Synthetic Methods

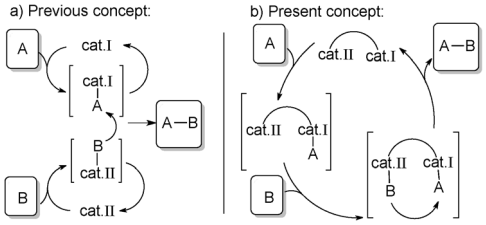
Deutsche Ausgabe: DOI: 10.1002/ange.201411601
Internationale Ausgabe: DOI: 10.1002/anie.201411601

Cooperative Catalysis: Enantioselective Propargylic Alkylation of Propargylic Alcohols with Enecarbamates Using Ruthenium/Phosphoramide Hybrid Catalysts**

*Yasushi Senda, Kazunari Nakajima, and Yoshiaki Nishibayashi**

Abstract: *The diastereo- and enantioselective propargylic alkylation of propargylic alcohols with E-enecarbamates in the presence of a catalytic amount of thiolate-bridged diruthenium complexes bearing an optically active phosphoramide moiety gives the corresponding propargylic alkylated products (up to 97% ee).*

Considerable attention has been paid to the development of reactions undergoing cooperative catalysis using distinct catalysts.[1] This methodology realizes unprecedented transformations. In particular, the development of reactions undergoing cooperative catalysis using transition-metal catalysts and organocatalysts has opened up new fields in organic synthesis.[2,3] Many such reactions have been achieved by simple mixing of two distinct catalysts as shown in Scheme 1 a.

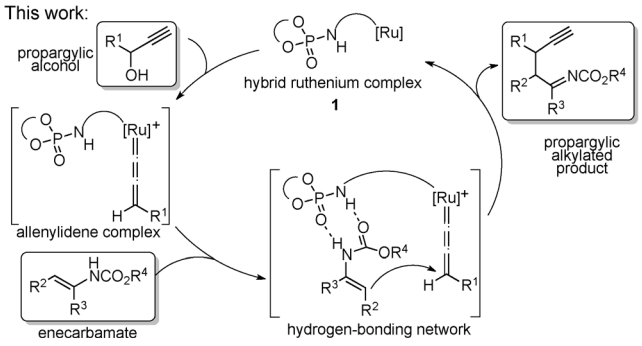


Scheme 1. a) Reactions involving cooperative catalysis by simple mixing of two distinct catalysts. b) Reactions involving cooperative catalysis using hybrid transition-metal complexes bearing an organocatalyst.

To develop a new type of cooperative catalysis, we envisaged the use of hybrid catalysts derived from both transition-metal catalysts and organocatalysts within the same molecule (Scheme 1 b). The use of such hybrid catalysts may increase the reactivity and enantioselectivity of the reactions. As a result, the development of new types of cooperative transformations is anticipated by using the hybrid catalysts.

As an extension of our study,[4,5] we have recently found the application of cooperative catalytic reaction systems, having two distinct catalysts, to enantioselective reactions of propargylic alcohols with carbon-centered nucleophiles, such as aldehydes, to give the corresponding propargylic alkylated products in high yields with an excellent enantioselectivity.[6] In these reaction systems, ruthenium complexes activate the propargylic alcohols to afford the corresponding allenylidene complexes, and organocatalysts, such as optically active amines, activate the carbon-centered nucleophiles to afford the corresponding enamines. As a result, the activated carbon-centered nucleophiles attack the electrophilic γ-carbon atom in the allenylidene ligand to give the corresponding propargylic alkylated products with a high enantioselectivity. However, unfortunately, available nucleophiles are quite limited in these cooperative catalytic reaction systems.[7]

Based on this background, we have now designed novel hybrid catalysts such as thiolate-bridged diruthenium complexes bearing a phosphoramide moiety which is based on the BINOL skeleton (**1**).[8] The phosphoramide moiety in the ruthenium complex may activate nucleophiles such as enecarbamates[9] and control the nucleophilic attack by the allenylidene ligand on the ruthenium complexes (Scheme 2).



Scheme 2. Reactions involving cooperative catalysis using hybrid ruthenium complexes bearing a phosphoramide moiety as an organocatalyst.

In this reaction system, the intramolecular organocatalyst plays a crucial role in achieving high enantioselectivity. Herein, we report the reactions undergoing cooperative catalysis using hybrid transition-metal complexes bearing an organocatalyst.

