ChemPubSoc Europe

DOI: 10.1002/ejoc.201701177

EurJOC European Journal of Organic Chemistry

Communication

Asymmetric Catalysis

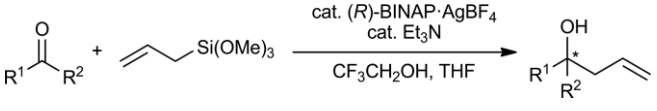
Asymmetric Allylation of Carbonyl Compounds Catalyzed by a Chiral Phosphine–Silver Complex

Akira Yanagisawa,*[a] Nan Yang,[a] and Kentaro Bamba[a]

Abstract: A catalytic, asymmetric allylation reaction of aldehydes or ketones with allyltrimethoxysilane was achieved by using a BINAP•$AgBF_4$ [BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] complex as the chiral precatalyst and triethylamine as the base precatalyst in the presence of 2,2,2-trifluoroethanol. Optically active homoallylic alcohols with up to 95 % *ee* were obtained in moderate to high yields through the in situ generated chiral allyl silver catalyst.

Introduction

The asymmetric allylation of carbonyl compounds is a useful method to obtain optically active homoallylic alcohols, which are frequently observed in natural products and other important organic molecules.[1] Various processes for the catalytic asymmetric addition of allylic stannanes or silanes to aldehydes or ketones have been reported to furnish such chiral allylated products in high yields and satisfactory optical purity; however, most of these processes use chiral Lewis acid catalysts[2] or chiral Lewis base catalysts,[3] and only a few employ chiral Brønsted acid catalysts.[4] The first example of the chiral silver(I)-catalyzed asymmetric allylation of aldehydes was reported by Yamamoto and Yanagisawa and colleagues, who found that a 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP)–silver(I) complex behaved as an efficient chiral Lewis acid catalyst.[5] Since then, diverse chiral phosphine–silver(I) complexes have been utilized as chiral catalysts in carbon–carbon bond-forming reactions.[6] Although these allylation reactions are able to yield the corresponding nonracemic products with high enantioselectivity, they have a disadvantage in that they require environmentally hazardous organotin reagents. To solve this problem, a Tol-BINAP•AgF-catalyzed enantioselective Sakurai–Hosomi-type allylation reaction of aldehydes was developed, in which allyltrimethoxysilane was used as the allyl donor.[7] We report herein the asymmetric allylation of aldehydes or ketones by using a BINAP•$AgBF_4$ complex as the chiral precatalyst and triethylamine as the base precatalyst in the presence of 2,2,2-trifluoroethanol (Scheme 1).



Scheme 1. Enantioselective allylation of carbonyl compounds with allyltrimethoxysilane catalyzed by a (*R*)-BINAP•$AgBF_4$ complex.

Results and Discussion

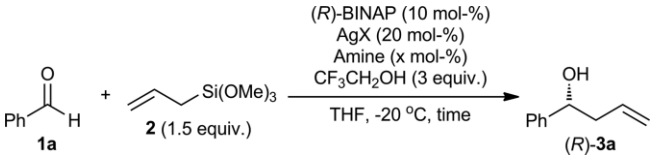
We reported that the BINAP•AgOMe complex could act as a catalyst in the presence of MeOH and a catalytic amount of *N*,*N*-diisopropylethylamine in the aldol reaction of alkenyl trihaloacetates with aldehydes.[8] The reaction was considered to take place via a chiral silver enolate and a BINAP•AgOMe complex was regenerated with the assistance of MeOH. We envisioned that if a chiral phosphine–allyl silver complex could be formed from a chiral phosphine–silver alkoxide complex and an allylsilane, and if an allylated product, a silver alkoxide of a homoallylic alcohol, could be readily protonated by an alcohol, the chiral silver alkoxide-catalyzed asymmetric allylation of aldehydes would be possible. Thus, we initially attempted to generate a BINAP•$AgOCH_2CF_3$ complex from BINAP, silver trifluoromethanesulfonate (AgOTf), and CF_3CH_2OH and to use it as a chiral catalyst in the reaction of allyltrimethoxysilane (**2**) with benzaldehyde (**1a**). Upon treating a 1.5:1 mixture of allyltrimethoxysilane (**2**)/benzaldehyde (**1a**) with (*R*)-BINAP (10 mol-%) and AgOTf (20 mol-%) in the presence of *N*,*N*-diisopropylethylamine (40 mol-%) and CF_3CH_2OH (3 equiv.) in THF at –20 °C for 20 h, desired (*R*)-1-phenyl-3-buten-1-ol [(*R*)-**3a**] was obtained in 8 % yield with 6 % *ee* (Table 1, entry 1). Then, we examined which silver salt would facilitate the generation of an allyl silver species and increase the chemical yield of homoallylic alcohol **3a**. We found that target product **3a** was obtained in 70 % yield if $AgBF_4$ was used as the silver salt (Table 1, entry 4). Even more significant was that the silver salt gave the (*R*)-enriched product with remarkable enantioselectivity (94 % *ee*). To attain better results, we next focused on the effect of a tertiary amine as an additive. Reducing the amount of *N*,*N*-diisopropylethylamine to 20 mol-% still gave (*R*)-**3a** in 61 % yield without any loss in the enantiomeric excess (Table 1, entry 5). However, in the absence of the amine, the desired adduct was not obtained at all (Table 1, entry 6). Among the amines (20 mol-%) tested, *N*,*N*-

