Cerium Photocatalysis

Literature seminar #2

M1 Shun Tanabe

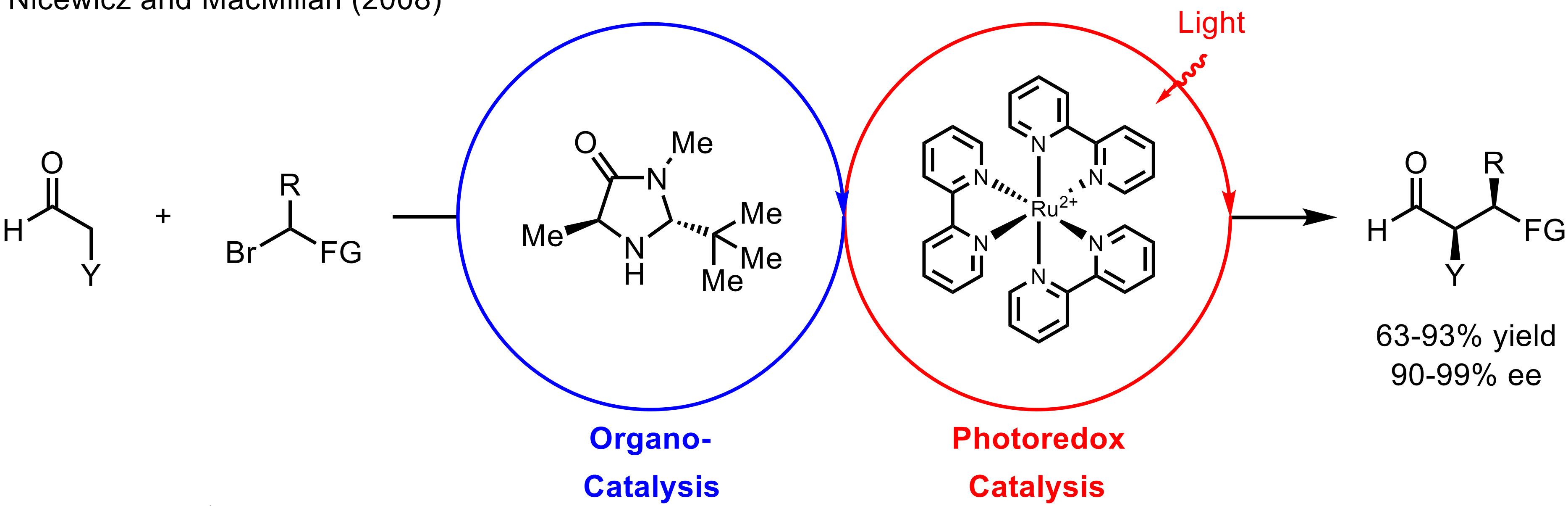
2019/5/9

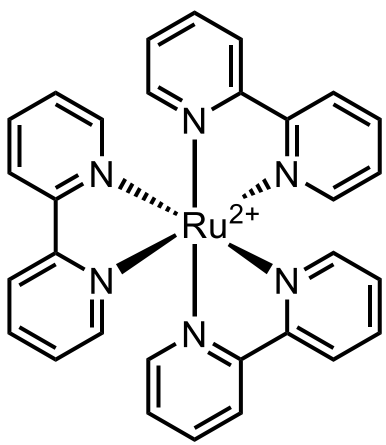
Contents

Introduction

- **Photoredox catalysis is a powerful tool for activation of molecules**

- Nicewicz and MacMillan (2008)





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

- Visible light absorption
- Long-lived excited state
- Potent SET catalyst

Chem. Rev. **2013**, *113*, 5322.

Nicewicz, D. A.; MacMillan, D. W. C. *Science*, **2008**, *322*, 77.

Introduction

- **Photochemistry of Ce(III)**

Ce(III)

- 4f $\rightarrow$ 5d transitions
- ~ns lifetimes
- broad absorption and emission bands

(other Ln(III): parity-forbidden 4f $\rightarrow$ 4f transitions)

Qiao, Y.; Schelter, E. J. *Acc. Chem. Res.* **2018**, *51*, 2926.

Introduction

- **Differences between cerium photocatalysis and transition-metal photocatalysis**

Ru Ir

- expensive
- SET catalysis

Ce

- earth-abundant
- **unique reactivities**

Chem. Rev. **2013**, *113*, 5322.

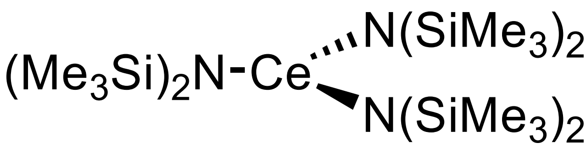
Qiao, Y.; Schelter, E. J. *Acc. Chem. Res.* **2018**, *51*, 2926.

Recent deveropement of cerium photocatalysis

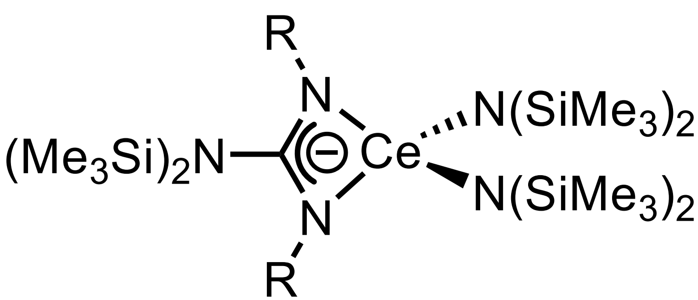
Ce(III) guanidinate-amide complexes

Ce(III) guanidinate-amide complexes

- **Photophysical properties of Ce(III) guanidinate-amide complexes**

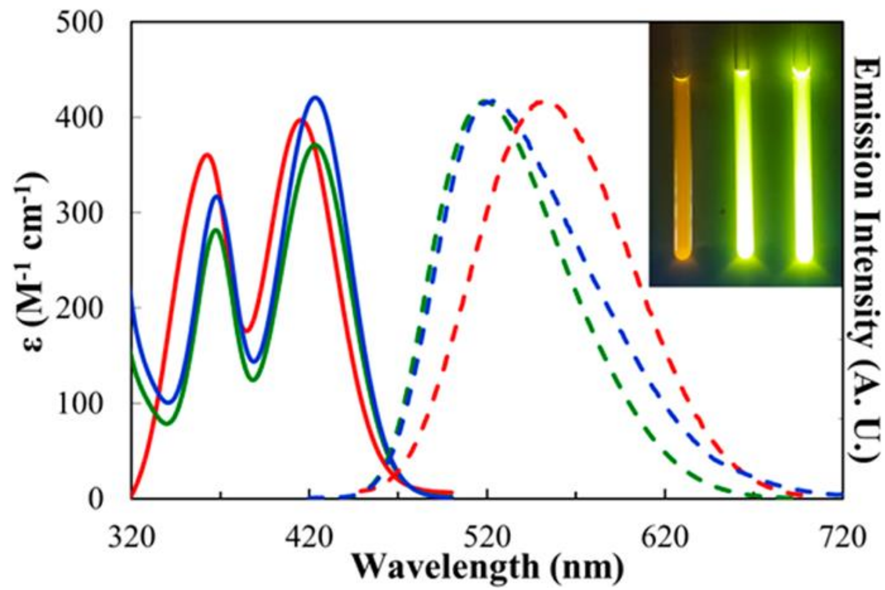


1 $\Phi_{PL} = 0.03$, $\tau = 24$ ns



R = *i*Pr: 1-*i*Pr $\Phi_{PL} = 0.46$, $\tau = 67$ ns

R = Cy: 1-Cy $\Phi_{PL} = 0.54$, $\tau = 61$ ns

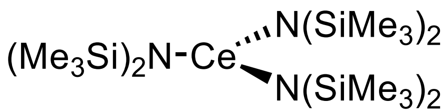


solid: absorption, dashed: emission
left: 1, middle: 1-*i*Pr, right: 1-Cy

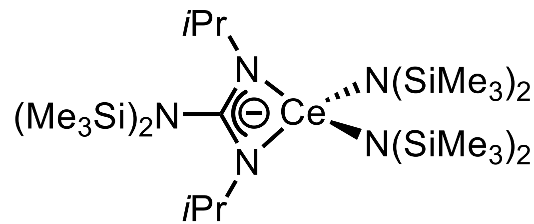
Anna, J. M.; Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2015**, *137*, 9234.

Ce(III) guanidinate-amide complexes

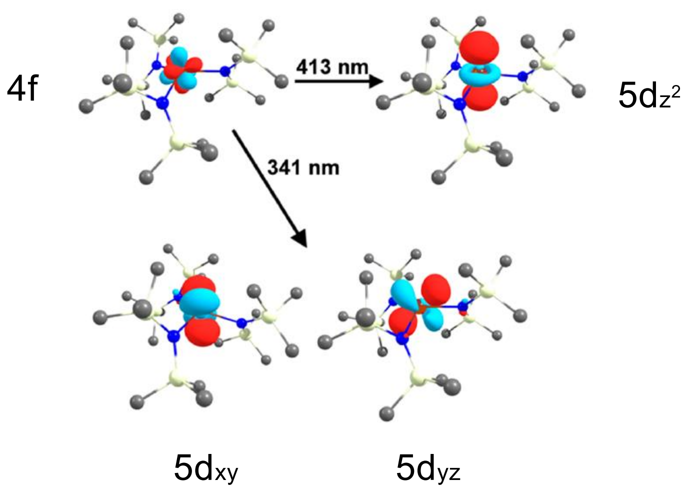
- **Photophysical properties of Ce(III) guanidinate-amide complexes**

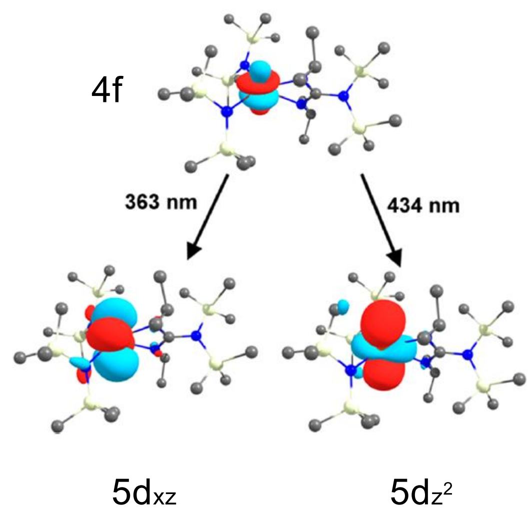


1



1-*i*Pr



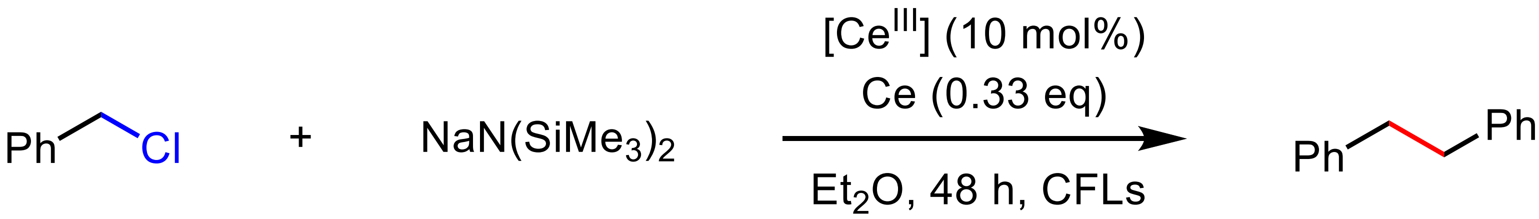


~420 nm absorption → from ground states of primarily 4f character to $5d_{z^2}$ orbital-based excited states

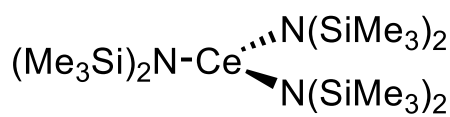
Anna, J. M.; Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2015**, *137*, 9234.

