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Copper Catalyzed Enantioselective Alkylation of Pyrrole with β,γ-Unsaturated α-Ketoesters: Application to One-Pot Construction of the Seven-Membered Ring by Merging a Gold Catalysis

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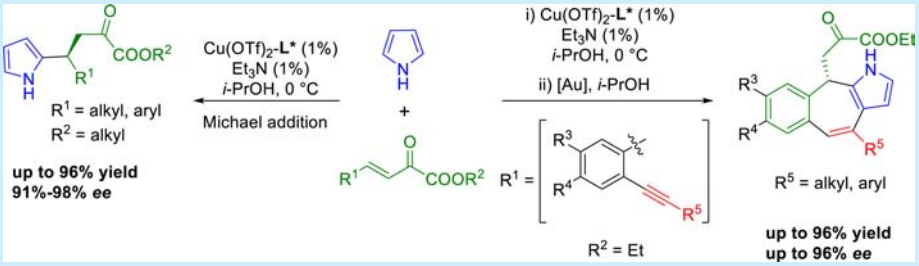
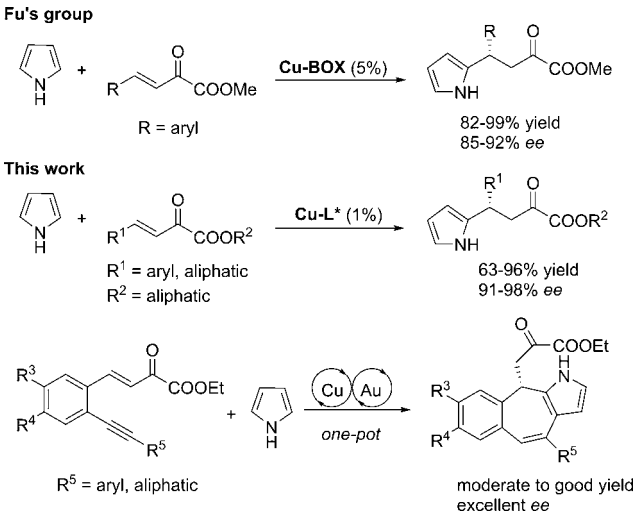
Supporting Information



ABSTRACT: A highly enantioselective Friedel−Crafts alkylation of pyrrole to β,γ-unsaturated α-ketoesters was developed by virtue of a chiral copper complex, affording the alkylated derivatives of pyrrole with good yields and excellent enantioselectivities. Moreover, merging copper catalysis with gold catalysis realized a one-pot construction of the seven-membered ring to give annulated pyrroles with moderate to good yields and high enantiomeric excesses.

Pyrrole and derivatives of pyrrole are prevalent in many natural products, pharmaceuticals, and biologically active molecules.[1] The Friedel−Crafts reaction as an important tool to build C−C bond is of considerable interest for chemists.[2] In the past decades, many asymmetric Friedel−Crafts reactions of pyrrole with various electrophiles were developed.[3] Meanwhile, β,γ-unsaturated α-ketoesters as the versatile molecules came into sight.[4] Recently, the Unaleroglu group designed homochiral pyrroles to access alkylated products with β,γ-unsaturated α-ketoesters via metal triflates.[5a] Then, unprotected pyrrole was employed in the same process to give the corresponding products that could be cyclized by itself via heating.[5b] In 2011, an asymmetric version of the Friedel−Crafts alkylation of *N*-methylated pyrrole to β,γ-unsaturated α-ketoesters was described by the Mikami group.[5c] High yields and good to excellent *ee*'s were achieved. Because of the high reactivity of the very electron-rich pyrrole[1a] and multifunctionality of β,γ-unsaturated α-ketoesters,[4a] the reaction of unprotected pyrrole to β,γ-unsaturated α-ketoesters is always challenging. The Fu group developed the Cu-BOX catalyst bearing the hetero-arylidene skeleton to facilitate the Friedel−Crafts alkylation of pyrrole to β,γ-unsaturated α-ketoesters (Scheme 1).[5d] The transformations were highly enantioselective and efficient. Very recently, the Feng group developed the Friedel−Crafts C3-alkylation of C2-sealed pyrrole to β,γ-unsaturated α-ketoesters through the Ni-*N*,*N*′-dioxide complex.[5e] Good yields and enantioselectivities were obtained. And yet, it is necessary to develop new catalytic systems to promote the important transformation. More importantly, a one-pot dual catalytic system has recently gained considerable interest due to the fact that the products were not acquired using either of the catalysts alone.[6]