Treatment of 1-phenyl-2-propyn-1-ol (**2a**) with 2 equivalents of methyl (*E*)-1-phenylbut-1-enylcarbamate (**3a**) in the

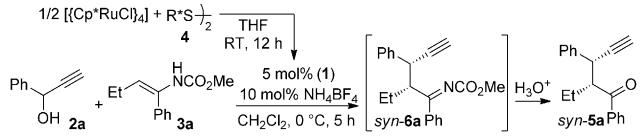
[*] Y. Senda, Dr. K. Nakajima, Prof. Dr. Y. Nishibayashi
Institute of Engineering Innovation, School of Engineering
The University of Tokyo
Yayoi, Bunkyo-ku, Tokyo 113-8656 (Japan)
E-mail: ynishiba@sogo.t.u-tokyo.ac.jp

[**] We thank Grants-in-Aid for Scientific Research (Nos. 26288044, 26620075, and 26105708) from the Japan Society for the Promotion of Science (JSPS) and the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201411601.

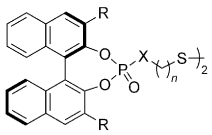
presence of a catalytic amount of a chiral thiolate-bridged diruthenium complex (**1a**), which was generated in situ from the tetranuclear ruthenium(II) complex [{Cp*RuCl}$_4$] (Cp* = η^5-C_5Me_5) and dialkyl disulfide bearing an optically active phosphoramide[10] (**4a**) in tetrahydrofuran (THF) at room temperature for 12 hours, and NH_4BF_4 in dichloromethane at 0 °C for 5 hours gave 2-ethyl-1,3-diphenylpent-4-yn-1-one (**5a**) in 79% yield (NMR) as a mixture of two diastereoisomers (*syn*-**5a**/*anti*-**5a** = 3:1), with 21% *ee* for *syn*-**5a**, after acid hydrolysis of the corresponding crude imine products (**6a**) (Table 1, entry 1). Separately, a similar result was

Table 1: Enantioselective propargylic alkylation of the propargylic alcohol **2a** with enecarbamate **3a**.[a]



Entry	4	1	5a Yield [%][b]	*syn*-5a/*anti*-5a[c]	*syn*-5a *ee* [%][d]
1	**4a**	**1a**	79	3:1	21
2[e]	**4a**	**1a**	84	3:1	20
3	**4b**	**1b**	80	6:1	30
4	**4c**	**1c**	84	6:1	14
5	**4d**	**1d**	74	6:1	14
6	**4e**	**1e**	64	19:1	8
7	**4f**	**1f**	79	6:1	64
8	**4g**	**1g**	89	4:1	56
9	**4h**	**1h**	82	7:1	35
10[f]	**4f**	**1f**	86 (68)	>20:1	85

[a] All reactions of **2a** (0.2 mmol) with **3a** (0.4 mmol) were carried out in the presence of **1** (0.01 mmol, generated in situ from [{Cp*RuCl}$_4$] and **4**) and NH_4BF_4 (0.02 mmol) in CH_2Cl_2 (5 mL). [b] Determined by ^{1}H NMR analysis. Yield of the isolated product given within parentheses. [c] Determined by ^{1}H NMR analysis. [d] Determined by HPLC analysis. [e] Isolated **1a** was used as a catalyst. [f] At −50 °C for 90 h.



R = H. X = NH, *n* = 2 (**4a**)
R = H. X = NH, *n* = 3 (**4b**)
R = H. X = NH, *n* = 4 (**4c**)
R = H. X = O, *n* = 3 (**4d**)
R = H. X = NMe, *n* = 3 (**4e**)
R = Me. X = NH, *n* = 3 (**4f**)
R = Et. X = NH, *n* = 3 (**4g**)
R = Ph. X = NH, *n* = 3 (**4h**)

observed when the isolated **1a** was used as a catalyst (entry 2). The molecular structure of **1a** was confirmed by X-ray analysis (see the Supporting Information for experimental details).[11] An ORTEP drawing of **1a** is shown in Figure 1. The use of a disulfide bearing an elongated carbon chain (**4b**) as a chiral ligand gave **5a** with slightly higher enantioselectivity (30% *ee*; entry 3). However, the use of a disulfide bearing an even longer carbon chain (**4c**) gave **5a** with lower enantioselectivity (14% *ee*; entry 4). A phosphoramide moiety (NH) in the chiral ligand was revealed to be an essential factor for achieving a good enantioselectivity. In fact, the use of phosphanate or *N*-methyl phosphoramide moiety gave only a low enantioselectivity of **5a** under the same reaction conditions (entries 5 and 6). The introduction of a methyl group at the 3,3′-positions of the naphthyl moiety

