Photoelectrochemistry in Organic Synthesis

Literature Seminar

2021/11/11 Ryo Kuroda

Contents

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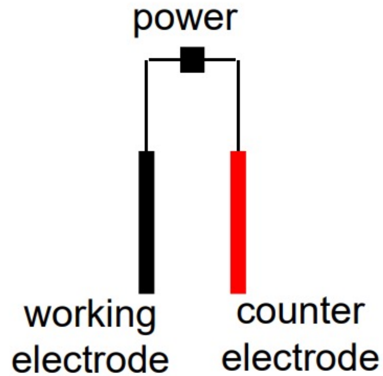
Synthetic Organic Electrochemistry

Electrochemical Cells

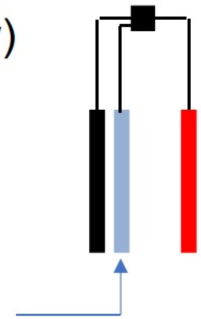
undivided cell



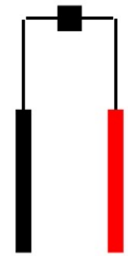
divided cell (“H” cell)

Modes of Operation

constant voltage (cv)



reference electrode

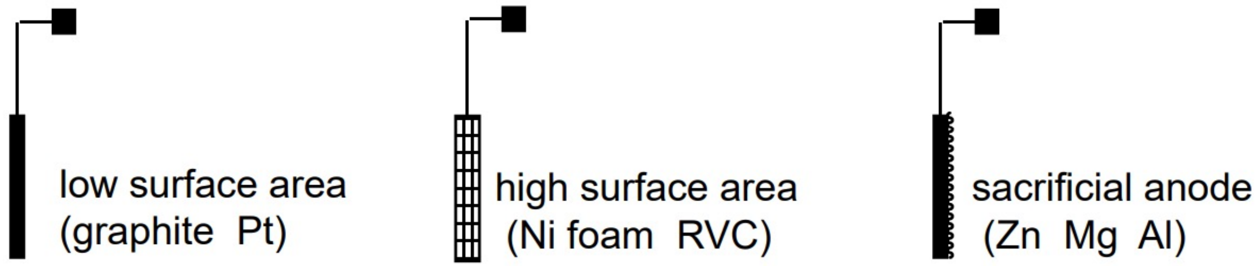


constant current (cc)

S. R. Waldvogel *et al. Chem. Sci.*, **2020**, *11*, 12386.

Synthetic Organic Electrochemistry

Electrodes



Solution

THF	DCM	Acetone	Methanol	MeCN	DMA	H_2O	
8	9	21	33	38	38	80	ε

more resistance → less resistance

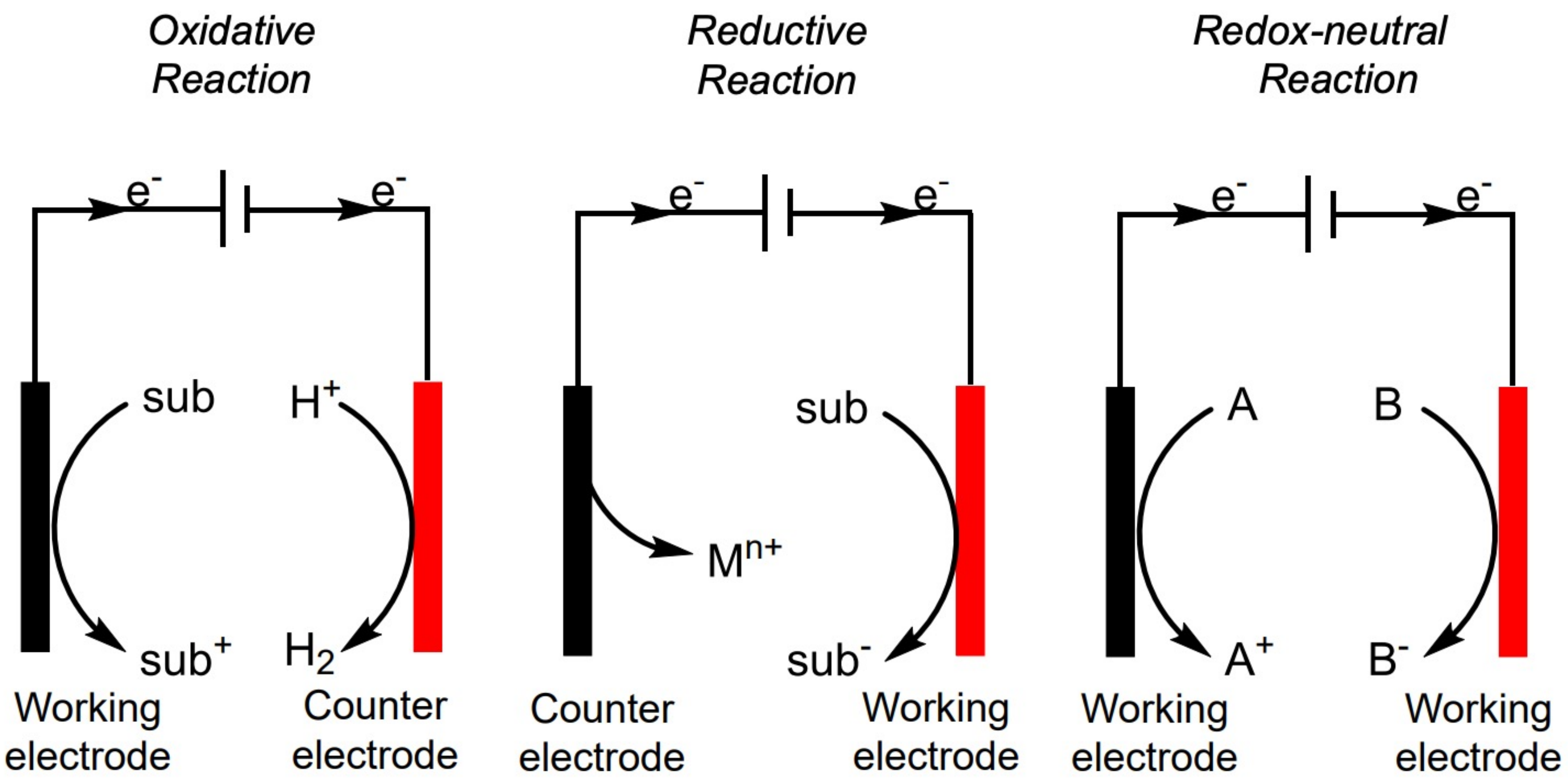
cations ↔ anions

Li^+ Na^+ Et_4N^+ Bu_4N^+ ⟷ ClO_4^- PF_6^- BF_4^- OAc^- I^- Br^-

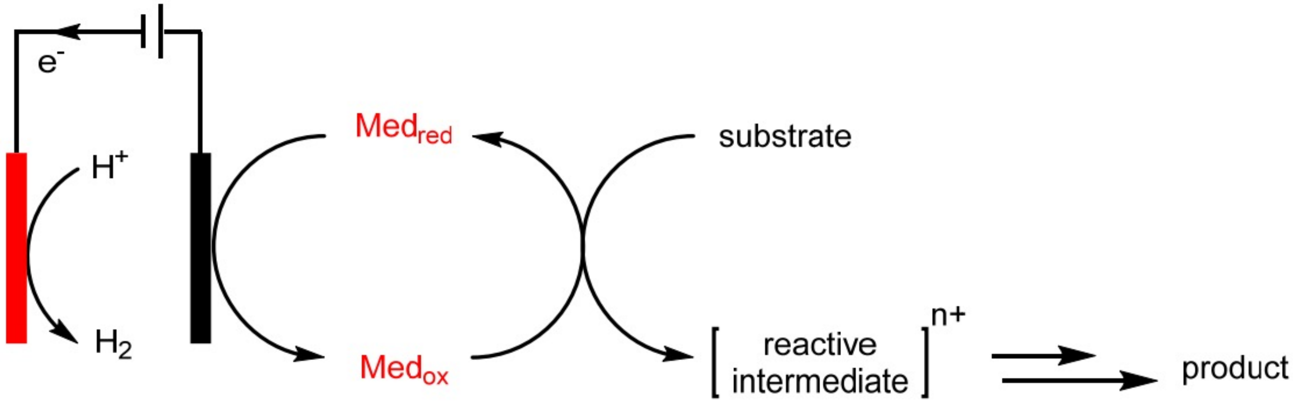
mix and match

P. S. Baran *et al. Acc. Chem. Res.* **2020**, *53*, 72.

Synthetic Organic Electrochemistry



Synthetic Organic Electrochemistry



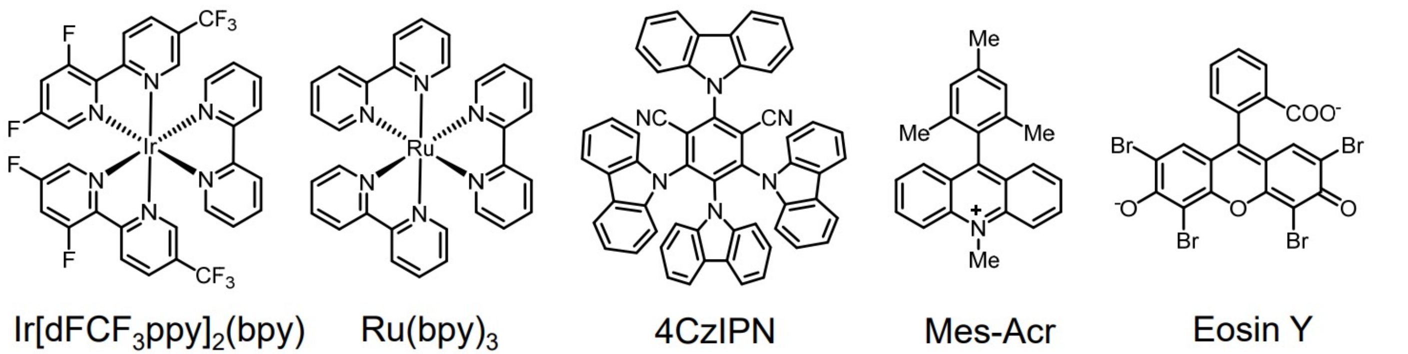
outer-sphere: Med_{ox} + SM $\rightleftharpoons$ (electron transfer) Med_{red} + SM^{n+} $\longrightarrow\longrightarrow$ (follow-up reactions)

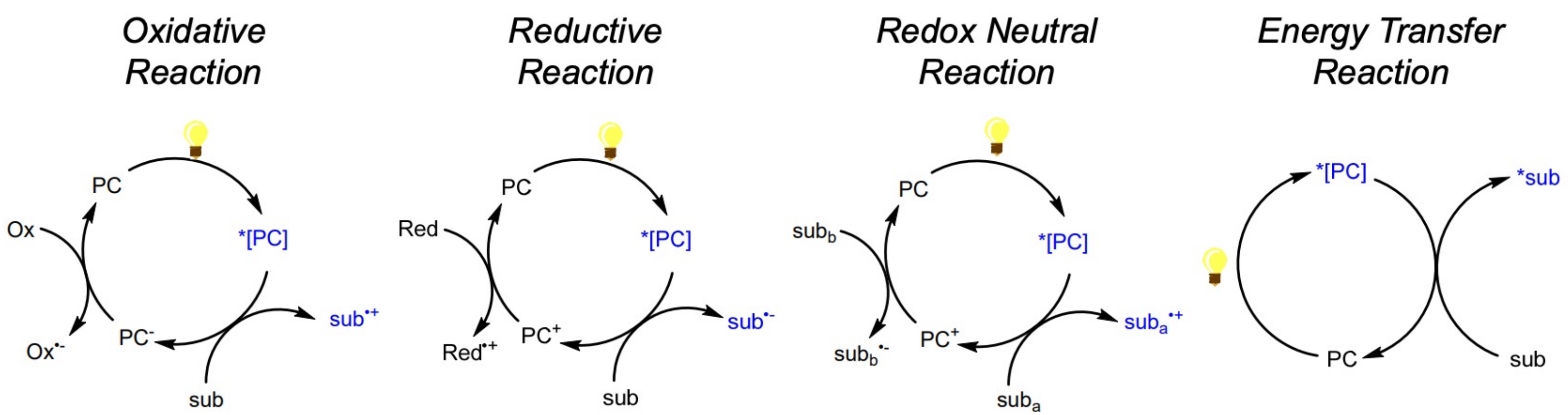
inner-sphere: Med_{ox} + SM $\rightleftharpoons$ (complex formation) Med_{ox}----SM $\longrightarrow$ Med_{red} + SM^{n+} $\longrightarrow\longrightarrow$ (follow-up reactions)

R. D. Little *et al. Chem. Soc. Rev.*, **2014**, *43,* 2492.

Photoredox Chemistry

Visible-Light Photoredox Catalysis

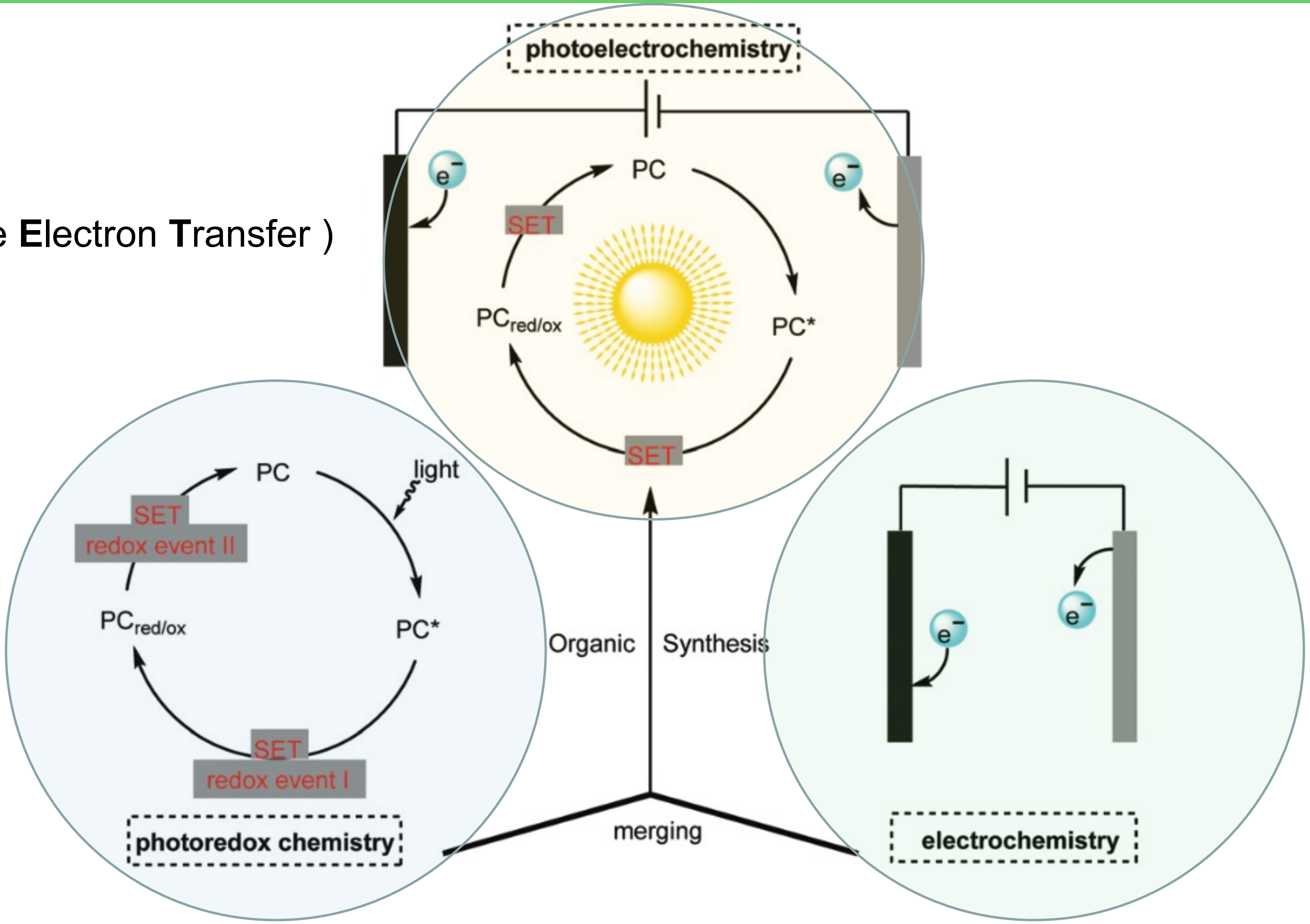




G. A. Molander *et al.* *ACS Catal.* **2017**, *7*, 2563.

Photoelectrochemical Organic Synthesis

SET
(**S**ingle **E**lectron **T**ransfer)



