铈参与的光催化有机合成

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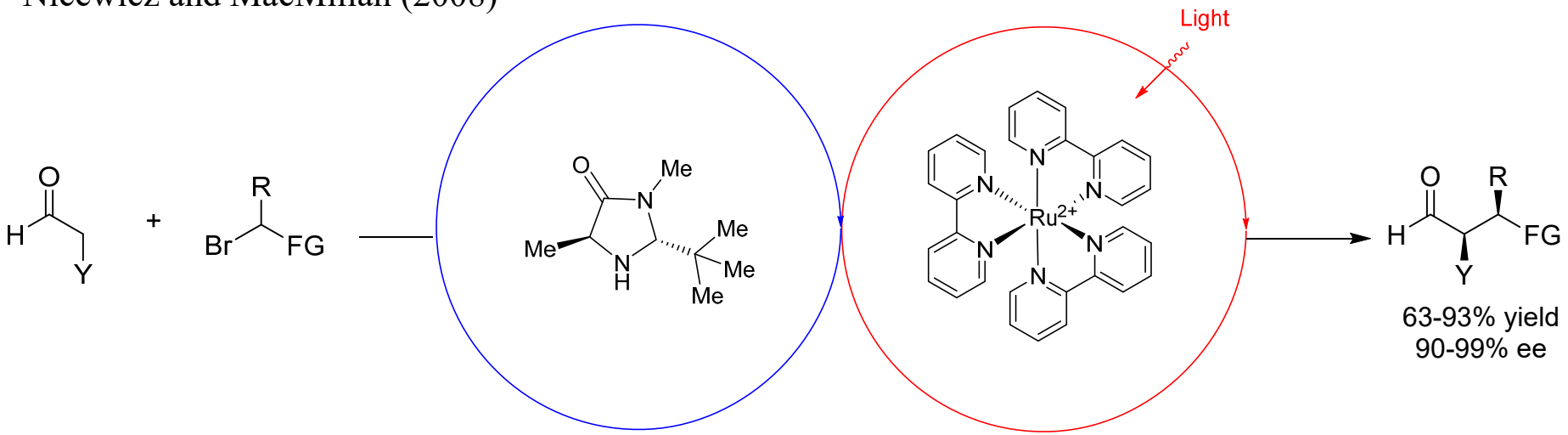
导师：麻生明

2019/9/20

目录

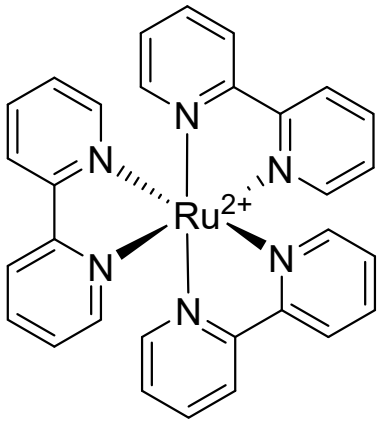
前言

• Nicewicz and MacMillan (2008)



Organo-catalysis

Photoredox catalysis



$Ru(bpy)_3^{2+}$

- 可见光激发
- 激发态寿命长
- 有用的单电子转移催化剂

MacMillan, D. W. C. and co-authors *Science* **2008**, *322*, 77.

- 铈的光化学

Ce(III)

- 地球上储量最丰富的稀土元素，价格低廉
- **4f →5d** 跃迁，价态常常是可以变化的
- 吸收和发射光谱带较宽
- 特殊的反应性
- 荧光寿命短

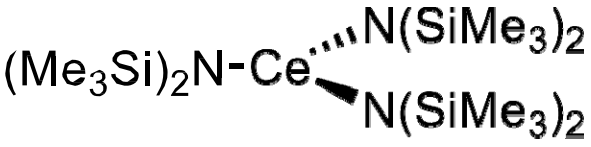
其他镧系金属

- **4f →4f** 禁戒跃迁，强度低，应用范围窄
- 基质对发光颜色变化不大
- 发射光谱呈线状，受温度影响小

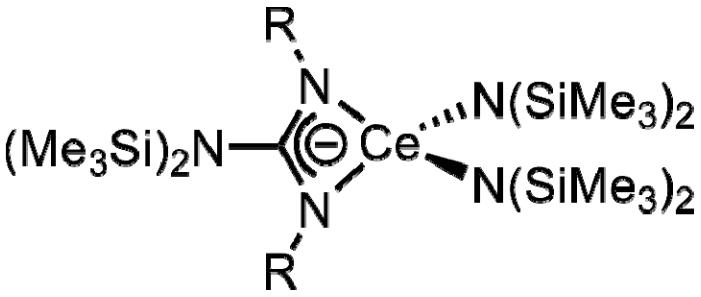
Schelter, E. J. and co-authors *Acc.Chem. Res.* **2018**, *51*, 2926.

胍基-氨基铈(III)配合物催化的光反应

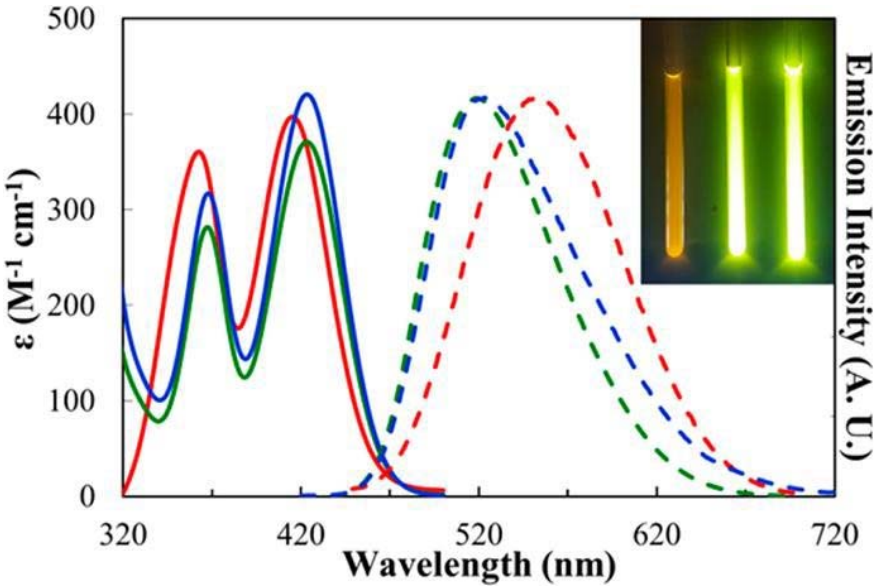
配合物的物理性质



1 Φ_{PL}= 0.03, Γ=24 ns



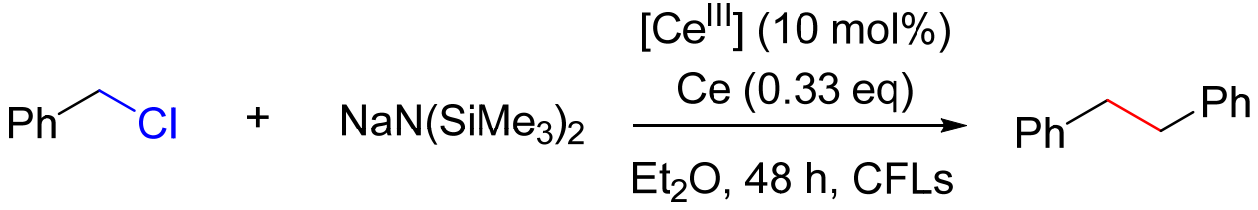
R=*i*Pr: 1-*i*Pr Φ_{PL}= 0.46, Γ=67 ns
R=Cy: 1-Cy Φ_{PL}= 0.54, Γ=61 ns



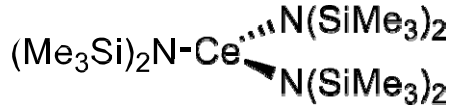
Solid: absorption, dashed: emission
Left: 1, middle: 1-*i*Pr, right: 1-Cy

Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2015**, *137*, 9234.

应用



entry	[Ce^{III}]	yield
1	1	68%
2	1-*i*Pr	17%
3	1-Cy	10%



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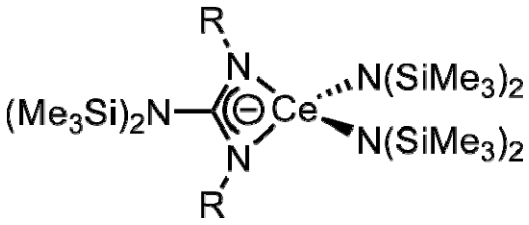

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R=Cy: 1-Cy Φ_{PL}= 0.54, Γ=61 ns

Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2015**, *137*, 9234.

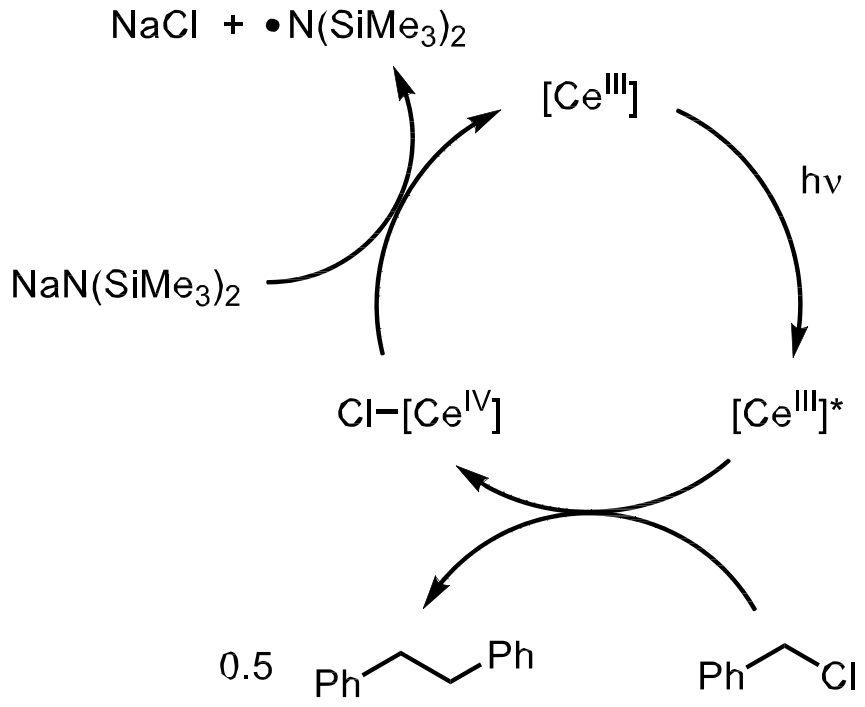
应用

•激发态还原电位

entry	[Ce^{III}]	$E_{1/2}$* (V)
1	1	-2.19
2	1-*i*Pr	-2.30
3	1-Cy	-2.24

• $PhCH_2Cl$: E_{pc} = -2.66 V

• 可能的机理

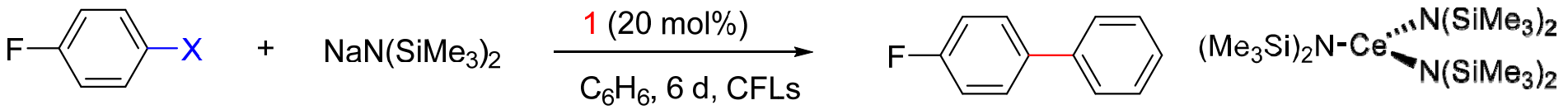


内层电子传递过程，反应中 Ce(IV)-Cl 键的形成促进了 C(SP^3)-Cl 键的活化

Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2015**, *137*, 9234.

应用

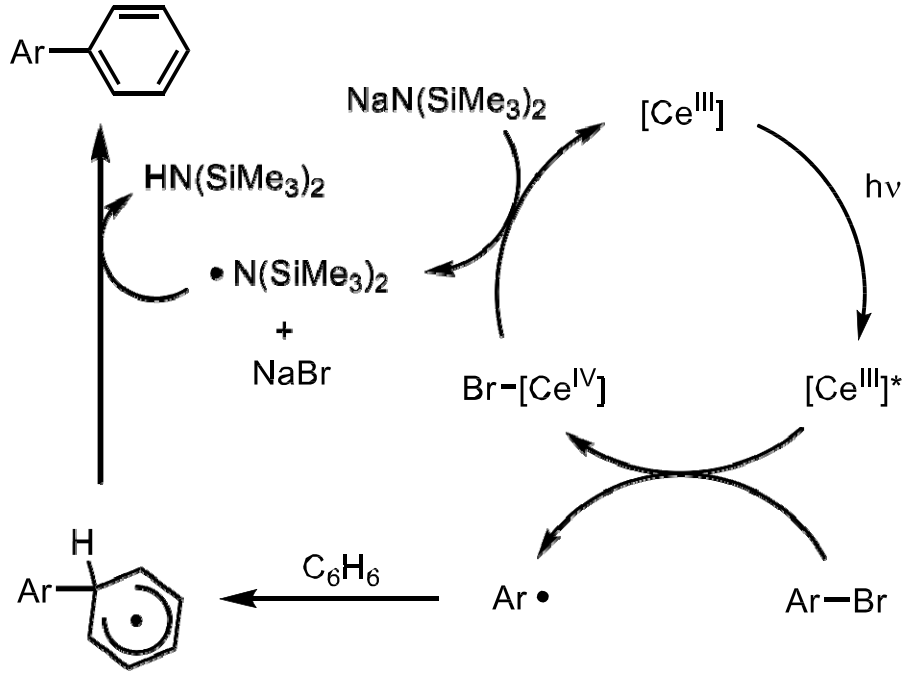
- 卤代苯的芳基化反应



1

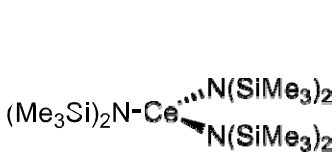
X=I: 68%
Br: 43%
Cl: No reaction

- Proposes catalytic cycle

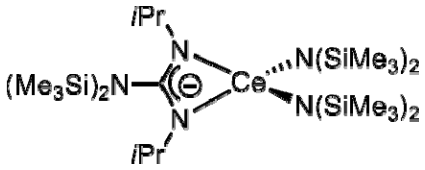


Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2015**, *137*, 9234.

