Organic LETTERS

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

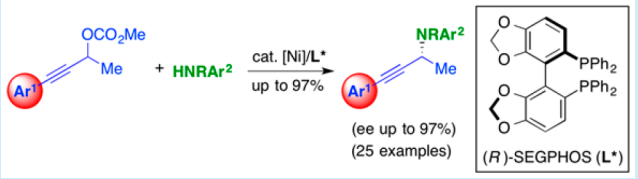
Nickel-Catalyzed Asymmetric Propargylic Amination of Propargylic Carbonates Bearing an Internal Alkyne Group

Kouichi Watanabe, Yusuke Miyazaki, Masataka Okubo, Biao Zhou, Hiroaki Tsuji,* and Motoi Kawatsura*

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

Supporting Information

ABSTRACT: We have achieved the nickel-catalyzed asymmetric propargylic amination of propargylic carbonates bearing an internal alkyne group. A wide variety of propargylic carbonates and *N*-methylaniline derivatives were tolerated under the reaction conditions, providing the corresponding chiral propargylic amines in up to 97% yield with up to 97% ee.

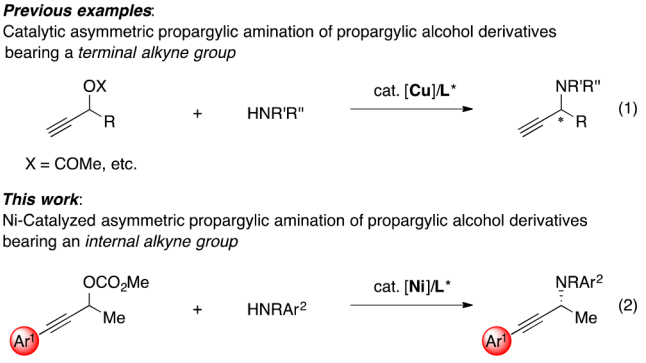


The catalytic asymmetric propargylic substitution reaction has been recognized as a powerful tool for the efficient synthesis of chiral propargylic compounds.[1] Since the pioneering work by Nishibayashi and co-workers in 2003,[2] the asymmetric propargylic substitution reaction of propargylic alcohol derivatives with carbon- and heteroatom-centered nucleophiles has been extensively studied using ruthenium[3] and copper[4] catalyst systems. However, these catalyst systems usually could not be applicable for the reaction of propargylic alcohol derivatives bearing an internal alkyne group,[5] because a terminal alkyne group is necessary for the formation of the metal-allenylidene intermediates,[6] which play a key role in the substitution reaction. Therefore, the catalytic asymmetric propargylic substitution reaction of these substrate classes is limited to only a few examples.[7] In this context, developing a catalyst system for achieving the asymmetric propargylic substitution reaction of propargylic alcohol derivatives bearing an internal alkyne group is highly desirable.

Chiral propargylic amines have attracted considerable attention because of their prevalence in synthetic intermediates and biologically active compounds.[8] The catalytic asymmetric propargylic amination of propargylic alcohol derivatives offers an important approach for accessing enantioenriched propargylic amines.[9] Although the catalytic asymmetric propargylic amination of propargylic alcohol derivatives bearing a terminal alkyne group has been well studied using copper catalysis (Scheme 1, eq 1),[4a−i] the use of propargylic alcohol derivatives bearing an internal alkyne group remains unexplored.[10] We describe herein the nickel-catalyzed asymmetric propargylic amination of propargylic alcohol derivatives having an internal alkyne group (Scheme 1, eq 2).

Inspired by the nickel-catalyzed asymmetric arylation of propargylic alcohol derivatives bearing an internal alkyne group,[7a,d] we chose a nickel catalyst system for the optimization of the reaction conditions (Table 1). We initially examined the reaction of propargylic carbonate **1a** bearing an internal alkyne group with *N*-methylaniline **2a** in the presence of 2.5 mol % of $Ni(cod)_2$ and 10 mol % of (*R*)-BINAP **L1** in

Scheme 1. Catalytic Asymmetric Propargylic Amination of Propargylic Alcohol Derivatives

