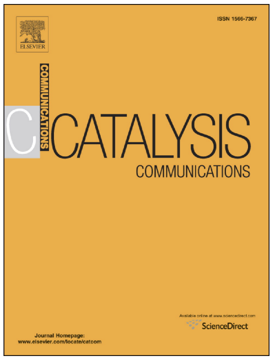

Copper porphyrin as efficient catalysts for esterification of allyl sp3 C-H bond with carboxylic acid

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Copper Porphyrin as Efficient Catalysts for Esterification of Allyl sp^3 C–H Bond with Carboxylic Acid

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ABSTRACT

We described that copper 5,10,15,20-tetrakis (ethoxycarbonyl)porphyrin (TECP) catalyzed oxidative cross dehydrogenative coupling of allyl sp^3 C–H bond with acid for the synthesis of allyl esters in a homogeneous system. This reaction proceeded with broad substrate scope and good functional group tolerance. In the gram-level test, the turnover number (TON) reached to 8100 at 0.01 mol% catalyst loading, with 81% yield.

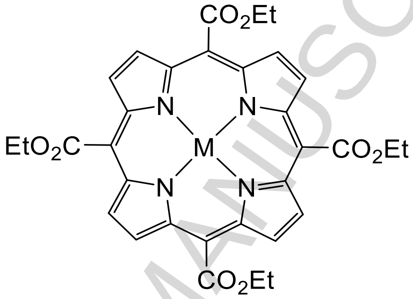
Keywords: Porphyrin, Copper, Cross dehydrogenative coupling, Allylic esterification

1. Introduction

Allylic esters are versatile key motifs with extensive applications in synthesis and importantly as ubiquitous cores in many natural products [1], pharmaceutical molecules, and fine chemicals [2, 3]. Therefore, continuous interests have been shown in the access of efficient, convenient, straightforward, and highly atom-economic methods for the synthesis of allylic esters through C-X (C, O, N, etc.) bond construction in recent years [2, 4]. The synthesis of allylic esters by direct oxidative cross dehydrogenative coupling (CDC) using allylic C–H substrates and acids as the starting materials is more atom-economic than by tandem C–H oxidative esterification between acid precursors (aldehydes, arylmethanes, alkenes, or alkynes) and alkenes [5-7]. Many transition metal catalysts such as iron [8], cobalt [9], copper [10, 11], copper-aluminum [12], and tetrabutylammonium iodide [13] have been developed for the esterification of allylic sp^3 C–H bond. However, the catalyst loadings are generally higher than 10 mol% in these systems and with the drawback of poor regioselectivity, diastereoselectivity, and enantioselectivity.

Metal porphyrin complex, as a bioinspired catalyst [2, 14], exhibits remarkable catalytic efficiency in many reactions such as oxidation [14, 15], radical hydrofunctionalization of olefins [16], nitrene [17], alkylation [18], carbene C–H insertions, and asymmetric synthesis [19-21]. Much efforts have been made to enhance the catalytic efficiency [22], regioselectivity [23], diastereoselectivity, and enantioselectivity [20] to achieve a significant breakthrough in these reactions. Despite that metal porphyrin-catalyzed reactions are very well documented, the utilization of metal porphyrin catalysts in CDC reactions is rarely explored. In 2013, Che and his co-workers used Pd (II) porphyrin as a catalyst (0.05 mol%) in the photochemical CDC reaction of tertiary amines and dimethyl malonate or diethyl phosphite [22]. Two years later, Guo had also reported the application of copper porphyrin to achieve aerobic oxidative CDC of terminal alkynes

