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ARTICLE

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

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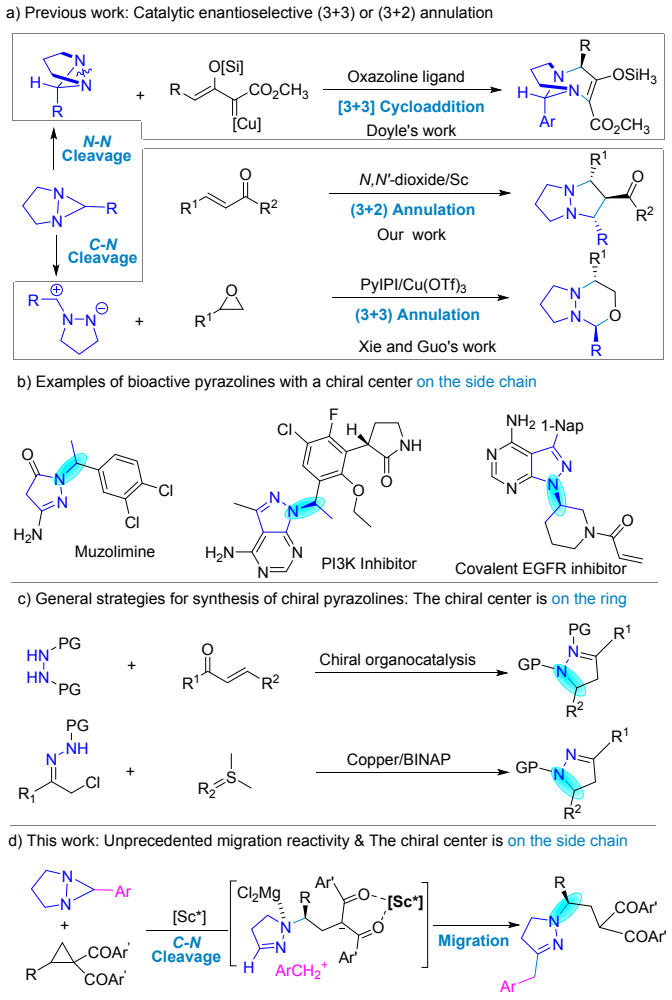
The ring-opening/cyclization represents a classic reactivity of bicyclic diaziridines. In this study, an unprecedented ring-opening/migration cascade process was discovered in the reaction between bicyclic diaziridines and donor-acceptor (D-A) cyclopropanes. By employing a chiral *N,N'*-dioxide/scandium(III) complex as the catalyst, a diverse array of chiral dihydro-1*H*-pyrazoles with a stereocenter in the side chain were 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. The work presents a novel method for accessing pyrazolines but also 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.[1] Due to this inherent structural trait, 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,[2] 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.[3] More recently, in 2025, Guo and Xie put forward a copper(II) - catalyzed asymmetric (3+3) annulation of diaziridines and oxiranes.[4] On the other hand, N–N cleavage paves the way for the creation 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 a chiral copper catalysis.[5]

On the other hand, pyrazolines featuring a chiral center on the side chain are ubiquitous in bioactive molecules (Scheme 1b).[6] Current methodologies for the asymmetric synthesis of pyrazolines primarily rely on two strategies (Scheme 1c): (1) organocatalytic cycloadditions between hydrazines/diazo compounds and α,β-unsaturated carbonyl compounds;[7] (2) Bolm's formal [4+1] cycloaddition of azoalkenes and sulfur ylides promoted by a chiral copper/BINAP complex.[8]




**Scheme 1** Enantioselective reactions of diaziridines and representative pyrazoline-incorporated derivatives.

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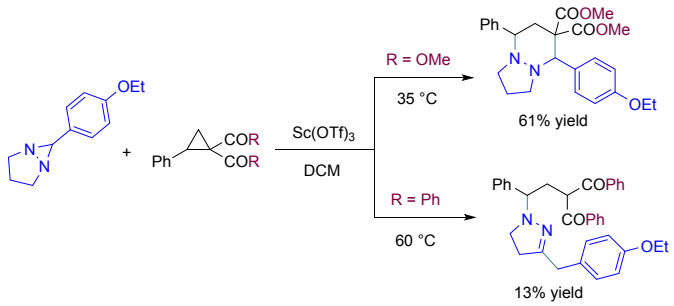
† Electronic Supplementary Information (ESI) available: [$^1$H, $^{13}$C{$^1$H} and $^{19}$F{$^1$H} NMR, HPLC and UPCC spectra. X-ray crystallographic data for **3ah**. CCDC: 2331716. or other electronic format see DOI: 10.1039/x0xx00000x

