Organic LETTERS

Letter

pubs.acs.org/OrgLett

Enantioselective 6-*exo*-Bromoaminocyclization of Homoallylic *N*-Tosylcarbamates Catalyzed by a Novel Monophosphine-Sc(OTf)$_3$ Complex

Weigang Liu,[†] Hongjie Pan,[†] Hua Tian,[†] and Yian Shi*[,†,‡,§]

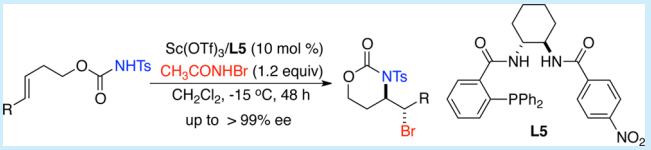
[†]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[‡]State Key Laboratory of Coordination Chemistry, Center for Multimolecular Organic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

[§]Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, United States

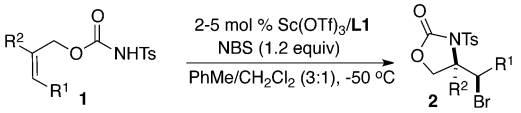
Supporting Information

ABSTRACT: A highly enantioselective 6-*exo*-bromoaminocyclization of (*E*)-homoallylic *N*-tosylcarbamates catalyzed by a novel monophosphine-Sc(OTf)$_3$ complex is described, giving a wide variety of optically active oxazinanones with high enantioselectivities.



Electrophilic halofunctionalization of olefins, one of the most fundamental organic reactions, allows the direct installation of two functional groups onto C−C double bonds in a stereoselective manner.[1] The resulting halides provide versatile intermediates for further transformations in organic synthesis. In recent years, asymmetric halogenation of olefins has received extensive attention,[2] which results in the development of various effective catalytic systems, including chiral Lewis acid,[3,4] chiral phosphoric acid or phosphate,[5,6] and chiral base.[7,8] Despite that significant progress has been made in this area, developing new catalytic systems to address unsolved challenges is highly desirable. During our studies, we have discovered that a Sc(OTf)$_3$-**L1** (Trost ligand[9]) complex is an effective catalyst for asymmetric bromocyclization of (*Z*)-allyl *N*-tosylcarbamates (**1**) (Scheme 1) (Figure 1).[10a]

Scheme 1



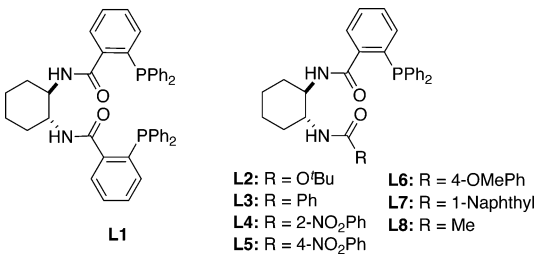
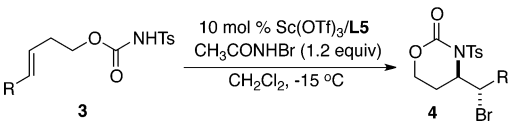


Figure 1. Selected examples of chiral ligands examined.

Mechanistic studies showed that the catalyst has stringent structural requirements for the ligand for the aforementioned bromocyclization. Two phosphines are essential for the reaction. To our surprise, optically active 1,3-oxazinan-2-ones (**4**) could be obtained with a monophosphine-Sc(OTf)$_3$ complex, but not with a Sc(OTf)$_3$-**L1** complex when (*E*)-homoallylic *N*-tosylcarbamates (**3**) were used as the substrate (Scheme 2). This observation prompted us to further investigate this reaction system. Herein, we wish to report our preliminary studies on this subject.