K. Y. Ye *et al. Org. Chem. Front.* **2020**, *7*, 131.

Photoelectrochemical Organic Synthesis

The limitation of **electrochemistry**

- ✔ **Low conductivity** of organic solvents
- ✔ **Unselective** redox processes
- ✔ **Limited potential** of mediators

The limitation of **photoredox chemistry**

- ✔ Energy **constrained**
- ✔ Energy **losses**
- ✔ Stoichiometric **oxidant or reductant**

Photoelectrochemistry

✔ Atom **efficient** ✔ **Large** redox window ✔ **High** selectivity / energy **efficiency**

Contents

1. Introduction

2. **Representative Researches**
   1. **Mechanistic Classification**
   2. Electrochemically Mediated PhotoRedox Catalysis (ePRC)
   3. Decoupled PhotoElectroChemistry (dPEC)
   4. Interfacial PhotoElectroChemistry (iPEC)

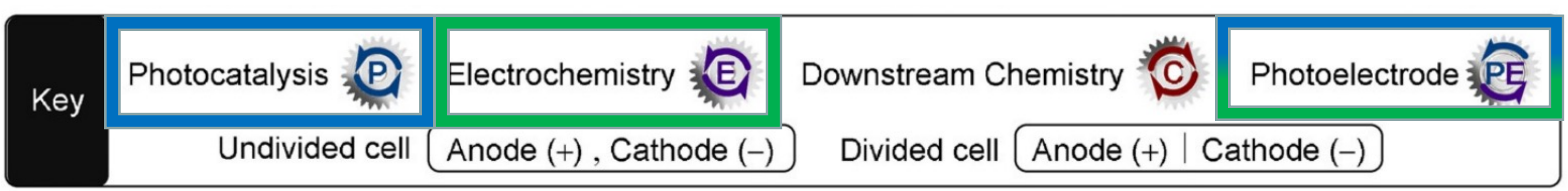
3. Summary

Mechanistic Classification

Electrochemical components
Photochemical components
↓
Interdependent roles

Electrochemical components
Photochemical components
↓
Separate roles

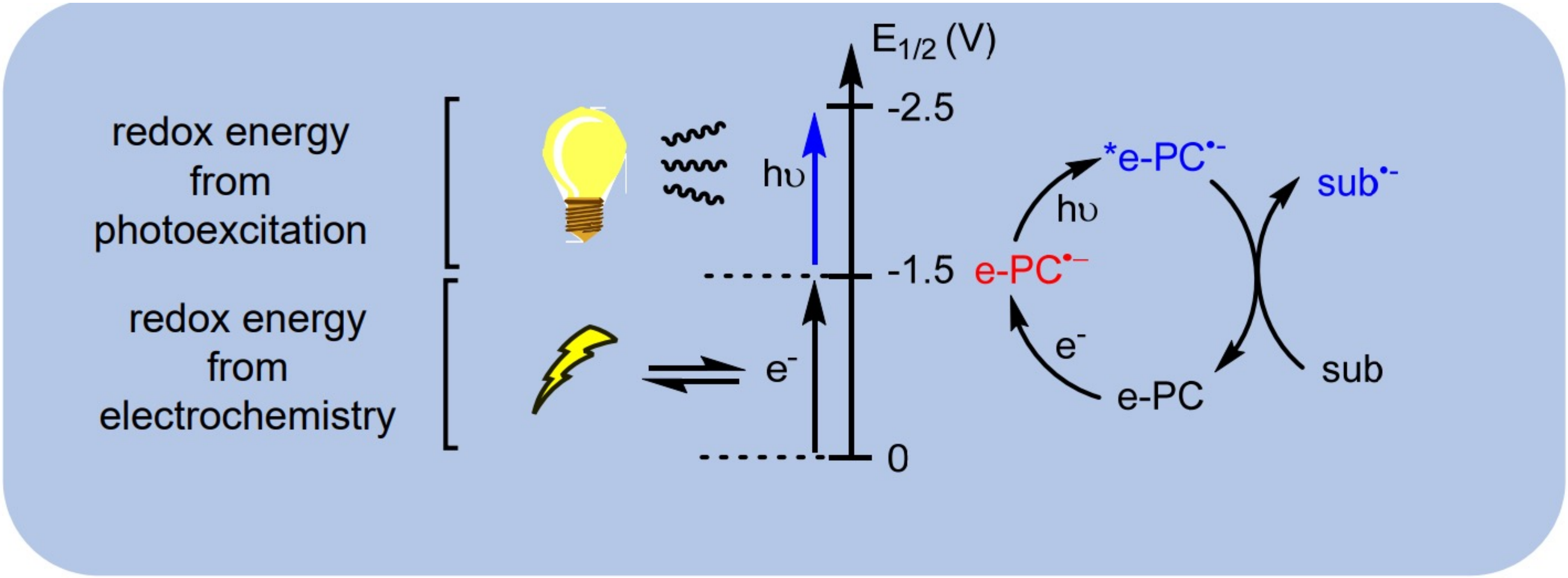
Reactions occur
at
Photoelectrode
surfaces



K. Y. Ye *et al. Org. Chem. Front.* **2020**, *7*, 131.

Contents

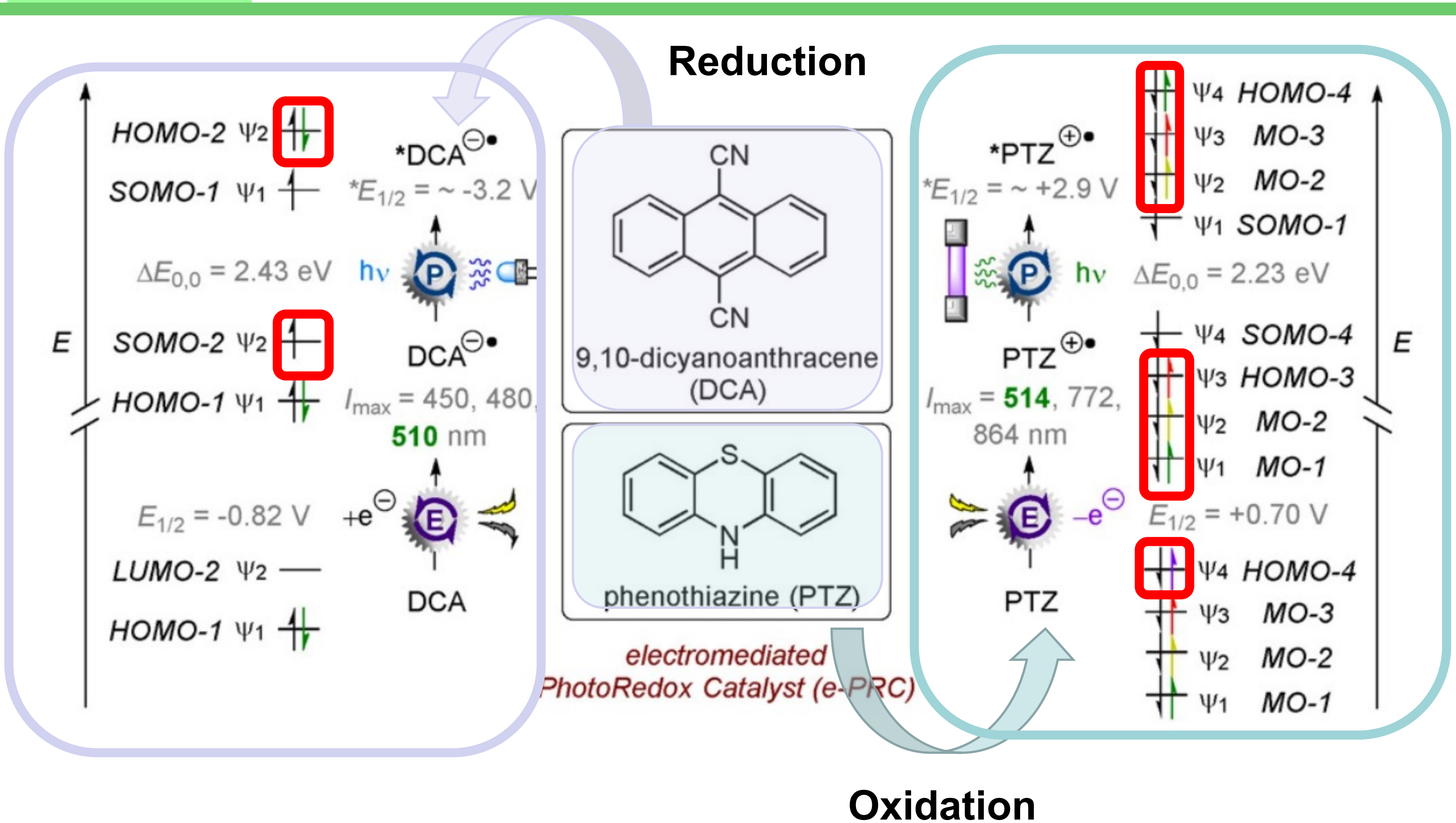
The Mechanism of ePRC



Tunable electrochemical redox + Selective light energy transfer

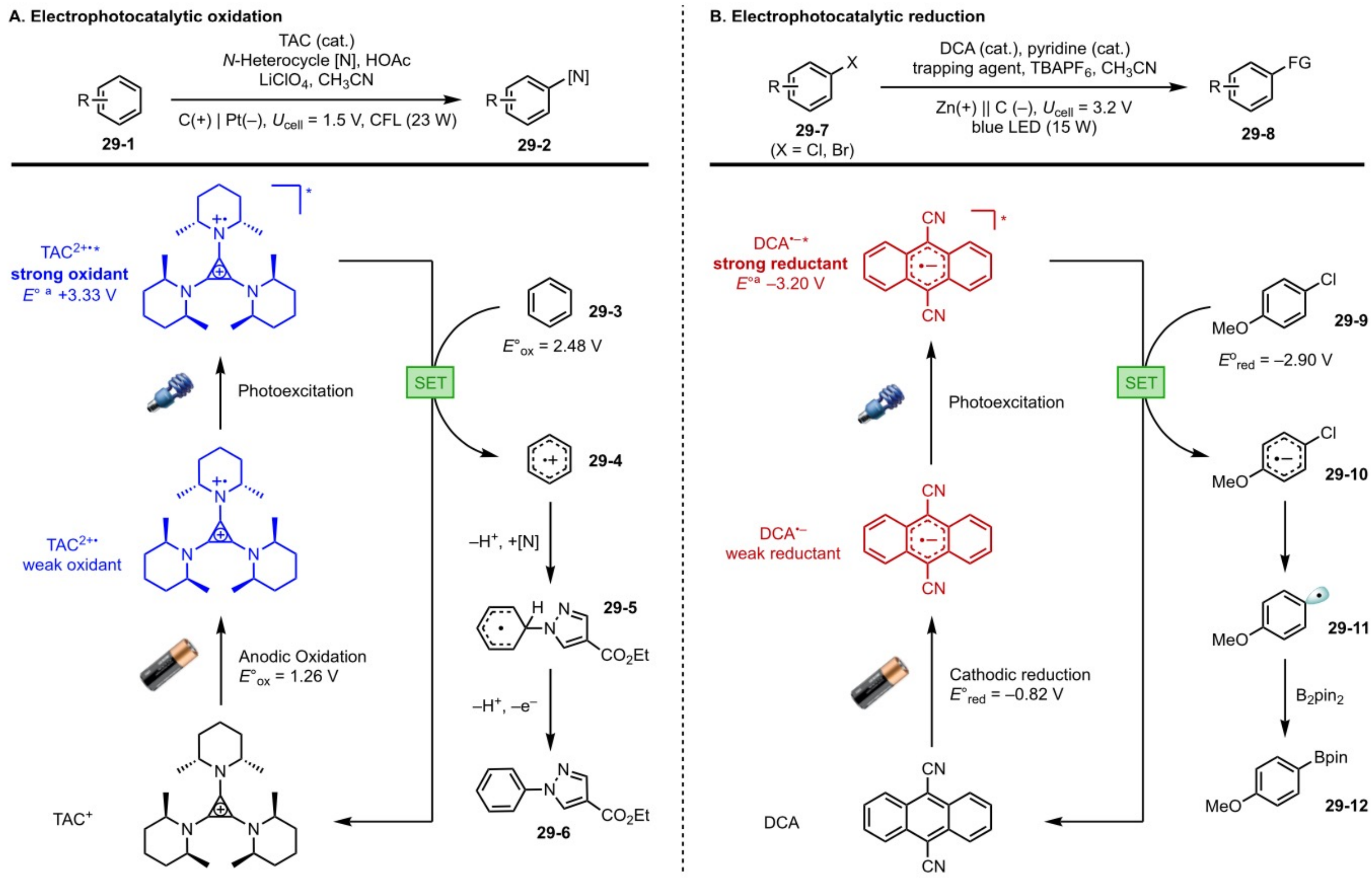
= Transient generation of **super-redox agent**

