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Copper Catalysis |*Hot Paper*|

Evidence of Cu^{I}/Cu^{II} Redox Process by X-ray Absorption and EPR Spectroscopy: Direct Synthesis of Dihydrofurans from β-Ketocarbonyl Derivatives and Olefins

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Abstract: The Cu^{I}/Cu^{II} and Cu^{I}/Cu^{III} catalytic cycles have been subject to intense debate in the field of copper-catalyzed oxidative coupling reactions. A mechanistic study on the Cu^{I}/Cu^{II} redox process, by X-ray absorption (XAS) and electron paramagnetic resonance (EPR) spectroscopies, has elucidated the reduction mechanism of Cu^{II} to Cu^{I} by 1,3-diketone and detailed investigation revealed that the halide ion is important for the reduction process. The oxidative nature of the thereby-formed Cu^{I} has also been studied by XAS and EPR spectroscopy. This mechanistic information is applicable to the copper-catalyzed oxidative cyclization of β-ketocarbonyl derivatives to dihydrofurans. This protocol provides an ideal route to highly substituted dihydrofuran rings from easily available 1,3-dicarbonyls and olefins.

Copper has been widely used as the catalyst in chemical synthesis. A wide variety of copper-catalyzed reactions, including Glaser–Hay and Ullmann–Goldberg couplings, have been employed as powerful tools for the preparation of biological and pharmaceutical active compounds.[1] This versatility in combination with low toxicity and cost make copper among the most promising transition metal in homogeneous catalysis. However, detailed mechanistic understanding of these homogeneous copper-catalyzed reactions is still incomplete.[1a,d,2] This is partially due to the fact that copper precursors are used in various available oxidation states and the metal center of copper complex can participate in either two-electron or single-electron processes, sometimes both in the same catalytic cycle.[3] The Cu^{I}/Cu^{III} catalytic cycle has been widely proposed in many copper-mediated coupling reactions. Some progress has been achieved in that several Cu^{III} complexes have been isolated, either with the help of very special ligands or under harsh conditions.[4] Although there is no solid evidence to show the presence of Cu^{III} species under live and realistic catalytic conditions, it provides for the possibility of this mechanism in copper catalysis.

Recently, copper-catalyzed oxidative coupling reactions have been extensively developed, in which copper salts are often proposed to serve as the one-electron oxidant to promote the single-electron transfer process.[5] Although several methodologies have been reported, the single-electron redox between the C/X–H compound and the copper salts has less been explored. Jutand and co-workers investigated Cu^{II} precursor supported by phenanthroline ligands, which could be reduced by alcohols or amines to generate the active Cu^{I} species, monitored by UV/Vis and NMR spectroscopies.[6] Recently, we used X-ray absorption spectroscopy (XAS) and electron paramagnetic resonance (EPR) spectroscopy to obtain information on the reduction of Cu^{II} to Cu^{I} species by alkynes in the presence of tetramethylethylenediamine (TMEDA).[7] XAS can provide direct information on the oxidation state and the coordination environment of the metal in solution.[8] Therefore, XAS can serve as a unique and powerful technique for probing the structures of reaction intermediates in homogeneous catalysis. Herein, we report a study on Cu^{I}/Cu^{II} redox mechanism by XAS and EPR spectroscopies. In addition, we have also used this mechanistic information to realize a copper-catalyzed oxidative cyclization of β-ketocarbonyl derivatives to dihydrofurans. This protocol provides an ideal route to highly substituted dihydrofuran rings from easily available 1,3-dicarbonyls and olefins under non-acidic conditions.

β-Diketone derivatives have been widely used as ligands in copper-mediated coupling reactions.[9] Revealing the mechanism of the interaction between the Cu center and the β-diketone ligand will help to better define the potential limits of catalytic reactions.[10] Initially, we commenced our study by investigating the interaction between CuX_2 (X = Br, Cl) and acetylacetone under nitrogen atmosphere by XAS (Figure 1). The X-ray absorption near edge structure (XANES) spectrum of

