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Chiral Phosphine Oxide–$Sc(OTf)_3$ Complex Catalyzed Enantioselective Bromoaminocyclization of 2-Benzofuranylmethyl *N*-Tosylcarbamates. Approach to a Novel Class of Optically Active Spiro Compounds

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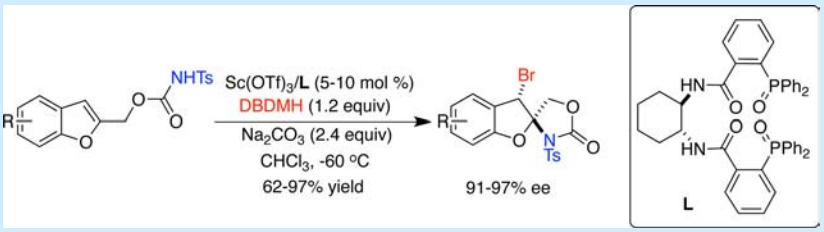
Supporting Information



ABSTRACT: An efficient enantioselective bromoaminocyclization of 2-benzofuranylmethyl *N*-tosylcarbamates catalyzed by a chiral phosphine oxide–$Sc(OTf)_3$ complex is described. A wide variety of optically active spiro benzofuran oxazolidinones can be obtained with high enantioselectivities.

Electrophilic halogenation of olefins is one of the most fundamental and classical transformations in organic chemistry, as it provides an effective approach for the functionalization of C–C double bonds with installation of two possible stereogenic centers. Asymmetric halogenations have received considerable attention in recent years,[1] and a variety of effective catalytic systems have been developed for both intramolecular[2−4] and intermolecular[5−7] processes. Expanding the substrate scope for an asymmetric halogenation process is highly desirable but is often difficult and unpredictable due to the complexity of the reaction system and the lack of clear understanding of the reaction mechanism. In our own studies, we recently reported a highly enantioselective bromoaminocyclization process of (*Z*)-allyl *N*-tosylcarbamates with $Sc(OTf)_3$ and chiral phosphine **L1** (Trost ligand[8]) complex as the catalyst (Scheme 1) (Figure 1).[9a] Subsequently, we developed a highly enantioselective 6-*endo*-bromoaminocyclization process for 2,4-dienyl *N*-tosylcarbamates with $Sc(OTf)_3$–chiral phosphine oxide (**L2**) complex (Figure 1).[9b] In our efforts to expand the substrate scope of these systems, we have found that 2-benzofuranylmethyl *N*-tosylcarbamates are highly effective substrates for the bromoaminocyclization, giving a novel class of spiro benzofuran oxazolidinones in high enantioselectivity (Scheme 2). Herein, we report our preliminary studies on this subject.

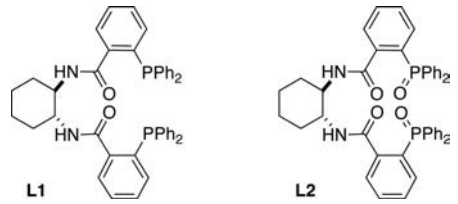
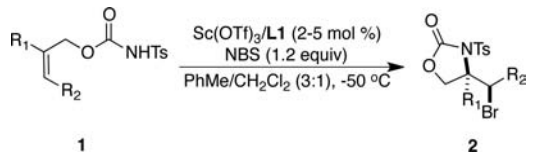
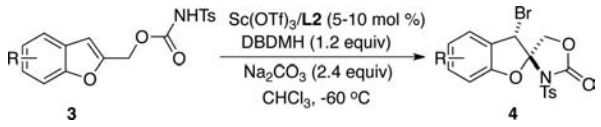


Figure 1. Selected examples of chiral ligands examined.

Scheme 1



Scheme 2



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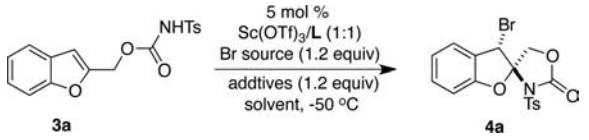
Our initial studies were carried out with 2-benzofuranylmethyl *N*-tosylcarbamate (**3a**) as the test substrate and 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) as the bromine source (Table 1).

