Asymmetric Catalysis

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Copper-Catalyzed Intermolecular Asymmetric Propargylic Dearomatization of Indoles**

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Abstract: *The first copper-catalyzed intermolecular dearomatization of indoles by an asymmetric propargylic substitution reaction was developed. This method provides a highly efficient synthesis of versatile furoindoline and pyrroloindoline derivatives containing a quaternary carbon stereogenic center and a terminal alkyne moiety with up to 86% yield and 98% ee.*

Furoindolines and pyrroloindolines with a chiral quaternary carbon center represent structural units widely embedded in biologically active natural products and pharmaceuticals (Figure 1).[1,2] Among them is the indoline scaffold with a propargylic group at the C3-position, a core which has been an attractive synthetic target owing to the versatile transformations of an alkyne group. Recently, the dearomatization strategy[3] has received much attention because of its efficiency towards the synthesis of furoindolines and pyrroloindolines, with a quaternary carbon center, under either transition-metal catalysis or organocatalysis.

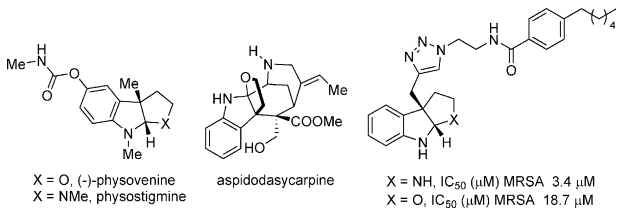
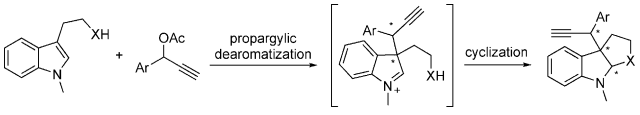


Figure 1. Selected naturally occurring and biologically active furoindolines and pyrroloindolines.

In contrast, transition-metal-catalyzed propargylic substitution reactions have been underdeveloped compared with allylic substitution reactions. Despite the fact that the Nicholas reaction, the substitution reaction of propargylic alcohol derivatives with a stoichiometric amount of a cobalt alkyne complex, was reported as early as in 1977,[4] the first copper-catalyzed propargylic substitution reaction was reported by Murahashi and co-workers in 1994.[5] Since then, great progress on the development of an asymmetric catalytic version of this reaction has been made.[6] In 2008, the groups of van Maarseveen and Nishibayashi independently reported the enantioselective copper-catalyzed propargylic amination reaction of propargylic acetates, thus providing the corresponding propargylic amines in up to 88% and 89% *ee*, respectively.[7] Later, Hou and co-workers disclosed the first copper-catalyzed asymmetric propargylic alkylation reaction with enamines as carbon nucleophiles.[8] Hu and co-workers realized the enantioselective decarboxylative propargylic alkylation with their newly developed chiral ketimine P,N,N-ligands, thus affording β-ethynyl ketones with up to 98% *ee*.[9] Recent elegant reports revealed that the copper allenylidene complexes are the key intermediates of the copper-catalyzed asymmetric propargylic substitution reactions.[10]

Despite these achievements, the copper-catalyzed asymmetric propargylic substitution reaction with prochiral carbon nuleophiles remains rare. To our knowledge, the asymmetric propargylic dearomatization reaction has not been reported.[11] Given our ongoing efforts towards the development of catalytic asymmetric dearomatization (CADA) reactions[12] and inspiration by recent rapid development of this field,[13] we envisioned that a copper-catalyzed asymmetric propargylic dearomatization of N-substituted tryptophol and tryptamine derivatives, including a propargylic substitution reaction and a subsequent cyclization, would afford furoindolines and pyrroloindolines, respectively (Scheme 1). Herein, for the first time we report the copper-catalyzed intermolecular dearomatization of indoles through a propargylic substitution reaction.

Our initial attempt was launched with the reaction of *N*-methyl tryptophol (**1a**) with the propargylic acetate **2a** in



Scheme 1. Copper-catalyzed propargylic dearomatization/cyclization cascade reaction.