[a] *Molecular Chirality Research Center, Department of Chemistry, Graduate School of Science, Chiba University*
Inage, Chiba 263-8522, Japan
E-mail: ayanagi@faculty.chiba-u.jp
http://moon.gmobb.jp/ohba/yanagisawa/index.html

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejoc.201701177.

dicyclohexylmethylamine (Cy_2NMe and Et_3N provided the best results with regard to chemical yield and enantiomeric excess (Table 1, entries 9 and 11). Decreasing the Et_3N loading to 10 mol-% further improved the enantioselectivity (Table 1, entry 12).

Table 1. Optimization of reaction conditions: silver salts and amines.[a]



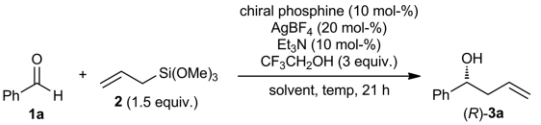
Entry	AgX	Amine (mol-%)	Time [h]	Yield[b] [%]	*ee*[c] [%]
1	AgOTf	iPr_2NEt (40)	20	8	6
2	$AgSbF_6$	iPr_2NEt (40)	19	<1	–
3	AgOAc	iPr_2NEt (40)	21	<1	–
4	$AgBF_4$	iPr_2NEt (40)	21	70	94
5	$AgBF_4$	iPr_2NEt (20)	21	61	94
6	$AgBF_4$	–	21	<1	–
7	$AgBF_4$	iPr_2NH (20)	21	48	94
8	$AgBF_4$	$CyNMe_2$ (20)	21	63	69
9	$AgBF_4$	Cy_2NMe (20)	21	83	95
10	$AgBF_4$	pyridine (20)	21	16	15
11	$AgBF_4$	Et_3N (20)	21	83	95
12	$AgBF_4$	Et_3N (10)	21	77	96
13	$AgBF_4$	Et_3N (40)	21	79	81

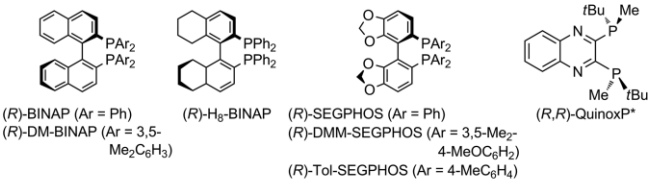
[a] Unless otherwise specified, the reaction was performed with (*R*)-BINAP (10 mol-%), silver salt (20 mol-%), benzaldehyde (**1a**, 1 equiv.), allyltrimethoxysilane (**2**, 1.5 equiv.), amine, and 2,2,2-trifluoroethanol (3 equiv.) in THF at –20 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis.

