RSC Advances

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2015, **5**, 103977

Received 28th October 2015
Accepted 24th November 2015

DOI: 10.1039/c5ra23950h

www.rsc.org/advances

β-Ketophosphonates formation *via* deesterification or deamidation of cinnamyl/alkynyl carboxylates or amides with H-phosphonates†

Yao Zhou,[a] Mingxin Zhou,[a] Ming Chen,[b] Jihu Su,[b] Jiangfeng Du[b] and Qiuling Song*[ac]

We report here an unprecedented Fe/Cu synergistically catalyzed deesterificative or deamidative oxyphosphorylation of unsaturated carboxylates or amides with H-phosphonates. The valuable β-ketophosphonates were obtained along with chemoselective cleavage of C_{sp^2}–C(CO) or C_{sp}–C(CO) bonds in good yields under oxygen atmosphere with a wide substrate scope.

Esters and amides are pivotal structural motifs in organic chemistry, pharmaceuticals and biologically active compounds, significant explorations have been made in the synthesis of these two types of compounds, however, surprisingly, direct utilization of esters or amides as synthetic blocks *via* deesterification[1] or deamidation[2] is very rare despite the wide existence and ready accessibility of these two types of compounds. There are three known ways for cleavage of C–C(COOR) bond: (a) direct cleavage of C–C(COOR) bond, rendering COOR as a leaving group;[1e–1g] (b) the two-step strategy: hydrolysis of ester to carboxylic acids first, then subsequent decarboxylation;[1a–1d] (c) decarboxylation of esters by releasing CO_2 gas.[3] The second strategy is step- and time-consuming, which is not suitable for late-stage modification when acid or base sensitive functional groups existing on the molecules; and the third one, in theory, belongs to decarboxylation; only the first strategy is the most straight-forward and efficient method to generate a new moiety by releasing COOR as a leaving group. However, very few precedent literatures have reported such transformation yet and the known deesterification was followed by a structural rearrangement. In term of deamidation reaction, even less examples have been reported.[2] α,β-Unsaturated (including C═C bonds and C≡C bonds) compounds are an important class of compounds in organic synthesis, they usually serve as Michael acceptors to lead to 1,4-adduct.[4] Recently, some elegant examples emerged on selective cleavage of C(sp^3)–C(CO) bonds in aryl alkyl ketones;[5] intriguingly, selective cleavage of C(sp^2) or C(sp)–C(CO) single bond of α,β-unsaturated compounds is scant.[6] and the known methods mainly focused on decarboxylative C–C cleavage of α,β-unsaturated carboxylic acids, such as decarboxylation of cinnamic acids[7] or alkynyl carboxylic acids.[8] To our knowledge, deesterification or deamidation *via* chemoselective cleavage of C(sp^2)–C(CO) or C(sp)–C(CO) bond in cinnamyl/alkynyl esters or amides has not been reported thus far. Therefore it is a challenge and would be highly desirable if efficient deesterification or deamidation of cinnamyl/alkynyl esters or amides could be developed.

Organophosphorus compounds are of great importance and widely applied in organic synthesis, material sciences, biology and pharmaceuticals.[9] It is always appealing for organic chemists to develop new and highly efficient strategy for construction of C–P bonds.[10] In 2011, Yang and his coworkers firstly reported a Cu-catalyzed decarboxylative phosphonation of cinnamic acids and arylalkynyl carboxylic acids with diphenylphosphine oxide (Scheme 1a).[7a] Very recently we reported an efficient method converting cinnamic acids or alkynyl carboxylic acids into β-ketophosphonates with H-phosphonates *via* decarboxylative oxyphosphorylation reaction (Scheme 1b).[7d,8c] As our continuous interests in activation of C–C single bond[11]/functionalization of C–C multiple bonds,[7d,8c] herein, we report an unprecendent Fe/Cu cocatalyzed deesterification and deamidation of cinnamyl/alkynyl esters or amides *via* chemoselective cleavage of C(sp^2)–C(CO) or C(sp)–C(CO) bond as well as difunctionalization of C═C or C≡C bonds to construct new C–P bonds under mild conditions. Compared with other precious noble metals, Fe and Cu are inexpensive, nontoxic, earth-abundant and user friendly for academia as well as for industry. Currently, Cu/Fe-cocatalyzed reactions have gained

