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Cooperative Catalytic Reactions Using Organocatalysts and Transition Metal Catalysts: Enantioselective Propargylic Alkylation of Propargylic Esters with Aldehydes

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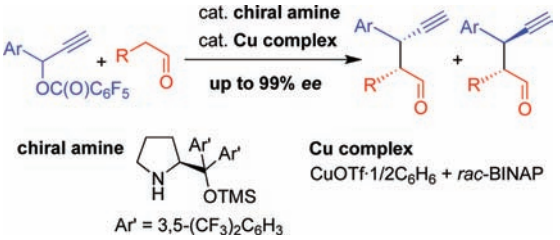
ABSTRACT



The enantioselective propargylic alkylation of propargylic esters with aldehydes in the presence of a copper complex and an optically active secondary amine as cocatalysts has been found to give the corresponding propargylic alkylated products in good yields as a mixture of two diastereoisomers with a high enantioselectivity.

Quite recently, we have found the enantioselective propargylic alkylation of propargylic alcohols with aldehydes in the presence of a thiolate-bridged diruthenium complex and an optically active secondary amine as cocatalysts to give the corresponding propargylic alkylated products in excellent yields as a mixture of two diastereoisomers with a high enantioselectivity (up to 99% *ee*) (Scheme 1).[1] This catalytic reaction is considered to provide a new type of enantioselective propargylic substitution reaction,[2] where the enamines generated in situ from aldehydes enantioselectively attack the γ-carbon atom of the ruthenium−allenylidene complexes.[3] In this reaction system, both the transition metal catalyst (ruthenium complex) and organocatalyst[4] (secondary amine)

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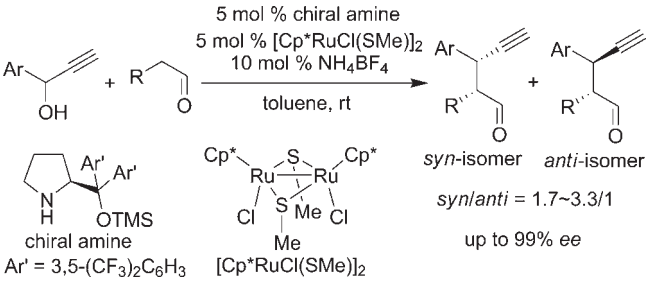
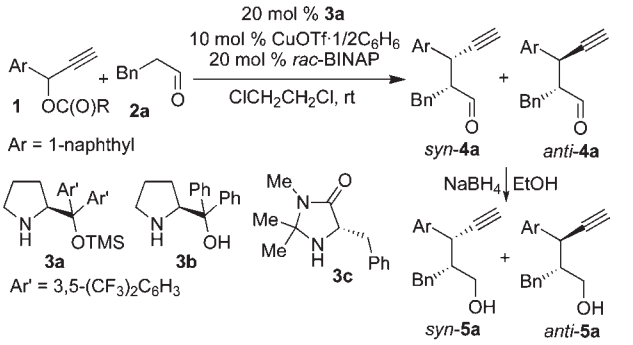
Scheme 1



Scheme 2



R (**1**)	time (h)	yield of **5a** (%)	*syn*-**5a**/*anti*-**5a**	*ee* (%) *syn*-**5a**	*ee* (%) *anti*-**5a**
C_6F_5 (**1a**)	1.5	53	3.2/1	98	96
3,4,5-$F_3C_6H_2$ (**1b**)	30	19	2.0/1	99	95
C_6H_5 (**1c**)	30	0	—	—	—
CH_3 (**1d**)	30	0	—	—	—

activate propargylic alcohols and aldehydes, respectively, and both catalysts cooperatively and simultaneously work to promote the propargylic alkylation enantioselectively.

On the other hand, we have found the copper-catalyzed enantioselective propargylic amination of propargylic acetates with amines to give the corresponding propargylic amines in high yields with a high to excellent enantioselectivity (up to 98% *ee*).[5−7] The result of the density functional theory calculation on the model reaction supports the concept that the catalytic amination proceeds via a copper−allenylidene complex, where the attack of amines to the γ-carbon atom of the allenylidene ligand is a key step although the isolation of copper−allenylidene complexes has not yet been successful.

As an extension of our continuous study on the enantioselective propargylic substitution reactions, we have now envisaged the cooperative catalytic reactions by using both a copper catalyst and an organocatalyst. In fact, we have found that reactions of propargylic esters with aldehydes in the presence of a copper complex bearing racemic diphosphine and an optically active secondary amine as cocatalysts give the corresponding propargylic alkylated products in good yields as a mixture of two diastereoisomers with a high enantioselectivity. We believe that the method described in this communication may provide a new type of dual catalytic reactions using both organocatalysts and transition metal catalysts.[8,9] Preliminary results are described here.