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 an unprecedented migration reactivity of 1,5-diaza-bicyclo[3.1.0]hexanes in the reaction with D-A cyclopropanes[9] 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-methoxyl-1,5-diazabicyclo-[3.1.0]hexane indeed afforded a (3+3) adduct in the presence of $Sc(OTf)_3$ as the catalyst, which is consistent with the (3+3) addition reaction reported by Ivanova and Trushkov for cyclopropane esters reacting with diaziridines under $Ni(ClO_4)_2$ catalysis.[10] 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.[11] 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.

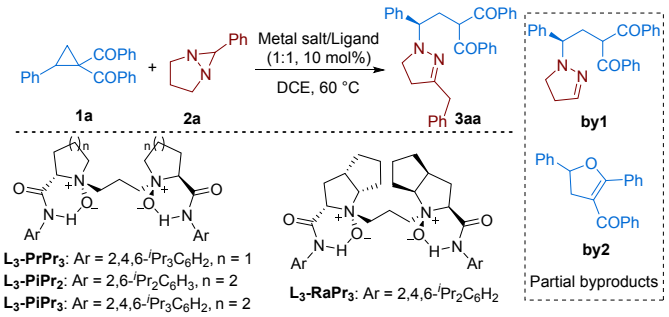



**Scheme 2** Discovery of migration reactivity.

## Results and discussion

Then, the optimization of reaction conditions was conducted (Table 1). Investigation of metal salts by complexing with chiral $_L$-pipecolic acid-derived *N,N'*-dioxide **$L_3$-PiPr$_3$** revealed that numerous metal salts, including $Mg(OTf)_2$, $MgCl_2$ and $Ni(OTf)_2$, were ineffective for the reaction.[12] Both yield and enantioselectivity remained low (Table 1, entries 1-3). Notably, rare-earth metal salts $Y(OTf)_3$, $La(OTf)_3$ improved the enantioselectivity (Table 1, entries 4-5). Specifically, $Sc(OTf)_3$ afforded 91% ee despite a modest yield of 27% (Table 1, entry 6). Ligand screening demonstrated both chiral skeleton and amide substituent significantly impacted enantioselectivity. $_L$-Proline-derived **$L_3$-PrPr$_3$** reduced enantioselectivity to 73% ee (Table 1, entry 7), while the $_L$-Ramipril-derived **$L_3$-RaPr$_3$** 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 $MgCl_2$ further enhanced the yield to 63%

**Table 1** Optimization of reaction conditions.[a]




| | metal salt | ligand | Add. | Yield | ee/% |
|---|---|---|---|---|---|
| 1 | $Mg(OTf)_2$ | **$L_3$-PiPr$_3$** | - | 15 | 14 |
| 2 | $MgCl_2$ | **$L_3$-PiPr$_3$** | - | 12 | 15 |
| 3 | $Ni(OTf)_2$ | **$L_3$-PiPr$_3$** | - | 13 | 11 |
| 4 | $Y(OTf)_3$ | **$L_3$-PiPr$_3$** | - | 26 | 53 |
| 4 | $La(OTf)_3$ | **$L_3$-PiPr$_3$** | - | 18 | 49 |
| 5 | $Sc(OTf)_3$ | **$L_3$-PiPr$_3$** | - | 27 | 91 |
| 6 | $Sc(OTf)_3$ | **$L_3$-PrPr$_3$** | - | 26 | 73 |
| 8 | $Sc(OTf)_3$ | **$L_3$-RaPr$_3$** | - | 22 | 8 |
| 9 | $Sc(OTf)_3$ | **$L_3$-PiPr$_2$** | - | 22 | 55 |
| 10[b] | $Sc(OTf)_3$ | **$L_3$-PiPr$_3$** | - | 42 | 92 |
| 11[b] | $Sc(OTf)_3$ | **$L_3$-PiPr$_3$** | $MgCl_2$ | 63 | 92 |

[a] The reactions were performed with metal salt/ligand (1:1, 10 mol%), **1a** (0.2 mmol), **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. [b] 1,1,2,2-Tetrachloroethane (1.0 mL) as the solvent,**1a** (2.2 equiv.).