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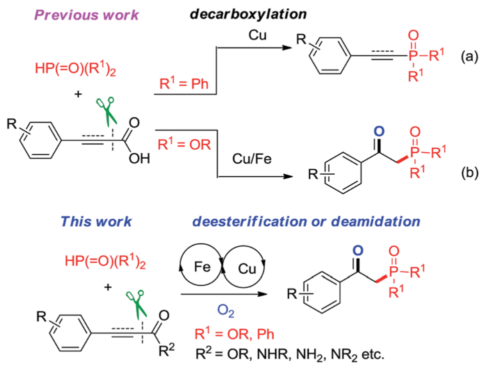
[a] *Institute of Next Generation Matter Transformation, College of Chemical Engineering, College of Materials Science & Engineering at Huaqiao University, 668 Jimei Blvd, Xiamen, Fujian, 361021, P. R. China. E-mail: qsong@hqu.edu.cn; Fax: +86-592-6162990*

[b] *Hefei National Laboratory for Physical Sciences at Microscale, Department of Modern Physics, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China*

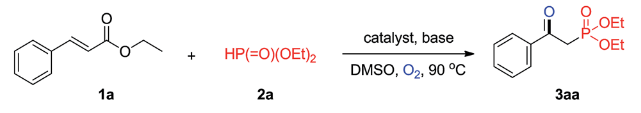
[c] *Beijing National Laboratory for Molecular Sciences, Beijing, 100190, P. R. China*

† Electronic supplementary information (ESI) available: Full experimental and optimization details, characterization of the synthesized products. See DOI: 10.1039/c5ra23950h



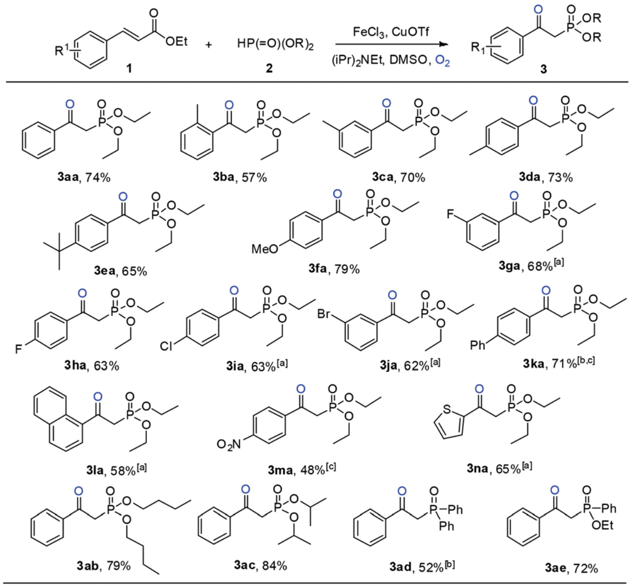
Scheme 1 Transition-metal-catalyzed phosphonation reactions between α,β-unsaturated carbonyl compounds and H-phosphonates.

Table 1 Optimization of the reaction parameters[a]



Entry	[Cu] cat.	[Fe] cat.	Base (1 equiv.)	Yield[b] (%)
1	CuOTf (5 mol%)	$FeCl_3$ (10 mol%)	Et_3N	(69)[c]
2	CuOTf (5 mol%)	$FeCl_2$ (10 mol%)	Et_3N	67
3	CuOTf (5 mol%)	$FeBr_2$ (10 mol%)	Et_3N	54
4	CuOTf (5 mol%)	$FeCl_3$ (10 mol%)	$(iPr)_2NEt$	(70)[c]
5[d]	**CuOTf (5 mol%)**	**$FeCl_3$ (10 mol%)**	**$(iPr)_2NEt$**	**(79)**[c]
6[e]	**CuOTf (5 mol%)**	**$FeCl_3$ (10 mol%)**	**$(iPr)_2NEt$**	**(74)**[c]
7	CuOTf (5 mol%)	$FeCl_3$ (5 mol%)	$(iPr)_2NEt$	58
8	CuOTf (10 mol%)	$FeCl_3$ (10 mol%)	$(iPr)_2NEt$	65
9[f]	CuOTf (5 mol%)	$FeCl_3$ (10 mol%)	$(iPr)_2NEt$	—
10[g]	CuOTf (5 mol%)	$FeCl_3$ (10 mol%)	$(iPr)_2NEt$	47
11	—	$FeCl_3$ (10 mol%)	$(iPr)_2NEt$	7
12	CuOTf (5 mol%)	—	$(iPr)_2NEt$	—

[a] Reaction conditions: ethyl cinnamate **1a** (0.5 mmol), H-diethyl phosphate **2a** (1.5 mmol), Cu catalyst and Fe cocatalyst in DMSO (1 mL), Et_3N (0.5 mmol), O_2 atmosphere, 90 °C, 17 h, in a sealed tube. [b] GC yield. [c] Isolated yield in parenthesis. [d] 24 h. [e] 1.3 mmol of **2a** was used for 24 h. [f] The reaction was performed under N_2 atmosphere. [g] The reaction was performed under air.



