

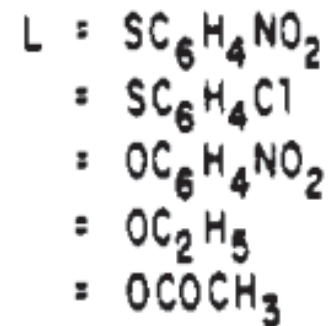
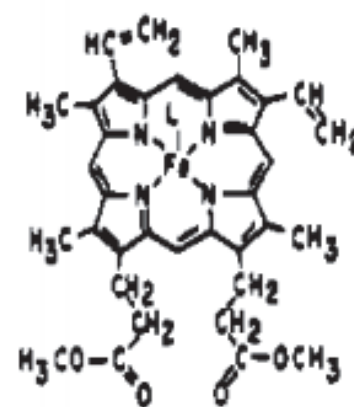
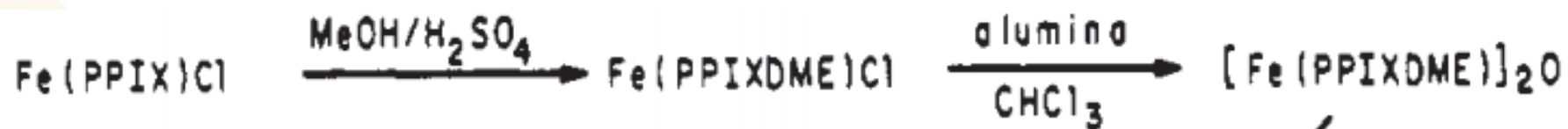
## Topic

# 具有自由基性质的Fe-O/S配合物

李连杰

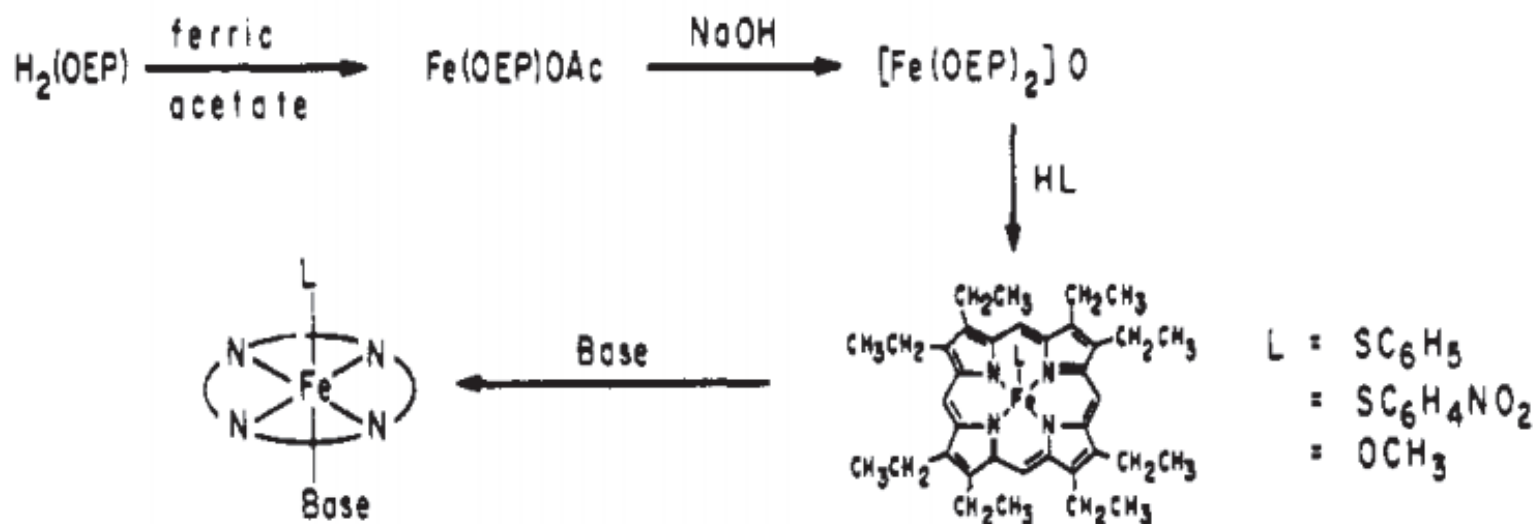
2024.03.22

# Fe-S 配合物



Holm, R. H. *J. Am. Chem. Soc.* 1976, 98, 2414–2434.

# Fe-S配合物



**Figure 1.** Synthetic scheme for the preparation of iron(III) PPIXDME and OEP complexes. The indicated five-coordinate complexes were isolated; six-coordinate base adducts were generated in situ and were not isolated.

Holm, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 2414–2434.

# Fe-S配合物

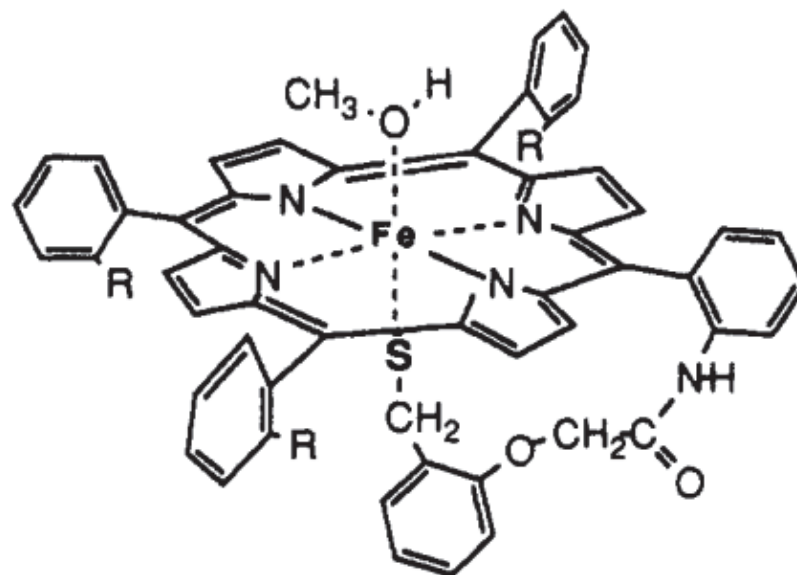


$\text{Fe}(\text{TPP})\text{Cl} (-0.20\text{V}) > \text{Fe}(\text{PPIXDME})\text{Cl} (-0.31\text{V}) > \text{Fe}(\text{OEP})\text{Cl} (-0.39\text{V})$

- Fe-S配合物在氧气中极不稳定，极易被氧化。
- Fe-S配合物的P卟啉配体为OEP的稳定性要大于TPP。
- 烷基硫键稳定性小于芳基硫键。

Holm, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 2414–2434.

# Fe-S配合物

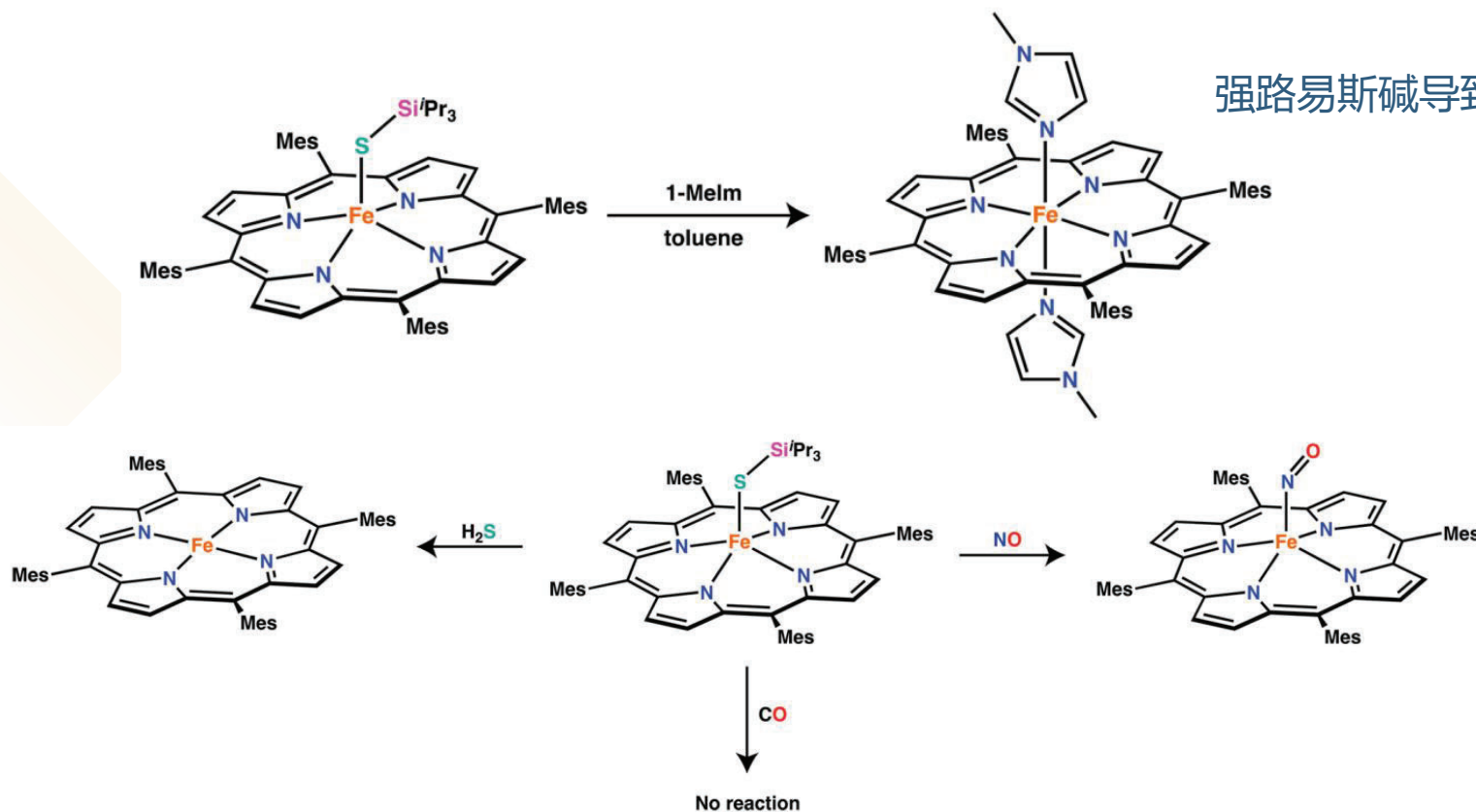


**Figure 1. Complex 1: R = NHCOC(CH<sub>3</sub>)<sub>3</sub>.**

在卟啉分子的RS配位面上引入大基团，能够高度稳定并防止氧化，在0°C空气下保存数月，并可在空气下进行柱层析。第一个由烷基硫配位的可分离的铁卟啉的合成。

Hirobe, M. *J. Am. Chem. Soc.* **1990**, *112*, 7051–7053.

# Fe-S配合物



大位阻的卟啉配体会让Fe-S配合物在空气下更稳定。

Tonzetich, Z. *J. Inorg. Chem.* **2013**, *52*, 12468–12476.

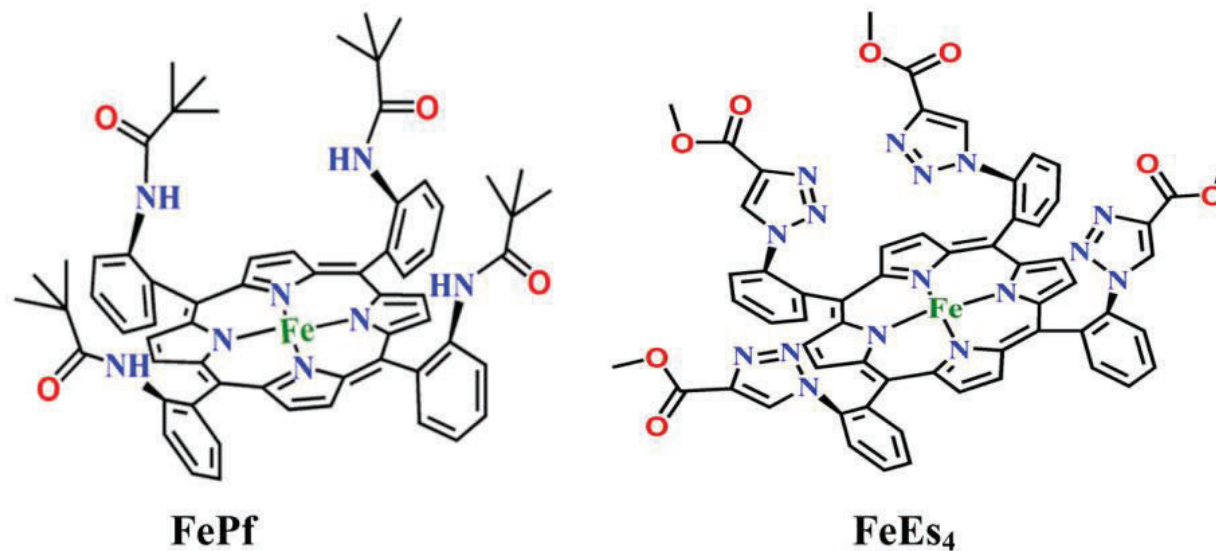


Figure 1. Models investigated in this manuscript.

