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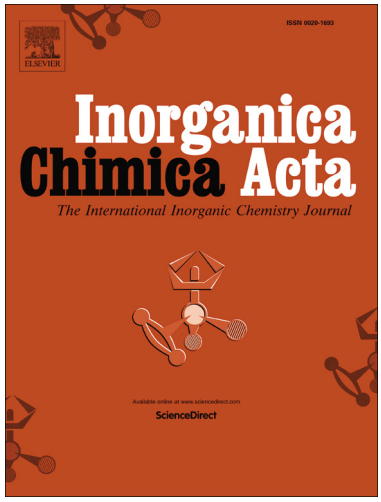

Research paper

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Copper-Catalyzed Oxidative Dehydrogenative Functionalization of Alkanes to Allylic Esters

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Abstract. Herein, we report a general, efficient and solvent-free method for the one-pot synthesis of allylic esters via dehydrogenation of unactivated alkanes and subsequent oxidative cross coupling with different substituted carboxylic acids. A simple, well defined and air stable Cu(II)-complex, [Cu(MeTAA)], featuring a tetraaza-macrocyclic ligand (tetramethyltetraaza[14]annulene (MeTAA)) is used as the catalyst. A wide variety of substituted allylic esters were synthesized in high yields starting from readily available starting materials. Control reactions were carried out to understand the reaction sequence and the plausible mechanism.

Introduction. Esters are common functional motifs found in many naturally occurring and synthetic organic compounds [1]. They are used as bulk chemicals in pharmaceutical and polymer industries [2]. They are also widely applied in synthetic organic chemistry as versatile intermediates for further synthetic transformations. Consequently, significant effort has been devoted over the years for the development of practical and efficient methods for ester synthesis [3-5]. Esters are usually synthesized via the reaction of acids and their derivatives (acyl chlorides and anhydrides) with alcohols [3]. Transition metal-catalyzed oxidative esterification of alcohols or aldehydes has also been developed in the last few years [4,5]. Despite significant advances, these methods have several drawbacks, such as limited substrate scope, harsh reaction conditions, and formation of large amounts of unwanted side products. Therefore, development of new efficient, atom-economic and straightforward alternatives is still desirable.

In this perspective, transition metal catalyzed cross dehydrogenative coupling (CDC) of carboxylic acids with alkanes under oxidative condition offers an attractive atom-economic one-pot synthetic approach for the synthesis of a wide variety of esters from various readily available starting precursors [6]. It allows to avoid the tedious multi-step synthetic procedures such as preparation of pre-functionalized starting precursors, activated reagents, etc. and thus makes the synthetic route shorter and more effective.

Over the past decade, much attention has been paid to develop new efficient catalysts and synthetic methods for C–C and C–X (X = N, O, S) bond formation via CDC under oxidative conditions [6-12]. Several new CDC methods were developed; among them most of the CDC reactions have been explored for the C–C bond formation [7]. The examples of carbon-heteroatom bond formation reactions, however, are still limited. Only in recent years, this method has been successfully extended for carbon-heteroatom (C–X, X = N, O, S) bond formation [8-10]. A few metal-free methodologies were also developed [11].

Despite of several advantages over the other classical synthetic approaches, the CDC reactions suffers from some severe drawbacks such as poor yield, limited substrate scope and requirement of expensive noble metal catalysts. Therefore, exploring new catalysts for the dehydrogenative functionalization of alkanes followed by meticulous investigations of the reaction steps are desirable to address the current limitations of the CDC reactions.

It is noteworthy to mention that the well-known Kharasch−Sosnovsky reaction involving the Cu(I)-catalyzed reaction of alkenes with carboxylic acids to form the corresponding allylic ester is well known since 1957 [13]. We recently reported a new copper(II)-complex containing a tridentate 2-pyrazol-(1,10-phenanthroline) pincer ligand and studied its application towards dehydrogenative functionalization of alkanes to esters via oxidative dehydrogenative coupling with carboxylic acids [12]. Esters were obtained in moderate to good yields from the dehydrogenative coupling of alkanes and acids in presence of 3.0 equiv. of *tert*-butylhydroperoxide (TBHP) and 2.0 mol% of the copper(II)-catalyst in benzene at 80°C. During this work we realized that the solubility of the copper catalyst plays a key role in the overall efficiency of the catalytic cycle. We envisioned that a more soluble copper catalyst, preferably soluble in alkanes, would allow us to avoid the use of carcinogenic benzene as the solvent and be more effective with low catalyst loading.

Keeping this in mind, we started screening various well-defined copper complexes available in our laboratory to study dehydrogenative functionalization of alkanes to esters via oxidative dehydrogenative coupling with carboxylic acids. Among the various available copper catalysts, the square planar Cu(II)-complex [Cu(MeTAA)] (**1**) containing a tetraaza macrocyclic ligand was found to be highly soluble in alkanes and exhibited promising activity in the dehydrogenative functionalization of alkanes to esters via oxidative CDC of a wide range of alkanes and carboxylic acids in neat conditions. Various allylic esters were synthesized in moderate to good yields starting from the corresponding alkanes and acids. A few control experiments and spectroscopic studies were performed for better understanding of the reaction sequence and shed light on the plausible mechanism.

