Chemistry of First-Row Transition Metal Photocatalysts

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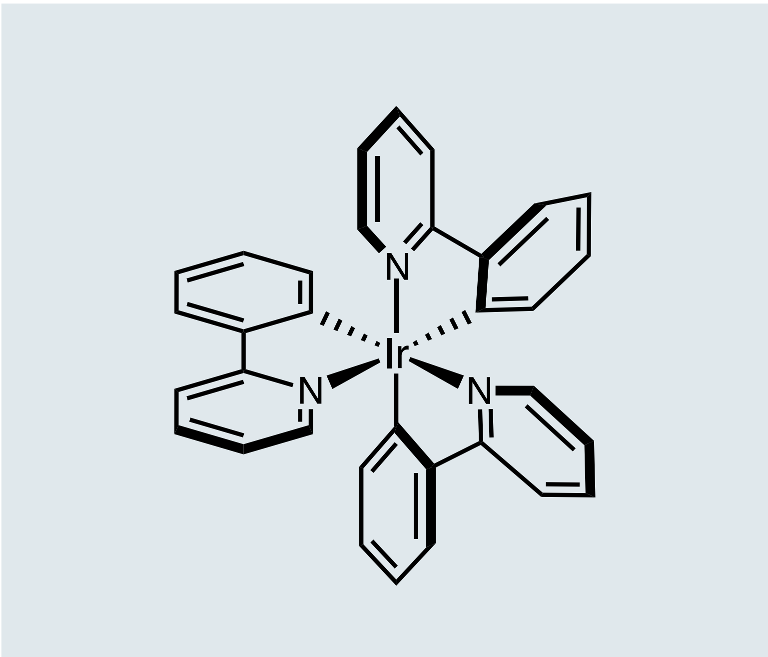
MacMillan Group Meeting
10/17/2018

Introduction

Why should we care about first-row transition metal photocatalysts?

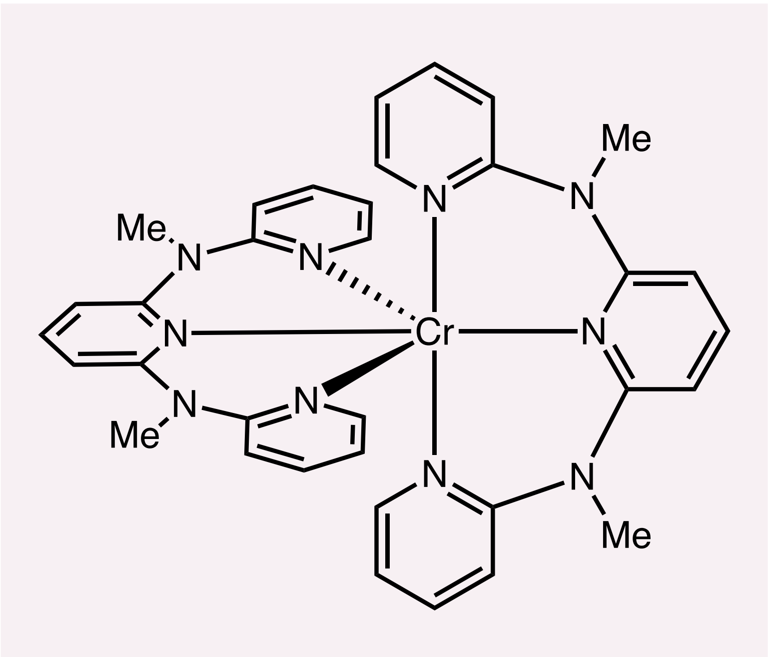
Properties of Organometallic Photocatalysts

2nd and 3rd row TM Photocatalysts



- Long lived phosphorescent T_1 state
- Tunable oxidation and reduction potential
- Singlet ground state
- Highly optimized for SET

First row transition metal photocatalysts



- Weak fluorescence, usually TADF
- Ligand dependent absorption spectra
- Singlet or higher spin ground states
- Can do SET and other chemistry

Wenger, O. *Chem. Eur. J.* **2018**, *24*, 2039

Introduction

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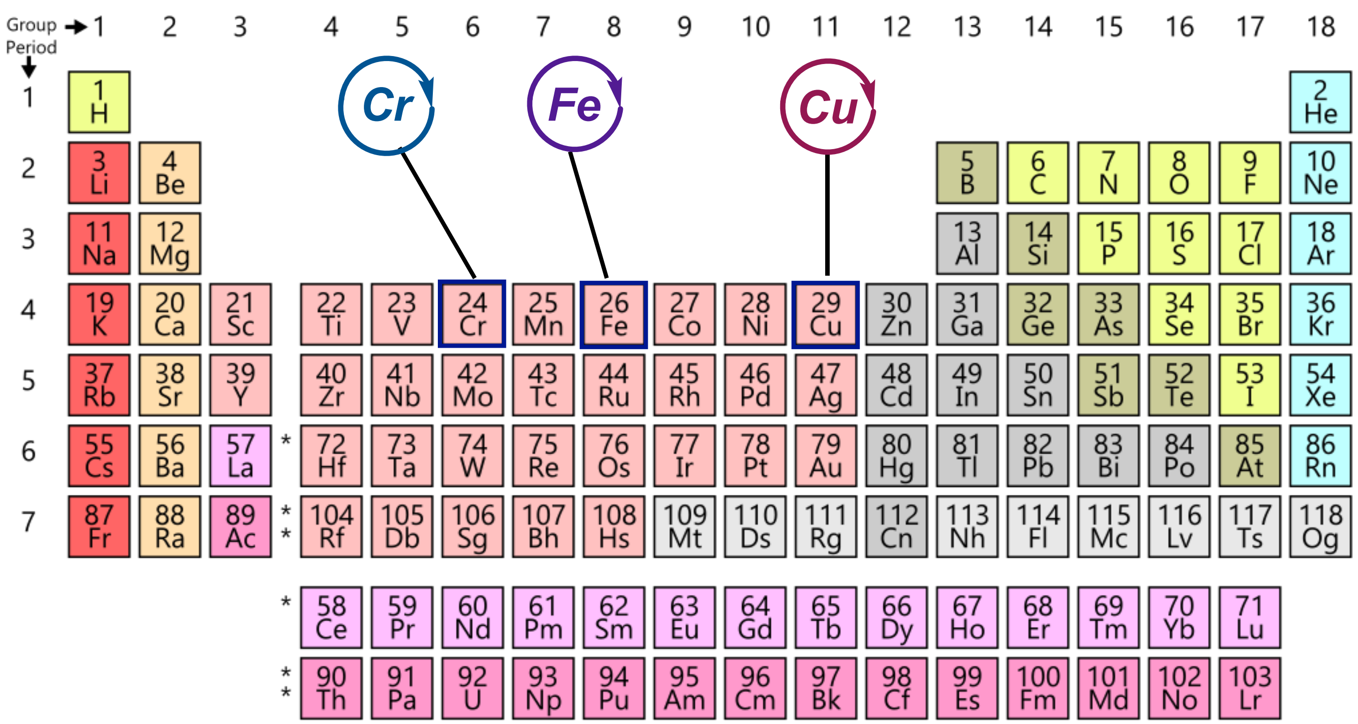
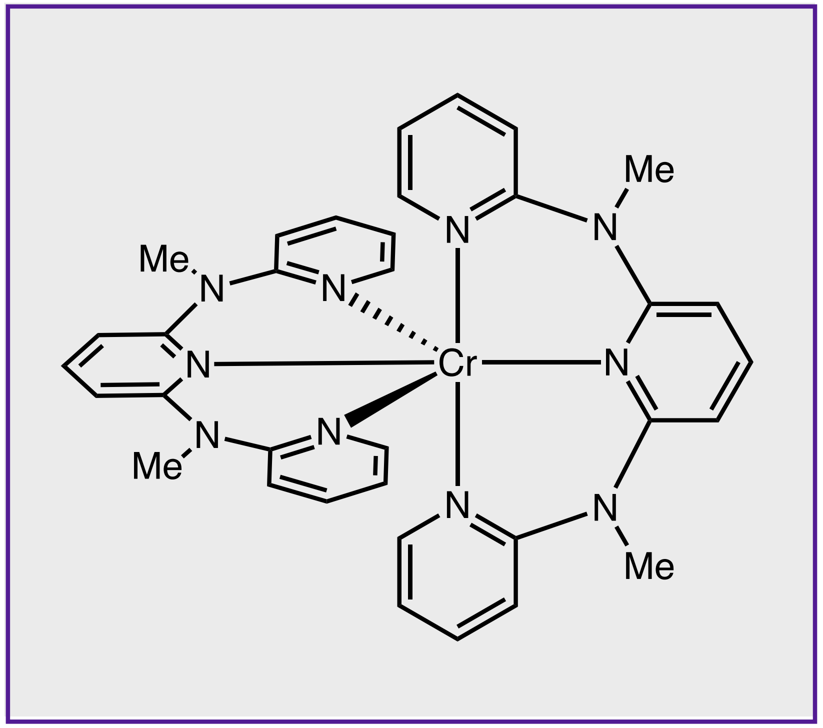
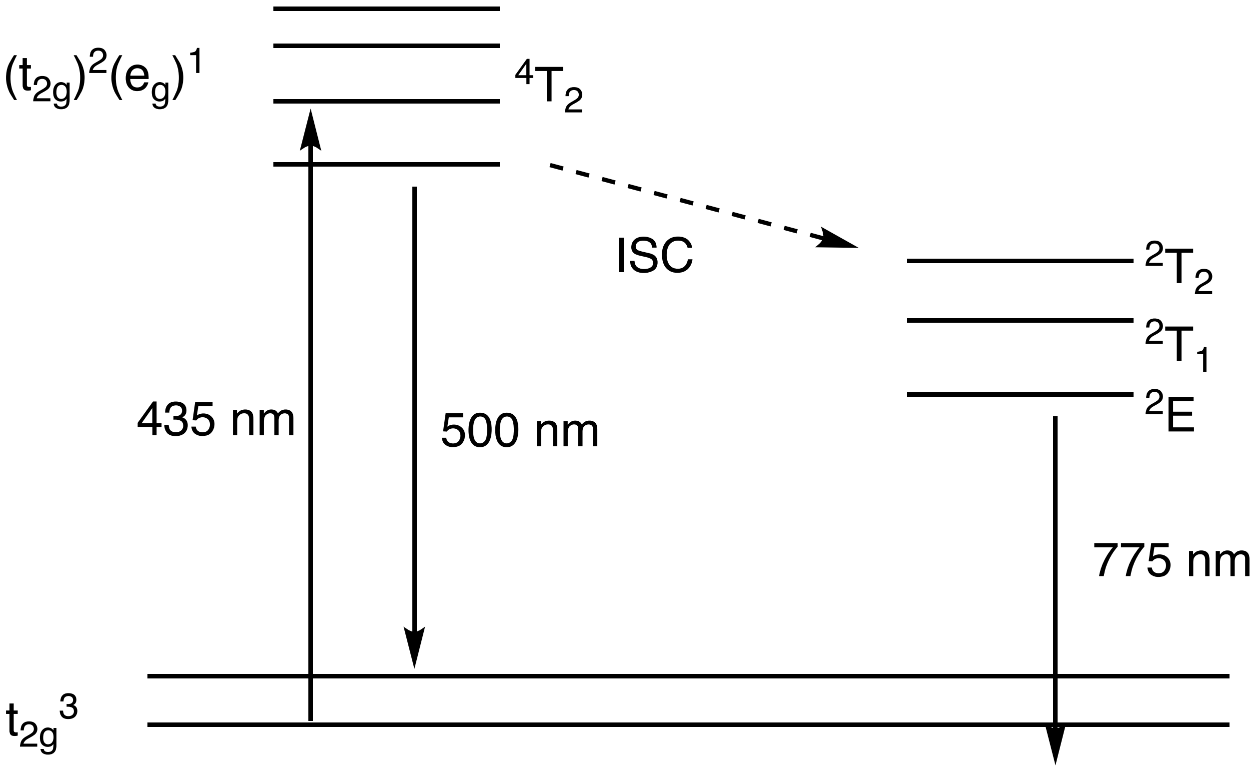
- **Triplet Sensitization with chromium**
- **Ligand-directed photochemistry with copper**
- **Direct photo-HAT with iron**



Chromium-Based Photocatalysts



$^4A_2$ ground state



- Quartet ground state (3 unpaired electrons)
- High photon absorption, Φ = 12.1% ($Cr[bpy]^{3+}$, Φ = 0.09%)
- Long-lived lifetimes of 899, 898, 1164 µs ($Cr[bpy]^{3+}$, 63 µs)

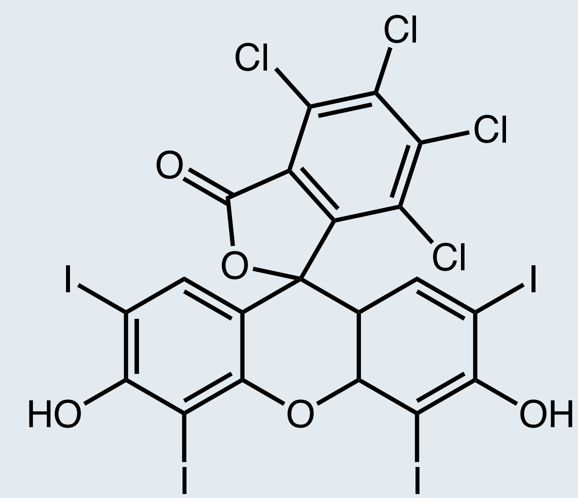
Heinze, K., *Angew. Chem. Int. Ed.*, **2015**, *54,* 11572

Oxygen Sensitization with Organic Dyes

Singlet Oxygen Production

$$^{3}O_2 \xrightarrow[\text{photosensitizer}]{\text{light}} {}^{1}O_2$$

Photobleaching of photosensitizer can be problematic



Rose bengal

$\{^{3}D \text{ - - - - - - } ^{3}A\}^{*}$ ***pentet***

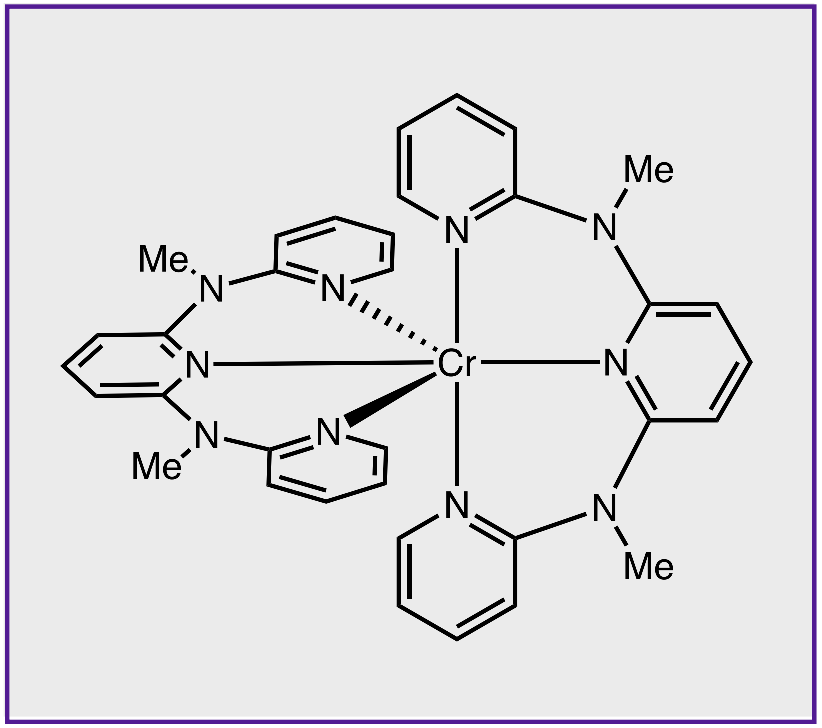
$\{^{3}D \text{ - - - - - - } ^{1}A\}^{*}$ ***triplet***

