Heterocycles

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Enantioselective Dearomative [3+2] Cycloaddition Reactions of Benzothiazoles

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Dedicated to Professor Yaozhong Jiang on the occasion of his 80th birthday

Abstract: *A highly enantioselective dearomative [3+2] cycloaddition of benzothiazole has been successfully developed. A wide range of benzothiazoles and cyclopropane-1,1-dicarboxylates are suitable substrates for this reaction. The desired hydropyrrolo[2,1-b]thiazole compounds were obtained in excellent enantioselectivity and yields (up to 97% ee and 97% yield). With the same catalytic system, a highly efficient kinetic resolution of 2-substituted cyclopropane-1,1-dicarboxylates was also realized.*

The hydrothiazole ring as an important structural motif has been often observed in natural products and pharmaceuticals.[1,2] For example, mirabazoles isolated from the blue-green algae *Scytonemea mirabile*, bistratamides produced by *Lissoclinum patella*, and the penicillin family of β-lactam antibiotics (**1**; Figure 1) are all hydrothiazole derivatives. As analogues of β-lactam antibiotics, the γ-lactams based on a hydropyrrolo-thiazole scaffold showed good antiviral and anticholinergic activities.[2a,3–5] For instance, hydropyrrolo-thiazole γ-lactams (**2**)[4a,b] are a selective HIV-1 reverse transcriptase inhibitor. The multisubstituted γ-lactams **3**[4c] are used as remedies for diabetes and obesity. The γ-lactams containing hydropyrrolo[2,1-*b*]benzothiazole (**4**)[4d] are effective against bicuculline-induced seizures in mice. Hydropyrrolo[2,1-*b*]thiazole compounds (**5**)[5] are dipeptidyl peptidase inhibitors. Therefore, searching for an efficient method to construct hydropyrrolo-thiazoles is in great demand.

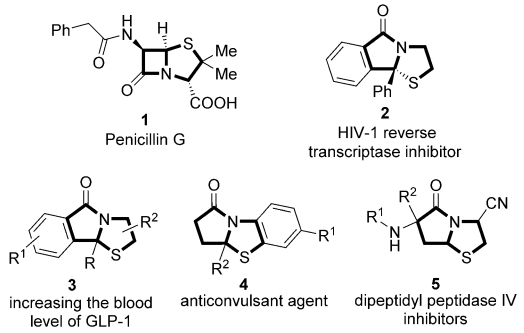

Figure 1. Examples of natural products and bioactive compounds containing a hydrothiazole unit.

Dearomatization reactions have been of interest for a long time since they have the potential to construct various ring systems including fused, bridged, and spiro heterocyclic or carbocyclic rings.[6] In particular, catalytic asymmetric dearomatization (CADA) reactions recently received great attention as these reactions provide direct access to three-dimensional complex molecules in their enantioenriched forms from simple planar aromatic compounds.[6c] In the course of our ongoing efforts towards the development of CADA reactions of electron-rich aromatics including indoles,[7a,b] pyrroles,[7c,d] and naphthols,[7e,f] we also became interested in exploring the reactions of electron-poor heteroarenes, which have been rarely studied.[8] Despite of the great importance of benzothiazoles and their related dearomatized structures, to our knowledge, catalytic asymmetric dearomatization reactions of benzothiazoles have not been reported yet. Recently, the [3+2] cycloaddition reactions of cyclopropane-1,1-dicarboxylates[9–12] with various unsaturated double bonds (C=C, C=O, N=O, N=N) have been elegantly conducted by the groups of Kerr, Tang, Johnson, Waser, and others. Especially, Johnson and co-workers[11a,b] reported an elegant dynamic kinetic asymmetric [3+2] cycloaddition of cyclopropanes with aldehydes and aldimines. Tang and co-workers[11d,e] developed an exceptional asymmetric [3+2] cycloaddition reaction of indole with cyclopropane-1,1-dicarboxylates. We envisaged that benzothiazoles might be suitable substrates for an asymmetric dearomative [3+2] cycloaddition with cyclopropane-1,1-dicarboxylates, thus providing highly enantioenriched hydropyrrolo-thiazoles. Herein, we report the first catalytic asymmetric dearomatization reaction

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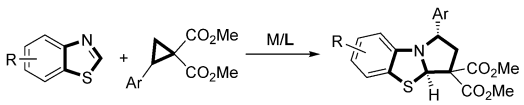


Scheme 1. Enantioselective dearomative [3+2] cycloaddition reactions of benzothiazoles.

