



Iron porphyrin-catalyzed C(sp³)-H activation for the formation of C–O bond via cross-dehydrogenative coupling of cycloether and aromatic acid

Wei-Hong Wen^a, An-Na Xie^a, Hua-Hua Wang^a, Dong-Xu Zhang^a, Atif Ali^a, Xiao Ying^b, Hai-Yang Liu^{a,*}

^a Department of Chemistry, Key Laboratory of Functional Molecular Engineering of Guangdong Province, South China University of Technology, Guangzhou 510641, China

^b Department of Applied Physics, South China University of Technology, Guangzhou 510641, China

ARTICLE INFO

Article history:

Received 9 August 2017

Received in revised form

16 October 2017

Accepted 17 October 2017

Available online 28 October 2017

Keywords:

Porphyrin

Iron

Cross-dehydrogenative coupling

Cycle ether

C–H activation

ABSTRACT

An efficient cyclic ether benzoxylation was achieved by using iron porphyrin as the catalyst and di-*tert*-butyl peroxide oxidant. The benzoic acid substrates bearing electron donating or withdrawing groups could react with cyclic ether smoothly to afford the desired products. It was found iron porphyrin catalyzed oxidative C(sp³)-H activating esterification had the advantage of short reaction time and low catalyst loading. The reaction had been proved to proceed via a radical process.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The development of efficient, convenient, straightforward and environmentally benign methods for C–X (C, O, N, etc.) bonds formation has attracted continuous interest in recent years.¹ Cross-dehydrogenative coupling (CDC) reaction plays an important role for the construction of C–X bond, in which transition metals such as palladium,² ruthenium,³ nickel,⁴ indium⁵ are the most commonly used catalysts. An alternative catalyst is iron. Since the first report of FeCl₂ catalyzed CDC reactions in 2007,⁶ lots of effort has been devoted to the iron catalyzed CDC reactions.⁷ It demonstrated that iron catalyst was available for C–O bond formation by the coupling of C(sp³)-H with O(sp³)-H⁸ or O(sp²)-H.⁹ and C(sp²)-H with O(sp²)-H.¹⁰ via CDC reactions. The direct esterification of a-C(sp³)-H bonds is one of the most important application of CDC reaction, which may prepare some biologically active ester of practical usage in medicine like artemisinin.¹¹ Compared to conventional esterification reactions, the CDC reaction has the advantage of using

alkane instead of alcohol substrates. In 2014, Han et al. had reported the iron-catalyzed oxidative CDC esterification of cyclic ether C–H bonds with carboxylic acids, the reaction was carried out at 20 mol % catalyst loading for 24 h at temperature 120 °C.¹² The reaction time could be further reduced to 12 h by using copper catalyst.¹³

Metalloporphyrins are a class of versatile catalysts.¹⁴ It shows good catalytic activity in many reactions such as olefin oxidation,¹⁵ cyclopropanation,¹⁶ olefination,¹⁷ asymmetric synthesis,¹⁸ three-component reactions¹⁹ and C–H bond insertion reactions.²⁰ Although there are many reports on metalloporphyrin catalyzed reactions, the use of metalloporphyrin catalysts in CDC reactions is scarce. In 2014, metal porphyrin was firstly used in catalytic CDC reaction which enables direct activation of two different sp³ C–H bonds of isoquinoline and nitromethane under solvent-free conditions.²¹ Two years later, Guo and his co-workers had also reported the application of metal porphyrin in CDC reaction,²² in which they had successfully achieved aerobic oxidative coupling of terminal alkynes. More recently, our group has also reported the esterification of C(sp³)-H via copper-porphyrin catalyzed CDC reaction.²³ To continue our efforts in the metalloporphyrin catalyzed CDC reactions, we here wish to report the CDC esterification of cyclic ether

* Corresponding author.

