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A catalytic highly enantioselective allene approach to oxazolines†

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Oxazolines are a very important class of heterocyclic compounds. However, catalytic enantioselective syntheses are very limited. Here, a highly enantioselective palladium-catalyzed coupling-cyclization of readily available *N*-(buta-2,3-dienyl) amides with aryl or 1-alkenyl iodides has been developed for the asymmetric construction of oxazoline derivatives. Many synthetically useful functional groups are tolerated in this reaction. The absolute configuration of the chiral center in the products has been established by X-ray diffraction study. A model for prediction of the absolute configuration of the chiral center in the products from this cyclic enantioselective nucleophilic allylation has been proposed. The synthetic potentials based on the unique structure of the products formed have also been demonstrated.

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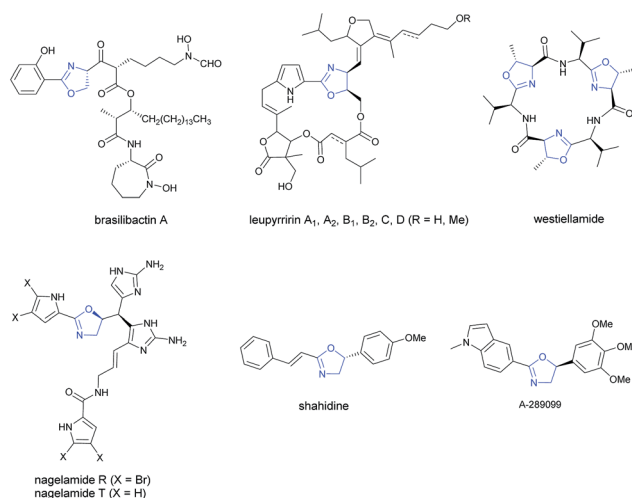
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Introduction

As a very important class of heterocyclic compounds, optically active oxazoline is not only present in many biologically active natural and unnatural compounds^{1–7} (Scheme 1), but also a very versatile functional group in organic synthesis.^{8–11}

They are usually synthesized from stoichiometric amounts of optically active amino alcohols, which instead are prepared from optically active amino acids. However, catalytic enantioselective approaches to optically active oxazolines are still very limited. Enantioselective alkylation of oxazolines under the catalysis of optically active phase-transfer catalyst^{12–14} and desymmetrization of *N*-(1,3-dihydroxy-2-alkyl) amides¹⁵ have been developed for the synthesis of optically active oxazolines with a chiral center at the 4-position. Enantioselective reactions of oxazolines,^{16–18} *meso*-aziridines,¹⁹ and 2-isocyanocarboxylates^{20–27} have been realized by applying different chiral catalysts for the synthesis of optically active oxazolines with chiral centers at both 4- and 5-positions. On the other hand, the ruthenium-catalyzed chemo- and enantioselective hydrogenation of the C=C bond in pre-formed oxazoles with 50 atm of H₂²⁸ and enantioselective halocyclization of

stereodefined *N*-(2-alkenyl) amides with an organocatalyst^{29–33} have been reported for oxazoline derivatives with a chiral center at the 5-position (Scheme 2A). These two pioneering contributions suffer from limitation of the starting materials and products. Thus, due to the importance of oxazolines, development of new catalytic enantioselective protocols for the efficient preparation of optically active oxazolines from readily available common chemicals is of current interest. On the other hand, we have been interested in developing enantioselective cyclization of allenes with a nucleophilic functionality for the catalytic asymmetric synthesis of heterocyclic compounds.^{34–39} Based on our recent development of straightforward method for the synthesis of



Scheme 1 Oxazoline natural products and drug. Selected examples of natural products and drugs containing oxazoline with chiral centers at 4- or 5-position.

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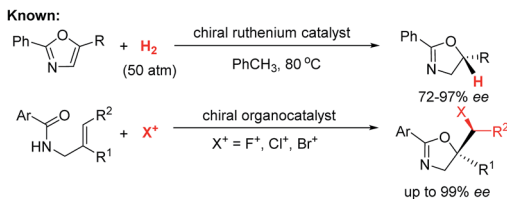
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† Electronic supplementary information (ESI) available: Experimental section, characterization of all compounds, and copies of ¹H and ¹³C NMR spectra of selected compounds. CCDC 1506167. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7sc04079b

