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Copper-mediated cross-coupling–cyclization–oxidation: a one-pot reaction to construct polysubstituted pyrroles†

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A novel and efficient procedure for the synthesis of polysubstituted pyrroles has been developed in this work. The polysubsituted pyrroles were synthesized directly from terminal alkenes, amines and β-keto esters through cross-coupling–cyclization–oxidation in the presence of a catalytic amount of cuprous chloride. This method provides a one-pot synthesis route from terminal alkenes to polysubstituted pyrroles for the first time and opens a new area in cuprous catalysis.

Pyrroles are privileged structures that have been found in numerous biologically active compounds such as natural products, pharmaceuticals, and agrochemicals.[1,2] This key heterocyclic core has been widely used in both organic synthesis and materials science.[3] In this regard, there are many reports for the synthesis of pyrroles,[4] such as the classical Knorr reaction,[5] Hantzsch reaction,[6] and Paal–Knorr condensation reaction.[7] Another type of synthesis procedures with metal-catalyzed reactions have also been developed.[8] However, some of these methods require tedious workup, harsh reaction conditions and long reaction times. Others involve multistep synthetic operations or result in low yields. Therefore, a straightforward, convenient, and highly regioselective route to synthesize pyrroles using basic chemical materials is highly attractive. To the best of our knowledge, the construction of pyrroles from simple terminal alkenes has not been reported.

Novel reactions that can selectively functionalize carbon–hydrogen bonds are of intense interest to the chemical community because they offer new strategic approaches for synthesis chemistry.[9] Since the last decade, transition-metal-catalyzed C–H functionalization of terminal alkynes has become an important type of organic reaction, as it provides a direct and reliable approach to synthesize a variety of valuable products.[10] In contrast, transition-metal-catalyzed C–H functionalization of terminal alkenes is relatively rare because the C(sp^2)–H bond of simple alkenes is less reactive toward transition metals than alkynes. Therefore, an efficient and atom-economic synthesis of multifunctional heterocycles *via* direct C–H functionalization–cyclization of terminal alkenes is very challenging but attractive. As a result of development on the transition-metal-catalyzed C–H functionalization of alkenes in our group,[11] herein, we report, for the first time, an efficient and straightforward protocol for synthesis of pyrroles with terminal alkenes under mild conditions. This protocol is also novel for the copper catalyzed sequential reaction.

To optimize the reaction conditions for the three-component cross-coupling–cyclization–oxidation process, a variety of catalysts and solvents were screened with styrene **1a**, aniline **2a** and ethyl acetoacetate **3a** as model substrates (Table 1). Initially, the reaction of **1a** (0.75 mmol), **2a** (0.5 mmol), and **3a** (0.5 mmol) in the presence of 10 mol% CuCl in DMSO at 80 °C for 24 h gave the substituted pyrroles **4aaa** in 78% yield (Table 1, entry 1). In addition, in the presence of other catalysts such as $BiCl_3$, $ZnCl_2$, $InCl_3$, $FeCl_3$, $PdCl_2$, $RhCl_3$ or $RuCl_3$, most of the starting material **1a** was recovered (Table 1, entries 2–8). The reaction with $AuBr_3$ as a catalyst yielded no target product **4aaa** at all (Table 1, entry 9). More catalysts were also screened but none of them gave higher yields than CuCl (see ESI†). Solvent plays a key role in this reaction too. Compared to the reaction in DMSO, the reactions in DCE and 1,4-dioxane produced much lower pyrrole yields under the same conditions (Table 1, entries 10 and 11 *vs.* entry 1). Other solvents including PhCl, CH_3NO_3, CH_3COOH, $PhCH_3$ and DMF are not desired (Table 1, entries 12–16). Hence, the optimized reaction conditions for this Cu-mediated cross-coupling–cyclization–oxidation process are 10 mol% CuCl in DMSO at 80 °C with a reaction time of 24 h.