Result and Discussion.

Synthesis and Characterization of the Catalyst. The macrocyclic ligand, H_2MeTAA (tetramethyltetraaza[14]annulene) and the Cu(II)-macrocycle complex [Cu(MeTAA)] (**1**) were synthesized following known literature methods [14]. Reaction of equimolar amounts of copper(II)acetate mono-hydrate and H_2MeTAA in acetonitrile at 70^{o}C for 0.5 h afforded dark green colored copper(II)-macrocyclic complex [Cu(MeTAA)] (**1**). Routine characterization along with positive-ion ESI mass spectrometry convincingly supports its formulation.

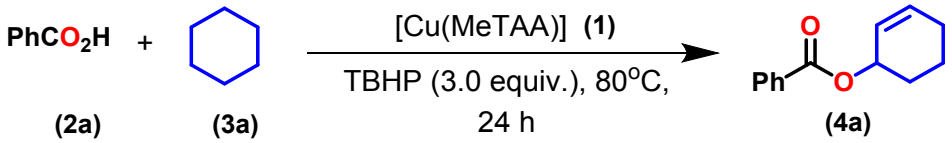
The structure of [Cu(MeTAA)] (**1**) was confirmed by the single crystal XRD. Slow evaporation of a dichloromethane-hexane solution of [Cu(MeTAA)] (**1**) produced single crystals of the complex. The ORTEP of [Cu(MeTAA)] (**1**) having ellipsoids at 50% probability level is displayed in Figure S1. The geometry around the central copper metal is saddle shaped with the benzene rings and the diiminato chelate rings tilted on opposite sides of the Nitrogen coordination plane [14c]. To confirm the +2 oxidation state of the central copper ion, low temperature X-Band EPR and room temperature magnetic moment measurements were carried out (see SI). A typical axial EPR spectrum along with μ_{eff} value of $1.76\mu_B$ is in complete agreement with the +2 oxidation state of copper [15].

Dehydrogenative Functionalization of Alkanes to Allylic Esters. To explore the activity of air-stable [Cu(MeTAA)] (**1**) towards dehydrogenative functionalization of simple alkanes to esters via oxidative dehydrogenative coupling with carboxylic acids, the reaction of benzoic acid (**2a**) and cyclohexane (**3a**) were studied under various reaction conditions to obtain the optimal reaction parameters. The reaction proceeds smoothly in benzene while no desired allylic ester (**4a**) was obtained in $CHCl_3$, CH_3OH, CH_3CN, DMF and DMSO (Table 1, entries 2-6). In benzene **4a** was obtained at a maximum yield of 90% when the dehydrogenative coupling of **2a** and **3a** were performed at 80°C in presence of 1.0 mol% catalyst loading and 3.0 equiv. of TBHP. The catalyst, [Cu(MeTAA)] (**1**), is highly soluble almost in all organic solvents including the substrate cyclohexane. Therefore, we decided to explore the catalytic reaction in neat condition in presence of 3.0 equiv. of TBHP and 1.0 mol% of [Cu(MeTAA)] (**1**). We were pleased to find that even in absence of benzene as solvent, the reaction proceeds smoothly and **4a** was obtained in almost identical yields (Table 1, entry 7). Furthermore, in neat conditions, a catalyst loading of 0.5 mol% is sufficient enough to afford the highest yield (92%) of **4a** (Table 1, entry 8). Other available oxidants such as di-*tert*-butylperoxide (DTBP), O_2, H_2O_2, benzoyl peroxide [$(PhCOO)_2$] or benzoquinone (BQ) were found to be less effective or ineffective compared to TBHP (Table 1, entries 8-13). No notable change in the yield of **4a** was observed upon increasing the temperature, reaction time or varying the amounts of TBHP beyond the optimized conditions. However, the yield of **4a** decreased significantly when the reaction was performed at temperature below 80°C. To further improve the yield of **4a**, the reaction of **2a** and **3a** was carried out in presence of a series of inorganic bases such as K_2CO_3, Cs_2CO_3, K_3PO_4, MO^tBu (M = Li, Na, K), and NaOH respectively (Table 1, entries 14-20). However, the yield of

4a was found to decrease significantly in presence of these bases. In all further catalytic studies we therefore focused on reactions at 80°C in presence of 0.5 mol% of [Cu(MeTAA)] (**1**) and 3.0 equiv of TBHP in neat conditions.

To check the background reaction, a few control experiments were carried out under the optimal reaction parameters (Table 1, entry 8). The coupling of **2a** and **3a** did not proceed in absence of [Cu(MeTAA)] (**1**) or TBHP. Commonly available copper salts like $CuCl_2$, CuI_2, CuCl, CuI, $Cu(OAc)_2$ were found to be less effective, only in presence of $Cu(OAc)_2$ the yield of **4a** reached up to 40% [16b]. A 1:1 mixture of H_2MeTAA and $Cu(OAc)_2.H_2O$ was also found to be less effective affording **4a** in only 72% yield (Table 1, entry 22).

