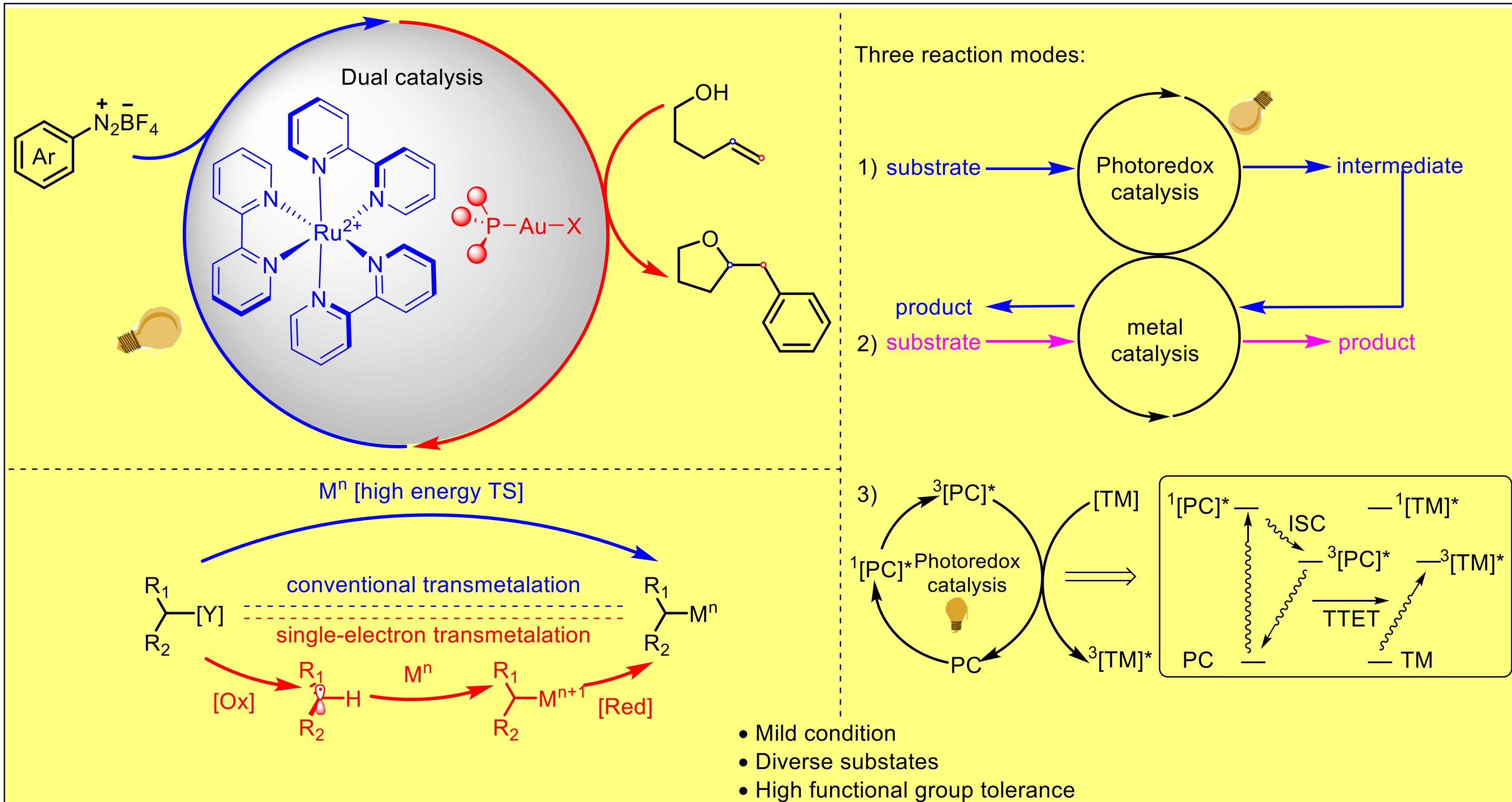
Merging Visible Light Photoredox Catalysis with Nickle & Gold Catalysis



Reporter: Fengjin Wu

Supervisor: *Prof*. Huang

Date: 02. 27. 2017

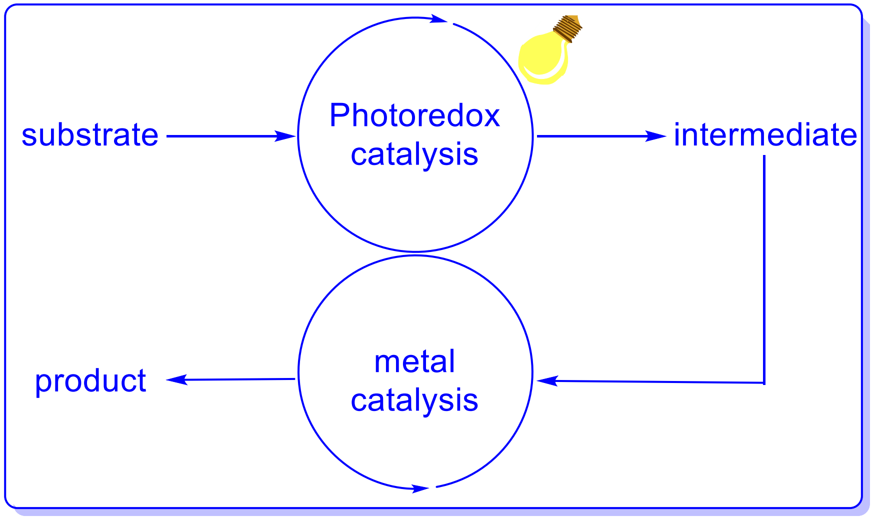
Outline:

1. Introduction
2. Merging visible light photoredox and nickle catalysis
   - 2.1. Catalysis of downstream steps
   - 2.2. Catalysis of redox steps
   - 2.3. Photoinduced energy transfer
3. Merging visible light photoredox and gold catalysis
4. Conclusion
5. Acknowledgement

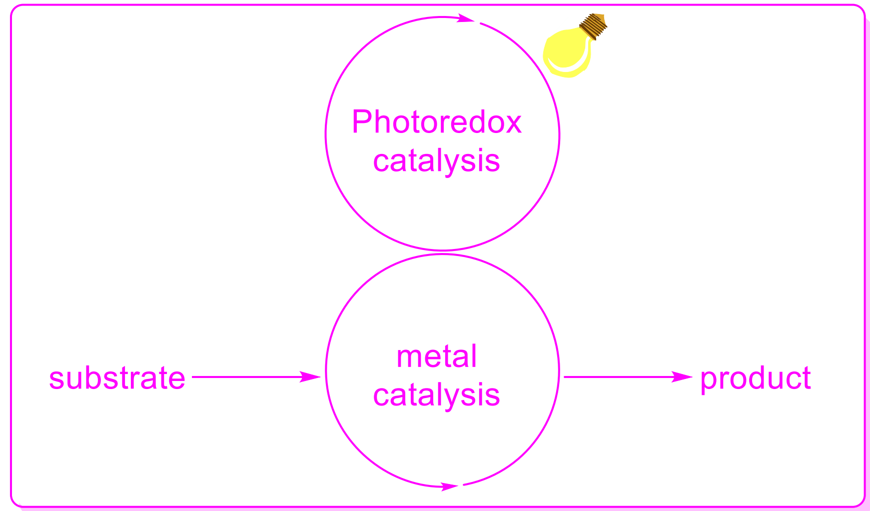
1. Introduction

Common modes of tandem transition metal and photocatalysis:

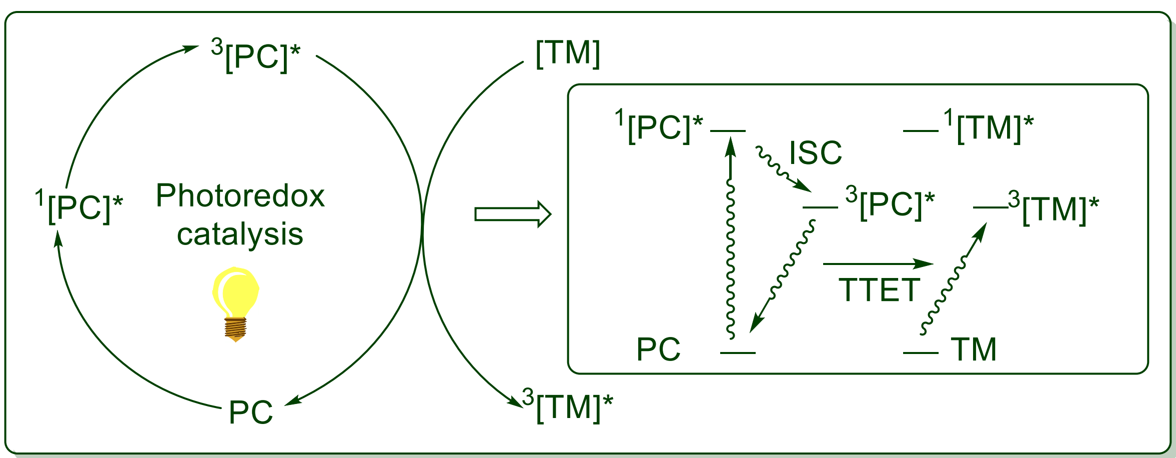
A. Catalysis downstream steps



B. Catalysis redox steps



C. Photoinduced energy transfer

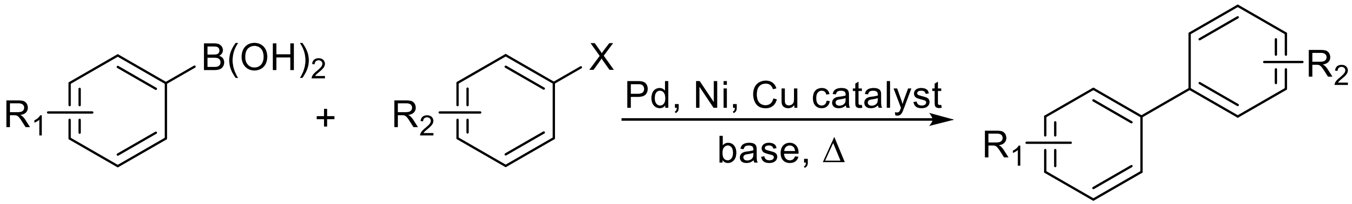


Outline:

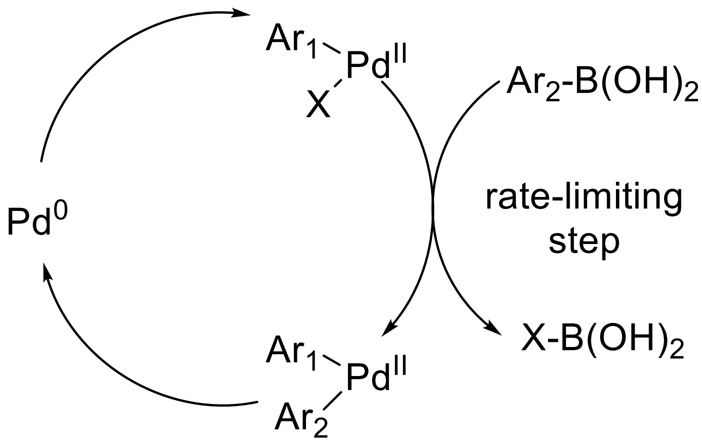
1. Introduction
2. Merging visible light photoredox and nickle catalysis
    2.1. Catalysis of downstream steps
    2.2. Catalysis of redox steps
    2.3. Photoinduced energy transfer
3. Merging visible light photoredox and gold catalysis
4. Conclusion
5. Acknowledgement

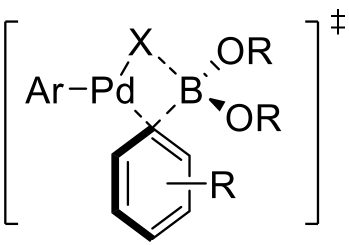
2. Merging visible light photoredox and Nickle catalysis

Conventional Suzuki-Miyaura cross-coupling:



Traditional cross-coupling: two electron transformation:

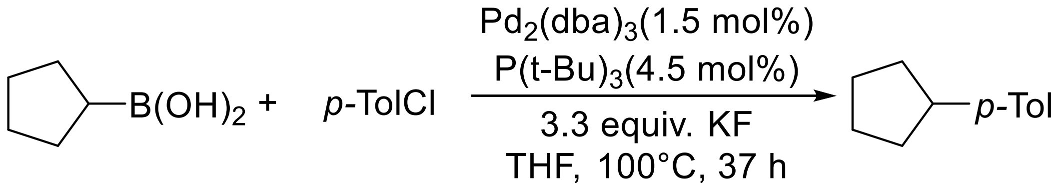


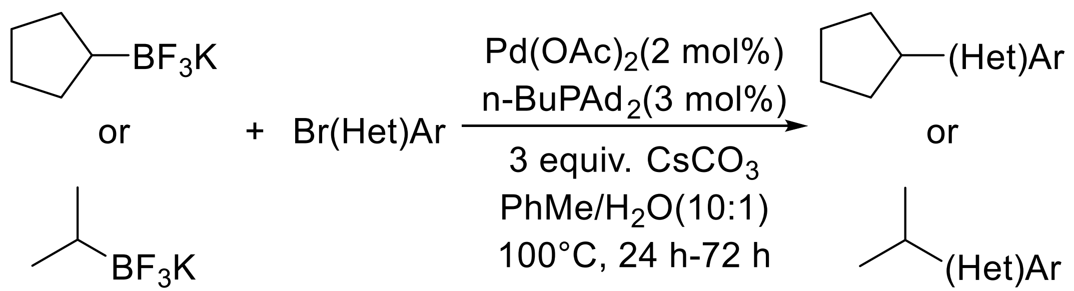


reaction rate: $C_{SP} > C_{SP}^2 > C_{SP}^3$

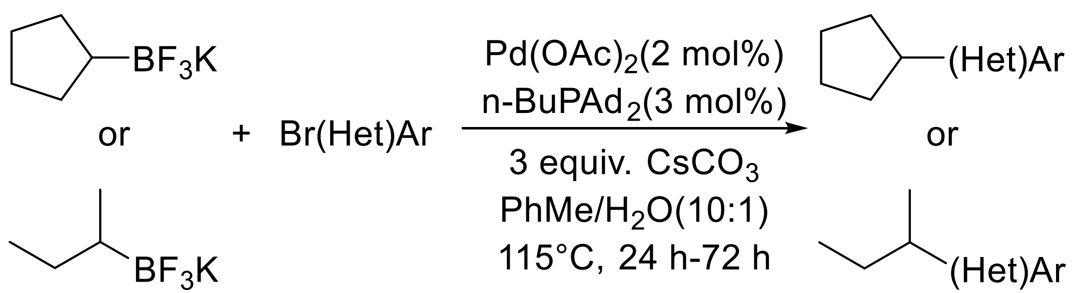
However, the application of secondary alkylboron reagents in these transformation was limited.

