可见光下丰产金属参与的自由基均裂(VLIH)反应构建C-C键

报 告 人：张 杰

导 师：陆 平 教授

2024-10-11

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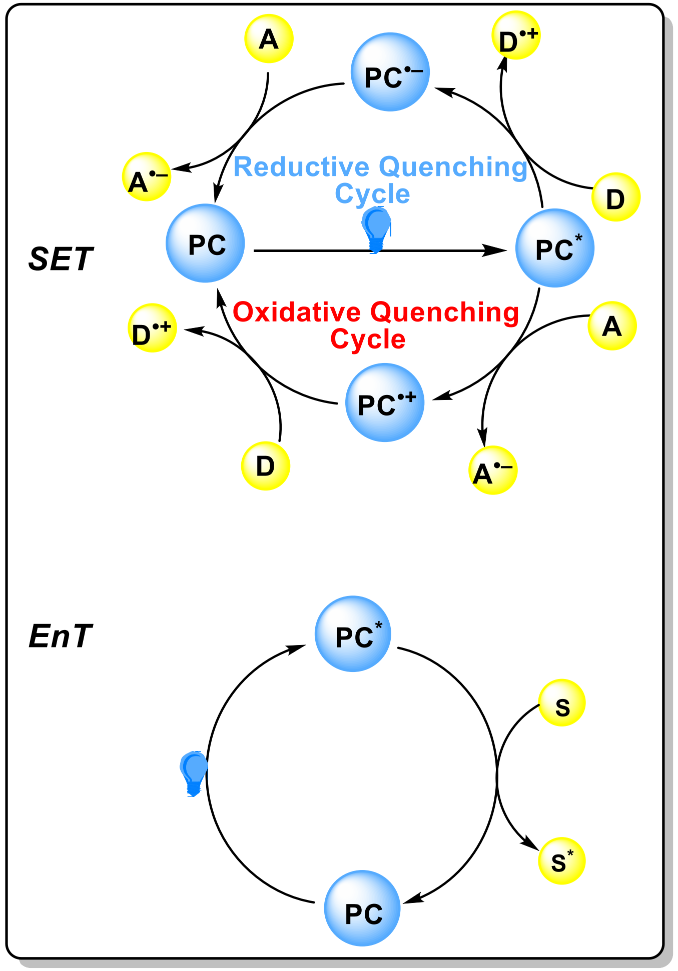
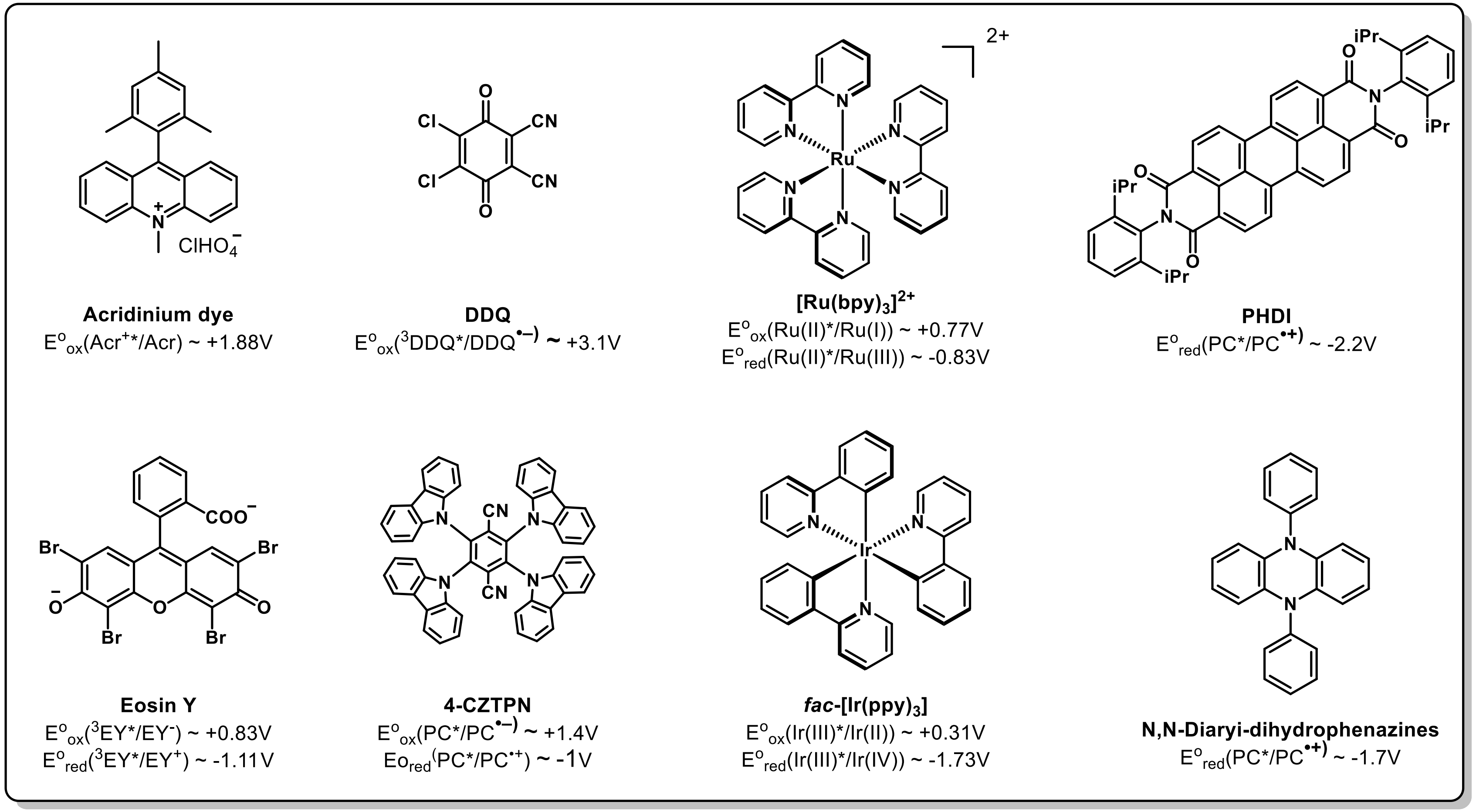
背景介绍-光催化剂的发展

➢ General Mechanisms of Photocatalysis



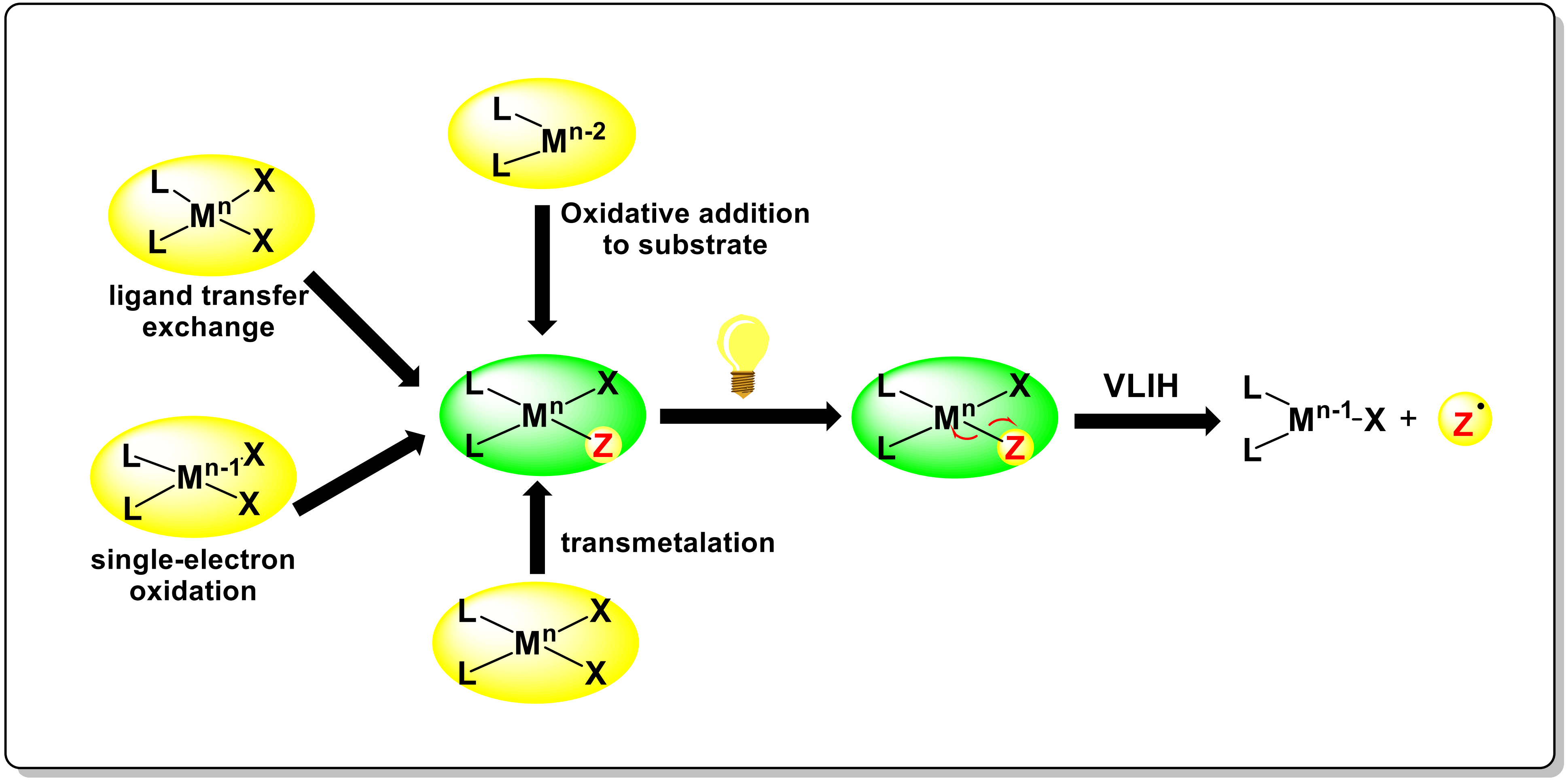
➢ Typical photoredox catalysts



[1]. V. Gevorgyan, et. al. *Chem. Rev.* **2022**, *122*, 1543-1625. [2]. B. König, et. al. *Angew. Chem. Int. Ed.* **2018**, *57*, 10034-10072.
[3]. M. Fagnoni, et. al. *Chem. Rev.* **2016**, *116*, 9850-9913. [4]. O. Reiser, et. al. *Angew. Chem. Int. Ed.* **2021**, *60*, 21100-21115.

背景介绍-VLIH概念的提出

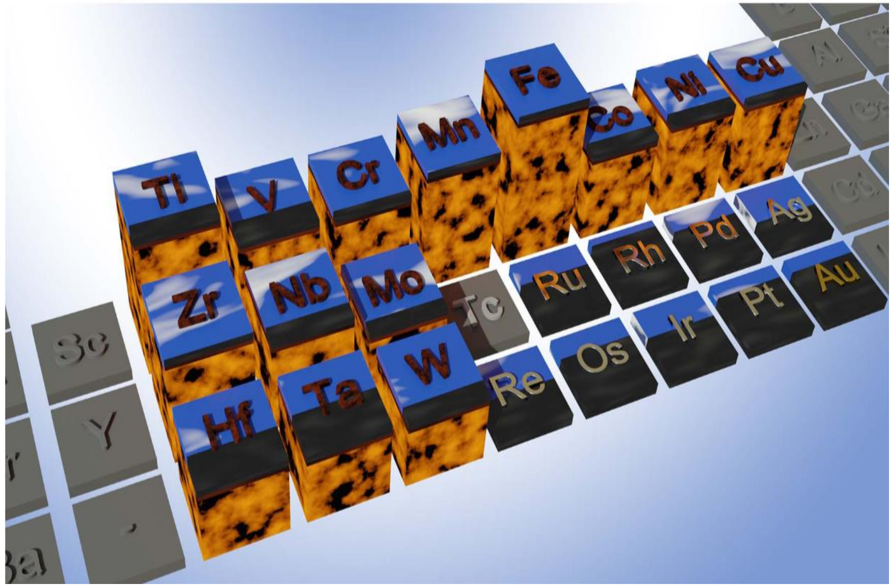
➢ **Visible-light-induced homolysis (VLIH) in photoredox catalysis.**



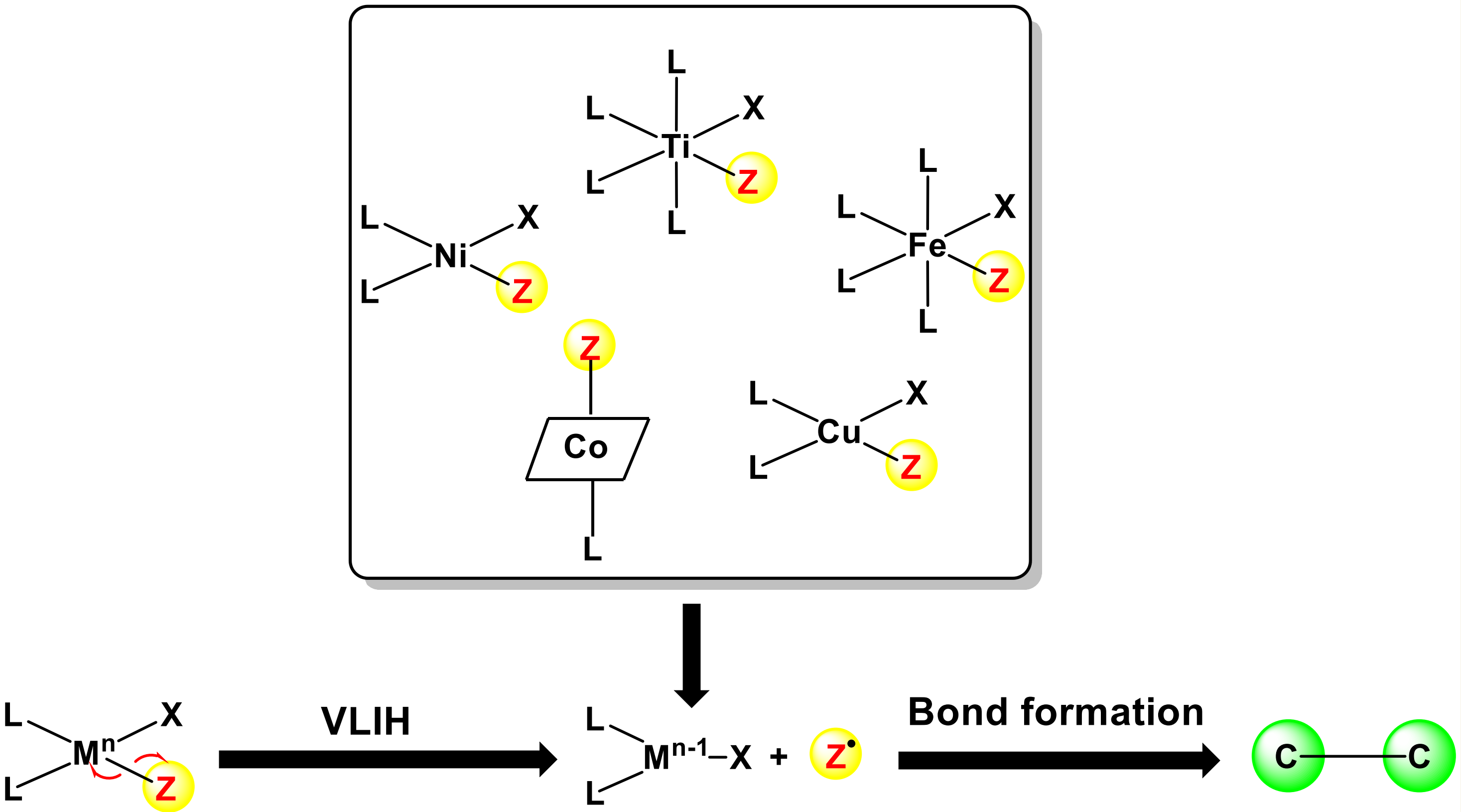
O. Reiser, et. al. *Angew. Chem. Int. Ed.* **2021**, *60*, 21100– 21115.

背景介绍-丰产金属参与VLIH反应

C-C键构建：过渡金属催化的交叉偶联反应和自由基链式反应，以及有机分子催化等



丰产金属



z =alkyl, halogen, Azide, carbonyl......

Y. Surendranath, et al. *Science*, **2020**, *369*, 786-796.

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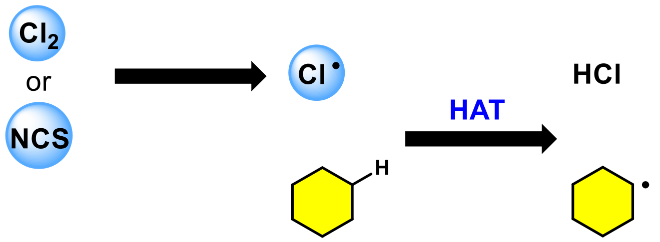
可见光下Ni催化构建C-C键

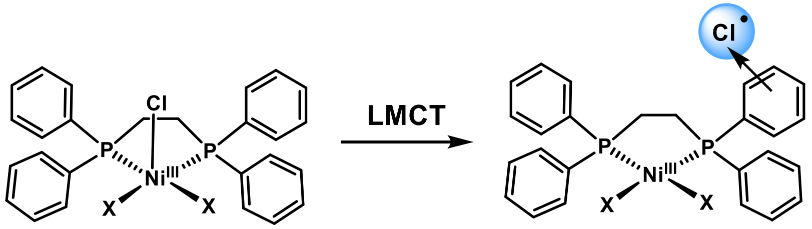
➢ **Direct $C(sp^3)$−H Cross Coupling Enabled by photoredox and nickel dual catalysis.**

◆ Interfacing chlorine radical $C(sp^3)$−H bond activation

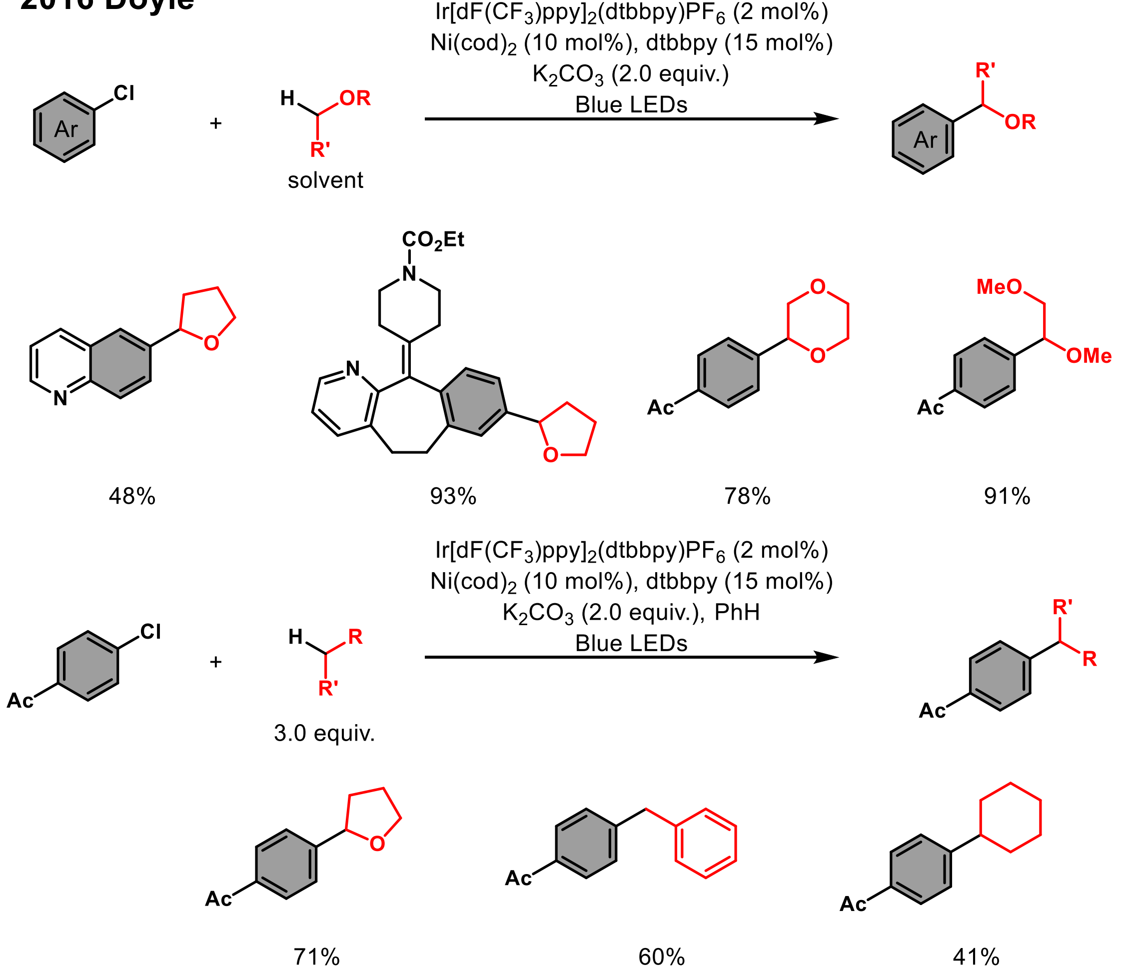


◆ Chlorine radical generation via photolysis of high-valent nickel chloride complexes.