[24]. Yuan reported cobalt corrolazine-catalyzed aerobic CDC of sp^2 C-H and thiols for C-S bond formation in water [25]. 5,10,15,20-Tetrakis (ethoxycarbonyl)porphyrin (TECP) is a kind of electron-deficient flat macrocyclic ligand [26, 27]. Manganese TECP was found recyclable with a high conversion efficiency in the oxidation of styrene using TBHP as oxidant [28]. Recently, we had successfully used TECP copper [29] and iron [30] complex in (CDC) esterification reaction between 1,4-dioxane C(sp^3)–H and carboxylic acids. To further our study along this line, here we report the CDC esterification reaction between allyl C(sp^3)–H and benzoic acid derivatives. Manganese, iron, cobalt, nickel, copper, palladium, and silver TECP complexes had been used in the screening tests (Scheme 1), of which only iron and copper TECP exhibited catalytic activity. Surprisingly, in the gram-level test, when CuTECP catalyst loading was 0.01 mol% using DTBP as oxidant at 100 ℃ for 72 h, TON of oxidative coupling of benzoic acid and cyclohexene sp^3 C–H bonds was up to 8100 with 81% yield, demonstrating the highest TON of this reaction recorded thus far [8-10, 12, 13]. Furthermore, we had also checked the scope of benzoic acid derivatives and regioselectivity of allylic esterification by using asymmetric olefins.



M=Mn, Fe, Co, Ni, Cu, Pd, Ag

Scheme 1. Molecular structure of metal TECP

2. Experimental Procedures

2.1 Materials and methods

All reagents were of commercial grade and purified according to the established procedures, and solvents were of analytical purity. Extracts were dried over anhydrous sodium sulfate. All solvents were concentrated in a rotary evaporator under vacuum, and the resulting residue was purified using a silica gel column. UV–Visible absorption spectra were measured using a Hitachi 3900H spectrometer in a quartz cell of 1 cm optical path length at room temperature. NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^{1}H NMR (400 MHz) and ^{13}C NMR (100 and 150 MHz). HRMS spectra were recorded using a Bruker maXis impact mass spectrometer with an ESI source.

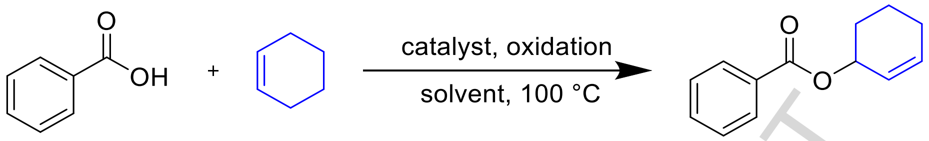
2.2 Synthetic procedure

Benzoic acids **1** (0.5 mmol), alkene **2** (5 mmol), DTBP (1 mmol), CuTECP (0.1 mol%), and benzene (1 mL) were added to a Schlenk tube and stirred at 100 ℃ for 24 h. The reaction mixture was concentrated to remove solvent in a rotary evaporator after the Schlenk tube was cooled to room temperature. The crude products were purified by silica gel (300-400 mesh size) column chromatography (hexane/ethyl acetate = 50:1).

3. Results and discussion

Table 1

Optimization of Reaction Condition. [a]



1 a 1a

Entry	Cat. (mol%)	Oxidant (equiv.)	time (h)	Yield [b]	TON
1	CuTECP (2.5)	DTBP (2.0)	4	99%	39.6
2	CuTECP (0.5)	DTBP (2.0)	12	95%	190
3	CuTECP (0.1)	DTBP (2.0)	24	91%	910
4	CuTECP (0.01)	DTBP (2.0)	72	80%	8000
5	CuTECP (0.5)	TBHP (2.0)	12	50%	100
6	CuTECP (0.5)	*m*-CPBA (2.0)	12	N.D. [c]	
7	CuTECP (0.5)	Oxone (2.0)	12	N.D.	
8	CuTECP (0.5)	PhIO (2.0)	12	N.D.	
9	CuTECP (0.5)	H_2O_2 (2.0)	12	N.D.	
10	FeTECPCl (0.5)	DTBP (2.0)	12	80%	160
11	$(FeTECP)_2O$ (0.5)	DTBP (2.0)	12	75%	150
12	AgTECP (0.5)	DTBP (2.0)	12	Trace	
13	MnTECPCl (0.5)	DTBP (2.0)	12	Trace	
14	CoTECP (0.5)	DTBP (2.0)	12	Trace	
15	NiTECP (0.5)	DTBP (2.0)	12	Trace	
16	PdTECP (0.5)	DTBP (2.0)	12	Trace	
17		DTBP (2.0)	12	N.D.	