Ce(III) guanidinate-amide complexes

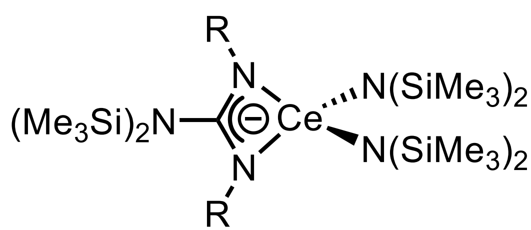
- **$PhCH_2Cl$ coupling reactions**



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



1 Φ_{PL} = 0.03, τ = 24 ns



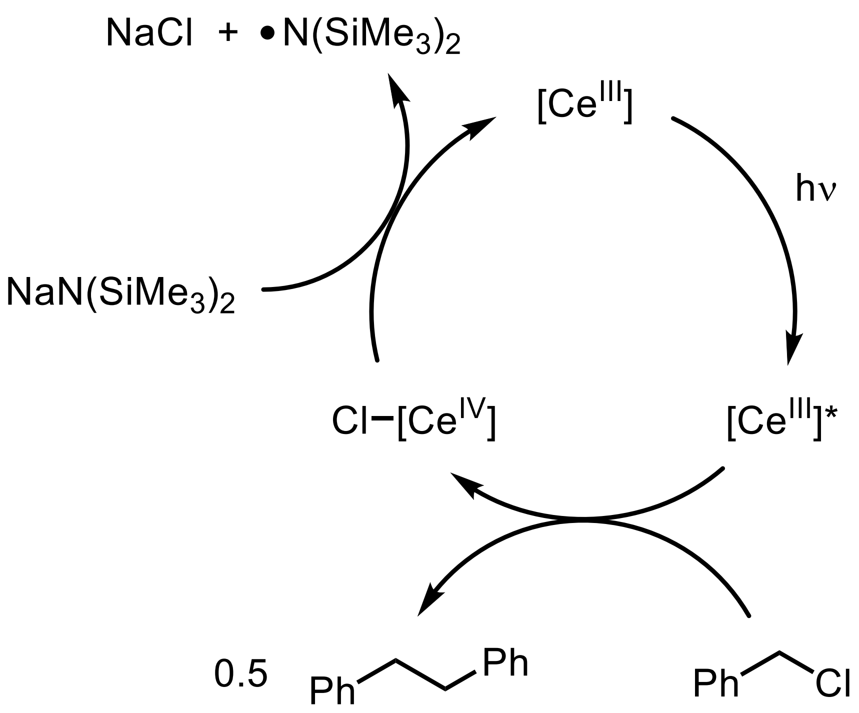
R = *i*Pr: 1-*i*Pr Φ_{PL} = 0.46, τ = 67 ns

R = Cy: 1-Cy Φ_{PL} = 0.54, τ = 61 ns

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

Ce(III) guanidinate-amide complexes

- **Proposed catalytic cycle**



- Estimated reduction potential for Ce(III) excited states

entry	$[Ce^{III}]$	$E_{1/2}$* (eV)
1	1	-1.84
2	1-*i*Pr	-2.36
3	1-Cy	-2.24

- $PhCH_2Cl$: E_{pc} = -2.66 V
- $[Ce^{IV}]$-Cl formation (by 1H NMR)

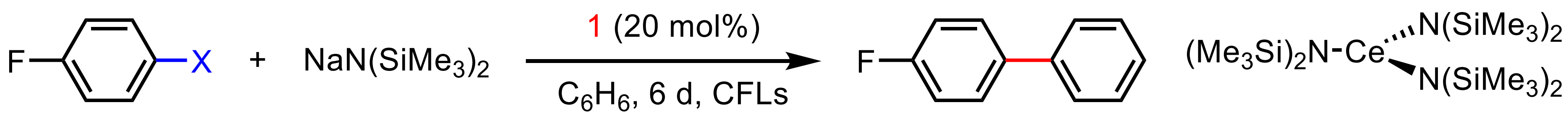
- Inner sphere SET (photoinduced halogen abstraction) pathway

→ The Ce(IV)-Cl bond formation enthalpy would drive the C(*sp*^{3})-Cl bond activation.

Qiao, Y.; Schelter, E. J. *Acc. Chem. Res.* **2018**, *51*, 2926.
Anna, J. M.; Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2015**, *137*, 9234.

Ce(III) guanidinate-amide complexes

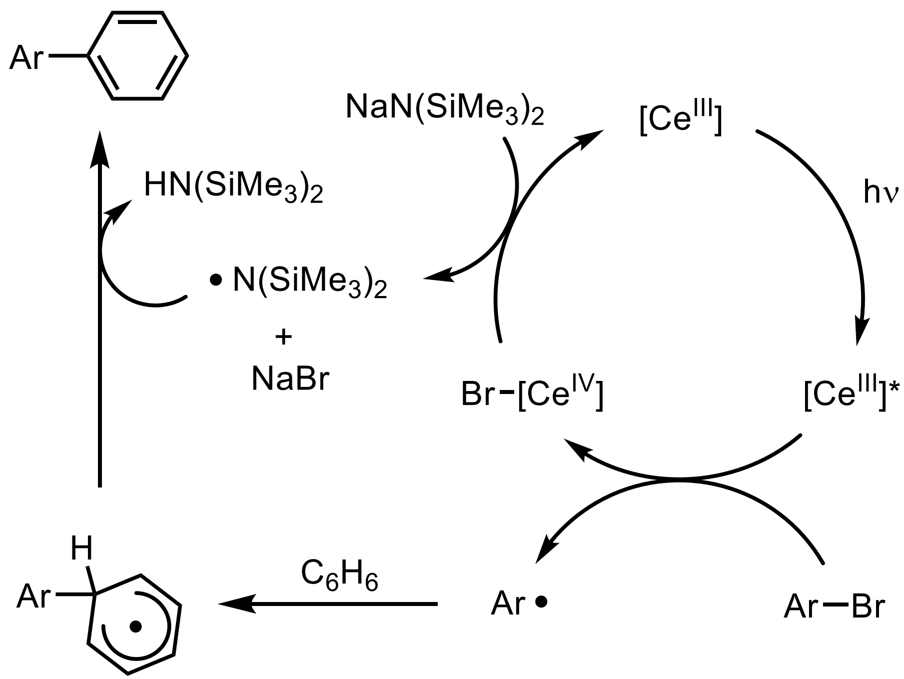
- **Arylations of benzene**



1

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

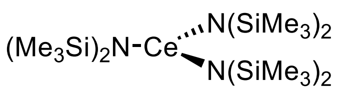
- Proposed catalytic cycle



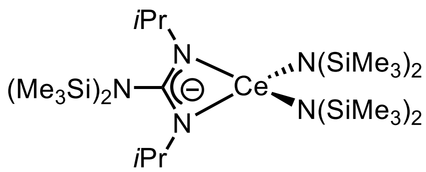
Qiao, Y.; Schelter, E. J. *Acc. Chem. Res.* **2018**, *51*, 2926.
Anna, J. M.; Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2015**, *137*, 9234.

Ce(III) guanidinate-amide complexes

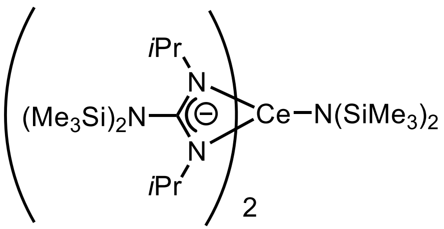
- **Structure-property rerationships**



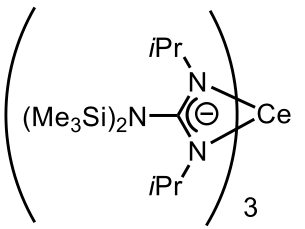
1-N



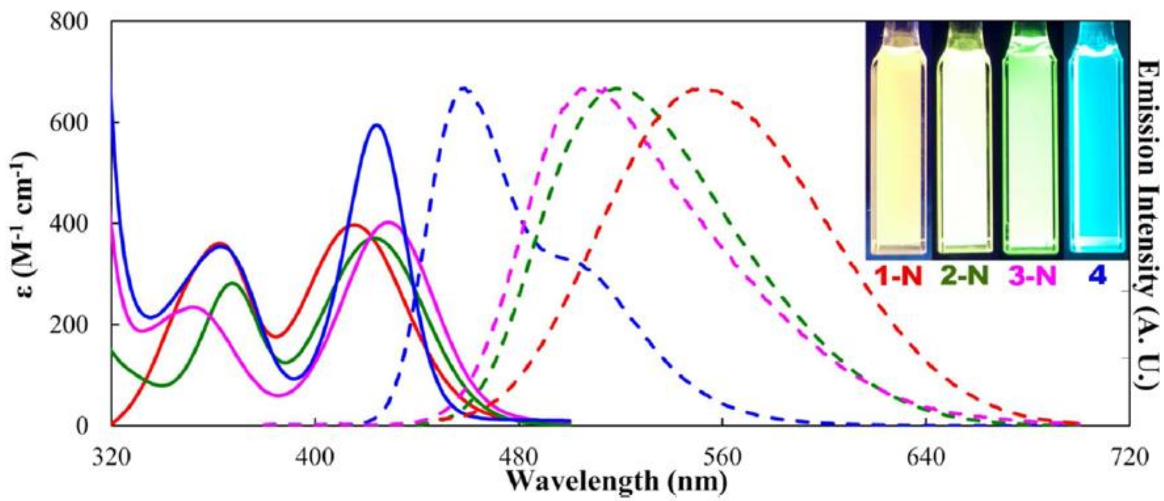
2-N



3-N



4



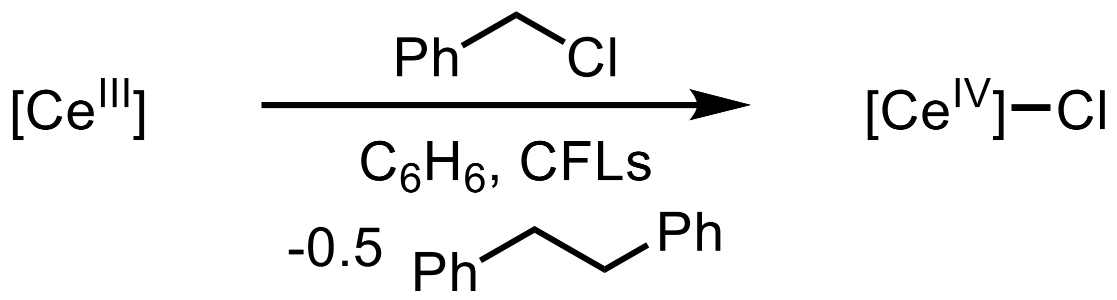
entry	$[Ce^{III}]$	Φ_{PL}	τ
1	1-N	0.03	24 ns
2	2-N	0.46	65 ns
3	3-N	0.79	117 ns
4	4	0.81	83 ns

- Emission colors of cerium complexes were determined by the ligand types and the rigidity of the structure.

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

Ce(III) guanidinate-amide complexes

- **Reactivity**



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

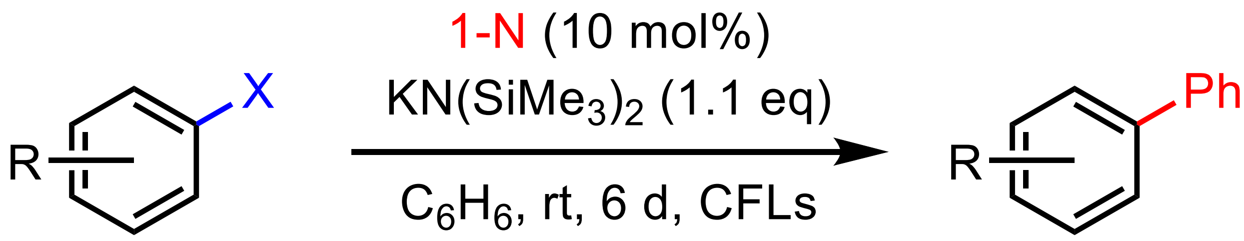
- Lack of reactivity for 3-N and 4

→ The steric congestion around Ce^{3+} cations is unfavorable for the substrate association in their excited states.

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

Ce(III) guanidinate-amide complexes

- **Further investigation for inner sphere SET mechanism**

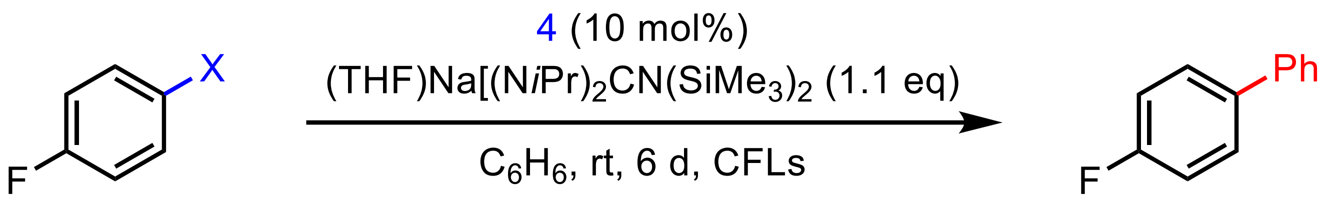


entry	X	R	conversion (%)	Yield (%)	entry	X	R	conversion (%)	Yield (%)
1	Br	4-Me	92	76	6	I	H	>99	85
2	Br	H	80	72	7	I	4-F	>99	91
3	Br	4-F	69	32	8	I	2-F	>99	87
4	Br	2-F	>99	86	9	I	3-Me	>99	88
5	I	4-Me	>99	76	10	I	2-Me	>99	23

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

Ce(III) guanidinate-amide complexes

- **Further investigation for inner sphere SET mechanism**



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

- Mechanistic insights from other experiments

  - Complex 4 was incapable of associating a Cl^- anion.

  - The isolation of $[4^+][BAr^F_4]$

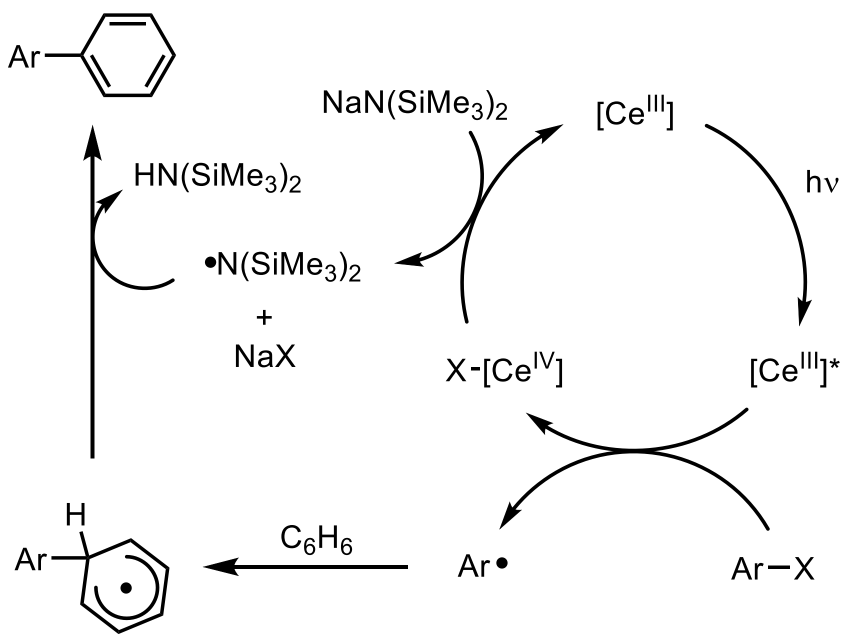
  → Outer sphere SET mechanism is a viable process.