Notable examples of secondary alkyl Suzuki cross-coupling:





High activation barrier of transmetalaiton



Limitation of using secondary alkylboron:

1. Elevated reaction temperature; 2. Using superstoichiometric aqueous base.

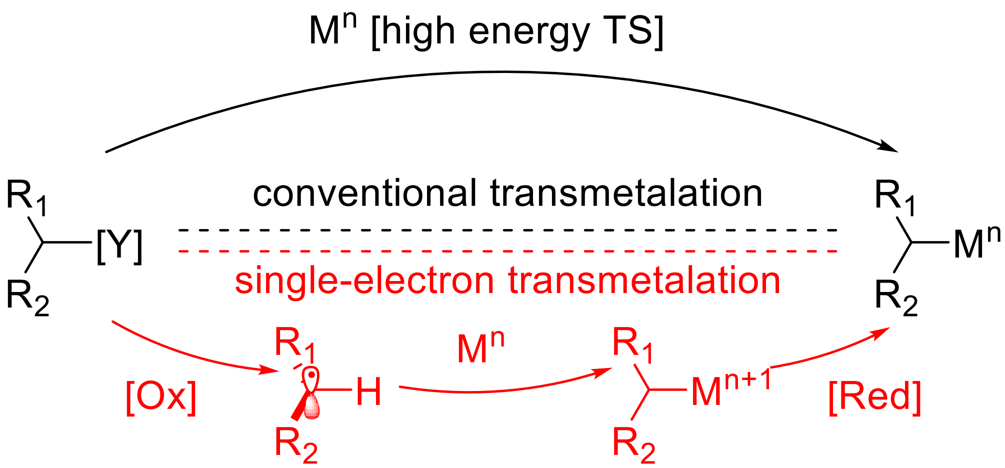
Littke,A.F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc*. **2000**, 122, 4020−4028.

Van den Hoogenband, A.; Visser, M. *Tetrahedron Lett*. **2008**, 49, 4122−4124.

Dreher, S. D.; Dormer, P. G.; Sandrock, D. L.; Molander, G. A. *J. Am. Chem. Soc*. **200**8, 130, 9257−9259.

2.1. Catalysis of downstream steps

Single-electron transmetalation in organoboron cross-coupling by photoredox/nickel dual catalysis

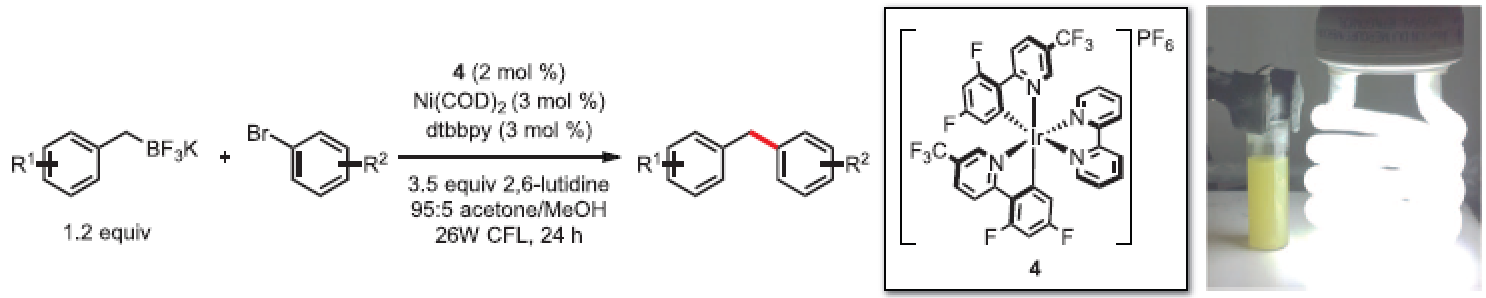


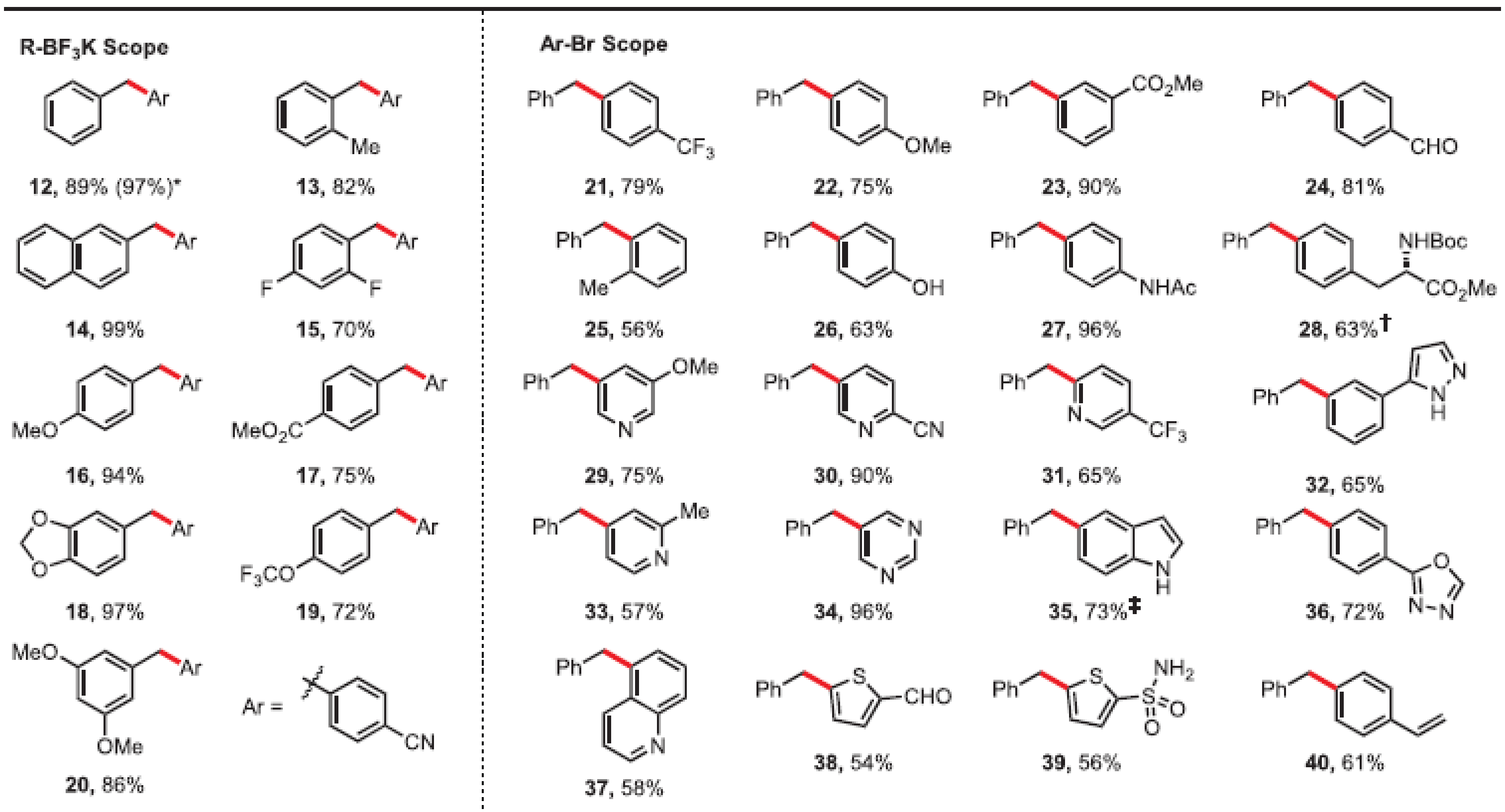
- Low activation energy
- Reactivity dictated by measurable redox potential
- Requires no base or heat
- SET rate: $C_{SP}^3 > C_{SP}^2 > C_{SP}$

Tellis, J. C.; Primer, D. N.; Molander, G. A. *Science.* **2014**, 345, 433−436.

2.1. Catalysis of downstream steps

Single-electron transmetalation in organoboron cross-coupling by photoredox/nickel dual catalysis

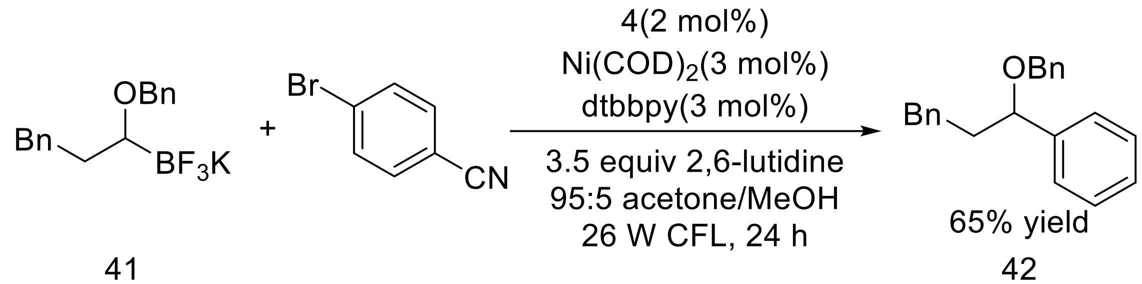




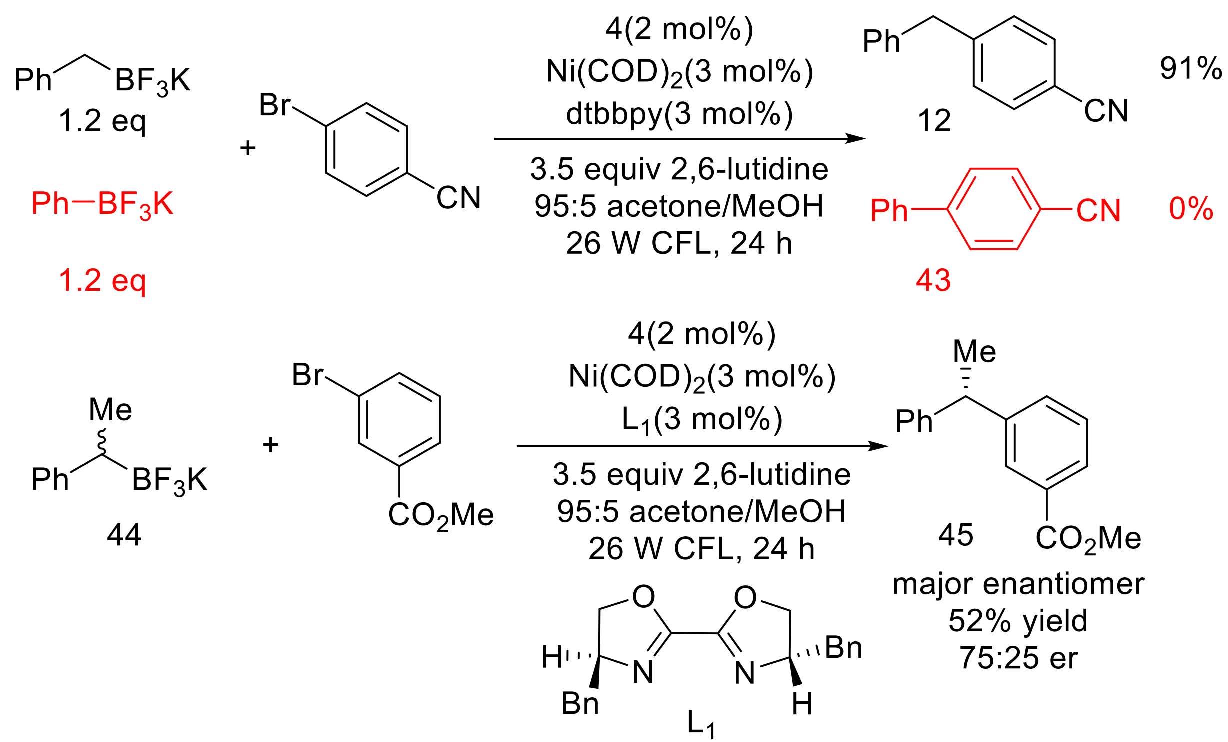
* Reaction performed on 1.0 g (5.5 mmol) ArBr with 1 mol % **4**, 1.5 mol % $Ni(COD)_2$, and 1.5 mol % dtbbpy. †Reaction performed with 3 mol % **4**, 5 mol % $Ni(COD)_2$, and 5 mol % dtbbpy. ‡55% isolated pure, 18% isolated as mixture with bromide starting material

2.1. Catalysis of downstream steps

Photoredox cross-coupling of secondary (*a*-alkoxy)alkyltrifluoroborate:



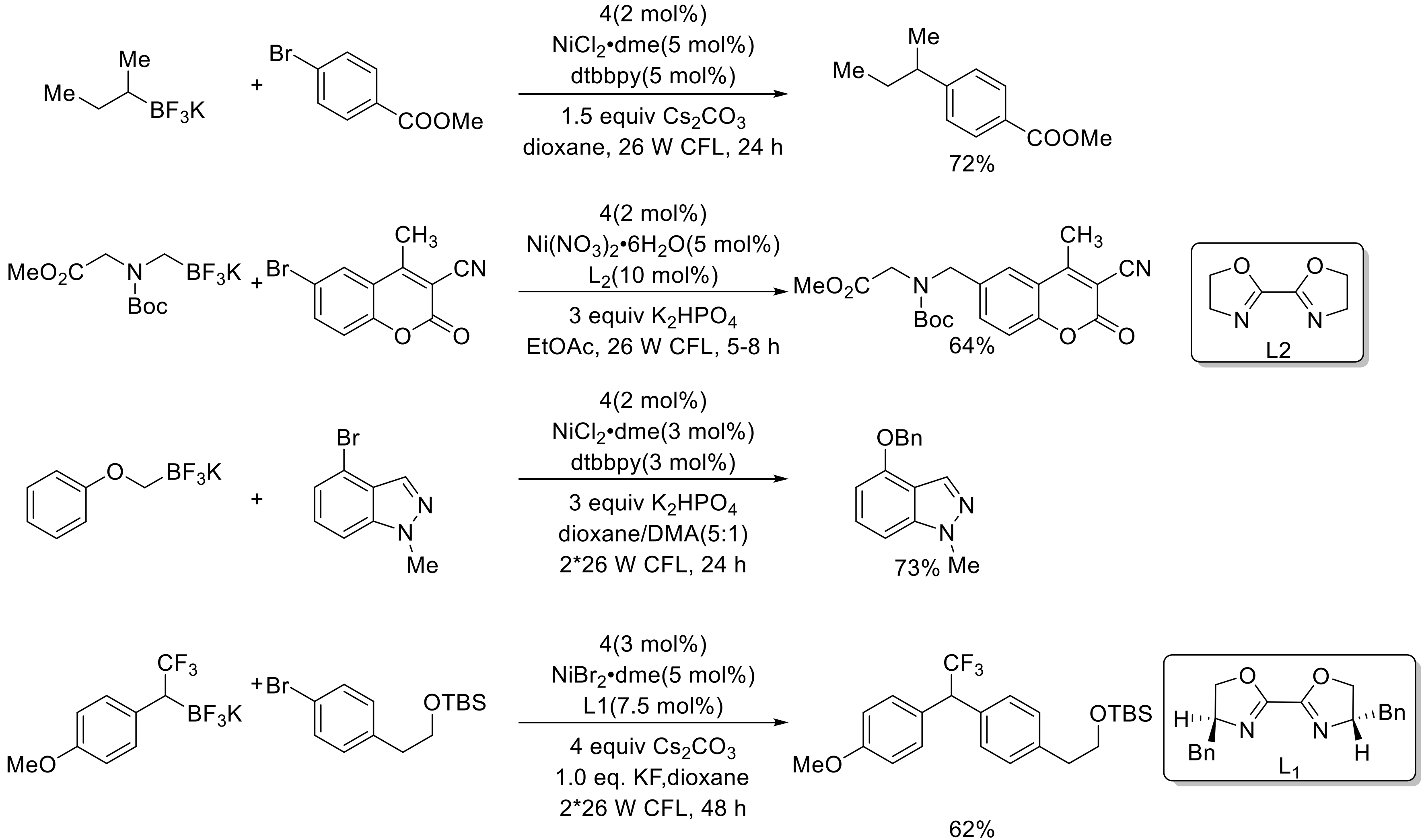
Probing chemo- and stereoselectivity:



Tellis, J. C.; Primer, D. N.; Molander, G. A. *Science*. **2014**, 345, 433–436.