Scheme 2

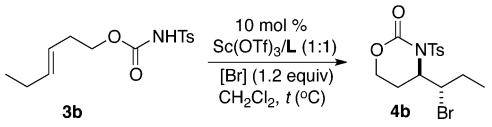


When (*E*)-hex-3-enyl tosylcarbamate (**3b**) was first treated with *N*-bromoacetamide and 10 mol % Sc(OTf)$_3$-**L1** complex, a messy mixture was obtained (Table 1, entry 1). It is clear that this reaction system is not effective for this class of substrates, which calls for the development of new catalysts. Various metals and ligands were subsequently examined. Ironically, high ee's were obtained with the monophosphine-Sc(OTf)$_3$ complex, which was previously shown to be ineffective for the asymmetric bromocyclization of (*Z*)-allyl *N*-tosylcarbamate (Scheme 1).[10a] For example, 1,3-oxazinan-2-one **4b** was obtained in 18% yield and 93% ee with monophosphine ligand **L2** (Table 1, entry 2). Further studies showed that the yield and ee were influenced by the amide

Received: June 19, 2015

DOI: 10.1021/acs.orglett.5b01779
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Studies on the Reaction Conditions[a]



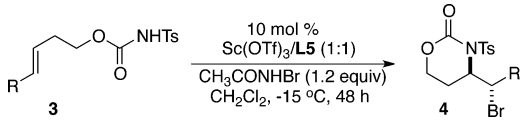
entry	Br source	L	t (°C)	yield (%)[b]	ee (%)[c]
1	$CH_3CONHBr$	**L1**	0	messy	–
2	$CH_3CONHBr$	**L2**	0	18	93
3	$CH_3CONHBr$	**L3**	0	39	97
4	$CH_3CONHBr$	**L4**	0	16	92
5	$CH_3CONHBr$	**L5**	0	63	99
6	$CH_3CONHBr$	**L6**	0	58	98
7	$CH_3CONHBr$	**L7**	0	43	97
8	$CH_3CONHBr$	**L8**	0	messy	–
9	PhCONHBr	**L5**	0	12	98
10	NBP	**L5**	0	messy	–
11	TBCO	**L5**	0	–	–
12	DBDMH	**L5**	0	24	93
13	NBS	**L5**	0	messy	–
14	$CH_3CONHBr$	**L5**	rt	39	98
15	$CH_3CONHBr$	**L5**	−15	66	>99
16[d]	$CH_3CONHBr$	**L5**	−30	60	>99
17[d]	$CH_3CONHBr$	**L5**	−50	32	>99
18[e]	$CH_3CONHBr$	**L5**	−15	44	99
19[f]	$CH_3CONHBr$	**L5**	−15	50	99
20[g]	$CH_3CONHBr$	**L5**	−15	53	99
21	$CH_3CONHBr$	–	−15	–	–
22[h]	$CH_3CONHBr$	**L5**	−15	messy	–

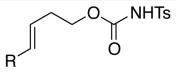
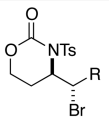
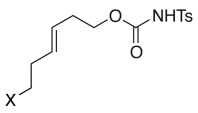
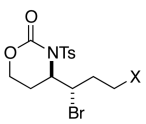
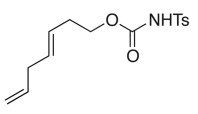
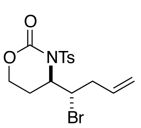
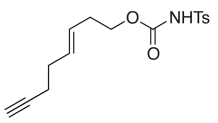
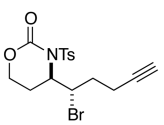
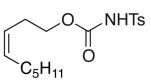
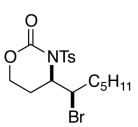
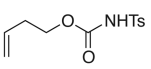
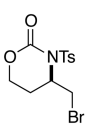
[a]The reactions were carried out with substrate **3b** (0.10 mmol), Br source (0.12 mmol), and $Sc(OTf)_3$-**L** (1:1) (0.010 mmol) in CH_2Cl_2 (1.0 mL) for 24 h unless otherwise stated. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]For 96 h. [e]With 3 Å MS (0.025 g). [f]With 4 Å MS (0.025 g). [g]With 5 Å MS (0.025 g). [h]Without $Sc(OTf)_3$.

substituents (Table 1, entries 2−8) with ligand **L5** being the best, giving **4b** in 63% yield and 99% ee in CH_2Cl_2 at 0 °C. Among the bromine sources examined (Table 1, entries 5, 9−13), *N*-Bromoacetamide was found to be the most effective for the reaction. The reaction temperature was further examined (Table 1, entries 5, 14−17), and the optimal results were obtained at −15 °C. Lower yields were obtained when the reaction was carried out in the presence of molecular sieves (Table 1, entries 18−20). Control experiments showed that both $Sc(OTf)_3$ and the ligand were crucial for the reaction. Little reaction was observed with $Sc(OTf)_3$ alone (Table 1, entry 21), and a messy mixture was formed with ligand **L5** in the absence of $Sc(OTf)_3$ (Table 1, entry 22).