Table 1. Screening for optimal reaction conditions of the [Cu(MeTAA)]-catalyzed dehydrogenative functionalization of alkanes to allylic esters.[a-e]



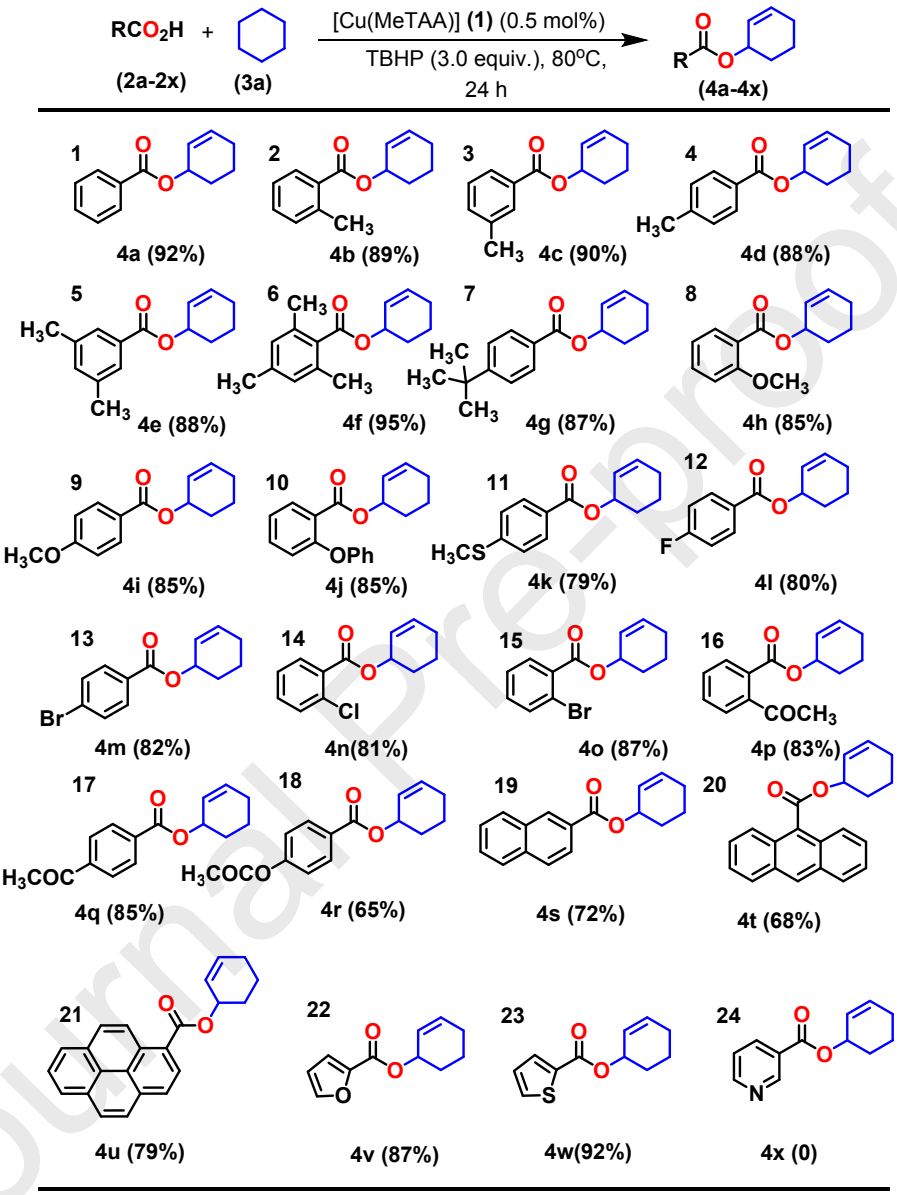
(2a) (3a) (4a)

