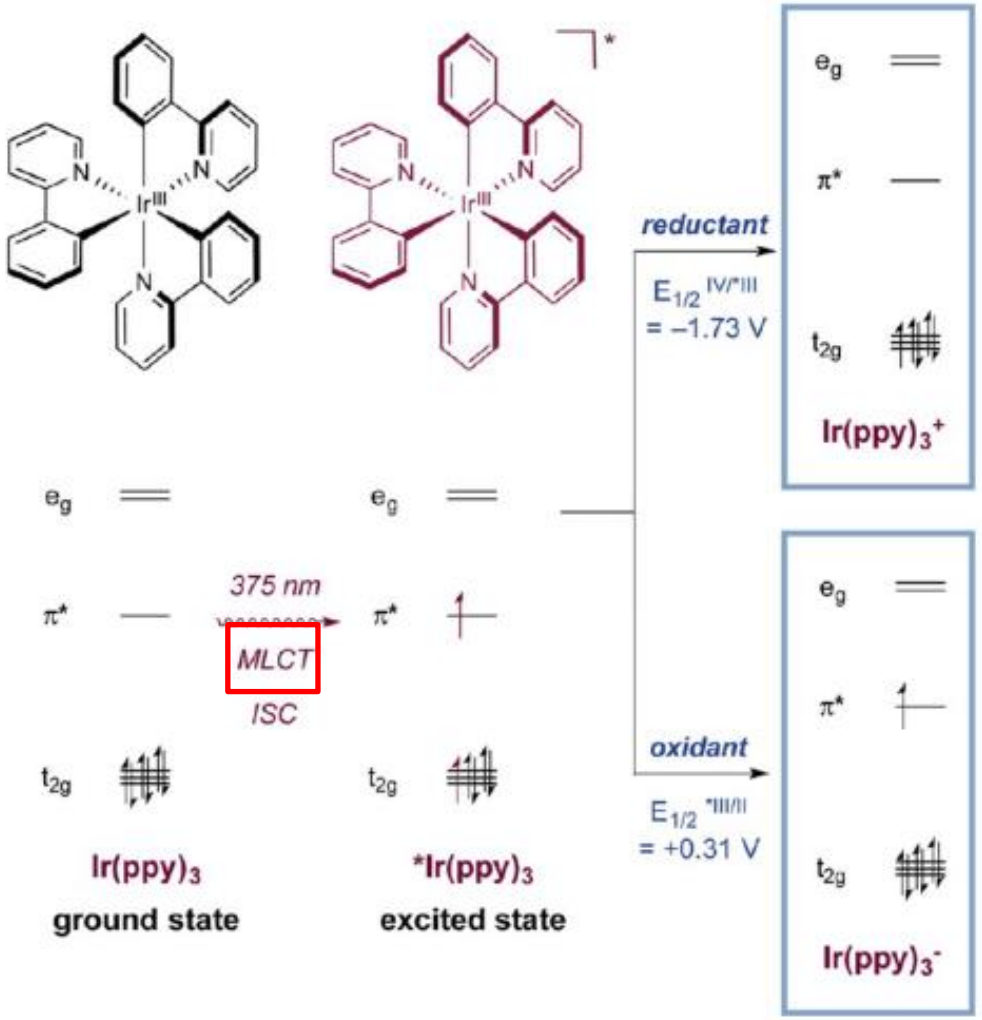
四种光催化模式

- 光氧化还原催化
- 光致能量转移
- 配体-金属光致均裂
- 光激发电子给体-受体复合物

汇报人：张利利
导师：杨泽鹏
2022.5.27

1. 光氧化还原催化（Photoredox Catalysis）



激发态PC的三种猝灭方式：

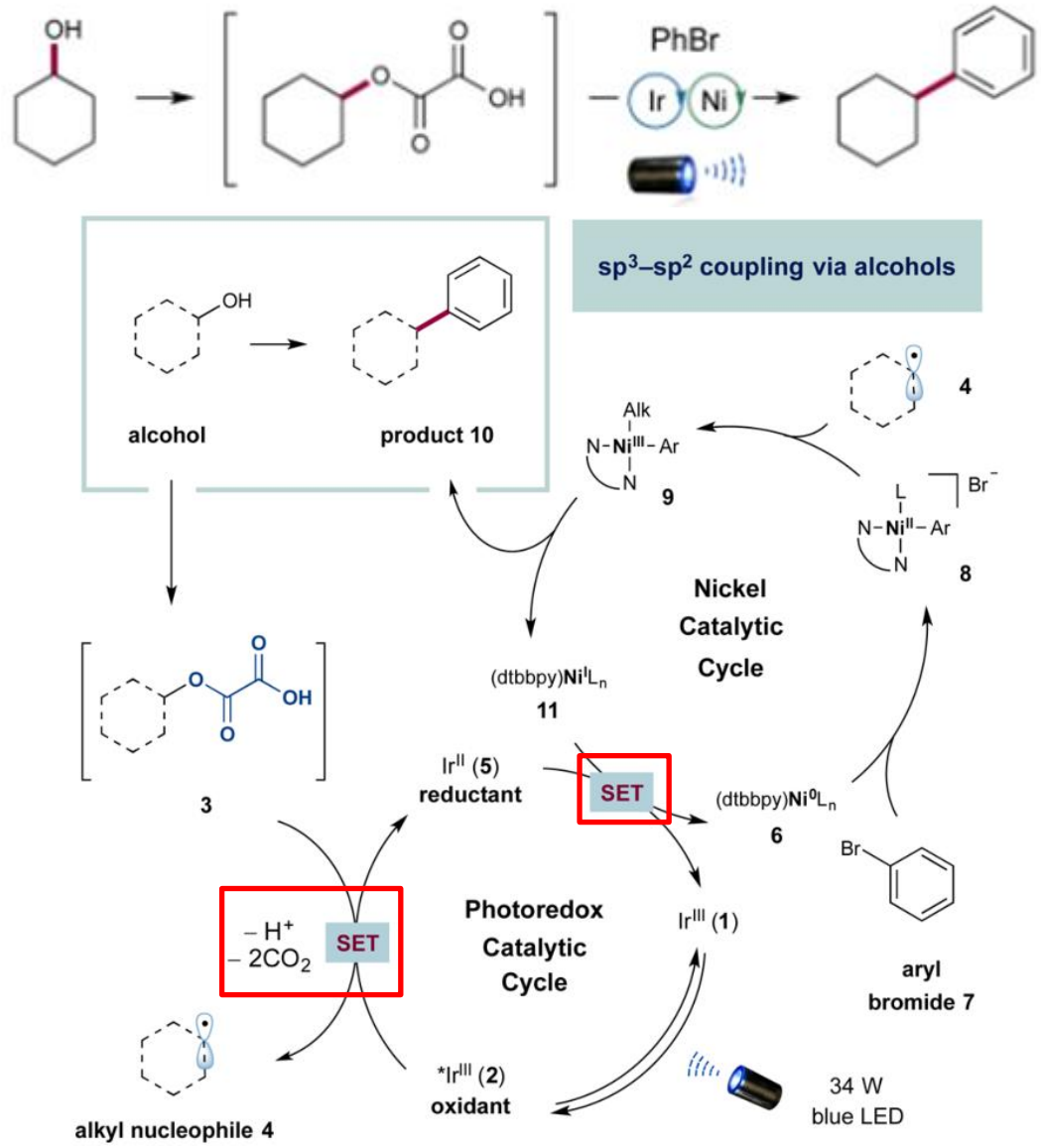