Treatment of 1-(1-naphthyl)-2-propynyl 2,3,4,5,6-pentafluorobenzoate (**1a**) with 3-phenylpropanal (**2a**) in the presence of catalytic amounts of (*S*)-α,α-bis[3,5-bis(trifluoromethyl)phenyl]-2-pyrrolidinemethanol trimethyl silyl ether (**3a**), a copper trifluoromethanesulfonate−benzene complex, CuOTf·1/2(C_6H_6) (10 mol %), and racemic BINAP[10] (20 mol %) in $ClCH_2CH_2Cl$ at room temperature for 1.5 h gave 2-benzyl-3-(1-naphthyl)-4-pentynal (**4a**) exclusively (Scheme 2). 2-Benzyl-3-(1-naphthyl)-4-pentyn-1-ol (**5a**) was isolated in 53% yield as an inseparable mixture of two diastereoisomers (*syn*-**5a**/*anti*-**5a** = 3.2/1) with 98% *ee* of *syn*-**5a** and 96% *ee* of *anti*-**5a** after the reduction of **4a** with $NaBH_4$ at 0 °C for 1 h. The nature of the ester group in propargylic esters plays a critical role in promoting the catalytic alkylation. When the reaction of 1-(1-naphthyl)-2-propynyl 3,4,5-trifluorobenzoate (**1b**) was carried out for a longer reaction time such as 30 h, **5a** was obtained in only 19% yield. On the other hand, no propargylic alkylation occurred at all when 1-(1-naphthyl)-2-propynyl benzoate (**1c**), 1-(1-naphthyl)-2-propynyl acetate (**1d**), or 1-(1-naphthyl)-2-propyn-1-ol was used in place of **1a**. Other secondary amines such as (*S*)-α,α-diphenyl-2-pyrrolidinemethanol (**3b**) and (5*S*)-2,2,3-trimethyl-5-benzyl-4-imidazolidinone (**3c**) did not work at all.

A significantly lower yield of the product was observed when the amount of **3a** was decreased to 10 mol %.

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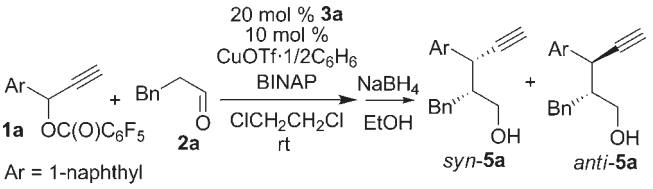
Scheme 3



BINAP (mol %)	time (h)	yield of 5a (%)	syn-5a/anti-5a	ee (%) syn-5a	ee (%) anti-5a
rac-BINAP (20)	1.5	53	3.2/1	98	96
rac-BINAP (10)[a]	4	60	2.7/1	97	95
(*R*)-BINAP (20)	1.5	67	3.4/1	99	96
(*S*)-BINAP (20)	1.5	71	3.5/1	99	95

[a] $CuOTf{\cdot}1/2C_6H_6$ (5 mol %) was used as a catalyst.

Expectedly, use of *ent*-**3a** ((*R*)-α,α,-bis[3,5-bis(trifluoromethyl)phenyl]-2-pyrrolidinemethanol trimethyl silyl ether) in place of **3a** as an organocatalyst gave *ent*-**5a** in 59% yield with a similar enantioselectivity. Separately, we confirmed that the use of only either **3a** or the copper complex did not promote the propargylic alkylation. This result indicates that both **3a** and the copper complex cooperatively worked as catalysts to promote the catalytic reaction enantioselectively.

Use of an excess amount (20 mol %) of BINAP is necessary to promote the catalytic reaction smoothly (Scheme 3). The excess amount of BINAP is considered to inhibit the dissociation of BINAP from the copper atom of the catalyst. A similar result was achieved when the amounts of a copper trifluoromethanesulfonate−benzene complex, $CuOTf{\cdot}1/2(C_6H_6)$ (5 mol %), and racemic BINAP (10 mol %) were decreased under the same reaction conditions. Interestingly, the stereochemistry of BINAP did not affect the enantioselectivity of the alkylated product. In fact, a similar result was achieved when (*R*)-BINAP or (*S*)-BINAP was used in place of racemic BINAP as a ligand to the copper complex. Although (*R*)-Cl-MeO-BIPHEP[11] worked as a suitable ligand for the propargylic alkylation, other diphosphines such as racemic BIPHEP,[12] (*R*)-SEGPHOS,[13] (*R*)-DTBM-SEGPHOS,[14] and dppe were not effective ligands. When the catalytic reaction was carried out in the absence of diphosphine, a complex mixture was formed with the alkylated products.