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

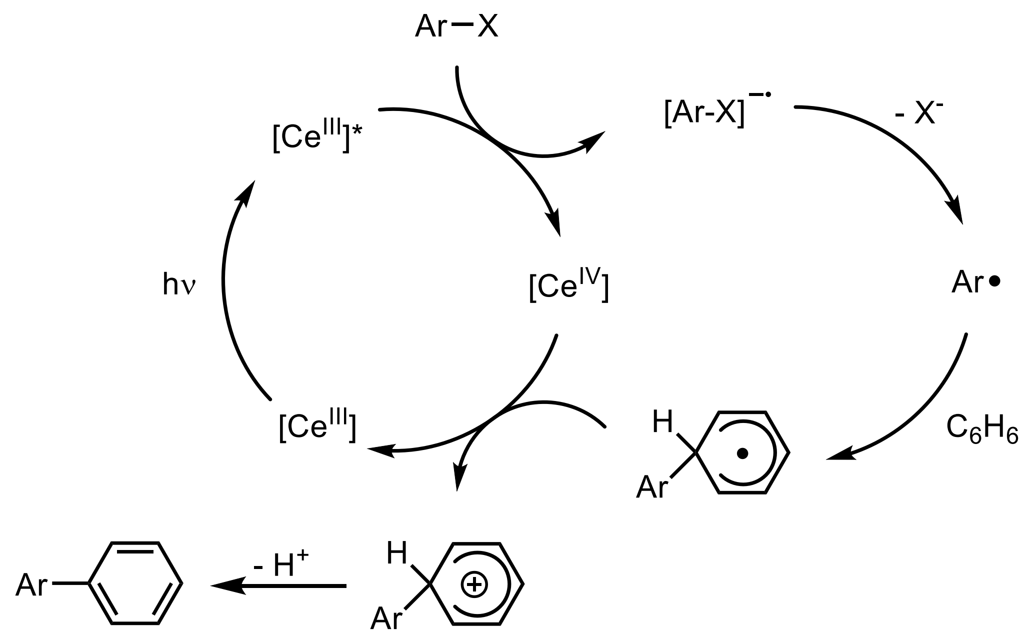
Ce(III) guanidinate-amide complexes

- **Proposed catalytic cycle**

- Inner sphere SET pathway with 1-N

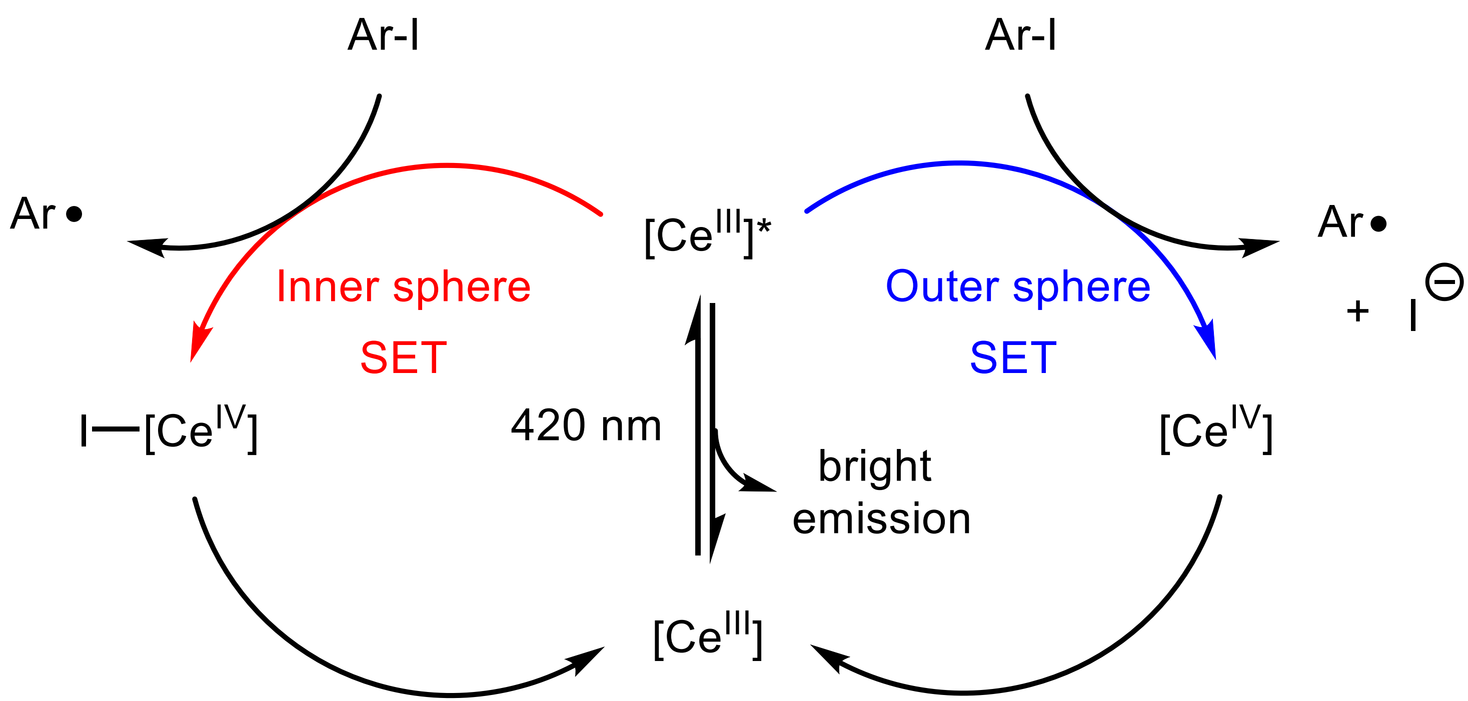


- Outer sphere SET pathway with 4



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

Short Summary



Drawbacks

- UV ~ visible light absorption (4f→5d)
- Inner sphere SET and outer sphere SET

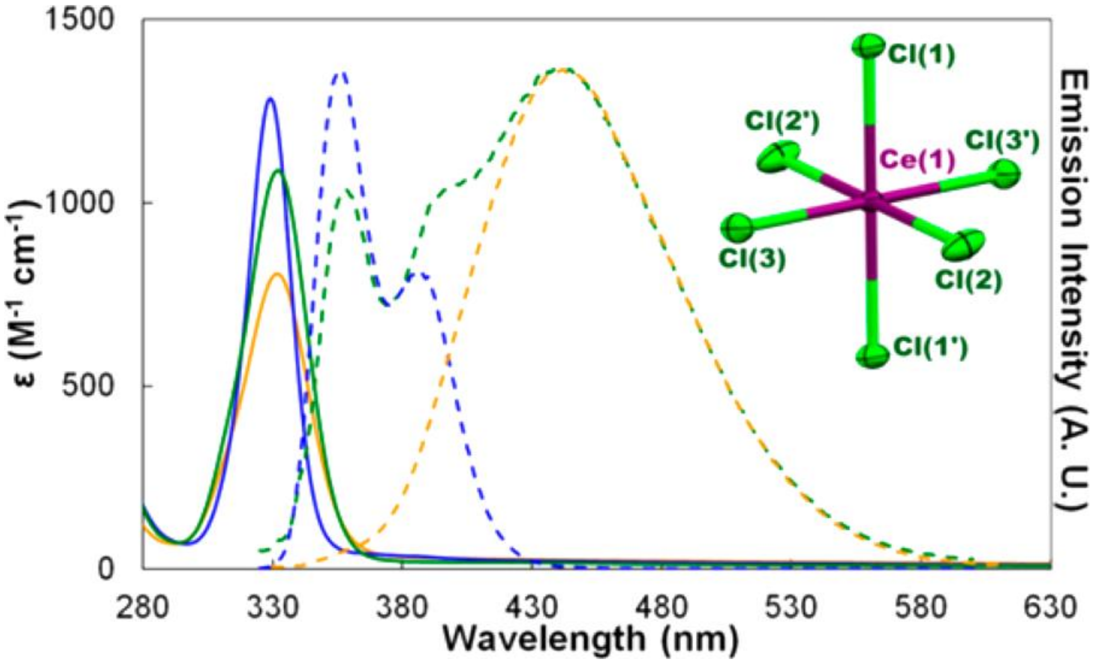
- Strong basic ligands
- Air and moisture sensitive

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

Hexachlorocerate(III) anion

Hexachlorocerate(III) anion

- **Photophysical properties of $CeCl_6^{3-}$ anion**



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: $[NEt_4]_3[Ce_2Cl_9]$

- UVA photoreductant

  λ_{ex} = 329 nm: interconfigurational transition

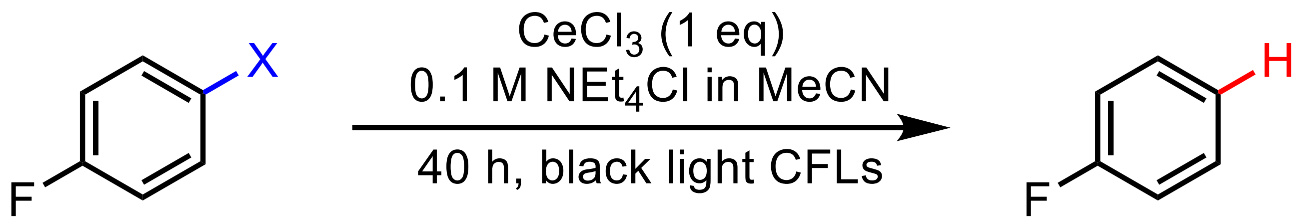
  4f $\rightarrow$ Ce-Cl π-anti bonding orbitals
  with predominant Ce^{III} $5d_{xy}$, $5d_{yz}$ and $5d_{xz}$ character

- Φ_{PL} = 0.61, τ = 22.1 ns

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

Hexachlorocerate(III) anion

- **Reductive dehalogenation of aryl halides**



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

- Estimated reduction potential of excited $[Ce^{III}Cl_6]^{3-}$: -3.45 V

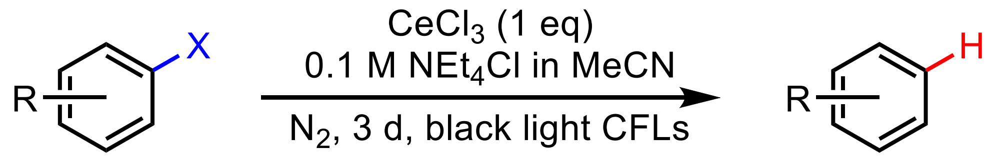
  ($E_{PhCl^{\bullet-}/PhCl}$ = -3.28 V)

- Aryl radical generation was supported by radical trapping experiments.

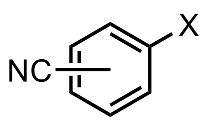
Anna, J. M.; Schelter, E. J. and co-authors *J. Am. Chem. Soc.* **2016**, *138*, 16266.

Hexachlorocerate(III) anion

- **Substrate scope**

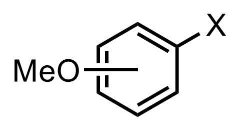


X = Cl, Br



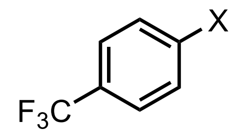
X = Cl: *o*-: 69%, *m*-: 45%, *p*-: 79%

X = Br: *p*-: >95%



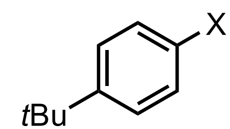
X = Cl: *o*-: 77%, *m*-: 52%, *p*-: 59%

X = Br: *p*-: 64%



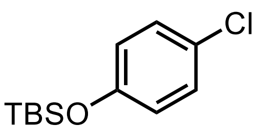
X = Cl: 49%

X = Br: 56%

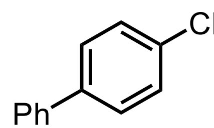


X = Cl: 34%

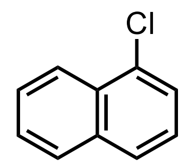
X = Br: 48%



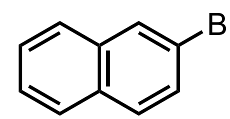
62%



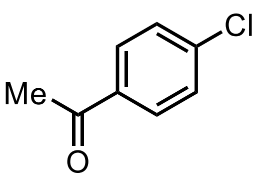
69%



66%



69%



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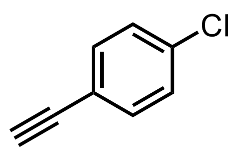

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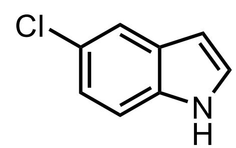