Scheme 1. Prior Work and This Work on the Friedel−Crafts Alkylation and Sequential Annulation



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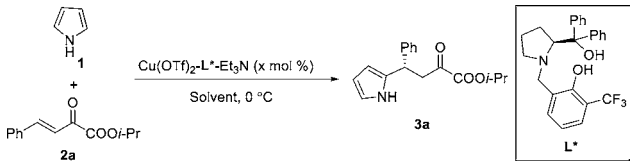
Herein, we employed a facile Cu-complex to catalyze the Friedel−Crafts alkylation of pyrrole to β,γ-unsaturated α-ketoesters. The reaction can be carried out smoothly with a low catalytic loading, and good yields and excellent enantiomeric excesses were acquired. Moreover, we installed the alkynyl group to the *ortho* group of aryl group of 2-oxo-4-arylbut-3-enoates since the molecules with medium-membered ring are very important in the pharmaceutical chemistry.[7] As a result, 7-*endo*-dig annulation was achieved to give seven-membered ring derivatives of pyrrole via a sequential gold catalysis.

Initially, (*E*)-isopropyl 2-oxo-4-phenylbut-3-enoate was selected as the model substrate to conduct the Friedel−Crafts alkylation. Based on our previous efforts on β,γ-unsaturated α-ketoesters, the chiral Cu-prolinol derivative complex was a suitable catalyst to deliver the chiral information through chelating with the double carbonyl group of the molecule.[8] The reaction solvent was first screened by using the Cu-prolinol derivative complex as the catalyst (Table 1). It was found that

Table 1. Optimization of the Friedel−Crafts Alkylation[a]



entry	*x*	solvent	yield[b]/%	*ee*[c]/%
1	10	toluene	11	28
2	10	$CHCl_3$	12	41
3	10	MTBE	34	54
4	10	MeOH	45	78
5	10	EtOH	43	93
6	10	*i*-PrOH	41	96
7[d]	10	*i*-PrOH	79	96
8[d]	5	*i*-PrOH	82	96
9[d]	2	*i*-PrOH	84	96
10[d]	1	*i*-PrOH	89	98

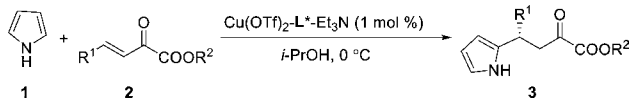
[a]Unless otherwise noted, all reactions were performed with **1** (0.3 mmol), **2a** (0.1 mmol), **L*** (*x* mol %), base (*x* mol %), and $Cu(OTf)_2$ (*x* mol %) in the solvent (1.0 mL) at 0 °C for 5−12 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]Reaction time was 0.3 h. Tf = trifluoromethanesulfonyl.

protonic solvent methanol is able to give a better yield and *ee* than nonprotonic solvents (entries 1−4). Then, other protonic solvents were tested for the Friedel−Crafts alkylation. Isopropyl alcohol showed a preferable result to give **3a** with 41% yield and 93% *ee* (entries 5−6).