Entry	Catalyst(mol%)	Solvent	Base	Oxidant	Temperature (°C)	Yield (%)
1	[Cu(MeTAA)] (1.0 mol%)	Benzene	-	TBHP	80°C	90
2	[Cu(MeTAA)] (1.0 mol%)	$CHCl_3$	-	TBHP	120°C	0
3	[Cu(MeTAA)] (1.0 mol%)	CH_3OH	-	TBHP	80°C	0
4	[Cu(MeTAA)] (1.0 mol%)	CH_3CN	-	TBHP	80°C	0
5	[Cu(MeTAA)] (1.0 mol%)	DMF	-	TBHP	80°C	0
6	[Cu(MeTAA)] (1.0 mol%)	DMSO	-	TBHP	80°C	0
7	[Cu(MeTAA)] (1.0 mol%)	Neat	-	TBHP	80°C	92
8	[Cu(MeTAA)] (0.5mol%)	Neat	-	TBHP	80°C	92
9	[Cu(MeTAA)] (0.5mol%)	Neat	-	DTBP	80°C	80
10	[Cu(MeTAA)] (0.5mol%)	Neat	-	O_2	80°C	0
11	[Cu(MeTAA)] (0.5mol%)	Neat	-	H_2O_2	80°C	0
12	[Cu(MeTAA)] (0.5mol%)	Neat	-	Benzoyl peroxide	80°C	Trace
13	[Cu(MeTAA)] (0.5mol%)	Neat	-	BQ	80°C	0
14	[Cu(MeTAA)] (0.5mol%)	Neat	K_2CO_3	TBHP	80°C	10
15	[Cu(MeTAA)] (0.5mol%)	Neat	K_3PO_4	TBHP	80°C	40
16	[Cu(MeTAA)] (0.5mol%)	Neat	Cs_2CO_3	TBHP	80°C	5
17	[Cu(MeTAA)] (0.5mol%)	Neat	Li^{t}BuO	TBHP	80°C	30
18	[Cu(MeTAA)] (0.5mol%)	Neat	Na^{t}BuO	TBHP	80°C	50
19	[Cu(MeTAA)] (0.5mol%)	Neat	K^{t}BuO	TBHP	80°C	45
20	[Cu(MeTAA)] (0.5mol%)	Neat	NaOH	TBHP	80°C	40
21	CuCl (0.5mol%)	Neat	-	TBHP	80°C	52
22	[(H_2MeTAA) : $Cu(OAc)_2$] (1:1)	Neat	-	TBHP	80°C	72

[a]In solvent: $PhCO_2H$ (0.5 mmol); cyclohexane (5.0 mmol); TBHP (0.3 mL); Under argon atmosphere. [b]In neat condition: $PhCO_2H$ (0.5 mmol); cyclohexane (10.0 mmol); TBHP (0.3 mL); Under argon atmosphere. [c]In neat condition: $PhCO_2H$ (0.5 mmol); cyclohexane (10.0 mmol); base (1.0 equiv.); TBHP (0.3 mL); Under argon atmosphere [d]Base : 1.0 equiv.; [e]Isolated yields after column chromatography.

With the optimized conditions in hand, we investigated the substrate scope of the present [Cu(MeTAA)] (**1**) catalyzed dehydrogenative functionalization of alkanes to esters. A number of reactions between various (poly)substituted carboxylic acids and alkanes were screened under the optimal conditions. Table 2 represents the yields of different allylic esters obtained from the reaction of different substituted benzoic acids (**2b-r**) with (**3a)** catalyzed by **1** under our optimal conditions. The reactions proceeded with benzoic acids containing both electron donating and -withdrawing functionalities. Irrespective of the positions of the substituents, benzoic acids (**2b-j**) containing different electron donating groups produced the respective allylic esters (**4b-j**) in 85-95% yield (Table 2, entries 2-10). Carboxylic acids (**2l-r**) bearing electron-withdrawing substituents also afforded the corresponding allylic esters (**4l-r**) in good to moderate yields (Table 2, entries 12-17). Despite of the strong oxidizing environment, 4-(methylthio)benzoic acid (**2k**) still produced **4k** in 79% isolated yield (Table 2, entry 11). Using 2-naphthoic acid (**2s**) and 9-anthracenecarboxylic acid (**2t**) the desired esters **4s** and **4t** were obtained in 72 and 68% yields respectively (Table 2, entry 19, 20). Reactions also proceeded with carboxylic acids containing heteroaryl rings. For example, **2v** and **2w** yielded the desired esters **4v** and **4w** in 87 and 92% yields respectively (Table 2, entries 22, 23). However, the reaction did not proceed with **2x** (Table 2, entry 24).

Table 2. [Cu(MeTAA)] (**1**)-catalyzed dehydrogenative functionalization of cyclohexane to various polysubstituted allylic esters.[a,b]

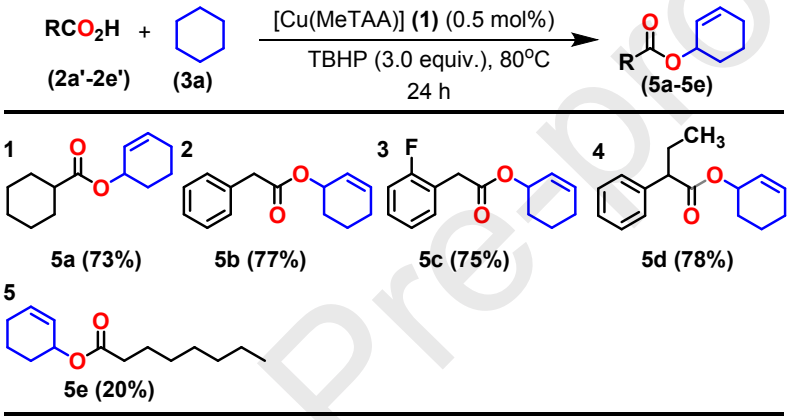


[a]In neat reagents: RCO_2H **(2a-2x)** (0.5 mmol); cyclohexane **(3a)** (10.0 mmol); TBHP (0.3 mL, 1.5 mmol); Under argon atmosphere. [b]Isolated yields after column chromatography