2015 Nocera



2016 Doyle



[1]. D. G. Nocera, et. al. *J. Am. Chem. Soc.* **2015**, *137*, 6472−6475. [2]. A. G. Doyle, et. al. *J. Am. Chem. Soc.* **2016**, *138*, 12719−12722.

可见光下Ni催化构建C-C键

◆ 从Ir的氧化还原电势看足以Ni完成催化循环

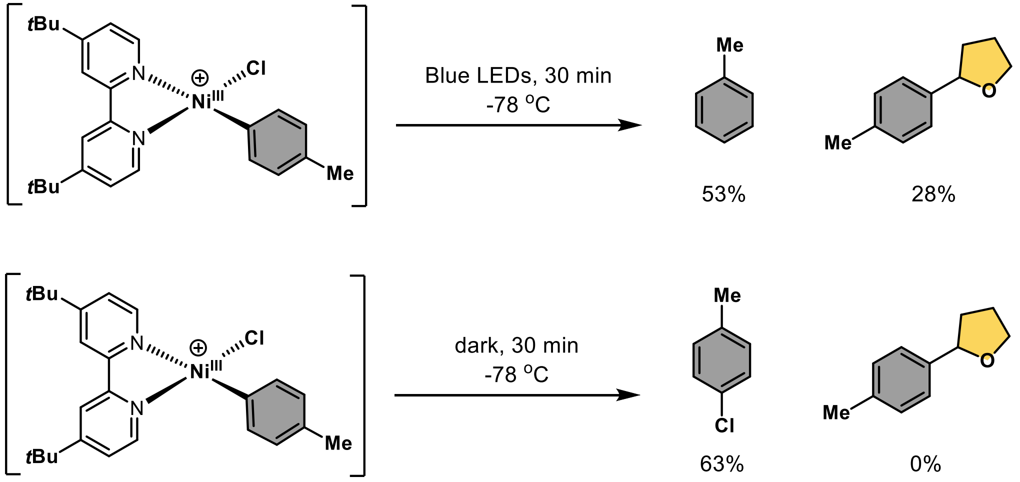
Ir^{III*} state ($^*E_{1/2}$ = 1.21 V vs. SCE in MeCN)

Ir^{II} species ($E_{1/2}$= −1.37 V vs. SCE in MeCN)

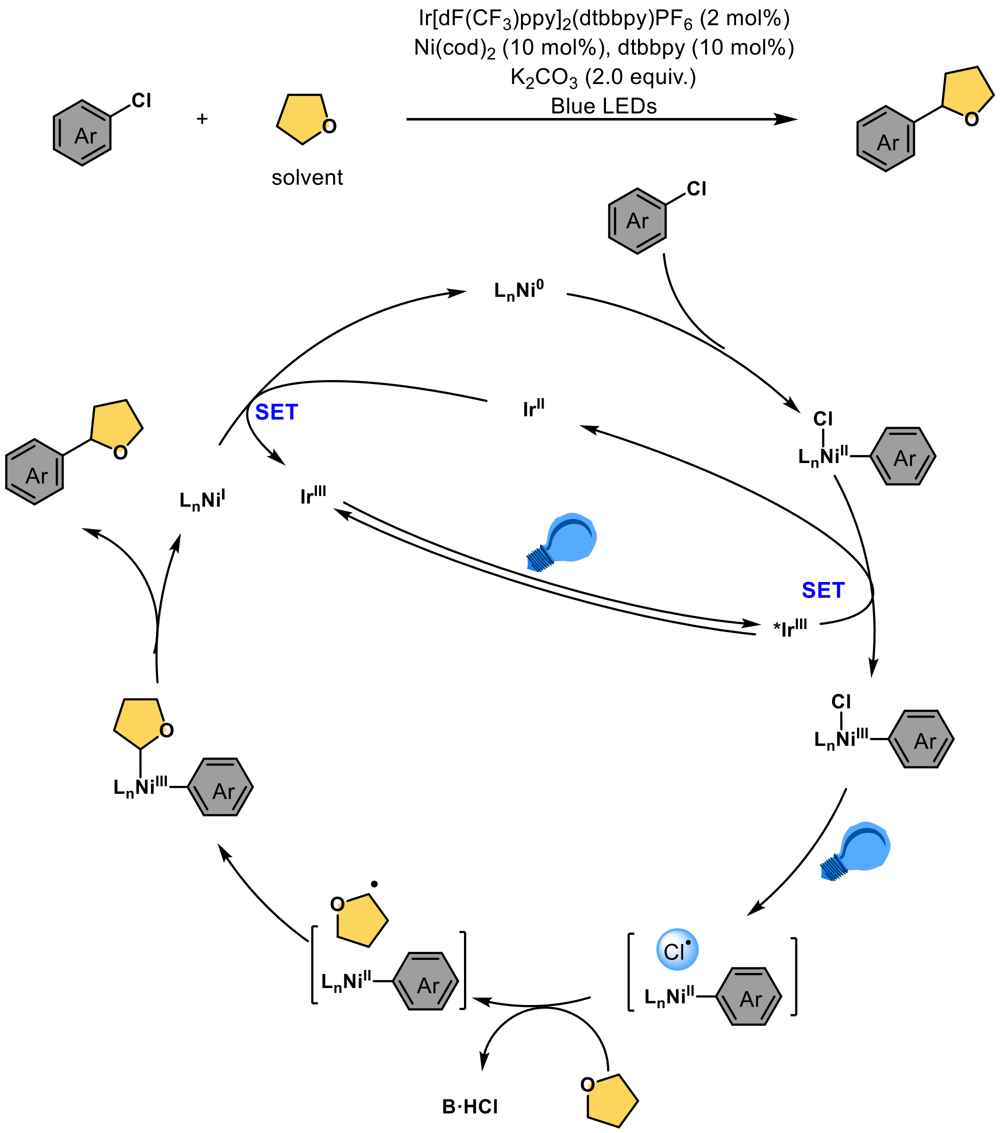
Ni^{I} species ($E_{1/2}$= − 1.17 V vs. SCE in MeCN)

Ni^{II} species ($E_{1/2}$= 0.85 V vs. SCE in MeCN)

◆ Ni^{III}中间体可以得到产物



◆ Doyle Proposed catalytic cycle.

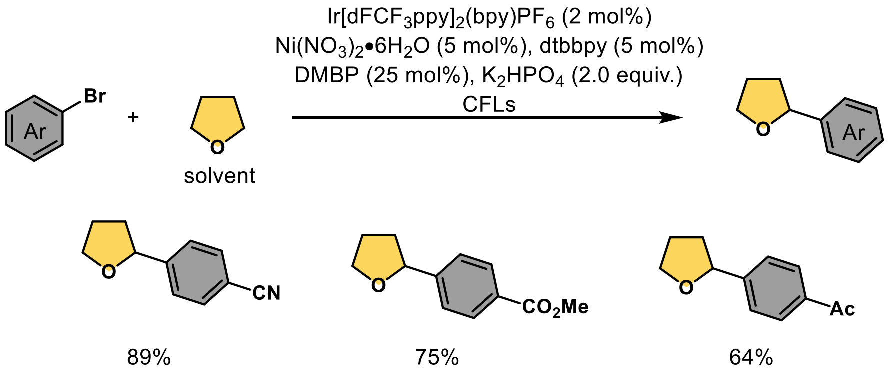


A. G. Doyle, et. al. *J. Am. Chem. Soc.* **2016**, *138*, 12719−12722.

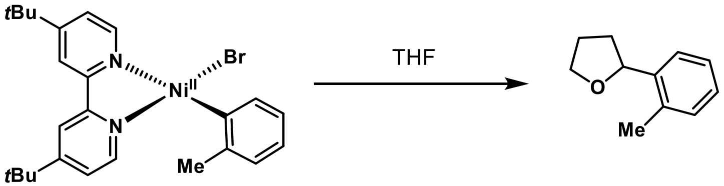
可见光下Ni催化构建C-C键

➢ **Direct C(sp³)−H Cross Coupling Enabled by photoredox and nickel dual catalysis.**

2016 Molander

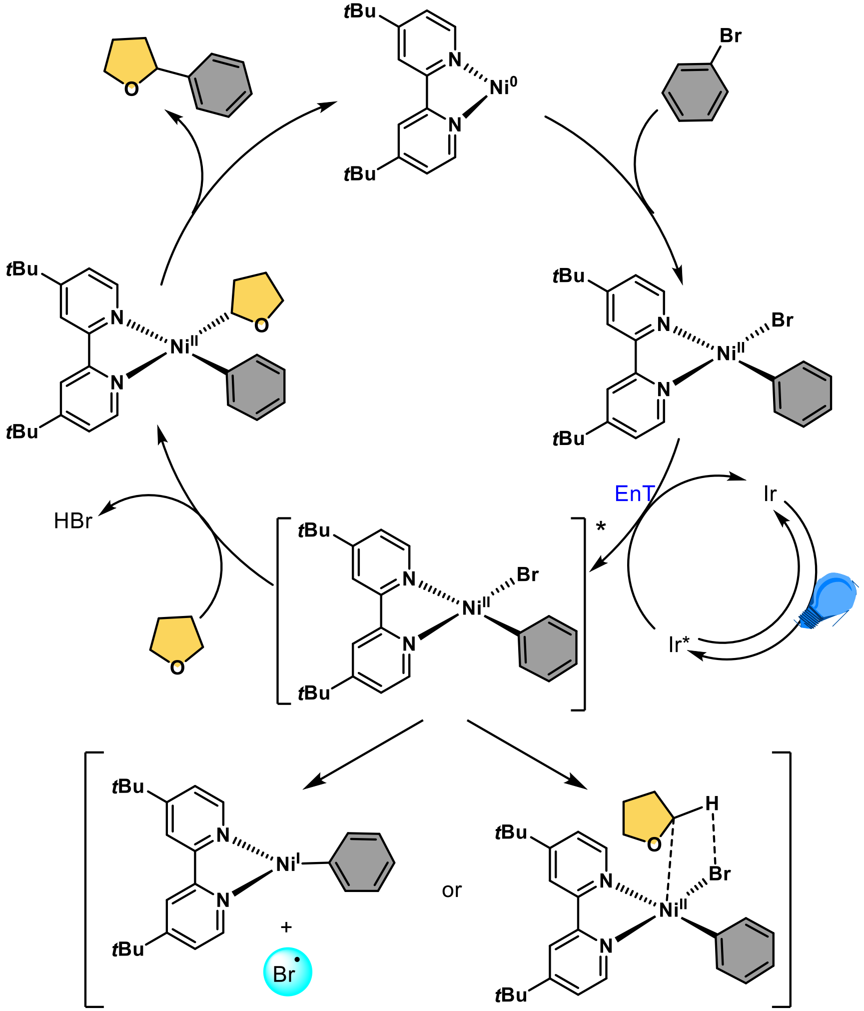


◆ Reactions of Ni(II) Oxidative Addition Complexes.



entry	photocatalyst	light source	result
1	$Ir[dFCF_3ppy]_2(bpy)PF_6$	26 W CFL	formed
2	none	26 W CFL	n.r.
3	none	UV light	formed

◆ Molander Proposed catalytic cycle.

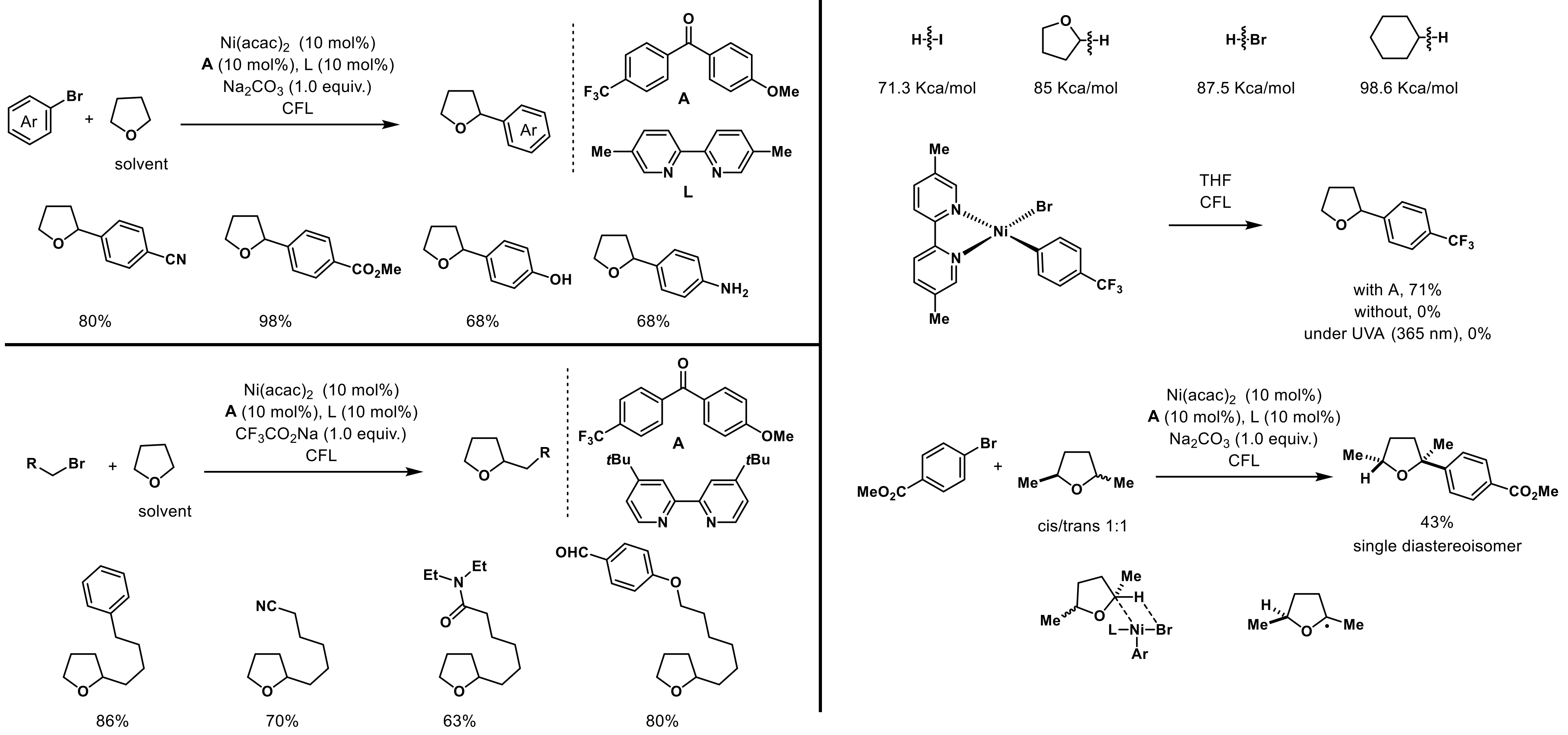


G. A. Molander, et. al. *J. Am. Chem. Soc*. **2016**, *138*, 12715−12718.

可见光下Ni催化构建C-C键

➢ **Direct C(sp³)−H Cross Coupling Enabled by Triplet Excited Ketones and Nickel Catalysts.**

2018 Martin

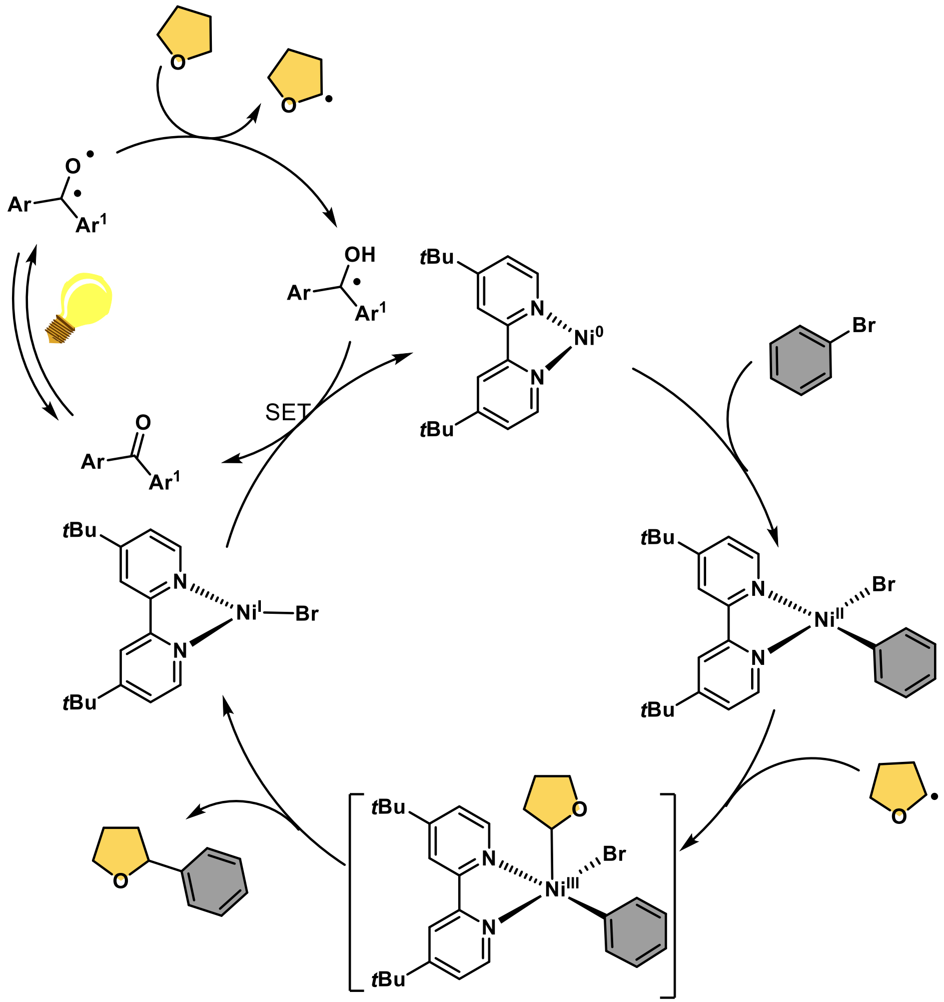


R. Martin, et. al. *J. Am. Chem. Soc.* **2018**, *140*, 12200−12209.

可见光下Ni催化构建C-C键

➢ **Direct C(sp³)−H Cross Coupling Enabled by Triplet Excited Ketones and Nickel Catalysts.**