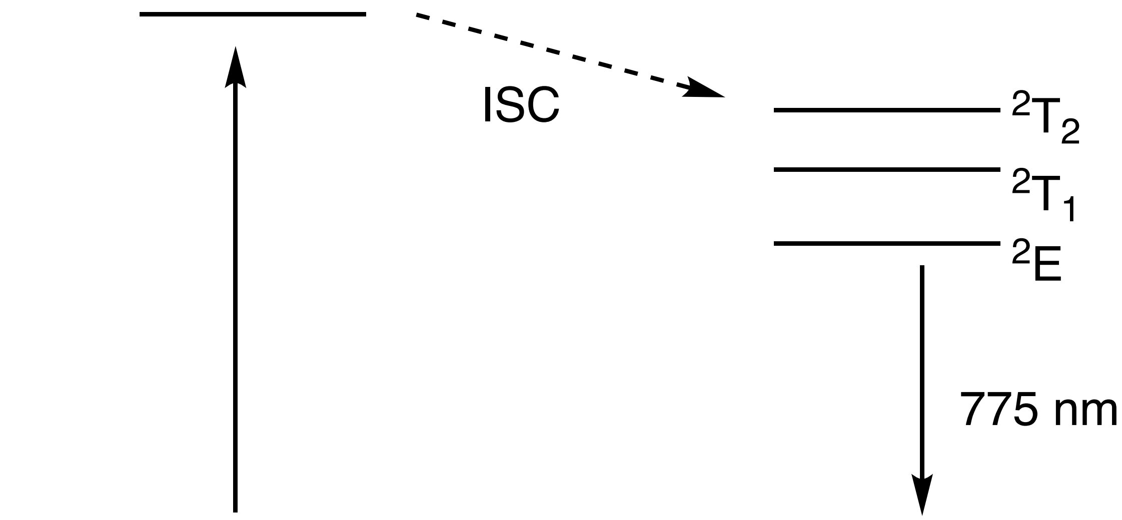
$\{^{1}D \text{ - - - - - - } ^{1}A\}^{*}$ ***singlet***

Spin statistics suggest that TTA produces an overall singlet state only 11% of the time (exclusions apply)

Heinze, K., *Angew. Chem. Int. Ed.*, **2015**, *54,* 11572

Oxygen Sensitization with Chromium





Excited state doublet

$$\left\{ {}^2D \text{ ------ } {}^3A \right\}^* \quad \textit{quartet}$$

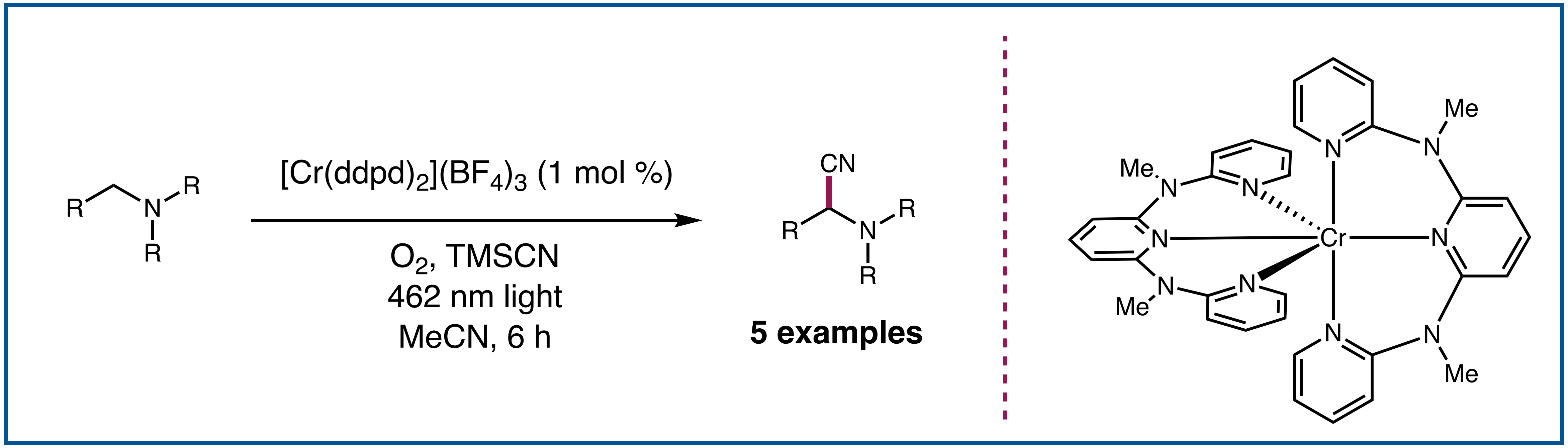
$$\left\{ {}^2D \text{ ------ } {}^1A \right\}^* \quad \textit{doublet}$$

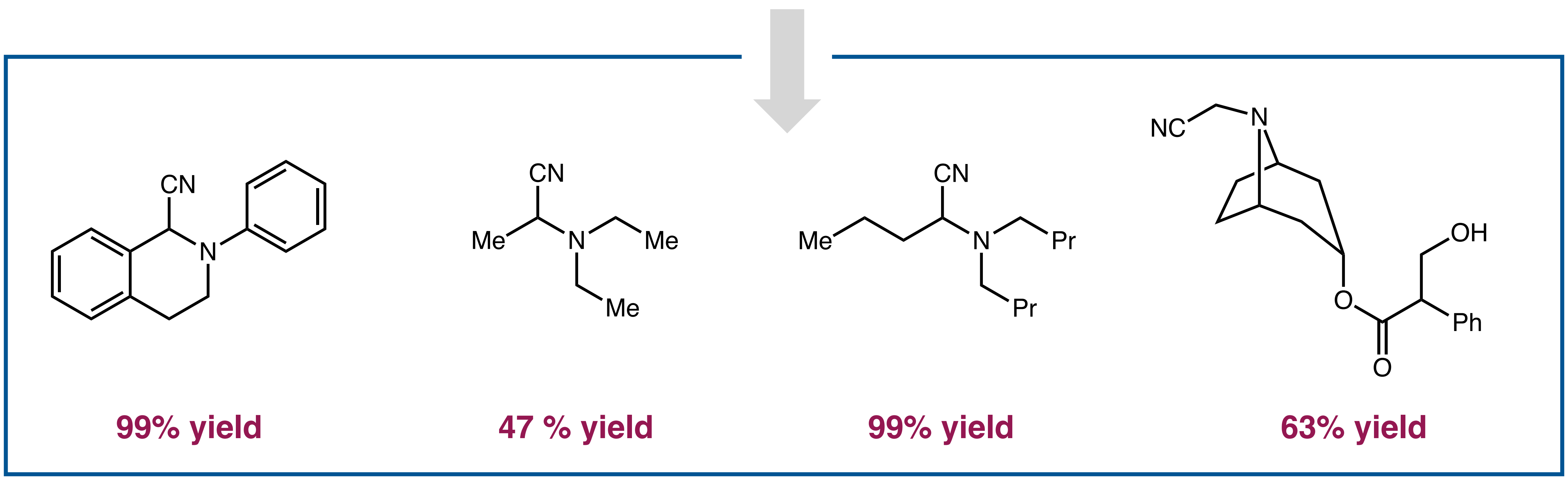
Quartet ground state carries away spin, so 4 out of 6 microstates lead to singlets

6-fold increase in collision efficiency

Heinze, K., *Angew. Chem. Int. Ed.* **2015**, *54*, 11572

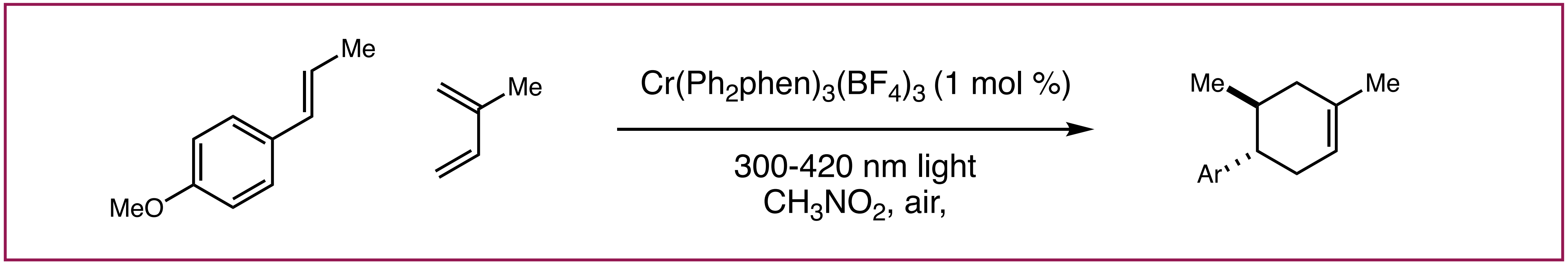
Amine α-cyanation with Cr

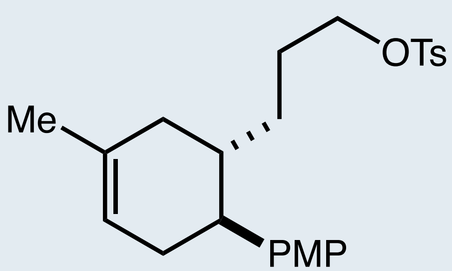




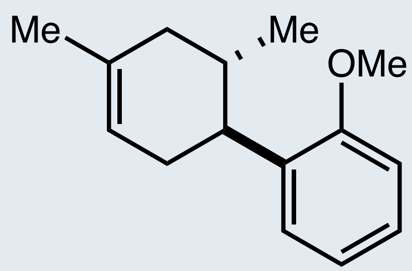
Opatz, T. *ChemPhotoChem*, 2017, **1**, 344

Radical Cation [4+2] with Chromium Photocatalysts

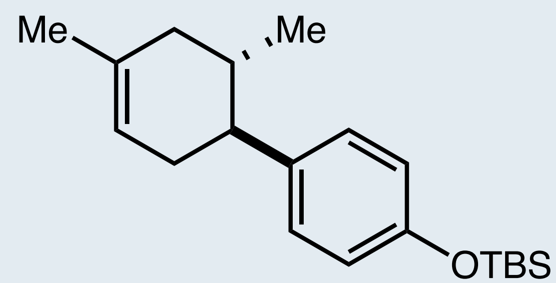




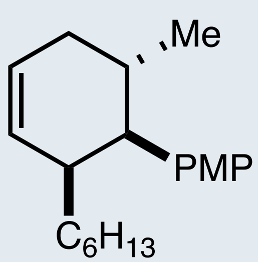
96% yield



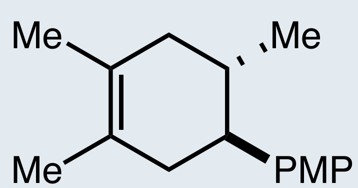
76% yield



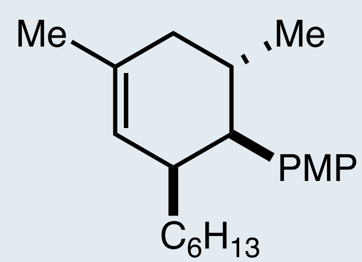
78% yield
23W CFL, 50% yield



89% yield
15:1 endo/exo



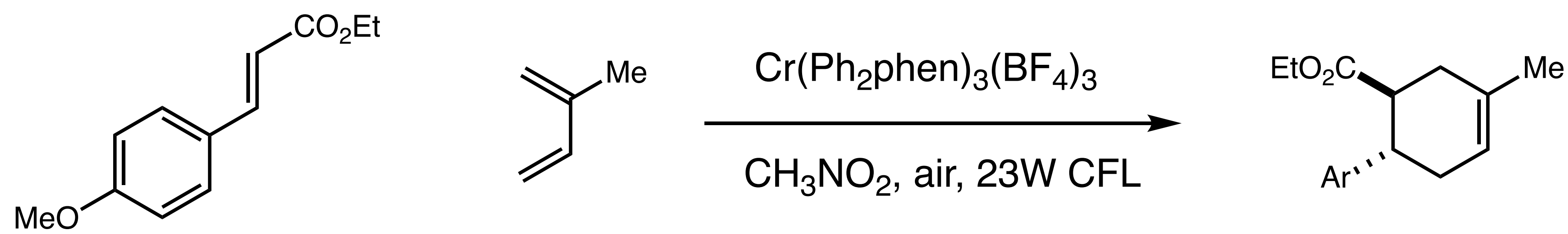
86% yield
19:1 d.r.

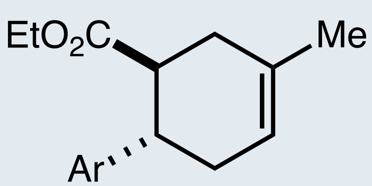


74% yield
6:1 endo:exo

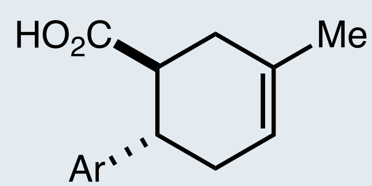
Ferreira, E. M. *Angew. Chem. Int. Ed.* **2015**, *54*, 6506

Radical Cation [4+2] with Chromium Photocatalysts

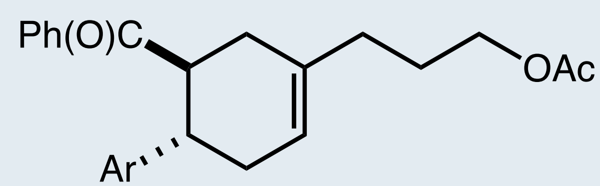




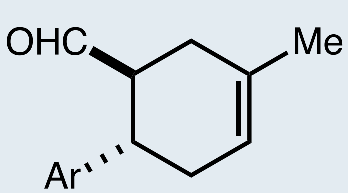
75% yield
19:1 r.r.



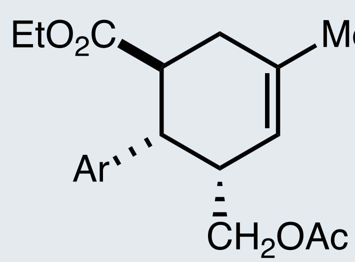
57% yield
17:1 r.r.



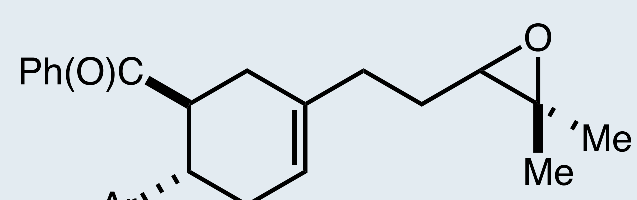
61% yield
7:1 r.r.



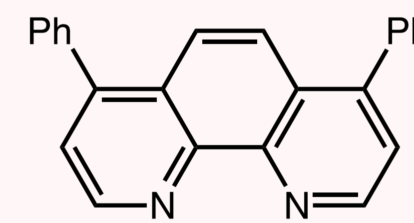
53% yield
11:1 r.r.



78% yield
6:1 r.r.

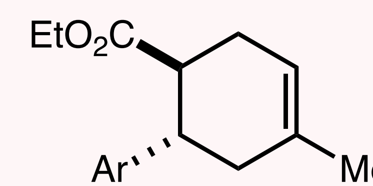


72% yield
7:1 r.r.