Subsequently, we investigated the asymmetric induction ability of chiral phosphines other than BINAP and reconfirmed that BINAP was the chiral ligand of choice (Table 2, entry 1 vs. entries 2–7). DM-BINAP was also a possible alternative in terms of chemical yield and enantioselectivity (Table 2, entry 3). In contrast, the use of QuinoxP* led to unsatisfactory results, and allylated product (*R*)-**3a** was obtained in 9 % yield with low optical purity (Table 2, entry 7). Then, we studied the reaction conditions, particularly the optimum solvent and temperature. Initially, we inspected the appropriateness of toluene and dichloromethane as solvents in place of THF, because less-polar solvents were expected to be more suitable for the formation of a rigid transition-state structure. However, we found that those less-polar solvents were disadvantageous from the point of view of enantioselectivity and yield of the product (Table 2, entries 8 and 9 vs. entry 1). Lowering the reaction temperature to –40 °C resulted in a significant deceleration of the reaction (Table 2, entry 12 vs. 1). There was no substantial damage to the enantioselectivity if the reaction was performed at 0 °C (Table 2, entry 13).

We further studied the ratio of BINAP to $AgBF_4$, and the results are shown in Table 3. If the amount of BINAP was increased to 20 mol-%, the yield of isolated product (*R*)-**3a** decreased slightly without any loss in enantioselectivity (Table 3, entry 1 vs. 3). A 1:1 mixture of (*R*)-BINAP (10 mol-%)/$AgBF_4$ (10 mol-%) still induced the allylation with 90 % *ee*, but the product was isolated in a lower yield (42 %; Table 3, entry 4).

Table 2. Optimization of reaction conditions: chiral phosphines, solvents, and temperatures.[a]





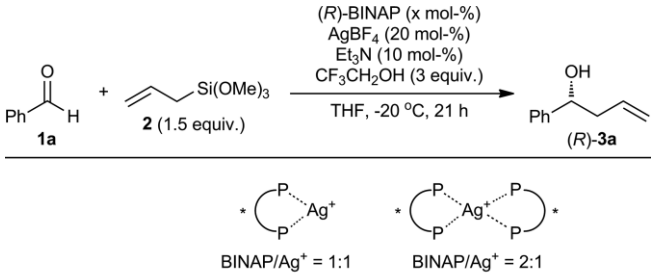
Entry	Chiral phosphine	Solvent	*T* [°C]	Yield[b] [%]	*ee*[c] [%]
1	(*R*)-BINAP	THF	–20	77	96
2	(*R*)-H_8-BINAP	THF	–20	77	88
3	(*R*)-DM-BINAP	THF	–20	71	94
4	(*R*)-SEGPHOS	THF	–20	59	79
5	(*R*)-DMM-SEGPHOS	THF	–20	56	85
6	(*R*)-Tol-SEGPHOS	THF	–20	60	71
7	(*R*,*R*)-QuinoxP*	THF	–20	9	10
8	(*R*)-BINAP	toluene	–20	39	78
9	(*R*)-BINAP	CH_2Cl_2	–20	6	88
10	(*R*)-BINAP	DMF	–20	7	30
11	(*R*)-BINAP	ether	–20	<1	–
12	(*R*)-BINAP	THF	–40	5	–
13	(*R*)-BINAP	THF	0	67	94

[a] Unless otherwise specified, the reaction was performed with chiral phosphine (10 mol-%), silver tetrafluoroborate (20 mol-%), benzaldehyde (**1a**, 1 equiv.), allyltrimethoxysilane (**2**, 1.5 equiv.), triethylamine (10 mol-%), and 2,2,2-trifluoroethanol (3 equiv.) in solvent for 21 h. [b] Yield of isolated product. [c] Determined by HPLC analysis.

However, the use of a 2:1 mixture of these catalysts reduced both the yield and the enantioselectivity to a great extent (Table 3, entry 5). In our aforementioned previous study on the chiral silver(I)-catalyzed asymmetric Sakurai–Hosomi-type allylation of aldehydes,[7] we showed that a considerable amount of an inert 2:1 complex[9] of BINAP/silver(I) salt was formed accompanied by a reactive 1:1 complex if BINAP was added to an equimolar amount of the silver(I) salt in CH_3OH. In the reaction, a 0.6:1 mixture of BINAP/silver(I) salt was found to give the desired 1:1 complex without the formation of the 2:1 complex. As a result, in the present allylation, a 1:1 complex (BINAP/Ag^+ = 1:1) equally showed catalyst activity that was superior to that shown by the 2:1 complex (BINAP/Ag^+ = 2:1).

