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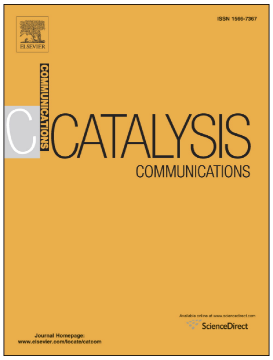

Copper ferrite nanoparticles catalyzed formation of β-Ketophosphonates via oxyphosphorylation of styrenes with H-phosphonates: A DFT study on UV–vis absorption spectra

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Copper Ferrite Nanoparticles Catalyzed Formation of β-Ketophosphonates via Oxyphosphorylation of Styrenes with H⁻ Phosphonates: A DFT study on UV-Vis absorption spectra

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Abstract: Typical copper ferrite nanoparticles ($CuFe_2O_4$) were used as a catalyst for one-pot synthesis of β-ketophosphonates via the reaction of alkenes with *H*-phosphonates under conventional heating conditions. The catalyst was prepared by using the coprecipitation method and was analyzed by physiochemical techniques. By using this catalyst system, several types of useful and new β-ketophosphonate products were obtained in very good to excellent yields under optimized reaction conditions in a novel way. Furthermore, the catalyst is recyclable and reusable from the reaction

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Keywords: oxyphosphorylation, $CuFe_2O_4$, styrenes, β-ketophosphonates, heterogeneous catalyst, DFT, UV–visible spectroscopy

1. Introduction

The construction of a C–P bond is highly important in organic synthesis, since organophosphorus compounds are important intermediates for the synthesis of many biological active compounds and natural products [1-6].

Dialkyl H-phosphonates are an important class of building blocks for the synthesis of organophosphorus compounds, which have been applied for the synthesis of β-Ketophosphonates, α-hydroxy phosphonates, bisphosphonates, alkynylphosphonates, phosphoramides, α-aminophosphonates, etc [7].

Between them, β-ketophosphonates are an enormously useful class of phosphorus-containing organic compounds, due to their bioactivity and applications in synthetic chemistry [8-10]. Because of their importance, extensive research has been performed in the development of new protocols for their preparation [11, 12].

In 2011, Ji's group found a new way to synthesize β-ketophosphonates by reacting alkenes with dioxygen and H-phosphonates in the presence of copper/iron cocatalysts (Scheme 1a) [13].

Recently, Tan Jian Gu and Chun Cai reported homogeneous catalyst for the synthesis of β-ketophosphonates. Copper/iron catalyzed phosphorylation of styrenes with the aid of DTBP (di-tert-butyl peroxide) as the oxidant (Scheme 1b) [14].

Chen and co-workers reported the synthesis of β-ketophosphonates via homogeneous catalyst $CuSO_4{\cdot}5H_2O$ in CH_3CN under open air conditions. In a sharp contrast to Song's method, the most prominent advantage of this reaction is using common and inexpensive $CuSO_4{\cdot}5H_2O$, instead of expensive CuOTf as catalyst. The advantages also include a base free condition and extensive reaction scope (Scheme 1c) [15, 16].

Exploration of new substrates for β-ketophosphonates with alkynes or alkynyl carboxylic acids under different conditions were employed [16]. Transition metal catalysts were used for the direct phosphorylation of alkynes. Zhao group reported the synthesis of β-ketophosphonates directly from alkynes and H-phosphonates in the presence of $AgNO_3/CuSO_4$ and $K_2S_2O_8$.

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Over the past few years, the use of both α,β-alkynyl carboxylic acids and α,β-alkenyl carboxylic acids as terminal alkyne and alkene equivalents, began to be developed in the literature [17]. Some advantages of α,β-alkynyl carboxylic acids and α,β-alkenyl carboxylic acids are no unpleasant smell, and easy handling and storage due to their states as solid compounds [15].

However, almost all of these methods have limitations such as recycling and reuse of the catalyst, tedious procedures, relatively harsh reaction conditions, or losing a large amount of catalyst during work-up of the reaction.

Therefore, the development of mild, convenient, efficient, and environmentally benign methods to access β-ketophosphonates is still highly desirable in synthetic chemistry.

