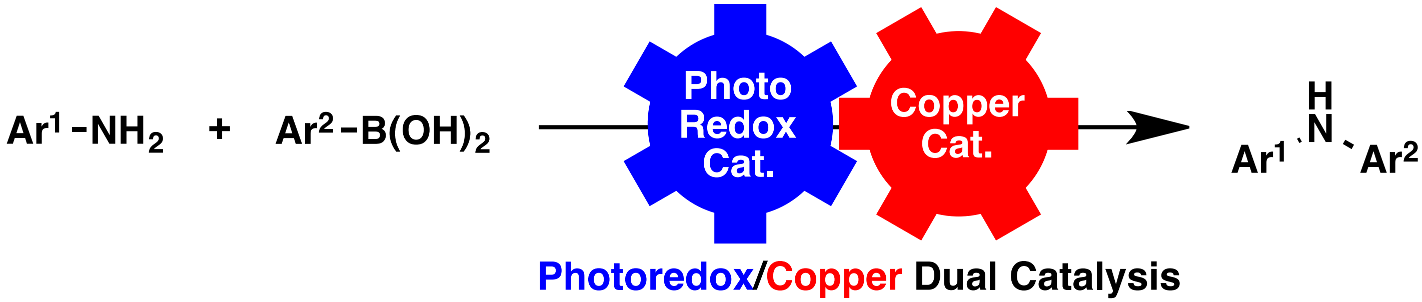
62% (19%*)

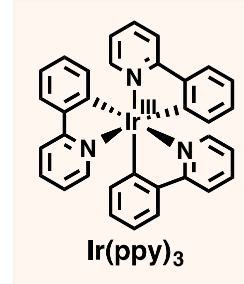


65% (17%*)

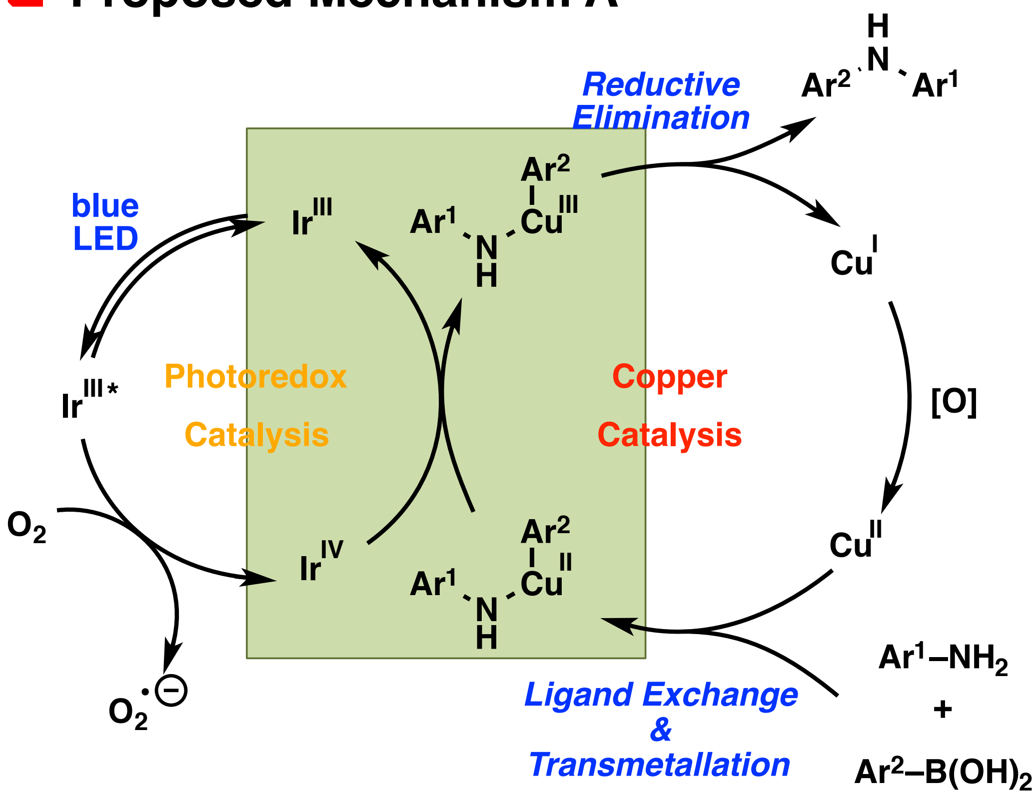
*in the absence of $Ir(ppy)_3$ and blue LED irradiation.

Mechanistic Study (1)





❑ Proposed Mechanism A



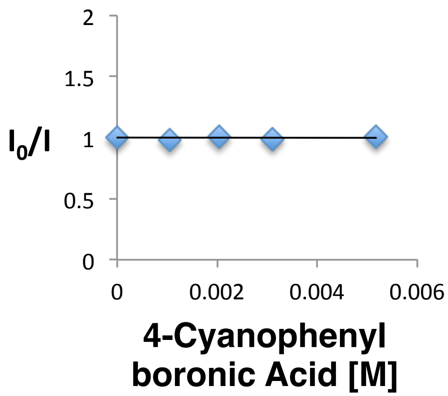
Visible light photoredox catalyst helps the formation of Cu(III) species.

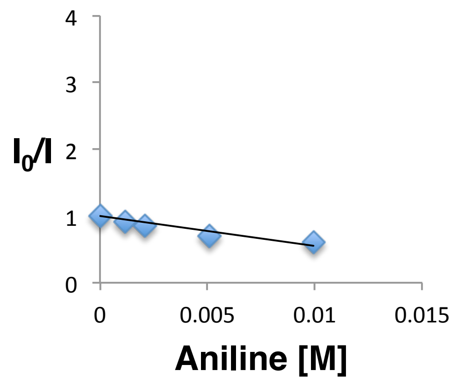
- ❑ Stern–Volmer Plot
- ❑ Kinetic Study
- ❑ Anaerobic Reaction

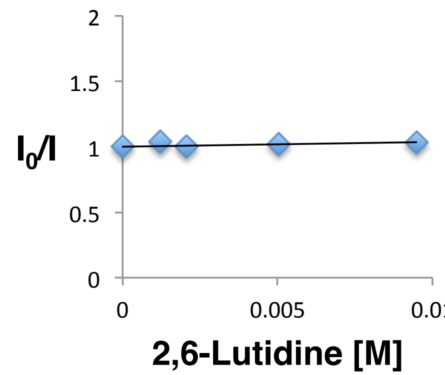
Mechanistic Study (2)

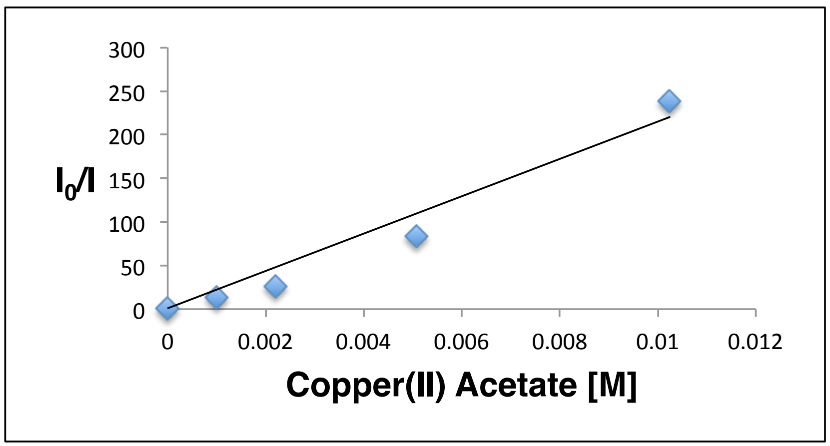
❑ Stern-Volmer Plot Study

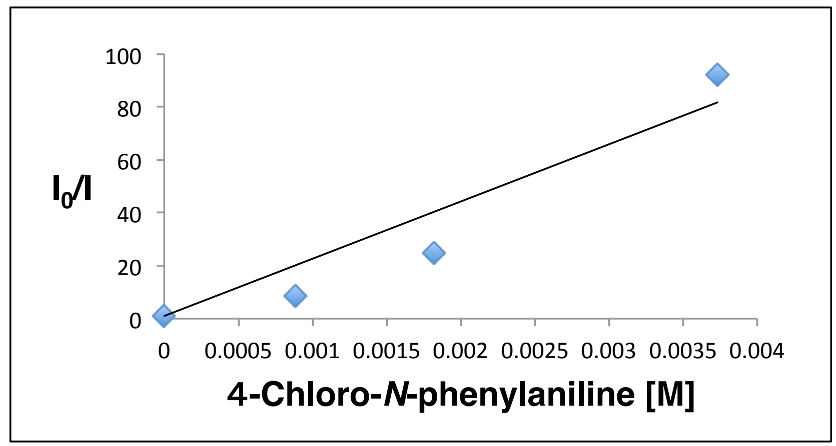
fac-Ir(ppy)$_3$ solutions (0.0122 mM in MeCN) were excited at 320 nm and the emission intensity at 518 nm was observed.







