Cascade Reactions

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Rhodium-Catalyzed Cascade Reactions of Dienynes Leading to Substituted Dihydronaphthalenes and Naphthalenes**

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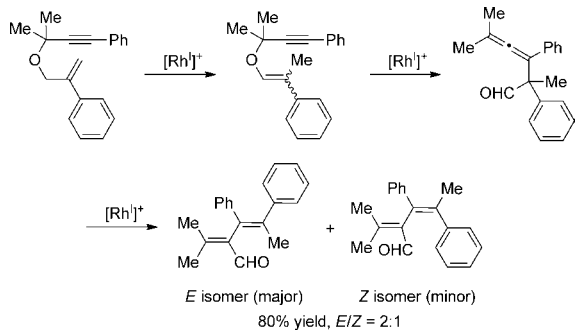
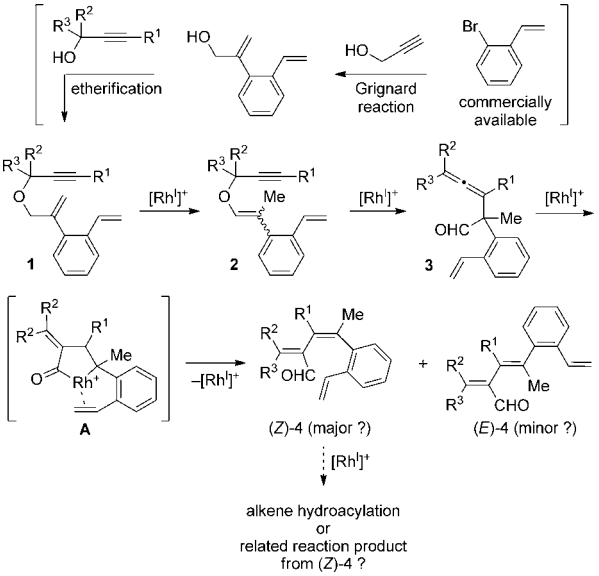
The elimination of a number of reaction steps, the avoidance of toxic reagents, and the reduction of hazardous waste are important subjects in modern organic synthesis.[1] To solve these problems, the development of novel cascade reactions, in which multiple reactions proceed in one step to afford complex molecules, is attractive. Obviously, the development of catalytic versions is even more attractive, and the use of a single multifunctional catalyst that is able to catalyze multiple fundamentally different transformations is ultimately desired. We recently reported cascade reactions catalyzed by a cationic rhodium(I)/dppf complex, including the olefin isomerization,[2] the propargyl Claisen rearrangement,[3] and the carbonyl migration reaction,[4] which transform allyl propargyl ethers to allenic aldehydes and dienals.[5–7] In these cascade reactions, the single multifunctional cationic rhodium(I)/dppf catalyst sequentially activates the allylic[8] and aldehyde C–H bonds,[9,10] and the alkyne π bond.[11,12] In the reaction of an enyne that possesses a phenyl-substituted alkene moiety, the corresponding dienal was obtained in high yield as a mixture of stereoisomers (Scheme 1).



Scheme 1. Previously reported olefin isomerization/propargyl Claisen rearrangement/carbonyl migration cascade of an enyne.

The above-mentioned cascade reactions involve up to three fundamentally different reactions. We anticipated that if an allyl propargyl ether possessed an additional olefin moiety, the novel cascade reaction, which involves more than three different reaction steps, would succeed. Thus, we designed dienyne **1**, which can be readily synthesized by Grignard reaction of commercially available 2-bromostyrene and propargyl alcohol,[13] followed by etherification with a substituted propargyl alcohol. The olefin isomerization and the propargyl Claisen rearrangement of dienyne **1** by the cationic rhodium(I) catalyst would furnish allenic aldehyde **3** via enol ether **2**. We anticipated that as a result of the chelation of the styrene moiety to the cationic rhodium core, the subsequent carbonyl migration would furnish (*Z*)-dienal **4** as a major stereoisomer. (*Z*)-Dienal **4** would be further transformed into an alkene hydroacylation or related reaction product (Scheme 2). Herein, we disclose cascade reactions of dienynes catalyzed by the cationic rhodium(I) complex, involving up to five fundamentally different transformations, including the enantioselective carboformylation of alkenes with aldehydes[14] or the cycloisomerization of enallenes.