1、配体π*轨道提供一个电子（作为还原剂）；

2、金属外层空轨道接收一个电子（作为氧化剂）；

以上两个过程是光氧化还原催化的基础。

3、配体π*轨道回到金属外层空轨道（释放能量）此过程是光致能量转移的基础。

例：光氧化还原催化



David W. C. MacMillan. J. Am. Chem. Soc. 2016, 138, 13862-13865

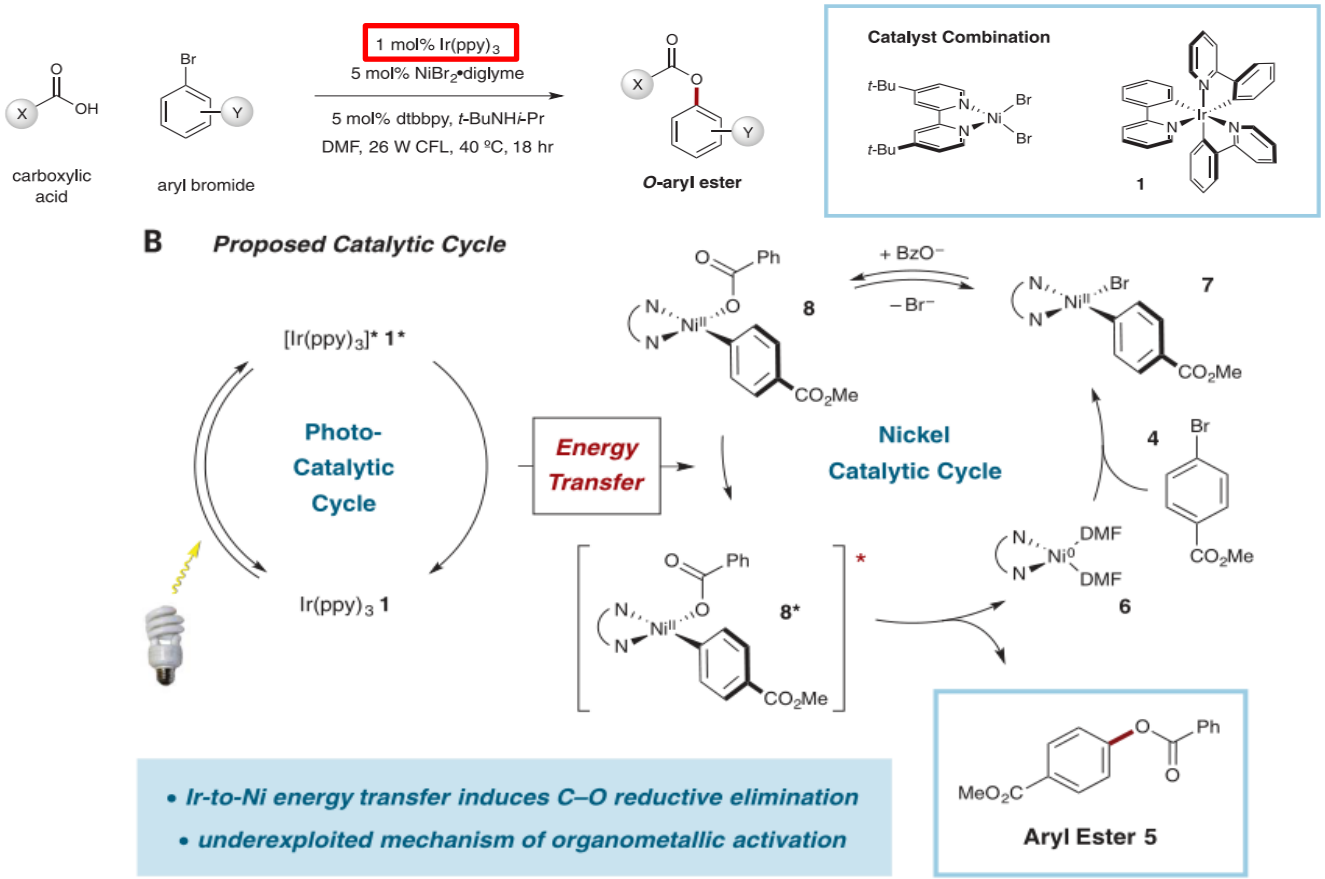