Scheme 2 Cooperative deesterificative tandem oxophosphorylation of cinnamates (**1**) with H-phosphonates under O_2 atmosphere. Reaction conditions: **1** (0.5 mmol), **2** (1.3 mmol), CuOTf (5 mol%), $FeCl_3$ (10 mol%), $(iPr)_2NEt$ (0.5 mmol), DMSO (1 mL), O_2 atmosphere, 90 °C, 24 h. [a]Methyl ester was used. [b]28 h. [c]**2** (1.5 mmol).

much attention due to their superior combined bimetallic catalytic reactivities.[12] In this strategy, environmentally benign Cu/Fe cocatalysts were for the first time employed to efficiently cleave $C(sp^2)$–C(CO) or C(sp)–C(CO) bond *via* deesterification or deamidation protocol in cinnamate or alkynyl carboxylates or amides under 1 atm dioxygen atmosphere and valuable β-ketophosphonates, which are key intermediates for the total synthesis of various natural products[13] and building blocks for a myriad of organic transformations,[14] were generated in good yields with a broad range of substrate scope in a one-pot protocol.

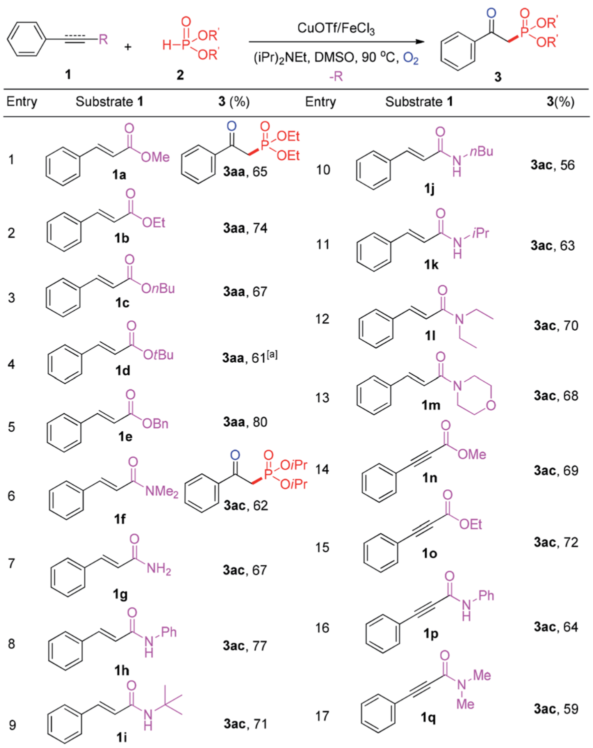
We commenced our study with ethyl cinnamate (**1a**) and H-diethyl phosphonate (**2a**) as substrates using 5 mol% CuOTf together with 10 mol% $FeCl_3$ as the cocatalyst system at 90 °C. To our delight, the desired product β-ketophosphonate was formed in 69% isolated yield in the presence of Et_3N in DMSO within 17 h *via* deesterification. Other iron salts, such as $FeCl_2$ or $FeBr_2$ gave lower yields (Table 1, entries 2–3). When the base was changed from Et_3N to $(iPr)_2NEt$, the isolated yield was slightly increased to 70% (entry 4). Reaction time was also important for the improvement of isolated yields: when the reaction time prolonged from 17 h to 24 h, the yield was increased to 79% (entry 5), yet when H-diethyl phosphonate (**2a**) was decreased from 3 equiv. to 2.6 equiv., the yield of desired product **3aa** was only slightly dropped to 74% (entry 6). Given the difficulty on the purification of final product **3aa** with excess amount of H-diethyl phosphonate (**2a**), we decided to take entry 6 as the optimal conditions. Control experiments suggested that molecular dioxygen, CuOTf and $FeCl_3$ were all indispensable to this reaction (entries 9–12).[15]

