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Chiral *N,N'*-dioxide/Mg(OTf)<sub>2</sub> complex-catalyzed asymmetric [2,3]-rearrangement of *in situ* generated ammonium salts†Qianchi Lin,<sup>ID</sup> Bowen Hu,<sup>ID</sup> Xi Xu,<sup>ID</sup> Shunxi Dong,<sup>ID</sup> Xiaohua Liu,<sup>ID</sup>\* and Xiaoming Feng<sup>ID</sup>\*Catalytic enantioselective [2,3]-rearrangements of *in situ* generated ammonium ylides from glycine pyrazoleamides and allyl bromides were achieved by employing a chiral *N,N'*-dioxide/Mg<sup>II</sup> complex as the catalyst. This protocol provided a facile and efficient synthesis route to a series of *anti*- $\alpha$ -amino acid derivatives in good yields with high stereoselectivities. Moreover, a possible catalytic cycle was proposed to illustrate the reaction process and the origin of stereoselectivity.

## Introduction

[2,3]-Rearrangements have been regarded as a class of synthetically powerful organic transformations due to their inherently high efficiency.<sup>1</sup> In particular, [2,3]-rearrangement of ammonium ylides has been extensively investigated for rapid construction of valuable nitrogen-containing molecules.<sup>2</sup> It is highly attractive to disclose asymmetric versions of such intriguing rearrangement,<sup>3–5</sup> but only a few examples concerning the catalytic enantioselective [2,3]-rearrangement of ammonium ylides have been reported to date.<sup>5</sup> In 2014, Smith and co-workers demonstrated the first example of chiral isothiurea-catalyzed [2,3]-rearrangement of allylic ammonium ylides to gain optically enriched *syn*-configured  $\alpha$ -amino acid derivatives (Scheme 1a).<sup>5a</sup> In 2017, they developed an elegant tandem *in situ* protocol utilizing Pd/chiral isothiurea relay catalysis, which provides a direct method for the synthesis of *syn*- $\alpha$ -amino acid derivatives from *N,N*-disubstituted glycine aryl esters and allylic phosphates (Scheme 1b).<sup>5c</sup> Recently, the group of Song reported an interesting study on an isothiurea catalyzed asymmetric [2,3]-rearrangement reaction of propargyl ammonium salts, which allows access to optically active allenyl  $\alpha$ -amino amides.<sup>5f</sup> Despite these impressive advances, there is still room for further development. For instance, chiral isothiurea is a unique catalyst with which *syn*- $\alpha$ -amino acid derivatives were preferentially afforded in current reports.<sup>5a–e</sup> Given the wide and versatile use of  $\alpha$ -amino acids in organic

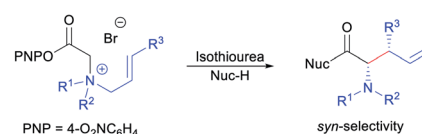
synthesis and pharmaceutical chemistry,<sup>6</sup> it is highly desirable to search for new catalytic systems for [2,3]-rearrangement of ammonium ylides in terms of the catalyst, substrate scope and the method of ammonium ylide formation, as well as stereo-divergence of products.<sup>7</sup>

Inspired by the achievements in enantioselective [2,3]-rearrangement<sup>1–5,8</sup> and our ongoing interest in synthesis of unnatural  $\alpha$ -amino acid derivatives,<sup>9</sup> we envisaged that chiral *N,N'*-dioxide-metal complex catalysts<sup>10</sup> developed by our group would be potentially useful in promoting asymmetric [2,3]-rearrangement of allylic ammonium ylides upon rationally introducing pyrazoleamide groups.<sup>11</sup> As depicted in Scheme 1c, pyrazoleamide ammonium salts generated from glycine

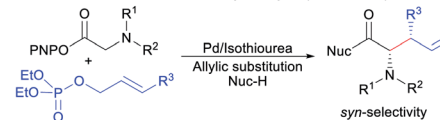
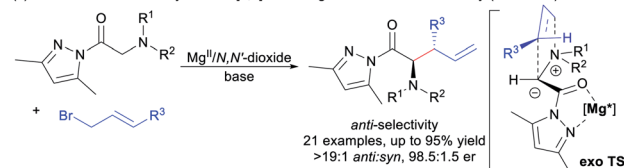
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† Electronic supplementary information (ESI) available: [<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}] and <sup>19</sup>F{<sup>1</sup>H} NMR, HPLC spectra, and CD spectra (PDF). X-ray crystallographic data for **4u** (CIF). CCDC 1960932. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc06342k