[a] Reaction condition: benzoic acid (0.5 mmol), cyclohexene (5 mmol), catalyst CuTECP (0.1 mol%), and benzene (1 mL) at 100 ℃ for 24 h. [b] isolated yield based on carboxylic acid. [c] not detected. DTBP = di-*tert*-butyl peroxide. TBHP = *tert*-butyl hydroperoxide (70% in H_2O). *m*-CPBA = 3-chloroperbenzoic acid. H_2O_2 (30% in H_2O). Oxone = potassium peroxymonosulfate.

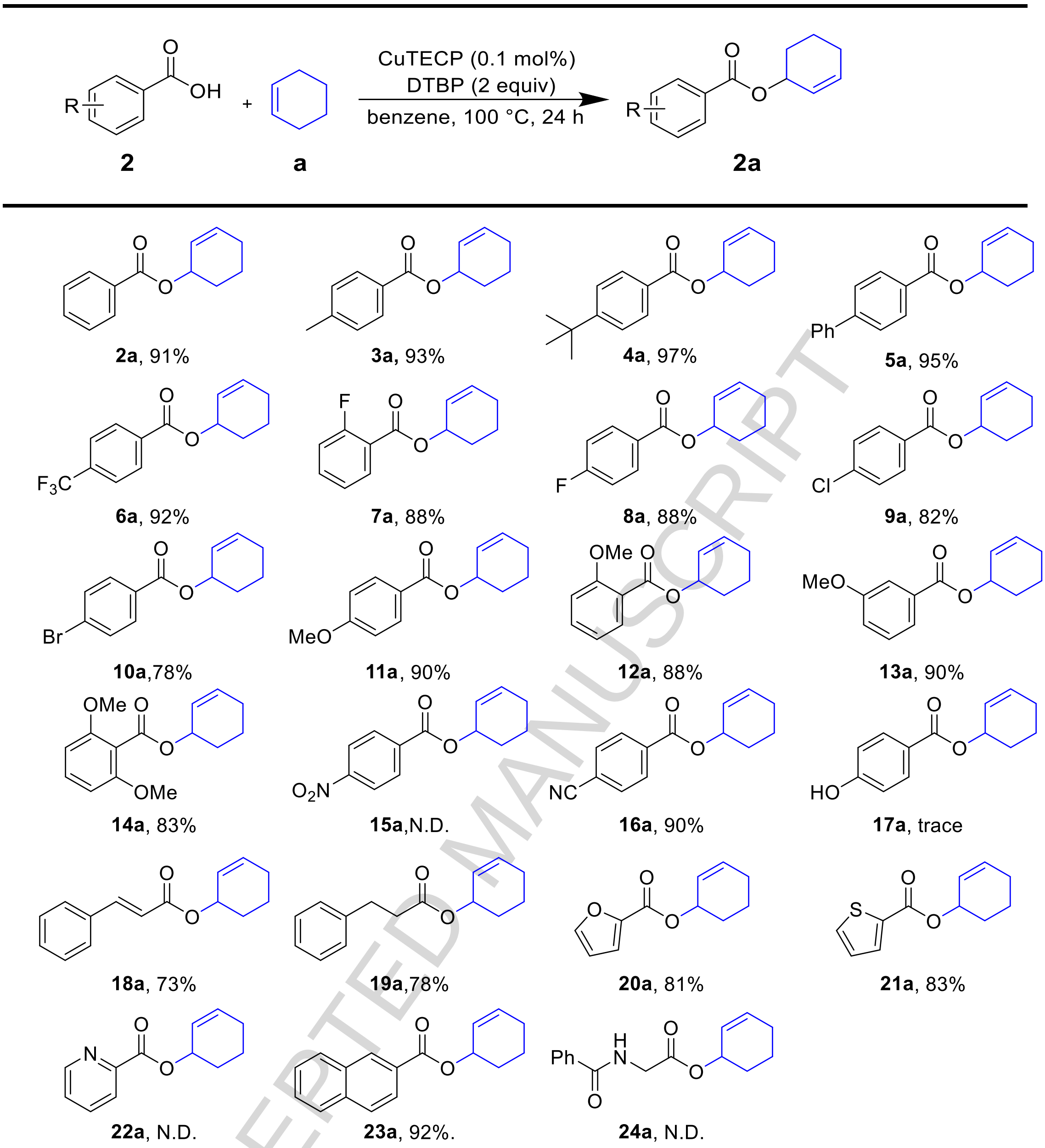
As seen in Table 1, the oxidative dehydrogenation coupling of benzoic acid and cyclohexene was selected as a model to investigate the catalytic activity of MTECPs (M = Mn, Fe, Co Ni, Cu, Pd, and Ag). Cyclohex-2-en-1-yl benzoate was observed to be the main product when FeTECPCl or CuTECP was used as the catalyst at 100 ℃ and DTBP as the oxidant. When the catalyst loading of CuTECP was 2.5 mol% (*vs*. benzoic acid), **1a** was obtained with an isolated yield of 99% in 4 h (Table 1, entry 1). When the concentration of catalyst loading was decreased to 0.5 mol%, the isolated yield of **1a** still reached to 95% after 12 h (Table 1, entry 2). To our surprise, the reaction of acid and cyclohexene in the presence of a catalytic amount of CuTECP (0.1 mol%) produced 2-cyclohexenyl benzoate **1a** with a yield of 91% in 24 h (Table 