Encouraged by the above results, we next explored the substrate scope (Scheme 2). Gratifyingly, a variety of ethyl cinnamate derivatives which bear either electron-donating (methyl, *p*-*t*-Bu, *p*-MeO) or electron-withdrawing (*p*-NO_2) groups on the aromatic rings of cinnamates were well tolerable in this transformation, affording the desired products in moderate to good yields (**3ba–3fa**, **3ma**). *Ortho*-, *meta*- and *para*-substituted groups gave the desired product in decent yields with *ortho* one in a relative low yield owing to the steric hindrance (**3ba–3da**). Halo-substituted cinnamates such as fluorine, chlorine and bromine were well compatible, leading to the corresponding products in 62–68% (**3ga–3ja**). Polyphenylene acrylate, for instance (*E*)-ethyl-3-([1,1′-biphenyl]-4-yl)acrylate and 1-naphthylacrylate are also good candidates for this transformation and gave the desired β-ketophosphonates in 71% and 58% yields respectively (**3ka** and **3la**). Heteroaromatic acrylate, like 2-thiopheneacrylate worked smoothly under standard conditions to give

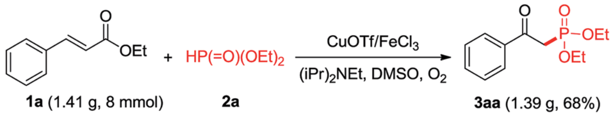
3na in 65% yield. It was noteworthy that di-*n*-butyl (**2b**), diisopropyl (**2c**), and diphenyl phosphoxide (**2d**) as well as ethyl phosphonate (**2e**) were all suitable substrates in addition to diethyl phosphonate (**2a**), generating β-ketophosphonates **3ab–3ae** in good to excellent yields.

To evaluate the generality of this tandem oxyphosphorylation reaction, a variety of other α,β-unsaturated systems were further employed under the standard conditions (Scheme 3). In addition to various cinnamates (**1a–1e**) (deesterification), to our delight, cinnamides (**1f–1m**) were also good substrates for this transformation *via* deamidation pathway regardless of primary, secondary or tertiary amides (entries 6–13). Meanwhile, 3-phenyl-propiolate (**1n–1o**) and 3-phenylpropiolamide (**1p–1q**) were both compatible for this transformation *via* chemoselective cleavage of C(sp)–C(CO) bonds and lead to the desired products in good yields (entries 14–17).

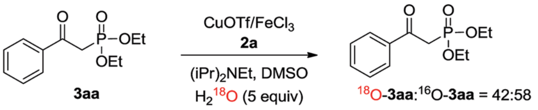
It is noteworthy that the reaction can be readily scaled up without loss of the efficiency: when **1a** (8 mmol) and **2a** (20.8 mmol) were exposed to the standard conditions, 68% (1.39 g) of desired product **3aa** was obtained (eqn (1)), which demonstrated the potential utility of this transformation in synthetic community, since β-keto-phosphonate is a key intermediate for the synthesis of various natural products such as (−)-blepharocalyxin D,[13a] (−)-diospongin B,[13b] 1-phosphono-3-azabicyclo[3.1.0] hexanes.[13c]



Scheme 3 α,β-Unsaturated compound scope. Unless otherwise noted, all reaction were run with **1** (0.5 mmol), **2a** or **2c** (1.3 mmol), CuOTf (5 mol%). $FeCl_3$ (10 mol%), $(iPr)_2NEt$ (0.5 mmol), DMSO (1 mL) in a sealed tube under O_2 atmosphere at 90 °C for 24 h. [a]80 °C, **2a** (1.5 mmol).



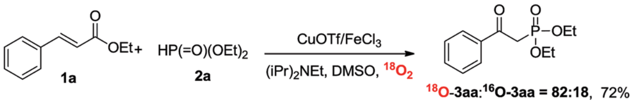
(1)



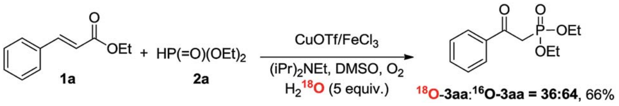
(2)

To understand the origination of the carbonyl oxygen atom of β-ketophosphonates, isotope labeling experiments were performed. Water scrambling experiment was firstly conducted with the product ^{16}O–**3aa** under the standard conditions in the presence of $H_2{}^{18}O$ (5 equiv.) to figure out the possibility of oxygen atom exchange with water, it turned out that 42% of product was incorporated by ^{18}O (eqn (2)), indicating that oxygen exchange with water occurred in the standard conditions.