铈配合物的结构与性质



1-N



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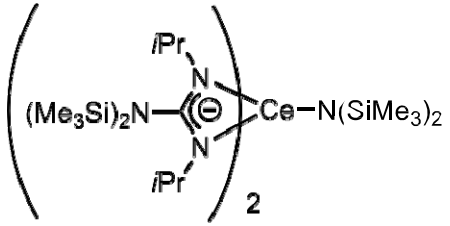

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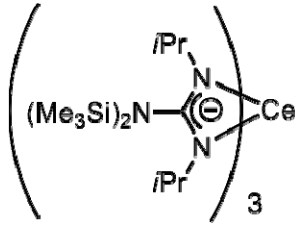

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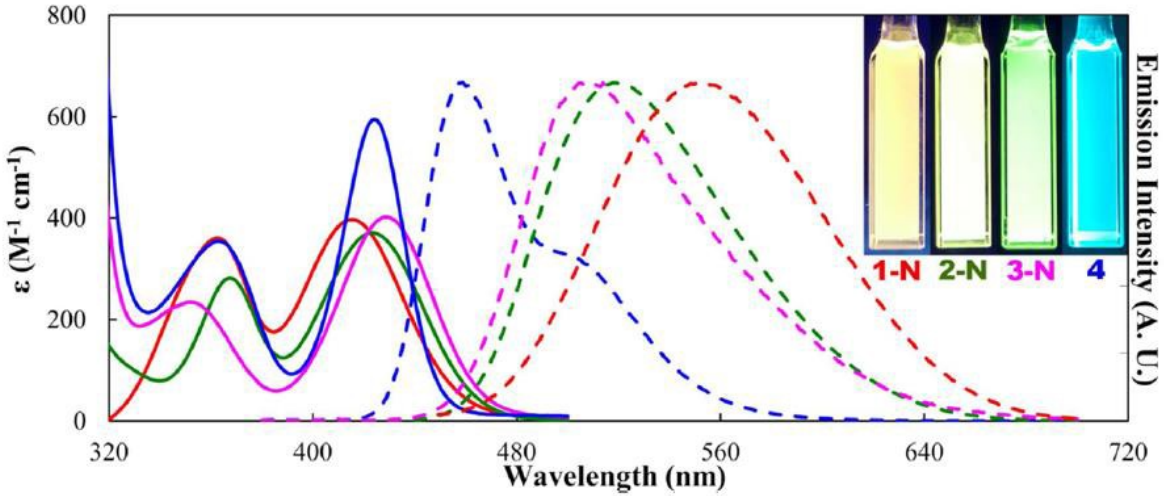
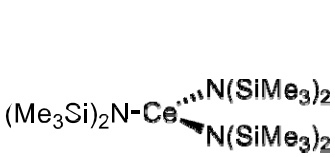


entry	[Ce^{III}]	Φ_{PL}	τ
1	1-N	0.03	24 ns
2	2-N	0.46	65 ns
3	3-N	0.79	117 ns
4	4	0.81	83 ns

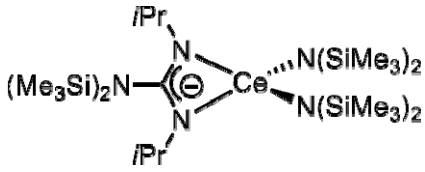
•铈配合物的发光颜色由配体类型和结构的刚性决定

Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2016**, *138*, 5984.

应用



1-N



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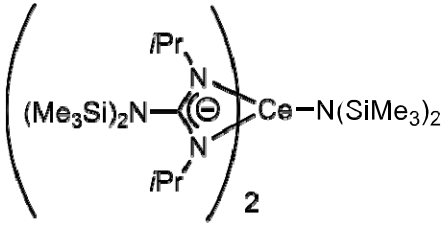

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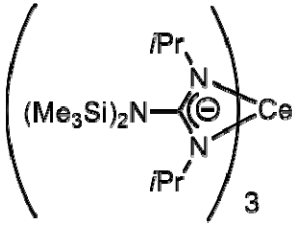

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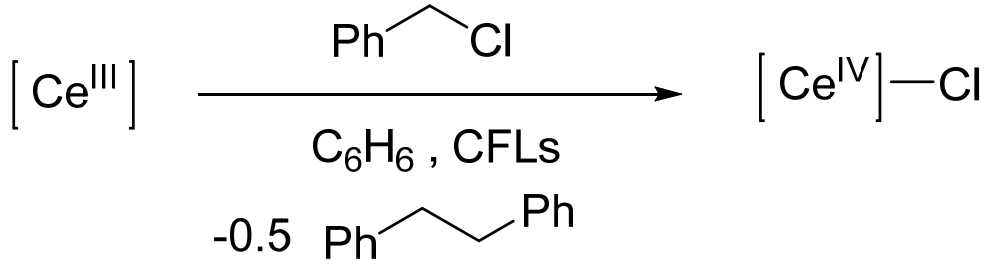
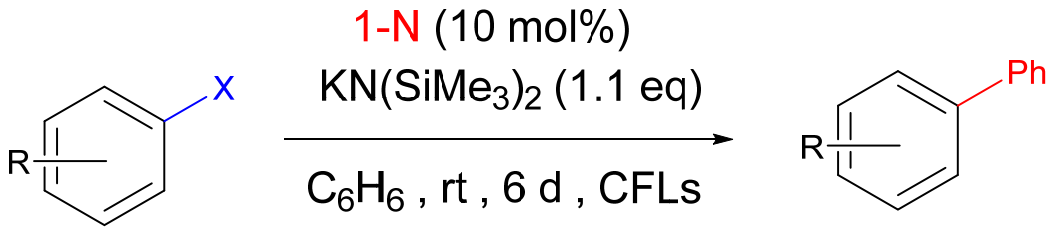


entry	[Ce^{III}]	$E_{1/2}$*(eV)	result
1	1-N	-2.19	proceeded
2	2-N	-2.30	proceeded
3	3-N	-2.59	no reaction
4	4	-2.92	no reaction

Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2016**, *138*, 5984.

应用

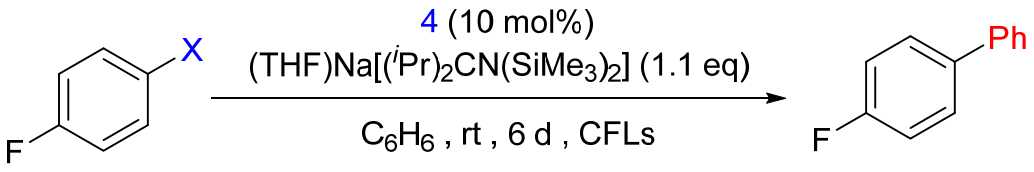
- 卤代苯的芳基化反应进一步底物拓展



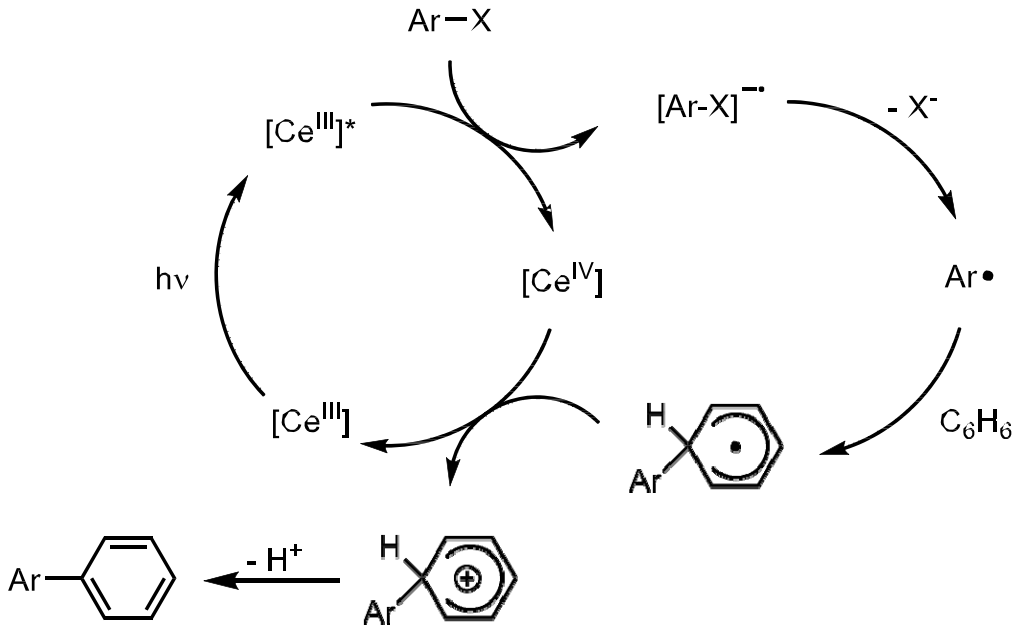
entry	X	R	conversion (%)	Yield (%)	entry	X	R	conversion (%)	Yield (%)
1	Br	4-Me	92	76	6	I	H	>99	85
2	Br	H	80	72	7	I	4-F	>99	91
3	Br	4-F	69	32	8	I	2-F	>99	87
4	Br	2-F	>99	86	9	I	3-Me	>99	88
5	I	4-Me	>99	76	10	I	2-Me	>99	23

Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2016**, *138*, 5984.

应用



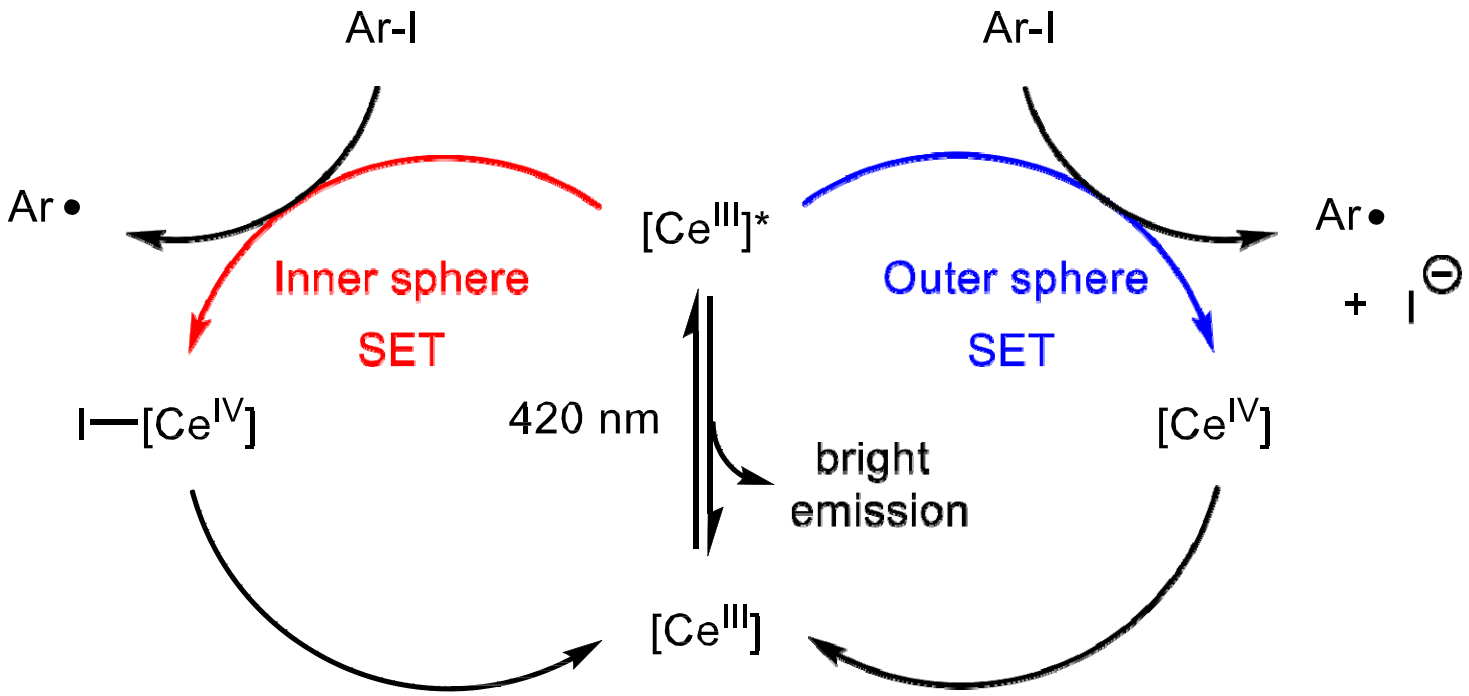
X = I: 35%
= Br: No reaction
= Cl: No reaction



4 + $[Cp_2Fe][BAr^F4]$ ⟶ $[4^+][BAr^F4]$ 单晶分析，证明了Ce^{IV}的存在

Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2016**, *138*, 5984.

小结

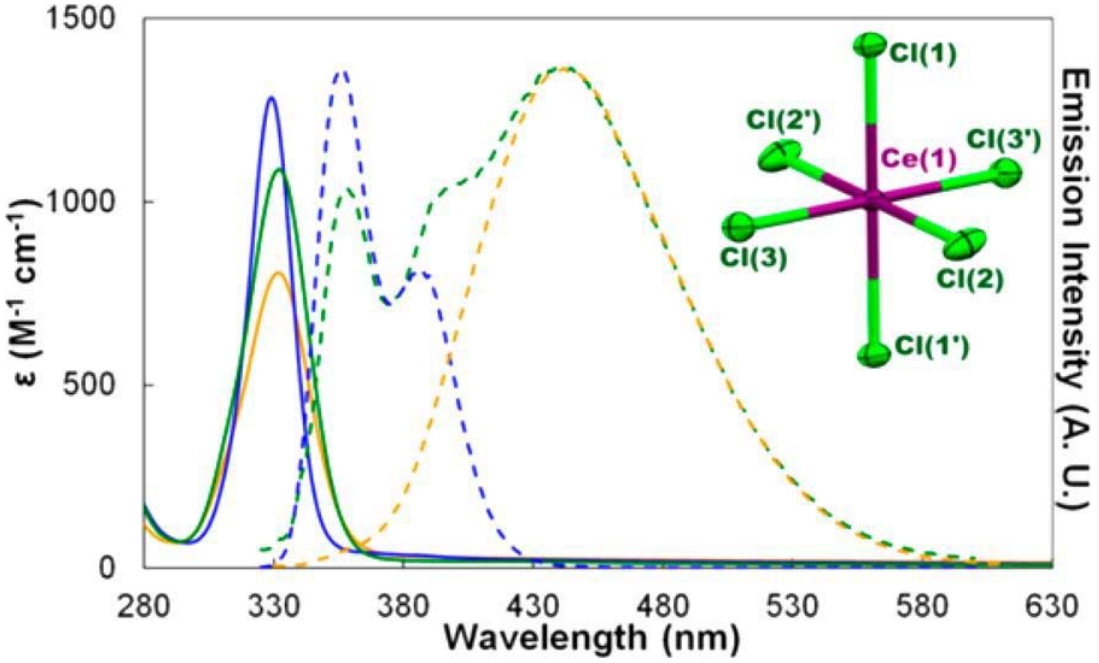


存在的问题：（1）铈催化剂对空气及湿度敏感
（2）反应效率偏低，反应时间长
（3）配合物光致发光量子产率低，对光能利用差

Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2016**, *138*, 5984.