Ph_2Phen

Φ = 0.21in degassed solvent

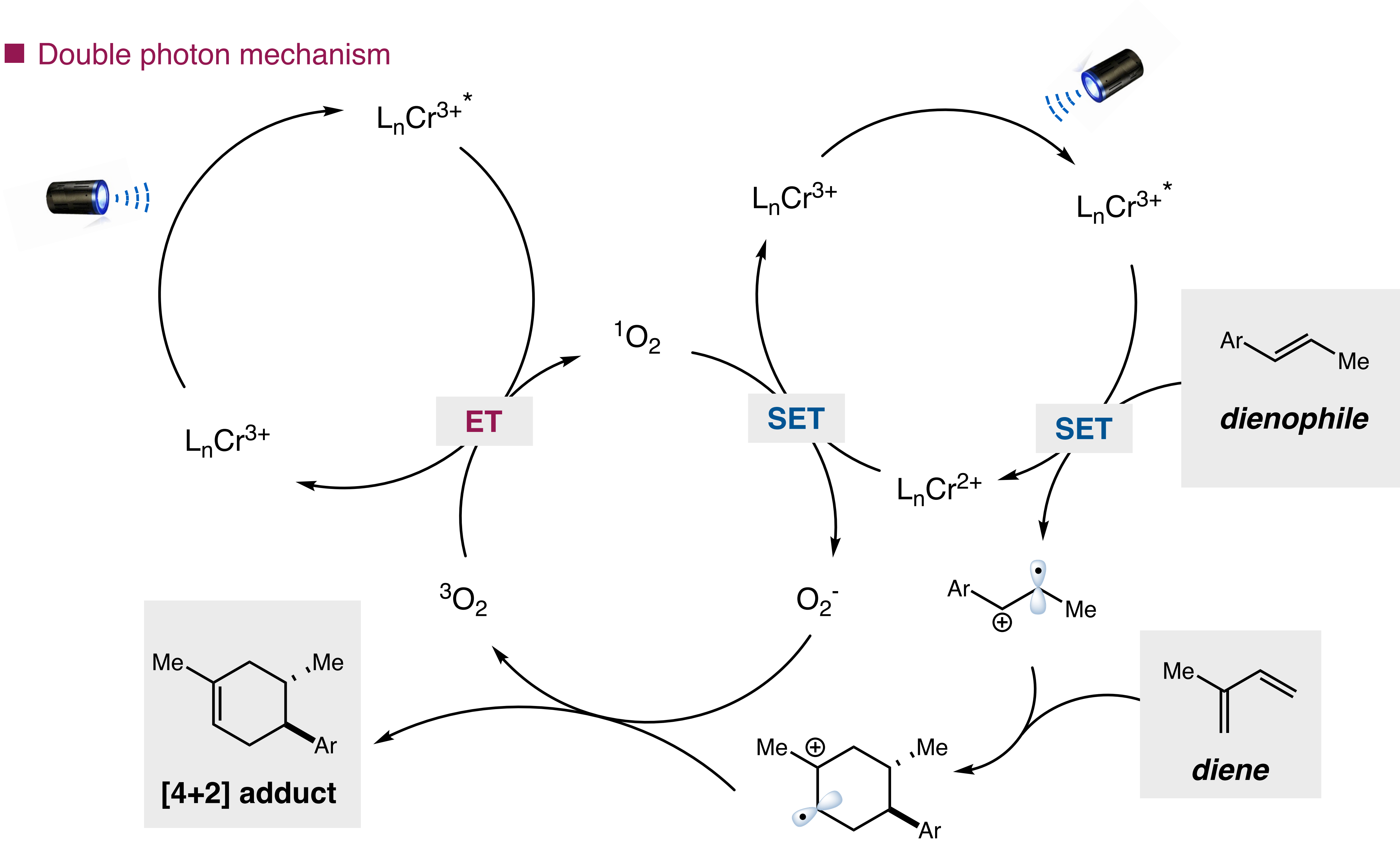


Reversed regioselectivity with respect to Diels Alder!

Shores, M. P. *J. Am. Chem. Soc.* **2016**, *138*, 5451

Oxygen Sensitization for [4+2] Cycloadditions

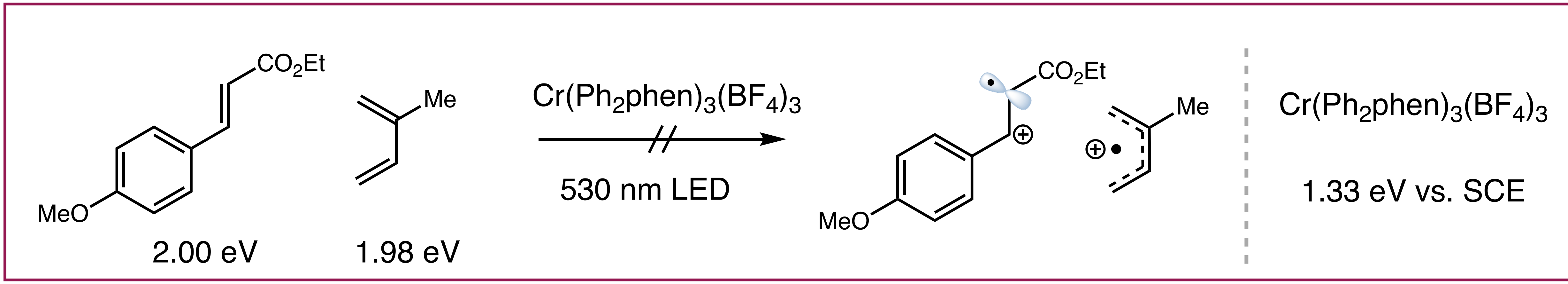
■ Double photon mechanism

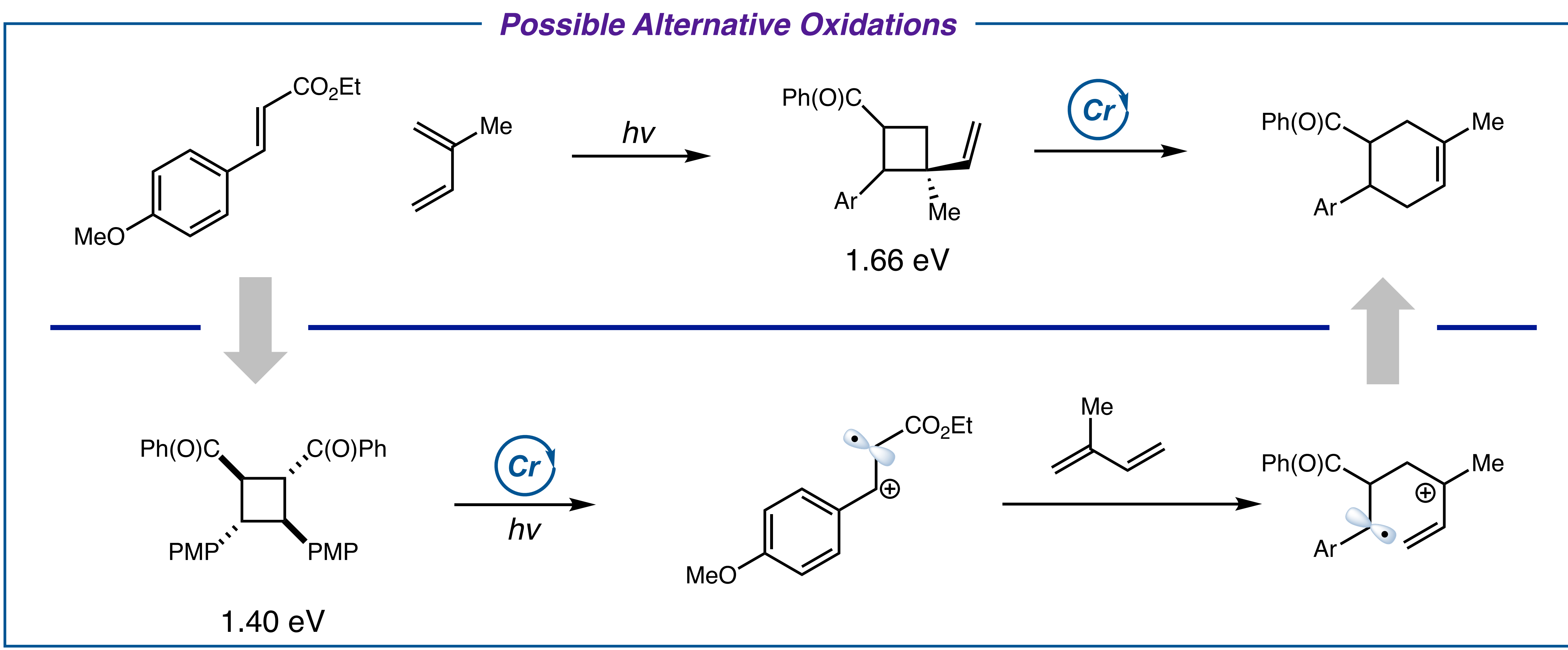


Energy transfer and electron transfer from same photocatalyst

Shores, M. P. *J. Am. Chem. Soc.* **2016**, *138*, 5451

Formation of Radical Cation Intermediate

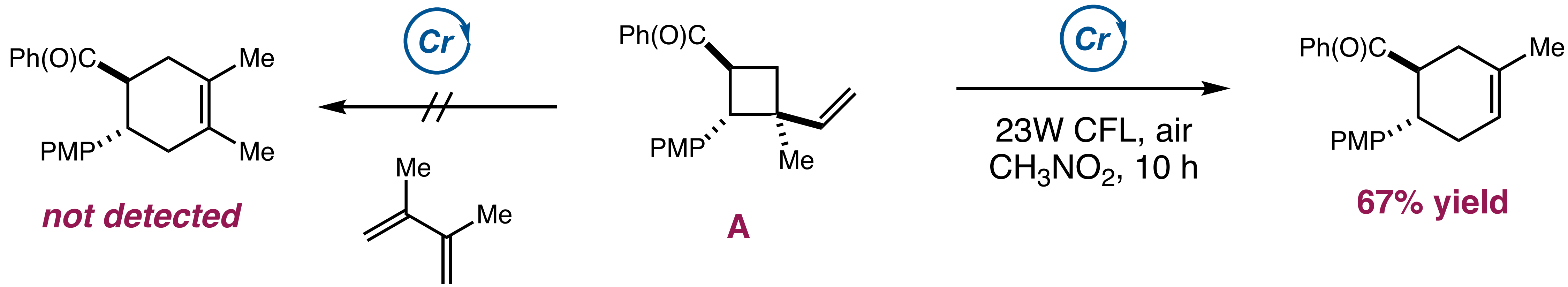




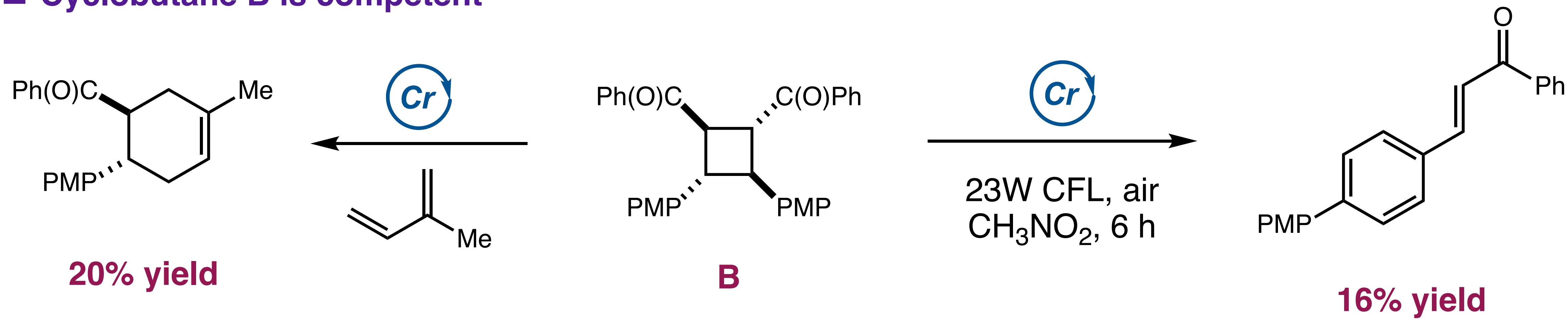
Shores, M. P. *J. Am. Chem. Soc.* **2016**, *138*, 5451

Convergent Reactivity

■ **Cyclobutane A is competent**



■ **Cyclobutane B is competent**



All roads lead to Rome!

Shores, M. P. *J. Am. Chem. Soc.* **2016**, *138*, 5451

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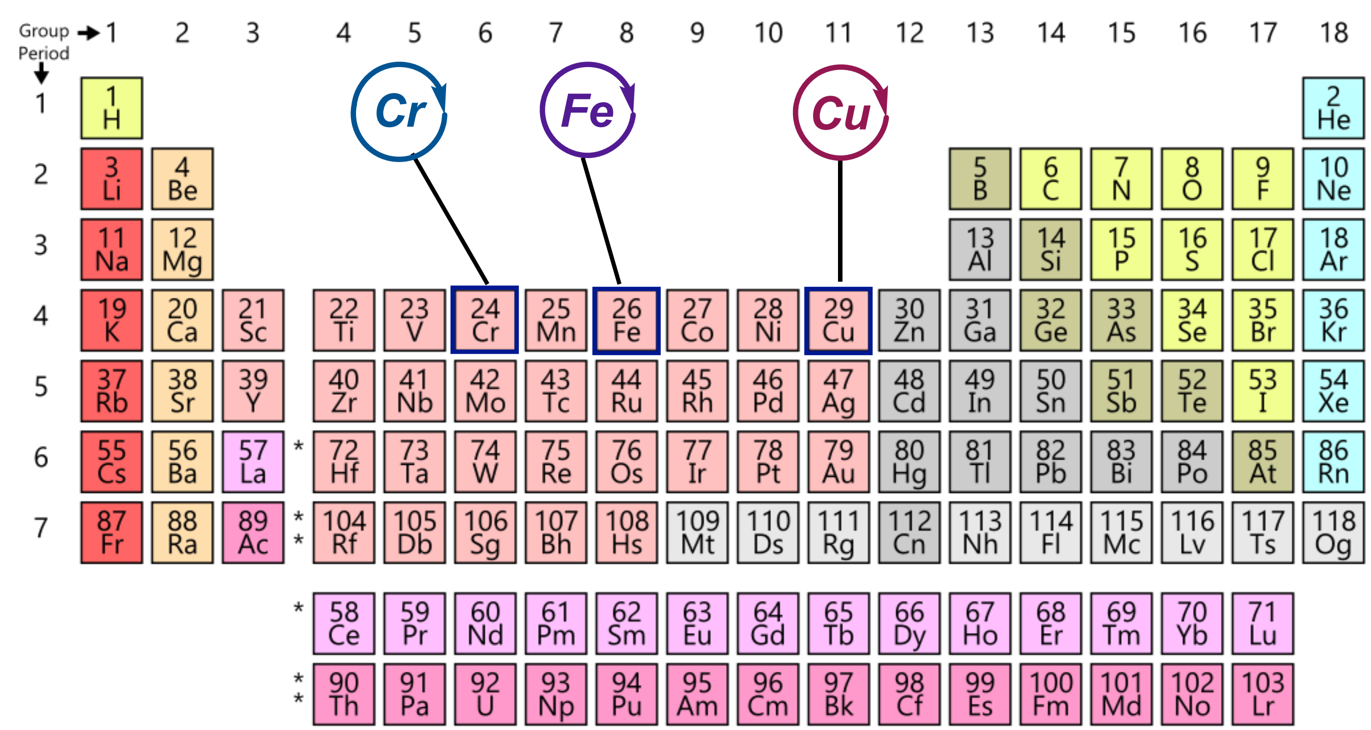
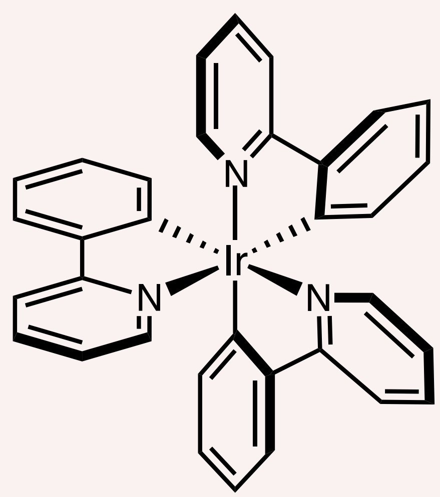
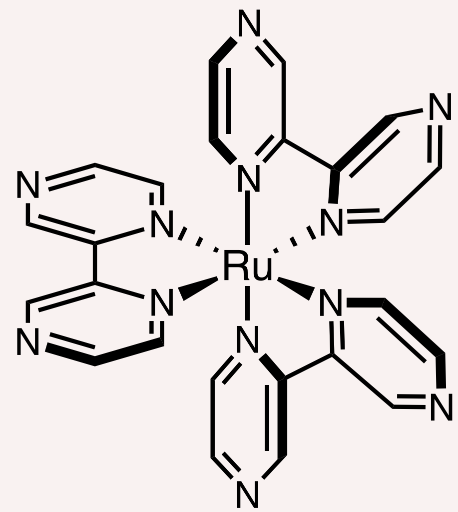