The Mechanism of ePRC



K. Y. Ye *et al. Org. Chem. Front.* **2020**, *7*, 131.

The Mechanism of ePRC

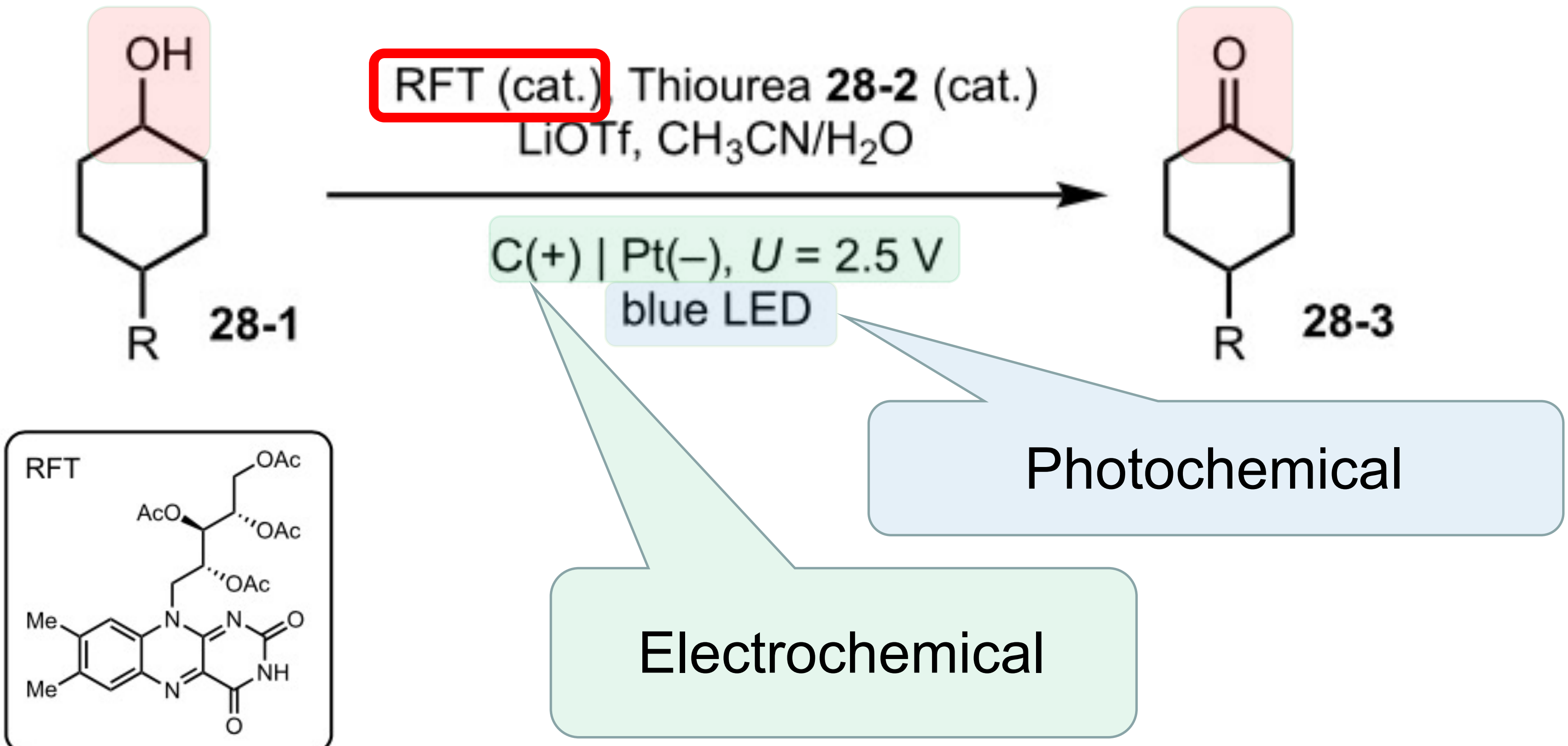


Oxidation **Reduction**

S. Lin *et al. ACS Cent. Sci.* **2020**, *6, 13.* 17−1340

The Example of ePRC

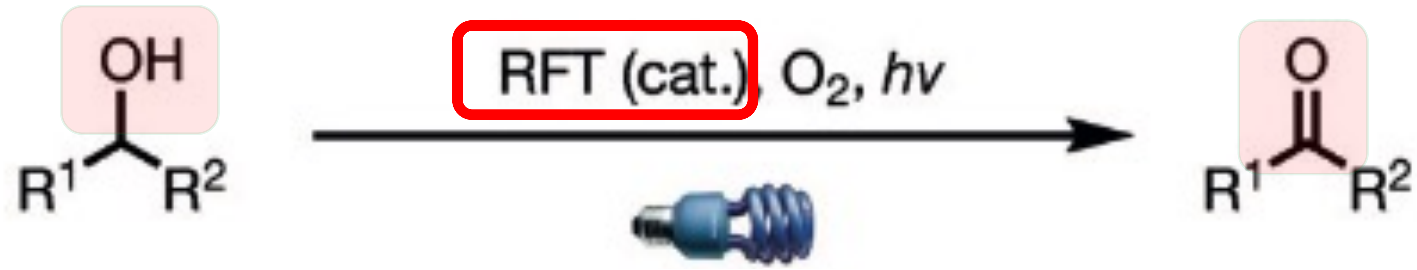
✔ Photoelectrocatalytic **oxidation** of unactivated **alcohols** under e-PRC using **RFT**

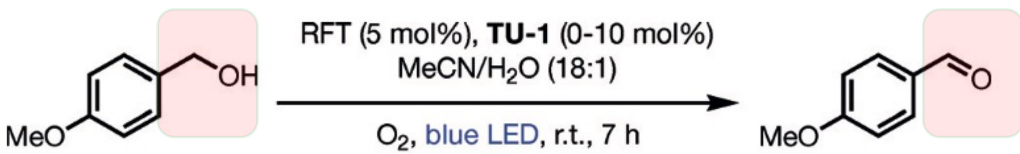


S. Lin *et al. Angew. Chem.* **2020**, *59 (1)*, 409−417.

The Limitation of Flavin-Catalyzed Oxidation of Alcohols

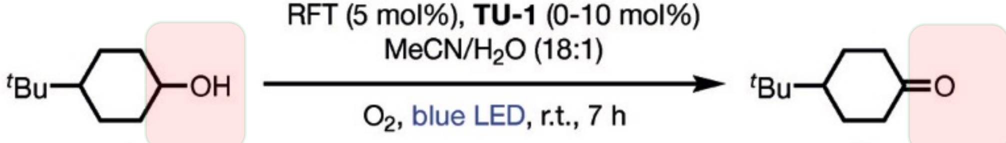
✔ **Flavin**-Catalyzed **Oxidation** of **Alcohols**





1a **2a**

Entry 1: w/o **TU-1**: 40% yield (with 21 mM H_2O_2)
Entry 2: 10% **TU-1**: 85% yield (with 34 mM H_2O_2)

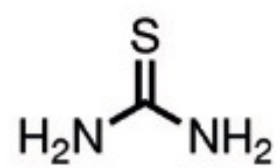


1b **2b**

Entry 3: w/o **TU-1**: 0% yield (H_2O_2 not detected)
Entry 4: 10% **TU-1**: 3% yield (with 2.6 mM H_2O_2)

✔ R_1 = **Ph**, **p-MeO-Ph**, R_2 = H, Me
→ **Successful** reaction

✔ R_1 = **alkyl**, R_2 = H, **alky**
→ **No** reaction

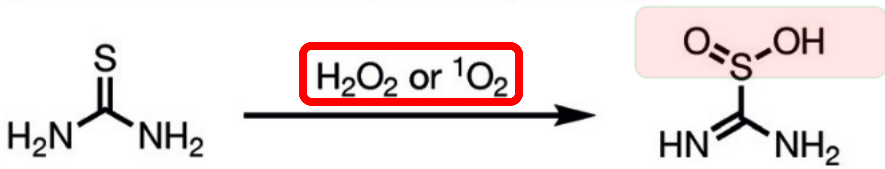


TU-1

S. Lin *et al. Angew. Chem.* **2020**, *59 (1)*, 409−417.

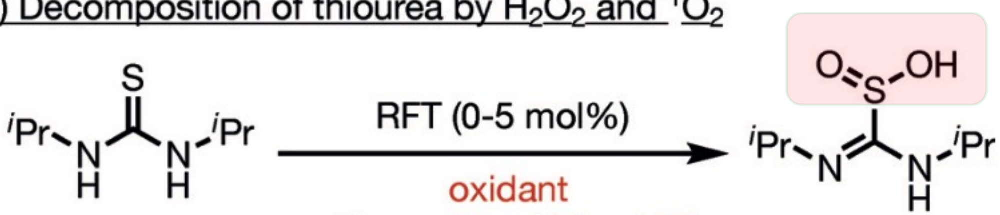
The Decomposition of Thiourea

(A) Proposed thiourea decomposition pathways



TU-1 TU-1•O_2

(B) Decomposition of thiourea by H_2O_2 and $^1O_2$



TU-2 TU-2•O_2

Entry	RFT	oxidant	**TU-2** recovered
1	5 mol%	H_2O_2 (1 equiv)	40%
2	none	H_2O_2 (1 equiv)	37%
3	5 mol%	O_2 + blue LED	0%
4	none	O_2 + blue LED	100%

✔ RFT + **O_2** or **H_2O_2** (BP)
→ **Decomposition** of thiourea

✔ **Influence** O_2 **>** H_2O_2

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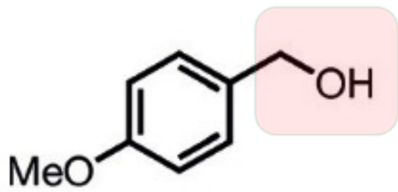
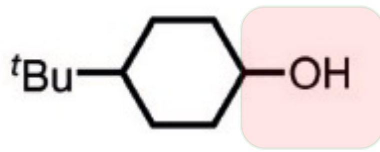
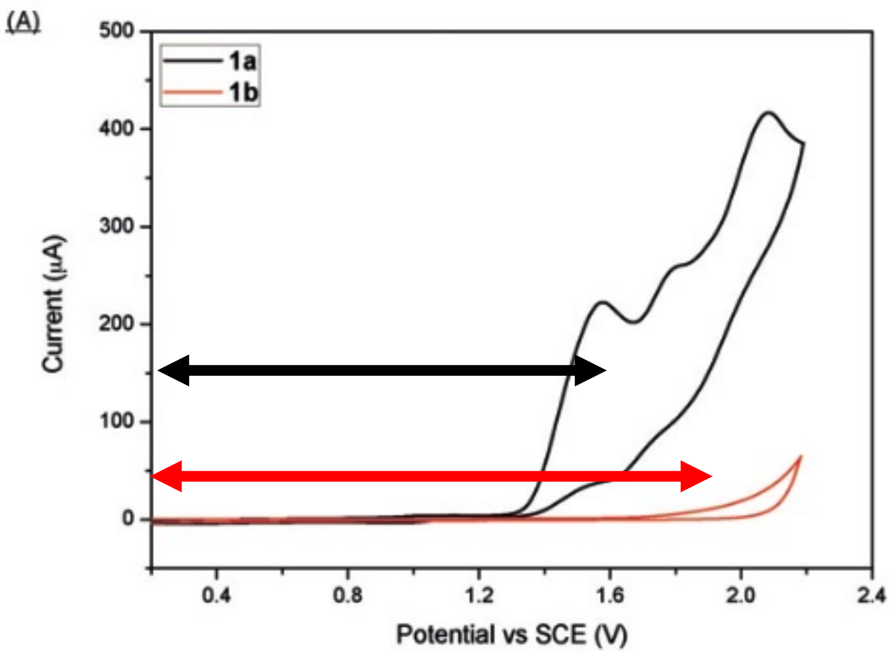
The Decomposition of Thiourea



1a



1b



✔ **Oxidation potential** **1a < 1b**

✔ **Speed**
Decomposition of thiourea **>** Oxidation of **1b**

✔ **Mild** conditions

= **Photoelectrochemistry**

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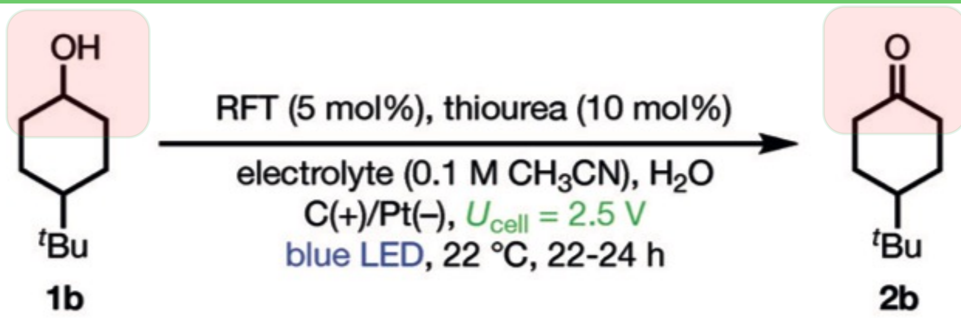
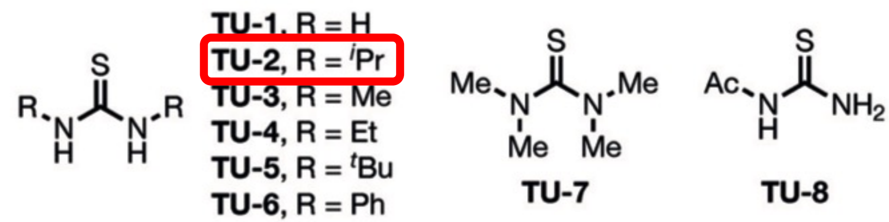
Optimization



Entry	Thiourea	Electrolyte	**1b** Conversion	**2b** Yield[b]
1	**TU-1**	$LiClO_4$	75%	67%
2	**TU-2**	$LiClO_4$	85%	78%
3	**TU-3**, **-4**, or **-5**	$LiClO_4$	27–30%	20–26%
4	**TU-6**	$LiClO_4$	7%	<5%
5	**TU-7**	$LiClO_4$	5%	<5%
6	**TU-8**	$LiClO_4$	27%	21%
7	**TU-2**	$TBABF_4$	24%	18%
8	**TU-2**	$TBAPF_6$	95%	56%
9	**TU-2**	LiOTf	>95%	96% (91%[c])
10[d]	**TU-2**	LiOTf	8%	<5%
11[e]	**TU-2**	LiOTf	8%	<5%
12[f]	**TU-2**	LiOTf	6%	<5%
13	none	LiOTf	11%	6%
14[g]	**TU-2**	LiOTf	12%	9%



Scheme 6. Photoelectrocatalytic oxidation of alcohols. [a] Reaction conditions: alcohol (0.2 mmol, 1 equiv), RFT (5 mol%), TU (10 mol%), electrolyte (3.5 mL, 0.1 M in MeCN), H_2O (0.2 mL), cell voltage U_{cell} = 2.5 V (initial anodic potential E_{anode} ≈ 0.8 V vs. SCE), blue LED. [b] Yield determined by ^{1}H NMR spectroscopy. [c] Yield of isolated product. [d] Without blue LED. [e] Without RFT. [f] Without electricity. [g] Electrolysis at a constant anodic potential of 0.58 V. [h] Reaction time 36 h.

✔ Electrical potential, blue LED, RFT, thiourea
→ All **essential**

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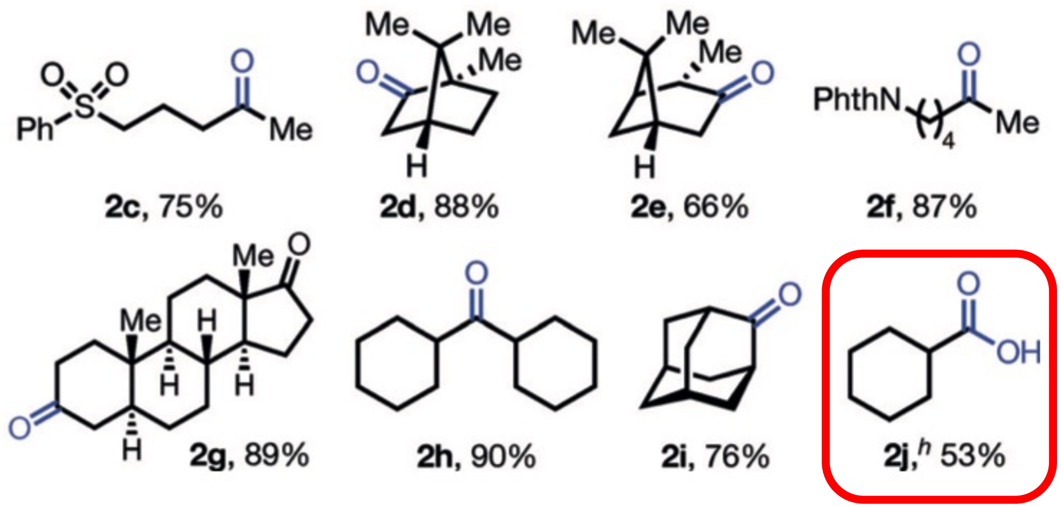
Substrate Scope

(B) Oxidation of several other alcohols[a,c]



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✔ 2c ~ 2d
Successful reactions