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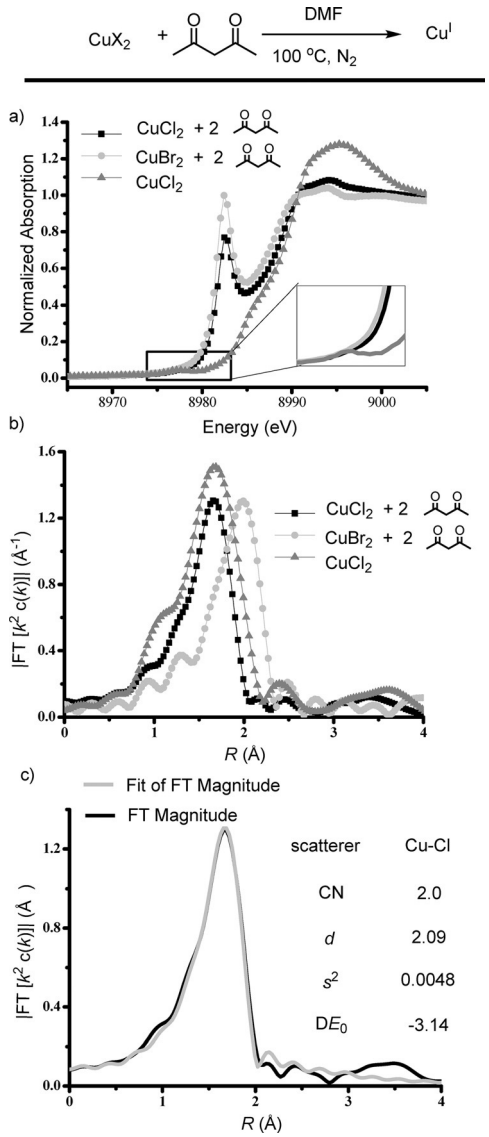


Figure 1. X-ray absorption spectra of various Cu species: a) XANES spectra; black line: $CuCl_2$ (0.5 mmol) and acetylacetone (1.0 mmol) in DMF (5.0 mL) at 100 °C; light gray line: $CuBr_2$ (0.5 mmol) and acetylacetone (1.0 mmol) in DMF (5.0 mL) at 100 °C; dark gray line: $CuCl_2$ (0.5 mmol) in DMF (5.0 mL) at RT. b) EXAFS spectra; black line: $CuCl_2$ (0.5 mmol) and acetylacetone (1.0 mmol) in DMF (5.0 mL) at 100 °C; light gray line: $CuBr_2$ (0.5 mmol) and acetylacetone (1.0 mmol) in DMF (5.0 mL) at 100 °C; dark gray line: $CuCl_2$ (0.5 mmol) in DMF (5.0 mL) at RT. c) k^2-weighted Fourier transform magnitudes of the *R*-space EXAFS spectrum. FT = Fourier transform; CN = coordination number; d = bond length; $\Delta\sigma^2$ = Debye–Waller factor; E_0 = threshold energy (2.96 Å^{-1} < k < 14.11 Å^{-1}; 1.12 Å < R < 1.99 Å).

the DMF solution of $CuCl_2$ gave a pre-edge at 8977.0 eV (Figure 1a, dark gray line). After the addition of acetylacetone at 100 °C, a new Cu species was detected with an edge energy of 8981.6 eV (Figure 1a, black line). This edge energy is very close to that of the CuCl standard sample (8982.0 eV), confirming that a Cu^I species was generated during this process. When mixing $CuBr_2$ and acetylacetone in DMF at 100 °C, a copper species with the same edge energy was detected (Figure 1a, light gray line). Interestingly, when performing the experiment in DMF as solvent at 100 °C, a very small amount of Cu^{II} was reduced to the Cu^I species (for details, see the Supporting Information), indicating that the Cu^{II} precursor can be reduced to Cu^I species by acetylacetone in DMF. Extended X-ray absorption fine structure (EXAFS) spectra were also taken to probe the local structures of the Cu species (Figure 1b). The EXAFS spectrum of the reaction between $CuCl_2$ and acetylacetone is very different from that of the reaction between $CuBr_2$ and acetylacetone, which suggests coordination of the halide ion to the Cu^I complex. Fitting of the R-space EXAFS spectrum revealed that the obtained Cu^I species had two coordinating Cl atoms (Figure 1c). The Cu–Cl bond length was determined as 2.09 Å. The structure of the obtained Cu^I species was thus assigned as a $[CuCl_2]^-$ ate complex.