Scheme 2. Design of the rhodium-catalyzed cascade reaction of dienyne **1**.

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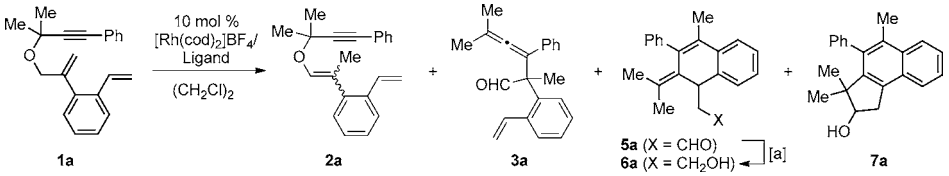
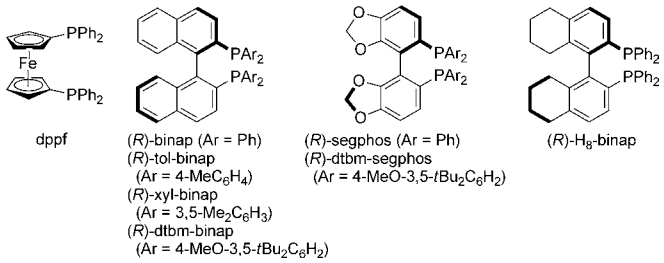
Table 1: Optimization of reaction conditions.



Entry	Ligand	Conditions	Conversion [%]	Yield[b] **2a** (*E*/*Z*)	**3a**	**5a** or **6a** and/or **7a**
1	dppf	RT, 16 h	100	71%[c] (1.7:1)	–	–
2	dppf	80°C, 16 h	100	<1%	<1%	**5a**: <5%, **7a**: 7%
3	(*R*)-binap	80°C, 40 h	100	–	–	**7a**: 34%[c] (51% *ee*)
4[a]	(*R*)-binap	40°C, 36 h	100	–	–	**6a**+**7a**: 49%[c] (**6a**/**7a** = 12:1, **6a**: 76% *ee*)
5[a]	(*R*)-H_8-binap	40°C, 36 h	100	37% (1:45)	<1%	**6a**: 9%[c] (79% *ee*)
6[a]	(*R*)-segphos	40°C, 36 h	98	18% (1:4)	7%	**6a**+**7a**: 26%[c] (**6a**/**7a** = 12:1, **6a**: 60% *ee*)
7	(*R*)-dtbm-segphos	40°C, 36 h	78	51% (1:8)	16%[c]	–
8[a]	(*R*)-tol-binap	40°C, 36 h	97	7% (1:3)	4%	**6a**+**7a**: 38%[c] (**6a**/**7a** = 18:1, **6a**: 57% *ee*)
9[a]	(*R*)-xyl-binap	40°C, 36 h	97	11% (1:3)	17%[c]	**6a**: 31%[c] (85% *ee*)
10	(*S*)-dtbm-binap	40°C, 36 h	19	5% (<1:>99)	2%	–
11[a]	(*R*)-xyl-binap	70°C, 24 h	96	4% (2:1)	<1%	**6a**: 45%[c] (80% *ee*)
12	(*R*)-xyl-binap	80°C, 40 h	100	–	–	**7a**: 43%[c] (67% *ee*)

[a] The crude reaction mixture containing aldehyde **5a** was treated with $NaBH_4$ (THF/MeOH, RT, 1 h) in order to isolate reduced alcohol **6a**. [b] Determined by ^1H NMR spectroscopy. [c] Yield of isolated product.