With the optimum reaction conditions in hand (Table 3, entry 1), we performed the chiral silver(I)-catalyzed asymmetric allylation reaction by using aldehydes **1a**–**m** (Table 4). The introduction of an electron-donating group in the *ortho* or *para* position of benzaldehyde (R = 2-$MeOC_6H_4$ and 4-$MeOC_6H_4$) promoted the reaction and yielded adducts **3b** and **3c** predominantly with 95 % *ee*, although the yield of isolated product **3c** was somewhat low (Table 4, entries 2 and 3). In addition, we executed the reaction of aromatic aldehydes **1d**–**h** having an electron-withdrawing group in the *meta* or *para* position and found that electron-deficient aromatic aldehydes **1d**–**f** showed high stereoselectivity and satisfactory product yields (Table 4,

Table 3. Optimization of reaction conditions: ratio of BINAP to $AgBF_4$.[a]

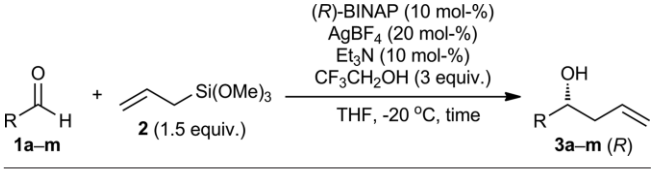


Entry	(*R*)-BINAP [mol-%]	Ratio (BINAP/$AgBF_4$)	Yield[b] [%]	*ee*[c] [%]
1	10	0.5:1	77	96
2	12	0.6:1	77	95
3	20	1:1	72	94
4[d]	10	1:1	42	90
5	40	2:1	11	<1

[a] Unless otherwise specified, the reaction was performed with (*R*)-BINAP, silver tetrafluoroborate (20 mol-%), benzaldehyde (**1a**, 1 equiv.), allyltrimethoxysilane (**2**, 1.5 equiv.), triethylamine (10 mol-%), and 2,2,2-trifluoroethanol (3 equiv.) in THF at –20 °C for 21 h. [b] Yield of isolated product. [c] Determined by HPLC analysis. [d] $AgBF_4$ (10 mol-%) was used.

entries 4–6). 1-Naphthaldehyde (**1i**), 2-pyridinecarboxaldehyde (**1k**), and 2-thiophenecarboxaldehyde (**1l**) were also promising substrates for the allylation (Table 4, entries 9, 11, and 12). α,β-Unsaturated aldehydes underwent the 1,2-addition, and indeed, the reaction of (*E*)-cinnamaldehyde (**1j**) with **2** gave (*R*)-(*E*)-1-phenyl-1,5-hexadien-3-ol (**3j**) almost exclusively (Table 4, entry 10). We also examined the reaction between cyclohexanecarboxaldehyde (**1m**) and allyltrimethoxysilane (**2**) at –20 to 0 °C for 19 h; however, we obtained target adduct **3m** in only 24 % yield, probably because of the low electrophilicity of this aliphatic aldehyde (Table 4, entry 13).

Table 4. Enantioselective allylation of aldehydes **1a**–**m** with allyltrimethoxysilane (**2**) catalyzed by (*R*)-BINAP•$AgBF_4$.[a]