Next, a few selected aliphatic carboxylic acids (**2a'-e'**) were screened as coupling partners with **3a** to explore the scope and limitation of [Cu(MeTAA)] (**1**) towards dehydrogenative synthesis of allylic esters. Cyclohexanecarboxylic acid (**2a'**), phenylacetic acid (**2b'**), 2-(2-fluorophenyl)acetic acid (**2c'**), 2-phenylbutyric acid (**2d'**) and octanoic acid (**2e'**) were reacted

with **3a** under the optimal conditions. Reactions proceeded smoothly with **2a'-d'** yielding the desired allylic esters **5a-5d** in 73-78% yields respectively (Table 3, entries 1-4). When long chain carboxylic acid **2e'** was used as the coupling partner, the ester **5e** was isolated in only 20% yield (Table 3, entry 5).

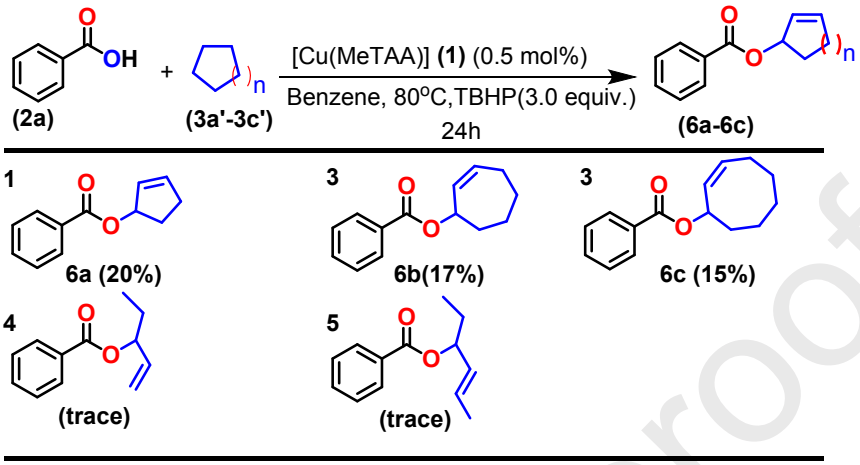
Table 3. [Cu(MeTAA)] (**1**)-catalyzed dehydrogenative functionalization of cyclohexane to various polysubstituted allylic esters via dehydrogenative coupling with various aliphatic carboxylic acids.[a,b]



[a]In neat reagents: RCO_2H **(2a'-2e')**(0.5 mmol); cyclohexane **(3a)** (10.0 mmol); TBHP (0.3 mL, 1.5 mmol); Under argon atmosphere. [b]Isolated yields after column chromatography

To further check the versatility of the present [Cu(MeTAA)] (**1**) catalyzed oxidative dehydrogenative functionalization of alkanes, reactions of **2a** with various other cyclic (**3b-d**) and acyclic (**3e, 3f**) alkanes were studied under the optimal reaction parameters. Reactions proceeded with cyclopentane (**3b**), cycloheptane (**3c**) and cyclooctane (**3d**), however, the respective esters **6a-c** were obtained in 15-20% yield (Table 4, entries 1-3). A slight increase in yields of **6a-c** was observed upon continuing the reaction for 48h. However, no significant improvement of yields were observed at higher temperature (150°C). The acyclic alkanes **3e** and **3f** were found to be ineffective yielding the respective products **6d** and **6e** only in trace quantities (Table 4, entries 4, 5).

Table 4. [Cu(MeTAA)] (**1**)-catalyzed dehydrogenative functionalization of various alkanes to allylic esters via dehydrogenative coupling with benzoic acid.[a,b]

