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Enantioselective Allylic Amination of Trifluoromethyl Group Substituted Racemic and Unsymmetrical 1,3-Disubstituted Allylic Esters by Palladium Catalysts

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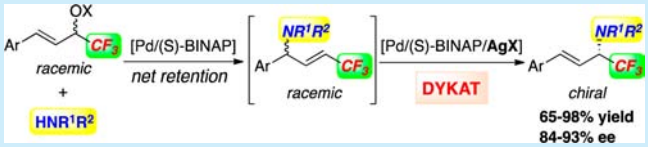
Supporting Information

ABSTRACT: The palladium-catalyzed regio- and enantioselective allylic amination of trifluoromethyl group substituted racemic and unsymmetrical 1,3-disubstituted allylic esters has been accomplished. The enantioselective formation of the α-type allylic amines was attained by the dynamic kinetic asymmetric transformation (DYKAT).



The palladium-catalyzed asymmetric allylic substitution reaction is a powerful synthetic method to construct chiral carbon−carbon or chiral carbon−heteroatom bonds, and several types of reactions have been reported.[1] Although there are many reports about the asymmetric allylic substitutions of symmetrical 1,3-disubstituted allylic esters[2] or monosubstituted allylic esters,[3] there are only limited examples of the asymmetric reaction for the unsymmetrical 1,3-disubstituted allylic esters.[4,5] In particular, the asymmetric reaction of racemic and acyclic unsymmetrical 1,3-disubstituted allylic esters is still very rare because the reaction generally proceeds via a net retention (double inversion) mechanism[4] or kinetic resolution process,[5,6] and there are only limited examples of the palladium-catalyzed dynamic kinetic asymmetric transformation (DYKAT).[7−9] For example, Hoberg[9a] and Gais[9b] reported the palladium-catalyzed DYKAT of acyclic unsymmetrical 1,3-disubstituted allylic substrates with oxygen nucleophiles, and the reactions with carbon nucleophiles were demonstrated by Pucheault in 2011.[9c] More recently, Liao realized the allylic indolylation of acyclic unsymmetrical 1,3-disubstituted allylic substrates.[9d] However, to the best our knowledge, there is no clear report about the palladium-catalyzed DYKAT of acyclic unsymmetrical 1,3-disubstituted allylic substrates with nitrogen nucleophiles in high yield.[10] On the other hand, we have studied the palladium-catalyzed regioselective allylic substitution of fluorine-containing allylic esters[11] and reported the regioselective allylic amination of the trifluoromethyl group substituted unsymmetrical 1,3-disubstituted allylic esters including the synthesis of an enatiomerically enriched product from a chiral substrate.[4g,6i,11b] During the course of our studies, we achieved the palladium-catalyzed allylic amination of the racemic trifluoromethyl group substituted unsymmetrical 1,3-disubstituted allylic esters that provide enatiomerically enriched allylic amines with both a high yield and enantioselectivity by DYKAT.

Based on our previous study,[6i] we first conducted the allylic amination of the trifluoromethyl group containing the racemic allyl ester **1a** with 1-phenylpiperazine (**2a**) by $[Pd(C_3H_5)(cod)]BF_4$ with (*S*)-BINAP at 25 °C, and the mixture of the γ-prodcut **3aa** (6% ee) and α-product **4aa** (94% ee) was obtained with a low regioselectivity (Table 1, entry 1). Although the yield of **4aa** was low, the formation of the enantiomerically enriched product from the racemic substrate is interesting and suggests that the reaction proceeds through the deracemization pathway; therefore, we attempted to obtain the enantiomerically enriched α-product in a high yield with a high enantioselectivity. The reaction at elevated temperature increased both the yield and α-selectivity, but the enantiomeric excess of **4aa** decreased (entries 2 and 3). We further examined other palladium catalysts and found that the combination of $[Pd(C_3H_5)Cl]_2$ with a silver salt effectively increased the yield of **4aa** with a high enantiomeric excess (entries 4 and 5). Although the role of silver salt is not clear, the reaction with the addition of 5 mol % of $AgPF_6$ exhibited better results and provided **4aa** in 88% isolated yield (91% α-selectivity) with 93% ee (entry 6). We also examined the reaction without silver salt and confirmed that the reaction proceeds with a low α-selectivity (8%) (entry 7).

