Photoelectrochemistry in Organic Synthesis

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2020-12-25

Contents

Contents

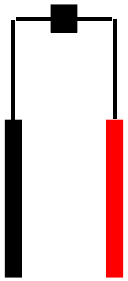
Introduction

Synthetic Organic Electrochemistry

Electrochemical Cells

undivided cell

power



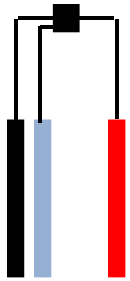
working electrode

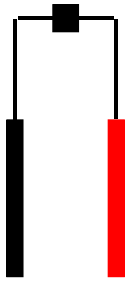
counter electrode

divided cell (“H” cell)

Modes of Operation

constant voltage (cv)





constant current (cc)

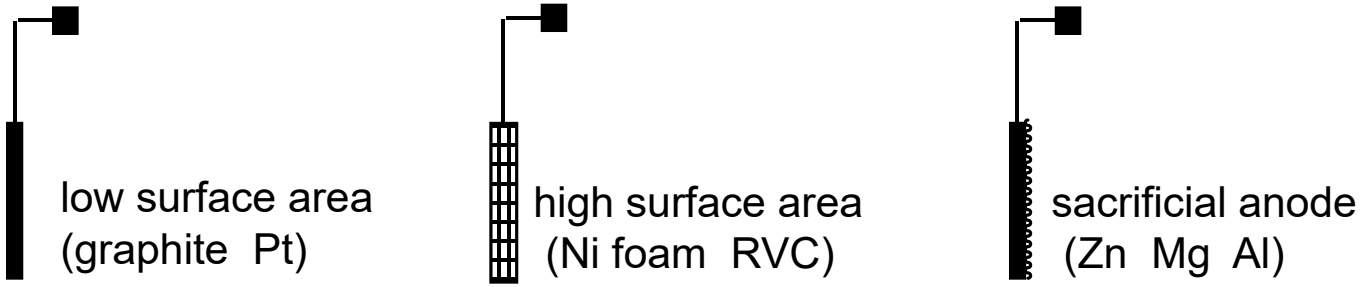
reference electrode

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

Introduction

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

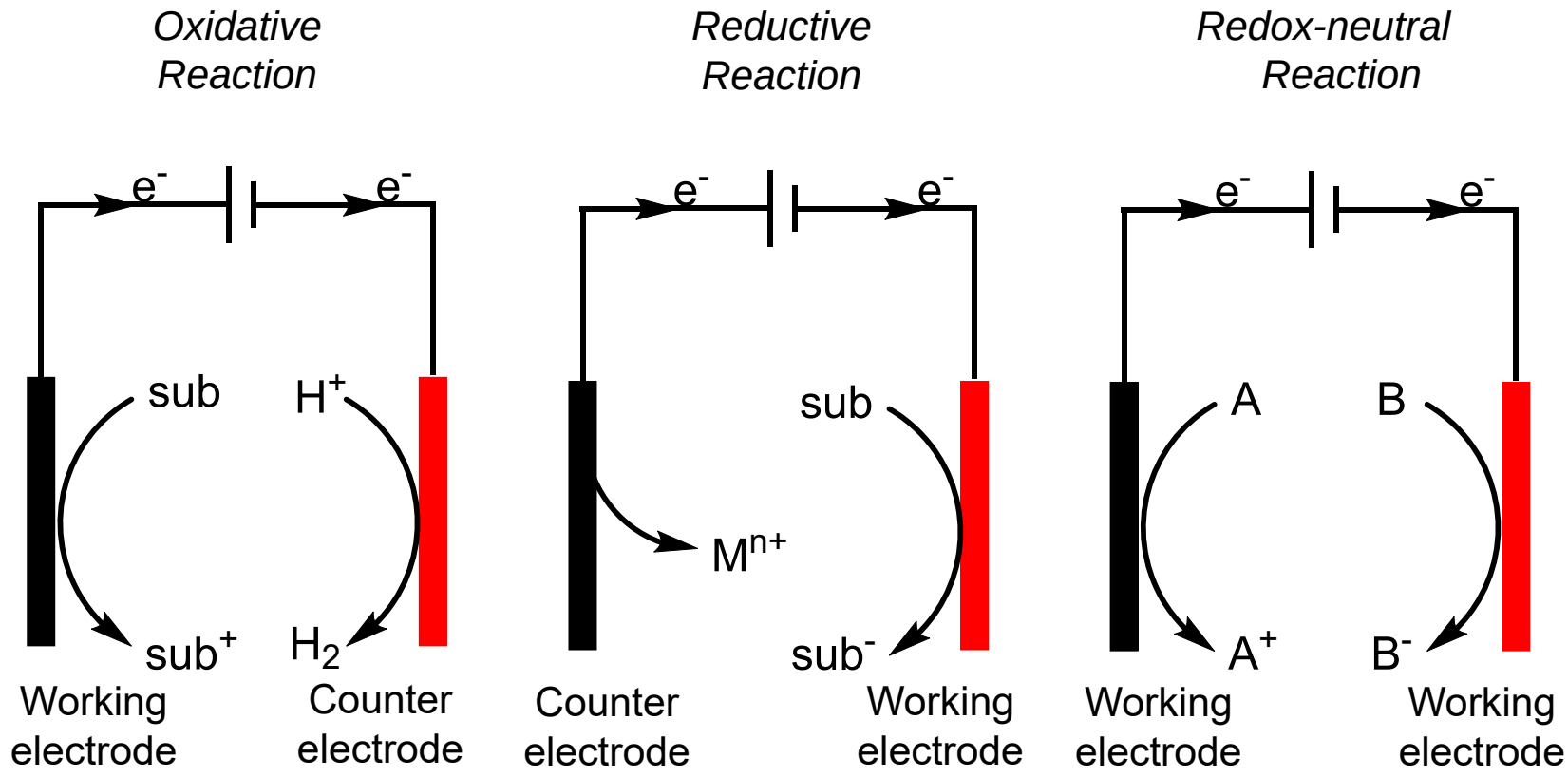
cations					anions					
Li^+	Na^+	Et_4N^+	Bu_4N^+	⟷	ClO_4^-	PF_6^-	BF_4^-	OAc^-	I^-	Br^-

mix and match

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

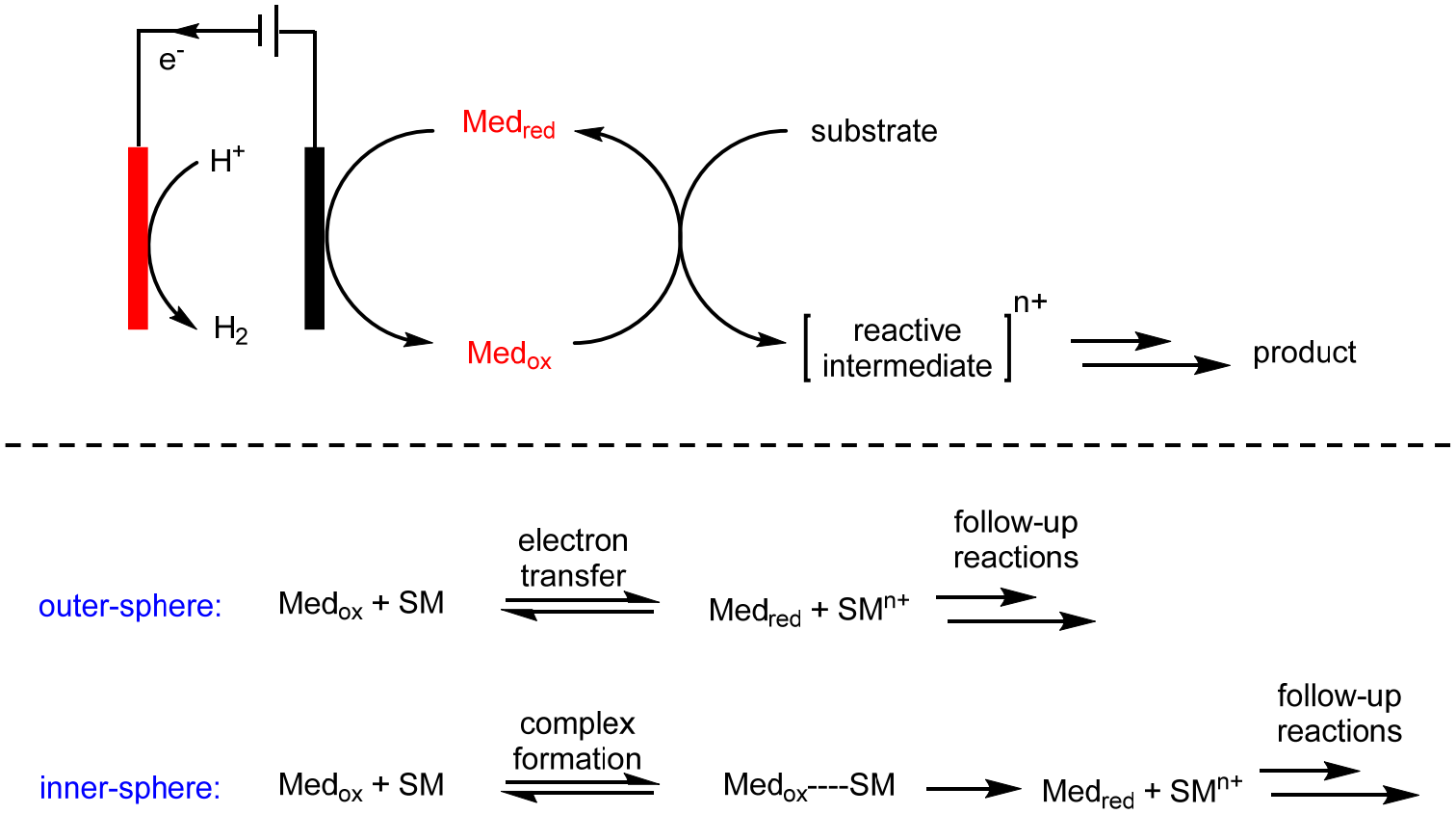
Introduction

Synthetic Organic Electrochemistry



Introduction

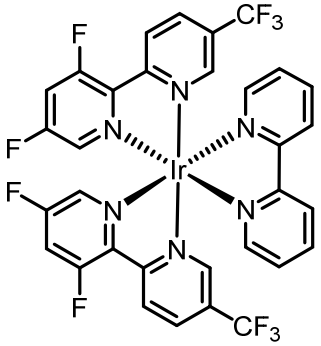
Synthetic Organic Electrochemistry



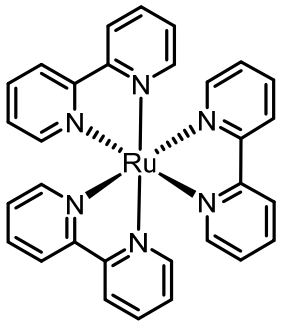
R. D. Little et al. *Chem. Soc. Rev.*, **2014**, 43, 2492.