We report the application of a highly active recyclable heterogeneous nanocopper ferrite catalyst for the oxyphosphorylation reaction of various styrenes under conventional heating conditions. Compared to previous homogenous unrecyclable catalysts, this is a low cost catalyst and prepared in a few steps from available starting materials (Scheme 1d).

On the other hand, because of its ferromagnetic nature, this catalyst completely and easily removed from the reaction, and it was possible to reuse it in consequent runs. This is a very important advantage because any remaining metal-based catalyst in the product is dangerous, particularly in cases where the end product is directly related to human life such as in pharmaceutical synthesis. Further, in comparison to ferromagnetic catalysts reported elsewhere,[18, 19] the rate of precipitation of the nanocopper ferrite catalyst on application of an external magnetic field is faster.

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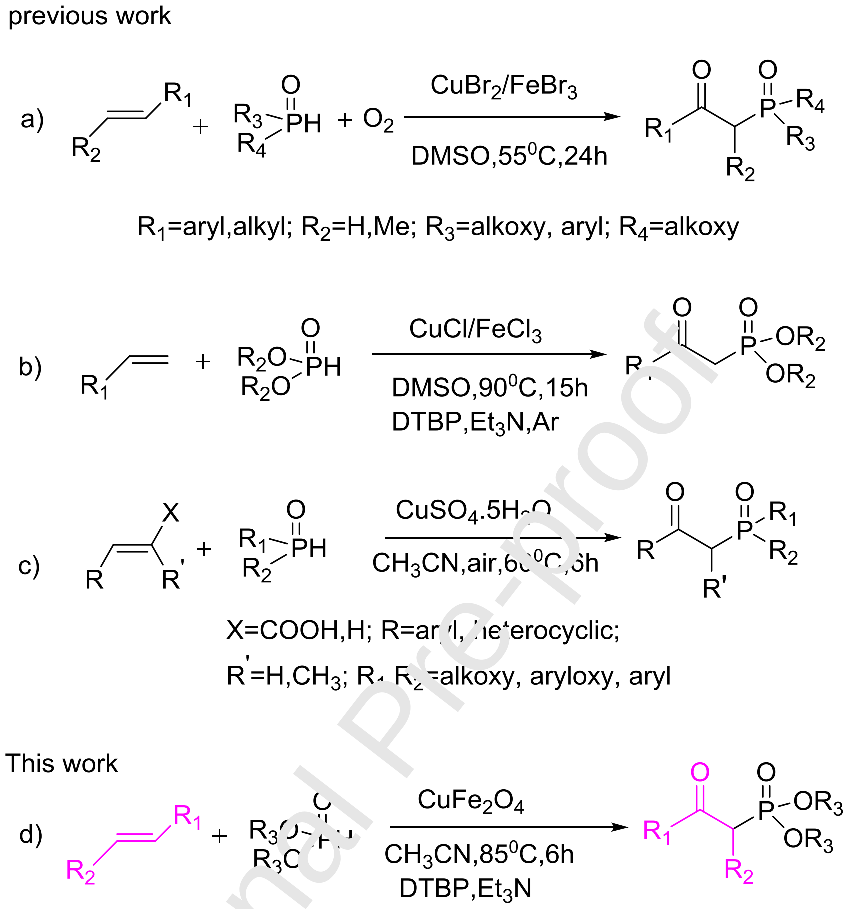

Scheme 1: Comparison of previous methods with this work.

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2. Experimental

2.1 Materials and Characterization Methods

All materials used are commercially available and were purchased from Merck and used without any additional purification. ^{1}H NMR and ^{31}P NMR spectra were recorded on a Bruker AVANCE DRX 500 MHz NMR spectrometer at RT. ^{1}H NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard and ^{31}P NMR spectra were obtained in H_3PO_4 as the internal standard. The XRF analysis was performed with a SPECTRO XEPOS spectrometer. The samples were characterized by crystallographic phase identification carried out with a Sradi P diffractometer using CuKa radiation and equipped with a graphite monochromator in the diffracted beam and an oscillation counter. FT-IR spectra of samples were obtained using an ABB Bomem MB-100 FT-IR spectrophotometer. Field emission scanning electron microscopy (MIRA3 TESCAN-RMRC) and transmission electron microscope (TECNAI F20) were used to characterize the morphologies and the particle size distribution of the nanoparticles. Magnetic measurements were performed at RT using an AGFM magnetometer.