As shown in Table 2, the bromocyclization with the $Sc(OTf)_3$-**L5** complex can be extended to a variety of (*E*)-homoallylic *N*-tosylcarbamates (Table 2, entries 1−9) (the X-ray structure of **4b** is shown in Figure 2). While the yield was moderate, the enantioselectivity was remarkably high (97−99% ee). Various functional groups such as OBn, Cl, N_3, alkene, and alkyne can be present in the side chains (Table 2, entries 5−9). The starting material largely remained when (*E*)-4-phenylbut-3-enyl tosylcarbamate was used as the substrate (R = Ph). For (*E*)-hexa-3,5-dienyl tosylcarbamate (R = vinyl), a messy mixture was obtained. Lower ee's were obtained for (*Z*)- and terminal substrates (Table 2, entries 10 and 11).

Table 2. Enantioselective Bromoaminocyclization of Homoallylic *N*-Tosylcarbamates[a]



entry	substrate	product[c]	yield (%)[d]	ee (%)[e]
				
1	**3a**; R = Me	**4a**	58	99
2	**3b**; R = Et	**4b**	57	> 99
3	**3c**; R = C_5H_{11}	**4c**	57	> 99
4	**3d**; R = CH_2Cy	**4d**	54	99
				
5	**3e**; X = OBn	**4e**	48	97
6[b]	**3f**; X = Cl	**4f**	45	99
7[b]	**3g**; X = N_3	**4g**	48	98
				
8	**3h**	**4h**	52	> 99
				
9	**3i**	**4i**	59	98
				
10	**3j**	**4j**	57	48
				
11	**3k**	**4k**	72	64

[a]The reactions were carried out with substrate **3** (0.50 mmol), $Sc(OTf)_3$-**L5** (1:1) (0.050 mmol), and $CH_3CONHBr$ (0.60 mmol) in CH_2Cl_2 (5.0 mL) at −15 °C for 48 h unless otherwise stated. [b]The reactions were carried out with DBDMH at 0 °C. [c]The absolute configurations of **4b** and **4f** were assigned based on their X-ray structures. For entries 1, 3−5, and 7−9, the absolute configurations were tentatively proposed by analogy. [d]Isolated yield. [e]Determined by chiral HPLC analysis.

The reaction can be carried out on a relatively large scale. As exemplified by **3b** (Scheme 3), 2.11 g of oxazinanone **4b**

DOI: 10.1021/acs.orglett.5b01779
Org. Lett. XXXX, XXX, XXX−XXX

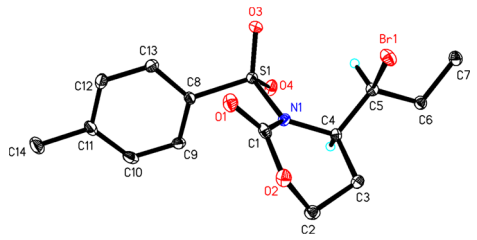
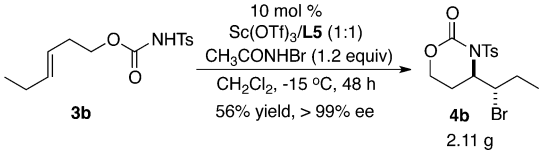


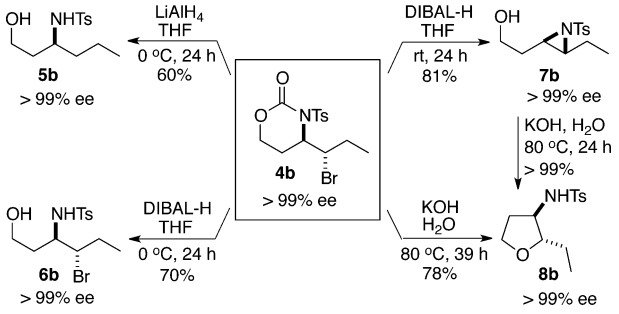
Figure 2. X-ray structure of **4b**.

