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Phosphine Oxide–$Sc(OTf)_3$ Catalyzed Highly Regio- and Enantioselective Bromoaminocyclization of (*E*)-Cinnamyl Tosylcarbamates. An Approach to a Class of Synthetically Versatile Functionalized Molecules

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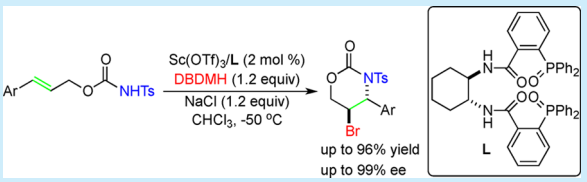
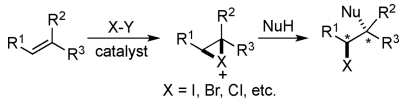
Supporting Information

ABSTRACT: A highly regio- and enantioselective bromoaminocyclization of (*E*)-cinnamyl tosylcarbamates catalyzed by a chiral phosphine oxide–$Sc(OTf)_3$ complex is described. A wide variety of optically active aryl 5-bromo-1,3-oxazinan-2-ones can be obtained with high yield and enantioselectivity.



Asymmetric halogenation of olefins provides an effective approach to stereoselectively introduce two heteroatoms onto C–C double bonds (Scheme 1)[1] and has been an active

Scheme 1. Catalytic Asymmetric Halogenation of Olefins



research area in recent years. Various effective catalytic systems, including a chiral Lewis acid,[2,3] chiral base,[4,5] and chiral phosphoric acid or phosphate,[6,7] have been developed. Developing catalytic systems with a broad substrate scope and great synthetic versatility is still highly desirable. In our own studies, we have shown that the complex of $Sc(OTf)_3$ with chiral phosphine **L1** (Trost ligand[8]) or chiral phosphine oxide **L2** (Figure 1) is a highly effective catalyst for asymmetric

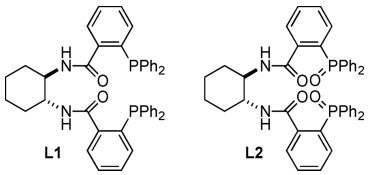
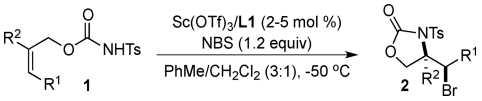


Figure 1. Selected examples of chiral ligands examined.

bromocyclization of (*Z*)-allyl *N*-tosylcarbamates (**1**) (Scheme 2)[9a] and 2,4-dienyl *N*-tosylcarbamates.[9b] In our efforts to further expand the reaction scope, we have found that (*E*)-cinnamyl tosylcarbamates (**3**) are highly effective substrates for the asymmetric 6-*endo*-bromoaminocyclization with the chiral $Sc(OTf)_3$ catalyst (Scheme 3). Herein, we wish to report our preliminary efforts on this subject.

Scheme 2



Scheme 3

Our initial studies were carried out with cinnamyl tosylcarbamate (**3a**) as a test substrate and 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) as the bromine source. Treating **3a** with DBDMH and 5 mol % $Sc(OTf)_3$–**L1** in $CHCl_3$ at −50 °C led to 5-bromo-1,3-oxazinan-2-one **4a** in 57% yield and 85% ee (Table 1, entry 1). A higher ee (95%) was obtained when phosphine oxide **L2** was used as the ligand (Table 1, entry 2). Various reaction conditions were subsequently examined with **L2**. No desired product **4a** was obtained with *N*-bromosuccinimide (NBS), $CH_3CONHBr$, PhCONHBr, and 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCO) (Table 1, entries 3–6). Among the solvents examined, $CHCl_3$ gave the best results (Table 1, entries 2, 7–10). Various additives were also investigated (Table 1, entries 11–15).[9b] When the reaction was carried out in the presence of 1.2 equiv of NaCl, compound **4a** was isolated in 83% yield and 96% ee (Table 1, entry 12). A lower yield and ee were obtained with **L1** under similar reaction conditions (Table 1, entry 16). A slightly higher yield was obtained when the catalyst loading was decreased to 2 mol %