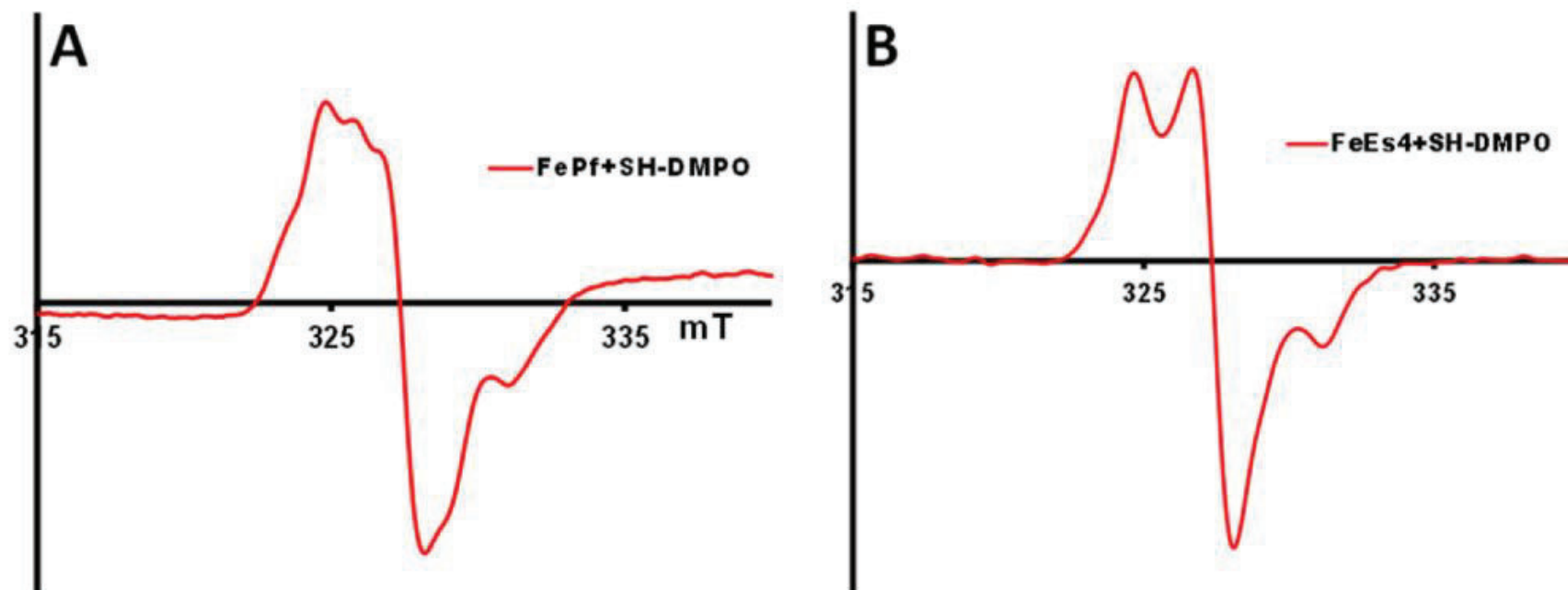


Figure 10. EPR of DMPO adduct of (A) FeEs<sub>4</sub> and (B) FePf. All spectra are recorded at 77 K.

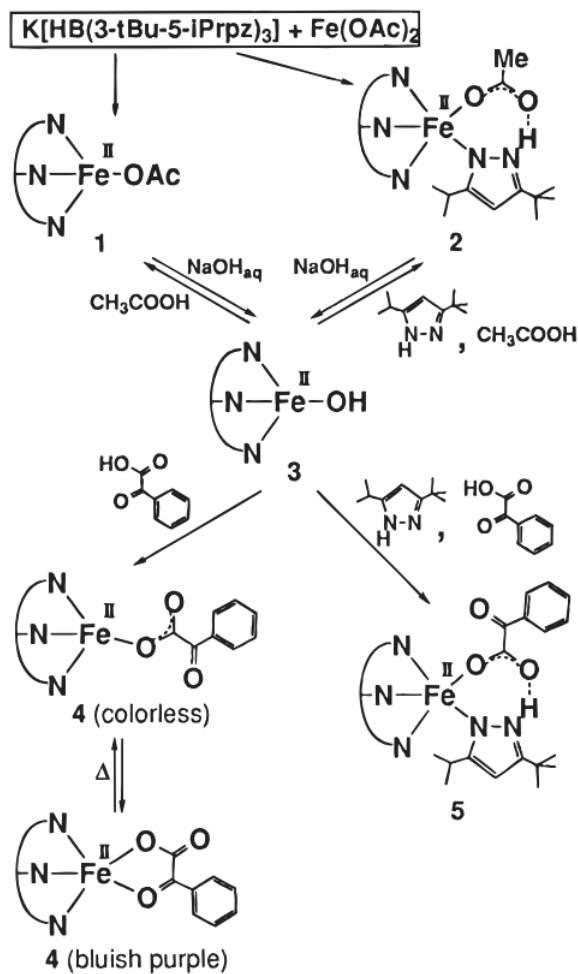
EPR显示了DMPO的巯基加成物的显性各向异性自由基信号。



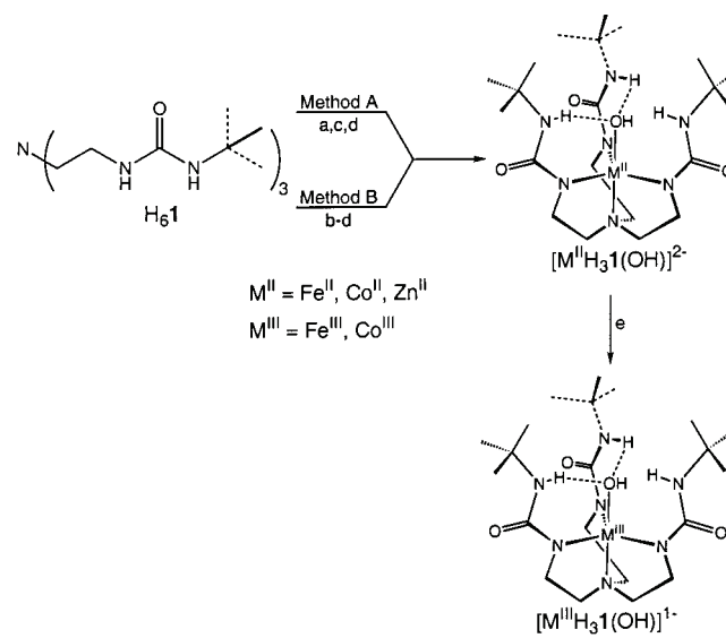
# Fe-O配合物



# Fe-O配合物

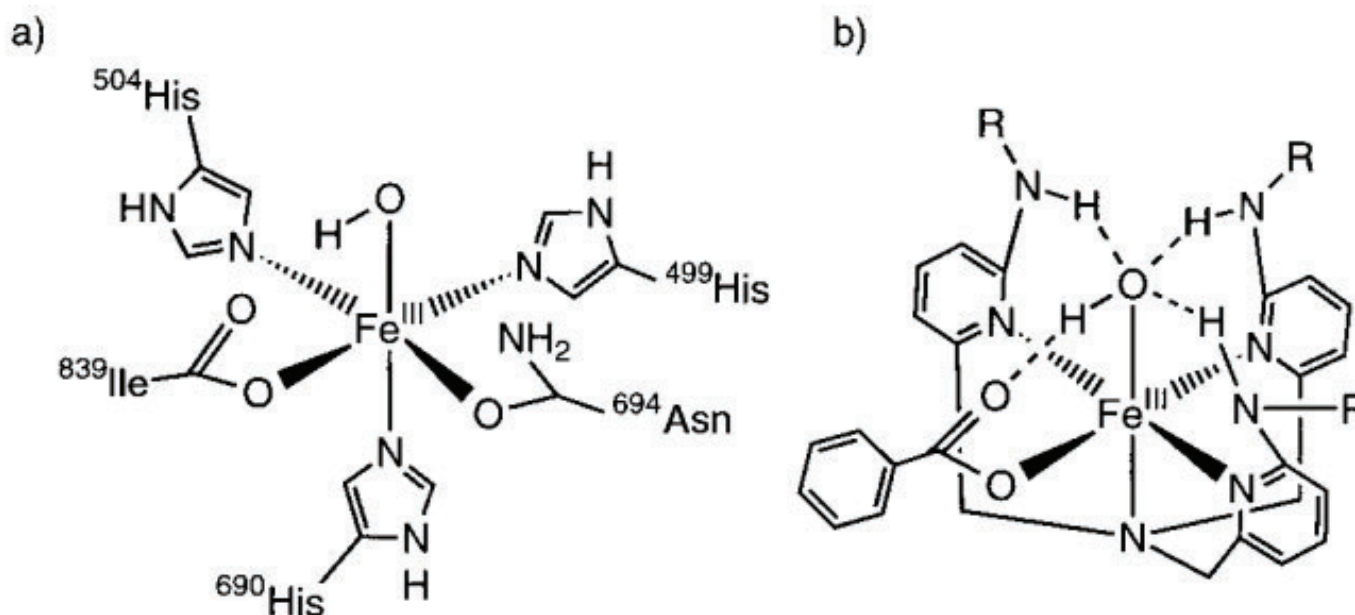


Scheme 1<sup>a</sup>

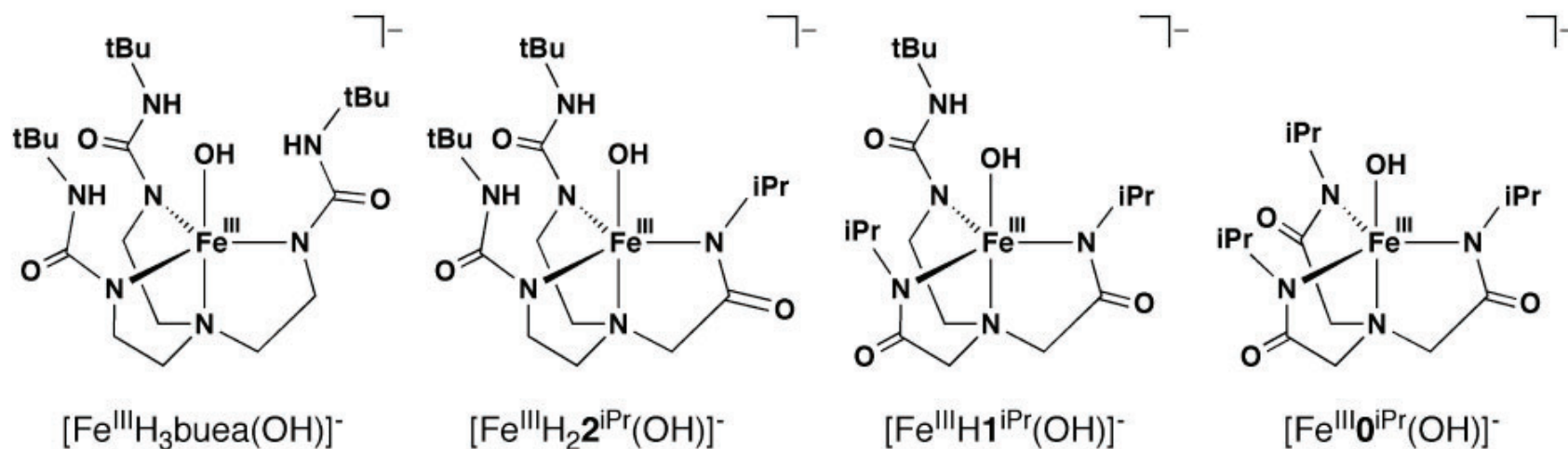


- 体积较大的三(吡唑基)硼酸盐衍生物配体
- 分子内氢键腔来保护Fe-OH键

Moro-oka, Y. *Inorg. Chem.* **1997**, *36*, 4539–4547.  
Borovik, A. S. *Inorg. Chem.* **2001**, *40*, 4733–4741.



Scheme 1. a) A proposed (hydroxo)iron(III) core structure of the active species in the catalytic cycle of soybean lipoxygenase-1. Adapted from ref. [1 a] p. 285. b) The six-coordinate (hydroxo)iron(III) complex **1**. Dashed lines represent intramolecular hydrogen bonds. R = CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>.

