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ARTICLE TYPE

Enantioselective Dearomative [3+2] Annulation of 5-Amino-isoxazoles with Quinone Monoimines

Hui Liu,[a,b,c] Yingkun Yan,[a,b,c] Jiayan Zhang,[a,b,c] Min Liu,[a,b,c] Shaobing Cheng,[a,b,c] Zhouyu Wang*[a] and Xiaomei Zhang*[a,b]

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The first enantioselective dearomative [3+2] annulation of 5-amino-isoxazoles with quinone monoimines was realized using a chiral phosphoric acid as catalyst. Various novel (bridged) isoxazoline fused dihydrobenzofurans bearing two continuous quaternary stereocenters were achieved in moderate to good yields (up to 94 %) with moderate to good enantioselectivities (up to 98 % ee). The absolute configurations of two products were assigned by X-ray crystal structural analyses and a plausible reaction mechanism was proposed.

Introduction

Isoxazolines are important building blocks of a large number of biologically active compounds.[1] Isoxazolines are also versatile intermediates for the synthesis of important organic molecules.[2] Consequently, many efficient strategies have been developed to construct structurally diverse isoxazolines.[3,4] However, catalytic asymmetric synthesis of enantioenriched isoxazolines has been rarely reported.[4a-4f]

2,3-Dihydrobenzofurans are important building blocks found in a wide range of natural products and pharmaceutical substances.[5] Therefore, the construction of 2,3-dihydrobenzofurans is of great interest to the researchers.[6]

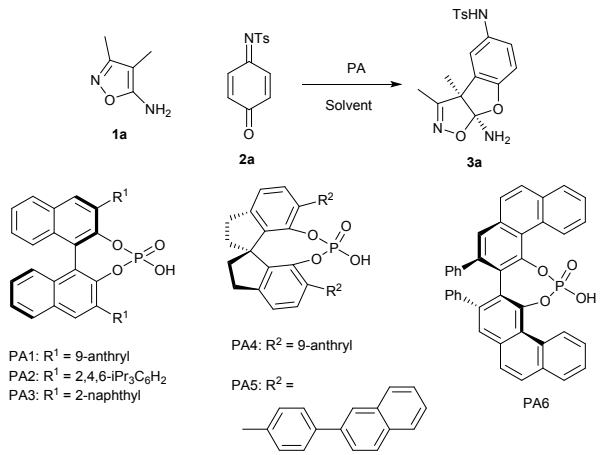
Asymmetric dearomative reactions[7] are efficient strategy to construct chiral heterocyclic compounds. In the last decade, many types of aromatic compounds have been employed in asymmetric dearomative reactions. However, dearomative reactions of isoxazoles have been rarely researched. Very recently, Qi and co-workers reported a three-component tandem reaction involving dearomative Michael addition of 5-amino-pyrazoles or 5-amino-isoxazole with nitroolephins followed by cyclization with cyclic ketones to provide a series of spiral fused polycyclic compounds with moderate to good yields in good diastereoselectivities.[8]

In recent years, great progress has been made in catalytic asymmetric reactions of quinone derivatives for the construction of novel chiral heterocyclic compounds.[6c,6e,6f,6h,6j,6m,6n,9,10] Our group has also been engaged in development of new asymmetric transformations of quinone derivatives.[6m,6n,10d] In continuation of our research on asymmetric reaction of quinone derivatives, herein we reported the first highly enantioselective dearomative [3+2] annulation of 5-amino-isoxazoles with quinone monoimines promoted by chiral phosphoric acids. In the presence of a chiral phosphoric acid, the reactions proceeded efficiently to provide various (bridged) isoxazoline fused dihydrobenzofurans with moderate to good yields in moderate to good enantioselectivities.

Results and Discussion

First, various chiral phosphoric acids were evaluated in the dearomative [3+2] coupling of 3,4-dimethylisoxazol-5-amine **1a** with 4-methyl-N-(4-oxocyclohexa-2,5-dienylidene)benzene-sulfonamide **2a** in dichloromethane at 0 °C. As can be seen in Table 1, all of the chiral phosphoric acids promoted the reaction smoothly to provide isoxazoline fused dihydrobenzofuran **3a** in moderate yields (Table 1, entries 1-6) and **PA3** which bears a 2-naphthyl group in the 3,3' position of BINOL, gave the product **3a** in quantitative yield with the highest *ee* value of 79% (Table 1, entry 3). Thus **PA3** was determined as the optimal catalyst and used in the following investigations.