Introduction

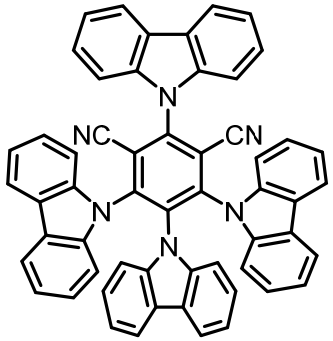
Visible-Light Photoredox Catalysis



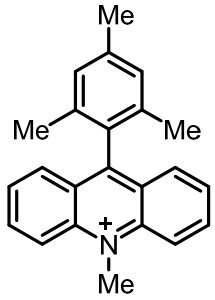
$Ir[dFCF_3ppy]_2(bpy)$



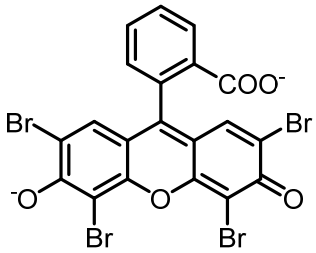
$Ru(bpy)_3$



4CzIPN

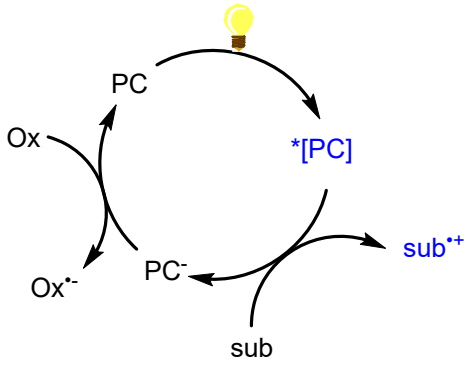


Mes-Acr

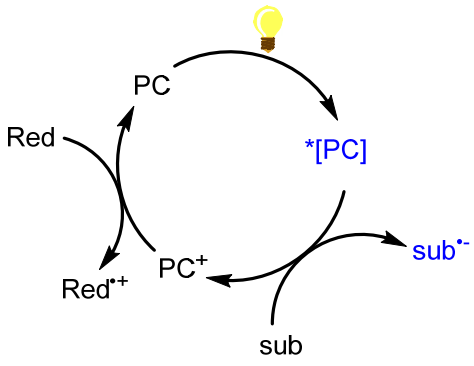


Eosin Y

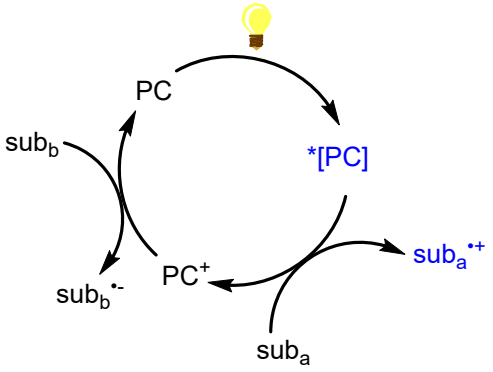
Oxidative Reaction



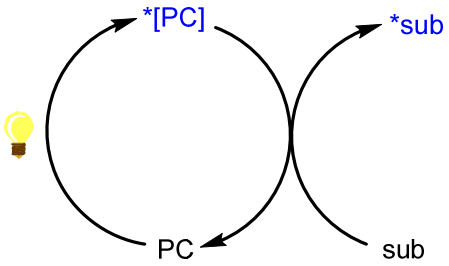
Reductive Reaction



Redox Neutral Reaction



Energy Transfer Reaction



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

Introduction

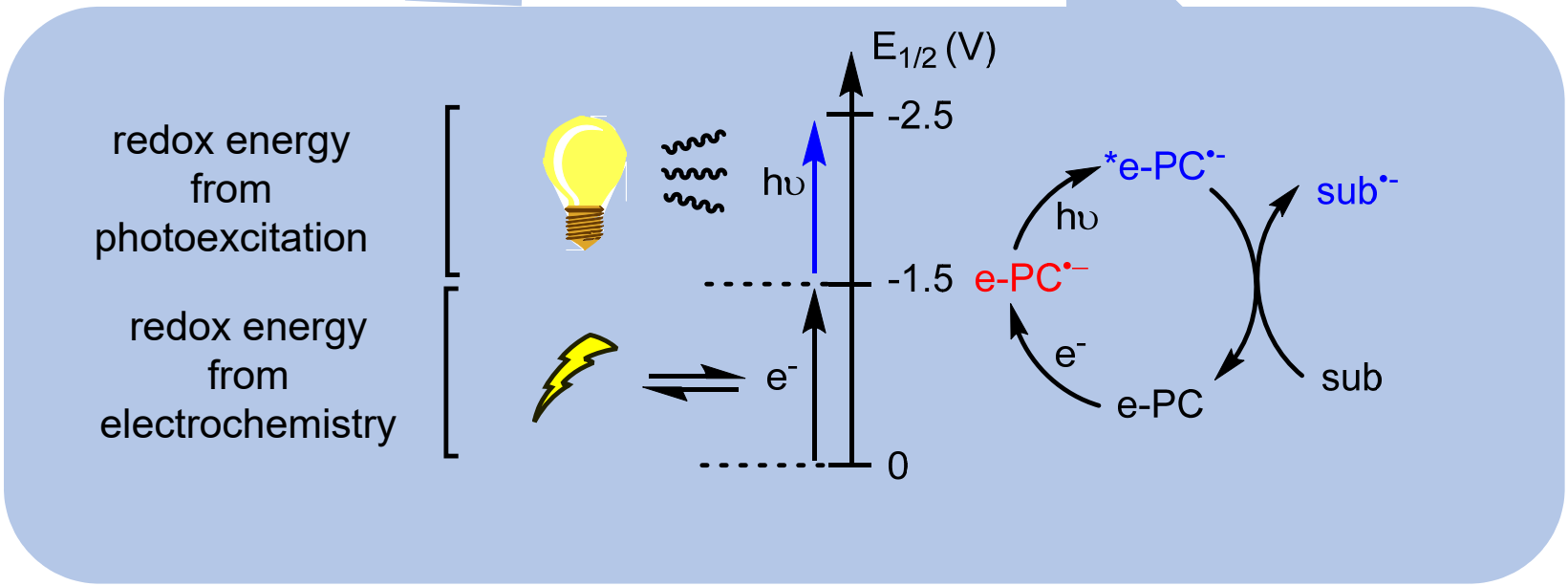
Photoelectrochemical Organic Synthesis

The limits of SOE

- low conductivity of organic solvents
- unselective redox processes
- limited mediators potential

The limits of PRC

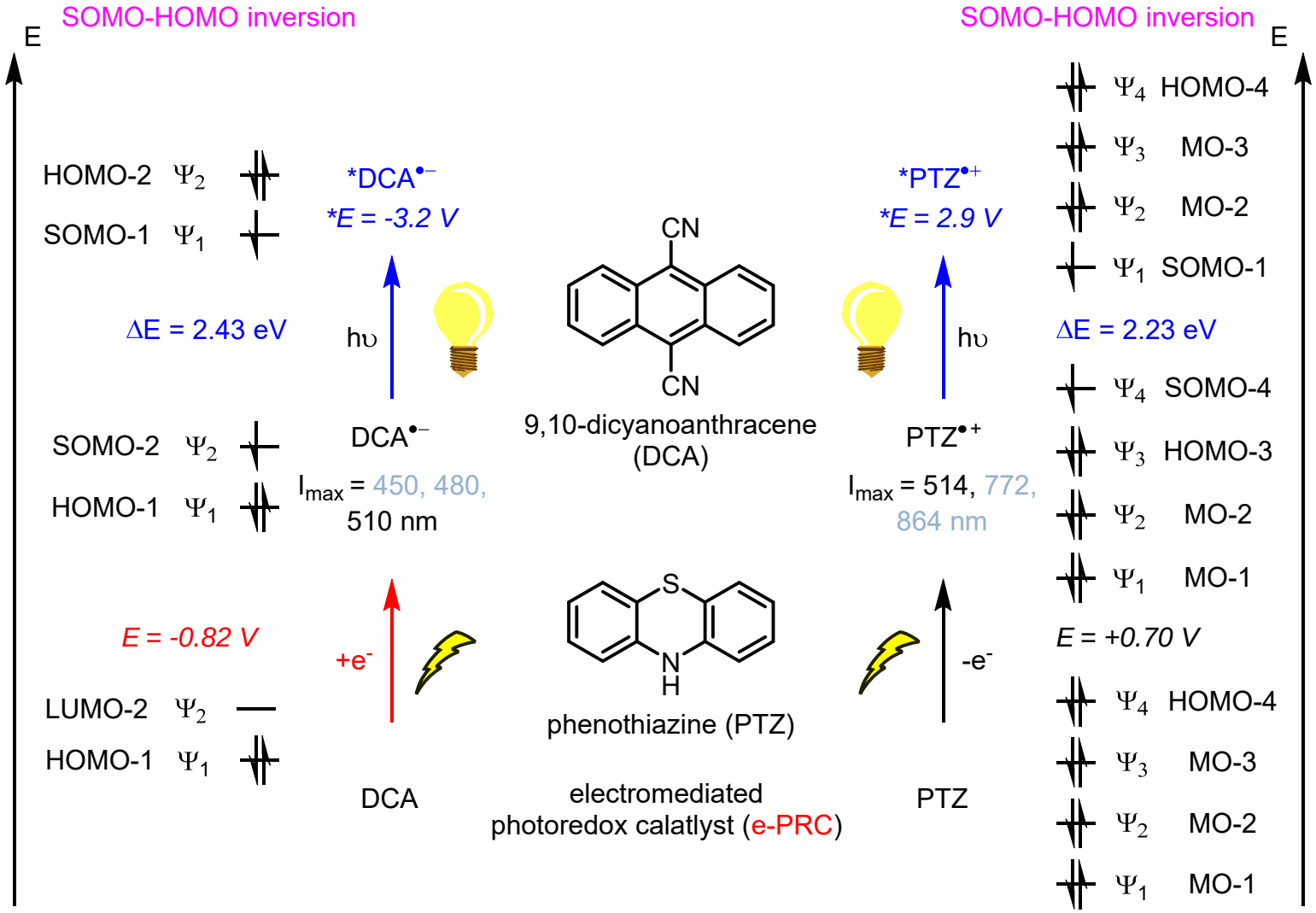
- energy constrained
- energy losses
- equivalent oxidizing or reducing agent



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

Introduction

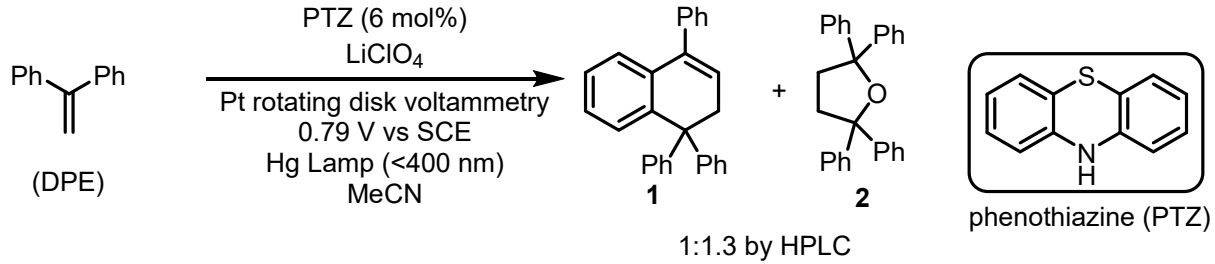
Photoelectrochemical Organic Synthesis

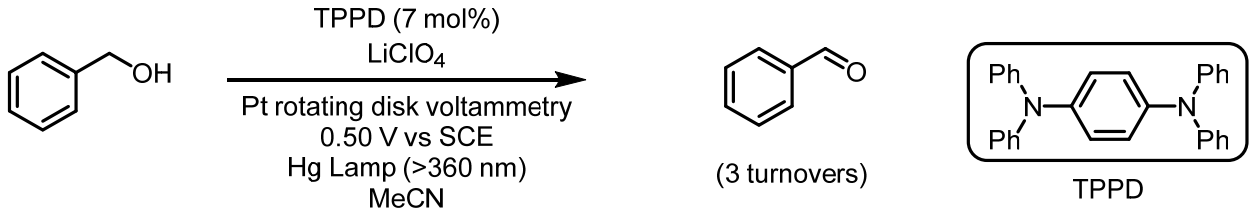


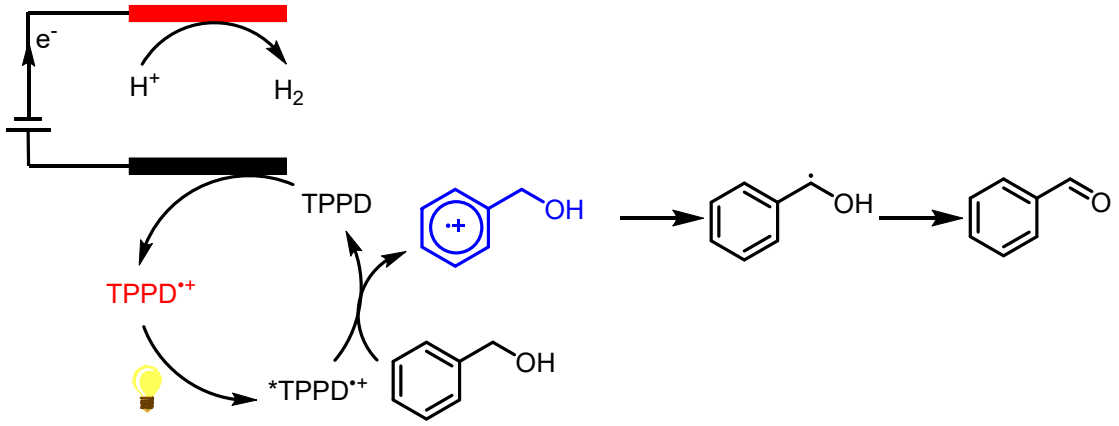
J. P. Barham et al. *Angew. Chem. Int. Ed*. **2020**, 59, 2.