The reaction of dienyne **1a** in the presence of the cationic rhodium(I)/dppf catalyst was investigated first. At room temperature olefin isomerization product **2a** was generated in high yield (Table 1, entry 1), on the other hand, at 80°C 1,2-dihydronaphthalene **5a** and naphthalene **7a** were generated in low yields (entry 2). The use of (*R*)-binap as a ligand furnished **7a** in significantly improved yield with a moderate *ee* value (Table 1, entry 3). We anticipated that **7a** was generated through the rhodium-catalyzed carbonyl ene reaction of aldehyde **5a** and thus lowered the reaction temperature to restrain this reaction. Pleasingly, when the reaction was conducted at 40°C for 24 hours, we obtained alcohol **6a** in moderate yield with good *ee* value after treatment with $NaBH_4$ (Table 1, entry 4). Thus, we screened various biaryl bisphosphine ligands (Scheme 3) at 40°C



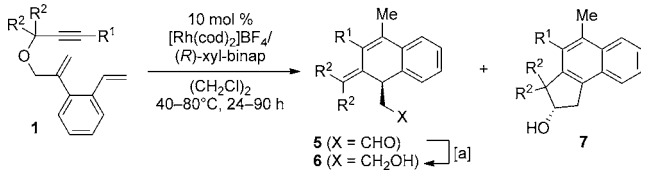
Scheme 3. Structures of bisphosphine ligands.

(Table 1, entries 5–10) and found that the use of (*R*)-xyl-binap furnished **6a** with the highest *ee* value, although the reaction rate decreased (Table 1, entry 9). Importantly, as the reactions with some sterically demanding ligands furnished the expected allene intermediate **3a** in isolatable amounts (Table 1, entries 7 and 9), the structure of **3a** was confirmed unambiguously by its spectral and analytical data. Finally, the reaction was conducted at 70°C for 24 hours to afford alcohol **6a** in improved yield with a high *ee* value (Table 1, entry 11), and alcohol **7a** could also be obtained in moderate yield with a good *ee* value by conducting the reaction at 80°C for 40 hours (entry 12).

Thus, the scope of the enantioselective 1,2-dihydronaphthalene synthesis was explored by using the cationic rhodium(I)/(*R*)-xyl-binap catalyst (Table 2).[15–17] Electronically diverse aryl groups could be incorporated at the alkyne terminus to give 1,2-dihydronaphthalenes **6a–f** in moderate yields with high *ee* values (Table 2, entries 1–6). As the *ee* value of **6d** was low (49% *ee*) when the reaction of **1d** was performed at 70°C, the reaction was conducted at 40°C for 72 hours (Table 2, entry 4). Interestingly, the *ee* value of *meta*-substituted phenyl derivative **6f** (Table 2, entry 6) was significantly higher than that of *para*-substituted phenyl derivative **6b** (entry 2). A primary alkyl group could also be incorporated at the alkyne terminus by using (*R*)-binap as a ligand, although lower enantioselectivity was observed (Table 2, entry 7). However, the reaction of dienyne **1h**, which possesses a secondary alkyl group at the alkyne terminus, was sluggish even at 80°C, and the *ee* value of product **6h** was very low (Table 2, entry 8). With respect to substituents at the propargylic position, the reactions of acetone- and cycloalkanone-derived tertiary propargyl ethers **1i** and **1j** proceeded at 40°C for 72 hours to give 1,2-dihydronaphthalenes **6i** and **6j**, respectively, with high *ee* values, although the yields of products decreased (Table 2, entries 9 and 10).

Next, the scope of the enantioselective naphthalene synthesis was explored at 80°C. The reactions of various substituted arylacetylene-derived dienynes **1a–f** proceeded to give the corresponding naphthalenes **7a–f** (Table 2, entries 11–16), however, the reaction of 4-chlorophenylacetylene-derived dienyne **1d** was sluggish (Table 2, entry 14)

Table 2: Asymmetric one-pot synthesis of substituted 1,2-dihydronaphthalenes **6** and naphthalenes **7** from dienynes **1**.