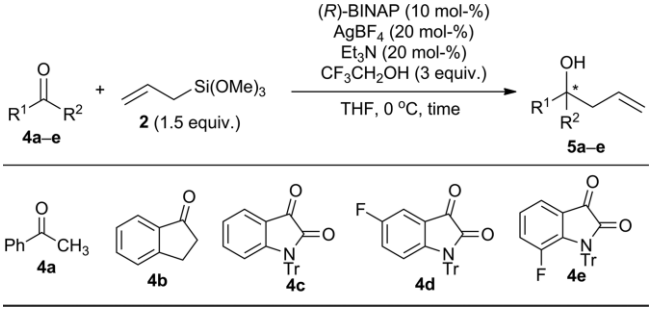


Entry	R (**1**)	Time [h]	Product	Yield[b] [%]	*ee*[c] [%]
1	Ph (**1a**)	21	**3a**	75	95
2	2-MeOC_6H_4 (**1b**)	26	**3b**	90	95
3	4-MeOC_6H_4 (**1c**)	40	**3c**	67	95
4	4-FC_6H_4 (**1d**)	22	**3d**	94	95
5	4-BrC_6H_4 (**1e**)	17	**3e**	94	94
6	4-F_3CC_6H_4 (**1f**)	20	**3f**	89	93
7	3-O_2NC_6H_4 (**1g**)	18	**3g**	82	88
8	4-O_2NC_6H_4 (**1h**)	18	**3h**	89	84
9	1-naphthyl (**1i**)	21	**3i**	87	95
10	(*E*)-PhCH=CH (**1j**)	18	**3j**	96	84
11[d]	2-pyridyl (**1k**)	26	**3k**	60	69
12	2-thienyl (**1l**)	18	**3l**	83	91
13[d]	Cy (**1m**)	19	**3m**	24	88

[a] Unless otherwise specified, the reaction was performed with (*R*)-BINAP (10 mol-%), silver tetrafluoroborate (20 mol-%), aldehyde **1a**–**m** (1 equiv.), allyltrimethoxysilane (**2**, 1.5 equiv.), triethylamine (10 mol-%), and 2,2,2-trifluoroethanol (3 equiv.) in THF at –20 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis. [d] The reaction was performed at –20 to 0 °C.

The aforementioned results further encouraged us to use ketones in the asymmetric allylation reaction. Initially, we attempted to perform the reaction of simple acyclic and cyclic ketones, such as acetophenone (**4a**) and 1-indanone (**4b**). However, desired allylated products **5a** and **5b** were not obtained at all (Table 5, entries 1 and 2). So, we focused on α-keto carbonyl compounds as the next target. We showed before that α-keto esters were good electrophiles for the BINAP•Ag^I-complex-catalyzed asymmetric aldol reaction of alkenyl trihaloacetates.[8,10] Treatment of *N*-tritylisatin (**4c**) with allyltrimethoxysilane (**2**) in the presence of (*R*)-BINAP (10 mol-%), $AgBF_4$ (20 mol-%), triethylamine (20 mol-%), and CF_3CH_2OH (3 equiv.) in dry THF at 0 °C for 21 h gave optically active allylation adduct **5c** in 57 % yield with 53 % *ee* (Table 5, entry 3). In addition to **4c**, fluorine-atom-substituted isatin derivatives **4d** and **4e** also reacted with allylating agent **2** enantioselectively, although products **5d** and **5e** had low enantiomeric excess values (Table 5, entries 4 and 5).

Table 5. Enantioselective allylation of ketones **4a**–**e** with allyltrimethoxysilane (**2**) catalyzed by (*R*)-BINAP•$AgBF_4$.[a]



Entry	Ketone	Time [h]	Product	Yield[b] [%]	*ee*[c] [%]
1[d]	**4a**	46	**5a**	<1	–
2[e]	**4b**	21	**5b**	<1	–
3	**4c**	21	**5c**	57	53
4	**4d**	21	**5d**	65	21
5	**4e**	21	**5e**	73	14

[a] Unless otherwise specified, the reaction performed with (*R*)-BINAP (10 mol-%), silver tetrafluoroborate (20 mol-%), ketone **4a**–**e** (1 equiv.), allyltrimethoxysilane (**2**, 1.5 equiv.), triethylamine (20 mol-%), and 2,2,2-trifluoroethanol (3 equiv.) in THF at 0 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis. [d] The reaction was performed at –78 to 0 °C. [e] The reaction was performed at 0 °C to r.t.

A plausible catalytic cycle is shown in Figure 1. Initially, (*R*)-BINAP•$AgBF_4$ reacts with trifluoroethanol in the presence of triethylamine to afford corresponding (*R*)-BINAP•$AgOCH_2CF_3$, which is the true catalyst in the present asymmetric allylation reaction. Next, the thus-generated chiral silver alkoxide attacks allyltrimethoxysilane (**2**) to yield chiral allyl silver species **6**. The following addition reaction of chiral allyl silver **6** with carbonyl compound **1** or **4** provides **7** as the chiral silver alkoxide of the homoallylic alcohol. Finally, protonation of **7** with CF_3CH_2OH results in the formation of optically active homoallylic alcohol

3 or **5** with regeneration of the chiral silver alkoxide. Rapid alcoholysis of silver alkoxide **7** promotes the catalytic cycle efficiently.