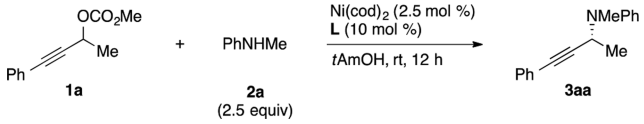


*t*AmOH at room temperature for 12 h (Table 1, entry 1). Fortunately, the desired propargylic amine **3aa** was obtained in 75% yield with 91% ee. To further improve the enantioselectivity, we tested other chiral bidentate phosphine ligands such as (*R*)-Tol-BINAP **L2**, (*R*)-SEGPHOS **L3**, and (*R*)-DTBM-SEGPHOS **L4** (Table 1, entries 2−4). Among these ligands, (*R*)-SEGPHOS **L3** showed high catalytic performance (Table 1, entry 3). On the other hand, (*S*,*S*)-*i*Pr-Pybox **L5** and (*S*,*S*)-*t*Bu-BOX **L6** were ineffective for the present reaction system (Table 1, entries 5 and 6). Based on these results, we chose (*R*)-SEGPHOS **L3** as the chiral ligand for further optimization studies. The amount of (*R*)-SEGPHOS **L3** could be reduced to 5 mol % while maintaining a high enantioselectivity, albeit with a low yield (Table 1, entry 7). When the reaction was carried out at 60 °C, the desired product **3aa** was obtained in 68% yield with 95% ee (Table 1, entry 8). Prolonging the reaction time from 12 to 48 h led to an increase of the yield of **3aa** without any loss of enantioselectivity (Table 1, entry 9). Finally, the use of 1.5

Received: July 26, 2018

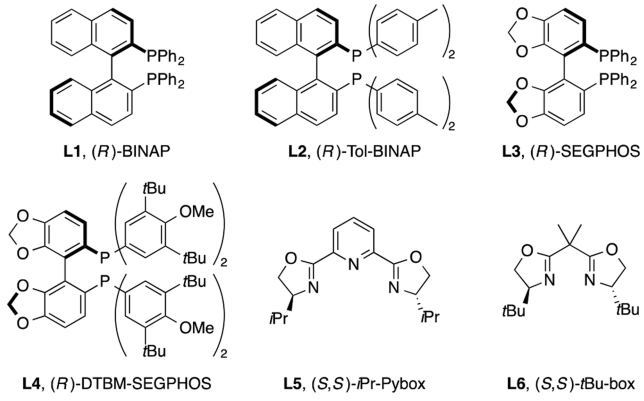
DOI: 10.1021/acs.orglett.8b02325
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Optimization of Reaction Conditions[a]



entry	L	temp (°C)	yield[b] (%)	ee[c] (%)
1	**L1**	rt	75	91
2	**L2**	rt	43	93
3	**L3**	rt	55	96
4	**L4**	rt	16	95
5	**L5**	rt	<1	–
6	**L6**	rt	<1	–
7[d]	**L3**	rt	38	96
8[d]	**L3**	60	68	95
9[d,e]	**L3**	60	86	96
10[d,e,f]	**L3**	60	91	95

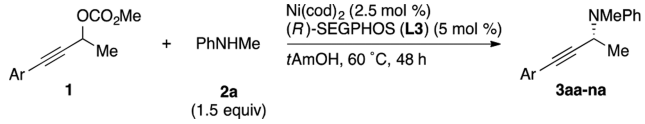
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), $Ni(cod)_2$ (0.005 mmol), **L** (0.02 mmol) in *t*AmOH (0.25 mL) at room temperature for 12 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]With 5.0 mol % of **L3**. [e]For 48 h. [f]With 1.5 equiv of **2a**.



equiv of *N*-methylaniline **2a** afforded the propargylic amine **3aa** in 91% yield with 95% ee (Table 1, entry 10).