(a) Isothiurea-Catalyzed Enantioselective Catalytic [2,3]-Rearrangement (Smith, 2014)



(b) Enantioselective Pd/Isothiurea Relay Catalysis (Smith, 2017)

(c) Lewis Acid-Enabled Asymmetric [2,3]-Rearrangement with *anti*-selectivity (This work)

## Features:

- First example of Lewis acid-catalyzed [2,3]-rearrangement of ammonium salts
- *Anti*-selectivity, good to excellent enantioselectivity under strong background reaction
- One-pot procedure, easy operation

Scheme 1 [2,3]-Rearrangements of allylic ammonium ylides.



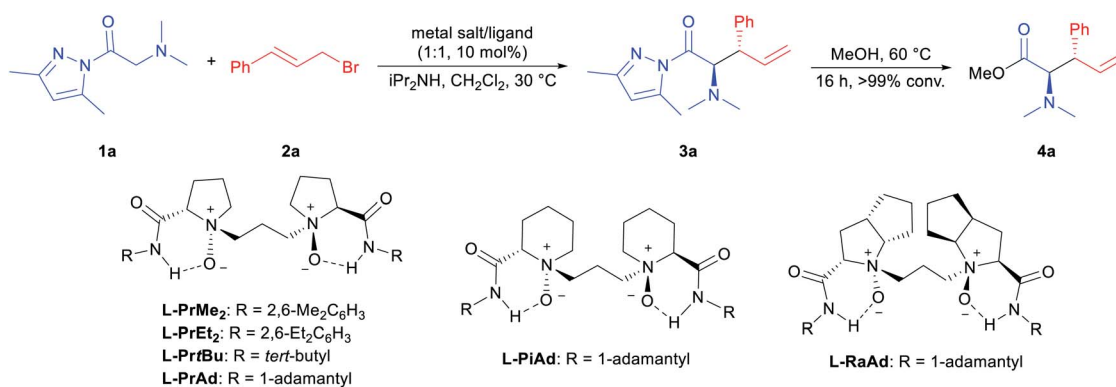
pyrazoleamides **1** and allyl bromides **2** were selected as the precursors of [2,3]-rearrangement. It was thought that such allylic ammonium salts could be activated by bidentate coordination with the chiral *N,N'*-dioxide–metal complex and then subjected to deprotonation with the assistance of an external base to afford ammonium ylides, which subsequently undergo [2,3]-rearrangement to deliver non-racemic  $\alpha$ -amino acid derivatives. There are some difficulties associated with the catalytic asymmetric [2,3]-rearrangement, such as the compatibility of all reactants with the catalyst<sup>5a,f</sup> and the background reaction in the presence of the external base.<sup>12</sup> Herein, we wish to disclose our effort toward one-pot asymmetric [2,3]-rearrangement of *in situ* formed allylic ammonium ylides. Chiral *N,N'*-dioxide/Mg(OTf)<sub>2</sub> (ref. 13) was found to promote the diastereo- and enantioselective rearrangement efficiently, and various *anti*- $\alpha$ -amino acid derivatives<sup>14</sup> were readily obtained in good yields with high stereoselectivities (up to 95% yield, >19 : 1 *anti* : *syn* and 98.5 : 1.5 er) from easily available glycine pyrazoleamides and allyl bromides.

## Results and discussion

In the initial study, *N,N*-dimethylglycine pyrazoleamide (**1a**) and cinnamyl bromide (**2a**) were selected as the model