Scheme 3. Bromoaminocyclization on a Gram Scale



was obtained in 56% yield with >99% ee. 1,3-Oxazinan-2-one **4b** can serve as a versatile chiral building block for further transformations as illustrated in Scheme 4. Treating **4b** with

Scheme 4. Synthetic Transformations of Bromide 4b



$LiAlH_4$ at 0 °C gave aminoalcohol **5b** in 60% yield. Bromoaminoalcohol **6b** was obtained in 70% yield with DIBAL-H at 0 °C. When the reaction was carried out at rt, aziridine **7b** was formed in 81% yield. The aziridine likely resulted from the cyclization of **6b** under the reaction conditions. When **4b** was reacted with KOH−H_2O at 80 °C, aminotetrahydrofuran **8b** was generated in 78% yield. Compound **8b** was formed from **4b** likely via aziridine **7b**. In all these transformations, no loss of optical purity was observed.

The different catalytic properties of $Sc(OTf)_3$-**L1** and $Sc(OTf)_3$-**L5** displayed in the bromocyclization of (*Z*)-allyl *N*-tosylcarbamates (**1**) and (*E*)-homoallylic *N*-tosylcarbamates (**3**) were intriguing. Attempts to elucidate the catalytic species involved in these reactions via NMR, MS, and X-ray spectroscopy were unsuccessful thus far. A better understanding of the reaction mechanism awaits further study.

In summary, we have developed a highly enantioselective 6-*exo*-bromoaminocyclization of (*E*)-homoallylic *N*-tosylcarbamates using *N*-bromoacetamide as the bromonium ion source and a novel chiral monophosphine-$Sc(OTf)_3$ complex as the catalyst, giving the corresponding 1,3-oxazinan-2-ones in up to >99% ee. The reaction is amenable to gram scale. The resulting optically active 1,3-oxazinan-2-ones can be further transformed into various useful functionalized compounds without loss of optical purity. It appears that a delicate combination of the catalyst system and the olefin substrate could bring opportunities to develop new reaction processes. Further efforts will be devoted to understanding the reaction mechanism, developing new catalytic systems, and expanding the substrate scope.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterizations, X-ray structures, data for determination of enantiomeric excess, and NMR spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01779.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Yian.Shi@colostate.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We gratefully acknowledge the National Basic Research Program of China (973 program, 2011CB808600), the National Natural Science Foundation of China (21172221), and the Chinese Academy of Sciences for the financial support.

■ REFERENCES

(1) For leading reviews on halogenation of olefins, see: (a) Dowle, M. D.; Davies, D. I. *Chem. Soc. Rev.* **1979**, *8*, 171. (b) Li, G.; Kotti, S. R. S. S.; Timmons, C. *Eur. J. Org. Chem.* **2007**, *2007*, 2745.

(2) For leading reviews on asymmetric halogenation of olefins, see: (a) Chen, G.; Ma, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 8306. (b) Castellanos, A.; Fletcher, S. P. *Chem. - Eur. J.* **2011**, *17*, 5766. (c) Tan, C. K.; Zhou, L.; Yeung, Y.-Y. *Synlett* **2011**, *2011*, 1335. (d) Hennecke, U. *Chem. - Asian J.* **2012**, *7*, 456. (e) Denmark, S. E.; Kuester, W. E.; Burk, M. T. *Angew. Chem., Int. Ed.* **2012**, *51*, 10938. (f) Murai, K.; Fujioka, H. *Heterocycles* **2013**, *87*, 763. (g) Chemler, S. R.; Bovino, M. T. *ACS Catal.* **2013**, *3*, 1076. (h) Tan, C. K.; Yeung, Y.-Y. *Chem. Commun.* **2013**, *49*, 7985. (i) Tripathi, C. B.; Mukherjee, S. *Synlett* **2014**, *25*, 163. (j) Cheng, Y. A.; Yu, W. Z.; Yeung, Y.-Y. *Org. Biomol. Chem.* **2014**, *12*, 2333. (k) Chen, J.; Zhou, L. *Synthesis* **2014**, *46*, 586. (l) Zheng, S.; Schienebeck, C. M.; Zhang, W.; Wang, H.-Y.; Tang, W. *Asian J. Org. Chem.* **2014**, *3*, 366.

