Organic LETTERS

Letter

pubs.acs.org/OrgLett

Ruthenium-Catalyzed Regio- and Enantioselective Allylic Amination of Racemic 1-Arylallyl Esters

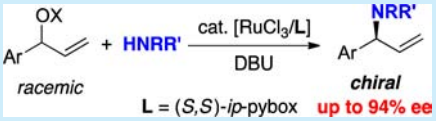
Motoi Kawatsura,*[,†] Kenta Uchida,[‡] Shou Terasaki,[†] Hiroaki Tsuji,[‡] Maki Minakawa,[†] and Toshiyuki Itoh*[,‡]

[†]Department of Chemistry, College of Humanities & Sciences, Nihon University, Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan

[‡]Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, Koyama, Tottori 680-8552, Japan

Supporting Information

ABSTRACT: The regio- and enantioselective allylic amination of racemic monosubstituted allylic esters, such as 1-arylallyl acetates, with cyclic secondary amines has been accomplished. The $RuCl_3$/(*S*,*S*)-*ip*-pybox catalyst system has effectively catalyzed the reaction to afford the enantiomerically enriched branch-type allylic amines with perfect regioselectivity and high enantioselectivity.



The transition-metal-catalyzed allylic amination of allylic substrates[1] is one of the most useful reactions to construct allylic amines, and its asymmetric reaction[2] is also a powerful method to prepare enantiomerically enriched allylic amines. For such a transition-metal-catalyzed asymmetric allylic amination, several types of allylic substrates can be used, including symmetrical 1,3-disubstituted allylic substrates, but the reaction of the unsymmetrical monosubstituted substrates is a more challenging system because the reaction requires controlling both the regioselectivity and enantioselectivity. To the best of our knowledge palladium,[3] iridium,[4−10] and rhodium[21] are known as effective catalysts for such an intermolecular asymmetric allylic amination of monosubstituted allylic substrates. The first example of the palladium-catalyzed reaction was reported by Hayashi and Ito in 1990.[3a] More recently, Hartwig's group investigated the highly enantioselective allylic amination of monosubstituted allylic esters and alcohols by an iridium catalyst.[4] Furthermore, Nguyen et al. reported rhodium-catalyzed asymmetric allylic amination of allylic trichloroacetimidates.[21]

However, still it is a challenging topic to discover an alternative transition metal catalyst, which allows the asymmetric allylic amination of racemic monosubstituted allylic compounds. Although there are several studies on the ruthenium-catalyzed asymmetric allylic substitution[11−17] after Onitsuka and Takahashi's report in 2001,[12a] there are still no reports about the intermolecular asymmetric allylic amination of racemic monosubstituted allylic substrates. During the course of our study on the ruthenium-catalyzed regioselective allylic substitution,[18] we succeeded in the intermolecular enantioselective allylic amination of racemic monosubstituted allylic esters with cyclic secondary amines.

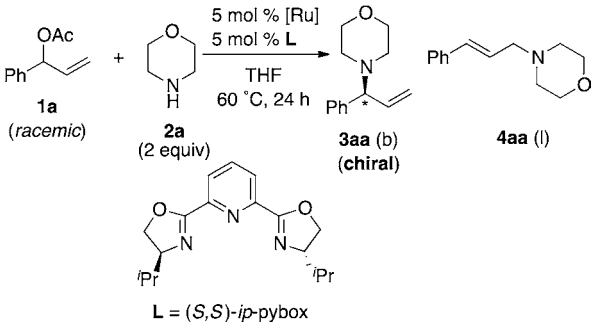
We first examined the allylic amination of the racemic 1-phenyl-2-propenyl acetate (**1a**) with morpholine (**2a**) by several chiral ruthenium catalysts, which were generated in situ from the ruthenium precatalyst and (*S*,*S*)-*ip*-pybox (**L**). As shown in Table 1, when the reactions were conducted without an additive, the desired branch-type product **3aa** was obtained in low yield or as a mixture of linear-type products **4aa** (entries 1−4). However, the addition of DBU (2 equiv to **1a**) to the reaction using $RuCl_2$(cod) or $RuCl_3$ effectively increased the branch selectivity (entries 6 and 8), and we observed a moderate enantioselectivity (54% ee) for the reaction using the $RuCl_3$ precatalyst with **L**. The higher enantioselectivity was attained by reducing the amount of DBU from 2 to 1 equiv at 40 °C (entries 9 and 10), and the highest enantioselectivity (85% ee) was obtained when the amount of **L** was increased from 5 to 10 mol % (2 equiv to Ru) (entry 11). We also examined other additives, such as DABCO, Et_3N, DMAP, or Cs_2CO_3, and confirmed that the DBU is a crucial additive for the perfect branch selectivity and high enantioselectivity (entries 12−15).