六氯合铈(III)离子催化的光反应

配合物的物理性质



Solid: absorption, dashed: emission

green: $[NEt_4]_3[Ce^{III}Cl_6]$

blue: $[NEt_4]_3[Ce^{III}Cl_6]$ in the presence of excess NEt_4Cl

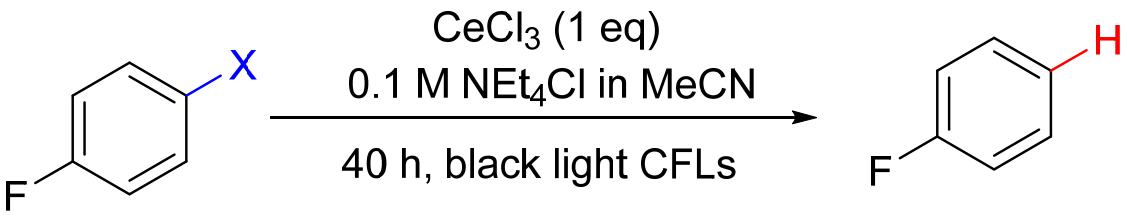
Yellow: $[NEt_4]_3[Ce_2Cl_9]$

- Φ_{PL}= 0.61, Γ=22.1 ns

Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2016**, *138*, 16266.

应用

- 芳基卤化物的还原脱卤反应



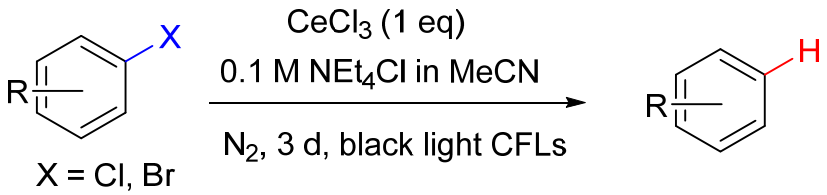
X = I: >95%
Br: 87%
Cl: 67%
F: No reaction

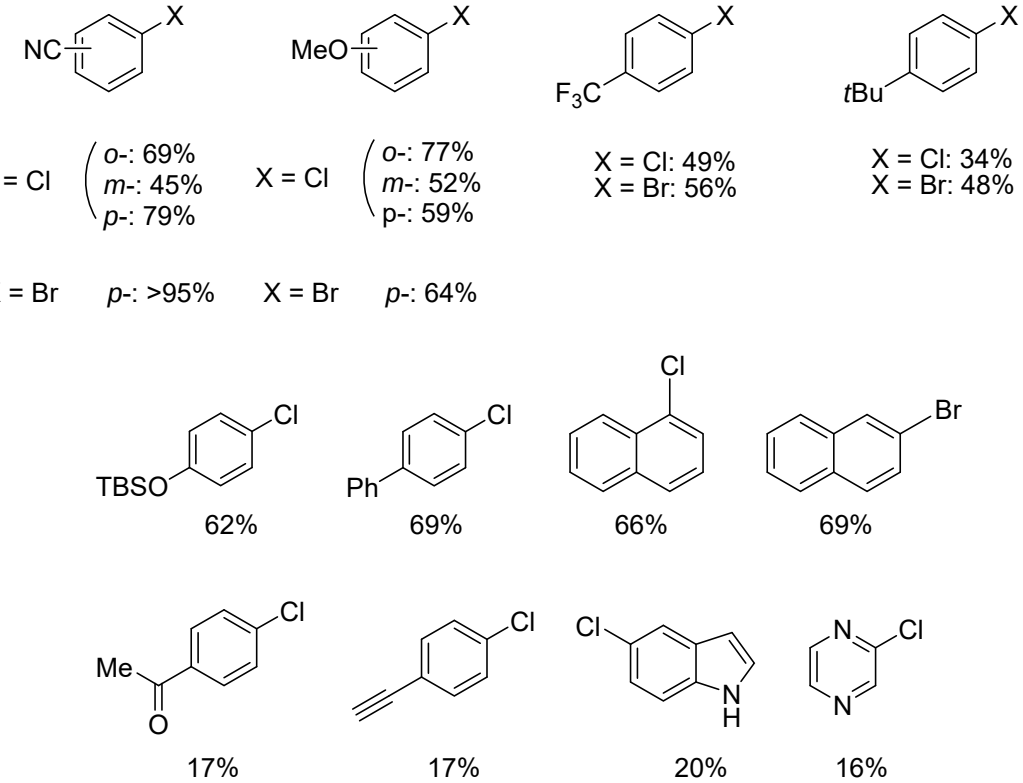
- 激发态 $[Ce^{III}Cl_6]^{3-}$的还原电位: -3.45 V　　($E_{PhCl^{\cdot -}/PhCl}$= -3.28 V)
- 自由基捕获实验证明了芳基自由基的存在

Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2016**, *138*, 16266.

应用

- 底物拓展

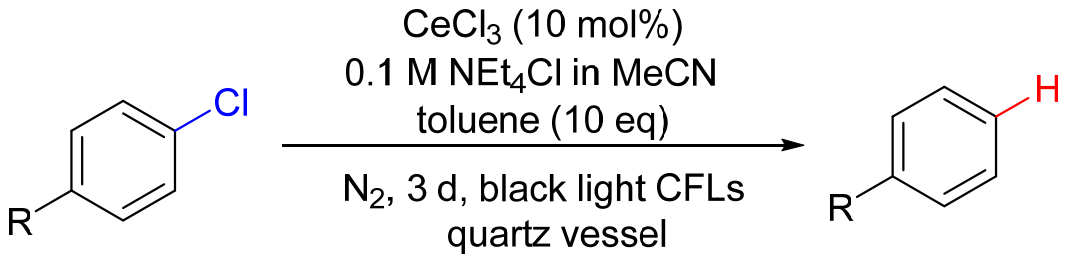


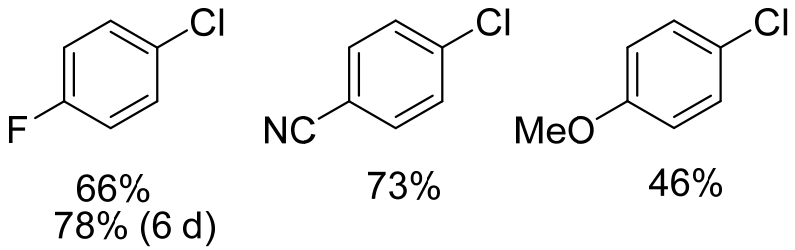


Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2016**, *138*, 16266.

应用

- 降低铈催化剂用量



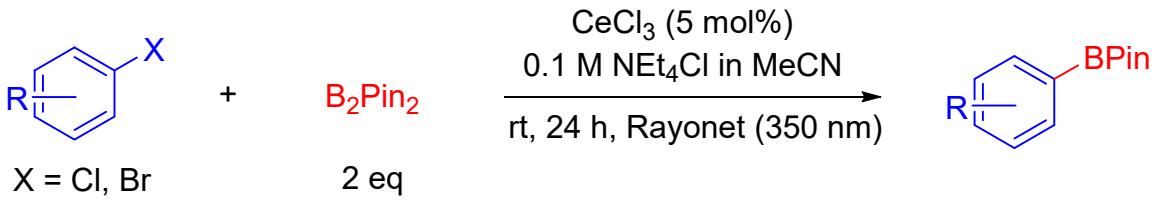


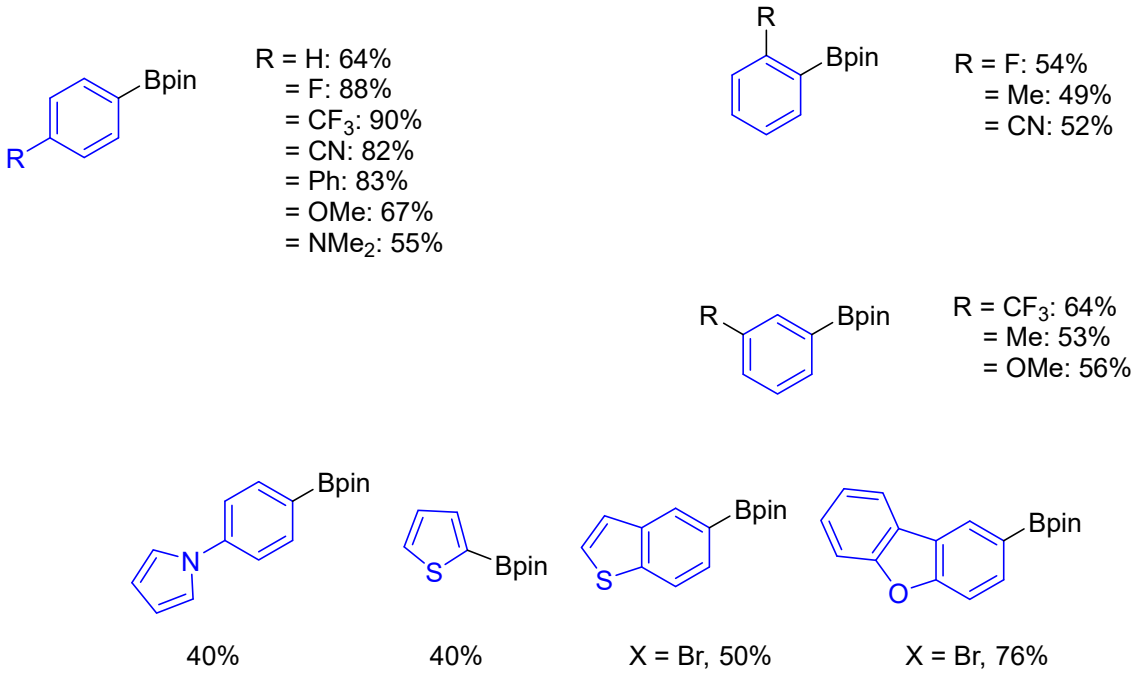
- 甲苯作为牺牲还原剂可以再生Ce(III)

Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2016**, *138*, 16266.

应用

- 光催化的硼化反应

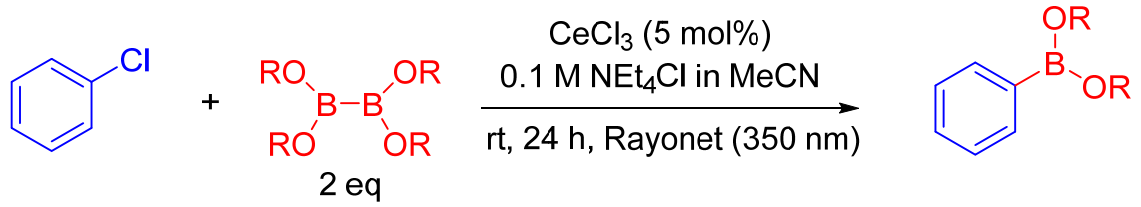


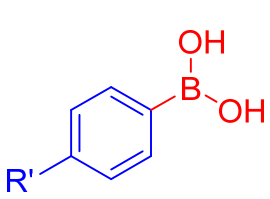


Schelter, E. J. and co-authors *Angew. Chem. Int. Ed.* **2018**, *57*, 10999.

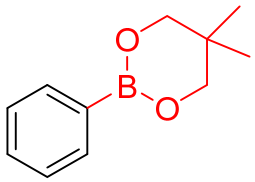
应用

•光催化的硼化反应

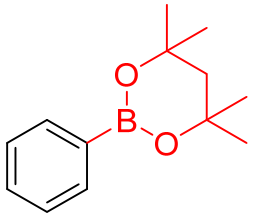




R' = H: 42%
= F: 50%
= CF_3: 61%
= OMe: 44%



63%



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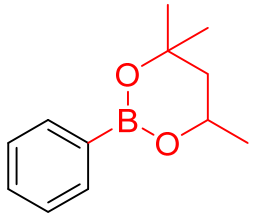
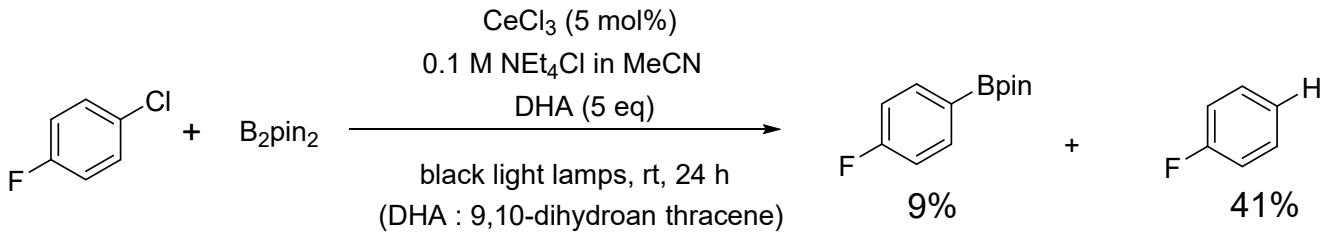


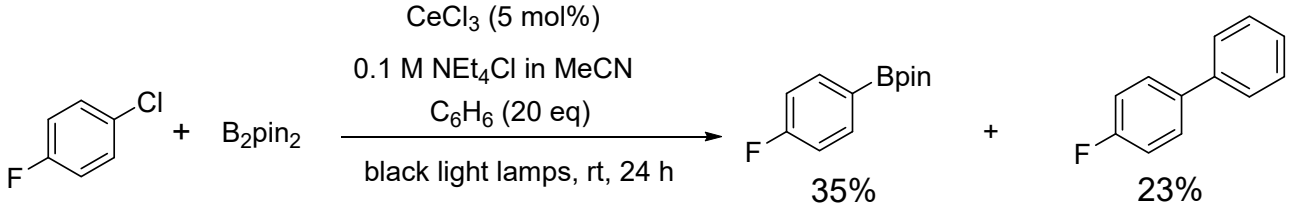
68%

Schelter, E. J. and co-authors *Angew. Chem. Int. Ed.* **2018**, *57*, 10999.