Table 1. Studies on the Reaction Conditions[a]



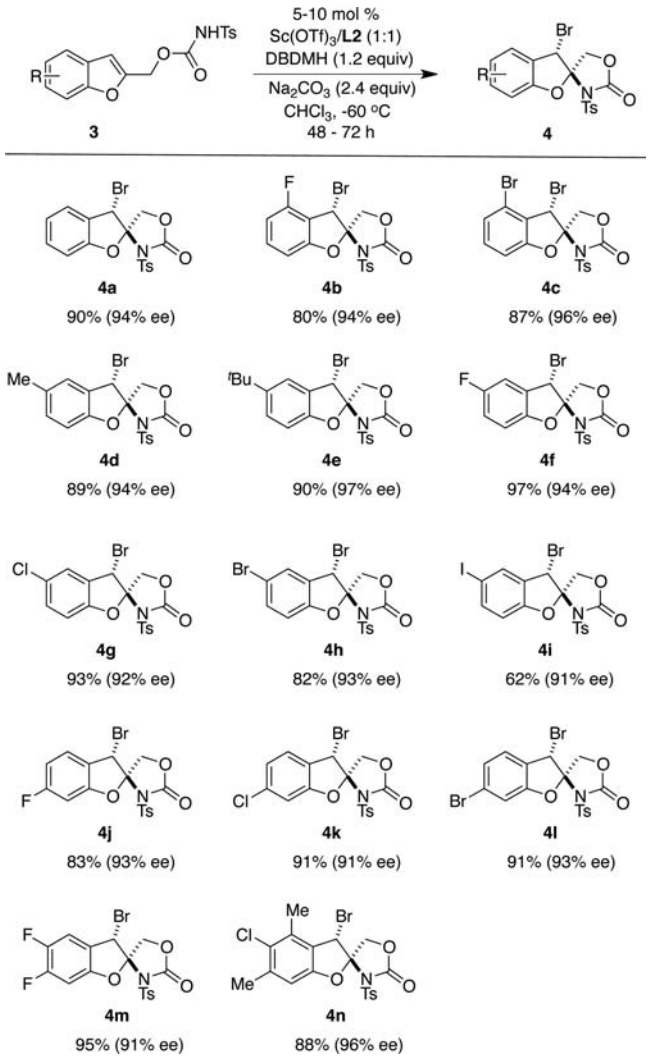
entry	L	Br source	additive	solvent	yield[b] (%)	ee[c] (%)
1	**L1**	DBDMH		$CHCl_3$	65	74
2	**L2**	DBDMH		$CHCl_3$	41	28
3	**L1**	DBDMH	PPh_3	$CHCl_3$	25	1
4	**L1**	DBDMH	$Ph_3P{=}O$	$CHCl_3$	23	78
5	**L1**	DBDMH	NaCl	$CHCl_3$	64	81
6	**L1**	DBDMH	$NaHCO_3$	$CHCl_3$	59	85
7	**L1**	DBDMH	Na_2CO_3	$CHCl_3$	76	85
8	**L1**	DBDMH	K_2CO_3	$CHCl_3$	75	86
9	**L1**	DBDMH	Py	$CHCl_3$	64	86
10	**L2**	DBDMH	NaCl	$CHCl_3$	65	68
11	**L2**	DBDMH	K_2CO_3	$CHCl_3$	76	74
12	**L2**	DBDMH	Na_2CO_3	$CHCl_3$	81	87
13[d]	**L2**	DBDMH	Na_2CO_3	$CHCl_3$	80	96
14[d]	**L2**	DBDMH	Na_2CO_3	$CHCl_3$	90	95
15[d]	**L2**	DBDMH	Na_2CO_3	THF	51	2
16[d]	**L2**	DBDMH	Na_2CO_3	EtOAc	37	3
17[d]	**L2**	DBDMH	Na_2CO_3	PhMe	29	31
18[d]	**L2**	DBDMH	Na_2CO_3	CH_2Cl_2	85	94
19[d]	**L2**	PhCONHBr	Na_2CO_3	$CHCl_3$	35	2
20[d]	**L2**	TBCO	Na_2CO_3	$CHCl_3$	13	2
21[d]	**L2**	NBS	Na_2CO_3	$CHCl_3$	43	30
22[d,e]	**L2**	DBDMH	Na_2CO_3	$CHCl_3$	35	0
23[d]		DBDMH	Na_2CO_3	$CHCl_3$	40	0