With these optimized reaction conditions in hand, we investigated the ruthenium catalyzed intermolecular asymmetric allylic amination of several racemic 1-arylallyl acetates **1a−j** with six-membered aliphatic amines, such as **2a−f** (Table 2). Most of the reactions proceeded smoothly, and we succeeded in obtaining the desired product in high yield with a high enantiomeric excess. Especially, the reaction of **1a** with phenylpiperazine (**2d**) gave the highest enantioselectivity (94% ee) (Table 2, entry 3). The reactions of **1b−d**, which have an electron-withdrawing group at the *para*-position on the phenyl group, also afforded good results (entries 6−11). On the other hand, we confirmed that the reaction of **1e**, which has a methoxy group at the *para*-position on the phenyl group, gave **3ea** in 60% yield with 12% ee (entry 12), but increasing the amount of ligand from 10 to 20 mol % significantly increased the enantiomeric excess up to 85% ee (entry 13). Furthermore, we examined the reaction of allyl acetates **1f−i** and succeeded in obtaining the intended enantiomercially enriched products with both acceptable yields and enantiomeric excess (entries 14−21). Unfortunately, the reactions of the 1-naphthyl group

Received: January 26, 2014
Published: February 13, 2014

dx.doi.org/10.1021/ol5002768 | *Org. Lett.* 2014, 16, 1470−1473

Table 1. Ru Catalysts for the Alkylation of 1a with 2a



entry	[Ru]	additive (2 equiv)	yield[a] (%) 3aa	yield[a] (%) 4aa	ee (%) of 3aa
1	[Ru-1][b]	–	<2	<2	nd
2	$RuCl_2$(cod)	–	47	39	0
3	$Ru_3(CO)_{12}$	–	7	73	nd
4	$RuCl_3$	–	6	40	0
5	[Ru-1][b]	DBU	37	<2	31
6	$RuCl_2$(cod)	DBU	78	4	16
7	$Ru_3(CO)_{12}$	DBU	<2	<2	–
8	$RuCl_3$	DBU	71	<2	54
9	$RuCl_3$	DBU[c]	75	<2	65
10[d]	$RuCl_3$	DBU[c]	80	<2	81
11[d,e]	$RuCl_3$	DBU[c]	90 (85)[f]	<2	85
12[d,e]	$RuCl_3$	DABCO	17	<2	0
13[d,e]	$RuCl_3$	Et_3N	18	<2	0
14[d,e]	$RuCl_3$	DMAP	<2	<2	nd
15[d,e]	$RuCl_3$	Cs_2CO_3	23	<2	12

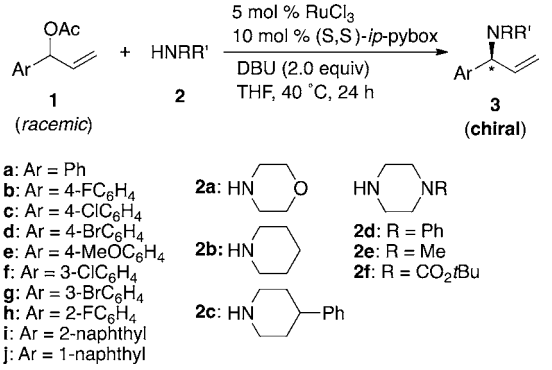
[a]The yields were determined by ^{1}H NMR of crude materials using an internal standard (trioxane). [b][Ru-1] = $[RuCl_2(p\text{-cymene})]_2$. [c]1 equiv of DBU was used. [d]Reactions were conducted at 40 °C. [e]10 mol % of **L** was used. [f]Isolated yield in parentheses.

substituted allyl acetate **1j** gave the desired products in low yield with low ee (entries 22 and 23).

