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Copper-Catalyzed Asymmetric Formal [3 + 2] Cycloaddition of Propargylic Acetates with Hydrazines: Enantioselective Synthesis of Optically Active 2-Pyrazolines

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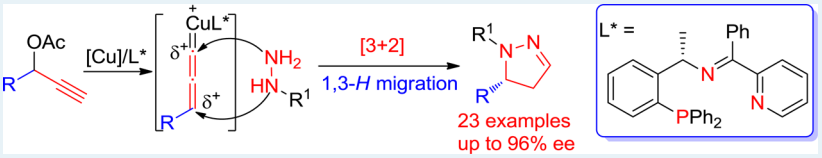
Supporting Information



ABSTRACT: A catalytic asymmetric [3 + 2] cycloaddition of hydrazines to bis-electrophilic C3 synthons generated from propargylic acetates, followed by an intramolecular 1,3-*H* migration, for the regio- and enantioselective construction of chiral 2-pyrazolines has been reported. By employment of copper catalysis in combination with a structurally rigid tridentate P,N,N-ligand, a variety of chiral 2-pyrazolines were obtained in good yields and with high enantioselectivities (up to 96% ee). A possible transition state has been proposed to explain the origin of the regio- and enantioselectivities.

KEYWORDS: *asymmetric catalysis, copper, cycloaddition, propargylic ester, 2-pyrazoline*

Pyrazolines are privileged and valuable five-membered aza-heterocycles, which are found in many bioactive compounds with antidepressant, anti-inflammatory, anticancer, antibacterial, and antiviral activities,[1] and also serve as important intermediates for organic synthesis.[2] The development of new chemical reactions for the synthesis of these aza-heterocycles, in particular in catalytic asymmetric versions, has therefore become an important issue. However, the number of available synthetic methodologies for the stereoselective construction of optically active pyrazolines is still very limited, and the methods mostly rely on two prominent strategies: (1) catalytic asymmetric 1,3-dipolar cycloadditions of diazoalkanes,[3] nitrile imine dipole precursors,[4] and azomethine imines[5] with alkenes or alkynes; (2) catalytic asymmetric Fischer's pyrazoline synthesis via a sequential aza-Michael addition/cyclocondensation process.[6,7] Despite these achievements, the development of novel strategies for the enantioselective construction of optically active pyrazolines with functional diversity remains a challenging and highly desirable task.

Recently, Nishibayashi's[8] and our[9] groups have demonstrated that propargylic derivatives can be used as bis-electrophilic C3 synthons via metal-allenylidene intermediates for the catalytic [3 + 3] cycloaddition, affording six-membered hetero- and carbocyclic motifs. However, the use of this new type of bis-electrophilic C_3 synthons in other cycloadditions remains unexploited.[10] In particular, no catalytic asymmetric [3 + 2] cycloaddition has yet been realized, thus severely narrowing their synthetic utility. To this end, we wondered about the possibility of a catalytic [3 + 2] cycloaddition of propargylic esters with hydrazines, possessing two adjacent nucleophilic nitrogen atoms, which should represent a novel strategy for stereoselectively producing optically active pyrazolines. However, the initial screening of the catalytic reaction of propargylic acetates with *N*,*N*′-diphenylhydrazine did not lead to any cycloadducts (Table 1, entry 1), clearly expressing the methodological difficulties. We envisioned that monosubstituted hydrazines should be more suitable bis-nucleophiles for realizing this transformation due to the clearly different steric properties of two nitrogen atoms toward the cycloaddition, which may be crucial to initiate the reaction in a chemo- and regioselective form. As a result, herein we disclose a highly regio- and enantioselective copper-catalyzed [3 + 2] cycloaddition of bis-electrophilic C3 synthons generated from propargylic acetates with monosubstituted hydrazines. Importantly, the initial cycloadducts are not stable under the reaction conditions, which undergo spontaneous 1,3-proton migration leading to thermodynamically more stable 2-pyrazolines (Scheme 1).[11] By employing a structurally rigid tridentate ketimine P,N,N-ligand, a variety of chiral 2-pyrazolines could be obtained in high yields and with good to excellent enantioselectivities.