2.2 Synthesis of Nickel/ Copper/ Cobalt Ferrite nanoparticles

The solutions of iron chloride ($FeCl_3.6H_2O$) (100 mL, 0.2 M) and nickel/ copper/ cobalt chloride ($NiCl_2.6H_2O$)/ ($CuCl_2.2H_2O$)/ ($CoCl_2.2H_2O$) (100 mL, 0.1 M) were prepared separately and mixed together. For pH to reach 13, a solution of NaOH (3M) was added slowly to the flask. Finally, oleic acid (3drops) was added to the solution as surfactant to prevent the aggregation and agglomeration of the nanoparticles. Then, the suspension was vigorously stirred using a magnetic stirring bar at 60 °C for 2 h. After complete precipitation, the residue was washed with double-distilled water (3× 25ml) and dried in an oven at 90 °C overnight. It was then calcinated at 500 °C for 3 h.

2.3 General Procedure for Synthesis of β-ketophosphonates from alkenes and H-phosphonates

A mixture of alkenes (0.5 mmol), H-phosphonates (1.5 mmol), $CuFe_2O_4$ (10 mol%), DTBP (1.0 mmol), and Et_3N (0.5 mmol) in CH_3CN (1.0 mL) was stirred at 85 °C for 6 h. The reaction was monitored by TLC plate and, after the completion of the reaction, the mixture was cooled to room temperature. The magnetic nanoparticles of the catalyst were collected with the help of a magnet. Then, 10 mL of water was added to the mixture and the product was extracted with ethyl

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acetate (4 × 10 mL). The organic layer was separated, washed with brine, and dried over Na_2SO_4. The volatiles were removed under vacuum to afford the crude product. The crude product was purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1:1) to afford the desired phosphonate as a yellow oil.

3. Results and discussion

Copper ferrite nanoparticles were synthesized using the coprecipitation method described in the Experimental Section. The activity of the copper ferrite nanoparticles in the β-ketophosphonates synthesis was investigated under conventional heating conditions.

The structures of catalysts were characterized using various physicochemical techniques including FT-IR, EDS, XRD, VSM, FE SEM, and TEM analysis.

Figure S1. shows the FT-IR spectrum of copper ferrite nanoparticles, in the range of 450-4,000 cm^{-1}. The spectrum presents characteristic bands at 3434, 540, and 470 cm^{-1}. The broad band at 3,434 cm^{-1} can be assigned to the absorbed water. The peaks at 470 and 540 cm^{-1} are assigned to the vibration of Fe-O and Cu-O bond, respectively, which confirm the structure of copper ferrite nanoparticles.

The XRD patterns of the copper ferrite nanoparticles are shown in Figure S2. The XRD patterns of catalyst indicating a particle size of 47.7 nm are calculated by the broadening of the most intense peak at 2θ= 35.75 using the Debye-Scherrer equation, which is in agreement with the average particle size obtained from TEM (Figure S3).

The magnetic properties of the nanoparticles were investigated at room temperature. According to the magnetization curve of the sample shown in Figure S4, $CuFe_2O_4$ nanoparticles have a

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superparamagnetic behavior with a small coercivity and can be easily attracted by a small external magnet.

The energy dispersive spectrum (EDS) shows the presence of Cu, Fe, and O in the catalyst structure (Figure S5).

To optimize the reaction conditions, various types of solvents and bases at different temperatures in the presence of various amounts of catalyst were surveyed in the reaction between the model substrates styrene and diethyl phosphite. The results are summarized in Table 1.

First, we performed an oxidant screening (entries 1-6). Oxidants such as O_2, $K_2S_2O_8$, DTBP, and H_2O_2 were examined. The result showed that the metal catalyst and DTBP were crucial for the reaction. As the next optimization step, a variety of ferrite nanoparticles were investigated, with the finding that copper ferrite nanoparticles were the optimal choice for the reaction (entries 7-8). In fact, the presence of copper was critical to the success of this oxyphosphorylation reaction and no product was detected when nickel ferrite was used as catalyst (entry 8).