(3) For leading references on Lewis acid catalyzed intramolecular enantioselective halogenation of olefins, see: (a) Inoue, T.; Kitagawa, O.; Ochiai, O.; Shiro, M.; Taguchi, T. *Tetrahedron Lett.* **1995**, *36*, 9333. (b) Inoue, T.; Kitagawa, O.; Saito, A.; Taguchi, T. *J. Org. Chem.* **1997**, *62*, 7384. (c) Kang, S. H.; Lee, S. B.; Park, C. M. *J. Am. Chem. Soc.* **2003**, *125*, 15748. (d) Kwon, H. Y.; Park, C. M.; Lee, S. B.; Youn, J.-H.; Kang, S. H. *Chem. - Eur. J.* **2008**, *14*, 1023. (e) Ning, Z.; Jin, R.; Ding, J.; Gao, L. *Synlett* **2009**, *2009*, 2291. (f) Bovino, M. T.; Chemler, S. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 3923. (g) Lee, H. J.; Kim, D. Y. *Tetrahedron Lett.* **2012**, *53*, 6984. (h) Miles, D. H.; Veguillas, M.; Toste, F. D. *Chem. Sci.* **2013**, *4*, 3427. (i) Filippova, L.; Stenstrøm, Y.; Hansen, T. V. *Tetrahedron Lett.* **2014**, *55*, 419. (j) Arai, T.; Sugiyama, N.; Masu, H.; Kado, S.; Yabe, S.; Yamanaka, M. *Chem. Commun.* **2014**, *50*, 8287. (k) Cai, Y.; Zhou, P.; Liu, X.; Zhao, J.; Lin, L.; Feng, X. *Chem. - Eur. J.* **2015**, *21*, 6386.

(4) For leading references on Lewis acid catalyzed intermolecular enantioselective halogenation of olefins, see: (a) Cai, Y.; Liu, X.; Hui, Y.; Jiang, J.; Wang, W.; Chen, W.; Lin, L.; Feng, X. *Angew. Chem., Int. Ed.* **2010**, *49*, 6160. (b) Cai, Y.; Liu, X.; Jiang, J.; Chen, W.; Lin, L.; Feng, X. *J. Am. Chem. Soc.* **2011**, *133*, 5636. (c) Cai, Y.; Liu, X.; Li, J.; Chen, W.; Wang, W.; Lin, L.; Feng, X. *Chem. - Eur. J.* **2011**, *17*, 14916. (d) Cai, Y.; Liu, X.; Zhou, P.; Kuang, Y.; Lin, L.; Feng, X.

DOI: 10.1021/acs.orglett.5b01779
Org. Lett. XXXX, XXX, XXX−XXX

Chem. Commun. **2013**, *49*, 8054. (e) Hu, D. X.; Shibuya, G. M.; Burns, N. Z. *J. Am. Chem. Soc.* **2013**, *135*, 12960. (f) Hu, D. X.; Seidl, F. J.; Bucher, C.; Burns, N. Z. *J. Am. Chem. Soc.* **2015**, *137*, 3795.

