Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

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Cite this: *Chem. Sci.*, 2025, **16**, 16584

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 1st July 2025
Accepted 9th August 2025

DOI: 10.1039/d5sc04846j

rsc.li/chemical-science

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.[1] 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,[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] 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.[5]

Meanwhile, 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]

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[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 a catalyst, which is consistent with the (3 + 3) addition reaction reported by Ivanova and Trushkov for cyclopropane esters reacting with diaziridines under $Ni(ClO_4)_2$ 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.

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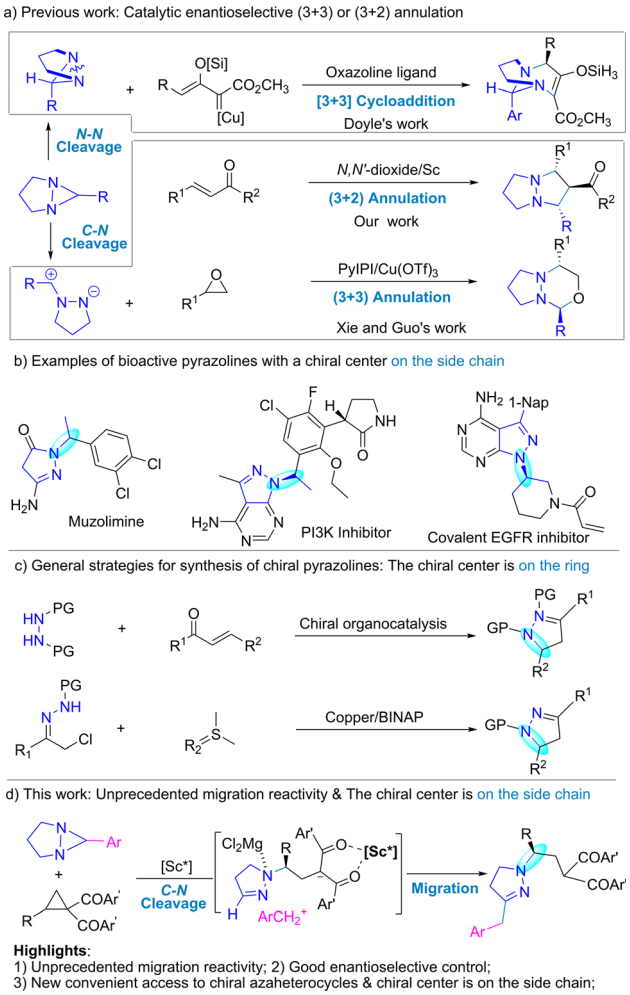
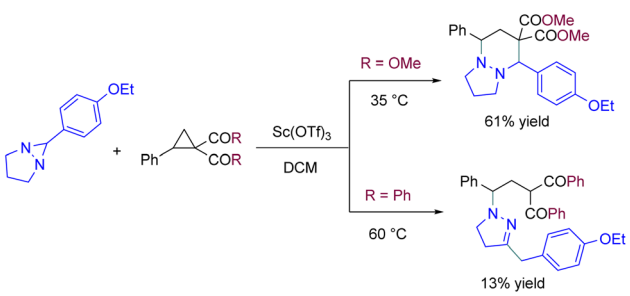


Scheme 1 Enantioselective reactions of diaziridines and representative pyrazoline-incorporating derivatives.

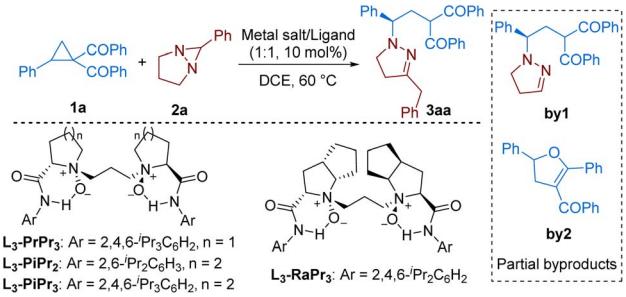


Scheme 2 Discovery of migration reactivity.

Results and discussion

Then, the optimization of the reaction conditions was conducted (Table 1). Investigation of metal salts by complexing with chiral $_L$-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 in the reaction.[12] Both yield and enantioselectivity remained low (Table 1, entries 1–3). Notably, rare-earth

Table 1 Optimization of reaction conditions[a]