substrates to optimize the reaction conditions. The preliminary study indicated that the tandem ammonium salt formation/[2,3]-rearrangement took place well in the presence of an external base, and the desired product **3a** was isolated in 91% yield with a 1 : 1 *anti* : *syn* ratio by using diisopropylamine as the base (see page 9 in the ESI† for more details). This result showed the difficulty in achieving the asymmetric version of such one-pot transformation. For the purpose of determination of the er value, compound **3a** was converted to **4a** quantitatively with MeOH at 60 °C for further analysis. Next, different metal salts coordinated with chiral *N,N'*-dioxide **L-PrMe<sub>2</sub>** were examined in CH<sub>2</sub>Cl<sub>2</sub> at 30 °C (Table 1, entries 1–4). Mg(OTf)<sub>2</sub> performed better than other metal salts, giving the desired rearranged product **3a** in 91% yield, 1.8 : 1 *anti* : *syn*, and 67.5 : 32.5 er for the major diastereomer (Table 1, entry 3). The complex of Mg(NTf)<sub>2</sub> provided a comparable result (Table 1, entry 4). Subsequently, the amide moiety in the ligand was evaluated, and it was found that sterically bulky 1-adamantyl amine derived **L-PrAd** afforded better stereoselectivities (Table 1, entry 7 *vs.* entries 5 and 6). Further investigations on the chiral backbone in the ligand showed that the *L*-ramipril-derived **L-RaAd** was superior to the *L*-proline-derived **L-PrAd** and (*S*)-pipercolic acid-derived **L-PiAd** in terms of enantioselectivity (91% yield, 3 : 1 *anti* : *syn*, and 81 : 19 er; entries 7–9).

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



Entry	Metal salt	Ligand	Yield of <b>3a</b> <sup>b</sup> (%)	<i>anti</i> : <i>syn</i> of <b>3a</b> <sup>c</sup>	er of <b>4a</b> <sup>d</sup>
1	Sc(OTf) <sub>3</sub>	<b>L-PrMe<sub>2</sub></b>	77	1 : 1	race/race
2	Ni(OTf) <sub>2</sub>	<b>L-PrMe<sub>2</sub></b>	90	1.1 : 1	54 : 46/57.5 : 42.5
3	Mg(OTf) <sub>2</sub>	<b>L-PrMe<sub>2</sub></b>	91	1.8 : 1	67.5 : 32.5/67.5 : 32.5
4	Mg(NTf) <sub>2</sub>	<b>L-PrMe<sub>2</sub></b>	93	1.6 : 1	65.5 : 34.5/64.5 : 35.5
5	Mg(OTf) <sub>2</sub>	<b>L-PrEt<sub>2</sub></b>	99	3 : 1	61 : 39/80 : 20
6	Mg(OTf) <sub>2</sub>	<b>L-Pr<i>t</i>Bu</b>	90	2 : 1	56.5 : 43.5/52.5 : 47.5
7	Mg(OTf) <sub>2</sub>	<b>L-PrAd</b>	98	5 : 1	75.5 : 24.5/57 : 43
8	Mg(OTf) <sub>2</sub>	<b>L-PiAd</b>	94	2 : 1	52.5 : 47.5/race
9	Mg(OTf) <sub>2</sub>	<b>L-RaAd</b>	91	3 : 1	81 : 19/54.5 : 45.5
10 <sup>e</sup>	Mg(OTf) <sub>2</sub>	<b>L-RaAd</b>	99	13 : 1	93.5 : 6.5
11 <sup>e,f</sup>	Mg(OTf) <sub>2</sub>	<b>L-RaAd</b>	82	12 : 1	95.5 : 4.5
12 <sup>e,f,g</sup>	Mg(OTf) <sub>2</sub>	<b>L-RaAd</b>	94	>19 : 1	97 : 3

<sup>a</sup> Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), *i*Pr<sub>2</sub>NH (0.15 mmol) and metal salt/ligand (1 : 1, 10 mol%) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) at 30 °C for 14 h. <sup>b</sup> Isolated yield of **3a**. <sup>c</sup> Determined by <sup>1</sup>H NMR. <sup>d</sup> Determined by HPLC on a chiral stationary phase. <sup>e</sup> Carried out in MeCN. The metal salt/ligand was pretreated in CH<sub>2</sub>Cl<sub>2</sub>. <sup>f</sup> –20 °C for 24 h. <sup>g</sup> NaBAR<sub>4</sub><sup>F</sup> {NaB[3,5-(F<sub>3</sub>C)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>4</sub>} (20 mol%) was added. The metal salt/ligand/NaBAR<sub>4</sub><sup>F</sup> was pretreated in EtOAc instead of CH<sub>2</sub>Cl<sub>2</sub>. Tf = trifluoromethanesulfonyl.



Other reaction parameters were investigated and the solvent was proven to play a significant role in the reaction. With MeCN as the solvent, the amino acid derivative **3a** was produced in 99% yield with 13 : 1 *anti* : *syn* and 93.5 : 6.5 er for the major diastereomer (entry 10). The enantioselectivity could be further enhanced when the reaction was performed at decreased temperature ( $-20\text{ }^{\circ}\text{C}$ )<sup>15</sup> while a slightly lower yield was obtained (82% yield, 12 : 1 *anti* : *syn*, 95.5 : 4.5 er; entry 11). To our delight, the addition of NaBAR<sub>4</sub><sup>F</sup> as an additive and preparation of the catalyst in EtOAc produced optimized results (entry 12; 94% yield, >19 : 1 *anti* : *syn*, 97 : 3 er).