(5) For leading references on chiral phosphoric acid and phosphate catalyzed intramolecular enantioselective halogenation of olefins, see: (a) Hennecke, U.; Müller, C. H.; Fröhlich, R. *Org. Lett.* **2011**, *13*, 860. (b) Rauniyar, V.; Lackner, A. D.; Hamilton, G. L.; Toste, F. D. *Science* **2011**, *334*, 1681. (c) Huang, D.; Wang, H.; Xue, F.; Guan, H.; Li, L.; Peng, X.; Shi, Y. *Org. Lett.* **2011**, *13*, 6350. (d) Denmark, S. E.; Burk, M. T. *Org. Lett.* **2012**, *14*, 256. (e) Wang, Y.-M.; Wu, J.; Hoong, C.; Rauniyar, V.; Toste, F. D. *J. Am. Chem. Soc.* **2012**, *134*, 12928. (f) Romanov-Michailidis, F.; Guénée, L.; Alexakis, A. *Angew. Chem., Int. Ed.* **2013**, *52*, 9266. (g) Xie, W.; Jiang, G.; Liu, H.; Hu, J.; Pan, X.; Zhang, H.; Wan, X.; Lai, Y.; Ma, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 12924. (h) Liu, H.; Jiang, G.; Pan, X.; Wan, X.; Lai, Y.; Ma, D.; Xie, W. *Org. Lett.* **2014**, *16*, 1908. (i) Müller, C. H.; Rösner, C.; Hennecke, U. *Chem. - Asian J.* **2014**, *9*, 2162. (j) Romanov-Michailidis, F.; Romanova-Michaelides, M.; Pupier, M.; Alexakis, A. *Chem. - Eur. J.* **2015**, *21*, 5561.

(6) For leading references on chiral phosphoric acid and phosphate catalyzed intermolecular enantioselective halogenation of olefins, see: (a) Li, G.-X.; Fu, Q.-Q.; Zhang, X.-M.; Jiang, J.; Tang, Z. *Tetrahedron: Asymmetry* **2012**, *23*, 245. (b) Alix, A.; Lalli, C.; Retailleau, P.; Masson, G. *J. Am. Chem. Soc.* **2012**, *134*, 10389. (c) Honjo, T.; Phipps, R. J.; Rauniyar, V.; Toste, F. D. *Angew. Chem., Int. Ed.* **2012**, *51*, 9684.

