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# Unveiling the migration reactivity of bicyclic diaziridines: enantioselective synthesis of chiral pyrazolines

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Ring-opening/cyclization represents a classic reaction of bicyclic diaziridines. In this study, an unprecedented ring-opening/migration cascade process was discovered in the reaction between bicyclic diaziridines and donor–acceptor (D–A) cyclopropanes. By employing a chiral *N,N'*-dioxide/scandium(III) complex as the catalyst, a diverse array of chiral dihydro-1*H*-pyrazoles with a stereocenter in the side chain was efficiently synthesized featuring excellent ee values. Control experiments indicated that the substitution on the D–A cyclopropane is of critical importance in determining the cyclization or migration process. When combined with DFT calculations, a plausible reaction mechanism was proposed, which involves a key transition state. This work presents a novel method for accessing pyrazolines and broadens the scope of diaziridine chemistry.

## Introduction

Bicyclic diaziridines, specifically 1,5-diazabicyclo[3.1.0]hexanes, are a distinct class of diaziridine compounds. These nitrogen-rich molecules contain a strained *cis* *N,N*-disubstituted diaziridine moiety.<sup>1</sup> Due to this inherent structural feature, they are inclined to undergo ring opening, which can occur through either selective C–N or N–N cleavage (Scheme 1a). The C–N cleavage pathway, which results in the formation of 1,3-dipole azomethine imine intermediates,<sup>2</sup> is well documented. These intermediates readily participate in annulation reactions with dipolarophiles. In 2020, our group disclosed an asymmetric (3 + 2) annulation reaction between diaziridines and chalcones, which was facilitated by a scandium(III) catalyst.<sup>3</sup> More recently, in 2025, Guo and Xie put forward a copper(II)-catalyzed asymmetric (3 + 3) annulation of diaziridines and oxiranes.<sup>4</sup> Conversely, N–N cleavage paves the way for the preparation of nitrogen-containing medium-sized rings. A notable example is Doyle's group's work in 2019. They reported a highly stereoselective formal [3 + 3] desymmetrization cycloaddition of diaziridines with enol diazo compounds to form bridged dinitrogen heterocycles through chiral copper catalysis.<sup>5</sup>

Meanwhile, pyrazolines featuring a chiral center on the side chain are ubiquitous in bioactive molecules (Scheme 1b).<sup>6</sup> Current methodologies for the asymmetric synthesis of pyrazolines primarily rely on two strategies (Scheme 1c): (1) organocatalytic cycloadditions between hydrazines/diazo

compounds and  $\alpha,\beta$ -unsaturated carbonyl compounds;<sup>7</sup> (2) Bolm's formal [4 + 1] cycloaddition of azoalkenes and sulfur ylides promoted by a chiral copper/BINAP complex.<sup>8</sup>

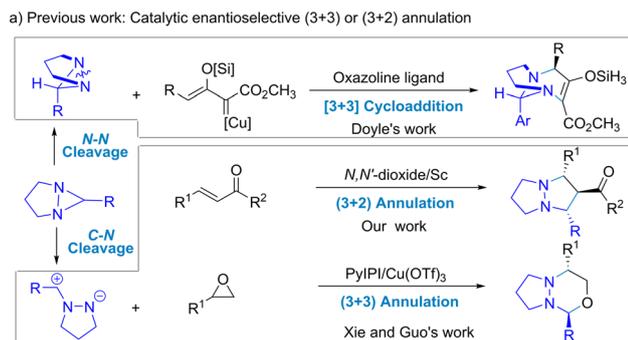
However, both approaches exclusively install the chiral center within the pyrazoline ring system. Given the prevalence of side-chain chirality in pharmacologically relevant pyrazolines, the development of efficient synthetic methods to access such scaffolds remains an unmet challenge and a compelling area of research.

Herein, we report the unprecedented migration reactivity of 1,5-diaza-bicyclo[3.1.0]hexanes in the reaction with D–A cyclopropanes<sup>9</sup> catalyzed by a chiral scandium catalyst (Scheme 1d). This protocol provides an efficient approach to access chiral 3-disubstituted pyrazolines featuring a chiral center on the side chain.