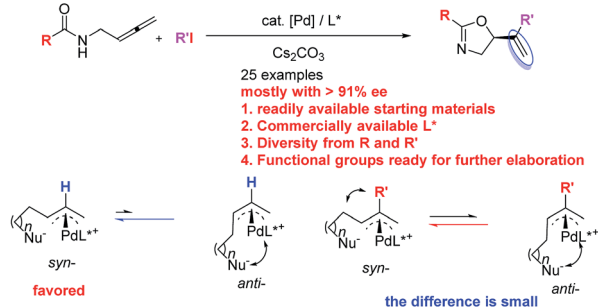
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A: Methods for oxazolines with a chiral center at 5-position



B: This work



Scheme 2 Enantioselective approaches to oxazolines. (A) Known methods for oxazolines with a chiral center at 5-position. (B) This work: palladium-catalyzed asymmetric cyclization protocol from readily available common chemicals.

allenes,⁴¹ we envisioned a catalytic enantioselective allene approach to this class of compounds *via* the *in situ* generation of 2-substituted π -allylic palladium intermediate and subsequent intramolecular allylic trapping by the oxygen atom in the amide functionality.^{40–42} Such an enantioselective allylation is challenging due to the presence of the 2-substituent (R'), which has greatly complicated the relative energy of the *syn*- and *anti*- π -allylic palladium intermediates (Scheme 2B). Herein, we wish

to report our recent results for identifying a chiral ligand for the catalytic highly enantioselective synthesis of oxazoline derivatives with a chiral center at the 5-position. Such a strategy enjoys the diversity from R and R' of both readily available starting materials and the construction of library for nagelamide R,⁵ shahidine,⁶ and the anticancer agents A-289099.⁷ In addition, the reactive functional groups in R and R' and the C=C bonds in the products make this method synthetically very attractive.

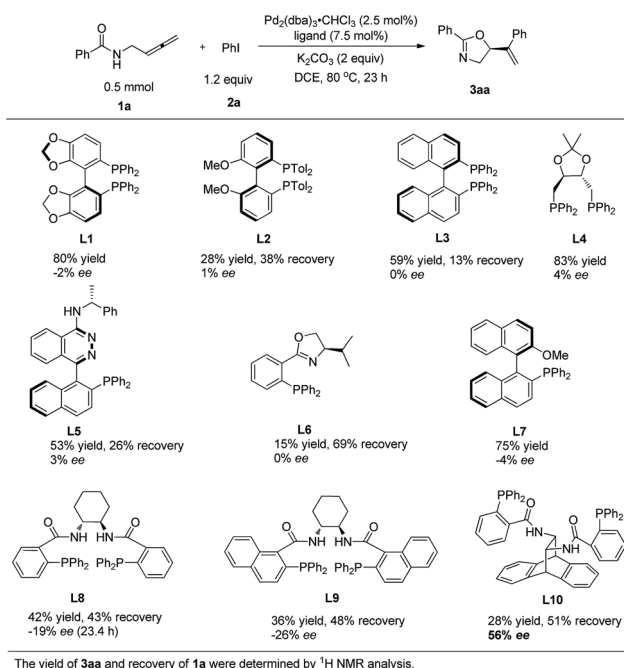
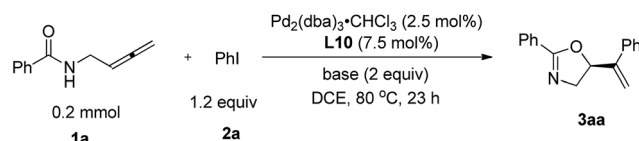
Results

Optimization of the reaction

N-(Buta-2,3-dienyl)amide **1a** and iodobenzene **2a** were selected for our preliminary study on asymmetric cyclizative coupling reaction. However, with the biaryl-based phosphine ligand (S)-SEGPHOS (**L1**), the desired oxazoline **3aa** was afforded in only 2% ee albeit with a high yield. The reaction with other ligands, such as P,P-ligands (**L2–L4**), P,N-ligands (**L5–L6**), and P,O-ligand (**L7**), still yielded almost a racemic product. To our delight, Trost ligands (**L8–L10**)^{43,44} performed better in this reaction, and **L10** was found to be the best (Scheme 3, For the results with more ligands, see Scheme S1 in the ESI†).

Further screening on the effect of bases led to the observation that Cs₂CO₃ is the best (Table 1, for the results with more bases, see Table S1 in the ESI†).

Table 1 The effect of base^a



Scheme 3 The effect of ligands. **L10** was found to be the best.