2.1. Catalysis of downstream steps

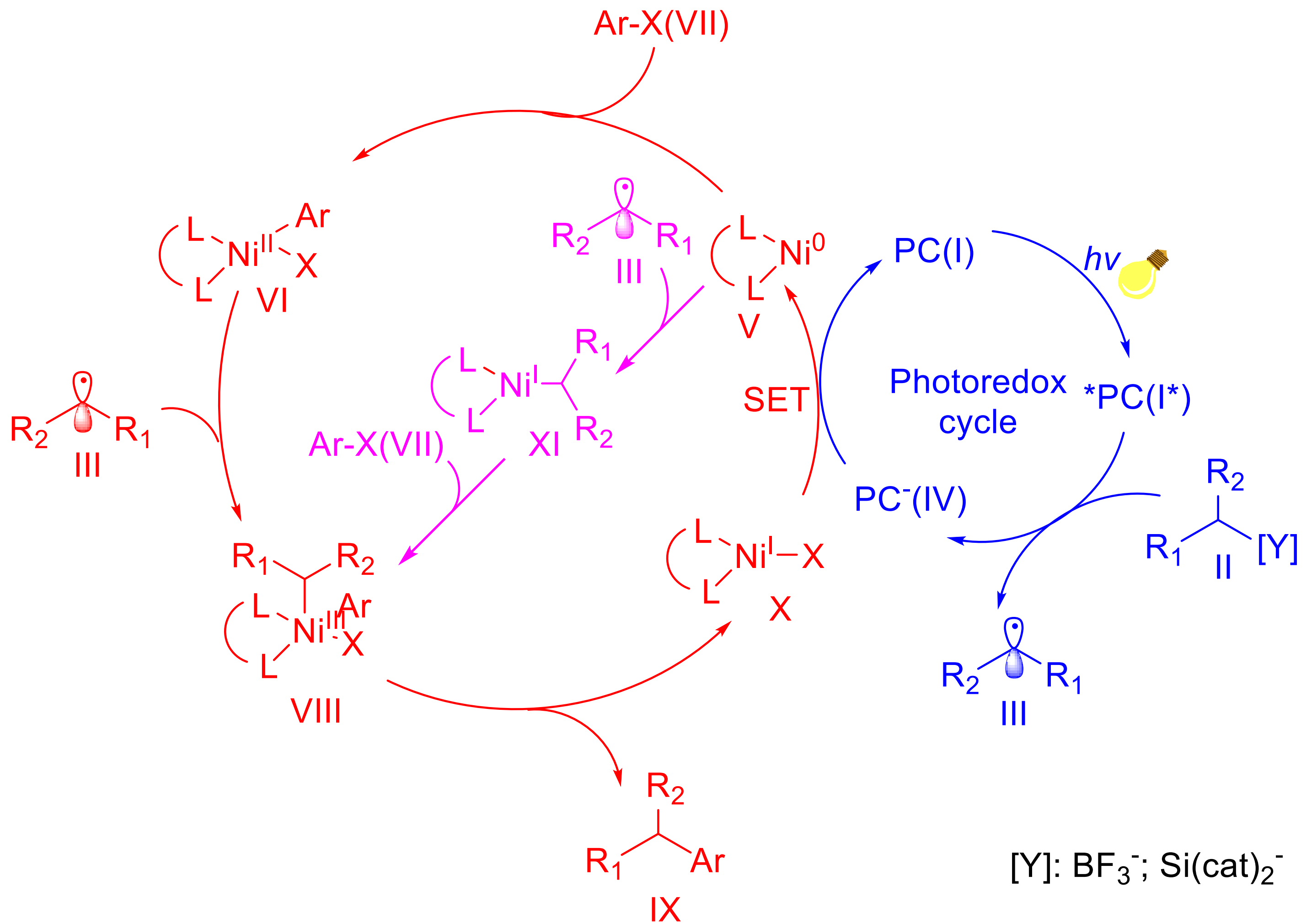
Photoredox cross-coupling of various alkylboron:



Primer, D. N.; Karakaya, I.; Tellis, J. C.; Molander, G. A. *J. Am. Chem. Soc.* **2015**, 137, 2195−2198.
El Khatib, M.; Serafim, R. A. M.; Molander, G. A. *Angew. Chem., Int. Ed.* **2016**, 55, 254−258.
Karakaya, I.; Primer, D. N.; Molander, G. A. *Org. Lett*. **2015**, 17, 3294−3297.
Ryu, D.; Primer, D. N.; Tellis, J. C.; Molander, G. A. *Chem. Eur. J.* **2016**, 22, 120−123.

2.1. Catalysis of downstream steps

the proposed single-electron transmetalation in photoredox/nickel cross-coupling:



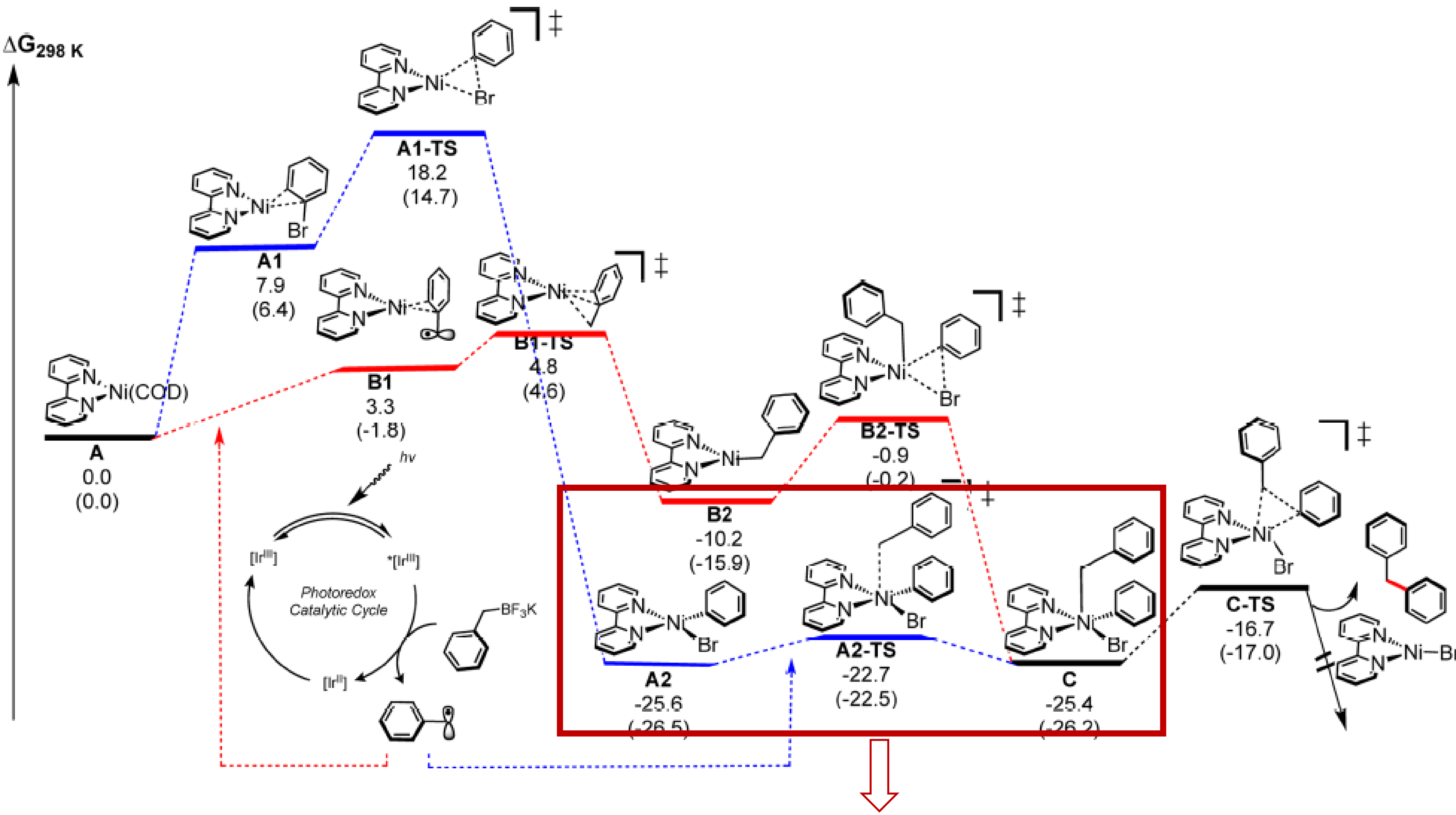
Q: 1. To which oxidation state of Ni does the radical add?

2. Which step is enantiodetermining?

Primer, D. N.; Karakaya, I.; Tellis, J. C.; Molander, G. A. *J. Am. Chem. Soc.* **2015**, 137, 2195–2198.

2.1. Catalysis of downstream steps

Stereoconvergence and mechanistic considerations:

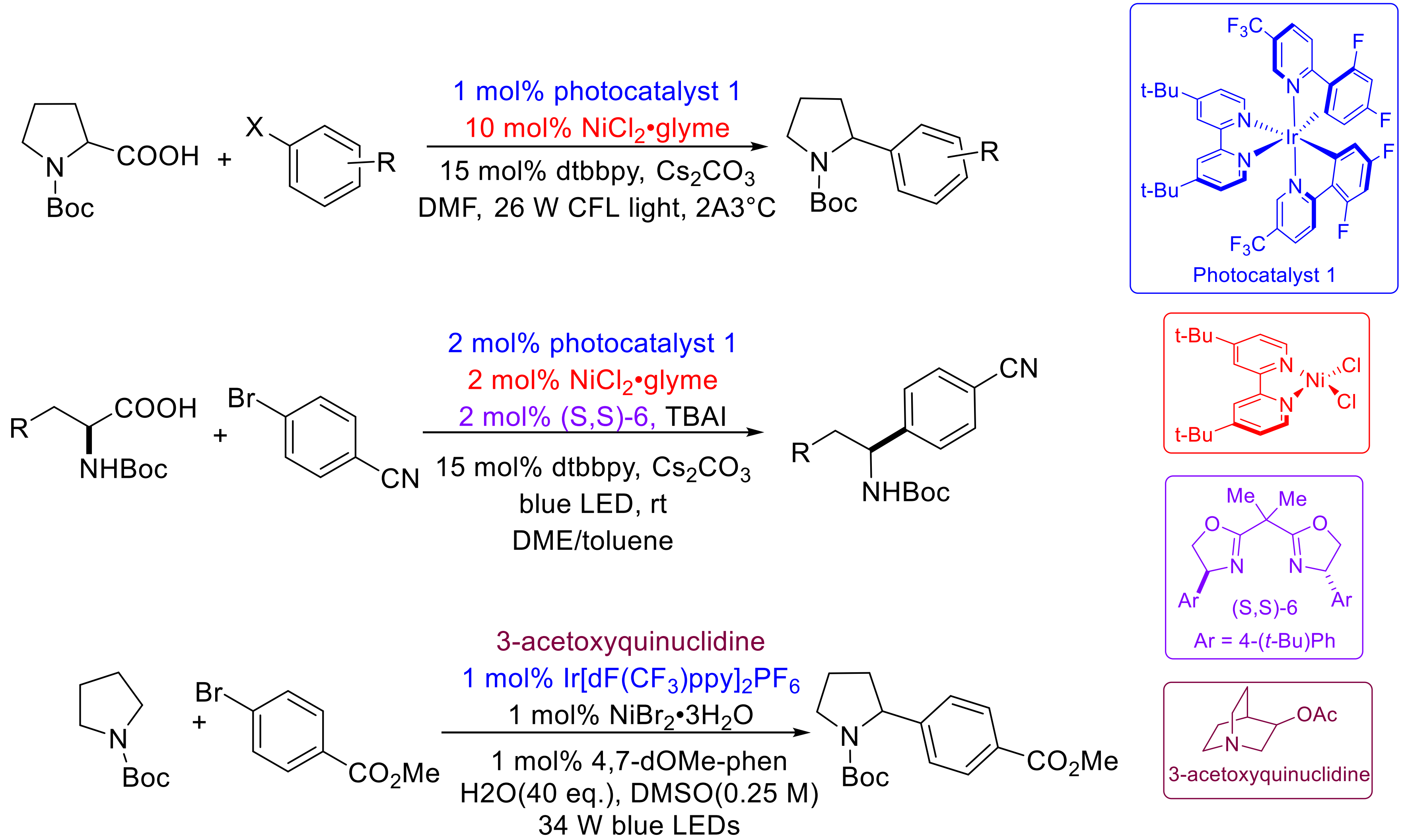


Ni(III) intermediate can dissociate the stabilized radical to form Ni(II) more rapidly than undergoing reductive elimination

Gutierrez, O.; Tellis, J. C.; Primer, D. N.; Molander, G. A.; Kozlowski, M. C. *J. Am. Chem. Soc.* **2015**, 137, 4896−4899.

