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Chiral *N,N′*-dioxide/Mg(OTf)$_2$ complex-catalyzed asymmetric [2,3]-rearrangement of *in situ* generated ammonium salts†

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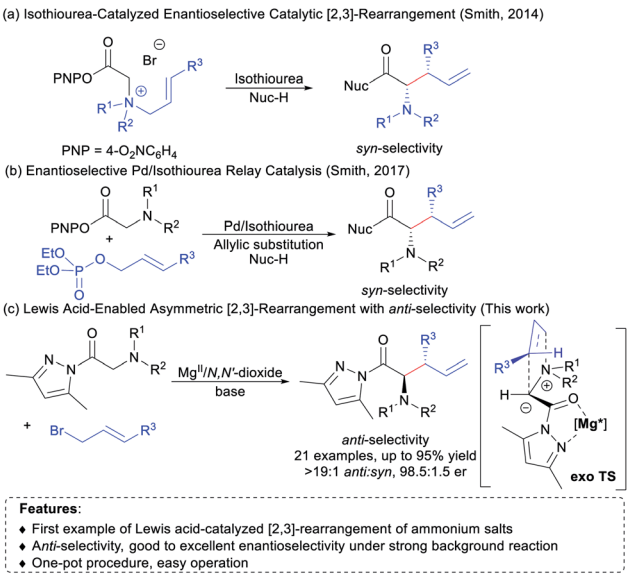
Catalytic enantioselective [2,3]-rearrangements of *in situ* generated ammonium ylides from glycine pyrazoleamides and allyl bromides were achieved by employing a chiral *N,N′*-dioxide/Mg^{II} complex as the catalyst. This protocol provided a facile and efficient synthesis route to a series of *anti*-α-amino 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.[1] In particular, [2,3]-rearrangement of ammonium ylides has been extensively investigated for rapid construction of valuable nitrogen-containing molecules.[2] It is highly attractive to disclose asymmetric versions of such intriguing rearrangement,[3–5] but only a few examples concerning the catalytic enantioselective [2,3]-rearrangement of ammonium ylides have been reported to date.[5] In 2014, Smith and co-workers demonstrated the first example of chiral isothiourea-catalyzed [2,3]-rearrangement of allylic ammonium ylides to gain optically enriched *syn*-configured α-amino acid derivatives (Scheme 1a).[5a] In 2017, they developed an elegant tandem *in situ* protocol utilizing Pd/chiral isothiourea relay catalysis, which provides a direct method for the synthesis of *syn*-α-amino acid derivatives from *N,N*-disubstituted glycine aryl esters and allylic phosphates (Scheme 1b).[5e] Recently, the group of Song reported an interesting study on an isothiourea catalyzed asymmetric [2,3]-rearrangement reaction of propargyl ammonium salts, which allows access to optically active allenyl α-amino amides.[5f] Despite these impressive advances, there is still room for further development. For instance, chiral isothiourea is a unique catalyst with which *syn*-α-amino acid derivatives were preferentially afforded in current reports.[5a–e] Given the wide and versatile use of α-amino acids in organic synthesis and pharmaceutical chemistry,[6] 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 stereodivergence of products.[7]

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



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

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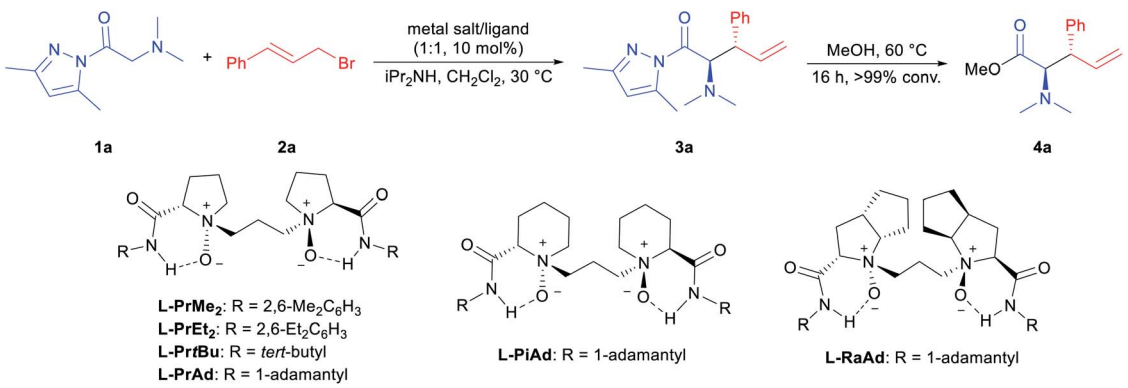
† Electronic supplementary information (ESI) available: [^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR, HPLC spectra, and CD spectra (PDF). X-ray crystallographic data for **4u** (CIF)]. CCDC 1960932. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9sc06342k