With the optimized reaction conditions in hand, we examined the applicability of the asymmetric nickel catalysis with respect to propargylic carbonates **1** bearing a wide variety of internal alkyne groups using *N*-methylaniline **2a** as the amine source (Table 2). The reaction of propargylic carbonate **1a** could be conducted on a 1 mmol scale, affording the desired product **3aa** without any loss of the catalytic performance (Table 2, entry 1). The reaction of propargylic carbonates **1b–e** bearing electron-donating and -withdrawing substituents on their phenyl rings proceeded well to give the corresponding propargylic amines **3ba–ea** in 74–92% yields with 94–96% ee (Table 2, entries 2–5). Propargylic carbonates **1f** and **1g** having fluoro and bromo atoms were tolerated under the reaction conditions to furnish the desired products **3fa** and **3ga** in 72% and 90% yields with 96% and 95% ee, respectively (Table 2, entries 6 and 7). The reaction of a biphenyl-group-containing substrate **1h** with 4-bromo-*N*-methylaniline **2b** instead of *N*-methylaniline **2a** gave the desired product **3hb** in 74% yield with 96% ee, and the absolute configuration of **3hb** was determined to be *R* by an X-ray crystallographic analysis (Table 2, entry 8). 3-Methyl phenyl (**1i**), 3-fluorophenyl (**1j**), 2-methyl phenyl (**1k**), 2-fluorophenyl (**1l**), and 1-naphthyl (**1m**) substituents showed no significant effect during the catalysis. Thus, chiral propargylic amines **3ia–ma** were obtained in 52–92% yields with 79–96% ee (Table 2, entries

Table 2. Scope of Propargylic Carbonates 1[a]



entry	1	Ar	3	yield[b] (%)	ee[c] (%)
1[d]	**1a**	Ph	**3aa**	96	95
2	**1b**	4-MeC_6H_4	**3ba**	92	96
3	**1c**	4-$MeOC_6H_4$	**3ca**	80	96
4	**1d**	4-$CF_3C_6H_4$	**3da**	85	94
5	**1e**	4-$(CO_2Et)C_6H_4$	**3ea**	74	95
6	**1f**	4-FC_6H_4	**3fa**	72	96
7	**1g**	4-BrC_6H_4	**3ga**	90	94
8[e]	**1h**	4-PhC_6H_4	**3hb**	74	96
9	**1i**	3-MeC_6H_4	**3ia**	85	94
10	**1j**	3-FC_6H_4	**3ja**	83	95
11	**1k**	2-MeC_6H_4	**3ka**	90	91
12	**1l**	2-FC_6H_4	**3la**	52	96
13	**1m**	1-naphtyl	**3ma**	92	79
14	**1n**	2-thienyl	**3na**	88	95

[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.3 mmol), $Ni(cod)_2$ (0.005 mmol), (*R*)-SEGPHOS (0.01 mmol) in *t*AmOH (0.25 mL) at 60 °C for 48 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]1 mmol of **1a** was used. [e]4-Bromo-*N*-methylaniline **2b** was used as the amine instead of *N*-methylaniline **2a**.

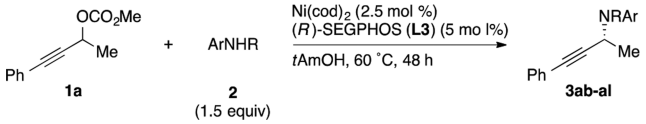
9–13). Propargylic carbonate **1n** bearing a 2-thienyl ring can be converted into propargylic amine **3na** in 88% yield with 95% ee (entry 14). Unfortunately, our catalyst system did not work for the reaction of propargylic carbonates having trimethylsilyl (Ar = TMS, R = Me) and terminal alkyne groups (Ar = H, R = Me). We also examined the reaction of propargylic carbonate bearing a trifluoromethyl group at the propargylic position instead of a methyl group, but the desired propargylic amines were not formed.

Encouraged by our success in the nickel-catalyzed asymmetric propargylic amination, we next investigated the reaction of propargylic carbonate **1a** with various aniline derivatives **2** (Table 3). *N*-Methylaniline derivatives **2b–e** having *para*-substituents (Me, MeO, F, Br) on their phenyl rings were smoothly reacted with propargylic carbonate **1a** under the optimized reaction conditions, providing the corresponding propargylic amines **3ab–ae** in high yields with excellent enantioselectivity (Table 3, entries 1–4). The reaction of *N*-methylaniline derivatives **2f** and **2g**, which possess *meta*-substituents on their phenyl rings, afforded propargylic amines **3af** and **3ag** in 91% and 40% yields with 95% and 96% ee, respectively (Table 3, entries 5 and 6). When *N*-methylaniline derivatives **2h** and **2i** were used as the amine source, the desired products **3ah** and **3ai** were obtained with excellent enantioselectivity, albeit with low yields (Table 3, entries 7 and 8). The present catalyst system was also effective not only for *N*-methylaniline derivatives but also *N*-benzylaniline **2j** and indoline **2k** (Table 3, entries 9 and 10). Aniline **2l** also underwent the reaction to furnish the amination product **3al** in 24% yield with 90% ee (Table 3, entry 11).