✔ 2j
The carboxylic acid → **Affordable**

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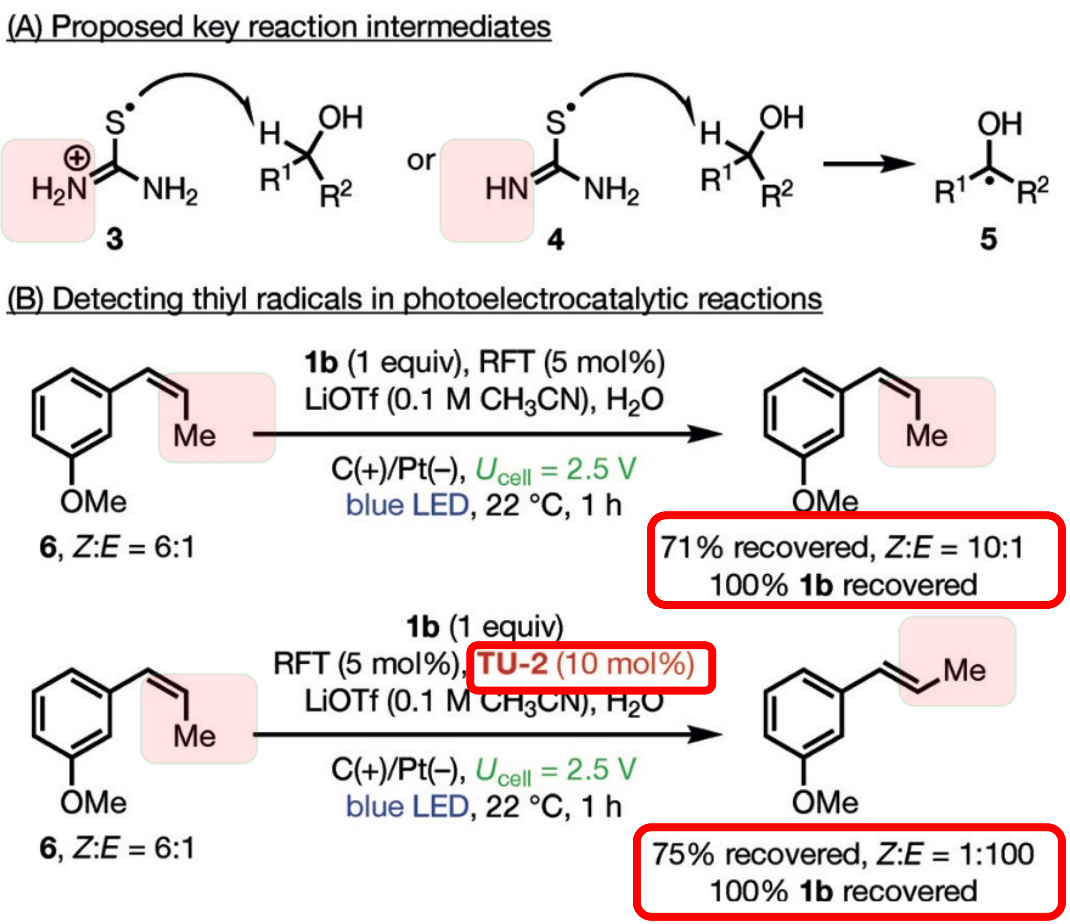
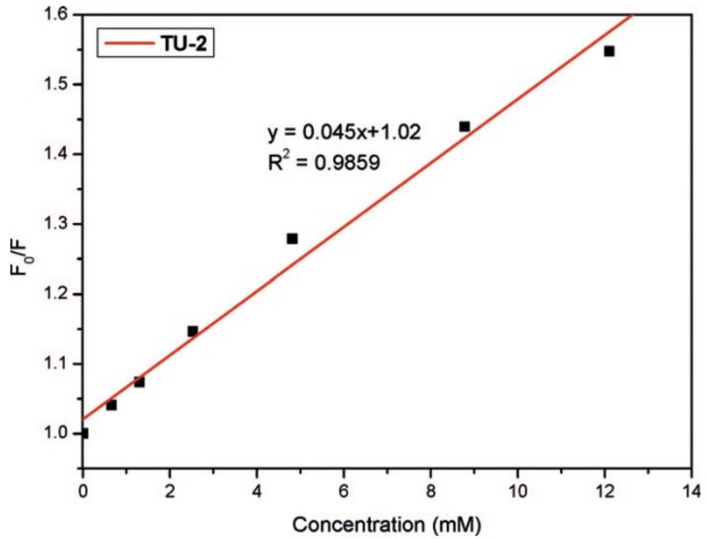
Probing the Role of Thiourea





✔Graph (Photoquenching of RFT)
Thiourea is **oxidized** by RFT*

✔ B
No TU-2 → Z **>** E (**stable**)
TU-2 → Z **<** E (**stable**)
→ TU-2 works as **radical** 3 or 4

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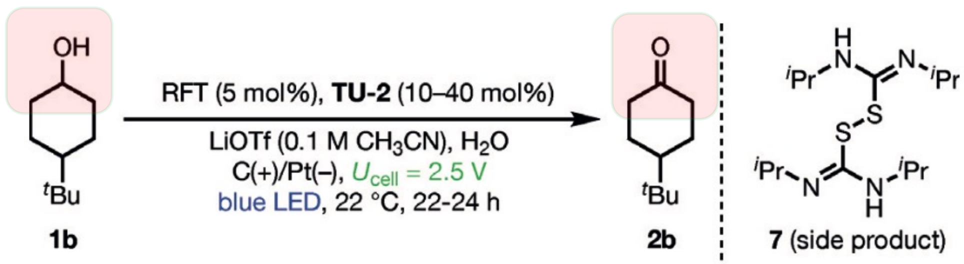
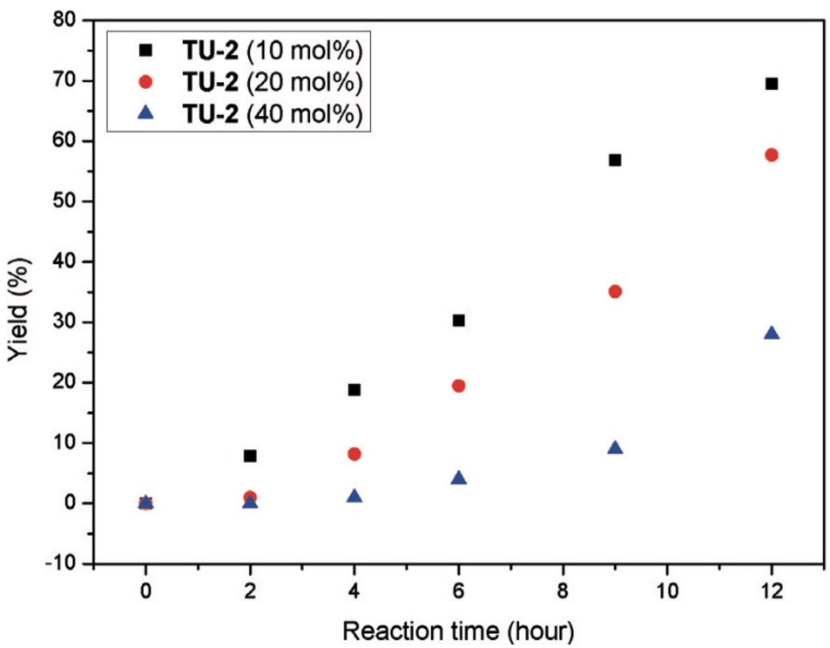
Probing the Role of Thiourea

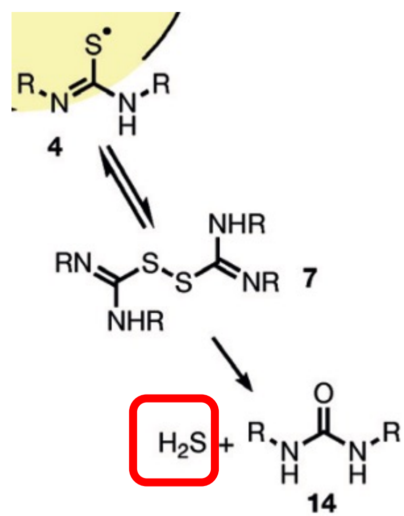




✔ Distinct odor of **H_2S**

✔ **More** TU-2, **less** desired reaction
← **More** TU-2, **more** Reaction 1

✔ TU-2 (40 mol%)
< 4h Desired reaction **<** Reaction 1
> 4h Desired reaction **>** Reaction 1



Proposed reaction
（ Reaction 1 ）

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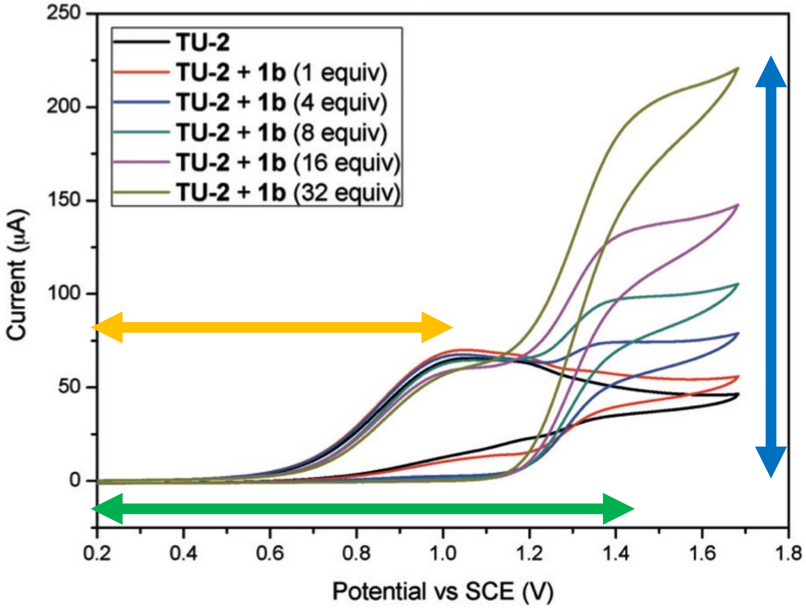
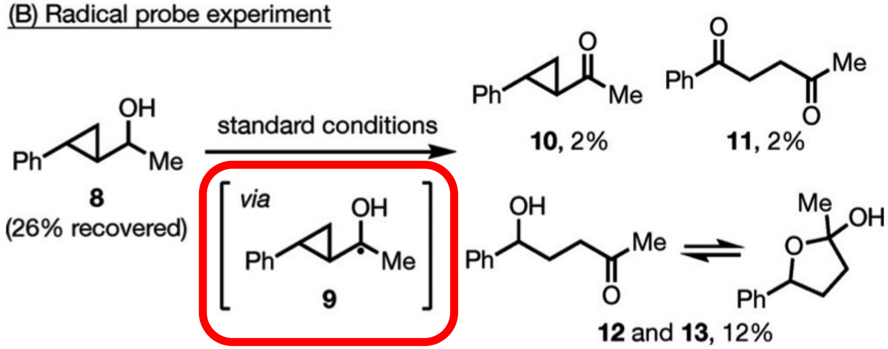
Probing the Role of Thiourea

(A) Cyclic voltammetry of **TU-2** in the absence and presence of **1b**



(B) Radical probe experiment



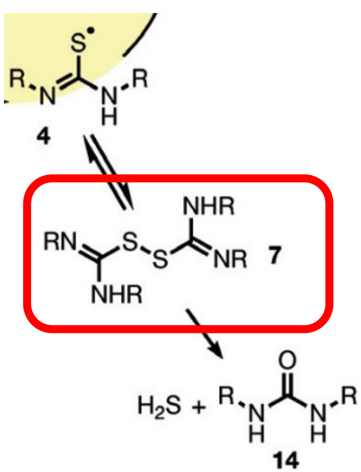
✔ **First peaks** : Including Reaction **1** ??

✔ **Second peaks** : Reaction **2**

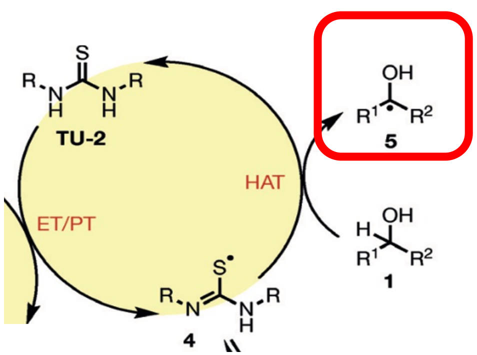
✔ More **1b**, **higher** second peaks
→ TU-2 is **catalyst**

✔ B
5 (**9**) is the **intermediacy**

Reaction 1



Reaction 2



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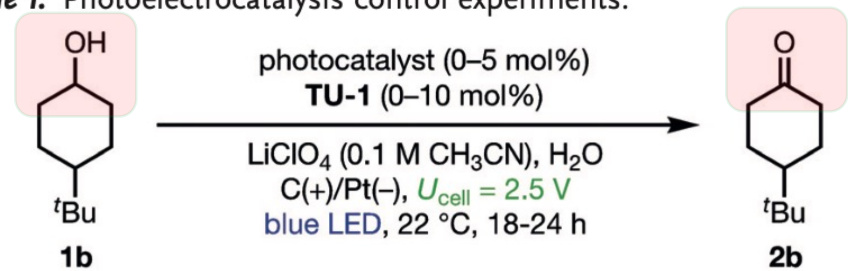
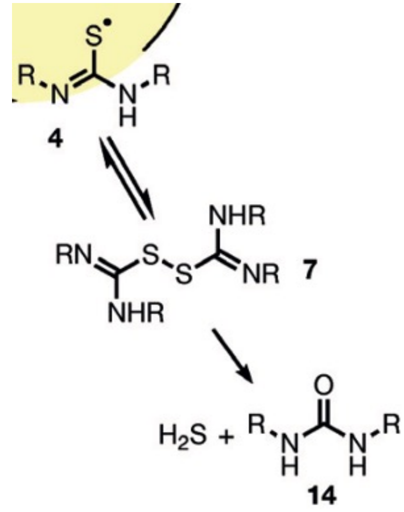
Understanding the Role of RFT

Table 1: Photoelectrocatalysis control experiments.



Entry	Photocatalyst	Thiourea	1b Conv. [%][a]	2b Yield [%][a]
1	RFT	yes	75	67
2	$[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$	yes	32	31
3	$[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$	no	5	< 5
4	$[Mes\text{-}Acr\text{-}Me]^+ClO_4^-$	yes	10	8
5	$[Mes\text{-}Acr\text{-}Me]^+ClO_4^-$	no	< 5	< 5
6	none	yes	13	< 5
7[b]	none	yes	7	< 5
8[c]	none	yes	8	< 5

[a] Determined by ^{1}H NMR spectroscopy. [b] Controlled potential electrolysis at E_{anode} = 1.09 V vs. SCE without light irradiation. [c] Controlled current electrolysis at i = 0.5 mA without light irradiation.