Although we succeeded in realizing that reactions of **1a**–**i** with six-membered aliphatic amines provided enantioenriched allylic amines in both good yields and high ee values, we also realized that the reaction with pyrrolidine (**2g**) gave a poor result (Table 3, entry 1). To improve these poor results, we reinvestigated the catalyst conditions for the reaction with **2f**. During the reaction of **1a** with **2g**, we observed the formation of the deacetylated allylic alcohol from **1a**; therefore we changed the leaving group of the allyl substrate from acetate to methyl carbonate **1a′** or *tert*-butyl carbonate **1a″**. Changing of the leaving group improved the reaction results, and **1a″** produced the desired aminated product **3af** in good yields (entries 3–5); the best result (82% yield with 80% ee) was attained when the reaction was conducted using 20 mol % of the pybox ligand (4 equiv to Ru) at 60 °C (entry 5). All the other reactions of **1e″**, **1f″**, or **1g″** with **2f** also gave enantiomerically enriched allylic amines with good enantioselectivities (81–84% ee) (entries 6–8).

We further examined the reaction of **1a** with other amines, such as azepane (**2h**) or acyclic amine **2i** (Table 4), but again our optimized conditions gave allylic amines in low yields and low enantiomeric excesses (entries 1 and 4). However, we succeeded in determining the suitable reaction conditions for the reaction with **2h** or **2i**, and acceptable results (93% yield with 82% ee for **2h**, and 92% yield with 82% ee for **2i**) were obtained by increasing the amount of amines and DBU to 3

Table 2. Ruthenium-Catalyzed Enantioselective Allylic Amination of Racemic 1-Arylallyl Acetates with Amines[a]



entry	1	2	yield[b] (%) of 3	% ee of 3
1	**1a**	**2b**	91 (**3ab**)	80
2	**1a**	**2c**	84 (**3ac**)	86
3	**1a**	**2d**	90 (**3ad**)	94
4	**1a**	**2e**	90 (**3ae**)	88
5	**1a**	**2f**	93 (**3af**)	86
6	**1b**	**2a**	88 (**3ba**)	86
7	**1b**	**2c**	87 (**3bc**)	90
8	**1b**	**2d**	87 (**3bd**)	93
9	**1c**	**2c**	83 (**3cc**)	90
10	**1c**	**2d**	88 (**3cd**)	94
11	**1d**	**2d**	81 (**3dd**)	94
12	**1e**	**2d**	60 (**3ed**)	12
13[c]	**1e**	**2d**	87 (**3ed**)	85
14	**1f**	**2b**	77 (**3fb**)	90
15	**1f**	**2d**	74 (**3fd**)	87
16	**1g**	**2b**	67 (**3gb**)	90
17	**1g**	**2d**	64 (**3gd**)	90
18	**1h**	**2d**	71 (**3hd**)	86
19	**1h**	**2e**	88 (**3he**)	86
20	**1i**	**2a**	78 (**3ia**)	81
21	**1i**	**2d**	90 (**3id**)	86
22	**1j**	**2a**	35 (**3ja**)	24
23	**1j**	**2d**	22 (**3jd**)	4

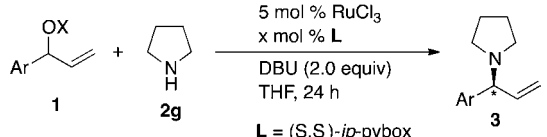
[a]Reaction conditions: **1a**–**j** (1.0 mmol), **2a**–**f** (2.0 mmol), DBU (2.0 mmol), 5 mol % of $RuCl_3$, and 10 mol % of (*S,S*)-*ip*-pybox in THF at 40 °C for 24 h. [b]Isolated yield. [c]20 mol % of **L** was used.

equiv and changing the solvents from THF to acetone (entries 3 and 5). We also demonstrated the reaction of other allylic acetates (**1b**–**d** and **1i**) with **2i** and could obtain enantiomerically enriched allylic amines with good enantiomeric excesses (entries 6–9). The details of the reaction mechanism of the $RuCl_3$/(*S,S*)-*ip*-pybox catalyzed enantioselective reaction, including the key intermediate, active ruthenium species, or the role of DBU, have not yet been clarified, but we believe that the reaction proceeds through (*S,S*)-*ip*-pybox ligated π-allyl and/or σ-allylruthenium complexes, and epimerization had occurred in those ruthenium intermediates to afford the enantiomerically enriched allylic amines.