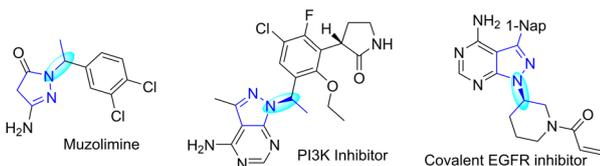
Before initiating the research using bicyclic diaziridines and D–A cyclopropanes as substrates, a (3 + 3) annulation is predicted. Our initial investigation using cyclopropane ester and 6-methoxy-1,5-diazabicyclo-[3.1.0]hexane indeed afforded a (3 + 3) adduct in the presence of Sc(OTf)<sub>3</sub> as a catalyst, which is consistent with the (3 + 3) addition reaction reported by Ivanova and Trushkov for cyclopropane esters reacting with diaziridines under Ni(ClO<sub>4</sub>)<sub>2</sub> catalysis.<sup>10</sup> However, when the ester group on the D–A cyclopropanes was simply changed to a ketone group, the unexpected 1,3-disubstituted pyrazoline was obtained as the product (Scheme 2). Notably, a benzyl group migration process occurred instead of cycloaddition.<sup>11</sup> Although the yield is low, this presents an opportunity to develop an efficient synthetic method for chiral diaziridines featuring a chiral center on the side chain.

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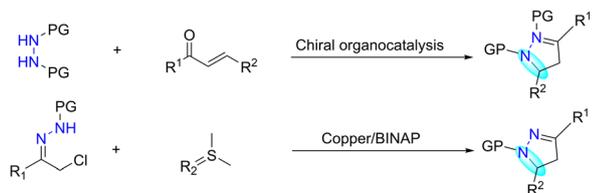




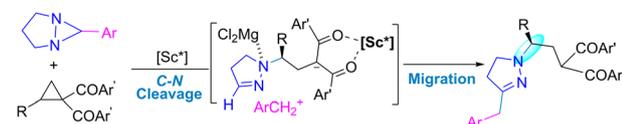
b) Examples of bioactive pyrazolines with a chiral center on the side chain



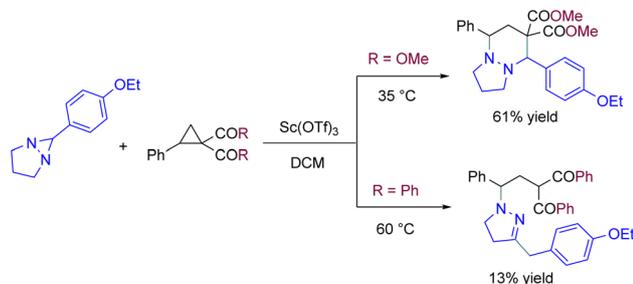
c) General strategies for synthesis of chiral pyrazolines: The chiral center is on the ring



d) This work: Unprecedented migration reactivity &amp; The chiral center is on the side chain

**Highlights:**

- 1) Unprecedented migration reactivity;
- 2) Good enantioselective control;
- 3) New convenient access to chiral azaheterocycles & chiral center is on the side chain;

**Scheme 1** Enantioselective reactions of diaziridines and representative pyrazoline-incorporating derivatives.**Scheme 2** Discovery of migration reactivity.

## Results and discussion

Then, the optimization of the reaction conditions was conducted (Table 1). Investigation of metal salts by complexing with chiral *L*-proline-derived *N,N'*-dioxide **L**<sub>3</sub>-**PiPr**<sub>3</sub> revealed that numerous metal salts, including Mg(OTf)<sub>2</sub>, MgCl<sub>2</sub>, and Ni(OTf)<sub>2</sub>, were ineffective in the reaction.<sup>12</sup> Both yield and enantioselectivity remained low (Table 1, entries 1–3). Notably, rare-earth