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 α-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[5a,f] and the background reaction in the presence of the external base.[12] 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/$Mg(OTf)_2$ (ref. 13) was found to promote the diastereo- and enantioselective rearrangement efficiently, and various *anti*-α-amino acid derivatives[14] 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$_2$** were examined in CH_2Cl_2 at 30 °C (Table 1, entries 1–4). $Mg(OTf)_2$ 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 $Mg(NTf)_2$ 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*)-pipecolic 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[a]



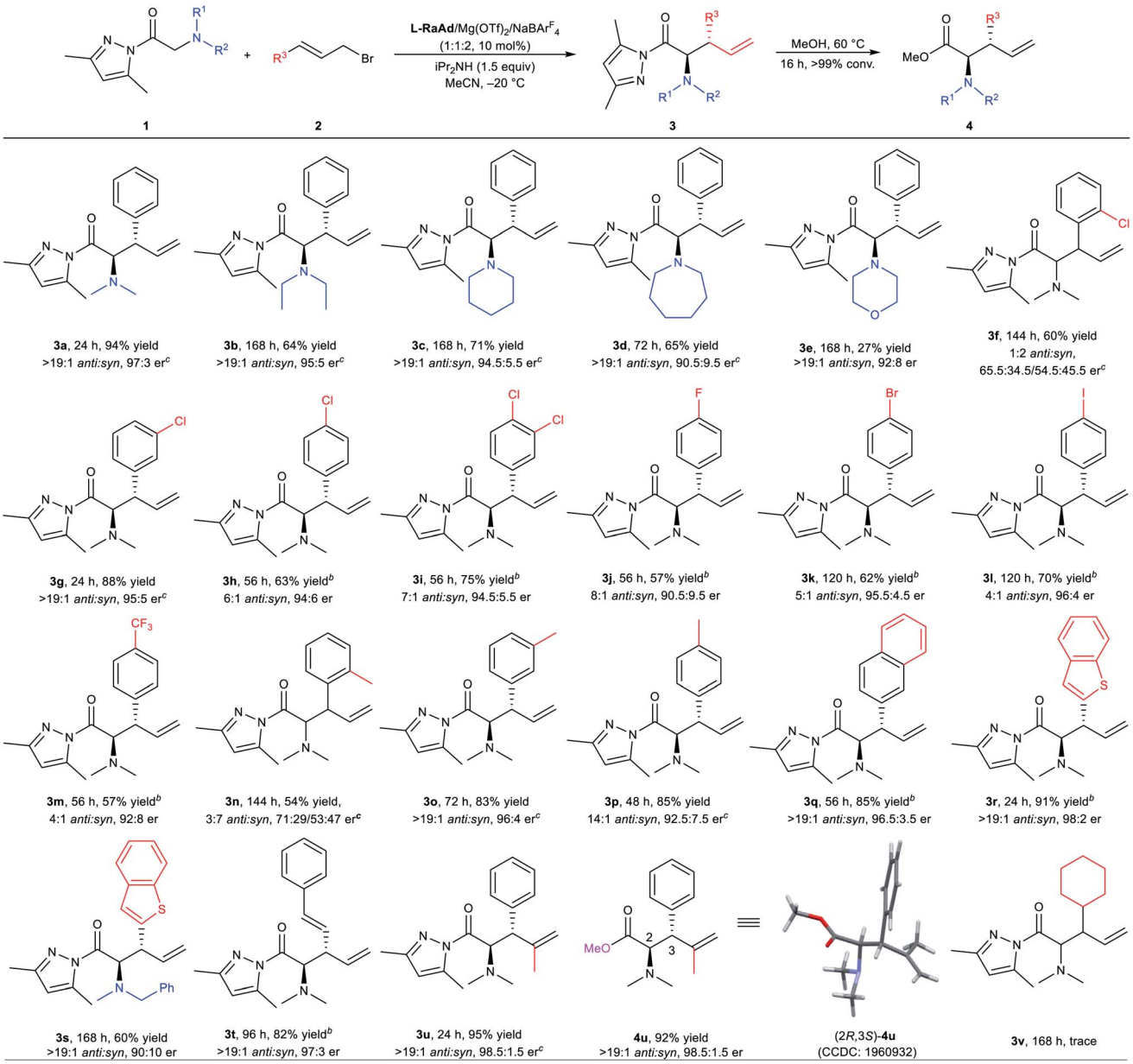
Entry	Metal salt	Ligand	Yield of **3a**[b] (%)	*anti* : *syn* of **3a**[c]	er of **4a**[d]
1	$Sc(OTf)_3$	**L-PrMe$_2$**	77	1 : 1	race/race
2	$Ni(OTf)_2$	**L-PrMe$_2$**	90	1.1 : 1	54 : 46/57.5 : 42.5
3	$Mg(OTf)_2$	**L-PrMe$_2$**	91	1.8 : 1	67.5 : 32.5/67.5 : 32.5
4	$Mg(NTf)_2$	**L-PrMe$_2$**	93	1.6 : 1	65.5 : 34.5/64.5 : 35.5
5	$Mg(OTf)_2$	**L-PrEt$_2$**	99	3 : 1	61 : 39/80 : 20