Introduction

Photoelectrochemical Organic Synthesis





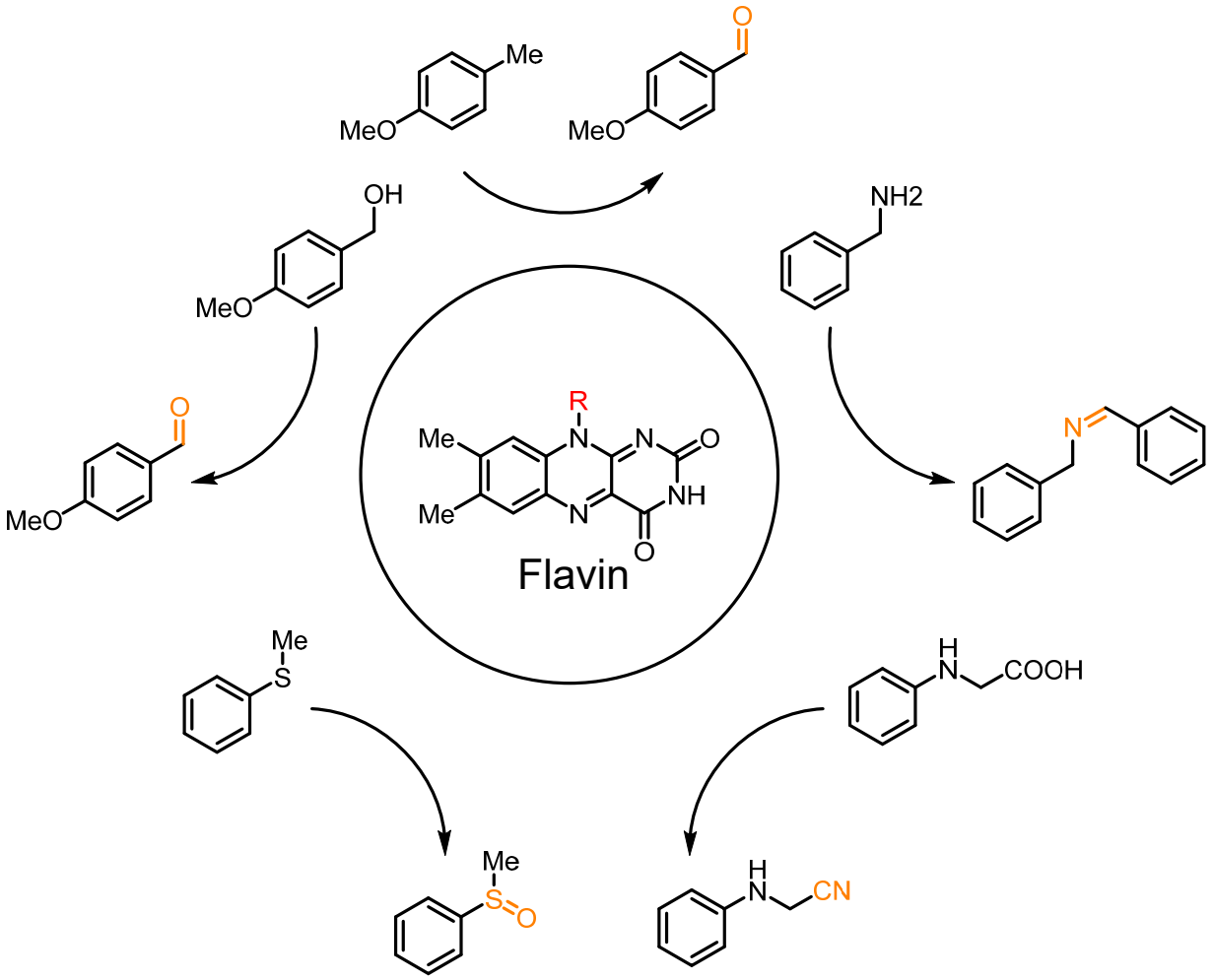


J.-C. Moutet, G. Reverdy. *Tetrahedron Lett.* **1979**, 20, 2389.
J.-C. Moutet, G. Reverdy. *J. Chem. Soc. Chem. Commun.* **1982**, 654.

Contents

Photoelectrochemical Organic Synthesis

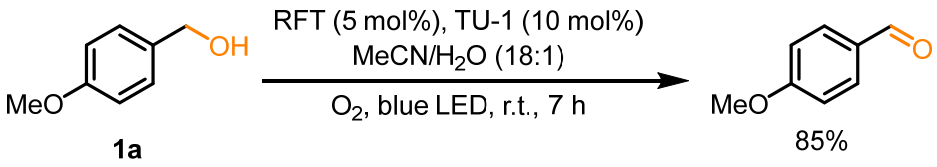
Electromediated Reaction with Photoredox Catalysis



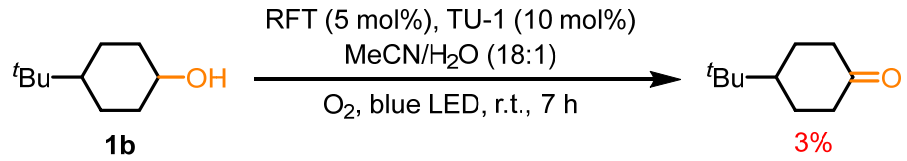
B. Konig et al. *Photochem. Photobiol. Sci*., **2010**, 9, 1367.
B. Konig et al. *Chem. Eur. J.* **2008**, 14, 1854.
D. R. Carbery et al. *Angew.Chem. Int.Ed*. **2015**, 54,8997.
B. Konig et al. *ChemCatChem.* **2012**, 4, 620.
J. C. Gonzalez-Gomez et al. *Organic Letters* **2019** *21* (5), 1368.

Photoelectrochemical Organic Synthesis

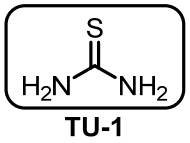
Electromediated Reaction with Photoredox Catalysis



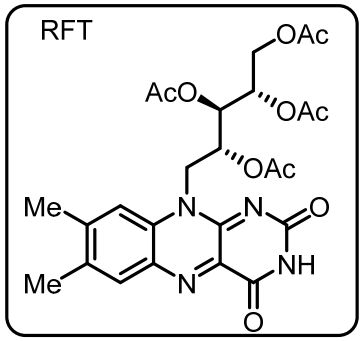
1a



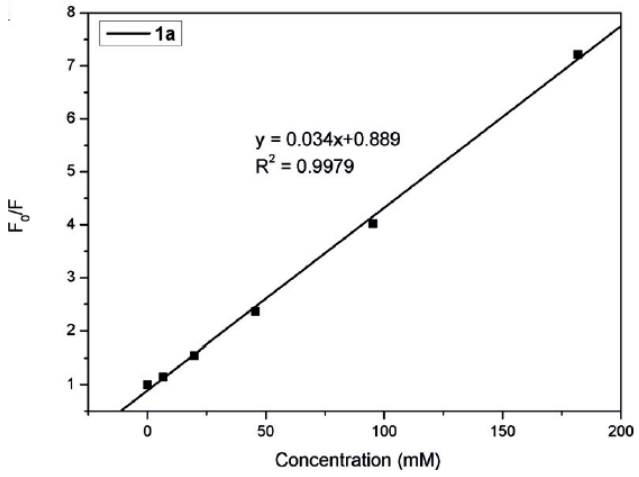
1b



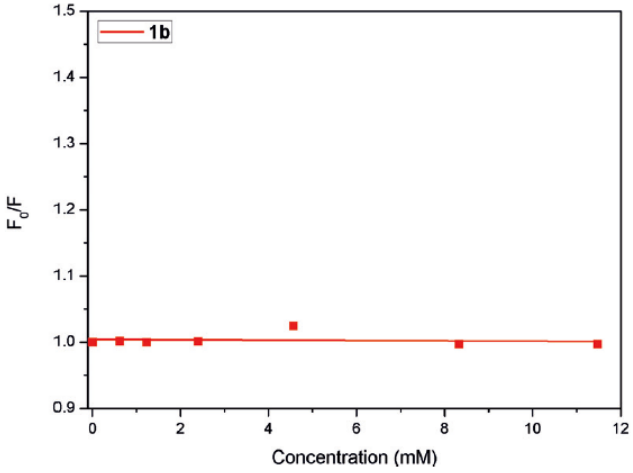
TU-1



1a: E ≈ 1.5 V
1b: E > 1.9 V
RFT*: E = 1.67 V



Fluorescence quenching of RFT with 1a

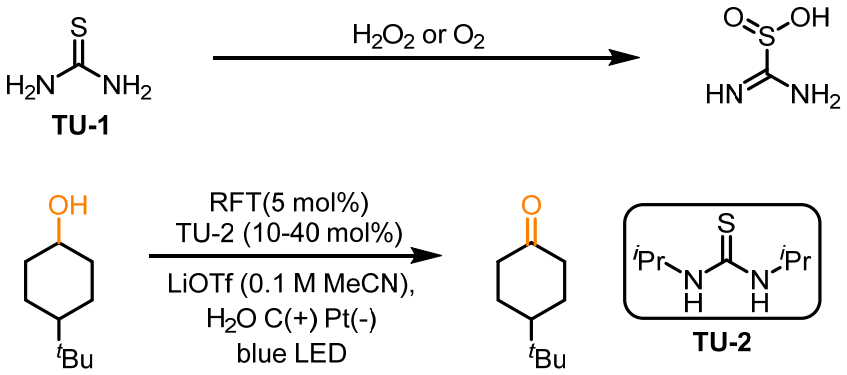


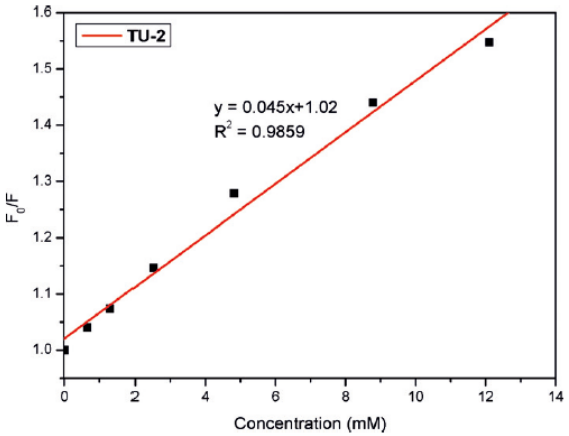
Fluorescence quenching of RFT with 1b

B. Konig et al. *Chem. Eur. J.* **2008**, 14, 1854.
S. Lin et al. *Angew. Chem. Int. Ed.* **2020**, 59, 409.

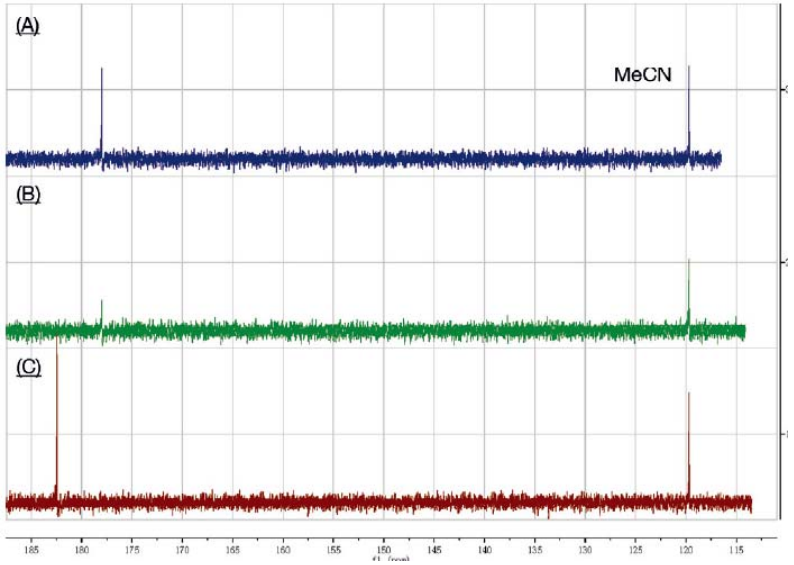
Photoelectrochemical Organic Synthesis

Electromediated Reaction with Photoredox Catalysis

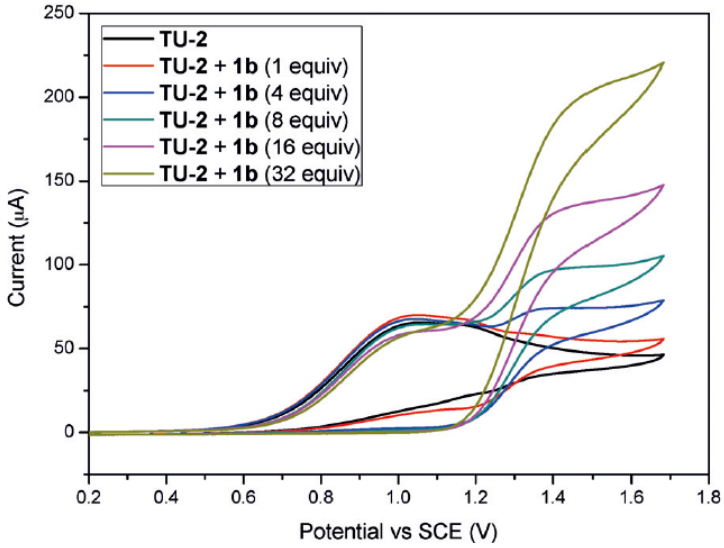




Fluorescence quenching of RFT with TU-2



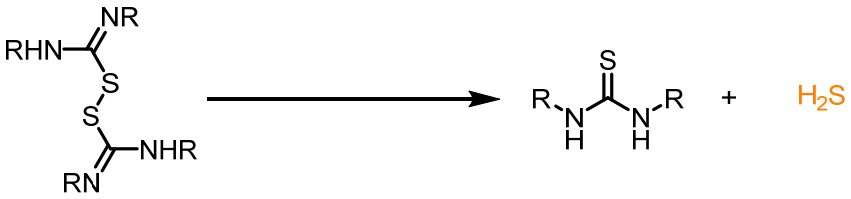
^{13}C NMR of (A) TU-1-O_2 (B) white precipitate (C) TU-1

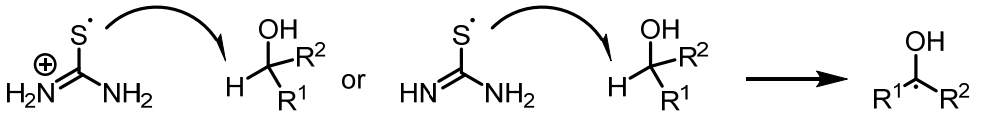


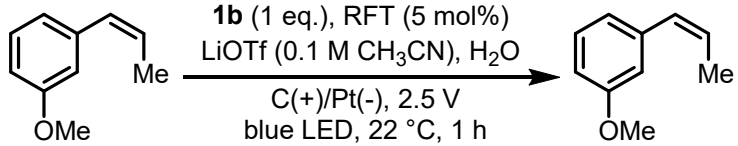
S. Lin et al. *Angew. Chem. Int. Ed.* **2020**, 59, 409.