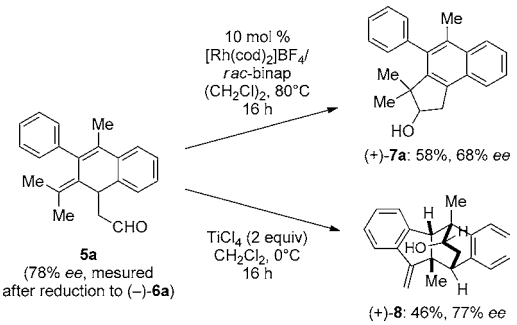
Entry	**1** (R^1/R^2,R^2)	Conditions	Yield of **6**+**7** [%][b] (**6**/**7**)[c]	**6** or **7** (% *ee*)
1[a]	**1a** (Ph/Me,Me)	70°C, 24 h	45 (**6a**)	(−)-**6a** (80)
2[a]	**1b** (4-$F_3CC_6H_4$/Me,Me)	70°C, 24 h	59 (13:1)	(−)-**6b** (78)
3[a]	**1c** (4-FC_6H_4/Me,Me)	70°C, 37 h	58 (13:1)	(−)-**6c** (77)
4[a]	**1d** (4-ClC_6H_4/Me,Me)	40°C, 72 h	49 (**6d**)	(−)-**6d** (85)
5[a]	**1e** (4-MeC_6H_4/Me,Me)	70°C, 38 h	47 (7:1)	(−)-**6e** (78)
6[a]	**1f** (3-$F_3CC_6H_4$/Me,Me)	70°C, 72 h	60 (**6f**)	(−)-**6f** (90)
7[a,d]	**1g** (*n*Bu/Me,Me)	60°C, 40 h	50 (2.3:1)	(−)-**6g** (40)
8[a,d]	**1h** (Cy/Me,Me)	80°C, 96 h	25[e] (**6h**)	(−)-**6h** (12)
9[a]	**1i** [Ph/$(CH_2)_4$]	40°C, 72 h	32 (**6i**)	(−)-**6i** (88)
10[a]	**1j** [Ph/$(CH_2)_5$]	40°C, 72 h	38 (**6j**)	(−)-**6j** (79)
11	**1a** (Ph/Me,Me)	80°C, 40 h	43 (**7a**)	(+)-**7a** (67)
12	**1b** (4-$F_3CC_6H_4$/Me,Me)	80°C, 65 h	51 (**7b**)	(+)-**7b** (64)
13	**1c** (4-FC_6H_4/Me,Me)	80°C, 90 h	50 (**7c**)	(+)-**7c** (62)
14	**1d** (4-ClC_6H_4/Me,Me)	80°C, 90 h	31[f] (**7d**)	(*S*)-(+)-**7d** (64)
15	**1e** (4-MeC_6H_4/Me,Me)	80°C, 72 h	29 (**7e**)	(+)-**7e** (63)
16	**1f** (3-$F_3CC_6H_4$/Me,Me)	80°C, 72 h	43 (**7f**)	(+)-**7f** (71)
17[d]	**1g** (*n*Bu/Me,Me)	40°C, 25 h; then 80°C, 24 h	40 (**7g**)	(+)-**7g** (31)

[a] Products were isolated after treatment with $NaBH_4$ (THF/MeOH, RT, 1 h). [b] Yields of isolated products. [c] Determined by ^{1}H NMR spectroscopy. [d] Ligand: (*R*)-binap. [e] Alkenyl ether **2h** was obtained in ca. 40% yield. [f] Aldehyde **5d** was obtained in ca. 20% yield.

and that of 4-methylphenylacetylene-derived dienyne **1e** afforded the corresponding naphthalene **7e** along with a complex mixture of unidentified products (entry 15). The reaction of alkylacetylene-derived dienyne **1g** could also furnish naphthalene **7g** by using (*R*)-binap as a ligand, however, the *ee* value was low (Table 2, entry 17). With cycloalkanone-derived substrates **1i** and **1j**, the carbonyl ene reaction did not even succeed at 80°C. A comparison of *ee* values of 1,2-dihydronaphthalenes **6a–g** (Table 2, entries 1–7) and naphthalenes **7a–g** (entries 11–17) showed that the present rhodium-catalyzed carbonyl ene reactions are moderately stereoselective. The absolute configuration of naphthalene (+)-**7d** was determined to be (*S*) by the anomalous dispersion method (Figure 1).[18,19]