6	$Mg(OTf)_2$	**L-PrtBu**	90	2 : 1	56.5 : 43.5/52.5 : 47.5
7	$Mg(OTf)_2$	**L-PrAd**	98	5 : 1	75.5 : 24.5/57 : 43
8	$Mg(OTf)_2$	**L-PiAd**	94	2 : 1	52.5 : 47.5/race
9	$Mg(OTf)_2$	**L-RaAd**	91	3 : 1	81 : 19/54.5 : 45.5
10[e]	$Mg(OTf)_2$	**L-RaAd**	99	13 : 1	93.5 : 6.5
11[e,f]	$Mg(OTf)_2$	**L-RaAd**	82	12 : 1	95.5 : 4.5
12[e,f,g]	$Mg(OTf)_2$	**L-RaAd**	94	>19 : 1	97 : 3

[a] Unless otherwise noted, all reactions were carried out with **1a** (0.10 mmol), **2a** (0.10 mmol), iPr_2NH (0.15 mmol) and metal salt/ligand (1 : 1, 10 mol%) in CH_2Cl_2 (1.0 mL) at 30 °C for 14 h. [b] Isolated yield of **3a**. [c] Determined by ^1H NMR. [d] Determined by HPLC on a chiral stationary phase. [e] Carried out in MeCN. The metal salt/ligand was pretreated in CH_2Cl_2. [f] −20 °C for 24 h. [g] $NaBAr^F_4$ {$NaB[3,5\text{-}(F_3C)_2C_6H_3]_4$} (20 mol%) was added. The metal salt/ligand/$NaBAr^F_4$ was pretreated in EtOAc instead of CH_2Cl_2. 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 °C)[15] 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 $NaBAr^F_4$ 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).