Table 1 Evaluation of the chiral phosphoric acids and optimization of the conditions.[a]



Entry	**PA** (mol%)	Solvent	T (℃)	t (h)	Yield (%)[b]	ee (%)[c]
1	**PA 1** (10)	CH_2Cl_2	0	0.3	94	59
2	**PA 2** (10)	CH_2Cl_2	0	0.3	95	41
3	**PA 3** (10)	CH_2Cl_2	0	4	99	79
4	**PA 4** (10)	CH_2Cl_2	0	0.3	99	9
5	**PA 5** (10)	CH_2Cl_2	0	4	85	13
6	**PA 6** (10)	CH_2Cl_2	0	4	67	8
7	**PA 3** (10)	DCE	0	10	99	79
8	**PA 3** (10)	$CHCl_3$	0	10	96	75
9	**PA 3** (10)	toluene	0	20	86	58

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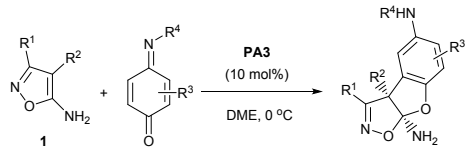
10	**PA 3** (10)	CH_3CN	0	5	89	77
11	**PA 3** (10)	Et_2O	0	45	73	79
12	**PA 3** (10)	MTBE	0	36	92	89
13	**PA 3** (10)	THF	0	10	83	92
14	**PA 3** (10)	DME	0	12	87	94
15	**PA 3** (10)	DME	-10	12	89	93
16	**PA 3** (5)	DME	0	12	81	92

[a] Unless otherwise specified, the reaction was carried out with 0.10 mmol of **1a**, 0.12 mmol of **2a**, and 0.01 mmol of the chiral phosphoric acid in 1 mL of solvent. [b] Isolated yield based on **1a**. [c] Enantiomeric excess was determined by HPLC analysis on a chiral stationary phase. Ts = 4-toluenesulfonyl.

Afterwards various solvents were screened in the reaction. Reactions in 1,2-dichloroethane, chloroform, acetonitrile and ether gave similar enantioselectivities to dichloromethane (Table 1, entries 7,8,10 and 11). Toluene delivered much lower enantioselection (Table 1, entry 9). To our delight, reaction in some ethereal solvents provided the product with obviously higher enantioselectivities (Table 1, entries 12-14), in which dimethoxyethane afforded the best result (Table 1, entry 14). Therefore dimethoxyethane was determined as the optimal solvent and used in the following investigations. When the reaction was performed at lower temperature (-10 °C), no better resukt was obtained (Table 1, entry 15). Furthermore, we also tried to lower the catalyst loading to 5 mol%, but both the yield and the enantioselectivity decreased (Table 1, entry 16).

With the optimized reaction conditions in hand, the scope of the reaction was investigated. The results were summarized in Table 2.

Table 2 Substrate scope of the enantioselective dearomative [3+2] annulation of 5-amino-isoxazoles **1** with quinone monoimines **2**.[a]



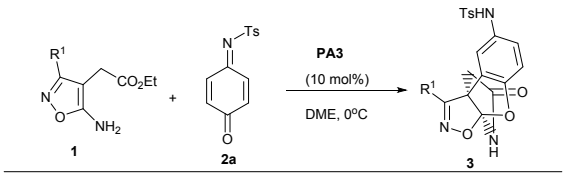
1 2 3

Entry	3	t	Yield (%)[b]	ee (%)[c,d]
1	**3aa**: R^1 = Me	12 h	87	94
2	**3ba**: R^1= *t*-Bu	12 h	63	87
3	**3ca**: R^1= Ph	12 h	79	94
4	**3da**: R^1 = 4-FC_6H_4	60 h	73	94
5	**3ea**: R^1 = 4-ClC_6H_4	40 h	64	93
6	**3fa**: R^1 = 4-BrC_6H_4	48 h	82	94
7	**3ga**: R^1= 4-$MeOC_6H_4$	7 d	58	93
8	**3ha**: R^1= 3-ClC_6H_4	40 h	79	94
9	**3ia**: R^1 = 2-thienyl	7 d	55	93
10	**3ja**: R^1 = 2-furanyl	48 h	60	94
11	**3ka**: R^2 = allyl	4 d	75	81
12	**3la**: R^2 = Bn	4 d	49	85
13	**3ma**: R^2 = 4-$FC_6H_4CH_2$	4 d	36	81
14	**3na**: R^2 = 4-$ClC_6H_4CH_2$	48 h	60	94
15	**3oa**: R^2 = Ph	48 h	NR	-
16	**3ab**: R^3 = Me	16 h	94	92
17	**3ac**: R^3 = Br	16 h	90	91
18	**3ad**: R^3 = OMe	16 h	35	85
19	**3ae**: R^4 = Ns	12 h	68	86
20	**3af**: R^4 = 4-$MeOC_6H_4SO_2$	12 h	90	91