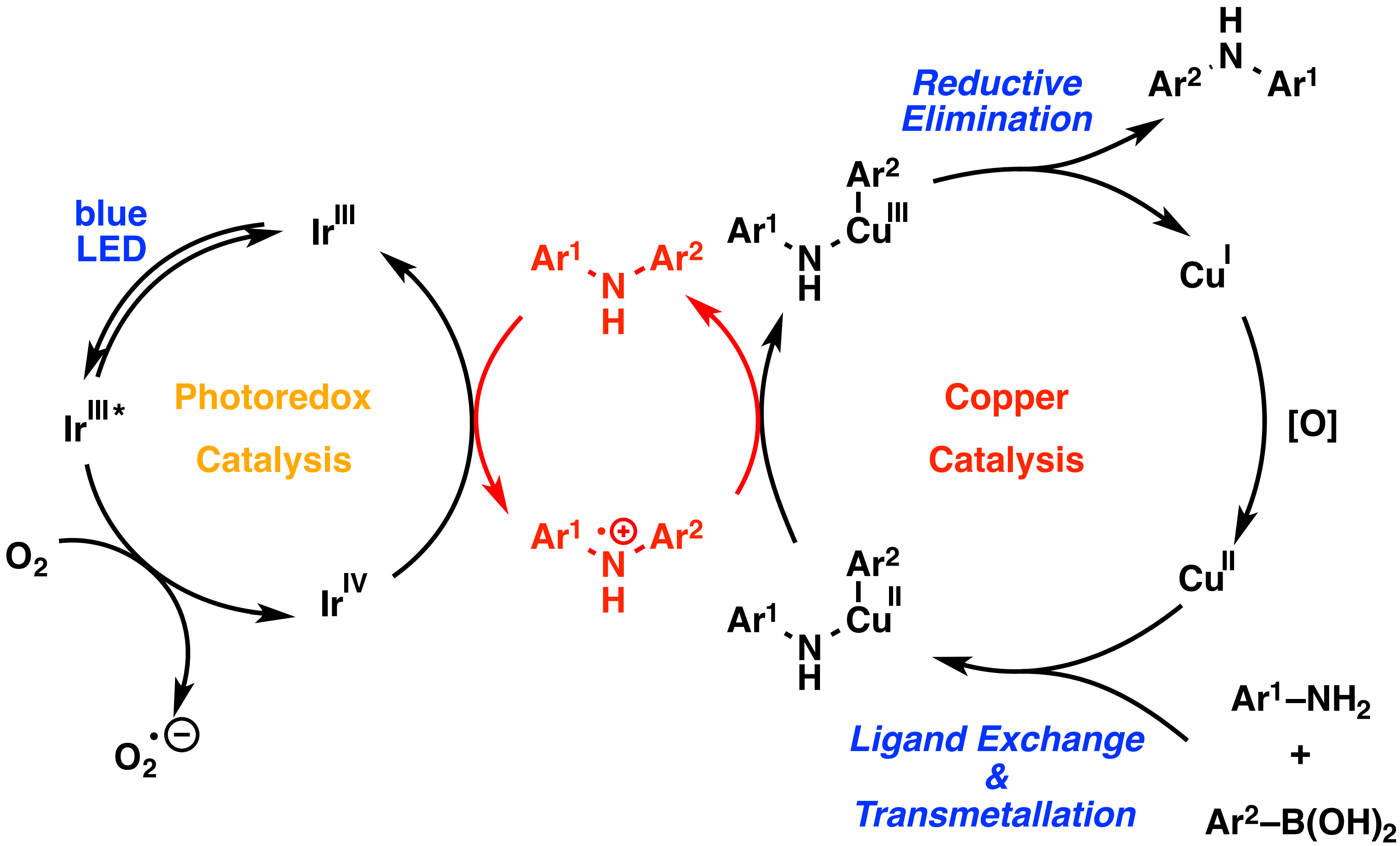




❑ Ir(ppy)$_3$* can react only with Cu(OAc)$_2$ and the product.

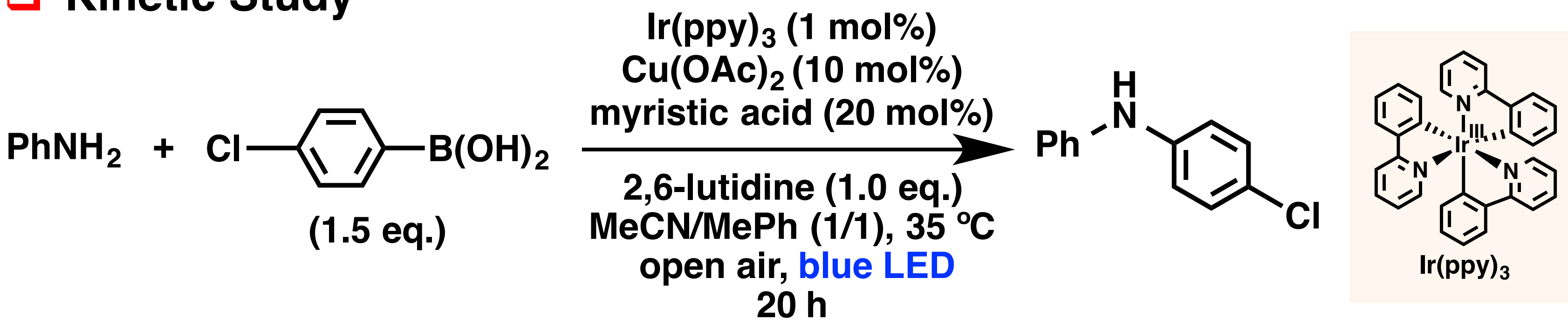
Mechanistic Study (3)

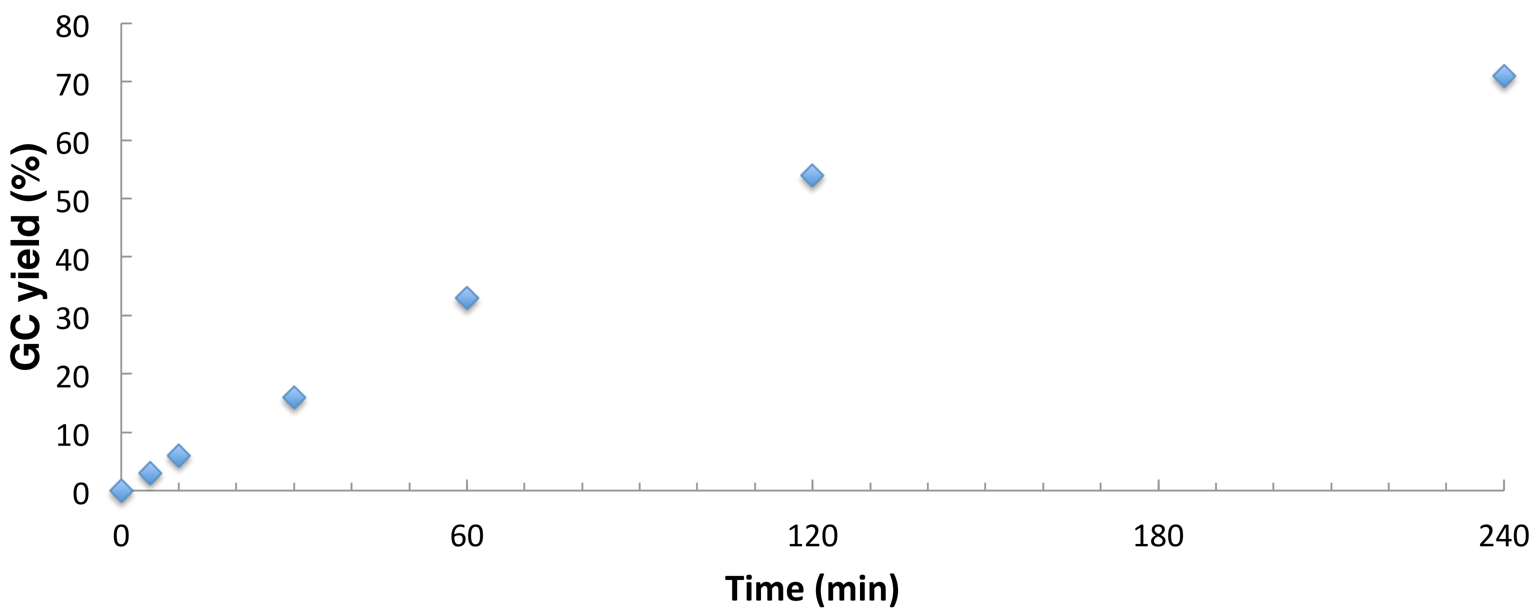
❑ Proposed Mechanism B



Mechanistic Study (4)