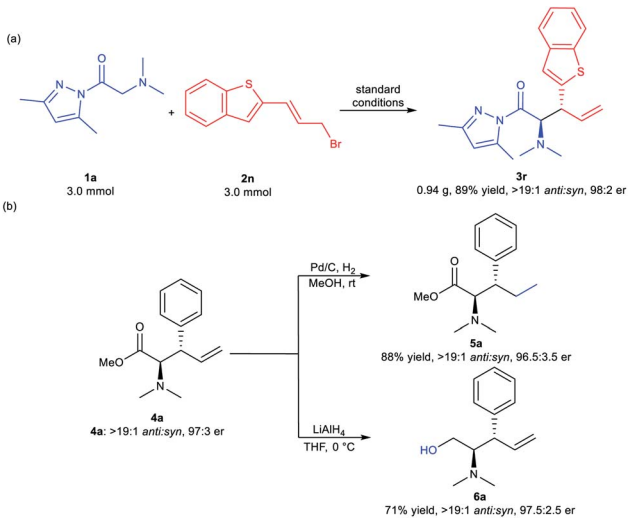
Table 2 Substrate scope for the [2,3]-rearrangement[a]



[a] All reactions were carried out with **L-RaAd**/$Mg(OTf)_2$/$NaBAr^F_4$ (1 : 1 : 2, 10 mol%), **1** (0.2 mmol), **2** (0.2 mmol), and iPr_2NH (0.3 mmol) in MeCN (2.0 mL) at −20 °C. Isolated total yield of product **3**. The *anti* : *syn* ratio was determined by ^1H NMR analysis. The er value was determined by HPLC on a chiral stationary phase. [b] Isolated yield of the major diastereomer **3**. [c] er value of product **4**.

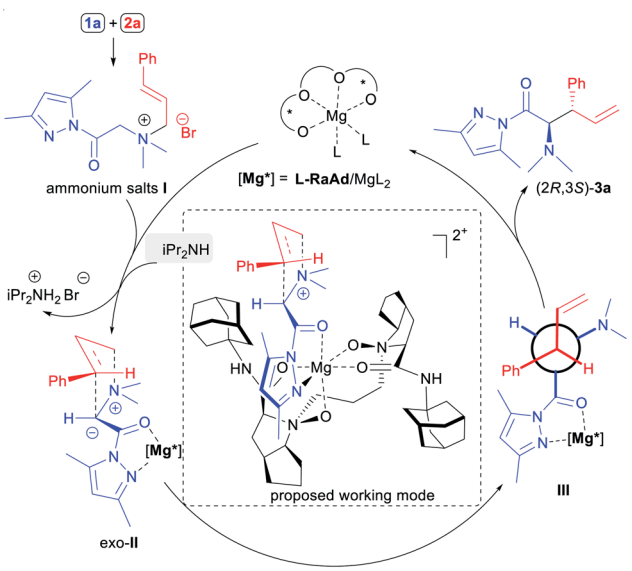
However, the reactivity and enantioselectivity dropped sharply with the increase of the ring size and steric hindrance of *N*-substituents (**3a–3e**). As shown in Table 2, the use of glycine pyrazoleamides bearing symmetrical *N*,*N*-dialkyl substituents, such as *N*,*N*-diethylglycine pyrazoleamide, 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_6H_4, 4-BrC_6H_4, and 4-IC_6H_4 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-$F_3CC_6H_4$ 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,[16] 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 $LiAlH_4$ 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,[17] 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 iPr_2NH 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,[14] the rearrangement occurred preferentially to afford the *anti*-configured α-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/$Mg(OTf)_2$ catalytic system benefited the rearrangement process efficiently, providing diverse chiral *anti*-α-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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15 Even at −20 °C, the background reaction still occurred, and the desired racemic product was isolated in 40% yield with a slightly lower *anti* : *syn* ratio (1 : 1.5).

16 CCDC 1960932 (**4u**)†

17 (*a*) W. W. Luo, X. Yuan, L. L. Lin, P. F. Zhou, X. H. Liu and X. M. Feng, *Chem. Sci.*, 2016, **7**, 4736; (*b*) D. Zhang, L. L. Lin, J. Yang, X. H. Liu and X. M. Feng, *Angew. Chem., Int. Ed.*, 2018, **57**, 12323.