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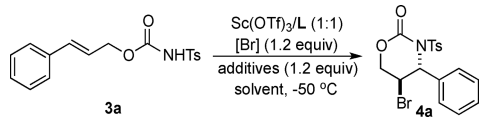
Table 1. Studies on the Reaction Conditions[a]



entry	L	Br source	solvent	additive	yield (%)[b]	ee (%)[c]
1	**L1**	DBDMH	$CHCl_3$	–	57	85
2	**L2**	DBDMH	$CHCl_3$	–	48	95
3	**L2**	NBS	$CHCl_3$	–	–	–
4	**L2**	$CH_3CONHBr$	$CHCl_3$	–	–	–
5	**L2**	PhCONHBr	$CHCl_3$	–	–	–
6	**L2**	TBCO	$CHCl_3$	–	–	–
7	**L2**	DBDMH	CH_2Cl_2	–	42	83
8	**L2**	DBDMH	THF	–	–	–
9	**L2**	DBDMH	PhMe	–	–	–
10	**L2**	DBDMH	EtOAc	–	–	–
11	**L2**	DBDMH	$CHCl_3$	LiCl	12	65
12	**L2**	DBDMH	$CHCl_3$	NaCl	83	96
13	**L2**	DBDMH	$CHCl_3$	KCl	78	96
14	**L2**	DBDMH	$CHCl_3$	NaBr	63	84
15	**L2**	DBDMH	$CHCl_3$	NaI	56	76
16	**L1**	DBDMH	$CHCl_3$	NaCl	59	87
17[d]	**L2**	**DBDMH**	**$CHCl_3$**	**NaCl**	**88**	**96**
18	–	DBDMH	$CHCl_3$	NaCl	–	–
19[e]	**L2**	DBDMH	$CHCl_3$	NaCl	38	0

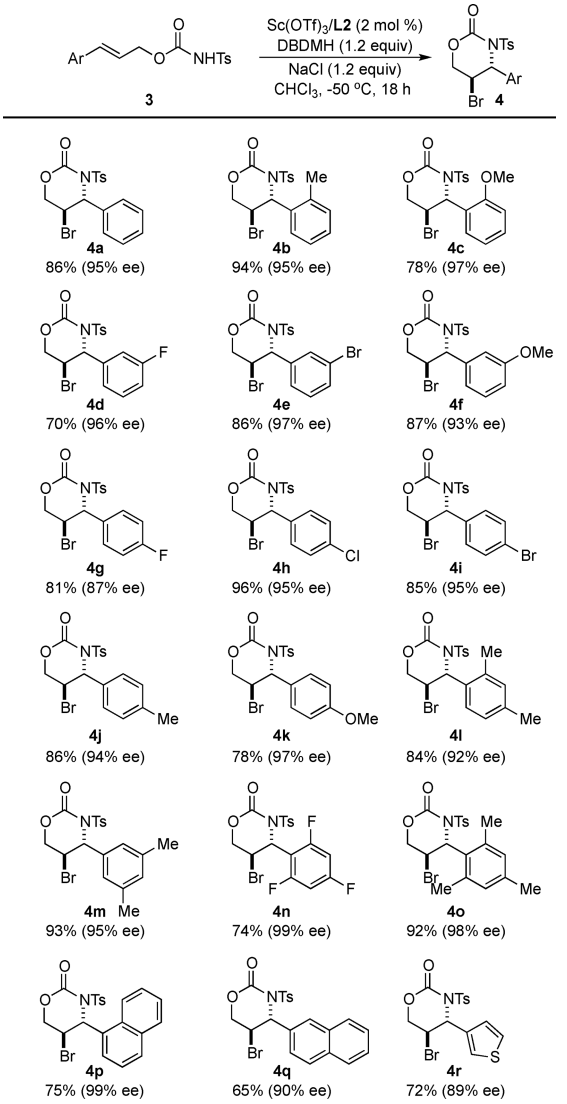
[a]The reactions were carried out with substrate **3a** (0.20 mmol), Br source (0.24 mmol), additive (0.24 mmol), and Sc(OTf)$_3$–**L** (1:1) (0.010 mmol) in $CHCl_3$ (2.0 mL) for 18 h unless otherwise stated. DBDMH = 1,3-dibromo-5,5-dimethylhydantoin; NBS = *N*-bromosuccinimide; TBCO = 2,4,4,6-tetrabromo-2,5-cyclohexadienone. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]With Sc(OTf)$_3$–**L** (1:1) (0.004 mmol). [e]Without Sc(OTf)$_3$.