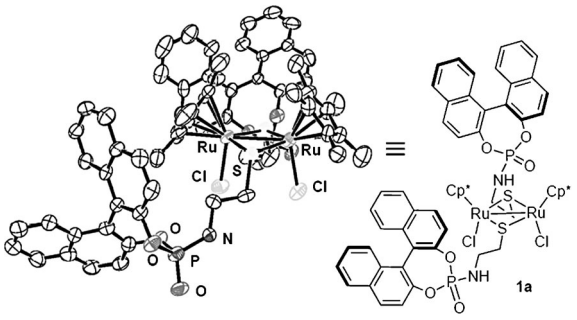
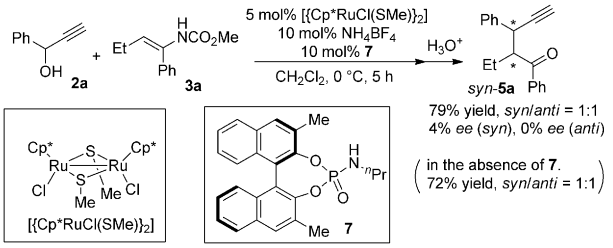


Figure 1. ORTEP drawing of **1a**.

in the chiral ligand (**4f**) dramatically increased the enantioselectivity of the product (entry 7). However, the introduction of more bulky substituents such as ethyl and phenyl groups at the same position (**4g** and **4h**) did not improve the enantioselectivity (entries 8 and 9). When the reaction using **4f** as a chiral ligand was carried out at −50 °C, **5a** was obtained in 86% yield (NMR; 68% isolated) with high diastereo- and enantioselectivities (85% *ee*), however a longer reaction time (90 h) was necessary to complete the reaction (entry 10).

To check the effect of the introduction of the phosphoramide moiety to the ruthenium complex, we investigated the reaction of **2a** with **3a** in the presence of catalytic amounts of methanethiolate-bridged diruthenium complex [{Cp*RuCl(μ-SMe)}$_2$] and an optically active phosphoramide (**7**) at 0 °C for 5 hours to give **5a** in 79% yield (NMR) as a mixture of two diastereoisomers (*syn*-**5a**/*anti*-**5a** = 1:1) with only 4% *ee* of *syn*-**5a** and 0% *ee* of *anti*-**5a** after acid hydrolysis (Scheme 3).

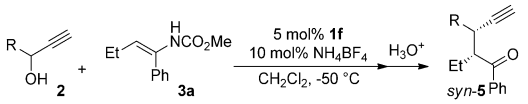


Scheme 3. Propargylic alkylation in the presence of an achiral ruthenium complex [{Cp*RuCl(SMe)}$_2$] and an optically active phosphoramide **7**.

Even in the absence of **7**, the reaction proceeded smoothly under the same reaction conditions. This outcome may show that the presence of the intramolecular phosphoramide moiety in the ruthenium complex, such as **4f**, realizes the high enantioselectivity in the present propargylic alkylation.

Next, propargylic alkylation of a variety of propargylic alcohols was carried out by using **4f** as a chiral ligand at −50 °C. Typical results are shown in Table 2. A high enantioselectivity was observed when substituents such as methyl, methoxy, and chloro groups were introduced at the *para*-position of the benzene ring of propargylic alcohols (entries 2–4). The position of the methyl group on the

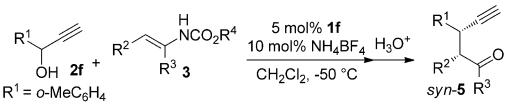
Table 2: Enantioselective propargylic alkylation of propargylic alcohols **2** with enecarbamate **3a**.[a]