2. 光致能量转移（Photoinduced Energy Transfer）

光致能量转移两种方式：

有PC：配体π*轨道回到金属外层空轨道，释放能量并传递至金属配合物；

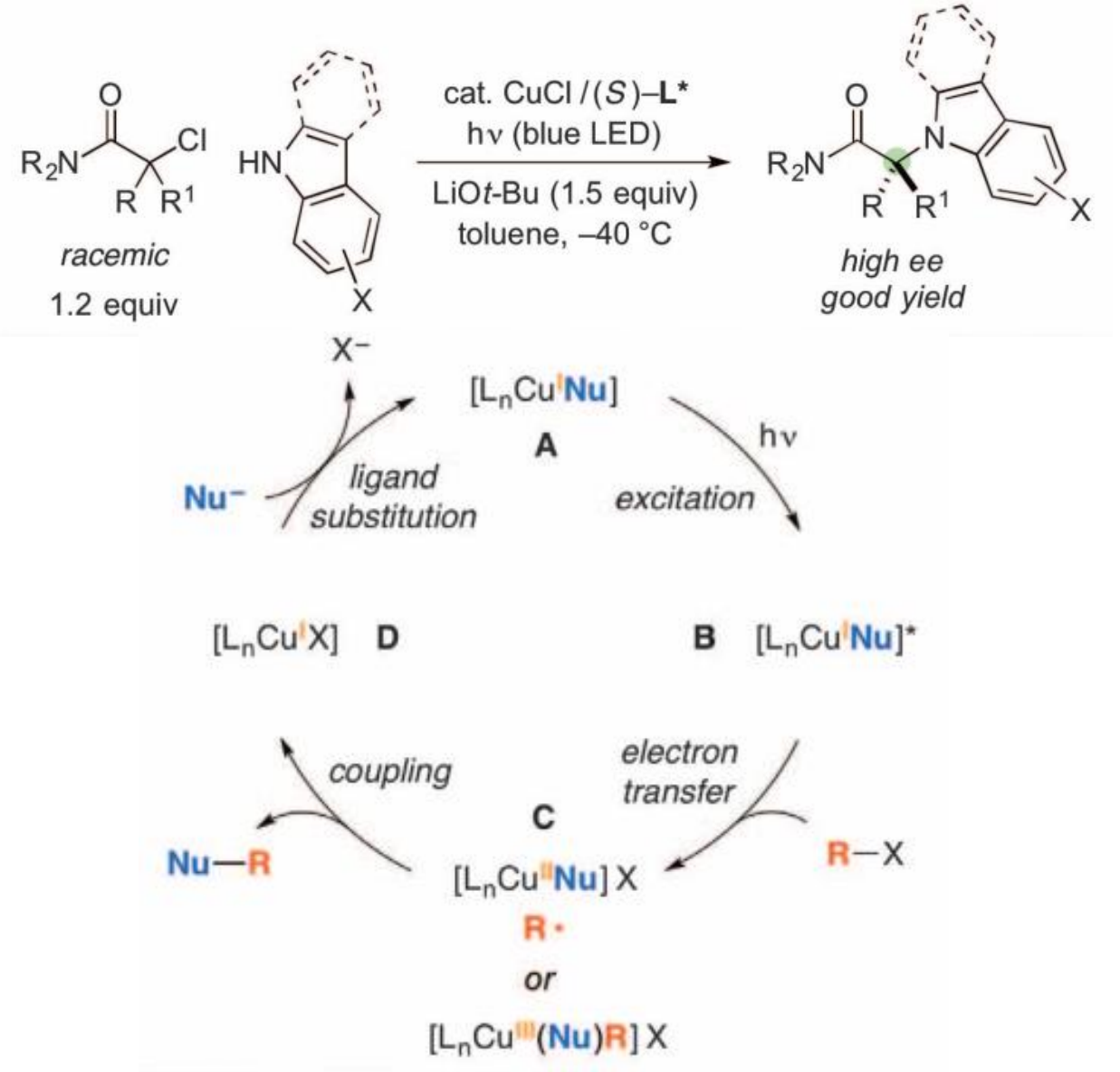
无PC：光通过辐射直接将能量传递至金属配合物。

例1：有PC



David W. C. MacMillan. Science 355, 380–385 (2017)

例2：光致能量转移—无PC