1, entry 3). These preliminary results motivated us to further decrease the catalyst loading to 0.01 mol%, and we found that **1a** was still obtained with an 80% yield with 8000 TON (Table 1, entry 4). Using TBHP instead of DTBP, the yield sharply dropped to 50% (Table 1, entry 5). When TBHP was replaced with some stronger oxidants such as *m*-CPBA, Oxone, PhIO, H_2O_2, and $PhI(OAc)_2$, no products were detected and the substrates were completely decomposed (Table 1, entries 6–9). When Mn, Fe, Co, Ni, Pd, and Ag-TECP catalysts were employed to catalyze the reaction with 0.5 mol% catalyst loading, only FeTECPCl and FeTECP-*μ*-oxo afforded **1a** with 80% and 75% yield, respectively. The other M-TECP complexes yielded trace product (Table 1, entries 10-16). As seen in Table S1, when catalysts were copper chloride and copper acetate with the same catalyst loading (0.1 mol%), the yield of **1a** was 21% and 25%, respectively. When CuTPP was used as the catalyst, 63% yield was obtained. With the increase of Lewis acidity of the catalyst, the yield of $CuF_{20}TPP$ was up to 74%. As we all know, the product **1a** was not observed in the absence of catalysts (Table 1, entry 17). This indicated that CuTECP had much better catalytic performance.