We propose the possible reaction pathways and stereochemical models as shown in Scheme 2. Initially, the addition of (*R*)- and (*S*)-propargylic carbonate **1a** to the nickel(0) species would occur in an *anti* fashion,[11] giving η^1-allenylnickels **I** and **II**.[12] Although the epimerization process in the present asymmetric nickel catalysis is still unclear, we

DOI: 10.1021/acs.orglett.8b02325
Org. Lett. XXXX, XXX, XXX–XXX

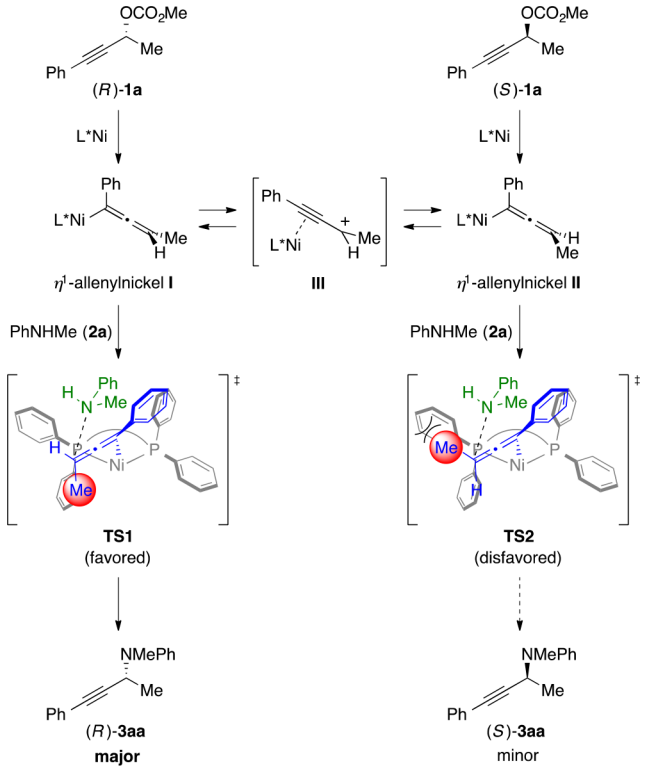
Table 3. Scope of Amines 2[a]



entry	2	Ar	R	3	yield[b] (%)	ee[c] (%)
1	2c	4-MeC_6H_4	Me	3ac	92	95
2	2d	4-$MeOC_6H_4$	Me	3ad	97	95
3	2e	4-FC_6H_4	Me	3ae	82	95
4	2b	4-BrC_6H_4	Me	3ab	76	96
5	2f	3-MeC_6H_4	Me	3af	91	95
6	2g	3-FC_6H_4	Me	3ag	46	96
7	2h	2-MeC_6H_4	Me	3ah	18	96
8	2i	2-FC_6H_4	Me	3ai	19	97
9	2j	Ph	Bn	3aj	86	89
10[d]	2k	–	–	3ak	73	94
11	2l	Ph	H	3al	24	90

[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $Ni(cod)_2$ (0.005 mmol), (*R*)-SEGPHOS (0.01 mmol) in *t*AmOH (0.25 mL) at 60 °C for 48 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]Indoline was used as the amine.

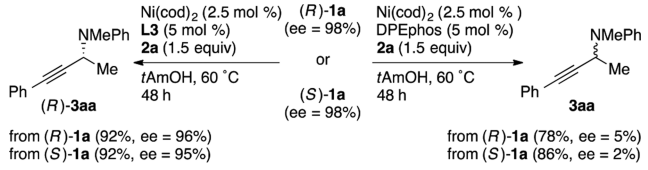
Scheme 2. Plausible Reaction Pathways and Stereochemical Models



assume that the epimerization would take place between the η^1-allenylnickels **I** and **II** via a propargylic cation intermediate **III**.[13] During the subsequent reaction of these two intermediates with *N*-methylaniline **2a**, the γ carbon atom of the η^1-allenylnickel **I** is attacked by the amine from its *Re*-face through the favored **TS1**, thus leading to (*R*)-**3aa** as a major stereoisomer. On the other hand, the reaction of the η^1-allenylnickel **II** with the amine through **TS2** seems to be disfavored due to the steric repulsion between the methyl group on the γ carbon atom of the η^1-allenylnickel **II** and the phenyl group on the phosphine moiety of (*R*)-SEGPHOS.