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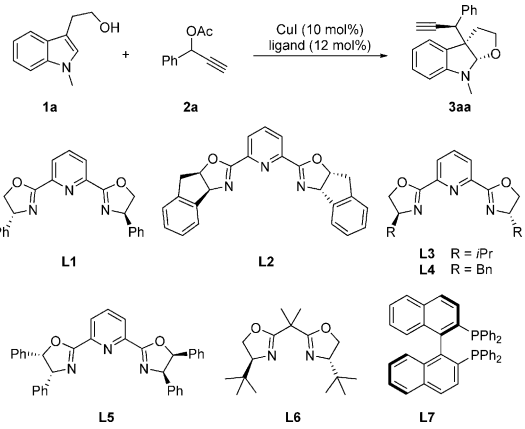
MeOH at room temperature in the presence of 1.0 equivalent of iPr$_2$NEt with a chiral copper catalyst prepared in situ from 10 mol% CuI and 12 mol% 2,6-bis(oxazolinyl)pyridine (**L1**; Table 1). The reaction delivered the desired furoindoline

Table 1: Optimization of reaction conditions.[a]



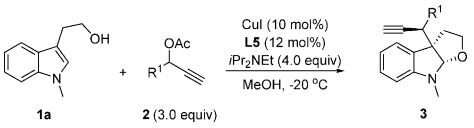
Entry	Ligand	T [°C]	t [h]	Yield [%][b]	d.r.[c]	*ee* [%][d] major	minor
1	**L1**	25	18	56	2.9:1	13	45
2	**L2**	25	18	34	1.1:1	13	40
3	**L3**	25	18	24	2.2:1	0	−20
4	**L4**	25	18	35	1.7:1	6	24
5	**L5**	25	2	58	4.0:1	58	6
6	**L6**	25	18	25	2.0:1	−12	−34
7[e]	**L7**	25	18	7	1.4:1	4	2
8	**L5**	0	24	60	6.4:1	73	14
9	**L5**	−10	84	44	10.1:1	93	18
10	**L5**	−20	132	24	13.0:1	96	21
11[f]	**L5**	−20	48	56	7.4:1	94	13

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), 10 mol% of CuI, 12 mol% of ligand, and iPr$_2$NEt (0.2 mmol) in 2.0 mL of MeOH at the indicated temperature. [b] Yield of both diastereoisomers (isolated products). [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Determined by HPLC analysis. [e] With 10 mol% CuI and 20 mol% ligand. [f] With 0.8 mmol of iPr$_2$NEt.

product **3aa** in 56% yield, 2.9:1 d.r., and 13% *ee* for the major diastereoisomer (entry 1). After evaluation of several other commercially available chiral ligands (entries 2–7), the chiral tridentate PYBOX **L5** was found to be optimal, thus providing **3aa** in 58% yield and 58% *ee* (entry 5). Encouraged by these results, further optimization with various solvents, such as CF_3CH_2OH, toluene, THF, and CH_2Cl_2, showed that the polar protic solvents were more favorable, and the best results were obtained in methanol.[14] By lowering the reaction temperature, the diastereoselectivity and enantioselectivity were improved significantly at the expense of the yield at a prolonged reaction time (entries 8–10). When 4.0 equivalents of iPr$_2$NEt were used, the reaction afforded **3aa** in 56% yield and 94% *ee* after a shortened reaction time (entry 11). Investigation of various copper salts and bases revealed that copper iodide and tertiary amines were beneficial for both yield and selectivity.[14]

Under the optimized reaction conditions, various propargylic acetates (**2b–n**) were reacted with **1a** to explore the generality of the process (Table 2). Substituents such as methyl, methoxy, fluoro, chloro, bromo, and phenyl groups at the *para*-position on the benzene ring of the propargylic acetate did not affect the enantioselectivity of the reactions

Table 2: The reaction substrate scope: propargylic acetates.[a]



