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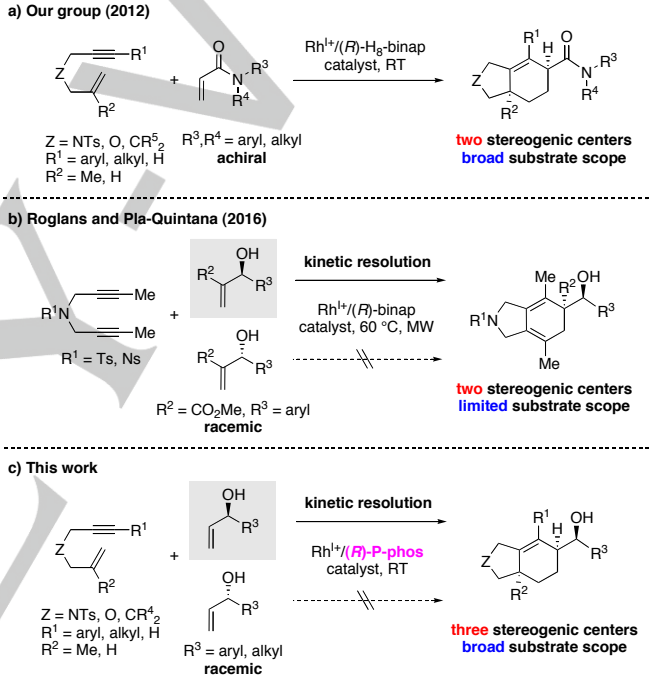
Rhodium-Catalyzed Asymmetric [2+2+2] Cycloaddition of 1,6-Enynes with Racemic Secondary Allylic Alcohols through Kinetic Resolution

Shunsuke Suzuki, Yu Shibata, and Ken Tanaka*

Abstract: It has been established that a cationic rhodium(I)/P-phos complex catalyzes the asymmetric [2+2+2] cycloaddition of 1,6-enynes with racemic secondary allylic alcohols to produce the corresponding chiral bicyclic cyclohexenes, possessing three stereogenic centers, as a single diastereomer with excellent *ee* values. Mechanistic experiments revealed that the present cycloaddition proceeds through the kinetic resolution of the racemic secondary allylic alcohols, in which one enantiomer preferentially reacts with the 1,6-enyne.

The transition-metal-catalyzed asymmetric [2+2+2] cycloaddition of 1,6-enynes with alkenes is a useful method for the construction of bicyclic cyclohexene frameworks.[1] For this asymmetric transformation, cationic rhodium(I)/axially chiral biaryl bisphosphine complexes show high catalytic activity and selectivity.[2] For example, our research group reported that a cationic rhodium(I)/H_8-binap complex is capable of catalyzing the regio-, diastereo-, and enantioselective [2+2+2] cycloaddition of 1,6-enynes[3,4] with acrylamides[5] giving chiral bicyclic cyclohexenes, possessing two stereogenic centers (Scheme 1a).[6] Not only acrylamides but also enamides[7] and oxabenzonorborna-dienes[8] could be employed in the rhodium-catalyzed asymmetric [2+2+2] cycloaddition with 1,6-enynes. In the reactions using acrylamides and enamides, the coordination of the amide carbonyl into rhodium induce high reactivity and selectivity, and suppress the undesired β-hydrogen elimination giving diene products.[6,7a,9]

In 2016, Roglans and Pla-Quintana reported that racemic secondary allylic alcohols[10] react with 1,6-diynes through the kinetic resolution[11] in the presence of a cationic rhodium(I)/binap complex to give bicyclic cyclohexadienes (Scheme 1b).[12] This reaction can construct contiguous two stereogenic centers as a single diastereomer with high *ee* values, while the substrate scope was somewhat limited (methoxycarbonyl- and aryl-substituted allylic alcohols, and sulfonamide-linked and dimethyl-substituted 1,6-diynes). In this Communication, we have established that a cationic rhodium(I)/P-phos complex is capable of catalyzing the regio-, diastereo-, and enantioselective [2+2+2] cycloaddition of 1,6-enynes with racemic secondary allylic alcohols through the kinetic resolution at room temperature giving chiral bicyclic cyclohexenes, possessing three stereogenic centers (Scheme 1c). This newly developed asymmetric catalysis shows a broad substrate scope concerning both 1,6-enyes and allylic alcohols.