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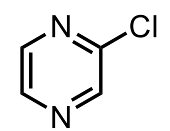
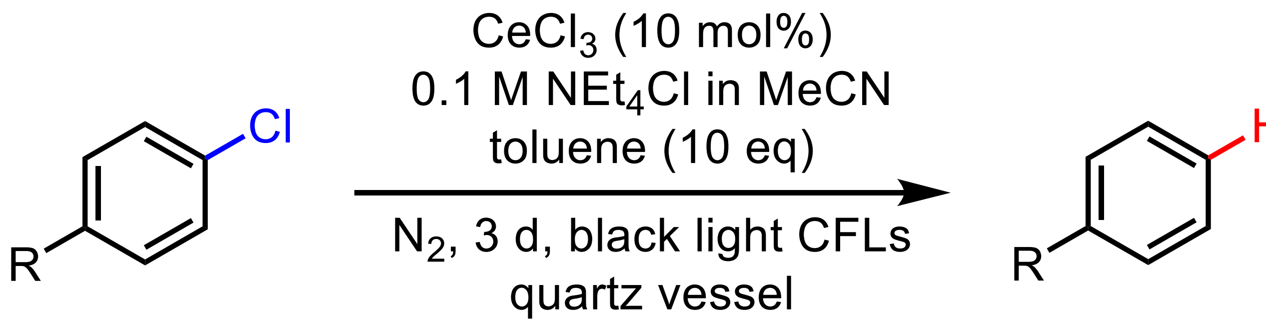


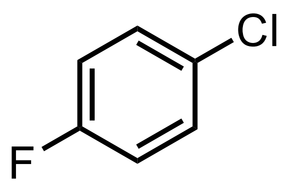
16%

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

Hexachlorocerate(III) anion

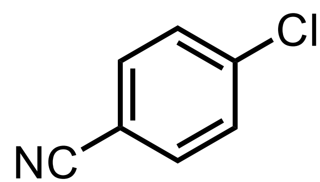
- **Catalytic reaction**



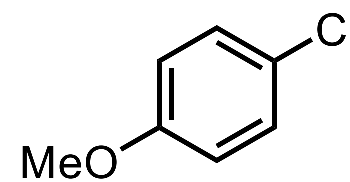


66%

78% (6 d)



73%



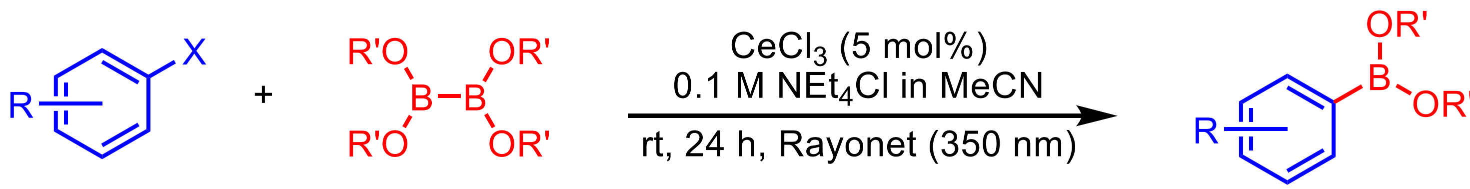
46%

- Toluene as a sacrificial reductant regenerates the Ce(III) catalysts.

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

Hexachlorocerate(III) anion

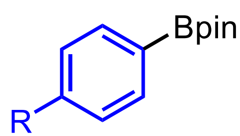
- **Photoinduced Miyaura borylation**



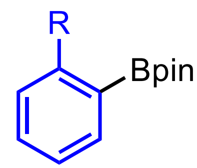
X = Cl, Br

2 eq

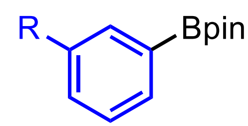
- Aryl halides



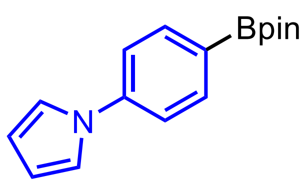
R = H: 64%
= F: 88%
= CF_3: 90%
= CN: 82%
= Ph: 83%
= OMe: 67%
= NMe_2: 55%



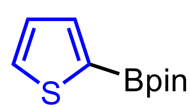
R = F: 54%
= Me: 49%
= CN: 52%



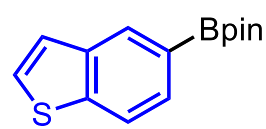
R = CF_3: 64%
= Me: 53%
= OMe: 56%



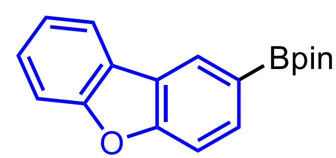
40%



40%



X = Br, 50%

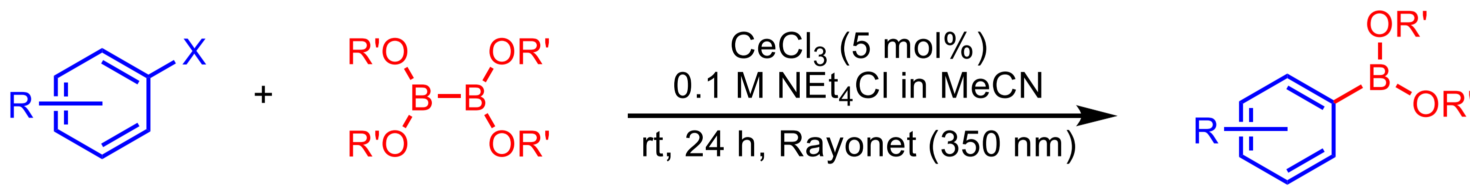


X = Br, 76%

Qiao, Y.; Yang, Q.; Schelter, E. J. *Angew. Chem. Int. Ed.* **2018**, *57*, 10999.

Hexachlorocerate(III) anion

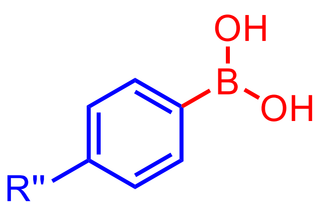
- **Photoinduced Miyaura borylation**



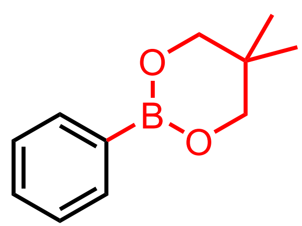
X = Cl, Br

2 eq

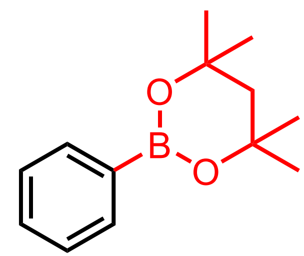
- Diboron reagents



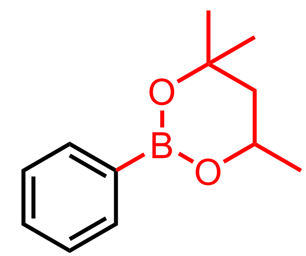
R'' = H: 42%
= F: 50%
= CF_3: 61%
= OMe: 44%



63%



77%

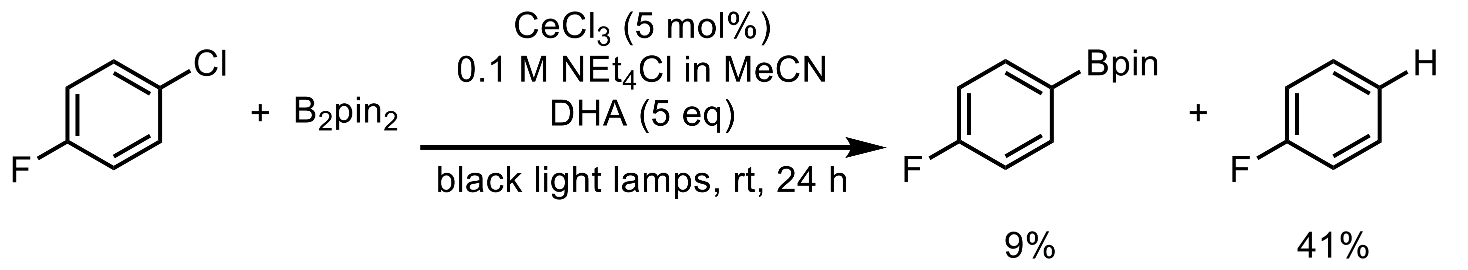


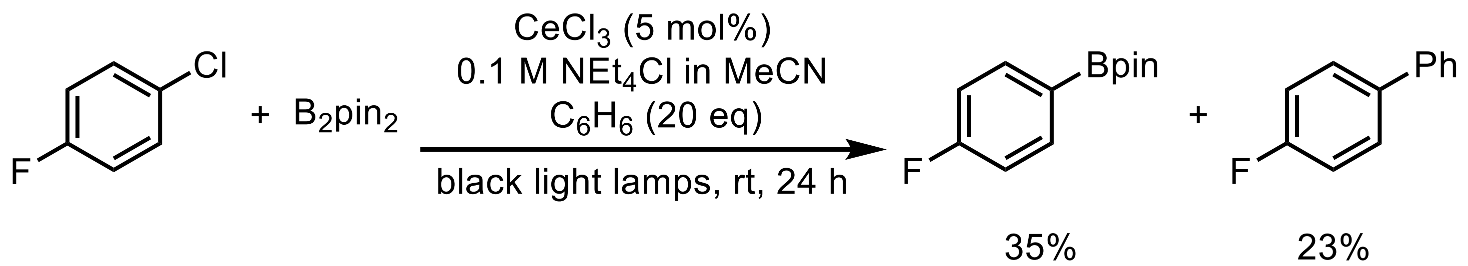
68%

Qiao, Y.; Yang, Q.; Schelter, E. J. *Angew. Chem. Int. Ed.* **2018**, *57*, 10999.

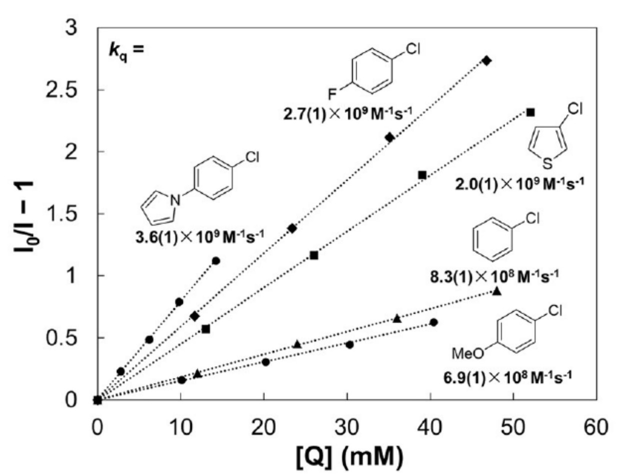
Hexachlorocerate(III) anion

- **Mechanistic studies**
  - Radical probing experiments





- Stern-Volmer experments



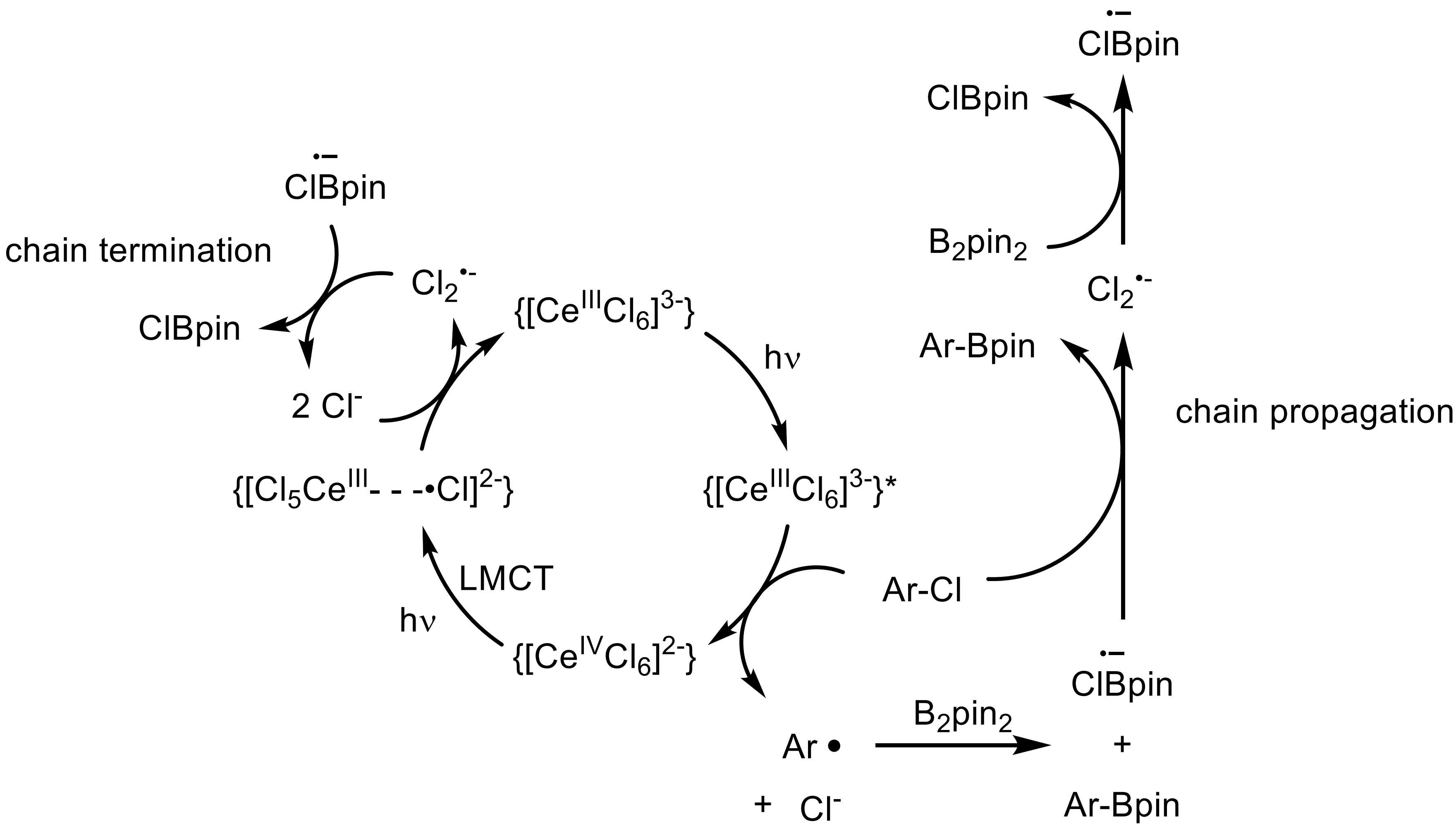
- The reaction quantum yield Φ = 6.1 and the shorter reaction time

→ Indicating radical propagation process

Qiao, Y.; Yang, Q.; Schelter, E. J. *Angew. Chem. Int. Ed.* **2018**, *57*, 10999.