2.1. Catalysis of downstream steps

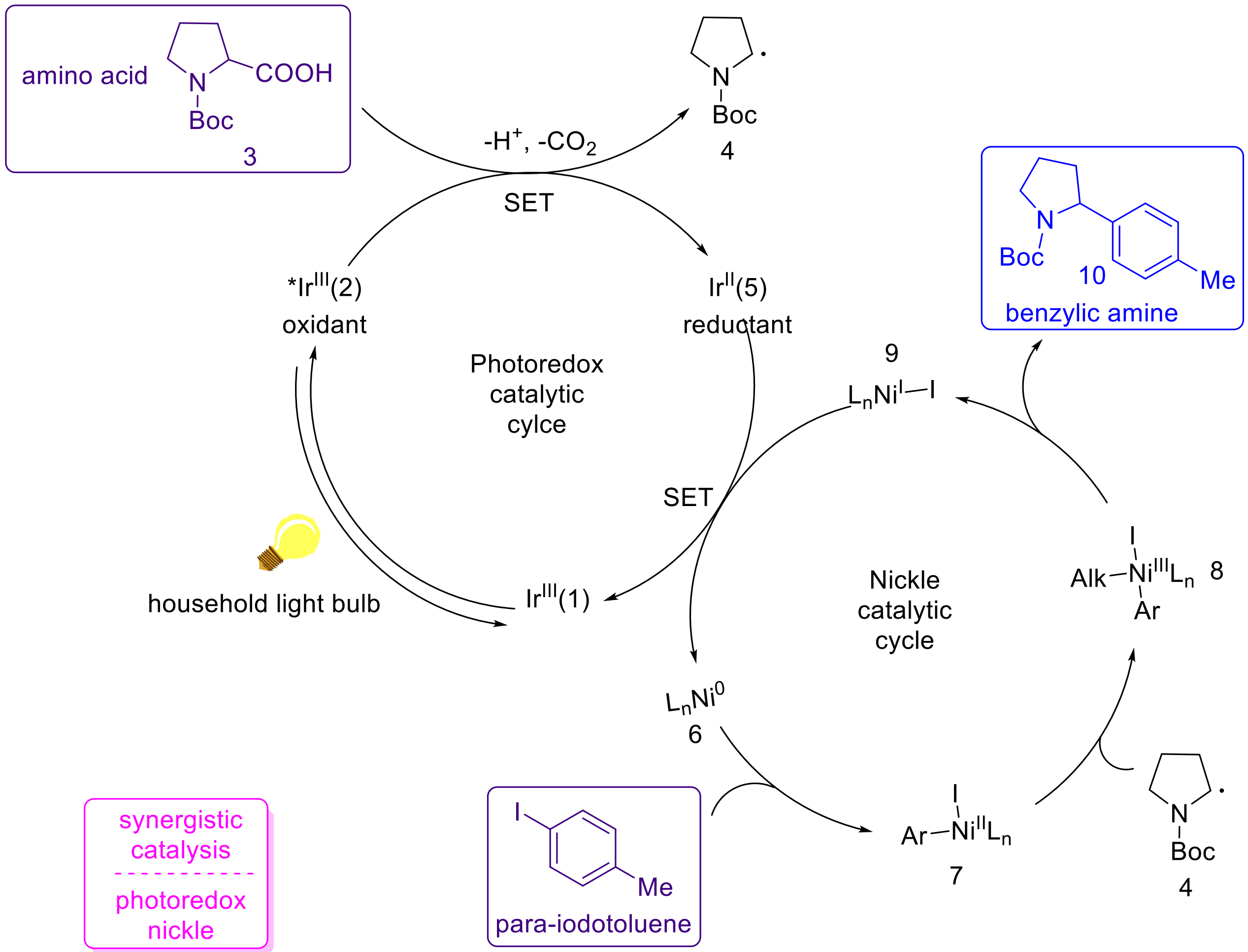
Photoredox & nickel-catalyzed decarboxylative and C-H arylation:



Zhiwei Zuo.; Derek T. Ahneman.; Lingling Chu.; Jack A. Terrett.; Abigail G. Doyle.; David W. C. MacMillan. *Science.* **2014**, 345, 437−440.
Zhiwei Zuo.; Huan Cong.; Wei Li.; Junwon Choi.; Gregory C. Fu.; David W. C. MacMillan. *J. Am. Chem. Soc.* **2016**, 138, 1832–1835.
Megan H. Shaw.; Valerie W. Shurtleff.; Jack A.; Terrett.; James D. Cuthbertson, David W. C. MacMillan. *Science*. **2016**, 352, 1304-1308.

2.1. Catalysis of downstream steps

Proposed mechanistic pathway of Photoredox & nickel-catalyzed decarboxylative arylation:

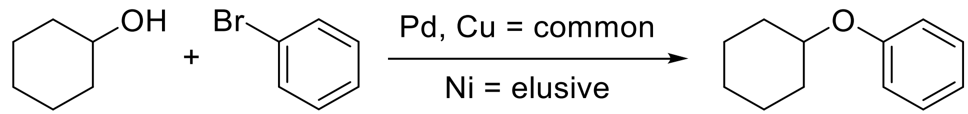


Zhiwei Zuo.; Derek T. Ahneman.; Lingling Chu.; Jack A. Terrett.; Abigail G. Doyle.; David W. C. MacMillan. *Science*, **2014**, 345, 437−440

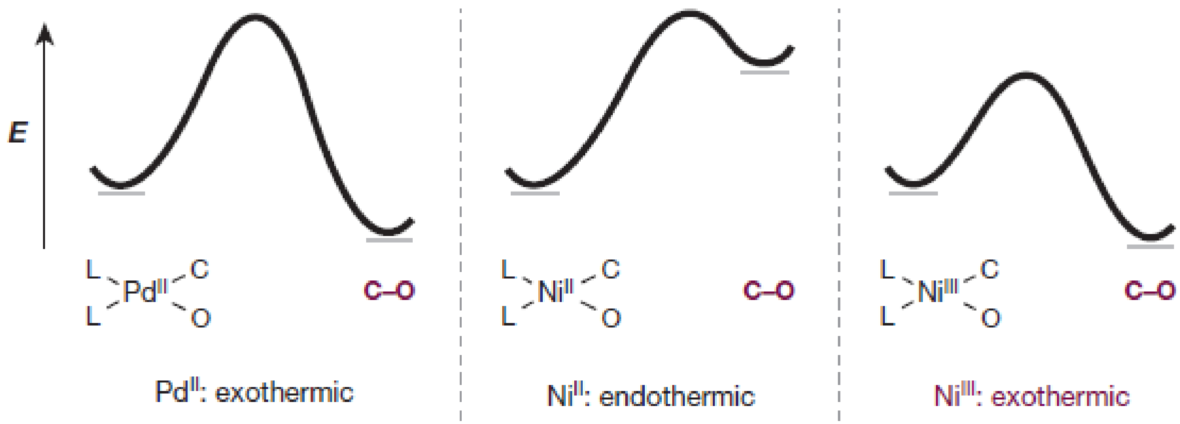
Outline:

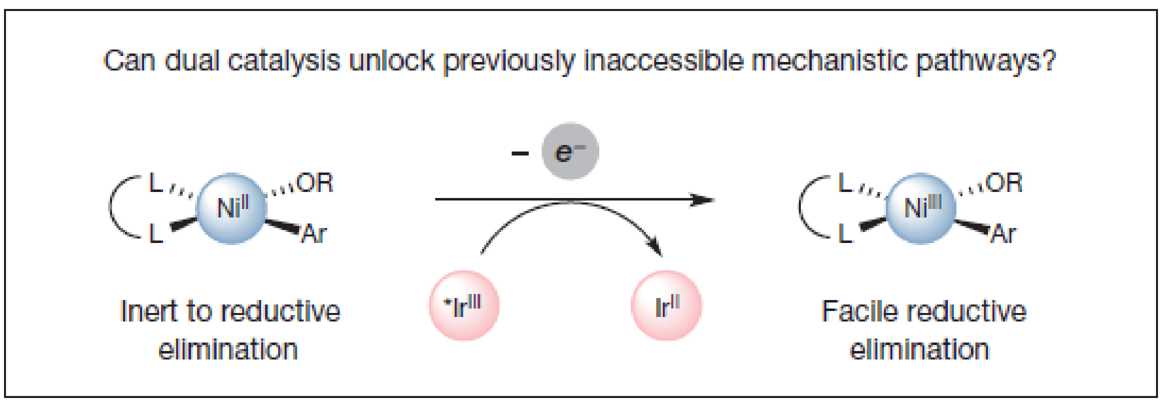
1. Introduction
2. Merging visible light photoredox and Nickle catalysis
    2.1. Catalysis of downstream steps
    2.2. Catalysis of redox steps
    2.3. Photoinduced energy transfer
3. Merging visible light photoredox and gold catalysis
4. Conclusion
5. Acknowledgement

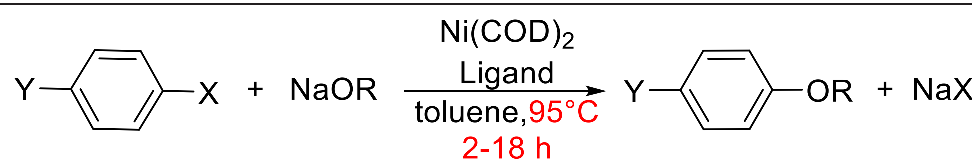
2.2. Catalysis of redox steps



Energetic profiles of reductive elimination reactions to form C–O bonds

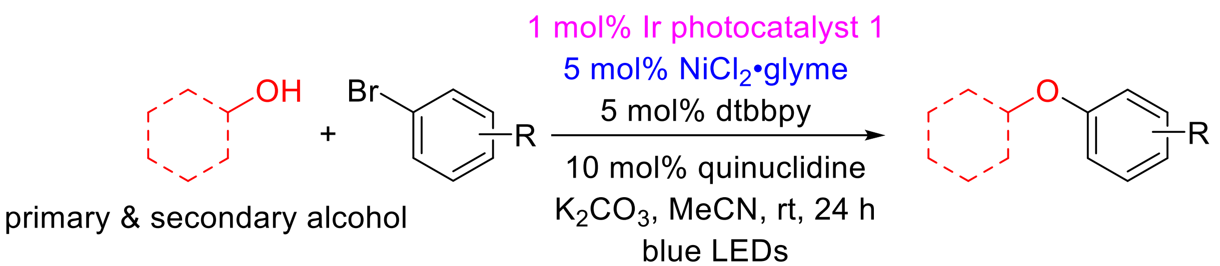


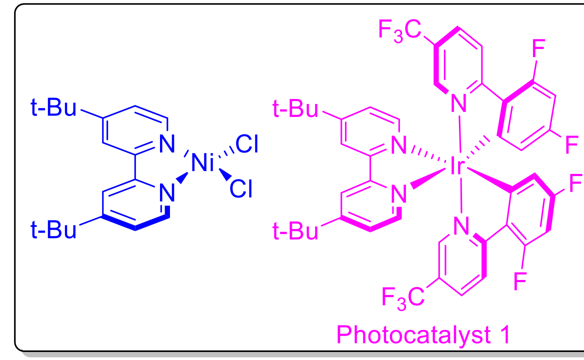


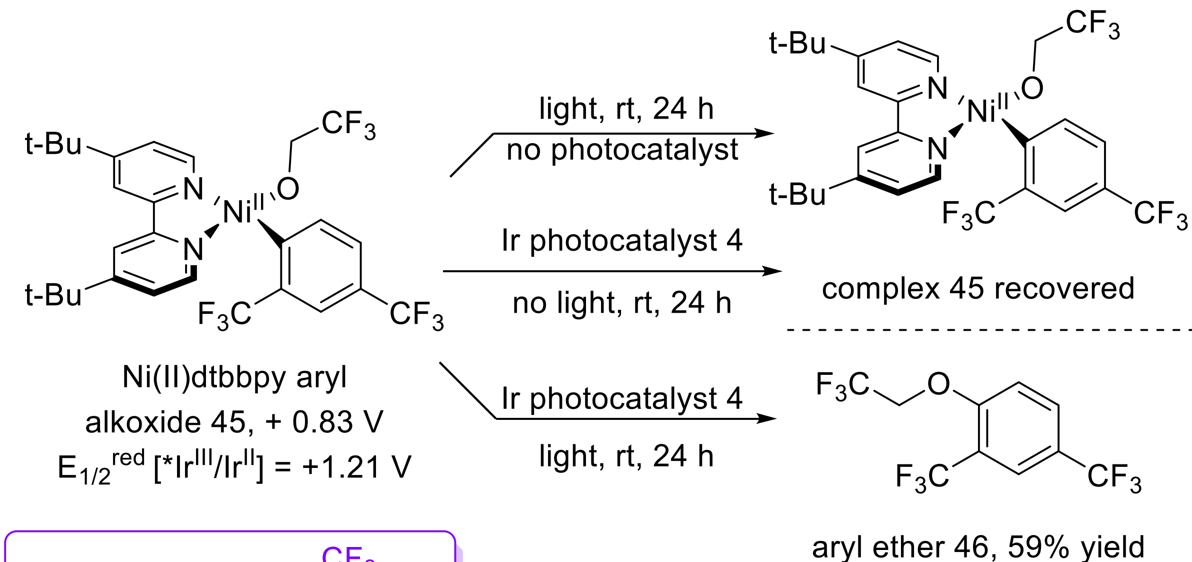


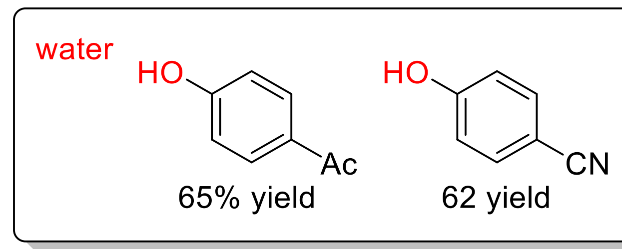
Jack A. Terrett.; James D. Cuthbertson.; Valerie W. Shurtleff.; David W. C. MacMillan. *Nature*, **2015**. 524, 330-334.
Mann, G. Hartwig, J. F. *J. Org. Chem*. **1997**, 62, 5413–5418.