3aa				
Entry	Base	Yield ^b (%)	ee ^c (%)	Recovery of 1a ^b (%)
1 ^d	Na ₂ CO ₃	4	n.d. ^e	85
2	K ₂ CO ₃	42	51	43
3	Rb ₂ CO ₃	67	66	27
4	Cs ₂ CO ₃	77	72	6
5	Na ₃ PO ₄	47	58	37
6	K ₃ PO ₄	66	71	16
7	LiOH	36	42	47
8	NaOH	64	45	19
9	KOH	27	62	47
10	Li ^t Bu	37	31	25
11	TEA	3	n.d. ^e	71

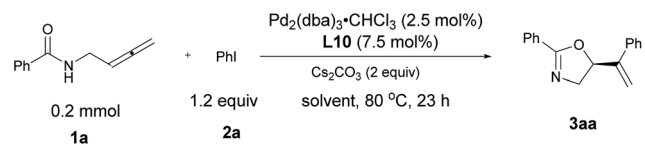
^a Unless indicated otherwise, the experiments were performed with **1a** (0.2 mmol), **2a** (0.24 mmol), Pd₂(dba)₃·CHCl₃ (0.005 mmol), **L10** (0.015 mmol), and base (0.4 mmol) in DCE (2 mL) at 80 °C under Ar atmosphere. ^b The yield and recovery were determined by ¹H NMR analysis using 1,3,5-trimethylbenzene as the internal standard. ^c The ee values were determined by HPLC analysis. ^d Reaction time: 22.5 h. ^e n.d. = not determined.



The striking effect of solvent

To further improve the enantioselectivity, we investigated the solvent effect (Table 2). Other halogen-containing solvents such as 1,1-dichloroethane and 1,1,1-trichloroethane failed to provide better results (Table 2, entries 1 and 2). Etheric solvents such as DME, THF, MTBE, and dioxane also failed to improve the enantioselectivity (Table 2, entries 3–6). Interestingly, when aromatic solvents were employed, higher enantioselectivity was constantly observed (Table 2, entries 7–11, 79–88% ee) albeit with some recovery of **1a**. It is surprising that the reaction with a slightly higher equiv. of **2a** and a low concentration in benzene at a higher temperature of 90 °C improved the ee to 94% (compare entry 11 with entry 12) (for more details, see Tables S2–S4 in the ESI†). Thus, we defined that the reaction of *N*-(buta-2,3-dienyl)amide **1a** (0.5 mmol) with iodobenzene **2a** (1.0 mmol) in benzene (6 mL) at 90 °C as the standard conditions.

Table 2 The effect of solvent^a

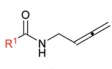
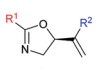
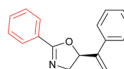
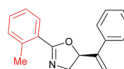
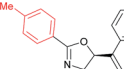
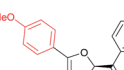
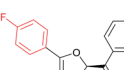
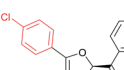
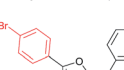
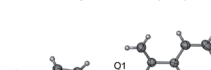
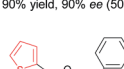
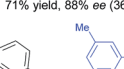
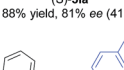
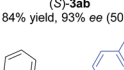
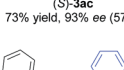
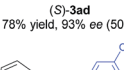
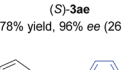
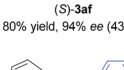
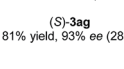
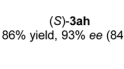
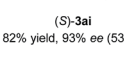
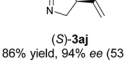
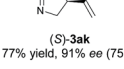
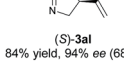
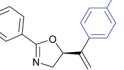
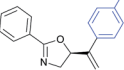
				
Entry	Solvent	Yield ^b (%)	ee ^c (%)	Recovery of 1a ^b (%)
1 ^d	CH ₃ CHCl ₂	60	64	30
2 ^e	CH ₃ CCl ₃	24	67	64
3 ^d	THF	6	n.d. ^f	94
4	DME	80	10	3
5	MTBE	59	52	—
6	Dioxane	54	46	34
7	PhCH ₃	68	79	5
8	<i>o</i> -Xylene	69	87	25
9	<i>m</i> -Xylene	66	88	27
10	<i>p</i> -Xylene	71	87	24
11 ^g	Benzene	69	85	27
12 ^h	Benzene	83ⁱ	94	—