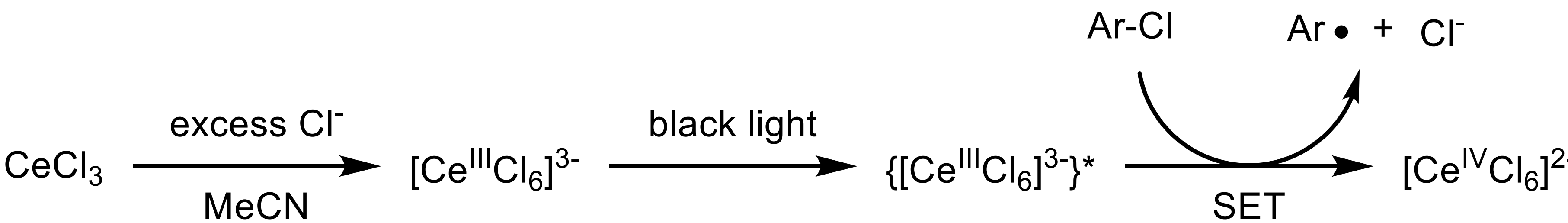
Hexachlorocerate(III) anion

- **Proposed catalytic cycle**



Qiao, Y.; Yang, Q.; Schelter, E. J. *Angew. Chem. Int. Ed.* **2018**, *57*, 10999.

Short Summary

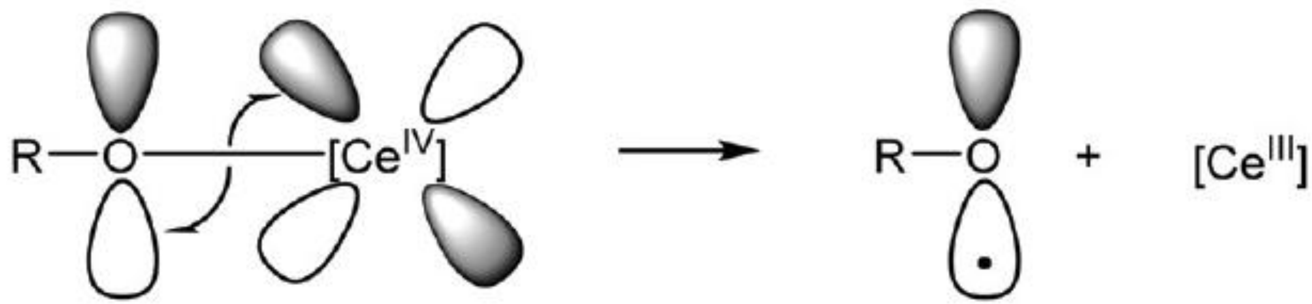


- UV absorption (4f→Ce-Cl π-anti bonding orbital)
- SET catalyst with strong negative reduction potential (-3.45 V)

Alkoxy radical mediated reactions by cerium photocatalysis

Alkoxy radical mediated reactions

- **Photoinduced LMCT by Ce(IV) and alcohol**



- UV ~ visible light absorption

  (π-bonding orbital electron from the ligand $\rightarrow$ the metal d orbital)

- Ce(III) and alkoxy radical generation after bond homolysis

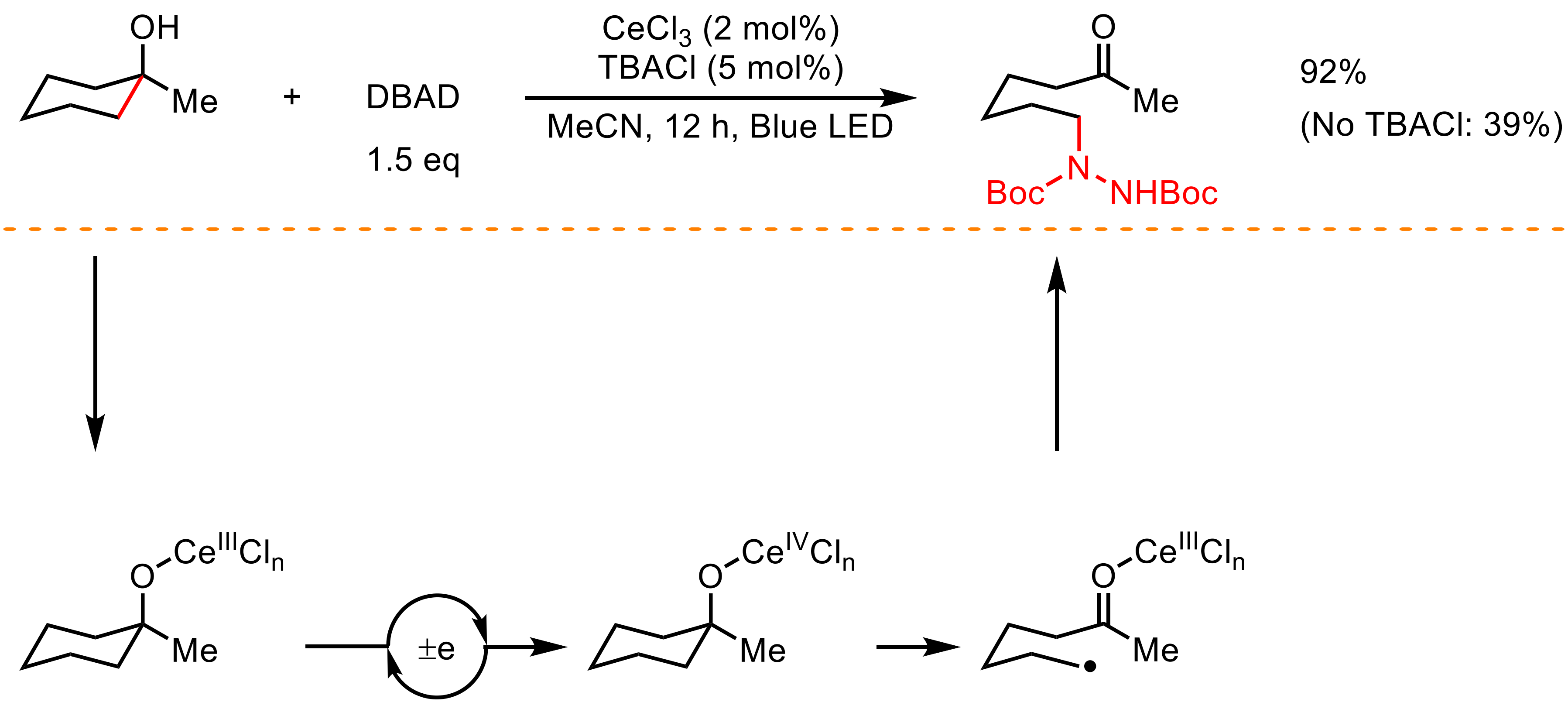
- LMCT mode activation probides a direct and more selective target heteroatom oxdation pathway.

Org. Chem. Front., **2018**, *5*, 3018.

Inorg. Chim. Acta **2006**, *359*, 4130.

Alkoxy radical mediated reactions

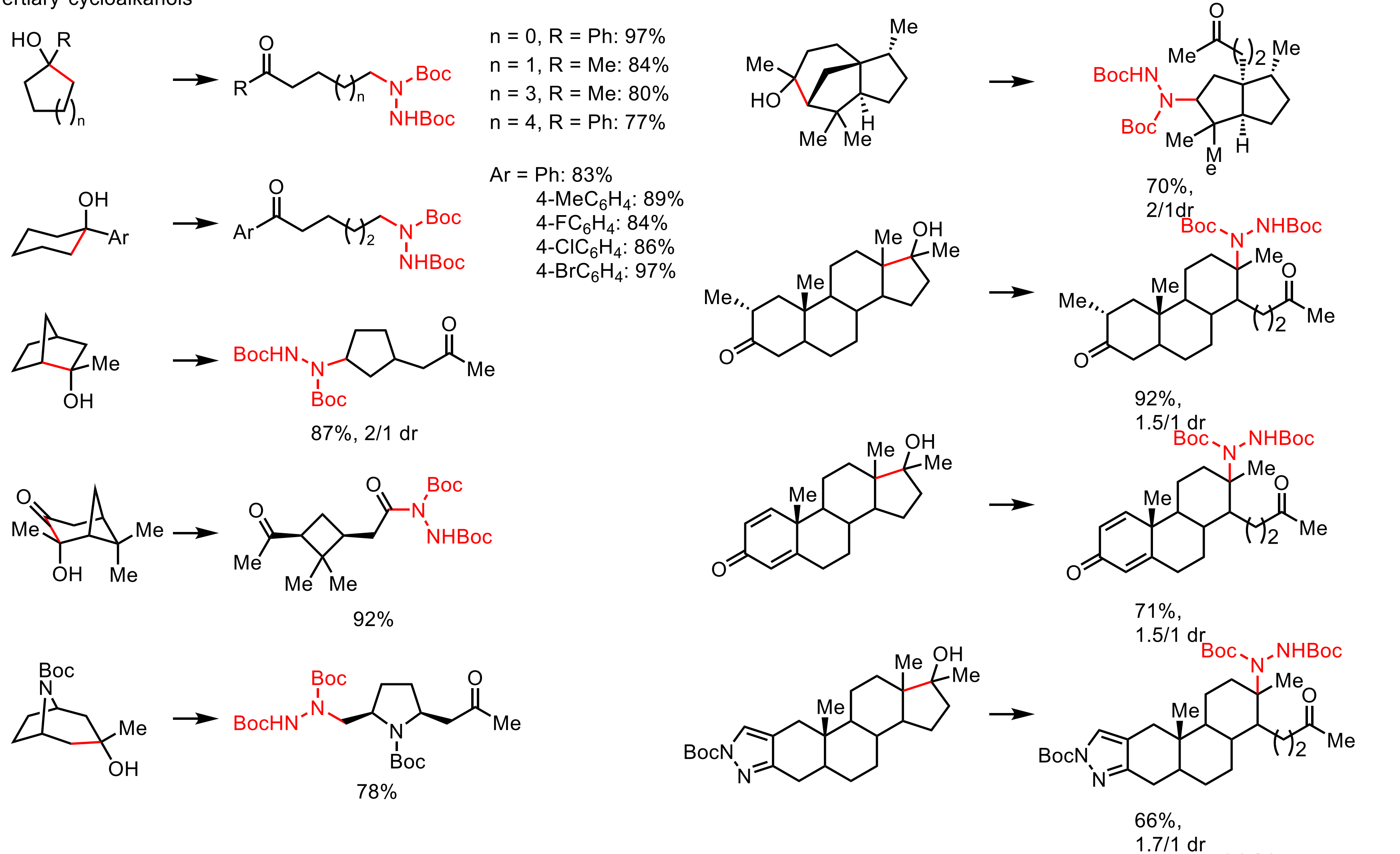
• **Photocatalytic C-C bond cleavage and amination of cycloalkanols**



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

Alkoxy radical mediated reactions

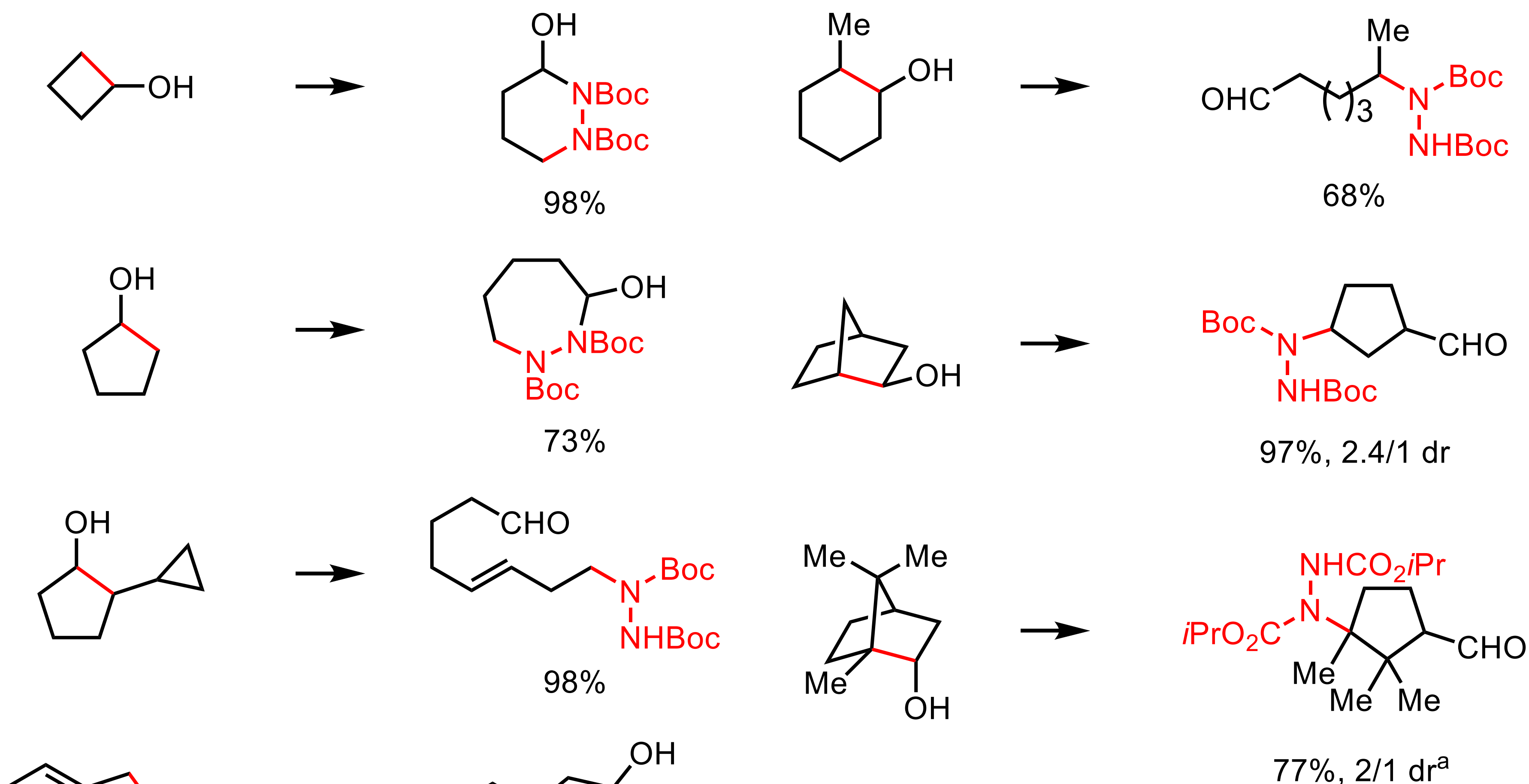
- **Substrate scope**
  - Tertiary cycloalkanols