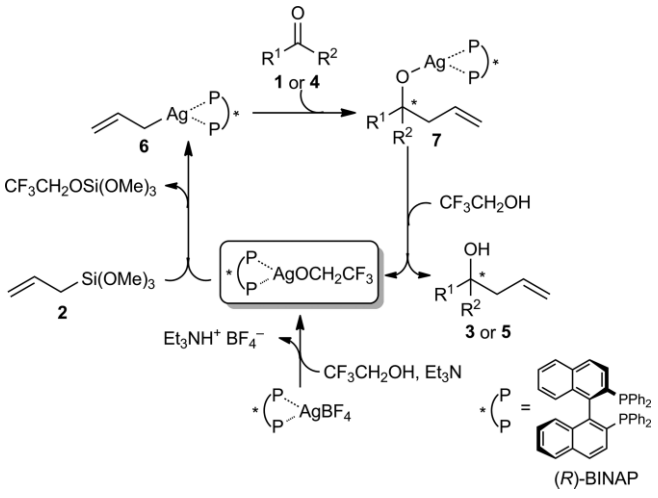


Figure 1. Plausible catalytic cycle for the asymmetric allylation catalyzed by chiral silver alkoxide.

A hypothesis for enantioface discrimination involving an aldehyde and an allyl silver in the present asymmetric allylation reaction catalyzed by (*R*)-BINAP•$AgBF_4$ is presented in Figure 2. Chiral allyl silver attacks the *Re* face of the aldehyde to avoid steric repulsion caused by a phenyl group of the chiral phosphine ligand through a six-membered cyclic transition-state structure. Thus, carbon–carbon bond formation occurs selectively to yield the (*R*)-homoallylic alcohol.

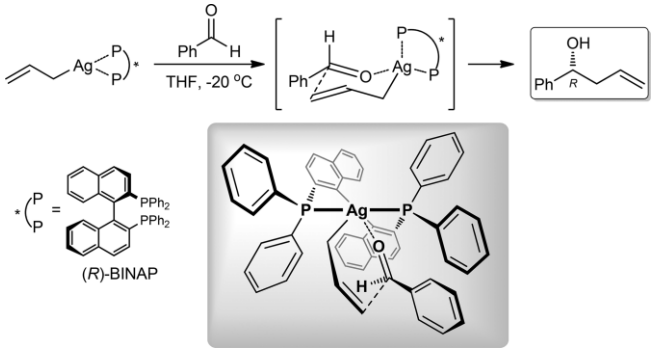


Figure 2. Proposed transition-state structure in the catalytic asymmetric allylation of aldehydes.

Conclusions

In summary, we demonstrated a novel example of an asymmetric allylation reaction of aldehydes or ketones with allyltrimethoxysilane catalyzed by an in situ generated chiral allyl silver species generated from BINAP•$AgBF_4$ and triethylamine. The procedure is simple, employs readily available chemicals, and yields various optically active homoallylic alcohols with up to 95 % *ee* not only from aromatic, α,β-unsaturated, and aliphatic aldehydes but also from isatin derivatives. To the best of our knowledge, this is the first example of the enantioselective allylation of carbonyl compounds catalyzed by a chiral silver alkoxide.[11] Further work is in progress on the asymmetric reaction.

Experimental Section

General Procedure for the Asymmetric Allylation of Aldehydes or Ketones Catalyzed by (*R*)-BINAP•$AgBF_4$ and Et_3N: A mixture of $AgBF_4$ (19.5 mg, 0.1 mmol) and (*R*)-BINAP (31.1 mg, 0.05 mmol) was dissolved in dry THF (5 or 2 mL) under an argon atmosphere with the exclusion of direct light, and the mixture was stirred at room temperature for 20 min. CF_3CH_2OH (108 μL, 1.5 mmol) and Et_3N (3.5 or 7 μL, 0.05 or 0.10 mmol) were successively added at a specified temperature (–20 or 0 °C). The mixture was stirred at the specified temperature for 10 min. Then, aldehyde **1a**–**m** or ketone **4a**–**e** (0.5 mmol) and allyltrimethoxysilane (**2**, 0.75 mmol) were successively added dropwise to the resulting solution at the specified temperature. After stirring at –20 °C for 17–40 h or 0 °C for 21–46 h, the mixture was treated with a mixture of 1 N HCl (5 mL) and solid KF (ca. 0.5 g) at ambient temperature for 30 min. Then, the resulting precipitate was filtered off by a glass filter funnel filled with Celite and silica gel. The filtrate was dried with Na_2SO_4 and concentrated in vacuo after filtration. The residual crude product was purified by column chromatography (silica gel, EtOAc/hexane) to give homoallylic alcohol **3a**–**m** or **5c**–**e** (Table 4 or 5). The enantiomeric ratio of the product was determined by HPLC analysis.