With these optimized reaction conditions in hand, we investigated the asymmetric allylic amination of racemic **1a** with several amines. As shown in Table 2, reactions with the optimized catalyst with six-membered cyclic amines, such as morpholine (**2b**), 1-methylpiperazine (**2c**), or 4-phenylpiperidine (**2d**), smoothly proceeded and produced the desired α-products **4ab**, **4ac**, and **4ad** with good enantioselectivities (Table 2, entries 1−3). The reaction of **1a** with pyrrolidine (**2e**) also exhibited a high enantioselectivity, but the yield was

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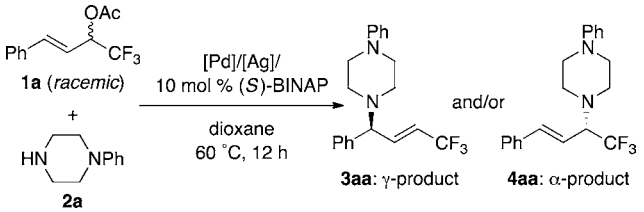
Table 1. Palladium-Catalyzed Allylic Amination of *rac*-1a with 2a



entry	[Pd] (mol %), [Ag] (mol %)	3:4[a]	yield[a] (%) of (3 + 4)	ee[b] (%) of 4aa
1[c]	$[Pd(C_3H_5)(cod)]BF_4$ (10)	77:23	69	94
2[d]	$[Pd(C_3H_5)(cod)]BF_4$ (10)	38:62	>98	87
3	$[Pd(C_3H_5)(cod)]BF_4$ (10)	9:91	>98	67
4	$[Pd(C_3H_5)Cl]_2$ (5), $AgBF_4$ (10)	33:67	94	77
5	$[Pd(C_3H_5)Cl]_2$ (5), $AgBF_4$ (5)	8:92	>98	86
6	$[Pd(C_3H_5)Cl]_2$ (5), $AgPF_6$ (5)	9:91	95 (88)[e]	93
7	$[Pd(C_3H_5)Cl]_2$ (5)	92:8	>98	87

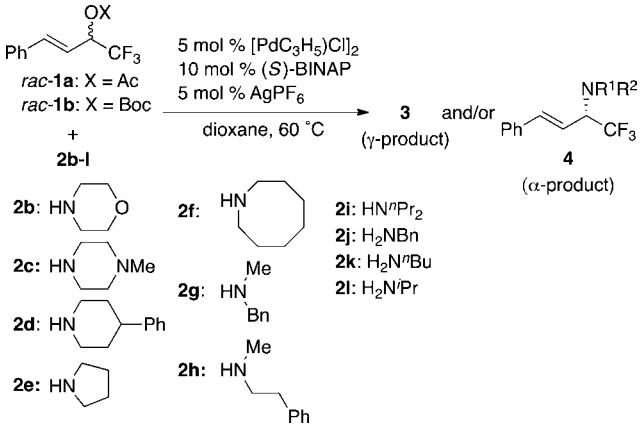
[a]The yields and ratios were determined by ^{1}H NMR of the crude materials using an internal standard. [b]Determined by HPLC. [c]The reaction was conducted at 25 °C. [d]The reaction was conducted at 40 °C. [e]Isolated yield in parentheses.

low due to deacylation of the allyl substrate **1a** with amine (entry 4). Fortunately, changing the leaving group of the allyl substrate from acetate to *tert*-butyl carbonate prevented the side reaction, and a good yield was then obtained (entry 5). The reaction with acyclic secondary amines **2g−i** also afforded the intended enantiomerically enriched α-products in moderate to good yields with a high ee value (entries 7−10). We further established that high enantioselectivities were attained for the reactions of **1b** with primary amines **2j−l** (entries 11−13).