- **Kinetic Study**

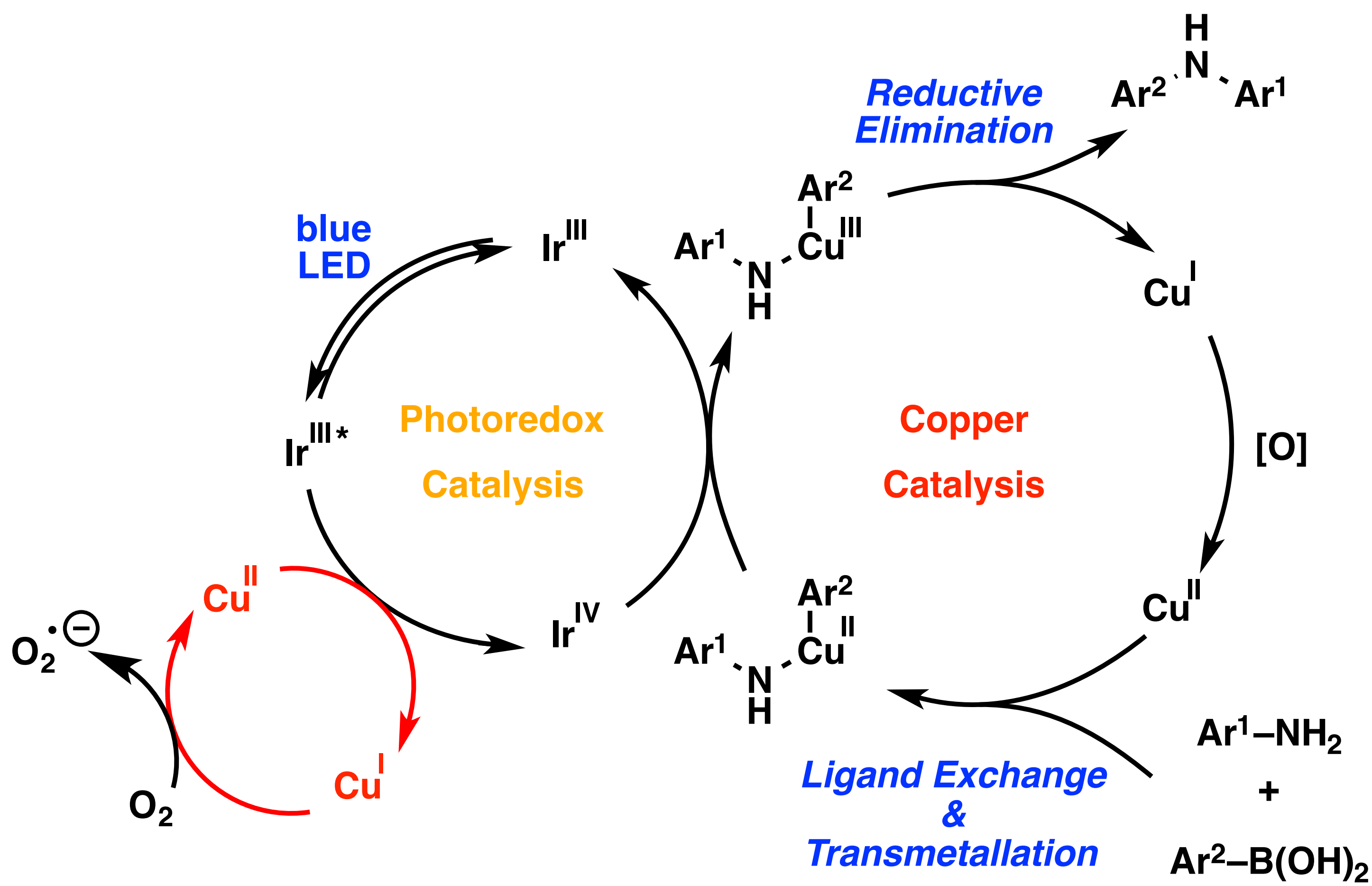




- **Proposed Mechanism B is not major pathway.**

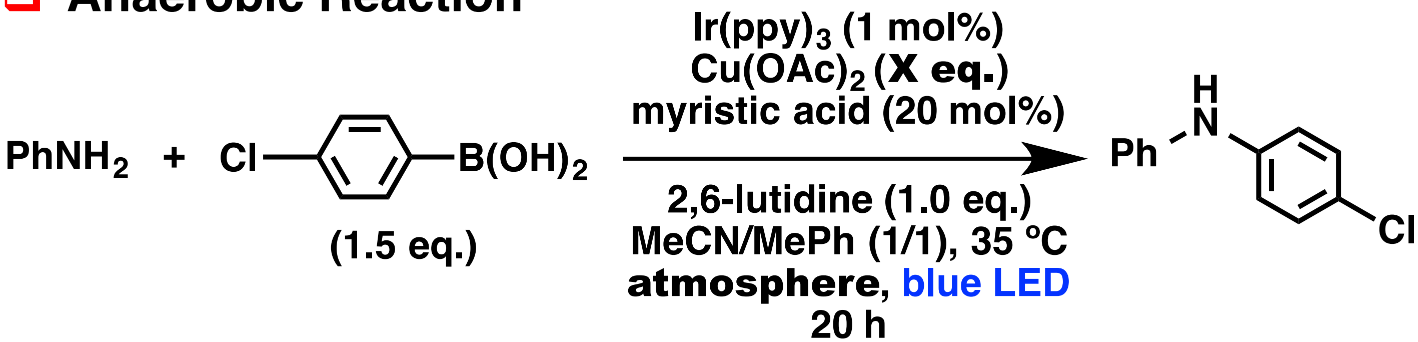
Mechanistic Study (5)

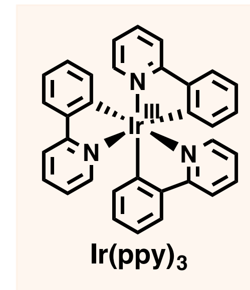
❑ Proposed Mechanism C



Mechanistic Study (6)

- **Anaerobic Reaction**





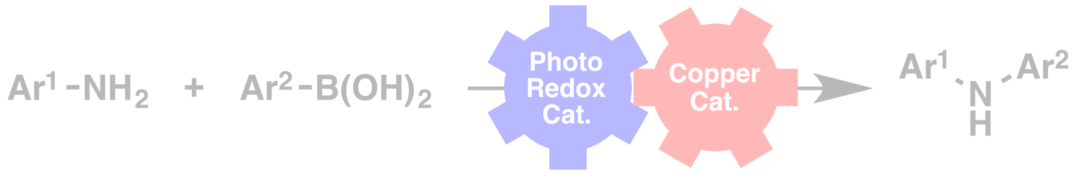
entry	$Ir(ppy)_3$	blue LED	$Cu(OAc)_2$ (X eq.)	atmosphere	yield [%][a]
1	✔	✔	10 mol%	O_2	93
2	✔	✔	2.0 eq.	Ar	38
3	×	×	2.0 eq.	Ar	28

[a] Isolated yield.

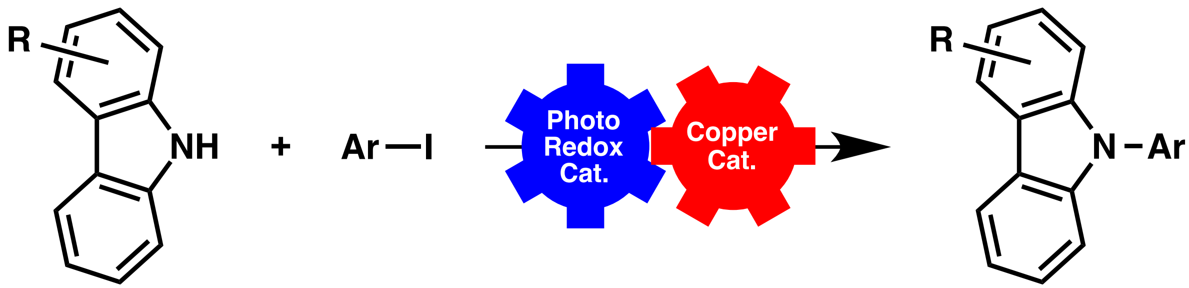
- **Proposed Mechanism C is not major pathway.**
- **<u>Proposed Mechanism A is most reasonable.</u>**

Topics

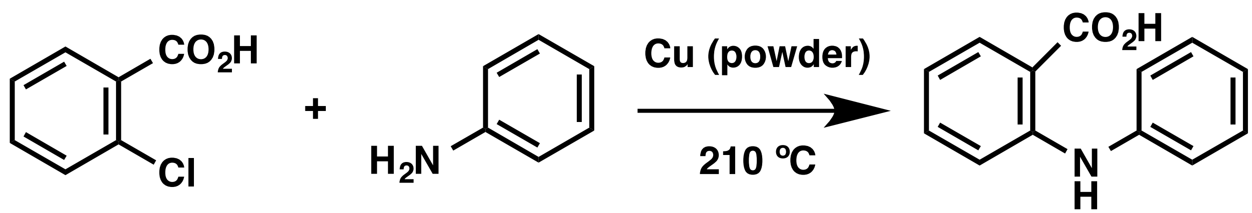
1. Visible-Light-Mediated Chan–Lam Coupling Reaction



2. Visible-Light-Mediated C–N Ullmann-type Coupling Reaction

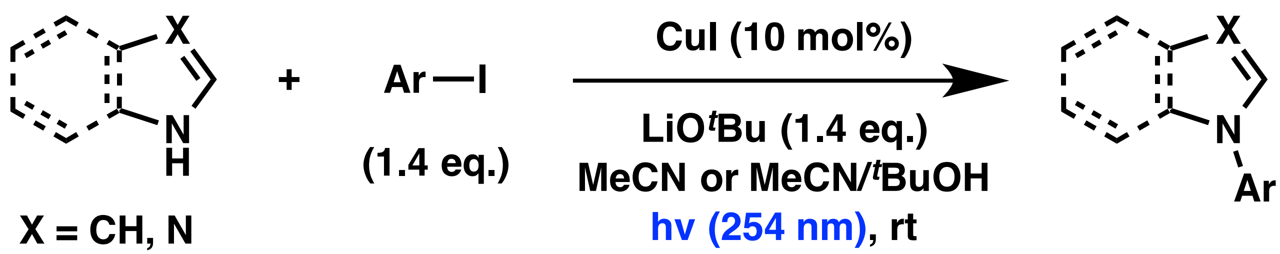


C–N Ullmann-type Coupling Reaction (1)



F. Ullmann, *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2382.

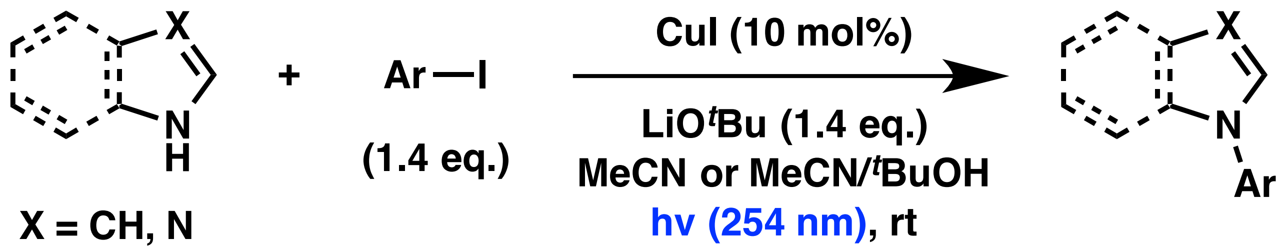
- **Stoichiometric Cu**
- **High temperature**

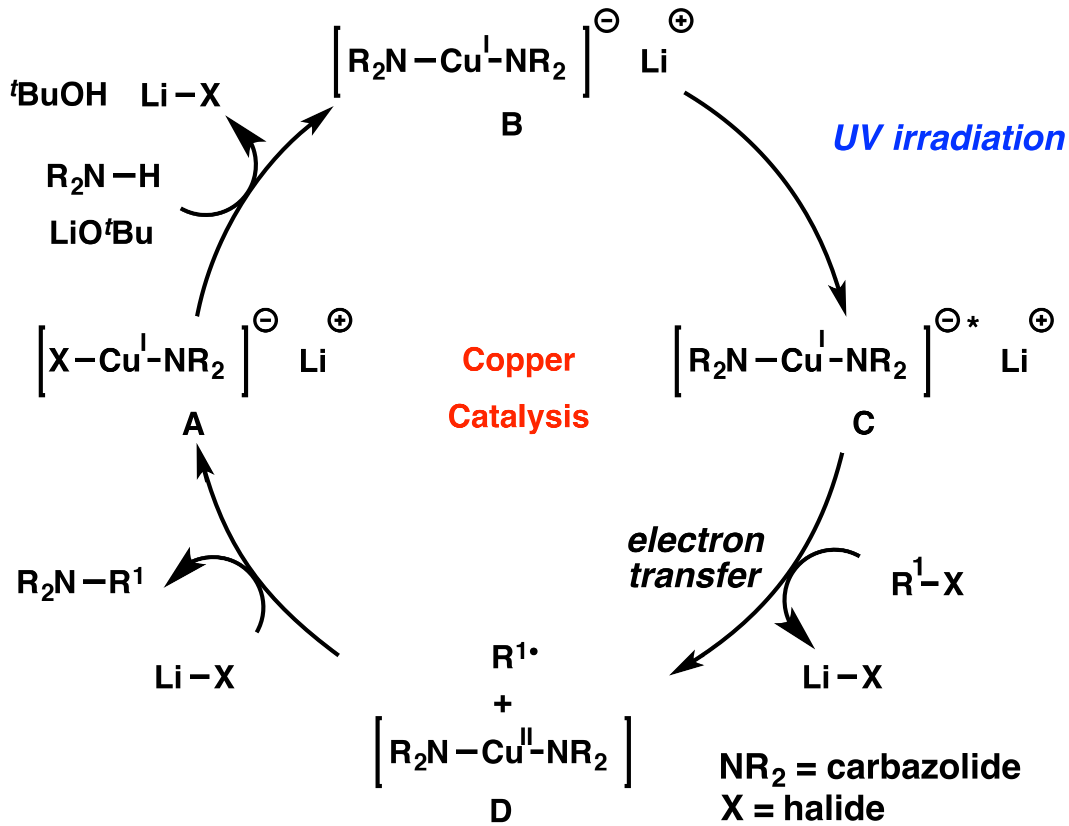


D. T. Ziegler, J. Choi, J. M. Muñoz-Molina, A. C. Bissember, J. C. Peters, G. C. Fu, *J. Am. Chem. Soc.* **2013**, *135*, 13107.