With the optimized reaction conditions in hand, various terminal alkenes **1** and amines **2** were reacted with different β-keto esters **3** to produce the corresponding pyrrole products **4** (Table 2). The reaction was readily extended to a variety of aryl-substituted terminal alkenes. Catalyzed by CuCl, almost all the reactions with aryl-substituted terminal alkenes produced a high yield of pyrrole under the

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† Electronic supplementary information (ESI) available. CCDC 972540. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc48728h

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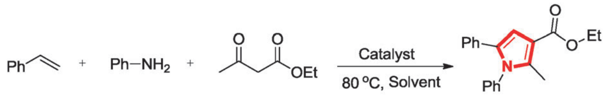
Table 1 Optimization of reaction conditions[a]

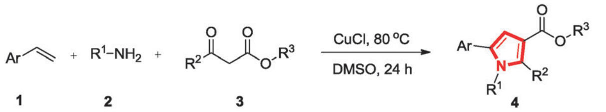


1a 2a 3a 4aaa

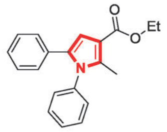
Entry	Catalyst	Solvent	Yield[b] (%)
1	CuCl	DMSO	78
2	$BiCl_3$	DMSO	0
3	$ZnCl_2$	DMSO	0
4	$InCl_3$	DMSO	0
5	$FeCl_3$	DMSO	0
6	$PdCl_2$	DMSO	0
7	$RuCl_3$	DMSO	0
8	$RhCl_3$	DMSO	0
9	$AuBr_3$	DMSO	0
10	CuCl	DCE	45
11	CuCl	1,4-Dioxane	36
12	CuCl	PhCl	0
13	CuCl	CH_3NO_3	0
14	CuCl	CH_3COOH	0
15	CuCl	$PhCH_3$	0
16	CuCl	DMF	0

[a] Reaction conditions: styrene **1a** (0.75 mmol), aniline **2a** (0.5 mmol), ethyl acetoacetate **3a** (0.5 mmol), catalyst (10 mol% to **2a**), solvent (4.0 mL), 80 °C, 24 h. [b] Isolated yield of the pure product based on **2a**.

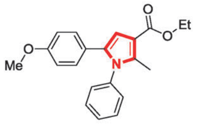
Table 2 Synthesis of polysubstituted pyrroles **4** catalyzed by CuCl[a,b]