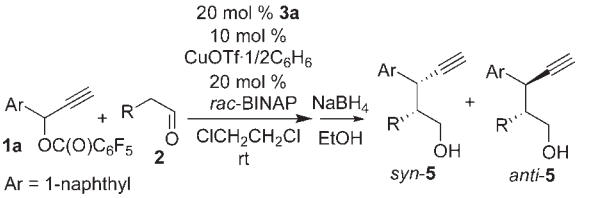
(11) (*R*)-Cl-MeO-BIPHEP = (*R*)-5,5′-dichloro-6,6′-dimethoxy-2,2′-bis(diphenylphosphino)-1,1′-biphenyl: (a) Huddleston, R. R.; Jang, H.-Y.; Krische, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 11488. (b) Jang, H.-Y.; Hughes, F. W.; Gong, H.; Zhang, J.; Brodbelt, J. S.; Krische, M. J. *J. Am. Chem. Soc.* **2005**, *127*, 6174. (c) Rhee, J. U.; Krische, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 10674. (d) Skucas, E.; Kong, J. R.; Krische, M. J. *J. Am. Chem. Soc.* **2007**, *129*, 7242.

(12) BIPHEP = 2,2′-bis(diphenylphosphino)-1,1′-biphenyl: Schmid, R.; Foricher, J.; Cereghetti, M.; Schönholzer, P. *Helv. Chim. Acta* **1991**, *74*, 370.

(13) (*R*)-SEGPHOS = (*R*)-5,5′-bis(diphenylphosphino)-4,4′-bi-1,3-benzodioxole: Nagasaki, I.; Matsumura, K.; Sayo, N.; Saito, T. *Acc. Chem. Res.* 2007, *40*, 1385 and references therein.

(14) (*R*)-DTBM-SEGPHOS = (*R*)-5,5′-bis[di(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino]-4,4′-bi-1,3-benzodioxole.

Table 1. Copper-Catalyzed Enantioselective Propargylic Alkylation of Propargylic Ester (**1a**) with Aldehydes (**2**)[a]



run	R (**2**)	time (h)	yield of **5** (%)[b]	*syn*-**5**/*anti*-**5**	ee (%)[c] *syn*-**5**	ee (%)[c] *anti*-**5**
1	Bn (**2a**)	1.5	53 (**5a**)	3.2/1	98	96
2	*p*-$ClC_6H_4CH_2$ (**2b**)	1.5	54 (**5b**)	3.8/1	99	97
3	$^cHexCH_2$ (**2c**)	1.5	52 (**5c**)	3.2/1	97	98
4	$Me(CH_2)_4$ (**2d**)	2	58 (**5d**)	3.5/1	83	94
5	$Cl(CH_2)_4$ (**2e**)	1.5	64 (**5e**)	3.5/1	84	94

[a] All reactions of **1a** (0.20 mmol) with aldehyde (**2**; 0.40 mmol) were carried out in the presence of $CuOTf{\cdot}1/2C_6H_6$ (0.02 mmol), *rac*-BINAP (0.04 mmol), and **3a** (0.04 mmol) in $ClCH_2CH_2Cl$ (5 mL) at room temperature. [b] Isolated yield of **5**. [c] Determined by HPLC (see the Supporting Information for experimental details).

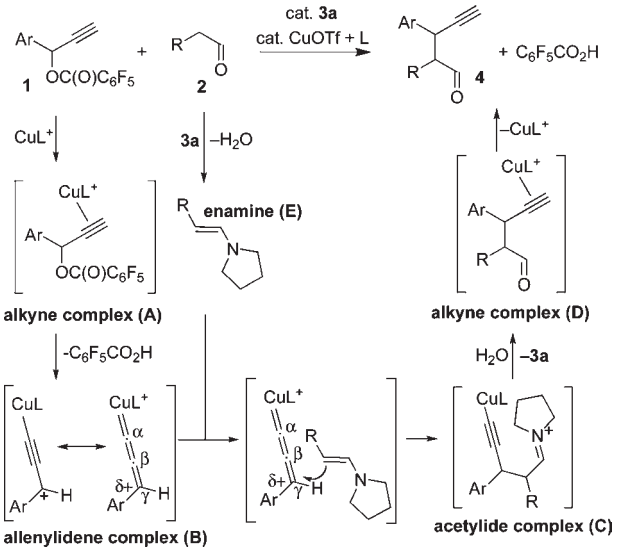
Propargylic alkylation with other aldehydes also proceeded smoothly to give the corresponding propargylic alkylated products with a high enantioselectivity. Typical results are shown in Table 1. The reaction of **1a** with 3-(4-chloro)phenylpropanal (**2b**) under the same reaction conditions gave the corresponding alkylated product with a similarly high enantioselectivity (Table 1, run 2). When other aldehydes such as 3-cyclohexylpropanal (**2c**), heptanal (**2d**), and 6-chlorohexanal (**2e**) were used in place of 3-arylpropanals, the corresponding propargylic alkyalted products were obtained in high yields as a mixture of two diastereoisomers with a high enantioselectivity (Table 1, runs 3−5). These results indicate that a variety of aldehydes are suitable for the propargylic alkylation.