In order to confirm whether the cationic rhodium(I) complex catalyzes the carbonyl ene reaction step, the isolated aldehyde (+)-**5a** (78% *ee*), prepared from **1a** by using the cationic rhodium(I)/(*R*)-xyl-binap catalyst, was treated with the cationic rhodium(I)/*rac*-binap complex (10 mol%) at 80°C. The desired alcohol (+)-**7a** was indeed obtained with almost the same level of chirality transfer as that obtained with the cationic rhodium(I)/(*R*)-xyl-binap complex (68% *ee*, Scheme 4). Therefore, the chirality of the rhodium(I) catalyst does not affect the chirality transfer from **5a** to **7a**. On the other hand, treatment of the same isolated aldehyde **5a** (78% *ee*) with $TiCl_4$ at 0°C furnished bridged pentacyclic alcohol (+)-**8** in moderate yield with an excellent level of chirality transfer (Scheme 4). The structure of (±)-**8** was unambiguously confirmed by the X-ray crystallographic analysis (Figure 2).[18] This transformation represents another synthetic utility of the present cascade reaction product.

In our previous report, isomerization of allyl propargyl ethers that possess a secondary propargyl ether moiety was terminated at the stage of the corresponding allenic aldehydes.[5] Therefore, the rhodium-catalyzed reaction of a dienyne that possesses



Scheme 4. Carbonyl ene reaction of isolated **5a** with the cationic rhodium(I)/*rac*-binap complex versus $TiCl_4$.

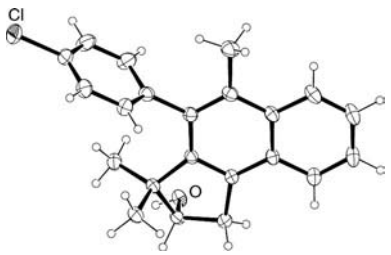


Figure 1. ORTEP drawing of (*S*)-(+)-**7d** with ellipsoids at 30% probability.

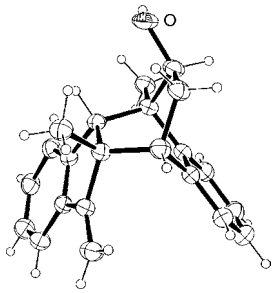
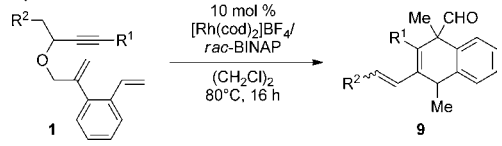


Figure 2. ORTEP drawing of (±)-**8** with ellipsoids at 30% probability.

a secondary propargyl ether moiety would furnish another product via allenic aldehyde **3** (Scheme 1). Indeed, the reaction of dienyne **1k** in the presence of the cationic rhodium(I)/*rac*-binap catalyst at 80 °C gave vinyl-substituted 1,4-dihydronaphthalene **9k**, instead of 1,2-dihydronaphthalene, in good yield as a mixture of diastereomers (Table 3, entry 1). The structure of **9k** was confirmed by X-ray crystallographic analysis (Figure 3).[18] The reactions of both arylacetylene- and alkylacetylene-derived dienynes **1l–n** furnished vinyl-substituted 1,4-dihydronaphthalenes **9l–n** in good yields (Table 3, entries 2–4).[15,16] Crotyl- and styryl-substituted 1,4-dihydronaphthalenes **9o** and **9p** could also be obtained in good yields (Table 3, entries 5 and 6).

Table 3: One-pot synthesis of substituted 1,4-dihydronaphthalenes **9** from dienynes **1**.[a]



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Entry	1	R^1	R^2	9	Yield[a] [%] (d.r., *E*/*Z*)
1	**1k**	Ph	H	**9k**	76 (1:1, –)
2	**1l**	4-ClC_6H_4	H	**9l**	64 (1:1, –)
3	**1m**	4-$MeOC_6H_4$	H	**9m**	68 (1:1, –)
4	**1n**	*n*Bu	H	**9n**	42 (1.3:1, –)
5	**1o**	Ph	Me	**9o**	61 (2:1, 8:1)
6	**1p**	Ph	Ph	**9p**	60 (2:1, 7:1)

[a] Yields of isolated products.