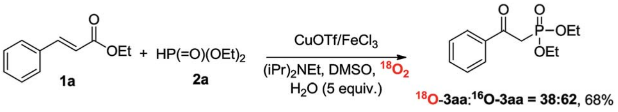
Subsequently, substrates **1a** and **2a** were performed under $^{18}O_2$ under the standard conditions, 82% of ^{18}O–labeled product **3aa** was detected (eqn (3)). When the reaction was conducted in the presence of 5.0 equiv. of $H_2{}^{18}O$ under O_2, 36% of ^{18}O–**3aa** and 64% of unlabeled products were detected with ethyl cinnamate **1a** (eqn (4)). From this reaction, we could tell that the oxygen of the carbonyl group should come from molecular oxygen. If the oxygen was from water, the ratio of ^{18}O–**3aa** : ^{16}O–**3aa** should be 5 : 1, that is *ca.* 82% ^{18}O–**3aa** should be detected since one equivalent of water was from the reaction, yet there was only 36% of ^{18}O–**3aa** was detected in the real system. Moreover, 38% ^{18}O-labeled and 62% unlabeled products were detected when the reaction of **1a** and **2a** was conducted in the presence of H_2O (5 equiv.) under $^{18}O_2$ (eqn (5)). On the basis of all above ^{18}O labeled experiments (eqn (2)–(5)), we can determine that the oxygen in carbonyl group should be exclusively from dioxygen, the low level of ^{18}O in desired product **3aa** in eqn (5) comes from the water scrambling reaction.



(3)



(4)



(5)

To elucidate and confirm our hypothesis for this oxidative radical involving tandem reaction, EPR (Electron Paramagnetic Resonance) experiments were further conducted under various reaction conditions with the addition of free radical spin trapping agent DMPO (5,5-dimethyl-1-pyrroline N-oxide). Firstly, the P-centered radical was determined by EPR since an EPR signal of phosphorous species ($A_P = 46.7$ G, $A_N = 14.3$ G, $A_{H\beta} = 18.9$ G) was detected in the reaction of **2a**, $FeCl_3$ and $(iPr)_2NEt$ in DMSO (Fig. 1a). Interestingly, no same phosphorous signal was detected in the reaction of **2a**, CuOTf and $(iPr)_2NEt$ in DMSO (Fig. 1b). These results suggested that $FeCl_3$ could promote diethyl H-phosphonate (**2a**) to generate P-centered radical, while the formation of the P-centered radical is independent on CuOTf. When DMPO was added to the reaction of **1a**, **2a**, CuOTf, $FeCl_3$ and $(iPr)_2NEt$ in DMSO, an EPR signal was observed ($A_N = 13.9$ G, $A_{H\beta} = 11.9$ G) (Fig. 1c), data analysis illustrated that it is different from the signal in Fig. 1b ($A_N = 12.9$ G, $A_{H\beta} = 10.3$ G, $A_{H\gamma} = 1.2$ G). Based on our hypothesis, we have reasons to believe that the peroxide signal in Fig. 1b is hydrogen peroxide, yet the peroxide signal in Fig. 1c should be $^{\bullet}OOR$.