Scheme 1. Research background. Ts = *p*-toluenesulfonyl. Ns = *o*-nitrobenzenesulfonyl. MW = microwave.

We first examined the reaction of tosylamide-linked 1,6-enyne **1a** and phenyl-substituted racemic secondary allylic alcohol **2a** (3 equiv) in the presence of the cationic rhodium(I)/(*R*)-binap catalyst (20 mol %). The desired [2+2+2] cycloaddition proceeded at room temperature to give bicyclic cyclohexene **3aa** with high *ee* value, but the yield of **3aa** was low due to the formation of the undesired β-hydrogen elimination product **4aa** (Table 1, entry 1). Increasing the steric bulk on the phosphorus significantly decreased the yields of both **3aa** and **4aa** (entry 2). Thus, axially chiral biaryl bisphosphine ligands with various biaryl backbones[13] were surveyed (entries 3–6). This survey revealed that the use of (*R*)-segphos, possessing the smallest dihedral angle, shows the highest ratio of **3aa**/**4aa** with retaining the high *ee* value of **3aa** (entry 6), on the contrary, the use of (*R*)-H_8-binap, possessing the largest dihedral angle, shows the lowest ratio of **3aa**/**4aa** (entry 3). We anticipated that the use of electron-deficient segphos-type ligands (entries 7–9) would facilitate the reductive elimination and increase the yield of **3aa** and decrease the yield of **4aa**. Pleasingly, the use of P-phos increased the yield of **3aa** to 57% and decreased the yield

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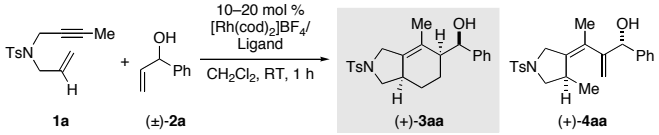
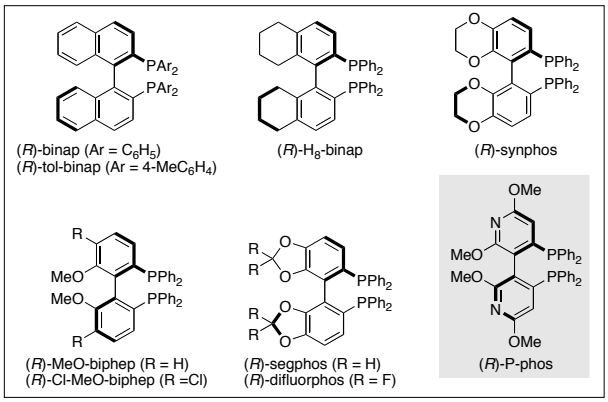
of **4aa** to 5% (entry 9). Increasing the amount of **2a** to 5 equiv further increased the yield of **3aa** to 64% (entry 10), but the further increase of **2a** to 10 equiv did not increase the yield of **3aa** (entry 11). Finally, the catalyst loading could be reduced to 10 mol %, with only a slight erosion of the yield of **3aa** (entry 12).

Table 1. Optimization of reaction conditions.[a]