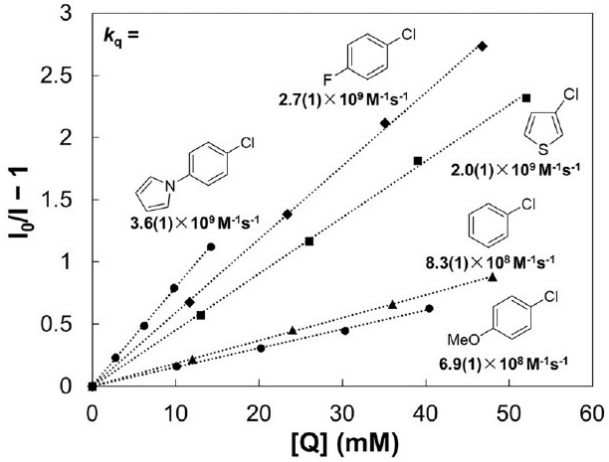
应用

- 机理实验





- Stern-Volmer experiments

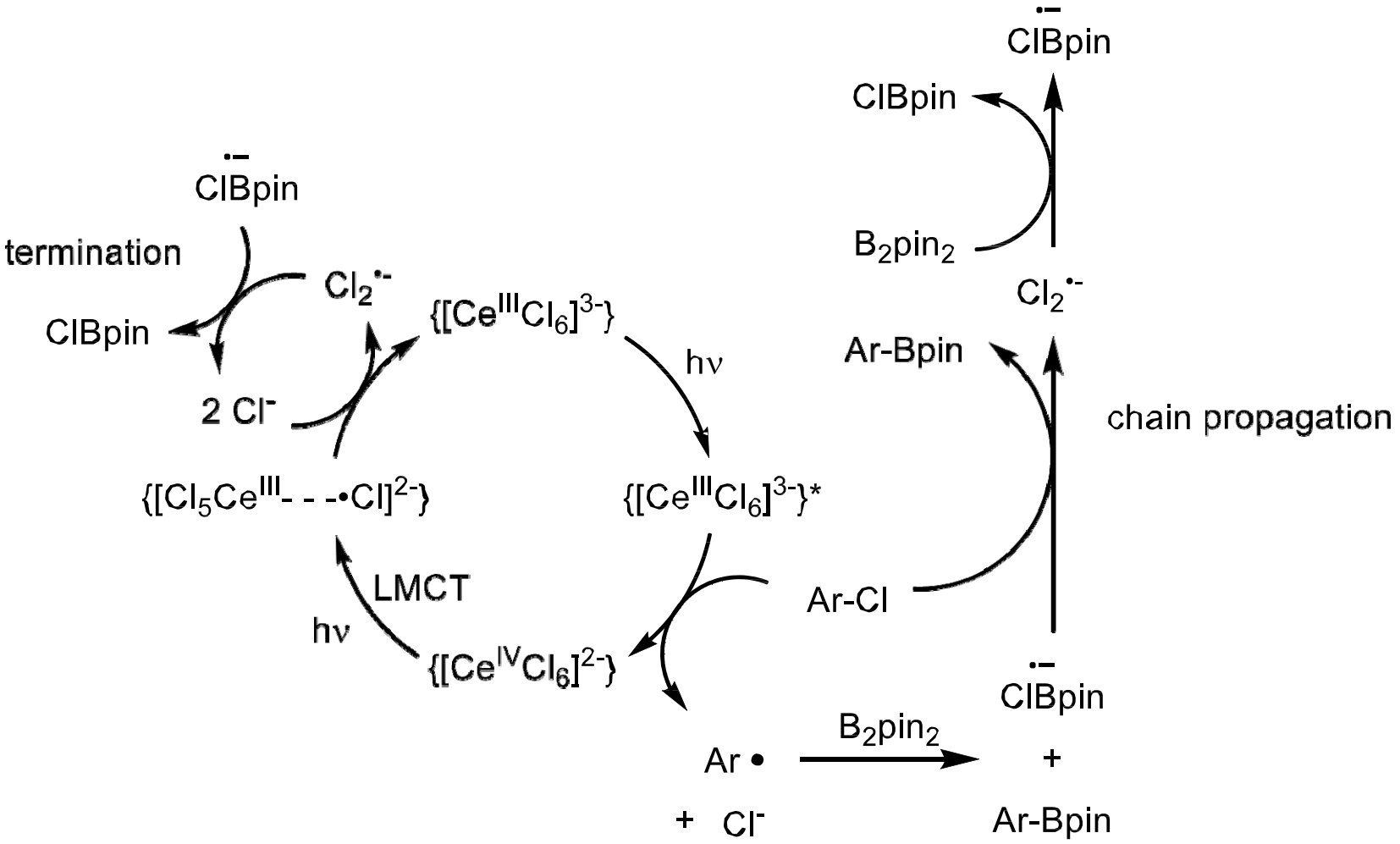


- 反应量子吸收效率：Φ= 6.1 (>1)，反应时间可缩短至24 h，证明了反应可能是自由基链式机理

Schelter, E. J. and co-authors *Angew. Chem. Int. Ed.* **2018**, *57*, 10999.

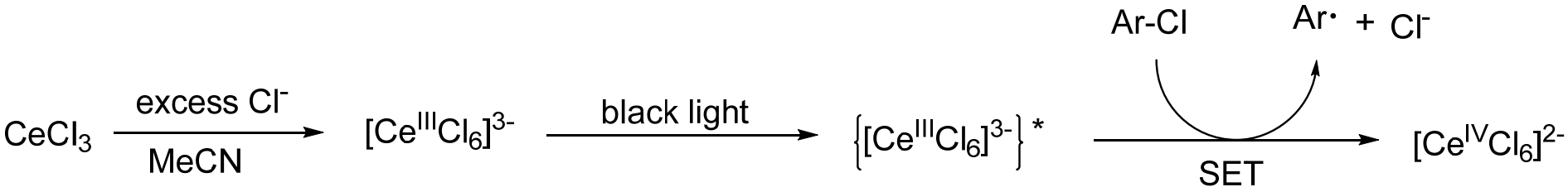
应用

- 可能的机理



Schelter, E. J. and co-authors *Angew. Chem. Int. Ed*. **2018**, *57*, 10999.

小结

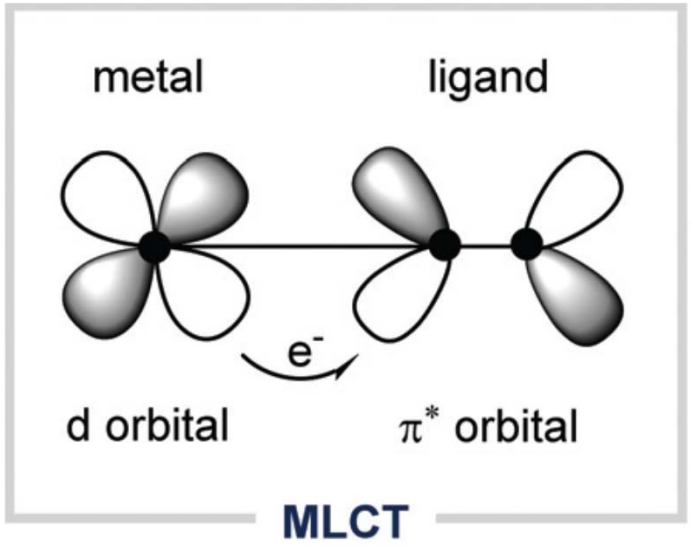


- 激发态 $[Ce^{III}Cl_6]^{3-}$的还原电位: -3.45 V

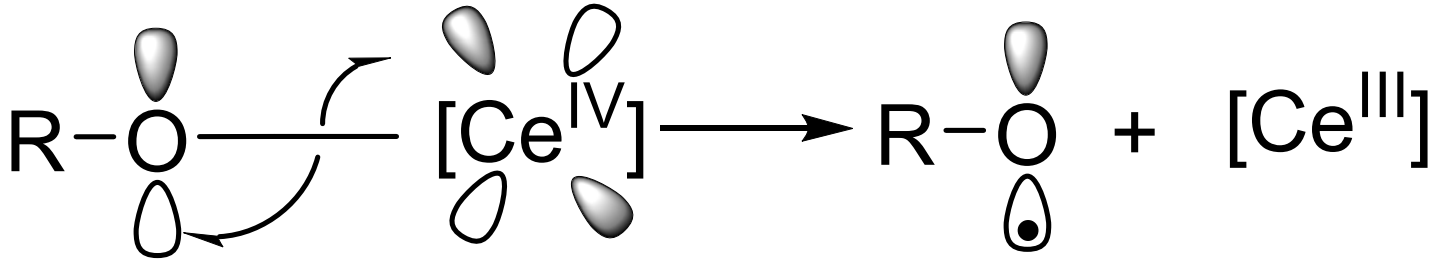
($[Ru(bpy)_3]^{2+}$: −1.21 V; fac-$Ir(ppy)_3$: −2.13 V; SmI_2-THF : −3.21 V)

烷氧基诱导的铈催化的光反应

光催化的 Ce(IV) 和醇的LMCT途径



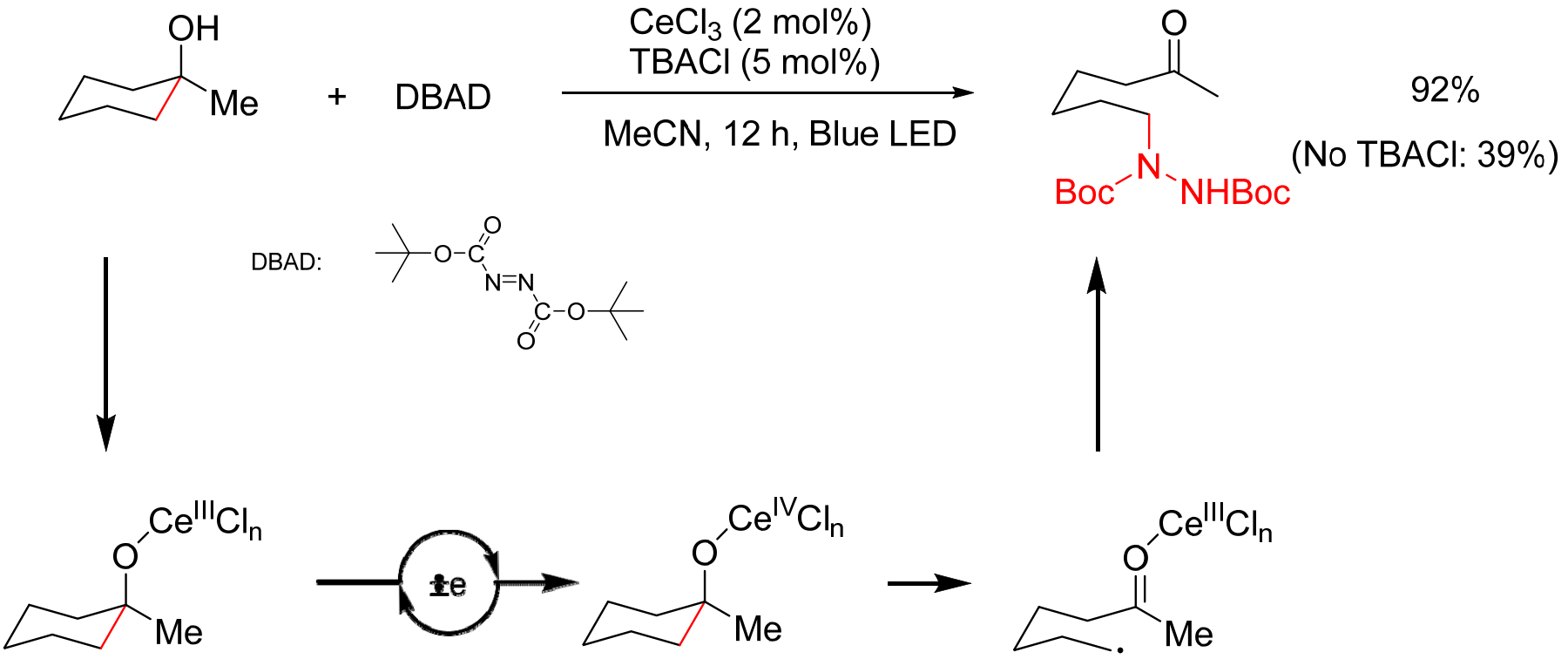
•传统MLCT（ metal-to-ligand charge transfer ）途径：金属催化剂需要历经系间跃迁和外层单子传递，把光能转化成化学能，过程中伴随着光能的部分损失。



•铈和醇参与的LMCT （ligand-to-metal charge transfer）途径：光照射后诱导配位键均裂形成有机自由基物种，减少中间态，从而最大程度地利用光能。