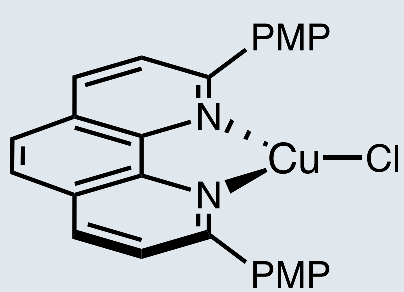
Ligand Substitution on Organometallic Photocatalysts



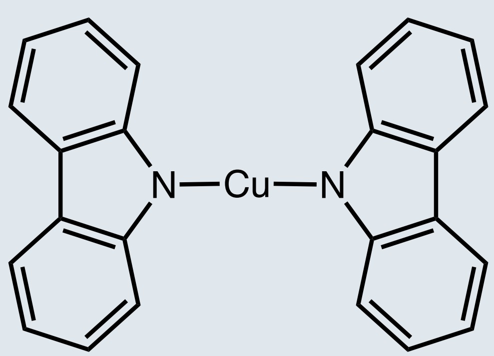
Ir(ppy)$_3$



Ru(bpz)$_3$



Cu(dap)Cl



LiCuCz$_2$

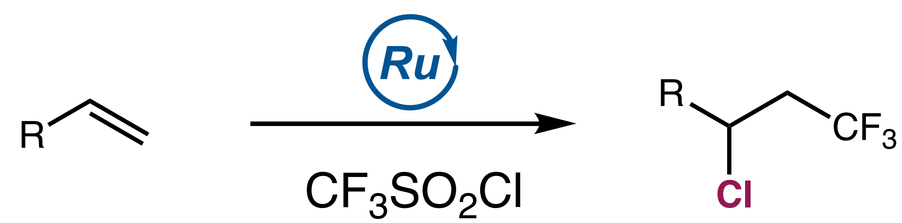
- Ir,Ru tris-complexes are usually inert to ligand exchange
- Ligand exchange is usually through two-point binding
- LMCT, MLCT bands interrupted by substitution

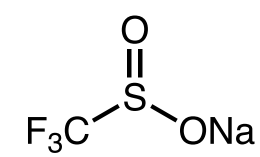
- Cu substitution is facile
- Ligand-Metal complex can be directly excited

Wenger, O. *Chem. Eur. J.* **2018**, *24*, 2039

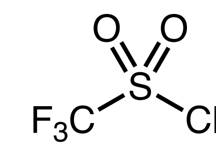
Ligand Directed Cu Photocatalysts

■ Trifluoromethylchlorination



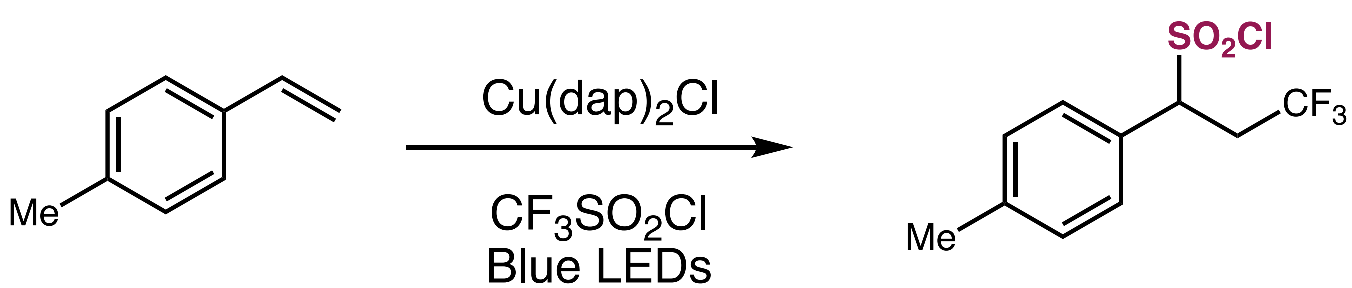


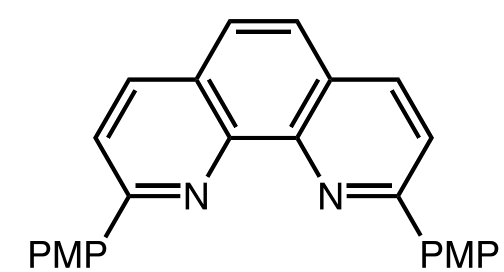
Langlois Reagent
source of CF_3 radical



ATRA reagent
for CF_3 and Cl transfer

■ Trifluoromethylsulfonylation



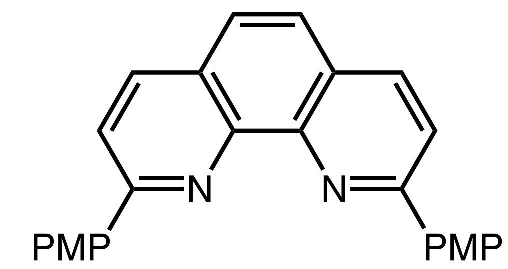


dap ligand

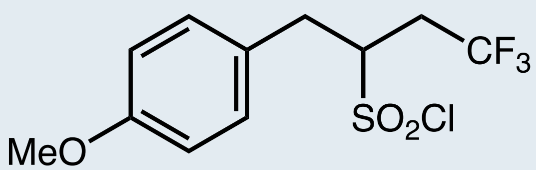
Ligation to photoactive metal center can directly affect radical stability

Han, S. B. *Org. Lett.* **2014**, *16*, 1310
Reiser, O. *Angew. Chem. Int. Ed.* **2015,** *127*, 6999

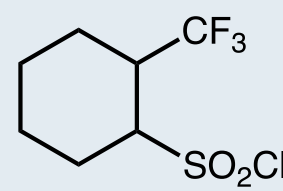
Trifluoromethylchlorosulfonylation with Copper



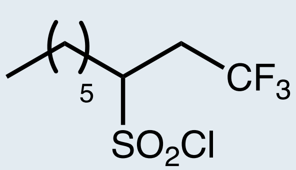
No Lewis Basic donors



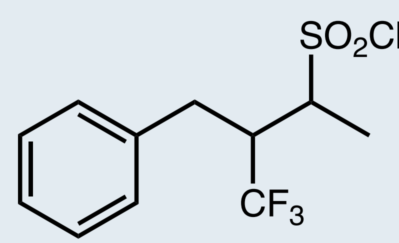
76% yield



56% yield

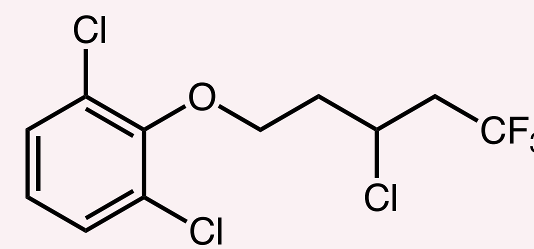


71% yield

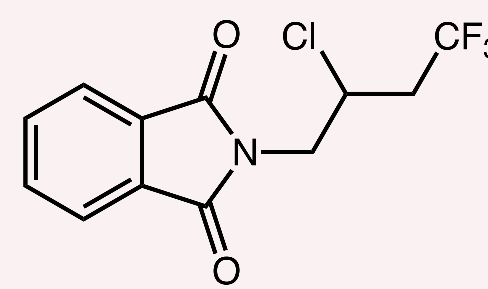


67 % yield
7:3 rr ratio

Lewis basic donors



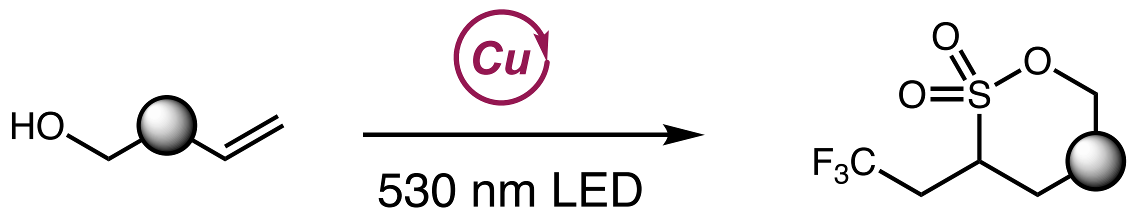
57% yield



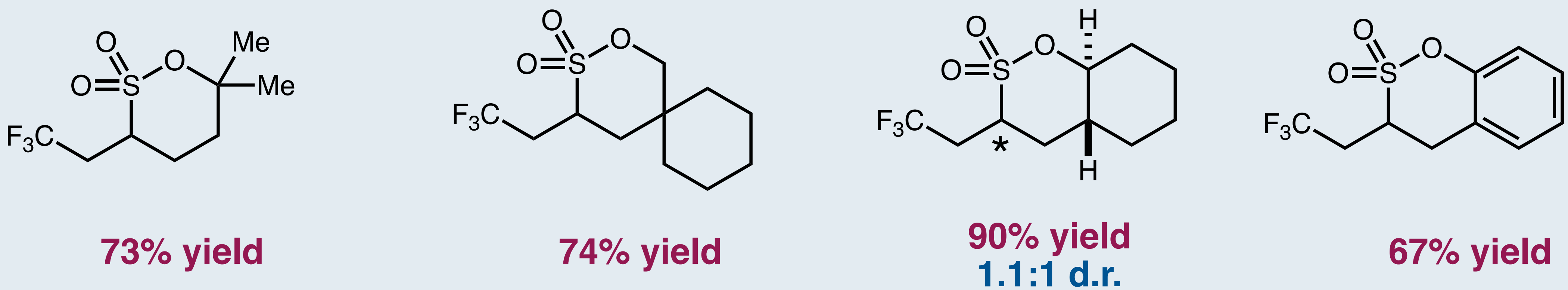
53% yield

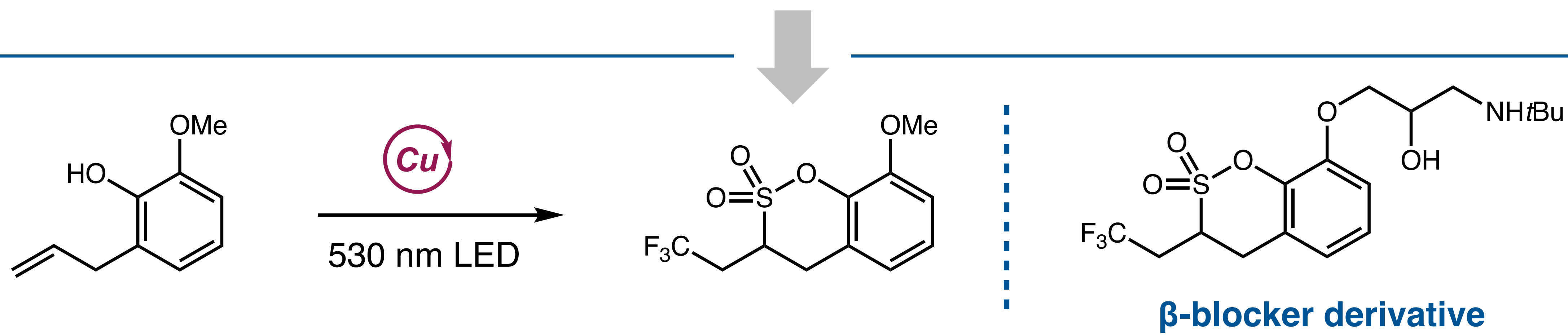
Reiser, O. *Angew. Chem. Int. Ed.* **2015,** *127*, 6999

Ligand-Directed Photocatalysis with Copper



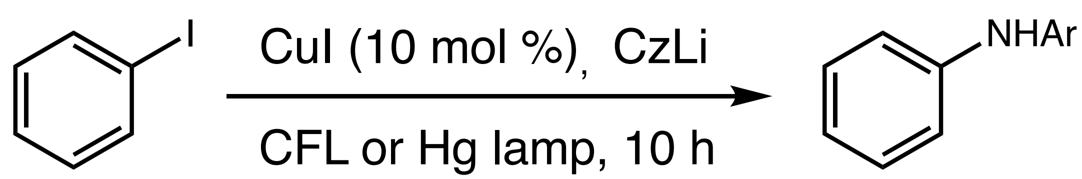
- Sultone formation is rare
- SO_2Cl moiety tolerates alcohols





Reiser, O. *J. Org. Chem.* **2016**, *81*, 7139

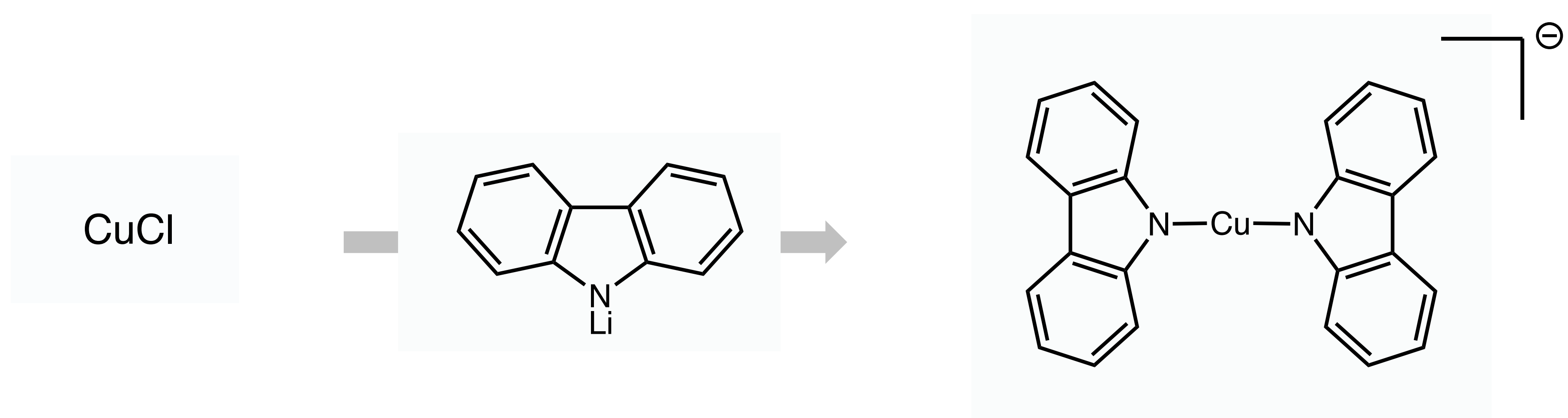
Ligand Excitation of Copper Complexes



65 % yield

- *Light necessary for reaction*
- *Amine deprotonation requires base*
- *Yield increased with Hg lamp*
- *Radical pathway*