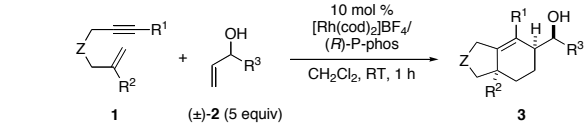


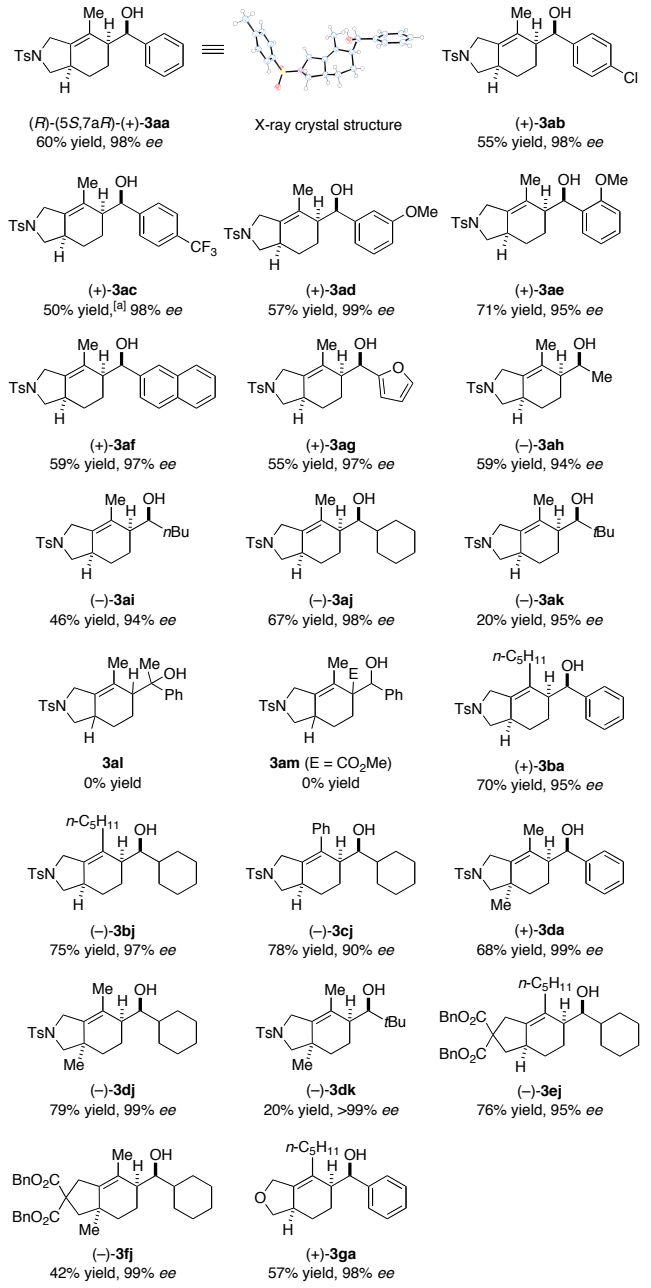


Entry	Ligand	(±)-**2a** (equiv)	Catalyst (mol %)	(+)-**3aa** % yield[b] (% *ee*)	(+)-**4aa** % yield[b] (% *ee*)
1	(*R*)-binap	3	20	39 (98)	24 (94)
2	(*R*)-tol-binap	3	20	18 (98)	13 (98)
3	(*R*)-H_8-binap	3	20	17 (97)	30 (99)
4	(*R*)-synphos	3	20	27 (98)	13 (89)
5	(*R*)-MeO-biphep	3	20	35 (99)	15 (92)
6	(*R*)-segphos	3	20	36 (98)	12 (90)
7	(*R*)-Cl-MeO-biphep	3	20	46 (98)	22 (95)
8	(*S*)-difluorphos	3	20	55 (96[c])	<5 (59[c])
9	(*R*)-P-phos	3	20	57 (98)	5 (75)
10	(*R*)-P-phos	5	20	64 (98)	6
11	(*R*)-P-phos	10	20	64 (98)	6
12	(*R*)-P-phos	5	10	60 (98)	5

[a] $[Rh(cod)_2]BF_2$ (0.0050–0.020 mmol), ligand (0.0050–0.020 mmol), **1a** (0.10 mmol), **2a** (0.30–1.00 mmol), and CH_2Cl_2 (2.0 mL) were used. [b] Isolated yield. cod = 1,5-cyclooctadiene.