应用

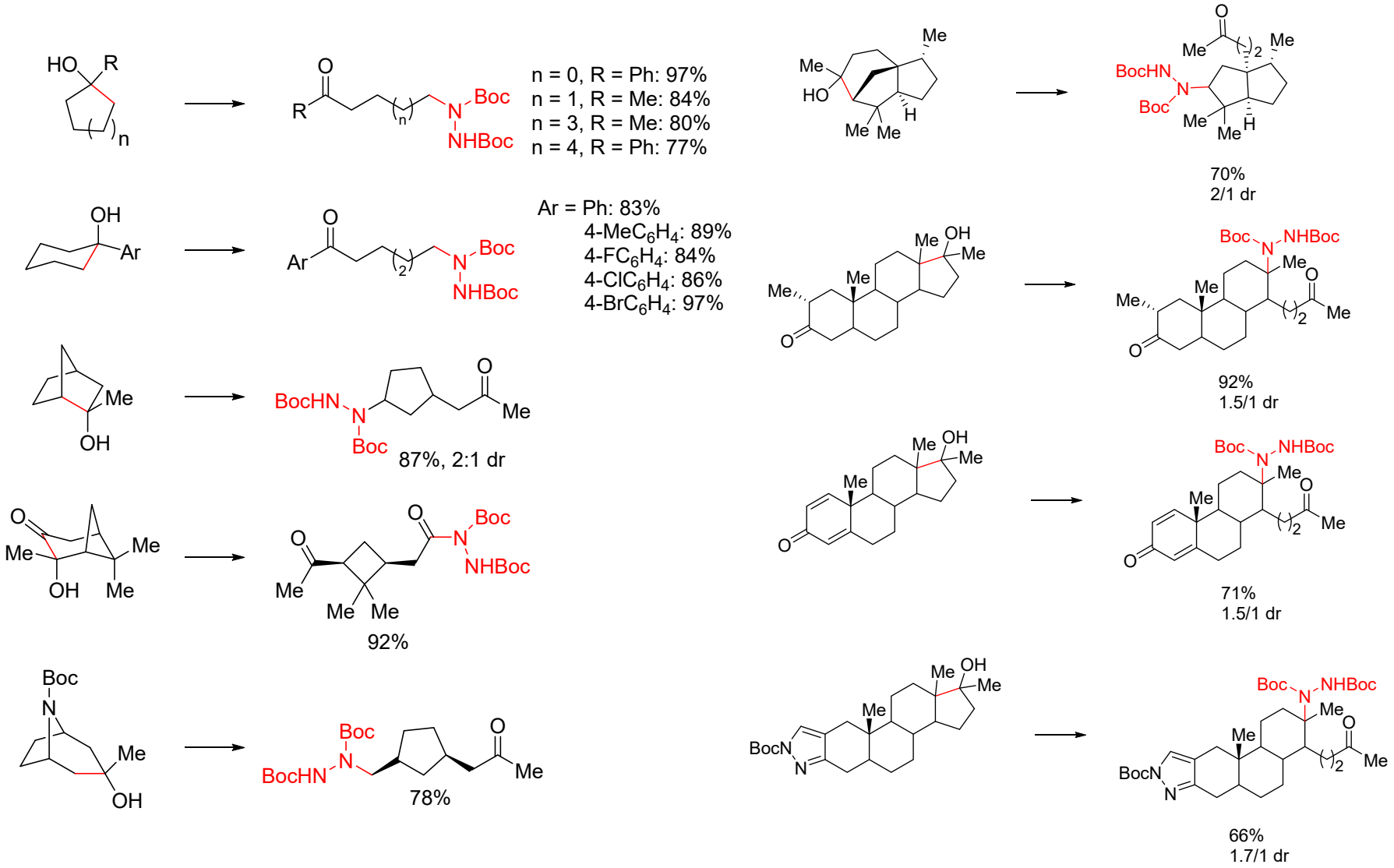
- 环状醇的C-C键断裂胺化反应



Zuo, Z. and co- authors *Angew. Chem. Int. Ed.* **2016**, *55*, 15319.

应用

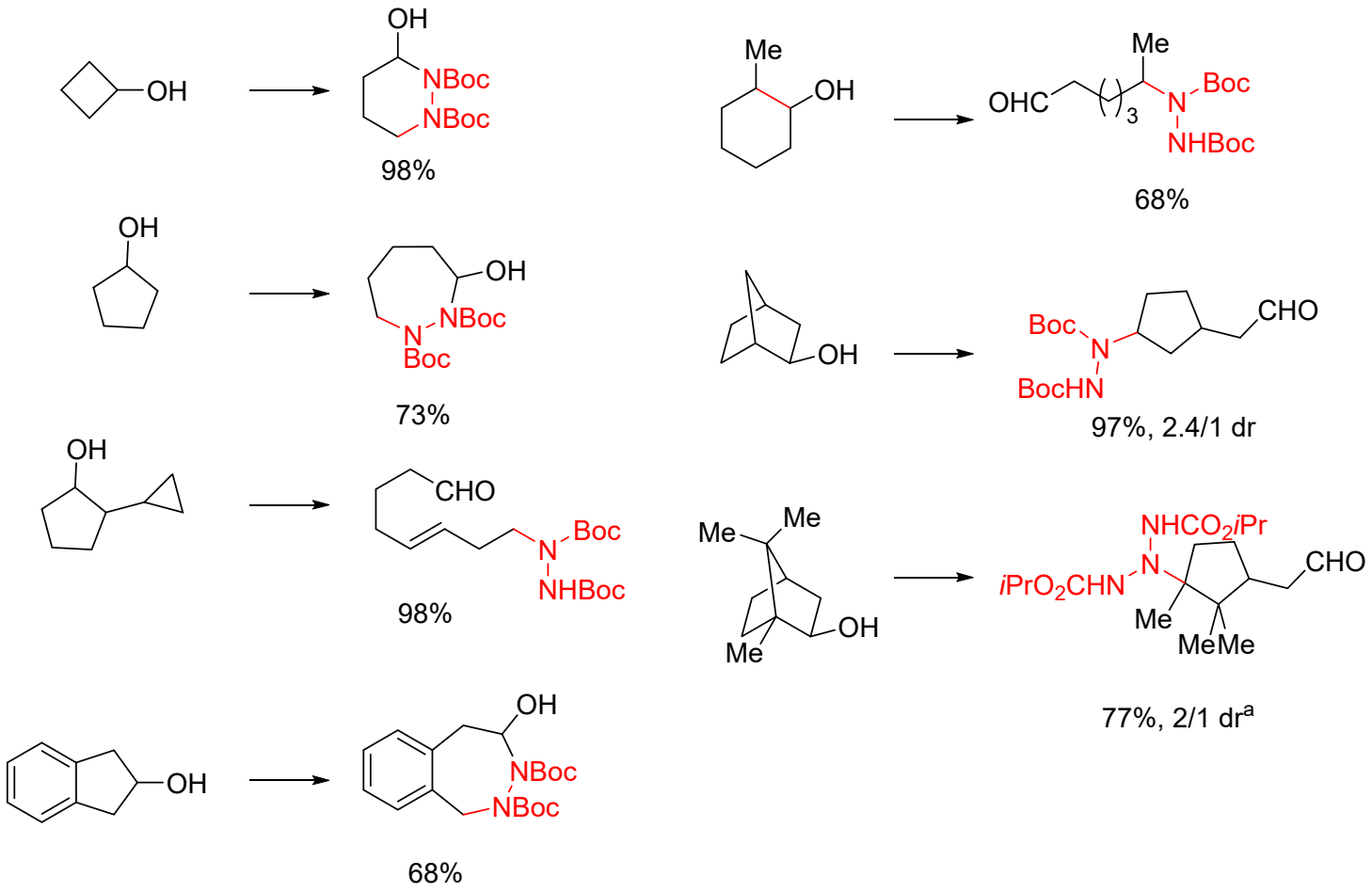
- 底物拓展



Zuo, Z. and co- authors *Angew. Chem. Int. Ed.* **2016**, *55*, 15319.

应用

- 底物拓展

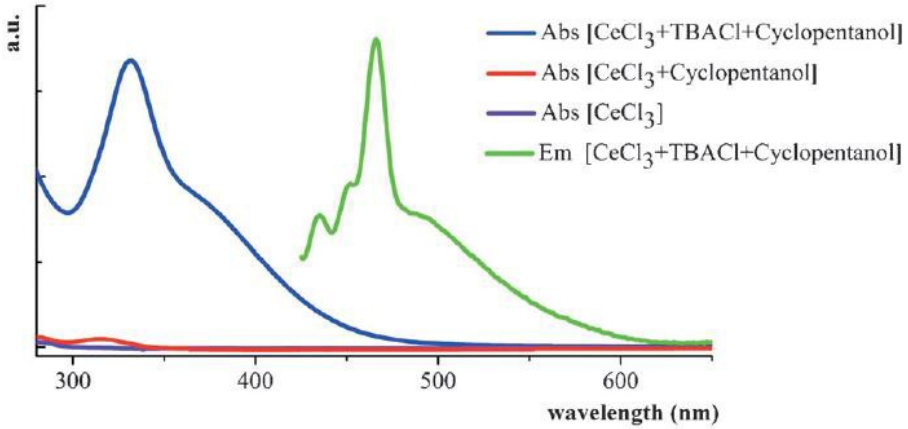


Zuo, Z. and co- authors *Angew. Chem. Int. Ed.* **2016**, *55*, 15319.

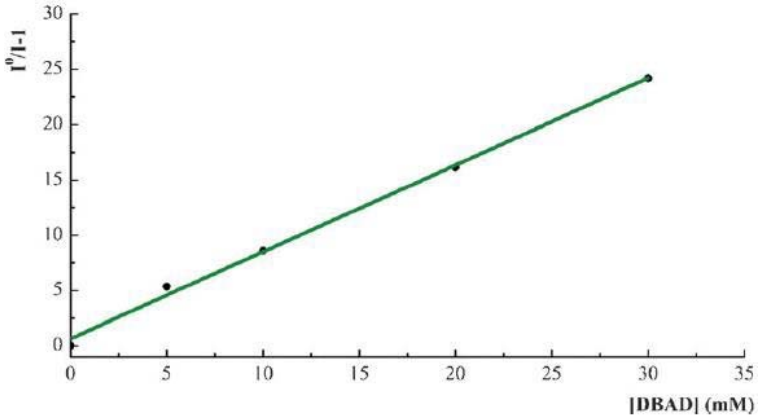
应用

- 机理实验

- **UV-Vis spectra**



- **Stern-Volmer experments**



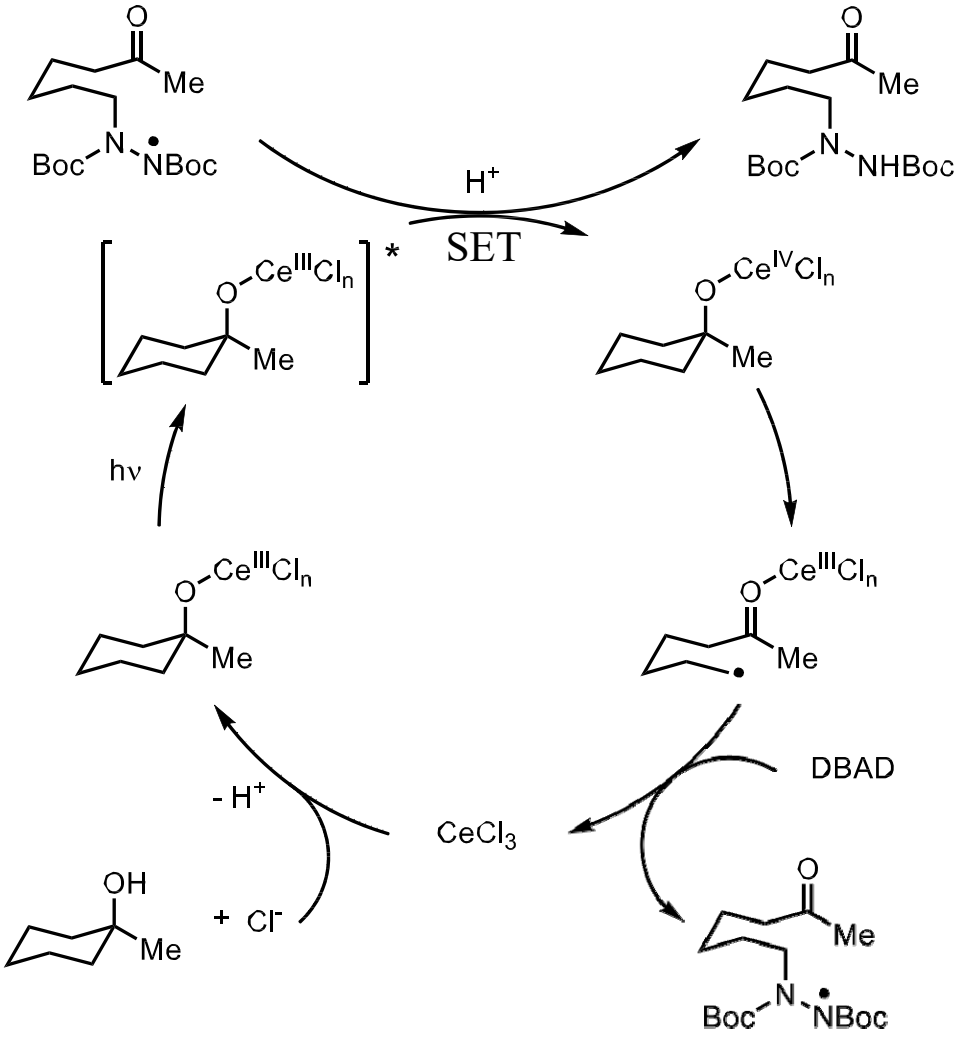
Cl⁻诱导的吸收增强可以导致更有效地光激发，从而增强催化效率

三氯化铈/醇配合物: $E_{1/2}$ (Ce^{IV}/*Ce^{III})= -2.2 V (vs SCE)
DBAD: $E_{1/2}^{red}$= -0.7 V (vs SCE)，可以进行单电子转移

Zuo, Z. and co- authors *Angew. Chem. Int. Ed.* **2016**, *55*, 15319.