Reaction 1

✔ 6~8

No photocatalyst (RFT)

Reaction 1 **predominates**

✔ 1

Reaction 1 is **suppressed** by the transient photoexcited state of **RFT**

→ **Successful** reaction

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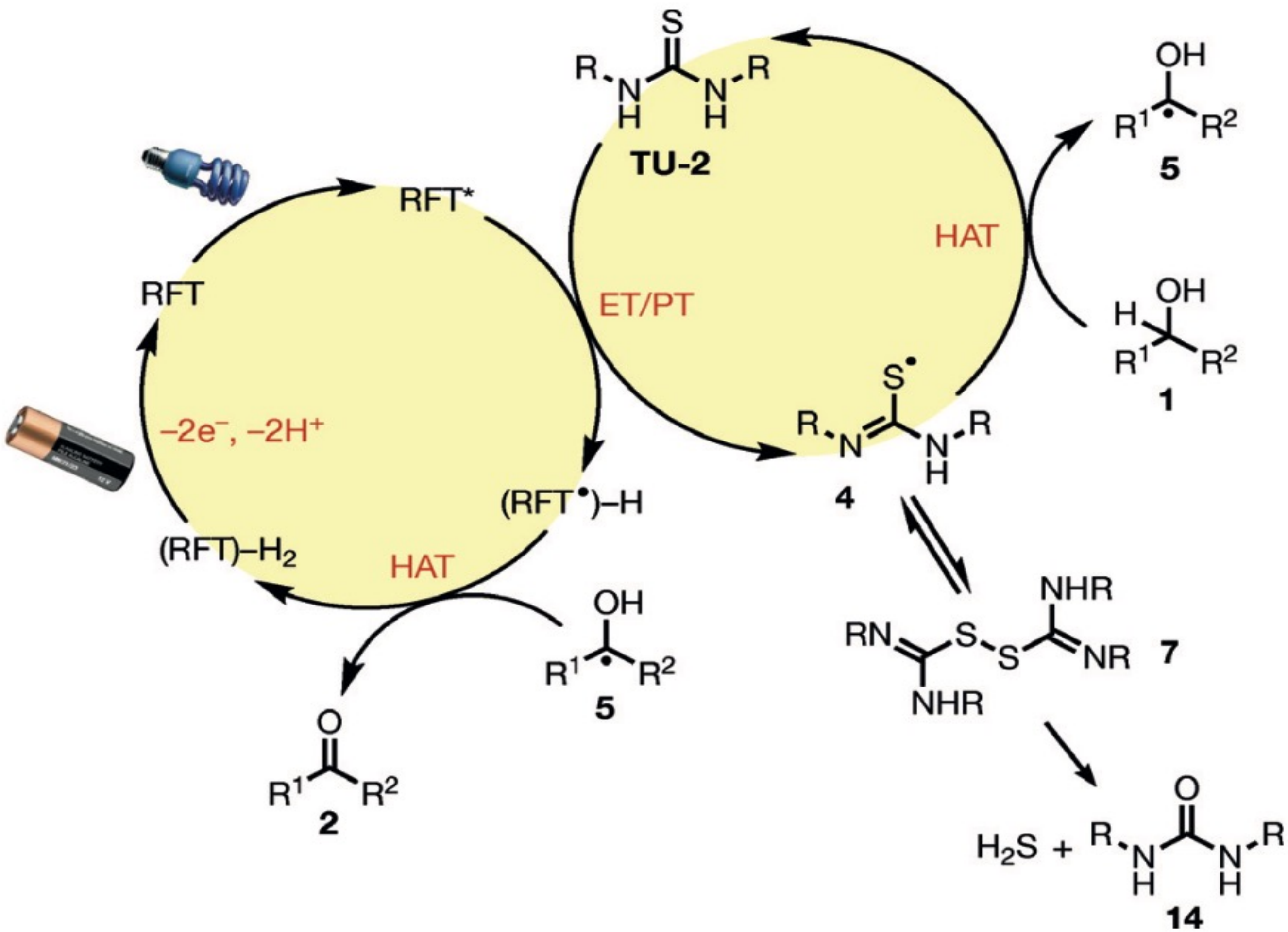
Proposed Catalytic Cycles



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Short Summary

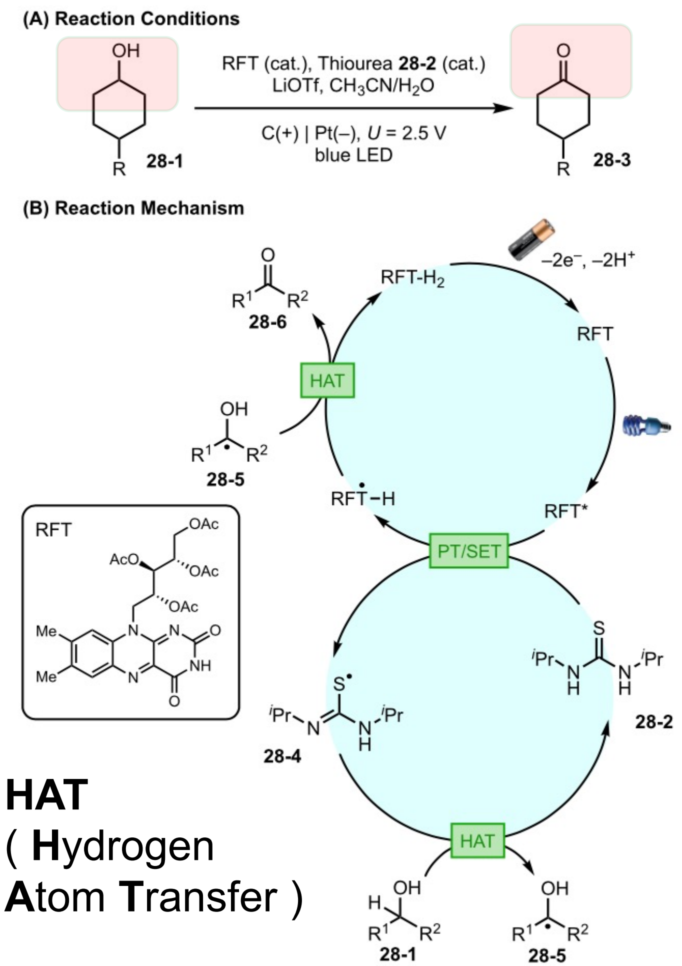

Figure 28. (A, B) EPC employing RFT as both electro- and photochemical catalyst in a single catalytic cycle.

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HAT
(**H**ydrogen
Atom **T**ransfer)

✔ Photoelectrocatalytic **oxidation** of unactivated **alcohols** under e-PRC using **RFT**

✔ **Advantage**

HAT of thiourea oxidizes previously untouched **aliphatic alcohols**

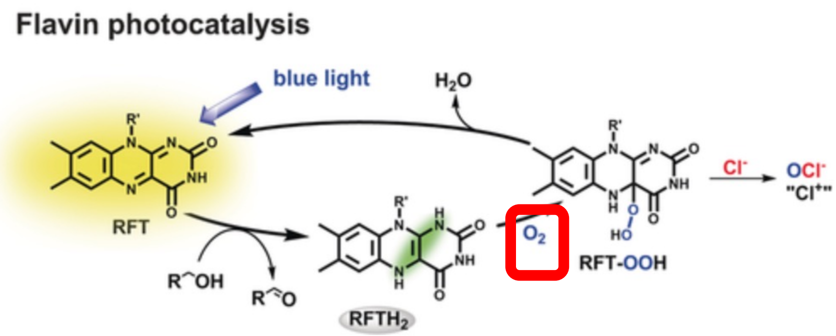
✔ **Good Point**

No O_2, Reduced H_2O_2

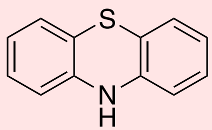
→ O_2 promotes **degradation** of thiourea

H_2O_2 is **byproduct**

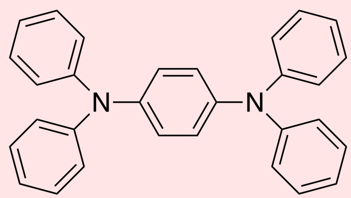
O_2 in traditional method (Flavin photocatalysis)



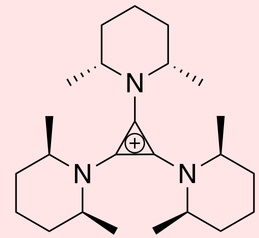
Other Examples of iPEC



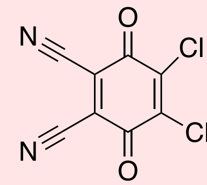
PTZ



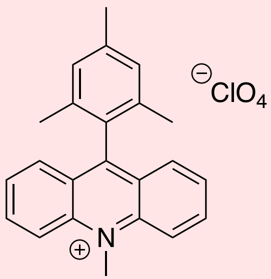
TPPD



TAC+



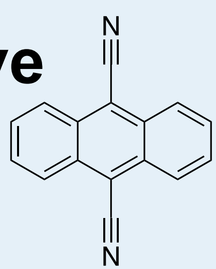
DDQ



Mes-Acr*

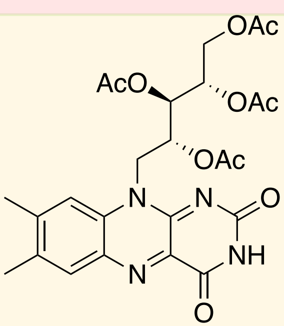
Oxidative

Reductive



DCA

HAT

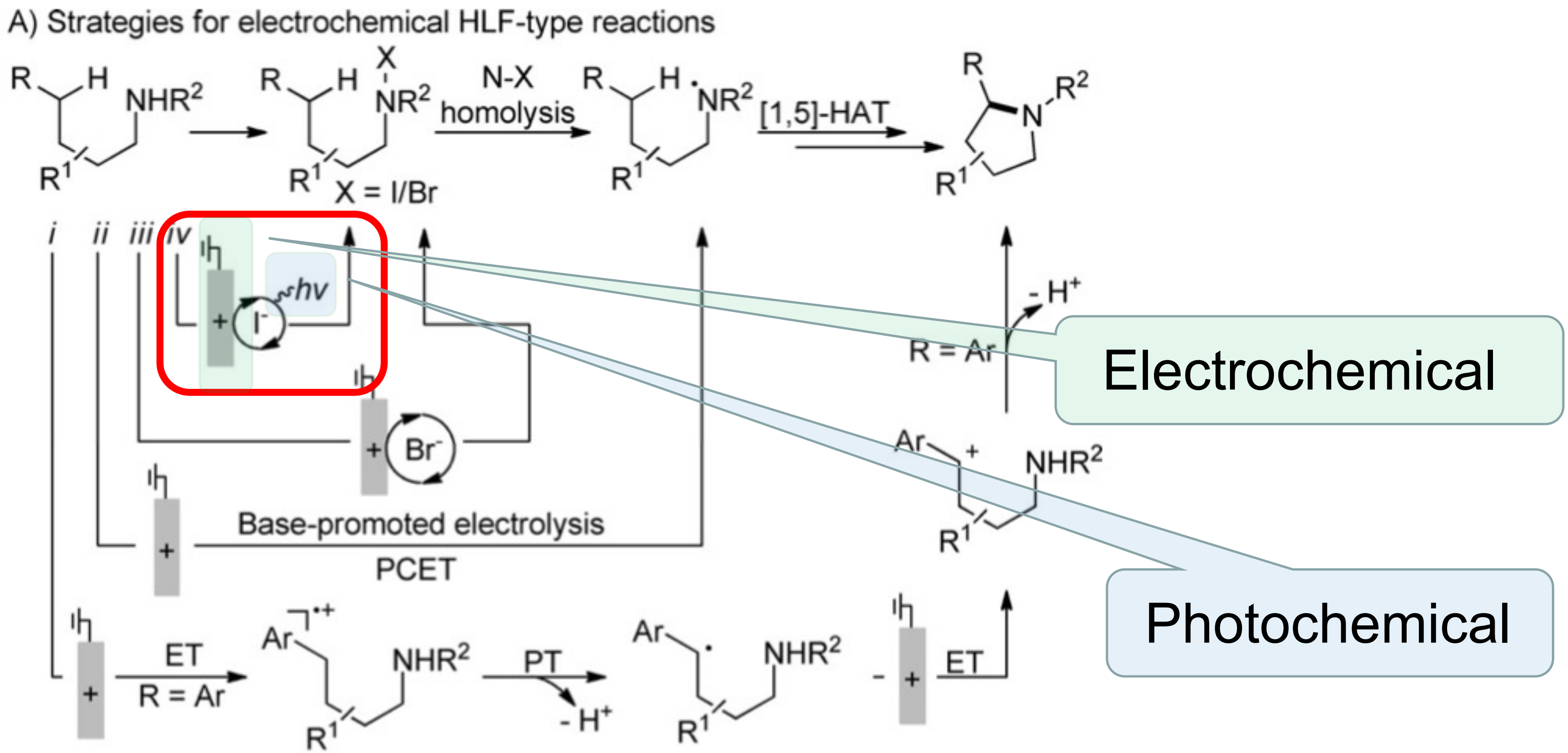


RFT

Contents

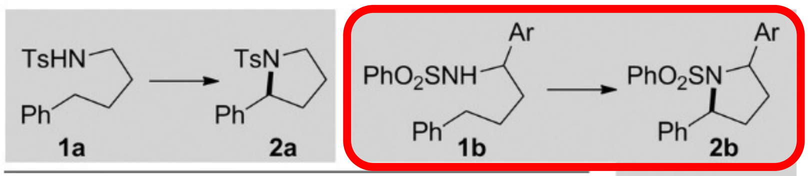
The Example of dPEC

✔ Hofmann–Lçffler–Freytag (**HLF**) **amination** of **C(sp3)-H** bonds under dPEC

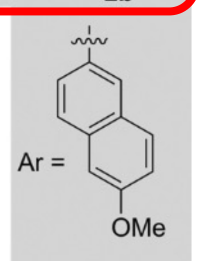


S. Stahl *et al. Angew. Chem.* **2019**, *131*, 6451 – 6456.

The Limitation of Previous Electrochemical HLF amination



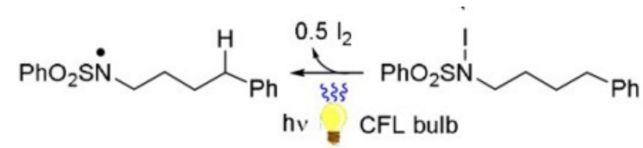
Electrochemical Method	Yield (conversion) 2a	2b
ET-PT-ET[a]	52% (84%)	n.d. (100%)
PCET[b]	86% (100%)	< 10% (100%)
Br^- [c]	71% (85%)	< 10% (100%)



Scheme 1. Comparison of previous electrochemical methods for C-(sp^3)–H amination. For detailed procedures, see Refs. [12–14] and the Supporting Information. Yields were determined by ^1H NMR spectroscopy with *m*-xylene as an internal standard. Conversion is shown within parentheses. [a] Reaction conditions: **1a** or **1b** (0.2 mmol) and $^nBu_4NPF_6$ (0.1 M) in HFIP (10 mL), 2.5 mA, RT. [b] Reaction conditions: **1a** or **1b** (0.2 mmol), NaOAc (0.2 mmol) and $^nBu_4NBF_4$ (0.2 mmol) in DCE/HFIP (6 mL, 2:1), 7.5 mA, RT. [c] **1a** or **1b** (0.4 mmol), NaOMe (0.2 mmol) and KBr (0.2 mmol) in methanol (6 mL) at 65 °C, 100 mA. DCE = 1,2-dichloroethane. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, n.d. = not detected, Ts = 4-toluenesulfonyl.

✔ 1a → 2a
Successful reaction

✔ 1b → 2b
No reaction



Reaction 1

✔ Promote Reaction 1

= **Photoelectrochemistry**

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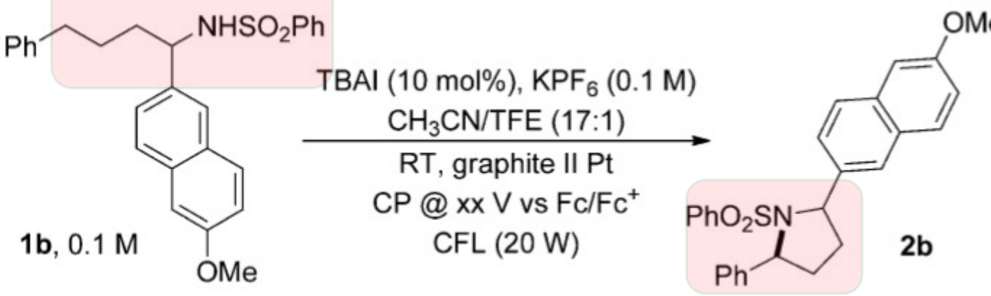
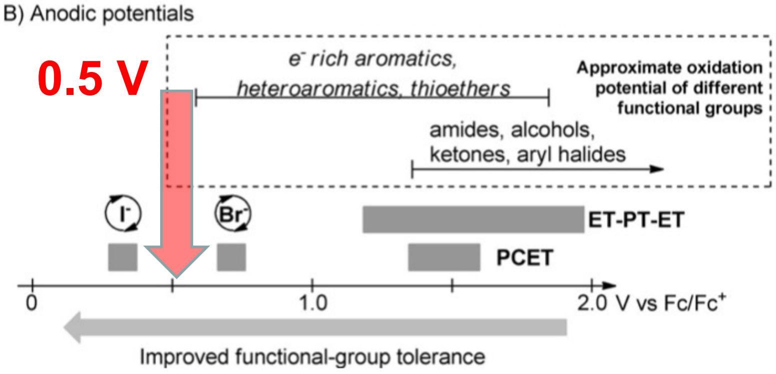
Optimization

Table 1: Combined electrochemical/photochemical iodide-mediated process for C–H amination.[a]



Entry	Potential/V vs. Fc/Fc$^+$	TBAI	Yield [%]
1	0.3	10 mol%	4
2	0.4	10 mol%	70
3	0.5	10 mol%	75 (72)
4	0.5	–	n.d.
5[b]	0.5	10 mol%	19

[a] The reaction was performed on a 0.5 mmol scale under constant potential (CP) conditions. Yields were determined by ^{1}H NMR spectroscopy with *m*-xylene as an internal standard. Yield of isolated product shown within parentheses. [b] Without irradiation. TFE = 2,2,2-trifluoroethanol, n.d. = not detected.



