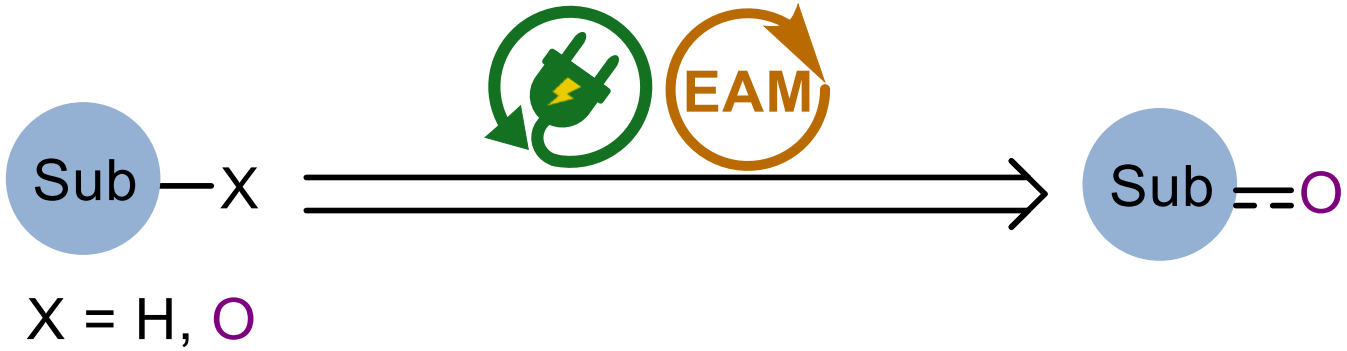
# 地壳丰产金属参与的电化学氧化反应进展




报告人：黄栋
指导老师：麻生明 教授
2022-11-18 Seminar

- 背景介绍
- 第八族金属参与的电氧化反应
- 其他地壳丰产金属参与的电氧化反应
- 总结与展望

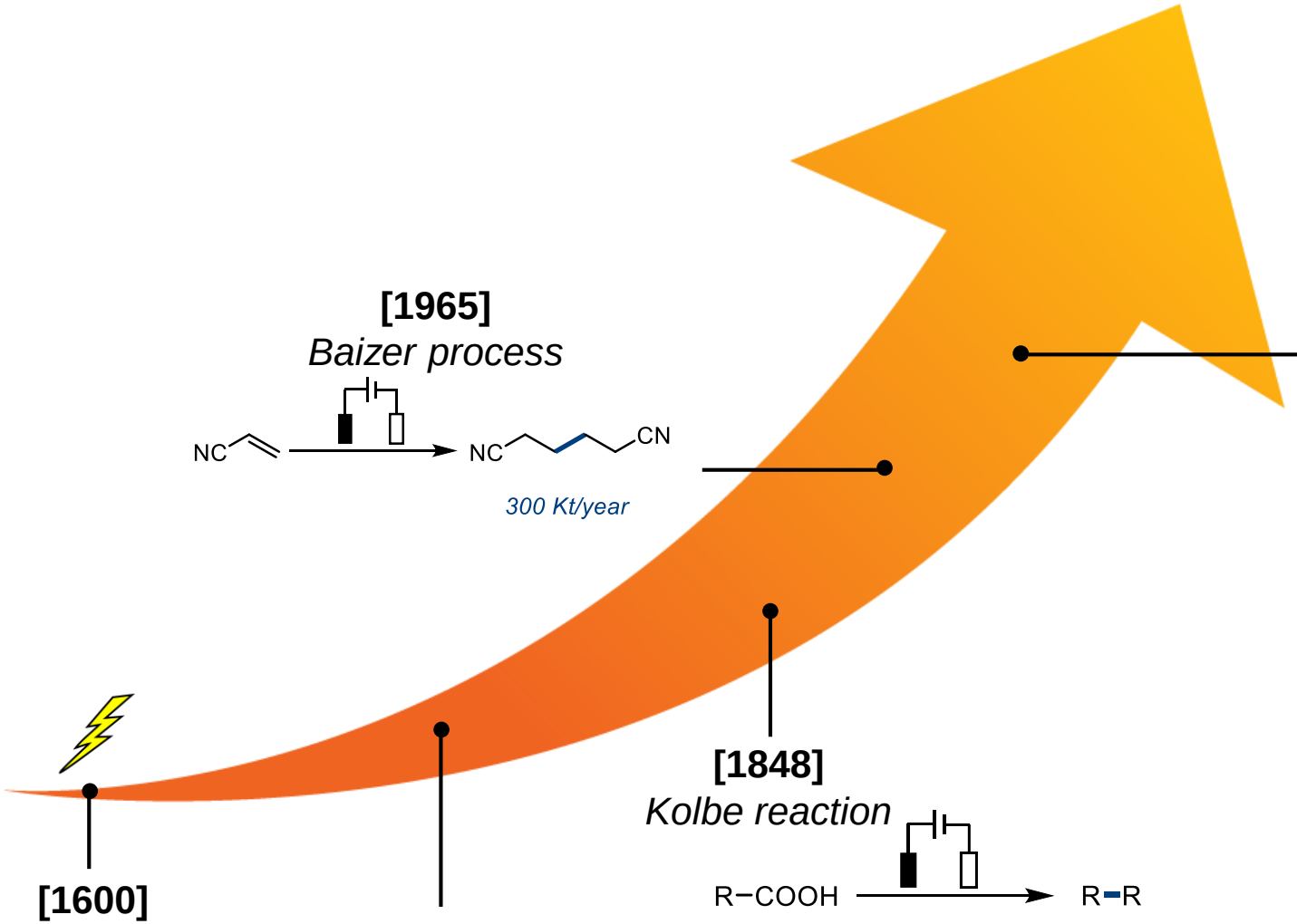
■背景介绍

■第八族金属参与的电氧化反应

■其他地壳丰产金属参与的电氧化反应

■总结与展望

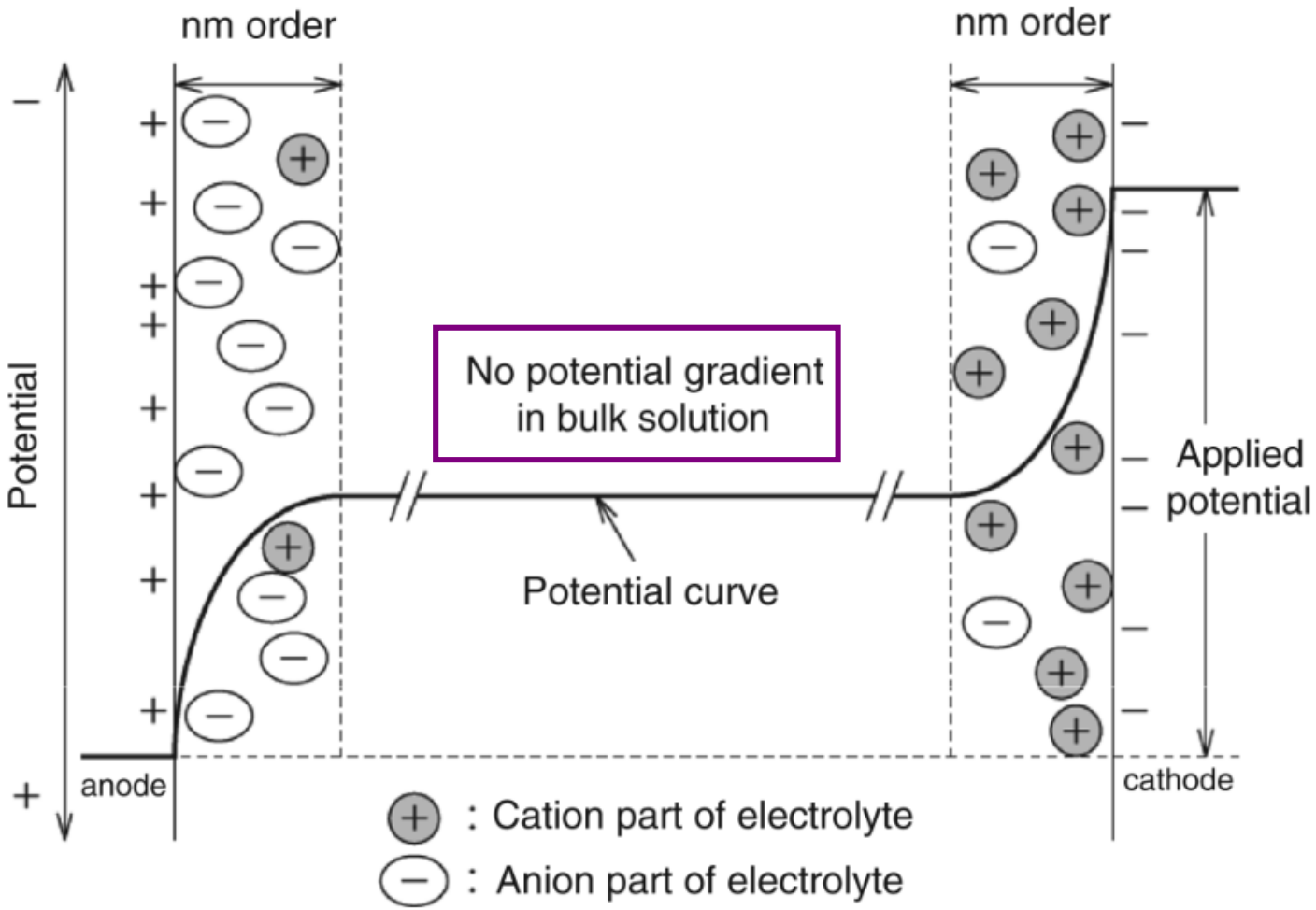
# 有机电化学发展时间线




**[Late 20th Century to the present]**

- *C-H activation*
- *Cross-coupling*
- *Flow chemistry*
- *photoelectrocatalysis*
- *Asymmetric catalysis*
- *Nature product synthesis*
- *Green oxidation*

# 电化学中的电子转移——双电层模型

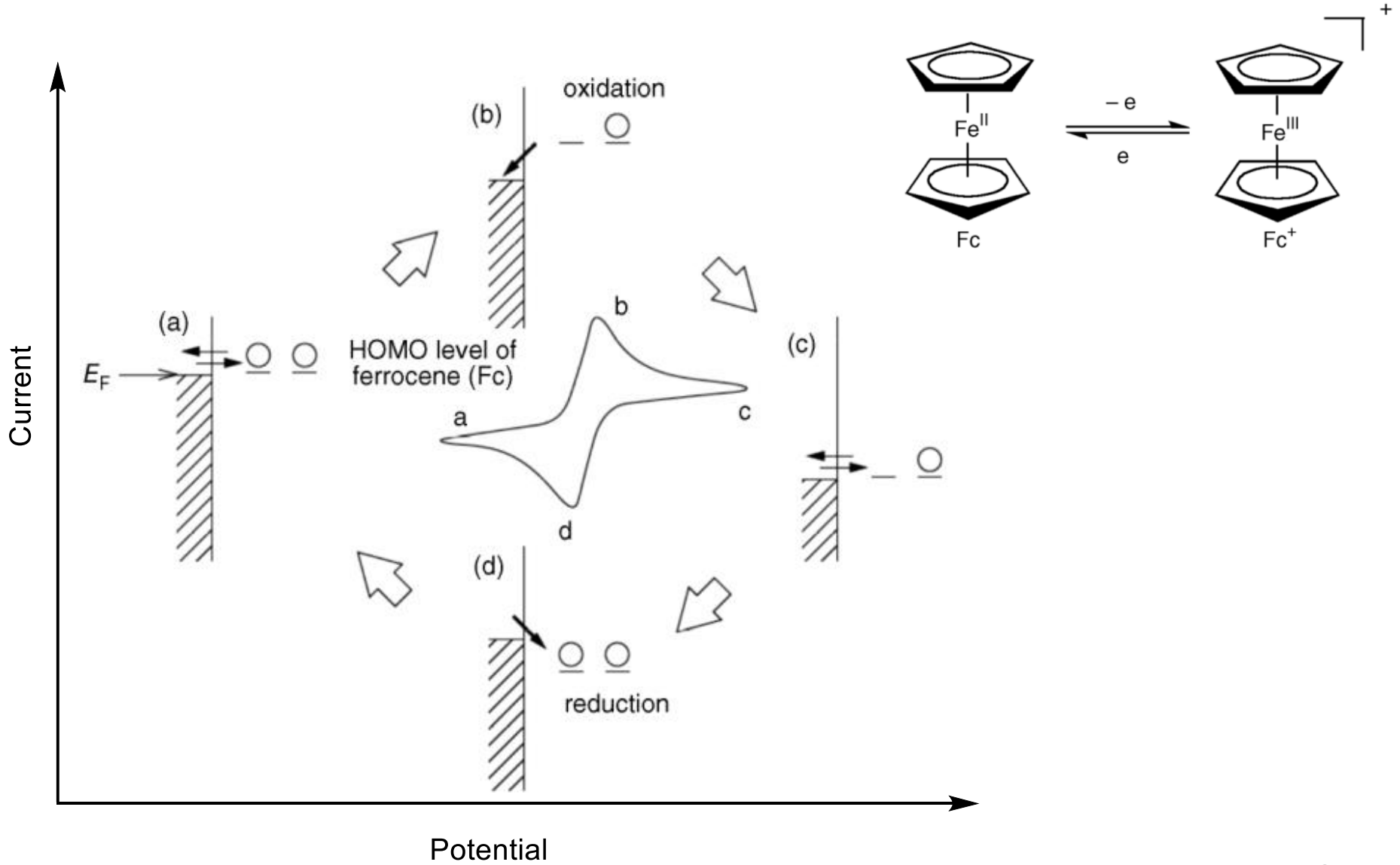



- *Form an electric double layer*
- *Neutralizing the charge imbalance after electrolysis*



Fuchigami, Toshio, Mahito Atobe, and Shinsuke Inagi. *Fundamentals and applications of organic electrochemistry: synthesis, materials, devices*. John Wiley & Sons, **2014**.

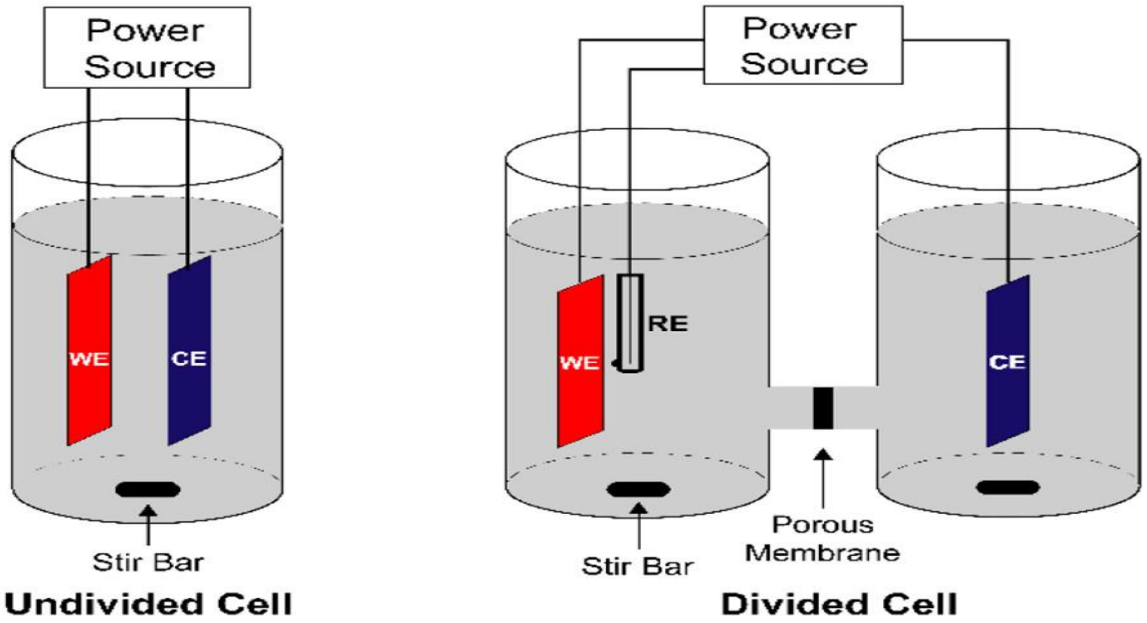
# 循环伏安法






Fuchigami, Toshio, Mahito Atobe, and Shinsuke Inagi. *Fundamentals and applications of organic electrochemistry: synthesis, materials, devices*. John Wiley & Sons, **2014**.