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data, and copies of the ^1H NMR and ^{13}C NMR spectra and HPLC traces.

Acknowledgments

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology (MEXT)/Japan Society for the Promotion of Science (JSPS) KAKENHI Grant Numbers 25410107 and 16K05766, the Naito Foundation, and the COE Program in Chiba University headed by Professor Takayoshi Arai. We acknowledge the generous gift of (*R*)-H_8-BINAP, (*R*)-DM-BINAP, (*R*)-SEGPHOS, (*R*)-DMM-SEGPHOS, and (*R*)-Tol-SEGPHOS from Takasago International Corporation and (*R*,*R*)-QuinoxP* from Nippon Chemical Industrial Co., Ltd.

Keywords: Aldehydes · Allylation · Asymmetric catalysis · Ketones · Silver

[1] For reviews on the catalytic asymmetric allylation of carbonyl compounds, see: a) S. E. Denmark, J. Fu, *Chem. Rev.* **2003**, *103*, 2763; b) A. Yanagisawa in *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Heidelberg, **2004**, supplement 2, p. 97; c) M. Yus, J. C. González-Gómez, F. Foubelo, *Chem. Rev.* **2011**, *111*, 7774.

[2] For recent notable examples of chiral Lewis acid catalyzed asymmetric allylations, see: a) Z. Li, B. Plancq, T. Ollevier, *Chem. Eur. J.* **2012**, *18*, 3144; b) N. V. Hanhan, Y. C. Tang, N. T. Tran, A. K. Franz, *Org. Lett.* **2012**, *14*, 2218; c) T. Wang, X.-Q. Hao, J.-J. Huang, J.-L. Niu, J.-F. Gong, M.-P. Song, *J. Org. Chem.* **2013**, *78*, 8712; d) Y. Murata, M. Takahashi, F. Yagishita, M. Sakamoto, T. Sengoku, H. Yoda, *Org. Lett.* **2013**, *15*, 6182; e) T. Wang, X.-Q. Hao, J.-J. Huang, K. Wang, J.-F. Gong, M.-P. Song, *Organometallics* **2014**, *33*, 194; f) J. Yadav, G. R. Stanton, X. Fan, J. R. Robinson, E. J. Schelter, P. J. Walsh, M. A. Pericas, *Chem. Eur. J.* **2014**, *20*, 7122; g) M. Takahashi, Y. Murata, F. Yagishita, M. Sakamoto, T. Sengoku, H. Yoda, *Chem. Eur. J.*

2014, *20*, 11091; h) Z.-Y. Cao, J.-S. Jiang, J. Zhou, *Org. Biomol. Chem.* **2016**, *14*, 5500.