✔ 3
0.5 V → **Best** Potential

✔ 4, 5
TBAI, irradiation → **Essential**

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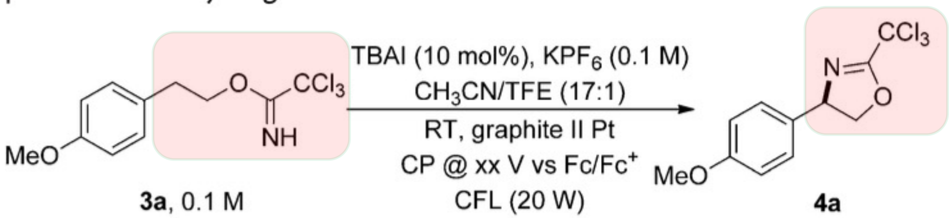
Optimization

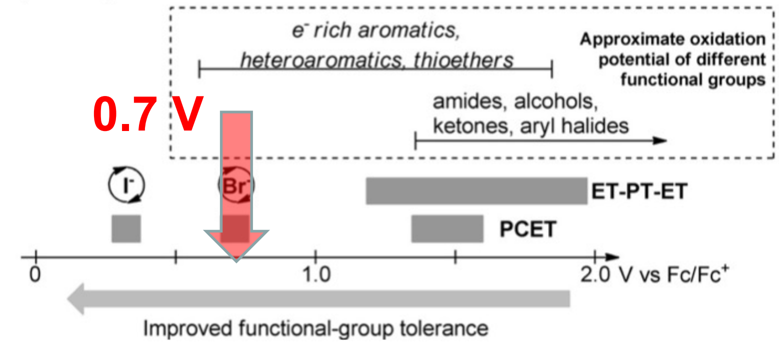
Table 2: Combined electrochemical/photochemical iodide-mediated process for dehydrogenative amination of imidate.[a]



Entry	Potential/V vs. Fc/Fc$^+$	TBAI (mol%)	Yield [%]
1	0.5	10	54
2	0.3	10	47
3	0.7	10	71
4[b]	0.7	10	82 (73)
5[b]	0.7	–	n.d.
6[b,c]	0.7	10	2

[a] The reaction was performed on a 0.5 mmol scale under constant potential (CP) conditions. Yields were determined by ^{1}H NMR spectroscopy with *m*-xylene as an internal standard. Yield of isolated product shown within parentheses. [b] With 1 equiv of pyridine. [c] Without irradiation.

B) Anodic potentials



✔ 4
0.7 V → **Best** Potential

✔ 5, 6
TBAI, irradiation → **Essential**

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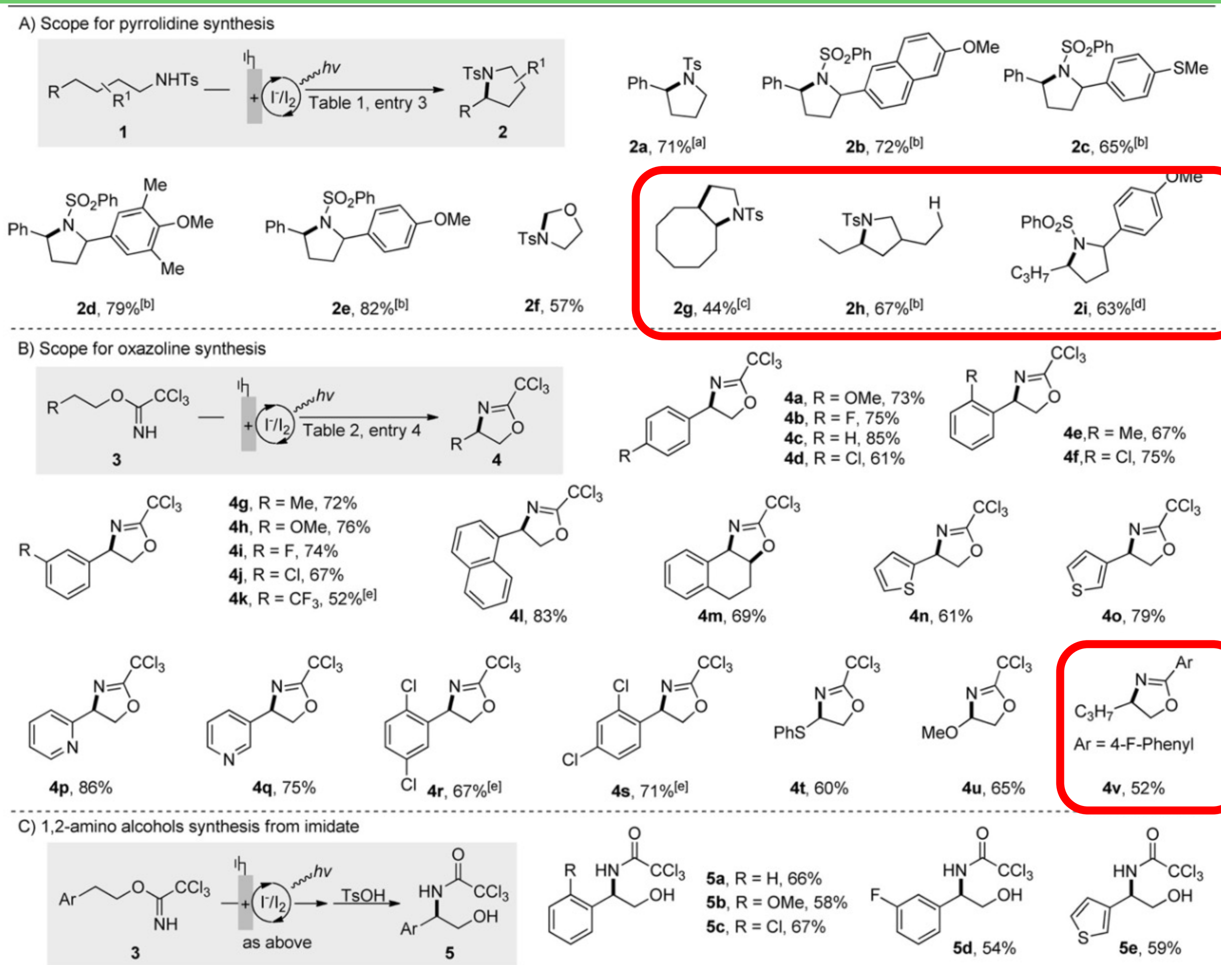
Substrate Scope



Unactivated aliphatic C-H bond

Scheme 2. Substrate scope of iodide-mediated dehydrogenative amination. The reactions were conducted on a 0.5 mmol scale. See the Supporting Information for details. All yields are those of the isolated products. [a] **2a** has also been produced under conditions with stoichiometric chemical oxidants: $PhI(OAc)_2$/*cat.* I_2, 90%;[11a] $PhI(OAc)_2/I_3^-$, 93%;[10g] mCPBA/*cat.* I_2, 54%;[11c] [b] dr = 1:1. [c] dr = 1.8:1. [d] dr = 1.2:1. [e] With 2,6-lutidine instead of pyridine as additive. TsOH = *p*-toluenesulfonic acid.

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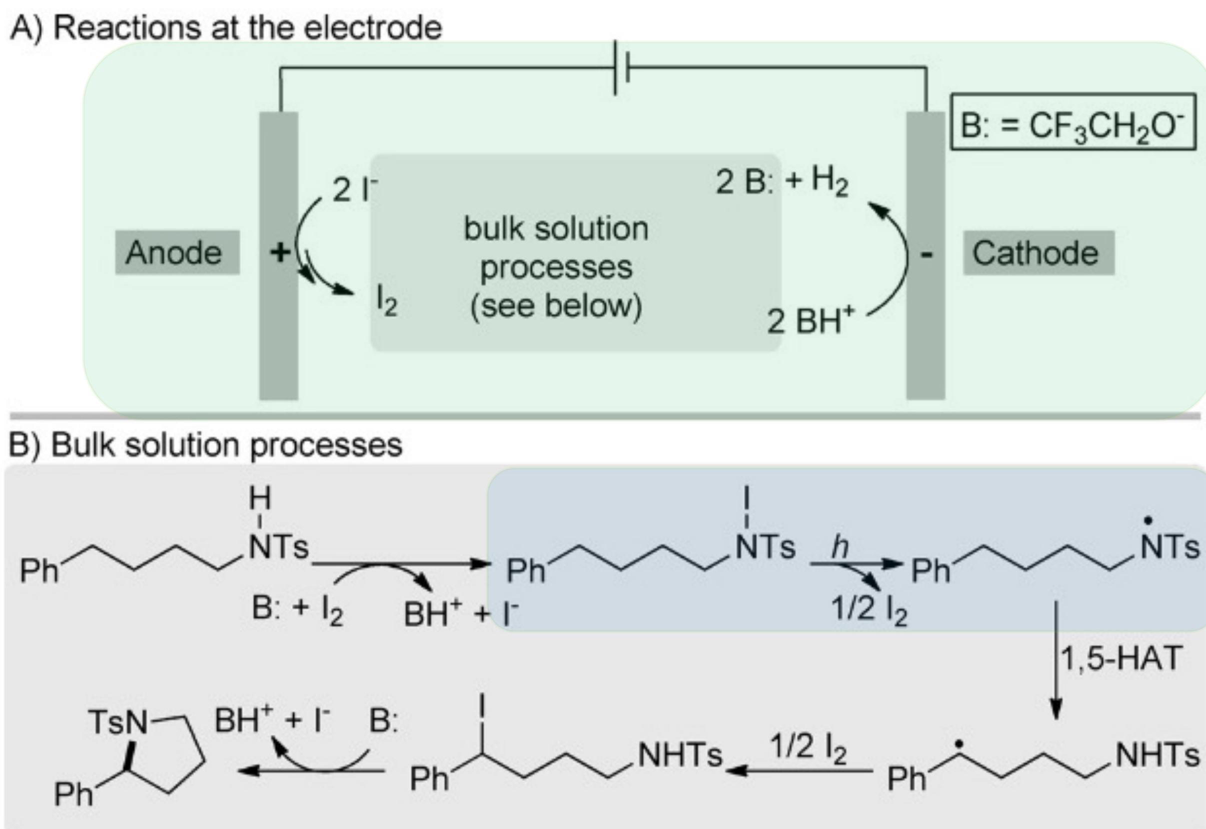
Proposed Mechanism



Scheme 3. Simplified mechanism for photo/electrochemical iodide-mediated dehydrogenative C–H/N–H coupling.

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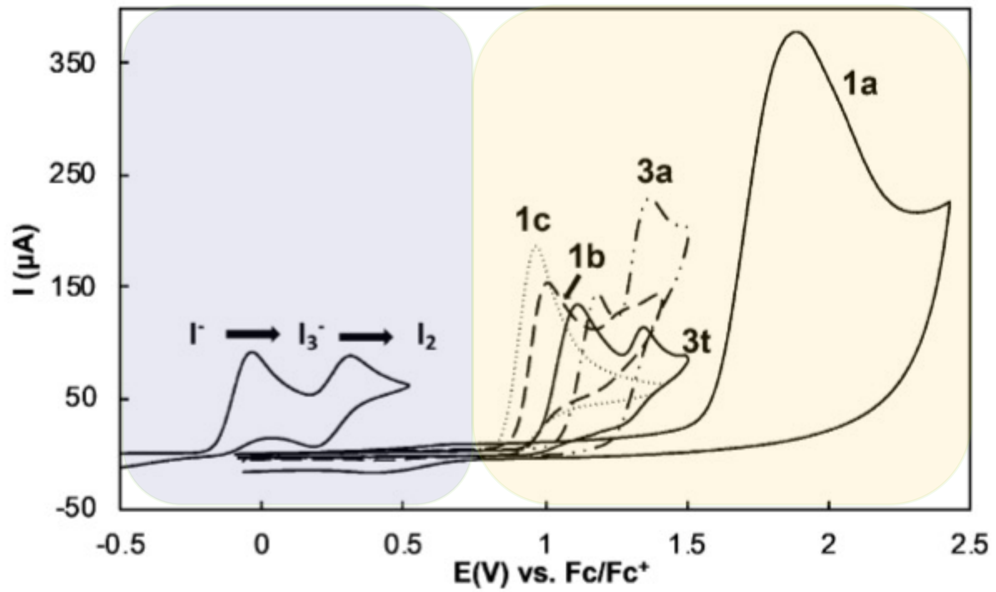
Functional-Group Tolerance

$I^- \rightarrow I_3^- \rightarrow I_2$



Substrates

Scheme 4. CVs of iodide and representative substrates. Conditions: 5 mM substate in acetonitrile with KPF_6 (0.1 M) as supporting electrolyte, glassy carbon as working electrode (≈7.0 mm^2), and a platinum wire counter electrode, scan rate = 100 $mV\,s^{-1}$.