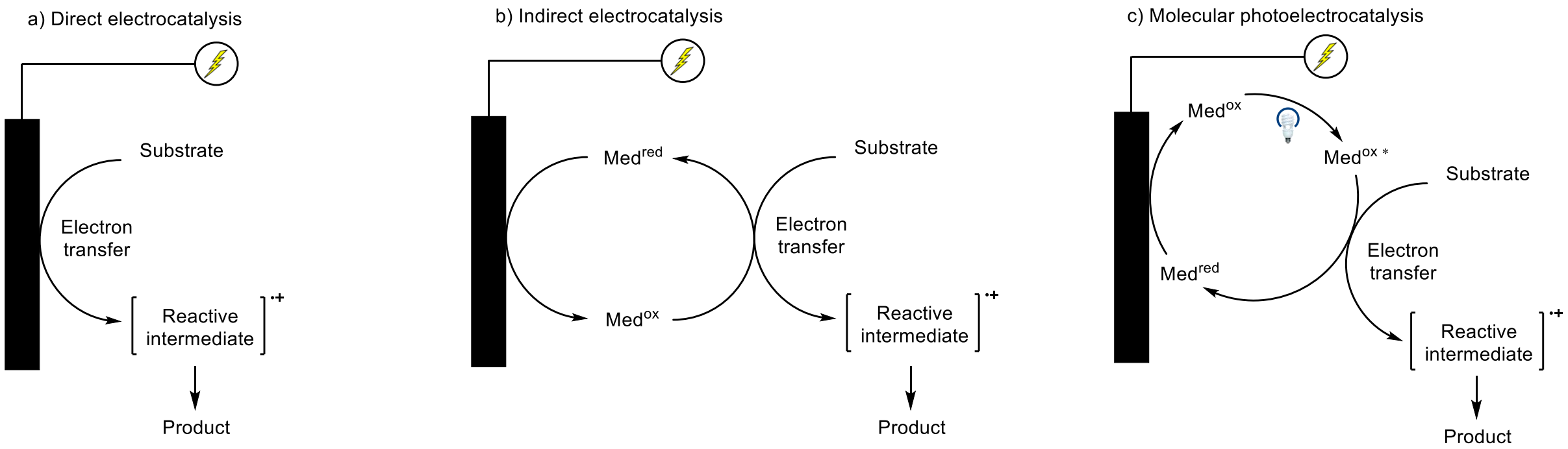
# 电解池类型以及电解模式




| Galvavostatic (constant current) | Potentiostatic (constant potential) |
|---|---|
| ☺ Easy setup | ☹ Only reproducible with reference electrode |
| ☺ Exact equivalents of electrons known | ☹ Equivalents of electrons not directly controlled |
| ☹ Voltage range not controlled | ☺ adjust the process potential to improve selectivity |

Little, R. D. *et al*. *Chem. Rev.* **2022**, *122,* 3292.
Willans, C. E. *et al*. *Green Chem.* **2020**, *22,* 3358.

# 有机电催化模式

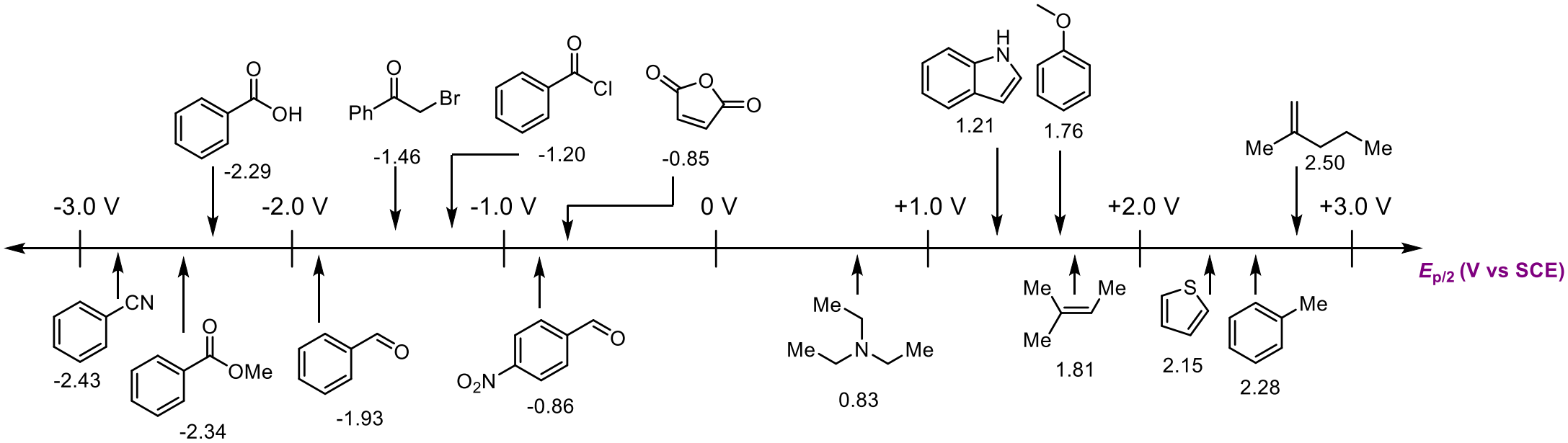



- *Indirect electrocatalysis is discussed in this topic*


Little, R. D. *et al. Chem. Soc. Rev.* **2014**, *43,* 2492.; Wang, F., Stahl, S. S. *Acc. Chem. Res.* **2020**, *53,* 561.
Baran, P. S. *et al. Acc. Chem. Res.* **2020**, *53,* 72.; Guo, C. *et al. Angew. Chem. Int. Ed.* **2020**, *59,* 12612.
Lennox, A. J. J. *et al. Angew. Chem. Int. Ed.* **2020**, *59,* 18866.; Lin, S. *et al. Chem. Soc. Rev.* **2021**, *50,* 7941.
Rovis, T. *et al. Chem. Rev.* **2022**, *122,* 2487.; Minteer, S. D. *et al. Chem. Rev.* **2022**, *122,* 3180.
Cheng, X., Lei, A., Mei, T.-S., Xu, H.-C., Xu, K., Zeng, C. *CCS Chem.* **2022**, *4,* 1120.

# 电化学氧化优势

■ ***Elctrochemical series of important organic compounds (potentials against SCE)***




***Common Oxidizing Agents***

| $F_2$ | $SO_4^{\bullet}$ | $S_2O_8^{\ominus}$ | $H_2O_2$ | $MnO_4^{\ominus}$ | HOCl | $O_2$ |
|---|---|---|---|---|---|---|
| 2.62 | 2.36 | 1.85 | 1.45 | 1.43 | 1.39 | 0.99 |

$\Delta G = -nFE^0_{cell}$

$\Delta\Delta G$ = 1.4 kcal, $\Delta K_{eq}$ = 10

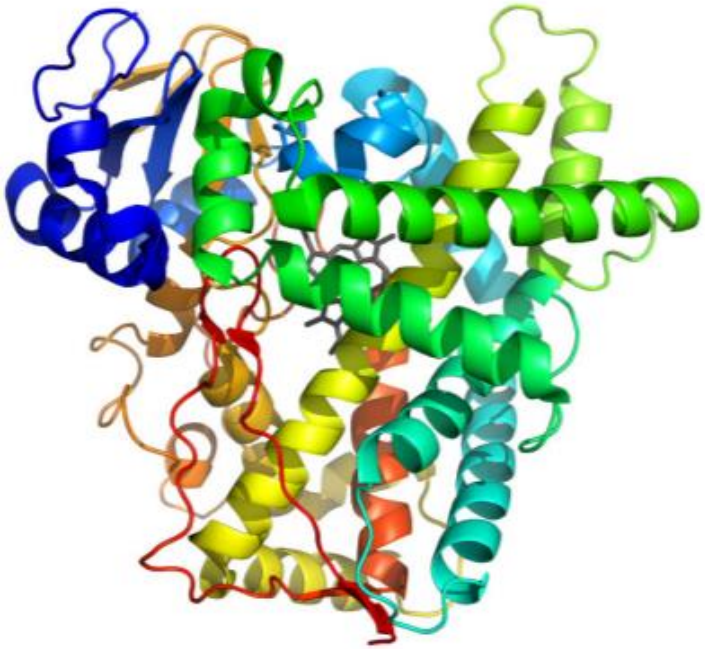
**60 mV** ~ 1.4 kcal ~ $\Delta K_{eq}$ = 10

***Benifits of electrooxidation***

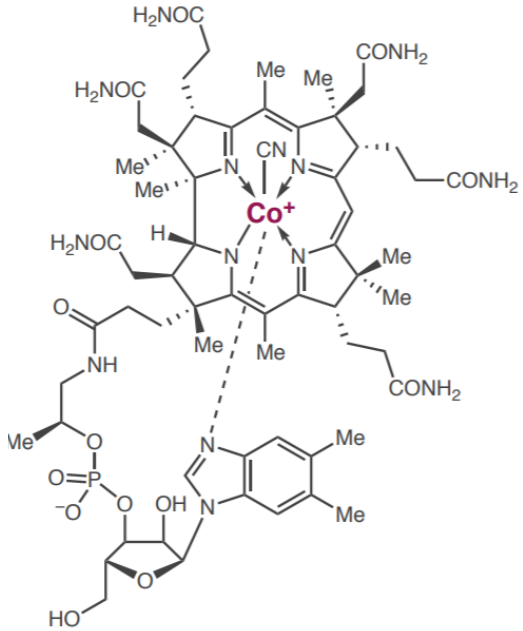
- ***Avoid equivalents of chemical reagents***
- ***Mild condition***
- ***Control electrode potential to control redox***

Nicewicz, D. A. *et al. Synlett* **2016**, *27*, 714.
Merker Photocatalysis Chart

# 地壳丰产金属(EAM)

***Cytochrome P450***




***Vitamin B12***

*Benefits of EAMs catalysis*

- *Naturally abundant in the earth's curst*
- *Low cost and low toxicity relative to other TM*
- *Present in various metalloproteins*
- *Multivalent and single-electron catalytic pattern make a diverse reactivity*

*Can we discover new reactivity that is unique to EAM elctrooxidation?*

J. Liu *et al*. *Chem. Rev.* **2014**, *114*, 4366.
Bullock R. M., Chen J. G., Gagliardi L. *et al. Science*, **2020**, *369*, 786.

■背景介绍

■第八族金属参与的电氧化反应

■其他地壳丰产金属参与的电氧化反应

■总结与展望

Fe

*electron configuration: $3d^6 4s^2$*
*range of oxidation state: 0 to +6*

Co

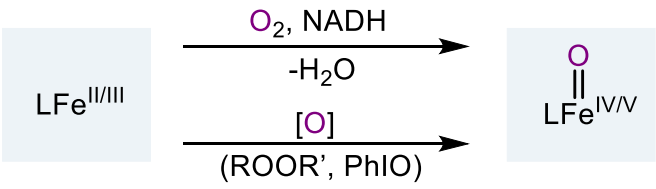
*electron configuration: $3d^7 4s^2$*
*range of oxidation state: -1 to +5*

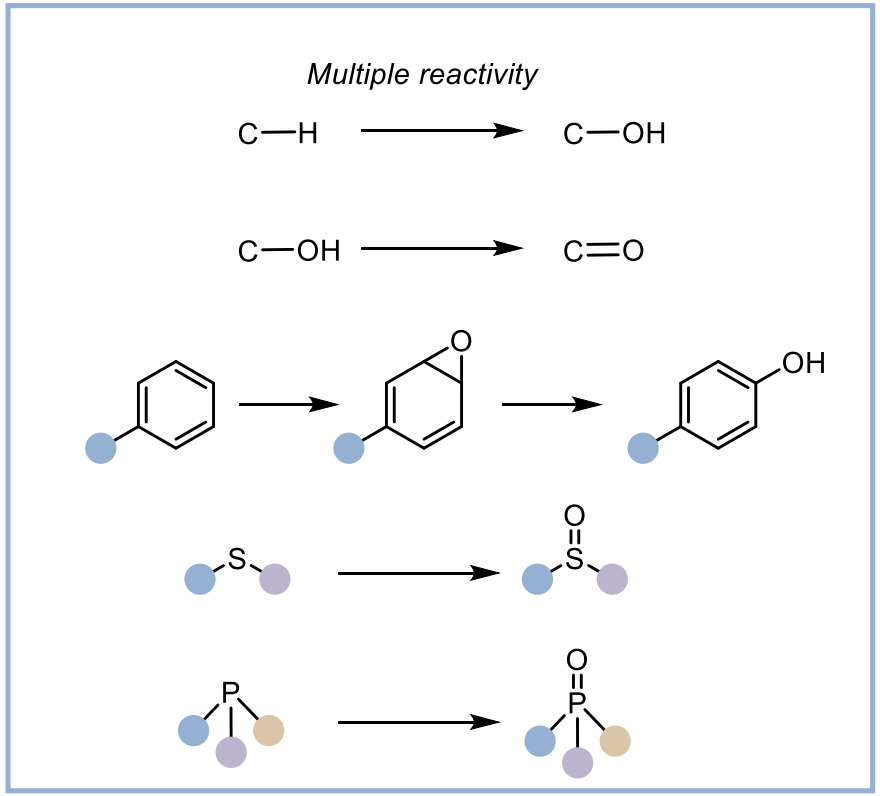
Ni

*electron configuration: $3d^8 4s^2$*
*range of oxidation state: 0 to +4*

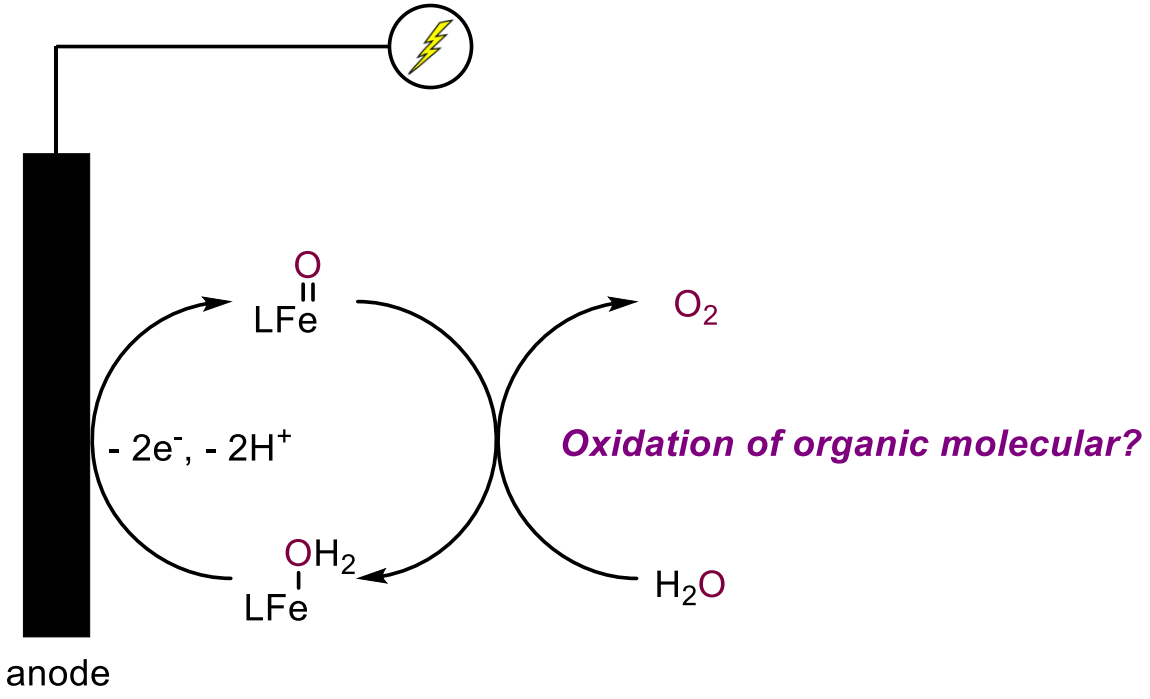
# 铁参与的电氧化反应

■ ***Different approaches for the generation of high-valent iron-oxo species***



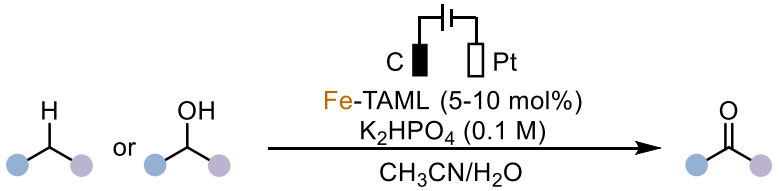

■ ***high-valent iron-oxo species generated in OER***



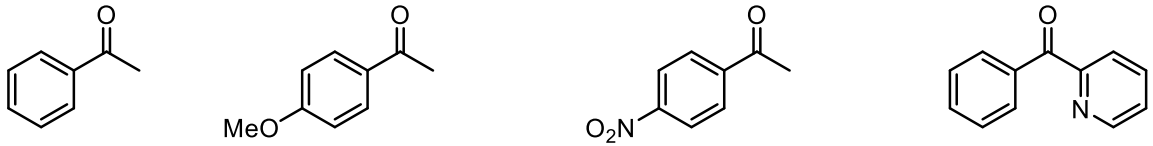

***Oxidation of organic molecular?***


J. H. Dawson *et al.Chem. Rev.*, **1996**, *96*, 2841.
J. T. Groves *et al. Chem. Rev.*, **2018**, *118*, 2491.
T. J. Meyer *et al. J. Am. Chem. Soc.*, **2014**, 136, 5531.