Encouraged by these results, the reaction conditions were further optimized. It was found that the reaction time was also crucial to the transformation. Long reaction times resulted in a decrease of the product **3a** gradually. However, no other reaction was observed except for the decomposition of the product when the reaction time was prolonged. The reaction yield was raised to 79% when the reaction time was 0.3 h (entry 7). The great catalytic efficiency reminded us of lowering the loading of the catalyst. 1% of the catalyst could also make the reaction working smoothly within 0.3 h to furnish **3a** with 89% yield and 98% *ee* (entries 8−10). However, <1 mol % of the catalytic loading could not efficiently catalyze the process. Therefore, the reaction conditions of entry 10 in Table 1 were chosen as the optimal conditions. The absolute configuration was assigned by comparison with the reported data.[5d]

With the optimal conditions in hand, the substrate scope of β,γ-unsaturated α-ketoesters for the Friedel−Crafts alkylation was explored (Table 2). First, the electronic effect was examined

Table 2. Scope of β,γ-Unsaturated α-Ketoesters[a]



entry	R^1, R^2 (**2**)	**3**	time	yield[b]/%	*ee*[c]/%
1	Ph, *i*-Pr (**2a**)	**3a**	0.3	89	98
2	*p*-MeC_6H_5, *i*-Pr (**2b**)	**3b**	0.9	73	96
3	*p*-$MeOC_6H_5$, *i*-Pr (**2c**)	**3c**	24	63	94
4	*p*-FC_6H_5, *i*-Pr (**2d**)	**3d**	1.0	79	97
5	*p*-ClC_6H_5, *i*-Pr (**2e**)	**3e**	1.3	84	91
6	*p*-BrC_6H_5, *i*-Pr (**2f**)	**3f**	1.3	79	94
7	*p*-$NO_2C_6H_5$, *i*-Pr (**2g**)	**3g**	5.3	96	96
8	*p*-$CF_3C_6H_5$, *i*-Pr (**2h**)	**3h**	0.5	86	94
9	*m*-ClC_6H_5, *i*-Pr (**2i**)	**3i**	0.5	82	98
10	*o*-ClC_6H_5, Et (**2j**)	**3j**	0.3	72	89
11	*m*-BrC_6H_5, *i*-Pr (**2k**)	**3k**	0.5	84	98
12	*o*-BrC_6H_5, Et (**2l**)	**3l**	1.0	85	96
13	2-naphthyl, *i*-Pr (**2m**)	**3m**	4.3	84	96
14	2-thienyl, *i*-Pr (**2n**)	**3n**	0.5	66	94
15	phenylpropyl, Et (**2o**)	**3o**	0.7	66	94
16	Ph, Me (**2p**)	**3p**	0.3	87	98
17	Ph, Et (**2q**)	**3q**	0.7	80	94
18	Ph, Bn (**2r**)	**3r**	3.5	80	95
19	Ph, *t*-Bu (**2s**)	**3s**	1.0	70	95

[a]Unless otherwise noted, all reactions were performed with **1** (1.2 mmol), **2** (0.4 mmol), **L*** (1 mol %), Et_3N (1 mol %), and $Cu(OTf)_2$ (1 mol %) in *i*-PrOH (2.0 mL) at 0 °C. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

by varying the *para*-substituents of R^1. As for the electron-donating groups, good yields and excellent enantiomeric excesses were obtained (entries 2−3). For the electron-withdrawing groups, such as fluoro-, chloro-, and bromo- groups, the reaction can be carried out smoothly, and these groups were also tolerated well (entries 4−6). Good yields and enantioselectivities were obtained when the intense electron-withdrawing groups were installed on the *para* position of R^1 (entries 7−8). These results indicated that electron-withdrawing groups could give better yields than the electron-donating ones. On the other hand, the position variation of substituents of R^1 showed little influence on the alkylations (entries 9−12). Moreover, the 2-naphthyl group and heterocyclic group were compatible with the catalytic system (entries 13−14). Significantly, the aliphatic substrate **2o** proceeded smoothly to afford the corresponding product **3o** with a moderate yield and excellent enantioselectivity (entry 15). Then, different ester groups R^2 were tested, which demonstrated that there is little influence on the alkylation in terms of the yields and enantioselectivities (entries 15−19). Most of these transformations were carried out rapidly and finished in 1 h. However, the reactions of some substrates required a long time due to the substrate solubility in *i*-PrOH (entries 3, 7, 13, 18).