✔ Potential $I^- \rightarrow I_3^- \rightarrow I_2$ **<** **Substrates**

→ Functional-group **tolerance** is achieved

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Short Summary

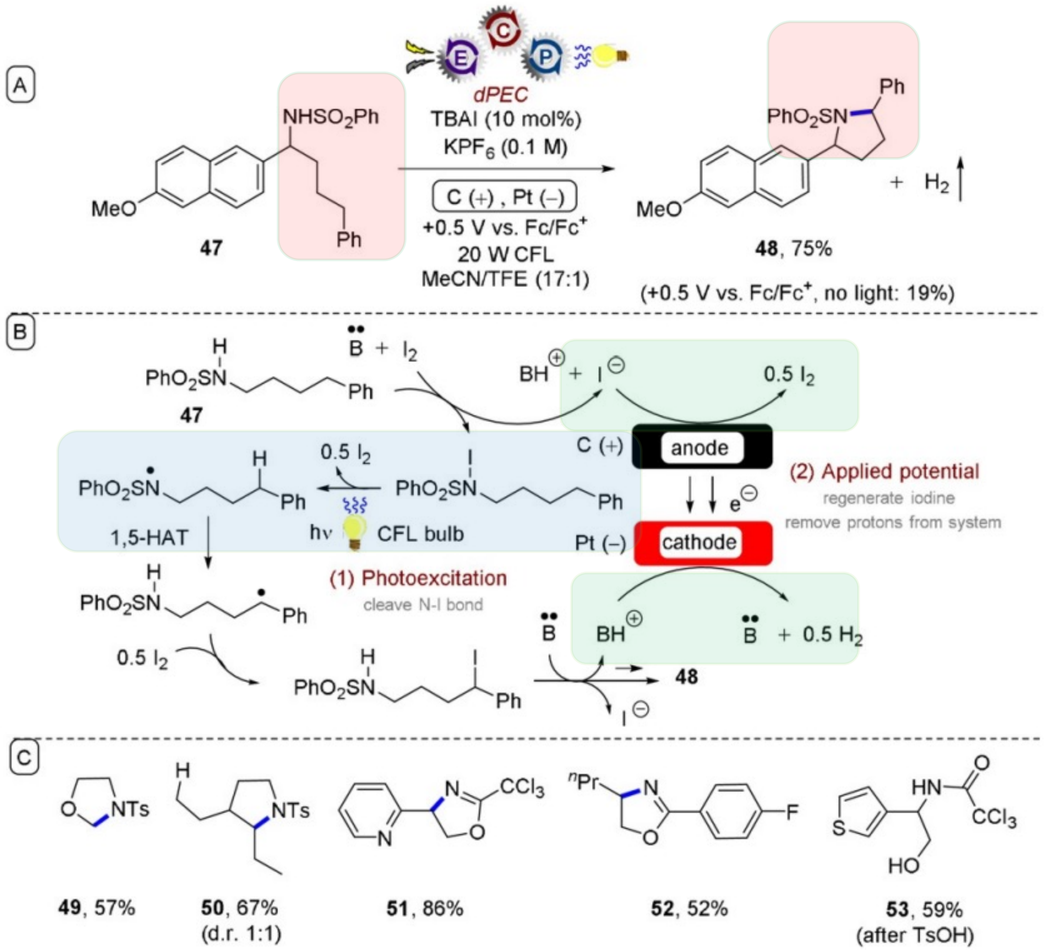

Figure 11. A) Hofmann–Löffler–Freytag amination of C(sp³)–H bonds under dPEC. B) Proposed mechanism. C) Example scope.

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✔ Hofmann–Lçffler–Freytag (**HLF**) **amination** of **C(sp3)-H** bonds under dPEC

✔ **Applied potential**
→ Regenerate iodine and remove protons from system

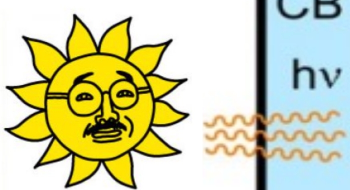
✔ **Photoexcitation**
→ Cleave N-I bond

✔ **Advantage**
= **Low** anodic potentials
→ **Mild condition**,
High selectivity

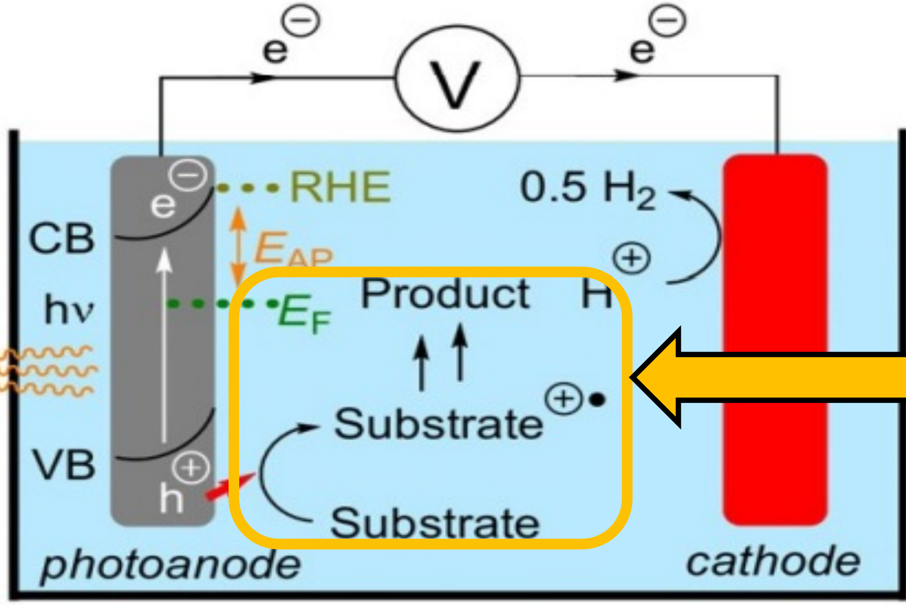
Contents

The Mechanism of iPEC

おっ!!サンテレビ



sunlight



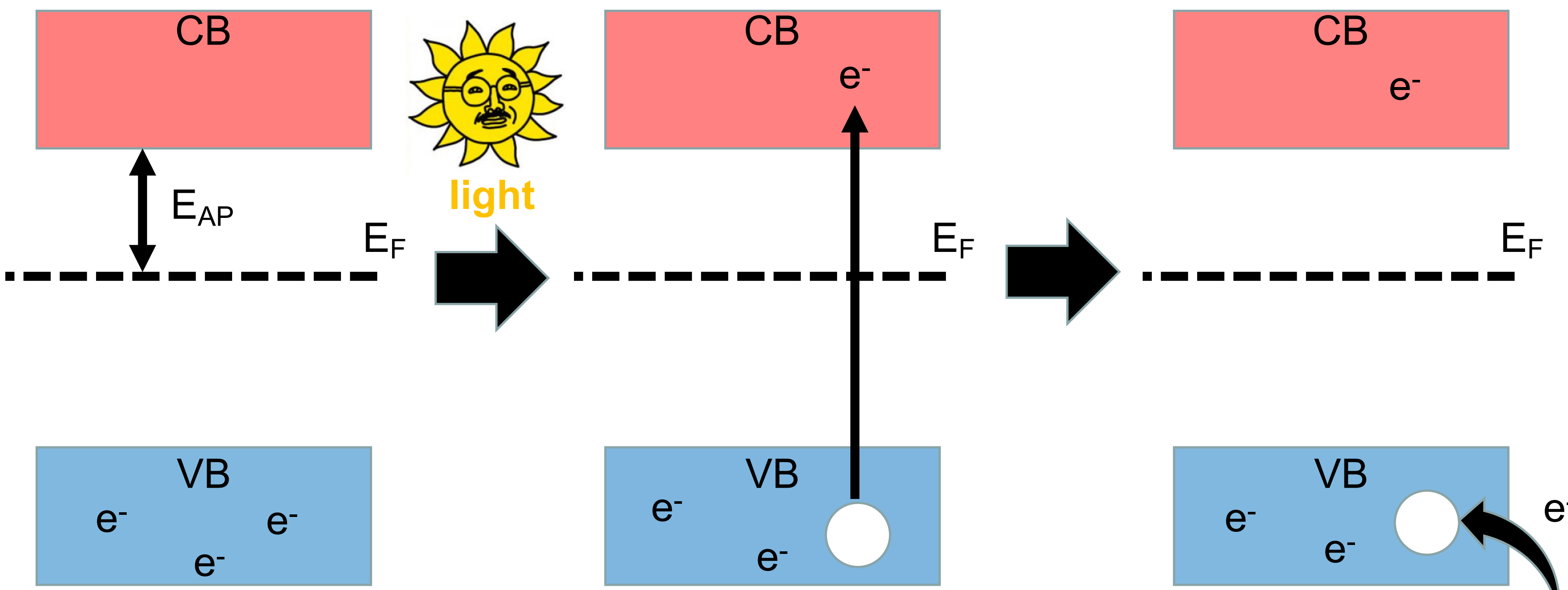
Reaction of
iPEC

Figure 12. Schematic of a photoanode used for oxidation of organic compounds. RHE: relative Hydrogen electrode; E_{AP}: applied potential; E_F: Fermi level; CB: conduction band; VB: valence band.

Photoelectrode is coated in a **photoresponsive material** (typically, **semiconductor**) whose **band gap** corresponds to the energy of a **visible-light photon**

K. Y. Ye *et al. Org. Chem. Front.* **2020**, *7*, 131.

The Mechanism of Photoanode



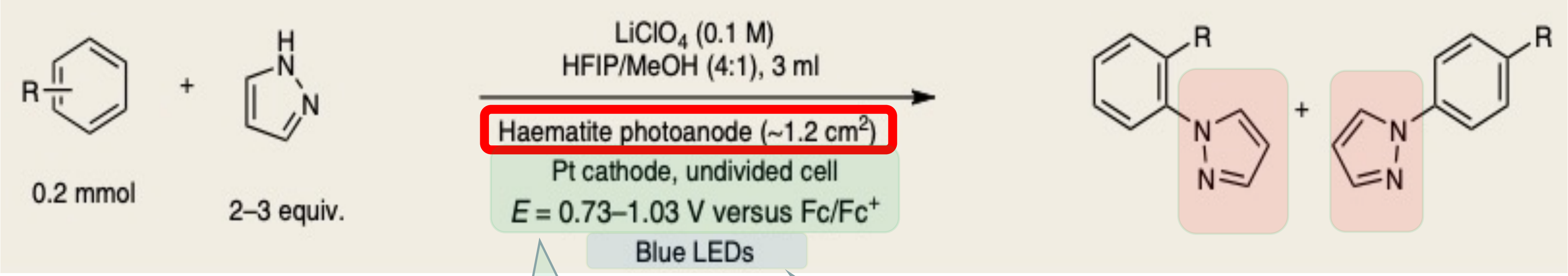
E_F : Fermi level
E_{AP} : applied potential
CB : conduction band
VB : valance band

E_{AP} is used to improve **charge carrier separation** upon **irradiation**
E_{AP} promotes **an electron from VB to CB**

Electron transfer generate **a hole** that is used for reaction

The Example of iPEC

✔ iPEC **C-H amination** of electron-rich **arenes** with a **α-Fe_2O_3** photoanode

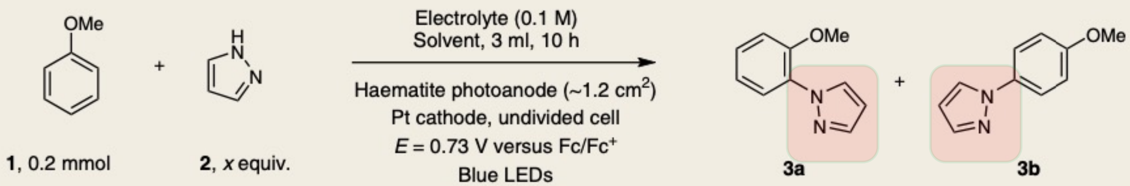


Electrochemical

Photochemical

X. Hu *et al. Nat. Catal.* **2019**, *2*, 366 – 373.

Optimization



Entry	**2** (x equiv.)	Electrolyte	Solvent	Yield (%)[a]	**3a:3b**
1	2.0	$TBAPF_6$	CH_3CN	0	--
2	2.0	$TBAPF_6$	CH_2ClCH_2Cl	14	1:1
3	2.0	$TBAPF_6$	HFIP/MeOH (4:1)	75	4:1
4	2.0	$TBAPF_6$	CF_3COOH/MeOH (4:1)	0	--
5	2.0	$TBAPF_6$	HFIP	0	--
6	2.0	$TBAPF_6$	MeOH	0	--
7	**2.0**	**$LiClO_4$**	**HFIP/MeOH (4:1)**	**77**	**6:1**
8	2.0	$LiClO_4$	HFIP/MeOH (3:1)	78	4:1
9	2.0	$LiClO_4$	HFIP/MeOH (5:1)	62	8:1
10	3.0	$LiClO_4$	HFIP/MeOH (4:1)	86	3:1
11[b]	2.0	$LiClO_4$	HFIP/MeOH (4:1)	0	--
12[c]	2.0	$LiClO_4$	HFIP/MeOH (4:1)	0	--
13[b,d]	2.0	$LiClO_4$	HFIP/MeOH (4:1)	58	2:1
14[b,e]	2.0	$LiClO_4$	HFIP/MeOH (4:1)	38	12:1

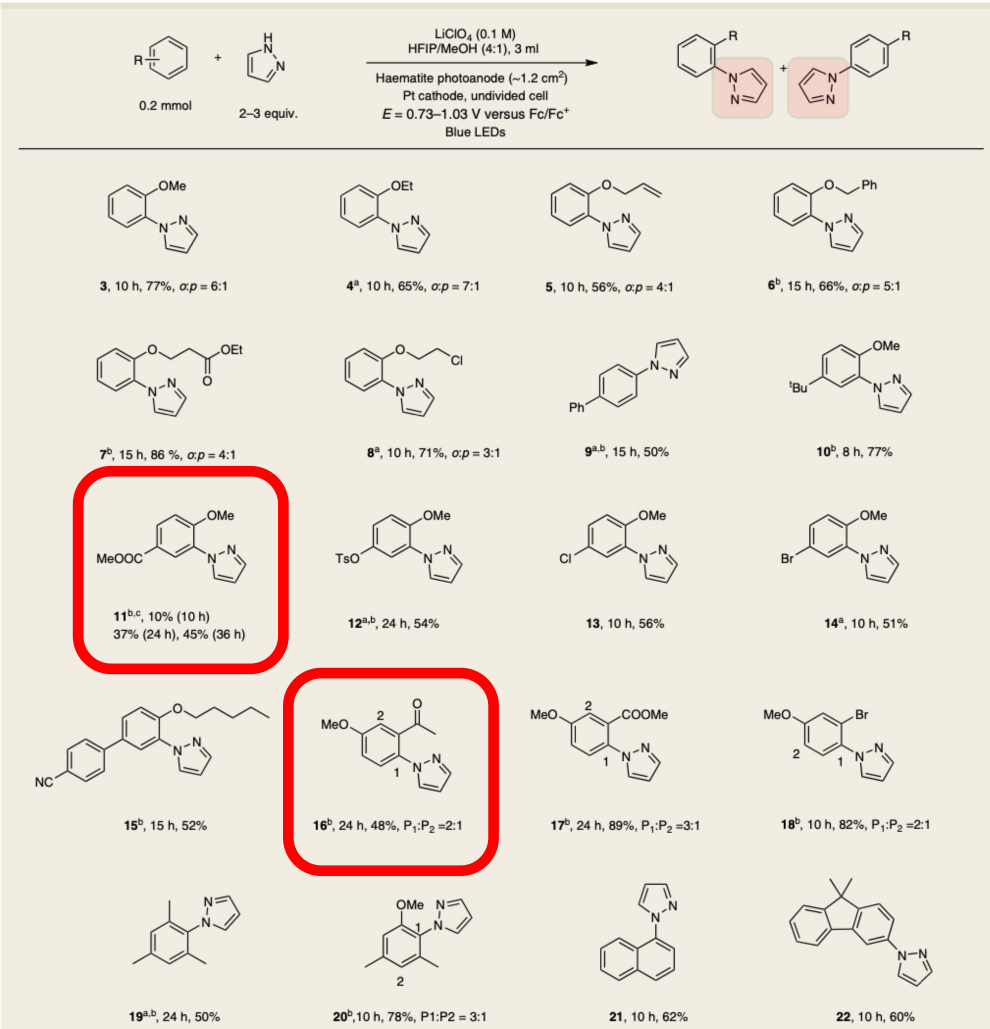
[a]Yield determined by gas chromatography. [b]Without light. [c]Without electricity. [d]Applied potential, $E = 1.53$ V versus Fc/Fc^+. [e]Glassy carbon (~1.2 cm^2) was used as the anode; applied potential, $E = 1.33$ V versus Fc/Fc^+.