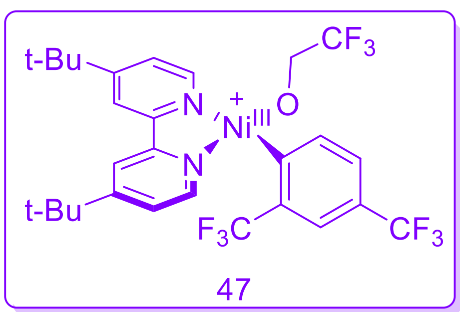
2.2. Catalysis of redox steps







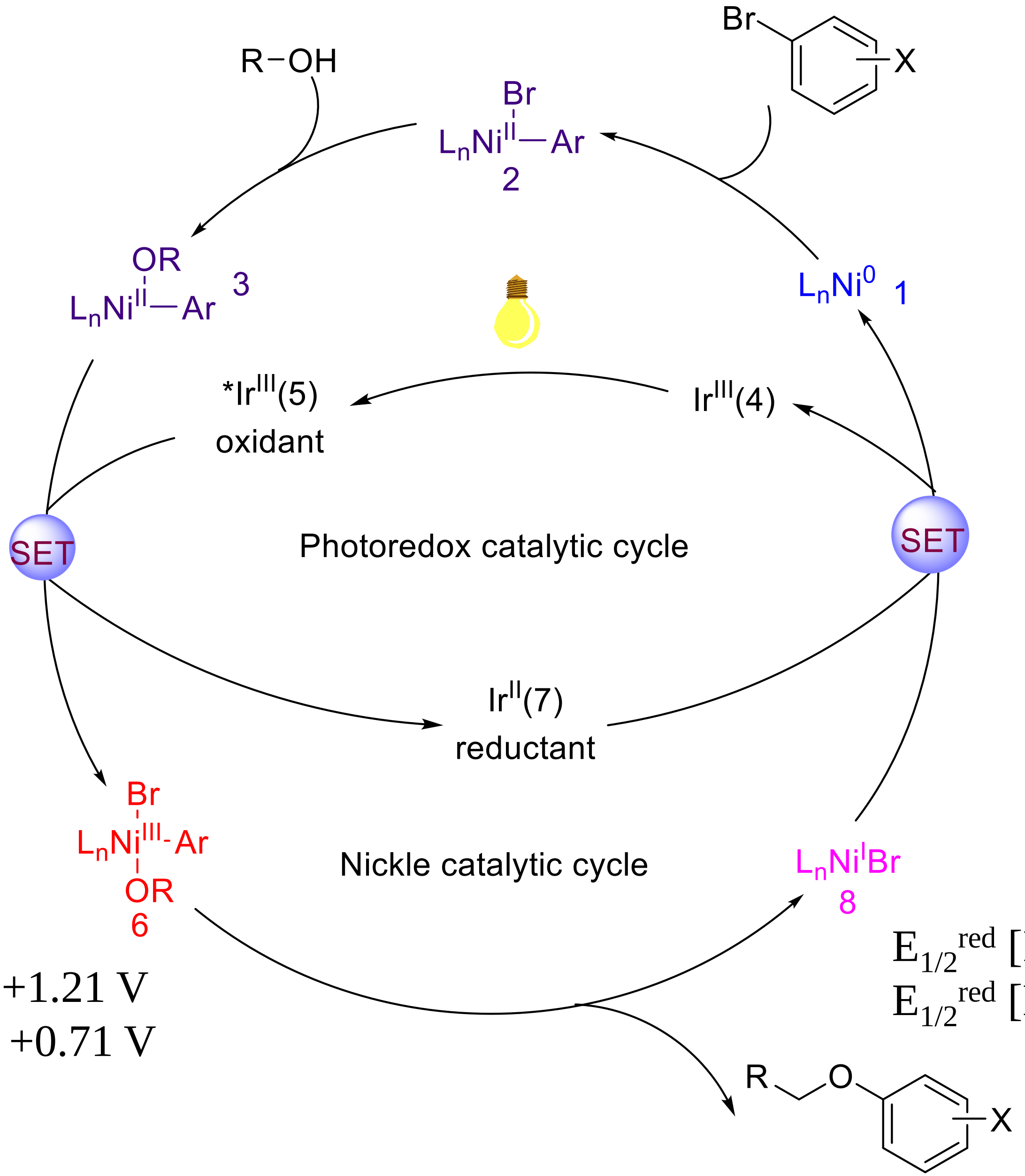




Transient Ni(III) complex required for C-O reductive elimination

Jack A. Terrett.; James D. Cuthbertson.; Valerie W. Shurtleff.; David W. C. MacMillan. *Nature*, **2015**, 524, 330-334.

2.2. Catalysis of redox steps

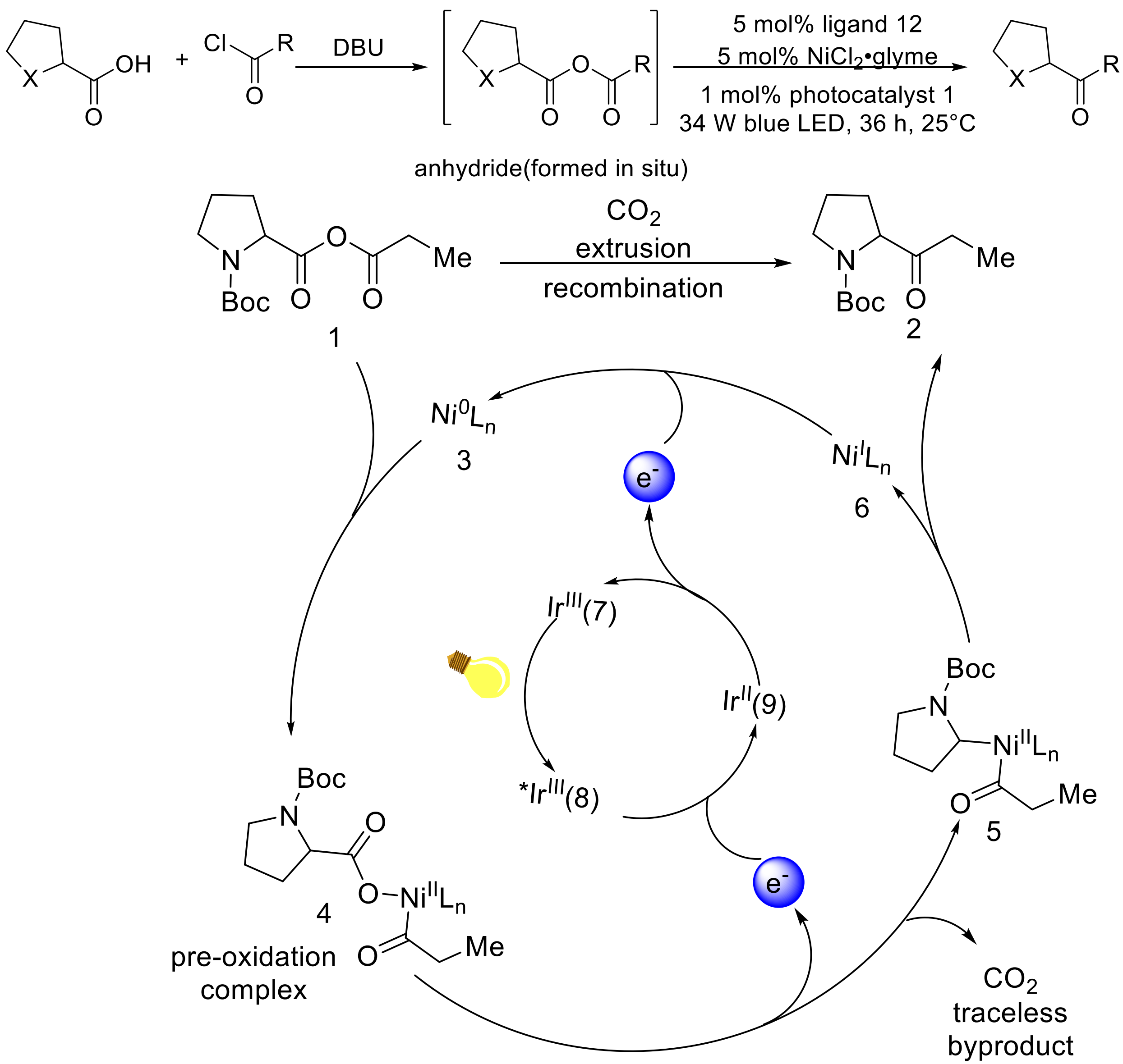


$E_{1/2}^{red}$ [$*Ir^{III}/Ir^{II}$] = +1.21 V
$E_{1/2}^{red}$ [Ni^{III}/Ni^{II}] = +0.71 V

$E_{1/2}^{red}$ [Ir^{III}/Ir^{II}] = -1.37 V
$E_{1/2}^{red}$ [Ni^{II}/Ni^{0}] = -1.2 V

Jack A. Terrett.; James D. Cuthbertson.; Valerie W. Shurtleff.; David W. C. MacMillan. *Nature*, **2015**, 524, 330-334.

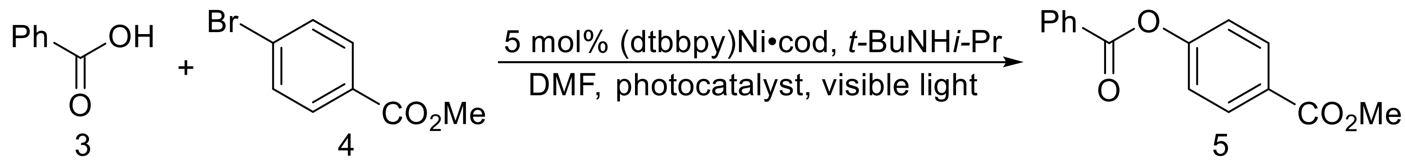
2.2. Catalysis of redox steps



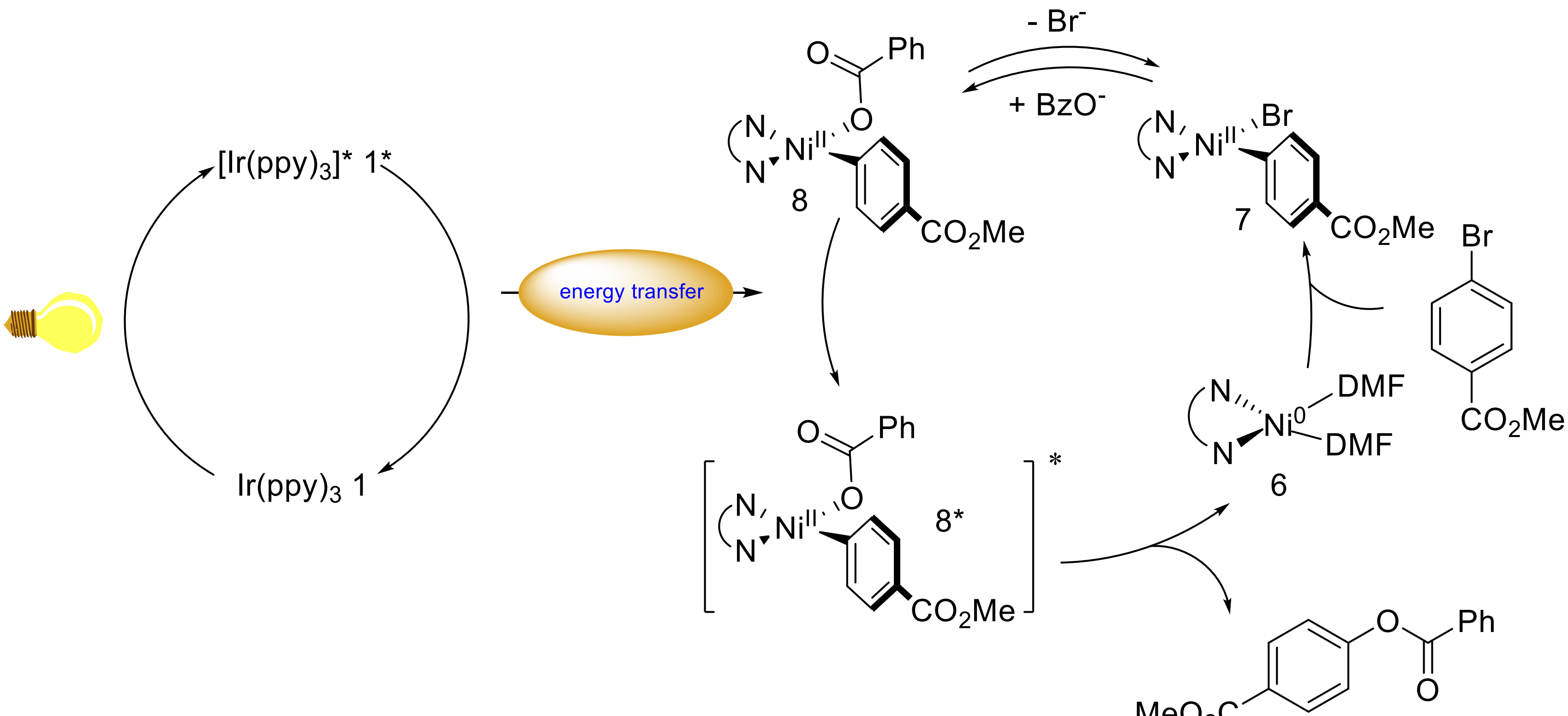
Chi “Chip” Le.; David W. C. MacMillan. *J. Am. Chem. Soc.* **2015**, 137, 11938–11941.

Outline:

2.2. Photoinduced energy transfer



Ir(ppy)$_3$: 18 hr, 85% yield Ph$_2$C=O: 18 hr, 25% yield no photocatalyst: 120 hr, 45% yield	catalytically active excited state accessed by sensitization or by direct excitation



Ir-to-Ni energy transfer induces C-O reductive elimination

Eric R. Welin.; Chip Le.; Daniela M. Arias-Rotondo.; James K. McCusker.; David W. C. MacMillan. *Science*. **2017**, 355, 380-385.