# 铁参与的电氧化反应

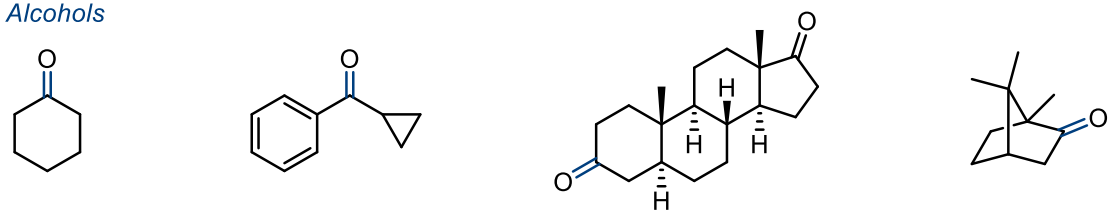



- *Benzylic C-H Bonds*

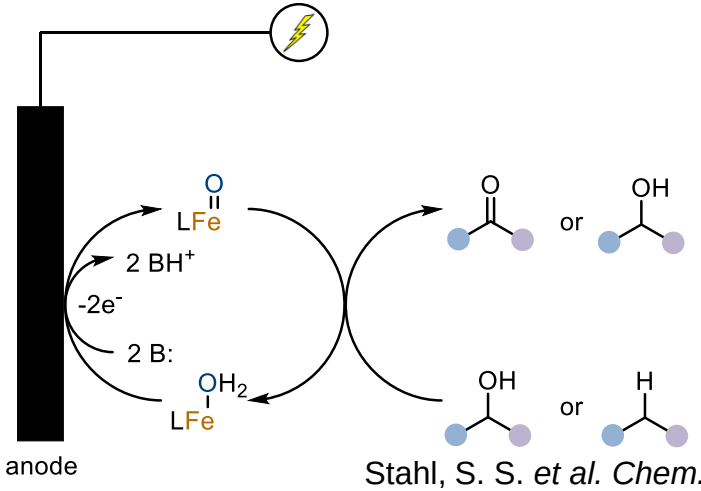


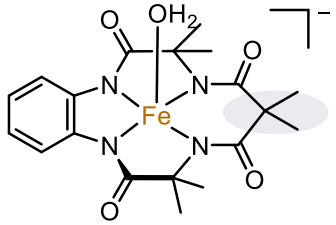

*79% yield* *77% yield* *31% yield* *45% yield*

- *Alcohols*




*85% yield* *95% yield* *94% yield* *84% yield*

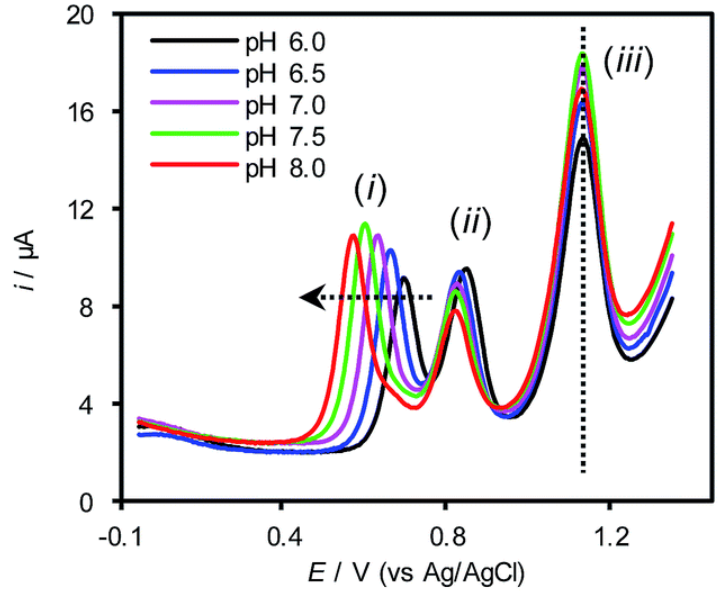


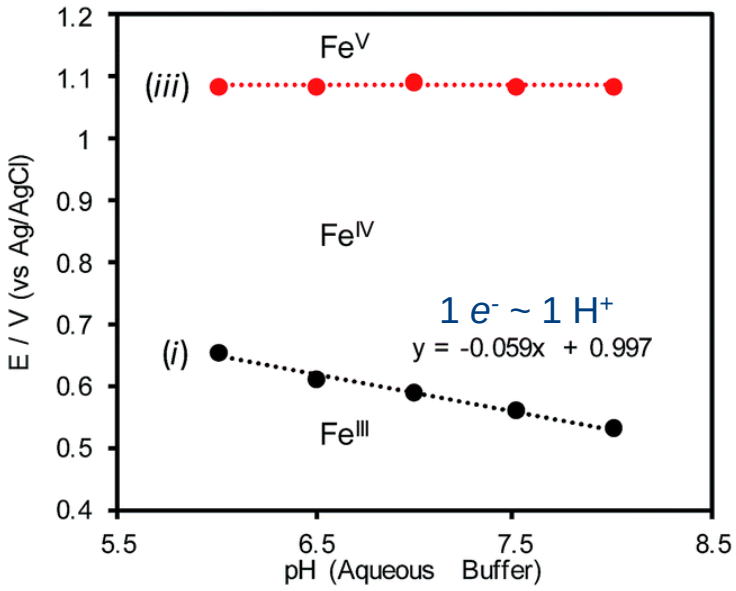



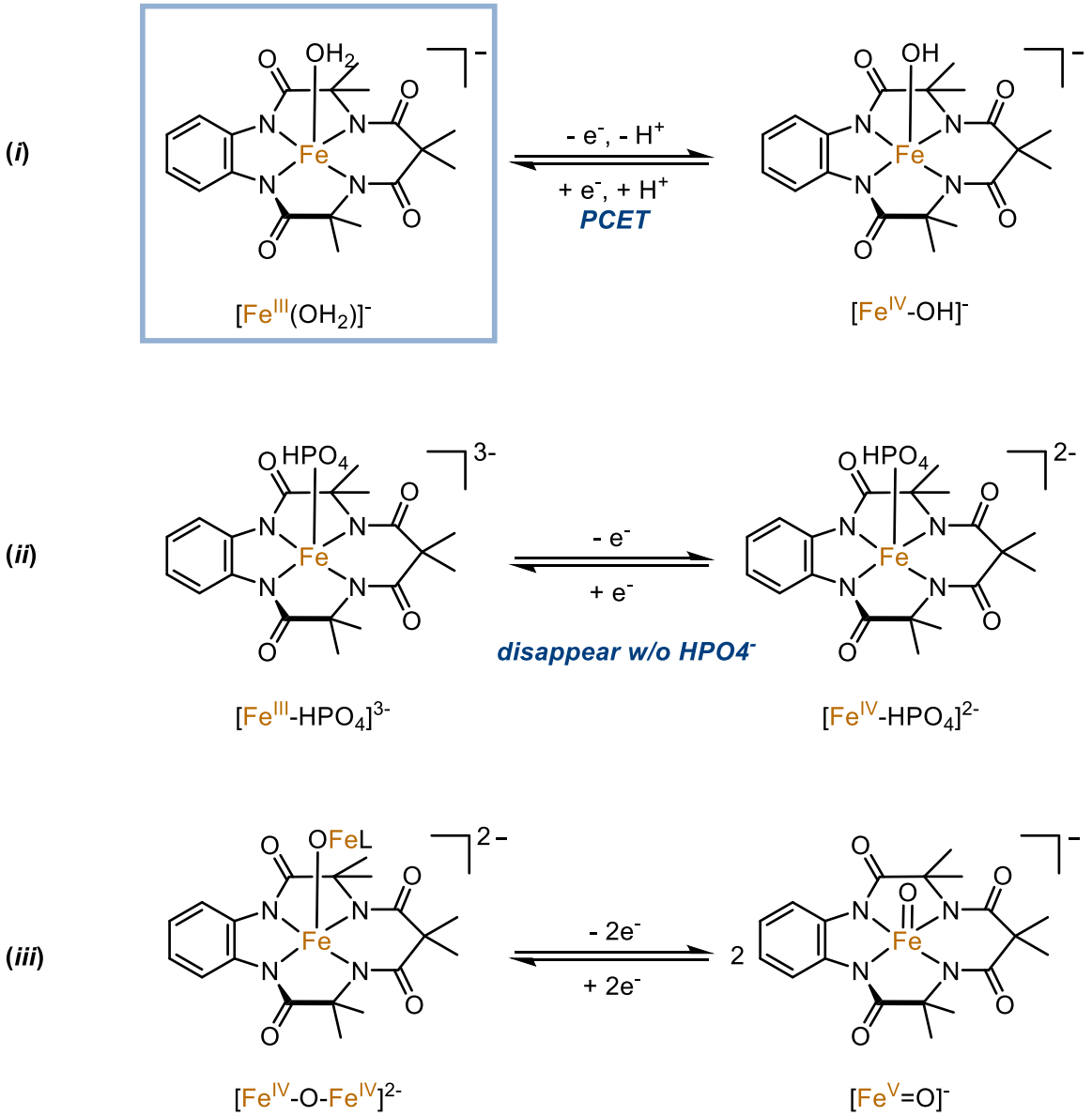

*Which oxidation state of Iron is the active species in catalytic cycle?*

Stahl, S. S. *et al. Chem. Sci.* **2019**, *10*, 7542.

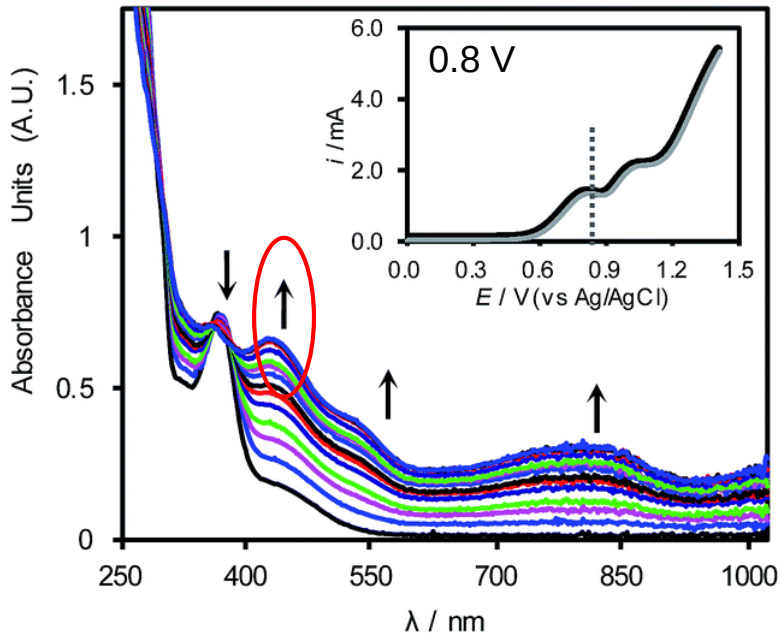
# 铁参与的电氧化反应机理研究

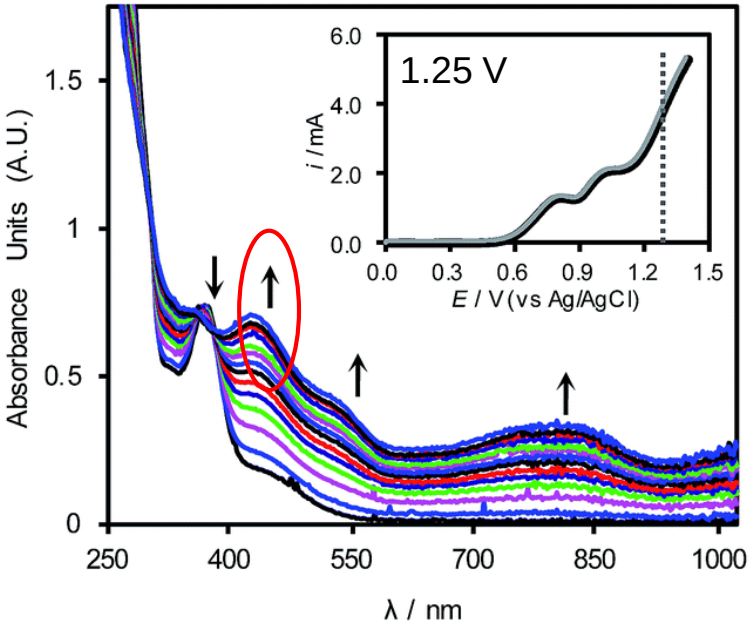


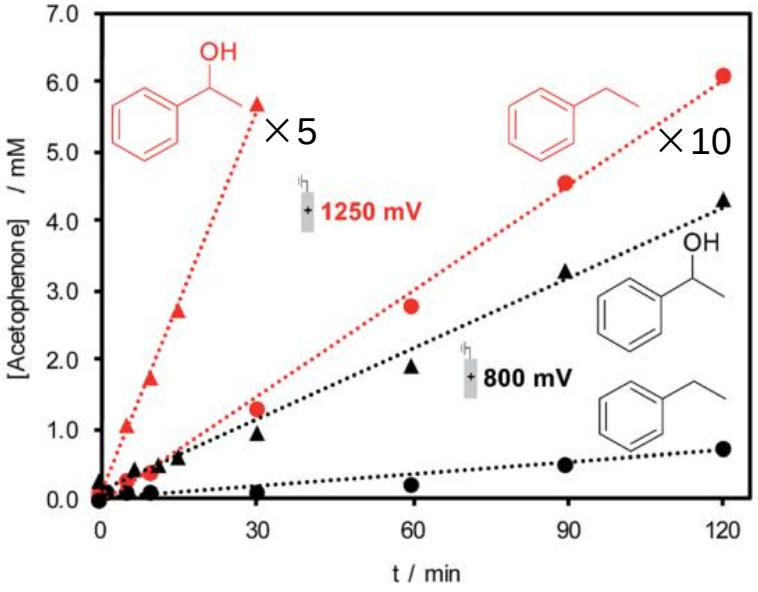



# 铁参与的电氧化反应机理研究

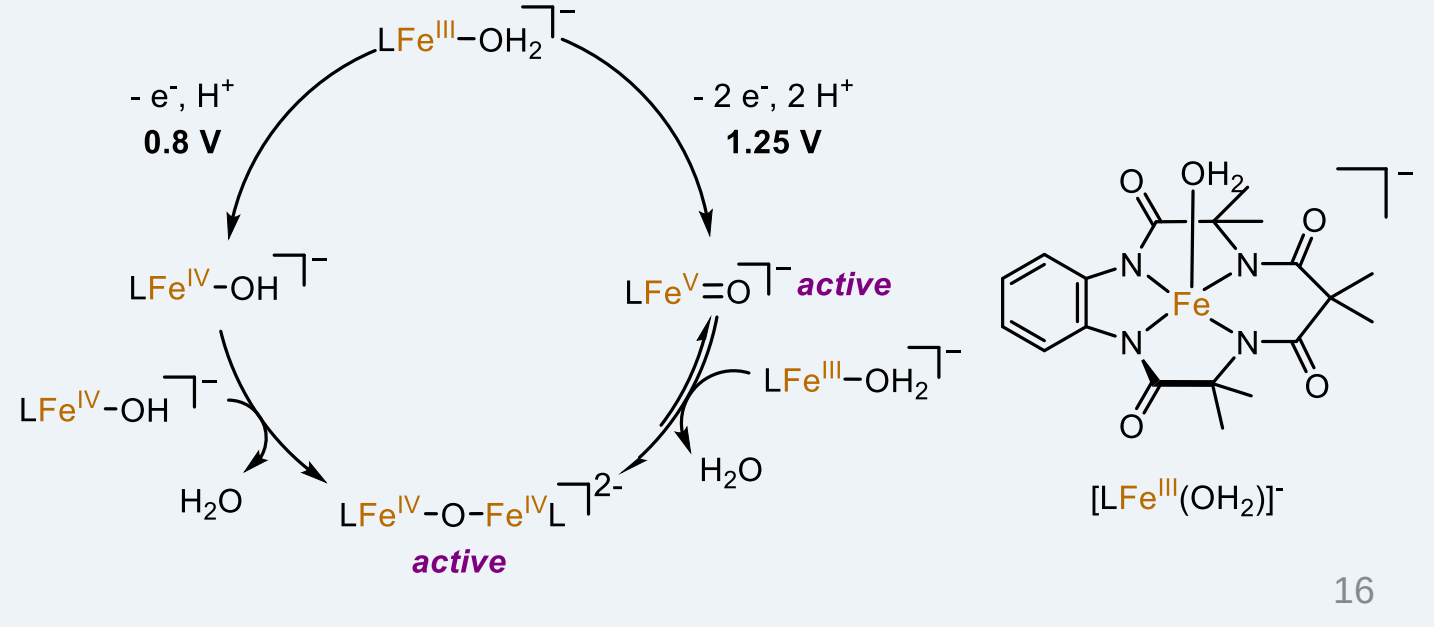


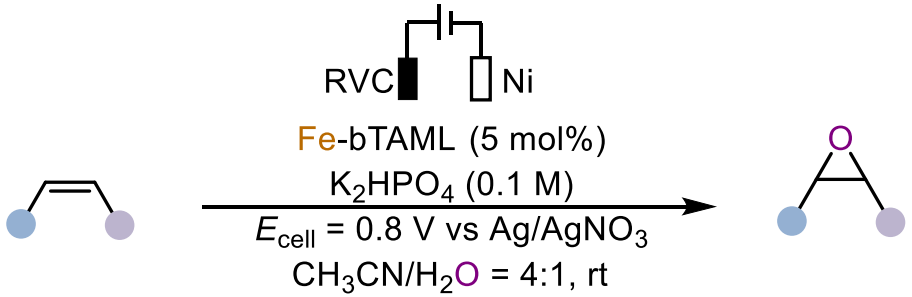




2 $LFe^{III}-OH_2^{\urcorner -}$ ⟹ $LFe^{IV}-O-Fe^{IV}L^{\urcorner 2-}$

*Comfirmed by in-situ UV-vis*

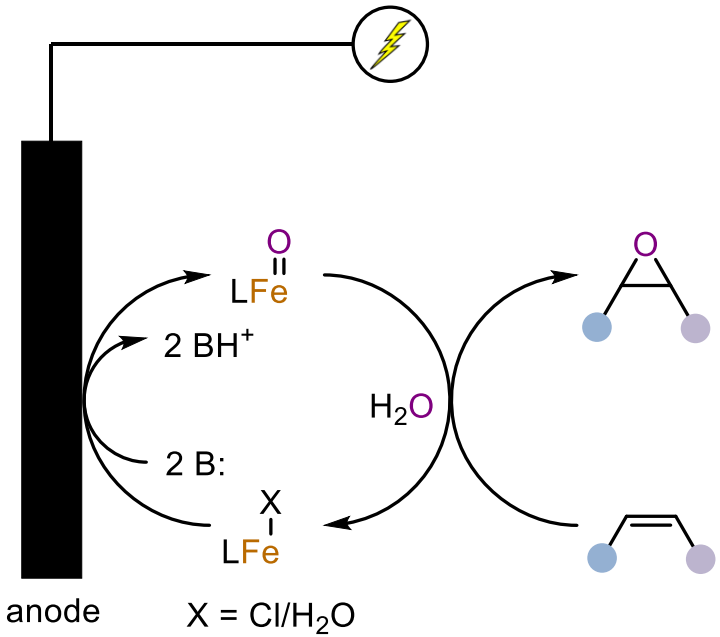


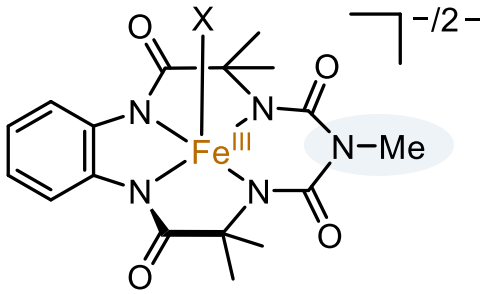
# 铁参与的电化学环氧化反应





*86% yield* *92% yield* *62% yield* *75% yield*



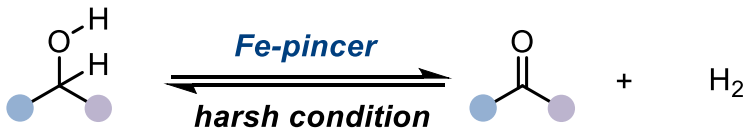




***Ligand modification***

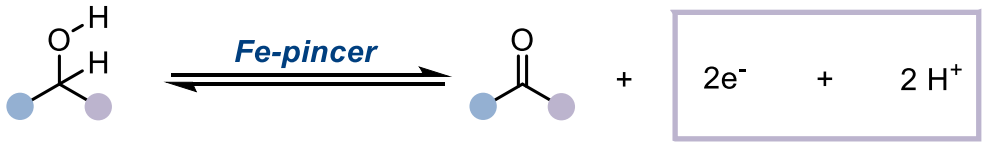
Gupta, S. S. *et al. Chem. Sci.* **2020**, *11*, 11877.