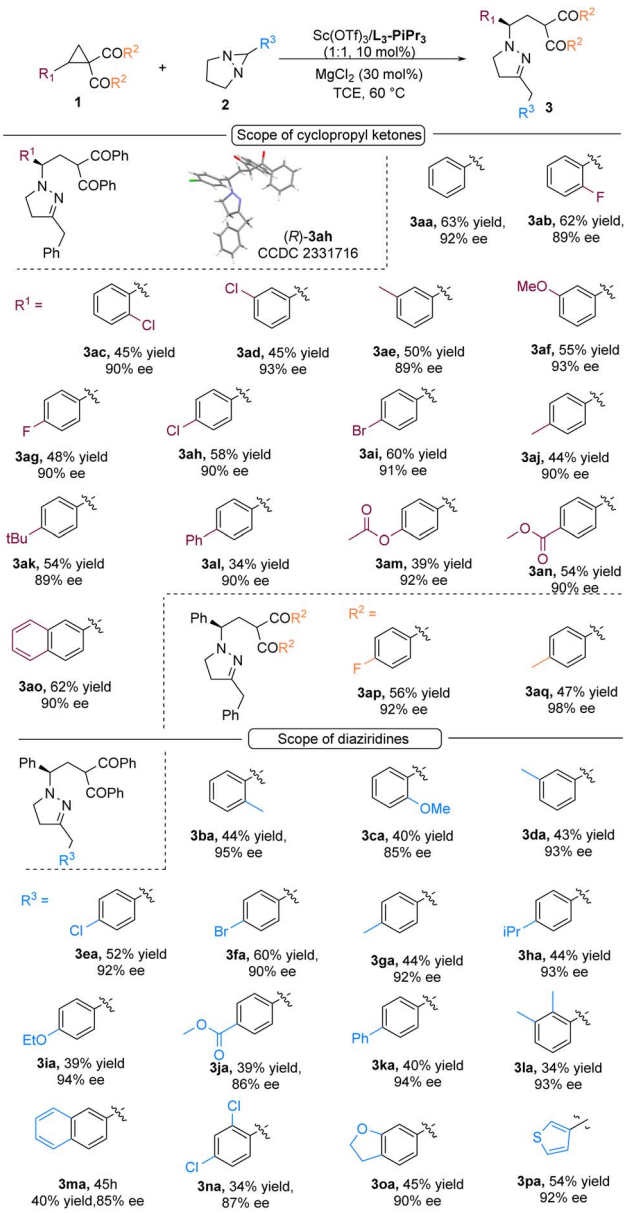
	Metal salt	Ligand	Add.	Yield	Ee/%
1	$Mg(OTf)_2$	**L_3-PiPr$_3$**	—	15	14
2	$MgCl_2$	**L_3-PiPr$_3$**	—	12	15
3	$Ni(OTf)_2$	**L_3-PiPr$_3$**	—	13	11
4	$Y(OTf)_3$	**L_3-PiPr$_3$**	—	26	53
4	$La(OTf)_3$	**L_3-PiPr$_3$**	—	18	49
5	$Sc(OTf)_3$	**L_3-PiPr$_3$**	—	27	91
6	$Sc(OTf)_3$	**L_3-PrPr$_3$**	—	26	73
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), 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. [b] 1,1,2,2-Tetrachloroethane (1.0 mL) as the solvent, **1a** (2.2 equiv.).

metal salts $Y(OTf)_3$ and $La(OTf)_3$ 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 that both the chiral skeleton and amide substituent significantly impacted the enantioselectivity. $_L$-Proline-derived **L_3-PrPr$_3$** reduced the enantioselectivity to 73% ee (Table 1, entry 7), while $_L$-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%.

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** 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-



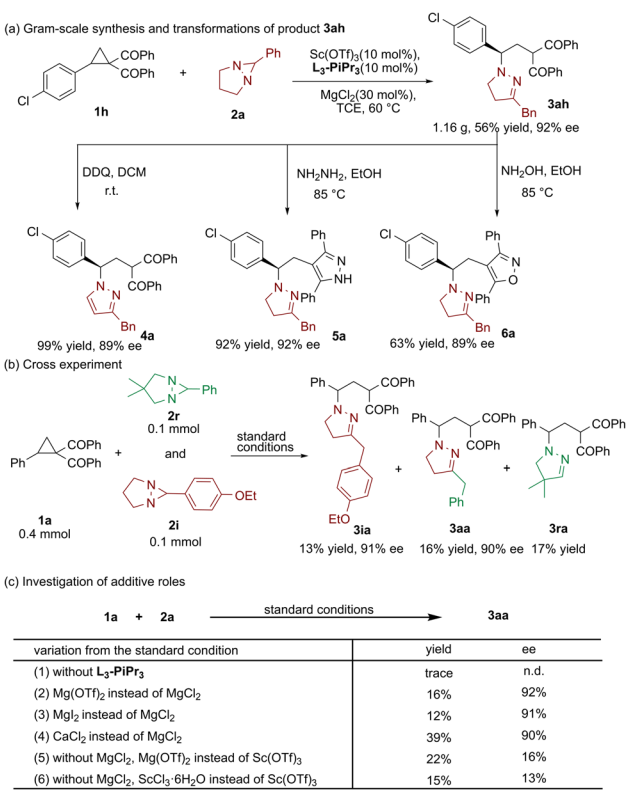
Scheme 3 Substrate scope. Unless otherwise noted, all reactions were performed with **1** (0.22 mmol), **2** (0.1 mmol), $Sc(OTf)_3$/L_3-$PiPr_3$ (1 : 1, 10 mol%), and $MgCl_2$ (30 mol%) in 1,1,2,2-tetrachloroethane (1.0 mL) at 60 °C for a defined amount of time. Isolated yields of the products were 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.[14] 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.