Formation of UV-active Cu Complexes



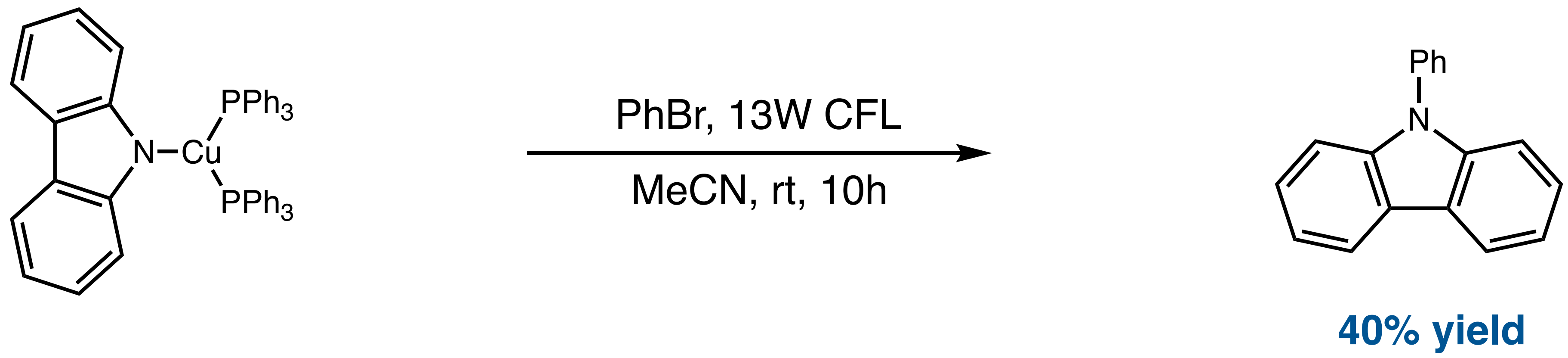
Non-absorptive

Absorbs at short and long UV
Competent intermediate for cross-coupling

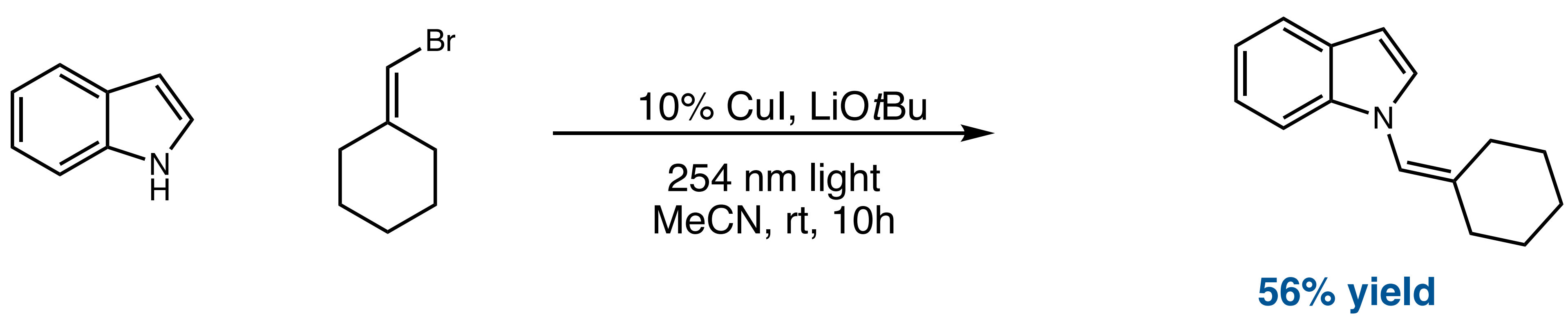
Fu, G. *Science*, **2012**, *338*, 647

Photoinduced Ullmann Couplings

N-Arylation of Heteroarenes



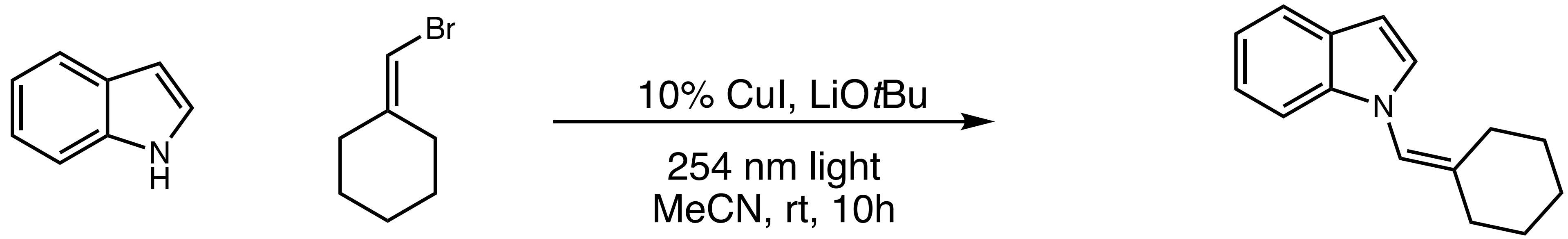
■ Catalytic copper can be used



Fu, G. *Science*, **2012**, *338*, 647

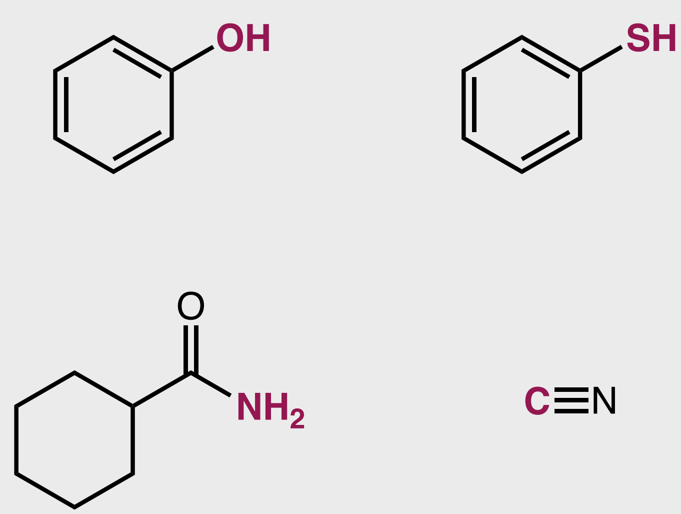
Photoinduced Ullmann Couplings

■ Catalytic Ullmann couplings

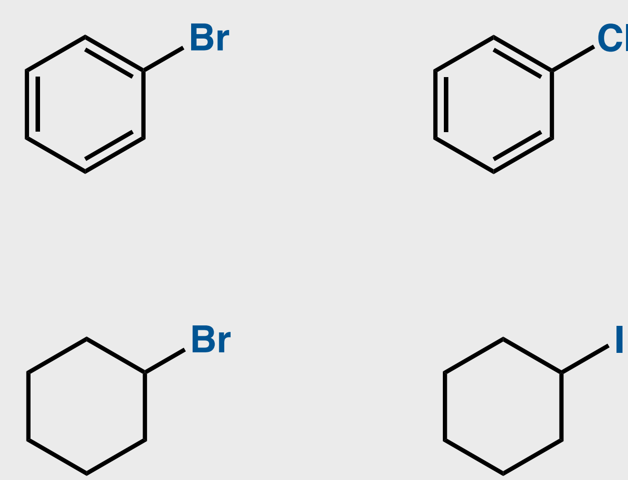


56% yield

■ Nucleophiles

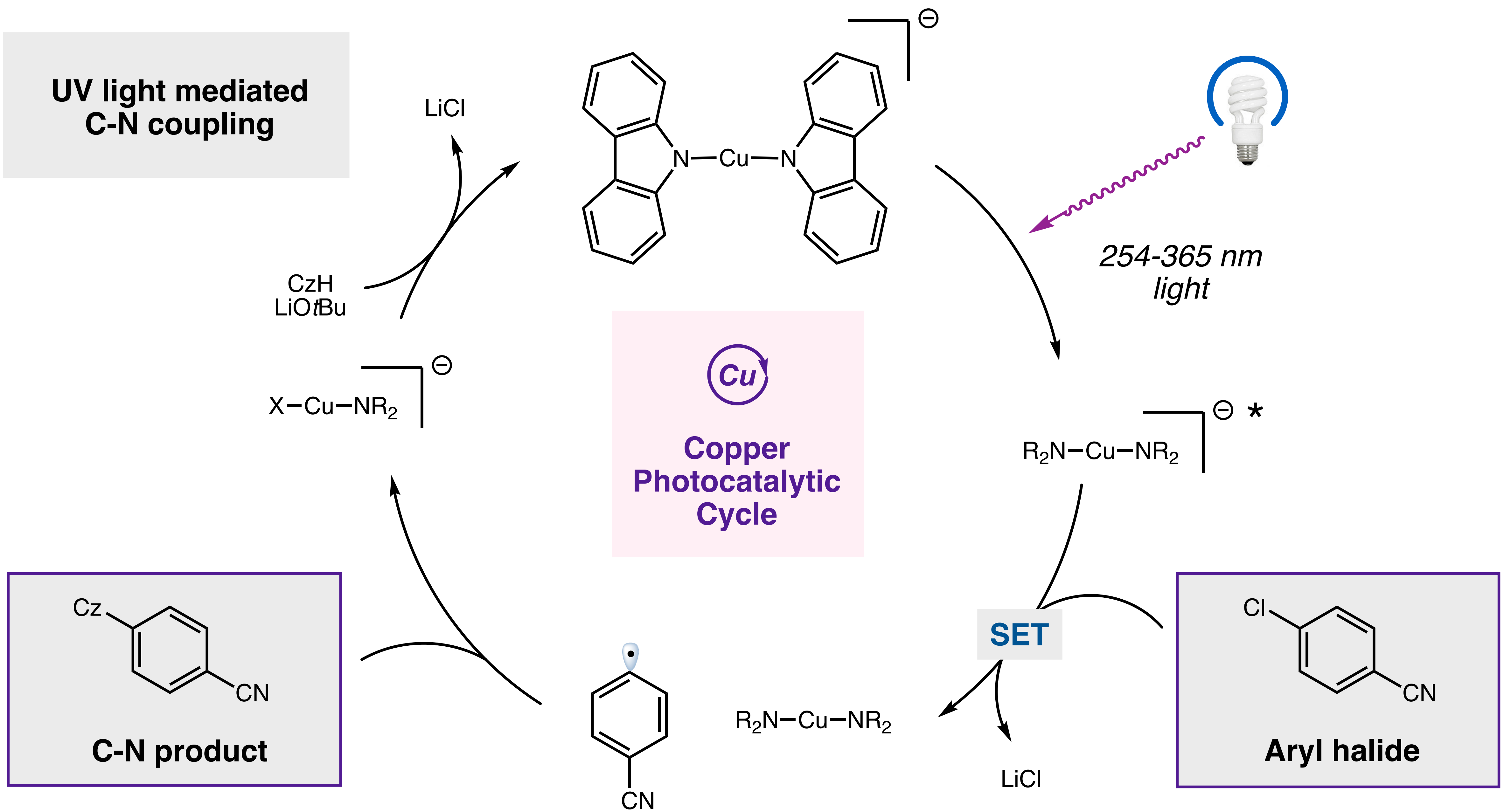


■ Electrophile



Fu, G. *J. Am. Chem. Soc.* **2014**, *136*, 2162
Fu, G. *Science*, **2012**, *338*, 647

Copper Arylation with UV Light

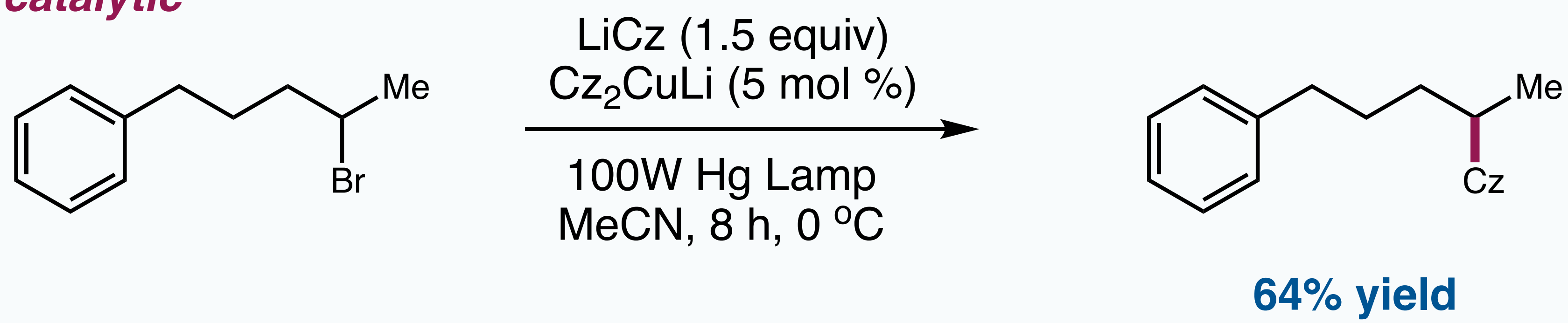


Fu, G. *J. Am. Chem. Soc.* **2013**, *135,* 13107

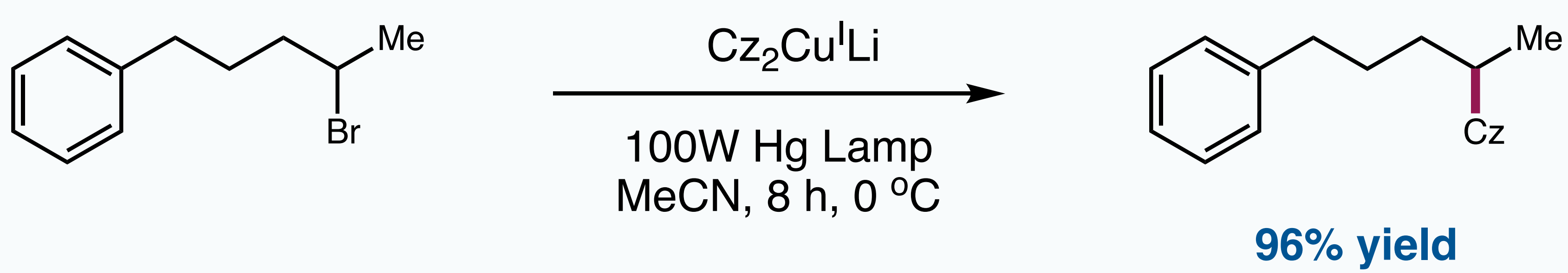
Mechanistic Investigation of CuCz System

- Copper carbazolide system selected for further study

catalytic

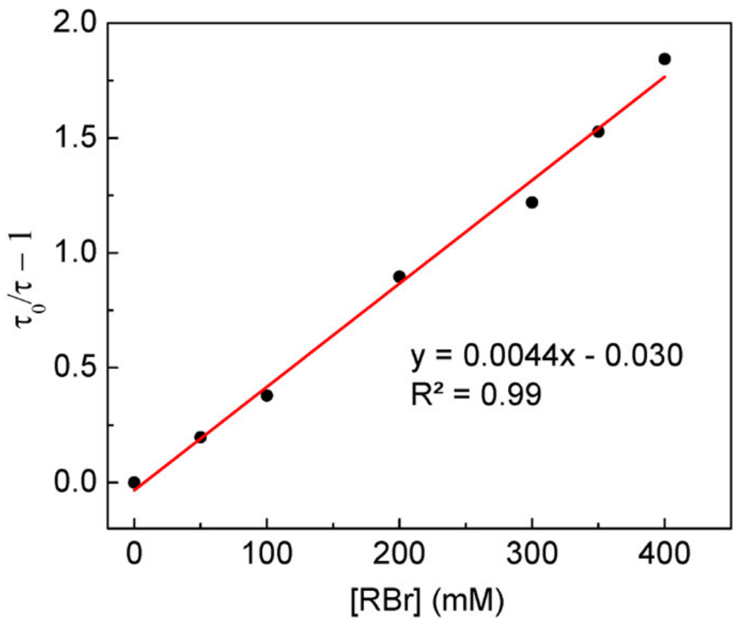


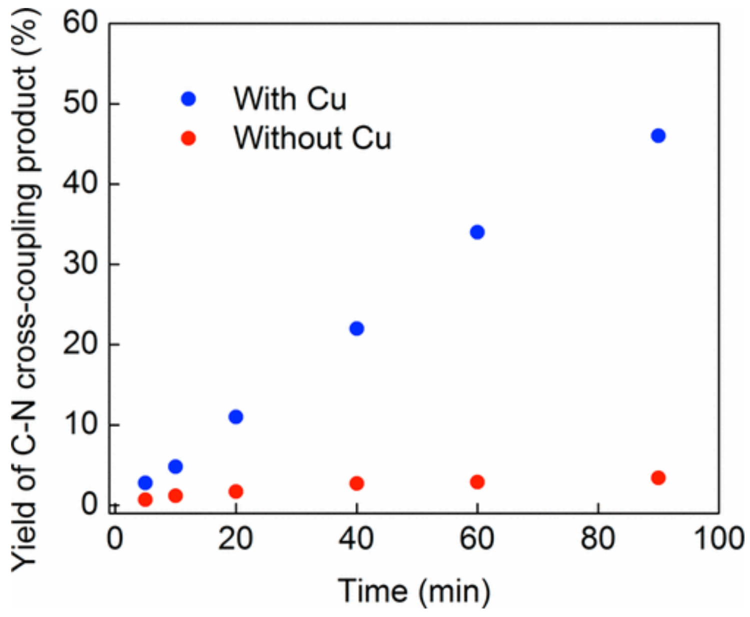
stoichiometric



Fu, G. *J. Am. Chem. Soc.* **2017** *139* 12716

Mechanistic Investigation of CuCz System





Cz_2CuLi is quenched by alkyl bromide

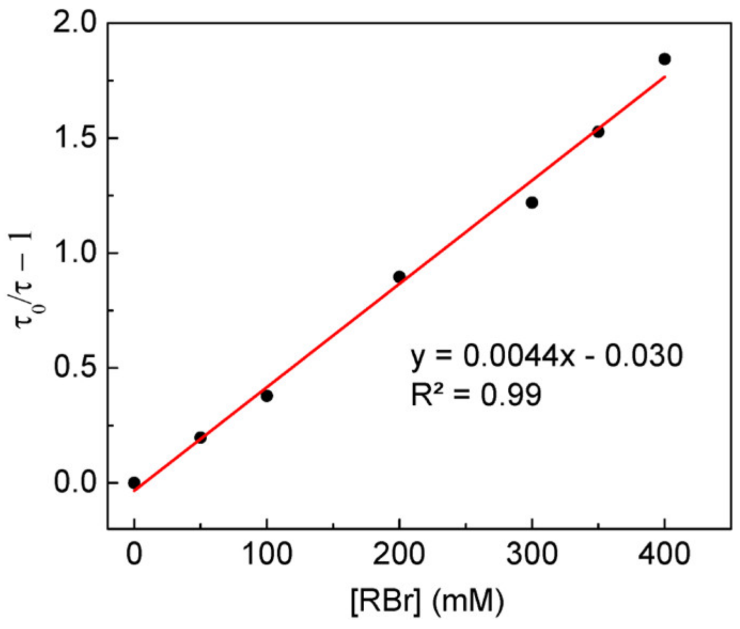
- $k_q = 4.8 \times 10^6\ M^{-1}\ s^{-1}$
- $t_{1/2,\ Cu} = 910$ ns