We next examined the reaction of other trifluoromethyl group substituted allyl acetates with **2a** (Table 3). The reactions of 1,1,1-trifluoro-4-arylbut-3-en-2-yl acetates **1c−f** with **2a** smoothly proceeded and provided the desired allylic amines in good yields with high ee values (entries 1−4). Unfortunately, we confirmed that **1g**, which has an alkyl group at the C-3 position instead of an aryl group, exhibited a low reactivity and produced the γ-product **3ga** (entry 5). The reaction of (*Z*)-**1a** gave a (*S*)-**4aa** in 90% yield with 91% ee, and the regioisomeric allyl acetate *rac*-**5** also provided (*S*)-**4aa** in 80% yield with 87% ee (entries 6 and 7). These results suggest that the reaction proceeds through the same reaction pathway including the π-allylpalladium intermediate.

To clarify the deracemization step in this enantioselective reaction of the racemic substrate, we examined the isomerization reaction of *rac*- or (*R*)-**3aa** (96% ee) (γ-product) to α-product **4aa** under several catalyst conditions (Table 4). We first confirmed that the isomerization had not occurred by the combinations of $[Pd(C_3H_5)Cl]_2/AgPF_6$ or $AgPF_6$/BINAP and recovered (*R*)-**3aa** without decreasing the ee value (entries 1 and 2). However, we observed that the racemization of (*R*)-**3aa** had occurred using the $[Pd(C_3H_5)Cl]_2$/BINAP catalyst without isomerization to the α-product **4aa** (entry 3). These results suggest that the BINAP-ligated palladium catalyst caused the epimerization between (*R*)-**3aa** and (*S*)-**3aa**. We further treated *rac*-**3aa** and (*R*)-**3aa** with $[Pd(C_3H_5)Cl]_2$/(*S*)-BINAP/$AgPF_6$

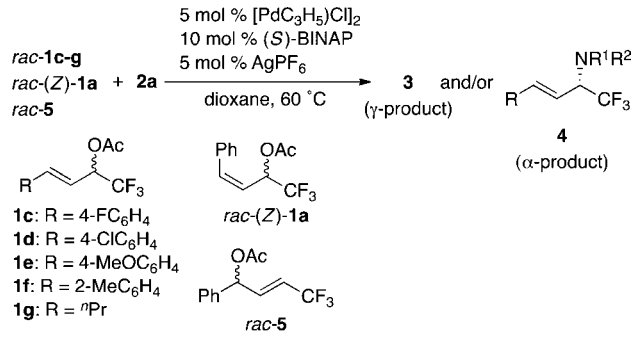
Table 2. Palladium-Catalyzed Enantioselective Allylic Amination of *rac*-1 with Several Amines



entry	1	2	time (h)	3:4[a]	yield[a,b] (%) of (3 + 4)	% ee[c] of 4
1	**1a**	**2b**	12	12:88	98 (83)	91 (**4ab**)
2	**1a**	**2c**	24	9:91	98 (82)	89 (**4ac**)
3	**1a**	**2d**	24	5:95	94 (90)	86 (**4ad**)
4	**1a**	**2e**	24	26:74	49 (41)	91 (**4ae**)
5	**1b**	**2e**	24	10:90	98 (77)	87 (**4ae**)
6	**1a**	**2f**	24	4:96	75 (59)	85 (**4af**)
7	**1a**	**2g**	24	7:93	90 (85)	91 (**4ag**)
8	**1a**	**2h**	36	7:93	90 (80)	87 (**4ah**)
9	**1a**	**2i**	72	8:92	60 (49)	86 (**4ai**)
10	**1b**	**2i**	72	8:92	65 (50)	86 (**4ai**)
11	**1b**	**2j**	96	3:97	77 (76)	93 (**4aj**)
12	**1b**	**2k**	36	2:>98	80 (58)	91 (**4ak**)
13	**1b**	**2l**	48	2:>98	67 (56)	92 (**4al**)

[a]The yields and ratios were determined by ^{1}H NMR of the crude materials using an internal standard. [b]Isolated yield in parentheses. [c]Determined by HPLC.