Furthermore, to improve the efficiency of the reaction, different bases were investigated under the same reaction conditions (entries 9-12). According to the results obtained, Et_3N shows the best reactivity and was chosen as the optimal base for this reaction.

Then, the effects of various polar and nonpolar solvents in this reaction were studied (entries 13–22). No product was detected when the reaction was performed in water and ethanol as green solvents (entries 18 and 20). Therefore, CH_3CN as a polar aprotic solvent was selected for performing the reaction.

Finally, the influence of temperature on the reaction was also investigated (entries 3, 23-24). The reaction efficiency was affected by the temperature, and 85 °C was found to be the optimal temperature for this reaction with higher conversion (entry 3).

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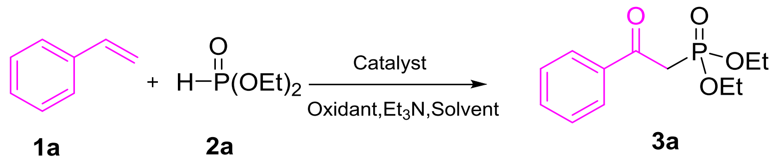
Table 1. Optimization of the reaction conditions[a]



Entry	Catalyst	Oxidant	Solvent	T (°C)	Base	Yield[b] (%)
1	$CuFe_2O_4$	-	CH_3CN	85	Et_3N	45
2	$CuFe_2O_4$	O_2	CH_3CN	85	Et_3N	55
3	**$CuFe_2O_4$**	**DTBP**	**CH_3CN**	**85**	**Et_3N**	**80**
4	$CuFe_2O_4$	$K_2S_2O_8$	CH_3CN	85	Et_3N	59
5	$CuFe_2O_4$	H_2O_2	CH_3CN	85	Et_3N	56
6[c]	$CuFe_2O_4$	DTBP	CH_3CN	85	Et_3N	81
7	$CoCuFe_2O_4$	DTBP	CH_3CN	85	Et_3N	77
8	$NiFe_2O_4$	DTBP	CH_3CN	85	Et_3N	NR
9	$CuFe_2O_4$	DTBP	CH_3CN	85	-	40
10	$CuFe_2O_4$	DTBP	CH_3CN	85	Et_2NH	42
11	$CuFe_2O_4$	DTBP	CH_3CN	85	DABCO	38
12	$CuFe_2O_4$	DTBP	CH_3CN	85	DIPEA	85
13	$CuFe_2O_4$	DTBP	DMF	85	Et_3N	35
14	$CuFe_2O_4$	DTBP	DMSO	85	Et_3N	45
15	$CuFe_2O_4$	DTBP	Toluene	85	Et_3N	28
16	$CuFe_2O_4$	DTBP	1,4-dioxane	85	Et_3N	40
17	$CuFe_2O_4$	DTBP	DCE	85	Et_3N	78
18	$CuFe_2O_4$	DTBP	H_2O	85	Et_3N	NR
19	$CuFe_2O_4$	DTBP	THF	66	Et_3N	65
20	$CuFe_2O_4$	DTBP	EtOH	78	Et_3N	NR
21	$CuFe_2O_4$	DTBP	EtOAC	77	Et_3N	65
22	$CuFe_2O_4$	DTBP	$CHCl_3$	60	Et_3N	70
23	$CuFe_2O_4$	DTBP	CH_3CN	r.t	Et_3N	NR
24	$CuFe_2O_4$	DTBP	CH_3CN	45	Et_3N	30

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.5 mmol), catalyst (10 mol%), base (0.5 mmol), solvent (1 mL), oxidant (1 mmol), 6 h. [b] Isolated yield. [c] Oxidant (2 mmol). NR = no reaction

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Having these optimized reaction conditions in hand, we next examined the scope of the phosphorylation of alkenes with H-phosphonates for the synthesis of β-ketophosphonates (Table 2).

As illustrated in Table 2, a variety of β-ketophosphonates can be conveniently and efficiently obtained by these copper ferrite nanoparticles in the oxyphosphorylation reaction of alkenes. In general, both electron-donating and electron-withdrawing substituents at the phenyl ring of styrene were suitable for this transformation and the corresponding oxidative coupling products were obtained in very good to excellent yields (**3a**–**3o**).