**Table 1** Optimization of reaction conditions<sup>a</sup>

$\text{1a} + \text{2a} \xrightarrow{\text{Metal salt/Ligand (1:1, 10 mol\%)}} \text{3aa}$  (DCE, 60 °C)

**L**<sub>3</sub>-**PrPr**<sub>3</sub>: Ar = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, n = 1  
**L**<sub>3</sub>-**PiPr**<sub>2</sub>: Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, n = 2  
**L**<sub>3</sub>-**PiPr**<sub>3</sub>: Ar = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, n = 2

	Metal salt	Ligand	Add.	Yield	Ee/%
1	Mg(OTf) <sub>2</sub>	<b>L</b> <sub>3</sub> - <b>PiPr</b> <sub>3</sub>	—	15	14
2	MgCl <sub>2</sub>	<b>L</b> <sub>3</sub> - <b>PiPr</b> <sub>3</sub>	—	12	15
3	Ni(OTf) <sub>2</sub>	<b>L</b> <sub>3</sub> - <b>PiPr</b> <sub>3</sub>	—	13	11
4	Y(OTf) <sub>3</sub>	<b>L</b> <sub>3</sub> - <b>PiPr</b> <sub>3</sub>	—	26	53
4	La(OTf) <sub>3</sub>	<b>L</b> <sub>3</sub> - <b>PiPr</b> <sub>3</sub>	—	18	49
5	Sc(OTf) <sub>3</sub>	<b>L</b> <sub>3</sub> - <b>PiPr</b> <sub>3</sub>	—	27	91
6	Sc(OTf) <sub>3</sub>	<b>L</b> <sub>3</sub> - <b>PrPr</b> <sub>3</sub>	—	26	73
8	Sc(OTf) <sub>3</sub>	<b>L</b> <sub>3</sub> - <b>RaPr</b> <sub>3</sub>	—	22	8
9	Sc(OTf) <sub>3</sub>	<b>L</b> <sub>3</sub> - <b>PiPr</b> <sub>2</sub>	—	22	55
10 <sup>b</sup>	Sc(OTf) <sub>3</sub>	<b>L</b> <sub>3</sub> - <b>PiPr</b> <sub>3</sub>	—	42	92
11 <sup>b</sup>	Sc(OTf) <sub>3</sub>	<b>L</b> <sub>3</sub> - <b>PiPr</b> <sub>3</sub>	MgCl <sub>2</sub>	63	92

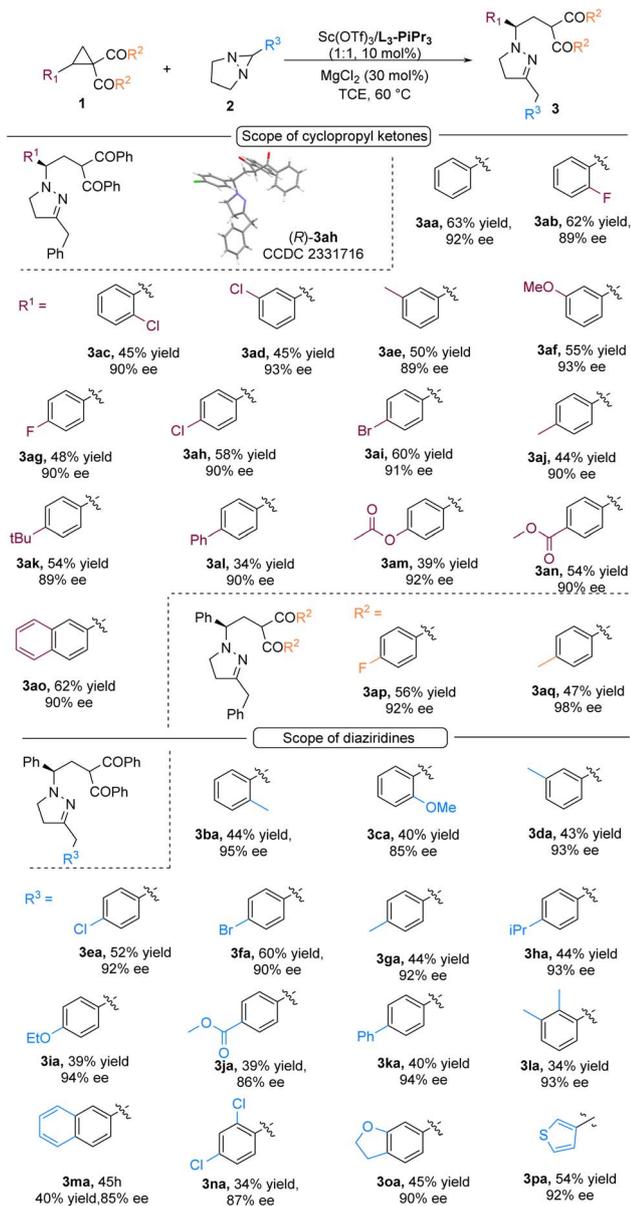
<sup>a</sup> The reactions were performed with metal salt/ligand (1 : 1, 10 mol%), **1a** (0.2 mmol), and **2a** (0.1 mmol), in 1,2-dichloroethane (1.0 mL) at 60 °C for 36 h. Isolated yield. The ee was determined by UPCC analysis on a chiral stationary phase. <sup>b</sup> 1,1,2,2-Tetrachloroethane (1.0 mL) as the solvent, **1a** (2.2 equiv.).

