Synthetic Methods

DOI: 10.1002/ange.201309182

Enantioselective Copper-Catalyzed Decarboxylative Propargylic Alkylation of Propargyl β-Ketoesters with a Chiral Ketimine P,N,N-Ligand**

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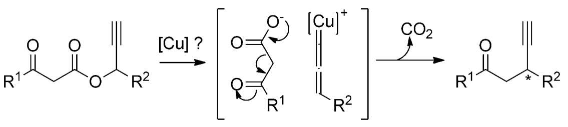
Abstract: *The first enantioselective copper-catalyzed decarboxylative propargylic alkylation has been developed. Treatment of propargyl β-ketoesters with a catalyst, prepared in situ from [Cu(CH$_3$CN)$_4$BF$_4$] and a newly developed chiral tridentate ketimine P,N,N-ligand under mild reaction conditions, generates β-ethynyl ketones in good yields and with high enantioselectivities without requiring the pregeneration of ketone enolates. This new process provides facile access to a range of chiral β-ethynyl ketones in a highly enantioenriched form.*

Transition-metal-catalyzed propargylic substitutions represent an important class of reactions because of their abilities to introduce an electron-rich triple bond which is a versatile entity for further chemical transformations.[1] Recent achievements have led to a catalytic asymmetric version of this reaction.[2] Although a variety of nitrogen and carbon nucleophiles are suitable reagents for these catalytic asymmetric propargylic substitutions, the use of simple ketone enolates as nucleophiles is still very limited.[3] The development of catalytic asymmetric propargylic alkylation with simple ketone enolates as nucleophiles remains a great challenge.

In the past decades, an excellent method for the generation of nonstabilized ketone enolates as nucleophiles in situ by decarboxylation under mild reaction conditions has been elegantly developed and known as transition-metal-catalyzed decarboxylative allylic alkylations.[4] In this method, the loss of CO$_2$ replaces the need to selectively prepare preformed enolate equivalents, and both the nucleophile and the electrophile are formed in situ in a catalytic concentration. It therefore can be envisaged that this strategy should also provide an ideal solution for the catalytic propargylic alkylation of simple ketones. However, few examples have been realized for the catalytic decarboxylative propargylic transformation to date,[5] and to the best of our knowledge, there is only one report, by Stoltz and co-workers, on the successful palladium-catalyzed asymmetric propargylation of enol carbonates with 12–44% *ee* .[6] Catalytic asymmetric decarboxylative propargylation is still a far less explored field.

Recent progress in the copper-catalyzed asymmetric propargylic substitution has indicated that the reaction proceeded via copper allenylidene complexes as key intermediates, which were formed by the elimination of an ester group from propargylic substrates.[7] We therefore envision that an asymmetric decarboxylatve propargylic alkylation may have occurred when a substrate, tethering the propargyl moiety and nucleophile together with an ester functional group, is subjected to a chiral copper catalyst (Scheme 1). As a result, herein we report the first copper-catalyzed enantioselective decarboxylative propargylic alkylation of propargyl β-ketoesters, which provides a new and facile approach for the synthesis of chiral β-ethynyl ketones in a highly enantioenriched form.[8]



Scheme 1. General reaction scheme for enantioselective copper-catalyzed decarboxylative propargylic alkylation.

An initial attempt to carry out a reaction using 1-phenyl-2-propynyl 3-oxo-3-phenylpropanoate (**1aa**)[9] was conducted in MeOH at room temperature in the presence of 1.2 equivalents of iPr$_2$NEt with 5 mol% of a chiral copper catalyst prepared in situ from Cu(OAc)$_2$·H$_2$O and (*S*)-binap. The reaction delivered the desired β-ethynyl ketone product **2aa** albeit in low yield with nearly no enantioselection (Table 1, entry 1). After the evaluation of several ligands which have proven to be efficient in copper-catalyzed asymmetric propargylic amination,[7] the chiral tridentate P,N,N-ligand (*R*)-**L4**[7j,10] developed in our group was identified as a promising ligand structure (Table 1, entry 4). We therefore evaluated the effects of modifications to the ligand structure of (*R*)-**L4** on the reaction outcome. Two new P,N,N-ligands (*S*)-**L5** and (*S*)-**L6**, bearing a ketimine moiety were then prepared as shown in Scheme 2. Pleasingly, (*S*)-**L6**, derived from 2-benzopyridine,

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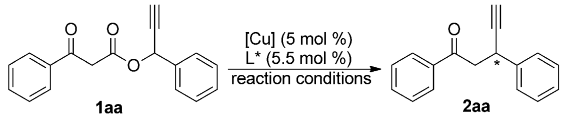
[**] Support for this research from the Dalian Institute of Chemical Physics (CAS) is gratefully acknowledged.