Jonas C. Peters, Gregory C. Fu. Science 351, 681–684 (2016)

3. 配体-金属光致均裂（Ligand-to-Metal Charge Transfer, LMCT ）

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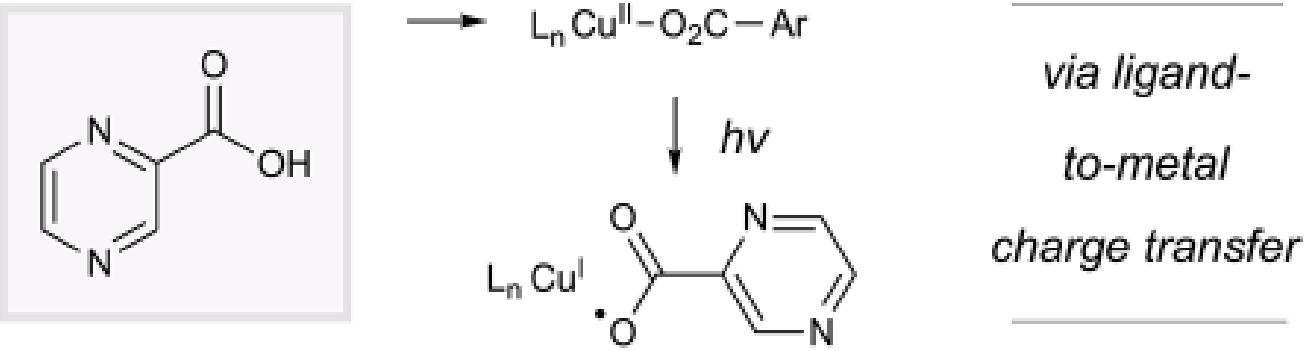
Article