X-ray absorption spectroscopy was also applied to explore the effect of the halide on the reduction of Cu^{II} species.[11] When mixing $Cu(OAc)_2$ and acetylacetone under the standard conditions, a Cu^{II} species was detected with a pre-edge at 8978.0 eV, indicating that the $Cu(OAc)_2$ cannot be reduced to Cu^I complex by acetylacetone (Figure 2, black line). After the addition of two equivalents of LiCl to the system, a Cu^I species was formed with an edge energy of 8981.8 eV, which revealed that Cl^- can promote the reduction of $Cu(OAc)_2$ to Cu^I species (Figure 2, light gray line).To further confirm this reduction process, a blank experiment, just mixing $Cu(OAc)_2$ and LiCl, was carried out, resulting in a Cu^{II} species with a pre-edge energy of 8976.6 eV. These results indicate that $Cu(OAc)_2$ cannot be reduced by LiCl. Therefore, the halide anion plays an important role in the reduction of Cu^{II} to Cu^I by acetylacetone.

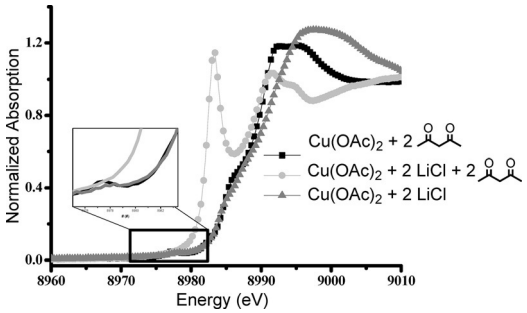


Figure 2. XANES spectra; black line: $Cu(OAc)_2$ (0.5 mmol) and acetylacetone (1.0 mmol) in DMF (5.0 mL) at 100 °C; light gray line: $Cu(OAc)_2$ (0.5 mmol), acetylacetone (1.0 mmol) and LiCl (1.0 mmol) in DMF (5.0 mL) at 100 °C; dark gray line: $Cu(OAc)_2$ (0.5 mmol) and LiCl (1.0 mmol) in DMF (5.0 mL) at 100 °C.

The above results suggest that acetylacetone can serve as the electron donor to transfer one electron to Cu^{II}, furnishing the reduced Cu^I complex. To make this process catalytic, an extra oxidant is needed to oxidize the Cu^I species. To prove our hypothesis, we used di-*tert*-butylperoxide (DTBP) as the oxidant to reoxidize the Cu^I species and monitored the reaction by XAFS and EPR spectroscopies (Figure 3). The XANES spectra (Figure 3a) indicate that the copper salts from the CuCl and $CuCl_2$ precursors react with DTBP in the presence of acetylacetone to generate a mixture of Cu^I and Cu^{II} species. Based on further EXAFS spectroscopic analysis (Figure 3b), the coordination environments of the generated Cu species from CuCl and