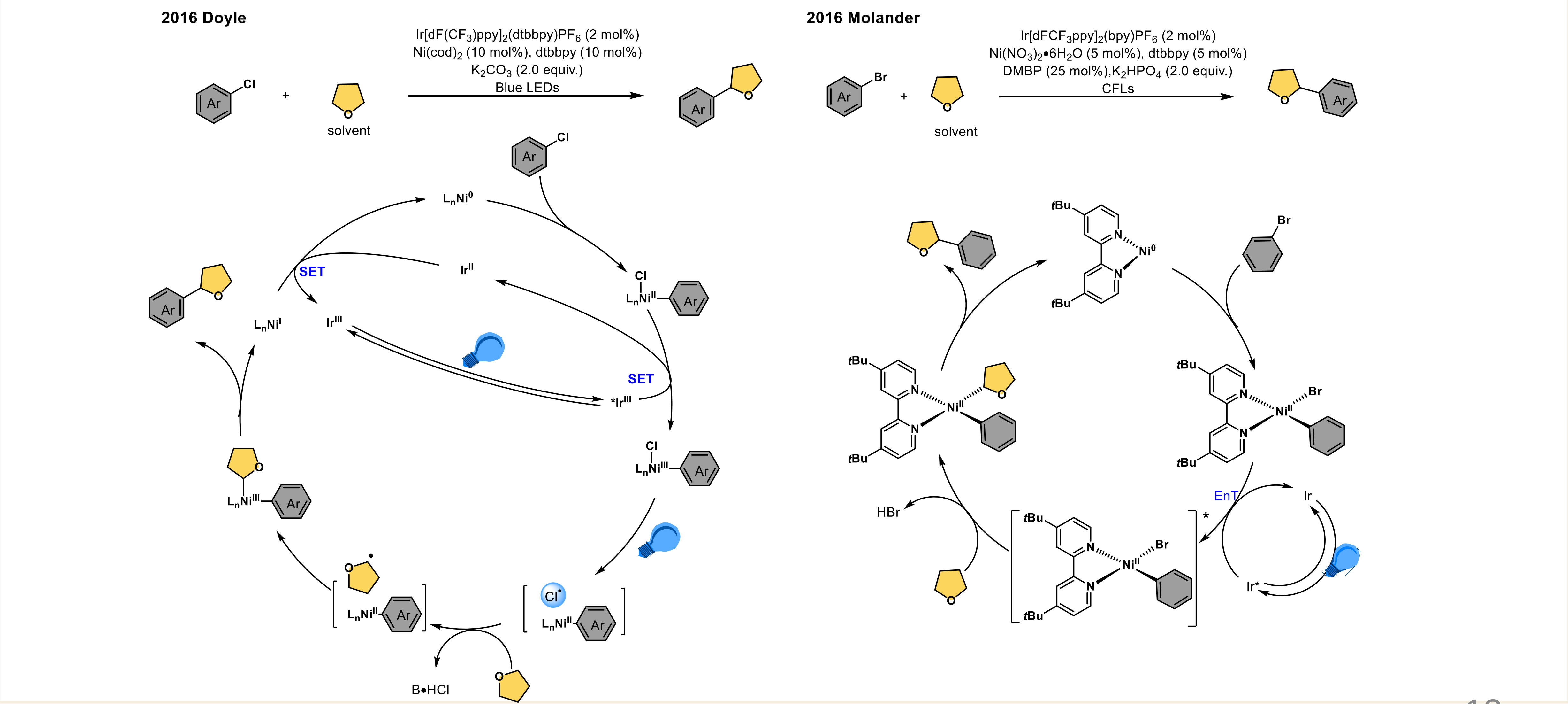
◆ Martin Proposed catalytic cycle.



R. Martin, et. al. *J. Am. Chem. Soc.* **2018**, *140*, 12200−12209.

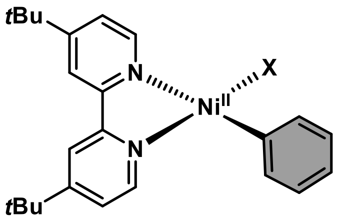
可见光下Ni催化构建C-C键

➤ **Representative triplet energy transfer and single electron transfer mechanisms for the C−H arylation of THF.**

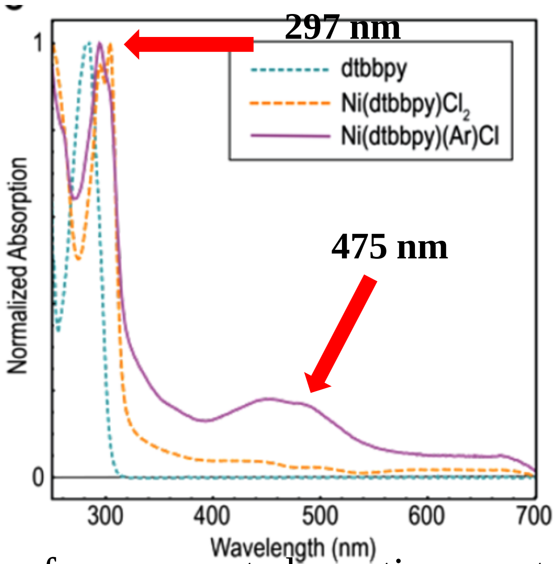


[1]. A. G. Doyle, et. al. *J. Am. Chem. Soc.* **2024**, *146*, 15331−15344. [2]. G. A. Molander, et. al. *J. Am. Chem. Soc.* **2016**, *138*, 12715−12718.

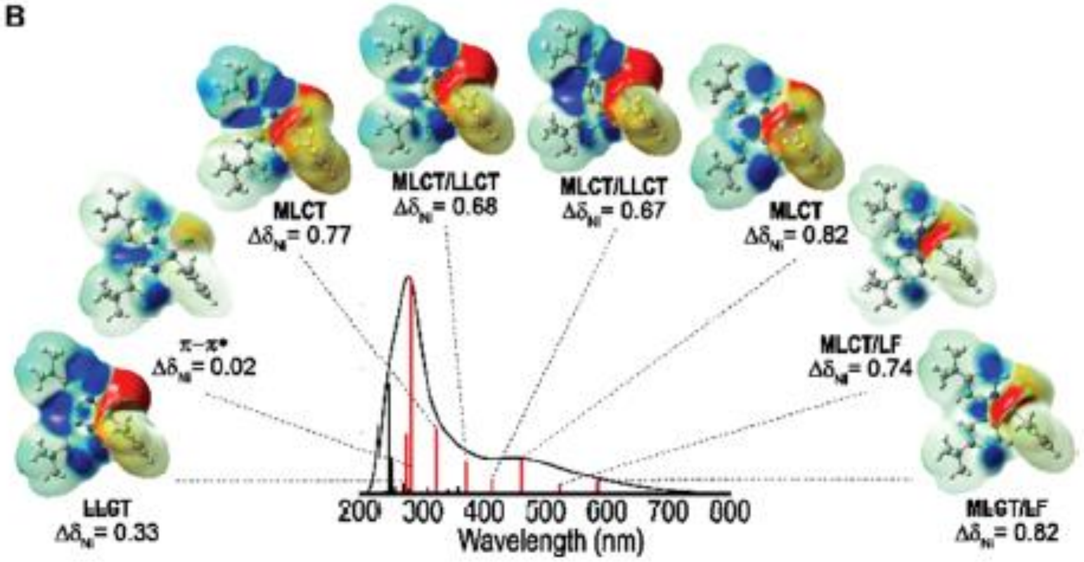
可见光下Ni催化构建C-C键



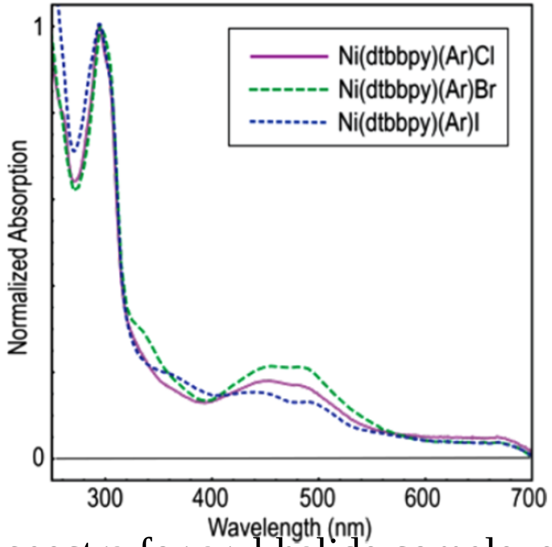
X=Cl/Br/I



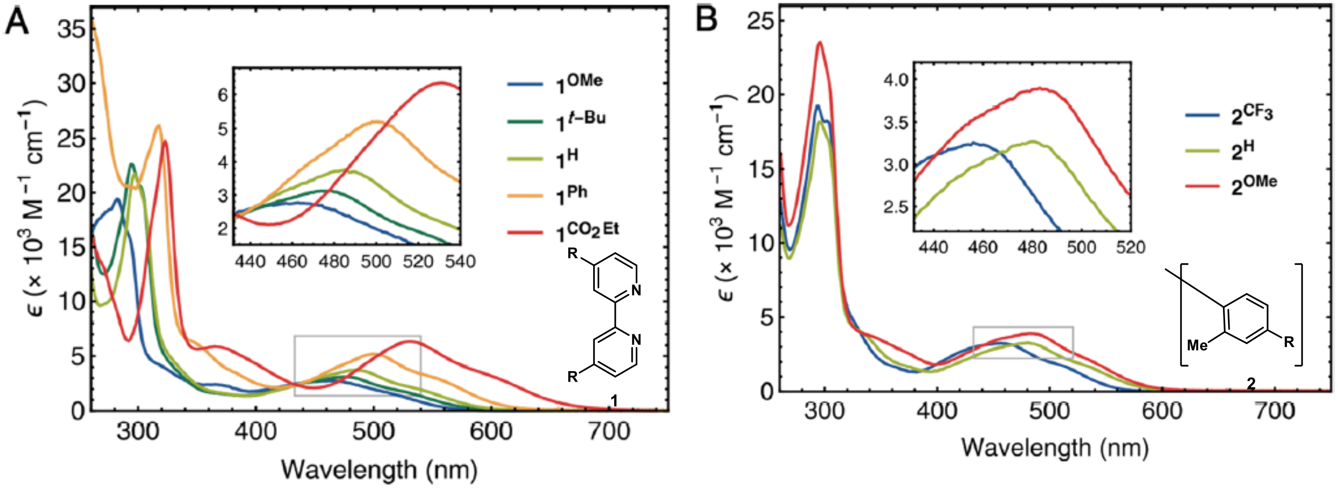
◆ Comparison of component absorption spectra.



◆ TD-DFT computed absorption spectrum.



◆ Absorption spectra for aryl halide complexes.

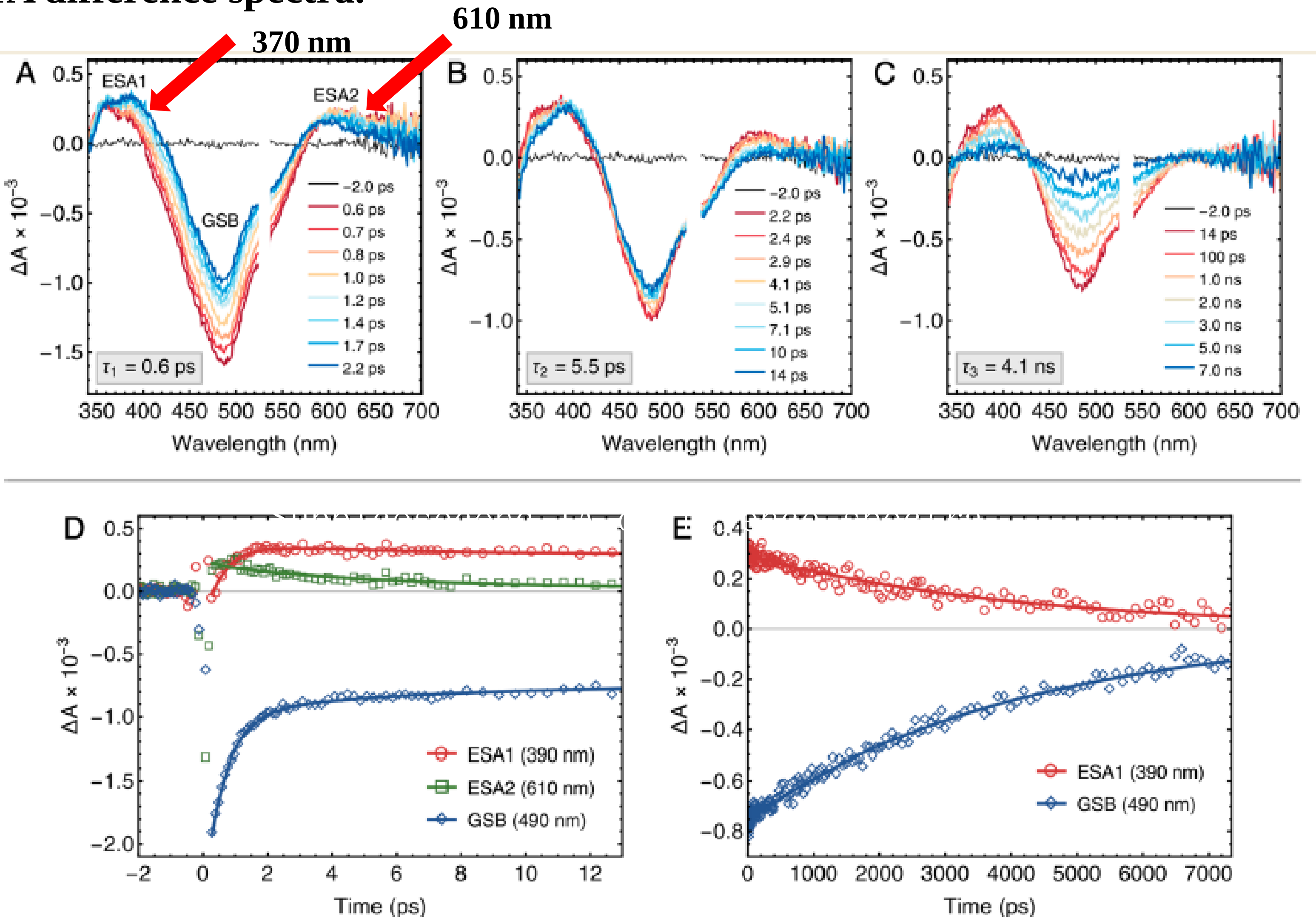


◆ UV−Vis absorption spectra in THF of (A) the bipyridine series

[1]. A. G. Doyle, et. al. *J. Am. Chem. Soc*. **2018**, *140*, 3035−3039. [2]. A. G. Doyle, et. al. *J. Am. Chem. Soc*. **2020,** *142*, 5800−5810.

可见光下Ni催化构建C-C键

- Subpicosecond TA difference spectra.

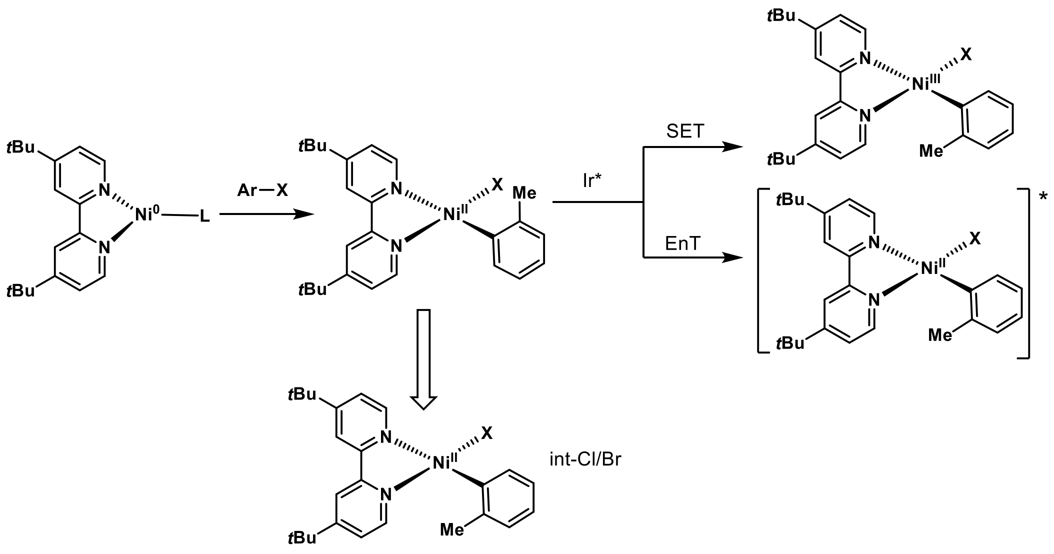


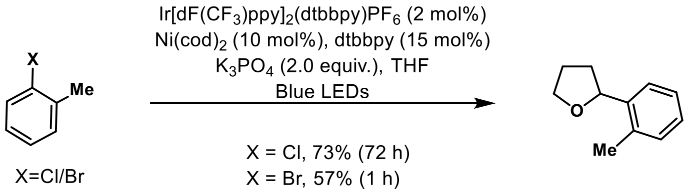
◆ (A) 0.6−2.2 ps, (B) 2.2−14 ps, (C) 14−7000 ps. (D) between −2 and 13 ps, (E) between 13 and 7300 ps.

[1]. A. G. Doyle, et. al. *J. Am. Chem. Soc*. **2018**, *140*, 3035−3039. [2]. A. G. Doyle, et. al. *J. Am. Chem. Soc*. **2020,** *142*, 5800−5810.