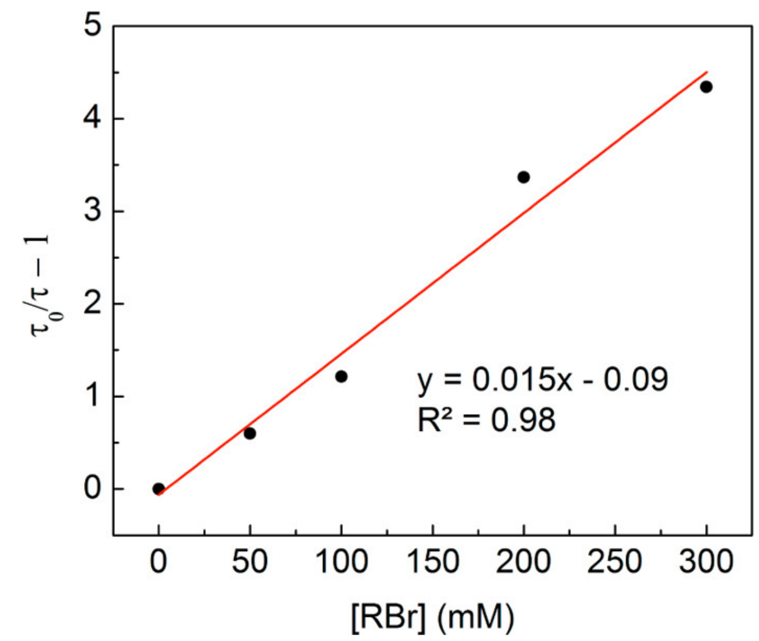
- *5% product obtained in absence of copper*
- *Yield increases over time*

What is the source of this background reactivity ?

Fu, G. *J. Am. Chem. Soc.* **2017** *139* 12716

Mechanistic Investigation of CuCz System





Cz_2CuLi is quenched by alkyl bromide

- $k_q = 4.8 \times 10^6\ M^{-1}\ s^{-1}$
- $t_{1/2,\ Cu}$ = 910 ns

LiCz also quenches alkyl bromide!

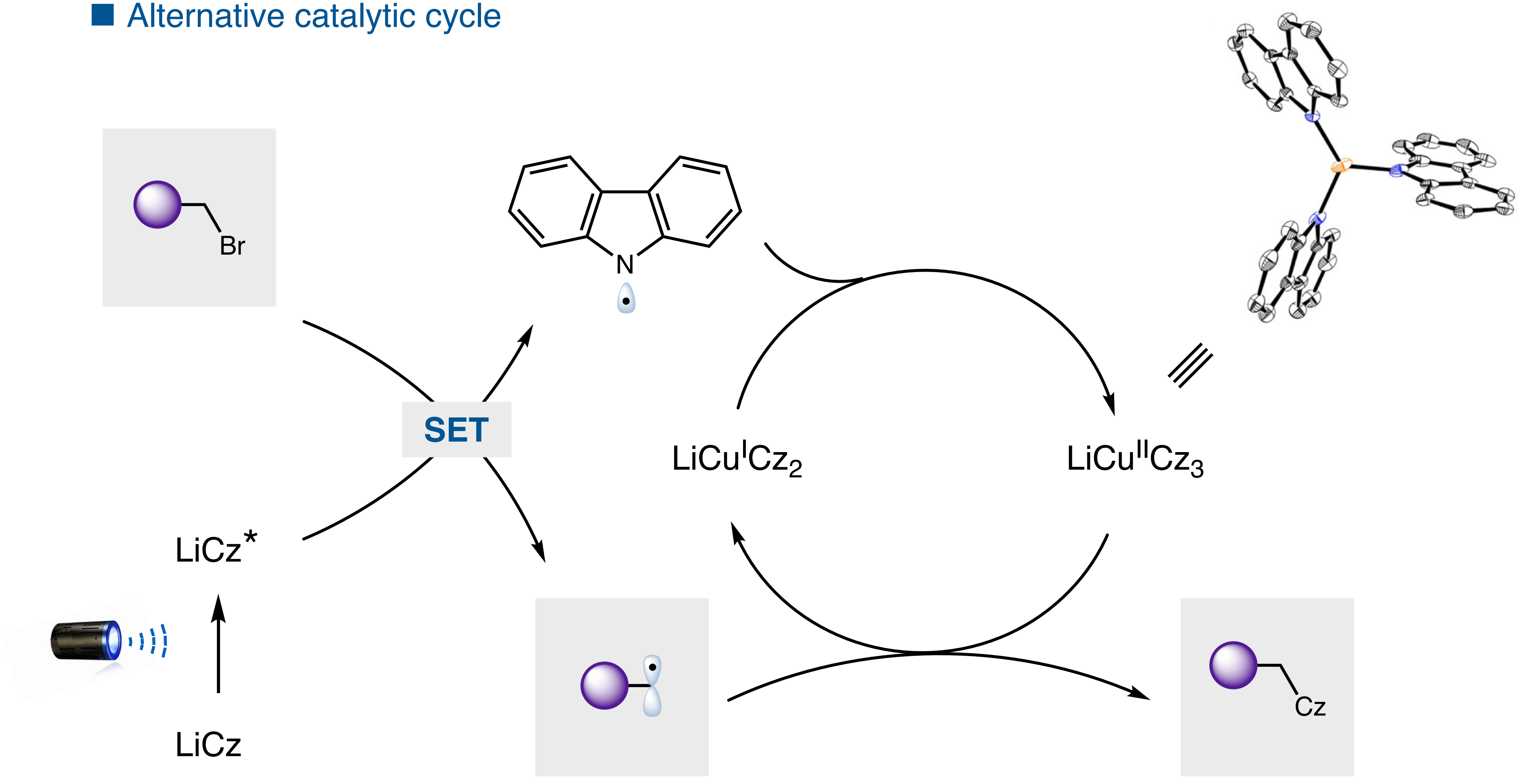
- $k_q = 4.9 \times 10^8\ M^{-1}\ s^{-1}$
- $t_{1/2,\ CzLi}$ = 31 ns

What is the source of this background reactivity ?

Fu, G. *J. Am. Chem. Soc.* **2017** *139* 12716

Mechanistic Investigation of CuCz System

■ Alternative catalytic cycle

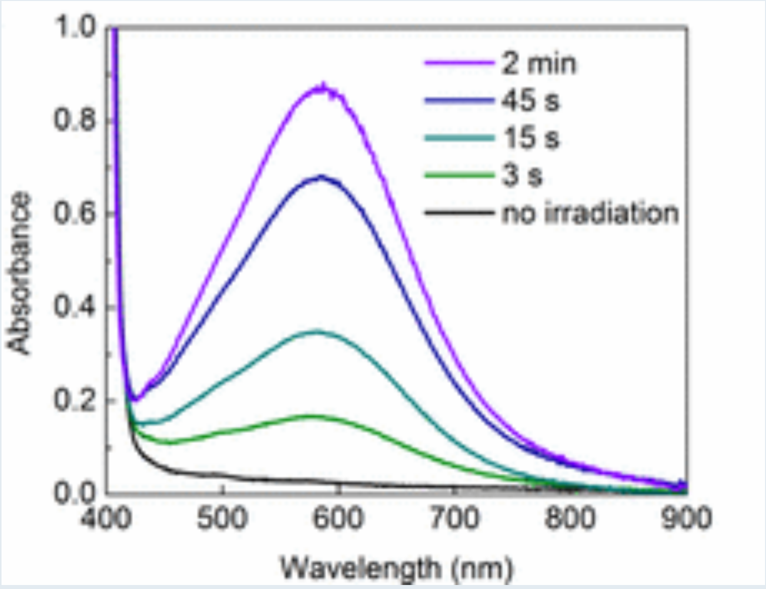


$LiCu^{II}Cz_3$ functions as a persistent radical

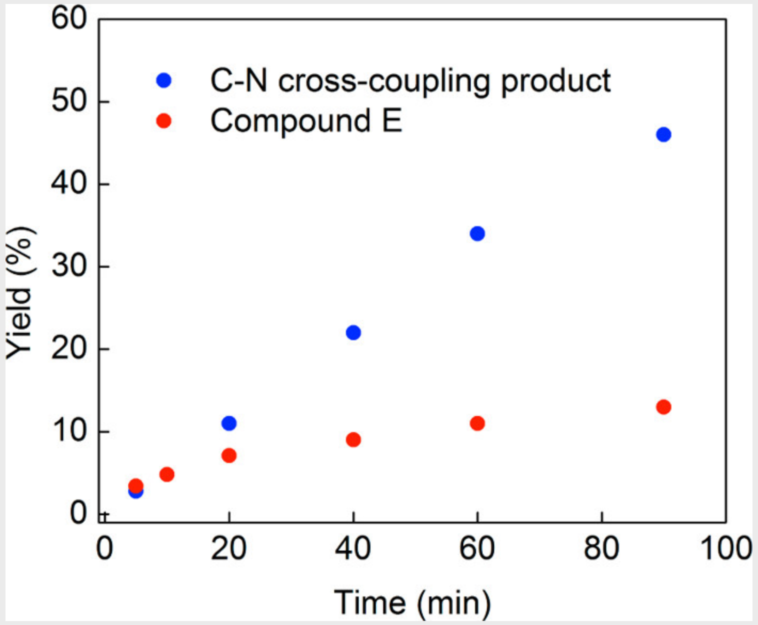
Fu, G. *J. Am. Chem. Soc.* **2017** *139* 12716

Mechanistic Investigation of CuCz System

- Off-cycle reactivity observed as concentration of key $LiCuCz_3$ builds up



Formation and change in absorption due to $LiCuCz_3$



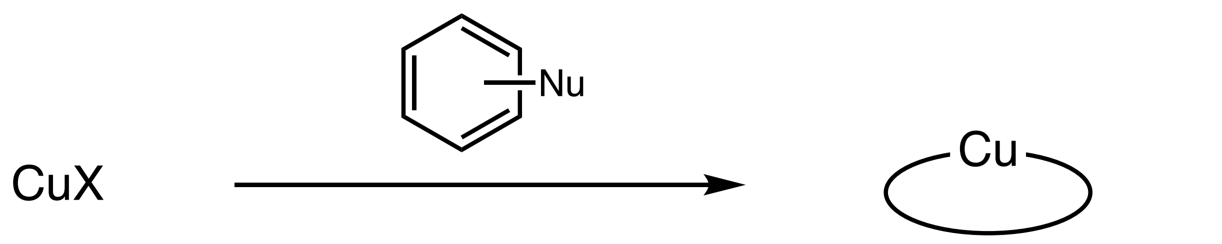
Ratio of Product/dimer increases over time

In photocatalysis with 1st row transition metals, multiple pathways are possible!

Fu, G. *J. Am. Chem. Soc.* **2017** *139* 12716

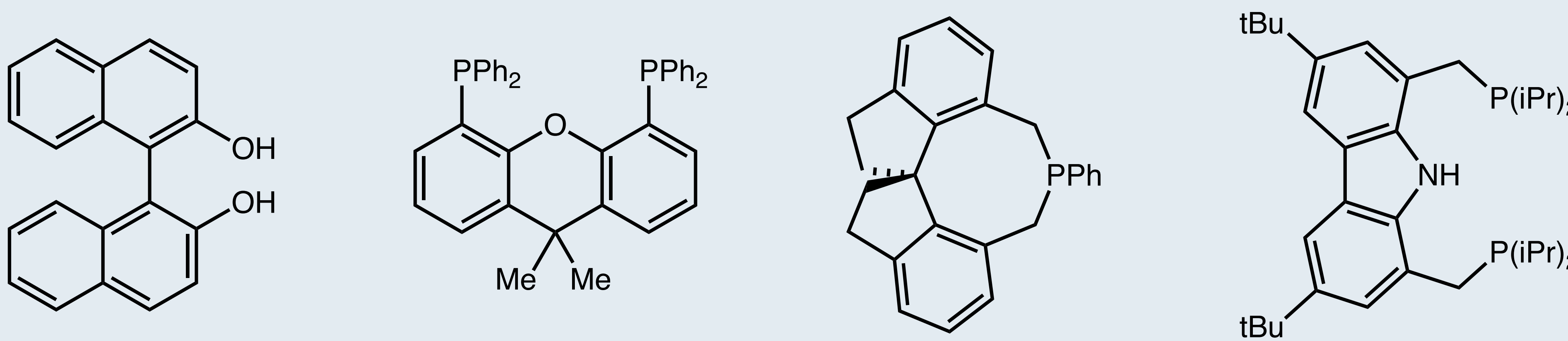
Traditional SET with Copper Catalysts

■ Formation of photoactive copper catalysts

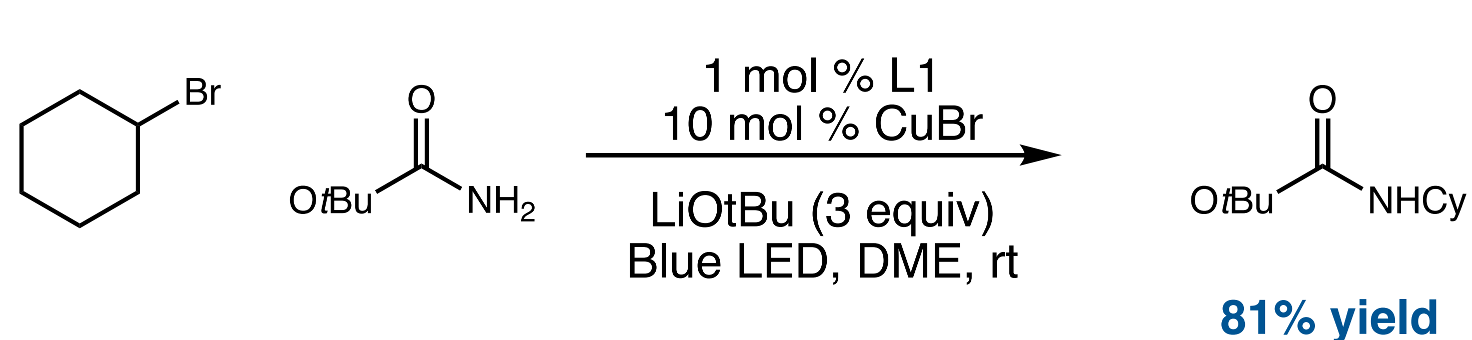


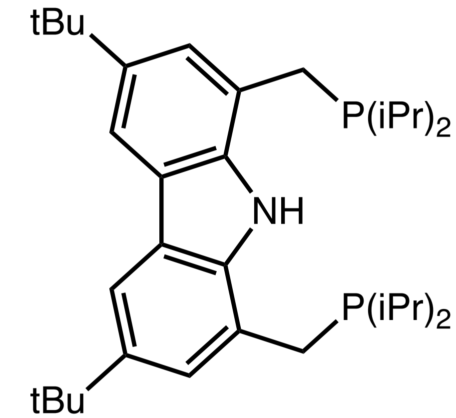
- ■ Substrate generality
- ■ Wavelength modulation
- ■ Catalyst Stability