2.2. Photoinduced energy transfer

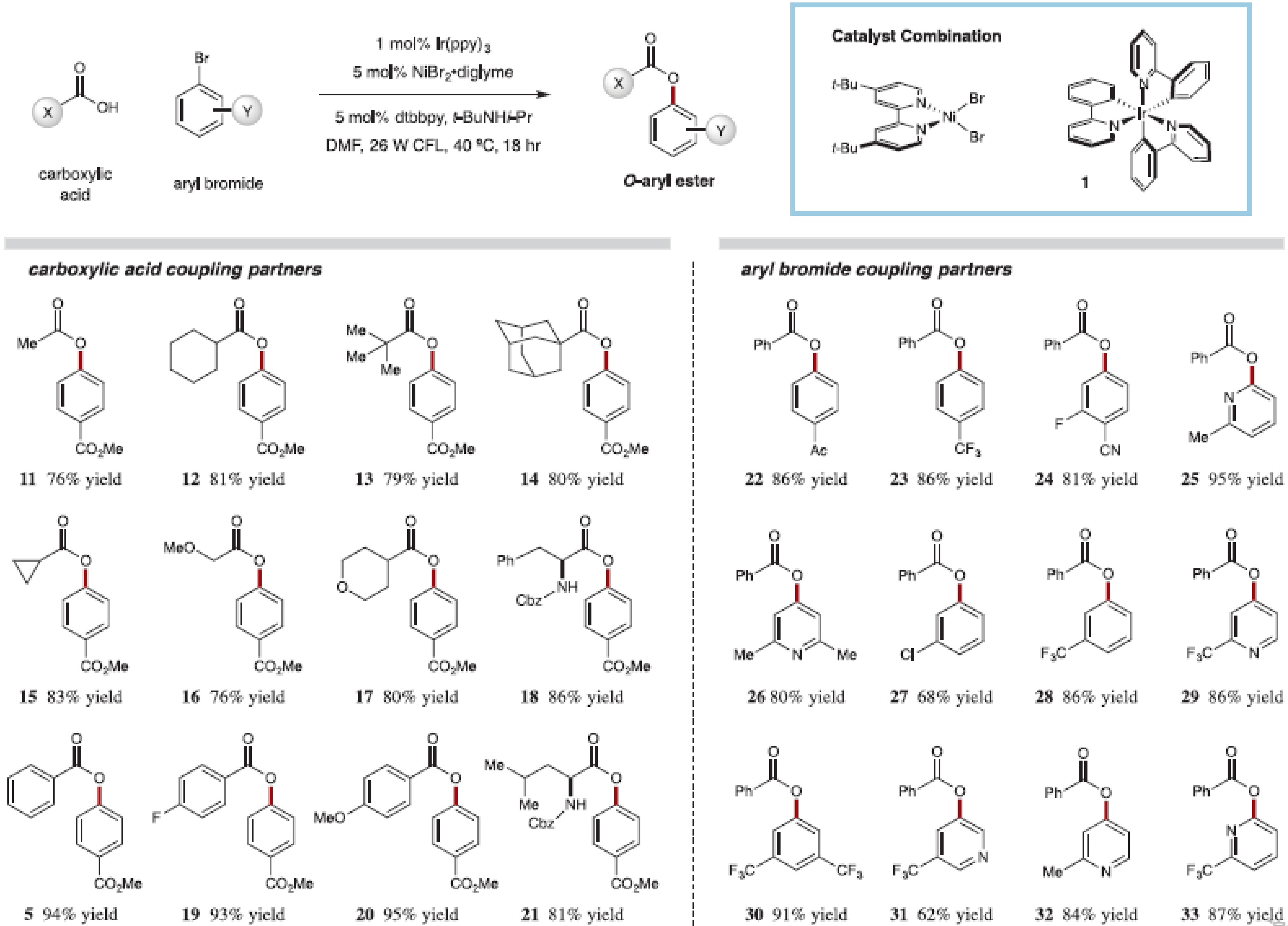
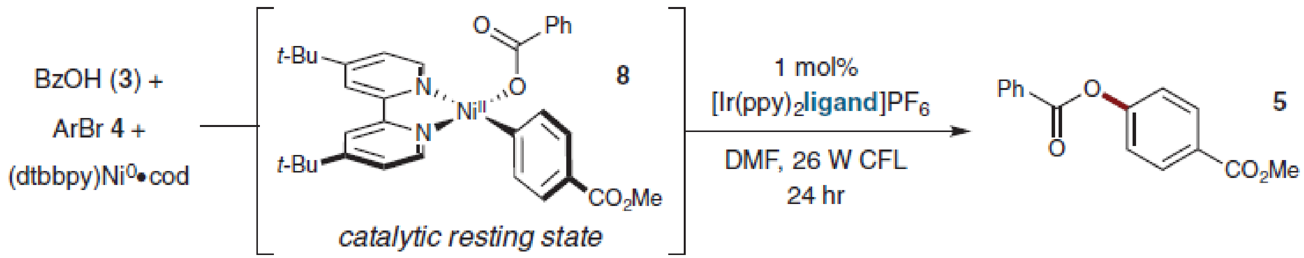


Fig. 4. Coupling of carboxylic acids with aryl halides. Substrate scope for the nickel-catalyzed coupling of aryl halides with carboxylic acids via excited-state catalysis. Cbz, benzyl carbamoyl.

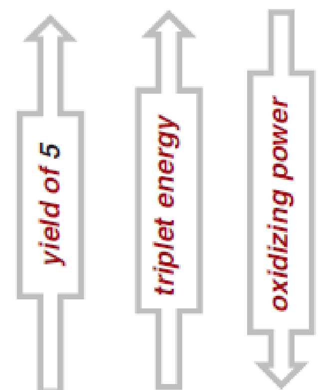
Eric R. Welin.; Chip Le.; Daniela M. Arias-Rotondo.; James K. McCusker.; David W. C. MacMillan. *Science*. **2017**, 355, 380-385.

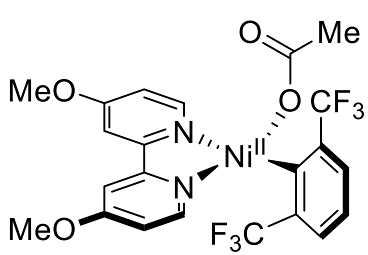
2.2. Photoinduced energy transfer

Reactivity of arylnickel(II) carboxylate is strongly dependent on photocatalyst ET:



ligand	yield **5**	E_T (kcal)	$E_{1/2}^{II/III*}$ (V)	$E_{1/2}^{III/IV}$ (V)
ppy (**1**)	85%	53.6	0.13	0.77
5,5'-Me_2bpy	80%	49.0	0.61	1.26
4,4'-$(MeO)_2$bpy	70%	47.7	0.58	1.22
4,4'-Me_2bpy	65%	47.6	0.59	1.25
bpy	50%	46.3	0.61	1.28
4,4'-Cl_2bpy	3%	42.6	0.72	1.32
4,4'-$(CO_2Me)_2$bpy	0%	39.7	0.70	1.34
4,4'-$(F_3C)_2$bpy	0%	39.2	0.74	1.37





9

$+ Ir(ppy)_3^* \longrightarrow 9^+ + Ir[(ppy)_3]^-$

ΔG^0_{ET} = +20 kcal/mol
oxidation by Ir(III)* is unfavorable

$+ [Ir^{IV}]^+ \longrightarrow 9^+ + Ir[(ppy)_3]$

ΔG^0_{ET} = +5.3 kcal/mol
oxidation by Ir(IV) is unfavorable

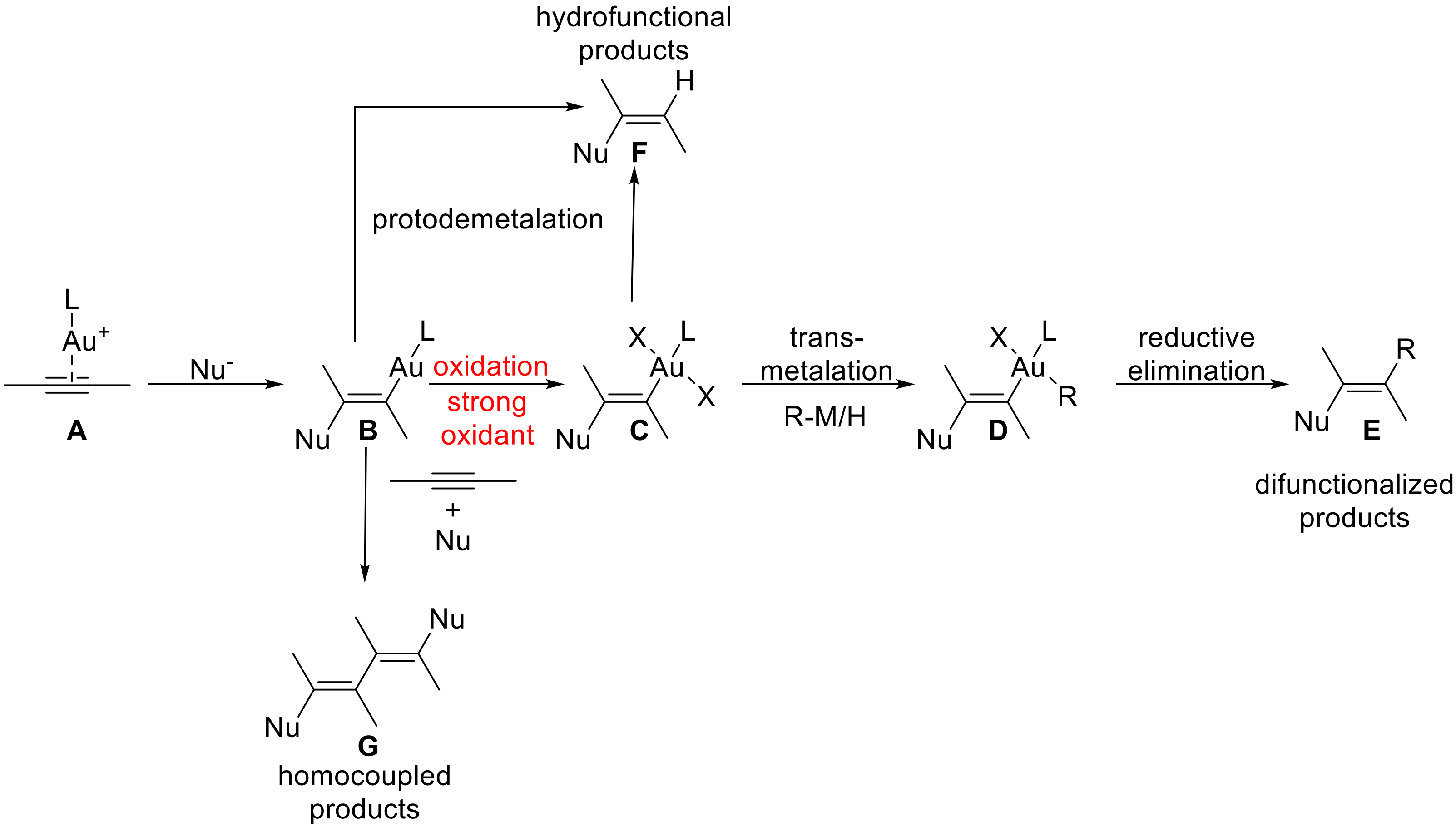
Eric R. Welin.; Chip Le.; Daniela M. Arias-Rotondo.; James K. McCusker.; David W. C. MacMillan. Science. **2017**, 355, 380-385.

Outline:

1. Introduction
2. Merging visible light photoredox and Nickle catalysis
    2.1. Catalysis of downstream steps
    2.2. Catalysis of redox steps
    2.3. Photoinduced energy transfer
3. Merging visible light photoredox and gold catalysis
4. Conclusion
5. Acknowledgement

3. Merging visible light photoredox and gold catalysis

Gold-catalyzed oxidative difunctionalization reactions using external oxidants:



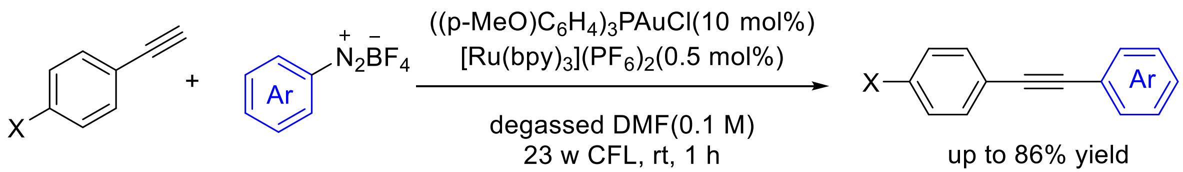
The redox potential of AuI/AuIII couple is significantly high (E_0 = 1.41 V)

Disadvantages:

1. Strong external oxidants;
2. Limitation of substrates;
3. Poor selectivity of cross-coupling and homodimers.

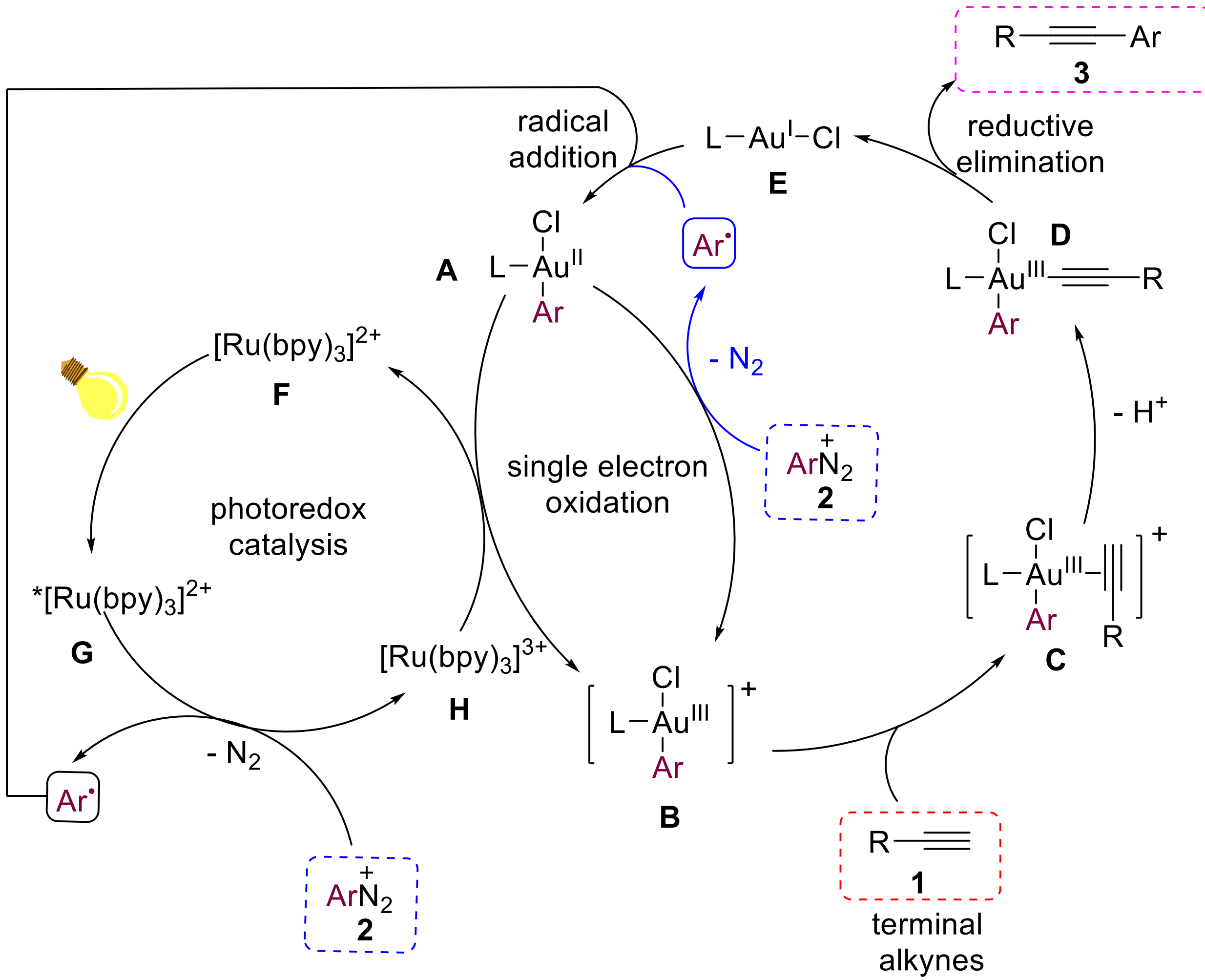
3. Merging visible light photoredox and gold catalysis

Dual gold /photoredox-catalyzed arylation of terminal alkynes



Oxidation first:

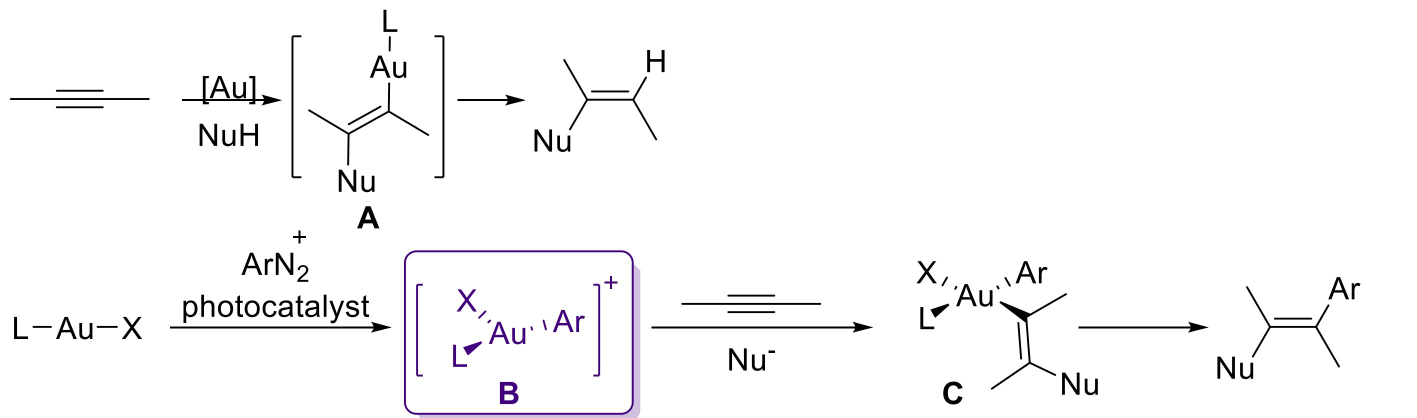
Also, high quantum yield (3.6) indicates more than one pathway



Tlahuext-Aca, A.; Hopkinson, M. N.; Sahoo, B.; Glorius, F. *Chem. Sci*. **2016**, 7, 89−93.