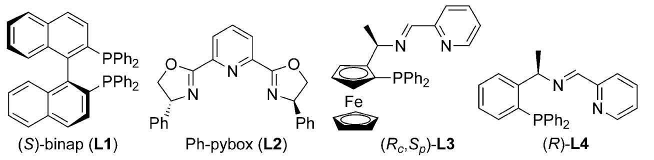
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201309182.

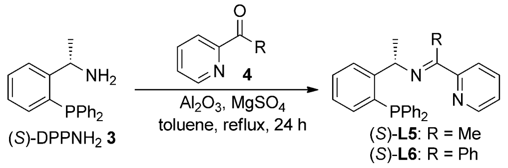
Table 1: Screening of chiral ligands and reaction conditions.[a]



Entry	[Cu]	L*	Solvent	Base	*T* [°C]	Yield [%][b]	*ee* [%][c]
1	$Cu(OAc)_2 \cdot H_2O$	**L1**	MeOH	*i*Pr_2NEt	25	38	<10
2	$Cu(OAc)_2 \cdot H_2O$	**L2**	MeOH	*i*Pr_2NEt	25	92	12
3	$Cu(OAc)_2 \cdot H_2O$	**L3**	MeOH	*i*Pr_2NEt	25	85	55
4	$Cu(OAc)_2 \cdot H_2O$	**L4**	MeOH	*i*Pr_2NEt	25	90	65
5	$Cu(OAc)_2 \cdot H_2O$	**L5**	MeOH	*i*Pr_2NEt	25	91	68
6	$Cu(OAc)_2 \cdot H_2O$	**L6**	MeOH	*i*Pr_2NEt	25	90	84
7	$Cu(CH_3CN)_4BF_4$	**L6**	MeOH	*i*Pr_2NEt	25	94	84
8	CuI	**L6**	MeOH	*i*Pr_2NEt	25	85	60
9	CuCl	**L6**	MeOH	*i*Pr_2NEt	25	84	55
10	$Cu(CH_3CN)_4BF_4$	**L6**	MeOH	*i*Pr_2NEt	0	93	92
11	$Cu(CH_3CN)_4BF_4$	**L6**	MeOH	none	0	–	–[d]
12	$Cu(CH_3CN)_4BF_4$	**L6**	MeOH	DBU	0	85	71
13	$Cu(CH_3CN)_4BF_4$	**L6**	MeOH	Et_3N	0	92	94
14	$Cu(CH_3CN)_4BF_4$	**L6**	CH_2Cl_2	Et_3N	0	95	94
15	$Cu(CH_3CN)_4BF_4$	**L6**	THF	Et_3N	0	92	92
16	$Cu(CH_3CN)_4BF_4$	**L6**	toluene	Et_3N	0	96	95

[a] Reaction conditions: **1aa** (0.3 mmol), [Cu] (0.015 mmol, 5 mol%), L* (0.0165 mmol, 5.5 mol%), base (0.36 mmol, 1.2 equiv), 1.2 mL of solvent, indicated temperature, 12 h. [b] Yield of isolated product. [c] The *ee* values were determined by HPLC analysis using a chiral stationary phase. [d] Not determined because of low conversion. THF = tetrahydrofuran.





Scheme 2. Synthesis of the new chiral tridentate P,N,N-ligands (*S*)-**L5** and (*S*)-**L6** bearing a ketimine moiety.

was found to be optimal and afforded **2aa** in 90% yield and with 84% *ee* (Table 1, entry 6). Other copper sources, including $[Cu(CH_3CN)_4BF_4]$, CuI, and CuCl, were also tested (Table 1, entries 7–9), and the results demonstrated that $[Cu(CH_3CN)_4BF_4]$ was the best choice (Table 1, entry 7). The tridentate coordination mode of (*S*)-**L6** with Cu^I was unambiguously confirmed by X-ray analysis of the CuCl/(*S*)-**L6** complex (Figure 1).[11]