E-mail address: chhyliu@scut.edu.cn (H.-Y. Liu).

by using iron chloro-5,10,15,20-tetra-(ethoxycarbonyl) porphyrin catalyst (**Scheme 1**, FeTECPCl) and TBHP oxidant. The reaction completed in 4 h with catalyst loading only 0.5%, showing iron porphyrin was efficient in this kind of reaction.

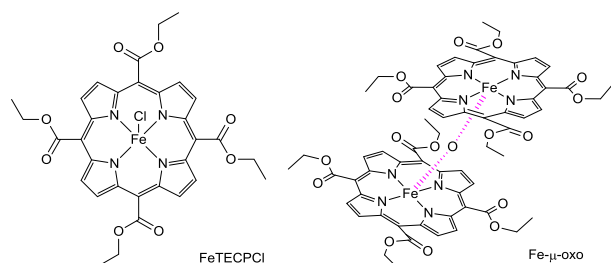
2. Result and discussion

X-ray diffraction analysis showed that the structure of FeTECPCl had a formulation unit in the cell in the orthorhombic P-1 space group, and no solvent molecule was crystallized. All crystallographically independent atoms are located in the usual position, except for the iron atom, which is located in the center of the inversion of the crystal. The 24-membered macrocyclic core of porphyrin is coplanar, and the five-coordinated iron atom is located at the center of this almost completely flat porphyrin macrocycle and forms a tetrahedron with four nitrogen atoms and one chlorine atom (**Scheme 2**).

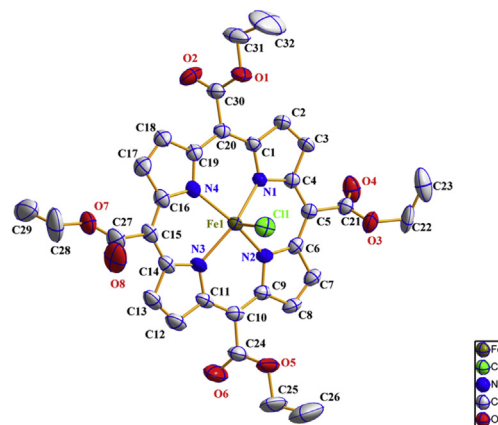
The Fe–N bond lengths range from 2.058 (4) to 2.066 (4) Å with an average value of 2.063 (4) Å, the Fe–Cl bond length is 2.2188 (15) Å, which is weaker interaction than the bond of metal iron and nitrogen atom (**Table 1**). The bond between the four nitrogen atoms (N1, N2, N3 and N4) and the iron atom and the chlorine atom is 99.60 (12), 104.11 (12), 101.46 (12), 104.16 (12).

Initially, the intermolecular oxidative reaction of benzoic acid (**1**) with 1,4-dioxane (**a**) was chosen as a model reaction to determine the optimum conditions. We commenced our investigation in the presence of FeTECPCl as the catalyst and DTBP as the oxidant under a solvent-free condition. At first, we discussed the quantity of catalyst from 0.05 to 1.0 mol %, the most efficiency of this transformation was 0.5 mol % (**Table 2**, entries 1–4). No significant improvement in the product yield was observed with 3 equiv of the DTBP (**Table 2**, entry 5). The effects of other oxidants and catalysts on the reaction was also investigated to pursue the higher yield (**Table 2**, entries 6–14). Unfortunately, we did not get satisfactory results. The yield decreased when the reaction was performed at 100 °C (**Table 2**, entries 15). No significant improvement in the yield was observed when the reaction was conducted at 140 °C (**Table 2**, entries 16). Note that the product **1a** was not observed in the absence of catalyst or oxidant (**Table 2**, entries 17–18).