3. Merging visible light photoredox and gold catalysis

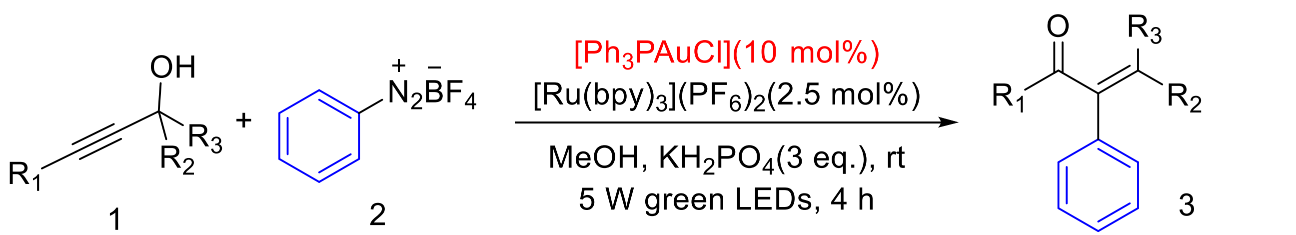
Alkyne Difunctionalization by Dual Gold/Photoredox Catalysis



simultaneous oxidation and aryl coupling partner coordination: **homocoupling suppressed**

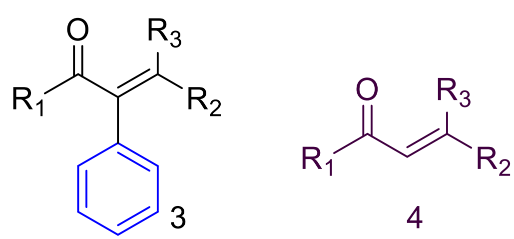
intermediate A not formed: **protodemetalation suppressed**

alkynes can be used as substrates with high selectivity



up to 82% yield E/Z > 95:5

$[Ph_3PAu]NTf_2$:



hyfrofunctionalized products

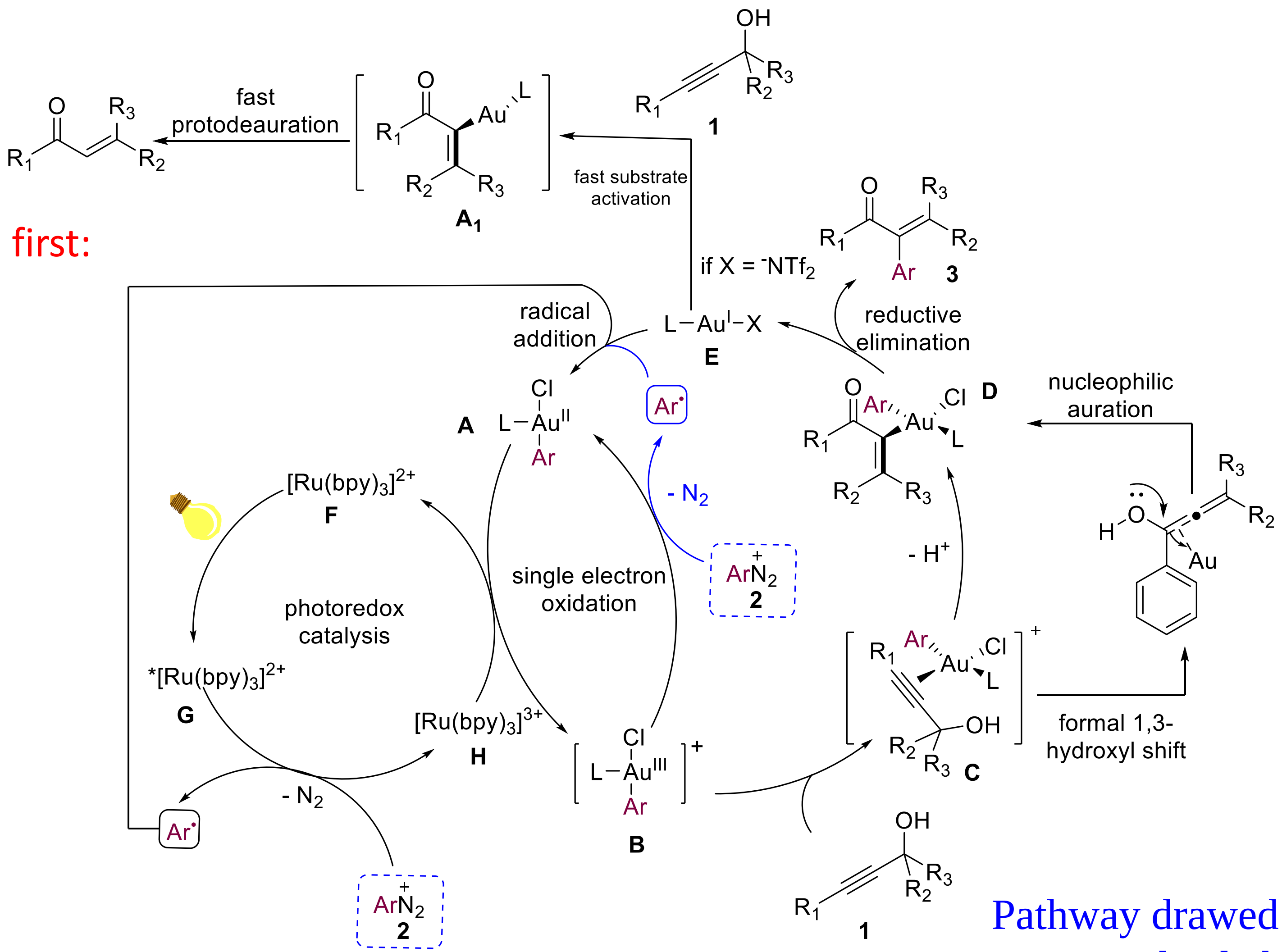
yield: 0% yield: 20%

Tlahuext-Aca, A.; Hopkinson, M. N.; Garza-Sanchez, R. A.;Glorius, F. *Chem. Eur. J.* **2016**, 22, 5909−5913.

3. Merging visible light photoredox and gold catalysis

Alkyne Difunctionalization by Dual Gold/Photoredox Catalysis

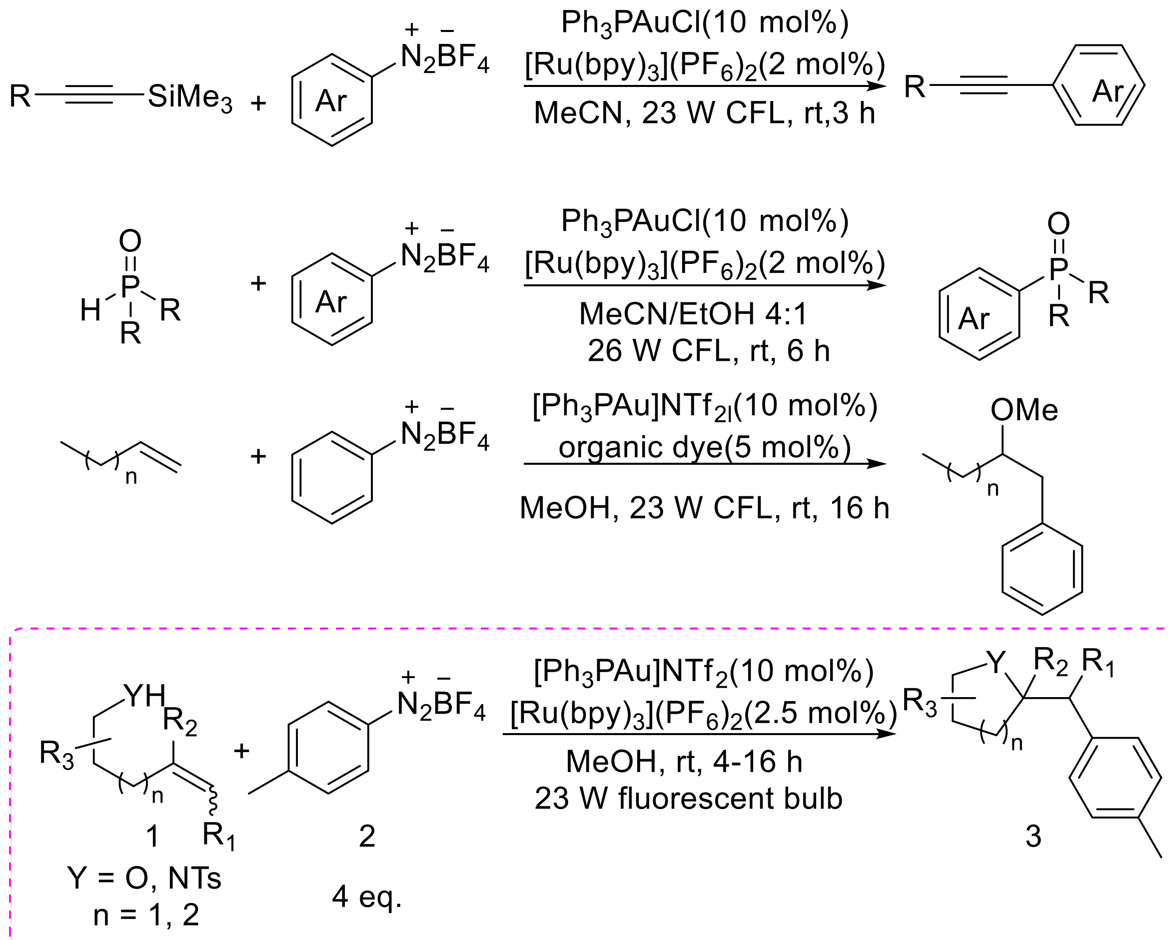
Oxidation first:



Pathway drawed in blue is radical chain

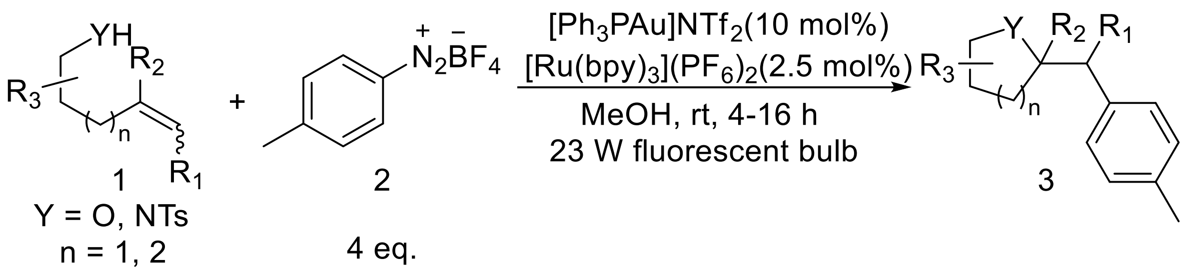
Tlahuext-Aca, A.; Hopkinson, M. N.; Garza-Sanchez, R. A.;Glorius, F. *Chem. Eur. J.* **2016**, 22, 5909−5913.

3. Merging visible light photoredox and gold catalysis



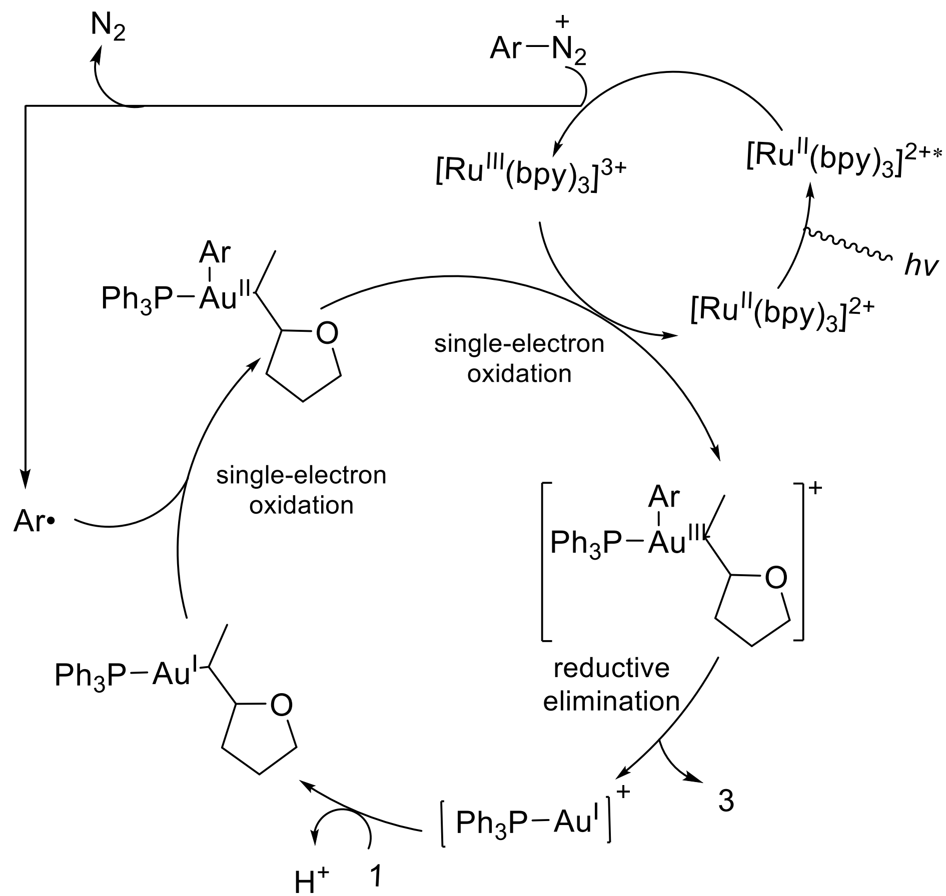
He, Y.; Wu, H.; Toste, F. D. *Chem. Sci*. **2015**, 6, 1194−1198.
Kim, S.; Rojas-Martin, J.; Toste, F. D. *Chem. Sci*. **2016**, 7, 85−88.
Hopkinson, M. N.; Sahoo, B.; Glorius, F. *Adv. Synth. Catal.* **2014**, 356, 2794−2800.
Tlahuext-Aca, A.; Hopkinson, M. N.; Garza-Sanchez, R. A.; Glorius, F. *Chem. Eur. J.* **2016**, 22, 5909−5913.