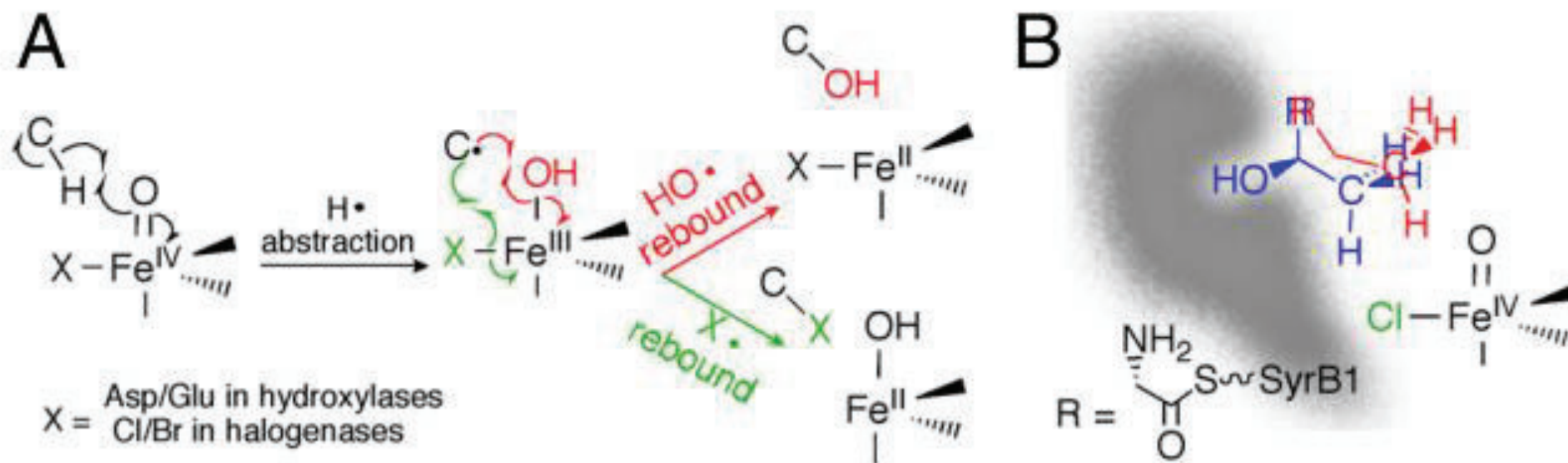


**Figure 1.**  $\text{Fe}^{\text{III}}\text{OH}$  complexes with varied H-bond networks used in this study.

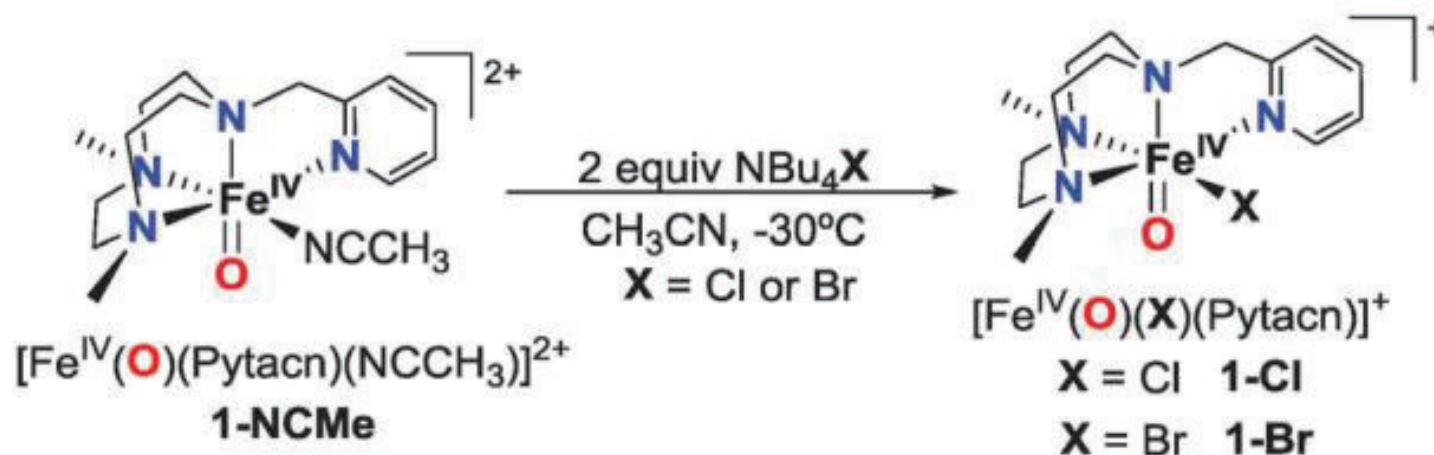
分子内氢键越多，Fe-O键越长。

Borovik, A. S. *Inorg. Chem.* **2008**, *47*, 5780–5786.

# Fe-O配合物



Bollinger, J. M. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 17723–17728.

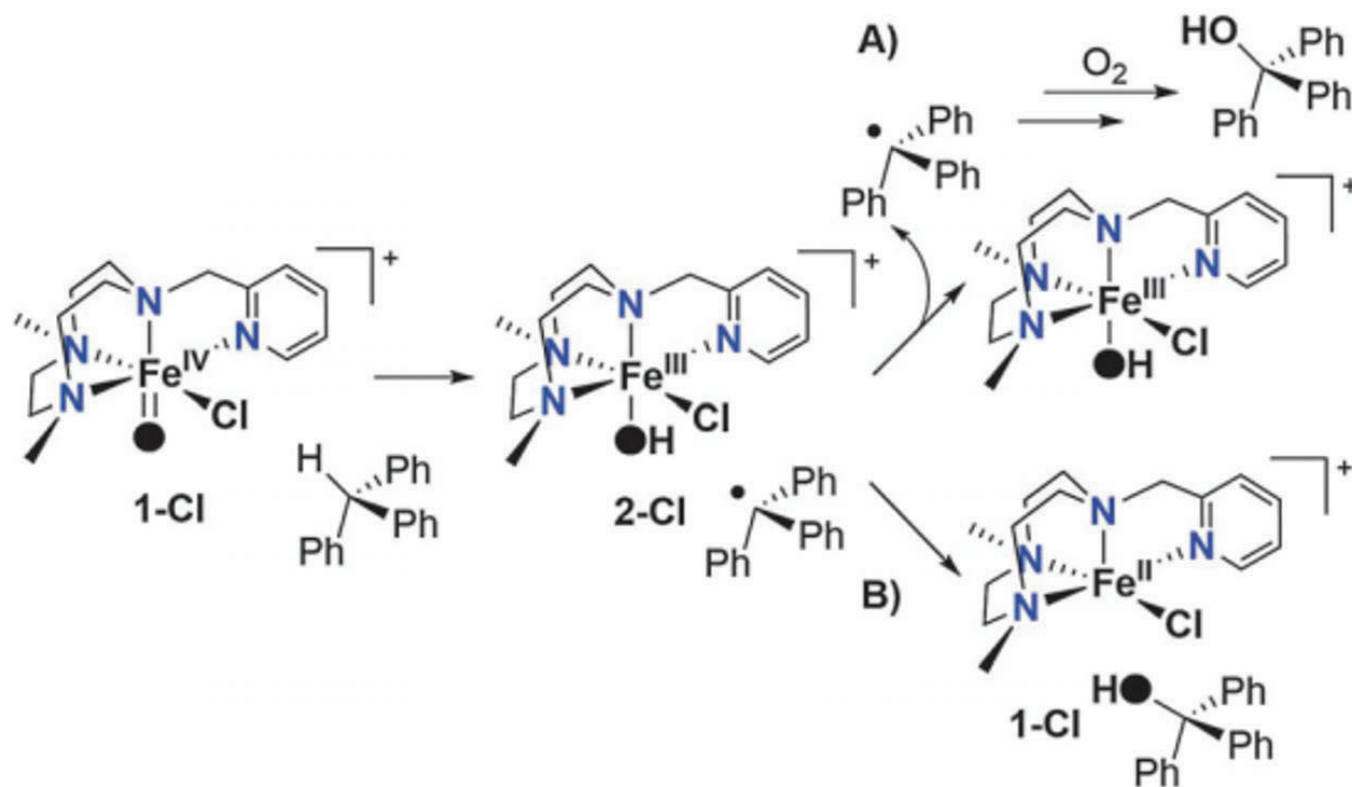


Scheme 1 Preparation of **1-Cl** and **1-Br** from **1-NCMe**.

首次报道这些配合物参与生物相关氧原子转移反应能力的反应性。

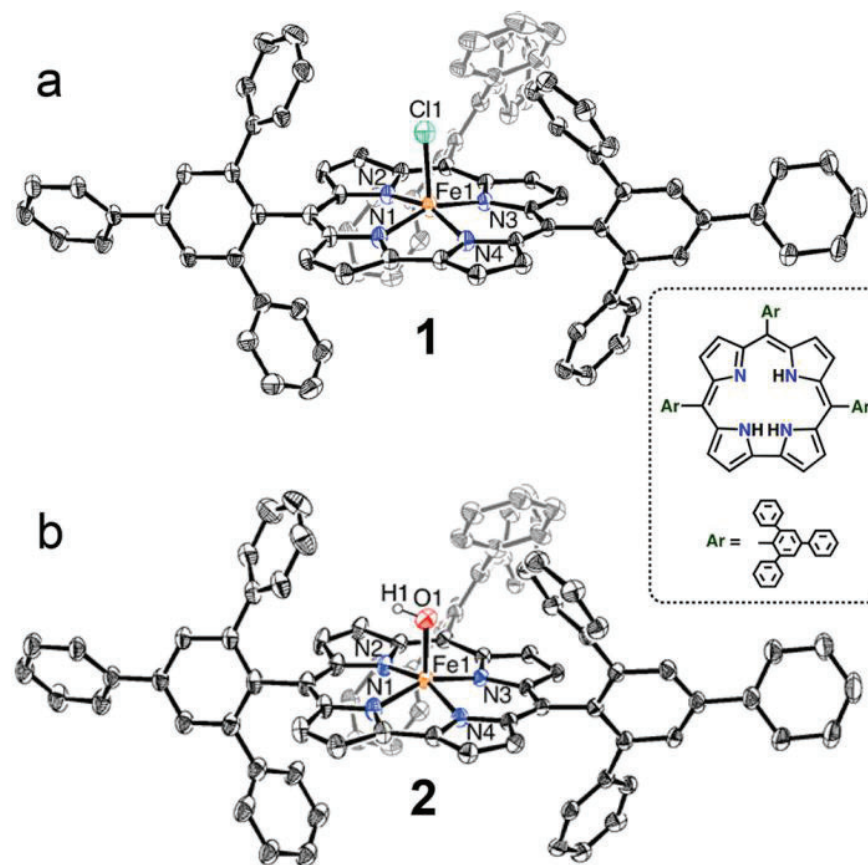
Costas, M. *Chem. Commun.* **2014**, 50, 10887–10890.

# Fe-O配合物



Costas, M. *Chem. Commun.* **2014**, *50*, 10887–10890.