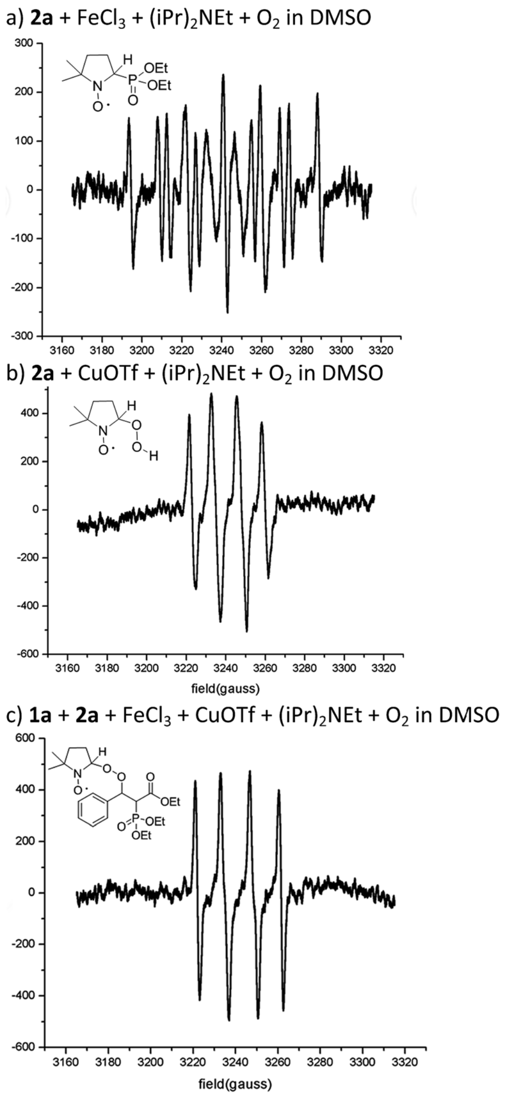
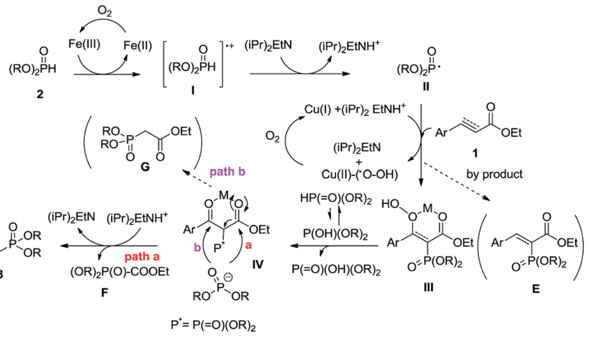


Fig. 1 The electron paramagnetic resonance (EPR) spectra of the reaction mixture under various conditions.

On the basis of all above results and previous reports,[7d,8c,16] a tentative mechanism for this tandem deesterificative or deamidative oxyphosphorylation is illustrated in Scheme 4: single electron transfers from iron(III) species to $HP(=O)(OR)_2$ in the presence of molecular oxygen, forming dialkyl phosphonate cation radical **I**. The H^+ from the dialkyl phosphonate cation radical **I** is grabbed by the base leading to dialkyl phosphonyl radical **II**. This radical is trapped by cinnamate **1** to afford an *in situ* generated C-centered radical, which further reacted with Cu(II)–($^{\bullet}$O–OH) species under dioxygen atmosphere to form hydroperoxide species **III**, trace amount of byproduct **E** was detected on GCMS, which might come from the β-hydrogen elimination. After reduction of the peroxide (one equivalent of H-phosphonate serves as reductant), α-ester-β-ketophosphonate **IV** was generated, whose existence was also proven by GCMS analysis, since a trace amount of $(OR)_2PCH_2COOEt$ **G** was detected on GCMS. Another one equivalent excess H-phosphonate acts as nucleophile to attack the carbonyl group in the ester, which also explains why *ca.* 3 equivalent of H-phosphonate was needed in order to get the optimized results (Table 1). Eventually the desired product **3** was afforded with the help of base.

In conclusion, a novel copper/iron-cocatalyzed aerobic deesterificative or deamidative oxyphosphorylation *via* cleavage of cinnamate or alkynyl carboxylate with H-phosphonates has been developed, this reaction leads to very valuable β-ketophosphonates in good yields with a broad spectrum of substrate scope. Environmentally benign catalysts system (copper and iron salts) and the use of O_2 as the oxidant plus readily available substrates make this transformation sustainable and practical. A putative mechanism is proposed on the basis of mechanistic studies, isotope labeling and EPR studies, suggesting that $FeCl_3$ was essential to generate P-centered radical which was responsible to initiate the whole process, yet the formation of the radical is independent on CuOTf, interestingly, CuOTf definitely has responsibility on the activation of molecular oxygen which was proven to be the source of the oxygen in the carbonyl group of β-ketophosphonates. Further exploration on the synthetic applications is under the way in our laboratory.



Scheme 4 Plausible reaction mechanism for oxyphosphorylation of cinnamates.

Acknowledgements

Financial support from the National Science Foundation of China (21202049), the Recruitment Program of Global Experts (1000 Talents Plan), Fujian Hundred Talents Plan, program of Innovative Research Team of Huaqiao University and Graduate innovation fund of Huaqiao Universityare gratefully acknowledged.

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