Photoelectrochemical Organic Synthesis

Electromediated Reaction with Photoredox Catalysis

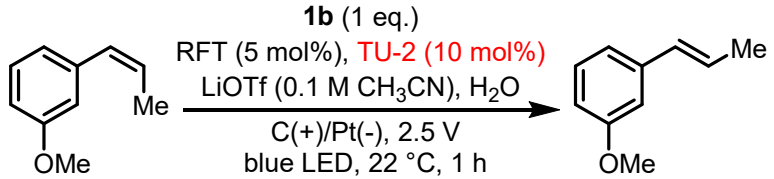






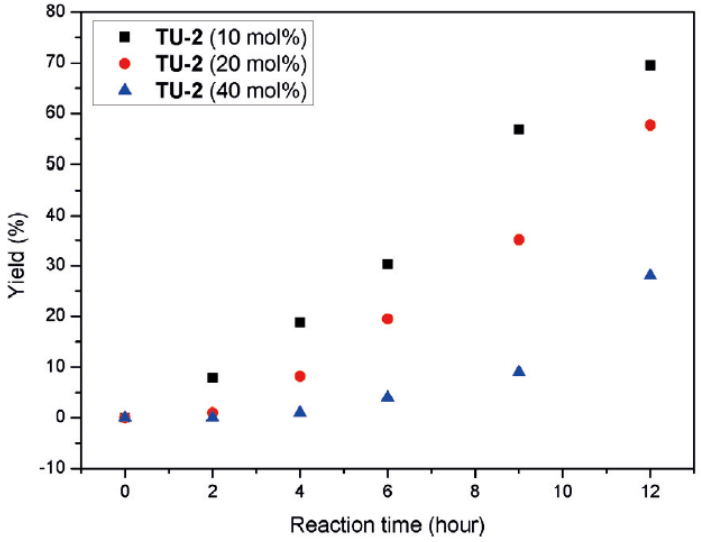
Z:E = 6:1

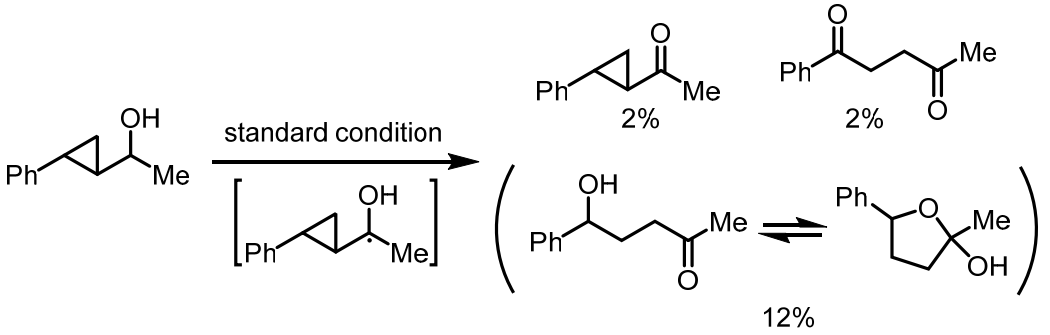
71% recovered, *Z:E* = 10:1
100% **1b** recovered



Z:E = 6:1

75% recovered, *Z:E* = 1:100
100% **1b** recovered

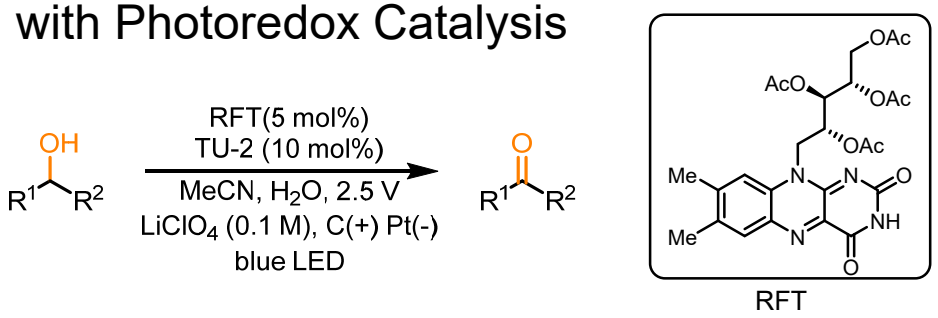


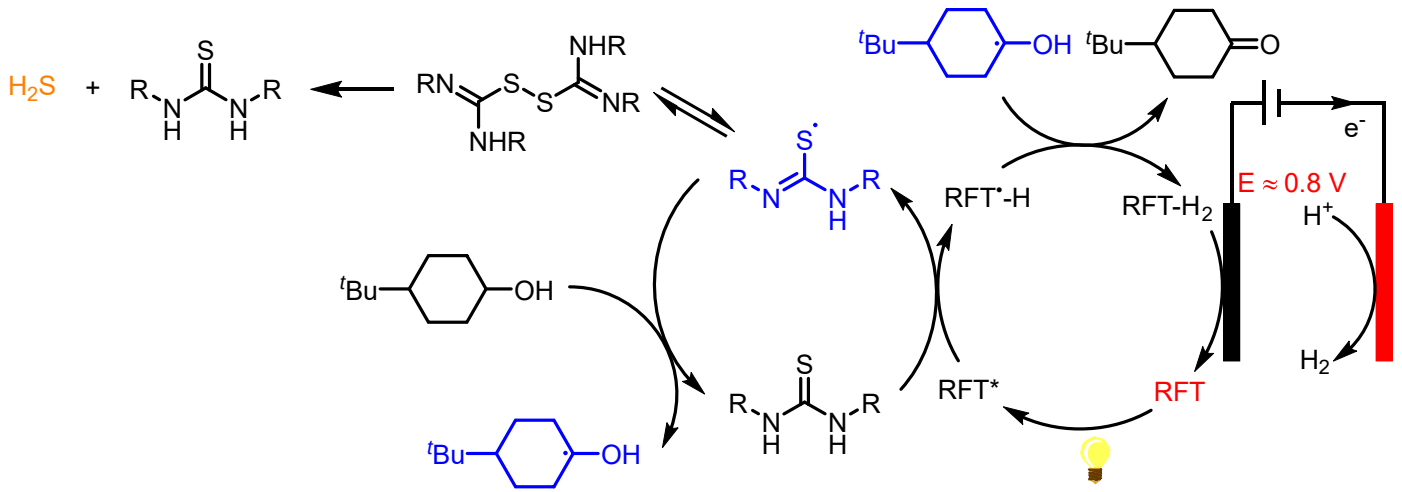


S. Lin et al. *Angew. Chem. Int. Ed.* **2020**, 59, 409.

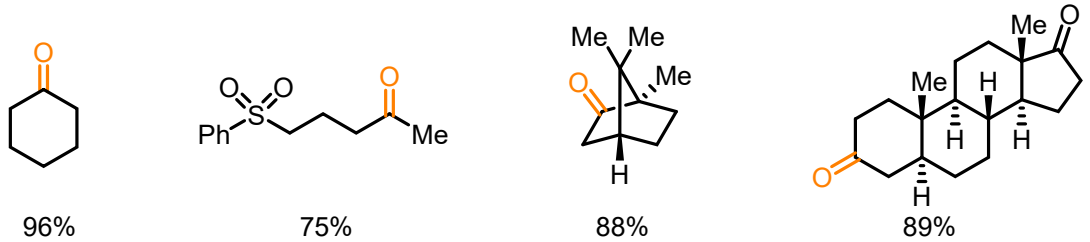
Photoelectrochemical Organic Synthesis

Electromediated Reaction with Photoredox Catalysis





Selected Substrates



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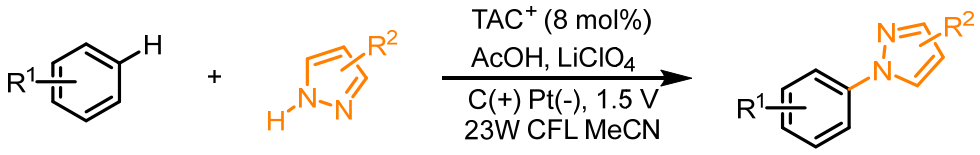
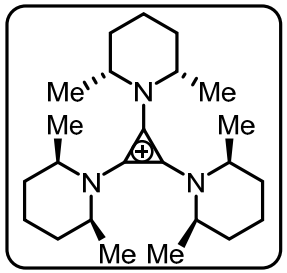
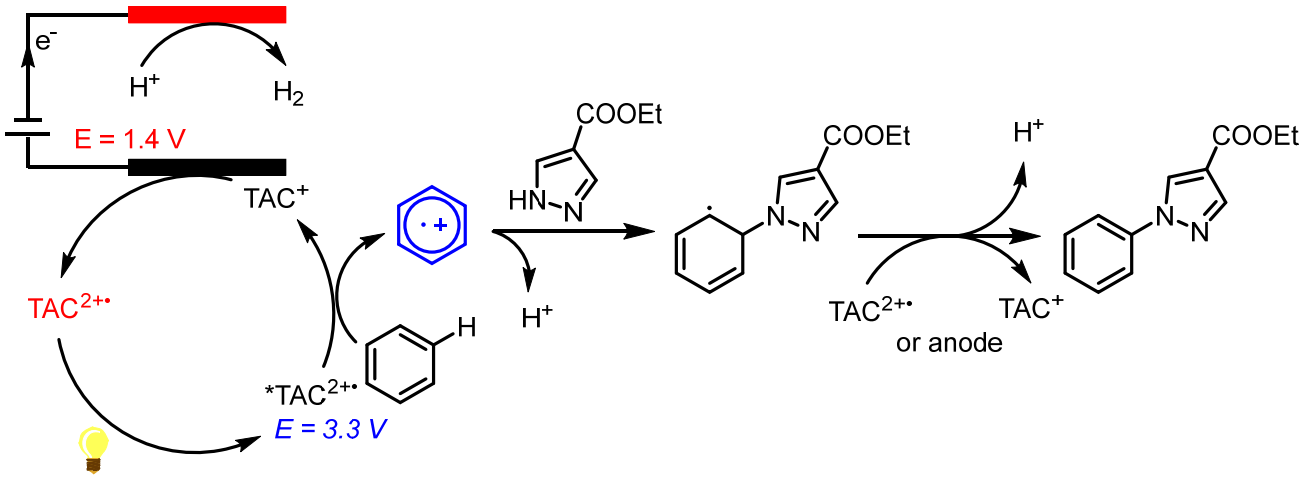
Photoelectrochemical Organic Synthesis

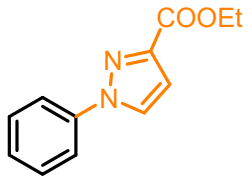
Electromediated Reaction with Photoredox Catalysis



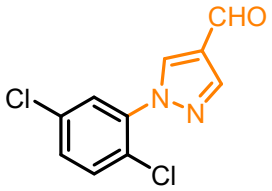




Selected Substrates



65%



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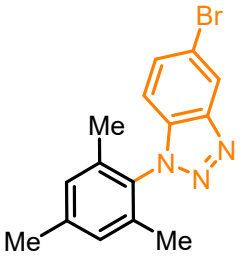
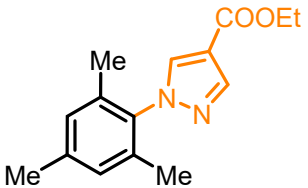