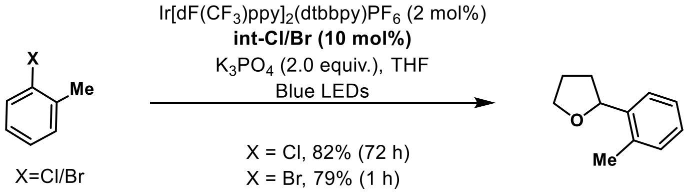
可见光下Ni催化构建C-C键

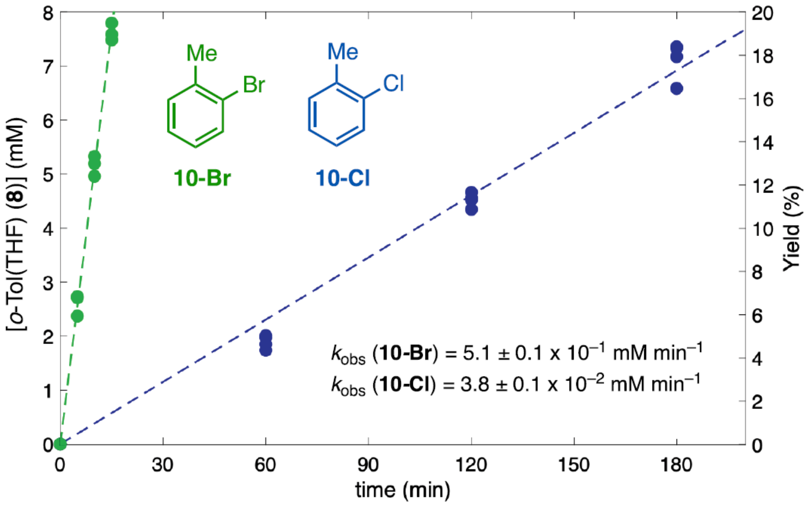
➢ 机理实验验证

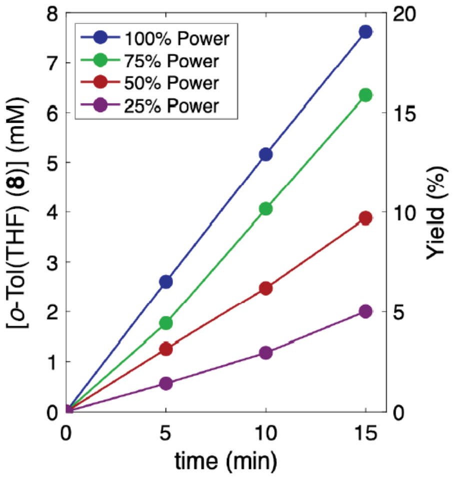


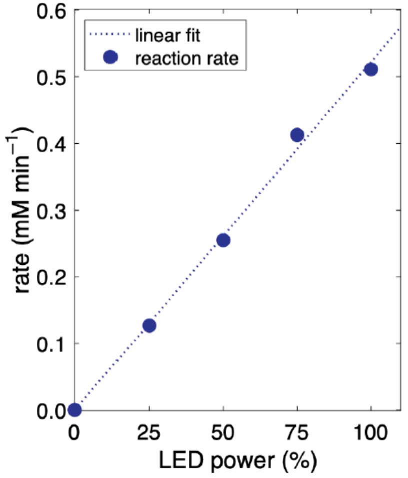


int-Cl/Br可能为活性中间体







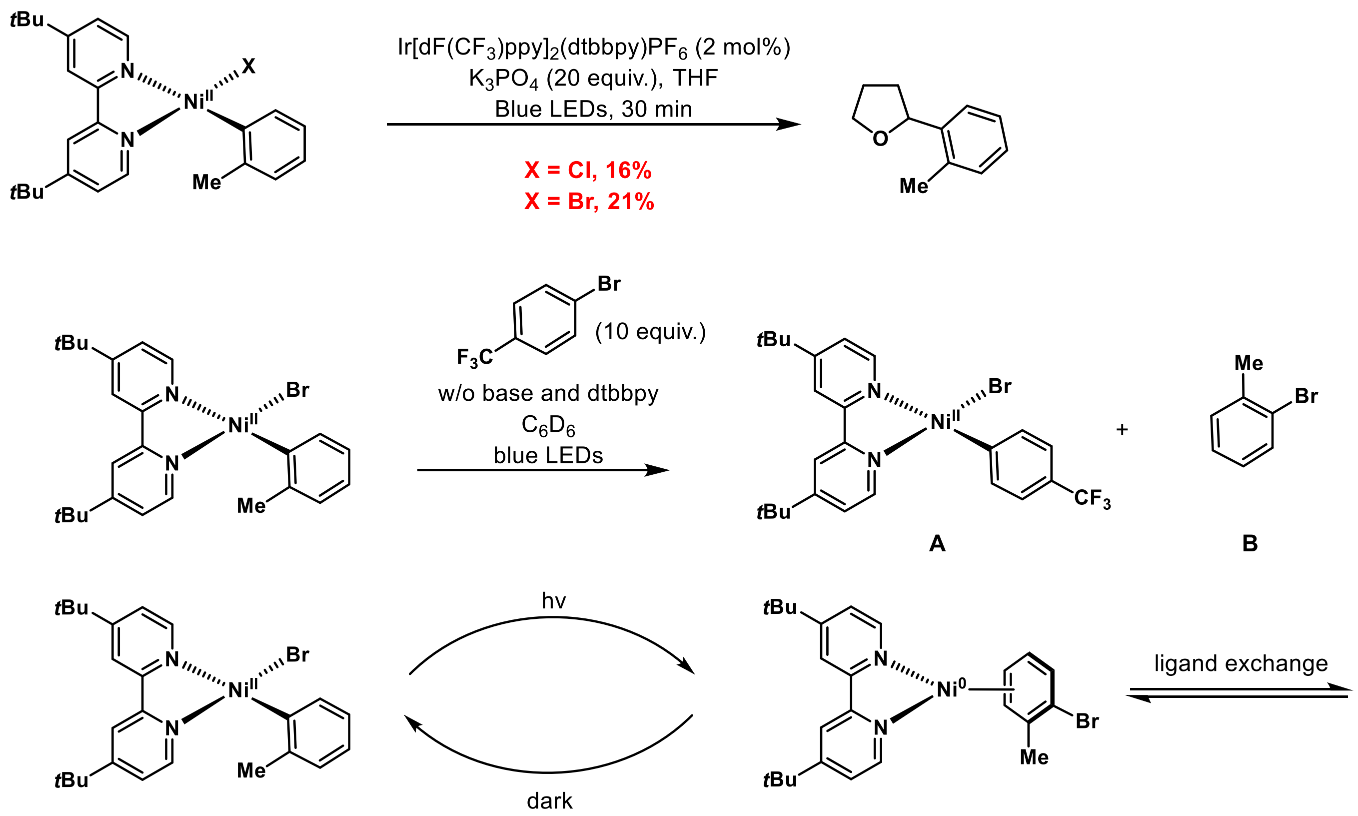


➢ Proposed role and competency of int-Cl/Br in catalysis.

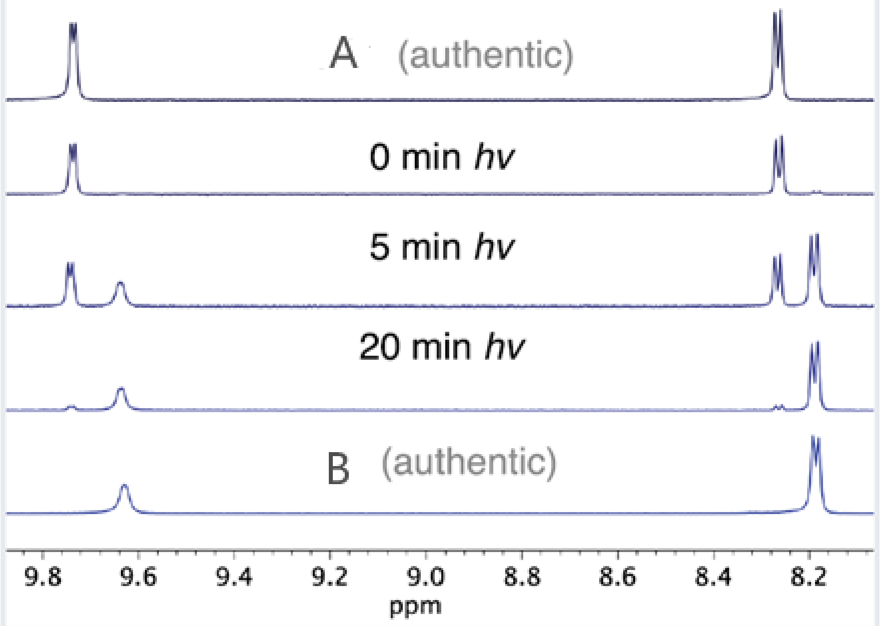
A. G. Doyle, et. al. *J. Am. Chem. Soc.* **2024**, *146*, 15331−15344.

可见光下Ni催化构建C-C键

➢ 机理实验验证



Photocatalyst	Time	Yield (%) A	Yield (%) B
1 (10 mol%)	5 min	95	100
none	5 min	43	46
none	20 min	84	87
none, dark	20 min	8	9



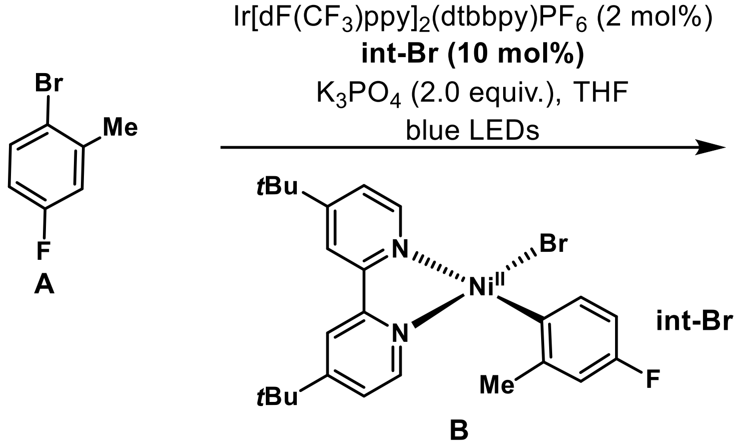
排除能量转移的历程。

A. G. Doyle, et. al. *J. Am. Chem. Soc.* **2024**, *146*, 15331−15344.

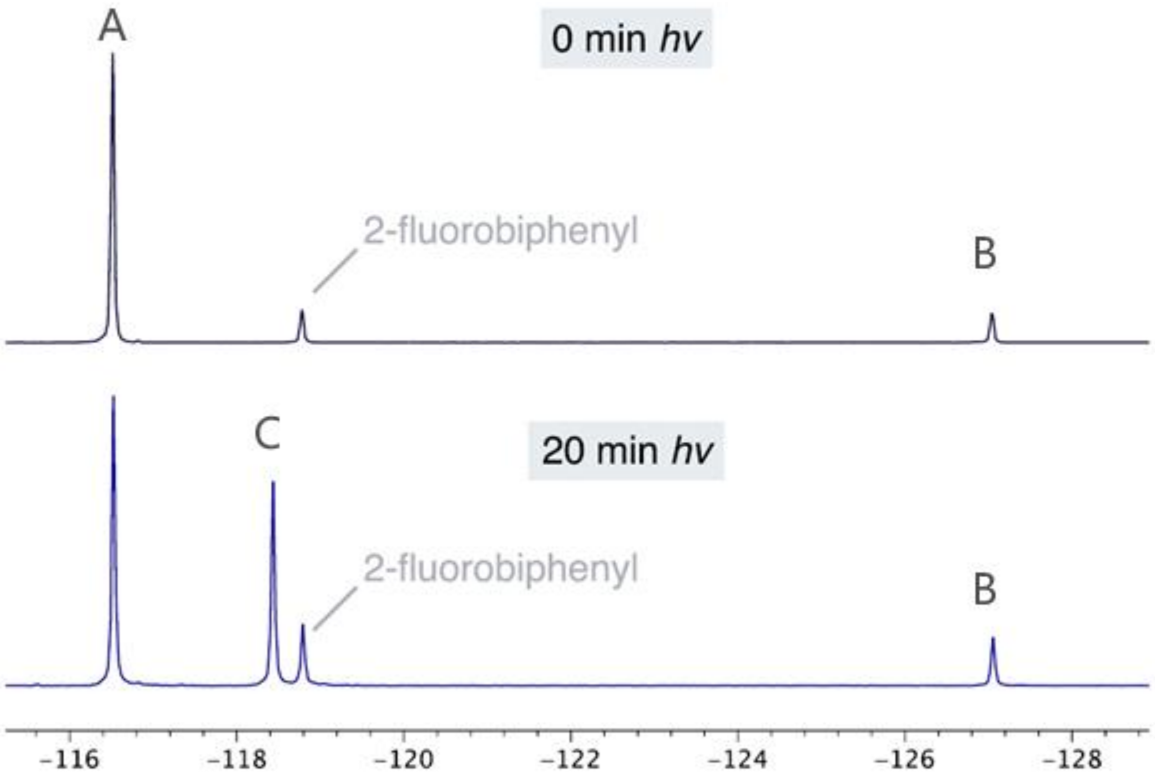
可见光下Ni催化构建C-C键

➢ **机理实验验证**

监测反应组分的分布：



34% yield after 20 min
77% int-Br remaining after 20min

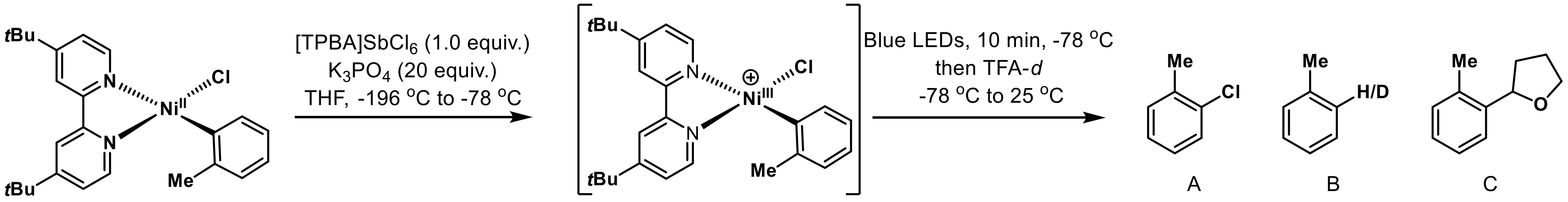


可能光照后发生还原消除反应又继续发生氧化加成，使得催化剂会大部分停留在这一步。

A. G. Doyle, et. al. *J. Am. Chem. Soc.* **2024**, *146*, 15331−15344.

可见光下Ni催化构建C-C键

➢ **机理实验验证**



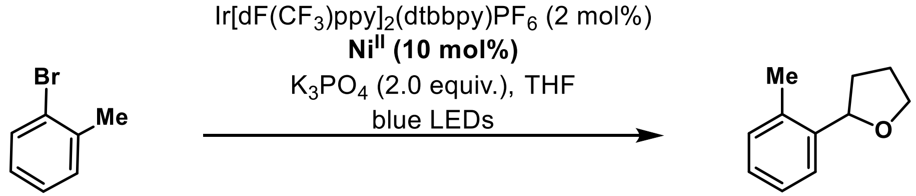
Oxidant	light	A	B	C
yes	no	89	2 (n.d.)	0
yes	yes	1	73 (3% D)	6
no	no	2	92 (80% D)	0
no	yes	1	92 (82% D)	0

排除单电子转移的历程。

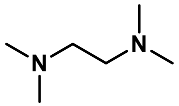
A. G. Doyle, et. al. *J. Am. Chem. Soc.* **2024**, *146*, 15331−15344.

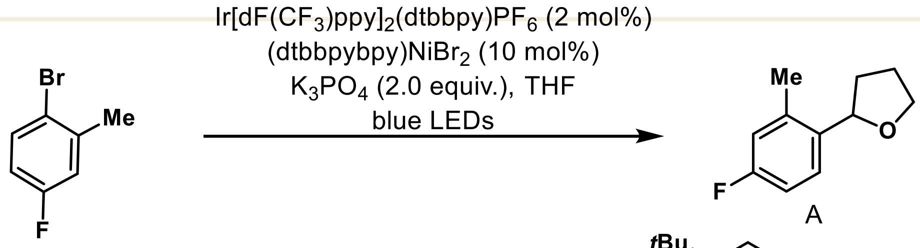
可见光下Ni催化构建C-C键

➢ 机理实验验证

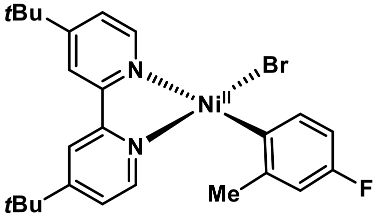


Oxidant	entry	Ir	LED	time	yield
(dtbbpy)Ni(o-Tol)Br	1	yes	427 nm	1	79
	2	no	427 nm	16	6
	3	no	370 nm	16	33
$(dtbbpybpy)NiBr_2$	4	yes	427 nm	1	76
	5	no	427 nm	24	0
	6	no	370 nm	24	26
$(dtbbpybpy)NiCl_2$	7	yes	427 nm	72	19
(TMEDA)Ni(o-Tol)Br	8	yes	427 nm	5	33

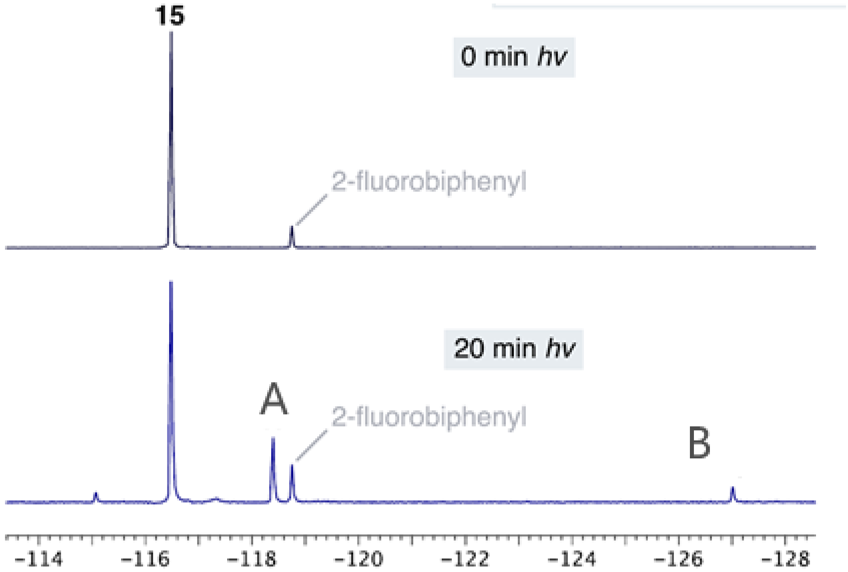
TMEDA: 