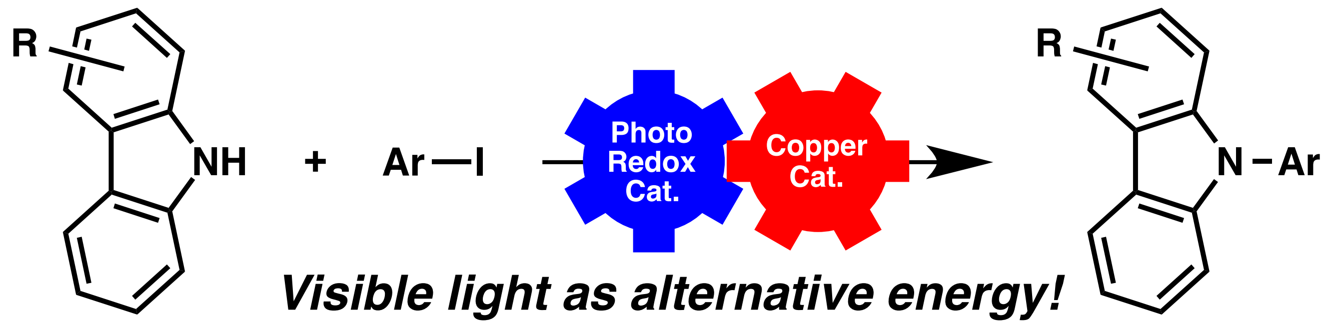
- **Catalytic Cu^{I}**
- **Room temperature**
- **Harmful light source, UV**

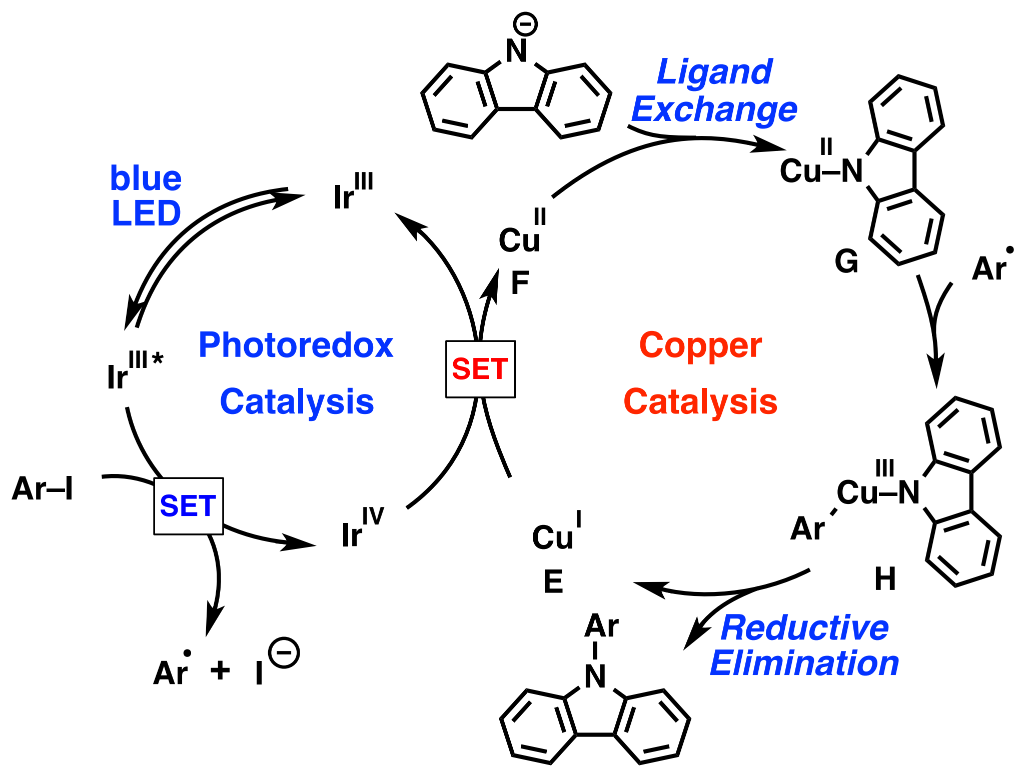
C–N Ullmann-type Coupling Reaction (1)



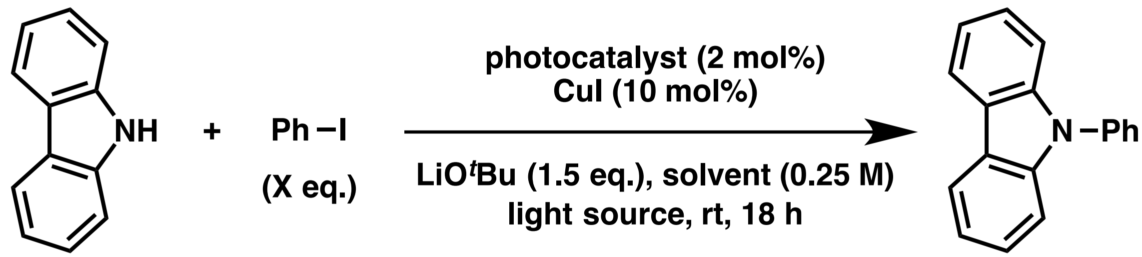


C–N Ullmann-type Coupling Reaction (2)



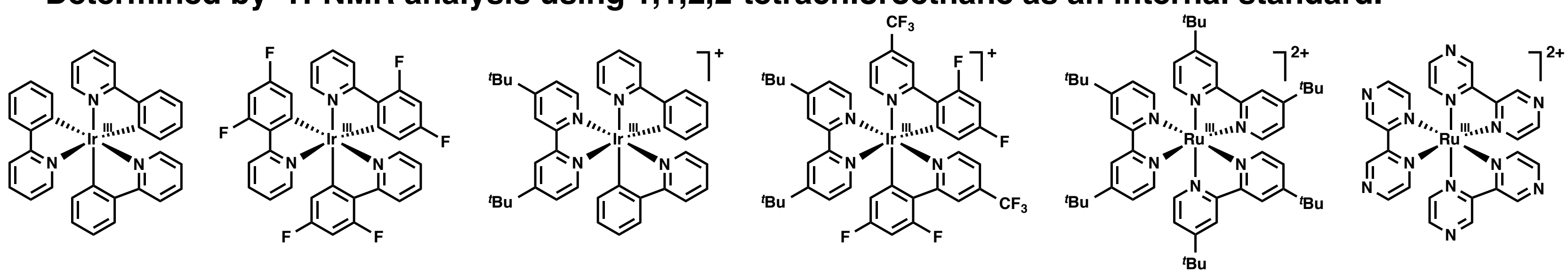


Optimization



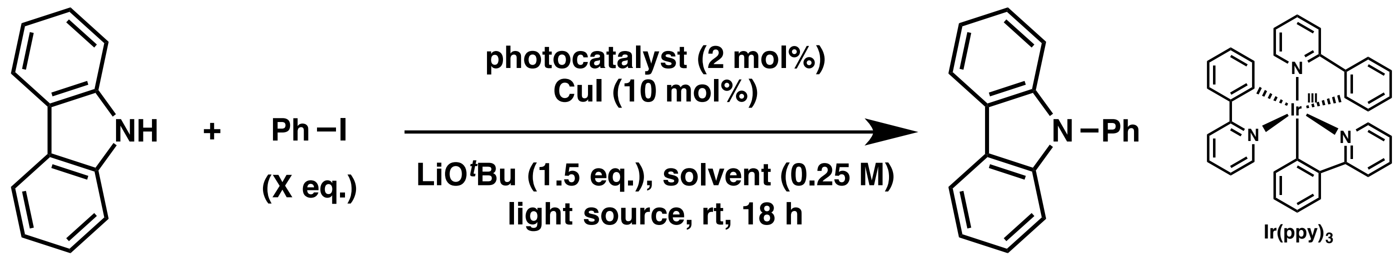
entry	solvent	photocatalyst	light source	X (eq.)	yield (%)[a]
1	DMSO	$Ir(ppy)_3$	white LED	1.5	72
2	DMSO	$Ir(dFppy)_3$	white LED	1.5	41
3	DMSO	$Ir(ppy)_2(dtbbpy)PF_6$	white LED	1.5	N.R.
4	DMSO	$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	white LED	1.5	14
5	DMSO	$Ru(dtbbpy)_3 2PF_6$	white LED	1.5	22
6	DMSO	$Ru(bpz)_3 2PF_6$	white LED	1.5	N.R.

[a] Determined by ^1H-NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.



$Ir(ppy)_3$ $Ir(dFppy)_3$ $Ir(ppy)_2(dtbbpy)^+$ $Ir(dF(CF)_3ppy)_2(dtbbpy)^+$ $Ru(dtbbpy)_3^{2+}$ $Ru(bpz)_3^{2+}$