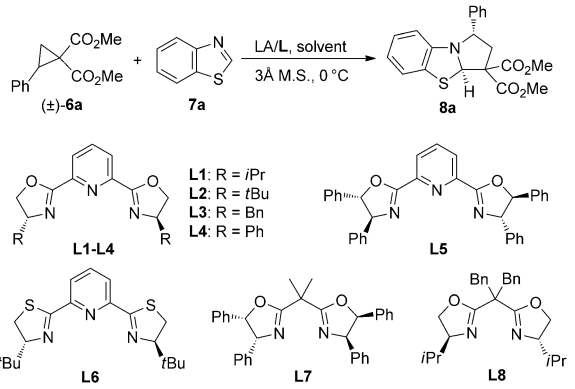
of benzothiazoles by [3+2] cycloaddition with cyclopropane-1,1-dicarboxylates (Scheme 1).

Initially, the cycloaddition reaction of racemic dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**6a**) with benzothiazole (**7a**) was examined (Table 1). Several Lewis acids, together with the *i*Pr-Pybox ligand **L1** were tested in DCM at 0 °C. As shown in Table 1, the results indicated that this reaction could be catalyzed by MgI_2, thus affording the desired product **8a** in moderate enantioselectivity and high yield (entry 3). Other Lewis acids hardly catalyzed the desired cycloaddition reaction (see Table S1 in the Supporting Information). To improve the enantioselectivity of the reaction, a series of chiral Pybox and Box ligands were tested. Except for the thio-Pybox **L6**, other ligands gave the desired cycloadducts in high yields (Table 1, entries 4–10), and the *t*Bu-Pybox **L2** gave the best enantioselectivity (entry 4). Subsequently, screening of solvents and molecular sieves (entries 11–14; see also Table S2) resulted in the isolation of the desired product in 94% yield and 95% *ee* when 4 Å M.S. were employed in PhCl (entry 14). In addition, when the reaction was carried out at room temperature, the *ee* value of the product was reduced to 93% (entry 15). When 5 mol% catalyst was employed, the *ee* value of the product was maintained but the yield was decreased (entry 16). When the ratio of **6a** and **7a** was changed to 1:1, the *ee* value and yield of **8a** fell significantly (entry 17). Thus, the optimized reaction conditions are obtained as follows: 10 mol% of MgI_2, 12 mol% of **L2**, 1.0 equivalent of **7a**, 2.4 equivalents of **6a**, and 4 Å M.S. in PhCl at 0 °C. When the reaction was carried out on a gram scale, similar excellent results were obtained (83% yield with 96% *ee*; see Scheme S1).

Subsequently, various cyclopropane-1,1-dicarboxylates were tested under the optimized reaction conditions. The results are summarized in Scheme 2. For the aryl groups at the 2-position of the cyclopropanes, those bearing either electron-rich or electron-deficient substituents led to the corresponding adducts with good *ee* values and yields (**8a–l**). In the case of the dichloro-substituted **6m**, the reaction gave the desired product **8m** in 97% *ee* and 39% yield. As for the naphthalen-2-yl cyclopropane **6n**, excellent enantioselectivity and yield (**8n**) were obtained. It should be noted that the reaction of the thiophen-2-yl cyclopropane **6o** gave desired product **8o** in 93% yield and 86% *ee* at −50 °C. The (*E*)-styryl cyclopropane **6p** was also a suitable substrate for this reaction, thus affording the desired product in excellent enantioselectivity and yield (**8p**, 93% yield, 90% *ee*), while dimethyl 2-cyclohexylcyclopropane-1,1-dicarboxylate failed to produce the desired product.

Then, benzothiazoles **7b–i** were employed under the optimized reaction conditions. As shown in Scheme 3, despite of the electronic property of the substituents, all the reactions

Table 1: Optimization of [3+2] cycloaddition of cyclopropanes with benzothiazole.[a]