metal salts Y(OTf)<sub>3</sub> and La(OTf)<sub>3</sub> improved the enantioselectivity (Table 1, entries 4–5). Specifically, Sc(OTf)<sub>3</sub> afforded 91% ee despite a modest yield of 27% (Table 1, entry 6). Ligand screening demonstrated that both the chiral skeleton and amide substituent significantly impacted the enantioselectivity. *L*-Proline-derived **L**<sub>3</sub>-**PrPr**<sub>3</sub> reduced the enantioselectivity to 73% ee (Table 1, entry 7), while *L*-ramipril-derived **L**<sub>3</sub>-**RaPr**<sub>3</sub> caused a drastic decrease to below 10% ee (Table 1, entry 8). Removal of the *para*-substituent on the amide benzene ring led to a reduction in enantioselectivity to 55% ee (Table 1, entry 9). Switching the solvent from 1,2-dichloroethane to 1,1,2,2-tetrachloroethane (TCE) and increasing the loading of **1a** to 2.2 equivalents improved the yield from 27% to 46% (Table 1, entry 10). The addition of MgCl<sub>2</sub> further enhanced the yield to 63%.

While maintaining 92% ee (Table 1, entry 11). Further yield improvement was hindered by the formation of numerous byproducts, including those from benzyl group cleavage and the self-cyclization of D-A cyclopropanes.

With the optimized conditions established, the substrate scope was evaluated (Scheme 3). First, the scope of D-A cyclopropanes was investigated *via* reaction with diaziridine **2a**. For *ortho*-substituted phenyl cyclopropyl ketones,<sup>13</sup> F or Cl substitution exerted no significant effect on yield or enantioselectivity (**3ab** and **3ac**). D-A cyclopropanes bearing electron-withdrawing or electron-donating substituents at the *meta*- or *para*-position of the aryl ring were efficiently converted to the corresponding products **3ad**–**3al** with 34–60% yield and 89–93% ee. The 2-