75%

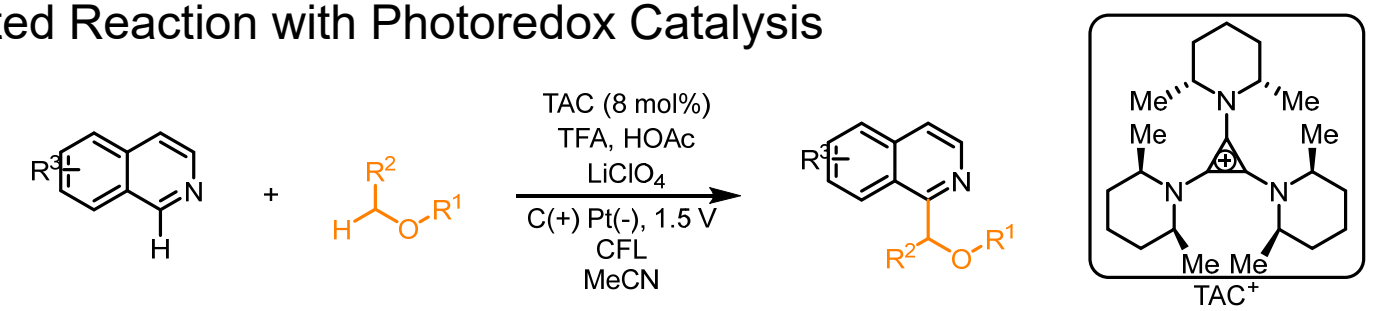


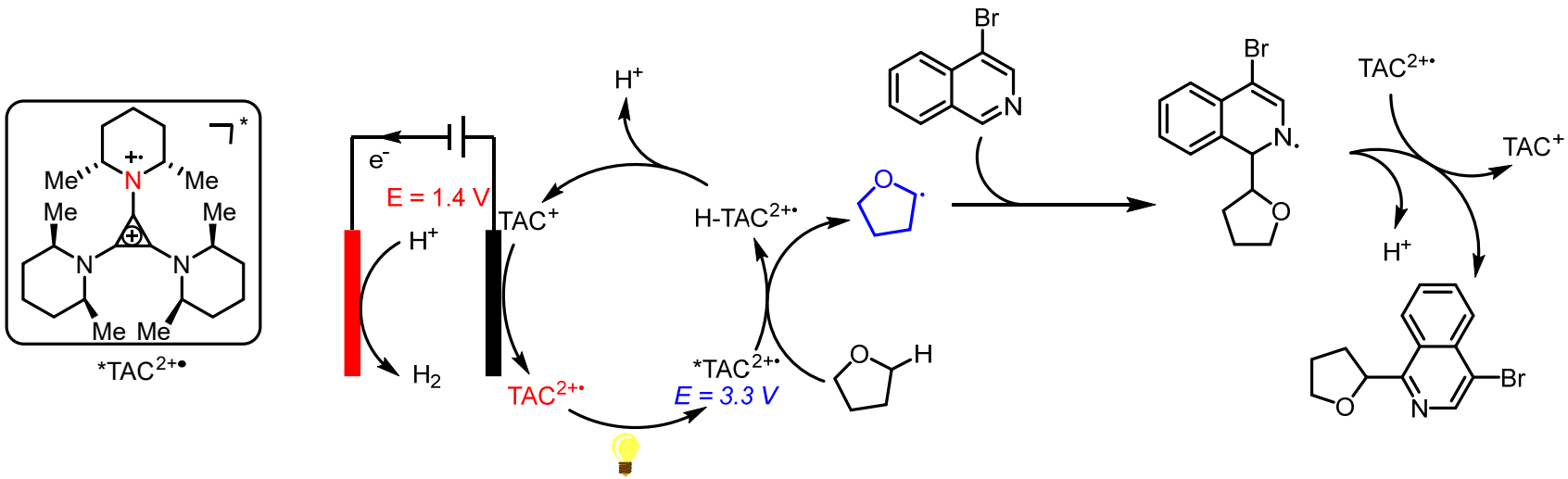
71%

T. H. Lambert et al. *Angew. Chem. Int. Ed.* **2019**, 58, 13318.

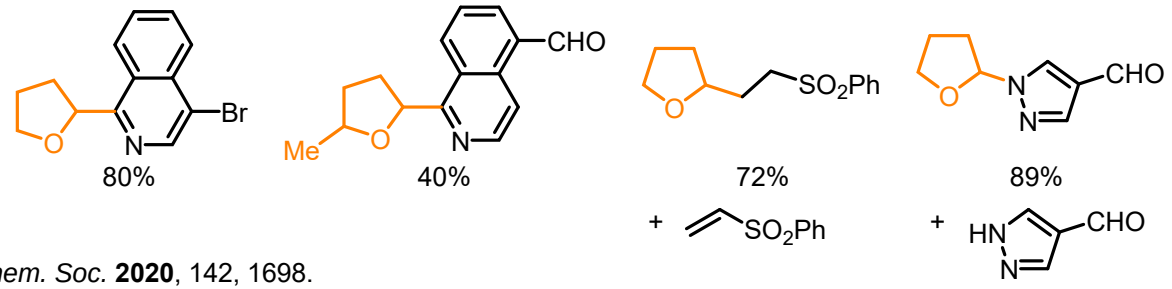
Photoelectrochemical Organic Synthesis

Electromediated Reaction with Photoredox Catalysis





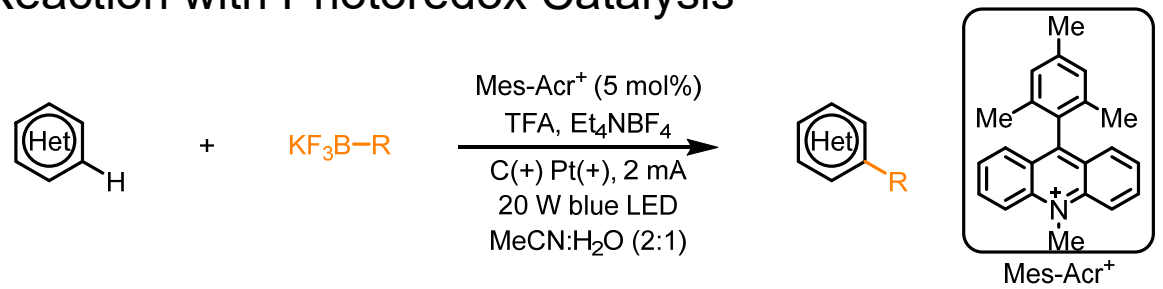
Selected Substrates

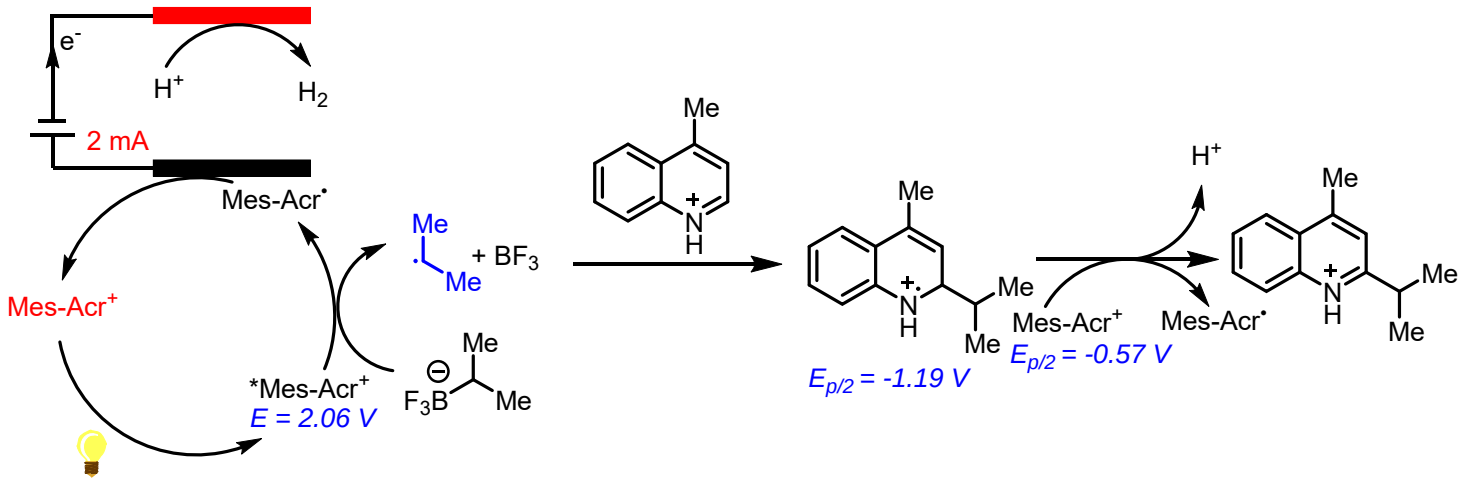


T. H. Lambert et al. *J. Am. Chem. Soc.* **2020**, 142, 1698.

Photoelectrochemical Organic Synthesis

Electromediated Reaction with Photoredox Catalysis





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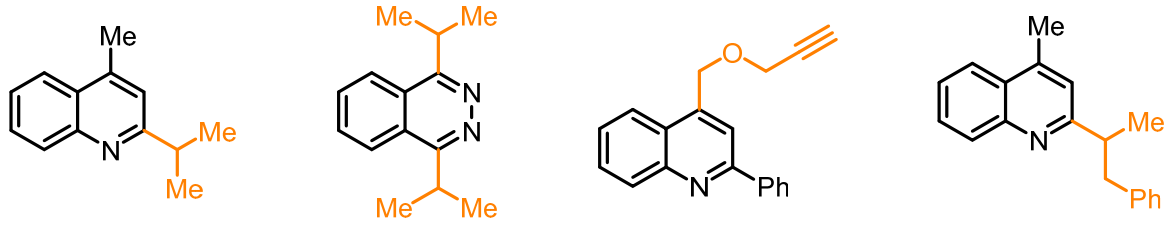
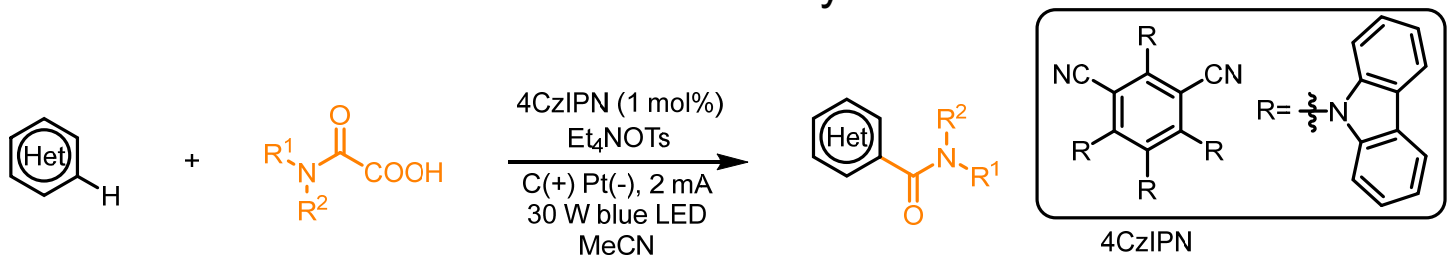


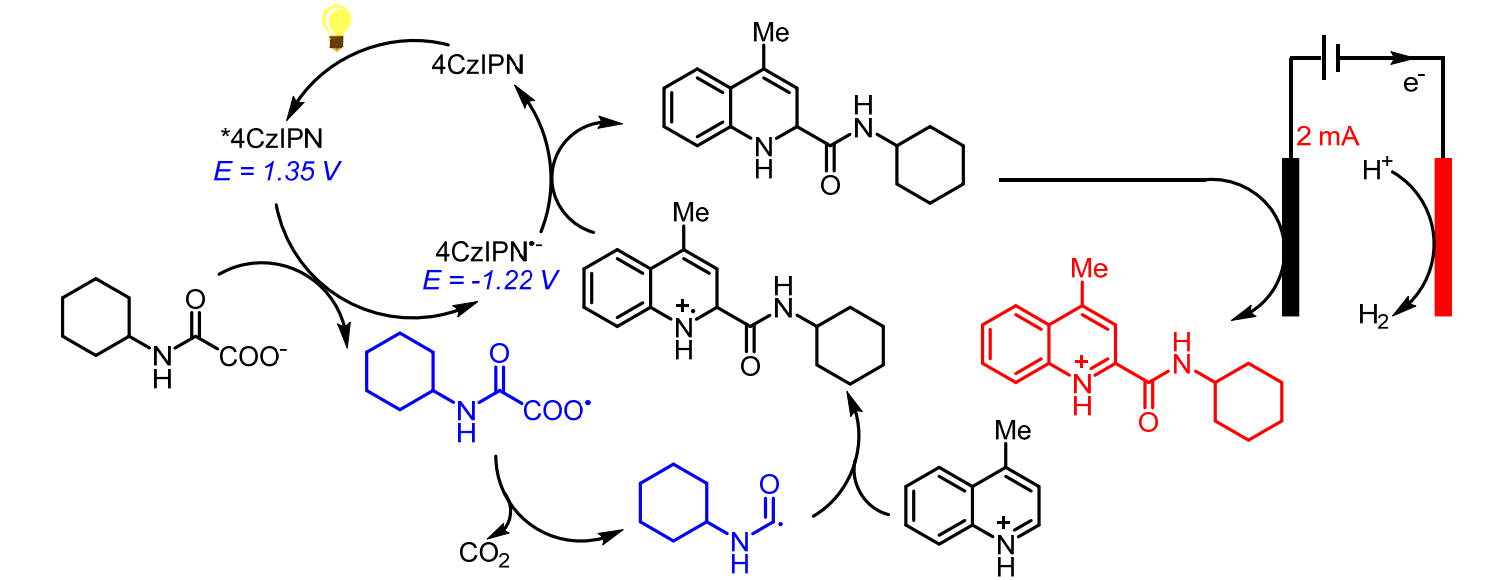
87% 47% 62% 71%

H.-C. Xu et al. *Angew. Chem. Int. Ed*. **2019**, 58,4592.