[a]The reactions were carried out with substrate **3a** (0.20 mmol), Br source (0.24 mmol), $Sc(OTf)_3$-L (1:1) (0.010 mmol), and additive (0.24 mmol) in solvent (2.0 mL) at −50 °C for 24 h unless otherwise stated. DBDMH = 1,3-dibromo-5,5-dimethylhydantoin; TBCO = 2,4,4,6-tetrabromo-2,5-cyclohexadienone; NBS = *N*-bromosuccinimide. [b]Isolated yield based on **3a**. [c]Determined by chiral HPLC analysis. [d]At −60 °C, for entries 14, 19−23, the reactions were carried out with Na_2CO_3 (0.48 mmol) for 48 h. [e]Without $Sc(OTf)_3$.

To our delight, spiro benzofuran oxazolidinone **4a** was isolated in 65% yield with 74% ee when **3a** was treated with DBDMH and 5 mol % of $Sc(OTf)_3$−**L1** complex in $CHCl_3$ at −50 °C (entry 1). Lower yield (41%) and ee (28%) were obtained when chiral phosphine oxide **L2** was used as the ligand (entry 2). A series of additives[9b] were subsequently screened with $Sc(OTf)_3$−**L1** complex as catalyst (entries 3−9). Both yield and ee were significantly improved with Na_2CO_3 and K_2CO_3 (entries 7 and 8). An even more dramatic additive effect was observed when the reaction was carried out with $Sc(OTf)_3$−**L2** complex as the catalyst (entries 10−12). Compound **4a** was isolated in 81% yield and 87% ee with Na_2CO_3 as additive (entry 12). The ee was increased to 96% when the reaction was conducted at −60 °C (entry 13). The yield was further improved to 90% with more Na_2CO_3 (2.4 equiv) and longer reaction time (48 h) (entry 14). Poorer results were obtained with other solvents examined except CH_2Cl_2 (entries 15−18). Much lower yield and ee were obtained with other bromine sources (entries 19−21). Studies showed that the asymmetric bromination required both $Sc(OTf)_3$ and the ligand. A racemate was obtained with the ligand or $Sc(OTf)_3$ alone (entries 22 and 23).

With the optimized reaction conditions in hand, the substrate scope of the reaction was subsequently investigated. As shown in Scheme 3, the asymmetric bromination can be extended to a

Scheme 3. Enantioselective Bromoaminocyclization of 2-Benzofuranylmethyl *N*-Tosylcarbamates[a]



[a]The reactions were carried out with substrate **3** (0.30 mmol), $Sc(OTf)_3$-L2 (1:1) (0.015 mmol), DBDMH (0.36 mmol), and Na_2CO_3 (0.72 mmol) in $CHCl_3$ (3.0 mL) at −60 °C for 48 h unless otherwise stated. For **4b**, **4c**, and **4m**, the reactions were carried out with $Sc(OTf)_3$−L2 (1:1) (0.030 mmol). For **4b**, **4c**, **4i**, **4m**, and **4n**, the reactions were carried out for 72 h. The yield was the isolated yield based on **3**. The absolute configurations of **4a**, **4h**, **4m**, and **4n** were determined from their X-ray structures. The absolute configurations of others were tentatively proposed by analogy.

variety of 2-benzofuranylmethyl *N*-tosylcarbamates containing various electron-rich or electron-deficient substituents at the C4, C5, and C6 positions, giving the corresponding spiro benzofuran oxazolidinones in 62−97% yield with 91−97% ee (Scheme 3, **4a**−**l**). High yield and ee were also obtained for di- and trisubstituted substrates (Scheme 3, **4m**,**n**) (the X-ray structure of **4a** is shown in Figure 2). As illustrated in Scheme 4, the asymmetric bromination process can be carried out at gram scale,