The electronic effects of the substituents attached to phenyl rings had no noticeable effect on the efficiency of oxyphosphorylation reactions. Bromo and chloro groups at the phenyl ring of styrene are useful for further functionalization at a later stage using cross coupling reactions (**3i**–**3l**). Fluorine has been recognized as an important element in materials science, and many fluorine-containing biologically active agents are finding applications as pharmaceuticals and agrochemicals (**3g**–**3h**). Additionally, stilbene was also a suitable substrate for this reaction, which highlights the potential application of this method (**3o**).

Table 2. Scope of the oxyphosphorylation of alkenes with H-phosphonates[a]

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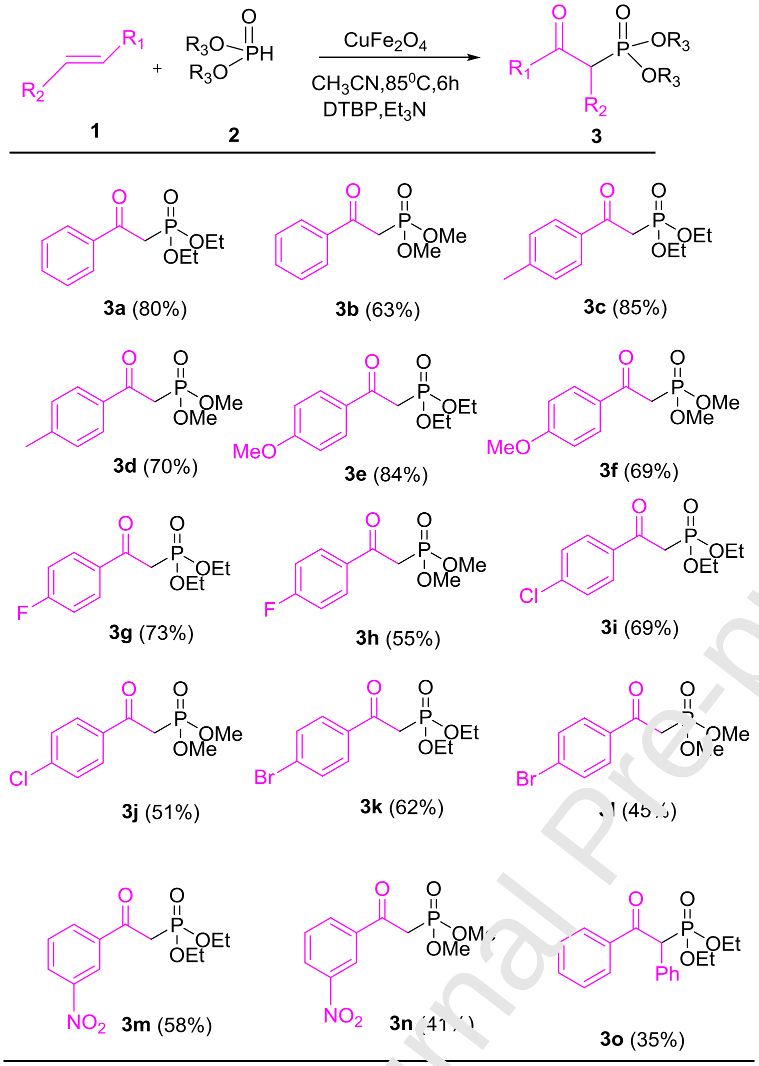

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.5 mmol), catalyst (10 mol%), base (0.5 mmol), solvent (1 mL), oxidant (1 mmol), 6 h. [b]all isolated yields

To determine if the oxyphosphorylation of alkynes and allylic compounds was feasible, we extended our study to phenylacetylene and safrole under the optimized reaction conditions. CuFe$_2$O$_4$ catalyzed oxyphosphorylation of phenylacetylene leading to β- ketophosphonates (**3p-3q**) [Eq. (S2)]. Surprisingly, through the reaction between safrole and dialkyl *H*-phosphonates, two unexpected products (**3r-3s**) were isolated which have not been reported to date [Eq. (S3)]. Further studies on mechanistic details and other substrates are currently underway in our group.