It is noteworthy that a higher diastereoselectivity on the copper-catalyzed propargylic alkylation described in this paper was achieved than that of the ruthenium-catalyzed propargylic alkylation[1] by using the same optically active amine as an organocatalyst. However, unfortunately, the catalytic activity of the copper complex is lower than that of the ruthenium complex although an excellent enantioselectivity was observed in both cases.

Reactions of other propargylic esters such as 1-(2-naphthyl)-2-propynyl (**1e**), 1-phenyl-2-propynyl (**1f**), 1-(4-chlorophenyl)-2-propynyl (**1g**), 1-(4-methylphenyl)-2-propynyl (**1h**), and 1-(2-methoxyphenyl)-2-propynyl (**1i**) 2,3,4,5,6-pentafluorobenzoates with **2a** under the same reaction conditions did not proceed smoothly to give the corresponding propargylic alkylated products in low yields with an excellent enantioselectivity (not shown).[15]

A proposed reaction pathway is shown in Scheme 4. The initial step is the formation of an allenylidene complex (**B**)

Scheme 4



by the reaction of propargylic ester **1** with the copper complex via an alkyne complex (**A**). Subsequent attack of an enamine (**E**) generated in situ from aldehyde **2** and amine **3a** upon the γ-carbon of **B** results in the formation of another alkyne complex (**D**) via an acetylide complex (**C**). Then, the alkylated product **4** is formed from **D** by ligand exchange with another propargylic ester **1**. In fact, we confirmed that no reaction occurred at all when reactions of propargylic esters bearing an internal alkyne moiety were carried out under the same reaction conditions. These results clearly indicate that this propargylic alkylation proceeded via copper−allenylidene complexes as key and reactive intermediates.[5]

To obtain some information on the enantioselective propargylic alkylation, the stereochemistry of the product *syn*-**5a** was compared with that of the propargylic alkylated product which were previously obtained from the reaction of 1-(1-naphthyl)-2-propyn-1-ol with **2a**.[1] This result indicates that the absolute configuration of *syn*-**5a** is [(2*R*,3*S*)]. The information on the stereochemistry of the propargylic alkylated products supports that the asymmetric induction of the propargylic alkylation catalyzed by the copper complex was achieved in a similar manner as that by the ruthenium complex, which was proposed in the previous paper.[1] Thus, for the formation of major products *syn*-**5**, enamine, generated from chiral amine and aldehyde, attacks from the *Si*-face of enamine upon the *Re*-face of the copper−allenylidene complex leading to the carbon−carbon bond formation.

(15) (a) Preliminary results are as follows: For **1e**, 27% yield (4.5 h), *syn*-isomer/*anti*-isomer = 1.8/1, 97% *ee* (*syn*-isomer) and 96% *ee* (*anti*-isomer). For **1f**, 20% yield (4 h), *syn*-isomer/*anti*-isomer = 1.7/1, 98% *ee* (*syn*-isomer) and 95% *ee* (*anti*-isomer). (b) Unfortunately, some other propargylic esters bearing an electron-rich aromatic moiety at the propargylic position such as 1-(4-methoxyphenyl)-2-propynyl (**1j**) and 1-(4-methoxynaphthyl)-2-propynyl (**1k**) 2,3,4,5,6-pentafluorobenzoates could not be prepared from the corresponding propargylic alcohols due to the instability of the pentafluorobenzoate esters (not shown).

In summary, we have found the enantioselective propargylic alkylation of propargylic esters with aldehydes in the presence of a copper complex bearing racemic BINAP and an optically active secondary amine as cocatalysts to give the corresponding propargylic alkylated products in good yields as a mixture of two diastereoisomers with a high enantioselectivity (up to 99% *ee*). This catalytic reaction is considered to provide a new type of enantioselective propargylic substitution reaction,[16] where the enamines generated in situ from aldehydes enantioselectively attack the copper−allenylidene complexes. In the present reaction system, both the transition metal catalyst (copper complex) and organocatalyst (secondary amine) activate propargylic esters and aldehydes, respectively, and both catalysts cooperatively and simultaneously work to promote the propargylic alkylation enantioselectively. We believe that the finding described here will open up a new aspect of not only dual catalytic reactions using both organocatalysts and transition metal catalysts but also the enantioselective α-alkylation of aldehydes.[17,18] Further work is currently in progress to apply this strategy to other reaction systems and to clarify the scope and limitations of the present propargylic alkylation.

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Supporting Information Available. Experimental procedures and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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