Table 3. Palladium-Catayzed Enantioselective Allylic Amination of Several Allylic Acetates with 2a



entry	1, 5	time (h)	3:4	yield[a,b] (%) of (3 + 4)	% ee[c] of 4
1	**1c**	42	8:92	98 (81)	88 (**4ca**)
2	**1d**	24	10:90	88 (83)	89 (**4da**)
3	**1e**	36	11:89	96 (88)	90 (**4ea**)
4	**1f**	36	5:95	85 (80)	84 (**4fa**)
5	**1g**	12	>98:2	31	nd
6	(*Z*)-**1a**	12	13:87	98 (90)	91 (**4aa**)
7	**5**	24	23:77	82 (80)	87 (**4aa**)

[a]The yields and ratios were determined by ^{1}H NMR of the crude materials using an internal standard. [b]Isolated yield in parentheses. [c]Determined by HPLC.

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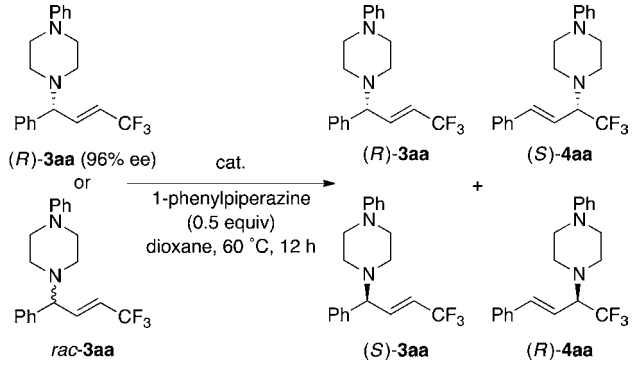
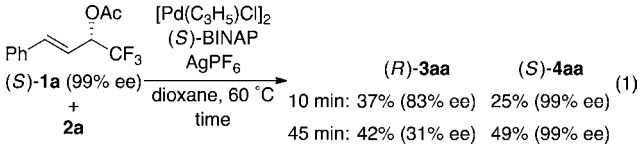
Table 4. Isomerization of 3aa to 4aa



entry	3aa	cat. (mol %)	yield[a] (%)/ee[b] of 3aa	4aa
1	*R*	$[Pd(C_3H_5)Cl]_2$ (5) $AgPF_6$ (5)	98/95 ee (*R*)	0
2	*R*	(*S*)-BINAP (10) $AgPF_6$ (5)	98/96 ee (*R*)	0
3	*R*	$[Pd(C_3H_5)Cl]_2$ (5) (*R*)-BINAP (10)	93/17 ee (*R*)	0
4	*R*	$AgPF_6$ (5)	90/96 ee (*R*)	0
5	*rac*	$[Pd(C_3H_5)Cl]_2$ (5) (*S*)-BINAP (10) $AgPF_6$ (5)	10/9 ee (*S*)	96/93 ee (*S*)
6	*R*	$[Pd(C_3H_5)Cl]_2$ (5) (*S*)-BINAP (10) $AgPF_6$ (5)	7/10 ee (*S*)	89/92 ee (*S*)
7	*R*	$[Pd(C_3H_5)Cl]_2$ (5) (*R*)-BINAP (10) $AgPF_6$ (5)	8/10 ee (*R*)	89/89 ee (*R*)

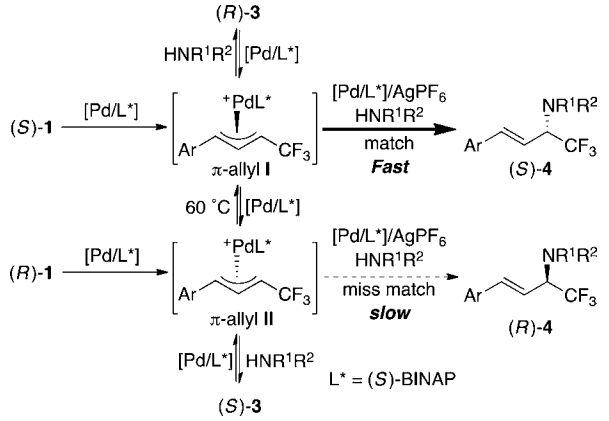
[a]The yields were determined by ^{1}H NMR of the crude materials using an internal standard. [b]Determined by HPLC.