^a Unless indicated otherwise, the experiments were performed with **1a** (0.2 mmol), **2a** (0.24 mmol), Pd₂(dba)₃·CHCl₃ (0.005 mmol), **L10** (0.015 mmol), and Cs₂CO₃ (0.4 mmol) in solvent (2 mL) for 23 h at 80 °C under Ar atmosphere. ^b The yield and recovery were determined by ¹H NMR analysis using 1,3,5-trimethylbenzene as the internal standard. ^c The ee values were determined by HPLC analysis. ^d The reaction was conducted at 70 °C. ^e Reaction time: 22.5 h. ^f n.d. = not determined. ^g Reaction time: 21 h. ^h The reaction was conducted with **1a** (0.5 mmol), **2a** (1.0 mmol), Pd₂(dba)₃·CHCl₃ (0.0125 mmol), **L10** (0.0375 mmol), and Cs₂CO₃ (1.0 mmol) in benzene (6 mL) for 0.5 h at rt, then 39 h at 90 °C under Ar atmosphere. ⁱ Isolated yield.

Substrate scope

With the optimized protocol in hand, we investigated the generality of this transformation. As shown in Table 3, a variety of optically active oxazoline derivatives could be prepared: *N*-(buta-2,3-dienyl)amides **1** with R¹ being electron-donating substituents, such as 2- or 4-methyl and 4-methoxy groups,

Table 3 Scope of palladium-catalyzed asymmetric coupling cyclization reaction of *N*-(buta-2,3-dienyl)amides and aryl iodides^a

$\text{Pd}(\text{dba})_3 \cdot \text{CHCl}_3$ (2.5 mol%) L10 (7.5 mol%) Cs_2CO_3 (2 equiv), benzene rt (0.5 h), then 90 °C (t)		
 1 0.5 mmol	$\text{R}^2\text{-I}$ 2 2 equiv	 3
 (S)-3aa 83% yield, 94% ee (39 h)	 (S)-3ba 64% yield, 93% ee (54 h)^b	 (S)-3ca 76% yield, 96% ee (36 h)
 (S)-3da 82% yield, 94% ee (57 h)	 (S)-3ea 88% yield, 92% ee (28 h)	 (S)-3fa 92% yield, 91% ee (28 h)
 (S)-3ga 90% yield, 90% ee (50 h)	 (S)-3ha 71% yield, 88% ee (36 h)	
 (S)-3ia 88% yield, 81% ee (41 h)	 (S)-3ab 84% yield, 93% ee (50 h)	 (S)-3ac 73% yield, 93% ee (57 h)
 (S)-3ad 78% yield, 93% ee (50 h)	 (S)-3ae 78% yield, 96% ee (26 h)^c	 (S)-3af 80% yield, 94% ee (43 h)^b
 (S)-3ag 81% yield, 93% ee (28 h)	 (S)-3ah 86% yield, 93% ee (84 h)	 (S)-3ai 82% yield, 93% ee (53 h)^b
 (S)-3aj 86% yield, 94% ee (53 h)	 (S)-3ak 77% yield, 91% ee (75 h)	 (S)-3al 84% yield, 94% ee (68 h)
 (S)-3am 86% yield, 93% ee (30 h)	 (S)-3an 75% yield, 88% ee (69 h)	 (S)-3ao 81% yield, 85% ee (52 h)
 (S)-3ap 85% yield, 94% ee (108 h)	 (S)-3aq 80% yield, 92% ee (108 h)	

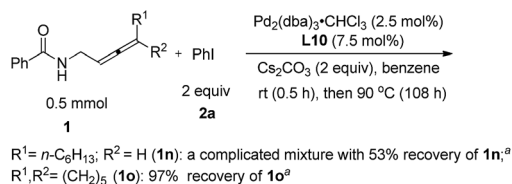
^a Unless indicated otherwise, the experiments were performed with **1** (0.5 mmol), **2** (1.0 mmol), Pd₂(dba)₃·CHCl₃ (0.0125 mmol), **L10** (0.0375 mmol), and Cs₂CO₃ (1.0 mmol) in benzene (6 mL) at rt (0.5 h) and 90 °C under Ar atmosphere. ^b The reaction was conducted in 4 mL of benzene. ^c With (S,S)-**L10** purchased from Sigma-Aldrich, 90% ee of (R)-**3ag** was obtained.