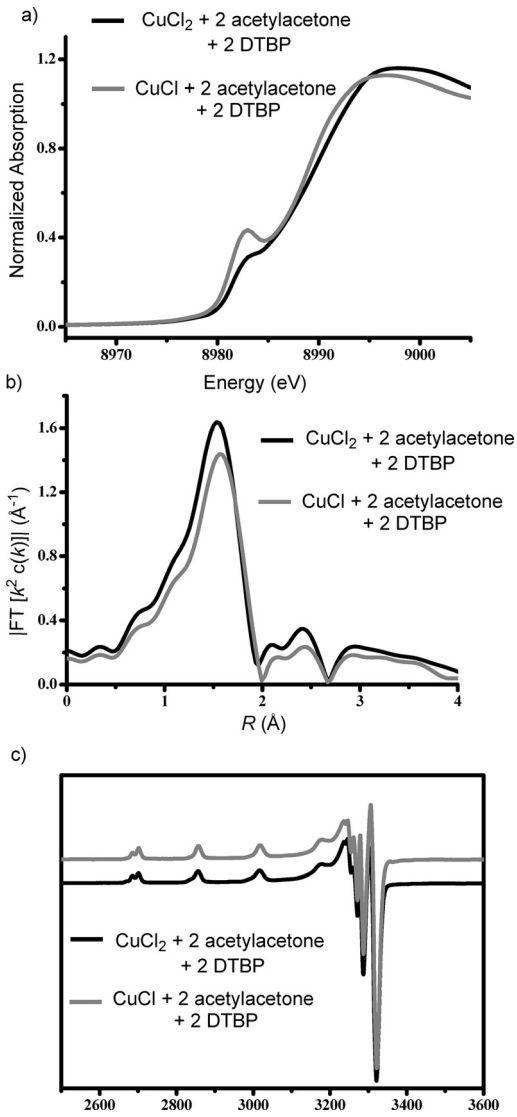
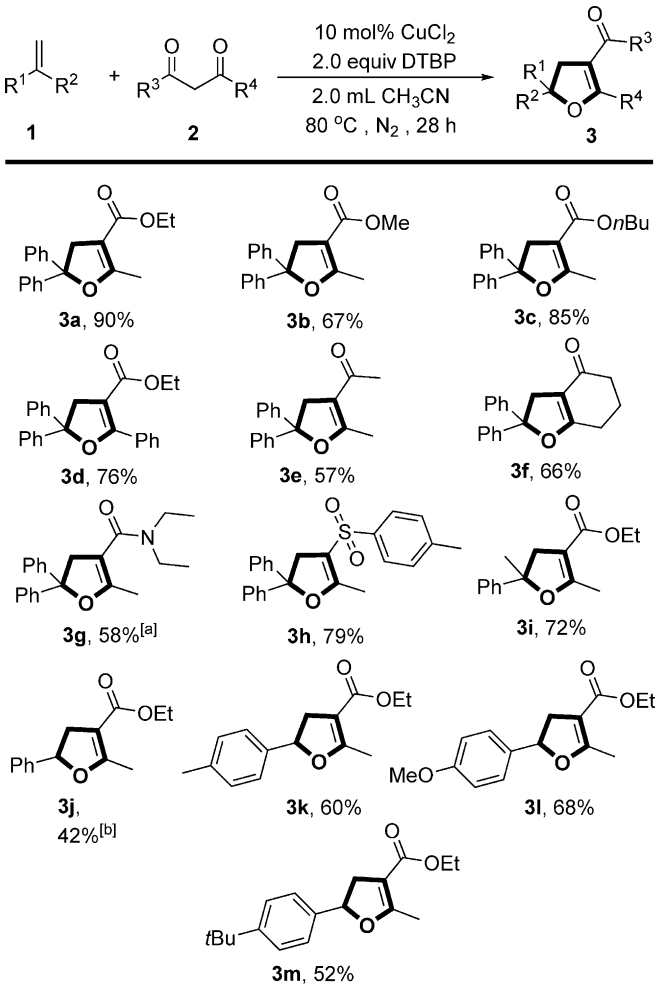


Figure 3. a) XANES spectra; b) EXAFS spectra; c) EPR spectra (X band, 9.4 GHz, 160 K); black line: $CuCl_2$ (0.5 mmol), DTBP (1.0 mmol) and acetylacetone (1.0 mmol) in DMF (5.0 mL) at 100 °C; gray line: CuCl (0.5 mmol), DTBP (1.0 mmol) and acetylacetone (1.0 mmol) in DMF (5.0 mL) at 100 °C.

$CuCl_2$ are similar. Furthermore, EPR spectroscopy was also used to monitor this oxidation process (Figure 3c). The same Cu^{II} species was formed from the reaction of CuCl or $CuCl_2$ with acetyl acetone and DTBP. Therefore, we have established that the CuX_2 could be reduced to the Cu^{I} species by acetylacetone. The XAS and EPR results also indicate that the Cu^{I} species could be oxidized by DTBP in the presence of acetylacetone.

During the last decade, radical addition of 1,3-dicarbonyl compounds to alkenes to synthesize dihydrofurans, a useful organic building block,[12] mediated by metal salts (Mn^{III}, Ce^{IV}, Co^{II}, and V^{V}) has received considerable attention in organic synthesis.[13] Although some remarkable progresses have been made, the required loading, cost, and toxicity impact of these metal salts, as well as the fact that most need more than fourfold excess alkene in acid solvent, have hindered its further application. Based on the mechanistic information on Cu^{I}/Cu^{II} redox process, we have successfully realized a copper-catalyzed oxidative cyclization of β-ketocarbonyl derivatives to dihydrofurans, utilizing DTBP as the oxidant (Scheme 1). This protocol provides an convenient route to highly substituted dihydrofuran rings from easily available 1,3-dicarbonyls and olefins.