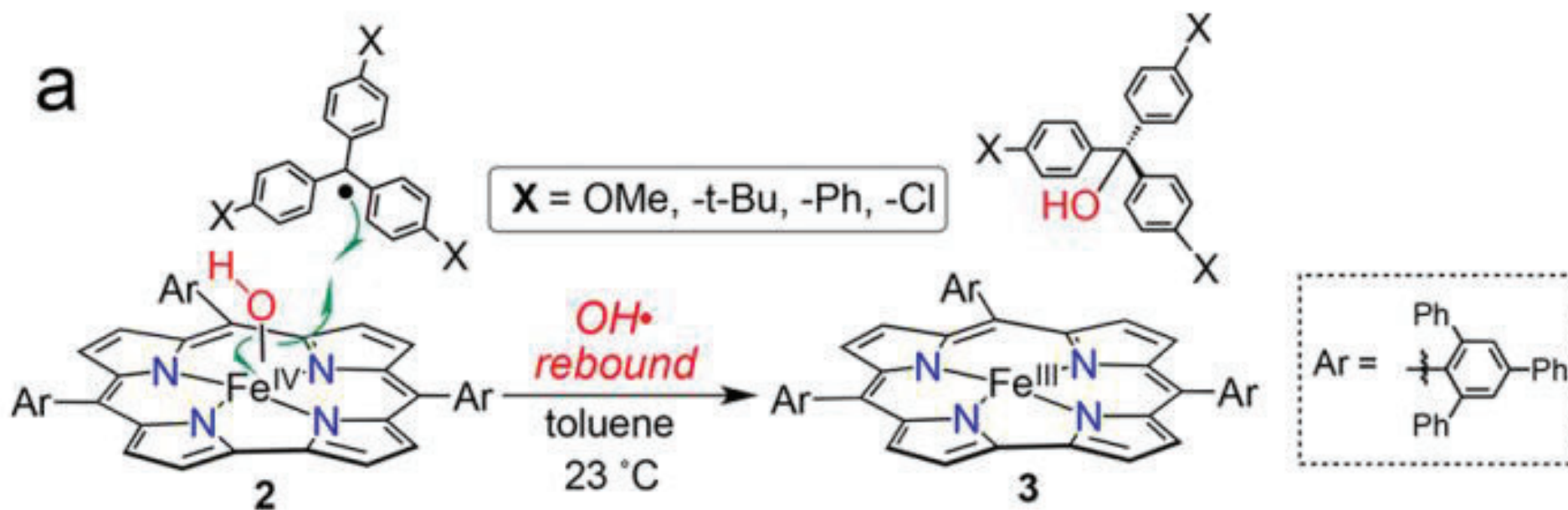
# Fe-O配合物

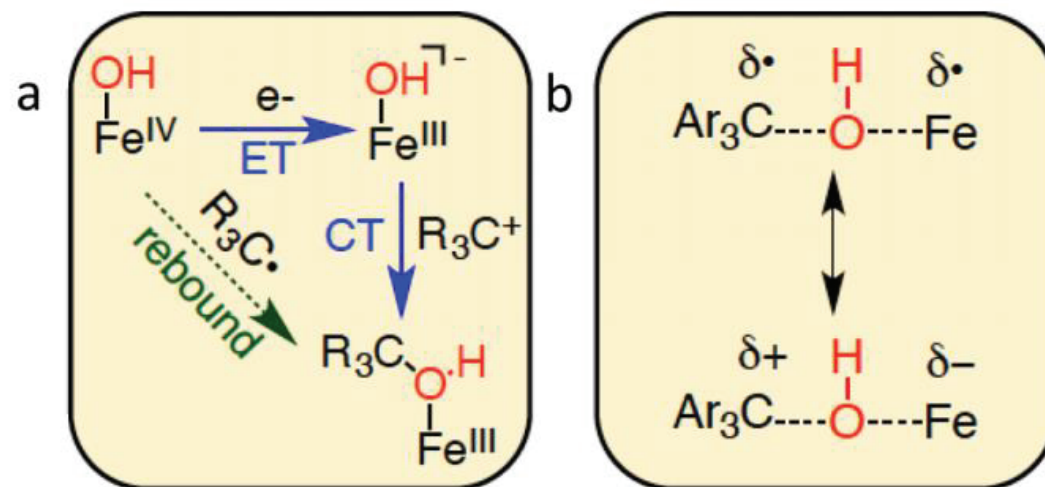
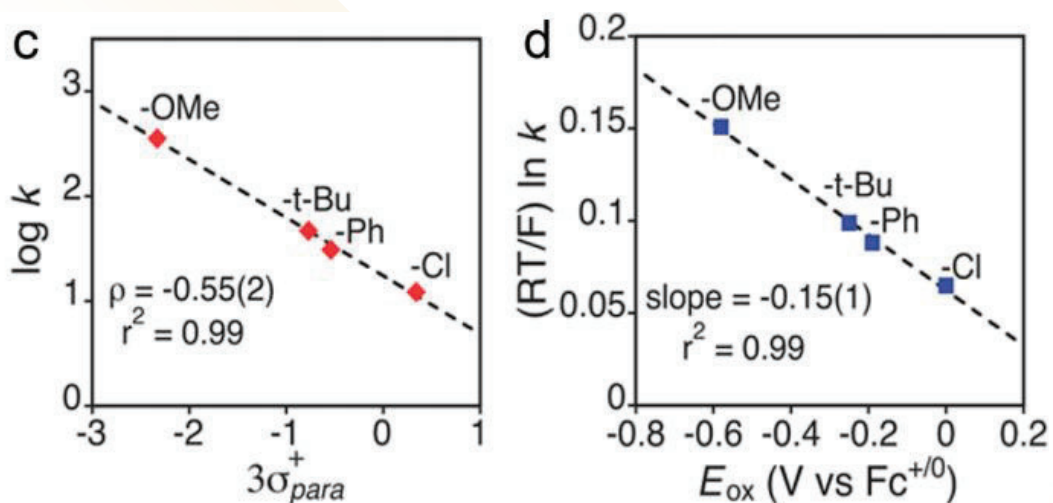


Goldberg, D. P. *J. Am. Chem. Soc.* **2017**, *139*, 13640–13643.



# Fe-O配合物

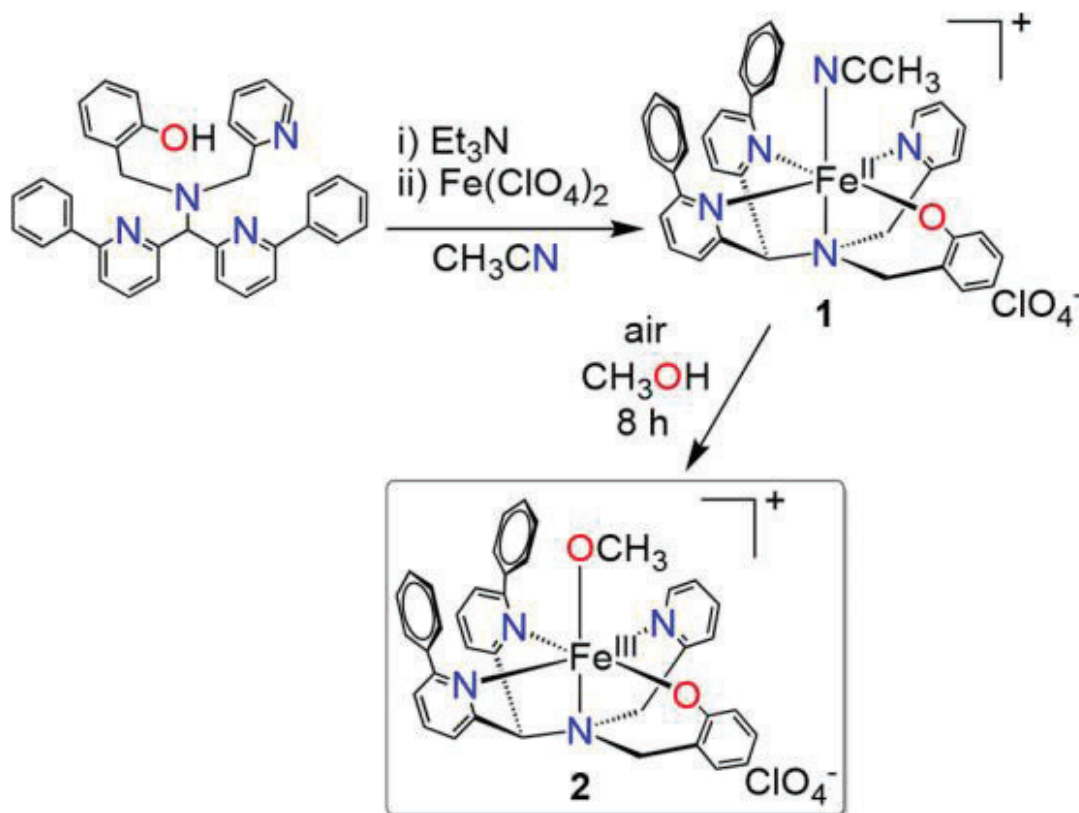




**Figure 3.** (a) Scheme depicting concerted and separated ET/CT steps for radical rebound. (b) Charge separation in the transition state of the rebound reaction.

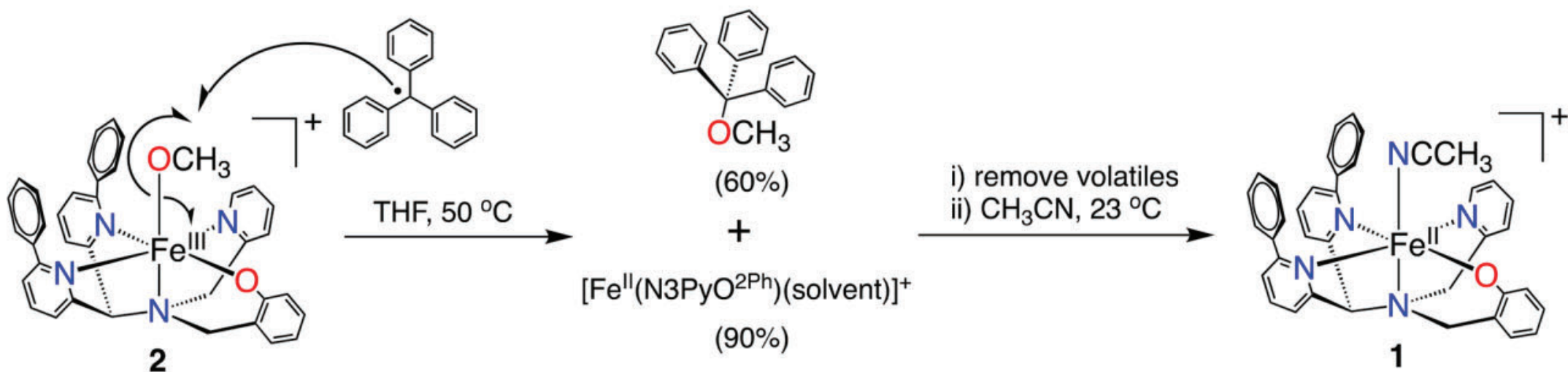
(c) Hammett plot and (d) Marcus plot.

# Fe-O配合物



Goldberg, D. P. *J. Am. Chem. Soc.* **2018**, *140*, 4191–4194.

# Fe-O配合物



# Fe-O配合物

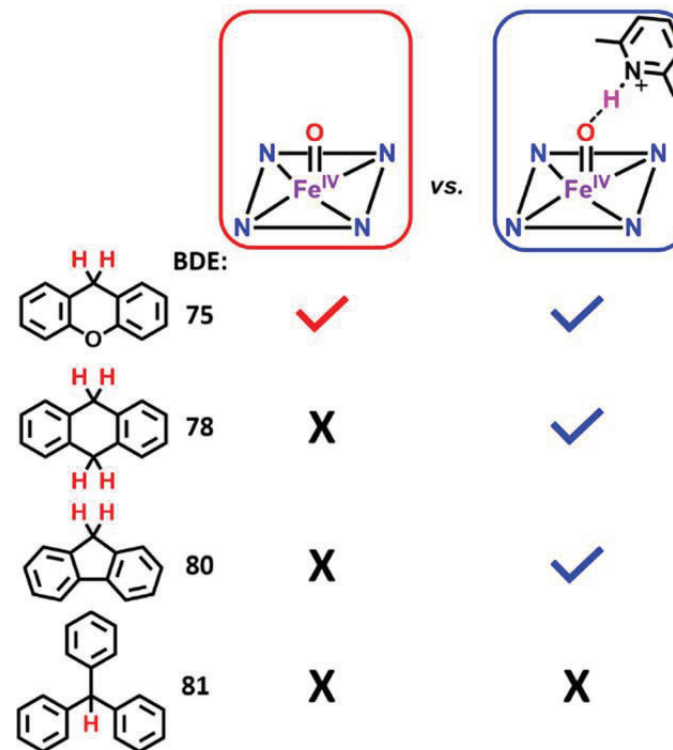
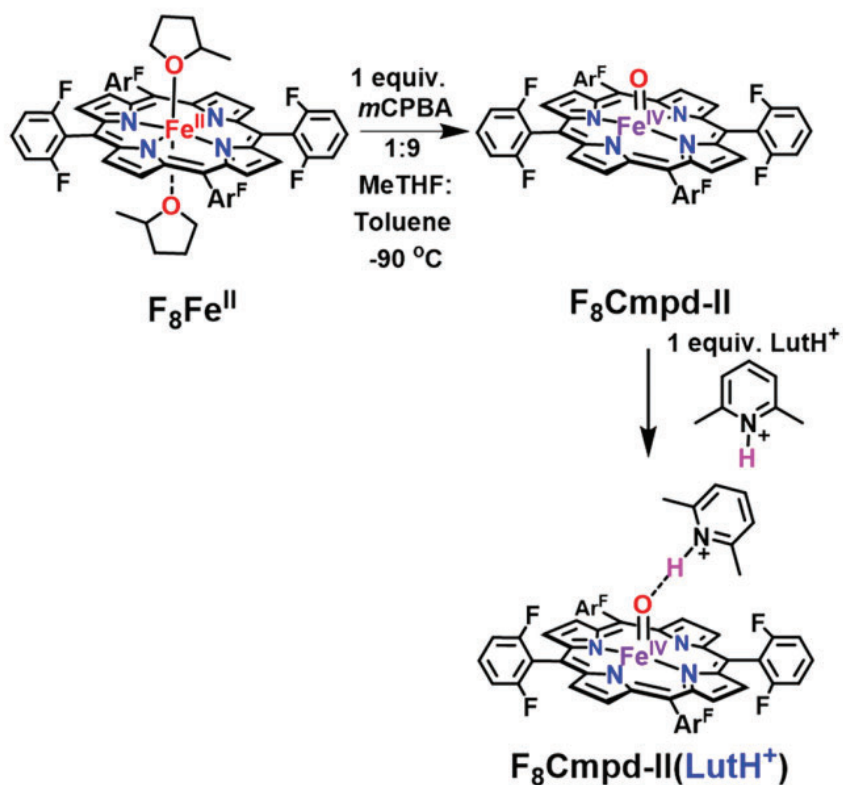
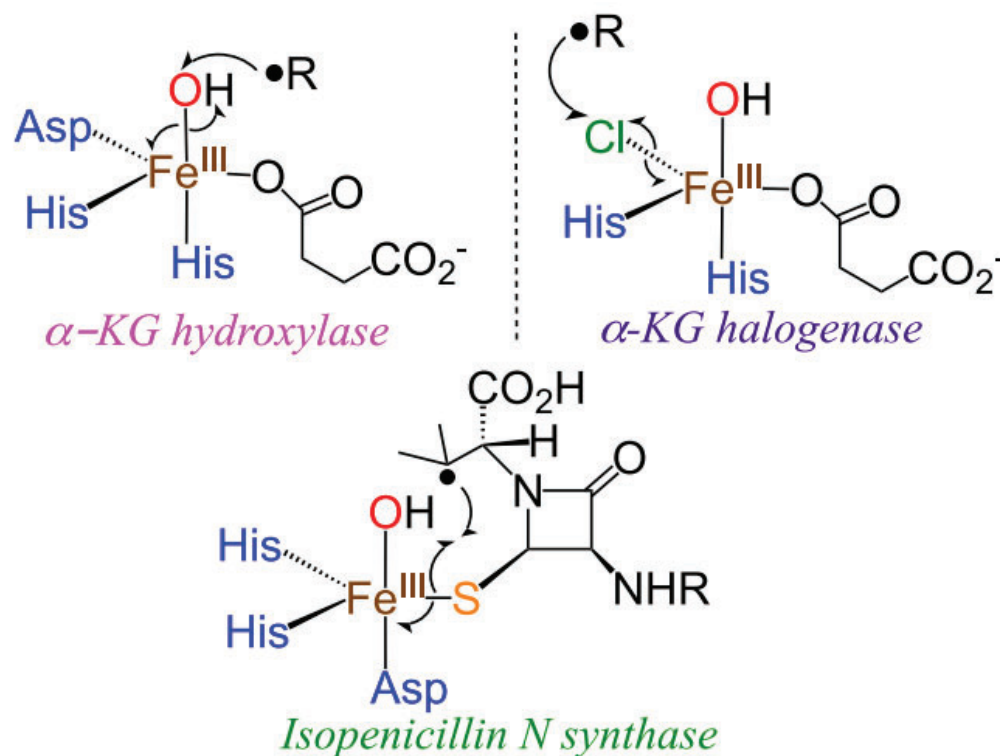