In conclusion, we demonstrated the $RuCl_3$/(*S,S*)-*ip*-pybox catalyzed allylic amination of racemic 1-arylallyl esters with amines (mainly aliphatic secondary amines)[19] and succeeded in obtaining enantiomerically enriched allylic amines with a high enantioselectivity with perfect regioselectivity. Further studies, such as the reaction of other allylic esters,[20] reaction with

dx.doi.org/10.1021/ol5002768 | Org. Lett. 2014, 16, 1470–1473

Table 3. Reaction with Pyrrolidine (2g)[a]

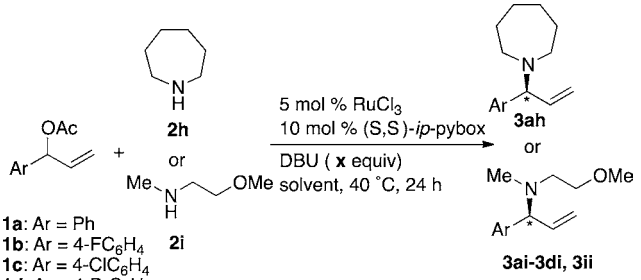


1a: Ar = Ph, X = Ac
1a': Ar = Ph, X = CO_2Me
1a": Ar = Ph, X = $CO_2{}^tBu$
1e": Ar = 3-FC_6H_4, X = $CO_2{}^tBu$
1f": Ar = 3-ClC_6H_4, X = $CO_2{}^tBu$
1g": Ar = 2-naphthyl, X = $CO_2{}^tBu$

entry	1	L (mol %)	temp (°C)	yield[b] (%) of 3	ee (%) of 3
1	1a	10	40	50 (3ag)	80
2	1a′	10	40	29 (3ag)	44
3	1a″	10	40	72 (3ag)	65
4	1a″	10	60	80 (3ag)	76
5	1a″	20	60	82 (3ag)	80
6	1e″	20	60	62 (3eg)	83
7	1f″	20	60	61 (3fg)	81
8	1g″	20	60	90 (3gg)	84

[a]Reaction conditions: **1** (1.0 mmol), **2g** (2.0 mmol), DBU (2.0 mmol), 5 mol % of $RuCl_3$, and 10 or 20 mol % of (*S,S*)-*ip*-pybox in THF for 24 h. [b]Isolated yield.

Table 4. Enantioselective Allylic Amination with 2h and 2i[a]



1a: Ar = Ph
1b: Ar = 4-FC_6H_4
1c: Ar = 4-ClC_6H_4
1d: Ar = 4-BrC_6H_4
1i: Ar = 2-naphthyl

entry	1	2 (equiv)	DBU (*x* equiv)	solvent	yield[b] (%) of 3	ee (%) of 3
1	1a	2h (2)	2	THF	29 (3ah)	44
2	1a	2h (3)	3	THF	88 (3ah)	70
3	1a	2h (3)	3	acetone	93 (3ah)	82
4	1a	2i (2)	2	THF	20 (3ai)	50
5	1a	2i (3)	3	acetone	92 (3ai)	82
6	1b	2i (3)	3	acetone	77 (3bi)	77
7	1c	2i (3)	3	acetone	82 (3ci)	81
8	1d	2i (3)	3	acetone	51 (3di)	81
9	1i	2i (3)	3	acetone	73 (3ii)	80

[a]Reaction conditions: **1** (1.0 mmol), **2h–i** (2.0 or 3.0 mmol), DBU (2.0 or 3.0 mmol), 5 mol % of $RuCl_3$, and 10 mol % of (*S,S*)-*ip*-pybox in THF or acetone at 40 °C for 24h. [b]Isolated yield.

aromatic amines, or study of the mechanistic details, are currently in progress in our group.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: kawatsur@chs.nihon-u.ac.jp.
*E-mail: titoh@chem.tottori-u.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was partially supported by Individual Research Expense of College of Humanities and Sciences at Nihon University for 2013.

■ REFERENCES

(1) (a) Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689. (b) Jørgensen, K. A. In *Modern Amination Methods*; Ricci, A., Ed.; Wiley-VCH: Weinheim, 2000; p 1. (c) Sundararaju, B.; Achard, M.; Bruneau, C. *Chem. Soc. Rev.* **2012**, *41*, 4467.

(2) (a) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258. (b) Trost, B. M. *J. Org. Chem.* **2004**, *69*, 5813. (c) Graening, T.; Schmalz, H.-G. *Angew. Chem., Int. Ed.* **2003**, *42*, 2580. (d) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921. (e) Dai, L.-X.; Tu, T.; You, S.-L.; Deng, W.-P.; Hou, X.-L. *Acc. Chem. Res.* **2003**, *36*, 669.