To support these suggested reaction pathways, we examined preliminary mechanistic studies as shown in Scheme 3. When

Scheme 3. Reaction of Chiral Propargylic Carbonates for Preliminary Mechanistic Studies[a]



[a]Reaction conditions: (*R*)- or (*S*)-**1a** (0.2 mmol), **2** (0.3 mmol), $Ni(cod)_2$ (0.005 mmol), DPEPHOS or (*R*)-SEGPHOS (0.01 mmol) in *t*AmOH (0.25 mL) at 60 °C for 48 h.

the reaction of (*R*)- or (*S*)-**1a** with *N*-methylaniline **2a** was carried out in the presence of 2.5 mol % of $Ni(cod)_2$ and 5 mol % of DPEphos, an almost racemic **3aa** was obtained. Furthermore, both (*R*)- and (*S*)-**1a** were converted into (*R*)-**3aa** under the optimized reaction conditions.[14] These results suggest that the epimerization of the η^1-allenylnickel species would proceed via the propargylic cation intermediates.[1c] The involvement of a μ–η^3-allenyl/propargyl dinuclear complex[15] and a radical species[16] could not be ruled out. The detailed mechanistic studies are under investigation.

In conclusion, we have accomplished the nickel-catalyzed asymmetric propargylic amination of propargylic carbonates bearing internal alkyne groups. A wide array of the propargylic carbonates can be transformed into the corresponding chiral propargylic amines in good yields with excellent enantioselectivities. Our nickel catalyst system enabled access to chiral propargylic amines bearing internal alkyne groups that are difficult to prepare using the conventional catalytic methods. Detailed mechanistic studies and further application of our catalyst system to other asymmetric transformations are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02325.

Experimental details and procedures; mechanistic studies; X-ray crystal structure of **3hb**; NMR spectra; HPLC chromatograms (PDF)

Accession Codes

CCDC 1815699 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: tsuji@chs.nihon-u.ac.jp.
*E-mail: kawatsur@chs.nihon-u.ac.jp.

DOI: 10.1021/acs.orglett.8b02325
Org. Lett. XXXX, XXX, XXX–XXX

ORCID

Biao Zhou: 0000-0002-4138-9425
Hiroaki Tsuji: 0000-0002-8899-3435
Motoi Kawatsura: 0000-0002-8341-6866

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research (C) from the Japan Society for the Promotion of Science (17K05794). We thank Mr. Mikihiro Saito (Nihon university) for his experimental support.

■ REFERENCES

(1) For selected reviews, see: (a) Miyake, Y.; Uemura, S.; Nishibayashi, Y. *ChemCatChem* **2009**, *1*, 342. (b) Detz, R. J.; Hiemstra, H.; van Maarseveen, J. H. *Eur. J. Org. Chem.* **2009**, *2009*, 6263. (c) Nishibayashi, Y. *Synthesis* **2012**, *2012*, 489. (d) Zhang, D.-Y.; Hu, X.-P. *Tetrahedron Lett.* **2015**, *56*, 283.

(2) Nishibayashi, Y.; Onodera, G.; Inada, Y.; Hidai, M.; Uemura, S. *Organometallics* **2003**, *22*, 873.

(3) For selected examples of alkylation, see: (a) Nishibayashi, Y.; Imajima, H.; Onodera, G.; Uemura, S. *Organometallics* **2005**, *24*, 4106. (b) Inada, Y.; Nishibayashi, Y.; Uemura, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7715. (c) Fukamizu, K.; Miyake, Y.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2008**, *130*, 10498. For selected examples of arylation, see: (d) Matsuzawa, H.; Miyake, Y.; Nishibayashi, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 6488. (e) Matsuzawa, H.; Kanao, K.; Miyake, Y.; Nishibayashi, Y. *Org. Lett.* **2007**, *9*, 5561. (f) Kanao, K.; Miyake, Y.; Nishibayashi, Y. *Organometallics* **2009**, *28*, 2920.