We began our experiments with the goal of identifying conditions that would allow for the stereoselective [3 + 2] cycloaddition of propargylic esters with monosubstituted hydrazines. To this end, initial experimentals were focused on the screening of the reaction between 1-phenyl-2-propynyl

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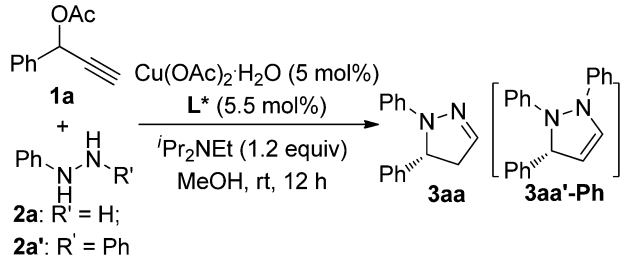
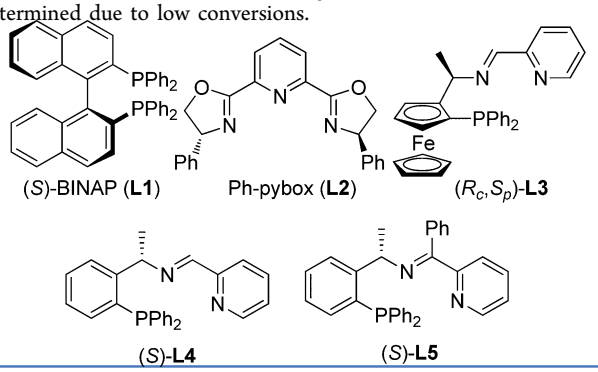
Table 1. Ligand and Substrate Screening for Cycloaddition[a]

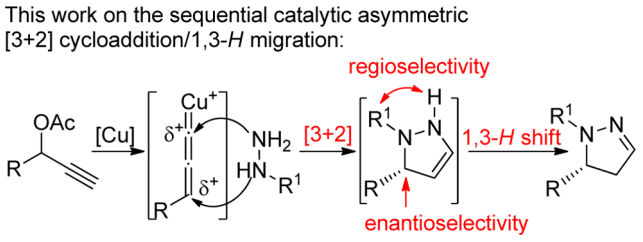


entry	L*	hydrazine	product	yield (%)[b]	ee (%)[c]
1	**L1**	**2a′**	**3aa′-Ph**	-	-[d]
2	**L1**	**2a**	**3aa**	28	76
3	**L2**	**2a**	**3aa**	30	42
4	**L3**	**2a**	**3aa**	52	80
5	**L4**	**2a**	**3aa**	80	84
6	**L5**	**2a**	**3aa**	90	94
7	**L5**	**2a′**	**3aa′-Ph**	-	-[d]

[a]Reaction conditions: **1a** (0.3 mmol), **2a** or **2a′** (0.36 mmol), [Cu] (0.015 mmol, 5 mol %), **L*** (0.0165 mmol, 5.5 mol %), $^{i}Pr_2NEt$ (0.36 mmol), 3 mL of MeOH, rt, 12 h. [b]Isolated yields of cycloadduct. [c]Determined by HPLC analysis using a chiral stationary phase. [d]Not determined due to low conversions.

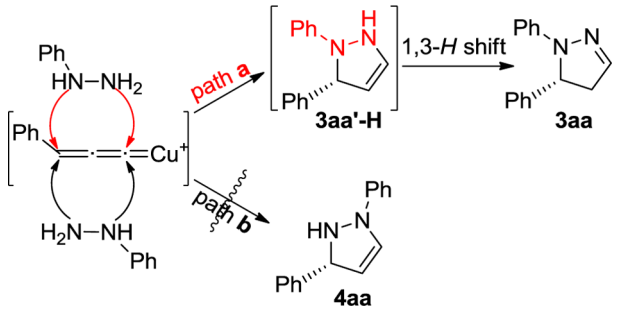


Scheme 1. Copper-Catalyzed [3 + 2] Cycloaddition of Propargylic Acetates with Monosubstituted Hydrazines