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,[13] F or Cl substitution exerted no significant effect on yield or enantioselectivity (**3ab**, **3ac**). D-A Cyclopropanes bearing electron-withdrawing or electron-donating substituents at *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-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 enhanced enantioselectivity to 98% ee (**3aq**). The absolute configuration of **3ah** was determined to be (*R*) by single-crystal X-ray diffraction analysis. [14] In addition, bis-ester substituted cyclopropane was employed to react with diaziridine **2a** under the optimized reaction conditions. Cycloaddition product was found in less than 10% yield with no migration product detected.

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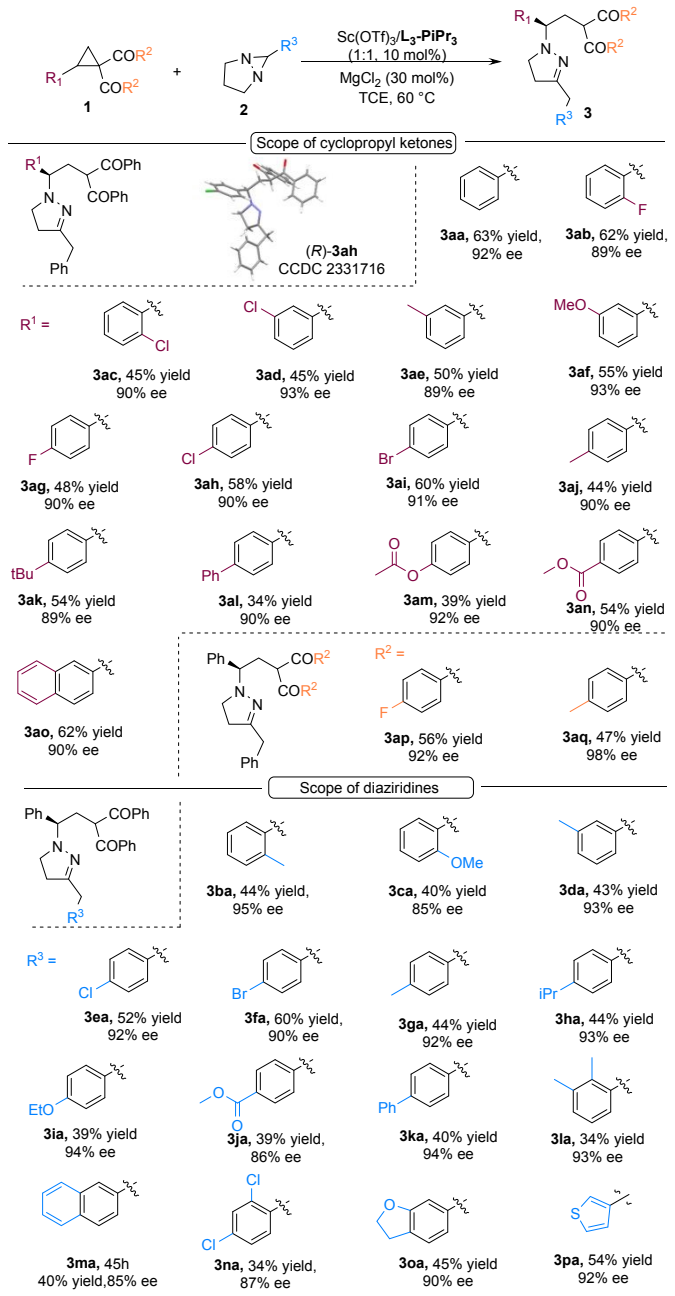
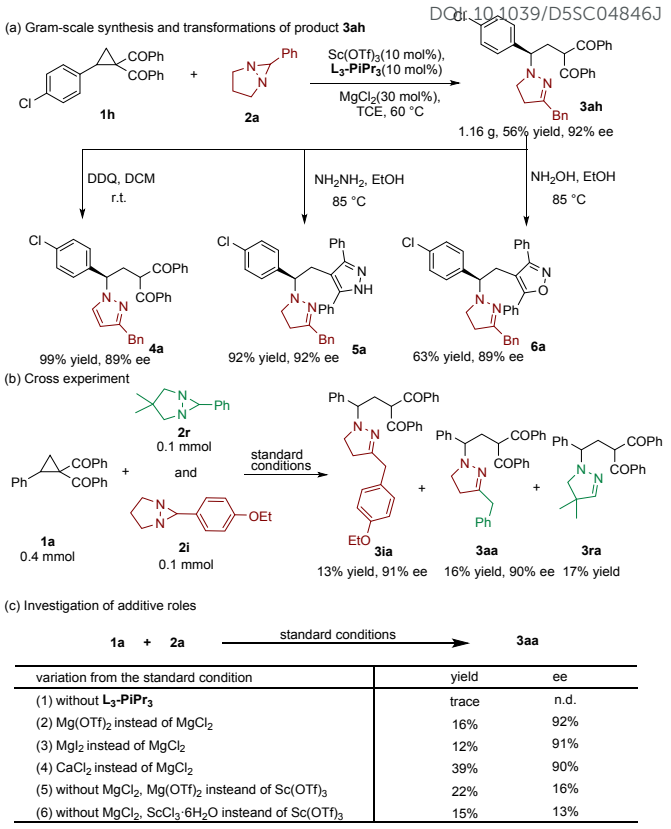