A Unified Approach to Decarboxylative Halogenation of (Hetero)aryl Carboxylic Acids

Tiffany Q. Chen,‖ P. Scott Pedersen,‖ Nathan W. Dow, Remi Fayad, Cory E. Hauke, Michael C. Rosko, Evgeny O. Danilov, David C. Blakemore, Anne-Marie Dechert-Schmitt, Thomas Knauber, Felix N. Castellano, and David W. C. MacMillan*



在光照条件下，电子从配体（ligand）向金属（metal）转移。

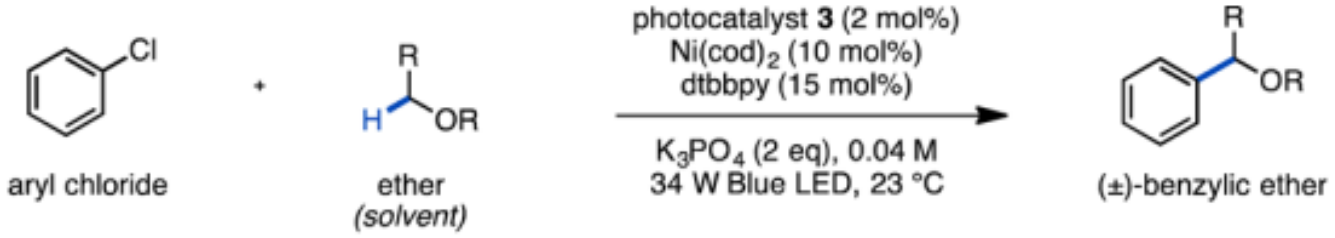