Entry	2	t [h]	5 Yield [%][b]	syn-5/anti-5[c]	syn-5 ee [%][d]
1	R = Ph (**2a**)	90	68 (**5a**)	>20:1	85
2	R = *p*-MeC$_6$H$_4$ (**2b**)	90	76 (**5b**)	>20:1	85
3	R = *p*-MeOC$_6$H$_4$ (**2c**)	120	74 (**5c**)	19:1	83
4	R = *p*-ClC$_6$H$_4$ (**2d**)	90	77 (**5d**)	>20:1	79
5	R = *m*-MeC$_6$H$_4$ (**2e**)	90	82 (**5e**)	>20:1	89
6	R = *o*-MeC$_6$H$_4$ (**2f**)	90	73 (**5f**)	20:1	97
7	R = *o*-PhC$_6$H$_4$ (**2g**)	120	80 (**5g**)	>20:1	92
8	R = 1-naphthyl (**2h**)	120	80 (**5h**)	6:1	86
9	R = cyclohexyl (**2i**)	90	0 (**5i**)	–	–

[a] All reactions of **2** (0.2 mmol) with **3a** (0.4 mmol) were carried out in the presence of **1f** (0.01 mmol; generated in situ from [{Cp*RuCl}$_4$] and **4f**) and NH_4BF_4 (0.02 mmol) in CH_2Cl_2 (5 mL). [b] Yield of the isolated product. [c] Determined by ^{1}H NMR analysis. [d] Determined by HPLC analysis.

Table 3: Enantioselective propargylic alkylation of propargylic alcohol **2f** with enecarbamates **3**.[a]



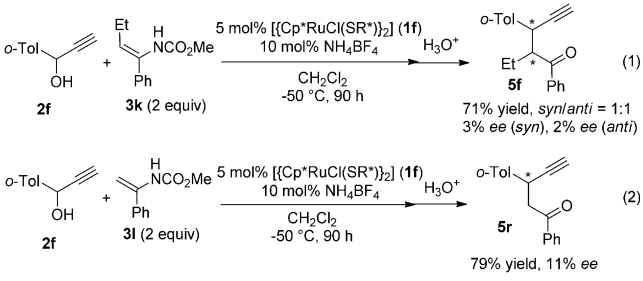
Entry	3	t [h]	5 Yield [%][b]	syn-5/anti-5[c]	syn-5 ee [%][d]
1[e]	R^2 = Et, R^3 = Ph, R^4 = Bn (**3b**)	120	86 (**5f**)	>20:1	95
2	R^2 = Me, R^3 = Ph, R^4 = Me (**3c**)	90	84 (**5j**)	18:1	90
3	R^2 = ^{n}Pr, R^3 = Ph, R^4 = Me (**3d**)	120	73 (**5k**)	20:1	96
4	R^2 = Et, R^3 = *p*-ClC$_6$H$_4$, R^4 = Me (**3e**)	90	79 (**5l**)	>20:1	97
5	R^2 = Et, R^3 = *p*-BrC$_6$H$_4$, R^4 = Me (**3f**)	120	67 (**5m**)	>20:1	92
6[f]	R^2 = Et, R^3 = *p*-MeO-C$_6$H$_4$, R^4 = Me (**3g**)	120	81 (**5n**)	15:1	95
7	R^2 = Et, R^3 = *p*-MeC$_6$H$_4$, R^4 = Me (**3h**)	120	81 (**5o**)	>20:1	96
8	R^2 = Et, R^3 = *m*-MeC$_6$H$_4$, R^4 = Me (**3i**)	90	71 (**5p**)	>20:1	96
9	R^2 = Et, R^3 = Me, R^4 = Me (**3j**)	120	58 (**5q**)	1:4	63[g]

[a] All reactions of **2f** (0.2 mmol) with **3** (0.4 mmol) were carried out in the presence of **1f** (0.01 mmol; generated in situ from [{Cp*RuCl}$_4$] and **4f**) and NH_4BF_4 (0.02 mmol) in CH_2Cl_2 (5 mL). [b] Yield of the isolated product. [c] Determined by ^{1}H NMR analysis. [d] Determined by HPLC analysis. [e] Bn = benzyl. [f] At −40 °C. [g] *ee* value of *anti*-**5q** was 57% *ee*.