performed well with iodobenzene, affording the desired oxazoline products **3ba–3da** with 64–82% yields and 93–96% ees. Synthetically attractive halogen groups (F, Cl, Br) in substrates **1** were also tolerated in this reaction with high yields and ee



values. The reaction of alkenyl or heteroaryl substituted amides proceeded smoothly to afford the corresponding products **3ha** or **3ia** in 71% and 88% yields, 88% and 81% ees, respectively. For aryl iodides, different electron-donating groups (Me, ⁱPr, OMe) or Ph (**2b–2g**) were tolerated with very limited influence on the yields and enantioselectivity (73–84% yields, 93–96% ees). When 4-acylphenyl iodide **2n** was subjected to the reaction, the corresponding oxazoline **3an** was obtained in 75% yield and 88% ee. Halogen group (F, Cl, Br)-substituted aryl iodides **2** are also suitable for this transformation, affording oxazoline derivatives **3ah–3am** in 77–86% yields and 91–94% ees. Sensitive functional groups such as primary amine (**2o**), ester (**2p**), and aldehyde group (**2q**) could be tolerated. The absolute configuration of **3ga** with **L10** was established as *S* by single-crystal X-ray diffraction study.⁴⁵

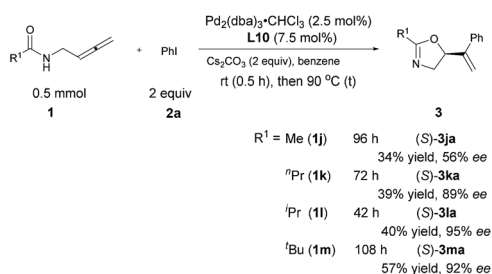
We also tried the reaction of non-terminal allenes **1n** and **1o** with phenyl iodide, however, neither of them afforded the corresponding oxazoline product (Scheme 4).



Scheme 4 The reaction of non-terminal allenes. ^aDetermined by ¹H NMR analysis using 1,3,5-trimethylbenzene as the internal standard.

The steric effect of the R¹ group

Interestingly, R^1 may also be an alkyl group albeit with a low yield and the ee increased with its steric hindrance: with R^1 being ⁱPr, the ee reached 95%, indicating that the steric hindrance of the R^1 group is also critical for enantioselectivity shown in Table 3. The reaction of *t*-butyl-substituted amide **1m** is much slower with an enantioselectivity of 92% (Scheme 5).



Scheme 5 Steric effect of the R^1 group.

The effect of the leaving group X

Moreover, the reactivity of phenyl chloride is too low resulting in 97% recovery of starting material **1a**; the reaction of phenyl bromide proceeded much slower (35% conversion in 65 hours); phenyl triflate afforded a complicated mixture (Table 4).

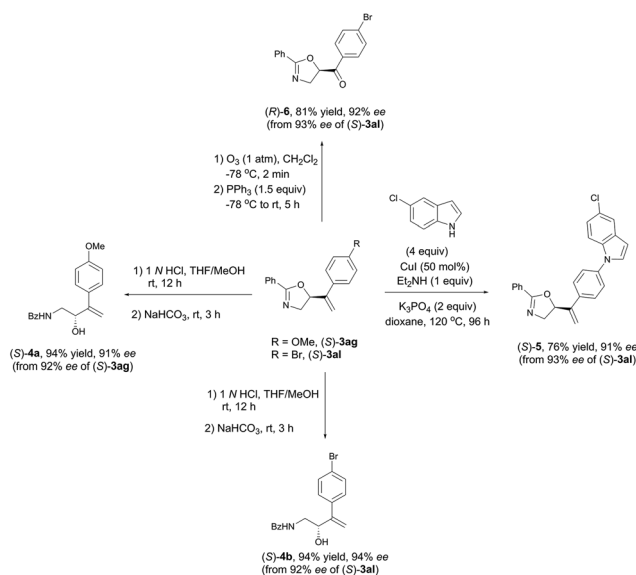
Table 4 The reaction of phenyl chloride, bromide, and triflate^a

Entry	X	Time (h)	Results ^a
1	Cl	65	97% recovery of 1a
2	Br	65	32% 3aa , 65% recovery of 1a
3	OTf	108	Complicated mixture

^a Determined by ¹H NMR analysis using 1,3,5-trimethylbenzene as the internal standard.