(4) For selected examples of amination, see: (a) Detz, R. J.; Delville, M. M. E.; Hiemstra, H.; van Maarseveen, J. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 3777. (b) Hattori, G.; Matsuzawa, H.; Miyake, Y.; Nishibayashi, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 3781. (c) Hattori, G.; Yoshida, A.; Miyake, Y.; Nishibayashi, Y. *J. Org. Chem.* **2009**, *74*, 7603. (d) Hattori, G.; Sakata, K.; Matsuzawa, H.; Tanabe, Y.; Miyake, Y.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2010**, *132*, 10592. (e) Detz, R. J.; Abiri, Z.; le Griel, R.; Hiemstra, H.; van Maarseveen, J. H. *Chem. - Eur. J.* **2011**, *17*, 5921. (f) Zhang, C.; Wang, Y.-H.; Hu, X.-H.; Zheng, Z.; Xu, J.; Hu, X.-P. *Adv. Synth. Catal.* **2012**, *354*, 2854. (g) Mino, T.; Taguchi, H.; Hashimoto, M.; Sakamoto, M. *Tetrahedron: Asymmetry* **2013**, *24*, 1520. (h) Zou, Y.; Zhu, F.-L.; Duan, Z.-C.; Wang, Y.-H.; Zhang, D.-Y.; Cao, Z.; Zheng, Z.; Hu, X.-P. *Tetrahedron Lett.* **2014**, *55*, 2033. (i) Shibata, M.; Nakajima, K.; Nishibayashi, Y. *Chem. Commun.* **2014**, *50*, 7874. For examples of etherfication, see: (j) Nakajima, K.; Shibata, M.; Nishibayashi, Y. *J. Am. Chem. Soc.* **2015**, *137*, 2472. (k) Shao, L.; Zhang, D.-Y.; Wang, Y.-H.; Hu, X.-P. *Adv. Synth. Catal.* **2016**, *358*, 2558. For selected examples of alkylation, see: (l) Fang, P.; Hou, X.-L. *Org. Lett.* **2009**, *11*, 4612. (m) Zhu, F.-L.; Wang, Y.-H.; Zhang, D.-Y.; Hu, X.-H.; Chen, S.; Hou, C.-J.; Xu, J.; Hu, X.-P. *Adv. Synth. Catal.* **2014**, *356*, 3231. (n) Zhao, L.; Huang, G.; Guo, B.; Xu, L.; Chen, J.; Cao, W.; Zhao, G.; Wu, X. *Org. Lett.* **2014**, *16*, 5584. (o) Zhu, F.-L.; Zou, Y.; Zhang, D.-Y.; Wang, Y.-H.; Hu, X.-H.; Chen, S.; Xu, J.; Hu, X.-P. *Angew. Chem., Int. Ed.* **2014**, *53*, 1410. (p) Han, F.-Z.; Zhu, F.-L.; Wang, Y.-H.; Zou, Y.; Hu, X.-H.; Chen, S.; Hu, X.-P. *Org. Lett.* **2014**, *16*, 588. (q) Huang, G.; Cheng, C.; Ge, L.; Guo, B.; Zhao, L.; Wu, X. *Org. Lett.* **2015**, *17*, 4894. (r) Shao, L.; Hu, X.-P. *Chem. Commun.* **2017**, *53*, 8192. For examples of arylation, see: (s) Tsuchida, K.; Senda, Y.; Nakajima, K.; Nishibayashi, Y. *Angew. Chem., Int. Ed.* **2016**, *55*, 9728. (t) Shao, L.; Hu, X.-P. *Org. Biomol. Chem.* **2017**, *15*, 9837.

(5) For exceptional examples, see: (a) Kondo, T.; Kanda, Y.; Baba, A.; Fukuda, K.; Nakamura, A.; Wada, K.; Morisaki, Y.; Mitsudo, T. *J. Am. Chem. Soc.* **2002**, *124*, 12960. (b) Inada, Y.; Nishibayashi, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 15172. (c) Yu, Y.-B.; Luo, Z.-J.; Zhang, X. *Org. Lett.* **2016**, *18*, 3302.