Optimization



entry	solvent	photocatalyst	light source	X (eq.)	yield (%)[a]
1	DMSO	$Ir(ppy)_3$	white LED	1.5	72
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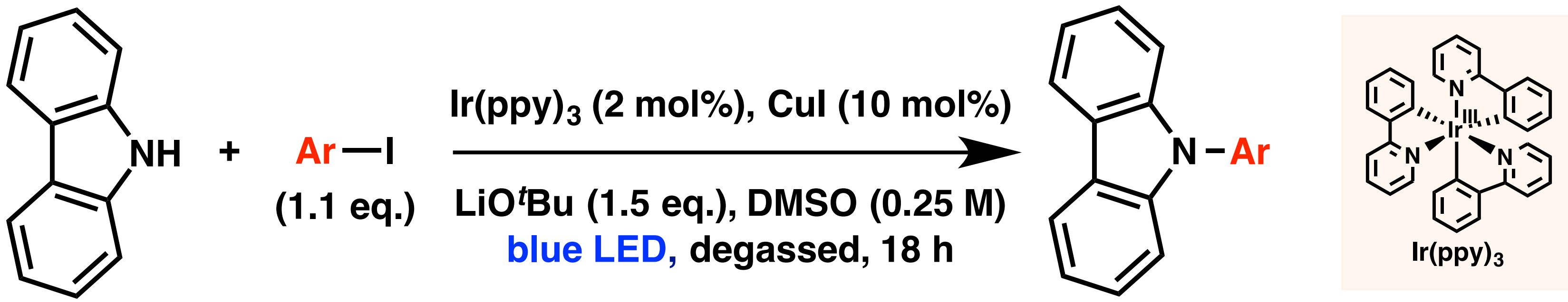
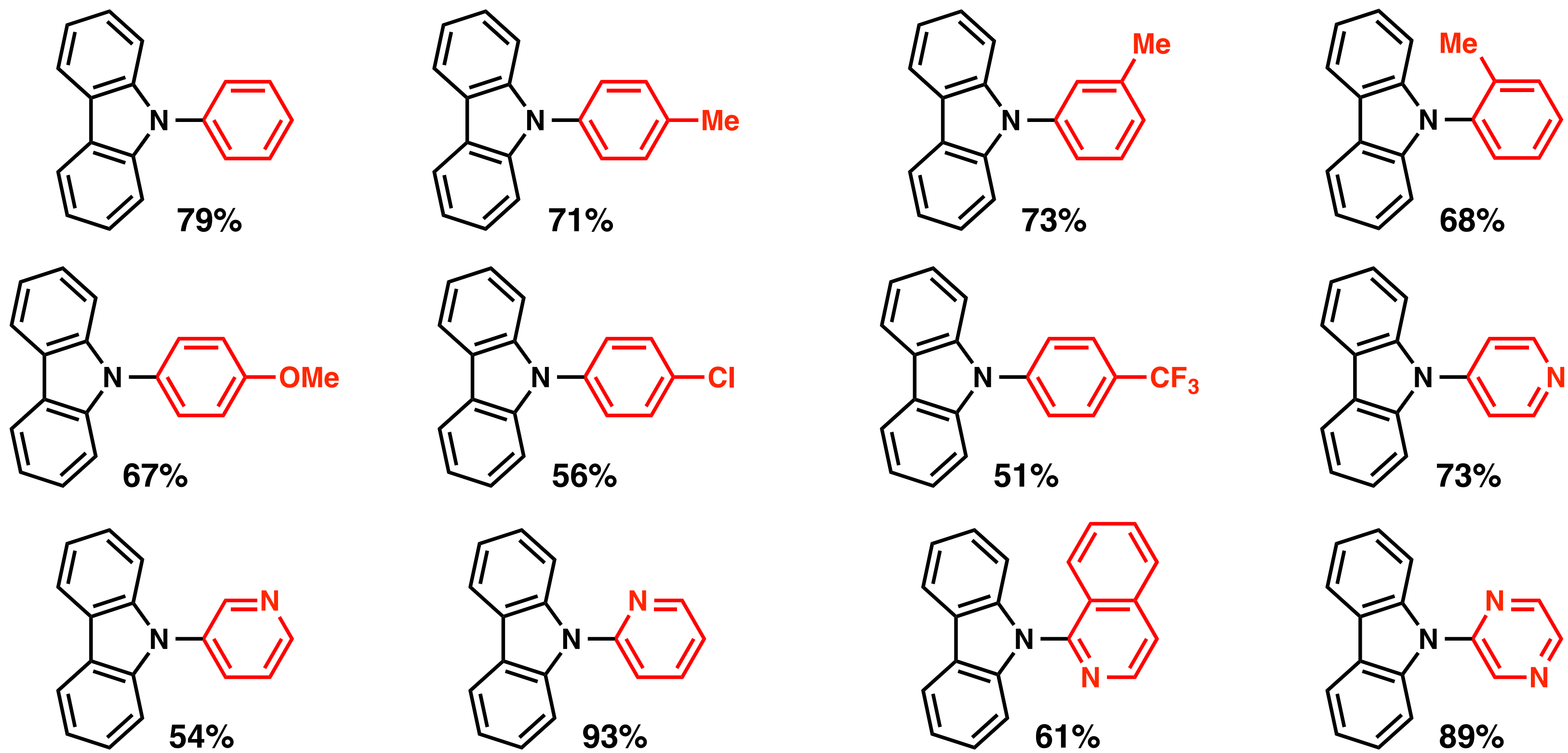
4	DMSO	$Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$	white LED	1.5	14
5	DMSO	$Ru(dtbbpy)_3 2PF_6$	white LED	1.5	22
6	DMSO	$Ru(bpz)_3 2PF_6$	white LED	1.5	N.R.
7	DMSO	$Ir(ppy)_3$	blue LED	1.5	80
8	DMSO	$Ir(ppy)_3$	blue LED	1.1	79

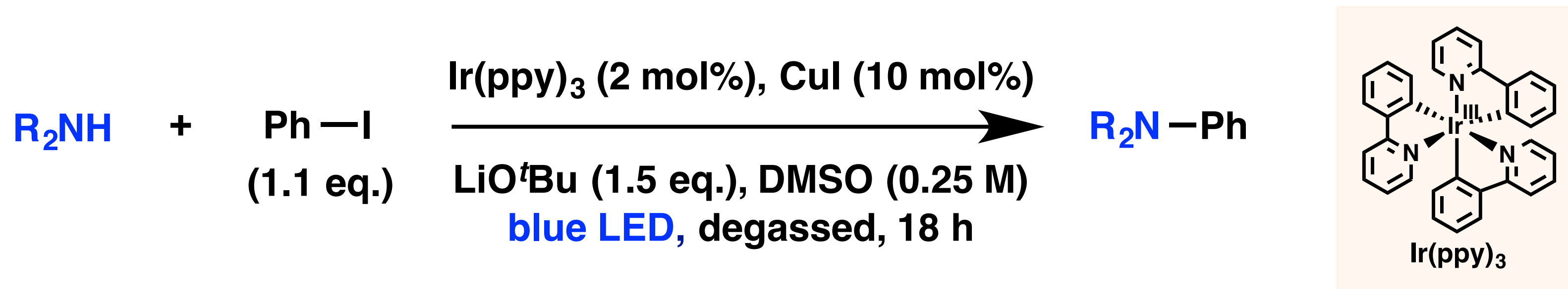
[a] Determined by ^{1}H-NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

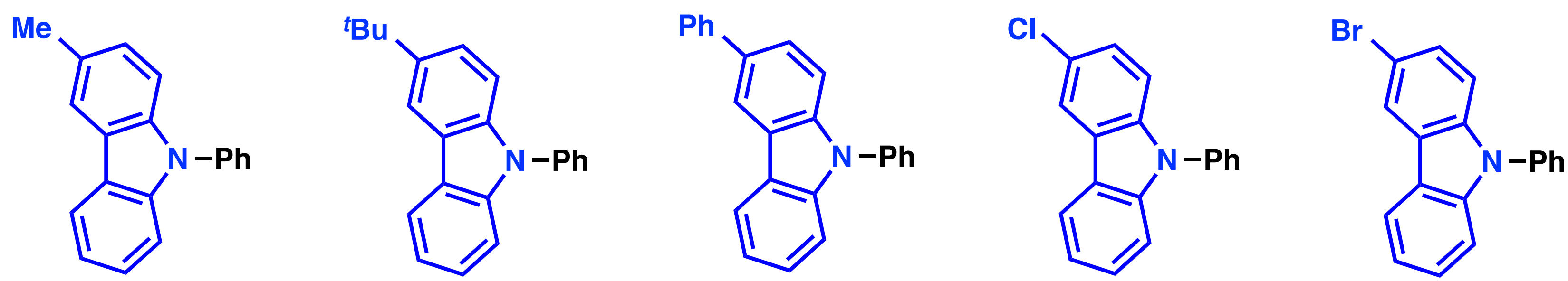
Substrate Scope (1)



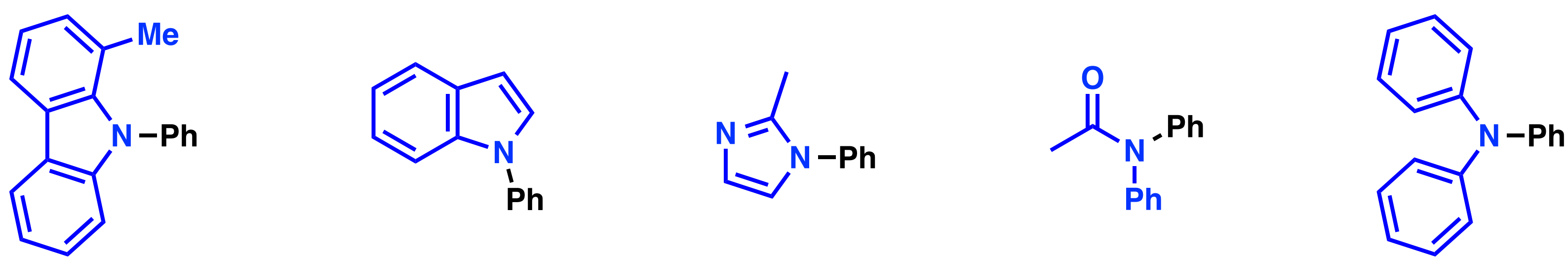


Substrate Scope (2)



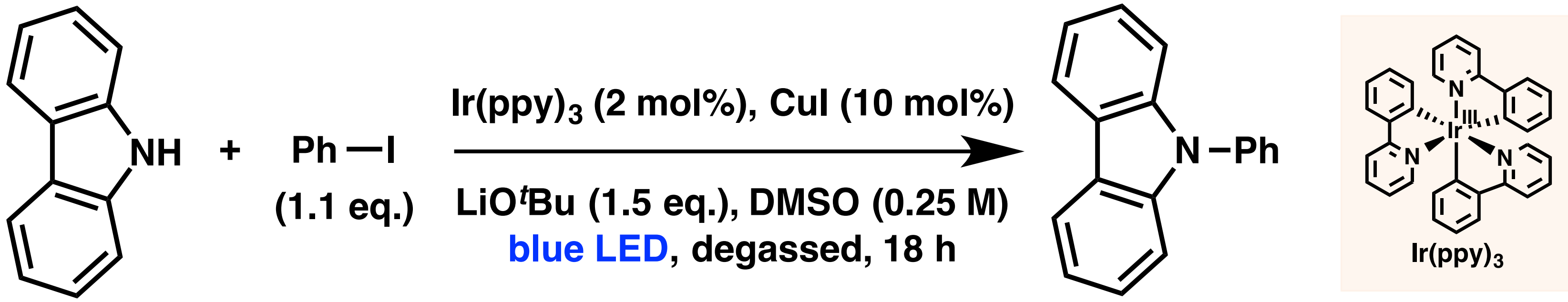


71% | 66% | 71% | 70% | 46%



44% | N.R. | 14% | 24% | 27%

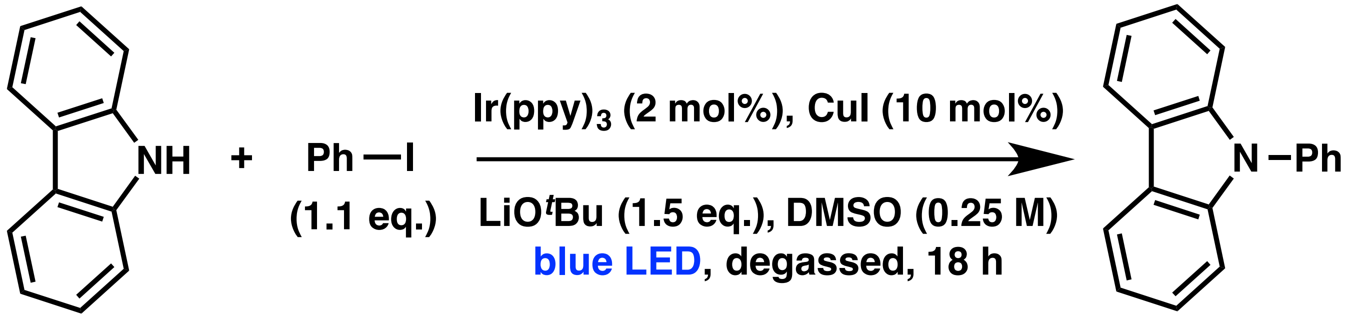
Control Experiments

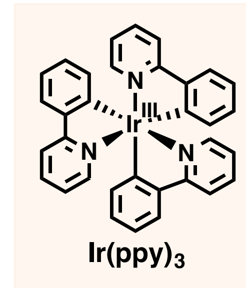


entry	$Ir(ppy)_3$	blue LED	CuI	yield (%)[a]
1	✔	✔	×	0
2	×	×	✔	0
3	×	✔	✔	39
4	✔	✔	✔	79