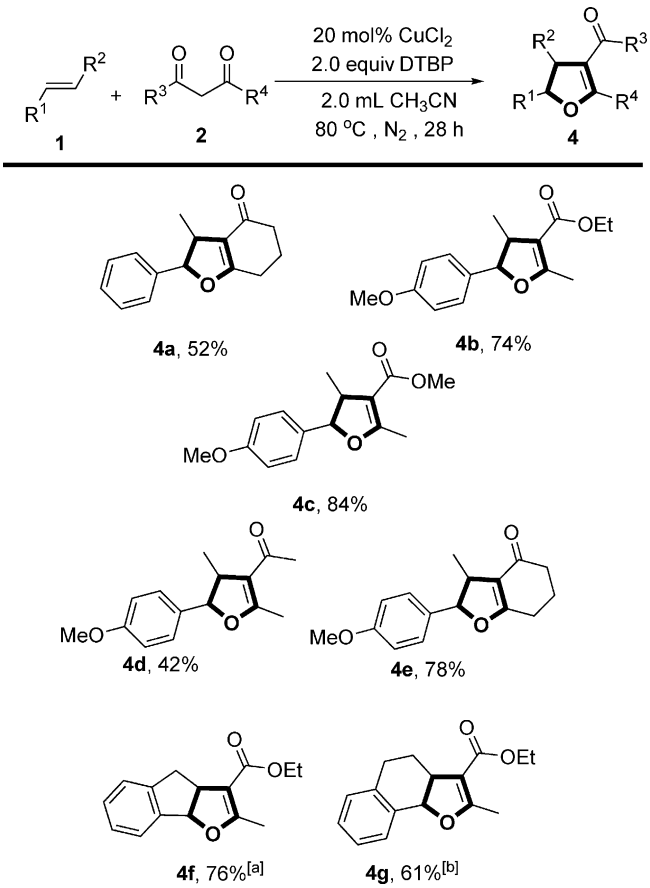
Scheme 1. Copper-catalyzed oxidative cyclization reactions of various 1,3-dicarbonyl compounds **2** with **1**. Reaction conditions (unless otherwise stated): **1** (0.80 mmol), **2** (0.50 mmol), $CuCl_2$ (0.05 mmol) and DTBP (1.0 mmol) in CH_3CN (2.0 mL) at 80 °C for 28 h. Yields refer to isolated products. [a] **1** (0.50 mmol), **2** (1.0 mmol), $CuCl_2$ (0.05 mmol); [b] **1** (1.0 mmol), **2** (0.50 mmol), $CuCl_2$ (0.10 mmol)

We started our evaluation of the reaction parameters with 1,1-diphenylethylene (**1a**) and ethyl acetoacetate (**2a**) as standard substrates (see the Supporting Information, Table S2). After exploring a wide array of conditions, we found that the oxidative cyclization product **3a** was obtained in excellent yield in the presence of 10 mol% $CuCl_2$, 2 equivalents of DTBP, and CH_3CN as the solvent at 80 °C (see the Supporting Information, Table S2, entry 13). With the optimal reaction conditions established, we tested various substituted 1,3-dicarbonyl compounds **2**, combined with **1a** (Scheme 1). Almost all of the β-keto esters were effective under the standard conditions. As shown in Scheme 1, ethyl, methyl, and *n*-butyl acetoacetates

all reacted smoothly, affording the desired products **3a**–**c** in good to excellent yields. Ethyl benzoylacetate was also suitable for this reaction (Scheme 1, **3d**). In addition, β-diketones could be readily introduced in the reaction, providing the corresponding dihydrofurans **3e** and **3f** in moderate yields. Furthermore, a 1,3-dicarbonyl compound bearing an amide group was also tolerated in the reaction with **1a**, affording the dihydrofuran product **3g** in moderate yield. The β-ketosulfone was also effective for this reaction and gave the desired product **3h** in 79% yield.

Under the same reaction conditions, α-methylstyrene could also react with ethyl acetoacetate (**2a**) yielding dihydrofuran **3i** in 72% yield. The reaction was also readily extended to a variety of aryl terminal alkenes. As shown in Scheme 1, *p*-methyl-, *p*-methoxy-, and *p*-*tert*-butylstyrenes all reacted smoothly, affording the desired products **3j**–**m** in moderate yields.