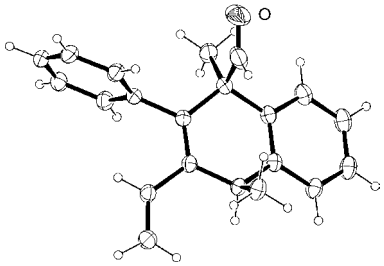
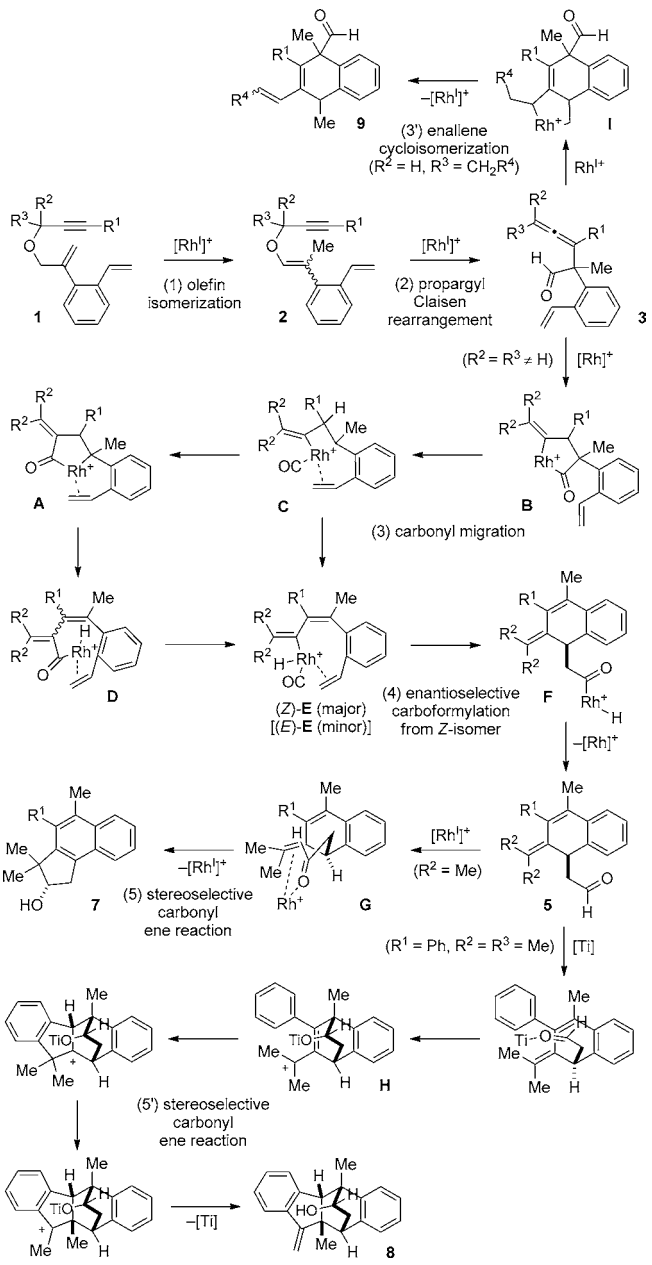


Figure 3. ORTEP drawing of **9k** with ellipsoids at 30% probability.

A plausible mechanism for the present cascade reactions is outlined in Scheme 5. The olefin isomerization of allyl ether **1** followed by the propargyl Claisen rearrangement furnishes allenic aldehyde **3** via enol ether **2**.[20] In the case of dienynes that possess a tertiary propargyl ether moiety, the carbonyl migration reaction proceeds via intermediates **B**, **C**, **A**, and **D** to afford rhodium carbonyl hydride **E**. However, we could not observe the formation of dienal **4**, and so the direct formation of intermediate **E** from intermediate **C** is more likely. In intermediate **E**, the styrene and the alkenylrhodium moieties would predominantly be in *Z* configuration as a result of the coordination of the alkene to the rhodium core. The enantioselective alkene carboformylation proceeds to afford 1,2-dihydronaphthalene **5** via intermediate **F**. At 80 °C, the stereoselective carbonyl ene reaction between the exo C=C bond and the formyl group catalyzed by the cationic rhodium(I) complex[21] further proceeds via chelating intermediate **G** to generate naphthalene **7**. On the other hand, the carbonyl ene reaction proceeds through sole activation of the formyl group with $TiCl_4$ to give cationic intermediate **H**.[22] The Friedel–Crafts alkylation followed by the methyl group migration affords **8**. We believe that the possible chelation of rhodium between the alkene moiety and formyl group in intermediate **G** may play an important role for the chemoselective carbonyl ene reaction of **5a** to **7a** instead of **8**. In the case of dienyne that possesses a secondary propargyl ether