acetate **1a** and *N*-phenylhydrazine **2a** in the catalysis of $Cu(OAc)_2·H_2O$ in combination with a variety of chiral ligands, inspired by recent success in the copper-catalyzed propargylic substitution.[12,13] Because both nitrogen atoms of hydrazines are suitable nucleophiles, one major concern in implementation of this cycloaddition is the possible formation of two regioisomeric cycloadducts **3aa′-H** and **4aa** via the competitive attack of secondary (path **a**) and primary (path **b**) *N*-atoms of hydrazines at the C_γ-atom of Cu-allenylidene complex, as shown in Scheme 2. To our delight, the first attempt with a catalyst composed of $Cu(OAc)_2·H_2O$ and (*S*)-BINAP led to only one cycloadduct, in low conversions (Table 1, entry 2). Interestingly, the structural determination of the resulting cycloadduct disclosed that a thermodynamically more stable 2-pyrazoline **3aa** instead of the expected 3-pyrazoline **3aa′-H** was

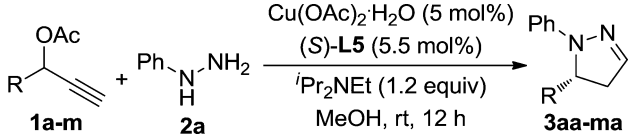
Scheme 2. Competitive Pathway for [3 + 2] Cycloaddition



obtained, suggesting that a cycloaddition via path **a** took place, followed by a spontaneous 1,3-proton migration under the reaction condition (path **a**, Scheme 2). Subsequent ligand screening revealed that the use of tridentate P,N,N-ligands increased the conversion and enantioselectivity, and in all cases, no regioisomeric cycloadduct **4aa** was detected (Table 1, entries 2−6). In particular, the bulky and structurally rigid ketimine-type P,N,N-ligand (*S*)-**L5**[13l] displayed good performance, affording 2-pyrazoline **3aa** in high yields (90%) and with excellent enantioselectivity (94% ee) (Table 1, entry 6). Under the optimal conditions,[14] no cycloadduct was detected with *N,N′*-diphenylhydrazine **2a′** as the substrate, suggesting a steric effect may dominate the cyclization process (Table 1, entry 7).

With the optimized conditions in hand, we next examined the substrate generality with respect to propargylic acetates, and the results are summarized in Table 2. The substitution pattern

Table 2. Substrate Scope of Propargylic Acetates[a]



entry	**1** (R)	**3**	yield (%)[b]	ee (%)[c]
1	**1a** (Ph)	**3aa**	90	94
2	**1b** (2-ClC_6H_4)	**3ba**	92	90
3	**1c** (3-ClC_6H_4)	**3ca**	91	94
4	**1d** (4-ClC_6H_4)	**3da**	89	92
5	**1e** (4-FC_6H_4)	**3ea**	90	91
6	**1f** (4-BrC_6H_4)	**3fa**	93	92
7	**1g** (4-$CF_3C_6H_4$)	**3ga**	88	91
8	**1h** (4-MeC_6H_4)	**3ha**	87	92
9	**1i** (4-$MeOC_6H_4$)	**3ia**	91	84
10	**1j** (2-naphthyl)	**3ja**	97	95
11	**1k** (2-thienyl)	**3ka**	91	87
12[d]	**1l** (Me)	**3la**	87	85
13[d]	**1m** (Bn)	**3ma**	85	94

[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.36 mmol), $Cu(OAc)_2·H_2O$ (0.015 mmol, 5 mol %), **L5** (0.0165 mmol, 5.5 mol %), $^{i}Pr_2NEt$ (0.36 mmol), 3 mL of MeOH, rt, 12 h. [b]Isolated yields of **3**. [c]Determined by HPLC analysis using a chiral stationary phase. [d]Pentafluorobenzoates instead of the corresponding acetates were used.

of functionality on the phenyl ring of propargylic acetates had little effect on this cycloaddition. Thus, all three substrates with a Cl group at the different position gave similar results (entries 2−4). The reaction also well tolerated both electron-donating and -withdrawing groups at the *para*-position of the phenyl ring, and gave the corresponding 2-pyrazolines in good yields