and confirmed that both reactions afforded the enantiomerically enriched (*S*)-**4aa** with 93% ee and 92% ee, respectively (entries 5 and 6). On the other hand, another isomerization reaction, which was conducted by changing the (*S*)-BINAP to (*R*)-BINAP, provided (*R*)-**4aa** with 89% ee (entry 7). Furthermore, we examined the reaction of (*S*)-**1a** (99% ee) and observed that the enantiomerc excess of γ-product (*R*)-**3aa** was lost immediately under the optimized catalyst conditions; the value of enantiomeric excess of (*R*)-**3aa** was 83% ee and 31% ee after 10 min[12] and 45 min, respectively (eq 1).



Based on these results and our previous work, we propose the possible reaction pathway for the formation of the enantiomerically enriched α-product (*S*)-**4** from the racemic allyl acetate **1** by (*S*)-BINAP as follows (Scheme 1): (1) The CF_3-group substituted π-allylpalladium intermediate **I** and **II**[13] were formed at the first step. (2) The π-allyl complex **I** provided both enantiomericallyl enriched (*R*)-**3** and (*S*)-**4** with a certain ratio by a net retention mechanism. (3) A rapid interconversion between π-allylpalladium complex **I** and **II** also occurred before the attack of nitrogen nucleophiles due to the Pd(0)/BINAP catalyst at 60 °C.[8g,9b,14] (4) The γ-product **3** also reformed π-allylpalladium complex with the C−N bond

Scheme 1. Possible Reaction Pathway of Enantioselective Allylic Amination by DYKAT



cleavage,[15] and the interconversion between (*R*)-**3** and (*S*)-**3** through the π-allyl complex **I** and **II** proceeded. (5) A highly selective dynamic kinetic resolution took place during the isomerization from **3** to **4** with Pd/chiral-BINAP/$AgPF_6$. Overall, the allylic amination of the racemic trifluoromethyl group containing allylic ester **1** proceeded through the dynamic kinetic asymmetric transformation (DYKAT) and provided the enantiomerically enriched α-product (*S*)-**4** in high yield with a high enantiomeric excess.

In conclusion, we demonstrated the enantioselective allylic amination of the racemic trifluoromethyl group containing allyl esters with amines using the $[Pd(C_3H_5)Cl]_2$/(*S*)-BINAP/$AgPF_6$ catalyst. The reaction proceeds through the dynamic kinetic asymmetric transformation (DYKAT) and the enantiomerically enriched α-type allylic amines in a high yield with a high ee value. Further investigation of the mechanistic details and reaction with other nucleophiles will be the subject of a future study.

■ 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.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (b) Johannsen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689. (c) Hayashi, T. *J. Organomet. Chem.* **1999**, *576*, 195. (d) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336. (e) Dai, L.-X.; Tu, T.; You, S.-L.; Deng, W.-P.; Hou, X.-L. *Acc. Chem. Res.* **2003**, *36*, 659. (f) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921. (g) Trost, B. M. *J.*

dx.doi.org/10.1021/ol5008229 | *Org. Lett.* 2014, 16, 2442−2445

Org. Chem. **2004**, *69*, 5813. (h) Trost, B. M.; Machacek, M. R.; Aponick, A. *Acc. Chem. Res.* **2006**, *39*, 747. (i) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258. (j) Diéguez, M.; Pàmies, O. *Acc. Chem. Res.* **2010**, *43*, 312.