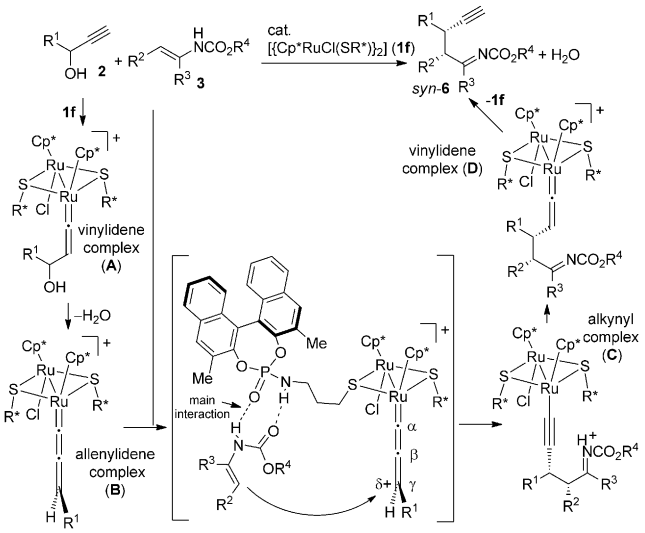
benzene ring affected the enantioselectivity. In fact, the introduction of methyl group at the *meta*- and *ortho*-positions increased the enantioselectivity (89% *ee* and 97% *ee*, respectively; entries 5 and 6). When a phenyl group was present at the *ortho*-position of the benzene ring of the propargylic alcohols, the enantioselectivity was also high (entry 7). The enantioselectivity was slightly lower when 1-(1-naphthyl)-2-propyn-1-ol (**2h**) was used as a substrate (entry 8). No reaction occurred at all under the same reaction conditions when 1-cyclohexyl-2-propyn-1-ol (**2i**) was used as a substrate (entry 9), thus indicating that the presence of an aryl group at the propargylic position is necessary to promote the present propargylic alkylation.

Propargylic alkylation with other enecarbamates as carbon-centered nucleophiles proceeded smoothly to give the corresponding propargylic alkylated products with a high enantioselectivity. Typical results are shown in Table 3. The reaction with benzyl (*E*)-1-phenylbut-1-enylcarbamate (**3b**) at −50 °C for 120 h gave the corresponding propargylic alkylated product **5f** in 86% yield with 95% *ee* for *syn*-**5f** (entry 1). When other alkyl moieties, such as methyl and *n*-propyl, were used in place of the ethyl group in **3a**, a similarly high enantioselectivity was observed in both cases (90% *ee* and 96% *ee*, respectively; entries 2 and 3). A variety of aryl groups can be used in place of the phenyl group in **3** to give the corresponding products with high diastereo- and enantioselectivities (entries 4–8). Unfortunately, when the methyl group was used in place of aryl group in **3**, only low diastereo- and enantioselectivities were observed (entry 9).

In sharp contrast to the use of *E*-enecarbamates, the reaction with the *Z*-enecarbamate **3k** at −50 °C for 90 hours gave **5f** in 71% yield (NMR) as a mixture of two diastereoisomers (*syn*-**5f**/*anti*-**5f** = 1:1) with only 3% *ee* for *syn*-**5f** and 2% *ee* for *anti*-**5f** [Eq. (1)]. In addition, the reaction with 2 equivalents of methyl 1-phenylvinylcarbamate (**3l**) under the same reaction conditions gave 1-phenyl-3-(*o*-tolyl)pent-4-yn-1-one (**5r**) in 79% yield with 11% *ee* [Eq. (2)]. These results indicate that the use of *E*-enecarbamates is necessary to achieve the high enantioselectivity.



A proposed reaction pathway is shown in Scheme 4. The initial step is the formation of an allenylidene complex[12] (**B**) by the reaction of **1f** with **2** via a vinylidene complex (**A**). The phosphoramide moiety in the chiral ligand activates **3** which then attacks the γ-carbon atom of **B** to result in the formation of another vinylidene complex (**D**) via the alkynyl complex **C**. After transformation of the **D** into the corresponding π-alkyne complex, the product **6**[13] is formed by ligand exchange with another propargylic alcohol **2**. The corresponding propargylic alkylated product **5** is obtained quantitatively after acid hydrolysis of **6**. Separately, we confirmed that no reaction occurred with a propargylic alcohol bearing an internal alkyne moiety under the same reaction conditions.

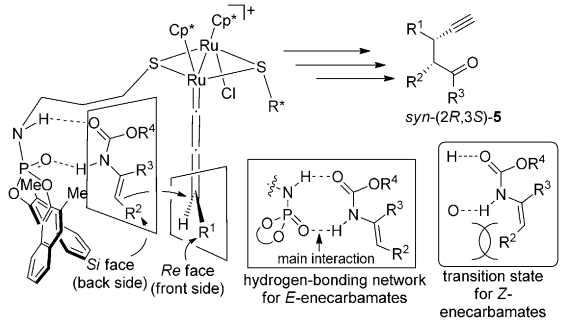


Scheme 4. Reaction pathway for the propargylic alkylation of propargylic alcohols with enecarbamates.