Lowering the reaction temperature to 0°C significantly improved the enantioselectivity to 92% *ee* without loss of the yield (Table 1, entry 10). The addition of a base proved to be crucial for this reaction, and none of the desired β-ethynyl ketone product **2aa** was observed in its absence (Table 1, entry 11). However, a stronger base, such as 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU), had a detrimental effect on both the yield and the enantioselectivity (Table 1, entry 12). The best result was obtained with Et_3N, in which **2aa** was obtained in 92% yield and 94% *ee* (Table 1, entry 13). The nature of the solvent showed little influence on both the yield and the enantioselectivity, and all of the solvents tested showed excellent performance, with toluene as the optimal in terms of the enantioselectivity (Table 1, entry 16). This result is different compared to those observed with the copper-catalyzed asymmetric propargylic substitution, in which only a polar protic solvent was found to be suitable.[7]

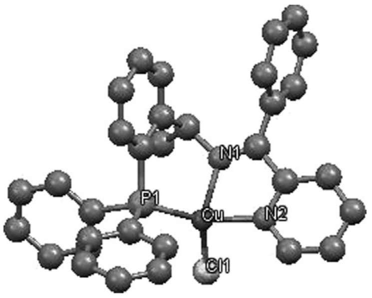
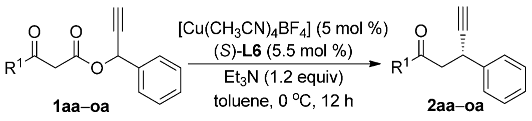


Figure 1. Crystal structure of CuCl/(*S*)-**L6** complex. Hydrogen atoms and solvent are omitted for clarity.

Having developed the optimized reaction conditions, we subsequently explored the scope of this process with respect to the ketone moieties of propargyl β-ketoesters. As shown in Table 2, a broad range of 1-phenyl-2-propynyl 3-oxo-3-arylpropanoates worked efficiently to provide the desired β-ethynyl ketones in good to excellent yields and with very high enantioselectivities (Table 2, entries 1–12). Electron-donating and electron-withdrawing substituents in the *para* (Table 2,

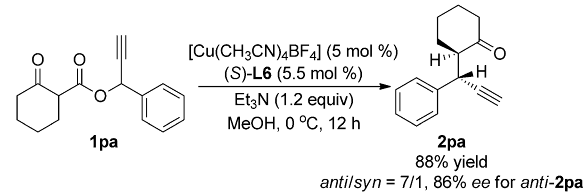
Table 2: Copper-catalyzed decarboxylative propargylic alkylation of β-ketoesters: scope of ketone moieties.[a]



Entry	Substrate	Product	Yield [%][b]	*ee* [%][c]
1	**1aa**: R^1 = Ph	**2aa**	96	95
2	**1ba**: R^1 = 2-ClC_6H_4	**2ba**	65	93
3	**1ca**: R^1 = 3-ClC_6H_4	**2ca**	92	95
4	**1da**: R^1 = 4-ClC_6H_4	**2da**	96	94
5	**1ea**: R^1 = 4-FC_6H_4	**2ea**	96	95
6	**1fa**: R^1 = 4-BrC_6H_4	**2fa**	95	95
7	**1ga**: R^1 = 4-MeC_6H_4	**2ga**	93	95
8	**1ha**: R^1 = 4-$MeOC_6H_4$	**2ha**	95	93
9	**1ia**: R^1 = 4-$NO_2C_6H_4$	**2ia**	96	94
10	**1ja**: R^1 = 2-naphthyl	**2ja**	95	96
11	**1ka**: R^1 = 6-MeO-2-naphthyl	**2ka**	96	98
12	**1la**: R^1 = thienyl	**2la**	91	95
13[d]	**1ma**: R^1 = Me	**2ma**	88	85
14[d]	**1na**: R^1 = *n*Pr	**2na**	85	86
15[d]	**1oa**: R^1 = Bn	**2oa**	90	83

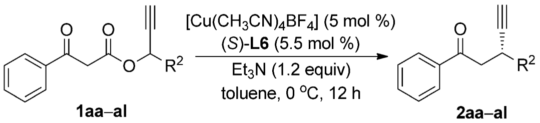
[a] Reaction conditions: **1** (0.5 mmol), $[Cu(CH_3CN)_4BF_4]$ (0.025 mmol, 5 mol%), (*S*)-**L6** (0.0275 mmol, 5.5 mol%), Et_3N (0.6 mmol, 1.2 equiv), 2 mL of toluene, 0°C, 12 h. [b] Yield of isolated product. [c] The *ee* values were determined by HPLC analysis using a chiral stationary phase. [d] The reaction was performed in MeOH at a catalyst loading of 10 mol%.