# 铁参与的电化学脱氢氧化反应

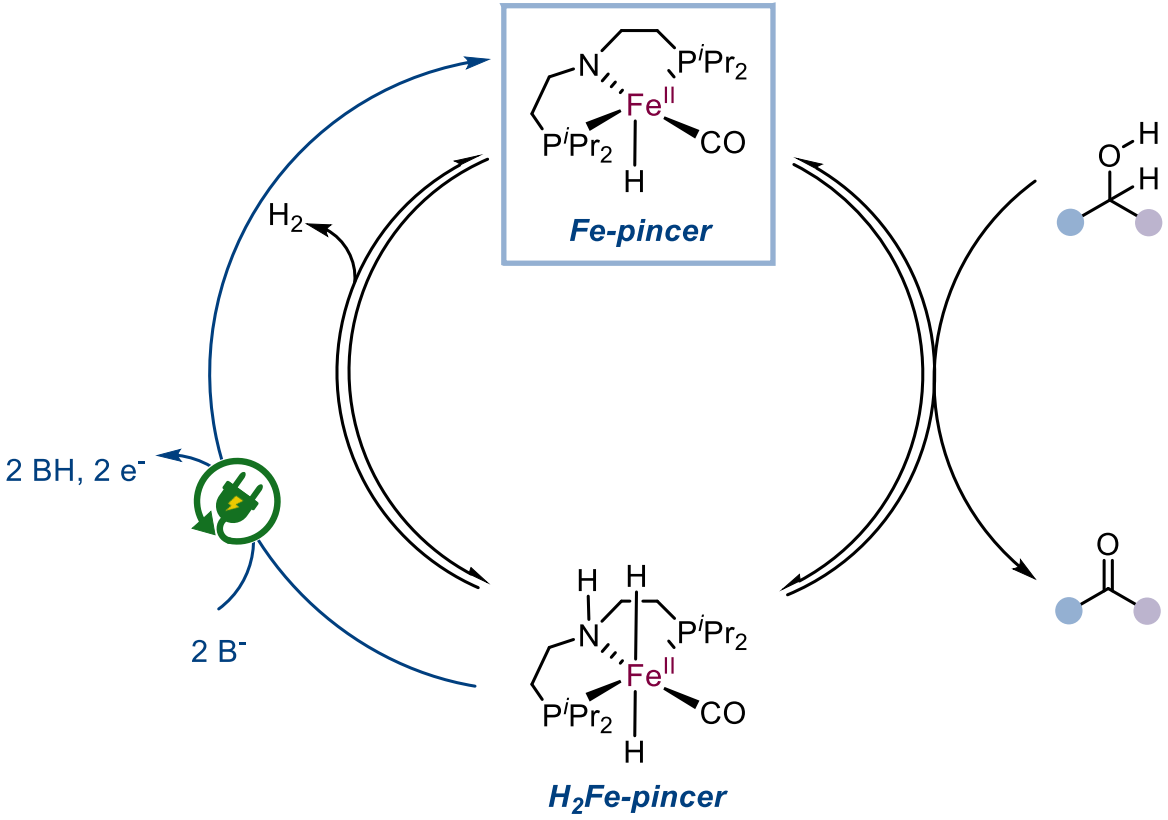
- ***Acceptorless alcohol dehydrogenation (AAD)***




- ***Electrocatalytic alcohol oxidation***



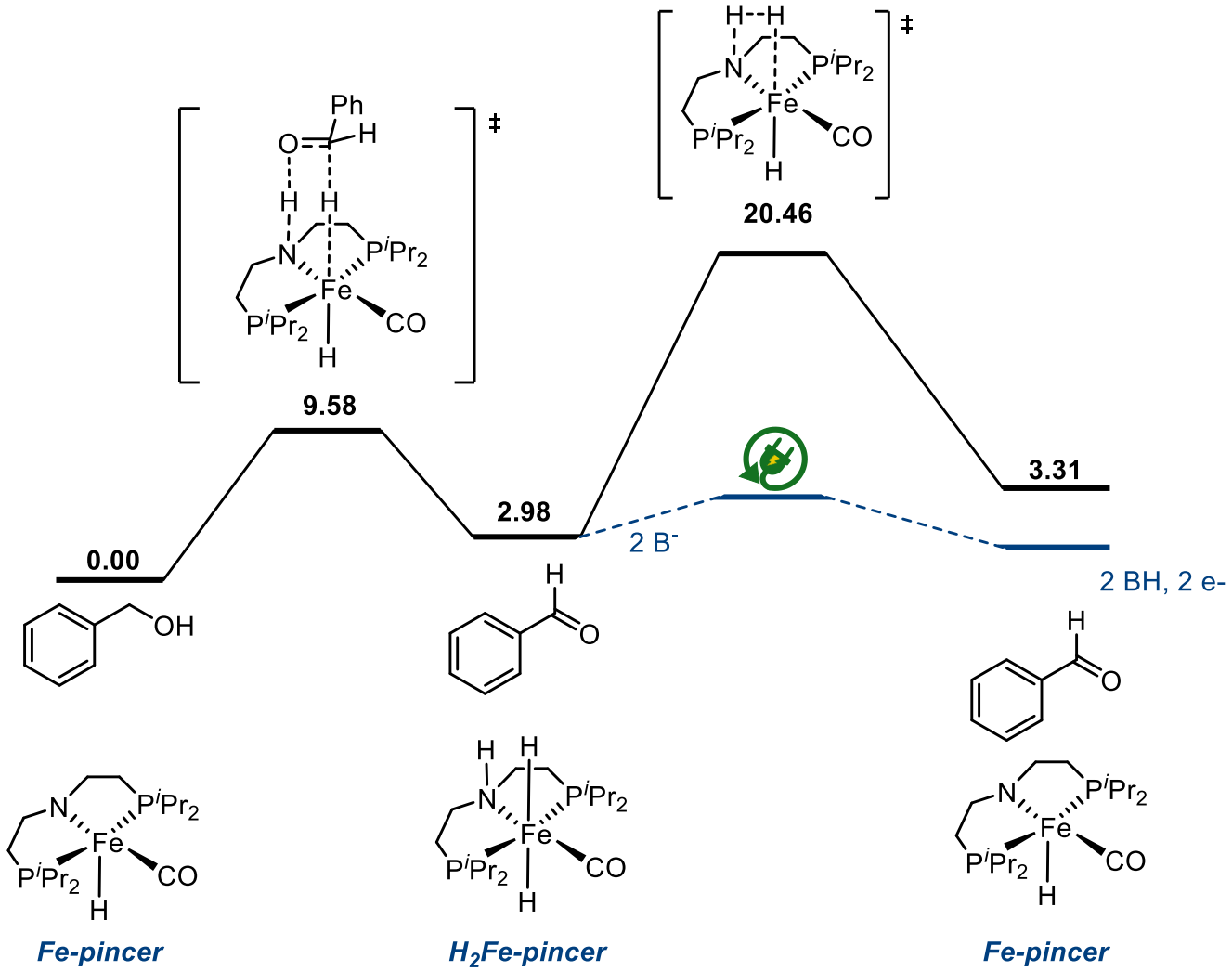

***Anode as $e^-$ acceptor***
***Base as $H^+$ acceptor***





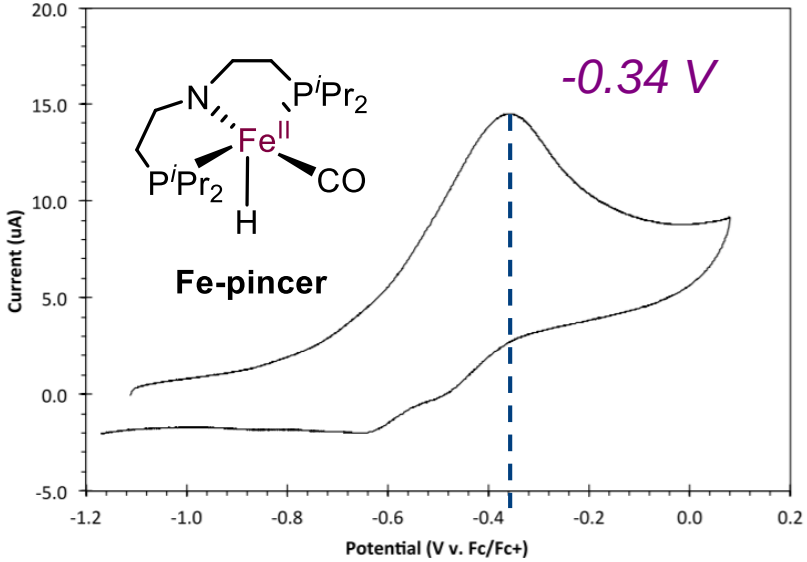
Crabtree, R. H. *et al.* Chem. Rev. **2017**, 117, 9228.
Shimizu, K. *et al. Green Chem.* **2018**, *20*, 2933.
Waymouth, R. M. *et al. Inorg. Chem.* **2020**, *59,* 1453.

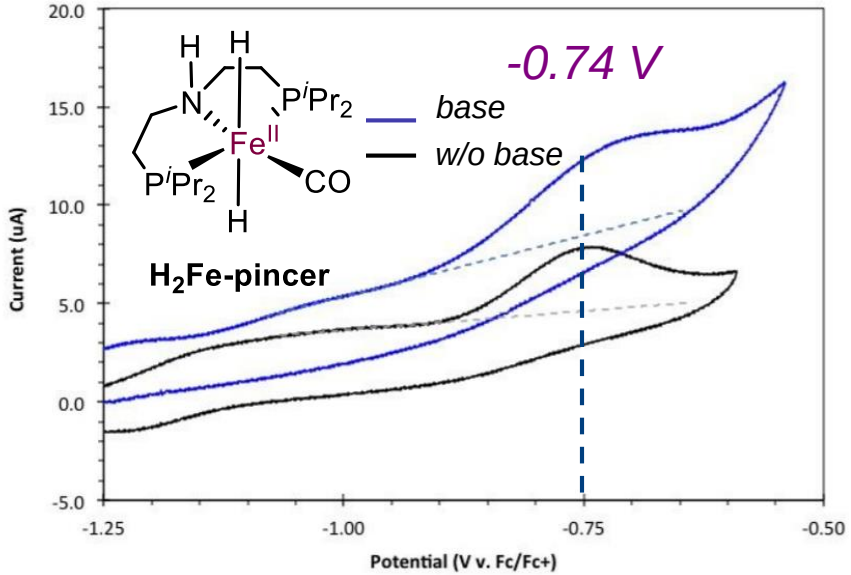
# AAD *vs* 电化学脱氢氧化

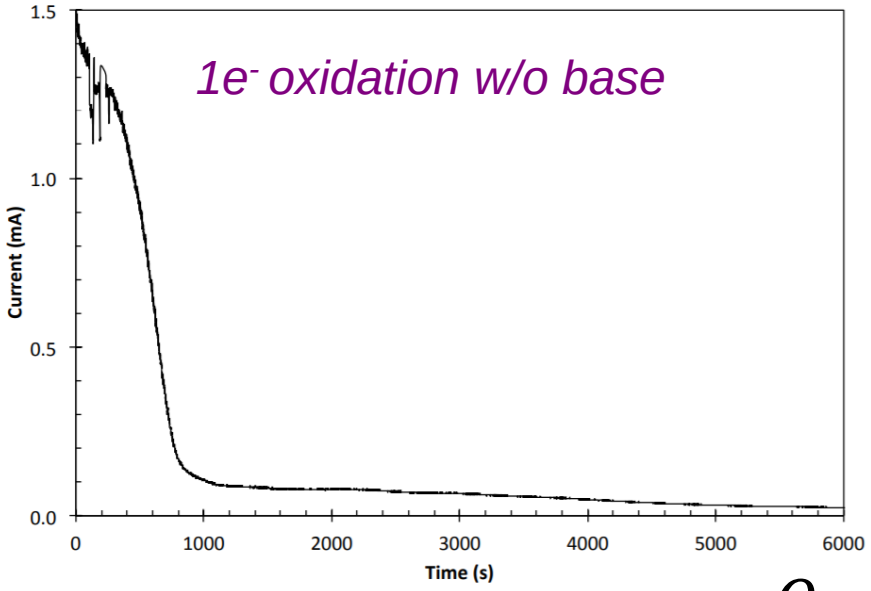


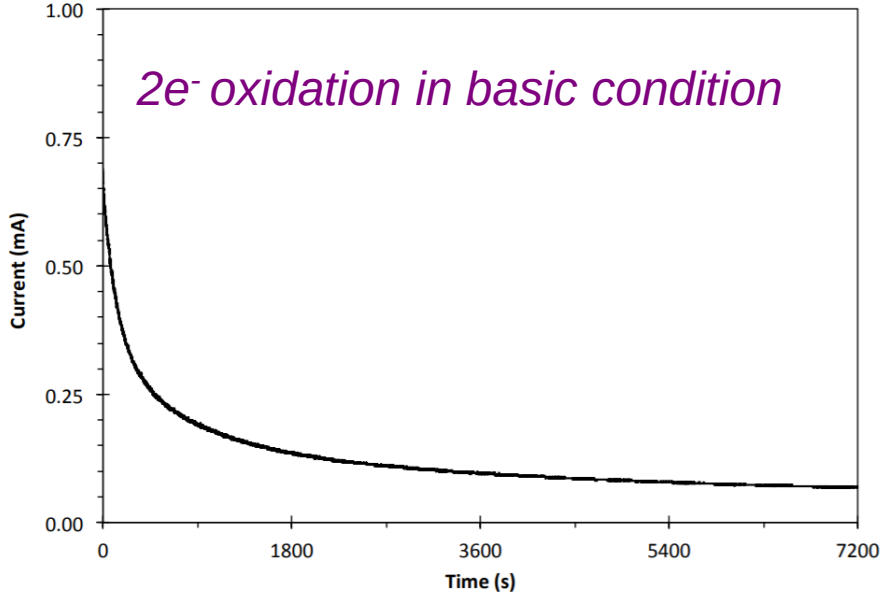

- ***pK$_a$ match between base and catalysts(or intermeidates)***
- ***Mediate potential to control electron transfer***