time	A	B
0	0	0
20 min	18%	4.4%

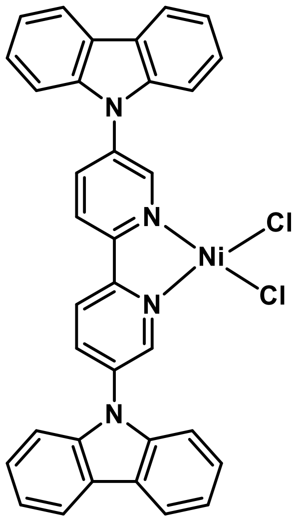


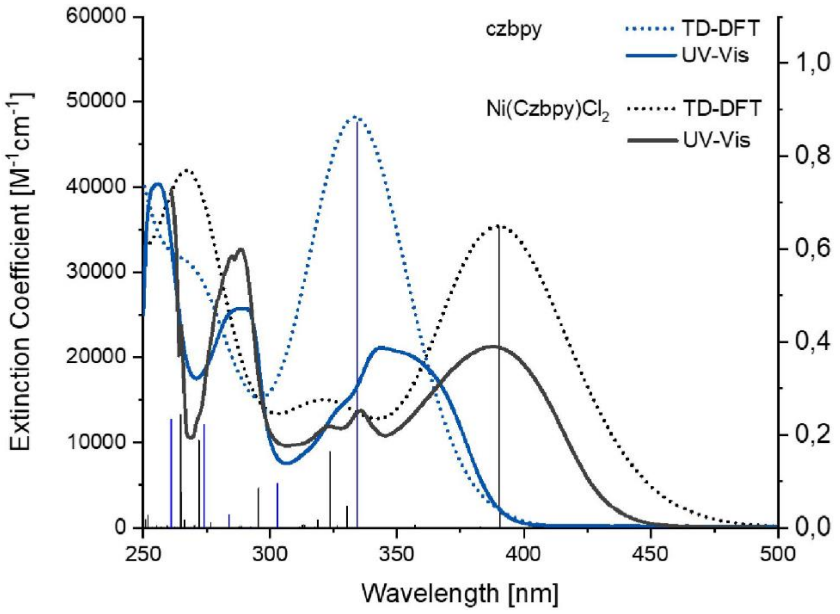
B

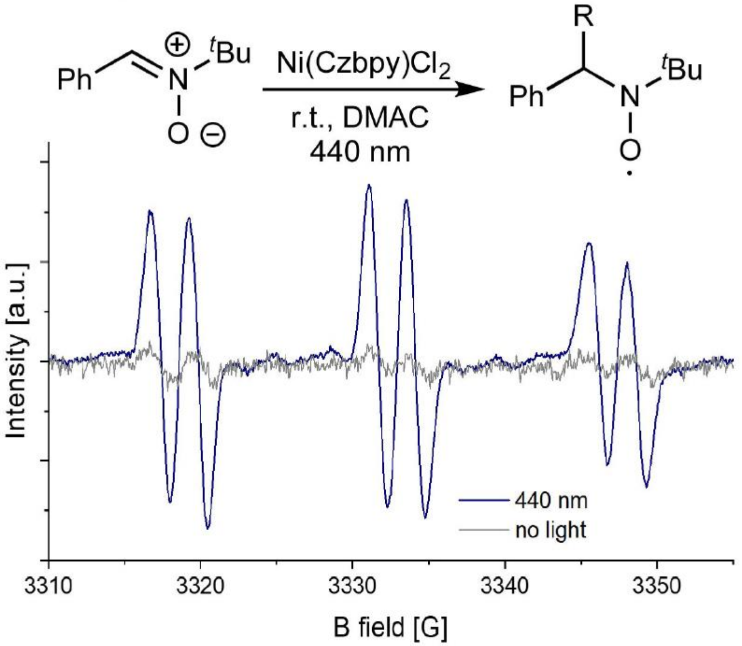


A. G. Doyle, et. al. *J. Am. Chem. Soc.* **2024**, *146*, 15331−15344.

ILCT (Intraligand Charge Transfer) 历程产生Ni^{I}证据





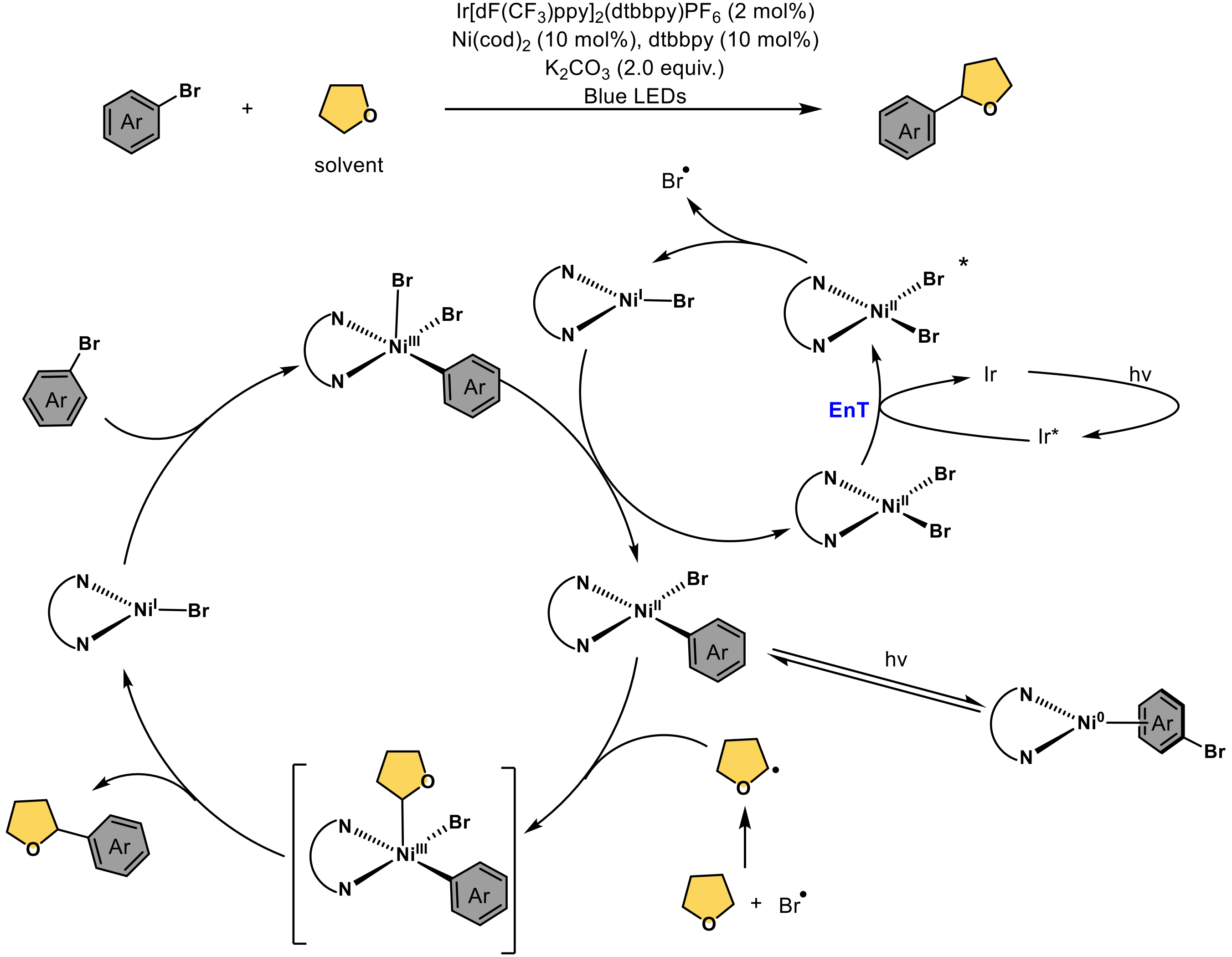


- 吸收光谱和计算可以得到激发态的镍经历了ILCT过程

B. Pieber, et. al. *Angew. Chem. Int. Ed.* **2022**, *61*, e202211433.

可见光下Ni催化构建C-C键

◆ Doyle Proposed catalytic cycle.

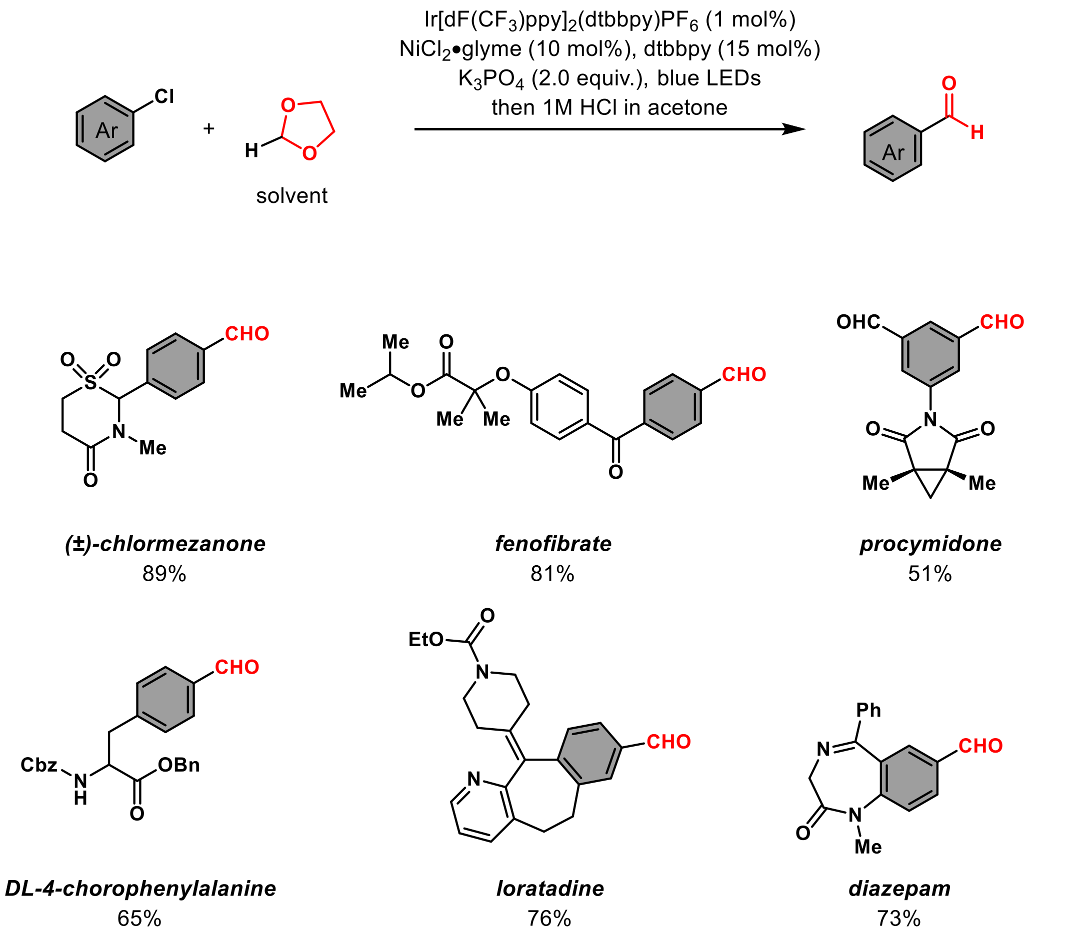


A. G. Doyle, et. al. *J. Am. Chem. Soc.* **2024**, *146*, 15331−15344.

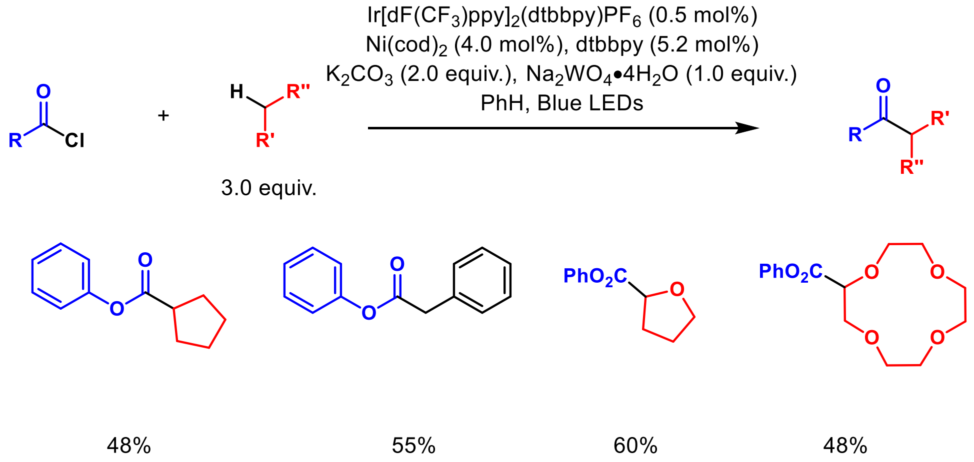
可见光下Ni催化构建C-C键

➢ **Direct C(sp^3)−H Cross Coupling Enabled by photoredox and nickel dual catalysis.**

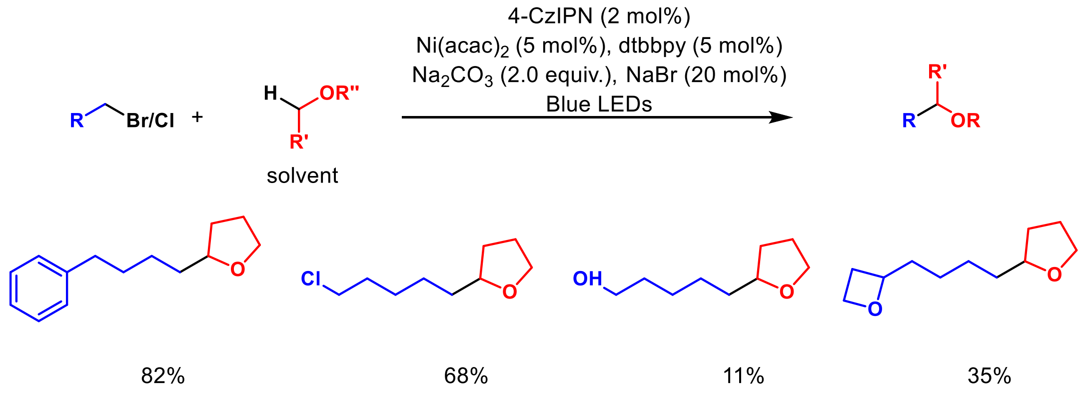
2017 Doyle



2018 Doyle



2020 König

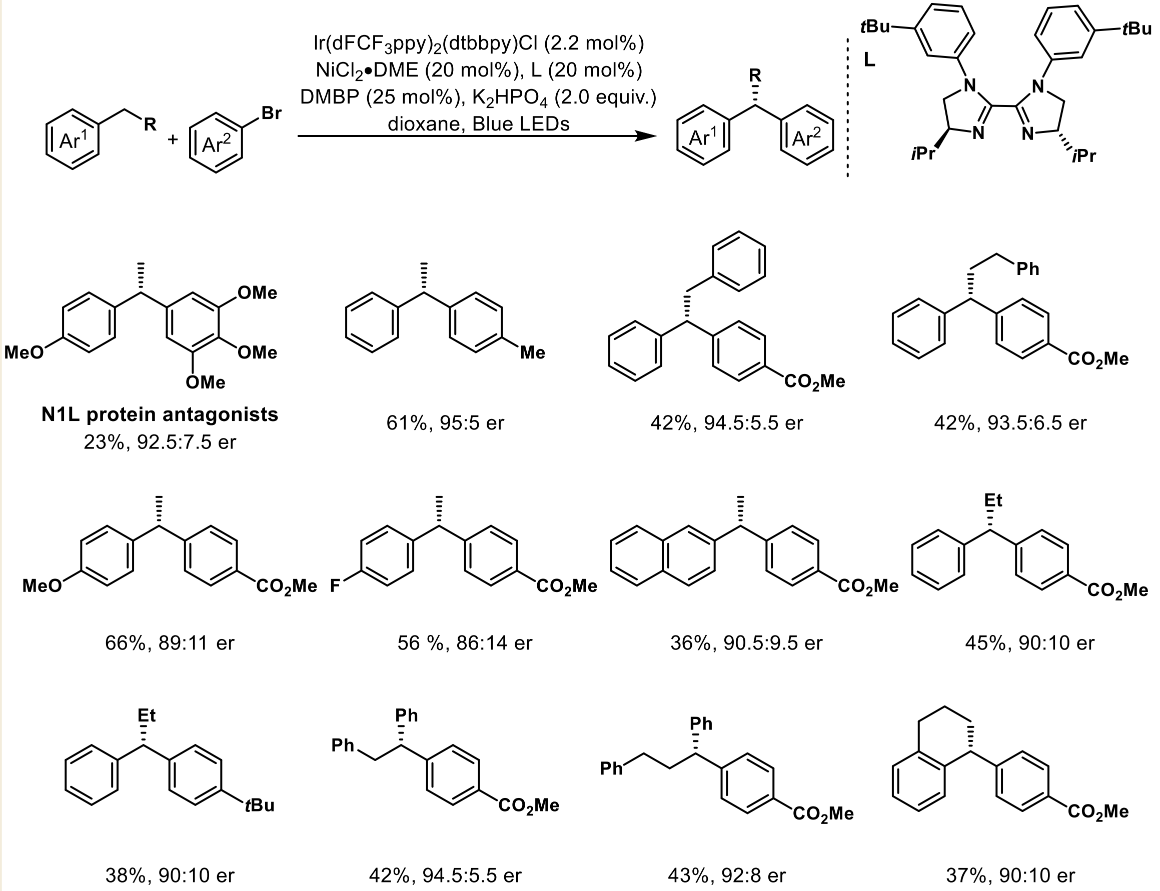


[1]. A. G. Doyle, et. al. *Angew. Chem.* **2017**, *129*, 7297 –7300. [2]. A. G. Doyle, et. al. *J. Am. Chem. Soc.* **2018,** *140*, 14059−14063.
[3]. B. K önig, et. al. *Adv. Synth. Catal*. **2020**, *362*, 2367– 2372.

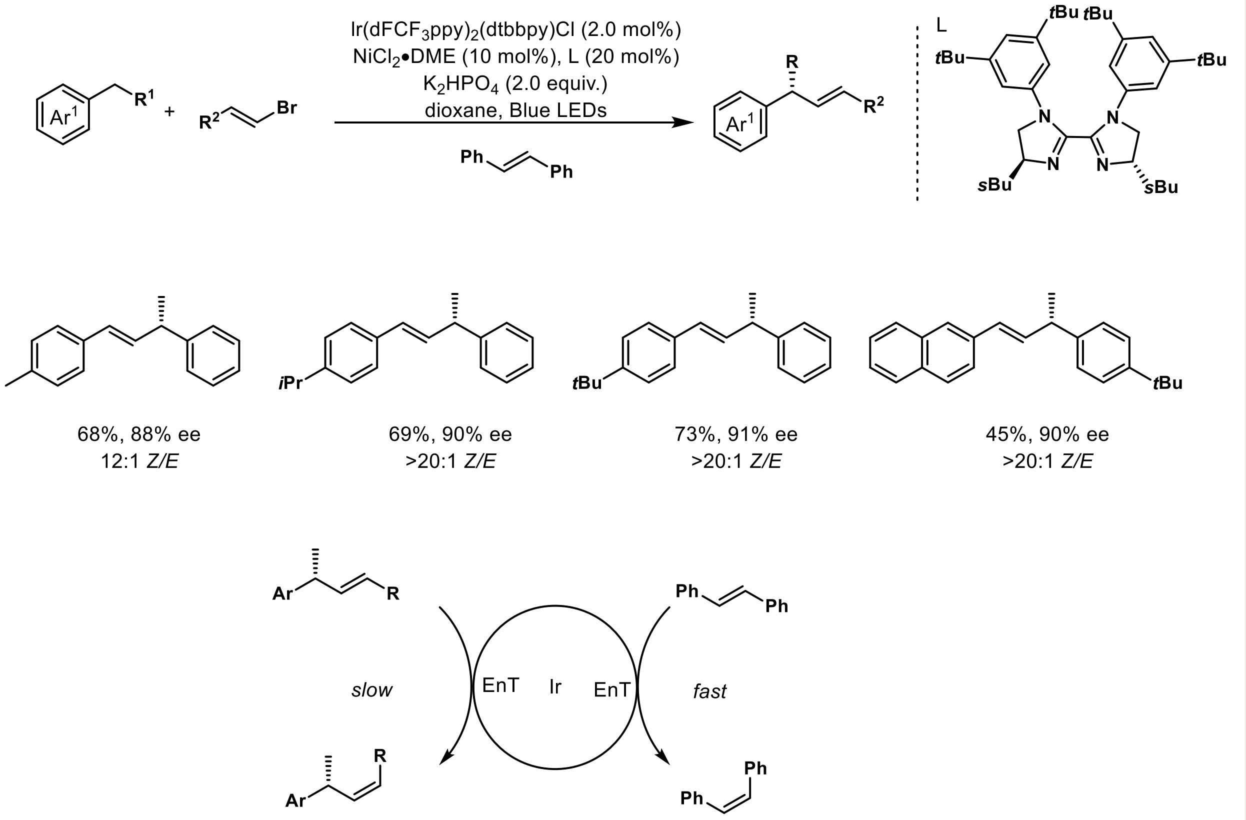
可见光下Ni催化构建C-C键

➢ **Enantioselective via photoredox and nickel dual catalysis.**

2019 Lu



2021 Lu



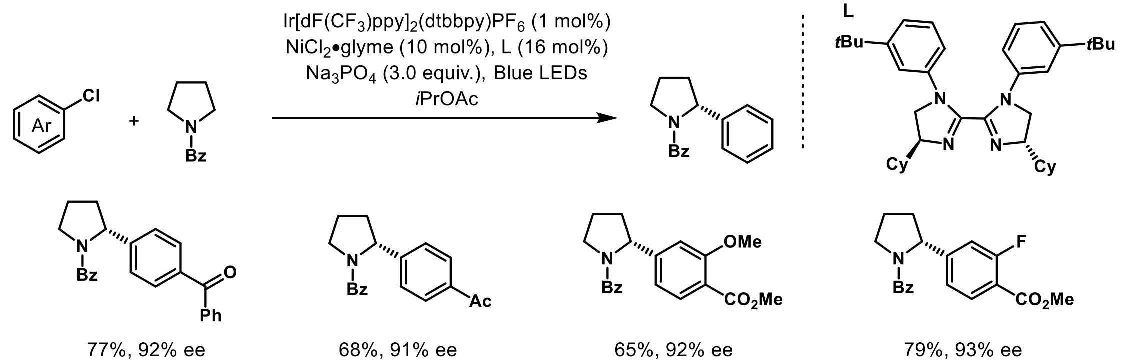
◆ Stilbene as the Triplet-Energy-Transfer inhibitor.