With the optimized reaction conditions in hand, we examined the substrate scope of this reaction by using (*R*)-P-phos as a ligand (Scheme 2). With regard to allylic alcohols, 1-phenylprop-2-en-1-ol derivatives **2a**–**e** with electronically and sterically diverse substituents on the benzene ring reacted with 1,6-enyne **1a** to give the corresponding cyclohexenes **3aa**–**ae** with good yields and high *ee* values. Naphthyl- and heteroaryl-substituted allylic alcohols **2f** and **2g** could participate in this reaction as well. Not only aryl but also primary, secondary, and tertiary alkyl-substituted allylic alcohols **2h**–**k** were suitable substrates for this process. However, tertiary allylic alcohol **2l** and methoxycarbonyl-substituted secondary allylic alcohol **2m** failed to react with **1a**. The scope of 1,6-enynes was also examined. Interestingly, the improved product (**3ba**, **3bj**, and **3cj**) yields were observed in the reactions of 1,6-enynes **1b** and **1c**, possessing the bulkier substituent than the methyl group at the alkyne terminus. Also, the improved product (**3da**, **3dj**, and **3dk**) yields and/or *ee* values were observed in the reactions of 1,6-enyne **1d**, possessing 1,1-disubstituted alkene moiety. Not only tosylamide- (**1a**–**d**) but also malonate- (**1e**,**f**) and ether (**1g**)-linked 1,6-enynes could be employed for this reaction. Importantly, in all cases, the cyclohexene products **3** were obtained as a single diastereomer with high *ee* values of 90–>99%. The relative and absolute configurations of (+)-**3aa** were determined to be (*R*)-(5*S*,7a*R*) by an X-ray crystallographic analysis.[14]





Scheme 2. Substrate scope. $[Rh(cod)_2]BF_2$ (0.015 mmol), ligand (0.015 mmol), **1** (0.15 mmol), **2** (0.75 mmol), and CH_2Cl_2 (2.0 mL) were used. The cited yields were of isolated products. [a] Determined by ^1H NMR using dimethyl sulfone as an internal standard.

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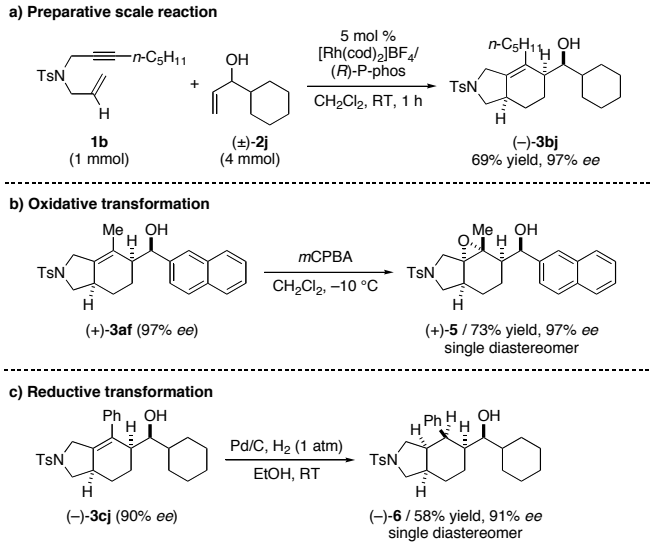
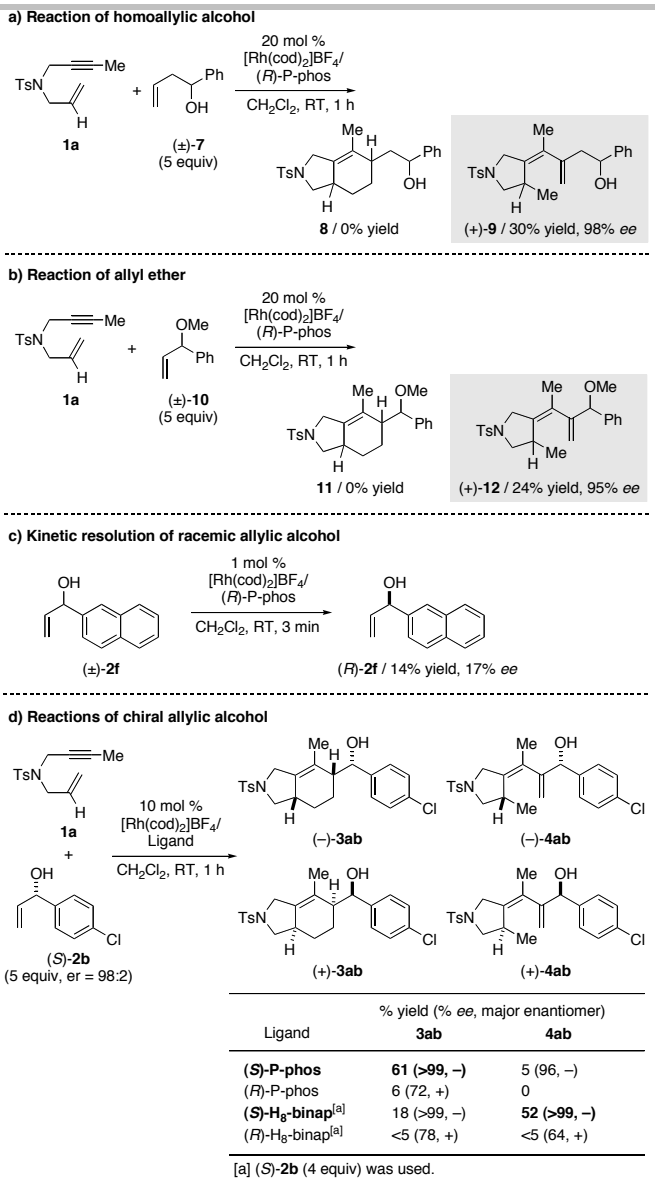
The present asymmetric [2+2+2] cycloaddition was scalable and thus the reaction using 1 mmol of **1b** proceeded by using reduced amounts of **2j** (4 equiv) and the Rh catalyst (5 mol %) to give cyclohexene product **3bj** with almost the same isolated yield and *ee* value comparing with the small scale reaction (Scheme 3a). Synthetic transformations of the cyclohexene products were also examined. Epoxide **5**, possessing five consecutive stereogenic centers, was isolated as a single diastereomer by oxidation of **3af** with *m*CPBA (Scheme 3b). Cyclohexane **6**, possessing five consecutive stereogenic centers, was also obtained as a single diastereomer by hydrogenation of **3cj** (Scheme 3c).