Photoactive Ligands

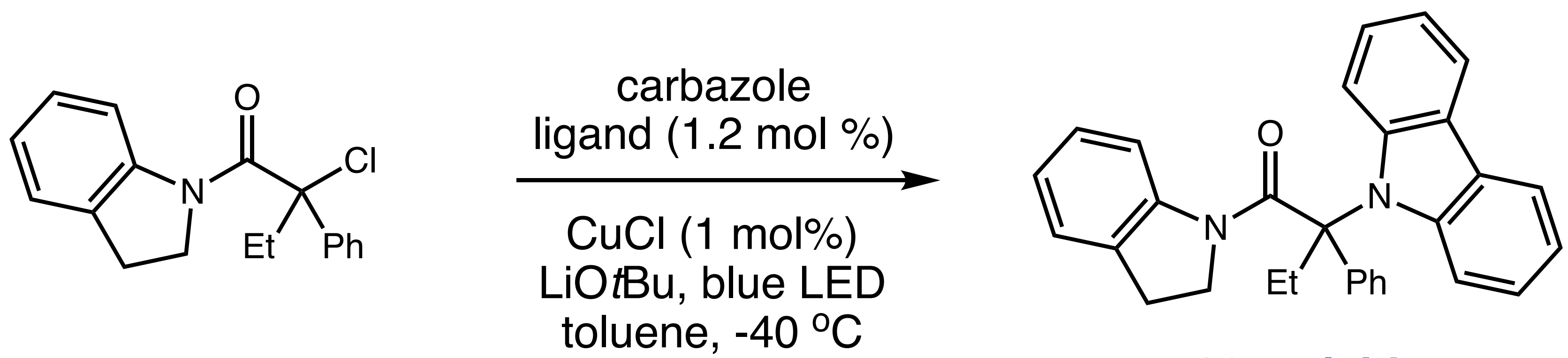


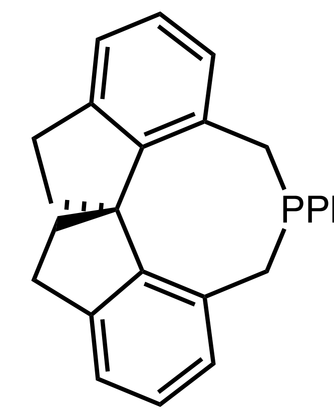
Traditional SET with Copper Catalysts





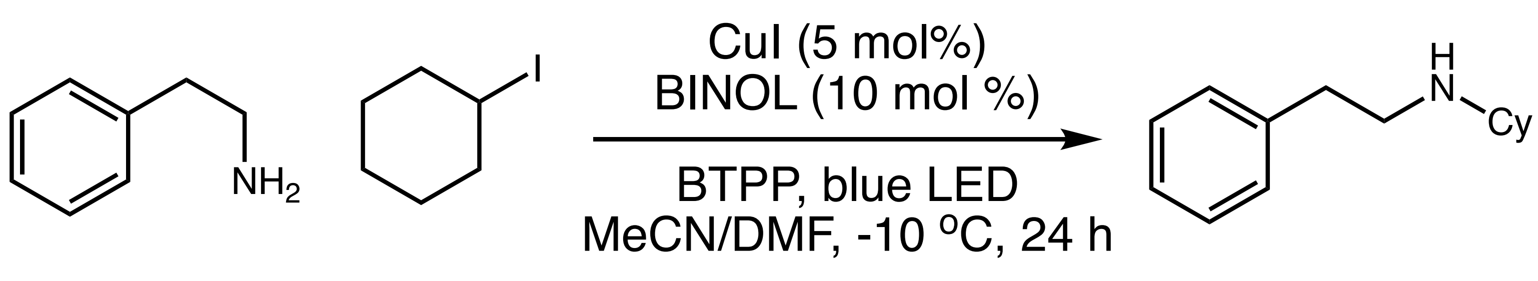
Fu, G. *J. Am. Chem. Soc.* **2017**, *139*, 17707

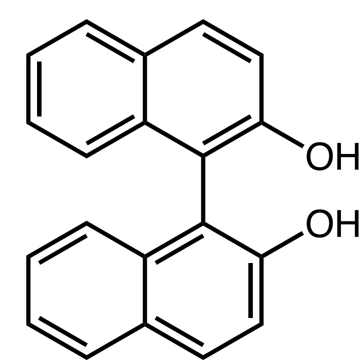




90% yield
94% ee

Fu, G. *Science* **2016**, *351*, 681





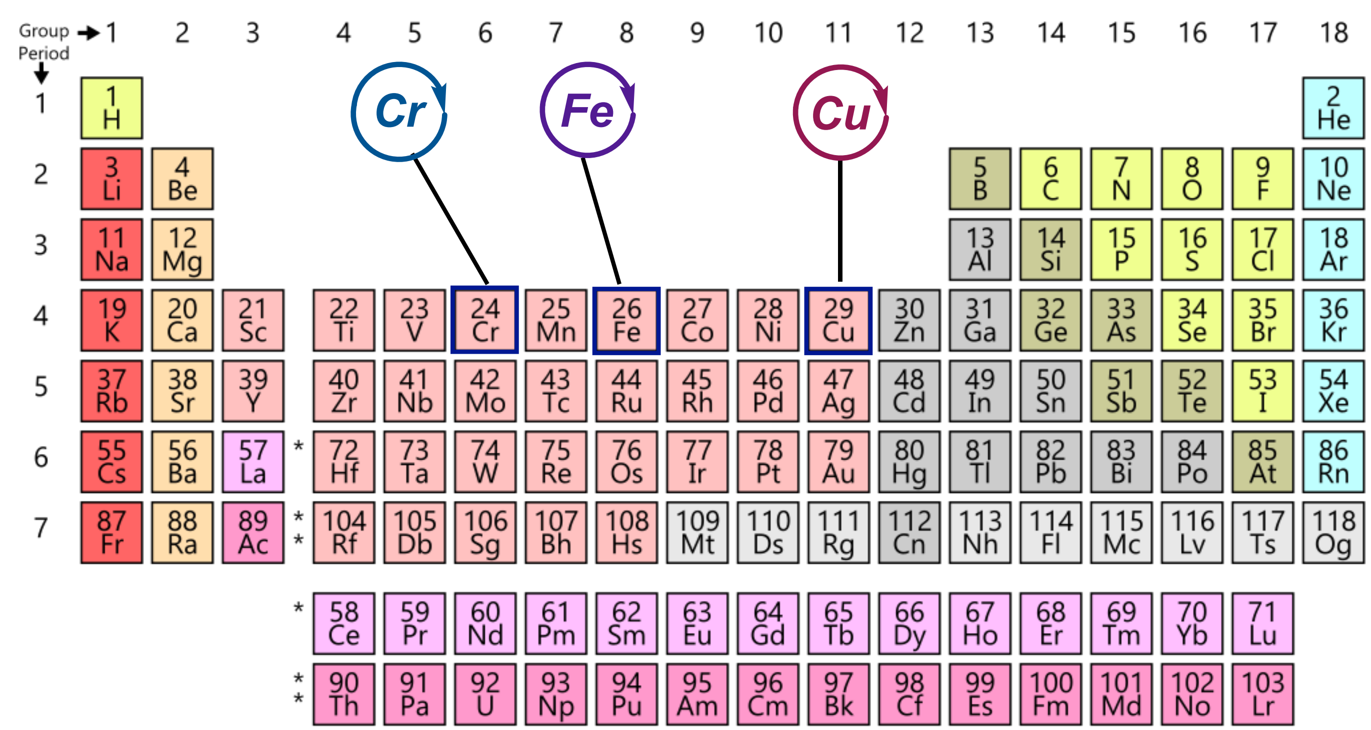
92% yield

Fu, G. *J. Am. Chem. Soc.* **2017**, *139*, 18101

Introduction

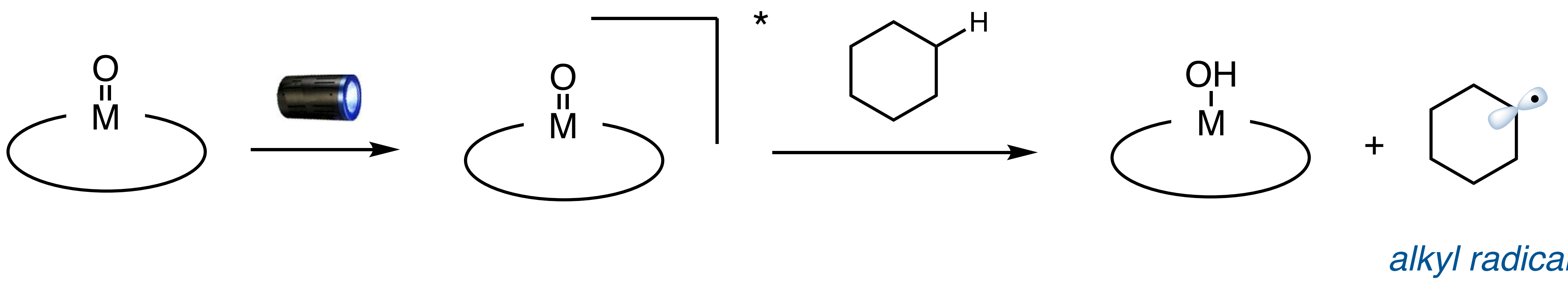
Why should we care about first-row transition metal photocatalysts?

- Triplet Sensitization with chromium
- Ligand-directed photochemistry with copper
- **Direct photo-HAT with iron**

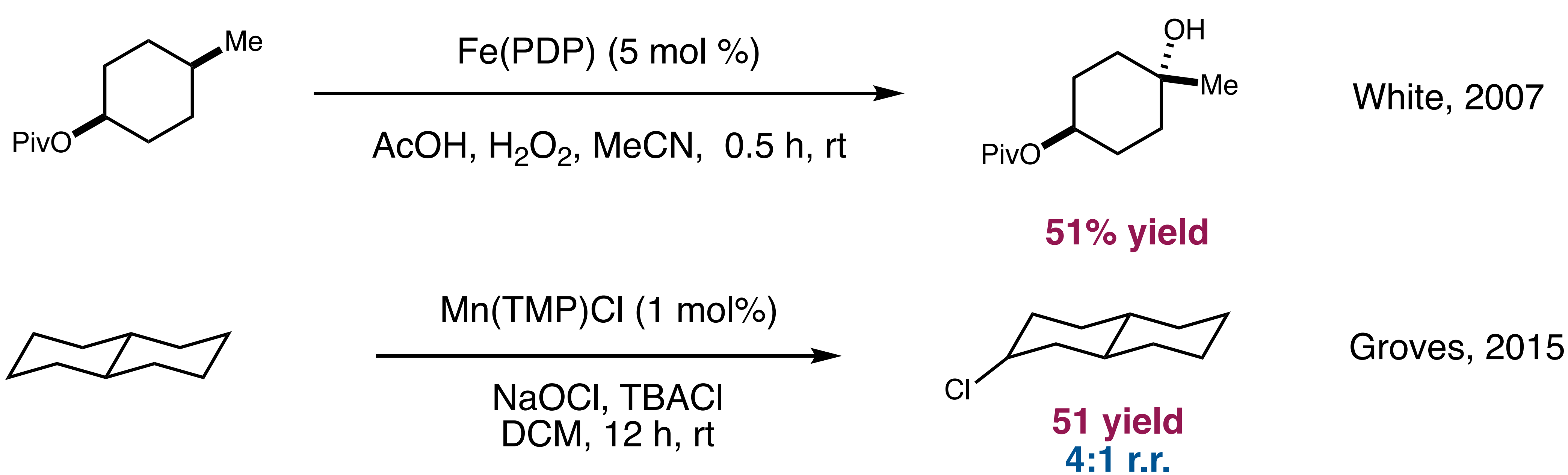


Direct HAT with Photocatalysts

Photo HAT

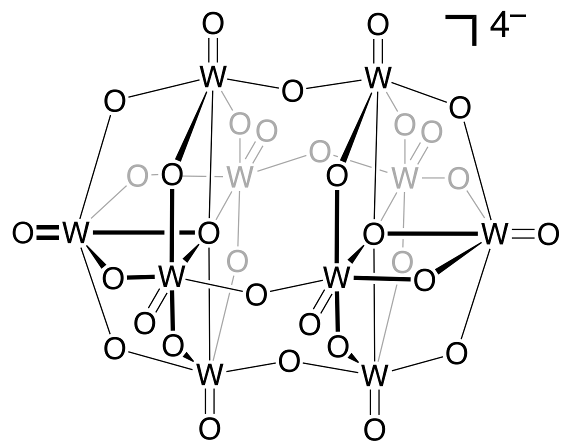


Non-Photo HAT

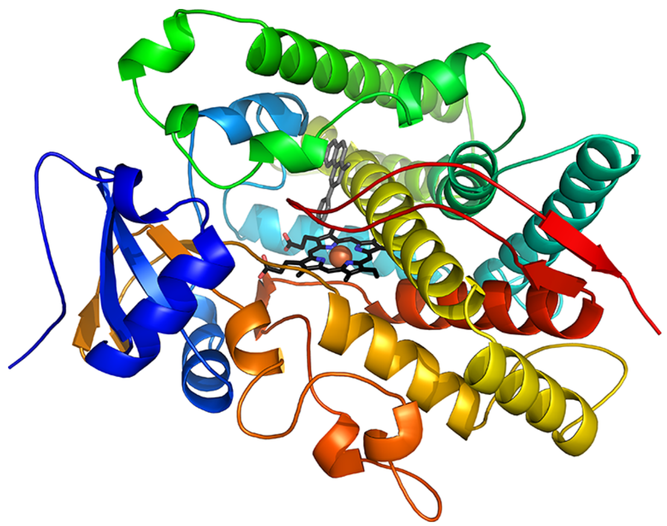


Wenger, O. S. *Chem. Eur. J.* **2018**, *24* 2039

Direct HAT with Photocatalysts



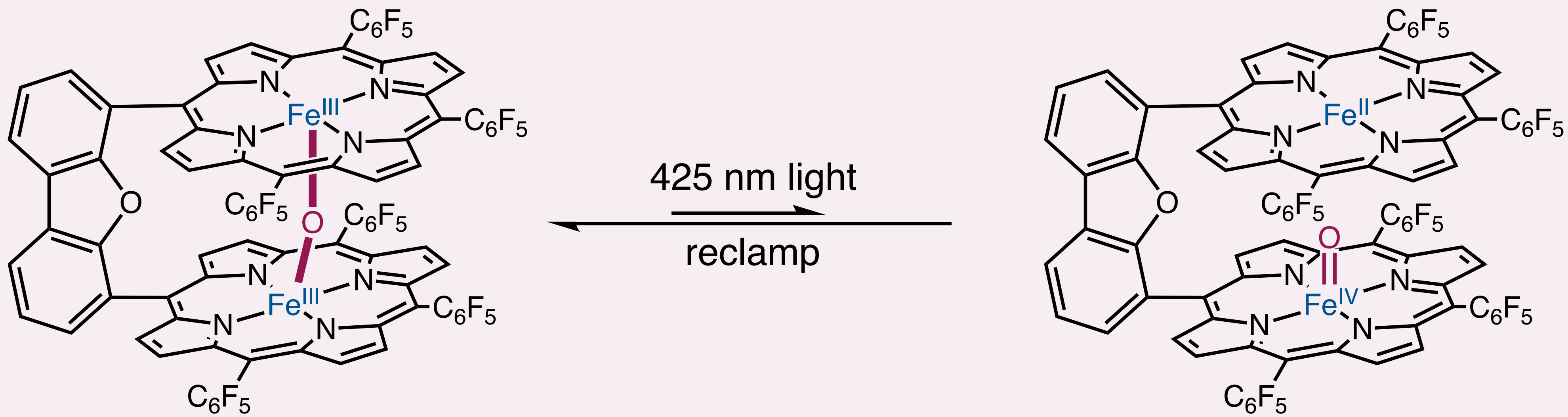
- ~390 nm excitation
- Powerful oxygen centered abstractor
- Selective C-H abstraction
- Electronic properties not tunable