理解1：金属离子被配体还原。

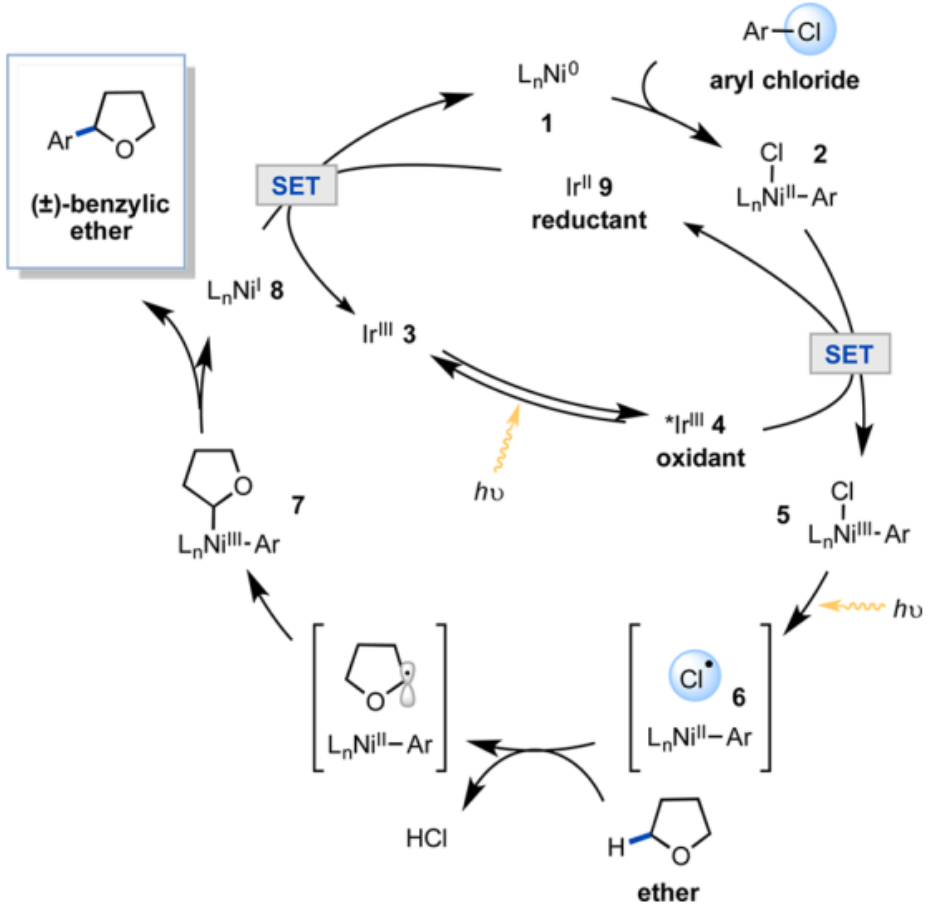
理解2：配体与金属间的离子键发生均裂。

比较：LMCT vs 基元反应中的配体解离

J. Am. Chem. Soc. 2022, 144, 8296-8305

例：配体-金属光致均裂





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Communication
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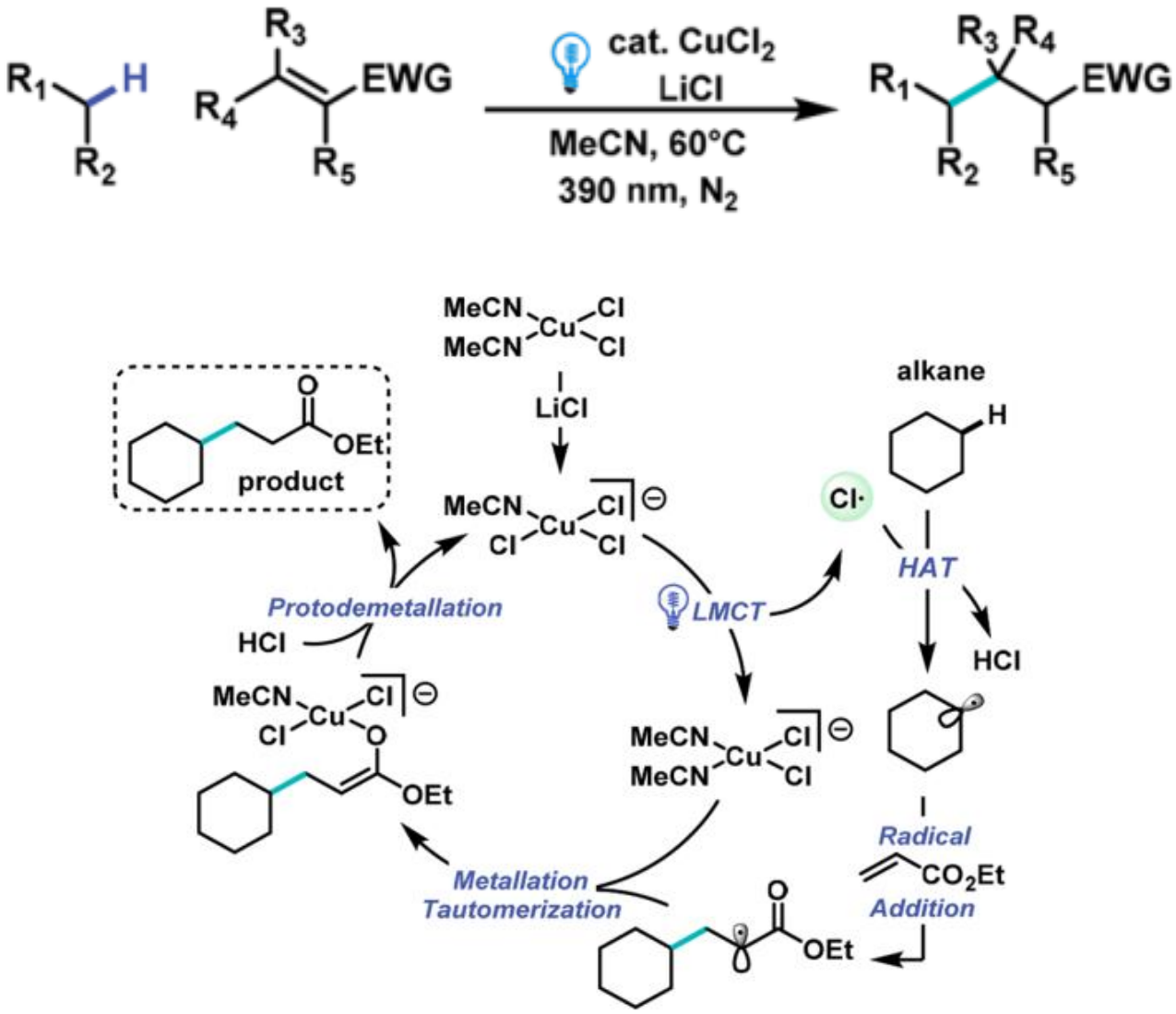
Direct C(sp^3)–H Cross Coupling Enabled by Catalytic Generation of Chlorine Radicals