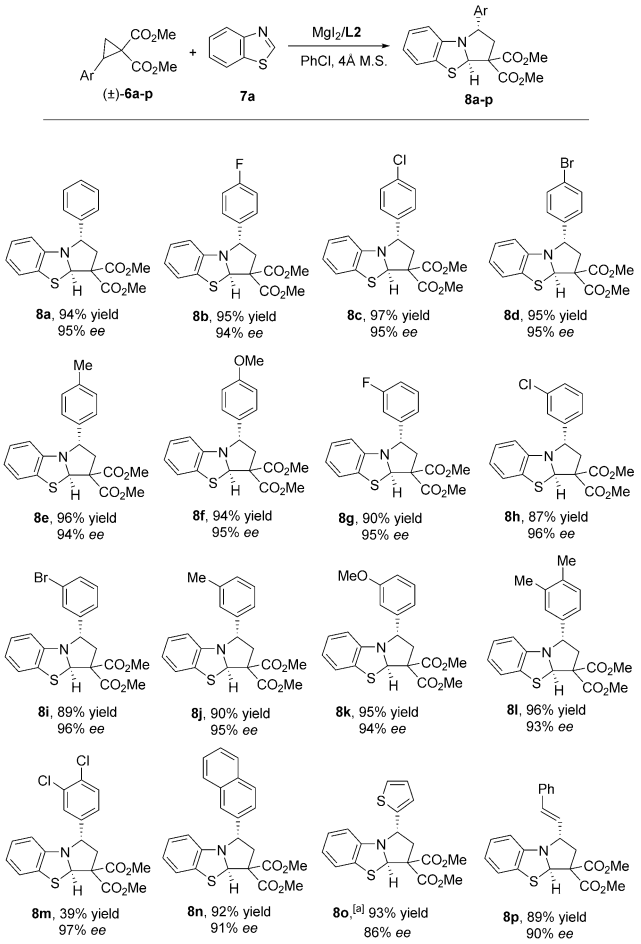


Entry	Lewis acid	L	Solvent	Yield [%][b]	*ee* [%][c]
1	$Sc(OTf)_3$	**L1**	DCM	5	41
2	$Cu(OTf)_2$	**L1**	DCM	n.r.	–
3	MgI_2	**L1**	DCM	96	51
4	MgI_2	**L2**	DCM	96	57
5	MgI_2	**L3**	DCM	93	24
6	MgI_2	**L4**	DCM	90	42
7	MgI_2	**L5**	DCM	94	−24
8	MgI_2	**L6**	DCM	25	13
9	MgI_2	**L7**	DCM	95	4
10	MgI_2	**L8**	DCM	97	−46
11	MgI_2	**L2**	$CHCl_3$	76	64
12	MgI_2	**L2**	PhCl	90	95
13	MgI_2	**L2**	PhCl	91	95[d]
14	MgI_2	**L2**	PhCl	94	95[e]
15	MgI_2	**L2**	PhCl	95	93[f]
16	MgI_2	**L2**	PhCl	69	95[g]
17	MgI_2	**L2**	PhCl	48	65[h]

[a] Reaction conditions: Lewis acid (10 mol%), **L** (12 mol%), **6a** (2.4 equiv), **7a** (1.0 equiv), $[\mathbf{7a}]_0 = 0.1$ M in solvent, 3 Å M.S., under N_2 at 0 °C for 5 days. [b] Yield of isolated product. The d.r. value was >20:1, as determined by ^{1}H NMR analysis of the crude reaction mixture. [c] The *ee* value was determined by chiralphase HPLC analysis. [d] 5 Å M.S. were used. [e] 4 Å M.S. were used. [f] 4 Å M.S. were used at room temperature. [g] MgI_2 (5 mol%) and **L2** (6 mol%) were used, 4 Å M.S. at 0 °C for 7 days. [h] The ratio of **6a**:**7a** = 1:1, 4 Å MS was used at 0 °C. DCM = dichloromethane, M.S. = molecular sieves, n.r. = no reaction, Tf = trifluoromethanesulfonyl.

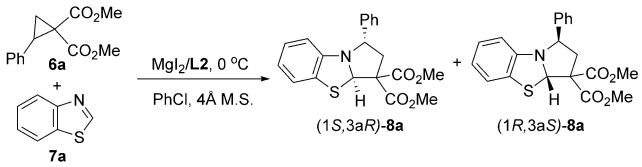
with (±)-**6a** proceeded smoothly, and their corresponding cycloadducts were obtained in excellent enantioselectivities and yields (**8q–x**).

In the [3+2] cycloaddition reactions described above, an excess amount of **6** (2.4 equiv) was used. The *ee* value of product was affected obviously by adjusting the ratio between the two substrates. Further experimental results are shown in Table 2. When 1.0 equivalent of *rac*-**6a** and 1.2 equivalents of **7a** reacted for one day, the product (1*S*,3a*R*)-**8a** was obtained with 97.3:2.7 e.r. and 44% yield, and the recovered **6a** was found to be enriched in the *S*-configured enantiomer with 92.7:7.3 e.r., and the S factor is 66. When (*R*)-**6a** was employed, a high conversion resulted and led to (1*S*,3a*R*)-**8a** with greater than 99% *ee* and 86% yield, and the remaining (*R*)-**6a** was recovered with 3.0:97.0 e.r. However, the utilization of (*S*)-**6a** afforded (1*R*,3a*S*)-**8a** with 5.4:94.6