Moreover, when the product with a low *anti* : *syn* ratio was subjected to the reaction conditions, it was found that both *anti* : *syn* ratios and er values did not change. This result implied that an ultimately high *anti* : *syn* ratio was obtained during the [2,3]-rearrangement rather than epimerization of the product during the reaction (for further details, see ESI,† page 11).

With the optimized reaction conditions in hand, the substrate scope of [2,3]-rearrangement was screened (Table 2). Varying *N*-substituents in the glycine pyrazoleamides had no effect on the *anti* : *syn* ratio of the reaction (>19 : 1 in all cases).

Table 2 Substrate scope for the [2,3]-rearrangement<sup>a</sup>

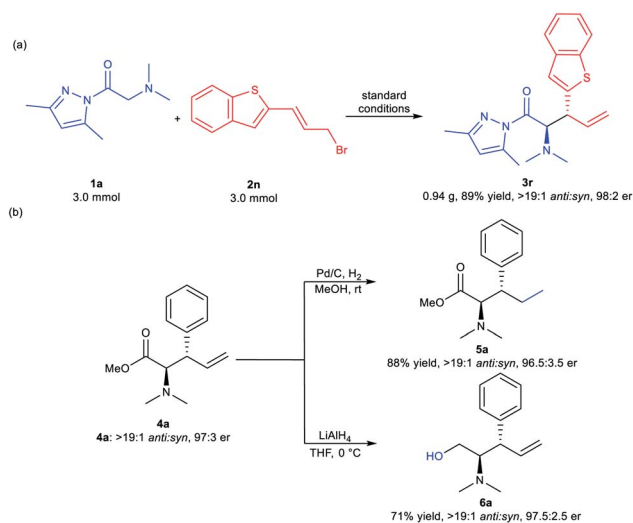
<b>3a</b> , 24 h, 94% yield >19:1 <i>anti</i> : <i>syn</i> , 97:3 er <sup>c</sup>	<b>3b</b> , 168 h, 64% yield >19:1 <i>anti</i> : <i>syn</i> , 95:5 er <sup>c</sup>	<b>3c</b> , 168 h, 71% yield >19:1 <i>anti</i> : <i>syn</i> , 94.5:5.5 er <sup>c</sup>	<b>3d</b> , 72 h, 65% yield >19:1 <i>anti</i> : <i>syn</i> , 90.5:9.5 er <sup>c</sup>	<b>3e</b> , 168 h, 27% yield >19:1 <i>anti</i> : <i>syn</i> , 92:8 er	<b>3f</b> , 144 h, 60% yield 1:2 <i>anti</i> : <i>syn</i> , 65.5:34.5/54.5:45.5 er <sup>c</sup>
<b>3g</b> , 24 h, 88% yield >19:1 <i>anti</i> : <i>syn</i> , 95:5 er <sup>c</sup>	<b>3h</b> , 56 h, 63% yield <sup>b</sup> 6:1 <i>anti</i> : <i>syn</i> , 94:6 er	<b>3i</b> , 56 h, 75% yield <sup>b</sup> 7:1 <i>anti</i> : <i>syn</i> , 94.5:5.5 er	<b>3j</b> , 56 h, 57% yield <sup>b</sup> 8:1 <i>anti</i> : <i>syn</i> , 90.5:9.5 er	<b>3k</b> , 120 h, 62% yield <sup>b</sup> 5:1 <i>anti</i> : <i>syn</i> , 95.5:4.5 er	<b>3l</b> , 120 h, 70% yield <sup>b</sup> 4:1 <i>anti</i> : <i>syn</i> , 96:4 er
<b>3m</b> , 56 h, 57% yield <sup>b</sup> 4:1 <i>anti</i> : <i>syn</i> , 92:8 er	<b>3n</b> , 144 h, 54% yield, 3:7 <i>anti</i> : <i>syn</i> , 71:29/53:47 er <sup>c</sup>	<b>3o</b> , 72 h, 83% yield >19:1 <i>anti</i> : <i>syn</i> , 96:4 er <sup>c</sup>	<b>3p</b> , 48 h, 85% yield 14:1 <i>anti</i> : <i>syn</i> , 92.5:7.5 er <sup>c</sup>	<b>3q</b> , 56 h, 85% yield <sup>b</sup> >19:1 <i>anti</i> : <i>syn</i> , 96.5:3.5 er	<b>3r</b> , 24 h, 91% yield <sup>b</sup> >19:1 <i>anti</i> : <i>syn</i> , 98:2 er
<b>3s</b> , 168 h, 60% yield >19:1 <i>anti</i> : <i>syn</i> , 90:10 er	<b>3t</b> , 96 h, 82% yield <sup>b</sup> >19:1 <i>anti</i> : <i>syn</i> , 97:3 er	<b>3u</b> , 24 h, 95% yield >19:1 <i>anti</i> : <i>syn</i> , 98.5:1.5 er <sup>c</sup>	<b>4u</b> , 92% yield >19:1 <i>anti</i> : <i>syn</i> , 98.5:1.5 er	<b>(2<i>R</i>,3<i>S</i>)-4u</b> (CCDC: 1960932)	<b>3v</b> , 168 h, trace