(6) For examples, see: (a) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, *122*, 11019. (b) Nishibayashi, Y.; Wakiji, I.; Ishii, Y.; Uemura, S.; Hidai, M. *J. Am. Chem. Soc.* **2001**, *123*, 3393. (c) Sakata, K.; Nishibayashi, Y. *Catal. Sci. Technol.* **2018**, *8*, 12 and also see refs 4d and 13.

(7) (a) Smith, S. W.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 12645. (b) Motoyama, K.; Ikeda, M.; Miyake, Y.; Nishibayashi, Y. *Eur. J. Org. Chem.* **2011**, *2011*, 2239. (c) Sinisi, R.; Vita, M. V.; Gualandi, A.; Emer, E.; Cozzi, P. G. *Chem. - Eur. J.* **2011**, *17*, 7404. (d) Oelke, A. J.; Sun, J.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 2966. For copper-catalyzed stereospecific propargylic arylation of chiral propargylic ammonium salts bearing an internal alkyne group, see: (e) Guisán-Ceinos, M.; Martín-Heras, V.; Tortosa, M. *J. Am. Chem. Soc.* **2017**, *139*, 8448.

(8) For examples, see: (a) Porco, J. A., Jr.; Schoenen, F. J.; Stout, T. J.; Clardy, J.; Schreiber, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 7410. (b) Nicolaou, K. C.; Hwang, C. K.; Smith, A. L.; Wendeborn, S. V. *J. Am. Chem. Soc.* **1990**, *112*, 7416. (c) Jiang, B.; Xu, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2543. (d) Fleming, J. J.; Du Bois, J. *J. Am. Chem. Soc.* **2006**, *128*, 3926 and also see ref 4e.

(9) The asymmetric alkynylation of imines is also an efficient approach to chiral propargylic amines. For reviews, see: (a) Zani, L.; Bolm, C. *Chem. Commun.* **2006**, 4263. (b) Trost, B. M.; Weiss, A. H. *Adv. Synth. Catal.* **2009**, *351*, 963. (c) Blay, G.; Monleon, A.; Pedro, J. R. *Curr. Org. Chem.* **2009**, *13*, 1498.

(10) For palladium-catalyzed stereospecific propargylic amination of chiral propargylic alcohol derivatives bearing an internal alkyne group, see: (a) Marshall, J. A.; Wolf, M. A. *J. Org. Chem.* **1996**, *61*, 3238. (b) Daniels, D. S. B.; Jones, A. S.; Thompson, A. L.; Paton, R. S.; Anderson, E. A. *Angew. Chem., Int. Ed.* **2014**, *53*, 1915.

(11) For examples, see: (a) Elsevier, C. J.; Stehouwer, P. M.; Westmijze, H.; Vermeer, P. *J. Org. Chem.* **1983**, *48*, 1103. (b) Elsevier, C. J.; Kleijn, H.; Boersma, J.; Vermeer, P. *Organometallics* **1986**, *5*, 716. (c) Yoshida, M.; Gotou, T.; Ihara, M. *Tetrahedron Lett.* **2004**, *45*, 5573 and references cited therein, and also see ref 10a.

(12) We propose the formation of η^1-allenylnickel species based on the studies of η^1-allenylpalladium and η^1-allenylplatinum species; see: (a) Kurosawa, H.; Ogoshi, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 973. (b) Chen, J.-T. *Coord. Chem. Rev.* **1999**, *190-192*, 1143. (c) Wojcicki, A. *Inorg. Chem. Commun.* **2002**, *5*, 82.

(13) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 11846 and references cited therein.

(14) We also carried out the reaction of *rac*-**1a** with **2a** in the presence of 2.5 mol % of $Ni(cod)_2$ and 5 mol % of (*R*)-SEGPHOS in tAmOH at 60 °C for 6 h to give (*R*)-**3aa** in 41% yield with 95% ee (52% conversion). We confirmed that the enantiomeric excess of recovered **1a** was 3%.

(15) Ogoshi, S.; Nishida, T.; Shinagawa, T.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 7164.

(16) Schley, N. D.; Fu, G. C. *J. Am. Chem. Soc.* **2014**, *136*, 16588.

DOI: 10.1021/acs.orglett.8b02325
Org. Lett. XXXX, XXX, XXX−XXX