[3] For notable examples of chiral Lewis base catalyzed asymmetric allylations, see: a) S. E. Denmark, J. Fu, *J. Am. Chem. Soc.* **2000**, *122*, 12021; b) S. E. Denmark, T. Wynn, *J. Am. Chem. Soc.* **2001**, *123*, 6199; c) S. E. Denmark, J. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 9488; d) S. E. Denmark, J. Fu, *J. Am. Chem. Soc.* **2003**, *125*, 2208; e) S. E. Denmark, J. Fu, D. M. Coe, X. Su, N. E. Pratt, B. D. Griedel, *J. Org. Chem.* **2006**, *71*, 1513; f) A. Kadlčíková, I. Valterová, L. Ducháčková, J. Roithová, M. Kotora, *Chem. Eur. J.* **2010**, *16*, 9442; g) B. Bai, L. Shen, J. Ren, H. J. Zhu, *Adv. Synth. Catal.* **2012**, *354*, 354; h) E. Gnanamani, N. Someshwar, C. R. Ramanathan, *Adv. Synth. Catal.* **2012**, *354*, 2101; i) Y. Huang, L. Yang, P. Shao, Y. Zhao, *Chem. Sci.* **2013**, *4*, 3275; j) M. Ogasawara, S. Kotani, H. Nakajima, H. Furusho, M. Miyasaka, Y. Shimoda, W.-Y. Wu, M. Sugiura, T. Takahashi, M. Nakajima, *Angew. Chem. Int. Ed.* **2013**, *52*, 13798; *Angew. Chem.* **2013**, *125*, 14043; k) P. S. O'Hora, C. A. Incerti-Pradillos, M. A. Kabeshov, S. A. Shipilovskikh, A. E. Rubtsov, M. R. J. Elsegood, A. V. Malkov, *Chem. Eur. J.* **2015**, *21*, 4551; l) S. Staniland, R. W. Adams, J. J. W. McDouall, I. Maffucci, A. Contini, D. M. Grainger, N. J. Turner, J. Clayden, *Angew. Chem. Int. Ed.* **2016**, *55*, 10755; *Angew. Chem.* **2016**, *128*, 10913.

[4] For notable examples of chiral Brønsted acid catalyzed asymmetric allylations, see: a) G.-H. Chen, L.-Y. Liu, X.-N. Wei, W.-X. Chang, J. Li, *Chem. Lett.* **2010**, *39*, 1013; b) M. Mahlau, P. García-García, B. List, *Chem. Eur. J.* **2012**, *18*, 16283; c) D. Ghosh, N. Gupta, S. H. R. Abdi, S. Nandi, N. H. Khan, R. I. Kureshy, H. C. Bajaj, *Eur. J. Org. Chem.* **2015**, 2801; d) M. Sai, H. Yamamoto, *J. Am. Chem. Soc.* **2015**, *137*, 7091; e) P. S. J. Kaib, L. Schreyer, S. Lee, R. Properzi, B. List, *Angew. Chem. Int. Ed.* **2016**, *55*, 13200; *Angew. Chem.* **2016**, *128*, 13394.

[5] a) A. Yanagisawa, H. Nakashima, A. Ishiba, H. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 4723; b) A. Yanagisawa, H. Nakashima, Y. Nakatsuka, A. Ishiba, H. Yamamoto, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1129.

[6] For reviews on chiral phosphine–silver(I)-complex-catalyzed asymmetric allylation of carbonyl compounds, see: a) H. Yamamoto, M. Wadamoto, *Chem. Asian J.* **2007**, *2*, 692; b) A. Yanagisawa, T. Arai, *Chem. Commun.* **2008**, 1165; c) H. Pellissier, *Chem. Rev.* **2016**, *116*, 14868.

[7] A. Yanagisawa, H. Kageyama, Y. Nakatsuka, K. Asakawa, Y. Matsumoto, H. Yamamoto, *Angew. Chem. Int. Ed.* **1999**, *38*, 3701; *Angew. Chem.* **1999**, *111*, 3916.

[8] A. Yanagisawa, R. Miyake, K. Yoshida, *Eur. J. Org. Chem.* **2014**, 4248.

[9] a) A. Yanagisawa, Y. Nakatsuka, K. Asakawa, H. Kageyama, H. Yamamoto, *Synlett* **2001**, 69; b) A. Yanagisawa, Y. Nakatsuka, K. Asakawa, M. Wadamoto, H. Kageyama, H. Yamamoto, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1477.

[10] A. Yanagisawa, Y. Terajima, K. Sugita, K. Yoshida, *Adv. Synth. Catal.* **2009**, *351*, 1757.

[11] Two examples of the synthesis of achiral silver alkoxides have been reported: a) I. S. Edworthy, M. Rodden, S. A. Mungur, K. M. Davis, A. J. Blake, C. Wilson, M. Schröder, P. L. Arnold, *J. Organomet. Chem.* **2005**, *690*, 5710; b) A. Reisinger, D. Himmel, I. Krossing, *Angew. Chem. Int. Ed.* **2006**, *45*, 6997; *Angew. Chem.* **2006**, *118*, 7153.

Received: August 22, 2017