Scheme 5. Plausible mechanism for the formation of products **5**, **7**, **8**, and **9** from dienynes **1**.

moiety, not the carbonyl migration but the enallene cycloisomerization[23] proceeds via rhodacycle **I** to afford 1,4-dihydronaphthalene **9**.

In conclusion, the catalytic cascade reactions of dienynes, leading to 1,2-dihydronaphthalenes, naphthalenes, and 1,4-dihydronaphthalenes, including the catalytic enantioselective carboformylation of alkenes with aldehydes or the cycloisomerization of enallenes have been developed by using the cationic rhodium(I)/xyl-binap or binap complex as a catalyst. It is noteworthy that the present cascade reactions involve up to five fundamentally different transformations, a goal which has not been achieved to date. Future studies will focus on further utilization of the multifunctional cationic rhodium(I) complex in catalytic cascade reactions.

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Keywords: carbonyl ene reactions · cascade reactions · cycloisomerizations · dienynes · rhodium

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[10] For selected recent examples of the rhodium(I)-catalyzed enantioselective hydroacylation of alkenes or allenes with aldehydes, see: a) M. C. Coulter, K. G. M. Kou, B. Galligan, V. M. Dong, *J. Am. Chem. Soc.* **2010**, *132*, 16330; b) D. T. H. Phan, K. G. M. Kou, V. M. Dong, *J. Am. Chem. Soc.* **2010**, *132*, 16354; c) Y. Shibata, K. Tanaka, *J. Am. Chem. Soc.* **2009**, *131*, 12552; d) M. M. Coulter, P. K. Dornan, V. M. Dong, *J. Am. Chem. Soc.* **2009**, *131*, 6932; e) J. D. Osborne, H. E. Randell-Sly, G. S. Currie, A. R. Cowley, M. C. Willis, *J. Am. Chem. Soc.* **2008**, *130*, 17232; f) R. T. Stemmler, C. Bolm, *Adv. Synth. Catal.* **2007**, *349*, 1185; g) K. Kundu, J. V. McCullagh, A. T. Morehead Jr., *J. Am. Chem. Soc.* **2005**, *127*, 16042; h) Y. Sato, Y. Oonishi, M. Mori, *Angew. Chem.* **2002**, *114*, 1266; *Angew. Chem. Int. Ed.* **2002**, *41*, 1218, and references therein. For the pioneering works, see: i) Y. Taura, M. Tanaka, X.-M. Wu, K. Funakoshi, K. Sakai, *Tetrahedron* **1991**, *47*, 4879; j) R. W. Barnhart, X. Wang, P. Noheda, S. H. Bergens, J. Whelan, B. Bosnich, *J. Am. Chem. Soc.* **1994**, *116*, 1821.

[11] For a recent review on transition-metal catalyses through activation of the alkyne π bond, see: Y. Yamamoto, *J. Org. Chem.* **2007**, *72*, 7817.