This result supports the proposed reaction pathway via ruthenium-allenylidene complexes as key reactive intermediates.

To obtain information on the enantioselective propargylic alkylation, the stereochemistry of the product *syn*-**5d** was determined. After one recrystallization of *syn*-**5d**, the diastereo- and enantiomerically pure *syn*-**5d** was isolated and its absolute configuration was determined as [(2*R*,3*S*)] by X-ray analysis (see the Supporting Information for experimental details).[11]

To account for the diastereo- and enantioselective formation of **5**, we propose a transition state between the ruthenium-allenylidene complex and the enecarbamate activated by the intramolecular phosphoramide moiety as shown in Scheme 5. A significant change of the N-H chemical shift of



Scheme 5. Proposed transition state.

the carbamate was observed when a mixture of **1f** and **3a** in CD_2Cl_2 at −50 °C was measured by ^1H NMR spectroscopy.[10] This result may show a hydrogen-bonded eight-membered ring between the phosphoramide moiety in the ruthenium complex and the carbamate moiety in **3** in the transition state, although the interaction between the P=O of the phosphoramide and the N-H of the enecarbamate plays a major role.[14] We believe that this interaction leads to the high enantioselectivity in the catalytic reaction. In sharp contrast to the result shown in Scheme 3, where the intermolecular phosphoramide did not work as an effective organocatalyst, the intramolecular phosphoramide moiety in the ruthenium complex plays an essential role in promoting the propargylic alkylation with high diastereo- and enantioselectivities. Although a similar secondary interaction through coordinate bonds between the reagent and the ligand in the transition-metal complexes has already been reported in other catalytic reactions,[2b,d,15,16] we consider the result described in this paper to provide one of the successful examples of the use of hybrid transition-metal complexes bearing an organocatalyst, in enantioselective catalytic reactions.

In summary, we have found the diastereo- and enantioselective propargylic alkylation of propargylic alcohols with *E*-enecarbamates in the presence of a catalytic amount of a thiolate-bridged diruthenium complex, bearing an optically active phosphoramide moiety, as an organocatalyst to give the corresponding propargylic alkylated products in high yields with high diastereo- and enantioselectivities (up to 97 % *ee*). The use of the hybrid catalysts involving both transition-metal catalysts and organocatalysts in the same molecule achieves the catalytic reactions with high diastereo- and enantioselectivities.

Keywords: alkynes · asymmetric catalysis · organocatalyst · ruthenium · synthetic methods

Zitierweise: *Angew. Chem. Int. Ed.* **2015**, *54*, 4060–4064
Angew. Chem. **2015**, *127*, 4132–4136

[1] For recent reviews, see: a) J. M. Lee, Y. Na, H. Han, S. Chang, *Chem. Soc. Rev.* **2004**, *33*, 302; b) M. Klussmann, *Angew. Chem. Int. Ed.* **2009**, *48*, 7124; *Angew. Chem.* **2009**, *121*, 7260; c) P. de Armas, D. Tejedor, F. Garcia-Tellado, *Angew. Chem. Int. Ed.* **2010**, *49*, 1013; *Angew. Chem.* **2010**, *122*, 1029; d) M. Rueping, R. M. Koenigs, I. Atodiresei, *Chem. Eur. J.* **2010**, *16*, 9350; e) N. Kumagai, M. Shibasaki, *Angew. Chem. Int. Ed.* **2011**, *50*, 4760; *Angew. Chem.* **2011**, *123*, 4856; f) S. Piovesana, D. M. Scarpino Schietroma, M. Bella, *Angew. Chem. Int. Ed.* **2011**, *50*, 6216; *Angew. Chem.* **2011**, *123*, 6340; g) N. T. Patil, V. S. Shinde, B. Gajula, *Org. Biomol. Chem.* **2012**, *10*, 211; h) A. E. Allen, D. W. C. MacMillan, *Chem. Sci.* **2012**, *3*, 633.