[1]. Z. Lu, et. al. *Nat Commun*. **2019**, *10*, 3549-3556. [2]. Z. Lu, et. al. *ACS Catal*. **2021**, *11*, 11059−11065.

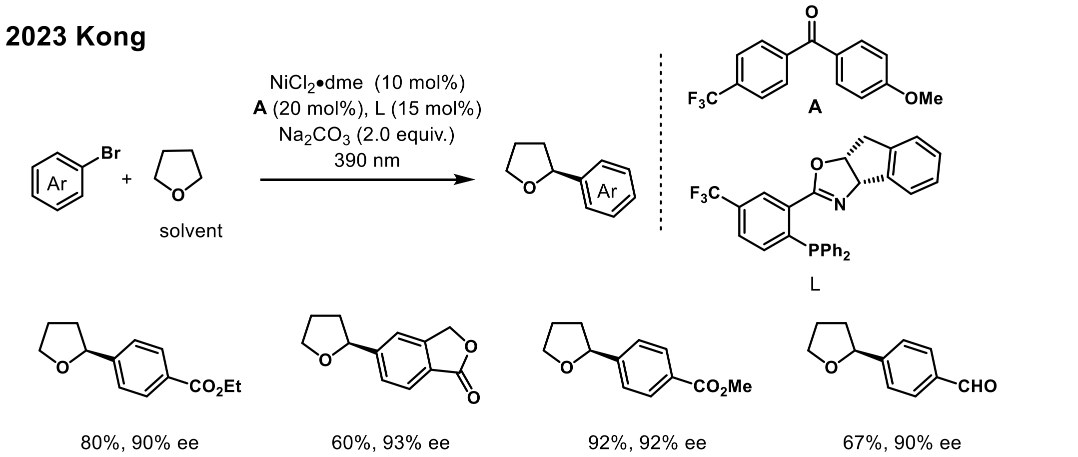
可见光下Ni催化构建C-C键

➢ **Enantioselective via photoredox and nickel dual catalysis.**

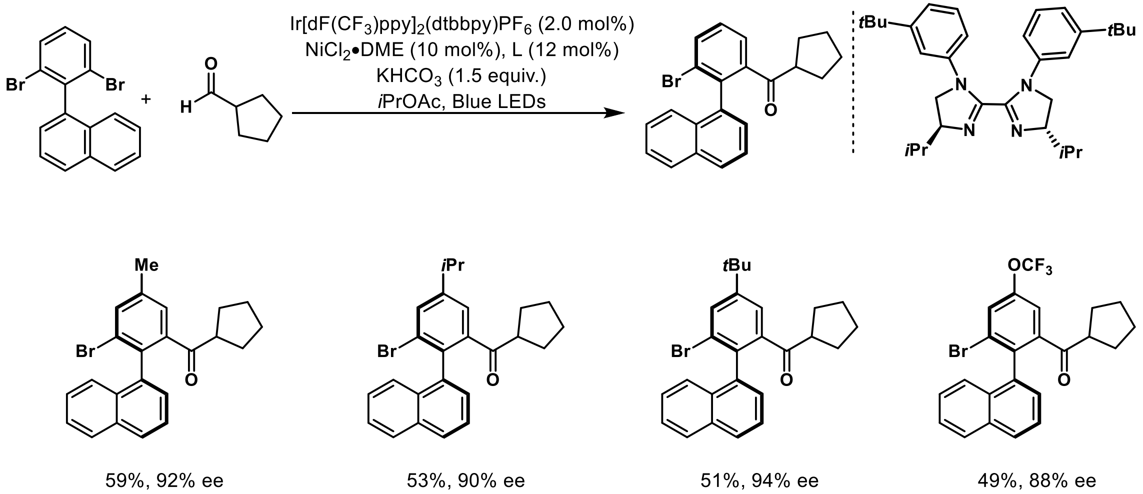
2022 Huo



2023 Kong



2024 Wang



[1]. H. Huo, et. al. *J. Am. Chem. Soc*. **2022**, *144*, 8797−8806. [2]. W. Kong, et. al. *J. Am. Chem. Soc.* **2023**, *145*, 5231−5241. [3]P. Wang, et. al. *ACS Catal.* **2024**, *14*, 13860−13866.

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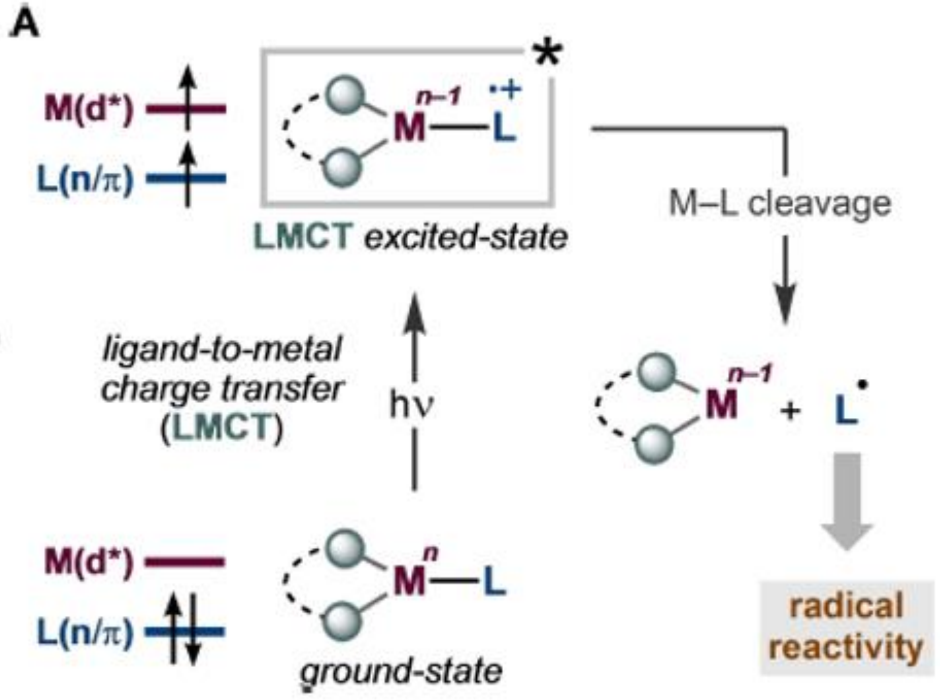
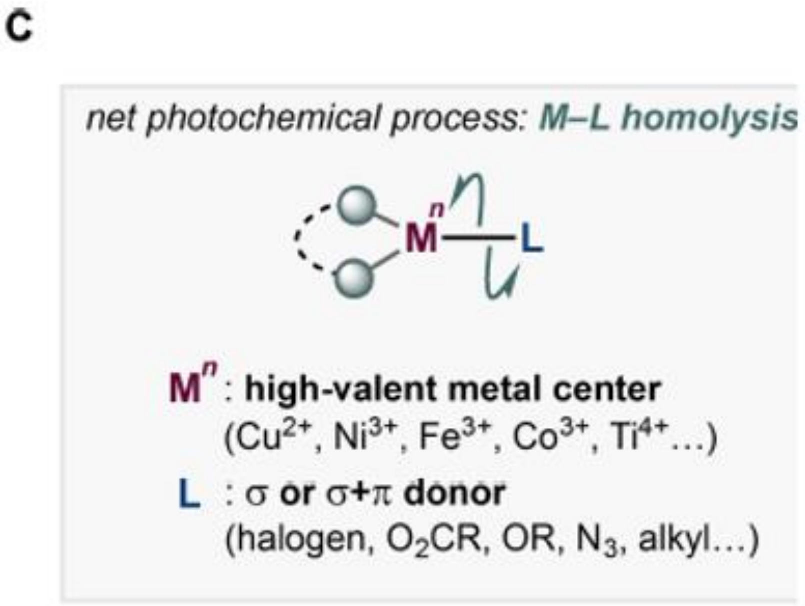


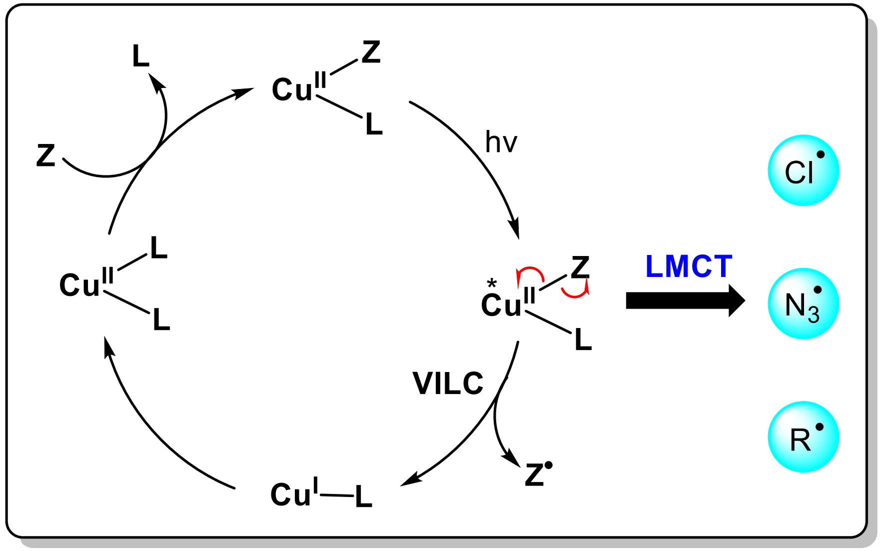
Photophysics and photochemistry of LMCT states.

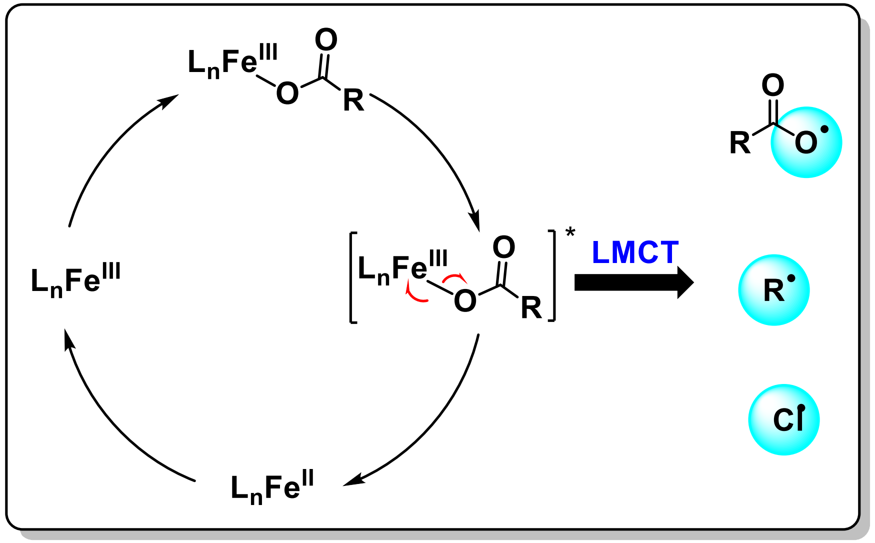


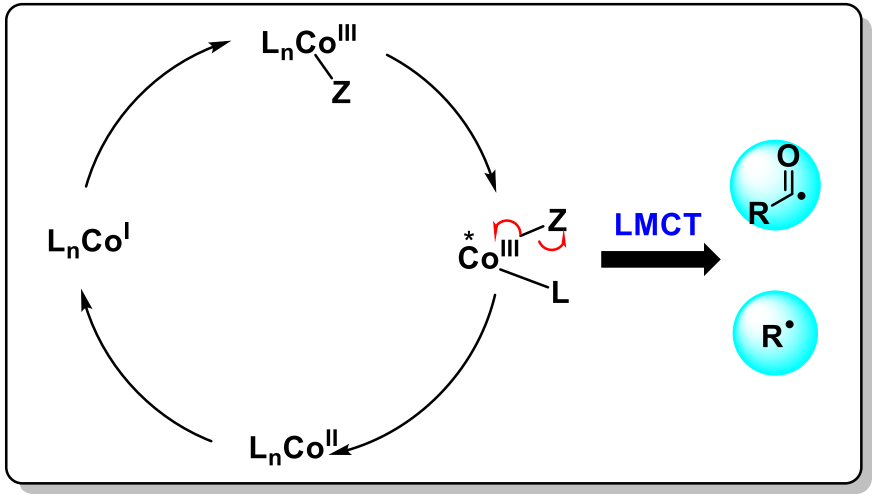
Overall chemical process via photoinduced LMCT homolysis.

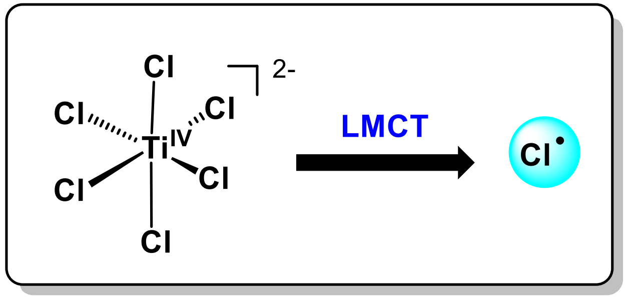
F. Julia. et. al. *ChemCatChem*. **2022**, *14*, e202200916.