(Table 1, entry 17). Control experiments showed that both Sc(OTf)$_3$ and the ligand were important for the reaction. No product **4a** was detected when the reaction was carried out with Sc(OTf)$_3$ alone (Table 1, entry 18). A racemate was isolated in 38% yield with **L2** alone (Table 1, entry 19).

With the optimized reaction conditions in hand, the substrate scope was subsequently explored. As shown in Scheme 4, a wide variety of (*E*)-cinnamyl tosylcarbamates can be bromocyclized to the corresponding 5-bromo-1,3-oxazinan-2-ones **4** in 65–96% yield and 87–99% ee (the X-ray structure of **4a** is shown in Figure 2). The aryl groups can be *ortho*- (Scheme 4, **4b** and **4c**), *meta*- (Scheme 4, **4d**–**4f**), and *para*-substituted (Scheme 4, **4g**–**4k**). The di- and trisubstituted substrates are also highly effective for the reaction (Scheme 4, **4l**–**4o**). The aryl groups can be other aromatics such as naphthalene and thiophene (Scheme 4, **4p**, **4q**, and **4r**). In all these cases, the bromoaminocyclization proceeded with high regioselectivity, and essentially only 6-*endo* products were obtained. When (*Z*)-cinnamyl tosylcarbamate (**3s**) was subjected to the reaction conditions, oxazolidinone **4s** was isolated in 20% yield and 48% ee (Scheme 5).

The reaction can also be carried out on a relatively larger scale. As shown in Scheme 6, 3.20 g of 5-bromo-1,3-oxazinan-2-one **4a** was obtained in 78% yield with 99% ee after recrystallization. Compound **4a** can serve as a versatile chiral synthetic intermediate for further transformations (Scheme 7). Treating **4a** with $LiAlH_4$ or DIBAL-H led to compounds **5a** and **6a** in 74% and 68% yield, respectively. When **4a** was treated with KOH–H_2O or K_2CO_3–MeOH, compounds **7a** and **8a** were obtained in 86% and 90% yield, respectively. These two compounds were

Scheme 4. Enantioselective Bromoaminocyclization of (*E*)-Cinnamyl Tosylcarbamates[a]



[a]The reactions were carried out with substrate **3** (0.50 mmol), Sc(OTf)$_3$–**L2** (1:1) (0.010 mmol), DBDMH (0.60 mmol), and NaCl (0.60 mmol) in $CHCl_3$ (5.0 mL) at −50 °C for 18 h. The yield was the isolated yield based on **3**. The absolute configurations of **4a**, **4k**, and **4n** were assigned based on their X-ray structures. The absolute configurations of the others were tentatively proposed by analogy.