As a result, the asymmetric alkylation of pyrrole with the β,γ-unsaturated α-ketoesters was developed. After that, we took into consideration the construction of the seven-membered ring on the basis of the developed alkylation. In recent decades, the enantioselective synthesis of the one-pot dual catalytic system

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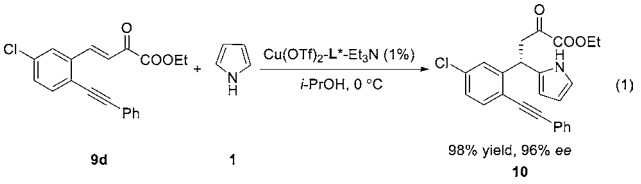
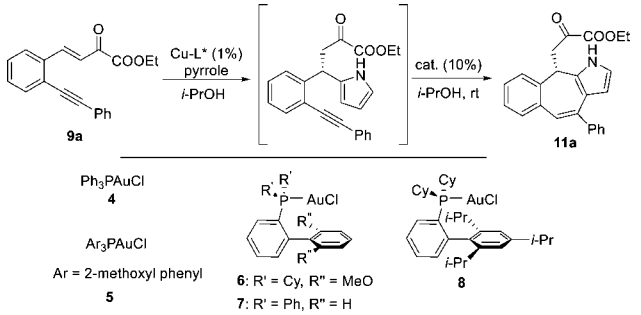
experienced rapid growth because the complexity of the molecules can be acquired via cooperative/relay/sequential catalysis.[9] Recently, the Enders group reported the synthesis of annulated indoles and pyrroles through merging organocatalysis and gold catalysis, realizing the preparation of challenging seven-membered ring molecules.[10] Inspired by these research results, we wondered whether the sequential gold catalysis could render an annulation via an attack of pyrrole to the alkynyl group in the *ortho* group of R^1 to fuse a seven-membered ring. (*E*)-Ethyl 4-(5-chloro-2-(phenylethynyl)phenyl)-2-oxobut-3-enoate **9d** was employed to examine this sequential annulation. As expected, the first alkylation proceeded smoothly to afford the product **10** in 98% yield and 96% *ee* via the copper catalysis (eq 1).



9d **1** **10**

The sequential annulation to access the seven-membered ring **11a** was then optimized by screening the various catalysts (Table 3). The substrate **9a** was converted to another intramolecular addition product from the N-1 position to the carbonyl group of keto ester when $AuCl_3$ and $AgNO_3$ were employed respectively (entries 1, 3). $AgNTf_2$ alone could not provide any desired product either (entry 2). A copper catalyst did not work in this annulation (entry 4). Finally, it was found that the combination of the gold catalyst **4** with $AgNTf_2$ could give rise to the desired seven-membered ring with a good yield and *ee* value (entries 5–7). After screening the different phosphine ligands (entries 8–11), the catalytic system of the Au(I) complex with phosphine **5** and $AgNTf_2$ was found to be the best catalyst for the transformation (entry 8).

Table 3. Optimization of Gold-Catalyzed Annulation[a]