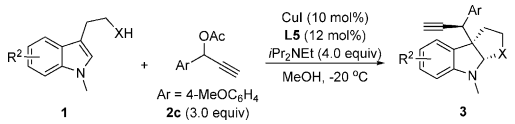
Entry	**2**, R^1	t [d]	Yield [%][b]	d.r.[c]	*ee* [%][d] major	minor
1	**2a**, Ph	3	**3aa**, 57	5.8:1	92	1
2	**2b**, 4-MeC_6H_4	3	**3ab**, 53	7.2:1	92	22
3	**2c**, 4-MeOC_6H_4	3	**3ac**, 55	12.5:1	97	46
4	**2d**, 4-FC_6H_4	2	**3ad**, 42	7.8:1	94	16
5[e]	**2e**, 4-ClC_6H_4	3.5	**3ae**, 57	8.0:1	92	10
6[e]	**2f**, 4-BrC_6H_4	7.5	**3af**, 60	7.4:1	93	14
7	**2g**, 4-PhC_6H_4	7.5	**3ag**, 52	9.2:1	96	30
8	**2h**, 3-MeC_6H_4	3	**3ah**, 46	3.6:1	92	8
9	**2i**, 2-naphthyl	5.5	**3ai**, 53	3.1:1	95	7
10[e]	**2j**, 1-naphthyl	7.5	**3aj**, 43	>19:1	83	–
11	**2k**, 2-furyl	3	**3ak**, 55	9.5:1	96	73
12	**2l**, 2-thienyl	5.5	**3al**, 67	12.3:1	94	38
13	**2m**, cinnamyl	5.5	**3am**, 52	10.0:1	98	56
14	**2n**, 2-MeC_6H_4	5.5	**3an**, 14	3.2:1	n.d.	n.d.

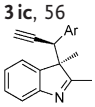
[a] Reaction conditions: **1a** (0.4 mmol), **2** (1.2 mmol), 10 mol% of CuI, 12 mol% of **L5**, and iPr$_2$NEt (1.6 mmol) in 2.0 mL of MeOH at −20°C. [b] Yield of both diastereoisomers (isolated products). [c] Determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Determined by HPLC analysis. [e] With 2.0 mmol of **2**. n.d. = not determined.

(entries 2–7). In the case of **2e** (4-Cl) and **2f** (4-Br), five equivalents of propargylic acetate and a longer reaction time were required to obtain acceptable yields (entries 5 and 6). The substrate with a *meta*-substituent tends to give slightly lower yield and enantioselectivity (entry 8). Propargylic acetates bearing 1-naphthyl, 2-naphthyl, 2-furyl, and 2-thienyl groups were compatible with the transformation (entries 9–12). The highest *ee* value was obtained when the cinnamyl derivative **2m** was used (98% *ee*; entry 13). However, the reaction was sensitive to the substituent at the *ortho* position of the benzene ring. A sharp decrease in yield was obtained when the substrate **2n**, bearing a 2-Me substituent, was used (entry 14). Furthermore, the reactions did not proceed at all when the aliphatic substrates, such as 3-isopropyl-3-propynyl acetate and propargylic acetate bearing an internal alkyne moiety, such as 1,3-diphenyl-2-propynyl acetate, were used as substrates. X-ray crystallographic analysis of a single crystal of enantiopure **3ai** confirmed its structure and disclosed the absolute configuration as 3a*R*, 8a*S*, *S*.[14]

Reactions of **2c** with various indole derivatives (**1b–j**) were next investigated (Table 3). Reactions of N-methyl-substituted tryptophols containing either a methyl or methoxy group at different positions of the indole ring (**1b–g**) proceeded smoothly to give the desired products (**3bc–gc**) in good yields with excellent enantioselectivity (entries 2–7). A slightly lower yield and enantioselectivity were observed when indole-3-propanol was used (entry 8). Notably, the

Table 3: The reaction substrate scope: indoles.[a]



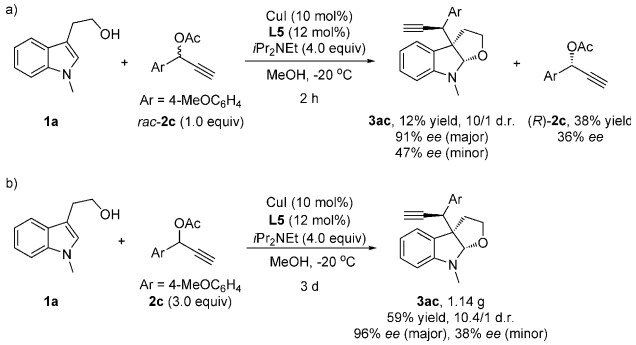
Entry	**1**, R^2, X	*t* [d]	Yield [%][b]	d.r.[c]	*ee* [%][d] major	minor
1	**1a**, H, O	3	**3ac**, 55	12.5:1	97	46
2	**1b**, 4-Me, O	2.5	**3bc**, 45	1.4:1	93	7
3	**1c**, 5-Me, O	4	**3cc**, 49	2.1:1	89	40
4	**1d**, 6-Me, O	2.5	**3dc**, 73	11.2:1	96	39
5	**1e**, 7-Me, O	2.5	**3ec**, 86	9.4:1	96	35
6	**1f**, 2-Me, O	2.5	**3fc**, 83	0.8:1	82	91
7	**1g**, 5-OMe, O	4	**3gc**, 73	7.5:1	94	42
8[e]	**1h**, H, CH_2O	1.5	**3hc**, 48	>19:1	79	–
9	**1i**, H, NTs	3	**3ic**, 56	12.2:1	95	n.d.
10	 **1j**	1.5	 **3jc**, 79	3.5:1	84	77