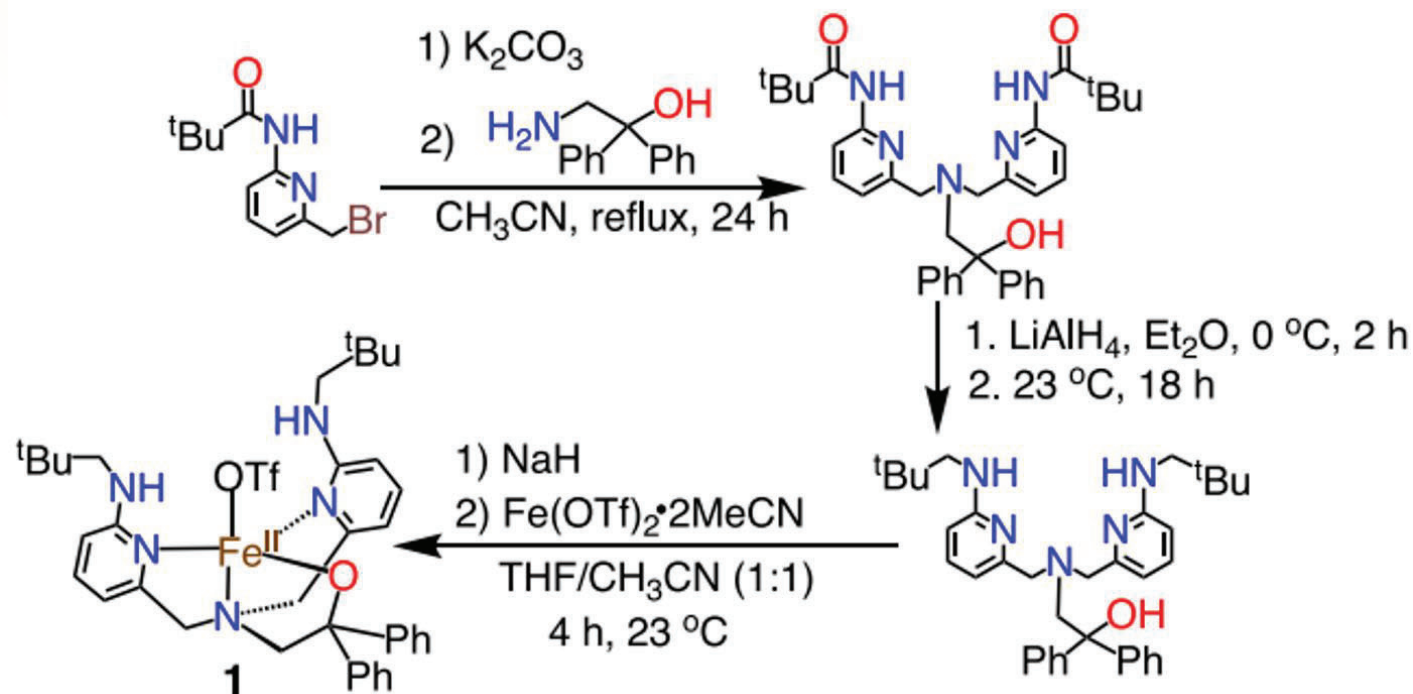
Figure 3. Reactivity between various C–H substrates (xanthene, dihydroanthracene (DHA), fluorene, and triphenylmethane) and  $\text{F}_8\text{Cmpd-II}$  or  $\text{F}_8\text{Cmpd-II(LutH}^+)$ . Also see the text for further details.

# Fe-O配合物

Scheme 1. Selective Rebound Step in Different Nonheme Iron Enzymes

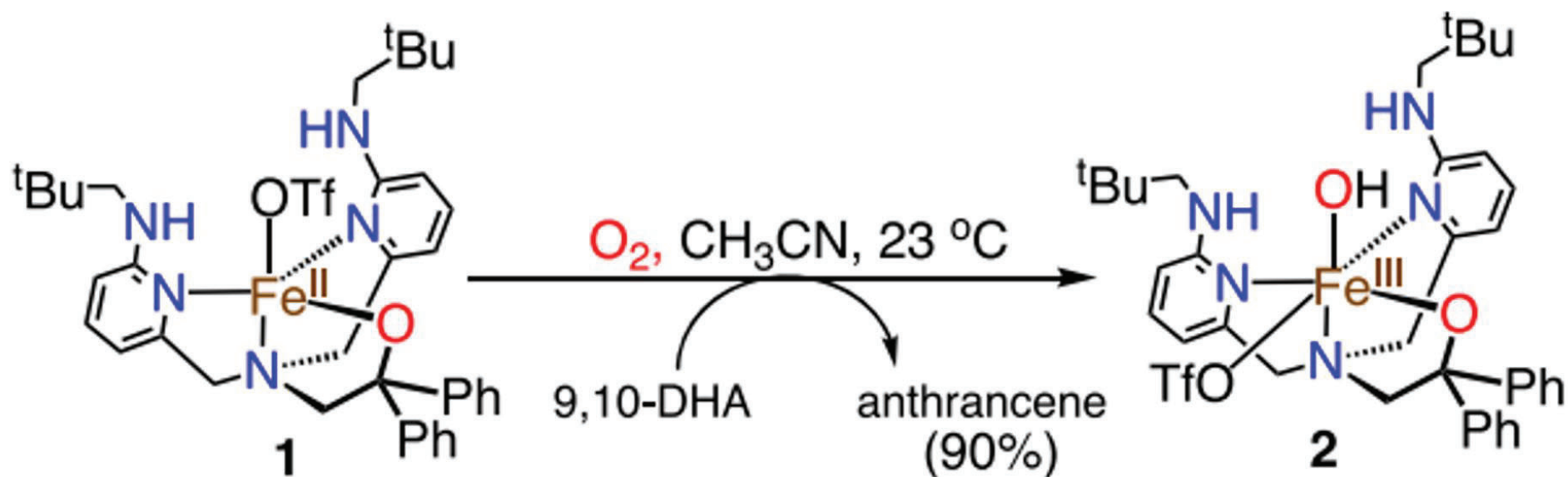


Scheme 2. Synthesis of BNPA<sup>Ph<sub>2</sub></sup>OH and Complex 1



- 氢键稳定FeIII(OH)单元
- FeII中心要被氧气氧化
- OH基团上含有开放位点

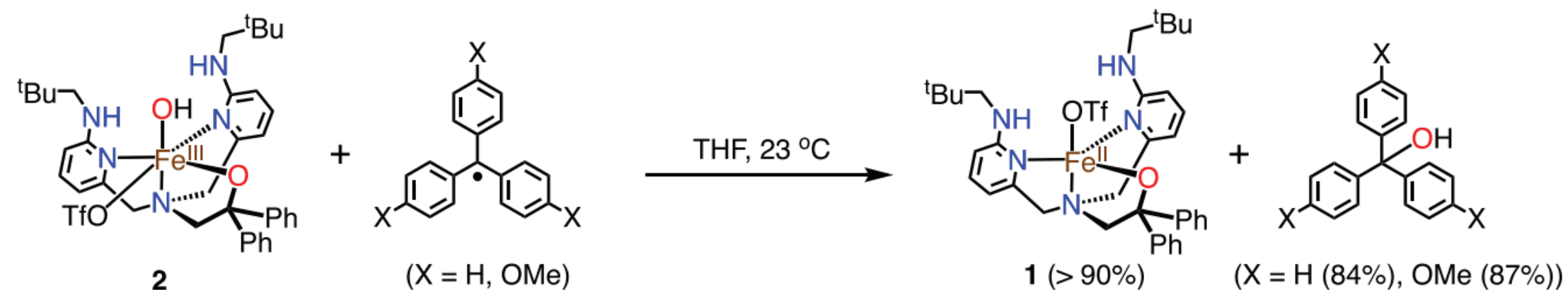
## Scheme 3. Activation of Dioxygen by 1



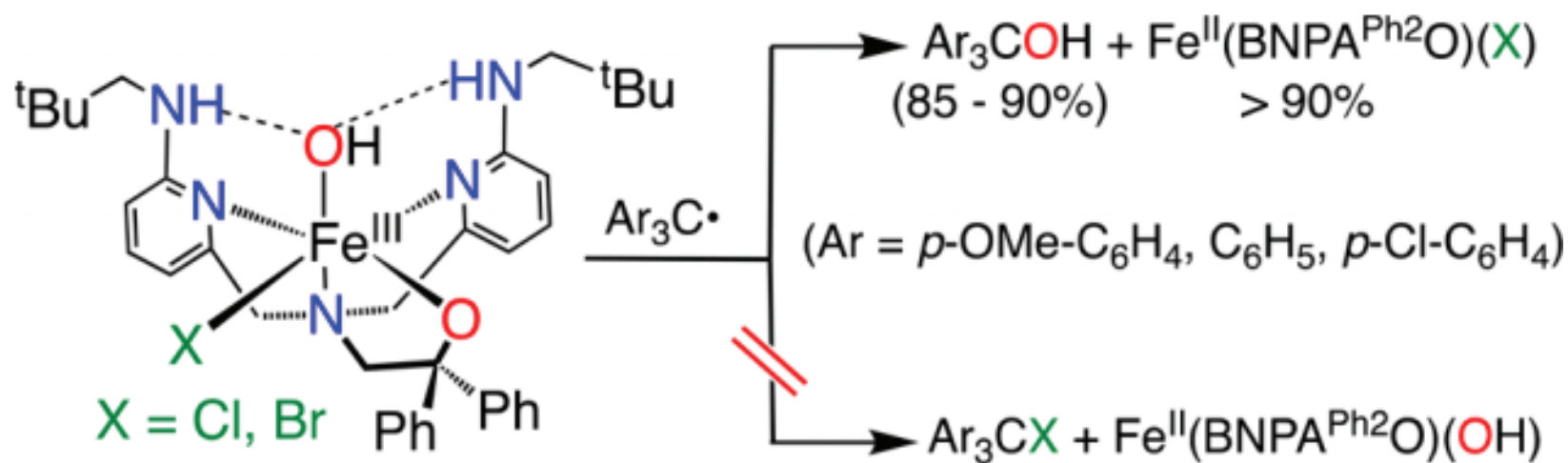


# Fe-O配合物

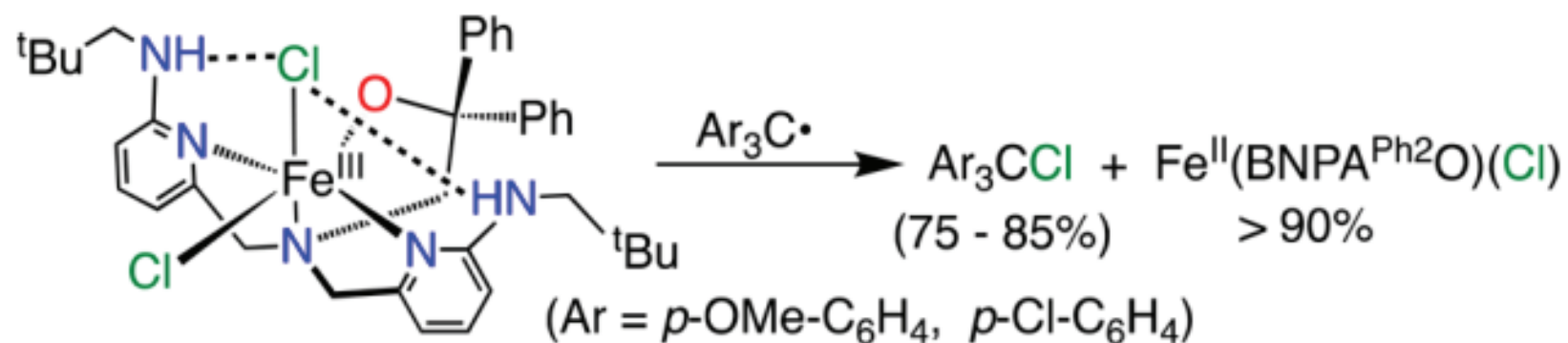
Scheme 4. Reaction between 2 and Triarylmethyl Radicals