应用

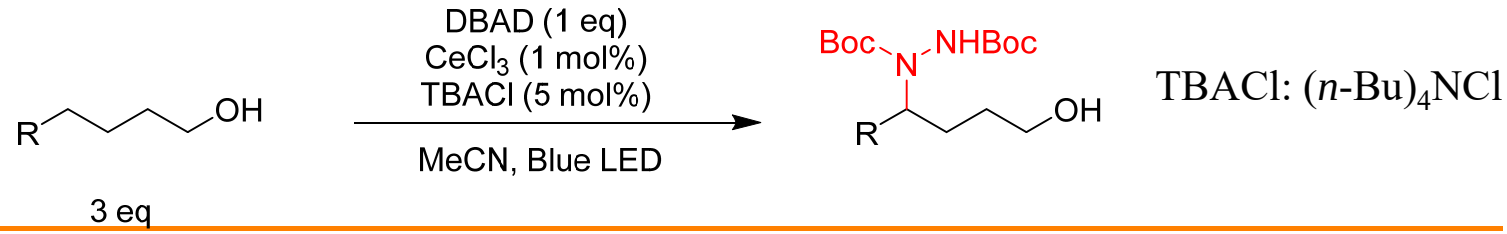
- 可能的机理

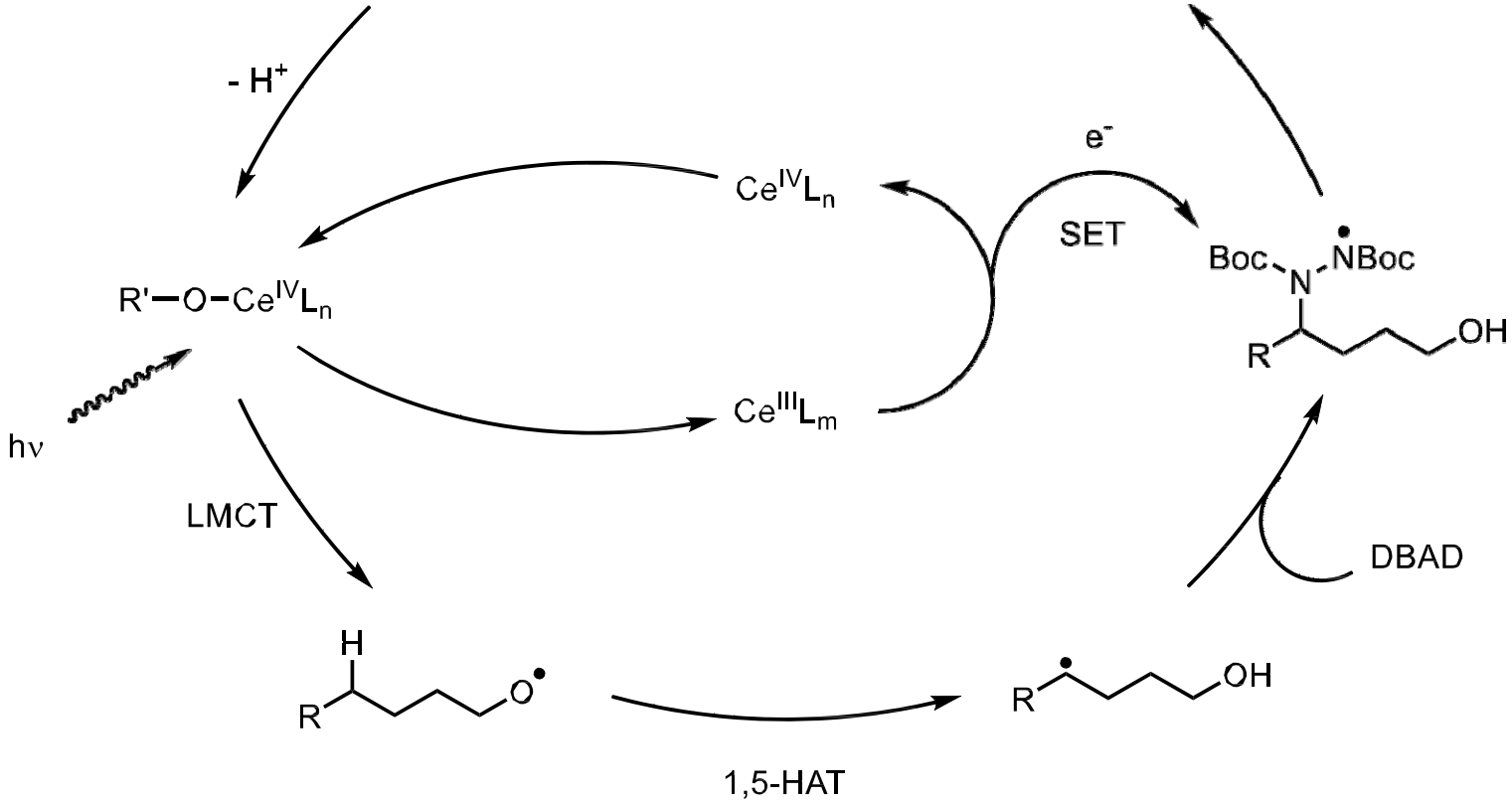


Zuo, Z. and co- authors *Angew. Chem. Int. Ed.* **2016**, *55*, 15319.

应用

- 伯醇的C-H键胺化反应

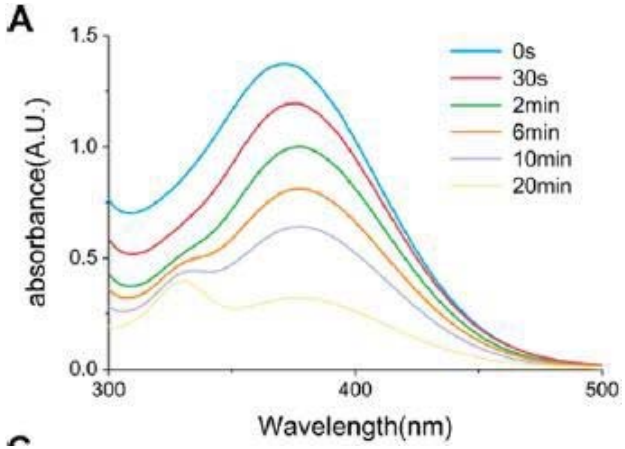




Zuo, Z. and co-authors *J. Am. Chem. Soc.* **2018**, *140*, 1612.

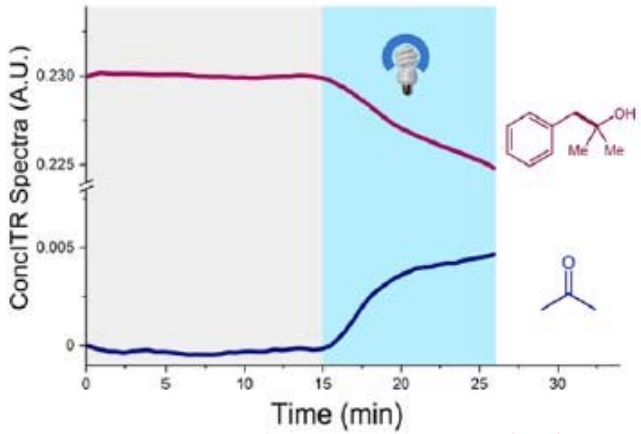
应用

- 机理实验
  - UV-Vis spectra of $Ce^{IV}(OC_5H_{11})Cl_n$

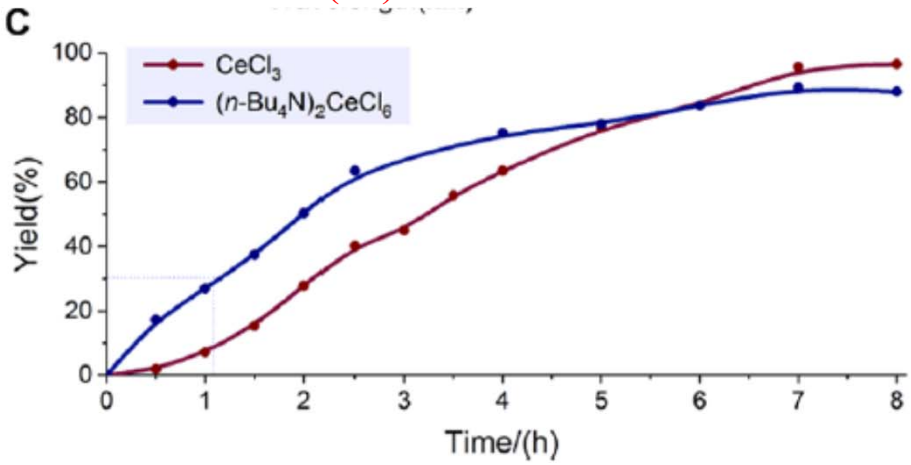


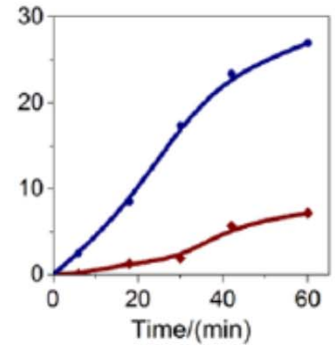
- 吸收峰的位移证明了Ce(III)的生成

  - Operando IR experiments



- 基态单电子转移不发生



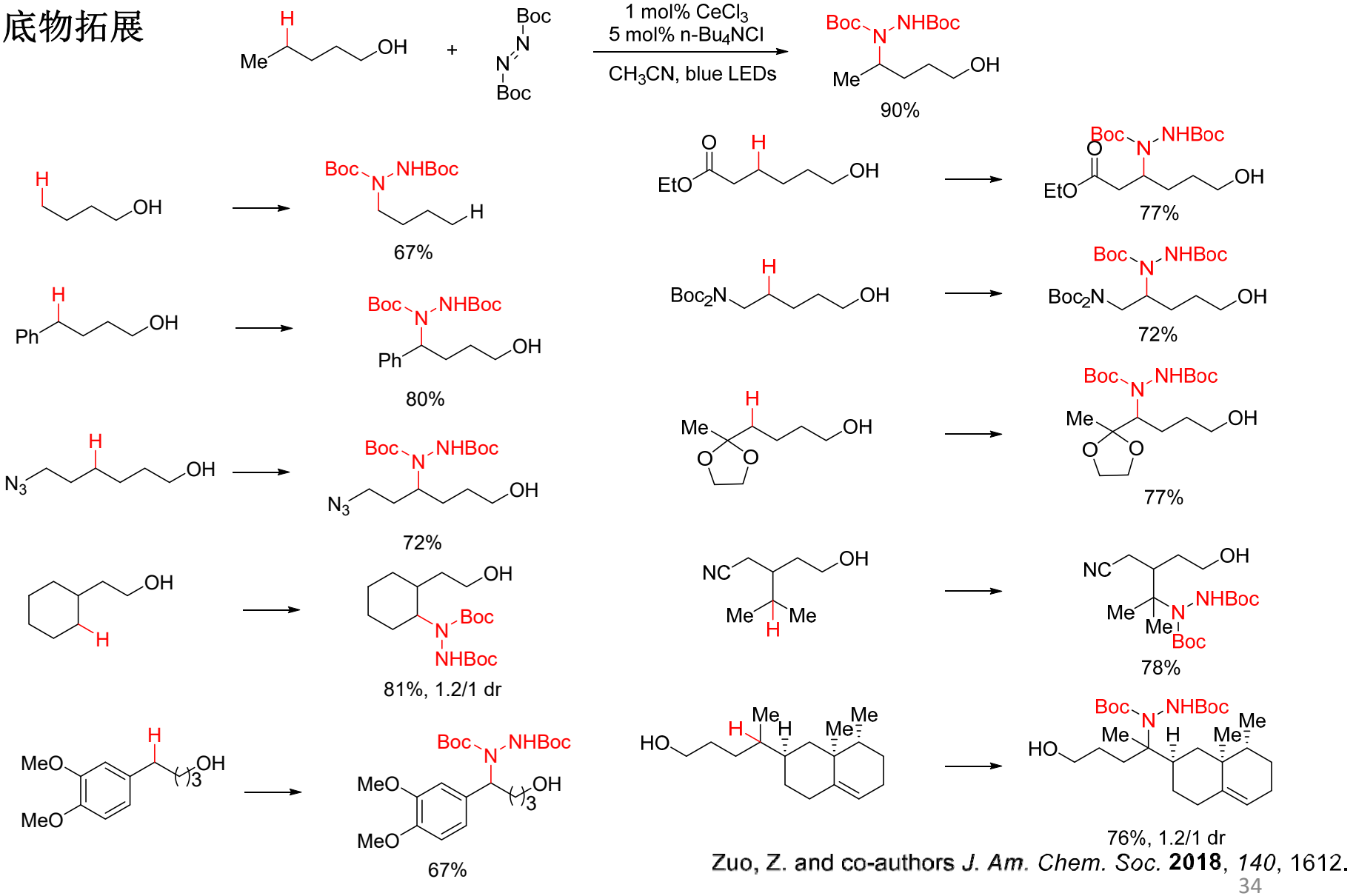


- $CeCl_3$作为催化剂前体会发生官能团化

Zuo, Z. and co-authors *J. Am. Chem. Soc.* **2018**, *140*, 1612.

应用

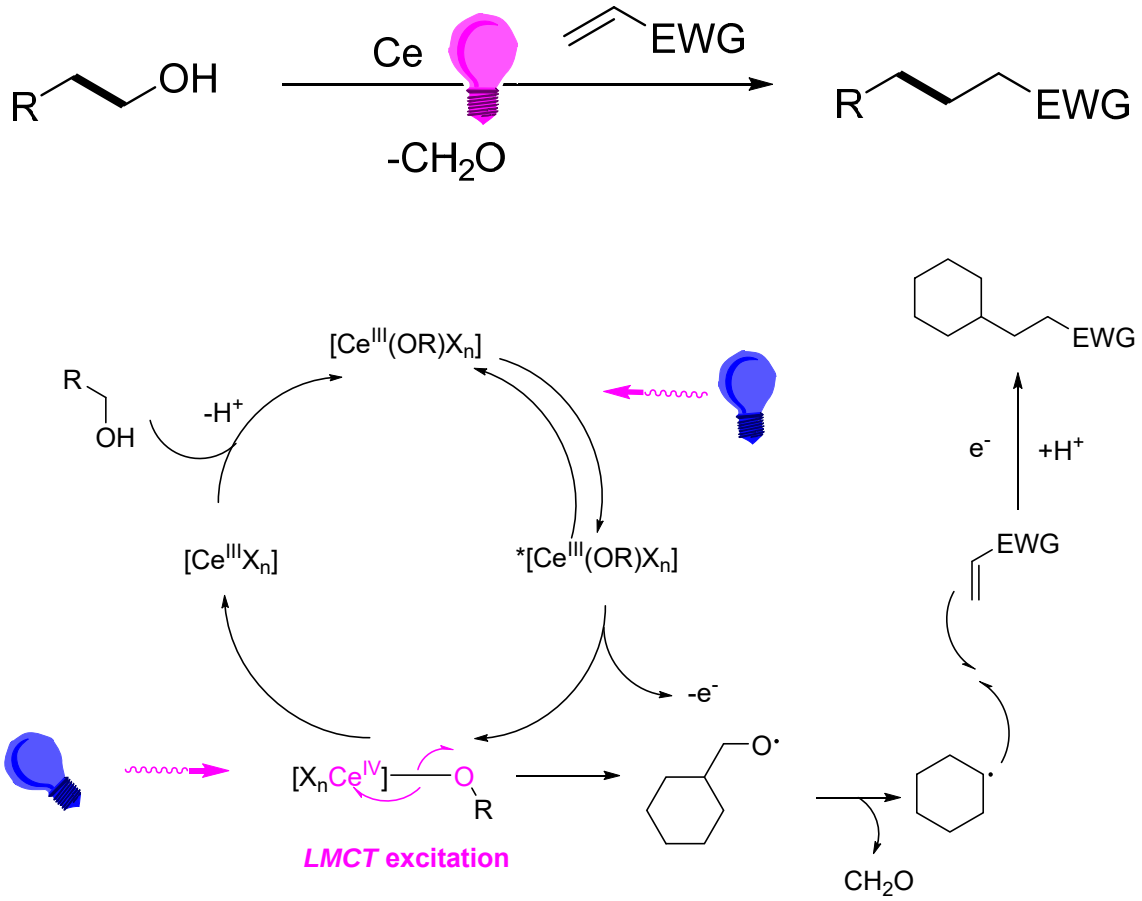
- 底物拓展



Zuo, Z. and co-authors *J. Am. Chem. Soc.* **2018**, *140*, 1612.