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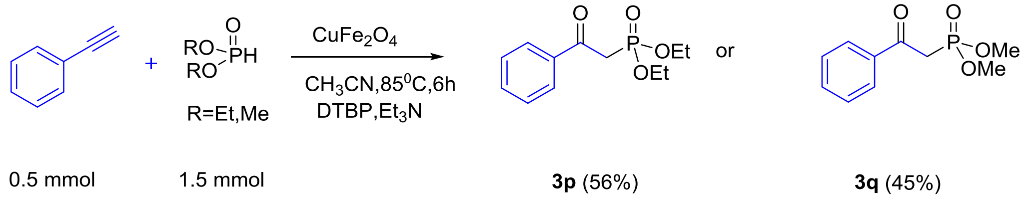
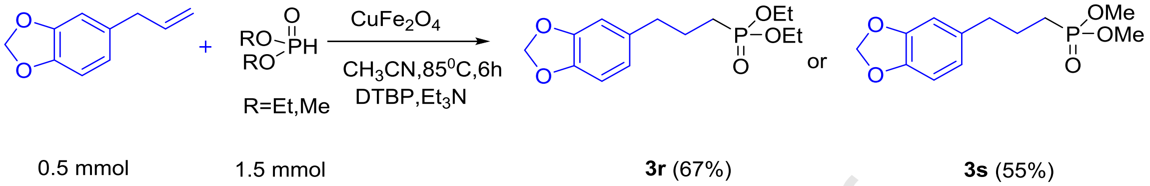


(S2)



(S3)

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To check the reusability of the catalyst, the oxyphosphorylation of styrene with diethyl phosphite was performed under the optimized reaction conditions. First, catalyst was recovered from the reaction mixture by a magnetic rod, washed twice with water, and dried in an oven at 100 ^{0}C. Then, recovered nanoparticles were employed in another run under the same reaction condition. This process was repeated six times, and each time the isolated yield was measured exactly. The results indicate that no considerable loss of activity was observed up to 6 cycles (Figure S6).

In order to study the surface morphology of the catalyst, FE SEM images were obtained (Figure 1). The FE SEM images of the catalysts before and after six runs of the reaction were obtained to confirm that the size, morphology, and dispersity of the nanoparticles were not approximately transformed during these runs. According to the images, it is obvious that the activity, efficiency, and morphology of the catalyst remains constant.

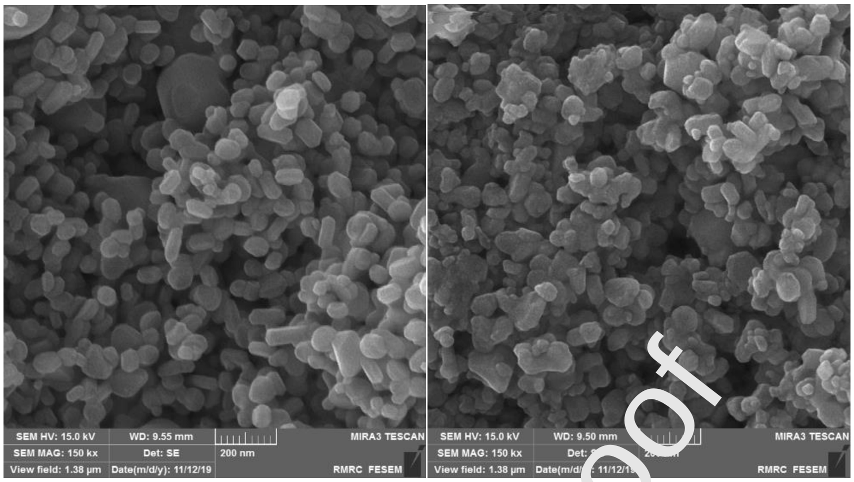

Figure 1. The FE SEM images of $CuFe_2O_4$ nanoparticles before employing as catalyst (left) and after six times reuse (right).

In order to gain reasonable insight into the reaction mechanism, radical trapping experiments were performed [Eq. (S1)]. By employing 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-di-tert-butyl-4-methylphenol (BHT) as radical scavengers along with styrene and diethyl phosphite under the standard conditions, the reaction was totally suppressed.