**Scheme 3** Substrate scope.[a] Unless otherwise noted, all reactions were performed with **1** (0.22 mmol), **2** (0.1 mmol), $Sc(OTf)_3$/**$L_3$-PiPr$_3$** (1:1, 10 mol%), and $MgCl_2$ (30 mol%) in 1,1,2,2-tetrachloroethane (1.0 mL) at 60 °C for indicated time. Isolated yields of the products. The ee values were determined by chiral UPCC analysis.

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**,**3na**). The 2-thienyl-substituted diaziridine substrate **2p** underwent smooth conversion, delivering




| variation from the standard condition | yield | ee |
|---|---|---|
| (1) without **$L_3$-PiPr$_3$** | trace | n.d. |
| (2) $Mg(OTf)_2$ instead of $MgCl_2$ | 16% | 92% |
| (3) $MgI_2$ instead of $MgCl_2$ | 12% | 91% |
| (4) $CaCl_2$ instead of $MgCl_2$ | 39% | 90% |
| (5) without $MgCl_2$, $Mg(OTf)_2$ insteand of $Sc(OTf)_3$ | 22% | 16% |
| (6) without $MgCl_2$, $ScCl_3{\cdot}6H_2O$ insteand of $Sc(OTf)_3$ | 15% | 13% |

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

the desired product in 54% yield with 92% ee. Diaziridines bearing a benzyl group with strong electron-withdrawing substituents, such as 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 diaziridines **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 $NH_2NH_2$ and $NH_2OH$ 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 a benzylic carbocation intermediate in the reaction pathway. To probe the roles of Mg(II) salt and the Sc(III)/**$L_3$-PiPr$_3$** complex, several control experiments were performed. In the absence of **$L_3$-PiPr$_3$**, the reaction mixture became complex, with only trace amounts of product detected. Changing the anion of the additive from $Cl^-$ to $OTf^-$ or $I^-$ caused a sharp decline in both yield and ee value (Scheme 4c, entries 2-3). Switching the additive cation to $Ca^{2+}$ or $Na^+$ reduced the yield but preserved excellent enantioselectivity. Additionally, using $ScCl_3 \cdot 6H_2O$/**$L_3$–PiPr$_3$** as the catalyst afforded the corresponding product **3aa** in only 15% yield with 13% ee. These control experiments indicate that magnesium chloride facilitates the formation of