# 铁参与的电化学脱氢氧化反应



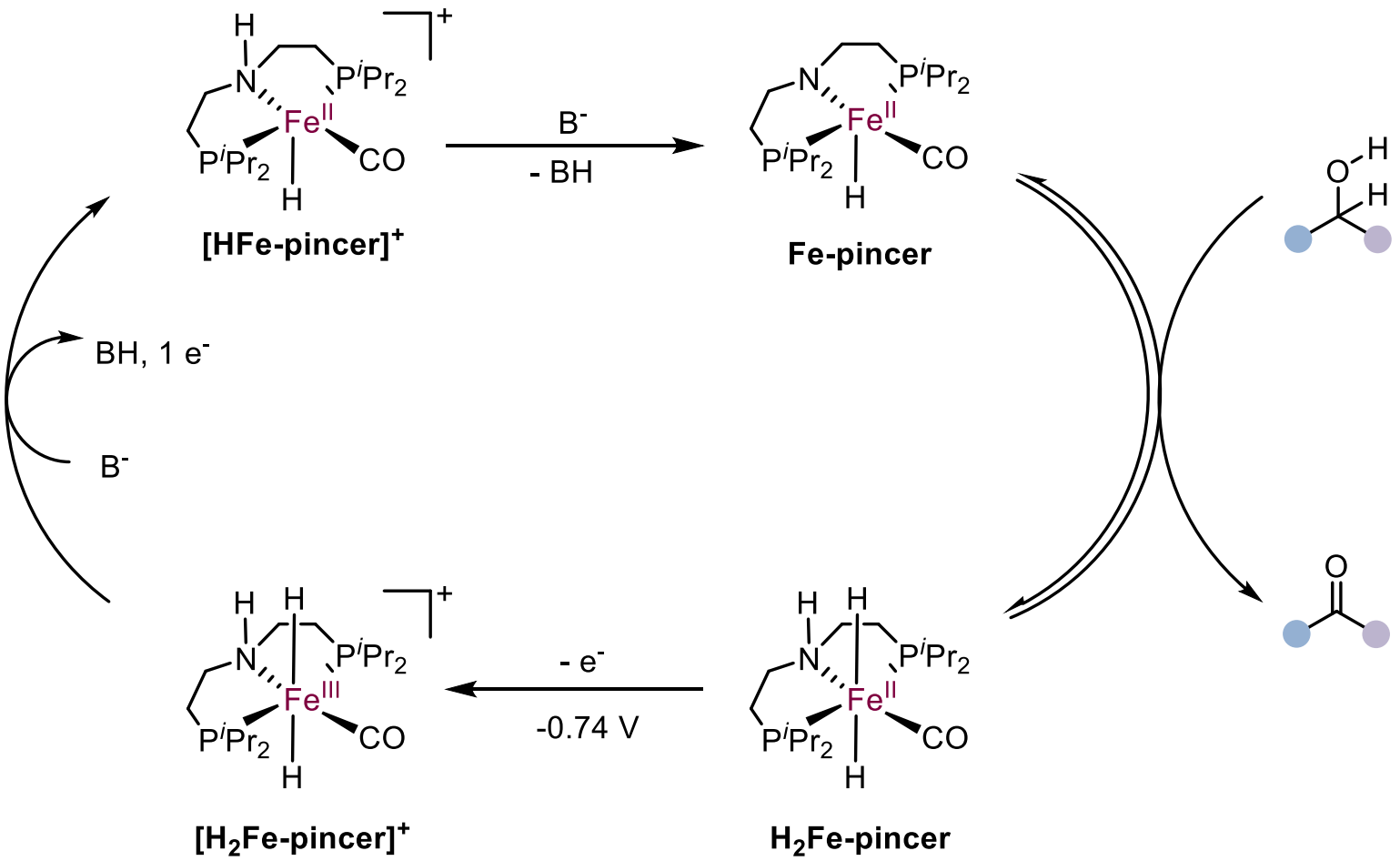




$$Q = nF\triangle N_{[H_2Fe\text{-pincer}]}$$

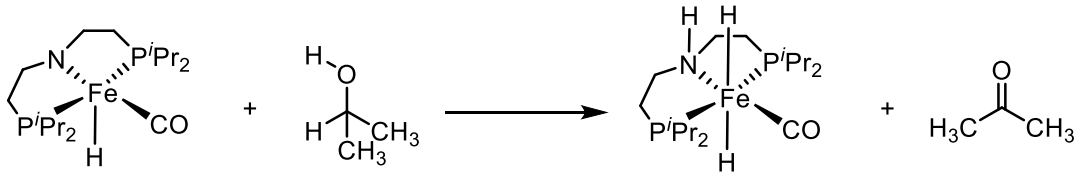
# 铁参与的电化学脱氢氧化反应

■ *A 2e⁻/2H⁺ ECEC pathway*



# 铁参与的电化学脱氢氧化反应

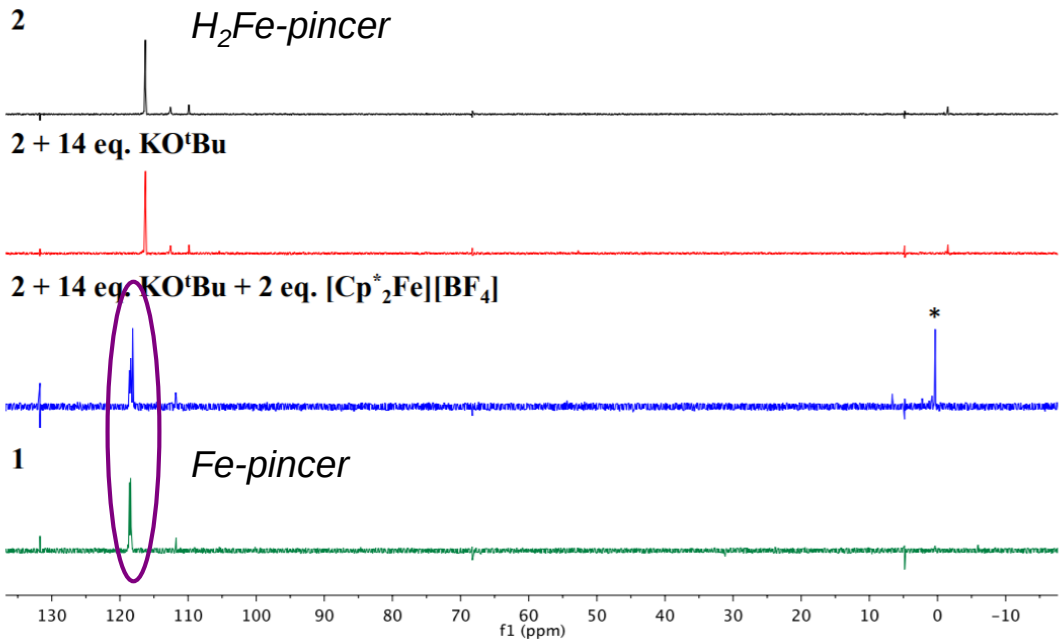
■ *Experiment and DFT calculation explain the $2e^-/2H^+$ ECEC pathway*




■ $H_2$Fe-pincer + KO$^t$Bu ⟶✗ Fe-pincer

$H_2$Fe-pincer + KO$^t$Bu + $[Cp^*_2Fe][BF_4]$ ⟶ Fe-pincer

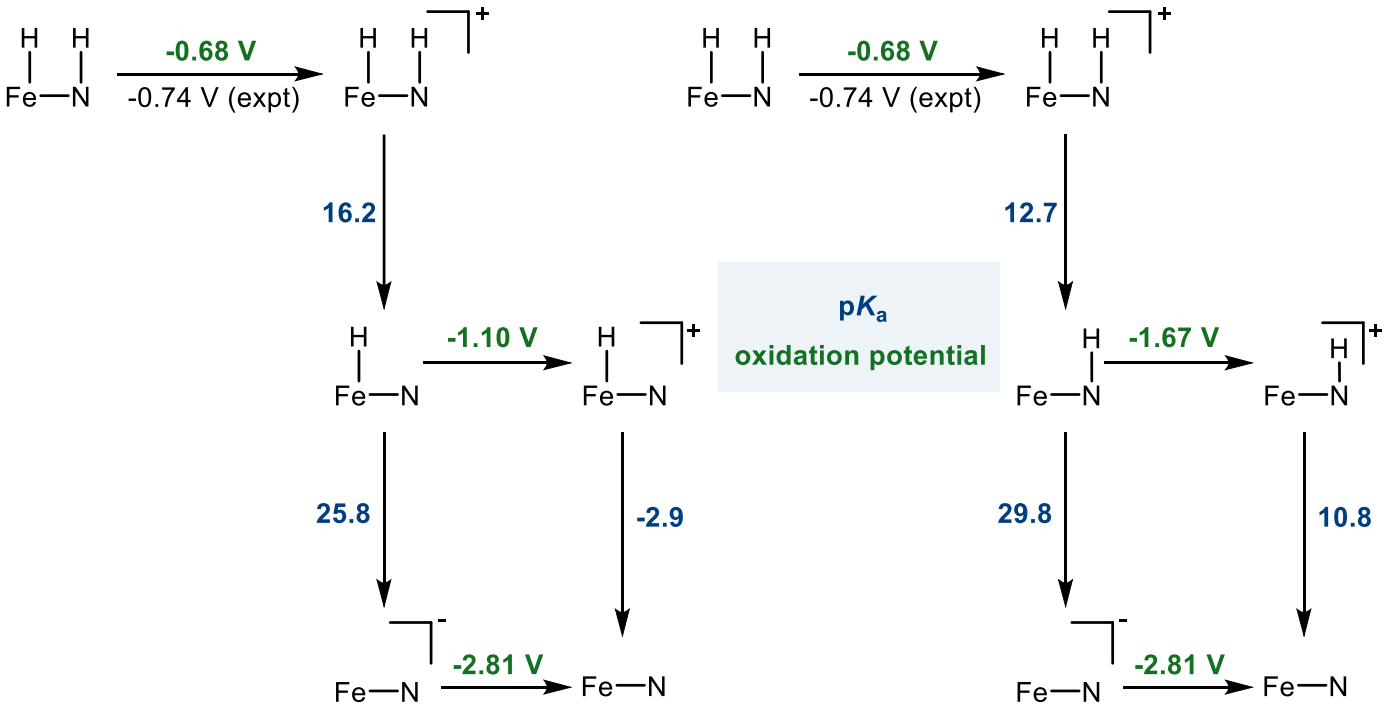
*via [Fe-pincer]$^+$*




$^{31}$P NMR spectra

Path A: N-H deprotonation first

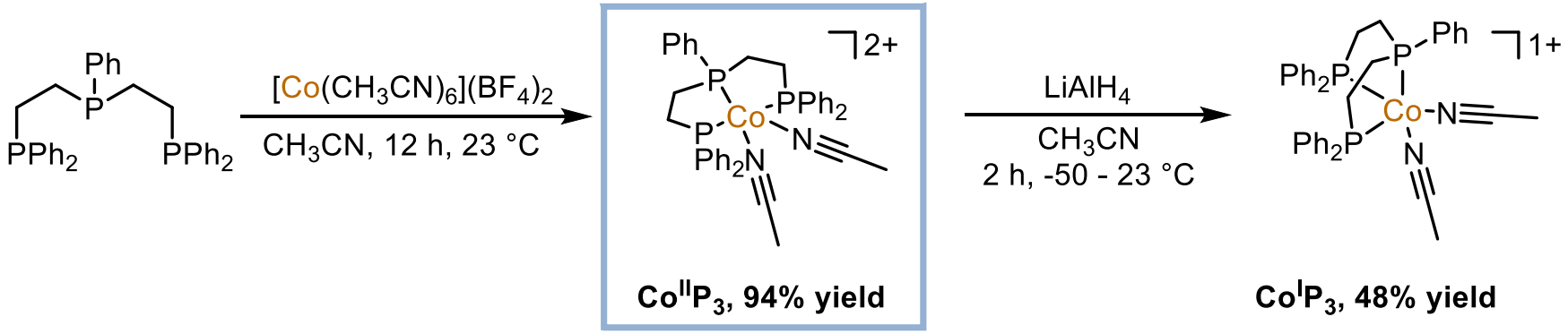
√ Path B: Fe-H deprotonation first



# 钴参与的电化学脱氢氧化反应

■ *A example of stoichiometric oxidation using $Co^{II}P_3$ complex*

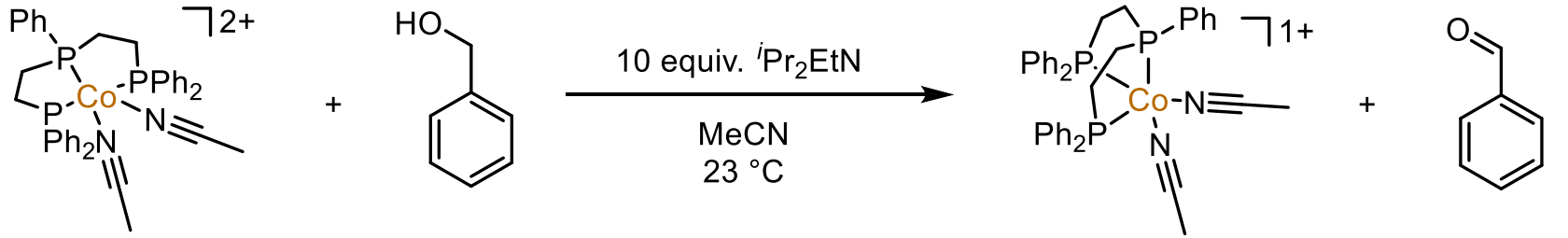
***Synthesis of Co complex***




$Co^{II}P_3$, 94% yield

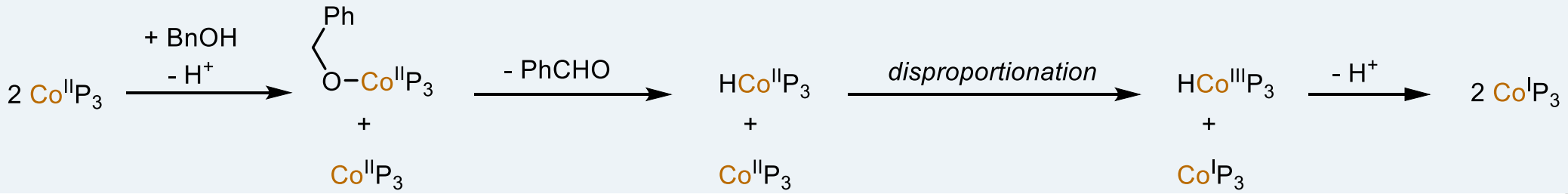
$Co^{I}P_3$, 48% yield

***Stoichiometric Oxidation***




2.0 equiv. $Co^{II}P_3$ 10 equiv. 2.0 equiv. $Co^{I}P_3$ **2:1** 1.0 equiv.

*99% yield*

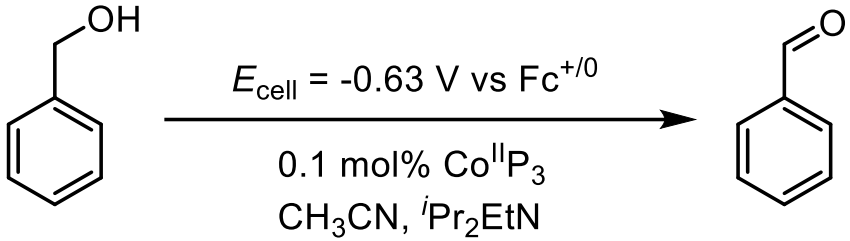


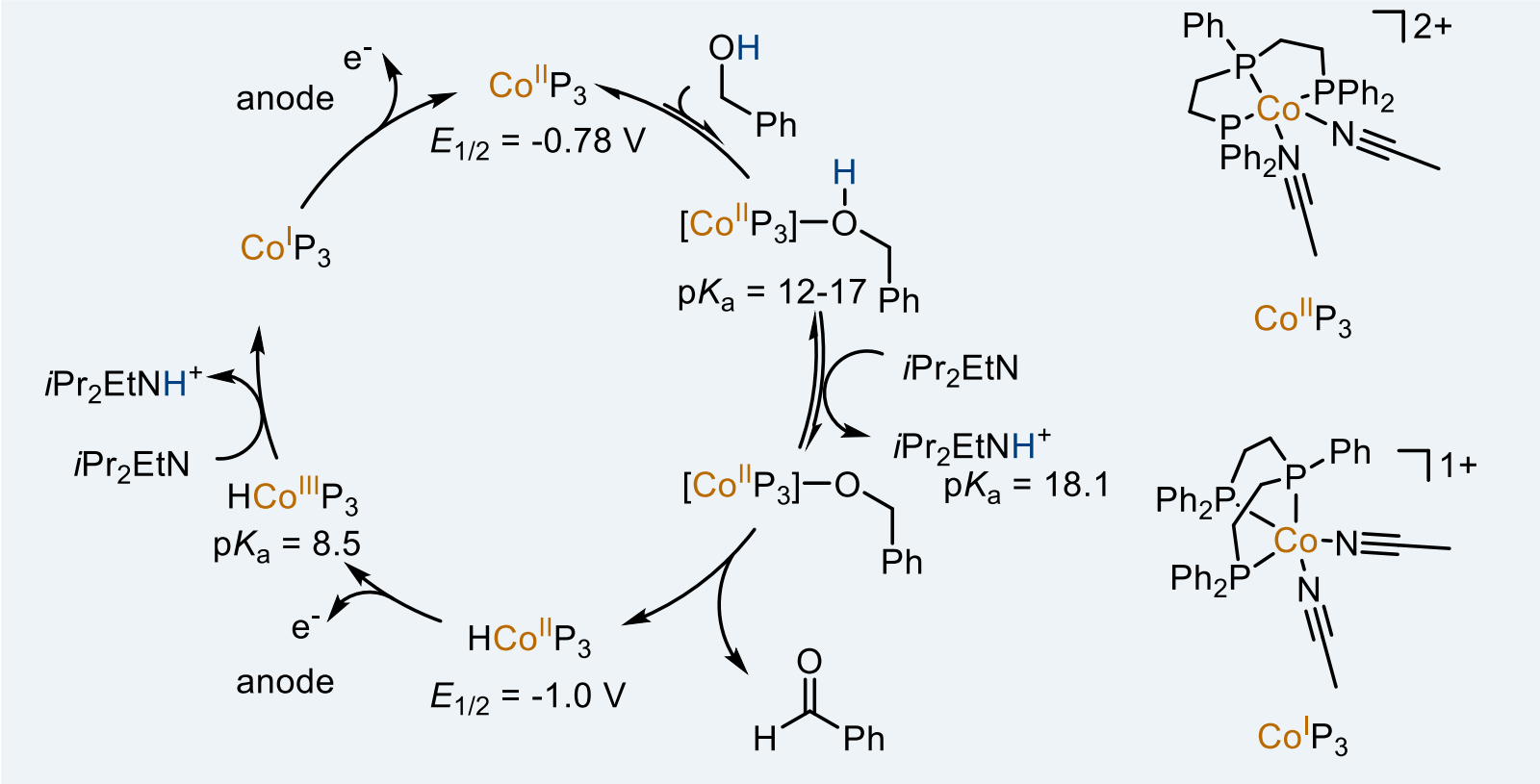



Appel, A. M. *et al. ACS Catal.* **2021**, *11*, 6384.