With the above optimized conditions in hand, the effects of catalyst concentration, solvent effect, reaction temperature, and cyclohexene concentration on the reaction results were investigated as shown in Table S1. The yield elevated from 87% to 92% with the increasing amount of oxidant from 1.5 to 3.0 equivalents. By screening common solvents for CDC reaction, we found that benzene had the best solvent effect compared with acetonitrile, acetone, dichloroethane, and chlorobenzene on catalyzing allyl esterification, and the highest yield was 92% with 0.1 mol% catalysts in 24 h. Unfortunately, the yield decreased when the reaction was performed at 80 °C, and no significant improvement in the yield was observed at 120 °C.

Under optimized reaction conditions (Table 1, entry 3), we subsequently explored the scope of acids in the CuTECP-catalyzed CDC allylic esterification reaction. Both electron-donating and -withdrawing aryl carboxylic acids reacted with cyclohexene and produced very good yields of the products of allyl esterification, as shown in Table 2. When the benzoic acid bears electron-donating groups, the yields were almost above 90% (**2a-5a**). The electron-withdrawing substituents obviously lower the yields (**6a-10a**). The monosubstituted group had no obvious effect on the yield of the corresponding products in ortho-position, meta-position, and para-position (**11a-13a**), but when there were two substituted groups in the ortho-position, the yield of allyl esterification decreased slightly (**14a**). In addition, the yield was 90% when the substituents were cyano (**16a**). However, in the presence of phenolic hydroxyl groups, pyridyl groups, or protected amino in the substrates, the esterification reaction could not proceed normally, possibly due to the strong axial coordination of heteroatoms and CuTECP (**15a**, **17a, 22a, 24a**). *Trans*-cinnamic acid, 3-phenylpropanoic acid, and other aryl carboxylic acids such as 2-furoic acid and 2-thiophene carboxylic acid afforded products of esterification in good yield (**18a-21a, 23a**).

Table 2

CuTECP-catalyzed CDC reaction of acids with cyclohexene. [a]



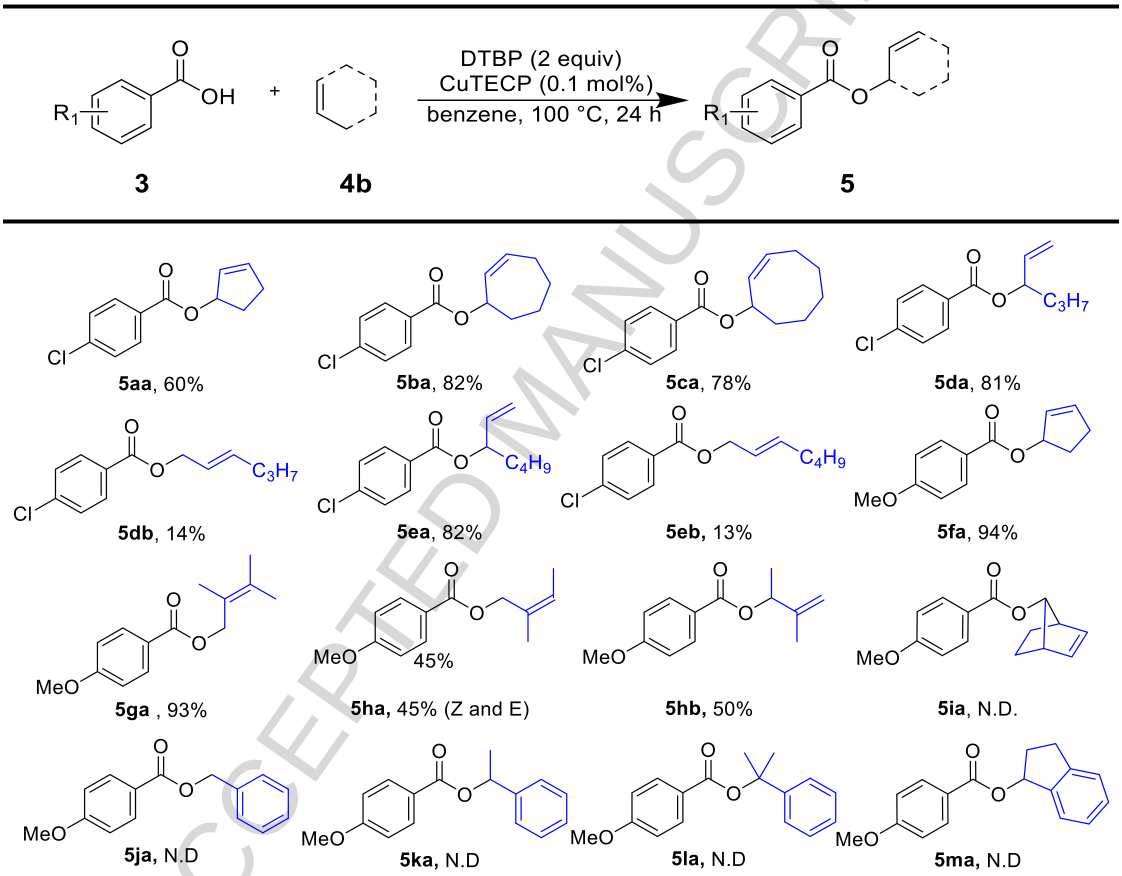
[a] Reaction condition: benzoic acid (0.5 mmol), cyclohexene (5 mmol), catalyst CuTECP (0.1 mol%), and benzene (1 mL) at 100 °C for 24 h. N.D. = not detected.