Synthetic applications

As shown in Table 3 and Scheme 5, these synthetically useful substituents such as Ar-OMe, Ar-Cl, Ar-Br, and Ar-acyl groups and the pre-installed (in (*S*)-**3ha**) or *in situ* formed C=C bonds in every case make these chiral oxazolines ready for further transformations as demonstrated in Scheme 6. Hydrolysis of (*S*)-**3ag** and (*S*)-**3al** under acidic conditions readily afforded the useful optically active β-amino alcohols (*S*)-**4a** and (*S*)-**4b** in 91% and 94% ees, respectively.⁴⁶ The C–N coupling of (*S*)-**3al** with 5-chloro-1*H*-indole was also realized using 50 mol% of CuI affording (*S*)-**5** in 76% yield and 91% ee.⁴⁷ Additionally, ozonolysis of the C=C bond in (*S*)-**3al** afforded the rather sensitive product, 5-acyl-substituted oxazoline (*R*)-**6**, without racemization.⁴⁸



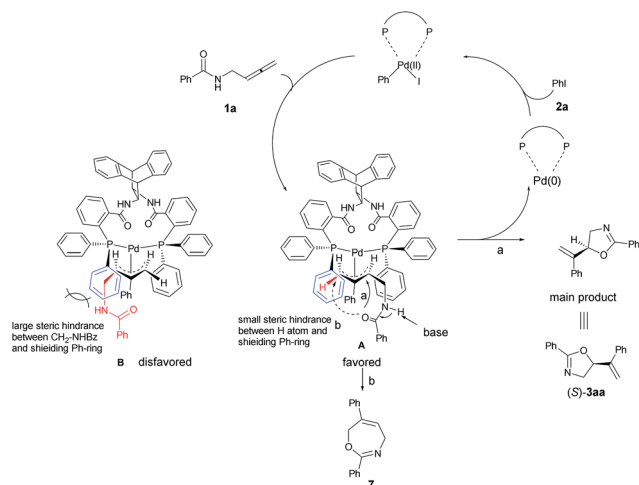
Scheme 6 Synthetic potentials of oxazoline products.

Discussion

A model for the prediction of absolute configuration in the products with the Trost ligand **L10** is shown below: oxidative

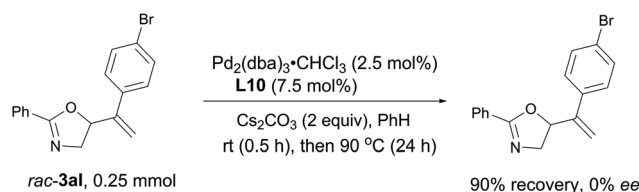


addition of Pd(0) with iodobenzene **2a** and subsequent carbopalladation with *N*-(buta-2,3-dienyl)amide **1a** would form two π -allylic palladium intermediates **A** or **B**. The intermediates **A** is preferred over **B** due to the steric interaction of the amide group with the axial phenyl group, thus, subsequent nucleophilic O-attack in intermediate **A** (path a) leads to the product **3aa** with the observed *S*-configuration (Scheme 7). In addition, the formation of the seven-membered product **7** is disfavored for the longer distance of nucleophilic O-centered nucleophile as compared to that for the formation the 5-membered **3aa** (path a vs. path b).



Scheme 7 A proposed mechanism and prediction of the absolute configuration of the product. Due to the steric interaction of the amide group with the axial phenyl group, the product **3aa** was observed with the absolute *S*-configuration.

Stirring racemic **3al** under the optimized reaction system for 24 hours, no ee was detected with the recovered oxazoline, which means that the allylic cleavage in *rac*-**3al** is not possible (Scheme 8).



Scheme 8 Mechanistic study. No ee was detected with the recovered oxazoline, which means that the nucleophilic O-attack in intermediate **A** of the mechanistic proposal is irreversible.

Conclusion

In conclusion, we have developed a completely different enantioselective approach for the asymmetric construction of oxazoline derivatives with an excellent enantioselectivity *via* the palladium-catalyzed coupling-cyclization of *N*-(buta-2,3-dienyl)

amides with aryl iodides. The easily accessible and diversified nature of both starting materials,^{40,49} the compatibility of useful functional groups, generality, and the synthetic potentials of the oxazoline and C=C bond make this method of high interest to both organic and medicinal chemists. Further studies in this area are being actively pursued in our laboratory.

Conflicts of interest

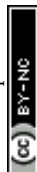
There are no conflicts to declare.

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