# 钴参与的电化学脱氢氧化反应

■ *Electrooxidation of $Co^{I}P_3$ to $Co^{II}P_3$ closed the cycle*

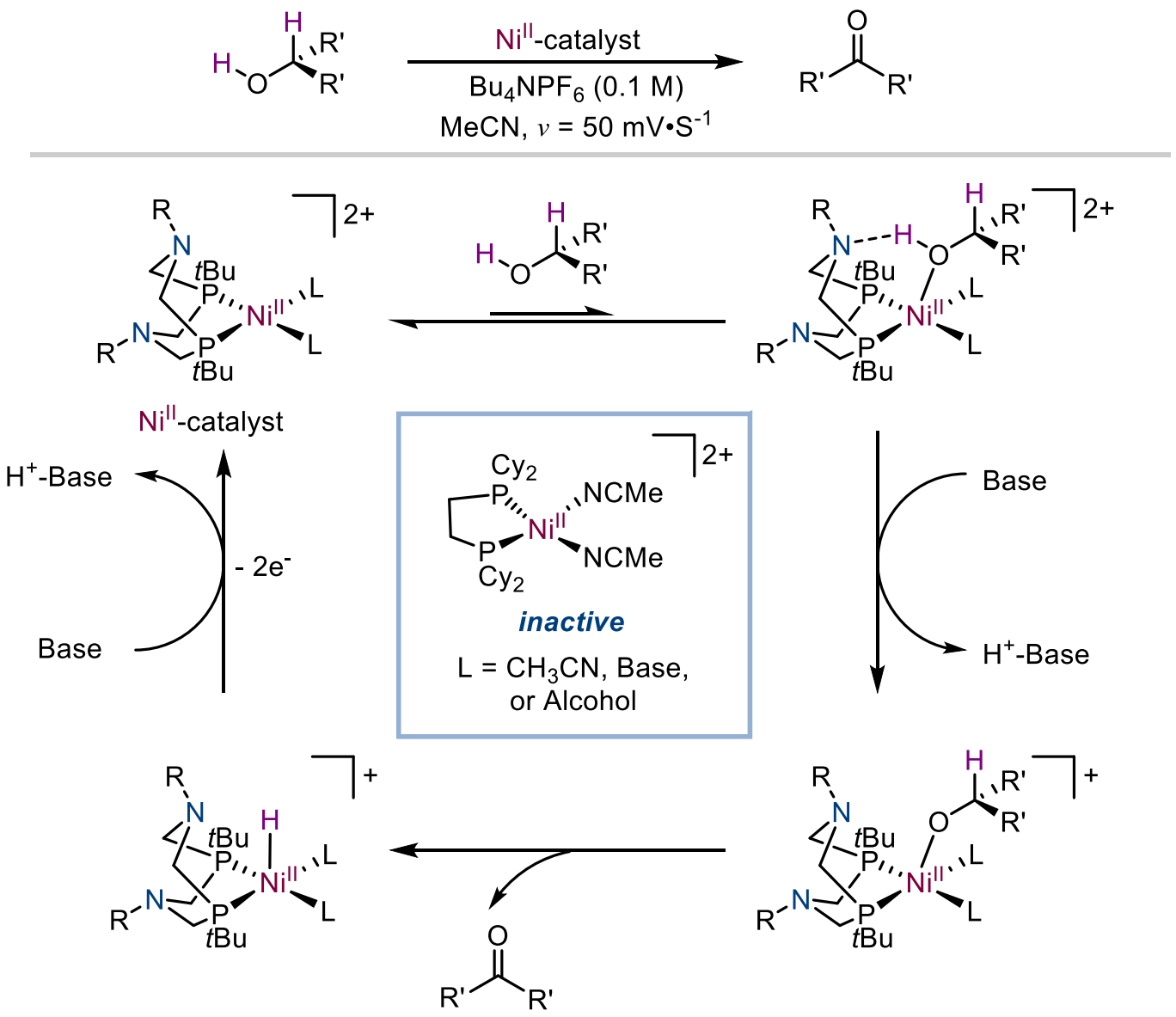




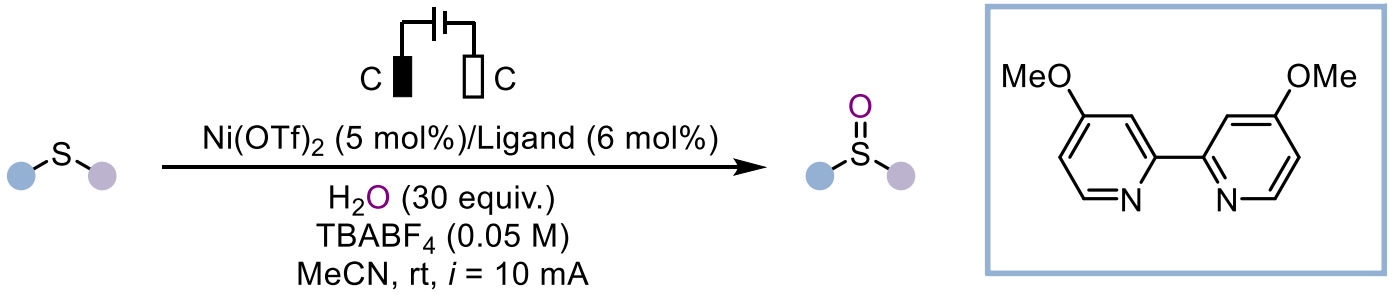

Appel, A. M. *et al. ACS Catal.* **2021**, *11*, 6384.

# 镍参与的电化学氧化反应



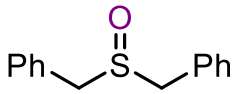

Appel, A. M. *et al. Chem. Commun.* **2015**, *51*, 6172.

# 镍参与的电化学氧化反应

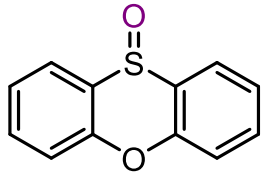




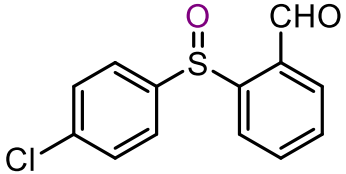




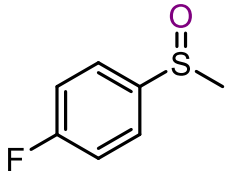

*78% yield*



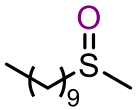

*74% yield*



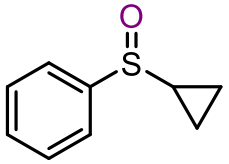

*53% yield*



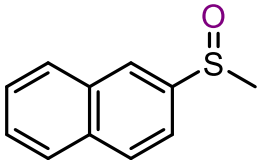

*83% yield*



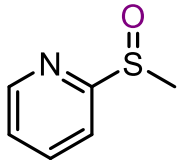

*63% yield*



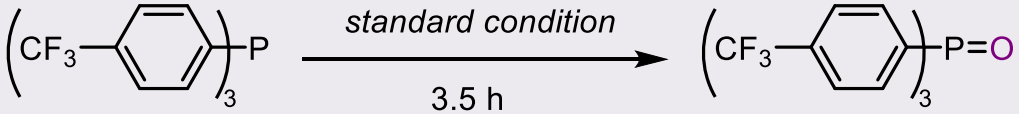

*76% yield*



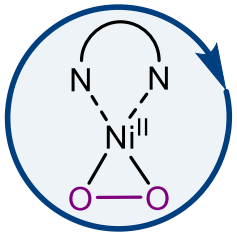

*79% yield*




*79% yield*

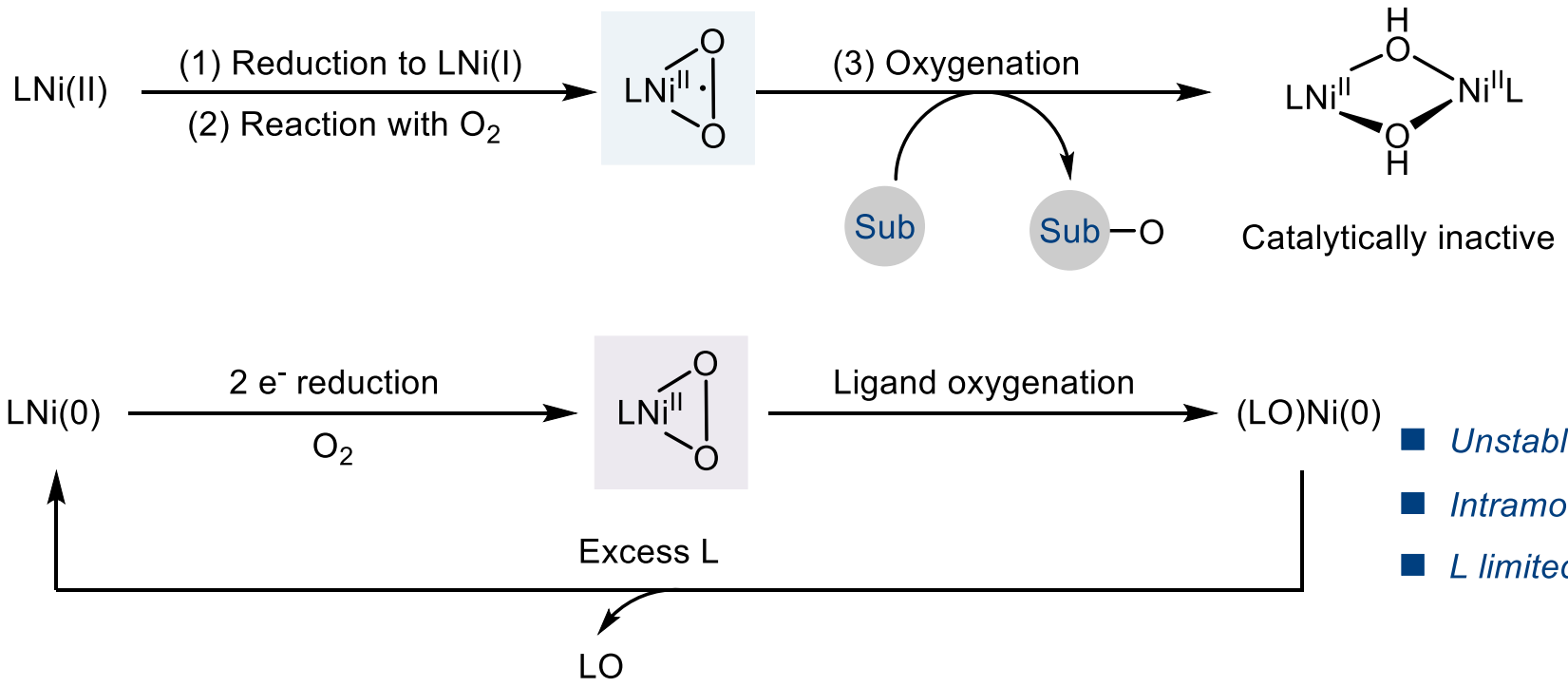



*90% yield*




Jiao, N. *et al. Nat. Catal.* **2021**, *4*, 116.

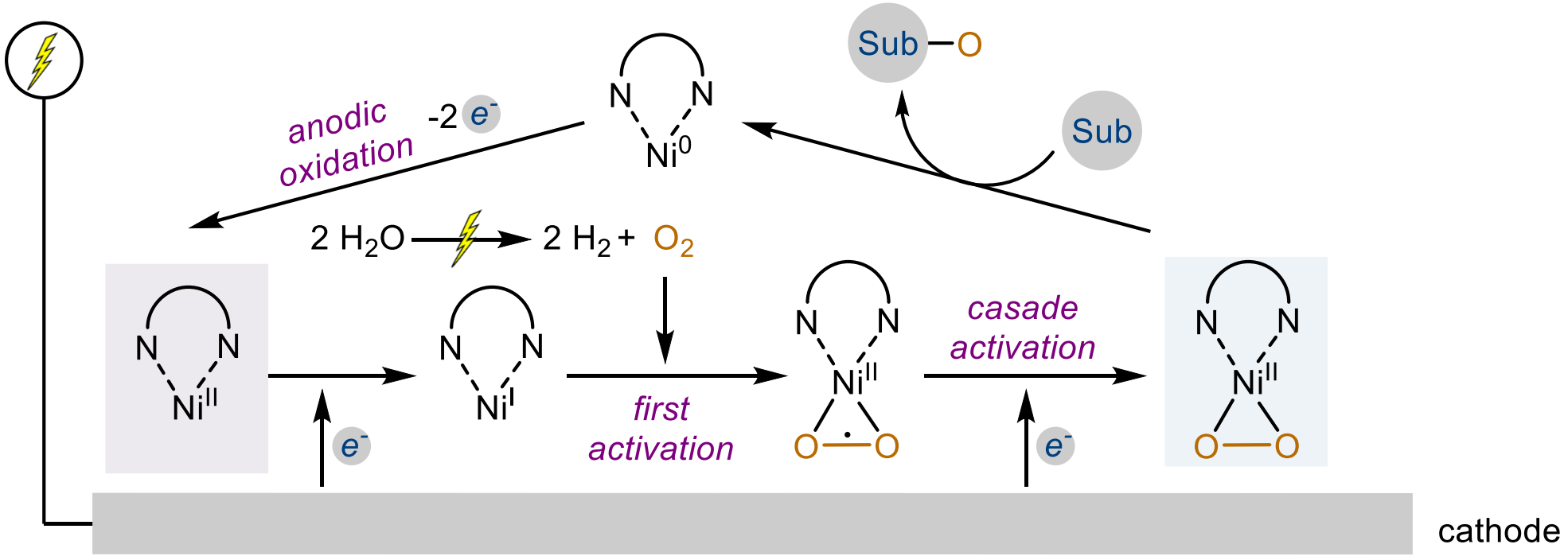
- *Pathways of the generation of Ni(II)-oxo species*




- *Unstable Ni(0) pre-catalyst*
- *Intramolecular oxygenation*
- *L limited to RNC or $PR_3$ ligand*

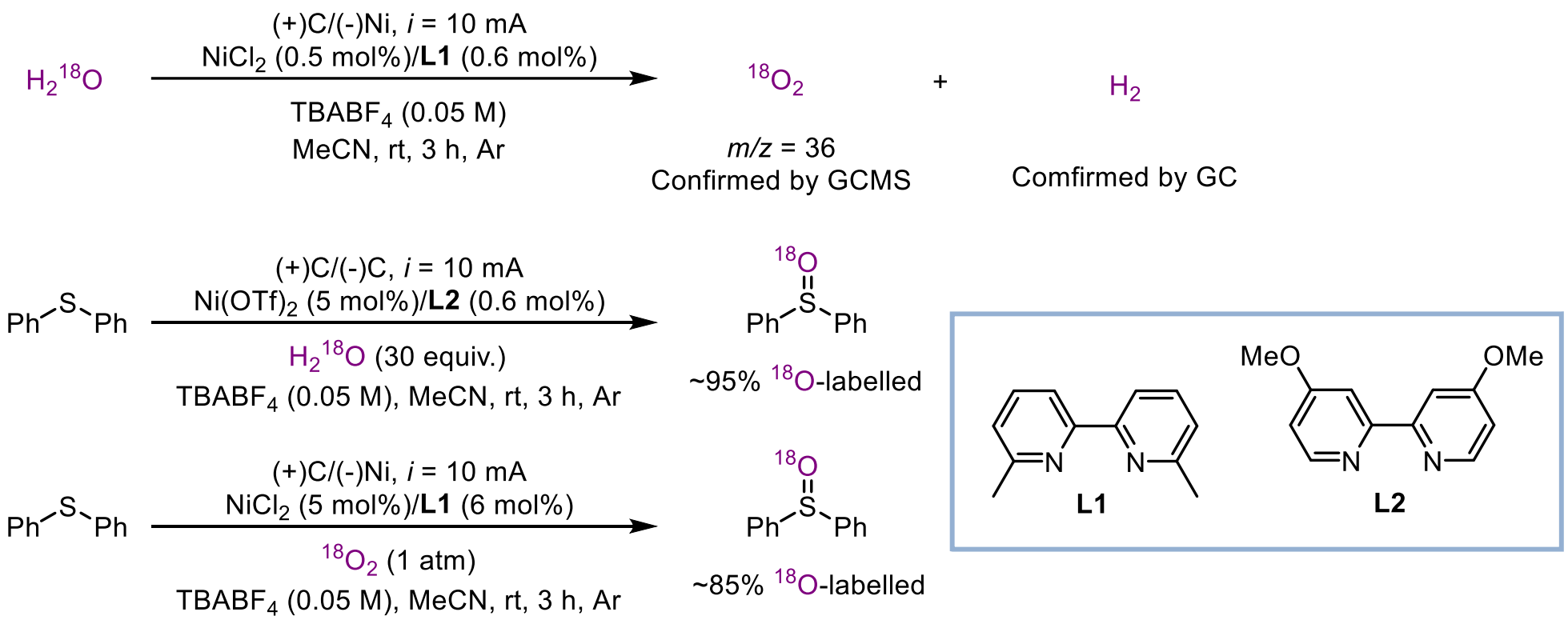
Fujita, K. *et al. Inorg. Chem.* **2004**, *43*, 3324.
Wieghardt, K., Driess, M. A. *et al.* Angew. Chem. Int. Ed. **2008**, *47*, 7110.