(7) For leading references on chiral base catalyzed intramolecular enantioselective halogenation of olefins, see: (a) Wang, M.; Gao, L. X.; Mai, W. P.; Xia, A. X.; Wang, F.; Zhang, S. B. *J. Org. Chem.* **2004**, *69*, 2874. (b) Sakakura, A.; Ukai, A.; Ishihara, K. *Nature* **2007**, *445*, 900. (c) Whitehead, D. C.; Yousefi, R.; Jaganathan, A.; Borhan, B. *J. Am. Chem. Soc.* **2010**, *132*, 3298. (d) Zhang, W.; Zheng, S.; Liu, N.; Werness, J. B.; Guzei, I. A.; Tang, W. *J. Am. Chem. Soc.* **2010**, *132*, 3664. (e) Zhou, L.; Tan, C. K.; Jiang, X.; Chen, F.; Yeung, Y.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 15474. (f) Veitch, G. E.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2010**, *49*, 7332. (g) Murai, K.; Matsushita, T.; Nakamura, A.; Fukushima, S.; Shimura, M.; Fujioka, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 9174. (h) Jaganathan, A.; Garzan, A.; Whitehead, D. C.; Staples, R. J.; Borhan, B. *Angew. Chem., Int. Ed.* **2011**, *50*, 2593. (i) Yousefi, R.; Whitehead, D. C.; Mueller, J. M.; Staples, R. J.; Borhan, B. *Org. Lett.* **2011**, *13*, 608. (j) Liu, N.; Werness, J. B.; Guzei, I. A.; Tang, W. *Tetrahedron* **2011**, *67*, 4385. (k) Zhou, L.; Chen, J.; Tan, C. K.; Yeung, Y.-Y. *J. Am. Chem. Soc.* **2011**, *133*, 9164. (l) Chen, Z.-M.; Zhang, Q.-W.; Chen, Z.-H.; Li, H.; Tu, Y.-Q.; Zhang, F.-M.; Tian, J.-M. *J. Am. Chem. Soc.* **2011**, *133*, 8818. (m) Tan, C. K.; Zhou, L.; Yeung, Y.-Y. *Org. Lett.* **2011**, *13*, 2738. (n) Lozano, O.; Blessley, G.; Campo, T. M.; Thompson, A. L.; Giuffredi, G. T.; Bettati, M.; Walker, M.; Borman, R.; Gouverneur, V. *Angew. Chem., Int. Ed.* **2011**, *50*, 8105. (o) Li, H.; Zhang, F.-M.; Tu, Y.-Q.; Zhang, Q.-W.; Chen, Z.-M.; Chen, Z.-H.; Li, J. *Chem. Sci.* **2011**, *2*, 1839. (p) Tan, C. K.; Chen, F.; Yeung, Y.-Y. *Tetrahedron Lett.* **2011**, *52*, 4892. (q) Müller, C. H.; Wilking, M.; Rühlmann, A.; Wibbeling, B.; Hennecke, U. *Synlett* **2011**, *2011*, 2043. (r) Chen, J.; Zhou, L.; Tan, C. K.; Yeung, Y.-Y. *J. Org. Chem.* **2012**, *77*, 999. (s) Zhang, W.; Liu, N.; Schienebeck, C. M.; Decloux, K.; Zheng, S.; Werness, J. B.; Tang, W. *Chem. - Eur. J.* **2012**, *18*, 7296. (t) Dobish, M. C.; Johnston, J. N. *J. Am. Chem. Soc.* **2012**, *134*, 6068. (u) Chen, J.; Zhou, L.; Yeung, Y.-Y. *Org. Biomol. Chem.* **2012**, *10*, 3808. (v) Tan, C. K.; Le, C.; Yeung, Y.-Y. *Chem. Commun.* **2012**, *48*, 5793. (w) Murai, K.; Nakamura, A.; Matsushita, T.; Shimura, M.; Fujioka, H. *Chem. - Eur. J.* **2012**, *18*, 8448. (x) Jiang, X.; Tan, C. K.; Zhou, L.; Yeung, Y.-Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 7771. (y) Paull, D. H.; Fang, C.; Donald, J. R.; Pansick, A. D.; Martin, S. F. *J. Am. Chem. Soc.* **2012**, *134*, 11128. (z) Tungen, J. E.; Nolsøe, J. M. J.; Hansen, T. V. *Org. Lett.* **2012**, *14*, 5884. (aa) Ikeuchi, K.; Ido, S.; Yoshimura, S.; Asakawa, T.; Inai, M.; Hamashima, Y.; Kan, T. *Org. Lett.* **2012**, *14*, 6016. (ab) Fang, C.; Paull, D. H.; Hethcox, J. C.; Shugrue, C. R.; Martin, S. F. *Org. Lett.* **2012**, *14*, 6290. (ac) Zhou, L.; Tay, D. W.; Chen, J.; Leung, G. Y. C.; Yeung, Y.-Y. *Chem. Commun.* **2013**, *49*, 4412. (ad) Chen, F.; Tan, C. K.; Yeung, Y.-Y. *J. Am. Chem. Soc.* **2013**, *135*, 1232. (ae) Zeng, X.; Miao, C.; Wang, S.; Xia, C.; Sun, W. *Chem. Commun.* **2013**, *49*, 2418. (af) Garzan, A.; Jaganathan, A.; Marzijarani, N. S.; Yousefi, R.; Whitehead, D. C.; Jackson, J. E.; Borhan, B. *Chem. - Eur. J.* **2013**, *19*, 9015. (ag) Brindle, C. S.; Yeung, C. S.; Jacobsen, E. N. *Chem. Sci.* **2013**, *4*, 2100. (ah) Wilking, M.; Mück-Lichtenfeld, C.; Daniliuc, C. G.; Hennecke, U. *J. Am. Chem. Soc.* **2013**, *135*, 8133. (ai) Murai, K.; Matsushita, T.; Nakamura, A.; Hyogo, N.; Nakajima, J.; Fujioka, H. *Org. Lett.* **2013**, *15*, 2526. (aj) Zhao, Y.; Jiang, X.; Yeung, Y.-Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 8597. (ak) Tripathi, C. B.; Mukherjee, S. *Angew. Chem., Int. Ed.* **2013**, *52*, 8450. (al) Sawamura, Y.; Nakatsuji, H.; Sakakura, A.; Ishihara, K. *Chem. Sci.* **2013**, *4*, 4181. (am) Yousefi, R.; Ashtekar, K. D.; Whitehead, D. C.; Jackson, J. E.; Borhan, B. *J. Am. Chem. Soc.* **2013**, *135*, 14524. (an) Jaganathan, A.; Staples, R. J.; Borhan, B. *J. Am. Chem. Soc.* **2013**, *135*, 14806. (ao) Yin, Q.; You, S.-L. *Org. Lett.* **2013**, *15*, 4266. (ap) Armstrong, A.; Braddock, D. C.; Jones, A. X.; Clark, S. *Tetrahedron Lett.* **2013**, *54*, 7004. (aq) Han, X.; Dong, C.; Zhou, H. *Adv. Synth. Catal.* **2014**, *356*, 1275. (ar) Tan, C. K.; Er, J. C.; Yeung, Y.-Y. *Tetrahedron Lett.* **2014**, *55*, 1243. (as) Tay, D. W.; Leung, G. Y. C.; Yeung, Y.-Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 5161. (at) Nakatsuji, H.; Sawamura, Y.; Sakakura, A.; Ishihara, K. *Angew. Chem., Int. Ed.* **2014**, *53*, 6974. (au) Yin, Q.; You, S.-L. *Org. Lett.* **2014**, *16*, 1810. (av) Yin, Q.; You, S.-L. *Org. Lett.* **2014**, *16*, 2426. (aw) Jaganathan, A.; Borhan, B. *Org. Lett.* **2014**, *16*, 3616. (ax) Ke, Z.; Tan, C. K.; Chen, F.; Yeung, Y.-Y. *J. Am. Chem. Soc.* **2014**, *136*, 5627. (ay) Wilking, M.; Daniliuc, C. G.; Hennecke, U. *Synlett* **2014**, *25*, 1701. (az) Tripathi, C. B.; Mukherjee, S. *Org. Lett.* **2014**, *16*, 3368. (ba) Murai, K.; Shimizu, N.; Fujioka, H. *Chem. Commun.* **2014**, *50*, 12530. (bb) Toda, Y.; Pink, M.; Johnston, J. N. *J. Am. Chem. Soc.* **2014**, *136*, 14734. (bc) Kawato, Y.; Kubota, A.; Ono, H.; Egami, H.; Hamashima, Y. *Org. Lett.* **2015**, *17*, 1244.