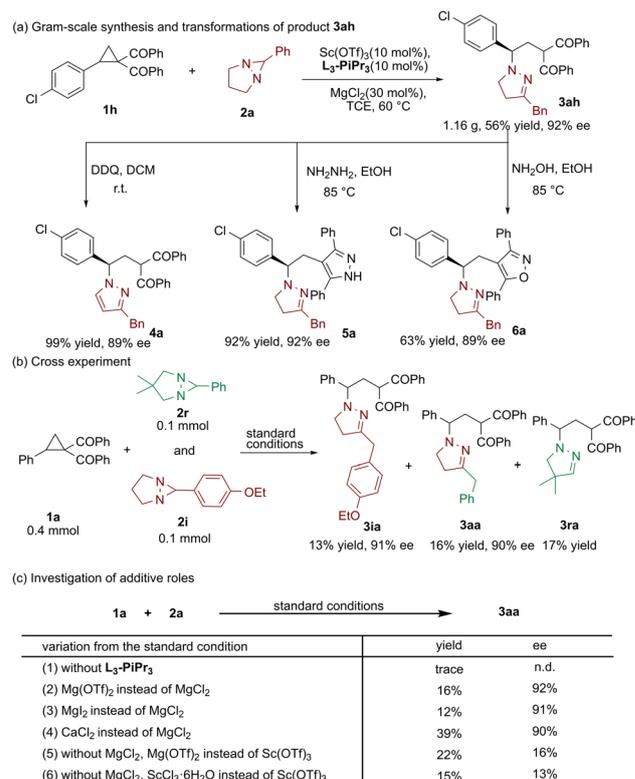
**Scheme 3** Substrate scope. Unless otherwise noted, all reactions were performed with **1** (0.22 mmol), **2** (0.1 mmol),  $\text{Sc}(\text{OTf})_3/\text{L}_3\text{-PIPr}_3$  (1 : 1, 10 mol%), and  $\text{MgCl}_2$  (30 mol%) in 1,1,2,2-tetrachloroethane (1.0 mL) at 60 °C for a defined amount of time. Isolated yields of the products were given. The ee values were determined by chiral UPCC analysis.

naphthyl substituted cyclopropyl ketone afforded product **3ao** in 62% yield with 90% ee. A *para*-F substituted benzoyl group at the 1-position of cyclopropanes showed no obvious influence on the reaction (**3ap**). Notably, the methylphenyl group increased the enantioselectivity to 98% ee (**3aq**). The absolute configuration of **3ah** was determined to be (*R*) by single-crystal X-ray diffraction analysis.<sup>14</sup> In addition, bis-ester substituted cyclopropane was employed to react with diaziridine **2a** under the optimized reaction conditions. The cycloaddition product was found in less than 10% yield with no migration product detected.

Subsequently, the scope of diaziridines was screened. Diaziridines bearing electron-withdrawing or electron-donating groups on their aryl rings were compatible, furnishing the desired products (**3ba–3ka**) in moderate yields (39–60%) with high enantioselectivities (85–95% ee). Efforts to enhance the yield by prolonging the reaction time were unsuccessful. The 2-naphthyl-substituted diaziridine **2m** was also suitable, affording product **3ma** in 40% yield with 85% ee. 2,3-Dimethyl and 2,4-dichloro substituents on the aryl ring of the diaziridine were also tolerated under this catalytic system (**3la** and **3na**). The 2-thienyl-substituted diaziridine substrate **2p** underwent smooth conversion, delivering the desired product in 54% yield with 92% ee. Diaziridines bearing a benzyl group with strong electron-withdrawing substituents, such as a *p*-nitro or *p*-trifluoromethyl group, failed to yield the corresponding products.

To demonstrate the synthetic utility of this methodology, a gram-scale synthesis of **3ah** was performed. As illustrated in Scheme 4a, 8.8 mmol of cyclopropyl ketone **1h** reacted smoothly with 4.0 mmol of diaziridine **2a** under standard conditions, affording 1.16 g of **3ah** in 56% yield with 92% ee. Oxidation with DDQ afforded the chiral product **4a** in 92% yield with 89% ee. Furthermore, pyrazole and isoxazole products **5a** and **6a** were obtained in the presence of  $\text{NH}_2\text{NH}_2$  and  $\text{NH}_2\text{OH}$  in EtOH.

To elucidate the reaction mechanism, a cross experiment was conducted (Scheme 4b). When **1a** was reacted with **2r** and 3,3-dimethyl diaziridine **2i** simultaneously, **3ia**, **3ra**, and cross-product **3aa** were isolated, suggesting the involvement of



**Scheme 4** (a) Gram-scale synthesis and transformations of product **3ah**; (b) cross experiment; (c) investigation of additive roles.





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- 14 CCDC 2331716, [3ah] contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