■ *Cascade-activation strategy for the electrochemical Ni(ii)-catalyzed oxygenation*

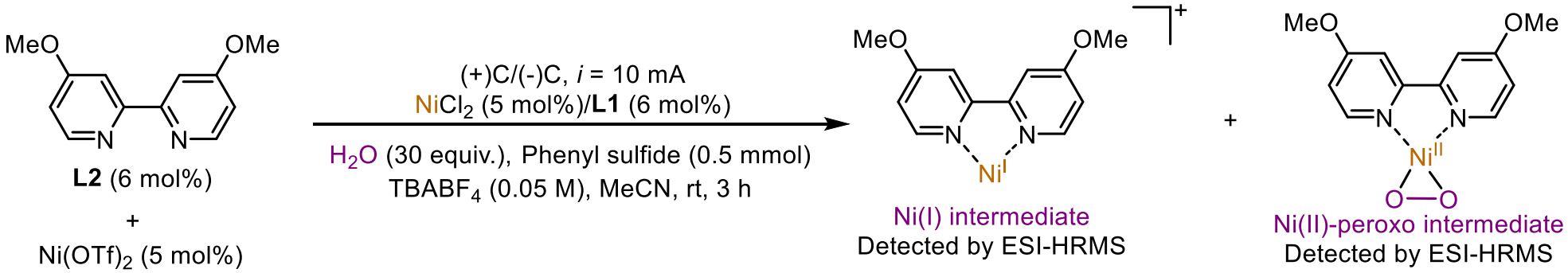


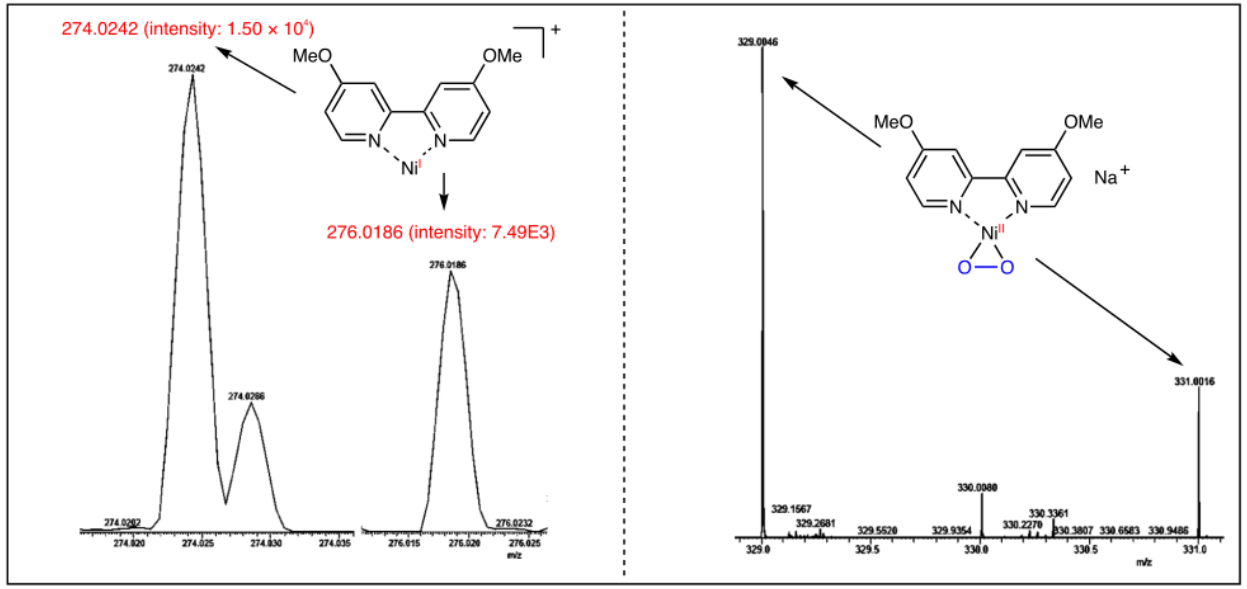

Jiao, N. *et al. Nat. Catal.* **2021**, *4*, 116.

## *Mechanism study of the electrochemical Ni(ii)-catalyzed oxygenation*

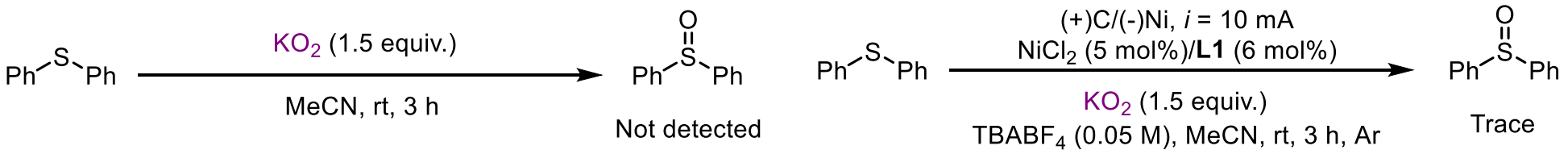


# 镍参与的电化学氧化反应机理研究




■ Exclude the pathway of $O_2^{\cdot-}$ generated via cathodic reduction



■背景介绍

■第八族金属参与的电氧化反应

■其他地壳丰产金属参与的电氧化反应

■总结与展望

Cu

*electron configuration: $3d^{10}4s^{1}$*
*range of oxidation state: 0 to +4*

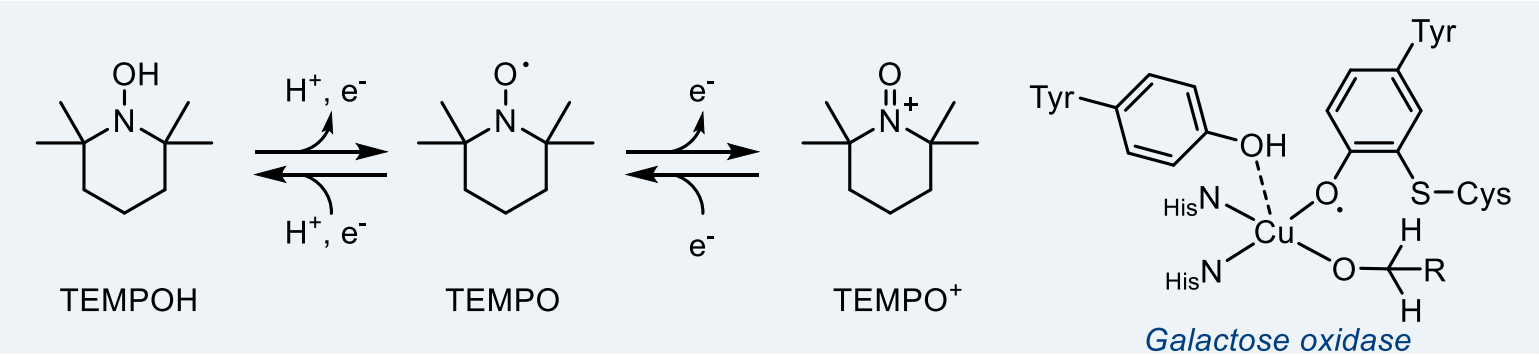
Mn

*electron configuration: $3d^{5}4s^{2}$*
*range of oxidation state: 0 to +7*

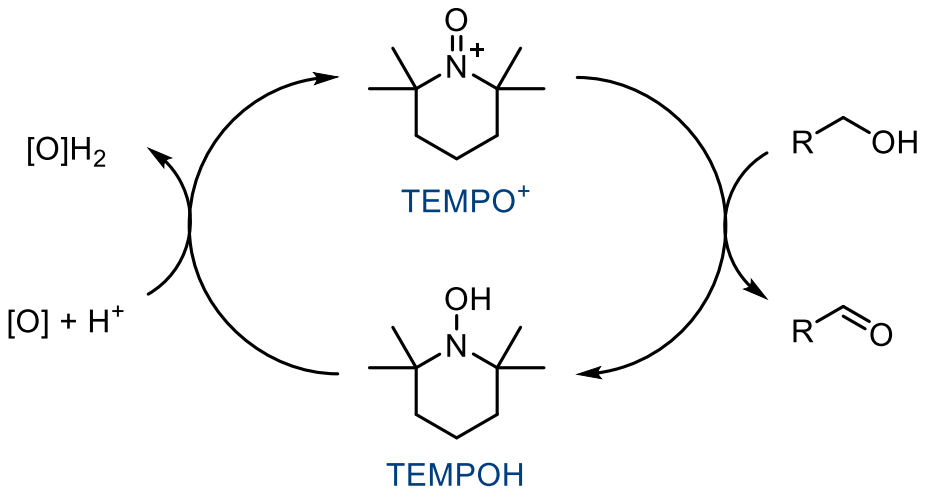
V

*electron configuration: $3d^{3}4s^{2}$*
*range of oxidation state: 0 to +5*

# 铜参与的电化学氧化反应

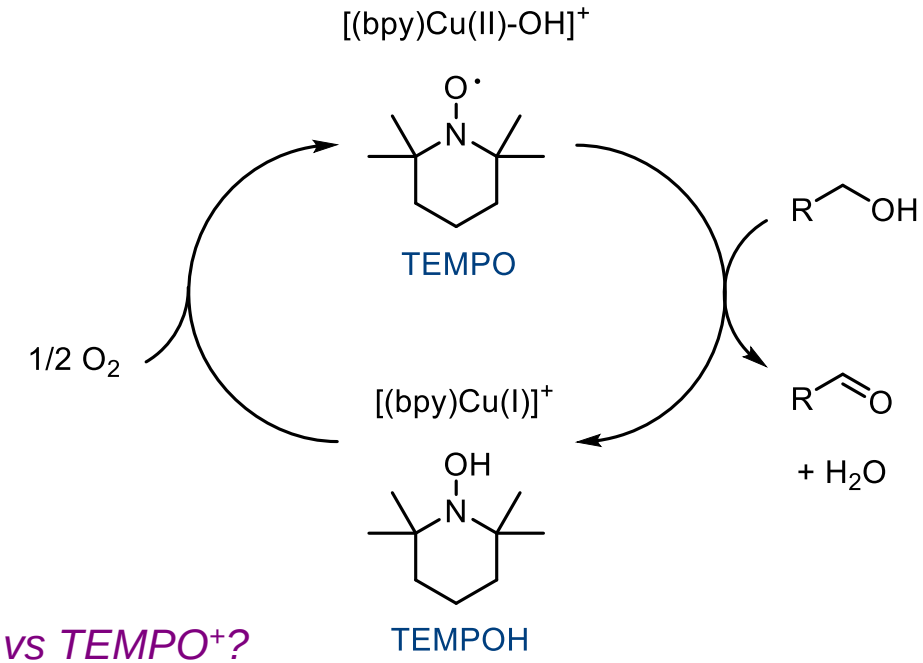



**TEMPO-only: 2-electron pathway**




[O] = NaOCl, $Br_2$, $PhI(OAc)_2$, catalyst $NO_x/O_z$, **electrode**

**Cu/TEMPO: 2 × 1-electron pathway**



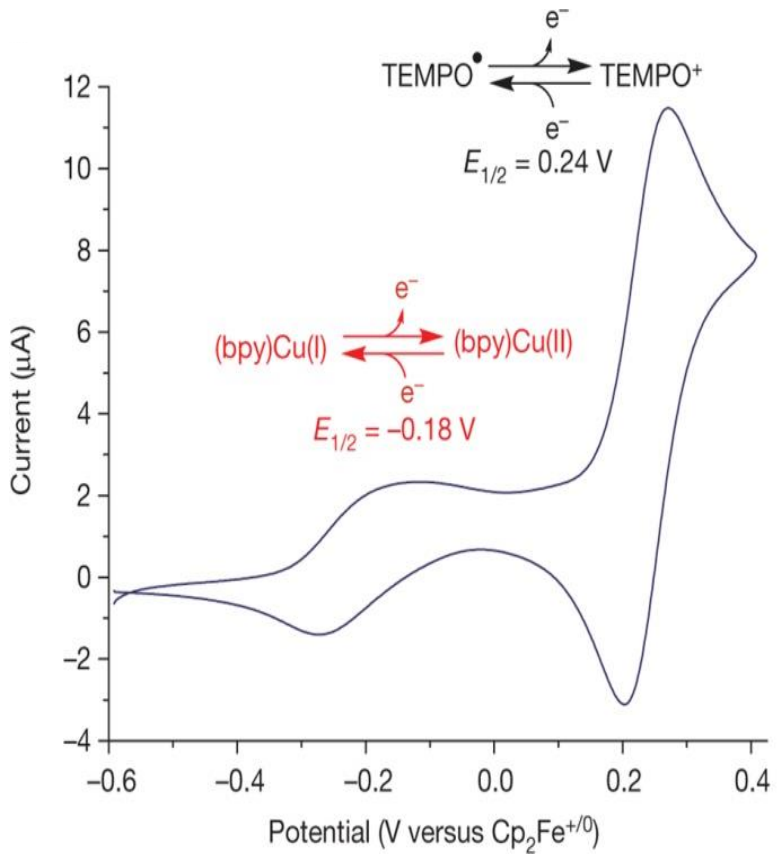

*Generate TEMPO• at much lower electrode potentials vs TEMPO⁺?*

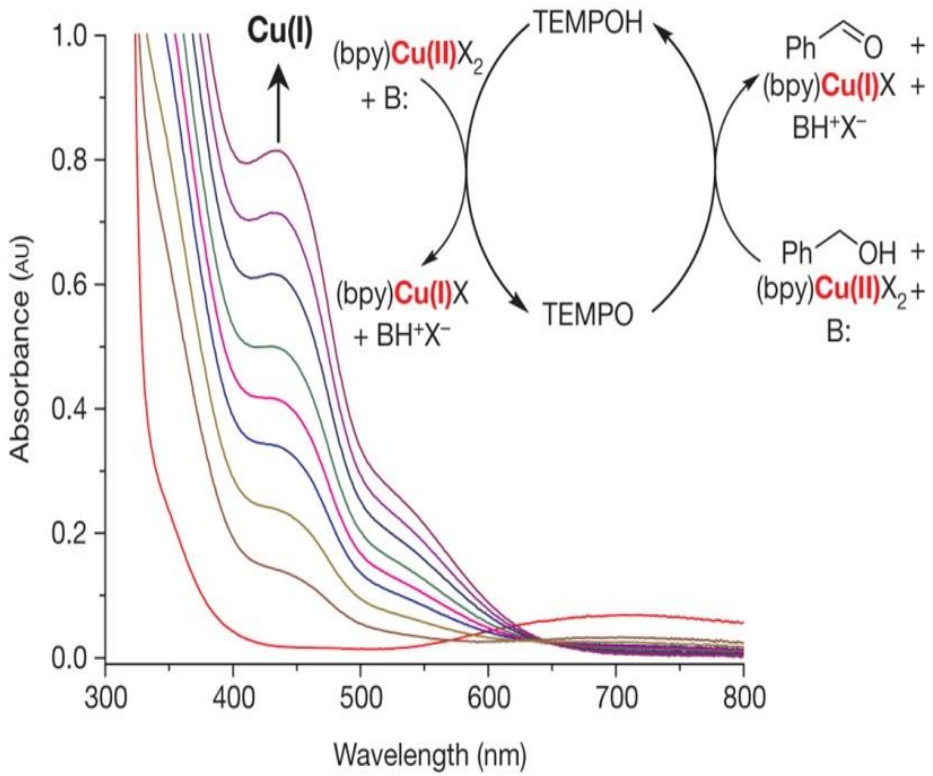

Stahl, S. S. *et al. Nature* **2016**, *535,* 406.
Ryland, B. L., Stahl, S. S. *Angew. Chem. Int. Ed.* **2014**, *53*, 8824.
Ma S. *et al. Org. Chem. Front*. **2019**, 6, 3101.