<sup>a</sup> All reactions were carried out with L-RaAd/Mg(OTf)<sub>2</sub>/NaBAR<sub>4</sub><sup>F</sup> (1 : 1 : 2, 10 mol%), **1** (0.2 mmol), **2** (0.2 mmol), and iPr<sub>2</sub>NH (0.3 mmol) in MeCN (2.0 mL) at  $-20\text{ }^{\circ}\text{C}$ . Isolated total yield of product **3**. The *anti* : *syn* ratio was determined by <sup>1</sup>H NMR analysis. The er value was determined by HPLC on a chiral stationary phase. <sup>b</sup> Isolated yield of the major diastereomer **3**. <sup>c</sup> er value of product **4**.



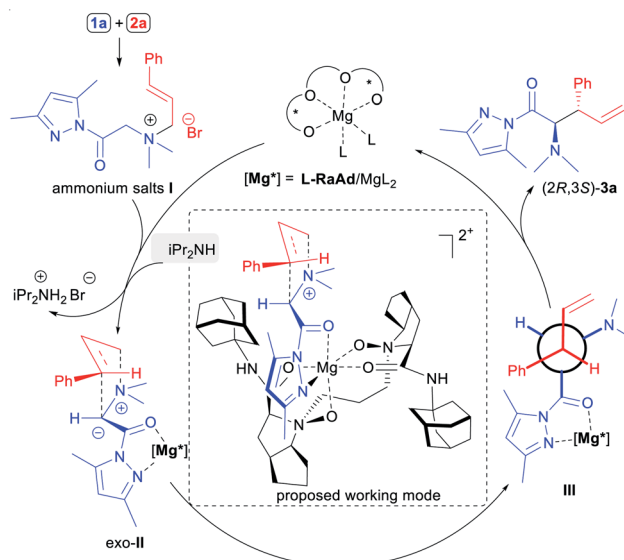
However, the reactivity and enantioselectivity dropped sharply with the increase of the ring size and steric hindrance of *N*-substituents (**3a–3e**). As shown in Table 2, the use of glycine pyrazoleamides bearing symmetrical *N,N*-dialkyl substituents, such as *N,N*-diethylglycine pyrazoleamide, gave the desired product **3b** in 64% yield with a 95 : 5 er value. Cyclic *N*-piperidinyl and *N*-azepanyl substituents were also tolerated in this reaction, delivering the products **3c** and **3d** in moderate yields with satisfactory enantioselectivities. Lower yield (27% yield) with a good enantiomeric ratio (92 : 8 er) was obtained for product **3e** bearing a *N*-heterocycle (morpholinyl) substituent. Next, the reaction of **1a** with allyl bromide compounds **2** bearing different cinnamic aryl substituents was evaluated. Both the position and electronic properties of substituents had obvious effects on the reaction. *Meta*-substituted (*E*)-(3-bromopropenyl)benzenes afforded the corresponding products (**3g** and **3o**) with better results than those with substituents at *ortho*- or *para*-positions (**3f**, **3h**, **3n**, **3p**). Generally, the substrate with an electron-rich group transformed into the rearrangement product with a slightly higher *anti* : *syn* ratio than the substrate with an electron-deficient group (**3h** and **3p**). Other *para*-halogen-substituted aryl rings, including 4-FC<sub>6</sub>H<sub>4</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>, and 4-IC<sub>6</sub>H<sub>4</sub> delivered the expected products (**3j–3l**) in 57–70% isolated yields of the major diastereomers with 90.5 : 9.5 to 96 : 4 er. The presence of the 4-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub> substituent led to acceptable outcomes (**3m**, 57% yield, 4 : 1 *anti* : *syn* and 92 : 8 er). The allyl bromide compounds bearing a 2-naphthyl group and heteroaromatic ring could also perform well to yield the desired products (**3q–3s**) with high diastereo- and enantioselectivities. Moreover, the allyl bromide compound **2** bearing a styryl functional group was suitable for the current reaction, producing the amino acid derivative **3t** in 82% yield with >19 : 1 *anti* : *syn* and 97 : 3 er. In addition, this rearrangement process of *N,N*-dimethylglycine pyrazoleamide **1a** with cinnamyl bromide bearing a methyl on the double bond gave the amino acid derivative **3u** in excellent yields (95% yield, >19 : 1 *anti* : *syn* and 98.5 : 1.5 er). Unfortunately, when cyclohexyl-substituted allyl bromide was employed, only a trace amount of the desired product (**3v**) was detected even with a prolonged reaction time (7 days). The absolute configuration of product **4u** was determined to be (2*R*,3*S*) by X-ray crystallography analysis,<sup>16</sup> and the others were assigned by comparing their CD spectra with that of **3u** (see pages 96–105 in the ESI† for more details).