With the above optimized conditions in hand, we explored the 1,4-dioxane with other benzoic acid derivatives and the results were listed in **Table 3**. The CDC reaction between methyl and methoxy substituent tolerated in moderate yields of 72–84% (**2a–4a**, **7a–9a**). Gratifyingly, 4-*tert*-butylbenzoic acid also examined and the desired product was obtained in 70% isolated yield (**5a**). Not only alkyl substituents were tested, but also 2-phenylbenzoic acid was investigated, affording **6a** with an isolated yield of 74%. There is no doubt that *ortho*, *meta*, *para*-benzoic acid has a good yield. The reaction yield of *ortho*-substituents is minimally reduced relative to *meta*- and *para*-positions. *ortho*-substituted acids were lower yields as compared to their *meta* and *para*-substituted analogues was due to steric hindrance imparted by *ortho*-substituents (**2a**, **7a**, **12a**, **15a**).



Scheme 1. Molecular Structures of FeTECPCl and Fe-μ-oxo.



Scheme 2. ORTEP plots of FeTECPCl. (Showing 50% probability thermal displacement ellipsoids, hydrogen atoms are omitted for clarity).

At the same time, we used *ortho* and *para*-halogen substituents and hydroxyl substituents to illustrate the substitution effect of the substrate on the reaction (**12a–18a**). Strikingly, Electron deficient aromatic acids such as 4-nitrobenzoic acid, 4-halogenbenzoic acid, and 4-cyanobenzoic acid have lower yields in comparison to electron donating groups (**19a–23a**). Unfortunately, 2-naphthoic acid is not suitable for this reaction (**24a**). Hydrocinnamic acid was used in this system to react with 1,4-dioxane under the typical reaction conditions, we were pleased to find that the reaction proceeded well and gave the corresponding product **25a** in 55% yield. 3-Phenoxypropanoic acid were reacted with 1,4-dioxane and gave the corresponding products **26a** (73%). Even more, the reaction did not work when furan-3-carboxylic acid was used as substrate in this system (**27a**).

After finishing the investigation of the 1,4-dioxane as a substrate, we attempted to extend the substrate range by using 1,3-dioxolane to explore the selectivity and activity of the reaction (**Table 4**). However, no reasonable yield of the product could be obtained with the same reaction conditions. When double the oxidant amount and prolong the reaction time to 8 h, the yield of **2b** may reach 40%, the further increasing of the reaction time did not affect the yield significantly. Interestingly, no **2b'** product could be isolated. The reaction of other benzoic acid derivatives bearing electron-donating or withdrawing groups such as 4-methylbenzoic acid (**2c**), 4-methoxybenzoic acid (**2d**), 2-phenylbenzoic acid (**2e**), 2-fluorobenzoic acid (**2f**), 4-*tert*-butylbenzoic acid (**2g**) and α,α,α -trifluoro-*p*-toluic acid (**2h**) with 1,4-dioxane provided moderate yield of 73–83%.

To investigate the reaction mechanism, a series of experiments was conducted. When the reaction was carried out in the presence of radical scavenger such as 2,2,6,6-tetramethylpyridine N-oxide (TEMPO) or butylated hydroxytoluene (BHT), no desired product could be obtained (**Scheme 3**), indicating the reaction via a radical mediated pathway. The intermolecular competing kinetic isotope effect (KIE) experiment showed a KIE effect of $k_H/k_D = 4$ (the KIE was determined by ^1H NMR spectroscopy by analyzing the ratio of **9a** and **[D]9a** (**Scheme 4**). This suggested that C (sp³)-H bond cleavage of 1,4-dioxane was the kinetic rate-determining step.²⁴ Interestingly, the UV–Vis spectra of the catalyst changed remarkably after adding oxidant (**Scheme 5**), such a spectra changes revealed the transformation of catalyst FeTECP to its Fe-μ-oxo species.²⁵ That is, the real catalyst is a porphyrin Fe-μ-oxo complex. (**Scheme 5**).

The TEMPO was detected by electron paramagnetic resonance (EPR) in the reaction mixture of benzoic acid, 1,4-dioxane and

Download English Version:

<https://daneshyari.com/en/article/7828047>

Download Persian Version:

<https://daneshyari.com/article/7828047>

[Daneshyari.com](https://daneshyari.com)