entries 4–9) or *meta* (Table 2, entry 3) position of the phenyl ring were compatible with this transformation. However, the reaction was sensitive to the substituent at the *ortho* position of the phenyl ring, and the use of the substrate **1ba**, bearing a 2-Cl substituent, resulted in a decreased yield (Table 2, entry 2). Although **1ba** was less reactive than its 3-Cl (**1ca**) and 4-Cl (**1da**) analogues, the observed selectivity was nonetheless excellent (Table 2, entry 2). Other aromatics and heteroaromatics, such as 1-naphthyl, 6-methoxy-1-naphthyl, and 2-thiophenyl groups proved to be good substrates for the reaction (Table 2, entries 10–12). Notably, the reaction could also be realized for aliphatic β-ketoesters although a catalyst loading of 10 mol % was required to reach complete conversion (Table 2, entries 13–15). The reaction also tolerated substituents at the α-position. Thus, the cyclic β-ketoester **1pa** also performed well under the optimized reaction conditions (Scheme 3).



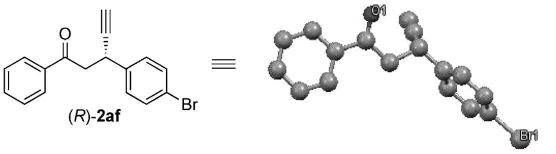
Scheme 3. Copper-catalyzed asymmetric decarboxylative propargylic alkylation of cyclic β-ketoester.

Table 3: Copper-catalyzed decarboxylative propargylic alkylation of β-ketoesters: scope of propargyl moieties.[a]



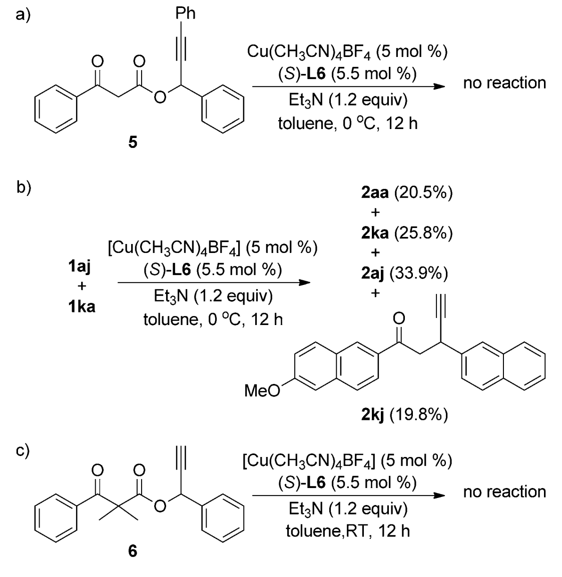
Entry	Substrate	Product	Yield [%][b]	*ee* [%][c]
1	**1aa**: R^2 = Ph	**2aa**	96	95
2	**1ab**: R^2 = 2-ClC_6H_4	**2ab**	92	93
3	**1ac**: R^2 = 3-ClC_6H_4	**2ac**	95	96
4	**1ad**: R^2 = 4-ClC_6H_4	**2ad**	96	95
5	**1ae**: R^2 = 4-FC_6H_4	**2ae**	96	94
6	**1af**: R^2 = 4-BrC_6H_4	**2af**	93	95
7	**1ag**: R^2 = 4-MeC_6H_4	**2ag**	91	89
8	**1ah**: R^2 = 4-$MeOC_6H_4$	**2ah**	94	85
9	**1ai**: R^2 = 4-$CF_3C_6H_4$	**2ai**	96	95
10	**1aj**: R^2 = 2-naphthyl	**2aj**	94	97
11	**1ak**: R^2 = thienyl	**2ak**	92	88
12	**1al**: R^2 = Me	**2al**	–	–[d]

[a] Reaction conditions: **1** (0.5 mmol), $Cu(CH_3CN)_4BF_4$ (0.025 mmol, 5 mol%), (*S*)-**L6** (0.0275 mmol, 5.5 mol%), Et_3N (0.6 mmol, 1.2 equiv), 2 mL of toluene, 0 °C, 12 h. [b] Yield of isolated product. [c] The *ee* values were determined by HPLC analysis using a chiral stationary phase. [d] Not determined because of low conversion.