Scheme 3. Synthetic applications. *m*CPBA = *m*-chloroperoxybenzoic acid.

To gain mechanistic insight into the present cycloaddition accompanied by the kinetic resolution, the following experiments were conducted. The reaction of homoallylic alcohol **7**[15] and allyl ether **10** with **1a** under the same reaction conditions as Scheme 2 afforded dienes **9** and **12** without the formation of cyclohexenes **8** and **11** (Schemes 4a and 4b). These results suggest that the strong bidentate coordination of the allylic alcohol into rhodium might deter the β-hydrogen elimination giving the diene product and promote reductive elimination giving the cyclohexene product. The rapid consumption of racemic allylic alcohol (±)-**2f** was observed at room temperature in the presence of a small amount (1 mol %) of the cationic rhodium(I)/(*R*)-P-phos complex to give unreacted allylic alcohol (*R*)-**2f** with low yield and *ee* value (Scheme 4c).[16] This result suggests that the major pathway of the kinetic resolution is not the reaction of allylic alcohol itself but that with the 1,6-enyne.[17]

Thus, the reactions of chiral allylic alcohol (*S*)-**2b** (er = 98:2) with **1a** were examined by using (*R*)- and (*S*)-axially chiral biaryl bisphosphine ligands (Scheme 4d). The use of (*S*)-P-phos and (*S*)-H_8-binap afforded (–)-**3ab** and (–)-**4ab**, respectively, in good yields with high *ee* values along with small amounts of (–)-**4ab** and (–)-**3ab**, respectively. The use of (*R*)-P-phos and (*R*)-H_8-binap did not afford (–)-**3ab** and (–)-**4ab**, and afforded trace amounts of (+)-**3ab**, and (+)-**3ab**/(+)-**4ab**, respectively. These results suggest that one enantiomer of the racemic allylic alcohol preferentially reacts with the 1,6-enyne to give both the cyclohexene and diene products. The selectivity between reductive elimination giving the cyclohexene and β-hydrogen elimination giving the diene is determined by the ligand used.



Ligand	% yield (% *ee*, major enantiomer) 3ab	4ab
(*S*)-P-phos	**61 (>99, –)**	5 (96, –)
(*R*)-P-phos	6 (72, +)	0
(*S*)-H_8-binap[a]	18 (>99, –)	**52 (>99, –)**
(*R*)-H_8-binap[a]	<5 (78, +)	<5 (64, +)

[a] (*S*)-**2b** (4 equiv) was used.