(2) For selected examples of Pd-catalyzed asymmetric substitution of symmetrical 1,3-disubstituted allylic substrates, see: (a) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031. (b) Bremberg, U.; Larhed, M.; Moberg, C.; Hallberg, A. *J. Org. Chem.* **1999**, *64*, 1082. (c) Ogasawara, M.; Yoshida, K.; Hayashi, T. *Organometallics* **2001**, *20*, 3913. (d) Oobora, N.; Katagiri, K.; Imamoto, T. *Tetrahedron: Asymmetry* **2003**, *14*, 2171. (e) Molander, G. A.; Burke, J. P.; Carroll, P. J. *J. Org. Chem.* **2004**, *69*, 8062. (f) Hayashi, T.; Suzuka, T.; Okada, A.; Kawatsura, M. *Tetrahedron: Asymmetry* **2004**, *15*, 545. (g) Imamoto, T.; Nishimura, M.; Koide, A.; Yoshida, K. *J. Org. Chem.* **2007**, *72*, 7413. (h) Trost, B. M.; Thaisrivongs, D. A. *J. Am. Chem. Soc.* **2008**, *130*, 14092. (i) Caldentey, X.; Pericàs, M. A. *J. Org. Chem.* **2010**, *75*, 2628. (j) Liu, Z.; Du, H. *Org. Lett.* **2010**, *12*, 3054. (k) Trost, B. M.; Thaisrivongs, D. A.; Hartwig, J. *J. Am. Chem. Soc.* **2011**, *133*, 12439. (l) Wang, Y.; Vaismaa, M. J. P.; Hämäläinen, A. M.; Tois, J. E.; Franzén, R. *Tetrahedron: Asymmetry* **2011**, *22*, 524. (m) Shi, C.; Chien, C.-W.; Ojima, I. *Chem.—Asian J.* **2011**, *6*, 674. (n) Lega, M.; Margalef, J.; Ruffo, F.; Pàmies, O.; Diéguez, M. *Tetrahedron: Asymmetry* **2013**, *24*, 995. (o) Philipova, I.; Stavrakov, G.; Dimitrov, V. *Tetrahedron: Asymmetry* **2013**, *24*, 1253. (p) Bravo, M. J.; Favier, I.; Saffon, N.; Ceder, R. M.; Muller, G.; Gómez, M.; Rocamora, M. *Organometallics* **2014**, *33*, 771.

(3) For selected examples of Pd-catalyzed asymmetric substitution of monosubstituted allylic substrates. see: (a) Hayashi, T.; Kishi, K.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1990**, *31*, 1743. (b) Prétôt, R.; Pfaltz, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 323. (c) Prétôt, R.; Lloyd-Jones, G. C.; Pfaltz, A. *Pure Appl. Chem.* **1998**, *70*, 1035. (d) Hayashi, T.; Kawatsura, M.; Uozumi, Y. *Chem. Commun.* **1997**, 561. (e) Kuwano, R.; Uchida, K.; Ito, Y. *Org. Lett.* **2003**, *5*, 2177. (f) Faller, J. W.; Wilt, J. C.; Parr, J. *Org. Lett.* **2004**, *6*, 1301. (g) Hou, X.-L.; Sun, N. *Org. Lett.* **2004**, *6*, 4399. (h) Zheng, W.-H.; Sun, N.; Hou, X.-L. *Org. Lett.* **2005**, *7*, 5151. (i) You, S.-L.; Zhu, X.-Z.; Luo, Y.-M.; Hou, X.-L.; Dai, L.-X. *J. Am. Chem. Soc.* **2001**, *123*, 7471. (j) Zheng, W.-H.; Zheng, B.-H.; Zhang, Y.; Hou, X.-L. *J. Am. Chem. Soc.* **2007**, *129*, 7718. (k) Liu, W.; Chen, D.; Zhu, X.-Z.; Wan, X.-L.; Hou, X.-L. *J. Am. Chem. Soc.* **2009**, *131*, 8734. (l) Lei, B.-L.; Ding, C.-H.; Yang, X.-F.; Wan, X.-L.; Hou, X.-L. *J. Am. Chem. Soc.* **2009**, *131*, 18250. (m) Chen, J.-P.; Ding, C.-H.; Liu, W.; Hou, X.-L.; Dai, L.-X. *J. Am. Chem. Soc.* **2010**, *132*, 15493. (n) Wang, X.; Meng, F.; Wang, Y.; Han, Z.; Chen, Y.-J.; Liu, L.; Wang, Z.; Ding, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 9276. (o) Tao, Z.-L.; Zhang, W.-Q.; Chen, D.-F.; Adele, A.; Gong, L.-Z. *J. Am. Chem. Soc.* **2013**, *135*, 9255. (p) Yu, Y.; Yang, X.-F.; Xu, C.-F.; Ding, C.-H.; Hou, X.-L. *Org. Lett.* **2013**, *15*, 3880. (q) Wang, X.; Guo, P.; Han, Z.; Wang, X.; Wang, Z.; Ding, K. *J. Am. Chem. Soc.* **2014**, *136*, 405.