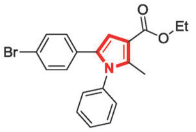
1 2 3 4



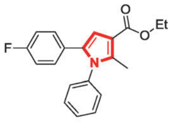
4aaa 78%



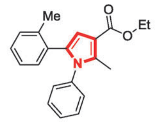
4baa 85%



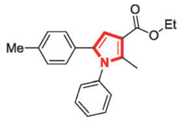
4caa 72%



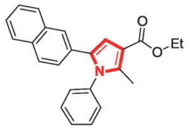
4daa 70%



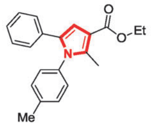
4eaa 81%



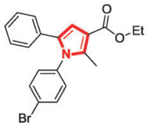
4faa 83%



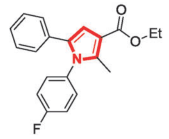
4gaa 75%



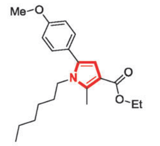
4aba 73%



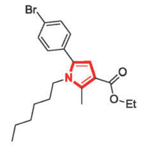
4aca 84%



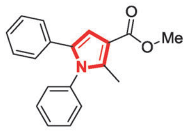
4ada 86%



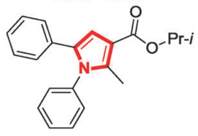
4bea[c] 69%



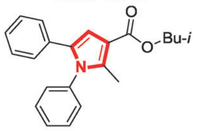
4cea[c] 65%



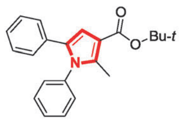
4aab 76%



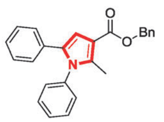
4aac 78%



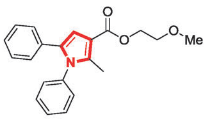
4aad 77%



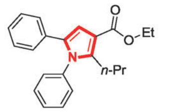
4aae 74%



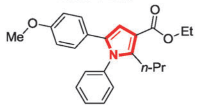
4aaf 72%



4aag 74%



4aah 73%



4bah 76%

[a] Reaction conditions: terminal alkenes **1a** (0.75 mmol), aromatic amines **2a** (0.5 mmol), β-keto esters **3a** (0.5 mmol), CuCl (10 mol% to **2a**), solvent (4.0 mL), 80 °C, 24 h. [b] Isolated yield of the pure product based on **2a**. [c] The reactions were carried out at 100 °C, for 36 h.

optimized conditions. Terminal aryl alkene **1b** with an electron-donating group at the aryl ring (Ar = 4-$MeOC_6H_4$) is reactive and yielded product **4baa** in 85% yield (Table 2, entry **4baa**). Substrates **1c** and **1d** possessing an electron-withdrawing group (Ar = 4-BrC_6H_4, 4-FC_6H_4) at the benzene ring are also reactive and afforded the desired products **4caa** and **4daa** in 72% and 70% yields, respectively (Table 2, entries **4caa** and **4daa**). Obviously, electron-rich terminal alkenes yield desired products in higher yields than electron-poor terminal alkenes do. It is striking that steric effects had no obvious effect on this sequential reaction. Regardless of the substitution pattern of the aryl ring (*ortho* or *para*), the aryl olefins used in the reactions gave the corresponding pyrrole products in 81–83% yields (Table 2, entries **4eaa** and **4faa**). Additionally, terminal alkenes containing a naphthalene moiety can also be employed to obtain the pyrrole scaffold in high yield (Table 2, entry **4gaa**). Unfortunately, when the acrylate esters (*e.g.* ethyl acrylate) and internal alkenes (*e.g.* trans-stilbene) were used, the reactions failed to afford the desired products. Substrate **2b** possessing an electron-donating group (R^1 = 4-MeC_6H_4) on the benzene ring produced the desired product **4aba** in 73% yield. Substrates **2c** and **2d**, with electron-withdrawing groups (R^1 = 4-BrC_6H_4, 4-FC_6H_4) on the benzene ring, produced the desired products **4aca** and **4ada** in 84% and 86% yields, respectively (Table 2, entries **4aca** and **4ada**). It was noticed that functional groups such as fluoro, bromo, methyl and methoxy were tolerated under the reaction conditions. When the *N*-phenyl groups were replaced with *N*-alkyl groups, the desired pyrroles could be obtained in high yields at higher reaction temperature with a longer reaction time (Table 2, entries **4bea** and **4cea**).

Various substituted β-keto esters **3** were also found as suitable reaction partners with terminal alkenes **1** and aromatic amines **2** in this reaction. The ester groups of **3**, including methyl, iso-propyl, iso-butyl, *tert*-butyl and benzyl ester, reacted with styrene **1a** and aniline **2a** to afford the corresponding pyrrole products in high yields (Table 2, entries **4aab**–**4aaf**). Crystallized **4aab** from ethanol is a single crystal and its molecular structure was confirmed by X-ray analysis (Fig. 1). The reaction of 2-methoxyethyl acetoacetate **3g** with **1a** and **2a** produced pyrrole **4aag** in 74% yield (Table 2, entry **4aag**). In addition, the corresponding pyrroles with different substituents on the 2-position were successfully synthesized in high yields (Table 2, entries **4aah** and **4bah**). This efficient and modular one-pot construction of pyrrole scaffolds from three simple and commercially available starting materials complements the Hantsch-type pyrrole synthesis and extends its applications.