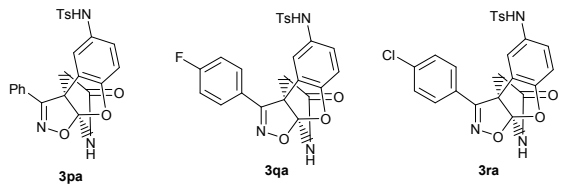
[a] Unless otherwise specified, the reaction was carried out with 0.10 mmol of **1**, 0.12 mmol of **2**, and 0.01 mmol of the chiral phosphoric acid **PA3** in 1 mL of 1,2-dimethoxyethane at 0 °C [b] Isolated yield based on **1**. [c] Enantiomeric excess was determined by HPLC analysis on a chiral stationary phase. [d] The absolute configuration of **3fa** was determined by an X-ray crystal structural analysis and the other products were assigned absolute configurations by analogy. Ts = 4-toluenesulfonyl, Ns = 4-nitrobenzenesulfonyl.

Generally, 5-amino-4-methylisoxazoles with different substituents on 3-position were tolerable in the reaction with quinone monoimine **2a** to afford the corresponding isoxazoline fused dihydrobenzofurans (Table 2, entries 1-10) in moderate to good yields with high *ee* values. However, lower enantioselectivities were observed with some 5-amino-3-methyl-isoxazoles with different substituents on 4-position (Table 2, entries 11-13), whereas 4-(4-chlorobenzyl)-3-methylisoxazol-5-amine **1n** exhibited good enantioselectivity in reaction with **2a** (Table 2, entry 14). When 3-methyl-4-phenylisoxazol-5-amine **1o** was subjected in reaction with **2a**, no reaction was observed (Table 2, entry 15). Furthermore, various quinone monoimines with different substituents on 3-position and quinone monoimines with different N-substituents were also tested in reaction with 3,4-dimethyl-isoxazol-5-amine **1a**. Generally the corresponding products were obtained with good *ee* values (Table 2, entries 16-20), although lower yields were observed with **3ad** and **3ae** (Table 2, entries 18 and 19). We also tried to use N-Boc-isoxazol-5-amine in this reaction. However, no reaction was observed, perhaps due to the decrease of electron density of the isoxazole ring.

Bridged polycyclic frameworks widely exist in natural products and pharmaceuticals. Construction of bridged polycyclic compounds has always been an attractive and challenging task for chemists.[11] Herein we presented the enantioselective synthesis of novel bridged isoxazoline fused dihydrobenzofurans **3pa**-**3xa** via tandem dearomative [3+2] annulation-cyclization of some ethyl 4-acetate-isoxazol-5-amines with quinone imine **2a**.



1 2a 3



3pa: 3d, 84% yield, 90% ee
3qa: 4.5d, 63% yield, 96% ee
3ra: 7d, 52% yield, 97% ee

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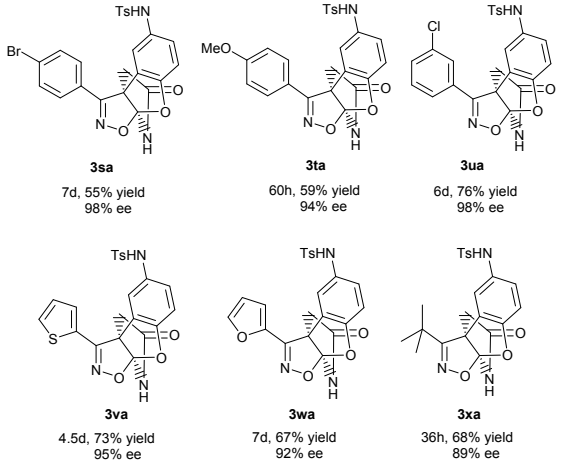


Scheme 1 Construction of bridged isoxazoline fused dihydrobenzofurans. Reaction conditions: Unless otherwise specified, the reactions were carried out with 0.10 mmol of **1**, 0.12 mmol of **2a**, and 0.01 mmol of **PA3** in 1 mL of 1,2-dimethoxyethane at 0 °C. Yields shown are of the isolated products and based on **1**. Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase. The absolute configuration of **3xa** was determined by an X-ray crystal structural analysis and the other products were assigned absolute configurations by analogy.