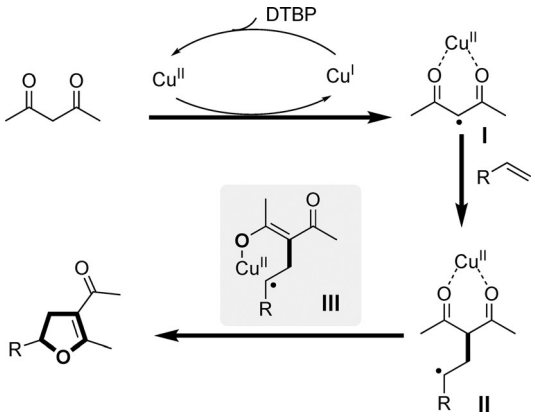
Notably, four-substituted dihydrofurans could also be obtained from this oxidative C–H/O–H cyclization (Scheme 2). (*E*)-β-Methylstyrene and (*E*)-anethole were selected to react with 1,3-dicarbonyl compounds (**2**). Various β-keto esters and β-diketones were effective for this transformation and the desired dihydrofurans **4a**–**e** were obtained in moderate to good yields.



Scheme 2. Copper catalyzed oxidative cyclization reactions of various 1,2-disubstituted alkenes **1** with **2**. Reaction conditions (unless otherwise stated): **1** (1.0 mmol), **2** (0.50 mmol), $CuCl_2$ (0.10 mmol) and DTBP (1.0 mmol) in CH_3CN (2.0 mL) at 80 °C for 28 h. Yields refer to isolated products. [a] **1** (1.0 mmol), **2** (0.5 mmol), $CuCl_2$ (0.05 mmol); [b] **1** (0.8 mmol), **2** (0.5 mmol), $CuCl_2$ (0.05 mmol).

The target tetrasubstituted dihydrofurans were obtained with *trans* stereochemistry (confirmed by NMR spectroscopy), which is a common structural moiety present in many natural products.[14] Interestingly, cyclic alkenes, such as indene and 1,2-dihydronaphthalene, could also be employed to give the target dihydrofuran scaffolds **4f** and **4g** without any difficulties (Scheme 2).

According to previous reports on the oxidative coupling between 1,3-dicarbonyl compounds and alkenes[13] and the above results, a proposed mechanism is described in Scheme 3. The acetylacetone is oxidized by the $CuCl_2$/DTBP



Scheme 3. Proposed mechanism.

system to generate the acetylacetone radical. The acetylacetone radical coordinates with copper to generate the radical **I**, which then attacks the alkene **1** to give another carbon radical **II**. The adduct **II** undergoes a keto–enol tautomerization to give intermediate **III**. Intermediate **III** undergoes intramolecular combination of the acetylacetate radical with Cu^{II} to form the C–O bond, giving the desired dihydrofuran product.

In conclusion, we have reported a mechanistic study of the Cu^{I}/Cu^{II} redox process by XAFS and EPR spectroscopy. The reduction of Cu^{II} to Cu^{I} by 1,3-diketone was evidenced by X-ray absorption spectroscopy (XAS). Detailed investigation revealed that the halide ion is very important for the reduction of Cu^{II}. The oxidative nature of the Cu^{I} was also investigated by XAS and EPR spectroscopy. The mechanistic findings were applicable to the oxidative cyclization of β-ketocarbonyl derivatives to give dihydrofurans with DTBP and copper catalyst. This process provides a convenient and efficient route to highly substituted dihydrofuran rings from simple chemical feedstocks.

Experimental Section

General procedure: A dried Schlenk tube equipped with a stir bar was charged with **1a** (0.80 mmol), **2a** (0.50 mmol), $CuCl_2$ (10 mol%), DTBP (1.0 mmol), and acetonitrile (2.0 mL) under an atmosphere of nitrogen. The mixture was then stirred at 80 °C for 28 h. After the completion of the reaction, it was quenched with ethyl acetate (3×20 mL) and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica

gel (gradient elution with of petroleum ether/ethyl acetate, 200:1–20:1) to give the pure product. **3 a** as a colorless liquid product in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.22 (m, 10H), 4.18 (q, J = 7.2 Hz, 2H), 3.63 (s, 2H), 2.38 (s, 3H), 1.30 ppm (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 165.9, 145.2, 128.3, 127.5, 125.7, 101.8, 91.5, 59.6, 44.2, 14.5, 14.3 ppm.

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Keywords: copper · homogeneous catalysis · oxidative coupling · redox chemistry · X-ray absorption spectroscopy

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