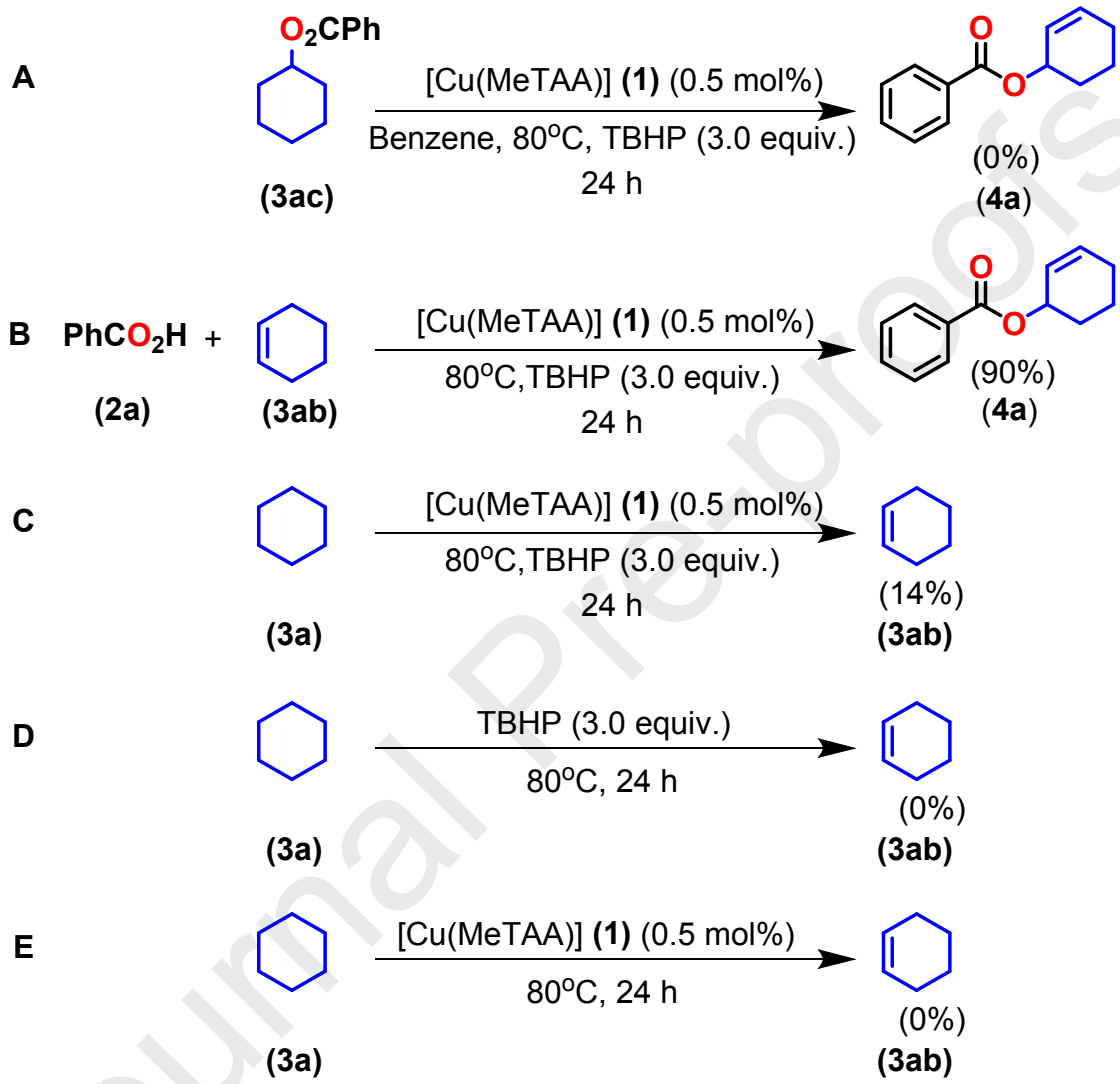


[a]In neat reagents: RCO_2H **(2a)** (0.5 mmol); cycloalkane **(3a'-3c')** (10.0 mmol); TBHP (0.3 ml, 1.5 mmol); Under argon atmosphere. [b]Isolated yields after column chromatography

Control Experiments and Mechanistic Investigation. The dehydrogenative functionalization of alkanes to allylic esters can proceed via either (i) initial formation of the C–O bond between the alkane and carboxylic acid followed by dehydrogenation of the *in situ* formed ester or (ii) initial dehydrogenation of alkanes to alkenes followed by allylic C–O bond formation [7,9]. Therefore, to investigate the reaction sequence and shed light on the plausible mechanism a few control experiments were performed.

When the pre-formed cyclohexyl benzoate (**3ac**) was subjected to dehydrogenation under the optimal reaction conditions we did not observe any formation of **4a** (Scheme 1, entry A). On the other hand, the reaction of cyclohexene (**3ab**) with **2a** under the optimal reaction conditions yielded **4a** in 90% yields (Scheme 1, entry B). It is worth mentioning that **3a** undergoes dehydrogenation to produce cyclohexene in presence of [Cu(MeTAA)] (**1**) and TBHP under the optimal reaction conditions (Scheme 1, entry C). The low yield may be attributed to the highly reactive nature of the cyclohexenyl radical species, which leads to decomposition or some other undesired product in absence of any other coupling partner. Both the copper catalyst **1** and TBHP are essential for the dehydrogenation of cyclohexane to cyclohexene. No cyclohexene formation was observed in absence of either catalyst **1** or TBHP (Scheme 1, entries D, E). These results are

in agreement with our previous result and available literature which indeed indicates that during the present [Cu(MeTAA)] (**1**)-catalyzed dehydrogenative functionalization of alkanes to allylic esters, dehydrogenation of olefins take place first followed by C–O bond formation [12].