[2] For recent reviews, see: a) C. Zhong, X. Shi, *Eur. J. Org. Chem.* **2010**, 2999; b) L. Stegbauer, F. Sladojevich, D. J. Dixon, *Chem. Sci.* **2012**, *3*, 942; c) Z. T. Du, Z. H. Shao, *Chem. Soc. Rev.* **2013**, *42*, 1337; d) Y. Deng, S. Kumar, H. Wang, *Chem. Commun.* **2014**, *50*, 4272; e) D.-F. Chen, Z.-Y. Han, X.-L. Zhou, L.-Z. Gong, *Acc. Chem. Res.* **2014**, *47*, 2365; f) D. M. Hodgson, A. Charlton, *Tetrahedron* **2014**, *70*, 2207.

[3] a) S. Krautwald, D. Sarlah, M. A. Schafroth, E. M. Carreira, *Science* **2013**, *340*, 1065; b) S. Krautwald, M. A. Schafroth, D. Sarlah, E. M. Carreira, *J. Am. Chem. Soc.* **2014**, *136*, 3020; c) K. Liu, M. T. Hovey, K. A. Scheidt, *Chem. Sci.* **2014**, *5*, 4026; d) Y. Zhu, L. Zhang, S. Luo, *J. Am. Chem. Soc.* **2014**, *136*, 14642.

[4] For enantioselective ruthenium-catalyzed propargylic substitution reactions, see selected examples: a) Y. Inada, Y. Nishibayashi, S. Uemura, *Angew. Chem. Int. Ed.* **2005**, *44*, 7715; *Angew. Chem.* **2005**, *117*, 7893; b) H. Matsuzawa, Y. Miyake, Y. Nishibayashi, *Angew. Chem. Int. Ed.* **2007**, *46*, 6488; *Angew. Chem.* **2007**, *119*, 6608; c) K. Fukamizu, Y. Miyake, Y. Nishibayashi, *J. Am. Chem. Soc.* **2008**, *130*, 10498; d) for a review, see:

Y. Miyake, S. Uemura, Y. Nishibayashi, *ChemCatChem* **2009**, *1*, 342.

[5] For enantioselective copper-catalyzed propargylic substitution reactions, see selected examples: a) R. J. Detz, M. M. E. Delville, H. Hiemstra, J. H. van Maarseveen, *Angew. Chem. Int. Ed.* **2008**, *47*, 3777; *Angew. Chem.* **2008**, *120*, 3837; b) G. Hattori, H. Matsuzawa, Y. Miyake, Y. Nishibayashi, *Angew. Chem. Int. Ed.* **2008**, *47*, 3781; *Angew. Chem.* **2008**, *120*, 3841; c) P. Fang, X.-L. Hou, *Org. Lett.* **2009**, *11*, 4612; d) G. Hattori, A. Yoshida, Y. Miyake, Y. Nishibayashi, *J. Org. Chem.* **2009**, *74*, 7603; e) G. Hattori, K. Sakata, H. Matsuzawa, Y. Tanabe, Y. Miyake, Y. Nishibayashi, *J. Am. Chem. Soc.* **2010**, *132*, 10592; f) R. J. Detz, Z. Abiri, R. le Griel, H. Hiemstra, J. H. van Maarseveen, *Chem. Eur. J.* **2011**, *17*, 5921; g) C. Zhang, Y.-H. Wang, X.-H. Hu, Z. Zheng, J. Xu, X.-P. Hu, *Adv. Synth. Catal.* **2012**, *354*, 2854; h) T. Mino, H. Taguchi, M. Hashimoto, M. Sakamoto, *Tetrahedron: Asymmetry* **2013**, *24*, 1520; i) F.-L. Zhu, Y. Zou, D.-Y. Zhang, Y.-H. Wang, X.-H. Hu, S. Chen, J. Xu, X.-P. Hu, *Angew. Chem. Int. Ed.* **2014**, *53*, 1410; *Angew. Chem.* **2014**, *126*, 1434; j) M. Shibata, K. Nakajima, Y. Nishibayashi, *Chem. Commun.* **2014**, *50*, 7874; k) F.-L. Zhu, Y.-H. Wang, D.-Y. Zhang, J. Xu, X.-P. Hu, *Angew. Chem. Int. Ed.* **2014**, *53*, 10223; *Angew. Chem.* **2014**, *126*, 10387; l) D.-Y. Zhang, F.-L. Zhu, Y.-H. Wang, X.-H. Hu, S. Chen, C.-J. Hou, X.-P. Hu, *Chem. Commun.* **2014**, *50*, 14459.