丰产金属催化LMCT机制构建C-C键





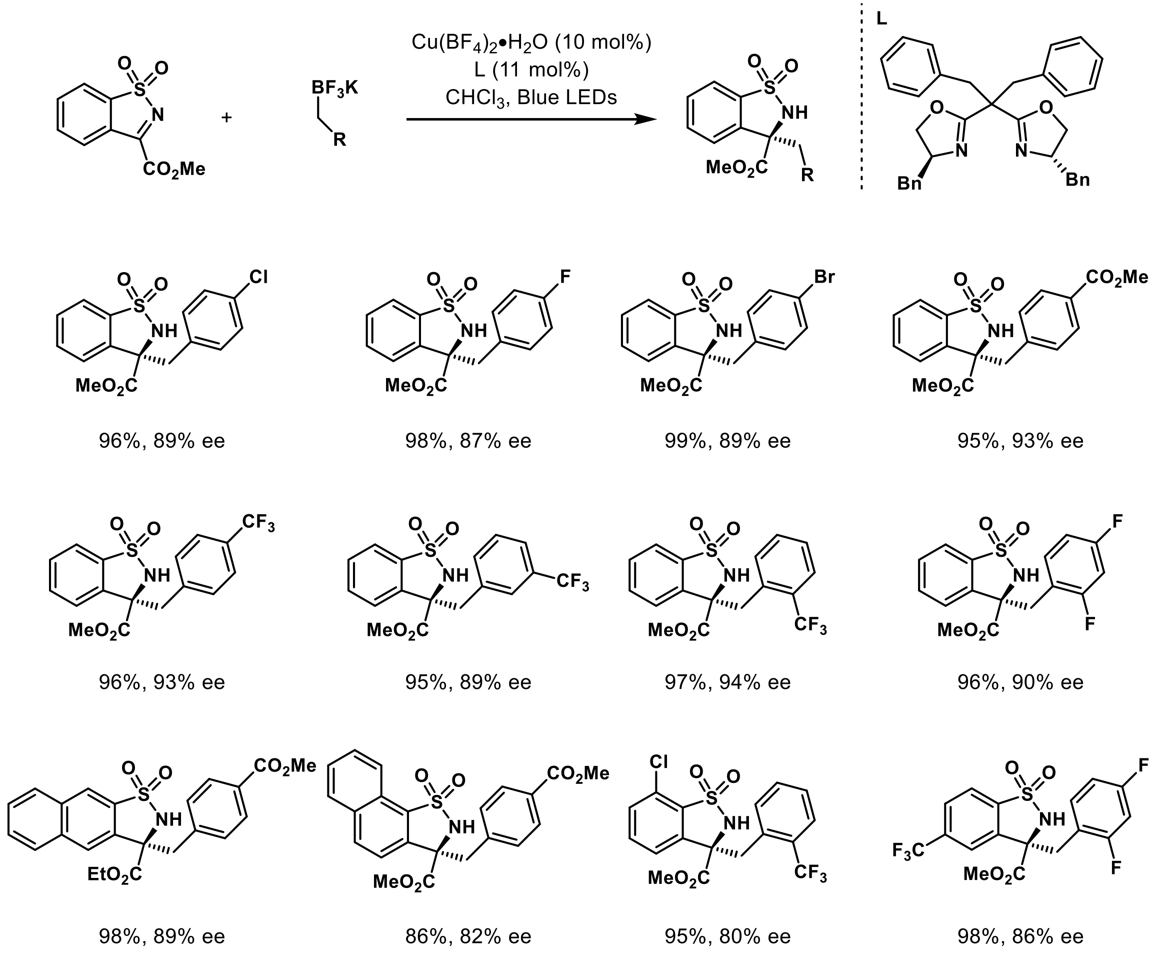


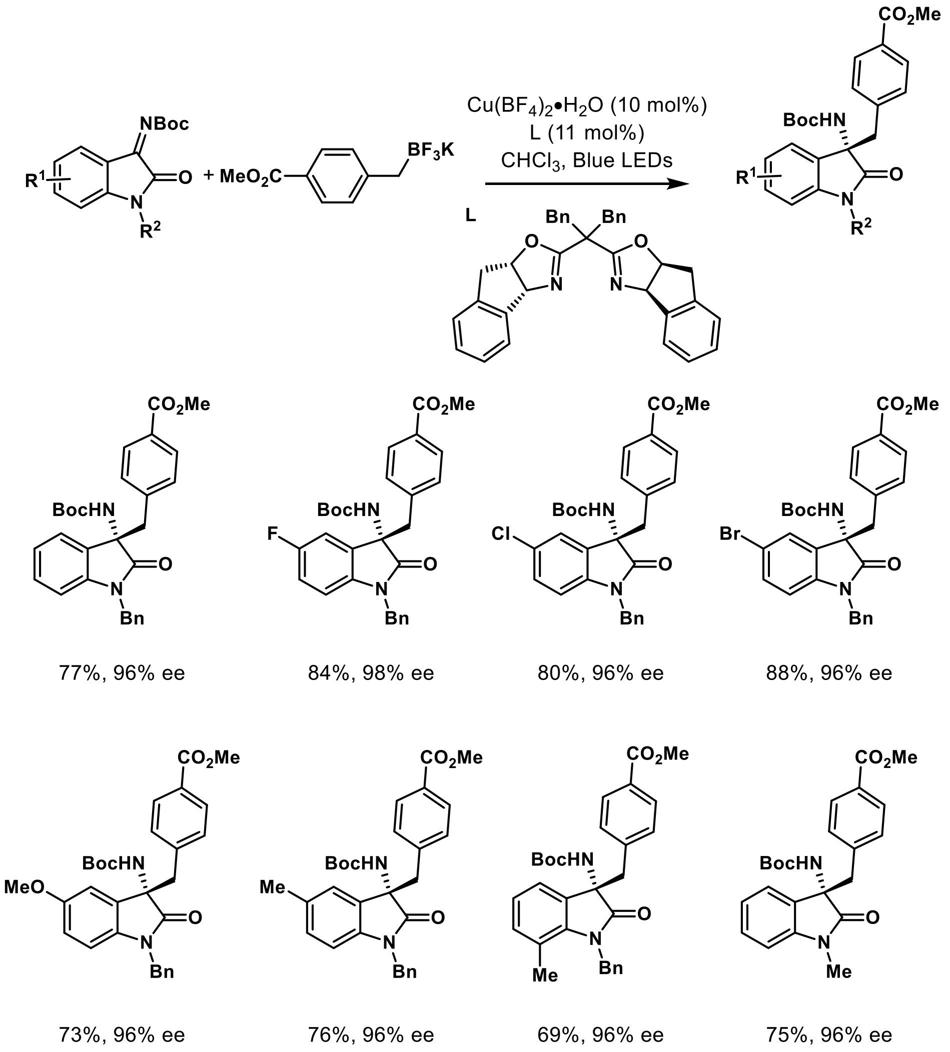


O. Reiser, et. al. *Angew. Chem. Int. Ed.* **2021**, *60*, 21100– 21115.

丰产金属催化LMCT机制构建C-C键

- **Copper(II)-Catalyzed Asymmetric Photoredox Reactions:**

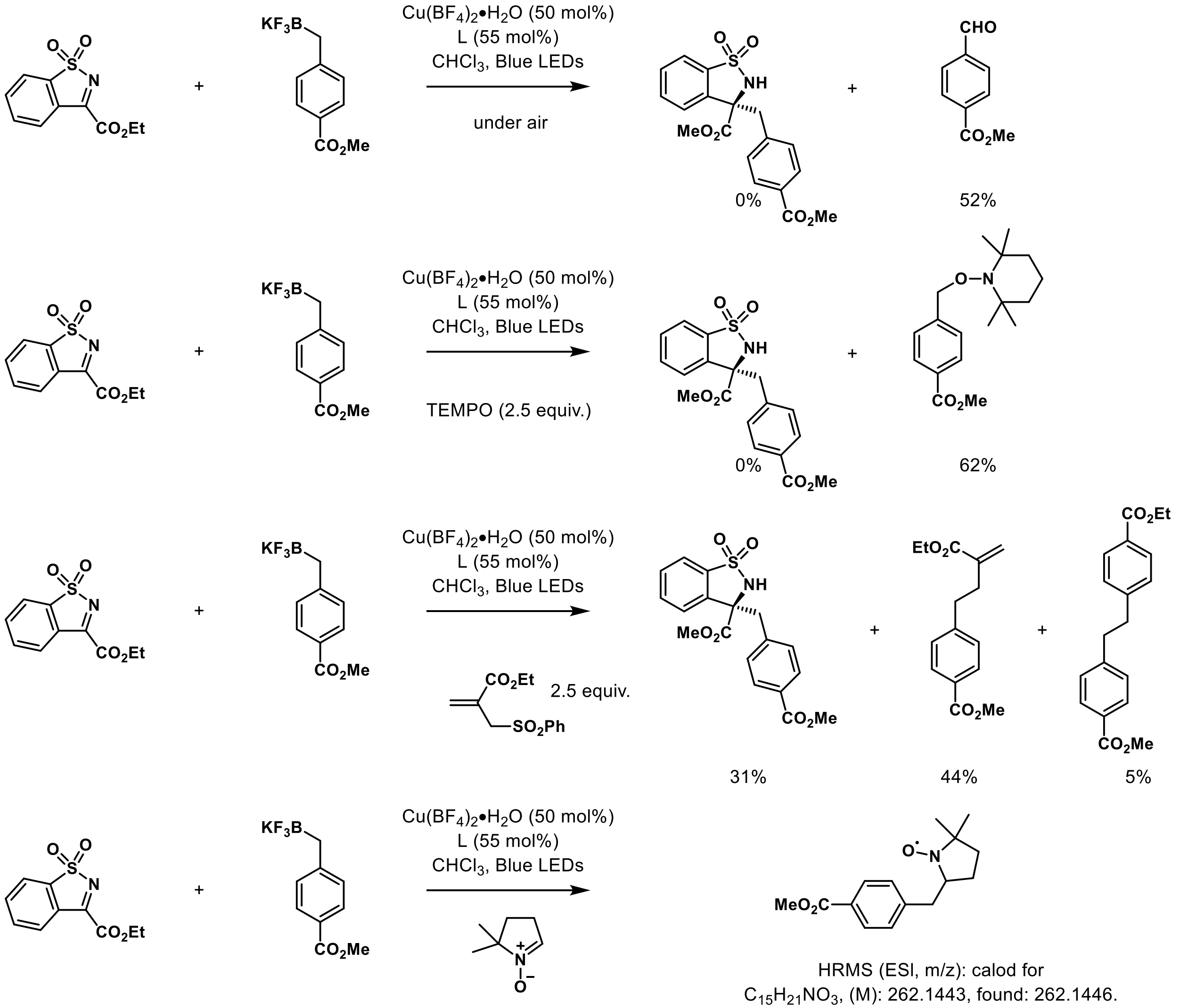


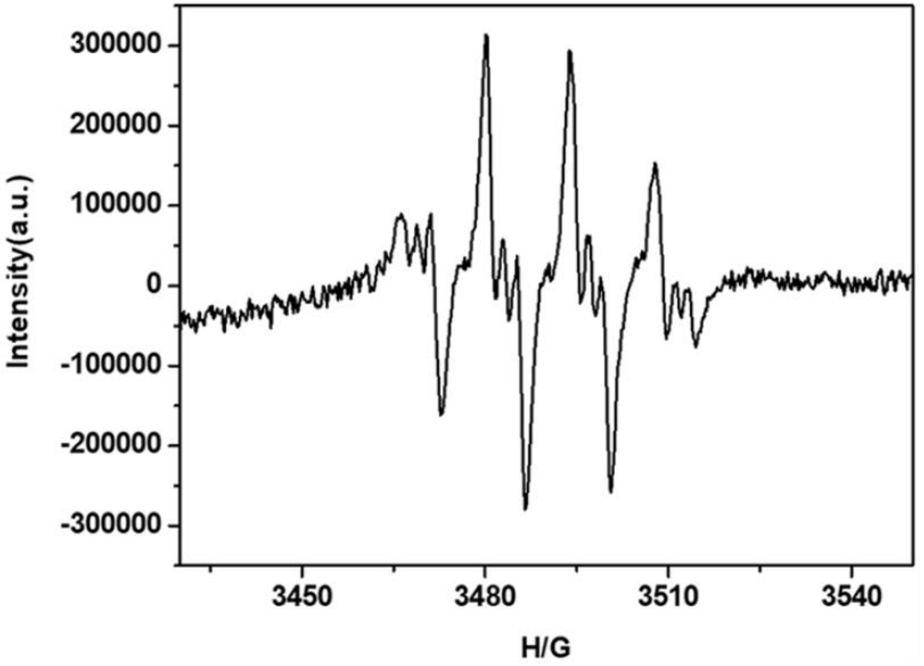


L. Gong, et. al. *J. Am. Chem. Soc*. **2018,** *140*, 15850−15858.

丰产金属催化LMCT机制构建C-C键

➢ 机理实验验证

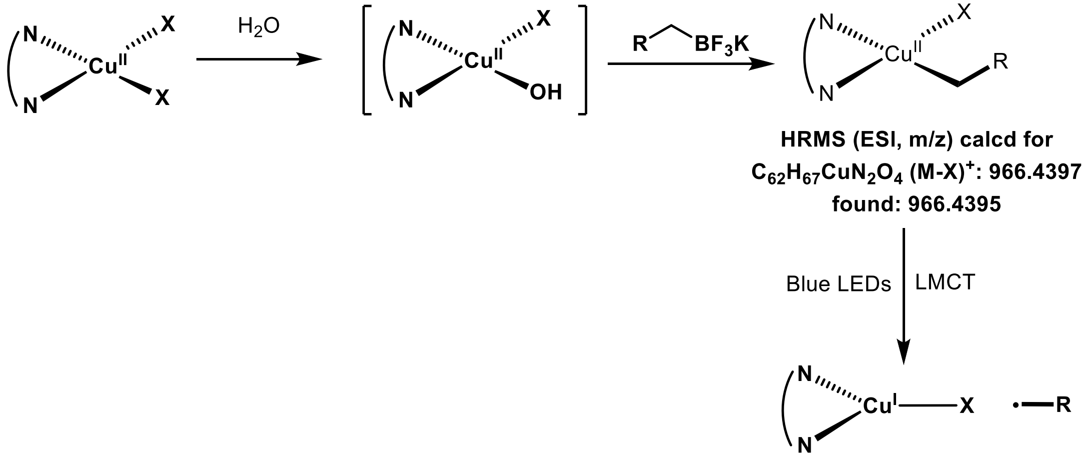


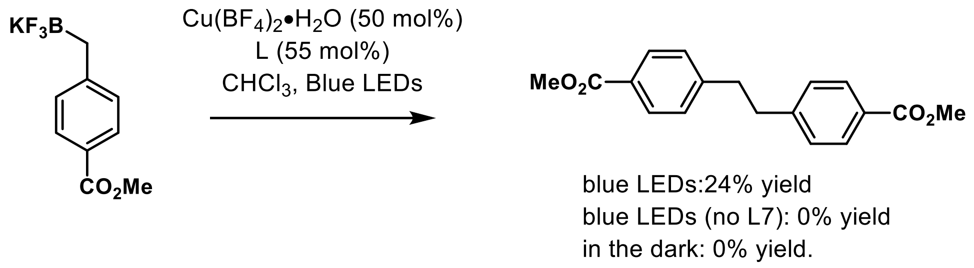


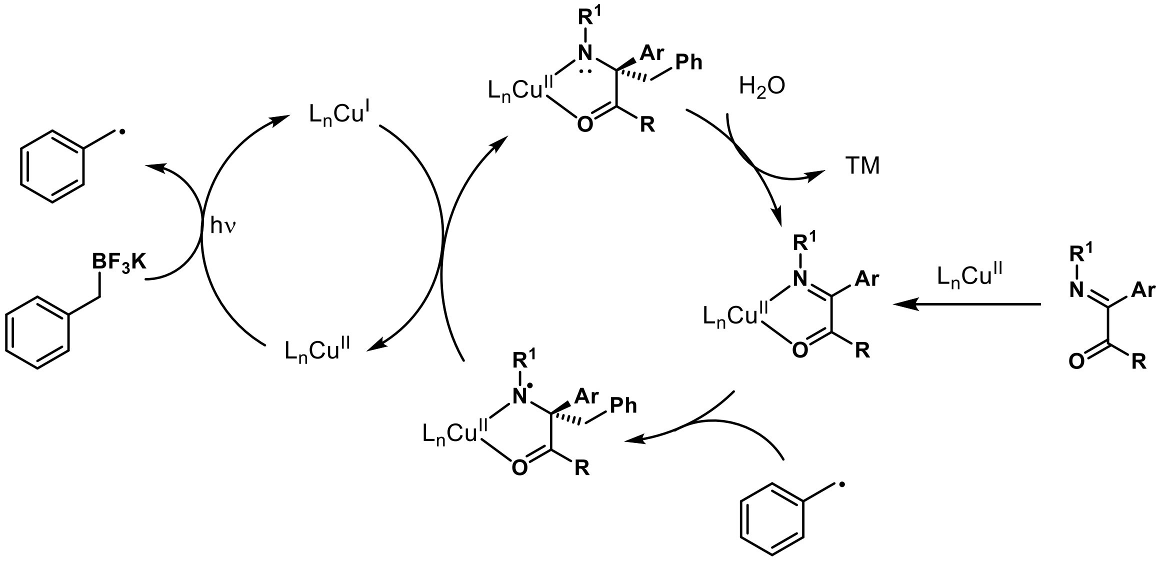
L. Gong, et. al. *J. Am. Chem. Soc*. **2018,** *140*, 15850−15858.

丰产金属催化LMCT机制构建C-C键

➢ 机理实验验证







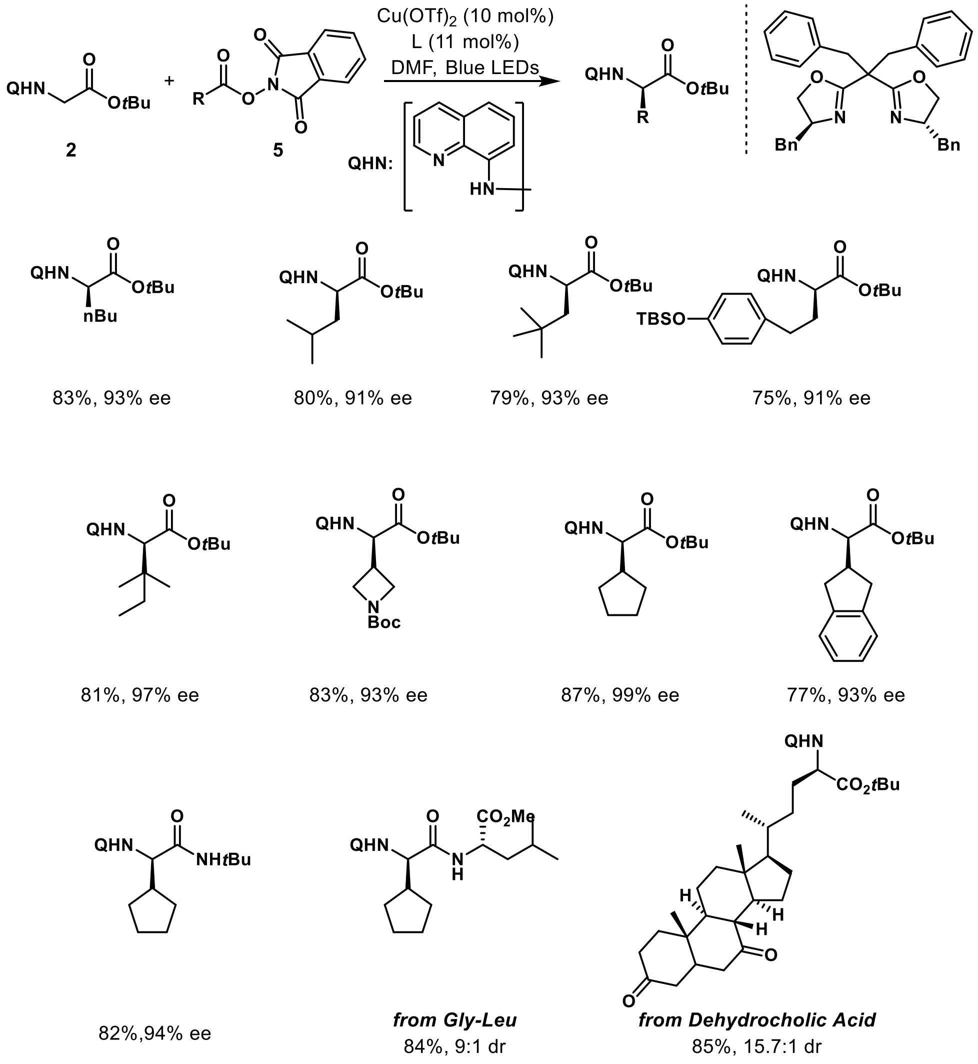
◆ Evidence for Light-Induced Oxidization of Alkyl Trifluoroborate by Cu.

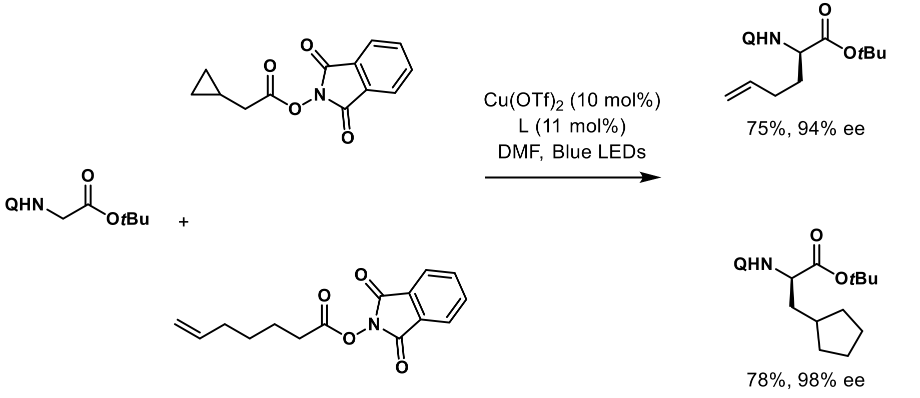
◆ A Proposed Reaction Mechanism

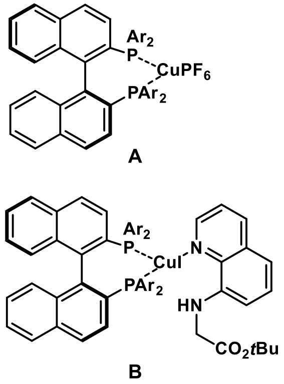
L. Gong, et. al. *J. Am. Chem. Soc*. **2018,** *140*, 15850−15858.