3. Merging visible light photoredox and gold catalysis



Transmetallation first:

How to differentiate transmetallation first or oxidation first



Tlahuext-Aca, A.; Hopkinson, M. N.; Garza-Sanchez, R. A.;Glorius, F. *Chem. Eur. J*. **2016**, 22, 5909−5913.

3. Merging visible light photoredox and gold catalysis

How to differentiate transmetallation first or oxidation first ?

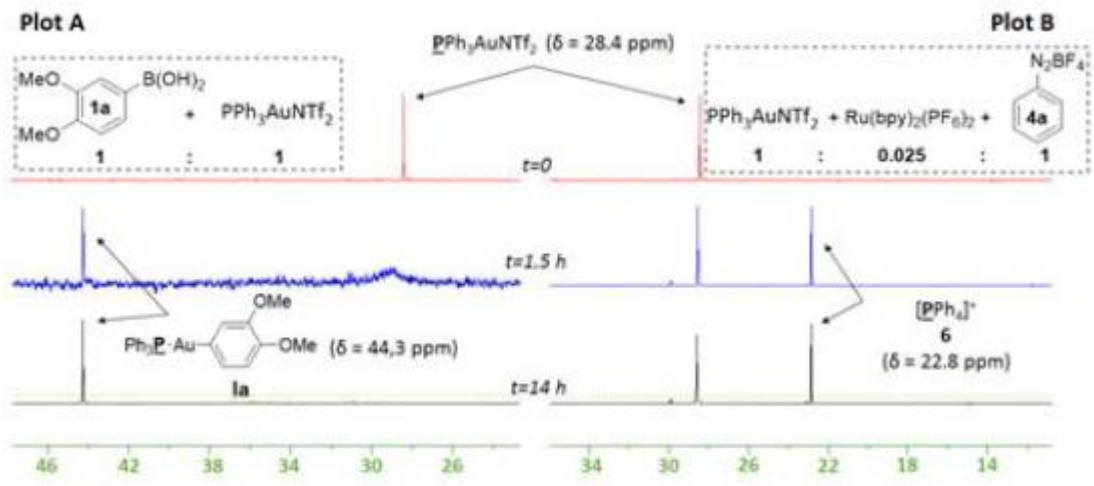


Figure 1 ^{31}P NMR studies in $CD_3CN:D_2O$

Cationic PPh_3AuNTf_2 undergoes transmetallation first.

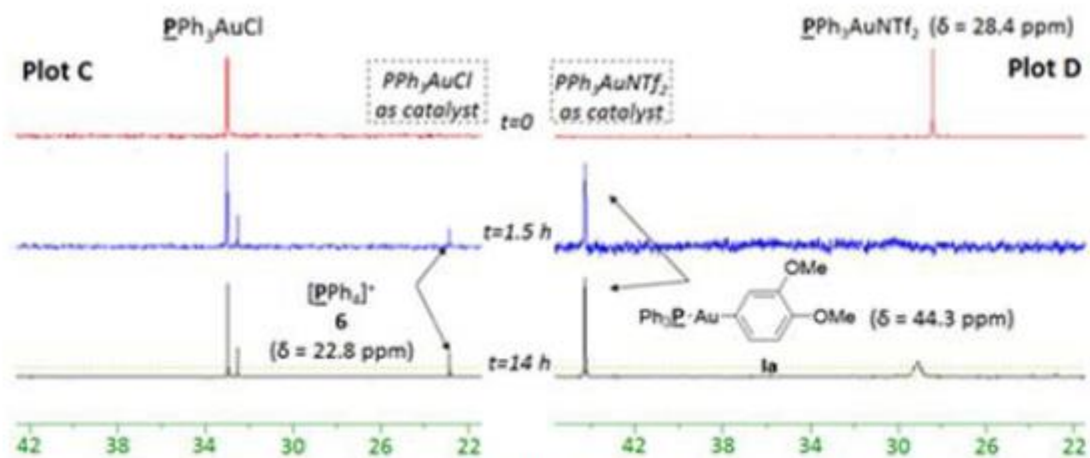


Figure 2 ^{31}P NMR monitoring of PPh_3AuCl-catalysed reaction (plot **C**) and PPh_3AuNTf_2-catalysed reaction (plot **D**)

neutral PPh_3AuCl undergoes the expected "oxidation first" pathway.

Gauchot, V.; Lee, A.-L. *Chem. Commun*. **2016**, 52, 10163−10166.

Outline:

1. Introduction
2. Merging visible light photoredox and Nickle catalysis
    2.1. Catalysis of downstream steps
    2.2. Catalysis of redox steps
    2.3. Photoinduced energy transfer
3. Merging visible light photoredox and gold catalysis
4. Conclusion
5. Acknowledgement

4. Conclusion

1. Dividing two electron transfer into two single electron transmetalation reduces the high activation barrier.

2. Unlock a new paradigm for sp^3-sp^2, sp-sp^2, sp^2-sp^2 cross-coupling.

3. Reacting under mild condition demonstrates greater functional group tolerance.

4. The mechanism about oxidation first or transmetallation first remained confused in dual gold/photoredox catalysis

Outlook

Can sp-sp^3 cross-coupling be realized through this dual gold/photoredox catalysis??

Acknowledgement

Prof. Huang

Wang leifeng

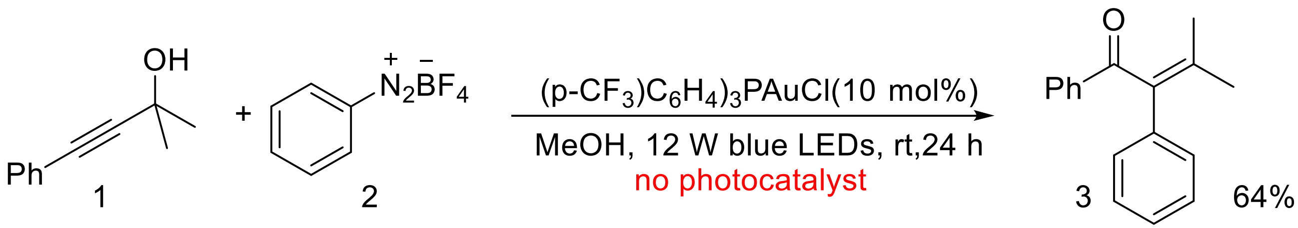
All members in E201

Everyone here

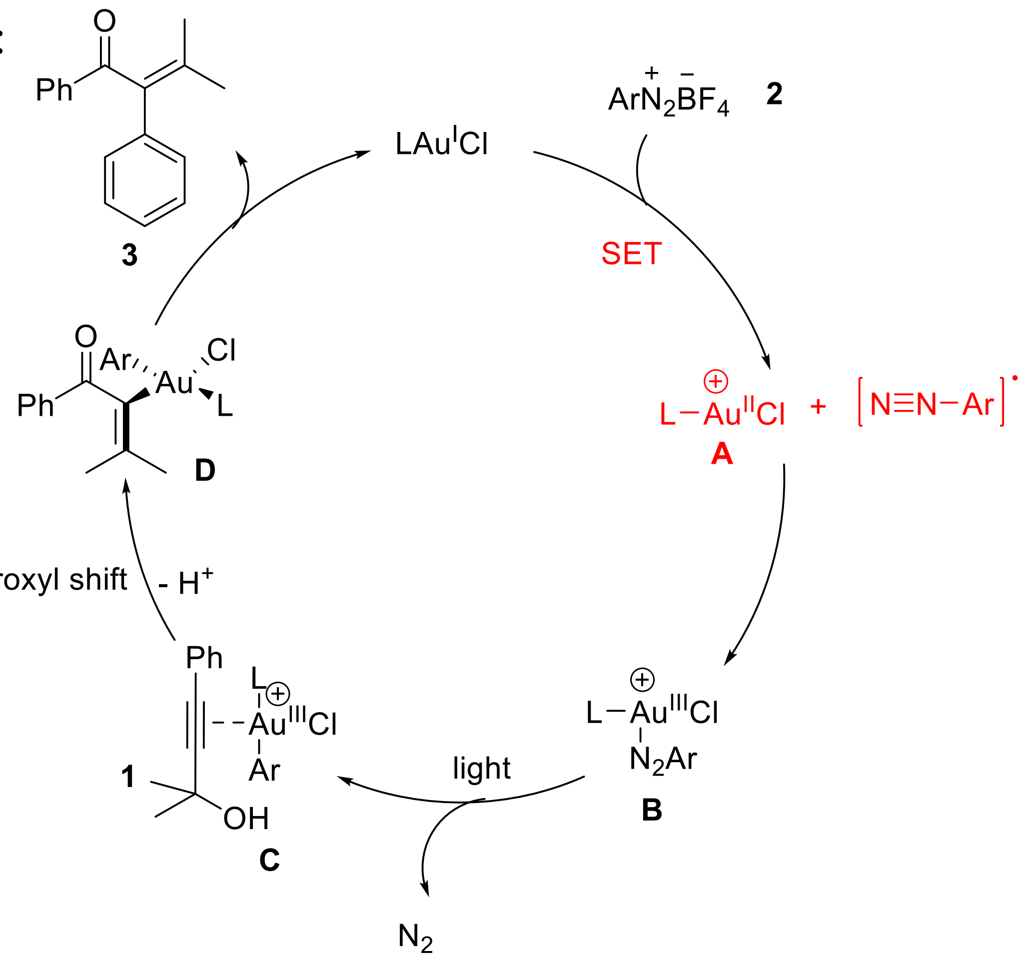
Thank you!

3. Merging visible light photoredox and gold catalysis

Photocatalyst-free gold-catalyzed difunctional of alkynes



Proposed mechanism:

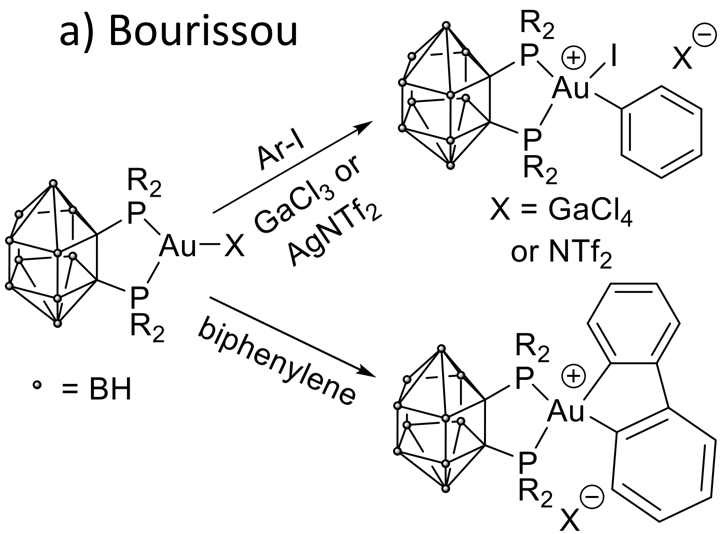


Huang, L.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem., Int. Ed*. **2016**, 55, 4808−4813.

3. Merging visible light photoredox and gold catalysis

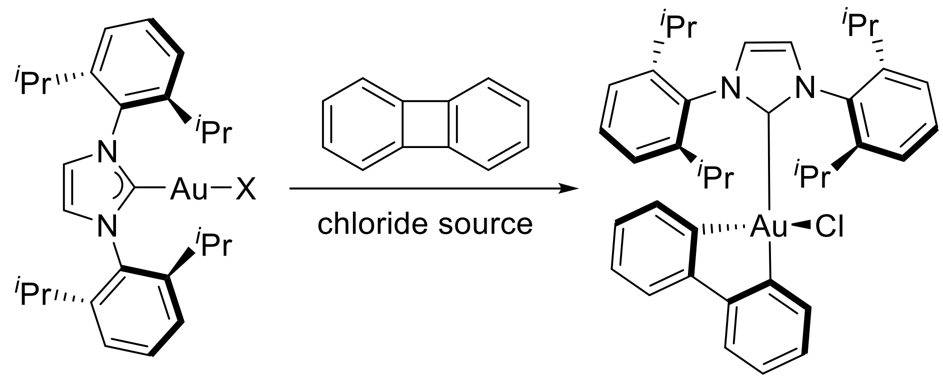
How to differentiate transmetallation first or oxidation first ?

a) Bourissou



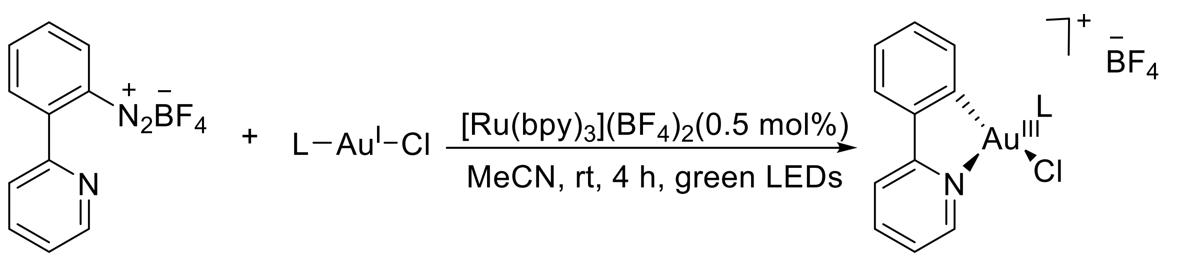
biphosphine ligand with a small bite angle:
preorganize the coordinaiton geometry around the metal center to accommodate rhe aquare planar arrangement.

b) Toste



X = ⁻OTf

c) Glorious



1a 2a 3aa 80% yield

square planar complex:
kinetically stable
resistant to reductive eliminaiton

Tlahuext-Aca, A.; Hopkinson, M. N.; Daniliuc, C. G.; Glorius, F. *Chem. Eur. J.* **2016**, 22, 11587−11592