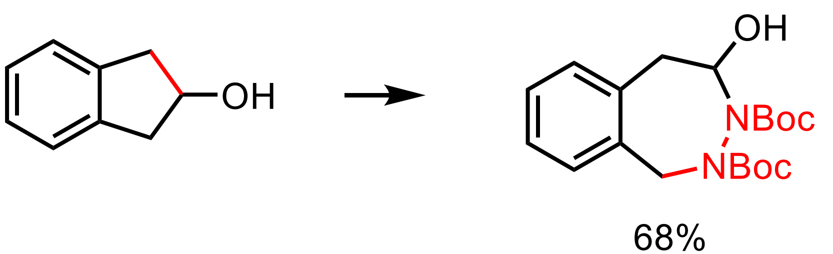


Zuo, Z. and co- authors *Angew. Chem. Int. Ed.* **2016**, *55*, 15319.

Alkoxy radical mediated reactions

- **Substrate scope**
  - Secondary cycloalkanols





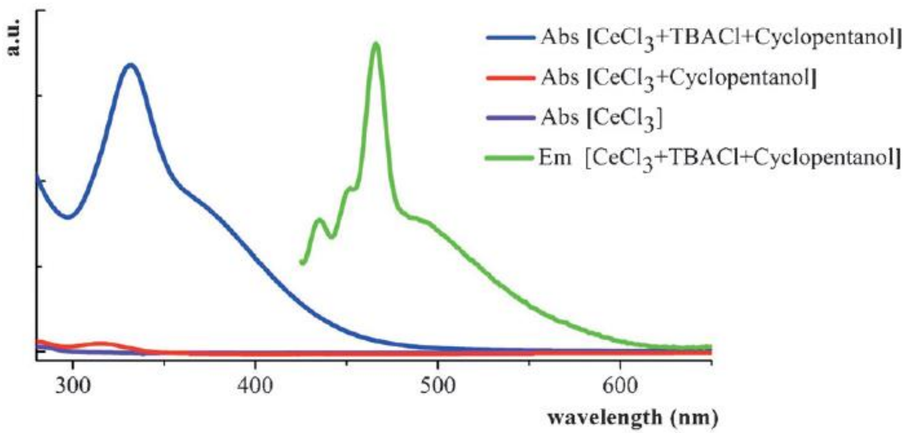
a: DIAD was used instead of DBAD.

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

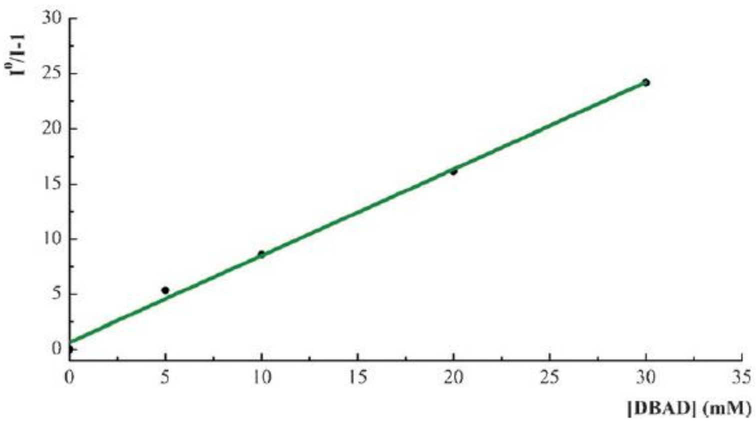
Alkoxy radical mediated reactions

- **Mechanistic studies**

- UV-Vis spectra



- Stern-Volmer experments



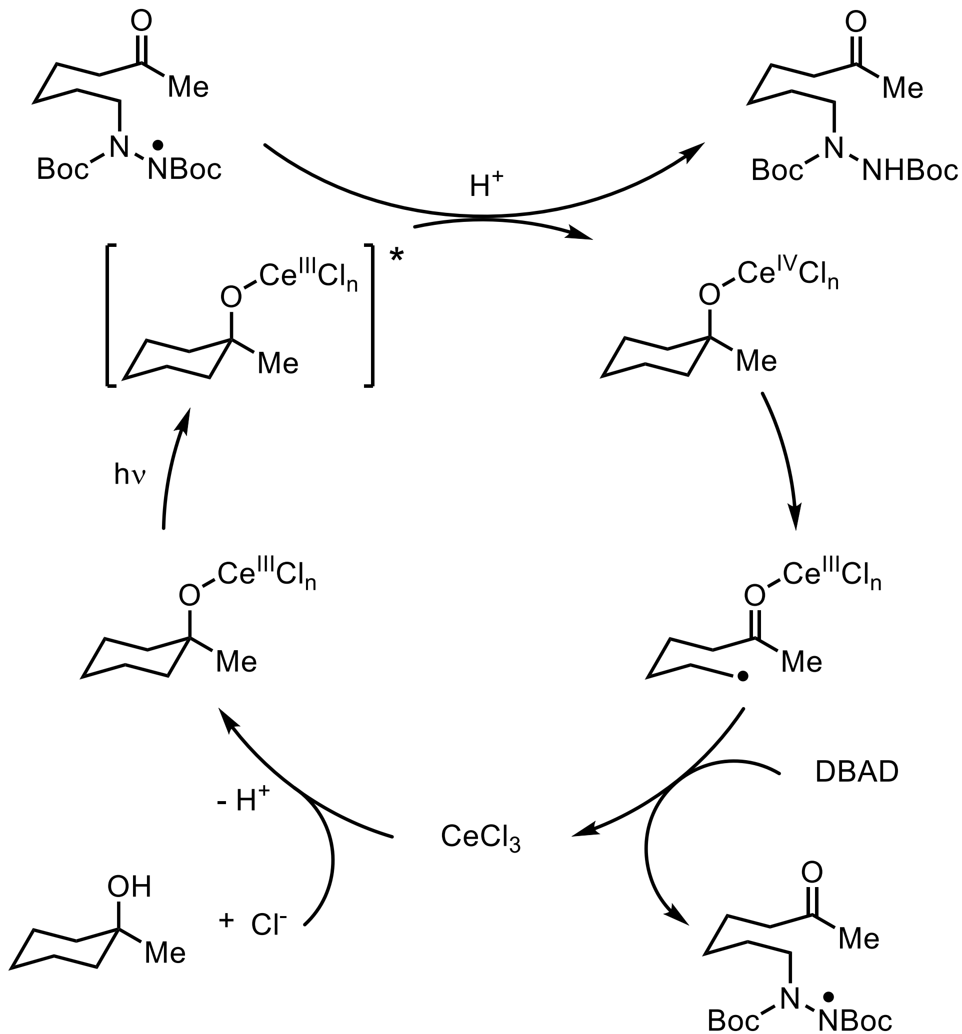
Cerium chloride/alcohol complex: $E_{1/2}(Ce^{IV}/{}^{*}Ce^{III})$ = -2.2 V (vs SCE)

DBAD: $E_{1/2}^{red}$ = -0.7 V (vs SCE)

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

Alkoxy radical mediated reactions

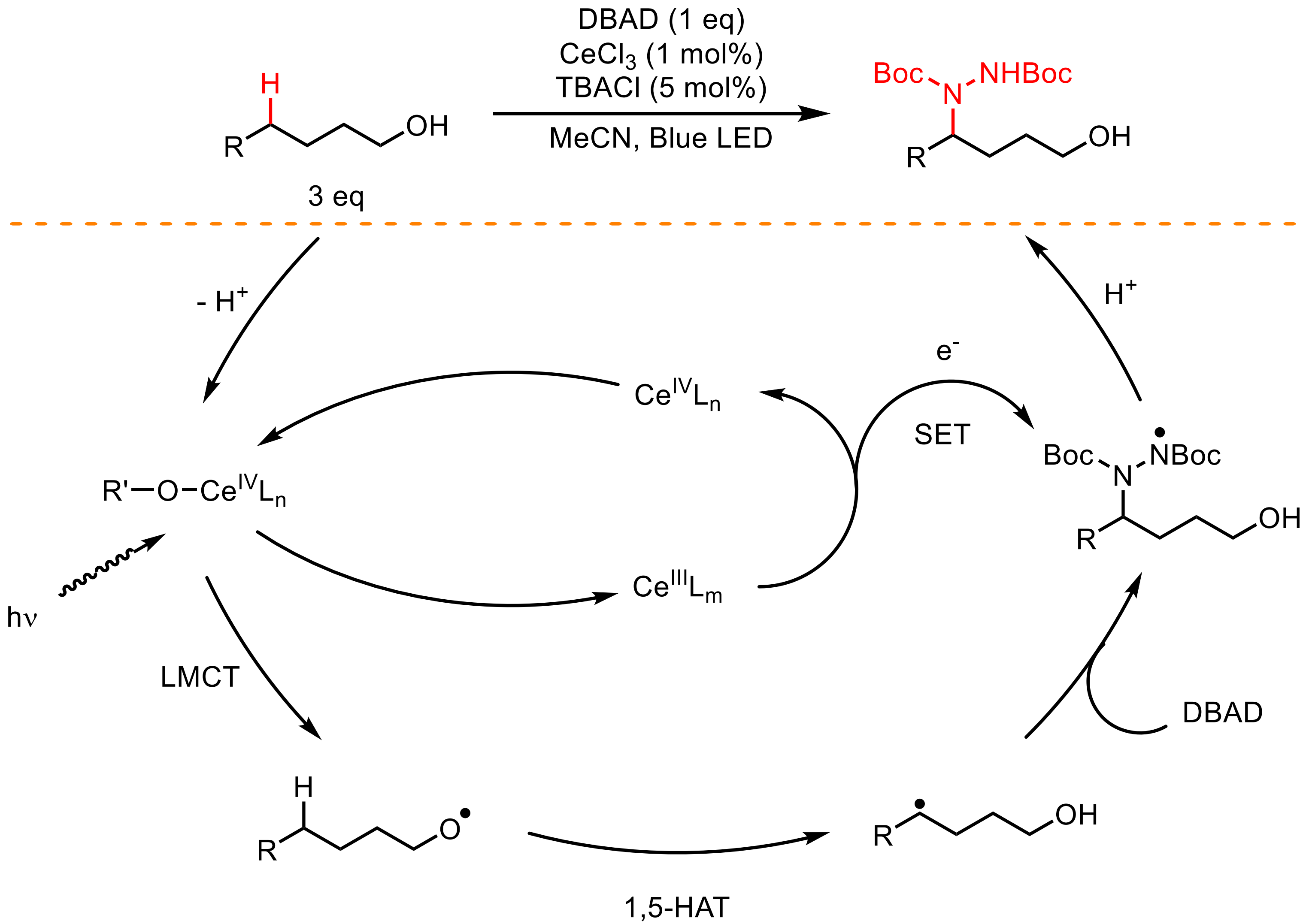
- **Proposed catalytic cycle**



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

Alkoxy radical mediated reactions

- **Alkanol δ C-H amination**

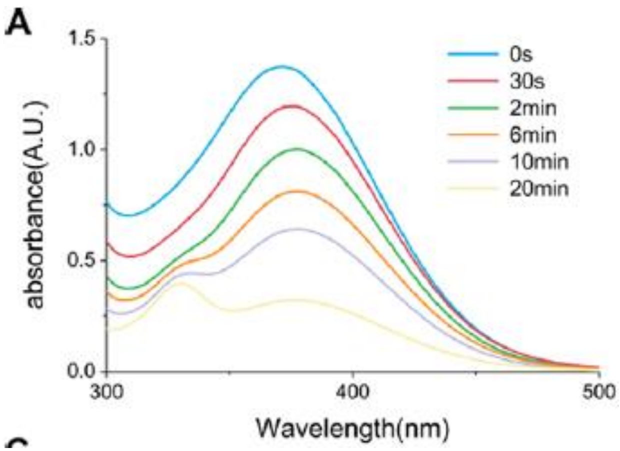


Zuo, Z. and co-authors *J. Am. Chem. Soc.* **2018**, *140*, 1612.