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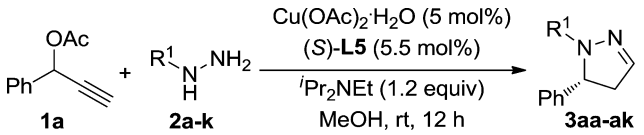
and high enantioselectivities (entries 4−8). An exception was the substrate **1i** bearing a *p*-methoxy substituent, which led to diminished enantioselectivity (84% ee, entry 9). 2-Naphthyl-substituted substrate worked well for this reaction, giving the cycloadduct **3ja** in 97% yield and with 95% ee (entry 10). Heterocycle-derived propargylic acetate **1k** was also a suitable substrate, providing the cycloadduct **3ka** in 91% yield and with 87% ee (entry 11). Moreover, aliphatic substrates **1l** and **1m** readily participated in this transformation, giving rise to the products **3la** and **3ma** with ee-values of 85% and 94%, respectively, although the pentafluorobenzoates were used instead of the corresponding acetates in these cases (entries 12−13).

The catalytic asymmetric [3 + 2] cycloaddition was then extended to other hydrazines. As shown in Table 3, an array of

Table 3. Substrate Scope of Hydrazines[a]



entry	2 (R^1)	3	yield (%)[b]	ee (%)[c]
1	**2a** (Ph)	**3aa**	90	94
2	**2b** (4-MeC_6H_4)	**3ab**	95	94
3	**2c** (4-$MeOC_6H_4$)	**3ac**	91	94
4	**2d** (4-$CF_3C_6H_4$)	**3ad**	84	95
5	**2e** (4-BrC_6H_4)	**3ae**	96	96
6	**2f** (4-FC_6H_4)	**3af**	92	94
7	**2g** (4-ClC_6H_4)	**3ag**	88	96
8	**2h** (3-ClC_6H_4)	**3ah**	89	93
9	**2i** (2-ClC_6H_4)	**3ai**	45	94
10	**2j** (2-MeC_6H_4)	**3aj**	65	94
11	**2k** ($HOCH_2CH_2$)	**3ak**	70	92
12	**2l** (H)	**3al**	-	-[d]

[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.36 mmol), $Cu(OAc)_2·H_2O$ (0.015 mmol, 5 mol %), **L5** (0.0165 mmol, 5.5 mol %), $^iPr_2NEt$ (0.36 mmol), 3 mL of MeOH, rt, 12 h. [b]Isolated yields of **3**. [c]Determined by HPLC analysis using a chiral stationary phase. [d]Not determined due to low conversion.

phenylhydrazines reacted smoothly, giving the corresponding cyclized products in high yields and with excellent enantioselectivities irrespective of the electronic property of the functionality at the *para*-position of the phenyl ring (entries 1−7). However, the reaction was sensitive to the substitution pattern on the phenyl ring (entries 7−9). Thus, the reaction with the substrates **2i** and **2j** bearing an *ortho*-substitutent resulted in the significantly decreased yield presumably due to the steric hindrance (entries 9 and 10). Remarkably, non-aromatic hydrazine **2k** also turned out to be a suitable reaction partner, providing the cycloadduct **3ak** in 70% yield and with 92% ee (entry 11). However, unsubstituted hydrazine **2l** was not efficient to the reaction, leading to the decomposition of **1a** to the corresponding propargylic alcohol (entry 12). The relatively weak nucleophilicity of primary amino group of hydrazine as observed in the Cu-catalyzed propargylic amination[13i] in combination with its relatively strong basicity should be responsible for this result.