[a] Determined by ^{1}H-NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

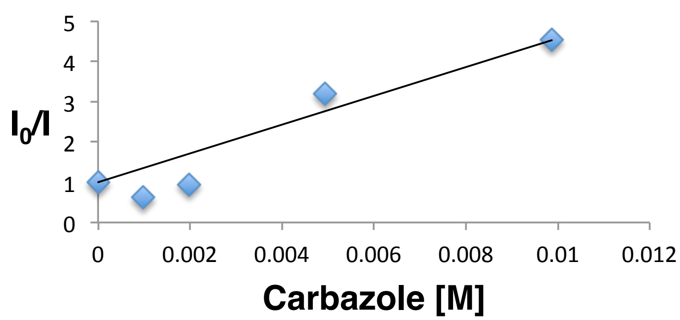
Mechanistic Study

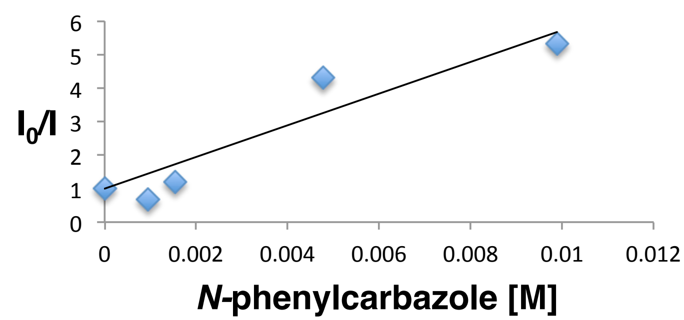


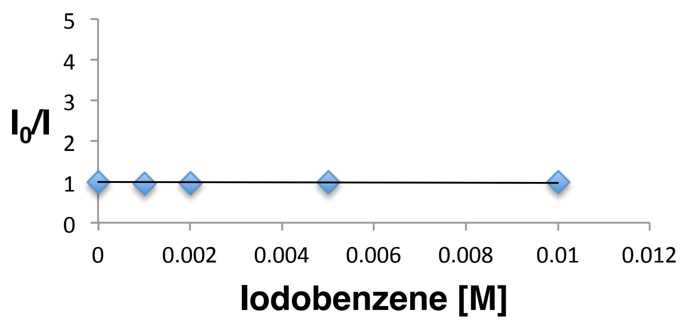


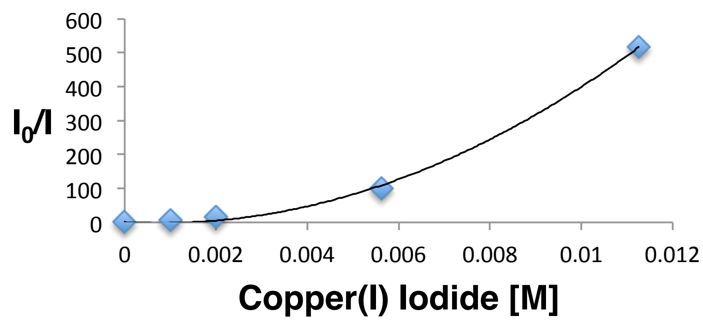
❑ Stern–Volmer Plot Study

fac-Ir(ppy)$_3$ solutions (0.0122 mM in DMSO) were excited at 320 nm and the emission intensity at 518 nm was observed.

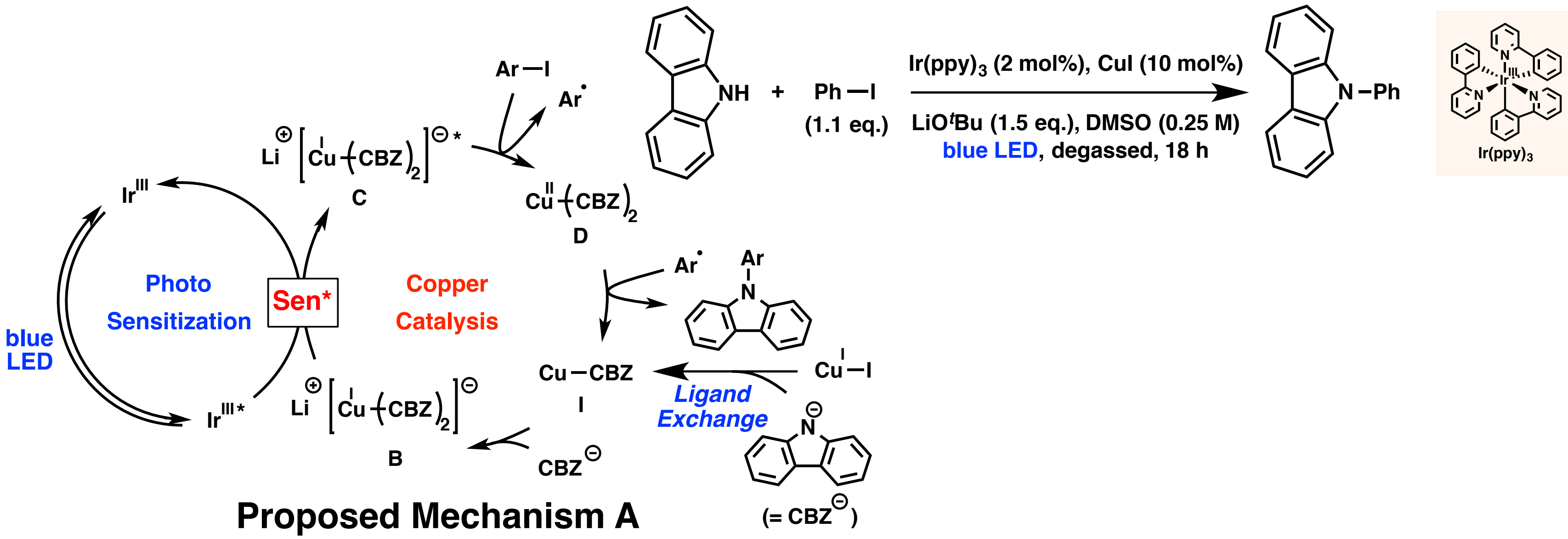






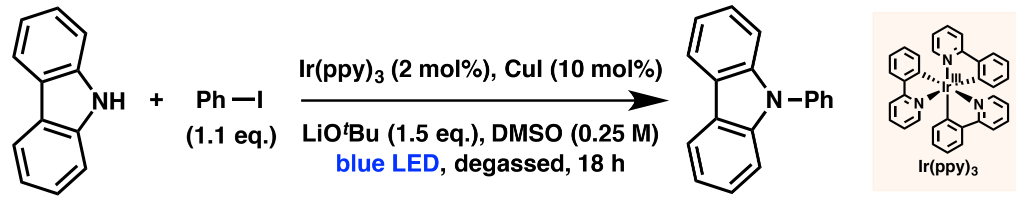


Proposed Mechanisms

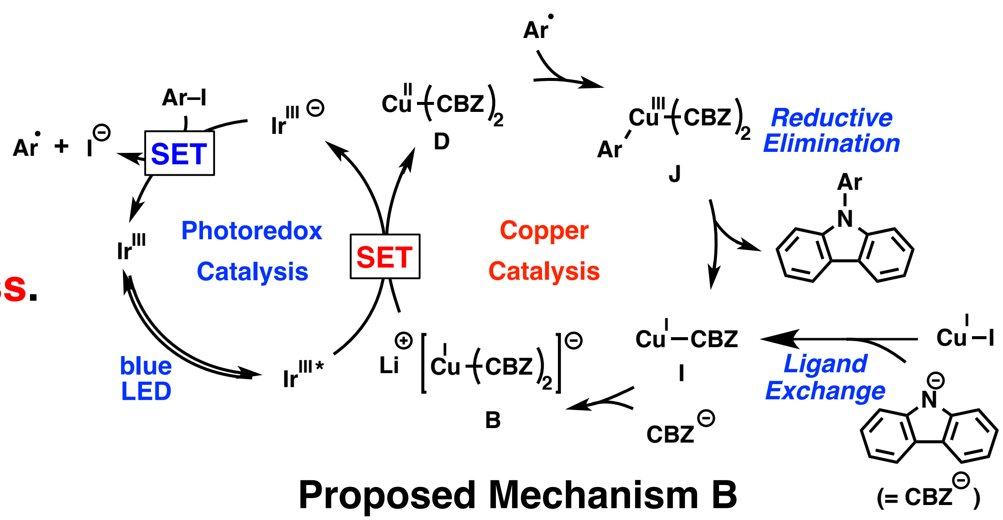


Proposed Mechanism A

Proposed Mechanisms



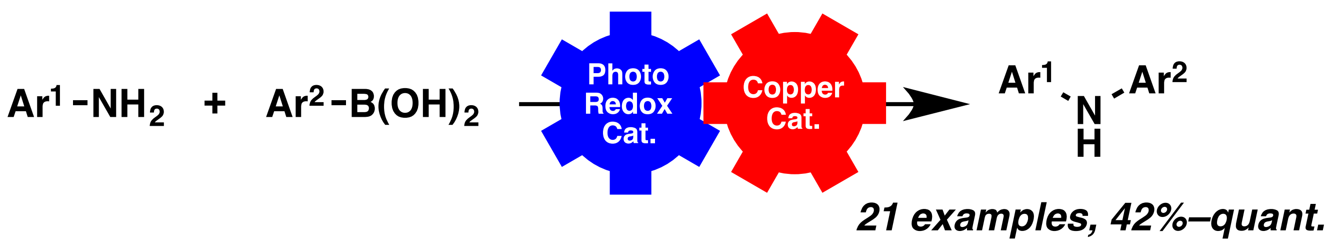
- Photocatalyst facilitates the **single-electron redox process**.