Scheme 4. Mechanistic experiments.

Proposed reaction mechanism is shown in Scheme 5a. 1,6-Enyne **1** reacts with rhodium to generate rhodacyclopentene **A**. Bidentate coordination of racemic allylic alcohol (±)-**2** to rhodium would generate four diastereomeric intermediates **B1**–**B4**. In intermediates **B2**–**B4**, there is steric repulsion between the equatorial phenyl group and R^1, and/or between the rhodacyclopentene moiety and R^3. On the contrary, no steric repulsion exists in intermediate **B1**. Thus, insertion of **2** predominantly proceeds in **B1** to generate rhodacycloheptene **C**, and the subsequent reductive elimination affords cyclohexene **3** as a single diastereomer with high *ee* value without the formation of cyclohexenes **3'**, **3''**, and **3'''**. The ligand-controlled β-hydrogen elimination[18] also proceeds in **C** to give diene **4** through intermediate **D**.

To confirm this mechanism, the reaction of sterically less demanding 1,6-enyne **1h** (R^1 = R^2 = H, Z = NTs in **1** of Scheme 5a) and racemic allylic alcohol (±)-**2h** (R^3 = Me in **2** of Scheme 5a) was examined. In this reaction, the steric repulsion between the equatorial phenyl group and R^1 can be minimized, and that between the rhodacyclopentene ring and R^3 would be small. Thus, a mixture of diastereomers was generated, and

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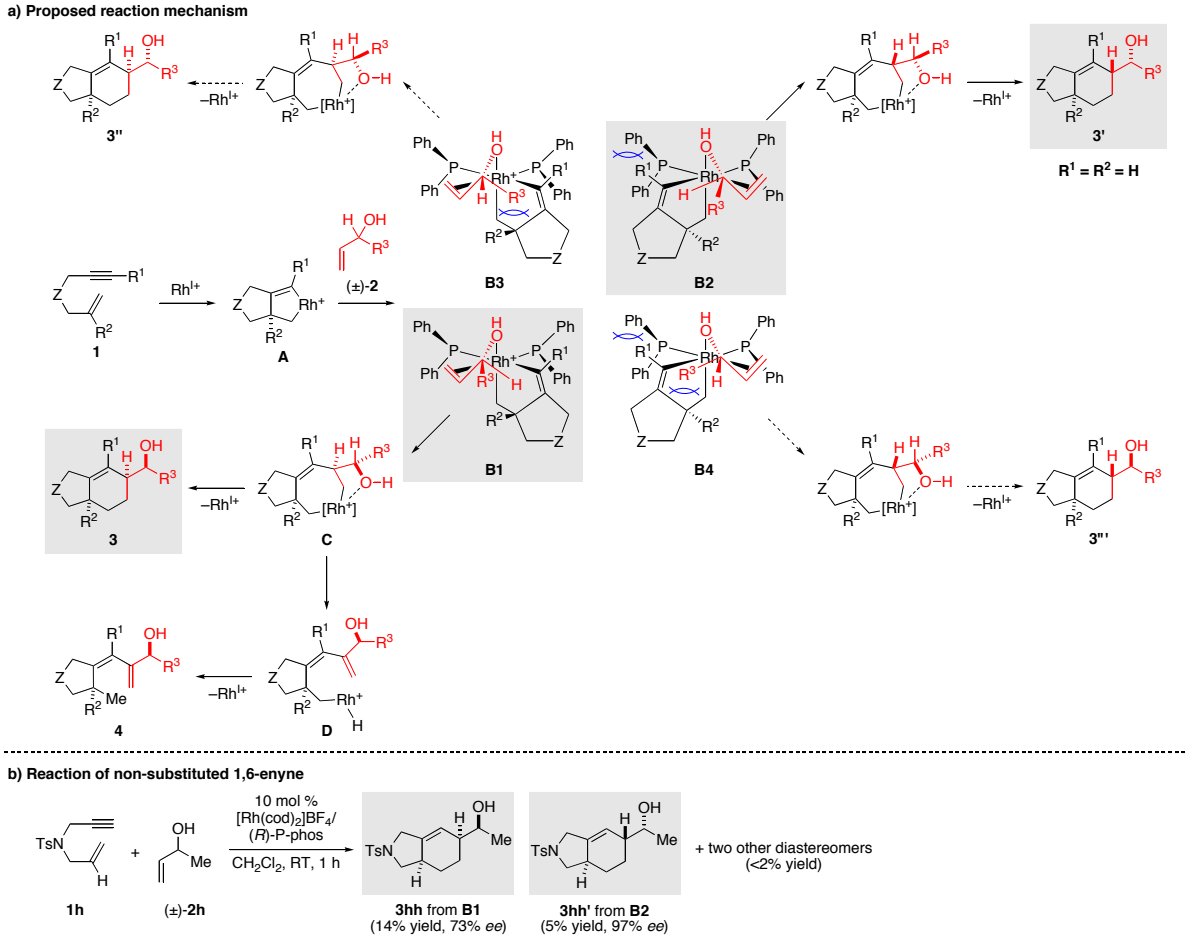
diastereomers **3hh** and **3hh'**, which are generated from sterically less demanding intermediates **B1** and **B2**, respectively, as major products (Scheme 5b).[19]