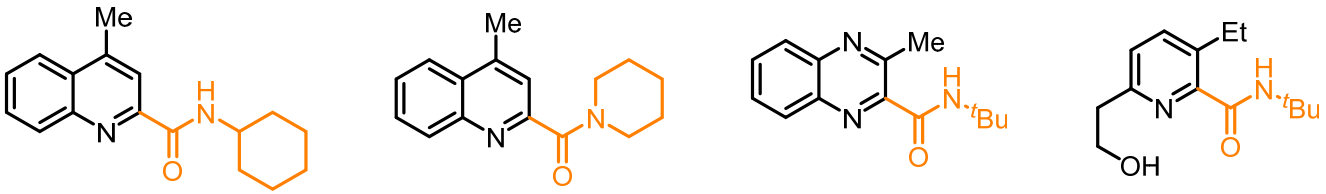
Photoelectrochemical Organic Synthesis

Electromediated Reaction with Photoredox Catalysis





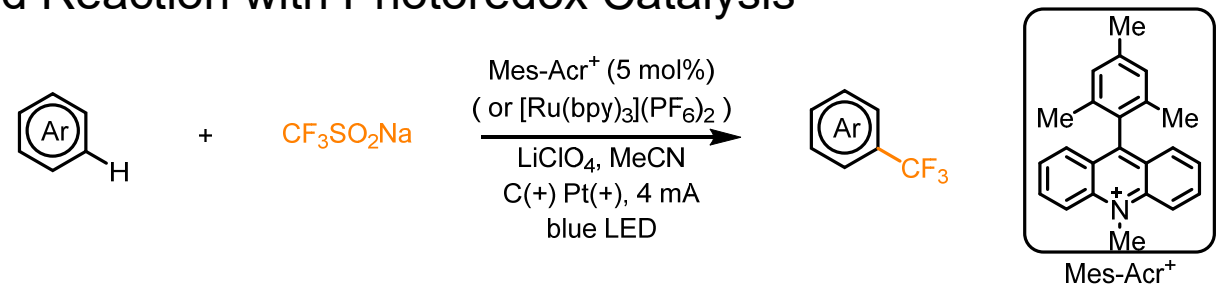
Selected Substrates

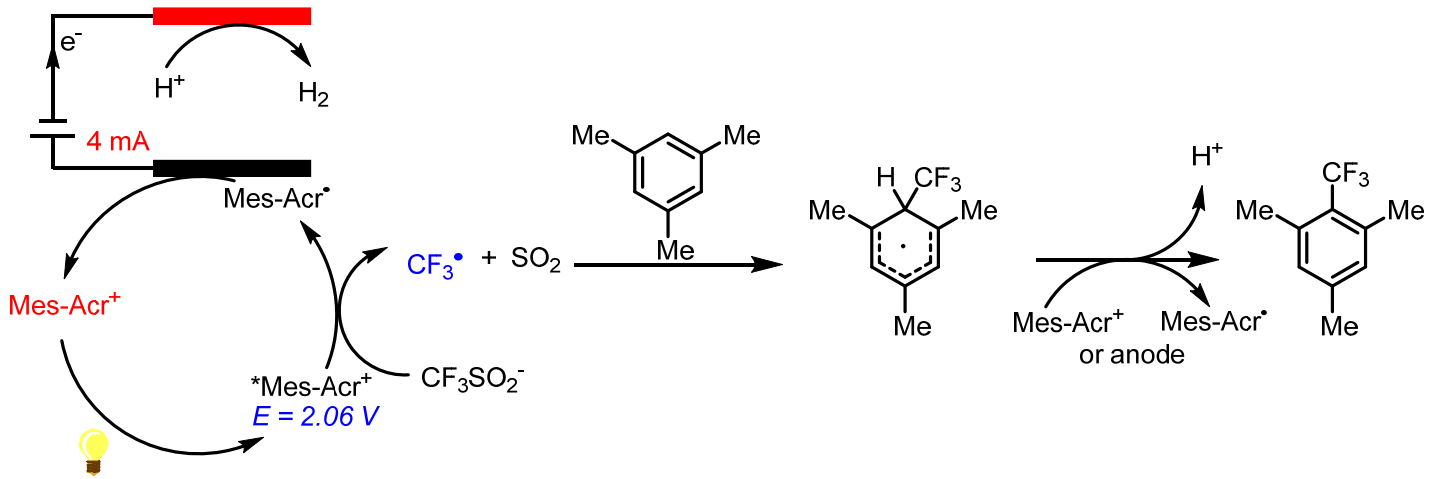


66% 40% 73% 86%

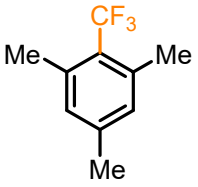
Photoelectrochemical Organic Synthesis

Electromediated Reaction with Photoredox Catalysis

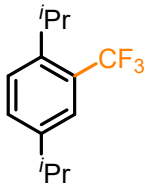




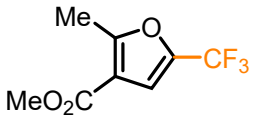
Selected Substrates



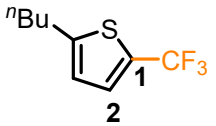
79%
with [Mes-Acr]ClO_4



67%
with $[Ru(bpy)_3](PF_6)_2$



71%
with $[Ru(bpy)_3](PF_6)_2$



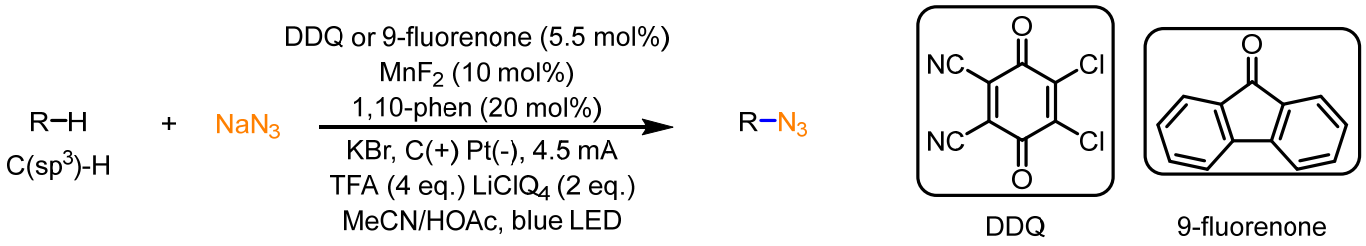
2

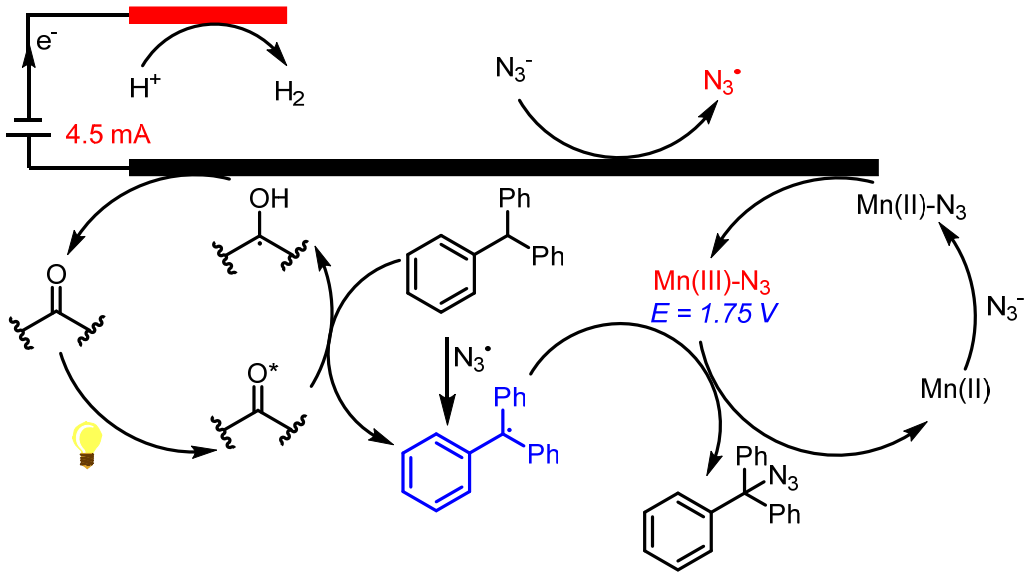
64% (**1**:**2** = 14:1)
with [Mes-Acr]ClO_4

L. Ackermann. et al. *Chem. Eur. J.* **2020**, 26, 3241.

Photoelectrochemical Organic Synthesis

Electromediated Reaction with Photoredox Catalysis





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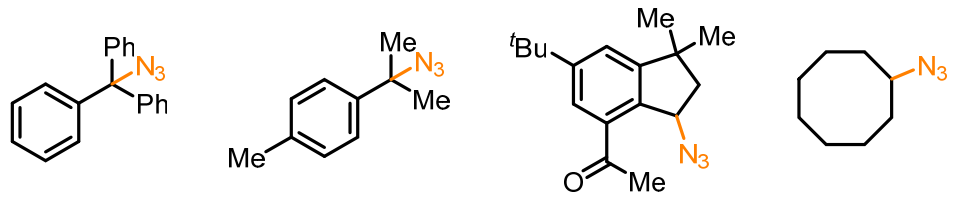
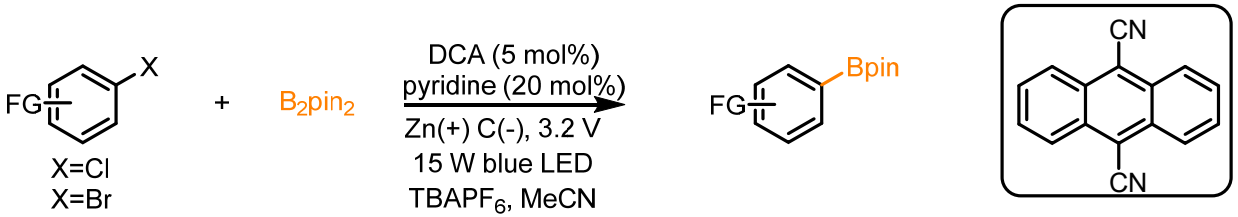


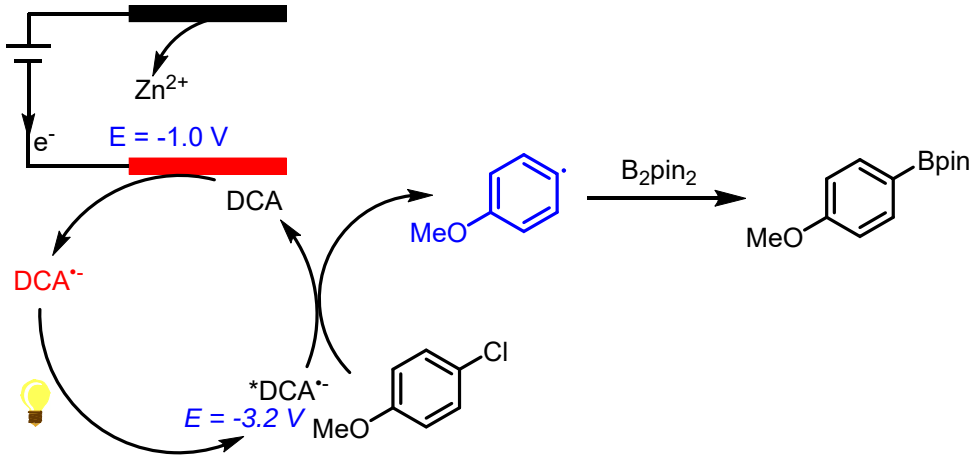
99% 51% 51% 41%

A.-W. Lei et al. *J. Am. Chem. Soc*. **2020**, 142, 17693.