To illustrate the potential utility of the methodology, a scale-up synthesis of **3r** was carried out under the optimized reaction conditions. As illustrated in Scheme 2a, 3 mmol of compound **1a** reacted smoothly with equal amounts of allyl bromide **2n**, furnishing the desired product **3r** in 89% yield with >19 : 1 *anti* : *syn* and 98 : 2 er. Further transformations of the product **4a** were conducted (Scheme 2b). Compound **4a** was easily reduced to **5a** in 88% yield with maintained stereoselectivities (>19 : 1 *anti* : *syn*, 96.5 : 3.5 er) by treatment with 10% Pd/C in methanol. Additionally, the reduction of **4a** with LiAlH<sub>4</sub> generated the corresponding alcohol **6a** in 71% yield (>19 : 1 *anti* : *syn*, 97.5 : 2.5 er).



Scheme 2 (a) Scale-up synthesis of **3r**; (b) further transformation of product **4a**.

Based on previous work,<sup>17</sup> the proposed catalytic cycle and a possible working mode of the enantioselective [2,3]-rearrangements of ammonium ylides are depicted in Scheme 3. Initially, the reaction of *N,N*-dimethylglycine pyrazoleamide (**1a**) and cinnamyl bromide (**2a**) produced the corresponding ammonium salt **I** which was activated by bidentate coordination with the *N,N*-dioxide–metal complex and subjected to deprotonation with the assistance of *i*Pr<sub>2</sub>NH to afford metal bonded ammonium ylide **II**. Due to the steric repulsion of the aryl group of the cinnamyl moiety of the substrate with the octahydrocyclopenta[*b*]pyrrole unit in the ligand **L-RaAd** as well as the pyrazoleamide unit in the *exo*-transition state,<sup>14</sup> the rearrangement occurred preferentially to afford the *anti*-configured  $\alpha$ -amino acid derivative (2*R*,3*S*)-**3a**, which was consistent with the experimental results.



Scheme 3 The proposed catalytic cycle and working mode.



## Conclusions

We have successfully developed the first Lewis acid catalyzed asymmetric [2,3]-rearrangement of quaternary ammonium ylides formed *in situ* from glycine pyrazoleamides and allyl bromides. The  $N,N'$ -dioxide/Mg(OTf)<sub>2</sub> catalytic system benefited the rearrangement process efficiently, providing diverse chiral *anti*- $\alpha$ -amino acid derivatives in good yields with high stereoselectivities (up to 95% yield, >19 : 1 *anti* : *syn* and 98.5 : 1.5 er). Besides, the potential use of the current method was illustrated by gram-scale synthesis and further transformations of products. A possible catalytic cycle along with the working mode was proposed to elucidate the reaction process and chiral induction. Further investigations on other reactions enabled by chiral  $N,N'$ -dioxide–metal complex catalysts are ongoing in our laboratory.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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