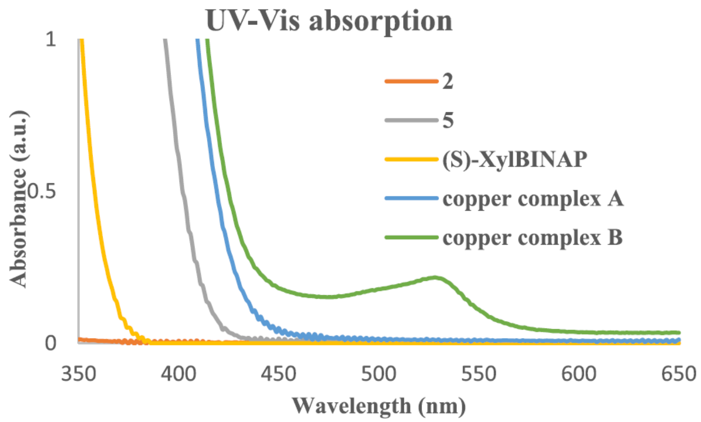
丰产金属催化LMCT机制构建C-C键

➢ Cu-Catalyzed Asymmetric C(sp^3)−H Alkylation





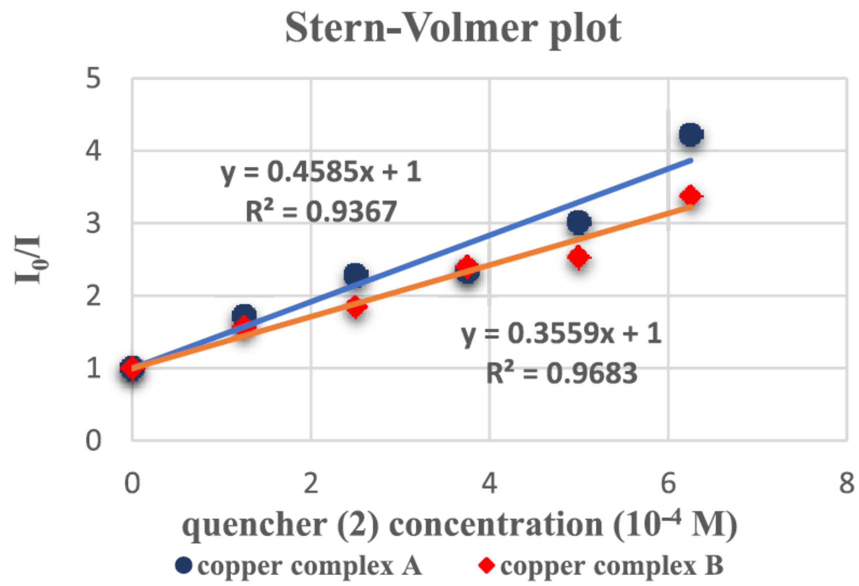


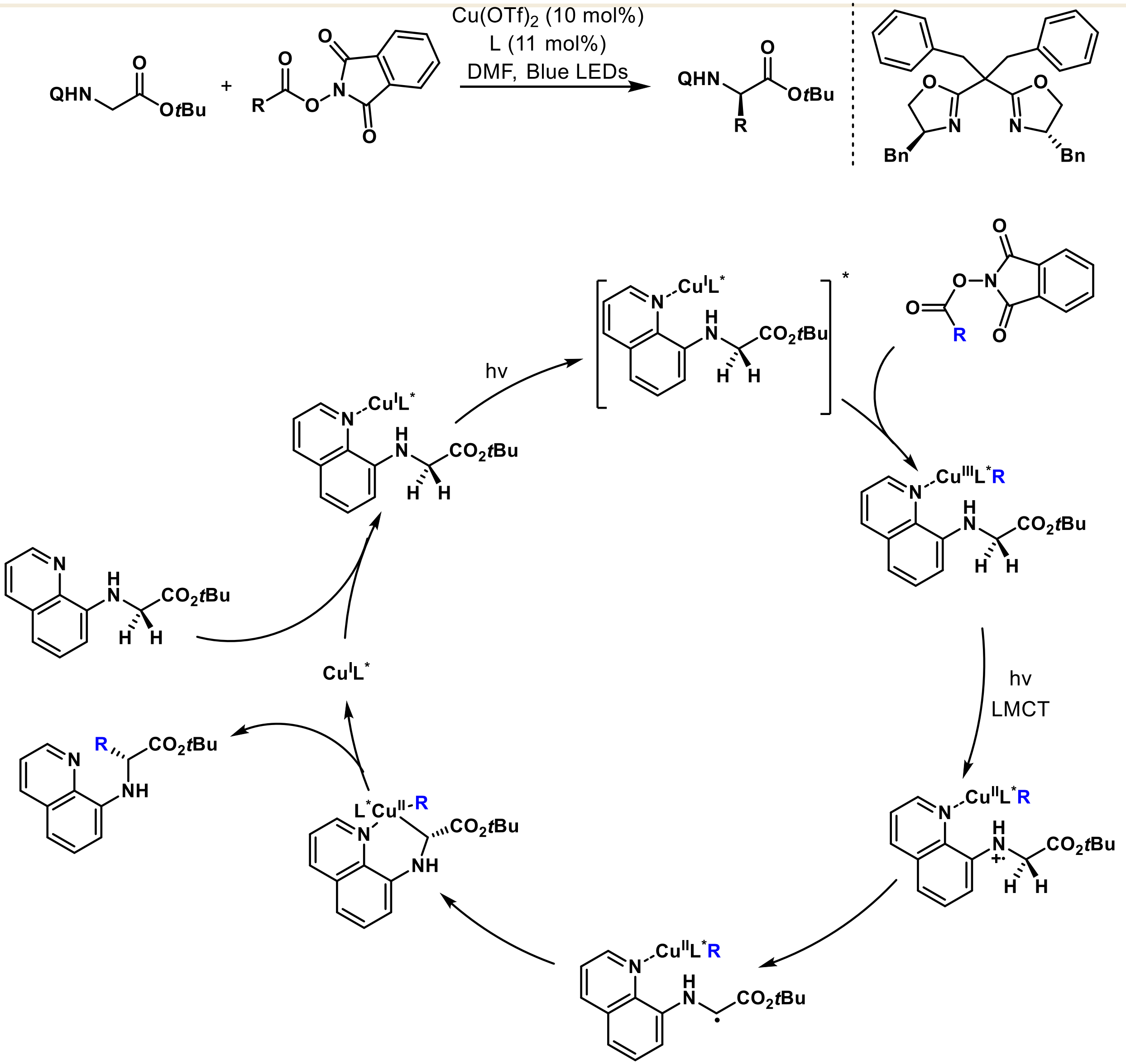


Z. Xu, et. al. *J. Am. Chem. Soc*. **2021**, *143*, 12777−12783.

丰产金属催化LMCT机制构建C-C键

◆ A Proposed Reaction Mechanism

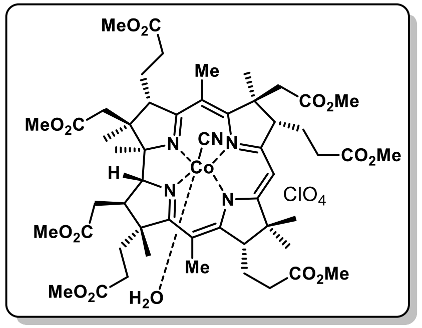


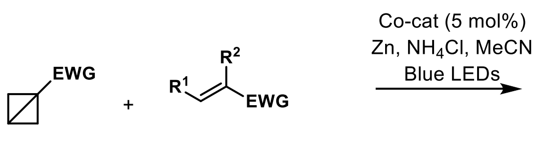


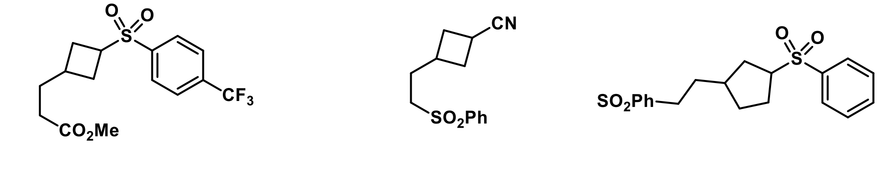
Z. Xu, et. al. *J. Am. Chem. Soc.* **2021**, *143*, 12777−12783.

丰产金属催化LMCT机制构建C-C键

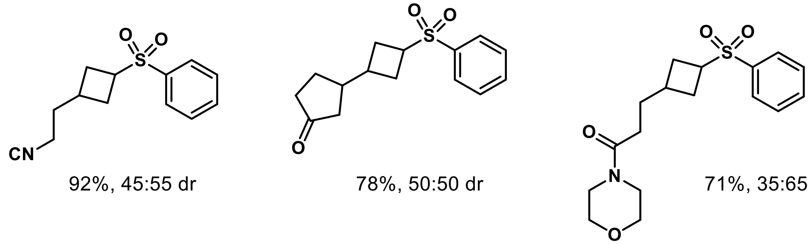
- Co催化构建C-C键



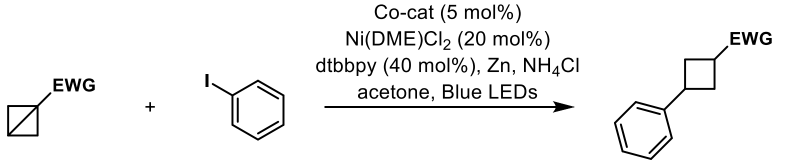


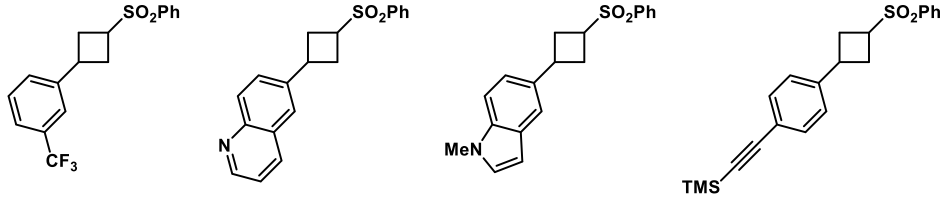


71%, 40:60 dr | 64%, 40:60 dr | 44%, 40:60 dr

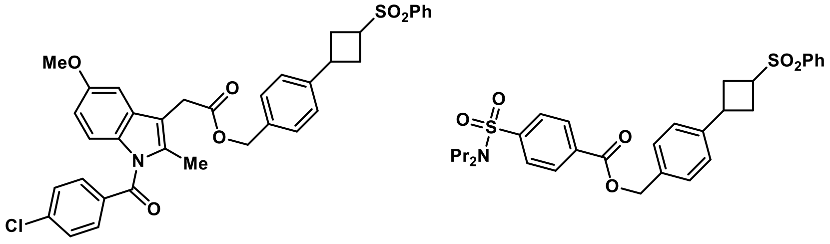


92%, 45:55 dr | 78%, 50:50 dr | 71%, 35:65 dr





54%, 60:40 dr | 75%, 75:25 dr | 49%, 55:45 dr | 66%, 60:40 dr

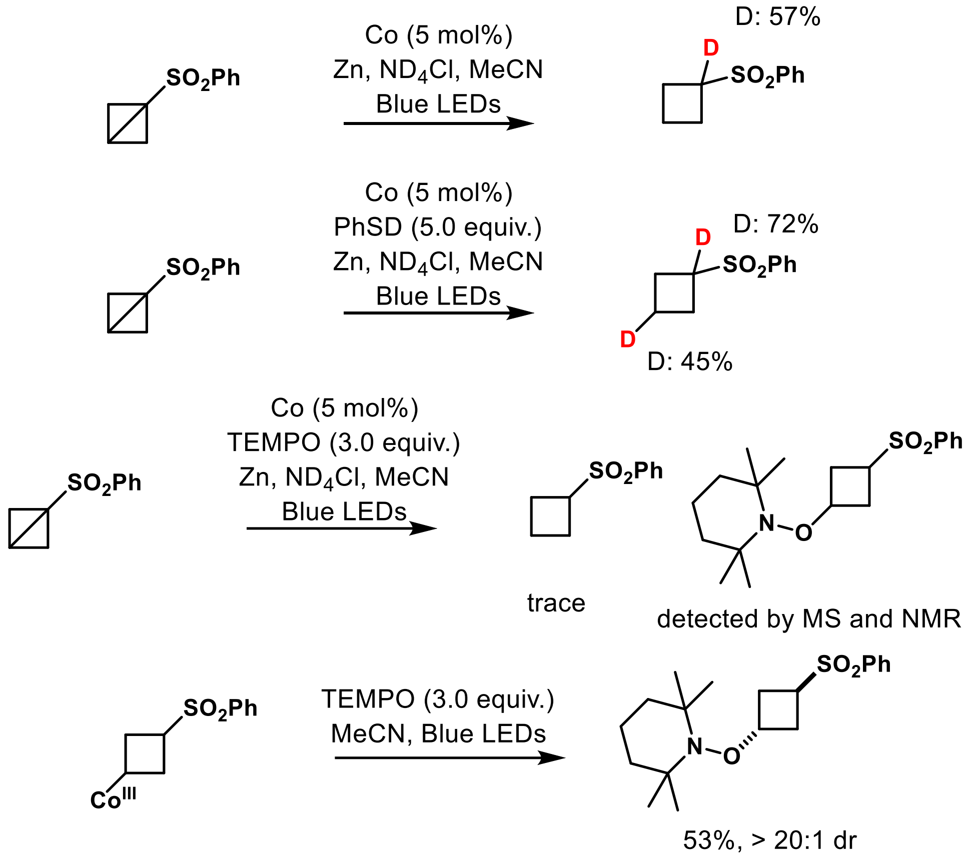


66%, 65:35 dr | 55%, 70:30 dr

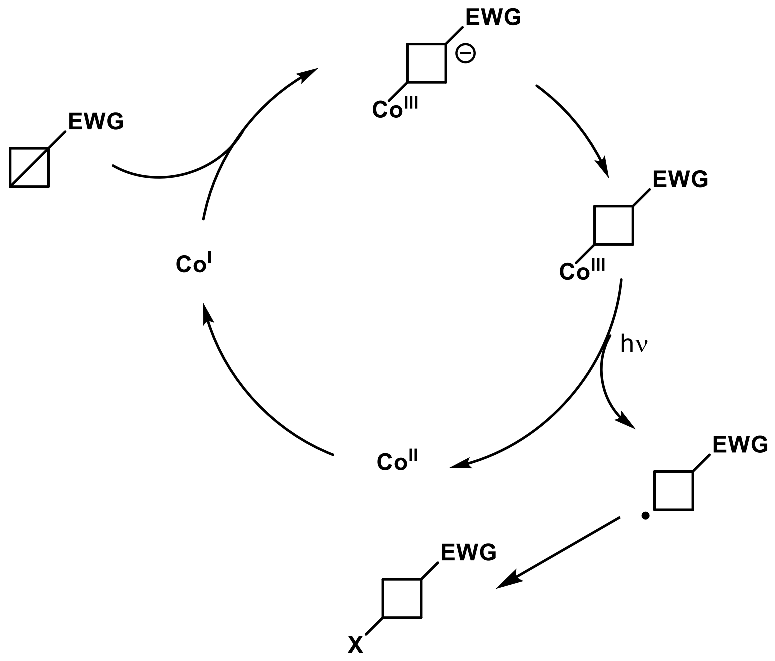
D. Gryko, et. al. *J. Am. Chem. Soc.* **2020**, *142*, 5355−5361.

丰产金属催化LMCT机制构建C-C键

➢ Co催化构建C-C键



◆ A Proposed Reaction Mechanism



D. Gryko, et. al. *J. Am. Chem. Soc.* **2020**, *142*, 5355−5361.

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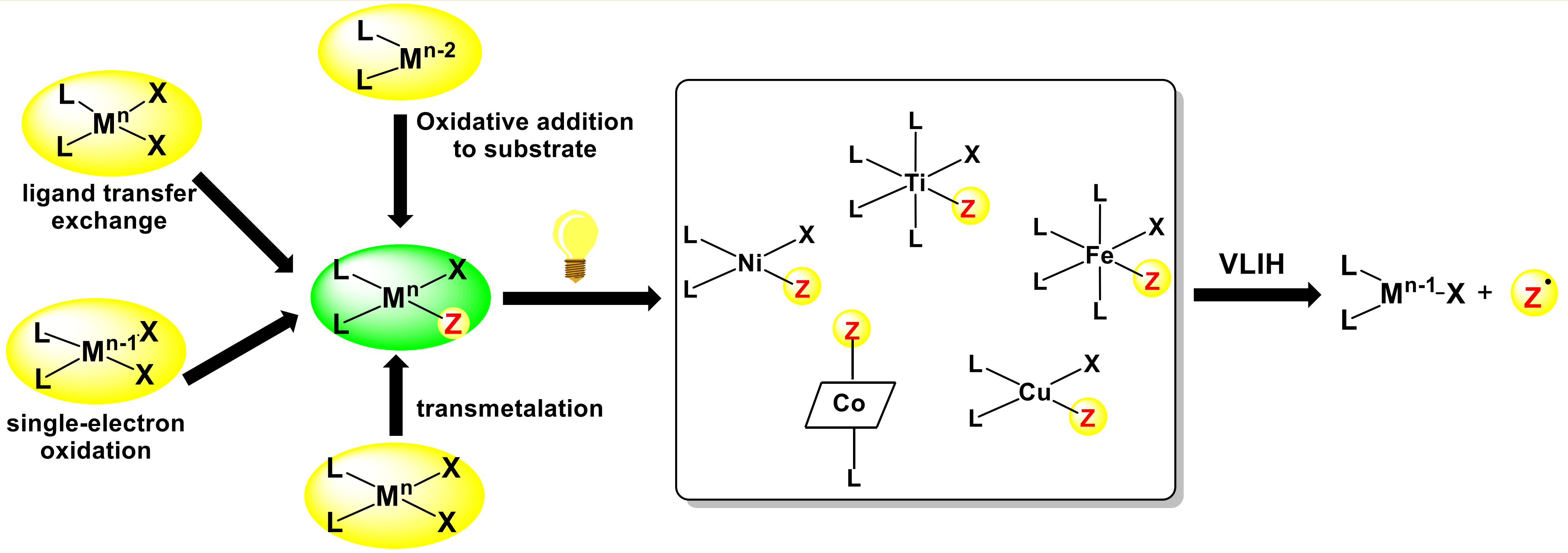
总结与展望

➢ **VLIH反应总结**



● 优势

➢ 原子经济效益好

➢ 反应条件温和

➢ 不对称催化

● 不足

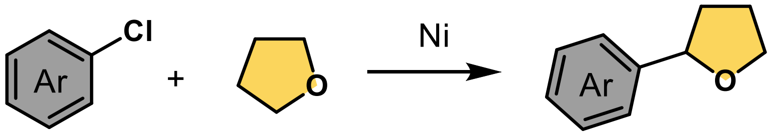
➢ 催化剂用量多

➢ 光稳定性不足

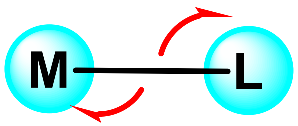
➢ 机理尚未明确

总结与展望

➢ 展望

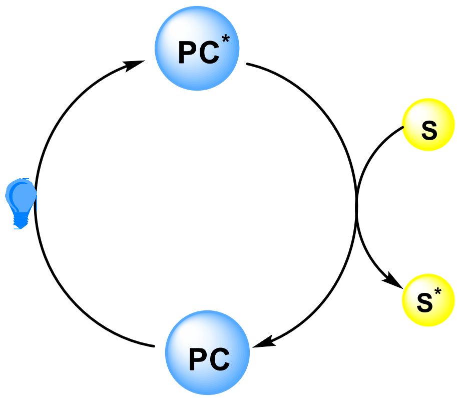


- 光/镍催化通用机理。
- 光/镍催化可见光直接激发。



[Mn], [Ti], [Zr],……

- 开发更多断键类型。



- 丰产金属Co,Ni作为光催化剂。
- 丰产金属作为手性光敏剂。

Thank you！ ！