应用

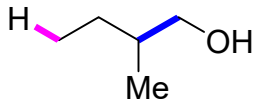
- 伯醇的脱羟甲基化反应



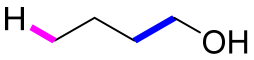
Zuo, Z. and co-authors *J. Am. Chem. Soc.* **2019**, *141*, 10556.

应用

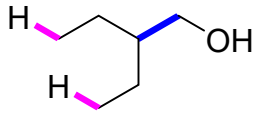
- 伯醇的脱羟甲基化反应



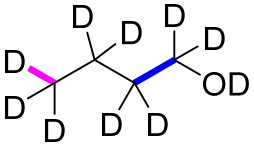
88% : 0%



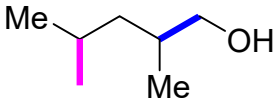
30% : 6%



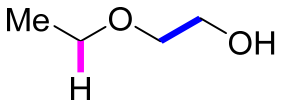
90% : 0%



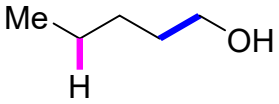
52% : 0%



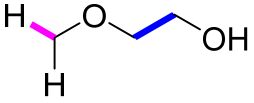
89% : 0%



66% : 4%



20% : 17%



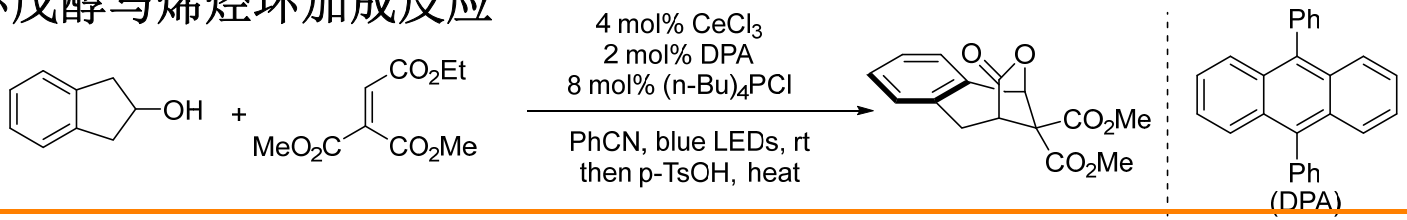
81% : 0%

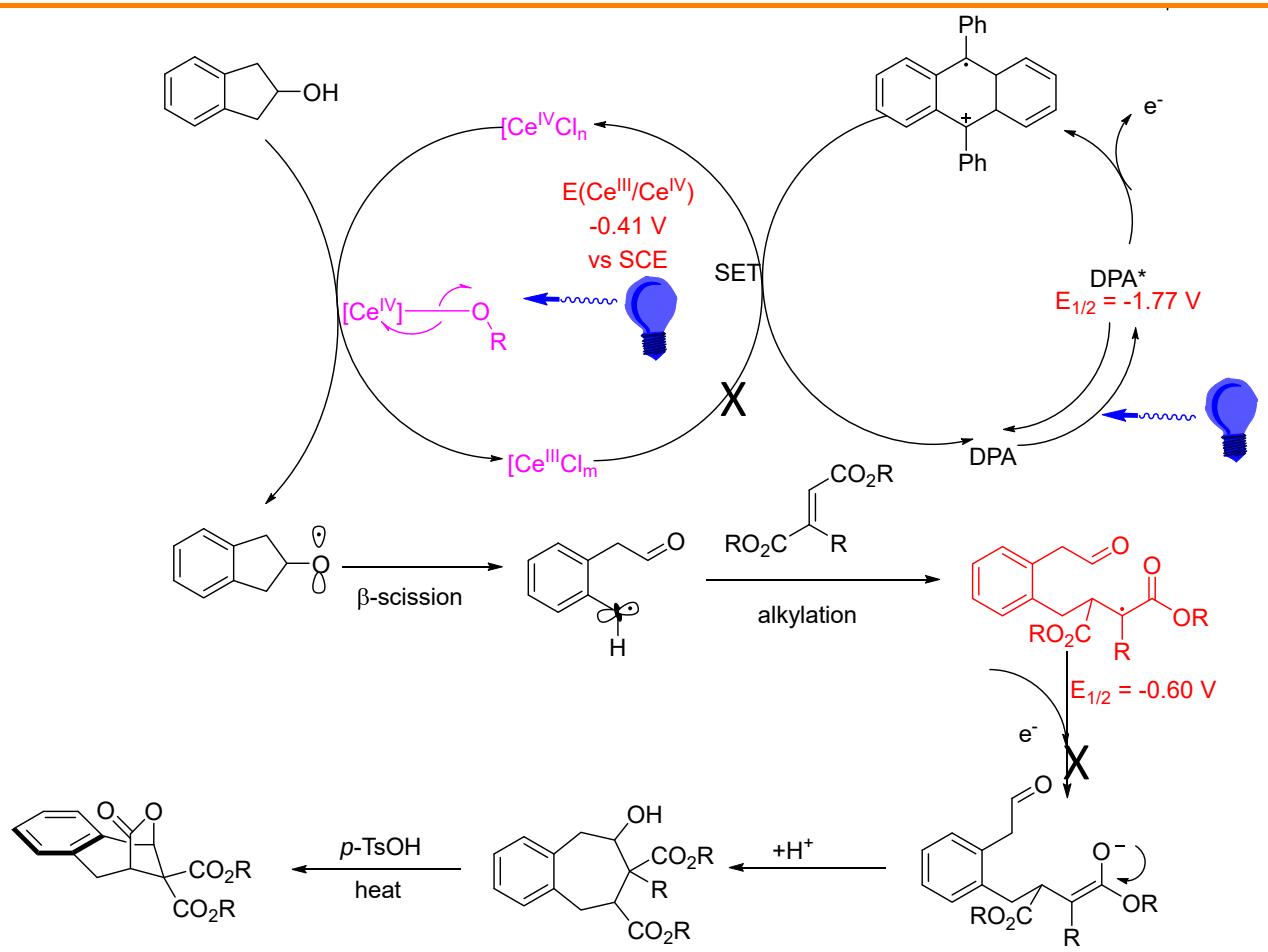
Conditions: 5 mol% $CeCl_3$, 3.0 eq $(n\text{-}Bu)_4NBr$, CH_3CN, LED light, rt, 12 h.

Zuo, Z. and co-authors *J. Am. Chem. Soc.* **2019**, *141*, 10556.

应用

- 双重激发环戊醇与烯烃环加成反应

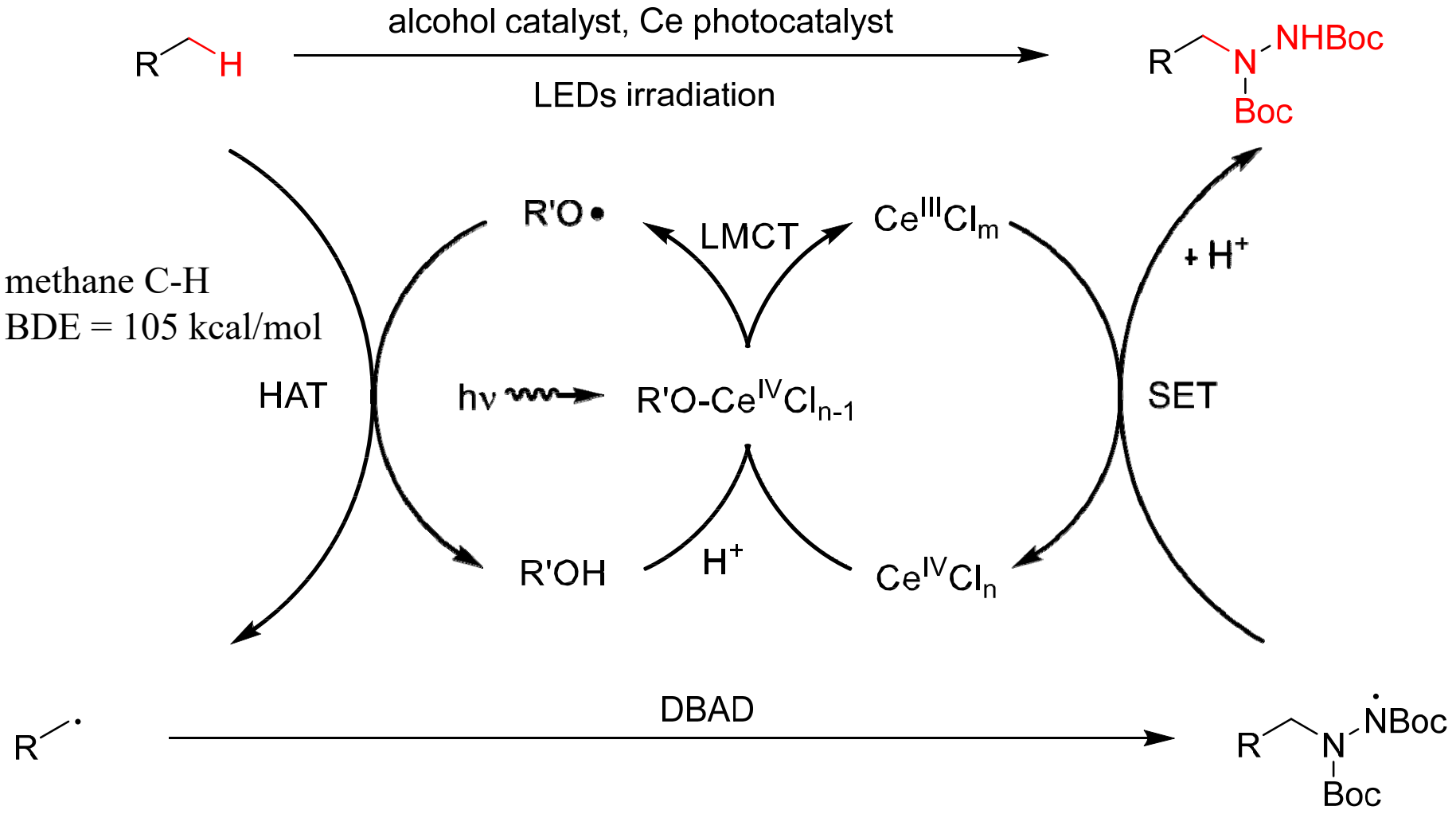




Zuo, Z. and co-authors *J. Am. Chem. Soc.* **2018**, *140*, 13580.

应用

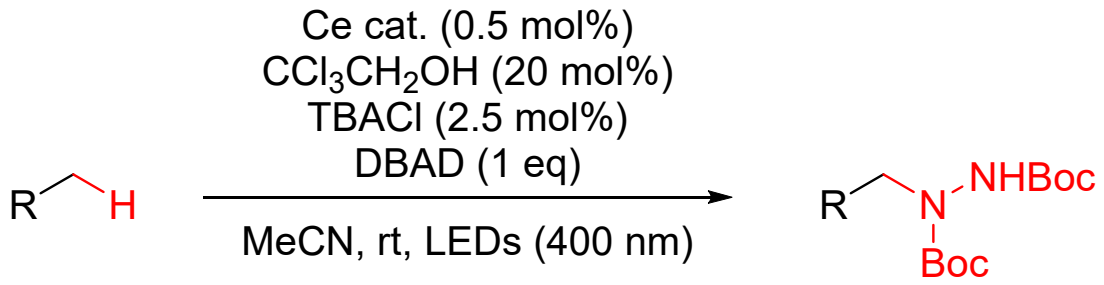
- 甲烷乙烷及其他烷烃的直接官能团化



Zuo, Z. and co-authors *Science* **2018**, *361*, 668.

应用

- 烷烃的胺化



Entry	alkane	Ce cat.	time	yield
1	methane (5000 kPa)	$(TBA)_2CeCl_6$	2 h	63%
2	ethane (101 kPa)	$CeCl_3$ (0.01 mol%)	4 h	97%
3	propane (101 kPa)	$CeCl_3$	9 h	70% (1/1 rr)
4	butane (101 kPa)	$CeCl_3$	6 h	76% (1/1.7 rr)
5	cyclohexane	$CeCl_3$	16 h	81%

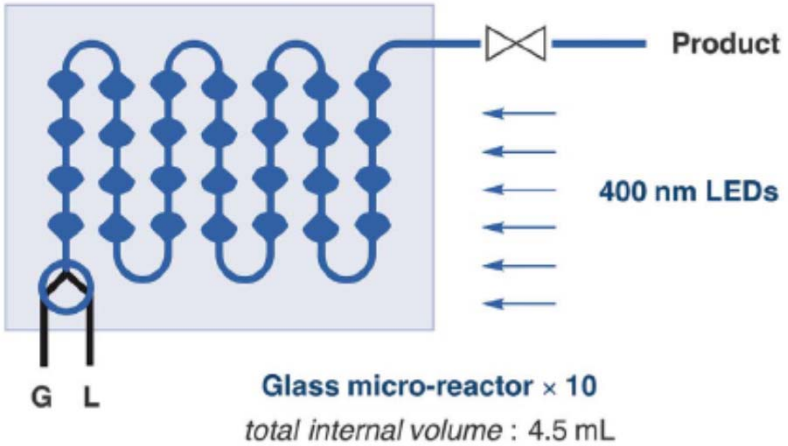
Zuo, Z. and co-authors *Science* **2018**, *361*, 668.