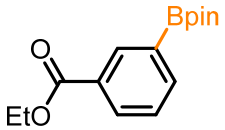
Photoelectrochemical Organic Synthesis

Electromediated Reaction with Photoredox Catalysis

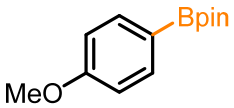




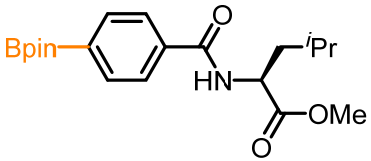
Selected Substrates



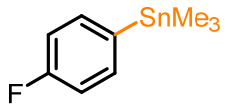
X = Cl 88%
X = Br 90%



X = Cl 53%
X = Br 68%



X = Br 75%

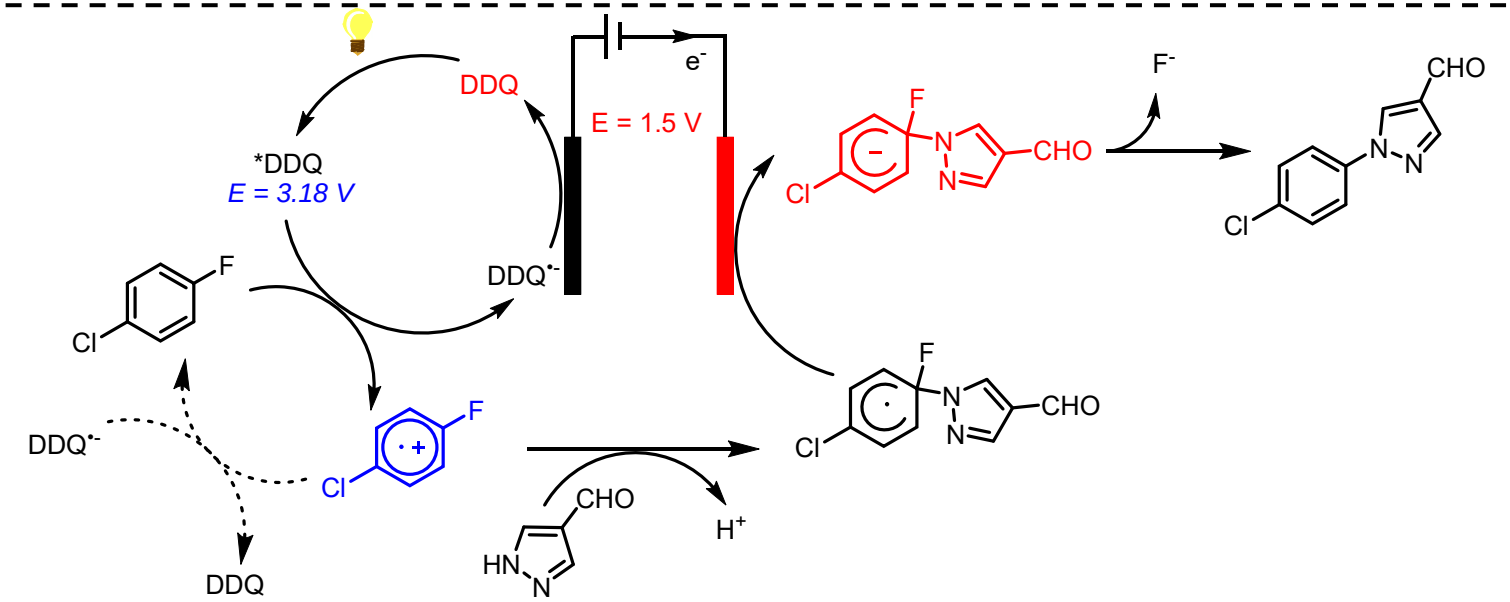


61%
$+(SnMe_3)_2$

S. Lin et al. *J. Am. Chem. Soc*. **2020**,142, 2087.

Photoelectrochemical Organic Synthesis

Electromediated Reaction with Photoredox Catalysis



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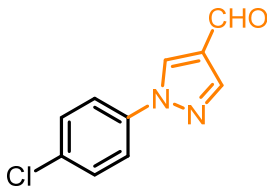
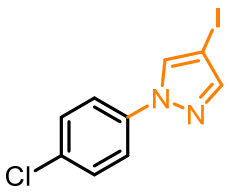
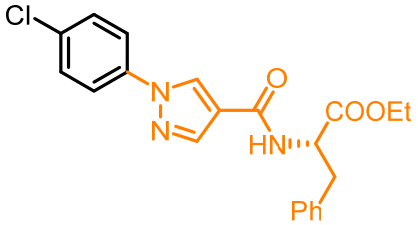


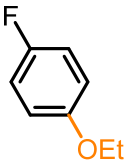
73%



53%



55%

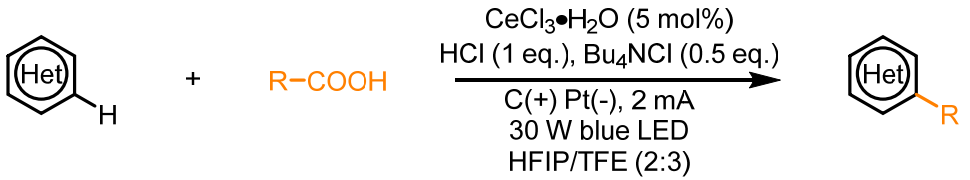


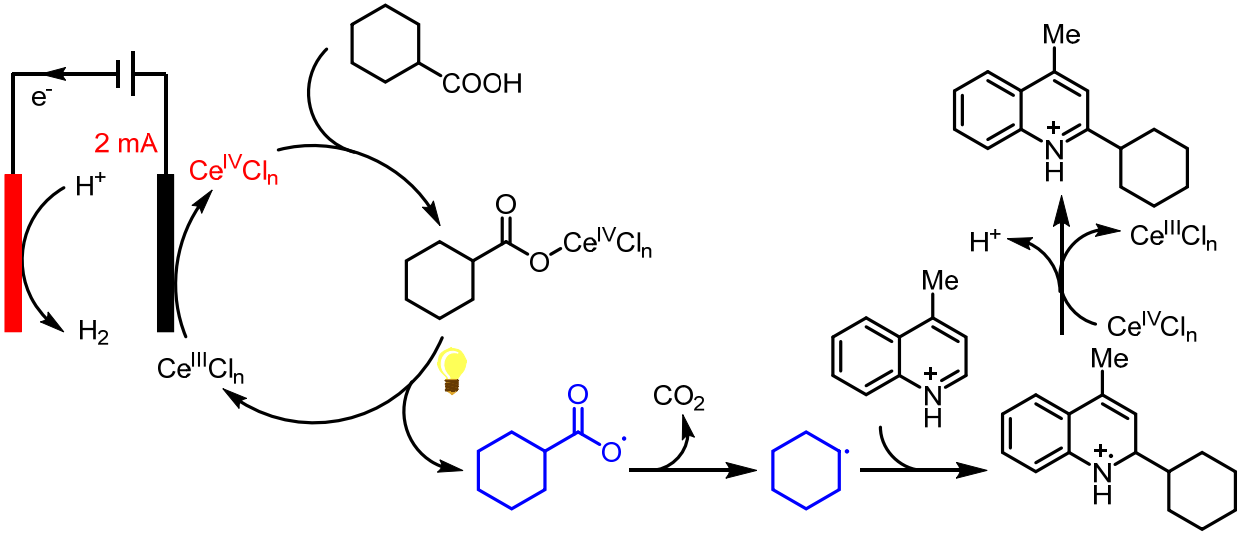
65%
(+ HOEt)

T. H. Lambert et al. *Angew. Chem. Int. Ed*. **2020**, 59, 658.

Photoelectrochemical Organic Synthesis

Electromediated Reaction involving Photo-induced Radical





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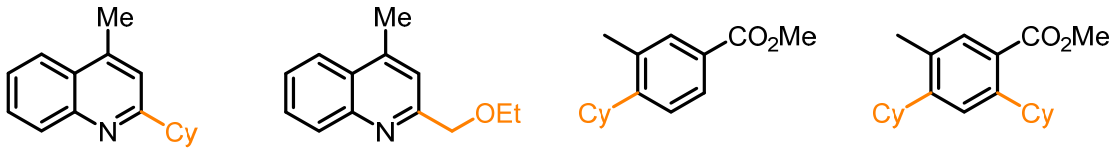
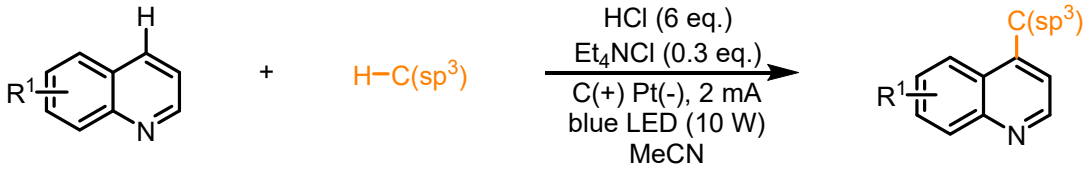


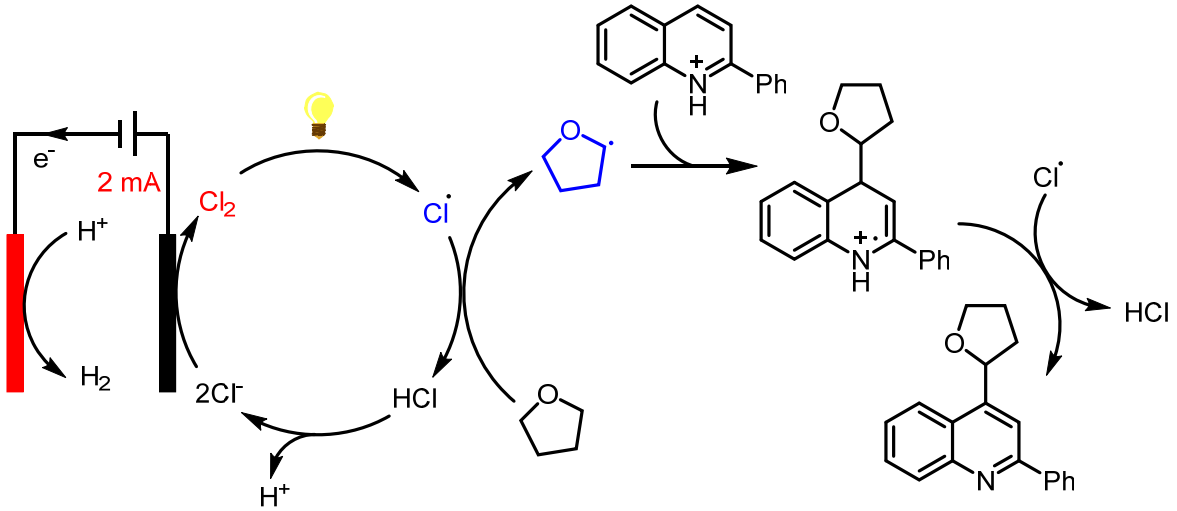
91% 78% 57% + 30%

H.-C. Xu et al. *Angew. Chem. Int. Ed*. **2020**, 59, 10626.

Photoelectrochemical Organic Synthesis

Electromediated Reaction involving Photo-induced Radical





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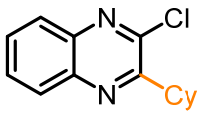
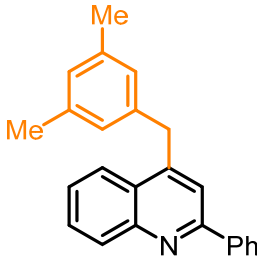
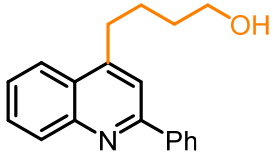


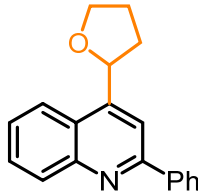
56%



97%



78%
with THF

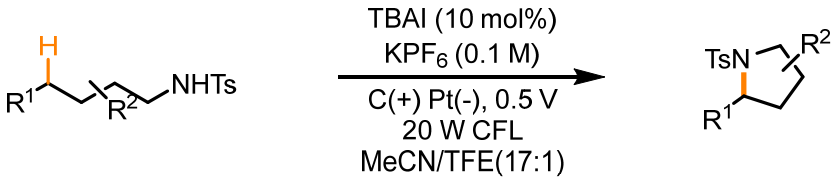


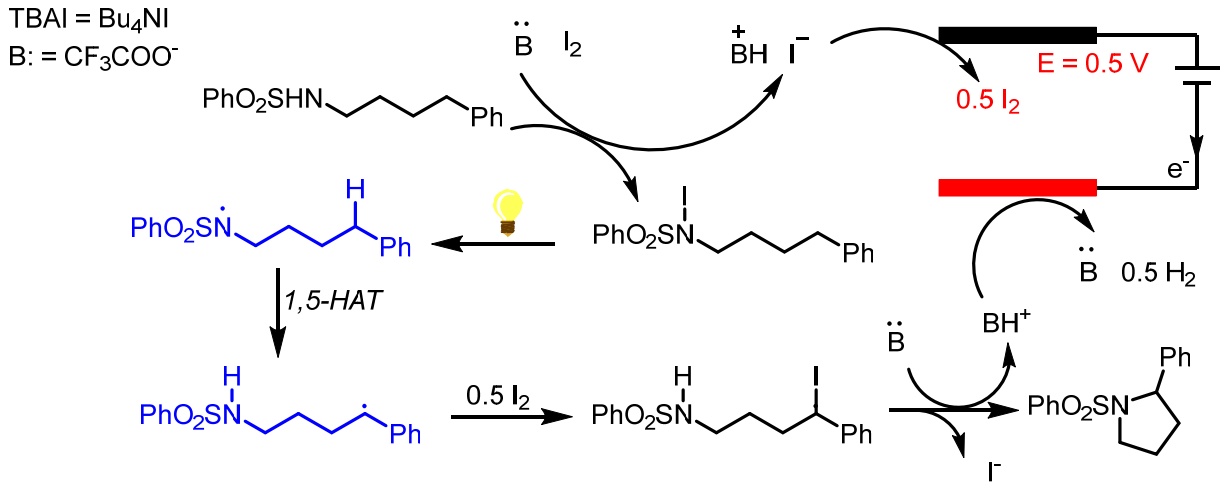
70%
with 2 eq. HCl

H.-C. Xu et al. *Angew. Chem. Int. Ed.* **2020**, 59, 14275.