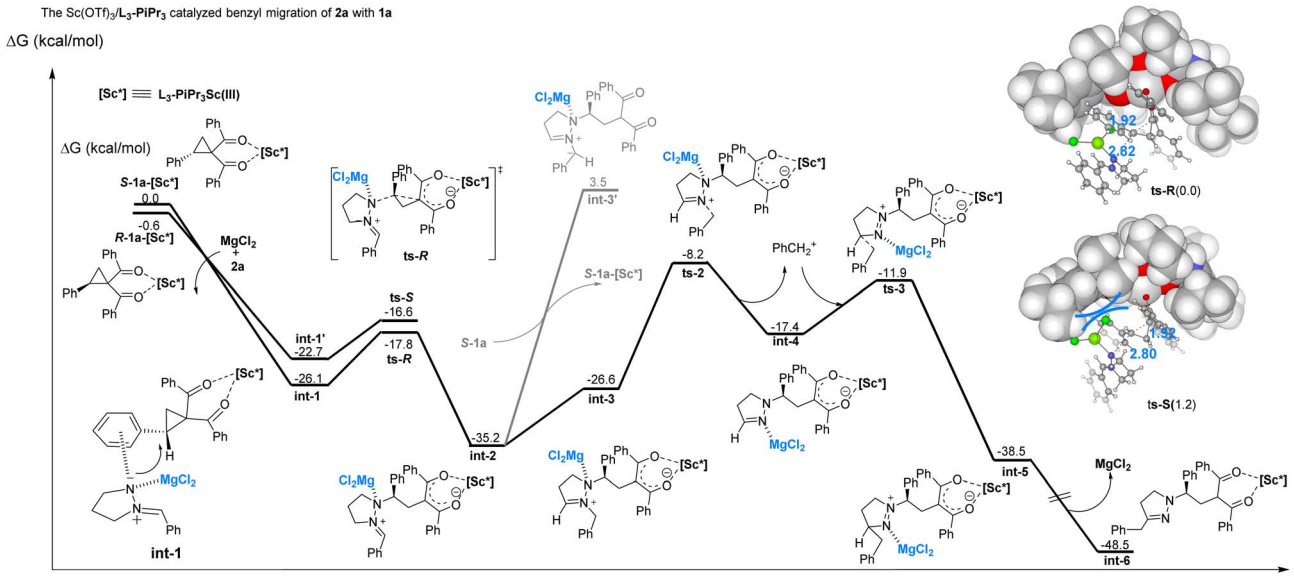
To demonstrate the synthetic utility of this methodology, a gram-scale synthesis of **3ah** was performed. As illustrated in Scheme 4a, 8.8 mmol of cyclopropyl ketone **1h** reacted smoothly with 4.0 mmol of diaziridine **2a** under standard conditions, affording 1.16 g of **3ah** in 56% yield with 92% 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 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



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 $MgCl_2$, $Mg(OTf)_2$ instead of $Sc(OTf)_3$	22%	16%
(6) without $MgCl_2$, $ScCl_3{\cdot}6H_2O$ instead 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.



Scheme 5 Plausible reaction mechanism.

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 the azomethine imine 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 on the cyclopropane carbon atom by the intermediate formed from the ring-opening product of **2a** in the presence of magnesium chloride. 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^{-1} 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**. **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^{-1}, 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 undergo spontaneous ring opening, indicating that it is energetically unstable and highlighting 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^{-1}. A final proton transfer, $MgCl_2$ and catalyst release then afford the observed product.

Conclusions

In summary, we 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 reaction 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.

Author contributions

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

Conflicts of interest

There are no conflicts to declare.

Data availability

Further details of the experimental procedure, ^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR, HPLC spectra, SFC spectra, and X-ray crystallographic data for complex **3ah** are available in the SI. See DOI: **https://doi.org/10.1039/d5sc04846j**.

Acknowledgements

We thank the National Key R&D Program of China (2023YFA1506700) and the National Natural Science Foundation of China (No. 22171189) for financial support. We are grateful to Dr Yuqiao Zhou from College of Chemistry, Sichuan University for the X-ray single-crystal diffraction analysis.

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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.