Proposed Mechanism B

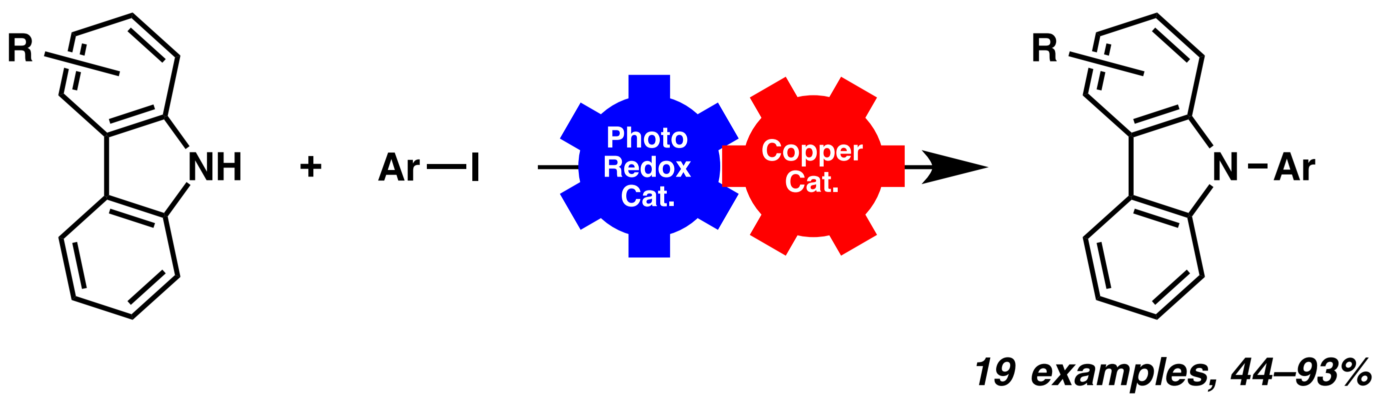
Summary of Master's Research

1. Visible-Light-Mediated Chan–Lam Coupling Reaction



W.-J. Yoo, T. Tsukamoto, S. Kobayashi, *Angew. Chem. Int. Ed.* **2015**, *54*, 6587.

2. Visible-Light-Mediated C–N Ullmann-type Coupling Reaction

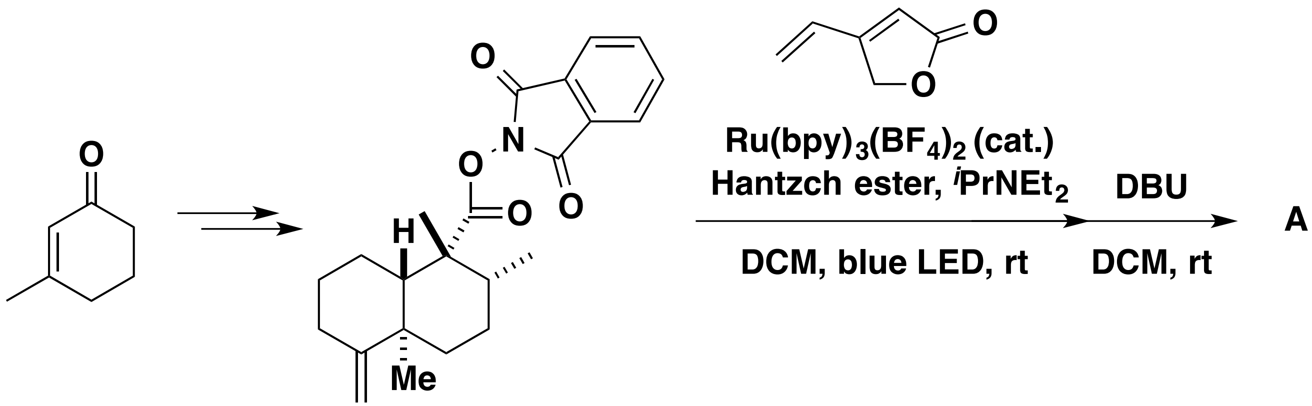


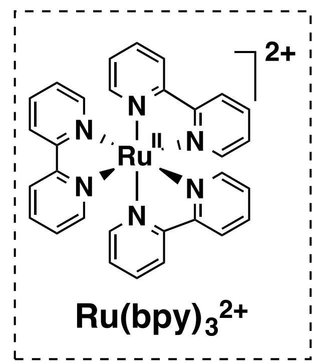
W.-J. Yoo, T. Tsukamoto, S. Kobayashi, *Org. Lett.* **2015**, *17*, 3640.

Thank you for your attention!

Questions

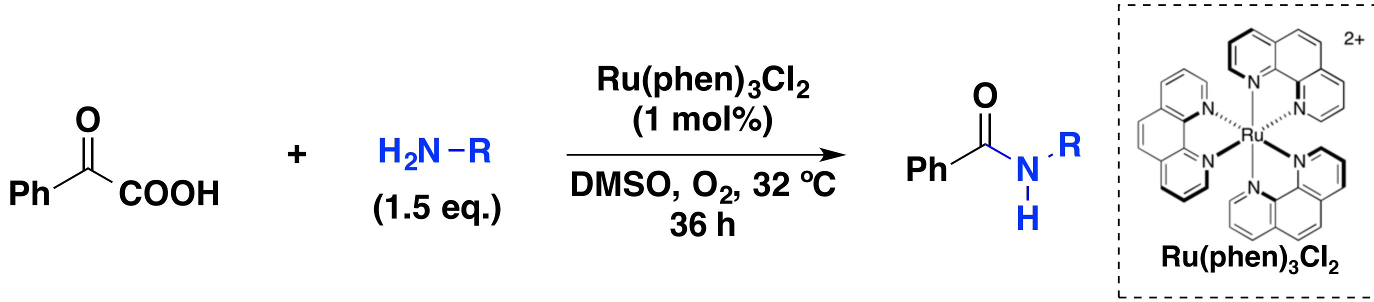
1. Please provide the product in the reaction below.

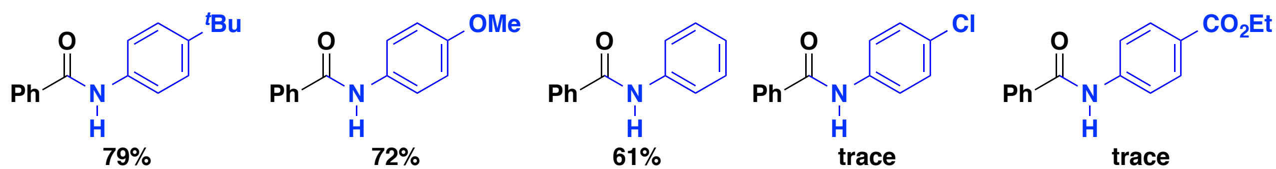


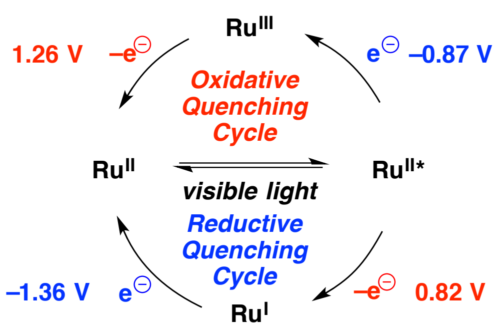


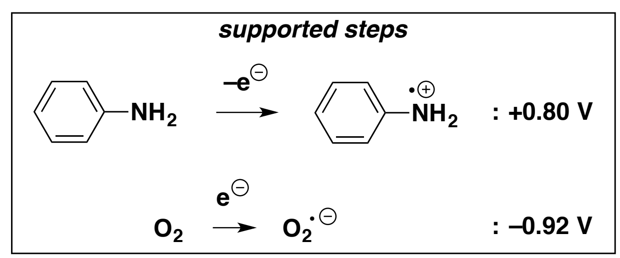
Questions

2. In which quenching cycle does the following reaction take place? (Ox. or Red.) Please also rationalize the results of substrate scope.