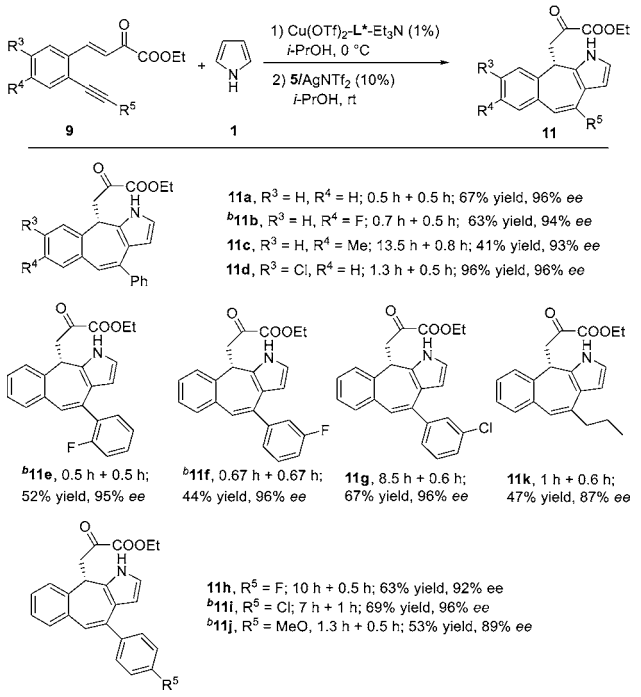


entry	catalyst	time/h	yield[b]/%
1[c]	$AuCl_3$	3.0	–
2	$AgNTf_2$	>24	–
3[c]	$AgNO_3$	3.0	–
4	$Cu(OTf)_2$	>24	–
5	**4**/AgOTf	0.3	62
6	**4**/$AgNTf_2$	0.3	81
7	**4**/$AgSbF_6$	0.3	75
8	**5**/$AgNTf_2$	0.3	86
9	**6**/$AgNTf_2$	0.3	73
10	**7**/$AgNTf_2$	0.3	84
11	**8**/$AgNTf_2$	0.3	66

[a]Unless otherwise noted, all reactions were performed with **9a** (0.1 mmol), and the catalyst (10 mol %) in *i*-PrOH (1.0 mL) at room temperature. [b]Isolated yield. [c]Another intramolecular addition product was detected from the 1-N position of pyrrole to the carbonyl group of keto ester.

With the optimized catalyst in hand, the scope of *β,γ*-unsaturated *α*-ketoesters with various substituents was explored to examine the compatibility of the dual-metal catalytic system (Scheme 2). To our delight, a variety of substituents of **9** could give good to excellent enantioselectivities. However, the electronic effect showed that there was an influence on the yields of the annulations. The yields of **9b** and **9d** bearing electron-withdrawing substituents were obviously higher than those of **9c** bearing an electron-donating substituent and **9a** bearing an electron-neutral substituent. However, the variation of aryl R^5 had little influence on the reaction. Moreover, aliphatic R^5 was also compatible with the sequential alkylation/annulation to afford **11k** with a good *ee* value in spite of the moderate yield. Nevertheless, the reaction rates of these substrates slowed down due to the solubility in *i*-PrOH (**9b**, **9e**, **9f**, **9i**, **9j**). The reaction temperature of these substrates was enhanced to room temperature from 0 °C in order to increase the reaction rate. Finally, we developed a one-pot alkylation/annulation of pyrrole with *β,γ*-unsaturated *α*-ketoesters to afford the chiral seven-membered ring derivatives with moderate to good yields and excellent *ee* values.

Scheme 2. Scope of the Sequential Friedel–Crafts Alkylation/Annulation[a]



[a]Unless otherwise noted, all reactions were performed with **9** (0.3 mmol), **1** (0.9 mmol) with 1 mol % copper catalyst at 0 °C in *i*-PrOH for the first step. Then to the residue after evaporation of solvent was added 10% gold catalyst at rt in *i*-PrOH (0.1 M). [b]The reaction temperature of the first step was at rt.

The mechanism of the sequential reaction is listed in the Supporting Information. At first, the nucleophilic addition of the C2 pyrrole to **9** furnished the asymmetric alkylated product. The chiral information was transferred through coordination of the

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Cu-complex and double carbonyl groups of β,γ-unsaturated α-ketoesters. In the second step, the gold catalyzed 7-*endo*-dig annulation was completed with retention of the enantioselectivity.[10b,11]

In summary, a highly enantioselective, efficient Friedel−Crafts alkylation of pyrrole with β,γ-unsaturated α-ketoesters was developed by virtue of the catalysis of a Cu-prolinol derivative complex. Good to excellent yields and excellent enantioselectivities were achieved with a low catalytic loading. More importantly, an alkylation/annulation sequence was realized in one pot to access the seven-membered ring molecules via a dual-metal system of copper and gold catalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01917.

Experimental procedures, characterization data, copies of ^{1}H NMR, ^{13}C NMR of new compounds, HPLC profiles (PDF)

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Notes

The authors declare no competing financial interest.

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