(3) (a) Hayashi, T.; Kishi, K.; Yamamoto, A.; Ito, Y. *Tetrahedon Lett.* **1990**, *31*, 1743. (b) You, S.-L.; Zhu, X.-Z.; Luo, Y.-M.; Hou, X.-L.; Dai, L.-X. *J. Am. Chem. Soc.* **2001**, *123*, 7471. (c) Faller, J. M.; Wilt, J. C. *Org. Lett.* **2005**, *7*, 633. (d) Faller, J. W.; Wilt, J. C. *Organometallics* **2005**, *24*, 5076. (e) Zheng, W.-H.; Sun, N.; Hou, X.-L. *Org. Lett.* **2005**, *7*, 5151. (f) Trost, B. M.; Fandrick, D. R.; Brodmann, T.; Stiles, D. T. *Angew. Chem., Int. Ed.* **2007**, *46*, 6123. (g) Chien, C.-W.; Shi, C.; Lin, C.-F.; Ojima, I. *Tetrahedron* **2011**, *67*, 6513. (h) Wang, X.; Meng, F.; Wang, Y.; Han, Z.; Chen, Y.-J.; Liu, L.; Wang, Z.; Ding, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 9276. (i) Wang, X.; Guo, P.; Han, Z.; Wang, X.; Wang, Z.; Ding, K. *J. Am. Chem. Soc.* **2014**, *136*, 405.

(4) (a) Ohmura, T.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 15164. (b) Kiener, C. A.; Shu, C.; Incarvito, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 14272. (c) Leitner, A.; Shekhar, S.; Pouy, M. J.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 15506. (d) Shekhar, S.; Trantow, B.; Leitner, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 11770. (e) Yamashita, Y.; Gopalarathnam, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2007**, *129*, 7508. (f) Pouy, M. J.; Leitner, A.; Weix, D. J.; Ueno, S.; Hartwig, J. F. *Org. Lett.* **2007**, *9*, 3949. (g) Stanley, L. M.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2009**, *48*, 7841. (h) pouy, M. J.; Stanley, L. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 11312. (i) Stanley, L. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 8971. (j) Hartwig, J. F.; Stanley, L. M. *Acc. Chem. Res.* **2010**, *43*, 1461.

(5) (a) Bartels, B.; García-Yebra, C.; Rominger, F.; Helmchen, G. *Eur. J. Inorg. Chem.* **2002**, 2569. (b) Weihofen, R.; Tverskoy, O.; Helmchen, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 5546. (c) Gnamm, C.; Förster, S.; Miller, N.; Brödner, K.; Helmchen, G. *Synlett* **2007**, 790. (d) Welter, C.; Dahnz, A.; Brunner, B.; Streiff, S.; Dübon, P.; Helmchen, G. *Org. Lett.* **2005**, *7*, 1239. (e) Gärtner, M.; Qu, J.; Helmchen, G. *J. Org. Chem.* **2012**, *77*, 1186. (f) Helmchen, G.; Dahnz, A.; Dübon, P.; Schelwies, M.; Weihofen, R. *Chem. Commun.* **2007**, 675. (g) Gärtner, M.; Weihofen, R.; Helmchen, G. *Chem.—Eur. J.* **2011**, *17*, 7605. (h) Satyanarayana, G.; Pflästerer, D.; Helmchen, G. *Eur. J. Org. Chem.* **2011**, 6788. (i) Hoecker, J.; Rudolf, G. C.; Bächle, F.; Fleischer, S.; Lindner, B. D.; Helmchen, G. *Eur. J. Org. Chem.* **2013**, 5149.

(6) (a) Nemoto, T.; Sakamoto, T.; Matsumoto, T.; Hamada, Y. *Tetrahedron Lett.* **2006**, *47*, 8737.

(7) (a) Roggen, M.; Carreira, E. M. *J. Am. Chem. Soc.* **2010**, *132*, 11917. (b) Lafrance, M.; Roggen, M.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 3470.

(8) (a) Xia, J.-B.; Liu, W.-B.; Wang, T.-M.; You, S.-L. *Chem.—Eur. J.* **2010**, *16*, 6442. (b) Ye, K.-Y.; He, H.; Liu, W.-B.; Dai, L.-X.; Helmchen, G.; You, S.-L. *J. Am. Chem. Soc.* **2011**, *133*, 19006. (c) Ye, K.-Y.; Dai, L.-X.; You, S.-L. *Org. Biomol. Chem.* **2012**, *10*, 5932.