Scheme 5. Proposed reaction mechanism.

In conclusion, we have established that a cationic rhodium(I) complex bearing the P-phos ligand, which is electron-deficient and possesses a small dihedral angle, catalyzes the asymmetric [2+2+2] cycloaddition of 1,6-enynes with racemic secondary allylic alcohols to produce the corresponding chiral bicyclic cyclohexenes, possessing three stereogenic centers, as a single diastereomer with excellent *ee* values. The strong bidentate coordination of the allylic alcohol into rhodium might deter the β-hydrogen elimination, and facilitate reductive elimination to give the cyclohexene product. The present cycloaddition proceeds through the kinetic resolution of the racemic secondary allylic alcohols, in which one enantiomer preferentially reacts with the 1,6-enyne. Future works will focus on the further development of the rhodium-catalyzed asymmetric [2+2+2] cycloaddition involving the kinetic resolution.

Acknowledgements

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Keywords: allylic alcohols • enynes • kinetic resolution • rhodium • asymmetric [2+2+2] cycloaddition

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[13] For a review , see: H. Shimizu, I. Nagasaki, T. Saito, *Tetrahedron* **2005**, *61*, 5405.

[14] CCDC 1971249 [(+)-**3aa**] contains 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.

[15] The rhodium-catalyzed enantioselective stereoconvergent isomerization of racemic secondary homoallylic and bishomoallylic alcohols was reported. See: R.-Z. Huang, K. K. Lau, Z. Li, T.-L. Liu, Y. Zhao, *J. Am. Chem. Soc.* **2018**, *140*, 14647.

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[17] In the reactions shown in Scheme 2, secondary allylic alcohols, which did not react with 1,6-enynes, were converted to a complex mixture of products presumably through the olefin isomerization. Therefore, the selectivity factor could not be determined.

[18] For examples of β-Hydride elimination from seven-membered rhodacycles, see: a) M. Ishida, Y. Shibata, K. Noguchi, K. Tanaka, *Chem. Eur. J*. **2011**, *17*, 12578; b) M. Kobayashi, K. Tanaka, *Chem. Eur. J*. **2012**, *18*, 9225. c) H. Ueda, K. Masutomi, Y. Shibata, K. Tanaka, *Org. Lett*. **2017**, *19*, 2913.

[19] For the structural determination for diastereomers **3hh** and **3hh'**, see the Supporting Information.

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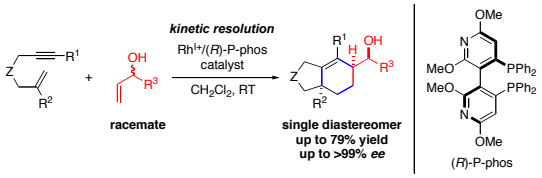

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Rhodium-Catalyzed Asymmetric [2+2+2] Cycloaddition of 1,6-Enynes with Racemic Secondary Allylic Alcohols through Kinetic Resolution