

Table 1. Studies on the Reaction Conditions^a

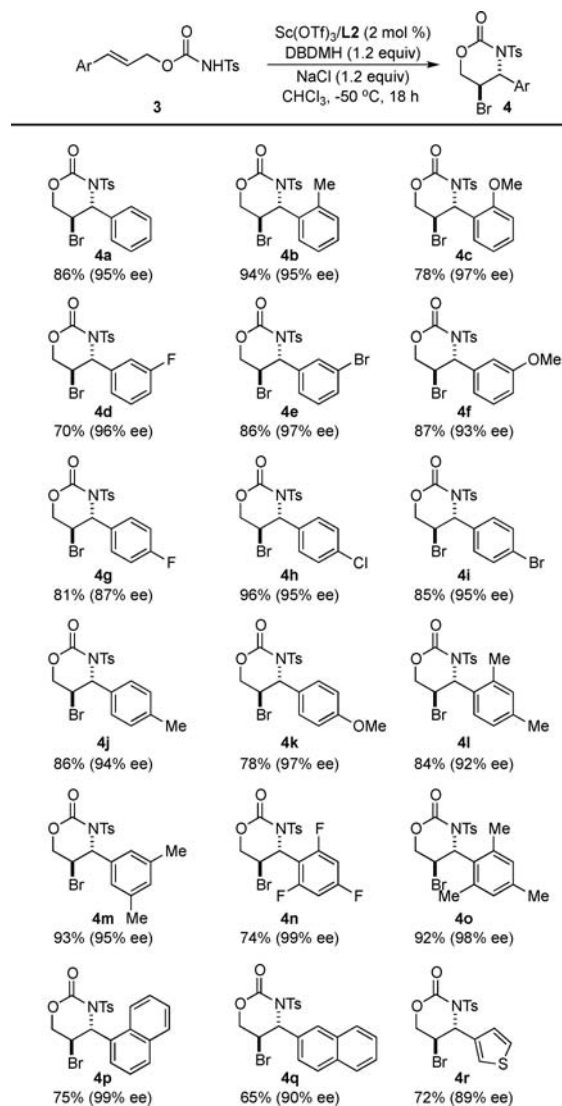
entry	L	Br source	solvent	additive	yield (%) ^b	ee (%) ^c
1	L1	DBDMH	CHCl ₃	—	57	85
2	L2	DBDMH	CHCl ₃	—	48	95
3	L2	NBS	CHCl ₃	—	—	—
4	L2	CH ₃ CONHBr	CHCl ₃	—	—	—
5	L2	PhCONHBr	CHCl ₃	—	—	—
6	L2	TBCO	CHCl ₃	—	—	—
7	L2	DBDMH	CH ₂ Cl ₂	—	42	83
8	L2	DBDMH	THF	—	—	—
9	L2	DBDMH	PhMe	—	—	—
10	L2	DBDMH	EtOAc	—	—	—
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

^aThe 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 CHCl₃ (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. ^bIsolated yield. ^cDetermined by chiral HPLC analysis. ^dWith Sc(OTf)₃-L (1:1) (0.004 mmol). ^eWithout Sc(OTf)₃.

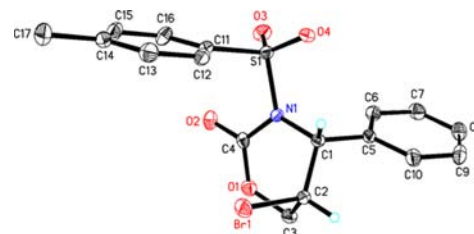
(Table 1, entry 17). Control experiments showed that both Sc(OTf)₃ and the ligand were important for the reaction. No product **4a** was detected when the reaction was carried out with Sc(OTf)₃ alone (Table 1, entry 18). A racemate was isolated in 38% yield with L2 alone (Table 1, entry 19).

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 LiAlH₄ or DIBAL-H led to compounds **5a** and **6a** in 74% and 68% yield, respectively. When **4a** was treated with KOH-H₂O or K₂CO₃-MeOH, compounds **7a** and **8a** were obtained in 86% and 90% yield, respectively. These two compounds were

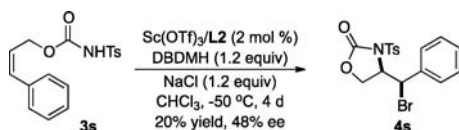
Scheme 4. Enantioselective Bromoaminocyclization of (*E*)-Cinnamyl Tosylcarbamates^a

^aThe 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 CHCl₃ (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.

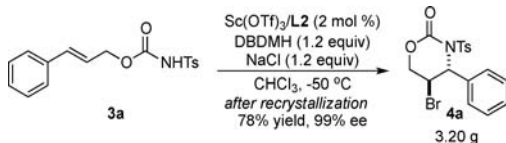
Figure 2. X-ray structure of compound **4a**.

likely formed via aziridine intermediate **9a**. This is supported by the fact that aziridine **9a**, obtained from **6a** with K₂CO₃-MeCN,¹⁰ can be converted to **8a** with K₂CO₃-MeOH in 87% yield. Azide **10a** can be obtained from **6a** in 86% yield with TMSN₃ and TBAF (Scheme 8) (for the X-ray structure of **10a**,

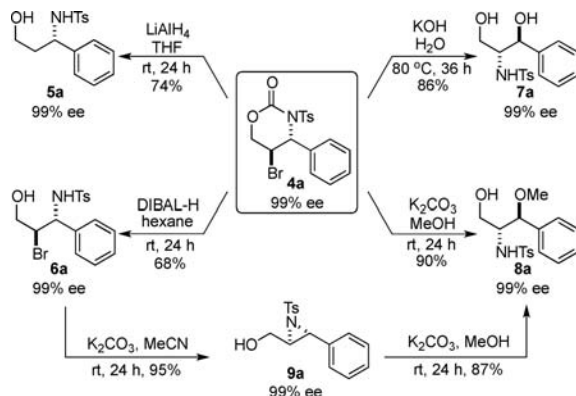
Scheme 5. Bromoaminocyclization of (Z)-Cinnamyl Tosylcarbamate



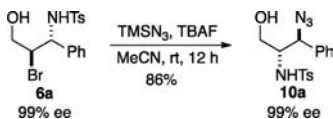
Scheme 6. Bromoaminocyclization on a Gram Scale



Scheme 7. Synthetic Transformations of Bromide 4a

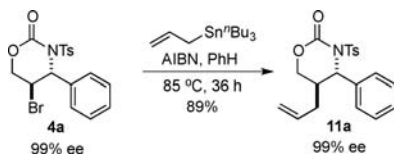


Scheme 8. Synthetic Transformation of Bromoaminoalcohol 6a



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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