To further explore the potential of our methodology, the substrate scope of various alkenes was explored, as shown in Table 3. The reaction of cyclopentene with 4-chlorobenzoic acid was achieved to the corresponding esterification products (**5aa**) in 60% yield. Similarly, the esterification products of expanded cyclic olefin substrate cycloheptene and cyclooctene were obtained in good yields (**5ba-5ca**). Comparatively, the esterification yield of 4-methoxy benzoic acid and cyclopentene was 94% (**5fa**). Notably, 2,3-dimethylbut-2-ene exhibited very high selectivity, merely affording the mono-esterification product **5ga** with a yield of 90%. Reactions of asymmetric alkene such as hex-1-ene and hept-1-ene with acids proceeded smoothly with regioselectivity of 5.7 to 1 and 6.1 to 1, respectively (**5da-5db, 5ea-5eb**). Interestingly, when

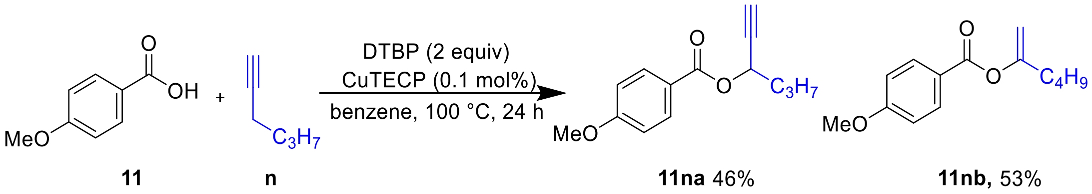
2-methylbut-2-ene reacted with 4-methoxybenzoic acid, 2-methylbut-2-en-1-yl 4-methoxybenzoate *cis-trans* isomers, and 3-methylbut-3-en-2-yl 4-methoxybenzoate were afforded at a ratio of 1 to 1.15 (**5ha-6ha**). With decreasing C-H bond strength, esterification products **5ja-5ma** were not detected because of a large number of byproducts. When norbornene was used as a substrate, esterification product **5ia** was not produced after 24 h with a large amount of benzoic acid remained. It is noteworthy, the reaction of hex-1-yne and 4-methoxy benzoic acid produced 46% **11na** and 53% **11nb** (Scheme 2) [31]. In addition, a gram-level reaction experiment was carried out for benzoic acid and cyclohexene CDC reaction: TON reached to 8100 with 0.01 mol% catalyst loading (Scheme 3).

Table 3.

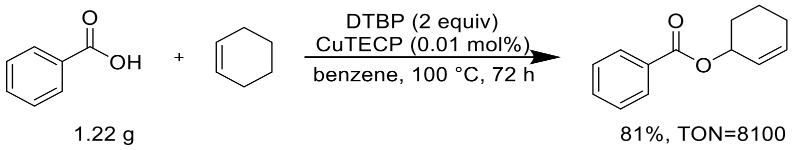
Esterification of benzoic acid with various alkenes. [a]



[a] Reaction condition: benzoic acid (0.5 mmol), alkene (5 mmol), catalyst CuTECP (0.1 mol%), and benzene (1 mL) at 100 °C for 24 h. N.D. = not detected.