# 铜参与的电化学氧化反应机理研究

- bpy + Cu(I)(OTf) + TEMPO

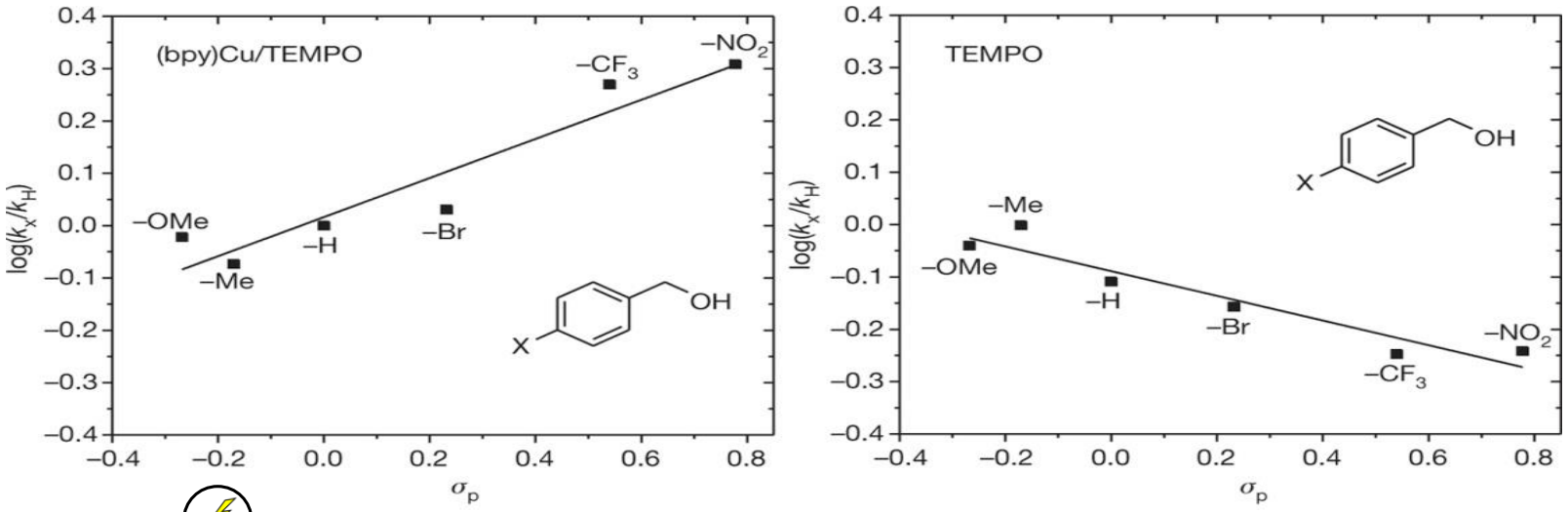
- Cu(II)$(OTf)_2$ + bpy + TEMPOH + 2,6-lutidine ⟶ bpyCu(I)(OTf) + TEMPO
- Cu(II)$(OTf)_2$ + bpy + TEMPO + 2,6-lutidine + BnOH ⟶ bpyCu(I)(OTf) + PhCHO

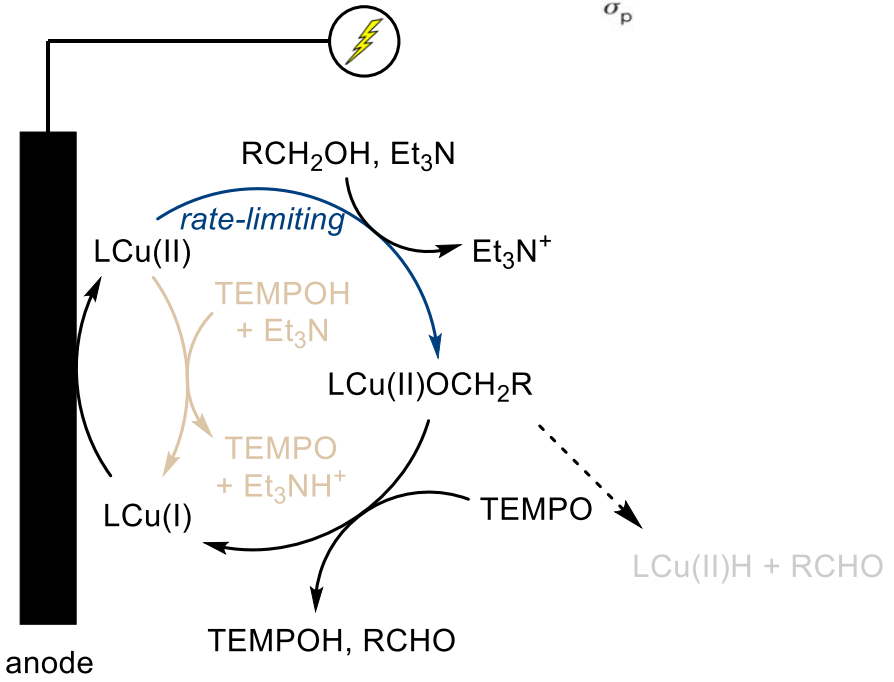


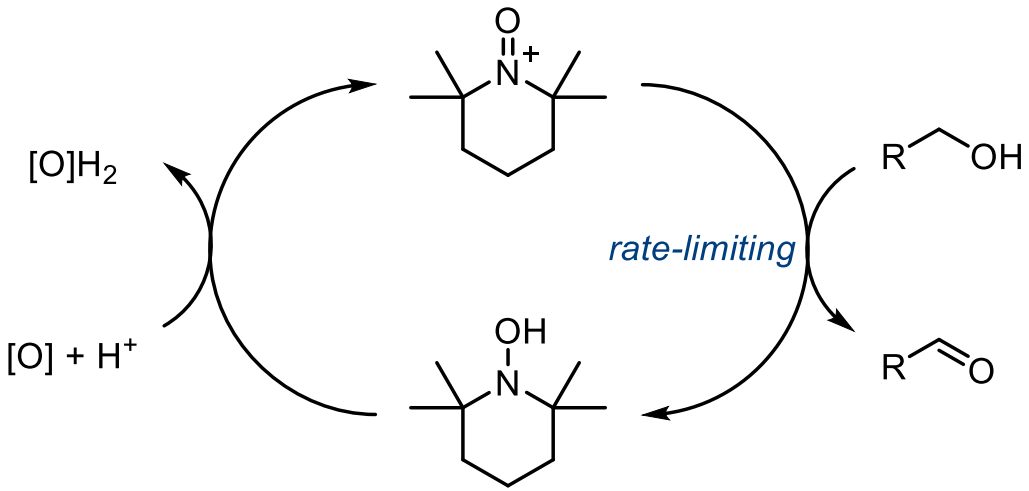




- *No TEMPO/TEMPOH redox feature in the lack of [H+] source*
- *Cu(II) promoted the oxidation of BnOH and TEMPOH in the basic condition*

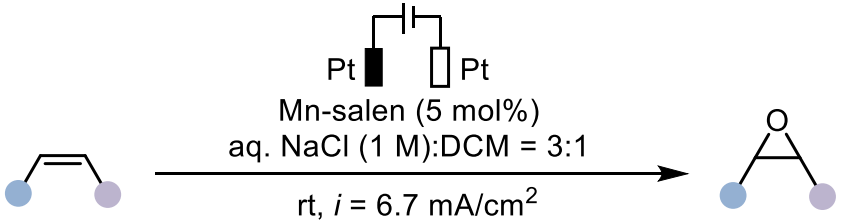
# 铜参与的电化学氧化反应机理研究



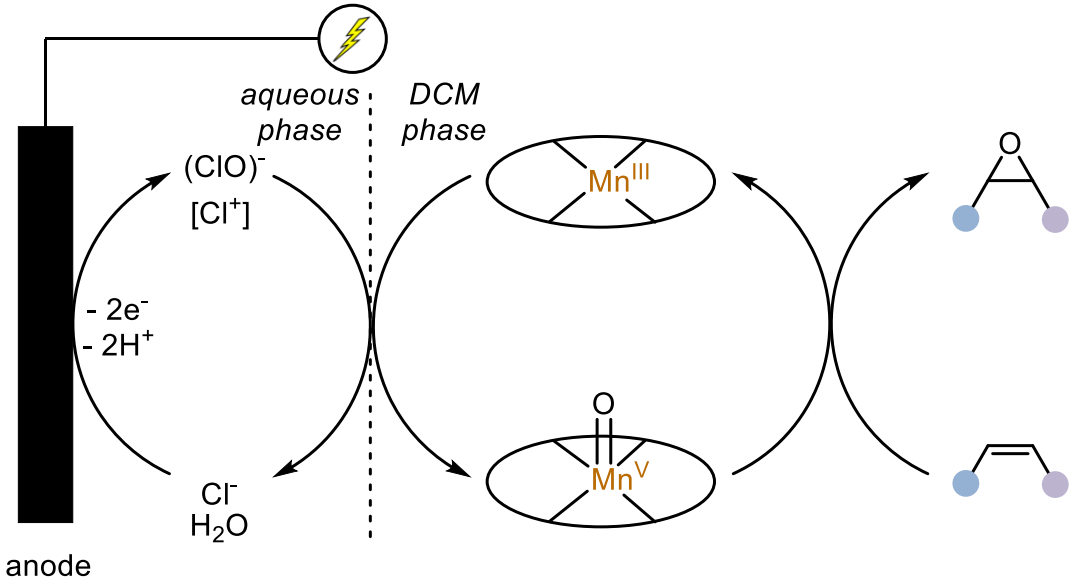



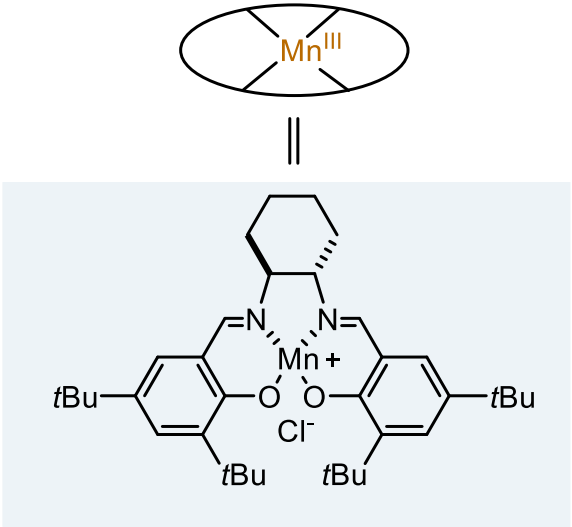
# 锰参与的电化学氧化反应





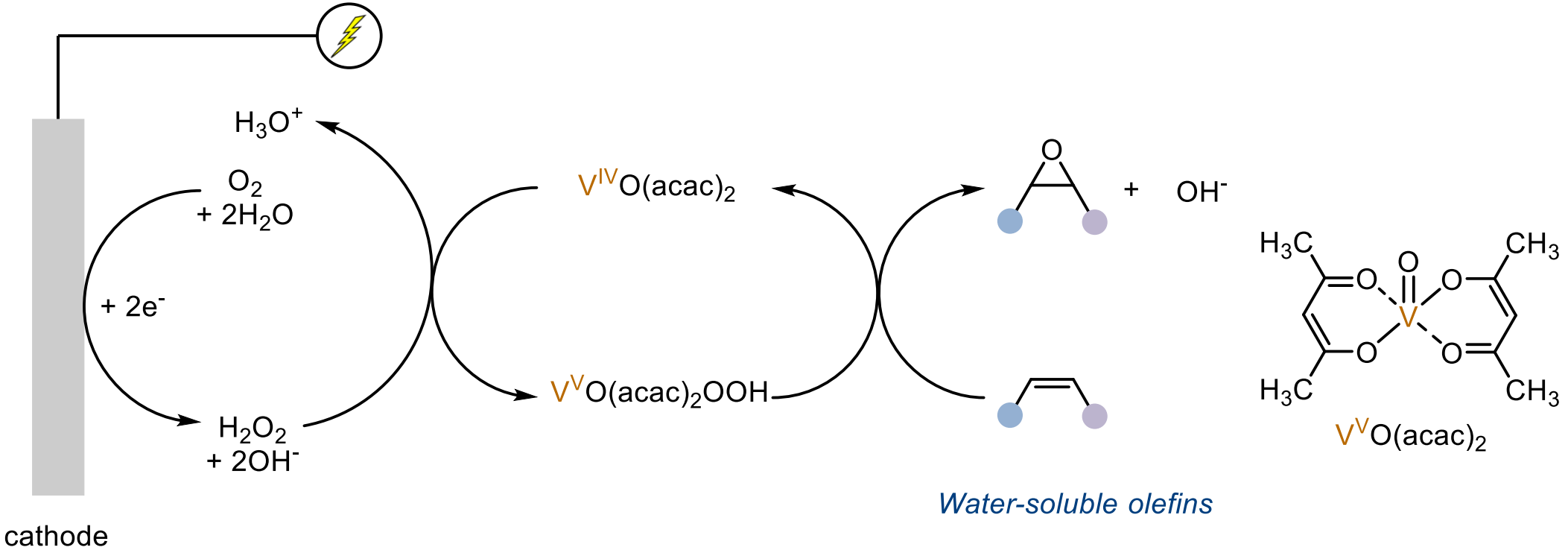
*93% yield, 87% ee* *69% yield, 43% ee* *80% yield, 81% ee* *30% yield, 26% ee*




Tanaka, H. *et al. J. Electroanal. Chem.* **2001**, *507*, 75.

# 钒参与的电化学氧化反应




Atobe, M. *et al. Electrochim. Acta* **2003,** *48,* 1041.

■背景介绍

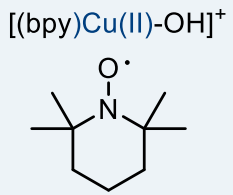
■第八族金属参与的电氧化反应

■其他地壳丰产金属参与的电氧化反应

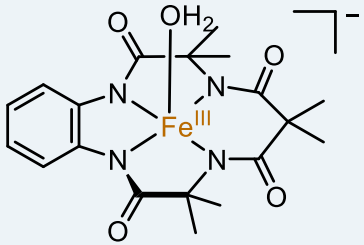
■总结与展望

# 总 结

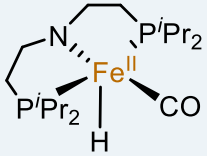
***Oxidation of alcohol***



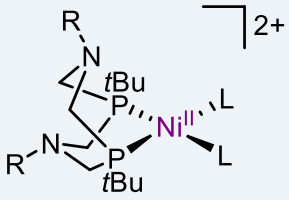

Stahl, **2016**



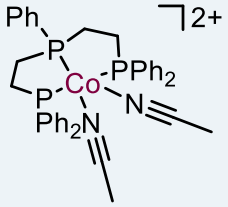
Stahl, **2019**
*oxidation of activated C-H*



Waymouth, **2019**

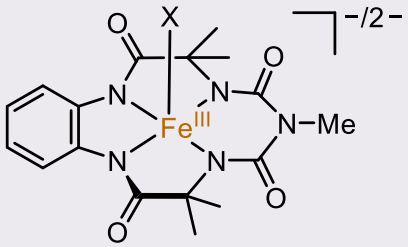


Appel, **2015**

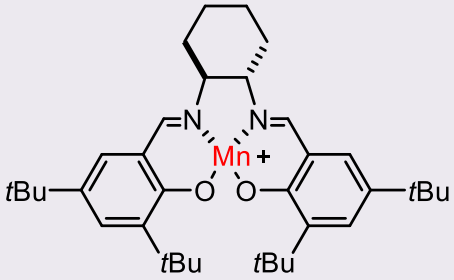


Appel, **2021**

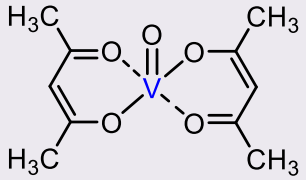
***Epoxidation of olefins***



Gupta, **2020**

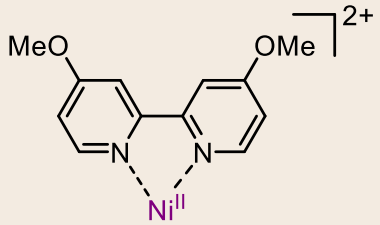


Tanaka, **2000**



Atobe, **2002**

***S/P-oxidation***

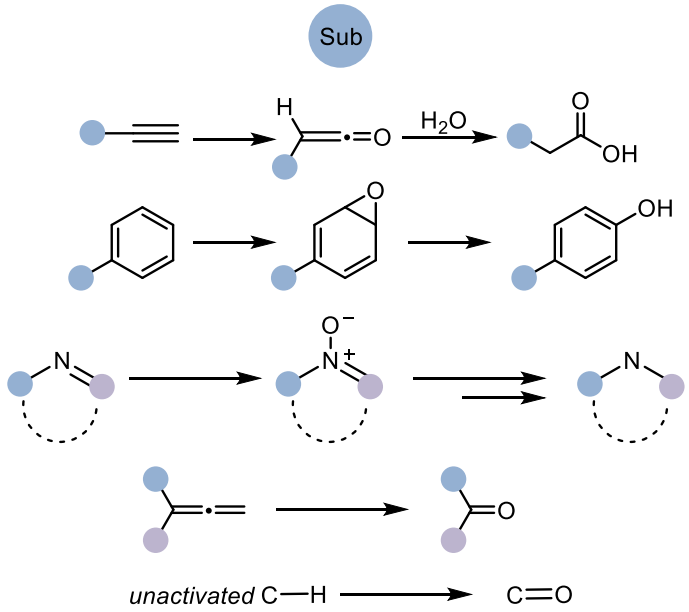


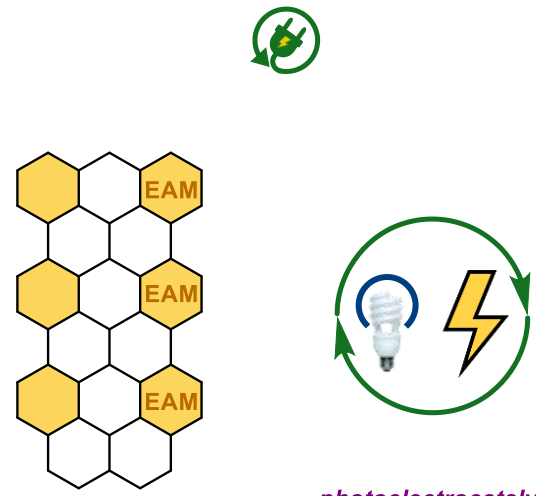
Ning Jiao, **2021**

■ ***Obstacle remain:***

1. ***High-valent metal complexs are unstable in a relatively high potential***
2. ***Reaction pattern is still relatively single***
3. ***Rare examples of enantioselective transformation***

# 展 望

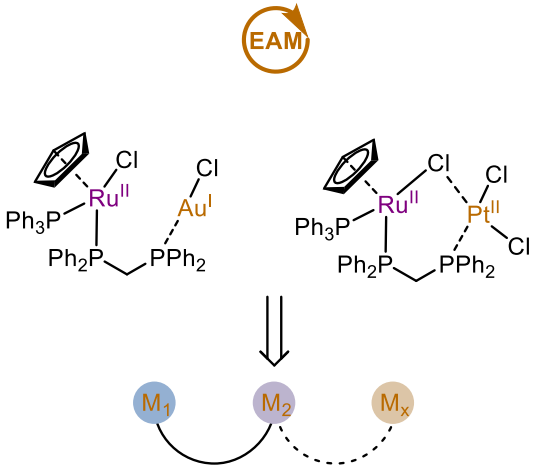




*modified electrode*

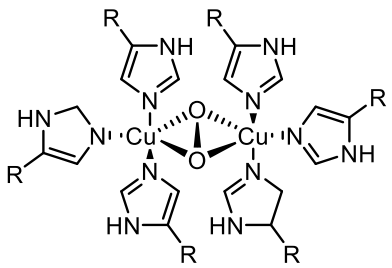


*photoelectrocatalysis*
*lower potential*
*better selectvity*




*$M_1$, $M_2$, $M_x$ = EAMs*
*Bi/multimetallic complex*

***Key: Ligand design***




***Hemocyanin***

***Biomimetic catalysis***

# 谢谢大家

# 恳请各位老师同学批评指正