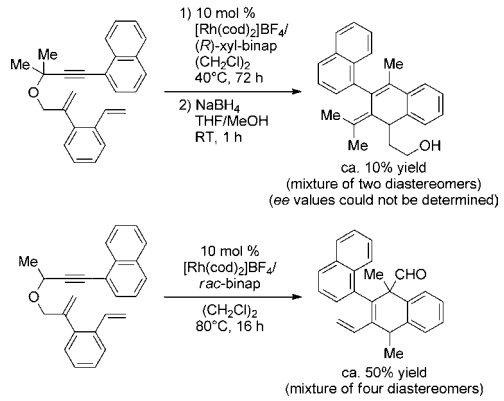
[12] For examples of the rhodium(I)-catalyzed Claisen rearrangement through activation of the alkyne π bond, see: a) A. Saito, S. Oda, H. Fukaya, Y. Hanzawa, *J. Org. Chem.* **2009**, *74*, 1517; b) A. Saito, A. Kanno, Y. Hanzawa, *Angew. Chem.* **2007**, *119*, 4005; *Angew. Chem. Int. Ed.* **2007**, *46*, 3931.

[13] J. G. Duboudin, B. Jousseaume, *J. Organomet. Chem.* **1979**, *168*, 1.

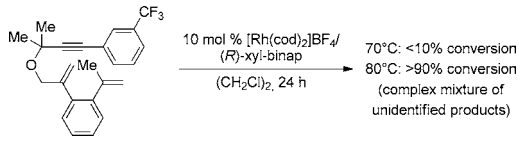
[14] Although the carboformylation of alkenes with aldehydes has not been reported, the palladium-catalyzed carboformylation of alkenes with aryliodides, $Ph_2Si(Me)H$, and CO was reported. See: S. Brown, S. Clarkson, R. Grigg, W. A. Thomas, V. Sridharanb, D. M. Wilson, *Tetrahedron* **2001**, *57*, 1347.

[15] In the reactions shown in Tables 2 and 3, no major by-product was obtained. An unidentified complex mixture was generated instead of the desired products.

[16] Although reactions of 1-naphthyl-substituted dienynes were also examined, the corresponding products were obtained as a mixture of two or four diastereomers, because of the existence of axial chirality.



[17] The reaction of α-methylstyryl-substituted allyl propargyl ether was also examined. The reaction rate was low at 70 °C and a complex mixture of unidentified products was generated at 80 °C.



[18] CCDC 809043 ((*S*)-(+)-**7d**), CCDC 869802 ((±)-**8**), and CCDC 809042 (**9k**) 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.

[19] Based on the proposed mechanism shown in Scheme 5, the absolute configuration of (−)-**6d** is estimated to be (*R*).

[20] The propargylic ene reaction and cyclization reaction under thermal conditions have recently been reported, see: a) J. M. Robinson, T. Sakai, K. Okano, T. Kitawaki, R. L. Danheiser, *J. Am. Chem. Soc.* **2010**, *132*, 11039; b) T. Sakai, R. L. Danheiser, *J. Am. Chem. Soc.* **2010**, *132*, 13203. Therefore, the behavior of dienyne **1a** was examined at 80 °C in the sole presence of the phosphine ligand or without additives. In both cases, no reaction was observed, the rhodium catalyst is thus necessary for the present cascade reaction.

[21] The rhodium(I)-catalysed hydroformylation of dienes followed by carbonyl ene reaction was reported. See: R. Roggenbuck, P. Eilbracht, *Tetrahedron Lett.* **1999**, *40*, 7455.

[22] For an example of the $TiCl_4$-mediated carbonyl ene reaction, see: A. Barbero, C. García, F. J. Pulido, *Tetrahedron* **2000**, *56*, 2739.

[23] Few examples of the transition-metal-catalyzed enallene cycloisomerizations were reported. For palladium, see: a) K. Närhi, J. Franzén, J.-E. Bäckvall, *Chem. Eur. J.* **2005**, *11*, 6937. For ruthenium, see: b) C. Mukai, R. Itoh, *Tetrahedron Lett.* **2006**, *47*, 3971. For the palladium-catalyzed carbocyclization of allenic allylic carboxylates, see: c) J. Franzén, J. Loefstedt, J. Falk, J.-E. Bäckvall, *J. Am. Chem. Soc.* **2003**, *125*, 14140. For the palladium-catalyzed oxidative enallene cycloisomerization, see: d) J. Piera, K. Naerhi, J.-E. Bäckvall, *Angew. Chem.* **2006**, *118*, 7068; *Angew. Chem. Int. Ed.* **2006**, *45*, 6914.