To account for high regio- and enantioselectivities, a transition state of Cu-allenylidene complex with chiral P,N,N-ligand (*S*)-**L5** is proposed, as shown in Figure 1, on the basis of the previous report by Nishibayashi,[13f] the crystallographic

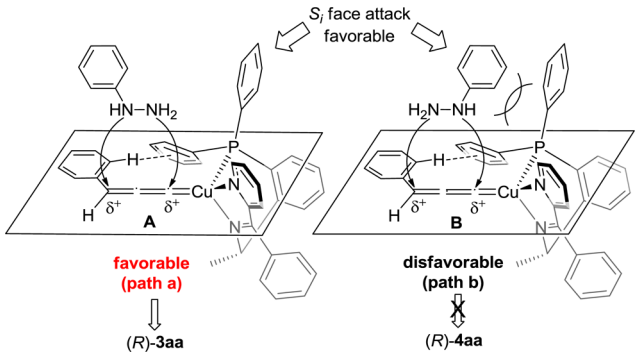
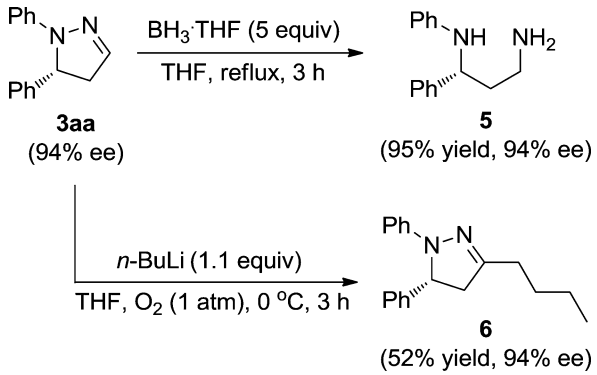


Figure 1. Proposed regio- and stereochemical model.

structure of CuCl/(*S*)-**L5** complex,[13l] and on the experimental results. The edge-to-face aromatic interaction and the steric hindrance of ligand make the attack of phenylhydrazine favorably from the *Si* face as in the reaction models **A** and **B**, thus facilitating the cycloaddition to give the experimentally observed (*R*)-cycloadduct confirmed by X-ray analysis of (*R*)-**3ae**.[15] The steric congestion imparted by the phenyl group of hydrazines close to the copper center in the reaction model **B** inhibits the cyclization, and the reaction proceeds via less sterically encumbering **A** to give the observed cycloadduct. This also explains why *N,N′*-diphenylhydrazine did not serve well with respect to the cycloaddition (Table 1, entry 7). For aliphatic propargylic substrates, a similar edge-to-face interaction between a sp^3 C−H bond of the substrate and a phenyl group at the pseudoequatorial position of chiral ligand led to the same sense of enantioinduction as that with aromatic substrates as proposed by Nishibayashi.[13g]

In an attempt to exhibit the synthetic utility of our method for generating interesting and useful chiral building blocks, some transformations were carried out on the cycloadduct obtained in the course of our studies (Scheme 3). For example,

Scheme 3. Synthetic Application



the enantioenriched 2-pyrazoline **3aa** can be readily converted into the corresponding chiral 1,3-diamine **5** without the deterioration of enantiomeric purity by the treatment with BH_3 in refluxing THF.[16] In addition, a substituent could be introduced into 3-position of **3aa** via a sequential addition/oxidation process, giving chiral 1,3,5-trisubstituted 2-pyrazoline **6** without any loss in enantioselectivity.

In summary, we have reported a highly regio- and enantioselective Cu-catalyzed [3 + 2] cycloaddition of propargylic acetates with monosubstituted hydrazines, followed by a spontaneous 1,3-proton migration, for the stereoselective

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construction of optically active 2-pyrazolines. The steric congestion imparted by the phenyl group of hydrazines close to the copper center has been proposed to explain the observed regioselectivity. By employing a structurally rigid tridentate ketimine P,N,N-ligand, we have efficiently coupled a wide range of propargylic acetates and hydrazines to generate useful chiral 2-pyrazolines in high enantiomeric excess (up to 96% ee). The methodology represents a novel strategy for the stereoselective access to enantioenriched 2-pyrazolines without a substituent at the 3-position that remain unavailable via other catalytic asymmetric methods. Studies utilizing this cycloaddition toward the synthesis of biologically active targets are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b01283.

Detailed experimental procedures (PDF)
Full characterization of new compounds (CIF)

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Notes

The authors declare no competing financial interest.

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