(4) For selected examples of net retention mechanism in the Pd-catalyzed allylic substitution, see: (a) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767. (b) Hayashi, T.; Yamamoto, A.; Hagihara, T. *J. Am. Chem. Soc.* **1986**, *51*, 723. (c) Kazmaier, U.; Zumpe, F. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 802. (d) Konno, T.; Nagata, K.; Ishihara, T.; Yamanaka, H. *J. Org. Chem.* **2002**, *67*, 1768. (e) Kawatsura, M.; Ikeda, D.; Ishii, T.; Komatsu, Y.; Uenishi, J. *Synlett* **2006**, 2435. (f) Amatore, C.; Génin, E.; Jutand, A.; Mensah, L. *Organometallics* **2007**, *26*, 1875. (g) Hirakawa, T.; Ikeda, K.; Ogasa, H.; Kawatsura, M.; Itoh, T. *Synlett* **2010**, 2887.

(5) For selected reviews on metal-catalyzed kinetic resolutions, see: (a) Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1988**, *18*, 249. (b) Cook, G. R. *Curr. Org. Chem.* **2000**, *4*, 869. (c) Keith, J. M.; Larrow, J. F.; Jacobsen, E. N. *Adv. Synth. Catal.* **2001**, *343*, 5. (d) Robinson, D. E. J. E.; Bull, S. D. *Tetrahedron: Asymmetry* **2003**, *14*, 1407.

(6) For selected examples of Pd-catalyzed kinetic resolution of allylic substrates: (a) Hayashi, T.; Yamamoto, A.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1090. (b) Ramdeehul, S.; Dierkes, P.; Aguado, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Osborn, J. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 3118. (c) Gais, H.-J.; Spalthoff, N.; Jagusch, T.; Frank, M.; Raabe, G. *Tetrahedron Lett.* **2000**, *41*, 3809. (d) Dominguez, B.; Hodnett, N. S.; Lloyd-Jones, G. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 4289. (e) Lüssem, B.; Gais, H.-J. *J. Am. Chem. Soc.* **2003**, *125*, 6066. (f) Gais, H.-J.; Jagusch, T.; Spalthoff, N.; Gerhards, F.; Frank, M.; Raabe, G. *Chem.—Eur. J.* **2003**, *9*, 4202. (g) Hou, X. L.; Zheng, B. H. *Org. Lett.* **2009**, *11*, 1789. (h) Lei, B.-L.; Ding, C.-H.; Yang, X.-F.; Wan, X.-L.; Hou, X.-L. *J. Am. Chem. Soc.* **2009**, *131*, 18250. (i) Hirakawa, T.; Ikeda, K.; Ikeda, D.; Tanaka, T.; Ogasa, H.; Kawatsura, M.; Itoh, T. *Tetrahedon* **2011**, *67*, 8238. (j) Mao, B.; Ji, Y.; Fañanás-Mastral, M.; Caroli, G.; Meersma, A.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2012**, *51*, 3168.