- ~420 nm Soret band
- Powerful oxygen centered abstractor
- Selective C-H abstraction
- Electronic properties highly tunable
- **Short-lived photoexcited state!**

Fagnoni, M. *Acc. Chem. Res.* **2016**, *49*, 2232
Emily Scott Lab Webpage, umich.edu

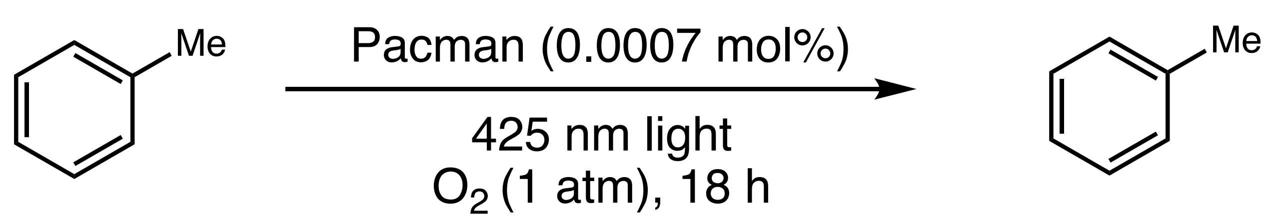
Iron Photosensitizers for HAT



Pacman-Complex

Active oxidation complex

Light-driven HAT from Toluene



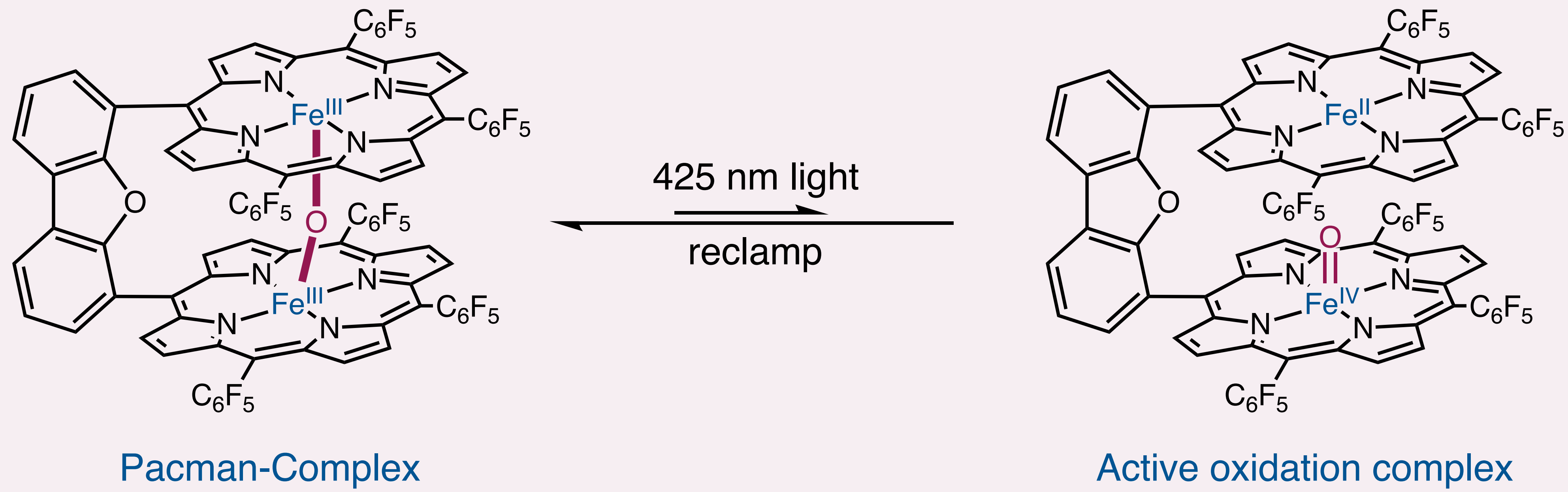
1 M in pyridine

76 TON
Φ_p =0.00151

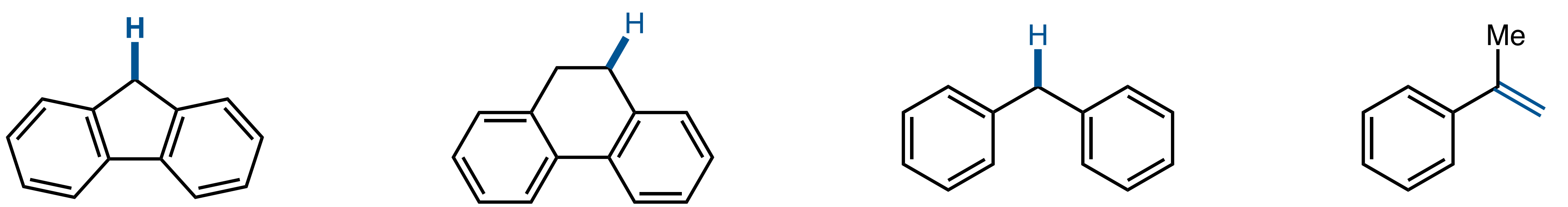
- Sole observed product
- Competitive reclamping
- K_H/K_D = 1.55

Nocera, D. G. *J. Am. Chem. Soc.* **2006**, *128*, 6546

Iron Photosensitizers for HAT



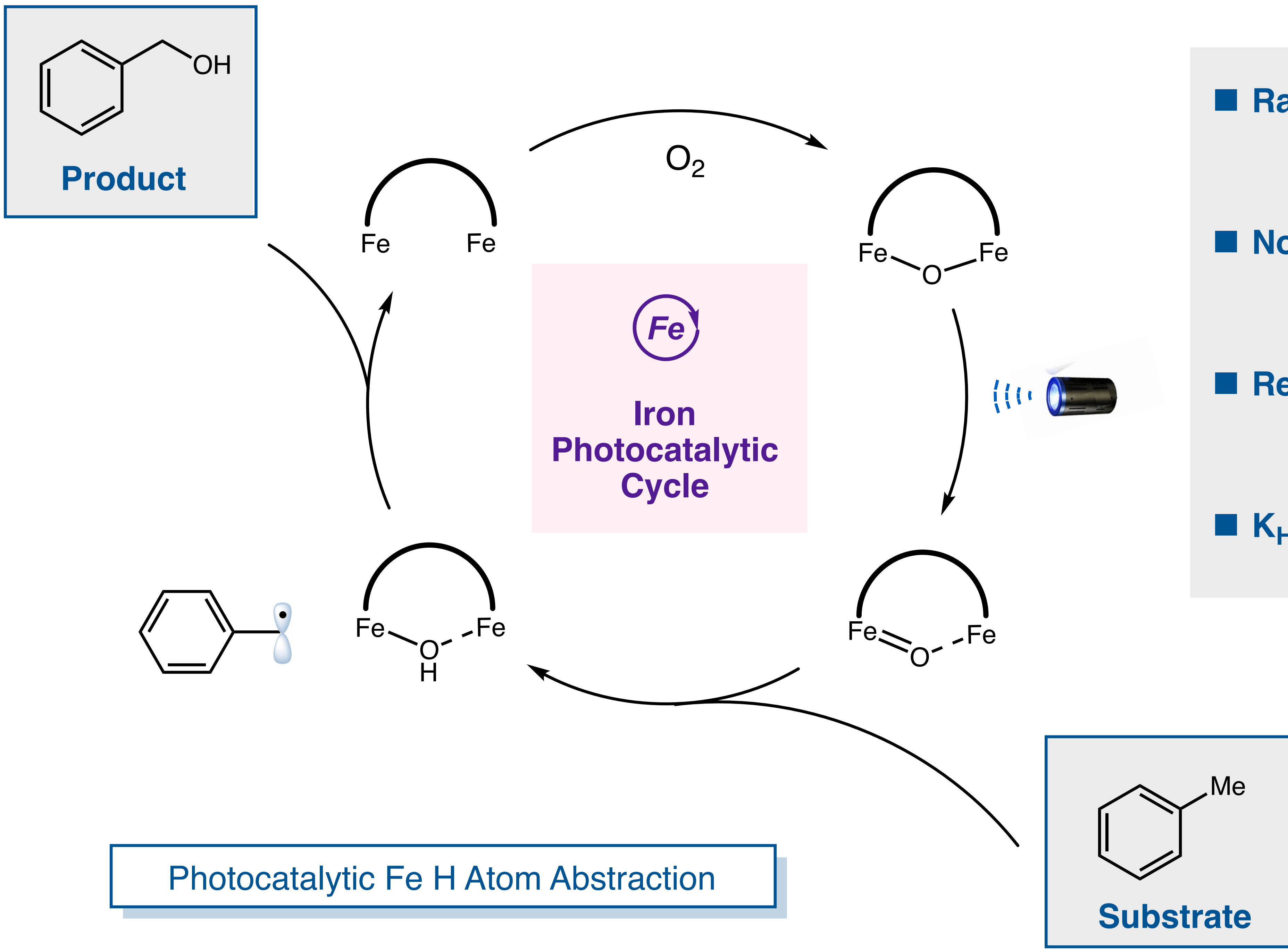
HAT from weak C-H bonds



287 TON	**235 TON**	**160 TON**	**143 TON**
Φ_p =0.0152	**Φ_p = ND**	**Φ_p =0.00276**	**Φ_p =0.00199**

Nocera, D. G. *J. Am. Chem. Soc.* **2006**, *128*, 6546

Iron Photosensitizers for HAT



Photocatalytic Fe H Atom Abstraction

- **Radical rebound**
- **No backgroud reaction**
- **Reclamp $t_{1/2}$ = 2.3 ns**
- **K_H/K_D > 1 suggests PCET**

Nocera, D. G. *J. Am. Chem. Soc.* **2006**, *128*, 6546

Introduction

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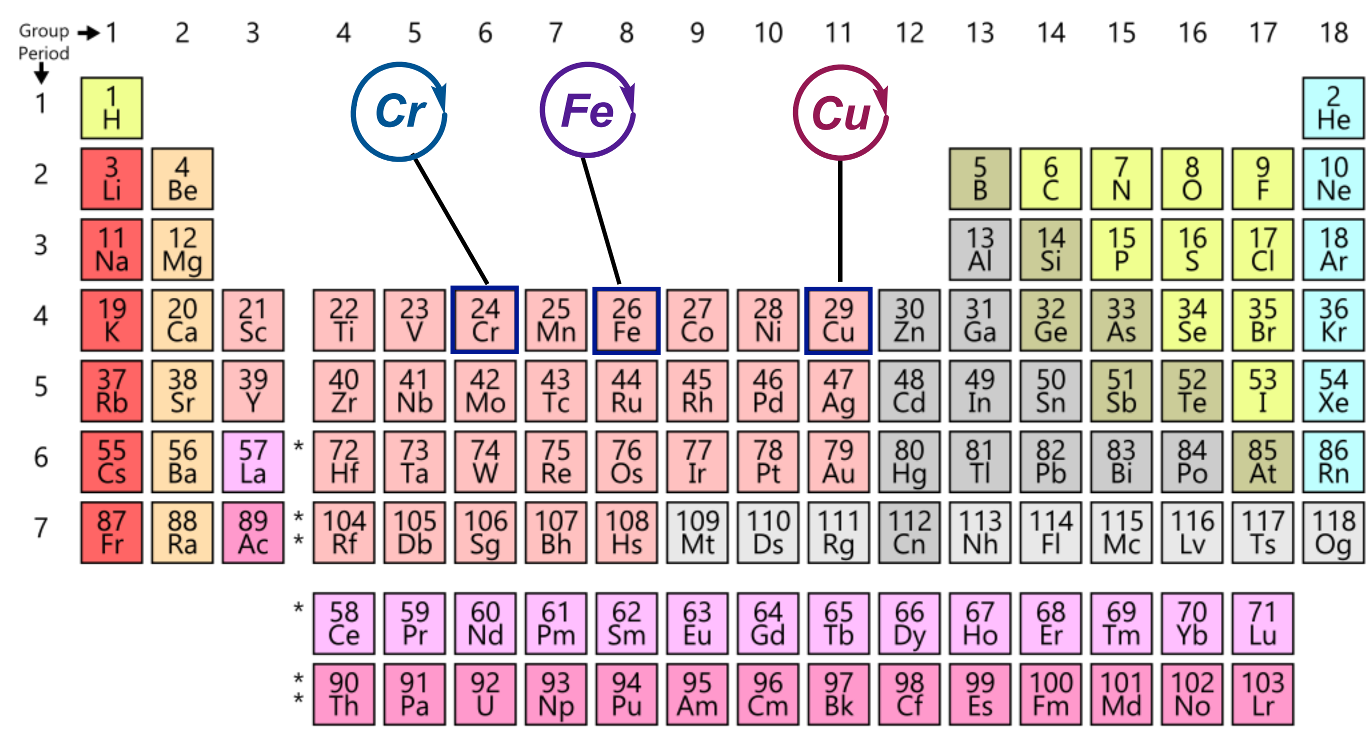

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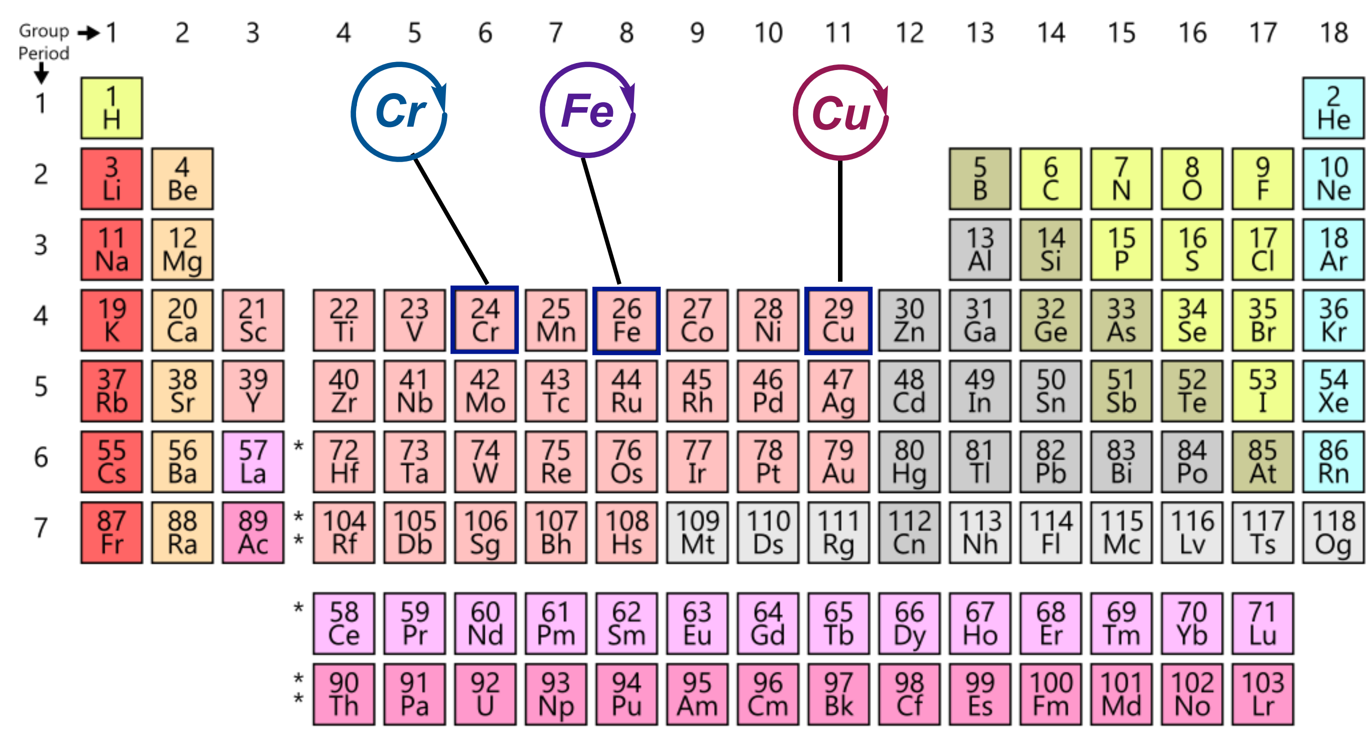

First row transition metal catalysts enable new photochemistry!

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Questions?

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