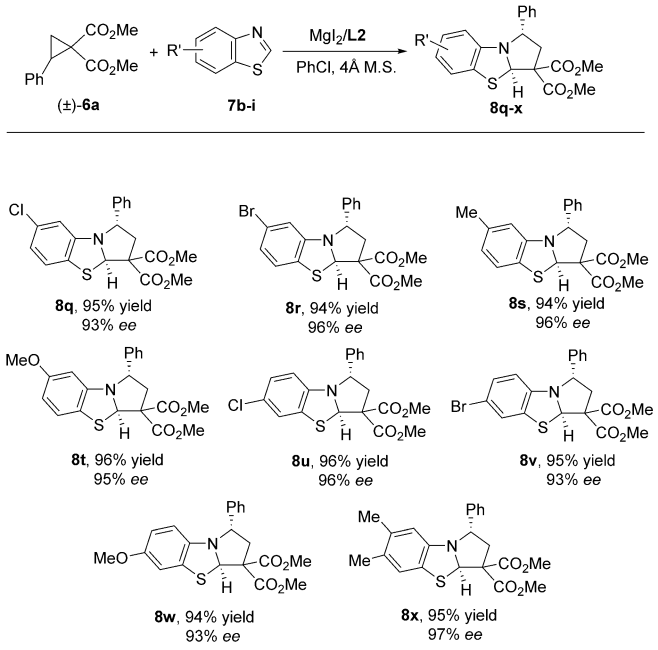
Scheme 2. [3+2] Cycloaddition of various cyclopropanes with benzothiazole. Reaction conditions: MgI_2 (10 mol%), **L2** (12 mol%), **6** (2.4 equiv), **7a** (1.0 equiv), $[\mathbf{7a}]_0 = 0.1$ M in PhCl, 4 Å M.S., under N_2 at 0°C for 5 days. Yields of isolated products are reported. For all the products, d.r. was >20:1, as determined by ^{1}H NMR analysis of the crude reaction mixture. The *ee* value was determined by chiral-phase HPLC analysis. [a] At −50°C.

Table 2: Stereochemical analysis.[a]



Substrate	Conversion [%][b]	Yield [%][c]	(1*S*,3a*R*)-**8a**/(1*R*,3a*S*)-**8a**[d]	(*S*)-**6a**/(*R*)-**6a**[d]
(±)-**6a**	48	44	97.3:2.7	92.7:7.3
(*R*)-**6a**	88	86	>99:1	3.0:97.0
(*S*)-**6a**	7	<5	5.4:94.6	>99:1

[a] Reaction conditions: MgI_2 (10 mol%), **L2** (12 mol%), **6a** (1.0 equiv), **7a** (1.2 equiv), $[\mathbf{6a}]_0 = 0.1$ M in PhCl, in the presence of 4 Å M.S. under N_2 atmosphere at 0°C for 24 h. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Yield of isolated **8a**. [d] The e.r. value was determined by chiral-phase HPLC analysis.



Scheme 3. [3+2] Cycloaddition of various benzothiazoles. Reaction conditions: MgI_2 (10 mol%), **L2** (12 mol%), **6a** (2.4 equiv), **7** (1.0 equiv), $[\mathbf{7}]_0 = 0.1$ M in PhCl, 4 Å M.S., under N_2 at 0°C for 5 days. Yields of isolated products are reported. For all the products, the d.r. was >20:1, as determined by ^{1}H NMR analysis of the crude reaction mixture. The *ee* value was determined by chiral-phase HPLC analysis.

e.r. and less than 5% yield, and the remaining (*S*)-**6a** was recovered with *ee* value unchanged. The results of the reactions for five days also suggested that a simple kinetic resolution rather than a dynamic kinetic resolution process dominates for the cycloaddition reaction (see Table S3). In addition, there is clearly a match scenario about the ligand and substrate, the benzothiazole selectively reacts with the *R*-configured enantiomer of the cyclopropane in the presence of ligand **L2**.

The experiments on dynamic kinetic transformation of the cyclopropanes **6f** and **6o** were conducted with this catalyst system (see Schemes S2 and S3). These results indicated that the cycloadditions of **6f** and **6o** with benzothiazole are also dominated by a simple kinetic resolution process. Notably, enantiopure (*S*)-**6a** reacted smoothly with **7a** in the presence of MgI_2 to afford **8a** without erosion of the enantiomeric purity (see Scheme S4). Therefore, both enantiomers of the hydropyrrolo[2,1-*b*]thiazole products could be obtained easily from racemic cyclopropane-1,1-dicarboxylate. The absolute configuration **8a** was determined to be (1*S*,3a*R*) by single-crystal X-ray diffraction analysis.[13]

In summary, we have successfully developed a highly enantioselective dearomative [3+2] cycloaddition reaction of benzothiazoles with cyclopropane-1,1-dicarboxylates. In the presence of a Pybox-MgI_2 catalyst, the cycloaddition reaction afforded a series of hydropyrrolo[2,1-*b*]thiazole compounds in excellent enantioselectivity (up to 97% *ee*) and yields (up to 97%). The reaction displays a general scope for both cyclopropanes and benzothiazoles. In addition, a highly

efficient kinetic resolution of 2-substituted cyclopropane-1,1-dicarboxylates was also realized, thus providing a facile way to access both enantiomers of hydropyrrolo[2,1-*b*]thiazole compounds.

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[13] CCDC 1498035 (**8a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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