Alkoxy radical mediated reactions

- **Mechanistic studies**

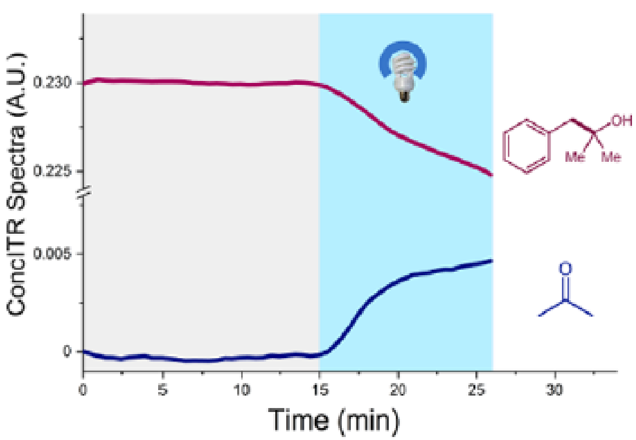
- UV-Vis spectra of $Ce^{IV}(OC_5H_{11})Cl_n$



- peak shifts after photo-irradiation from 370 nm to 330 nm

  → generation of Ce^{III}

- Operando IR experiments



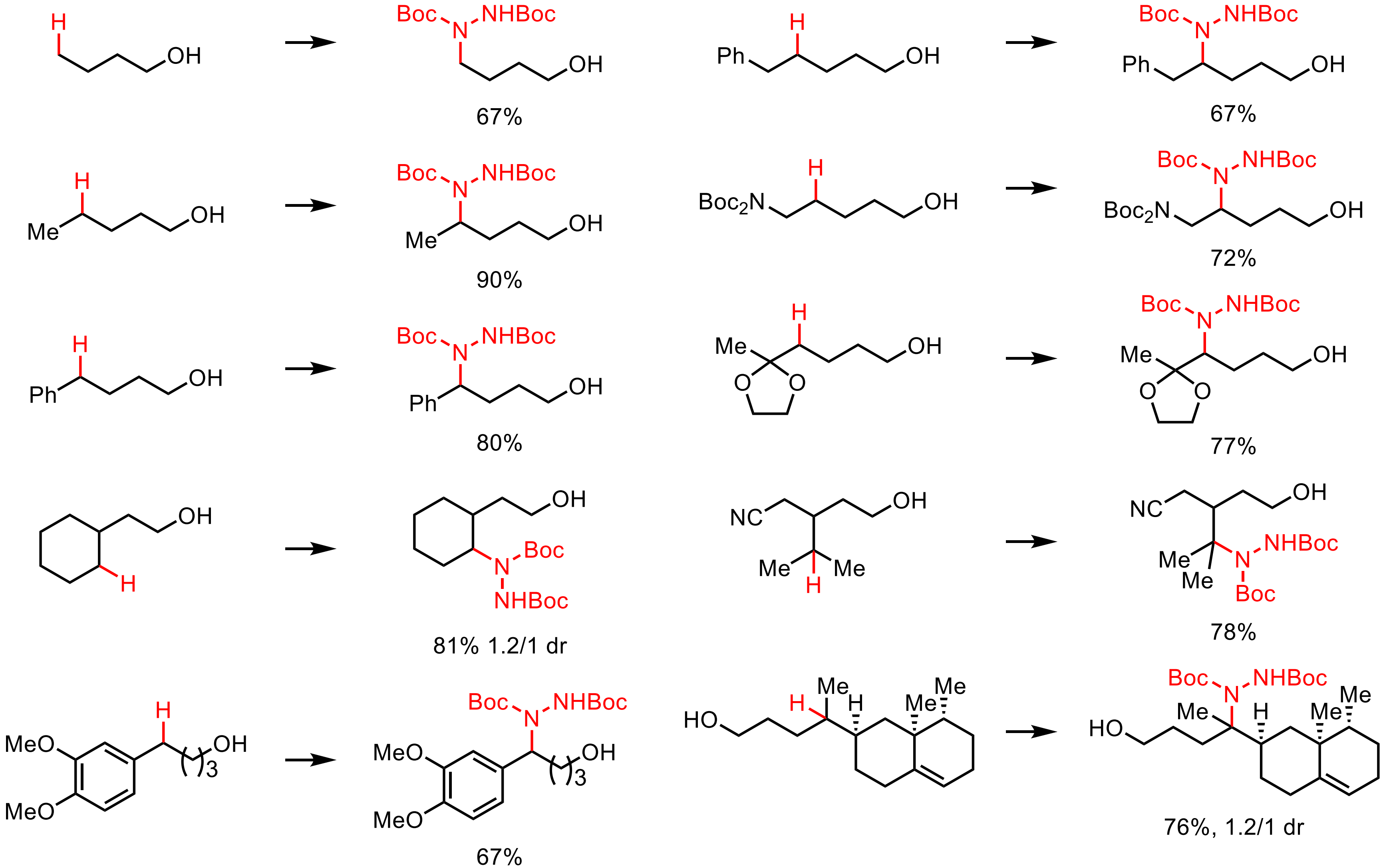
- stable in the dark

  → Ground-state SET is not operative.

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

Alkoxy radical mediated reactions

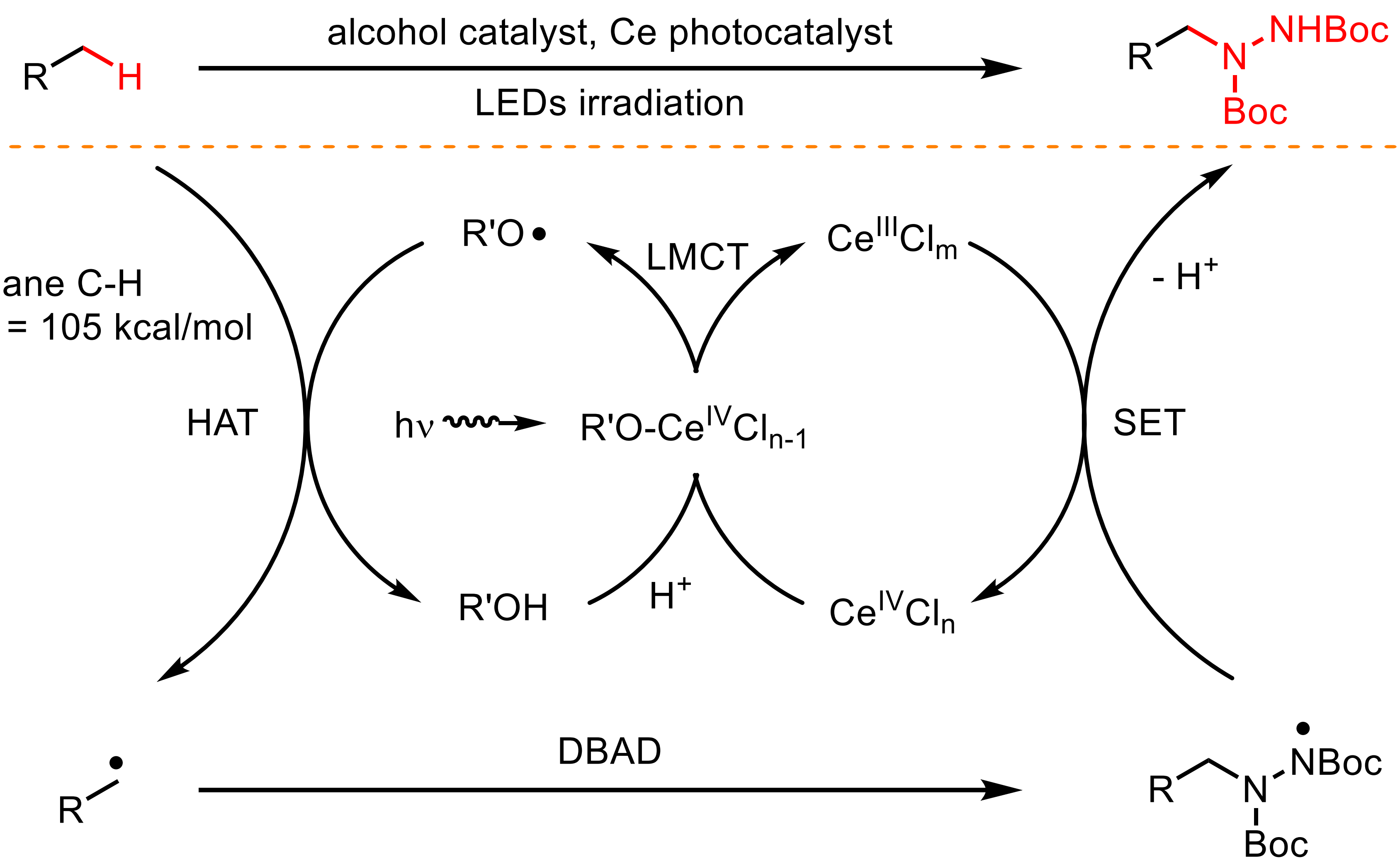
- **Substrate scope**



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

Alkoxy radical mediated reactions

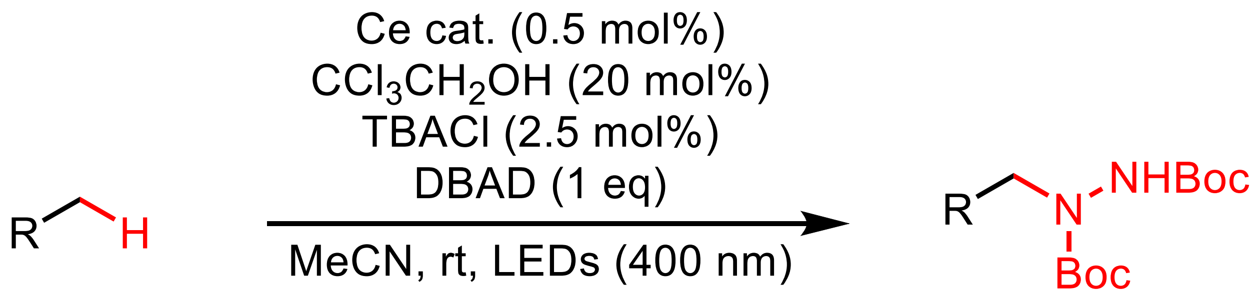
- **Functionalization of methane, ethane, and higher alkanes**



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

Alkoxy radical mediated reactions

- **Amination of alkanes**

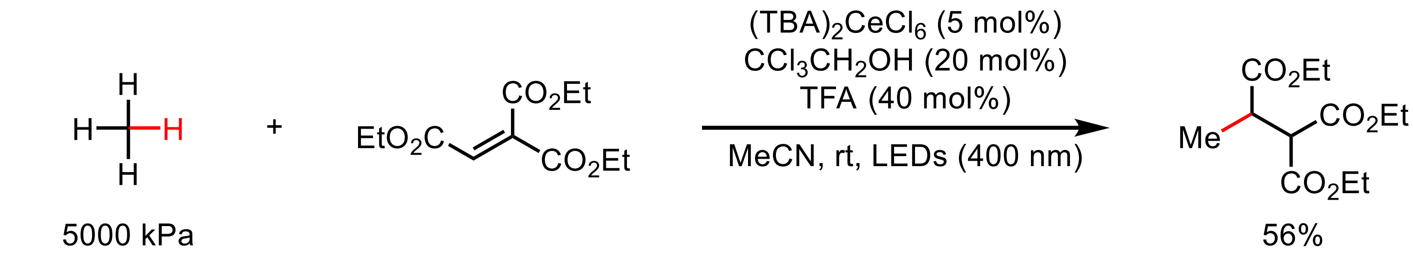


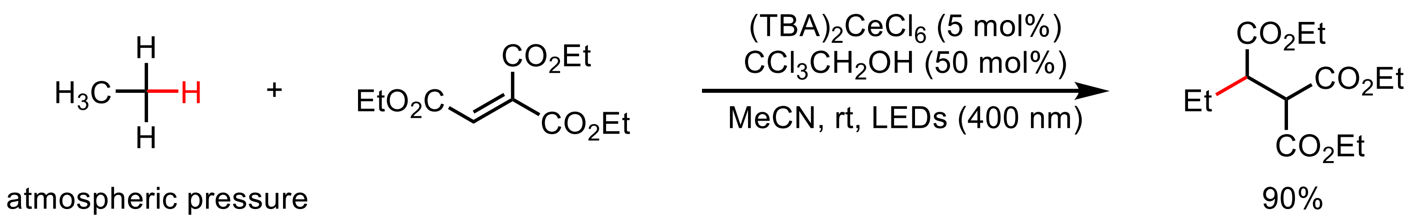
entry	alkane	Ce cat.	time	yield
1	methane (5000 kPa)	$(TBA)_2CeCl_6$	2 h	63 %
2	ethane (101 kPa)	$CeCl_3$ (0.01 mol%)	4 h	97 %
3	propane (101 kPa)	$CeCl_3$	9 h	70% (1/1 rr)
4	butane (101 kPa)	$CeCl_3$	6 h	76% (1/1.7 rr)
5	cyclohexane	$CeCl_3$	16 h	81%

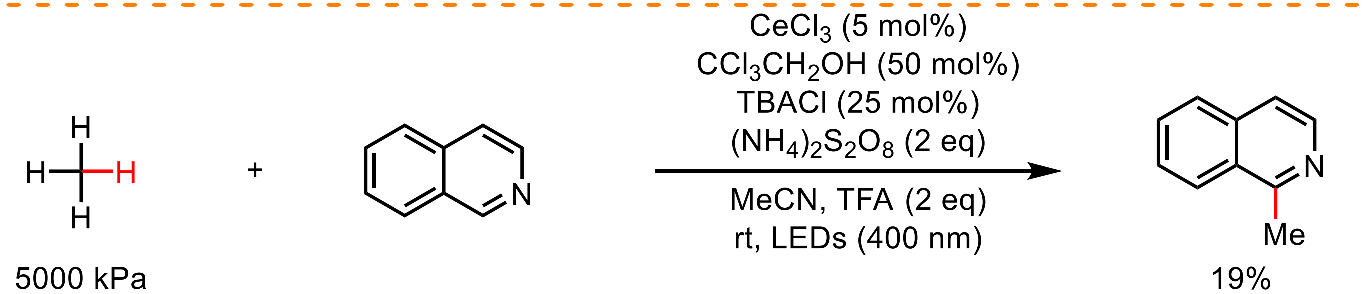
Zuo, Z. and co-authors *Science* **2018**, *361*, 668.