An extended example is β-enamino ester which underwent subsequent cross-coupling–cyclization–oxidation with terminal alkene

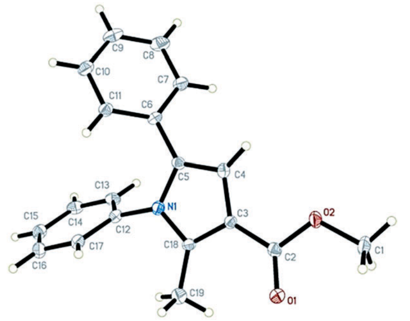
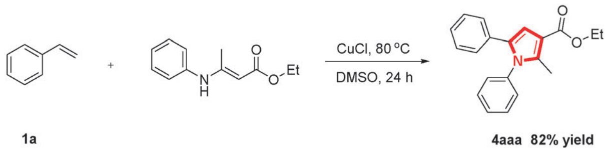
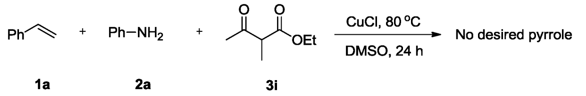


Fig. 1 X-ray crystal structure of **4aab**.



Scheme 1 Synthesis of pyrrole from β-enamino ester and styrene.



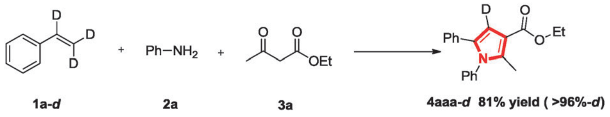
Scheme 2 Cross-coupling–cyclization–oxidation of styrene **1a**, aniline **2a** and ethyl 2-methylacetoacetate **3i**. Reaction conditions: **1a** (0.75 mmol), **2a** (0.5 mmol), **3i** (0.5 mmol), CuCl (10 mol%) in 4 mL of DMSO at 80 °C for 24 h.

1a. The reaction yielded the desired pyrrole product **4aaa** in 82% yield (Scheme 1).

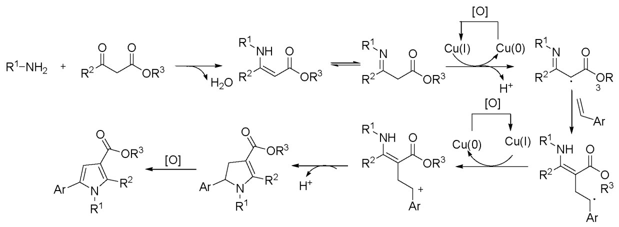
However, the reaction of ethyl 2-methylacetoacetate **3i** with **1a** and **2a** under the optimized conditions failed to afford the desired product (Scheme 2).

To explore the possible reaction pathway, isotope deuterium-labeled styrene **1a-*d*** was used to react with aniline **2a** and ethyl acetoacetate **3a**. The substituted pyrrole **4aaa-*d*** was obtained in 81% yield. Over 96% of deuterium was incorporated in the product (Scheme 3).

Based on other previous studies[12] and the isotope labeling experiment, a reaction mechanism is proposed as shown in Scheme 4. The reaction is initiated by the nucleophilic attack of amines to β-keto esters that produces a β-enamino ester through the loss of water. Single-electron oxidation of the carboanion of the β-enamino ester yields a radical intermediate. The subsequent single-electron inserts into styrene to cause C–C propagation, which is further oxidized by copper(I) to form a carbocation. Subsequent intramolecular condensation of this β-enamino ester intermediate is then oxidized by air to afford the final pyrrole product. It is noteworthy that this mechanism is in sharp contrast to that proposed in the synthesis of pyrazoles starting from β-imino esters and nitriles, where β-imino esters acts as nucleophiles that attack the nitrile.[13]



Scheme 3 Deuterium labeling experiment.



Scheme 4 Possible reaction mechanism.

In summary, we have developed an efficient approach to the synthesis of polysubstituted pyrroles *via* a copper-catalyzed three-component reaction of terminal alkenes, amines and β-keto esters under aerobic conditions. Due to the easy availability of the starting materials and potential applications of products, this method is highly prospective in organic synthesis and medicinal chemistry. This protocol also represents an extremely simple, efficient, and atom-economic way to construct the substituted pyrroles in good yield with high selectivity. Thus it complements the method for the rapid formation of multifunctional heterocycles.

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