[6] We have recently reported cooperative catalytic reactions using distinct catalysts. See selected examples: a) M. Ikeda, Y. Miyake, Y. Nishibayashi, *Angew. Chem. Int. Ed.* **2010**, *49*, 7289; *Angew. Chem.* **2010**, *122*, 7447; b) M. Ikeda, Y. Miyake, Y. Nishibayashi, *Chem. Eur. J.* **2012**, *18*, 3321; c) M. Shibata, M. Ikeda, K. Motoyama, Y. Miyake, Y. Nishibayashi, *Chem. Commun.* **2012**, *48*, 9528; d) for a recent review, see: Y. Nishibayashi, *Synthesis* **2012**, 489.

[7] Cozzi and co-workers have recently found cooperative catalytic reactions using distinct catalysts. See: a) M. G. Capdevila, F. Benfatti, L. Zoil, M. Stenta, P. G. Cozzi, *Chem. Eur. J.* **2010**, *16*, 11237; b) R. Sinisi, M. V. Vita, A. Gualandi, E. Emer, P. G. Cozzi, *Chem. Eur. J.* **2011**, *17*, 7404.

[8] In contrast to phosphoramides, phosphorimides (*N*-sunfonyl phosphoramides) have been known to work as effective bifunctional organocatalysts which mainly activate the electrophilic substrates via protonation. See recent reviews: a) T. Akiyama, *Chem. Rev.* **2007**, *107*, 5744; b) M. Terada, *Synthesis* **2010**, 1929; c) M. Rueping, B. J. Nachtsheim, W. Ieawsuwan, I. Atodiresei, *Angew. Chem. Int. Ed.* **2011**, *50*, 6706; *Angew. Chem.* **2011**, *123*, 6838; d) D. Parmar, E. Sugiono, S. Raja, M. Rueping, *Chem. Rev.* **2014**, *114*, 9047.

[9] a) M. Terada, K. Machioka, K. Sorimachi, *Angew. Chem. Int. Ed.* **2006**, *45*, 2254; *Angew. Chem.* **2006**, *118*, 2312; b) M. Terada, K. Machioka, K. Sorimachi, *J. Am. Chem. Soc.* **2007**, *129*, 10336; c) M. Terada, K. Soga, N. Moriyama, *Angew. Chem. Int. Ed.* **2008**, *47*, 4122; *Angew. Chem.* **2008**, *120*, 4190; d) M. Terada, K. Machioka, K. Sorimachi, *Angew. Chem. Int. Ed.* **2009**, *48*, 2553; *Angew. Chem.* **2009**, *121*, 2591.

[10] See the Supporting Information for details.

[11] CCDC 1034146 (**1a**·$C_4H_{10}O$) and 1034147 (*syn*-**5d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[12] For recent reviews of transition-metal–allenylidene complexes, see: a) C. Bruneau, P. H. Dixneuf, *Angew. Chem. Int. Ed.* **2006**, *45*, 2176; *Angew. Chem.* **2006**, *118*, 2232; b) *Metal Vinylidenes and Allenylidenes in Catalysis: From Reactivity to Applications in Synthesis* (Eds.: C. Bruneau, P. H. Dixneuf), Wiley-VCH, Weinheim, **2008**; c) V. Cadierno, J. Gimeno, *Chem. Rev.* **2009**, *109*, 3512; d) *Ruthenium in Catalysis* (Eds.: C. Bruneau, P. H. Dixneuf), Springer, Heidelberg, **2014**.

[13] The imine can be converted into the corresponding carbamate (**8**) without loss of optically purity.[10]

[14] a) M. Rueping, B. J. Nachtsheim, R. M. Koenigs, W. Ieawsuwan, *Chem. Eur. J.* **2010**, *16*, 13116; b) M. R. Monaco, S. Prevost, B. List, *Angew. Chem. Int. Ed.* **2014**, *53*, 8142; *Angew. Chem.* **2014**, *126*, 8280.

[15] For reviews, see: a) M. Sawamura, Y. Ito, *Chem. Rev.* **1992**, *92*, 857; b) M. Raynal, P. Ballester, A. Vidal-Ferran, P. W. N. M. van Leeuwen, *Chem. Soc. Rev.* **2014**, *43*, 1660.

[16] P. Dydio, R. J. Detz, B. de Bruin, J. N. H. Reek, *J. Am. Chem. Soc.* **2014**, *136*, 8418.

Received: December 2, 2014
Revised: December 23, 2014
Published online: February 4, 2015