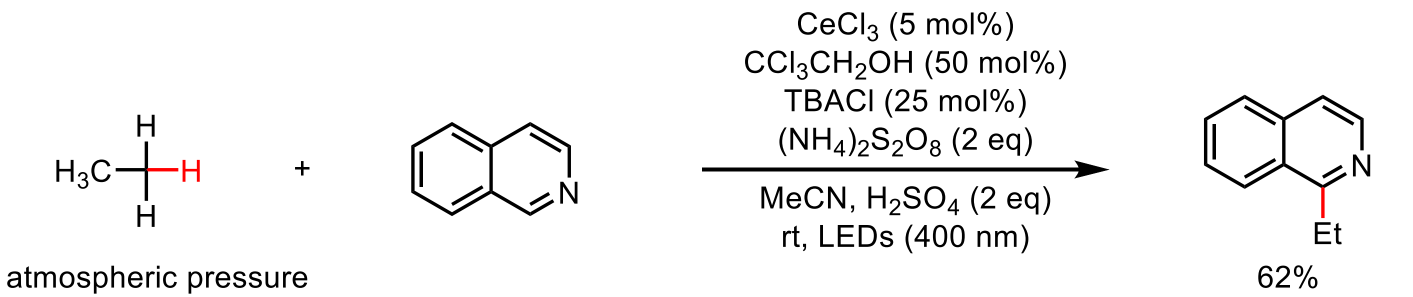
Alkoxy radical mediated reactions

• **C-H alkylation and arylation**





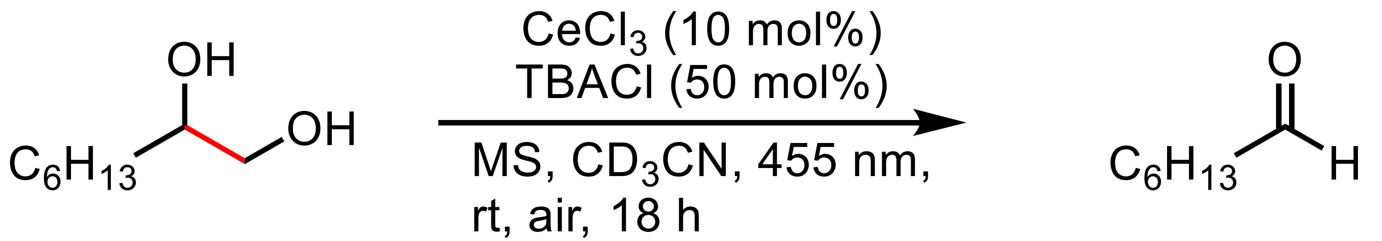




Zuo, Z. and co-authors *Science* **2018**, *361*, 668.

Alkoxy radical mediated reactions

- **Oxidative cleavage of 1,2-diols by cerium photocatalysis**

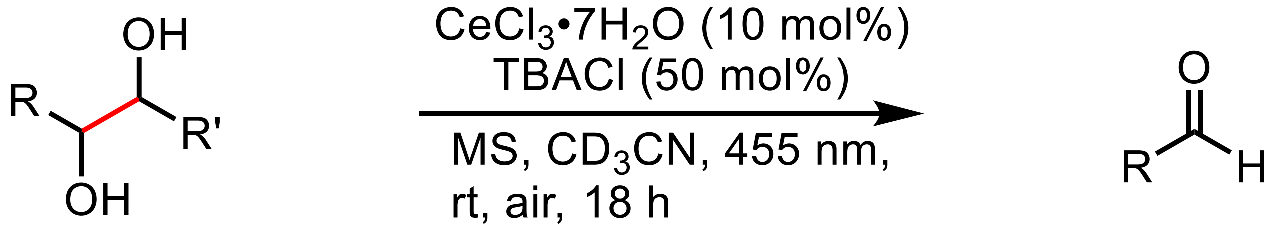


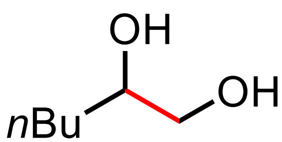
entry	deviation from standard conditions	yield (%)
1	none	87
2	No MS	67
3	No TBACl	45
4	under N_2	10
5	with $K_2S_2O_8$	6
6	$CeCl_3$•$7H_2O$	87

Schwarz, J.; König, B. *Chem. Commun.*, **2019**, *55*, 486.

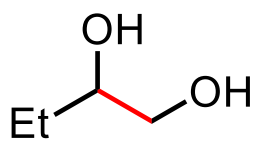
Alkoxy radical mediated reactions

- **Substrate scope**

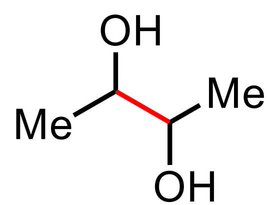




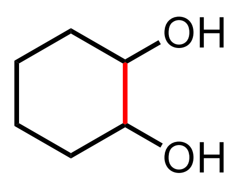
79%



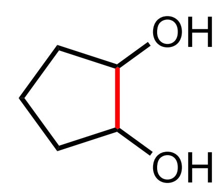
78%



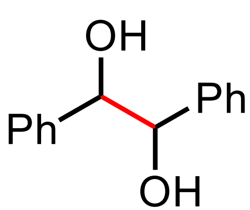
95%



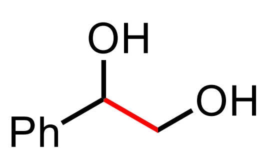
cis: 57%
trans: 69%



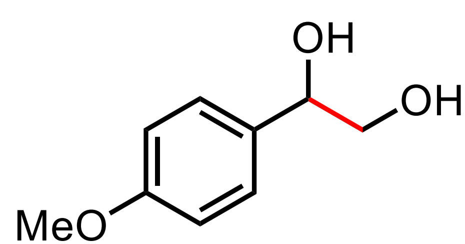
cis: 66%
trans: 69%



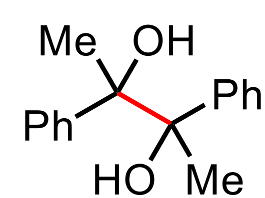
85%



86%



71%

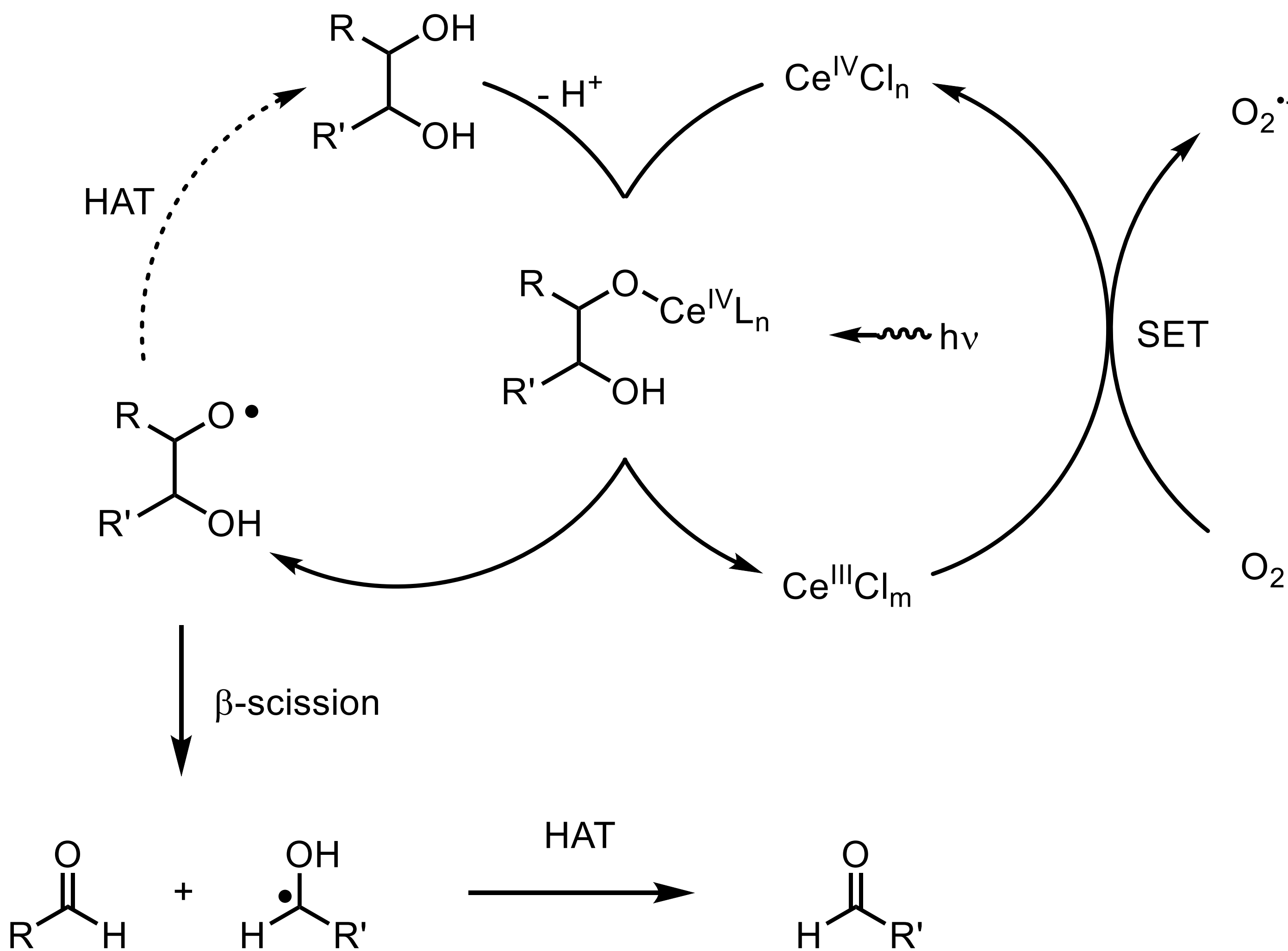


85%

Schwarz, J.; König, B. *Chem. Commun.*, **2019**, *55*, 486.

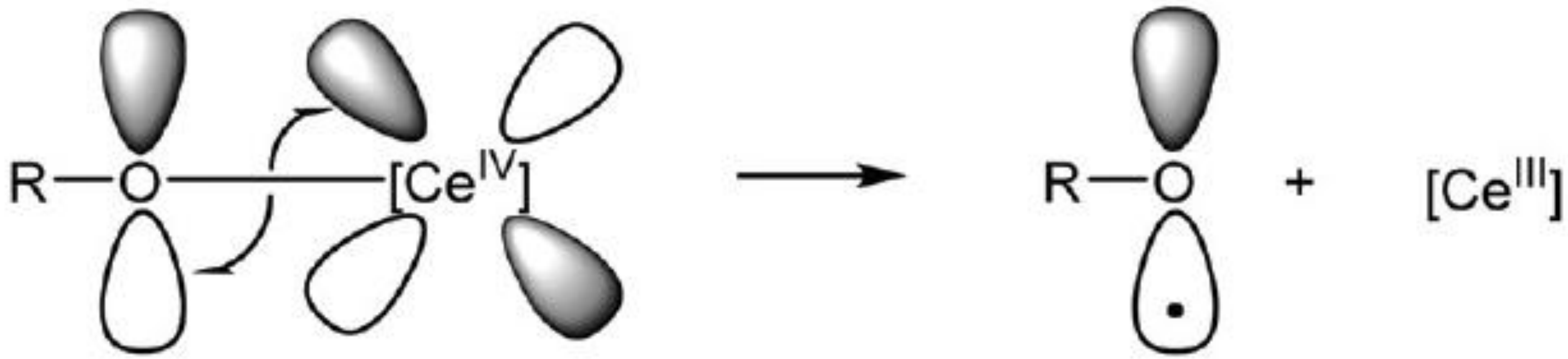
Alkoxy radical mediated reactions

- **Proposed catalytic cycle**



Schwarz, J.; König, B. *Chem. Commun.*, **2019**, *55*, 486.

Short Summary



- UV ~ visible light absorption (LMCT)
- Generation of Ce^{III} and alkoxy radical

Org. Chem. Front., **2018**, *5*, 3018.

Summary

- Earth-abundant cerium has economical and environmental benefits.
- Cerium photochemistry is rapidly developing in recent years.
- Cerium photoredox catalysts have unique reactivities compared to transition metal photoredox catalysts.