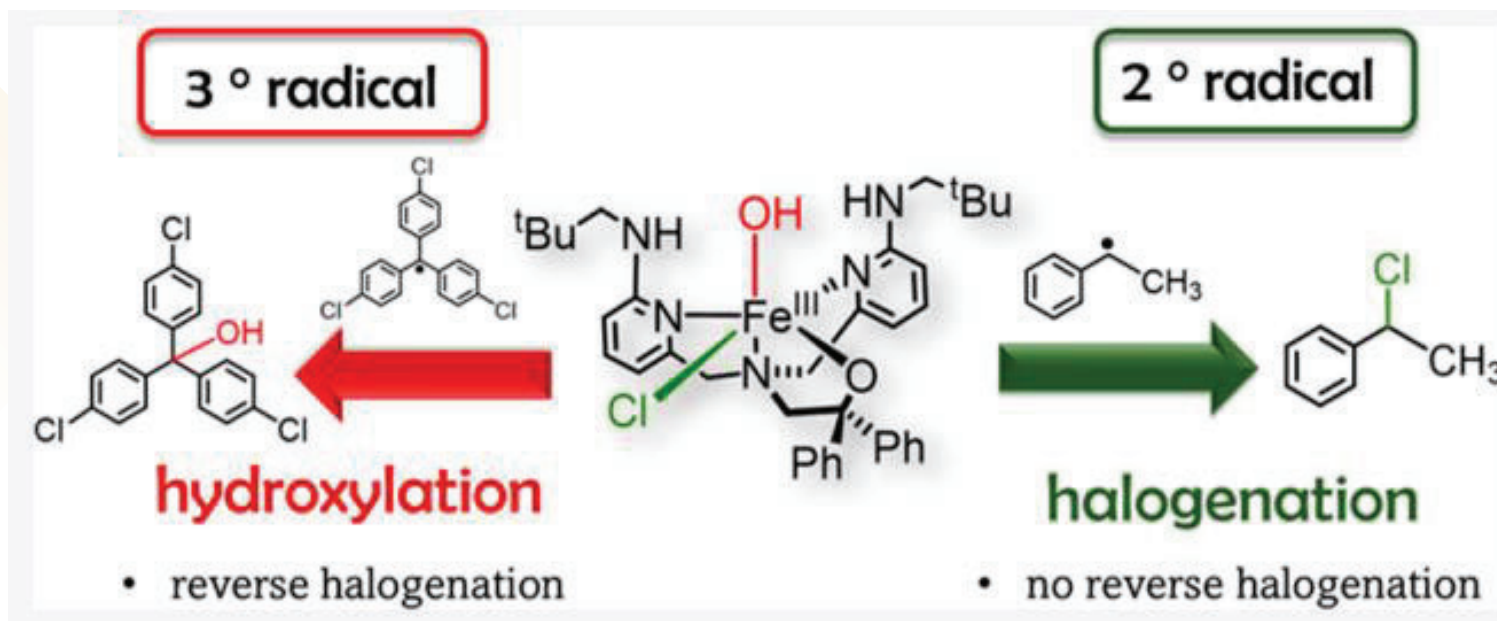
## Scheme 3. Reaction of 3 and 4 with Triphenylmethyl Radical Derivatives



## Scheme 4. Reaction of **5** with Triphenylmethyl Radical Derivatives

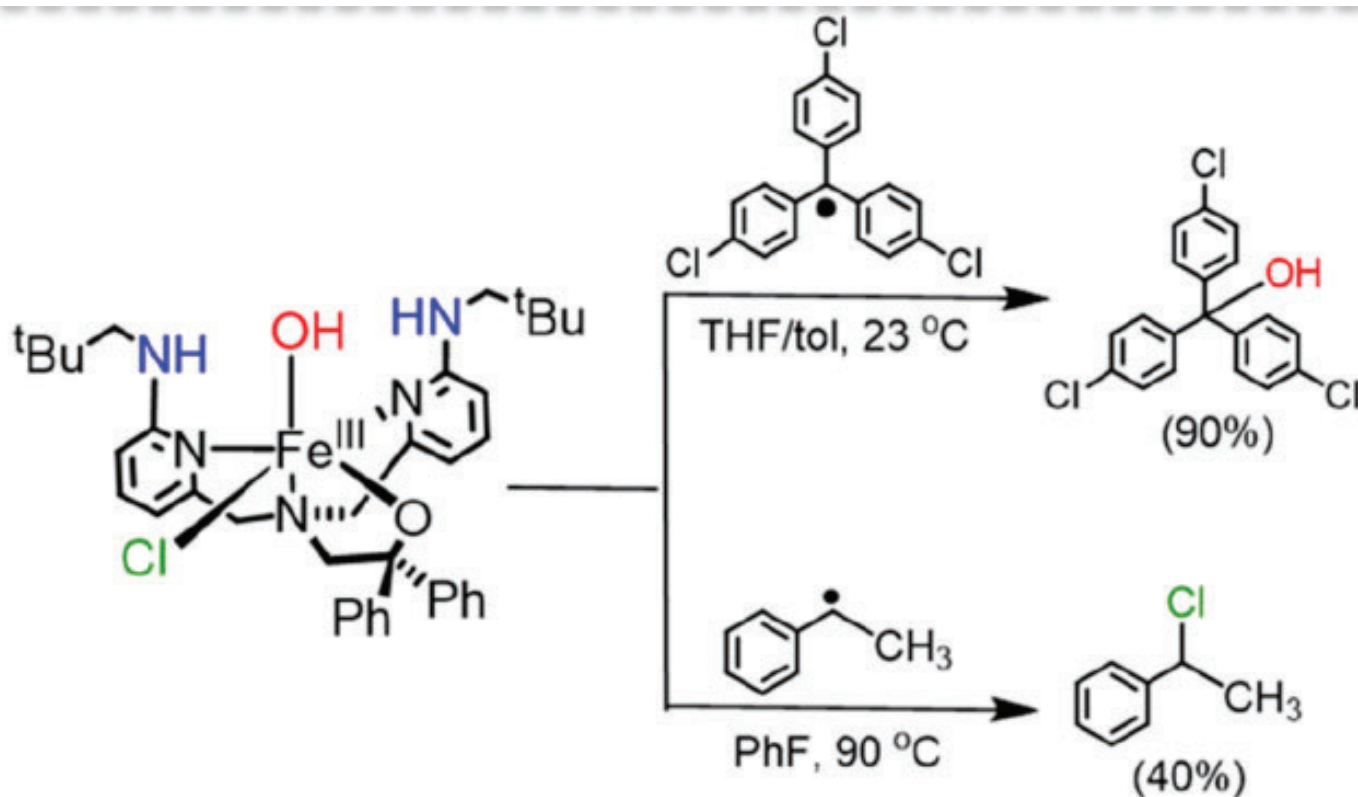


# Fe-O配合物



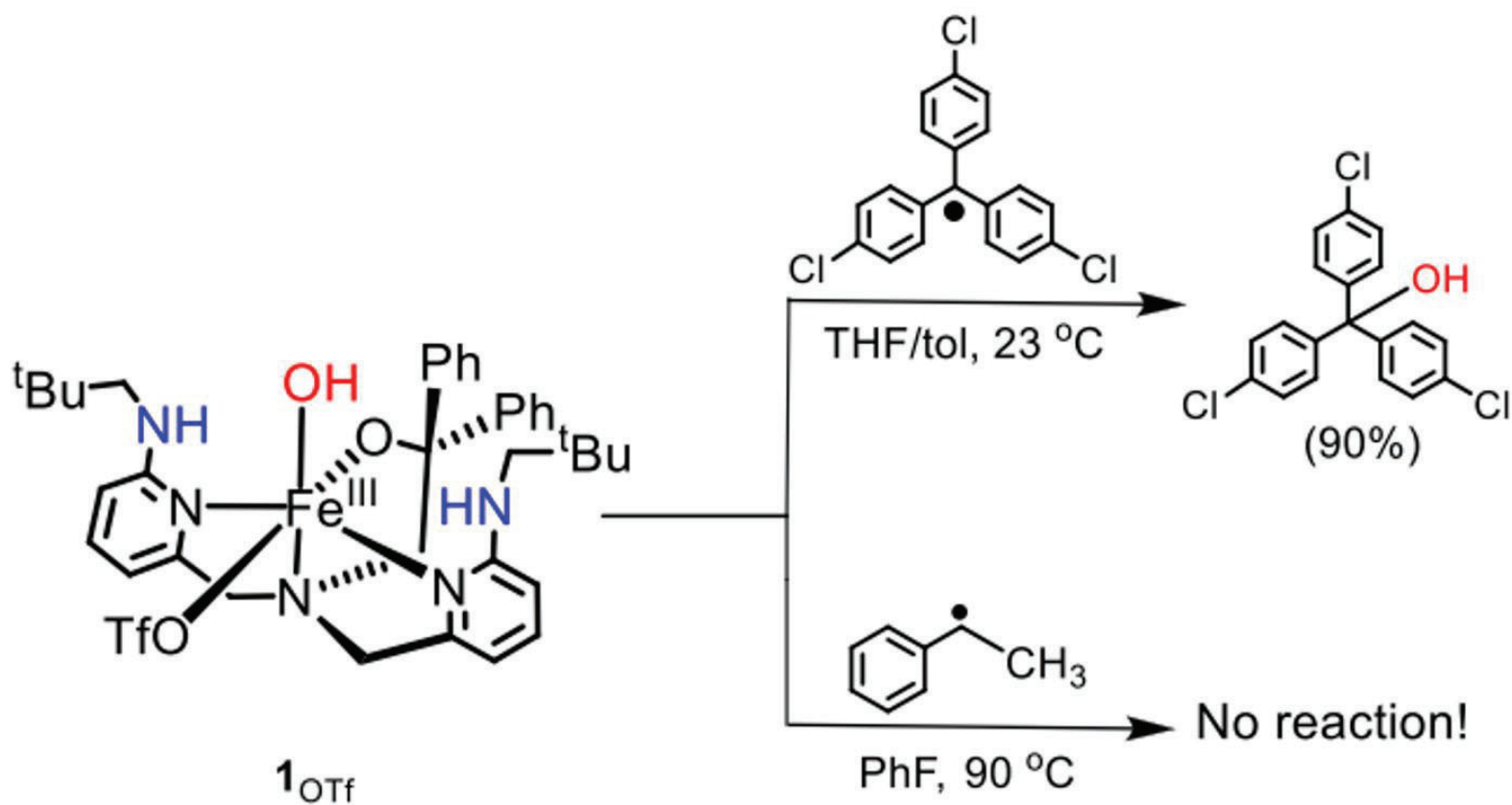
De Visser, S. P. J. *Am. Chem. Soc.* **2022**, *144*, 10752–10767.

# Fe-O配合物



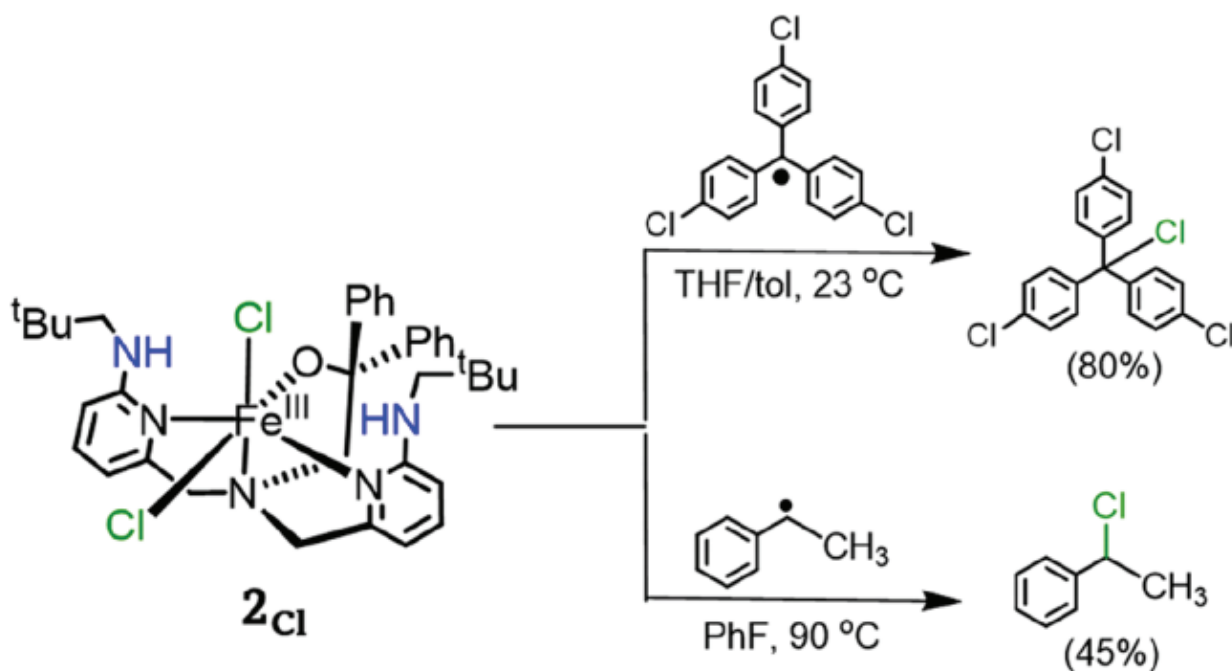
De Visser, S. P. J. *Am. Chem. Soc.* **2022**, *144*, 10752–10767.