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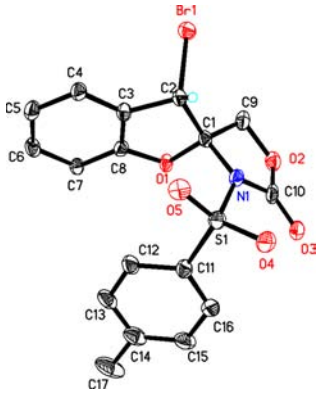
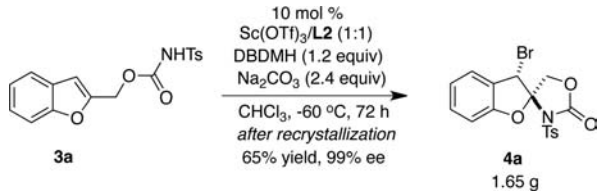


Figure 2. X-ray structure of **4a**.

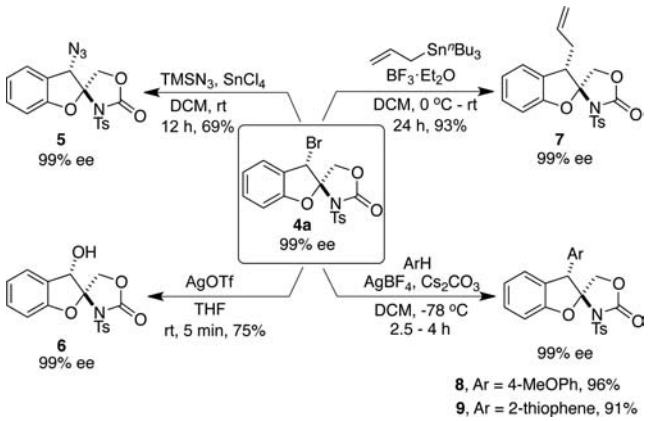
giving spiro benzofuran oxazolidinone **4a** in 65% yield with 99% ee after recrystallization.

Scheme 4. Bromoaminocyclization on a Gram Scale



As exemplified with **4a** (Scheme 5), the resulting bromide can be further transformed into other functionalized spiro

Scheme 5. Synthetic Transformations of Bromide 4a



benzofuran oxazolidinones. For example, bromide **4a** can be converted to azide **5** in 69% yield with $TMSN_3$, $SnCl_4$ in DCM at rt,[10] and alcohol **6** in 75% yield with AgOTf in undried THF.[11,12] The bromide can also be replaced with carbon nucleophiles. When **4a** was reacted with allyltributyltin and $BF_3{\cdot}Et_2O$, compound **7** was isolated in 93% yield.[13] Treating **4a** with $AgBF_4$, Cs_2CO_3, and anisole or thiophene led to Friedel–Crafts-type products **8** and **9** in 96% and 91% yield, respectively.[14] In general, these transformations went cleanly, giving essentially only one diastereoisomer without a loss of optical purity. The reactions likely proceeded via an S_N1-type process. The nucleophile approached the carbocation intermediate from the less hindered side (for the X-ray structures of **5**–**9**, see the SI).

In summary, we have developed a highly enantioselective bromoaminocyclization of 2-benzofuranylmethyl *N*-tosylcarbamates with DBDMH as the bromine source and chiral phosphine oxide–$Sc(OTf)_3$ complex as the catalyst, giving a novel class of spiro benzofuran oxazolidinones in 62–97% yield with 91–97% ee. The reaction can be performed on a gram scale. The resulting bromide can be stereoselectively transformed into other functionalized spiro benzofuran oxazolidinones without a loss of optical purity. The current work allows the further extension of the chiral phosphine (oxide)–$Sc(OTf)_3$ system to a new class of substrates for asymmetric bromination. Further efforts will be devoted to understanding the reaction mechanism, expanding the substrate scope, and developing new 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.5b02817.

Experimental procedures, characterizations, X-ray structures, HPLC data for the determination of enantiomeric excess, and NMR spectra (PDF)
X-ray data for **4a** (CIF)
X-ray data for **4h** (CIF)
X-ray data for **4m** (CIF)
X-ray data for **4n** (CIF)
X-ray data for **5** (CIF)
X-ray data for **6** (CIF)
X-ray data for **7** (CIF)
X-ray data for **8** (CIF)
X-ray data for **9** (CIF)

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Notes

The authors declare no competing financial interest.

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