As can be seen in Scheme 1, under the optimized conditions, the reactions proceeded for prolonged time to provide the bridged products in moderate yields with good enantioselectivities. The electron nature of 3-substituent has little effect on the result. Thus a facile strategy has been established to construct such kind of bridged polycyclic compounds with good enantioselection.

The absolute configurations of **3fa** and **3xa** were determined as (3a*R*,8a*S*) by X-ray crystal structural analyses[12] (Figure 1). Consequently, the other products can be assigned absolute configurations by analogy.

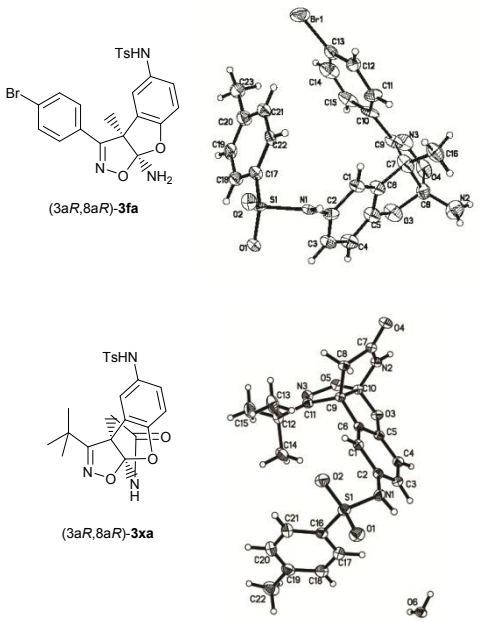
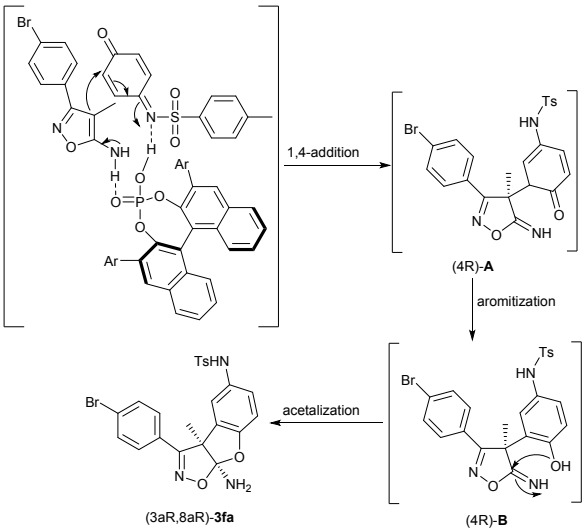


Figure 1. X-ray crystal structures of (3a*R*,8a*R*)-**3fa** and (3a*R*,8a*R*)-**3xa**.

Based on the absolute configuration of product **3fa**, a plausible reaction mechanism was proposed. As outlined in Scheme 2, first, bifunctional phophoric acid activated both isoxazole **1f** and quinone monoimine **2a**. Isoxazole **1f** attacked quinone monoimine **2a** to give the intermediate (4*R*)-**A** which underwent aromatization immediately to give phenol intermediate (4*R*)-**B**. Finally, intramolecular acetalization generated isooxazoline fused dihydrobenzofuran (3a*R*,8a*R*)-**3fa**.



Scheme 2. Plausible reaction mechanism.

Conclusions

In conclusion, we have developed an enantioselective dearomative [3+2] annulation of 5-amino-isoxazoles with quinone monoimines promoted by a chiral phosphoric acid. Through this transformation, various isoxazoline fused dihydrobenzofurans were approached with moderate to good yields in moderate to good enantioselectivities. Moreover, via tandem dearomative [3+2] annulation-cyclization, some bridged isoxazoline fused dihydrobenzofurans were also prepared with moderate yields in good enantioselectivities. The absolute configurations of a fused product and a bridged product were determined by X-ray crystal structural analyses. Accordingly, a plausible reaction mechanism was proposed.

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[a] *Department of Chemistry, Xihua University*
[b] *Asymmetric Synthesis and Chiraltechnology Key Laboratory of Sichuan Province, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, China, Fax: (+86)28-85257883; Tel: (+86)28-85257883; E-mail: xmzhang@cioc.ac.cn*
[c] *University of Chinese Academy of Sciences, Beijing,China.*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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