We interpret these results as evidence that our transformation occurs through a radical mechanism.

On the basis of the above control experiments and previous reports, a plausible mechanism for this catalytic reaction is proposed in Scheme 2.

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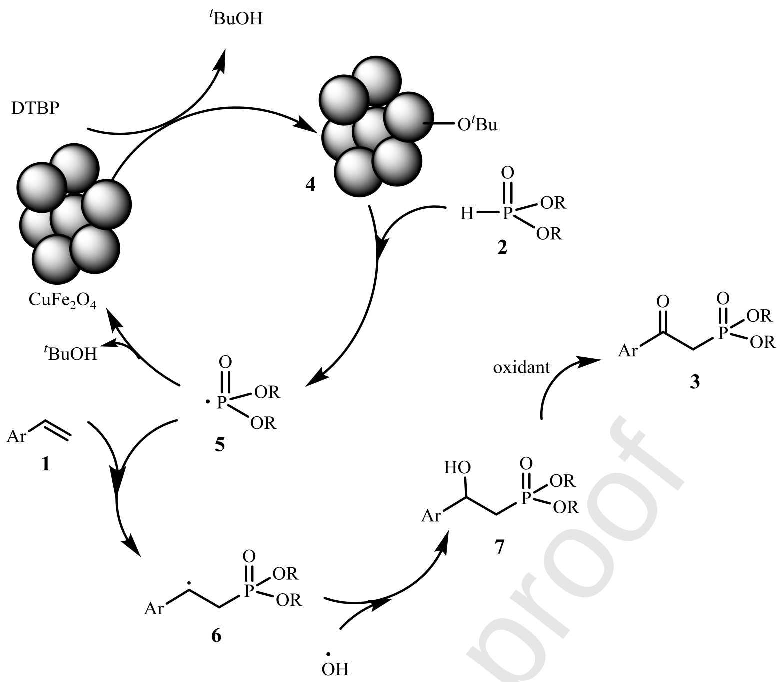

Scheme 2. Proposed mechanism.

First, DTBP reacts with copper ferrite to form intermediate **4** which adds to dialkyl phosphonate, and phosphonyl radical **5** is generated. Subsequently, addition of the phosphonyl radical **5** to the double bond of alkenes **1** produces the alkyl radical **6,** and copper ferrite was regenerated to continue the catalytic cycle. Because the reaction temperature is 85 °C, the formed radical **6** interacts with the hydroxyl radical. Finally, the intermediate **7** would undergo oxidation to give the desired product **3**.

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Conclusion

In summary, oxyphosphorylation of alkenes was performed successfully using ferromagnetic copper ferrite nanoparticles as a very efficient heterogeneous catalytic system.

The proposed conditions applied here for the oxyphosphorylation of alkenes compared to previous reports using homogeneous catalytic systems lead to a more convenient procedure and better yields. β-ketophosphonates are important intermediates for the synthesis of many biologically active compounds and natural products such as (-)-diospongin in the synthetic community [13]. By employing inexpensive, recyclable, and reusable ferromagnetic copper ferrite nanoparticles as catalyst, our transformation is both sustainable and practical.

Acknowledgement

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Manuscript title:

Copper Ferrite Nanoparticles Catalyzed Formation of β-Ketophosphonates via Oxyphosphorylation of Styrenes with H‐ Phosphonates: a DFT study on UV-Vis absorption spectra

1) **Firouz Matloubi Moghaddam:** Conceptualization, Methodology, Funding acquisition, Project administration, Validation (Corresponding Author).
2) **Maryam Daneshfar:** Investigation, Formal analysis, Software, Data Curation, Writing - Original Draft (First Co-Author).
3) **Reza Azaryan:** Resources, Visualization, Writing - Review and Editing (Second Co-Author).

4) **Jean-Luc Pirat:** Supervision (Third Co-Author).

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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- One-pot synthesis of β-ketophosphonates using a heterogeneous catalyst.
- Broad substrate scope and wide functional group tolerance.
- Formation of products in excellent yields and short reaction times.
- Recyclable and reusable catalyst without loss of activity.

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