(7) For reviews on palladium-catalyzed dynamic kinetic resolution of allylic substrates, see: (a) Trost, B. M.; Fandrick, D. R. *Aldrichimica Acta* **2007**, *40*, 59. (b) Gais, H.-J. In *Asymmetric Synthesis with Chemical and Biological Methods*; Enders, D., Jaeger, K.-E., Ed.; Wiley-VCH: Weinheim, 2007; p 215.

(8) For selected examples of dynamic kinetic resolution in palladium-catalyzed of allylic substitutions, see: (a) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1999**, *121*, 3543. (b) Cook, G. R.; Shanker, P. S.; Pararajasingham, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 110. (c) Choi, Y. K.; Suh, J. H.; Lee, D.; Lim, I. T.; Jung, J. Y.; Kim, M.-J. *J. Org. Chem.* **1999**, *64*, 8423. (d) Trost, B. M.; Tsui, H.-C.; Toste, F. D. *J. Am. Chem. Soc.* **2000**, *122*, 3534. (e) Trost, B. M.; Dudash, J.; Hembre, E. J. *Chem.—Eur. J.* **2001**, *7*, 1619. (f) Trost, B. M.; Crawley, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 9328. (g) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2003**, *125*, 3090. (h) Trost, B. M.; Brown, B. S.; McEachern, E. J.; Kuhn, O. *Chem.—Eur. J.* **2003**, *9*, 4442. (i) Kim, M.-J.; Kim, W.-H.; Han, K.; Choi, Y. K.; Park, J. *Org. Lett.* **2007**, *9*, 1157. (j) Trost, B. M.; Malhotra, S.; Olson, D. E.; Maruniak, A.; Du Bois, J. *J. Am. Chem. Soc.* **2009**, *131*, 4190. (k) Mangion, I.; Strotman, N.; Drahl, M.; Imbriglio, J.; Guidry, E. *Org. Lett.* **2009**, *11*, 3258.

(9) (a) Dong, Y.; Teesdale-Spittle, P.; Hoberg, J. O. *Tetrahedron Lett.* **2005**, *46*, 353. (b) Gais, H.-J.; Bondarev, O.; Hetzer, R. *Tetrahedron Lett.* **2005**, *46*, 6279. (c) Kukkadapu, K. K.; Ouach, A.; Lozano, P.; Vaultier, M.; Pucheault, M. *Org. Lett.* **2011**, *13*, 4132. (d) Du, L.; Cao, P.; Xing, J.; Lou, Y.; Jiang, L.; Li, L.; Liao, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 4207.

(10) Hoberg demonstrated the palladium-catalyzed enantioselective allylic amination of 1,3-disubstituted allylic substrate in ref 9a, but the yield is up to 52% and it is not clear if their reaction proceeded through the kinetic resolution or DYKAT.

(11) (a) Kawatsura, M.; Wada, S.; Hayase, S.; Itoh, T. *Synlett* **2006**, 2483. (b) Kawatsura, M.; Hirakawa, T.; Tanaka, T.; Ikeda, D.; Hayase, S.; Itoh, T. *Tetrahedron Lett.* **2008**, *49*, 2450. (c) Yamamoto, M.; Hayashi, S.; Isa, K.; Kawatsura, M. *Org. Lett.* **2014**, *16*, 700.

(12) We also confirmed that 25% of (*S*)-**1a** (99% ee) remained.

(13) Our several trials for observing and/or isolating the CF_3-group-containing π-allylpalladium complexes failed, and the details of the reaction mechanism have not yet been clarified.

(14) Granberg, K. L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1992**, *114*, 6858.

(15) For recent examples of C−N bond cleavage of allylic amines, see: (a) Bao, H.; Qi, X.; Tambar, U. K. *J. Am. Chem. Soc.* **2011**, *133*, 1206. (b) Zhao, X.; Liu, D.; Guo, H.; Liu, Y.; Zhang, W. *J. Am. Chem. Soc.* **2011**, *133*, 19354. (c) Wu, X.-S.; Chen, Y.; Li, M.-B.; Zhou, M.-G.; Tian, S.-K. *J. Am. Chem. Soc.* **2012**, *134*, 14694.