✔ 5, 6, 11, 12
HFIP, MeOH, light, electricity
→ All **essencial**

✔ 7
Most optimized

X. Hu *et al. Nat. Catal.* **2019**, *2*, 366 – 373.

Substrate Scope



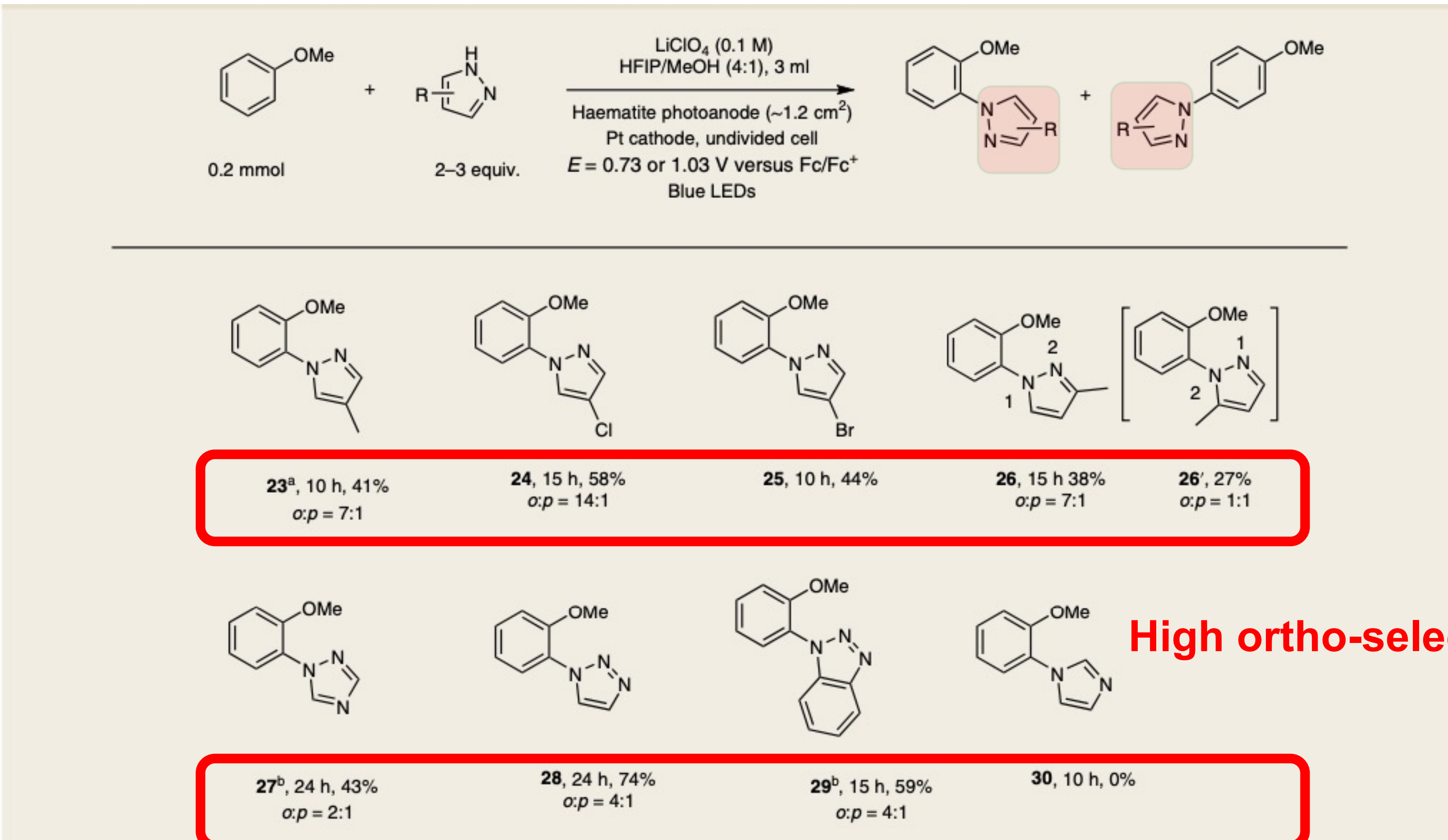
X. Hu *et al. Nat. Catal.* **2019**, *2*, 366 – 373.

✔ High **ortho**-selectivity

✔ 11, 16
Substrates with **high oxidative potentials** give **low yields**
← The oxidation was **inefficient**

✔ 11
Extend the reaction time
≠ Achieve a high yield

Substrate Scope



High ortho-selectivity

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Late-Stage Functionalization of Pharmaceuticals

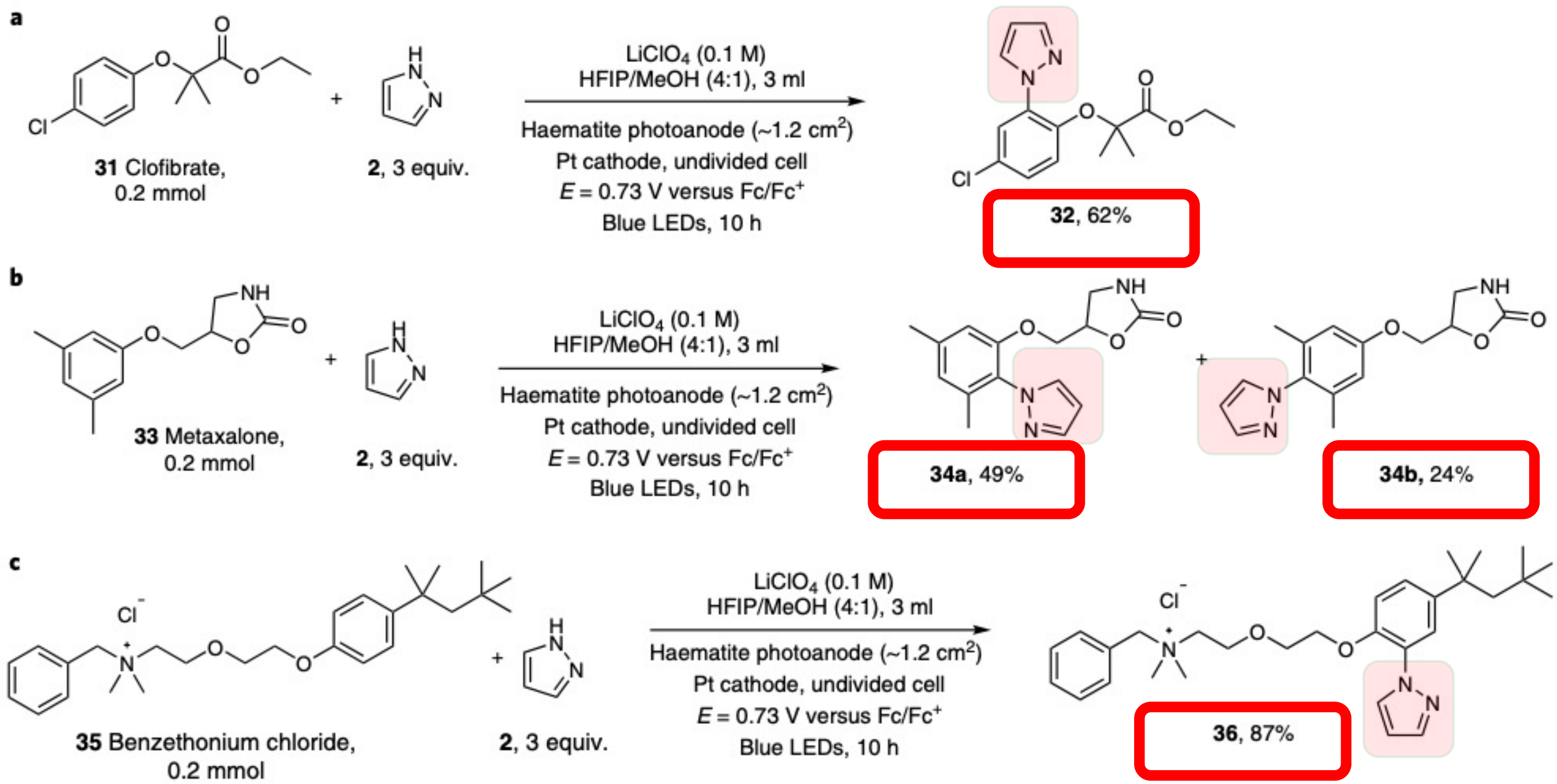
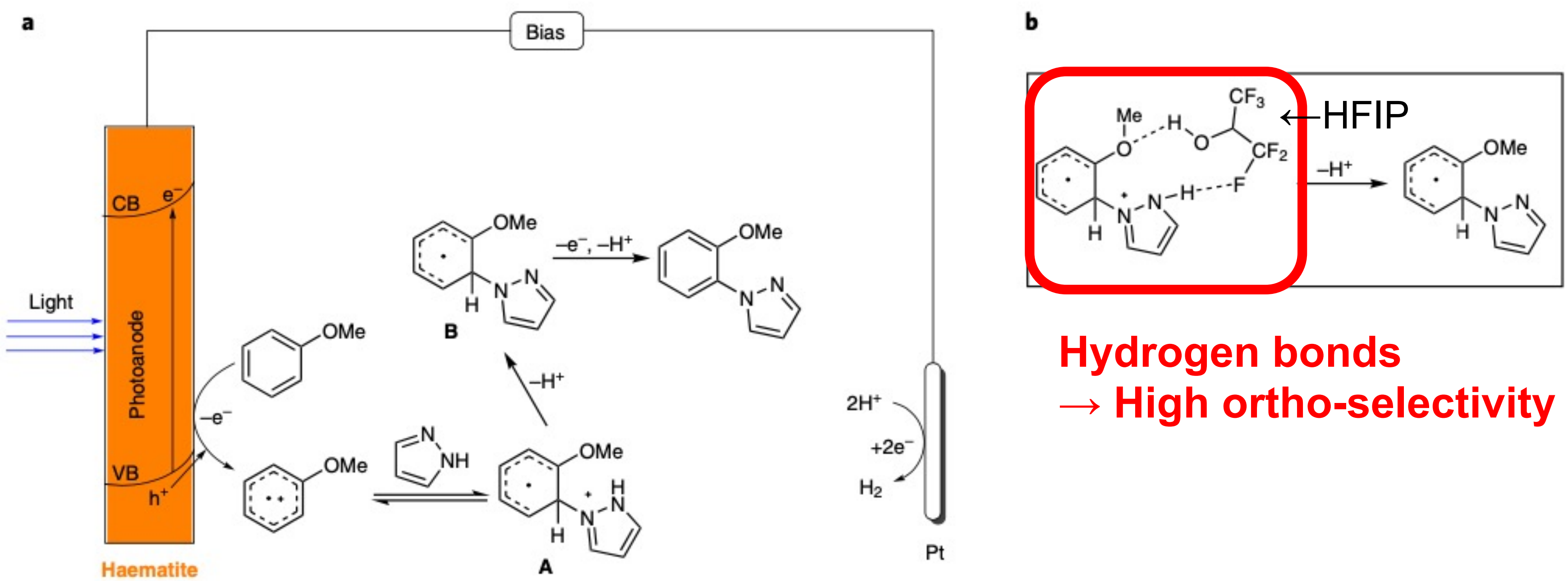


Fig. 3 | Late-stage functionalization of pharmaceuticals. a, C-H amination of clofibrate. **b**, C-H amination of metaxalone. **c**, C-H amination of benzethonium chloride.

X. Hu *et al. Nat. Catal.* **2019**, *2*, 366 – 373.

Proposed Mechanism



Hydrogen bonds
→ High ortho-selectivity

Fig. 5 | Mechanistic hypothesis. a, Proposed mechanism of C–N bond formation. **b**, Proposed hydrogen bonding among anisole, HFIP and pyrazole.

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Short Summary

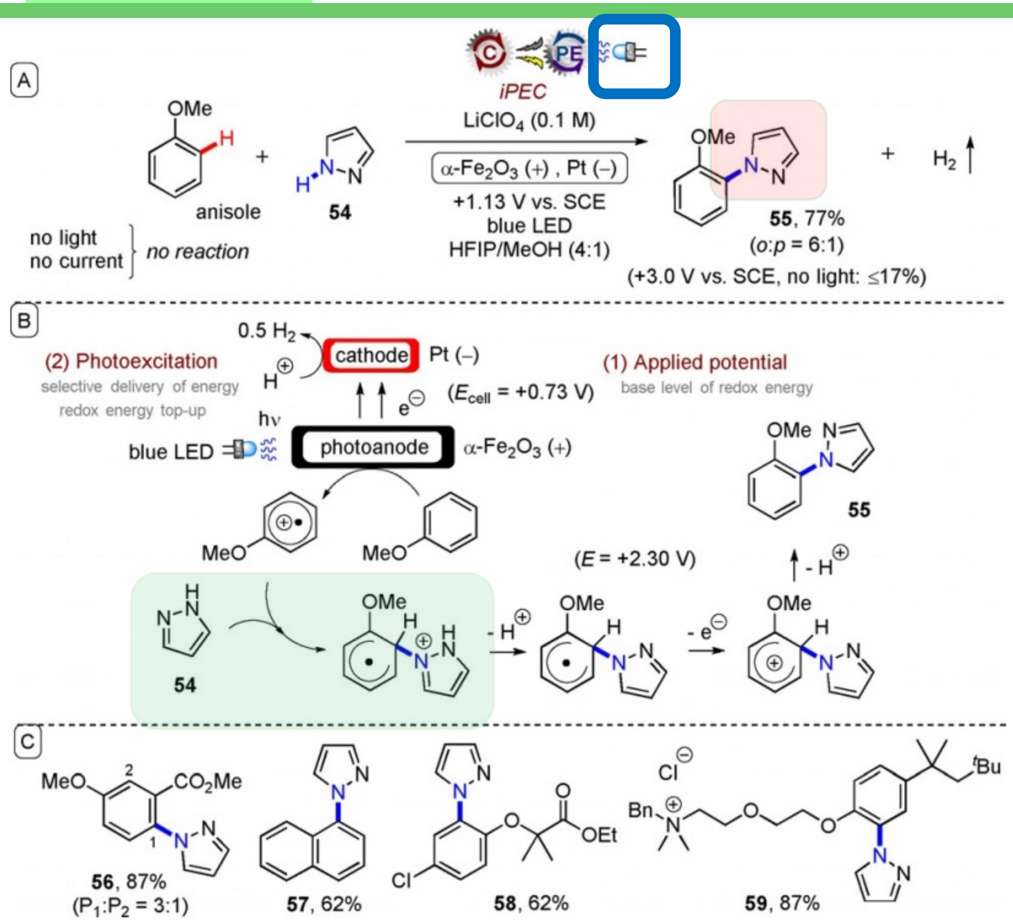


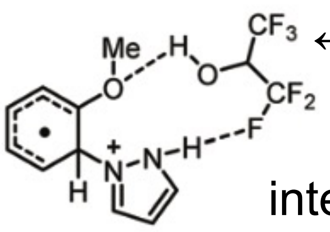
Figure 13. A) iPEC C–H amination of electron-rich arenes with a hematite photoanode. B) Proposed mechanism. C) Example scope.

✔ iPEC **C-H amination** of electron-rich **arenes** with a **α-Fe_2O_3** photoanode

✔ High **ortho**-selectivity

↑

Hydrogen bonds



✔ a-Fe_2O_3 photoanode + **Blue LEDs**
= **Highly oxidizing**

X. Hu *et al. Nat. Catal.* **2019**, *2*, 366 – 373.

Summary of iPEC

✔ **Advantages**

✔Leveraging the energy of visible light to **offset** the E_{AP}
→ **Better selectivity** and **energy efficiency**

✔ **Not only** a chromophore in solution
→ Substrates absorbing **no** visible light can be used

✔ **Disadvantages**

✔ **Energy benefits** iPEC **<** ePRC
← ePRC can access **very high** redox potentials

Contents

Summary

Advantages

- ✔ **Mild** condition
- ✔ **High** selectivity
- ✔ Atom / Energy **efficiency**
- ✔ **Large** redox window
- ✔ **Convenient** energy-input tuning
- ✔ **No** oxidant / reductant

Highly Promising Strategy!!!

- ✔ **Greenness**
- ✔ **Forming** difficult chemical bonds
- ✔ **More** potent catalyst
- ✔ **Meeting** the specific reaction`s requirements

Thank you for your attention !!!