Benjamin J. Shields and Abigail G. Doyle*

ABSTRACT: Here we report the development of a C(sp^3)–H cross-coupling platform enabled by the catalytic generation of chlorine radicals by nickel and photoredox catalysis. Aryl chlorides serve as both cross-coupling partners and the chlorine radical source for the α-oxy C(sp^3)–H arylation of cyclic and acyclic ethers. Mechanistic studies suggest that photolysis of a Ni(III) aryl chloride intermediate, generated by photoredox-mediated single-electron oxidation, leads to elimination of a chlorine radical in what amounts to the sequential capture of two photons. Arylations of a benzylic C(sp^3)–H bond of toluene and a completely unactivated C(sp^3)–H bond of cyclohexane demonstrate the broad implications of this manifold for accomplishing numerous C(sp^3)–H bond functionalizations under exceptionally mild conditions.

Abigail G. Doyle. J. Am. Chem. Soc. 2016, 138, 12719-12722

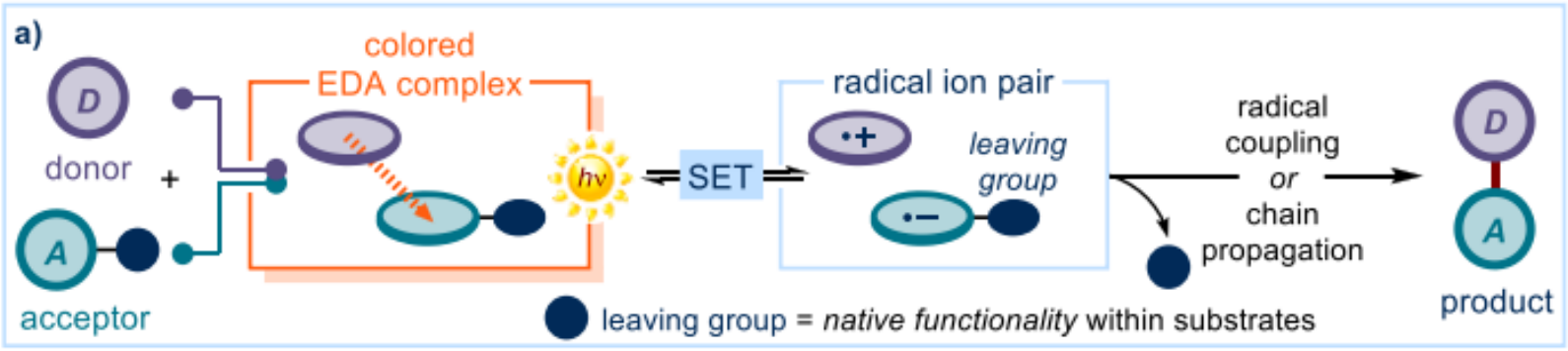
例：配体-金属光致均裂

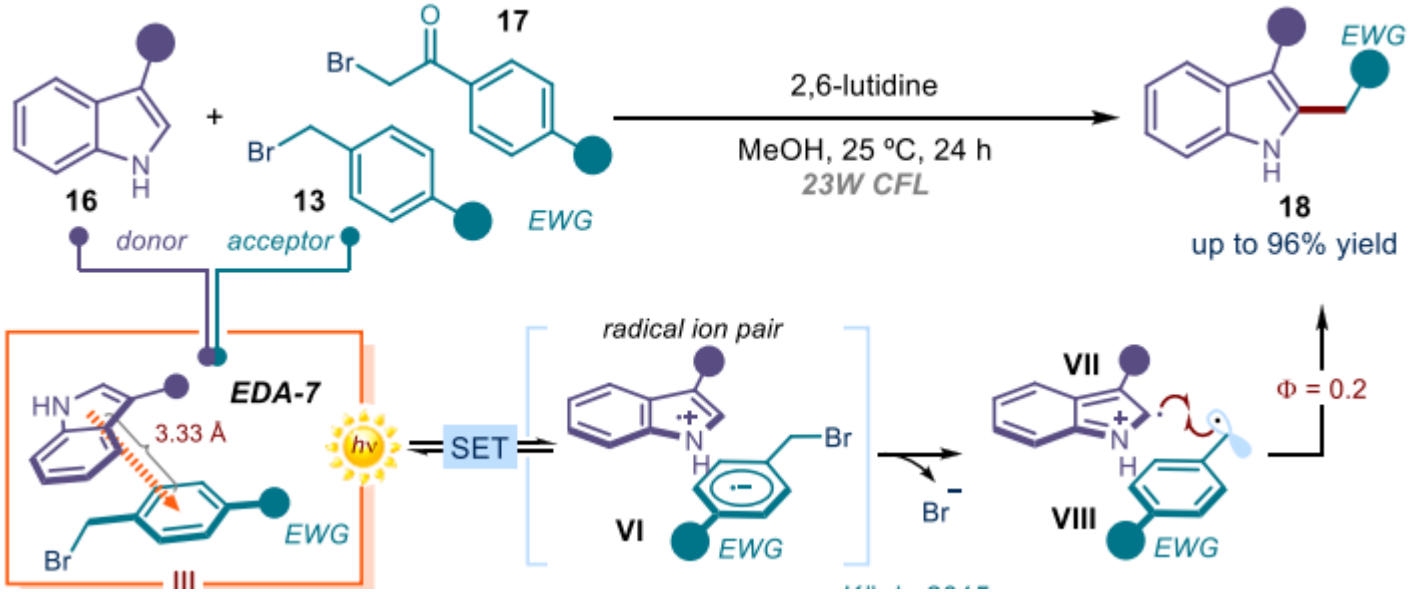


Tomislav Rovis. J. Am. Chem. Soc. 2021, 143, 2729-2735

4. 光激发电子给体-受体复合物（Photoactivity of Electron Donor–Acceptor Complexes）

反应模型：





特点：

1、不需要光催化剂；

2、A和D均不吸收光，EDA复合物吸收光；

3、 A和D均可带有离去基团。

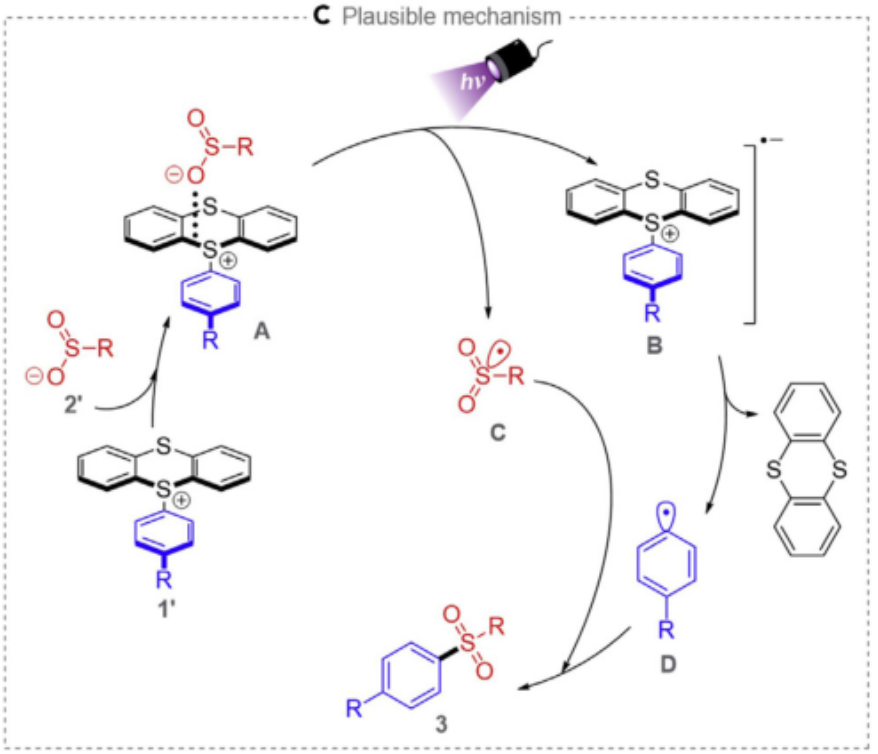
Paolo Melchiorre. J. Am. Chem. Soc. 2020, 142, 5461−5476

例：光激发电子给体-受体复合物

富电荷的分子+缺电荷的分子

或

富电子的盐+缺电子的盐



Gary A. Molander. Chem Catalysis 2, 898–907, April 21, 2022

总结

四种光催化模式

- 光氧化还原催化：需要PC，反应中同时经历氧化和还原两个过程；
- 光致能量转移：有无PC均可，能量传递至金属配合物，以提高金属中心的还原消除能力、氧化能力、或还原能力；
- 配体-金属光致均裂：不需PC，电子从配体向金属中心转移；
- 光激发电子给体-受体复合物：不需PC，电子从电子给体向电子受体转移。

Thanks!