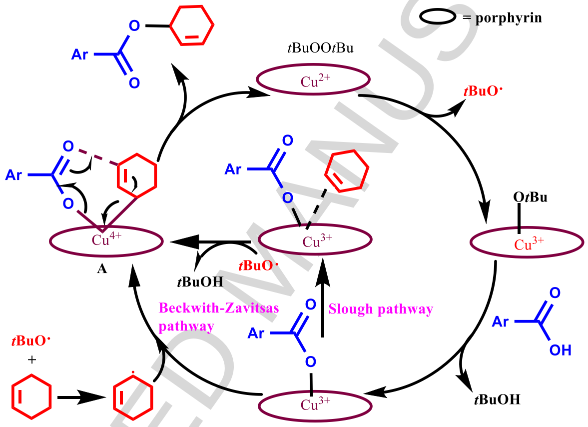


Scheme 2. Propargylic esterification of 4-methoxy benzoic acid and hex-1-yne.



Scheme 3. Gram-level reaction

Further experiments were conducted to elucidate the mechanism of the allylic esterification. The reaction of sodium benzoate and cyclohexene did not result in the formation of allylic ester **2a** (Scheme S1), which indicated that the reaction of a carboxylate anion and allyl cation was not involved in the allyl ester synthesis. When benzoyl peroxide was used as a substrate and oxidant for the reaction, the reaction generated allyl esterification products in moderate yield (Scheme S2). We succeeded to block this reaction by using radical scavengers butylated hydroxytoluene (BHT) or 2,2,6,6-tetramethylpyridine *N*-oxide (TEMPO) (Scheme S3), suggesting that the oxidative coupling reaction proceeded through the formation of an allylic radical intermediate.



Scheme 4. Proposed mechanism for allylic esterification.

In fact, the current reaction was found to follow Kharasch–Sosnovsky Reaction [32, 33]. According to the previous investigations on the mechanism of this reaction [34], there are three pathways to generate the key high-valent allyl-copper intermediate, which will result in the release of allylic ester: Beckwith–Zavitsas mechanism, Slough mechanism, and synergistic coordination mechanism. As free radical scavengers could block the reaction effectively, synergistic coordination mechanism may not play a key role in the present system. Suggested reaction mechanism is depicted in Scheme 4. TECPCu(II) catalyzed the splitting of DTBP to generate TECPCu(III)O*t*Bu and *t*BuO free radical. TECPCu(III)O*t*Bu then reacts with carboxylic acid to produce TECPCu(III)O_2CR, which will further turn into higher valent Cu(IV) intermediate A through the Beckwith–Zavitsas or Slough pathway and finally release the target product to complete the catalytic cycle. It should be pointed out that the reaction mechanism still needs more investigations, and the capture of these transient high-valent copper porphyrin intermediate species is a great challenge.

4. Conclusions

In summary, a series of metal complexes (Mn, Fe, Co, Ni, Cu, Pd, and Ag) of TECP were prepared and tested for the catalytic oxidative coupling of carboxylic acids and allylic sp^3 C–H bond for the synthesis of allylic esters. It was observed that CuTECP and FeTECP were effective for this CDC reaction, while the other tested metal complexes of TECP were not effective. Interestingly, in the gram-level test (0.01 mol% CuTECP catalyst loading at 100 °C, with DTBP as the oxidant), TON of the CDC reaction was up to 8100. The reaction proceeded smoothly with highly broad substrate scope and good functional group tolerance comprising various carboxylic acids, symmetric alkenes, asymmetric alkenes, and alkynes. In addition, the regioselective esterification of asymmetric alkene was also explored. CuTECP-catalyzed oxidative esterification of allylic C(sp^3)-H bond and acid progressed by a radical mechanism. Further studies on metal porphyrin-catalyzed asymmetric CDC reactions of C–O and C–C bond are currently underway in our laboratory.

Acknowledgments

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Appendix A. Supplementary data

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1. Metalloporphyrin catalyzed cross dehydrogenative coupling reaction.
2. Esterification of allyl sp^3 C–H bond with carboxylic acid using copper porphyrin.
3. Broad substrate scope and good functional group tolerance.
4. The best TON reached to 8100 with 81% yield under gram-level testing.