azomethine imine

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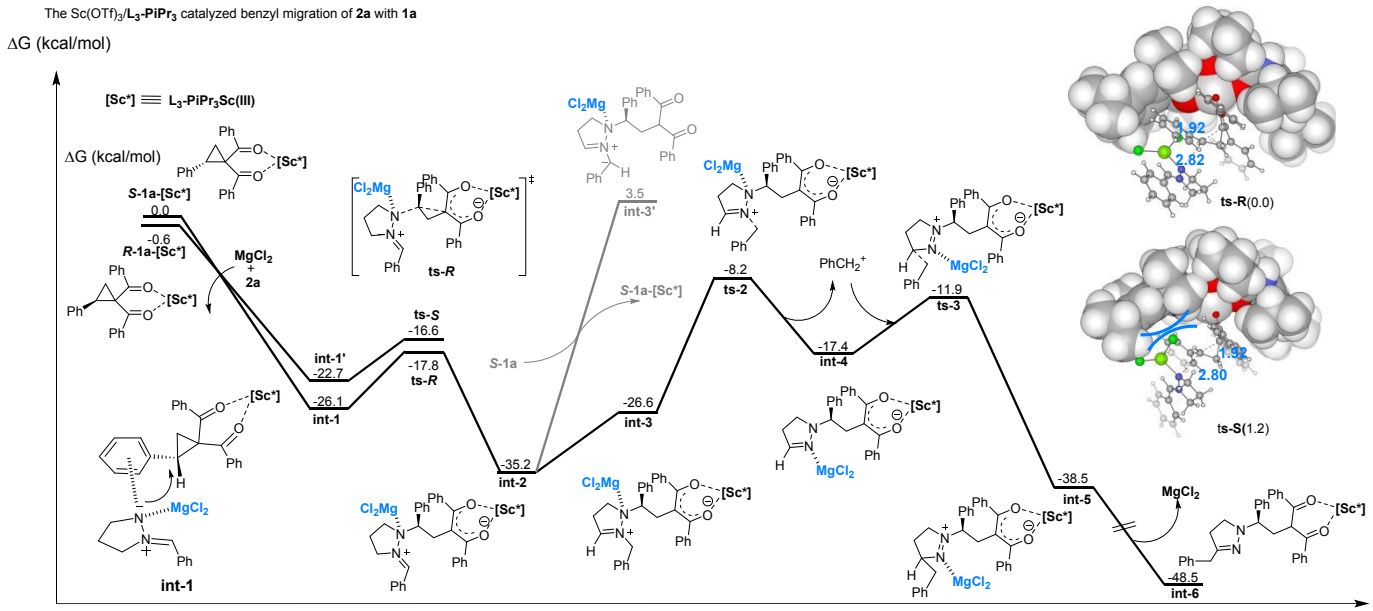


**Scheme 5** Plausible reaction mechanism.

intermediate and is critical for achieving high yield and enantioselectivity in the reaction.

Furthermore, DFT calculations (Scheme 5) were performed to clarify the reaction mechanism. The two enantiomers of compound **1a** coordinate with the catalyst, facilitating a nucleophilic attack by the intermediate formed after the combination of ring-opening product of **2a** with magnesium chloride on the cyclopropane carbon atom. This results in the opening of the cyclopropane ring and formation of intermediate **int-1**. The transformation proceeds via two possible transition states, **ts-R** and **ts-S**. Computational analysis indicates that **ts-R** is 1.2 kcal/mol lower in energy than **ts-S**. Structural analysis attributes this energy difference to significant steric hindrance between the phenyl group of the cyclopropane ring and the aryl substituent of the ligand's amide moiety in **ts-S**. The **int-2** undergoes a proton transfer to form intermediate **int-3**. **Int-3** undergoes benzyl cation release *via* transition state **ts-2**, with an associated activation barrier of 27 kcal/mol, identifying this step as the rate-determining step of the reaction. We also performed calculations on the intermediate leading to the [3+3] cycloaddition product. Upon optimization, this intermediate was found to spontaneously undergo ring-opening, indicating that it is energetically unfavorable and supporting the difficulty of forming the [3+3] product under the current conditions. Subsequently, the benzyl cation attacks the carbon center of **int-4** via transition state **ts-3**, forming intermediate **int-5** with an activation barrier of only 5.5 kcal/mol. A final proton transfer, $MgCl_2$ and catalyst release then afford the observed product.

## Conclusions

In summary, we have disclosed a benzyl migration process in the reaction of D-A cyclopropanes with 1,5-diazabicyclo[3.1.0]hexanes. The work not only uncovers a new reactivity of diaziridines but also provides a novel method for the enantioselective synthesis of chiral pyrazole derivatives bearing a chiral center on the side chain. In addition, this study expands the frontiers of diaziridine chemistry, thereby opening up new avenues for the synthesis of chiral heterocyclic compounds and the exploration of cascade reaction mechanisms.

## Data availability

Further details of experimental procedure, $^{1}H$, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR, HPLC spectra, SFC spectra, X-ray crystallographic data for **3ah** complex are available in the ESI.

## Author Contributions

Z. L. L. performed experiments and prepared the manuscript and ESI. L. C. N. conducted the DFT calculation. B. Q. Y. repeated some experiments. K. X. W. helped with modifying the paper and ESI. L. L. L. and X. M. F. conceived and directed the project.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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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

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Further details of experimental procedure, $^{1}H$, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR, HPLC spectra, SFC spectra, X-ray crystallographic data for **3ah** complex are available in the ESI.