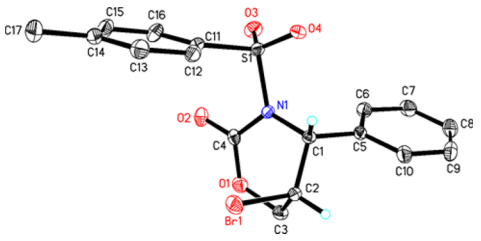


Figure 2. X-ray structure of compound **4a**.

likely formed via aziridine intermediate **9a**. This is supported by the fact that aziridine **9a**, obtained from **6a** with K_2CO_3–MeCN,[10] can be converted to **8a** with K_2CO_3–MeOH in 87% yield. Azide **10a** can be obtained from **6a** in 86% yield with $TMSN_3$ and TBAF (Scheme 8) (for the X-ray structure of **10a**,

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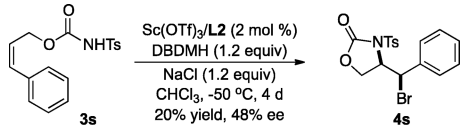
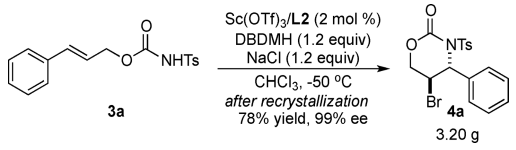
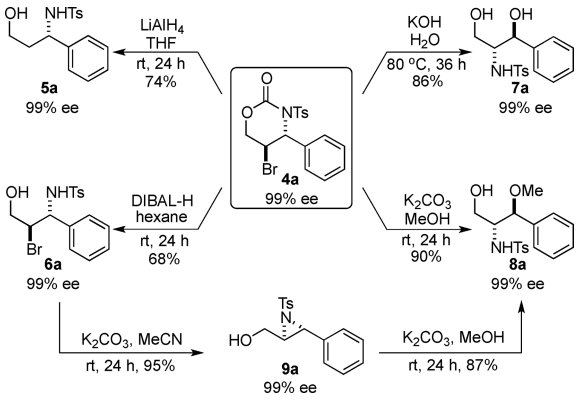
Scheme 5. Bromoaminocyclization of (*Z*)-Cinnamyl Tosylcarbamate



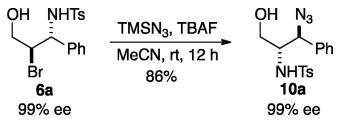
Scheme 6. Bromoaminocyclization on a Gram Scale



Scheme 7. Synthetic Transformations of Bromide 4a

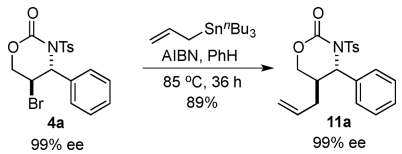


Scheme 8. Synthetic Transformation of Bromoaminoalcohol 6a



see Supporting Information).[10] A new C−C bond can also be stereoselectively formed from the C−Br bond. For example, compound **11a** was isolated in 89% yield when **4a** was reacted with allyltributyltin and AIBN at 85 °C (Scheme 9).[11] In all these transformations, the optical purity was maintained.

Scheme 9. Synthetic Transformation of Bromide 4a



In summary, we have developed a highly regio- and enantioselective bromoaminocyclization process for (*E*)-cinnamyl tosylcarbamates with DBDMH as the bromine source and chiral phosphine oxide−Sc(OTf)$_3$ complex as the catalyst. A wide of optically active aryl 5-bromo-1,3-oxazinan-2-ones have been obtained in 65−96% yield and 87−99% ee. The reaction can be performed on a gram scale. The resulting halides have been shown to be highly versatile synthetic intermediates and can be further transformed into various useful functionalized molecules. Further efforts will be devoted to understanding the reaction mechanism, expanding the substrate scope, and developing more effective catalytic systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03459.

Experimental procedures, characterizations, X-ray structures, HPLC data for the determination of enantiomeric excess, and NMR spectra (PDF)
Crystallographic data for **4a** (CIF)
Crystallographic data for **4k** (CIF)
Crystallographic data for **4n** (CIF)
Crystallographic data for **5a** (CIF)
Crystallographic data for **6a** (CIF)
Crystallographic data for **7a** (CIF)
Crystallographic data for **10a** (CIF)
Crystallographic data for **12a** (CIF)

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Notes

The authors declare no competing financial interest.

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