应用

- 放大反应

Gas input (G)
compressed gaseous alkane

Liquid input (L)
$(n\text{-}Bu_4N)_2CeCl_6$ (42 mg, 1 mol%)
CCl_3CH_2OH (149 mg, 20 mol%)
DBAD (1.15g, 5 mmol)
CH_3CN (100 ml)

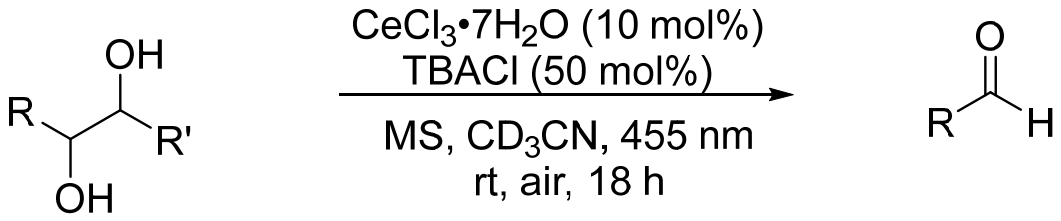


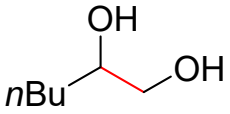
entry	Alkane	Flow rate	Residence time	yield (%)	productivity
1	methane (1800 kPa)	0.3 ml/min	15 min	15	0.6 mmol/d
2	ethane (1500 kPa)	0.75 ml/min	6 min	90	2.0 mmol/h
3	propane (800 kPa)	0.75 ml/min	6 min	76	1.7 mmol/h
4	butane (400 kPa)	0.75 ml/min	6 min	56	1.3 mmol/h
5	cyclohexane (22 ml)	0.5 ml/min	9 min	70	4.2mmol/h

Zuo, Z. and co-authors *Science* **2018**, *361*, 668.

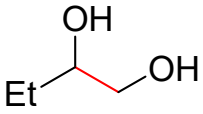
应用

- 光催化**1,2-**二醇的氧化断裂反应

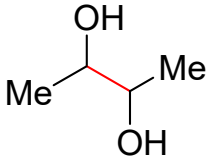




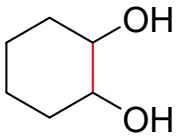
79%



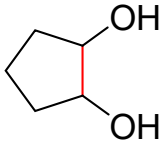
78%



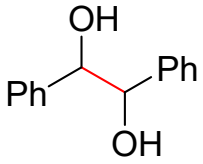
95%



cis: 57%
trans: 69%



cis: 66%
trans: 69%



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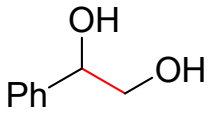

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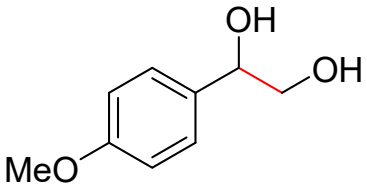

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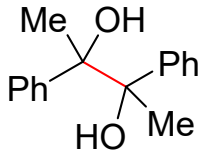
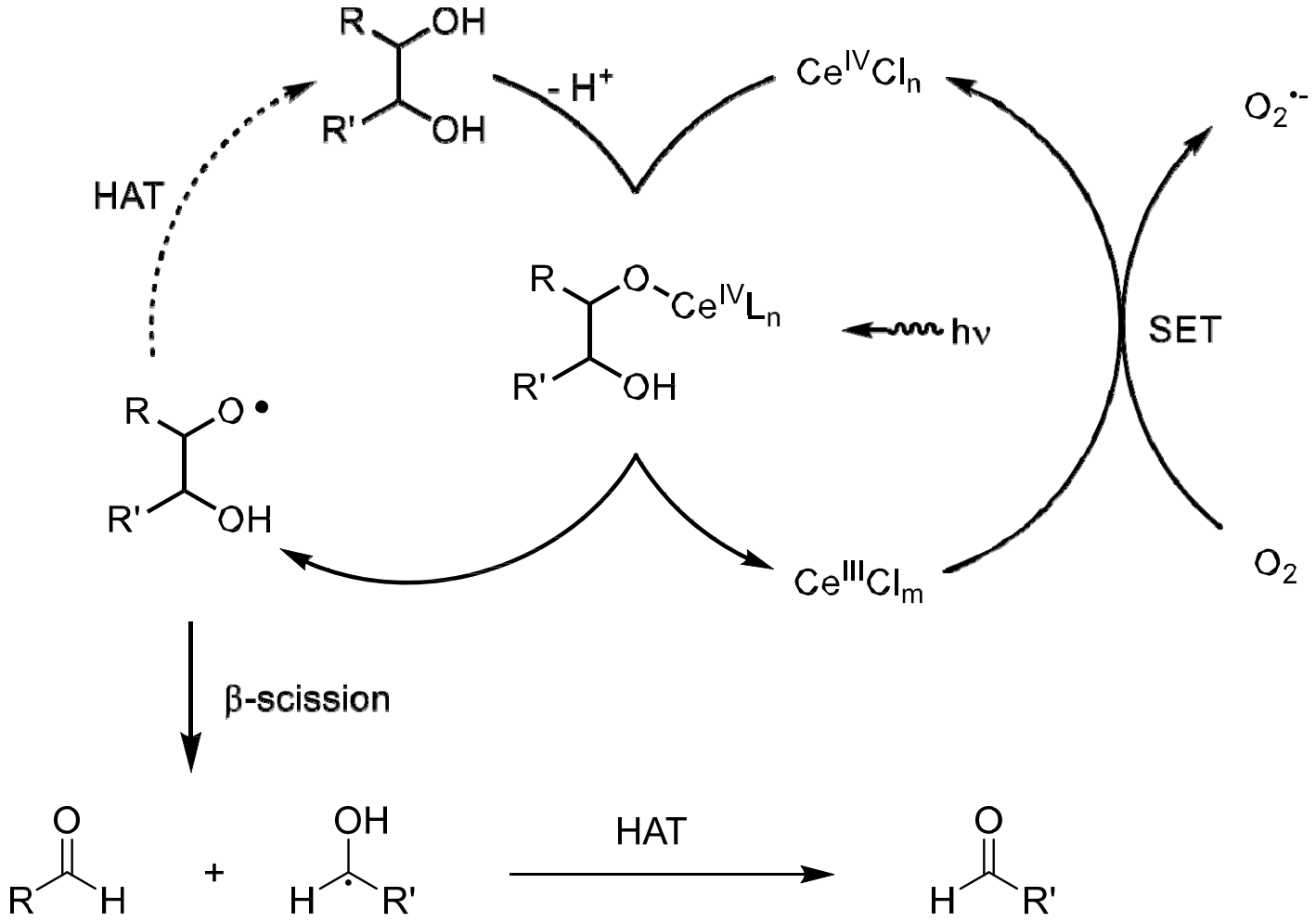


86%

König, B. and co-authors *Chem. Commun.*, **2019**, *55*, 486.

应用

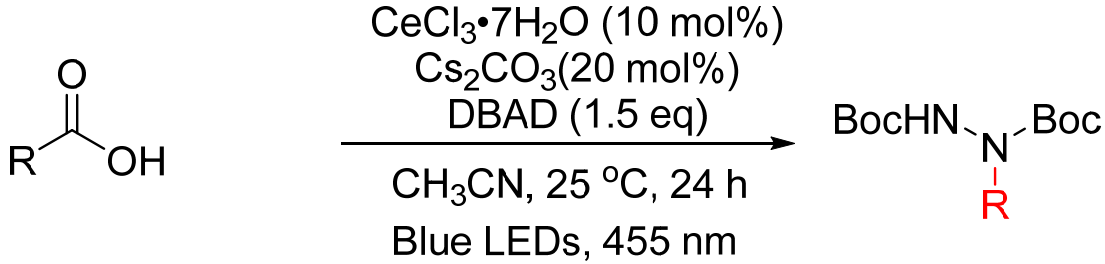
- 可能的机理

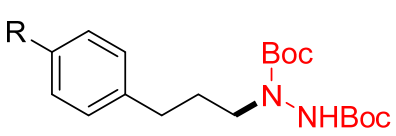


König, B. and co-authors *Chem. Commun.* **2019**, *55*, 486.

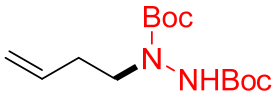
应用

- 羧酸的脱羧胺化反应

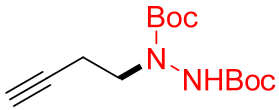




R= OMe, 80%
R= H, 54%
R= CN, 57%
R= Br, 51%
R= CO_2Et, 59%



60%



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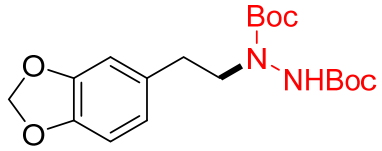

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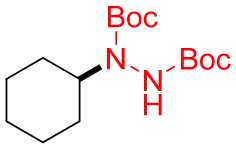

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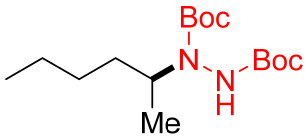

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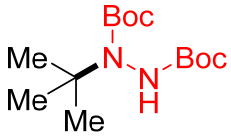
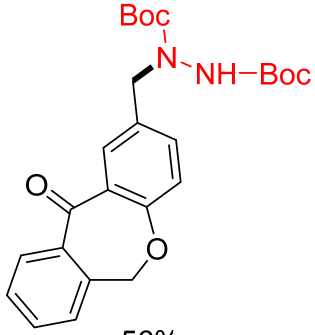


90%



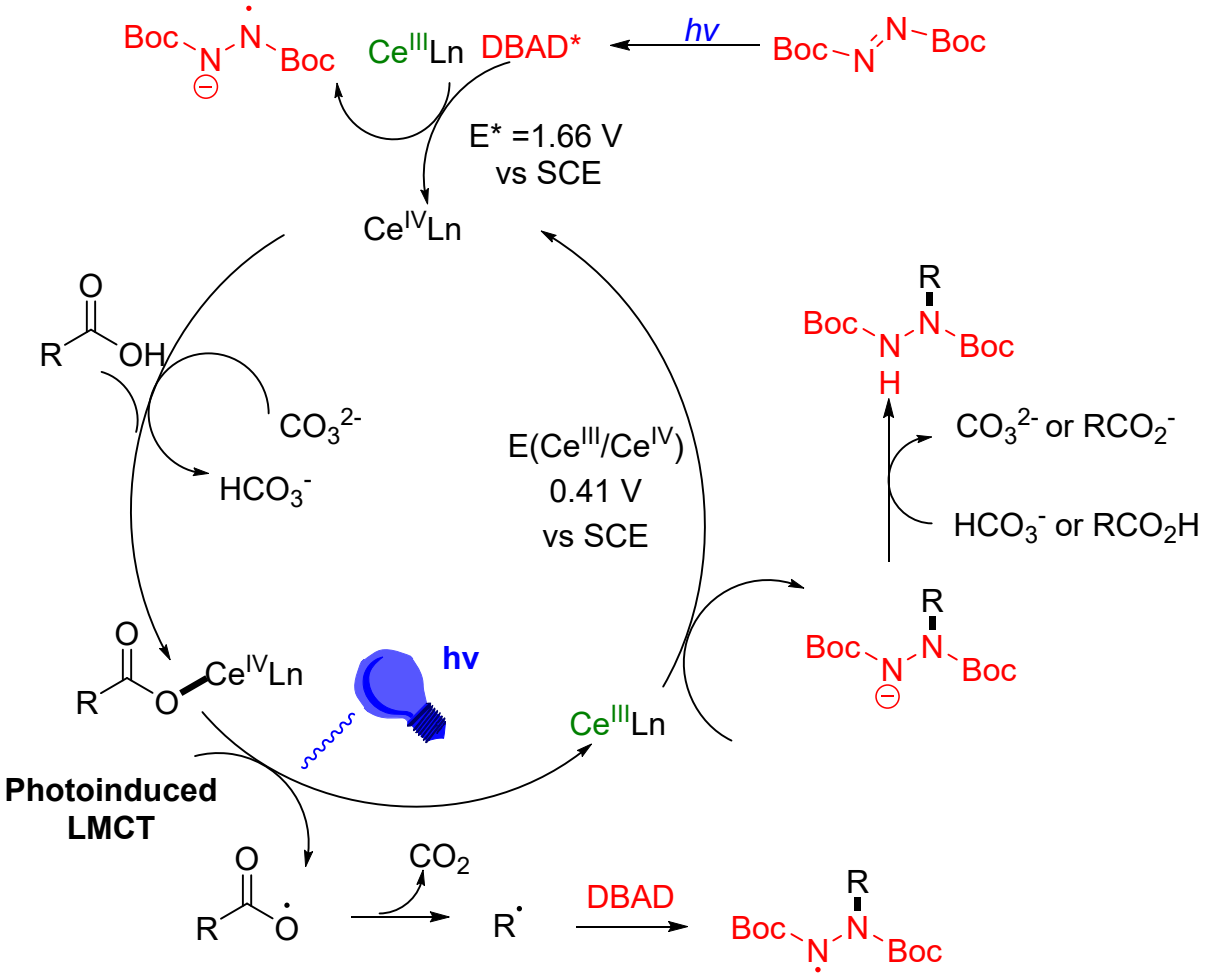
56%

from isoxepac

König, B. and co-authors *Chem. Commun.* **2019**, *55*, 3489.

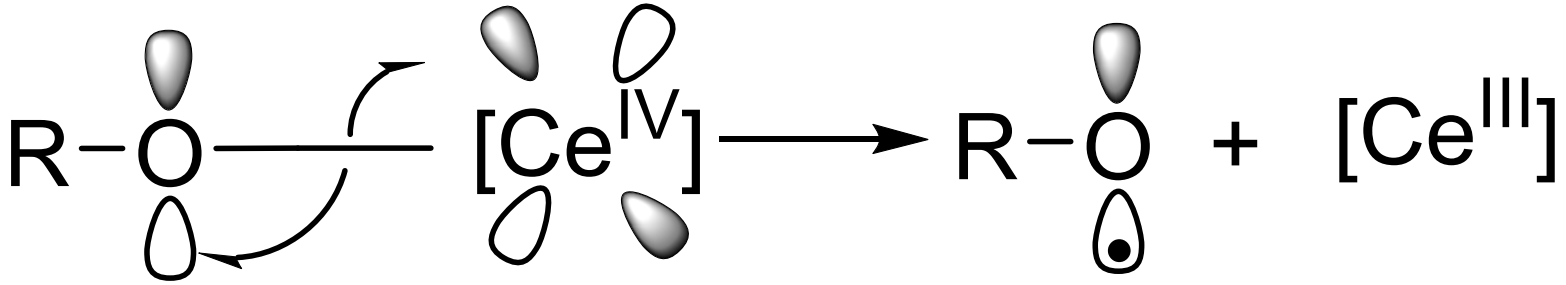
应用

- 可能的机理



König, B. and co-authors *Chem. Commun.* **2019**, *55*, 3489.

小结



总结

- 地球上储量大，价格便宜

- 近年来对金属铈物理化学性质的研究，促进了其在有机催化上的应用

- 与传统过渡金属催化的模式相比，铈催化的光反应会经历不同的过程

Thanks for your attention