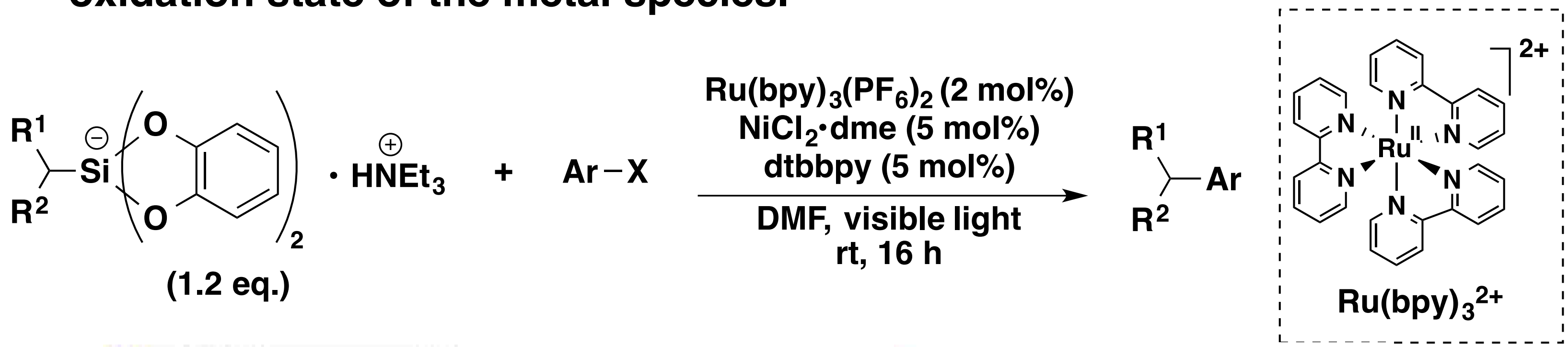


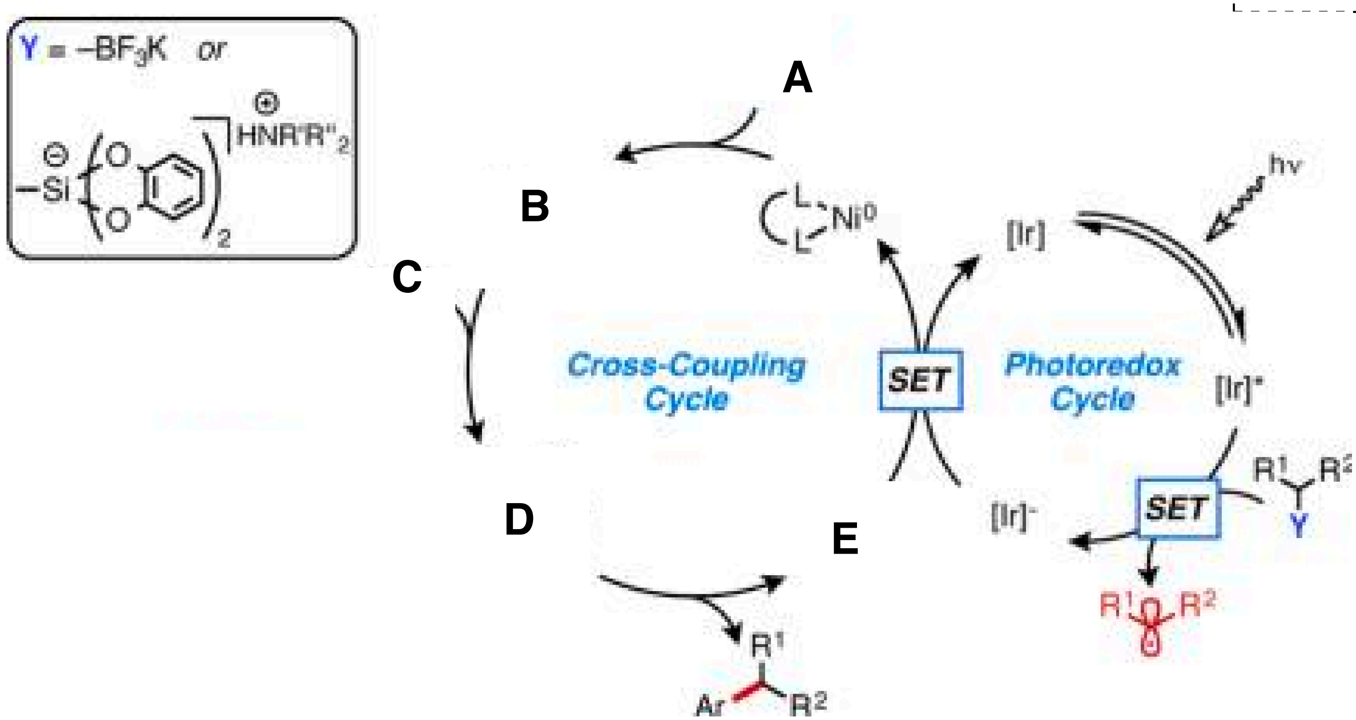




Questions

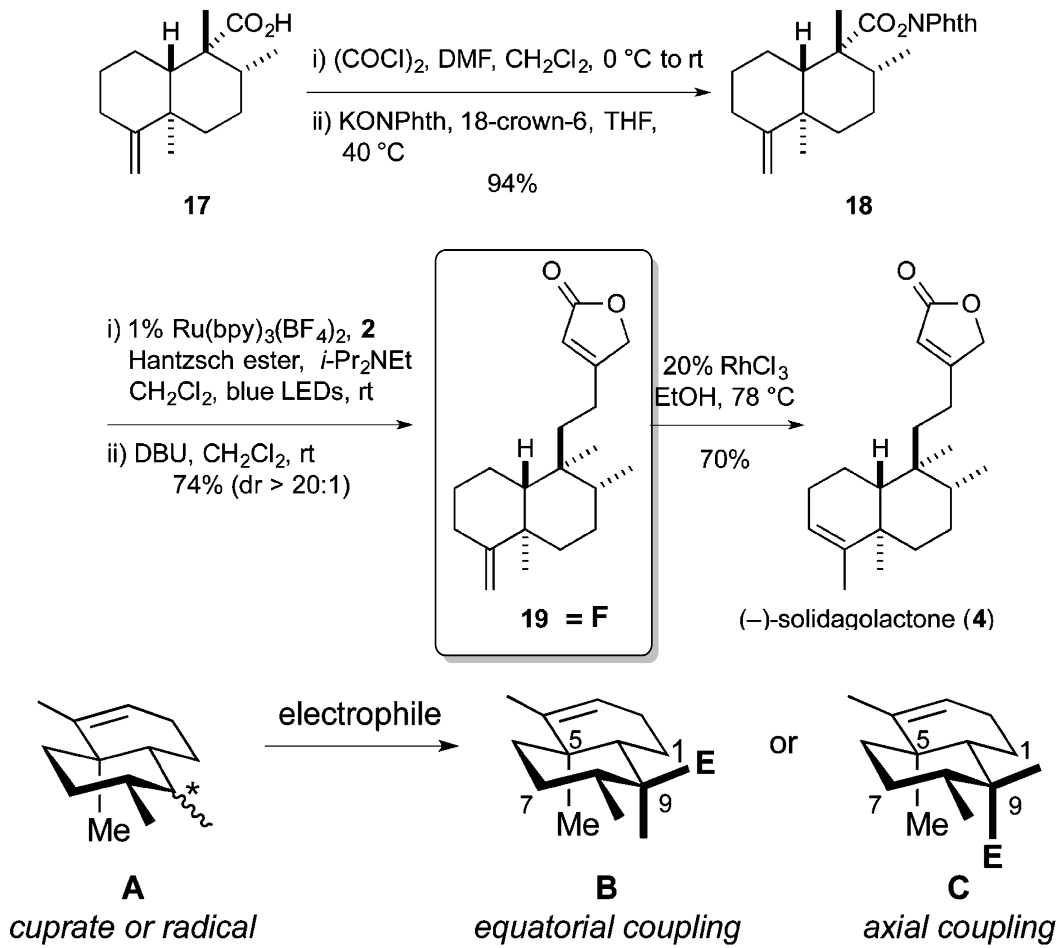
3. Please close the nickel catalysis filling in blanks A–E. Be sure to show oxidation state of the metal species.





Questions

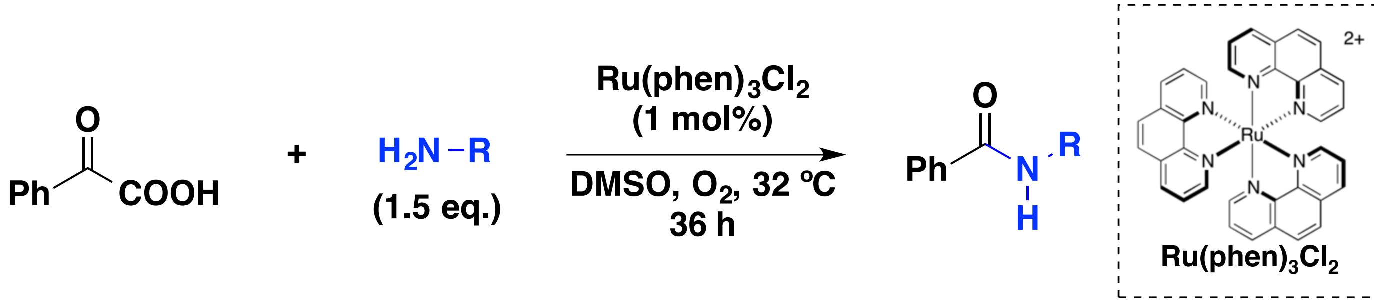
1. Please provide the product in the reaction below.



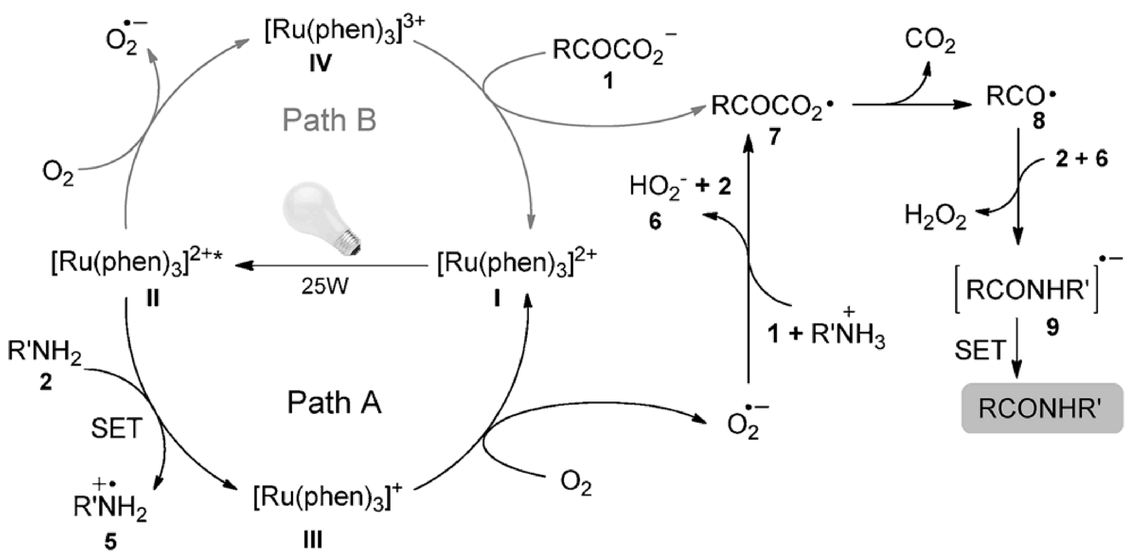
D. S. Müller, N. L. Untiedt, A. P. Dieskau, G. L. Lackner, L. E. Overman, *J. Am. Chem. Soc.* **2015**, *137*, 660.

Questions

2. **In which quenching cycle does the following reaction take place? (Ox. or Red.) Please also rationalize the results of substrate scope.**

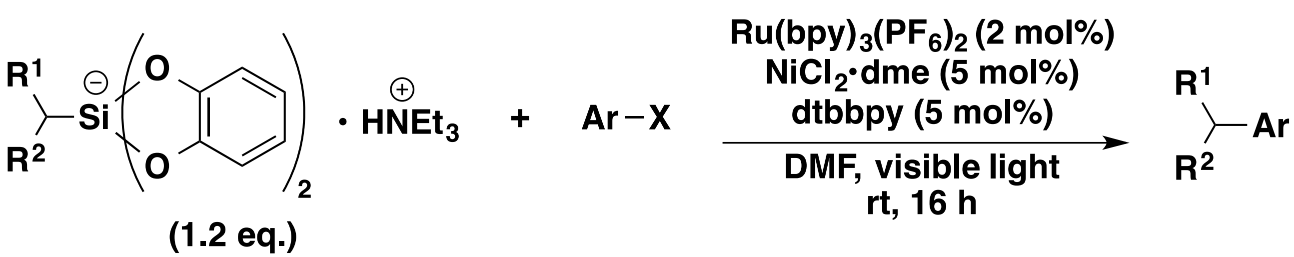


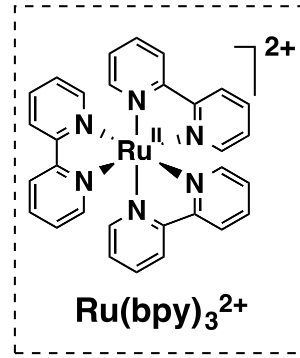
J. Liu, Q. Liu, H. Yi, C. Qin, R. Bai, X. Qi, Y. Lan, A. Lei, *Angew. Chem. Int. Ed.* **2014**, *53*, 502.



Questions

3. **Please close the nickel catalysis filling in blanks A–E. Be sure to show oxidation state of the metal species.**





M. Jouffroy, D. N. Primer, G. A. Molander, *J. Am. Chem. Soc.* **2015**, *ASAP*.