[a] Reaction conditions: **1** (0.4 mmol), **2c** (1.2 mmol), 10 mol% of CuI, 12 mol% of **L5**, and iPr_2NEt (1.6 mmol) in 2.0 mL of MeOH at −20°C. [b] Yield of both diastereoisomers (isolated products). [c] Determined by ^1H NMR analysis of the crude reaction mixture. [d] Determined by HPLC analysis. [e] With 2.0 mmol of **2c**. n.d. = not determined.

tosyl-protected tryptamine derivative was found to be compatible with the reaction conditions, thus giving the pyrroloindoline product in 56% yield, 12.2:1 d.r., and 95% *ee* (entry 9). When the commercially available 2,3-dimethyl indole (**1j**) was used, the reaction also occurred smoothly in 79% yield and good enantioselectivity for both diastereoisomers (entry 10).

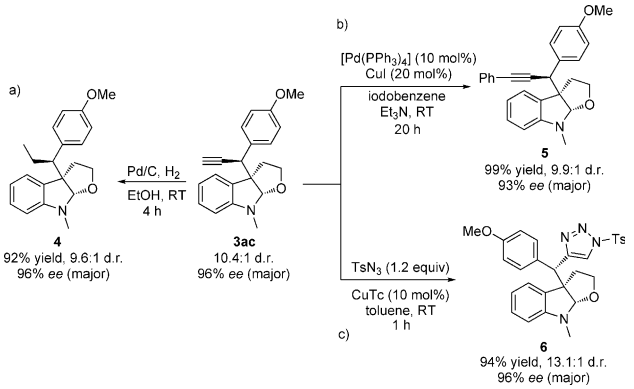
Next, the kinetic resolution behavior of *rac*-propagylic acetate in the reaction was examined by testing the reaction of **1a** with 1.0 equivalent of *rac*-**2c**. As shown in Scheme 2, both product and substrate were isolated in enantioenriched form, thus indicating that there exists a moderate kinetic resolution process (Scheme 2a). On a gram-scale (with 6.0 mmol of the substrate), the intermolecular propargylic dearomatization of **1a** with **2c** proceeded well to give **3ac** in 59% yield and 96% *ee* (Scheme 2b).

To further demonstrate the synthetic utility of the newly developed methodology, several transformations of the



Scheme 2. Kinetic resolution reaction and a gram-scale synthesis of **3ac**.

furoindoline **3ac** were carried out. The terminal alkyne group could be easily hydrogenated with 10% Pd/C, thus providing **4** in 92% yield and 96% *ee* (Scheme 3a). The furoindoline **3ac** underwent a Sonogashira coupling with



Scheme 3. Product transformations. Tc = thiophene-2-carboxylate, Ts = 4-toluenesulfonyl.

iodobenzene in the presence of 10 mol% $[Pd(PPh_3)_4]$ and 20 mol% CuI to afford **5**, which contains an internal acetylene, in a nearly quantitative yield (Scheme 3b). Copper-catalyzed 1,3-dipolar cycloaddition of **3ac** with TsN_3 gave **6** in 94% yield (Scheme 3c). No notable loss in the diastereomeric and enantiomeric purity was observed in all above transformations.

In summary, we have achieved the first copper-catalyzed intermolecular asymmetric propargylic dearomatization reaction of indole derivatives. With this new method, furoindolines and pyrroloindolines, bearing an all-carbon quaternary stereogenic center and a terminal alkyne, are easily accessed in moderate to good yields and with up to 98% *ee* from readily available propargylic acetates and indole derivatives under mild reaction conditions. Further development and application of this reaction as well as propargylic dearomatization reaction of other aromatics are currently under investigation in our laboratory.

Keywords: asymmetric catalysis · copper · dearomatization · heterocycles · synthetic methods

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[14] For details, see the Supporting Information.

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