(d) Liu, W.-B.; Zhang, X.; Dai, L.-X.; You, S.-L. *Angew. Chem., Int. Ed.* **2012**, *51*, 5183.
(9) Tosatti, P.; Horn, J.; Campbell, A. J.; House, D.; Nelson, A.; Marsden, S. P. *Adv. Synth. Catal.* **2010**, *352*, 3153.
(10) Trost, B. M.; Rao, M.; Dieskau, A. P. *J. Am. Chem. Soc.* **2013**, *135*, 18697.
(11) (a) Bruneau, C.; Renaud, J.-L.; Demerseman, B. *Pure Appl. Chem.* **2008**, *80*, 861. (b) Bruneau, C.; Achard, M. *Coord. Chem. Rev.* **2012**, *256*, 525.
(12) (a) Matsushima, Y.; Onitsuka, K.; Kondo, T.; Mitsudo, T.; Takahashi, S. *J. Am. Chem. Soc.* **2001**, *123*, 10405. (b) Onitsuka, K.; Okuda, H.; Sasai, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 1454. (c) Onitsuka, K.; Kameyama, C.; Sasai, H. *Chem. Lett.* **2009**, *38*, 444. (d) Kanbayashi, N.; Onitsuka, K. *J. Am. Chem. Soc.* **2010**, *132*, 1206. (e) Kanbayashi, N.; Onitsuka, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 5179. (f) Takii, K.; Kanbayashi, N.; Onitsuka, K. *Chem. Commun.* **2012**, *48*, 3872. (g) Kanbayashi, N.; Takenaka, K.; Okamura, T.; Onitsuka, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 4897.
(13) (a) Mbaye, M. D.; Renaud, J.-L.; Demerseman, B.; Bruneau, C. *Chem. Commun.* **2004**, 1870. (b) Sahli, Z.; Derrien, N.; Pascal, S.; Demerseman, B.; Roisnel, T.; Barrière, F.; Achard, M.; Bruneau, C. *Dalton Trans.* **2011**, *40*, 5625.
(14) (a) Tanaka, S.; Seki, T.; Kitamura, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 8948. (b) Miyata, K.; Kutsuna, H.; Kawakami, S.; Kitamura, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 4649. (c) Seki, T.; Tanaka, S.; Kitamura, M. *Org. Lett.* **2012**, *14*, 608.
(15) Trost, B. M.; Fraisse, P. L.; Ball, Z. T. *Angew. Chem., Int. Ed.* **2002**, *41*, 1059.
(16) Saporita, M.; Bottari, G.; Bruno, G.; Drommi, D.; Faraone, F. *J. Mol. Catal. A: Chem.* **2009**, *309*, 159.
(17) Zhang, X.; Yang, Z.-P.; Liu, C.; You, S.-L. *Chem. Sci.* **2013**, *4*, 3239.
(18) (a) Kawatsura, M.; Ata, F.; Wada, S.; Hayase, S.; Uno, H.; Itoh, T. *Chem. Commun.* **2007**, 298. (b) Kawatsura, M.; Ata, F.; Hayase, S.; Itoh, T. *Chem. Commun.* **2007**, 4283. (c) Kawatsura, M.; Ata, F.; Hirakawa, T.; Hayase, S.; Itoh, T. *Tetrahedron Lett.* **2008**, *49*, 4873. (d) Kawatsura, M.; Sato, M.; Tsuji, H.; Ata, F.; Itoh, T. *J. Org. Chem.* **2011**, *76*, 5485.
(19) Reactions of cinnamyl acetate or cinnamyl chloride with morpholine resulted in no reaction under our optimized conditions.
(20) Reactions with aniline, MeNHTs, or $(Boc)_2NH$ resulted in no reaction under our optimized conditions.
(21) (a) Arnold, J. S.; Nguyen, H. M. *J. Am. Chem. Soc.* **2012**, *134*, 8380. (b) Arnold, J. S.; Cizio, G. T.; Heitz, D. R.; Nguyen, H. M. *Chem. Commun.* **2012**, *48*, 11531. (c) Arnold, J. S.; Nguyen, H. M. *Synthesis* **2013**, *45*, 2101.

■ NOTE ADDED AFTER ASAP PUBLICATION

The version of this Letter published on February 13, 2014, did not cite related work by Nguyen et al. on rhodium-catalyzed asymmetric allylic amination of allylic trichloroacetimidates. Subsequently, the introductory paragraph has been revised and references 21a−c added in the corrected version that reposted on February 20, 2014.

dx.doi.org/10.1021/ol5002768 | *Org. Lett.* 2014, 16, 1470−1473