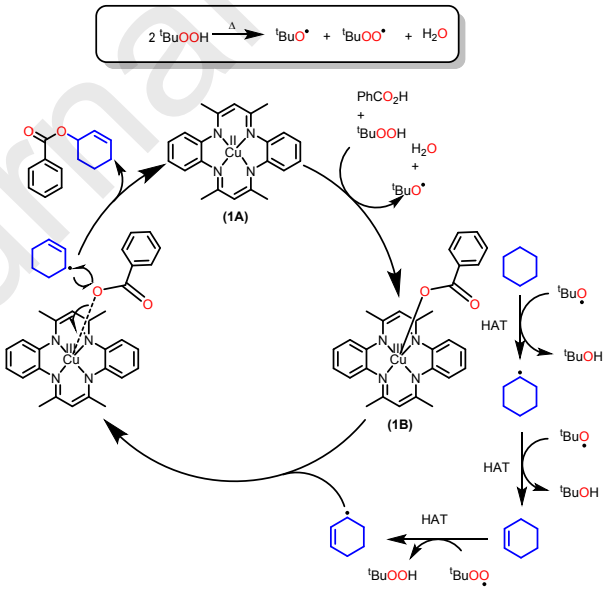


Scheme 1. Control Experiments to Test the Sequence of C=C and C-O Bond Formation.

To check the involvement of any organic radicals, the reaction of **2a** and **3a** was performed in presence of DPPH (2,2-diphenyl-1-picrylhydrazyl). Only a trace amount of **4a** was obtained, indicating the involvement of organic radical intermediates as reported by us and others in similar dehydrogenative coupling reactions [12]. Moreover, when **3a** was subjected to

dehydrogenation in presence of [Cu(MeTAA)] (**1**), DPPH and TBHP we did not observe any cyclohexene.

Based on the above experimental data and available literature [16a-f], we propose the reaction mechanism depicted in Scheme 2. In presence of catalyst, [Cu(MeTAA)] (**1**) and carboxylic acids, TBHP undergoes decomposition to the *tert*-butyloxy radical and the intermediate [Cu^{III}(MeTAA)(O_2CPh)] (**1B**) is formed. Under thermal conditions, TBHP also forms *tert*-butyloxy and *tert*-butylperoxy radicals, which dehydrogenate the alkanes to the corresponding alkenes via hydrogen-atom transfer (HAT) followed by a Kharasch−Sosnovsky-type process [13,16a-f]. This proceeds via HAT from alkanes to form alkanyl radical, which reacts with the intermediate [Cu^{III}(MeTAA)(O_2CPh)] species **1B** to form the respective allylic esters, thus regenerating the Cu(II)-catalyst. The proposed d^8 copper(III) intermediate **1B** should be a reactive short-lived species, that either rapidly captures the organic carbon radical directly or liberates a benzoyl radical with regeneration of Cu(II) upon homolysis of the Cu–O bond (followed by rapid C–O bond formation between the allyl radical and the benzoyl radical). We cannot fully exclude other reaction mechanisms, such as formation of naked cationic [Cu^{III}(MeTAA)]$^+$ species via outer sphere SET from Cu(II) to TBHP under the applied reactions conditions. However, we consider such pathways involving formation of charge-separated species (of opposite charge) rather unlikely in the applied apolar reaction media.



Scheme 2. Proposed Mechanism.

Conclusion. In conclusion we have described one pot dehydrogenative functionalization of alkanes to allylic esters via cross dehydrogenative coupling with carboxylic acids, catalyzed by a simple, earth abundant Cu(II)-catalyst, [Cu(MeTAA)] (**1**) under oxidative conditions. The catalyst, [Cu(MeTAA)] (**1**) used herein is cheap, easy to prepare, air stable and highly efficient as the reaction requires only 0.5 mol% catalyst loading. Furthermore, the high solubility of **1** enables us to achieve the catalytic reactions in neat condition, thereby avoiding the use and waste of solvent. This straightforward methodology is cost-effective and has a wide substrate scope. A wide range of allylic esters were prepared in moderate to good yields starting from various affordable and easily available raw materials in neat conditions.

Experimental Section

General Procedures. All the reactions were performed using standard Schlenk techniques under argon atmosphere. Benzene was refluxed over sodium/benzophenone, distilled under argon atmosphere, and stored over 4 Å molecular sieves. Methanol, DMF, hexane and $CHCl_3$ were refluxed with CaH_2 and distilled under argon atmosphere. All substituted benzoic acids and carboxylic acids were obtained from Sigma-Aldrich and TCI. All other reagents were purchased from commercial suppliers and used as received without further purification. Analytical TLC was performed on a Merck 60 F254 silica gel plate (0.25 mm thickness) and column chromatography was performed on Merck 60 silica gel (60-120 mesh). NMR spectra were recorded on a Bruker DPX-300(300 MHz), Bruker DPX-400(400 MHz) and Bruker DPX-500(500 MHz) spectrometers. TMS (tetramethylsilane) was used as the internal standard. Room temperature magnetic moment measurements for [Cu(MeTAA)] was carried out with Gouy balance (Sherwood Scientific, Cambridge, U.K.). EPR spectra in the X-band were recorded with a Bruker EMX plus spectrometer.