# Fe-O配合物



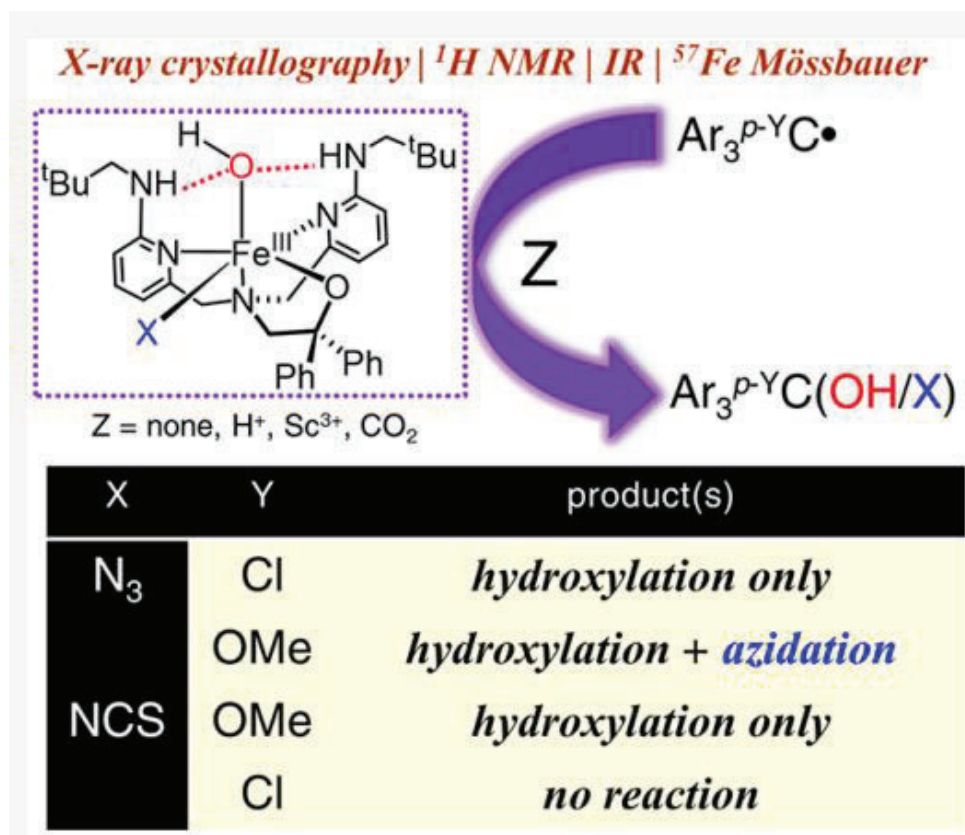
De Visser, S. P. J. *Am. Chem. Soc.* **2022**, *144*, 10752–10767.

## Scheme 5. Reactions of $2_{\text{Cl}}$ with Tertiary and Secondary Carbon Radicals



De Visser, S. P. J. *Am. Chem. Soc.* **2022**, *144*, 10752–10767.

# Fe-O配合物

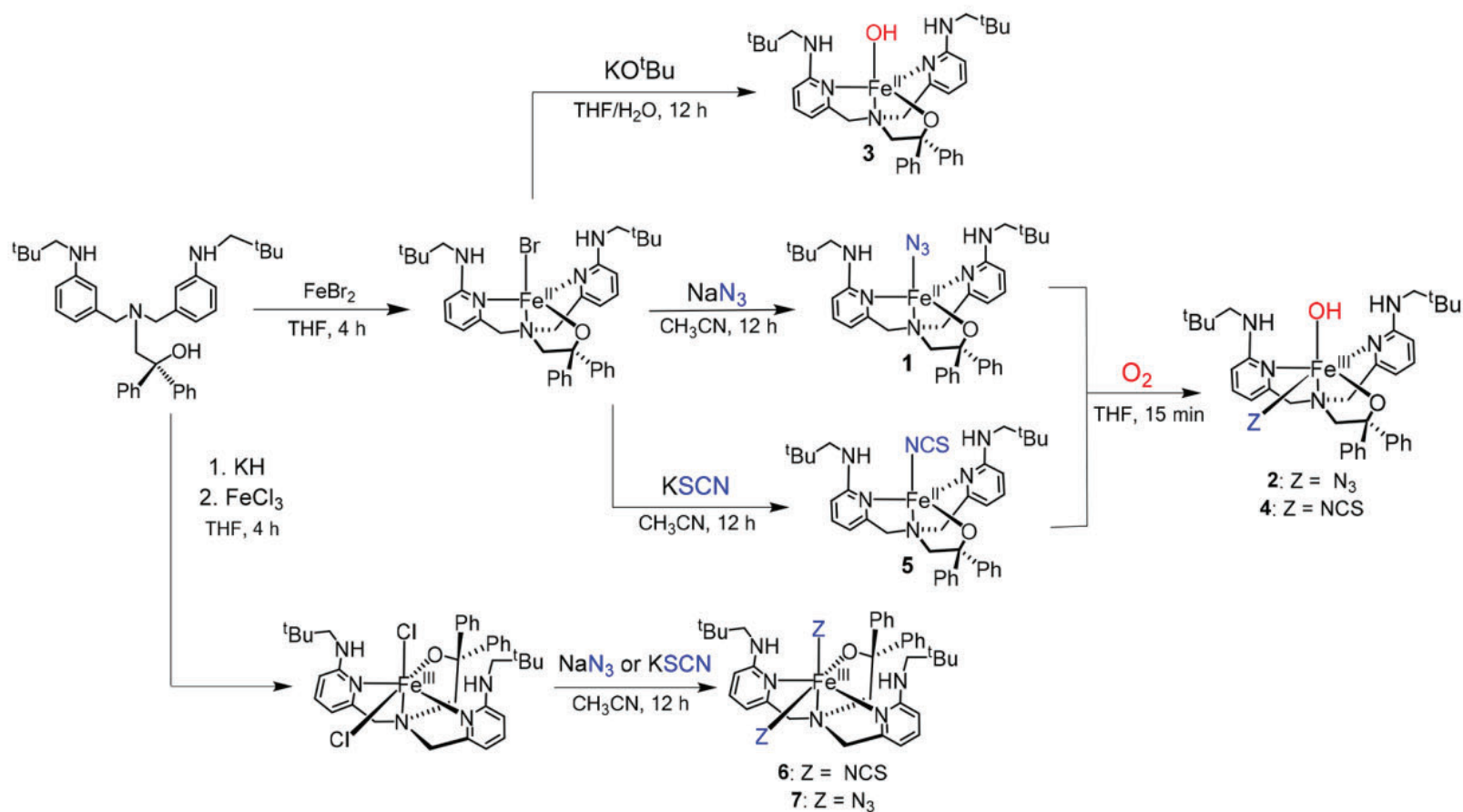


Goldberg, D. P. *J. Am. Chem. Soc.* **2022**, *144*, 20641–20652. **31**

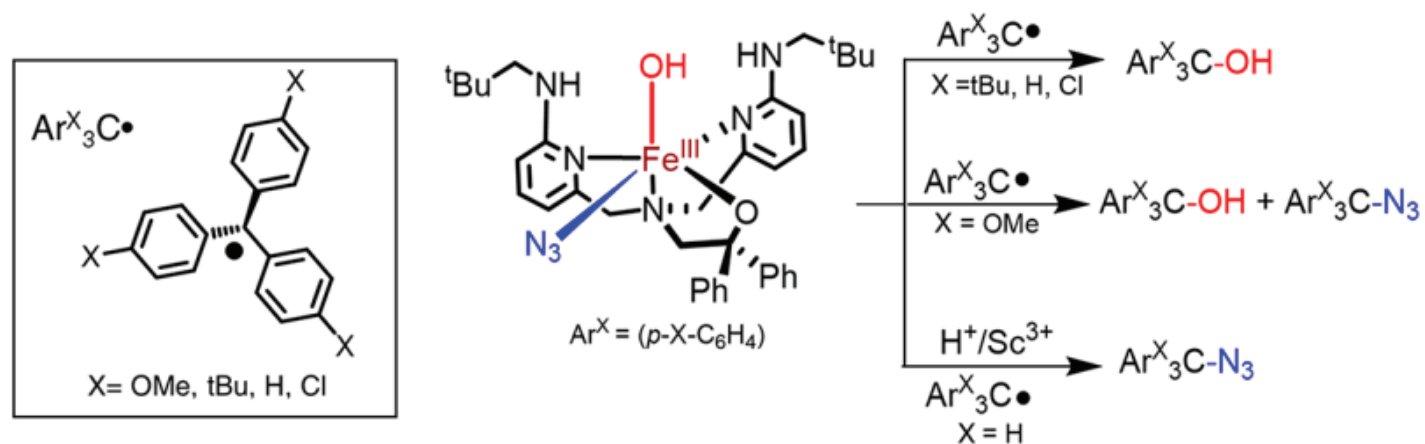


# Fe-O配合物

Scheme 2. Synthesis of Complexes 1–7<sup>a</sup>



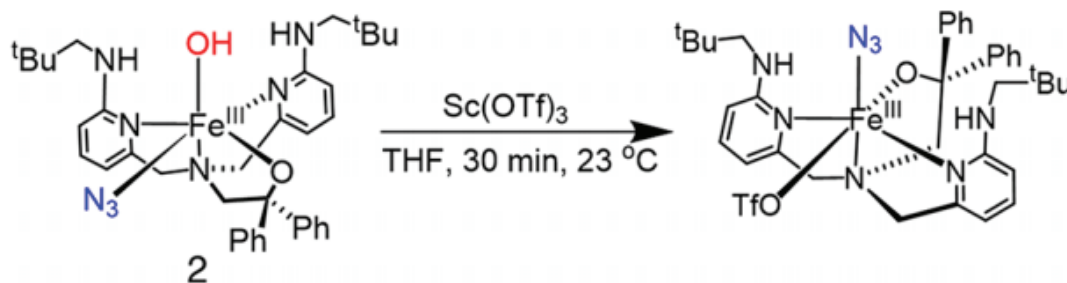
Scheme 3. Reaction of **2** with Triphenylmethyl Radical Derivatives