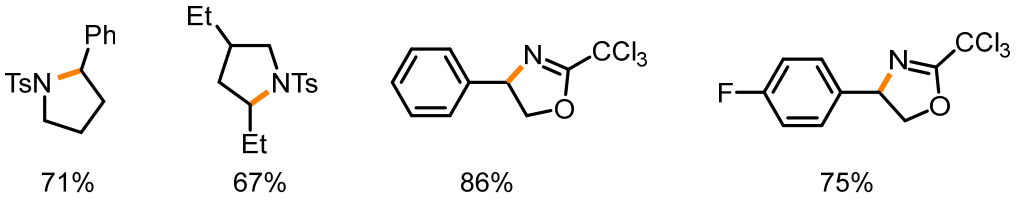
Photoelectrochemical Organic Synthesis

Electromediated Reaction involving Photo-induced Radical





Selected Substrates

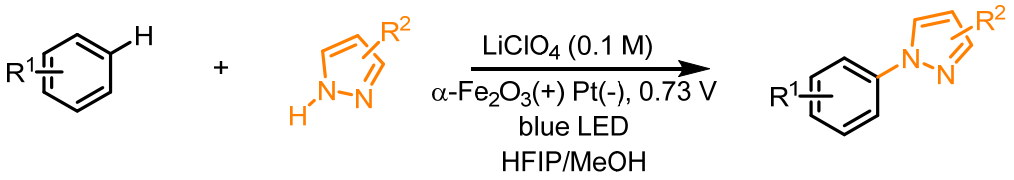


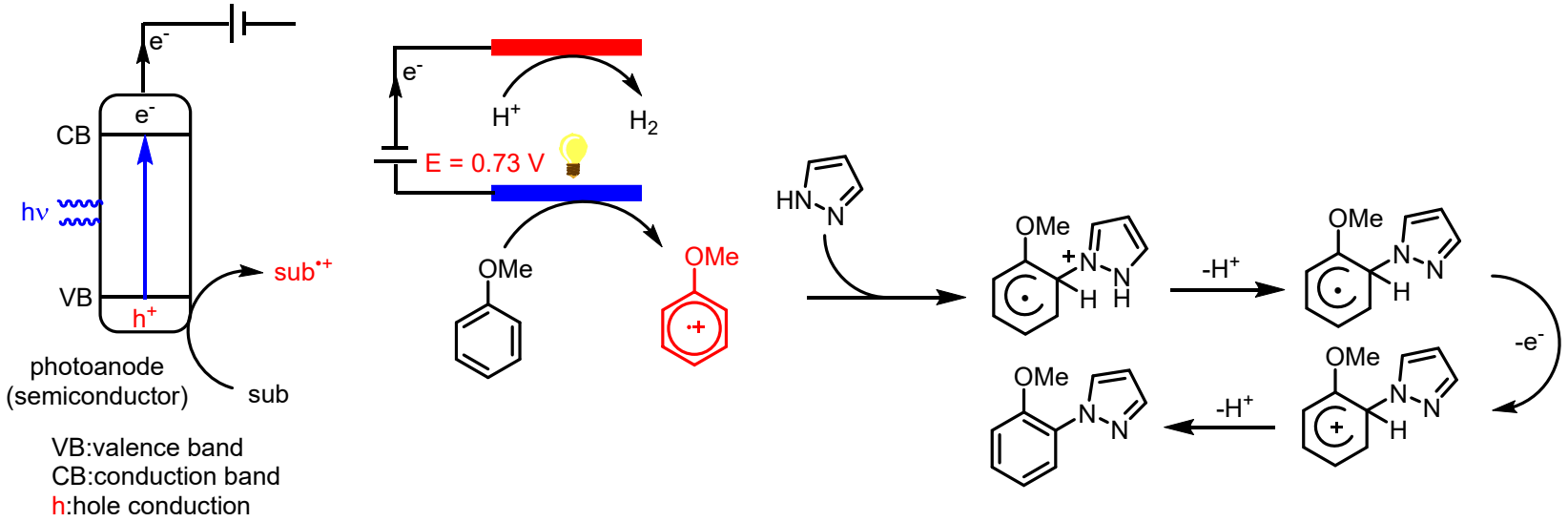
71% 67% 86% 75%

S. Stahl et al. *Angew. Chem. Int. Ed*. **2019**, 58, 6385.

Photoelectrochemical Organic Synthesis

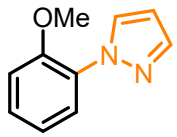
Interfacial Photoelectrochemistry



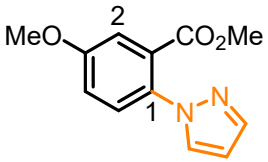


VB:valence band
CB:conduction band
h:hole conduction

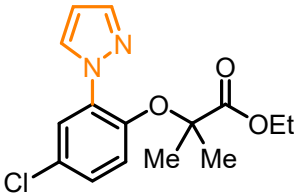
Selected Substrates



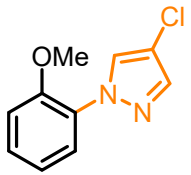
77%
o:p = 6:1



87%
(P_1:P_2=3:1)



82%

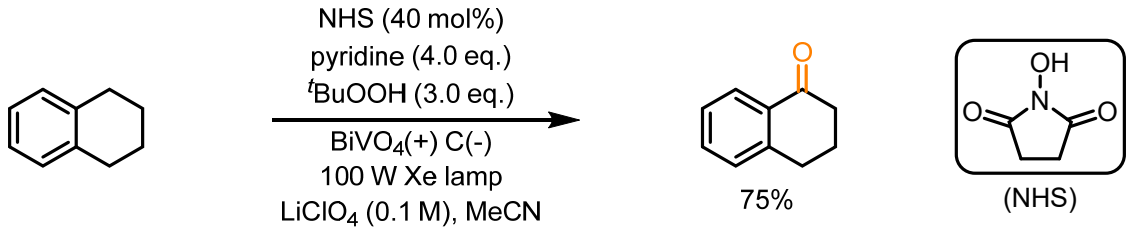


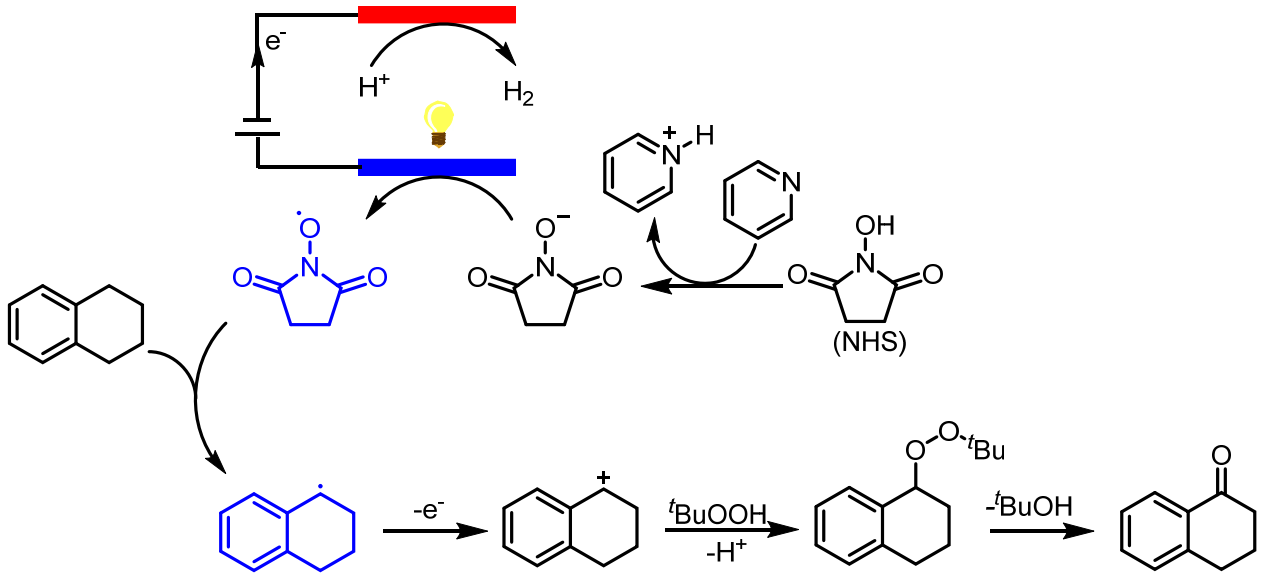
58%
o:p = 14:1

X.-L. Hu et al. *Nat. Catal*. **2019**, 2, 366.

Photoelectrochemical Organic Synthesis

Interfacial Photoelectrochemistry



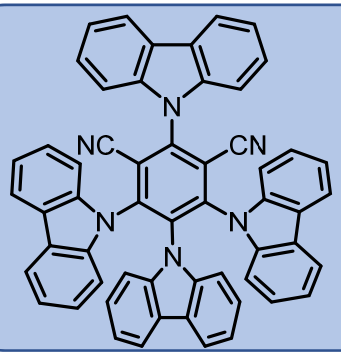


C. P. Berlinguette et al. *Nat. Commun*. **2017**, 8, 390.

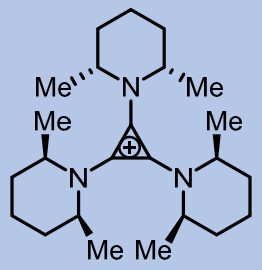
Contents

Summary and Prospection

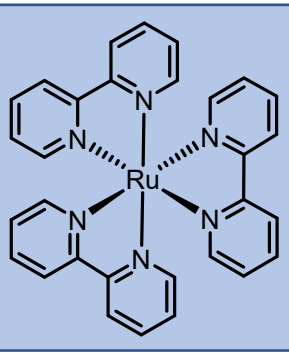
Oxidative



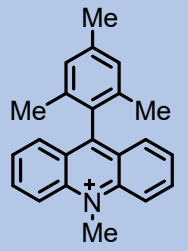
4czIPN



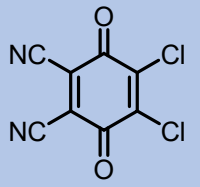
TAC



$Ru(bpy)_3$

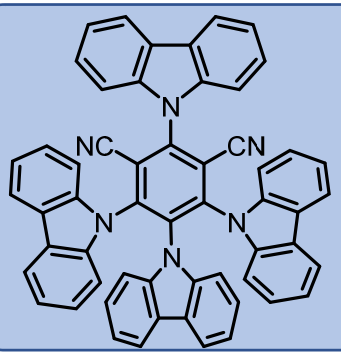


Mes-Acr



DDQ

Reductive



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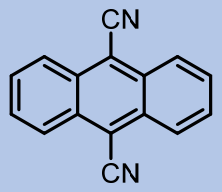
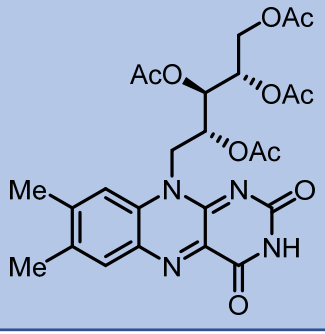
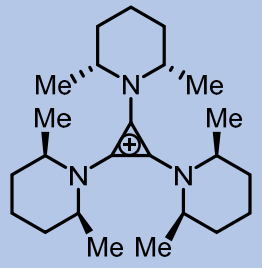


DCA

HAT



RFT



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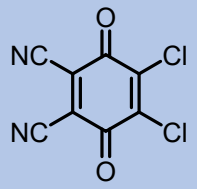
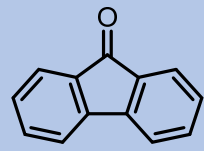
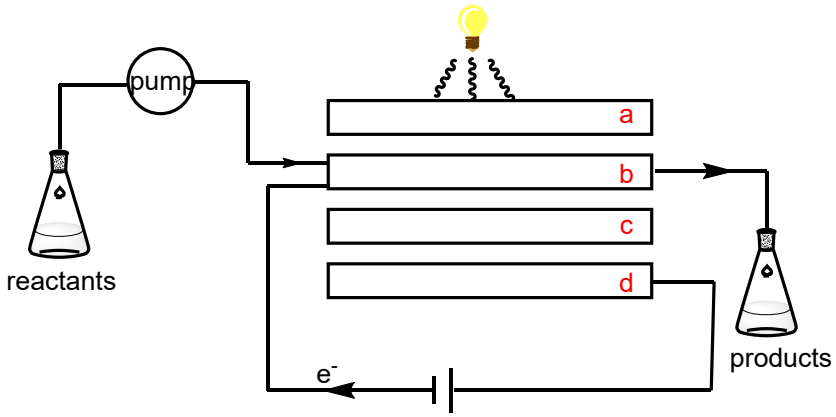


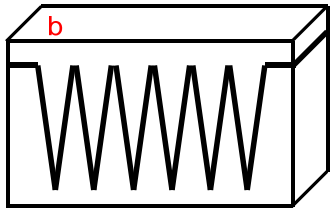
DDQ



9-fluorenone

Summary and Prospection





a:borosilicate glass cover
b:working electrode plate with groove channels
c:ion-exchange membrane
d:counter electrode plate

The limits of Photoelectrochemistry

- Rigorous control experiments
- Interelectrode ohmic drop
- Mass transfer

New reaction ?
New mediator ?
Chiral reaction ?

Thanks for your kind attention