Synthesis of [Cu(MeTAA)] (1). The free ligand H_2MeTAA was synthesized following a known template synthesis [14c]. [Cu(MeTAA)] was synthesized by directly reacting copper(II) acetate monohydrate with H_2MeTAA in presence of NEt_3 as base. In a round-bottom flask, 0.10 g of copper(II) acetate monohydrate salt (0.60 mmol) and 0.1 g of MeTAA (0.56 mmol) were added in 4.0 mL acetonitrile. To it 0.20 mL NEt_3 was added. Immediately after the addition of NEt_3, the color of the solution turned deep green. The reaction mixture was refluxed for 0.5 h and then placed in an ice-bath. Deep green microcrystalline complex thus formed was filtered and washed

with a small amount of acetonitrile and ether. Fractional crystallization using dichloromethane/hexane solvent mixture finally yielded the pure complex **1**. Yield: 52%.

General Procedures for Dehydrogenative Functionalization of Alkanes to Allylic Esters (in solvent). Under argon atmosphere, [Cu(MeTAA)] (2.0 mg, 0.005 mmol) and benzoic acid (61 mg, 0.5 mmol) were added in an oven-dried Schlenk tube containing a magnetic stir bar. The Schlenk tube was evacuated and backfilled with argon (3 cycles). 5.0 mmol cyclohexane (10 equiv), 1.50 mmol (3.0equiv) of TBHP and benzene (1.0 mL) were injected to the Schlenk tube via syringe. Then the Schlenk tube was placed into an oil bath and heated at 80°C for 24 hours. The reaction was monitored time to time using small TLC plates. After the reaction is complete, the solvent was evaporated under reduced pressure and the residue was dissolved in dichloromethane and purified by column chromatography using silica and hexane was used as eluent.

General Procedures for Dehydrogenative Functionalization of Alkanes to Allylic Esters (in absence of added solvent). Under an argon atmosphere, [Cu(MeTAA)] (2.0 mg, 0.005 mmol) and benzoic acid (61 mg, 0.5 mmol) were added in an oven-dried Schlenk tube containing a magnetic stir bar. The Schlenk tube was evacuated and back filled with argon (3 cycles). Subsequently 1.50 mmol (3.0 equiv) of TBHP and 1.0 mL cyclohexane were injected to the Schlenk tube via a syringe. Then the Schlenk tube was placed into an oil bath and heated at 80°C for 24 hours. Once the reaction was completed, the reaction mixture was concentrated in vacuum and the residue was dissolved in dichloromethane and purified by column chromatography using silica and hexane was used as eluent.

Control Experiments

To Test the Sequence of C=C and C-O Bond Formation.

(i) Under an argon atmosphere, a mixture of **1** (2.0 mg, 0.005 mmol) and cyclohexyl benzoate (102 mg, 0.500 mmol) were added in an oven-dried Schlenk tube with a magnetic stir bar. The schlenk tube was evacuated and backfilled with argon (3 cycles). Then a solution of TBHP (0.3 mL, 1.5 mmol) and benzene (1.0 mL) were injected via a syringe. Since the reactant and the catalyst were solid, we decided to perform the reaction in benzene solvent. Subsequently, the Schlenk tube was sealed with Teflon and placed into an oil bath at 80°C for 24 hours.

(ii) In an oven-dried Schlenk tube, **1** (2.0 mg, 0.005 mmol) and benzoic acid (61 mg, 0.50 mmol) were added with a magnetic stir bar. The Schlenk tube was evacuated and back filled with argon (3 cycles). A solution of cyclohexene (1.0 mL, 10.0 mmol) and TBHP (0.3 mL, 1.5 mmol) were injected to the Schlenk tube via a syringe. The Schlenk tube was tightly sealed with Teflon and placed into a preheated oil bath at 80°C for 24 hours.

(iii) In an oven-dried schlenk tube, **1** (2.0 mg, 0.005 mmol) was added with a magnetic stir bar. The schlenk tube was evacuated and backfilled with argon (3 cycles). A solution of cyclohexane (1.0 mL, 10.0 mmol) and TBHP (0.3 mL, 1.5 mmol) were injected to the Schlenk tube via a syringe. The Schlenk tube was tightly sealed with Teflon and placed into a preheated oil bath at 80°C for 24 hours.

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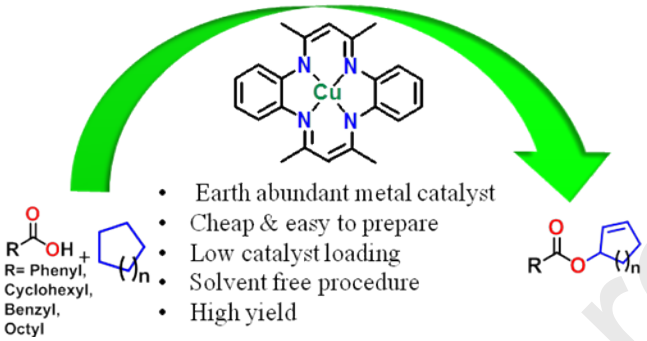
There are no conflicts to declare.



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