(8) For leading references on chiral base catalyzed intermolecular enantioselective halogenation of olefins, see: (a) Nicolaou, K. C.; Simmons, N. L.; Ying, Y.; Heretsch, P. M.; Chen, J. S. *J. Am. Chem. Soc.* **2011**, *133*, 8134. (b) Zhang, W.; Liu, N.; Schienebeck, C. M.; Zhou, X.; Izhar, I. I.; Guzei, I. A.; Tang, W. *Chem. Sci.* **2013**, *4*, 2652. (c) Zhang, Y.; Xing, H.; Xie, W.; Wan, X.; Lai, Y.; Ma, D. *Adv. Synth. Catal.* **2013**, *355*, 68. (d) Li, L.; Su, C.; Liu, X.; Tian, H.; Shi, Y. *Org. Lett.* **2014**, *16*, 3728. (e) Qi, J.; Fan, G.-T.; Chen, J.; Sun, M.-H.; Dong, Y.-T.; Zhou, L. *Chem. Commun.* **2014**, *50*, 13841.

(9) For a leading reference on the Trost ligand, see: Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327.

(10) (a) Huang, D.; Liu, X.; Li, L.; Cai, Y.; Liu, W.; Shi, Y. *J. Am. Chem. Soc.* **2013**, *135*, 8101. (b) Huang, H.; Pan, H.; Cai, Y.; Liu, M.; Tian, H.; Shi, Y. *Org. Biomol. Chem.* **2015**, *13*, 3566.

DOI: 10.1021/acs.orglett.5b01779
Org. Lett. XXXX, XXX, XXX−XXX