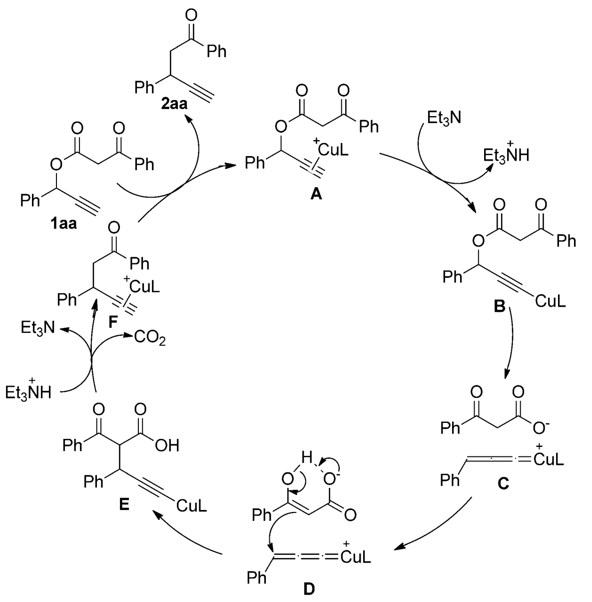


The scope of the propargyl moieties was next investigated (Table 3). We were pleased to find that the reaction proceeded smoothly for all 1-aryl-2-propynyl 3-oxo-3-phenylpropanoates tested, with the desired products obtained in good yields and with high levels of enantioinduction. The position of the substituent on the phenyl ring had less influence on this process. Thus, all three substrates having a Cl at the different positions on the phenyl ring gave similar results (Table 3, entries 2–4). It appears that the electronic properties of the substituent at the *para* position had some effect on the enantioselectivity, and the substrate with an electron-donating group tended to give lower enantioselectivity (Table 3, entries 7 and 8). 1-Naphthyl and 2-thiophenyl substrates were also suitable reaction partners, thus giving the corresponding β-ethynyl ketones in good results. However, the present catalytic system did not tolerate an aliphatic substrate (**1al**), thus giving very low conversions (Table 3, entry 12). This result is consistent with the observation in the catalytic asymmetric propargylic substitution.[7f–g] The absolute configuration of chiral β-ethynyl ketones was unambiguously determined by X-ray structure analysis of **2af**, and is assigned as having an *R* configuration.[11]

By considering all the experimental evidence (Scheme 4), a reaction pathway is proposed in Scheme 5. In the first step, a copper complex forms the π-complex **A** with the propargyl β-ketoester **1aa**. Deprotonation of **A** with Et_3N would then give the copper acetylide complex **B**, which would explain why a propargyl β-ketoester bearing an internal alkyne moiety did not react at all (Scheme 4a). The dissociation of **B** likely produces a copper allenylidene complex carboxylate ion pair (**C**),[7f] which isomerizes to give a copper allenylidene complex enolate ion pair (**D**). The crossover experiment in Scheme 4b suggested the dissociation of the copper allenylidene complex and the enolate ion during the reaction. The enolate attacks at the C_γ atom of the copper allenylidene



Scheme 4. Mechanistic investigations into the copper-catalyzed decarboxylative propargylic alkylation.



Scheme 5. Proposed mechanism.

complex with subsequent loss of CO_2 to give the copper π-alkyne complex **F**. The α,α-disubstituted ester **6** did not undergo the reaction (Scheme 4c) and may suggest that decarboxylation occurs after propargylic alkylation. However, the possibility that decarboxylation occurrs before propargylation alkylation is still not ruled out. Further investigations to elucidate the reaction mechanism are underway.

In conclusion, we have developed the first copper-catalyzed asymmetric decarboxylative propargylic alkylation of propargyl β-ketoesters with a new chiral ketimine P,N,N-ligand, and provides a new and facile access to a variety of β-ethynyl ketones in good yields and with high enantioselectivities. Since both the nucleophile and the electrophile are formed in situ in catalytic concentration by the loss of CO_2, instead of the need to prepare preformed enolate equivalents, we believe that this new reaction should provide a complementary strategy for catalytic asymmetric propargylic substitution. The further development and application of this reaction, as well as study of the mechanism, is underway in our laboratory.

Received: October 21, 2013

Keywords: alkylation · asymmetric catalysis · copper · ligand design · synthetic methods

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[11] CCDC 967239 [CuCl/(*S*)-**L6** complex] and CCDC 967238 [(*R*)-**2af**] contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.