叠氮化物配合物的回弹选择性受碳自由基的富电子性质的影响。

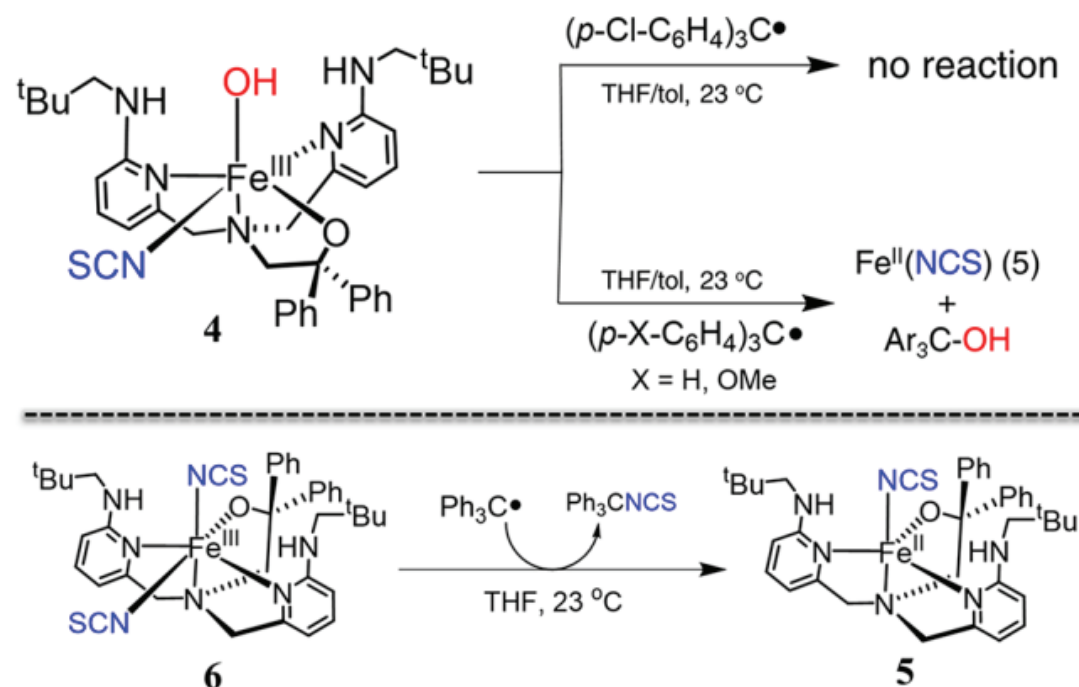
# Fe-O配合物

Scheme 4. Reaction of 2 with Sc(OTf)<sub>3</sub>

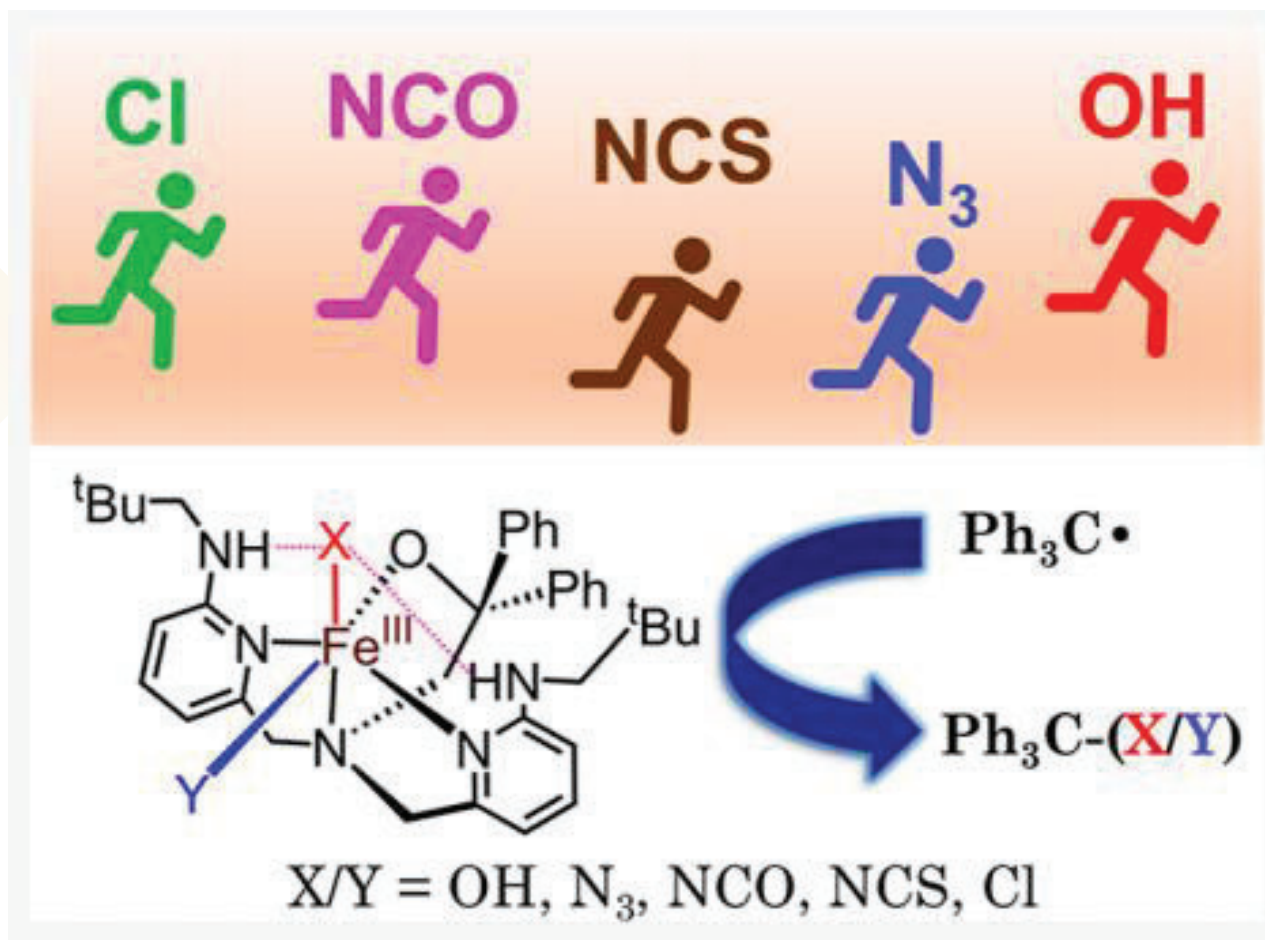


路易斯酸或布朗斯特酸的添加会导致只能分离到叠氮化产物。

Scheme 5. Reactions of Complexes 4 and 6 with Ar<sub>3</sub>C•

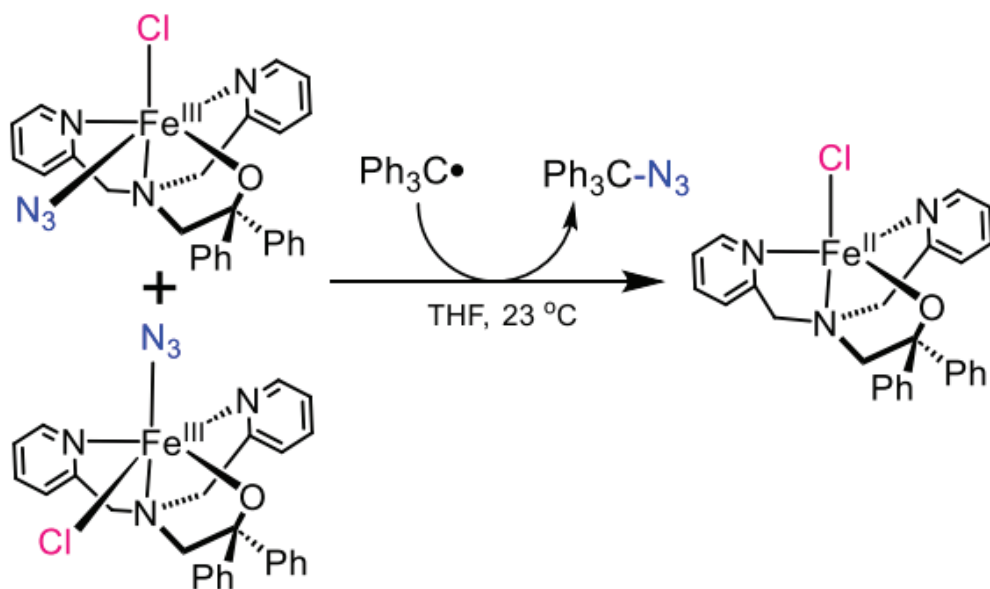


# Fe-O配合物

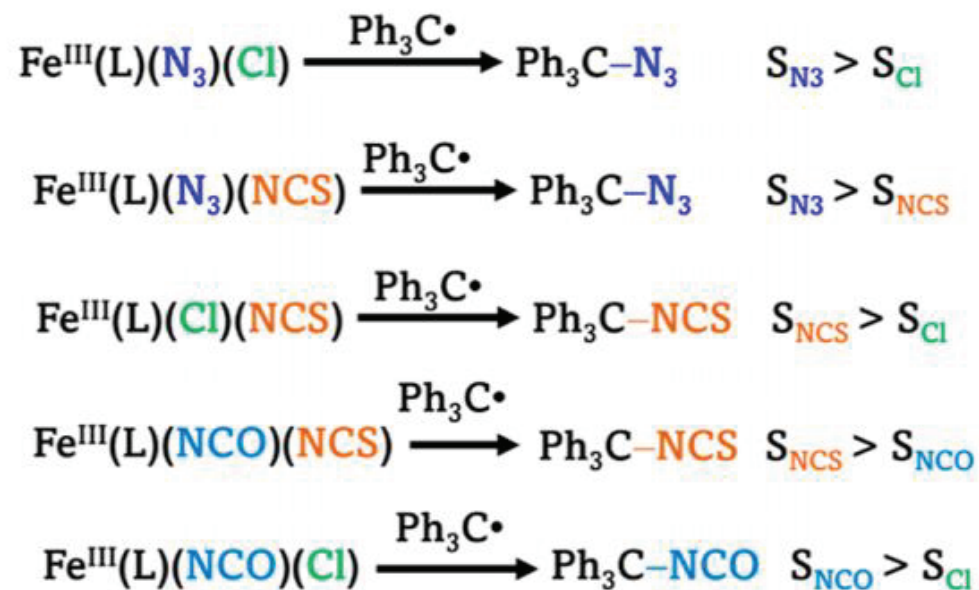


Goldberg, D. P. *Inorg. Chem.* **2023**, *62*, 17830–17842.

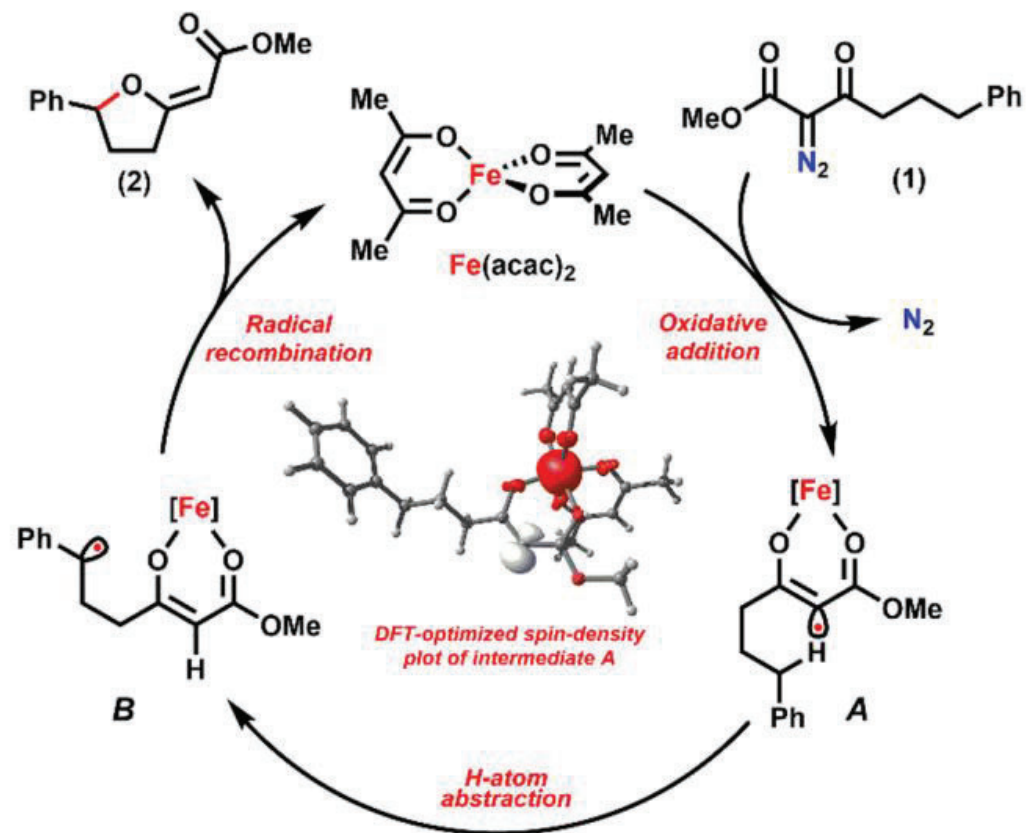
Scheme 9. Reaction of 13 with  $\text{Ph}_3\text{C}^\bullet$



Scheme 10. Relative Radical Transfer Selectivity ( $S$ )



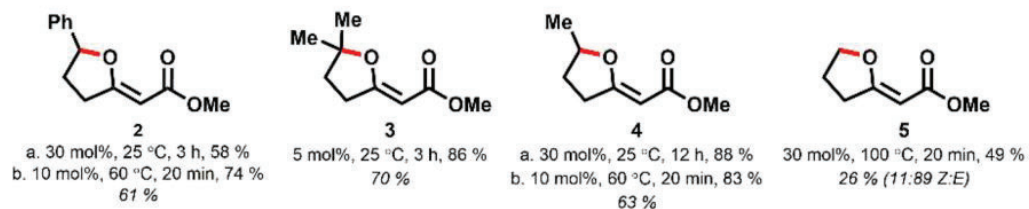
Overall trend :  $S_{\text{N}_3} > S_{\text{NCS}} > S_{\text{NCO}} > S_{\text{Cl}}$



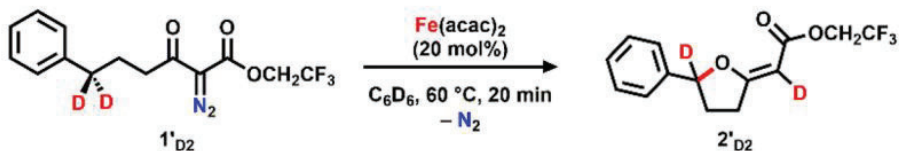
**Figure 4.** Proposed catalytic mechanism for the synthesis of substituted tetrahydrofurans.

Betley, T. A. *J. Am. Chem. Soc.* **2021**, *143*, 7480–7489.

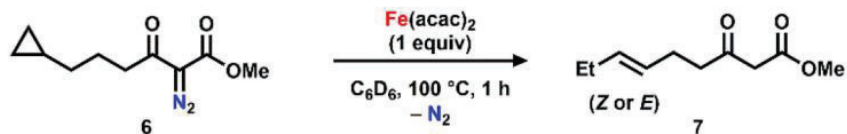
(a) *Canvassing substrate C-H bond strength accessibility*



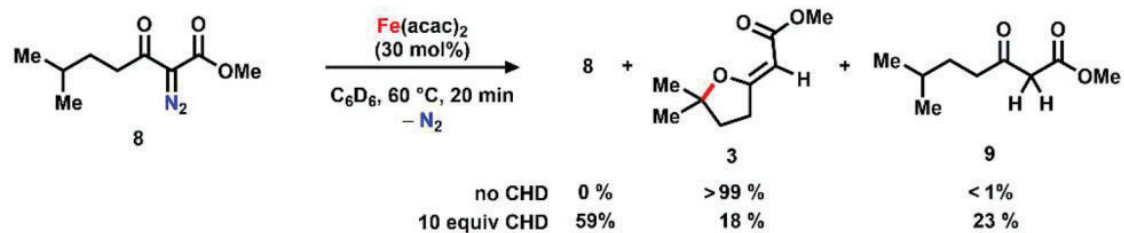
(b) *Tracking stepwise reaction through isotope labeling*



(c) *Radical clock ring opening*



(d) *Shunt reaction with sacrificial H-atom donor*



# THANKS!