SHORT COMMUNICATION

EurJOC European Journal of Organic Chemistry

DOI: 10.1002/ejoc.201300734

Rhodium-Catalyzed Cyclization Reactions of γ-Alkynyl Aldehydes with Carboxylic Acid Anhydrides

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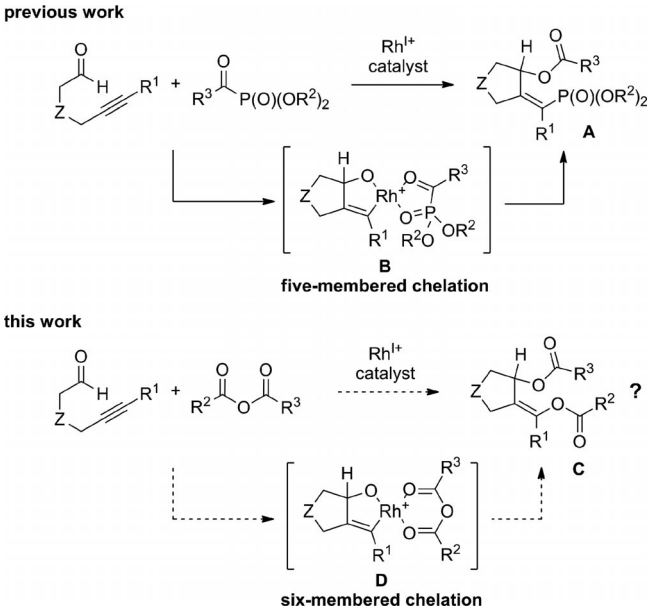
Keywords: Aldehydes / Alkynes / Anhydrides / Homogeneous catalysis / Rhodium

It has been established that a cationic rhodium(I)/H_8-binap or binap complex catalyzes two different modes of cyclization of γ-alkynyl aldehydes with carboxylic acid anhydrides to give cyclic aldehyde *gem*-dicarboxylates and cyclic alkenyl esters through cleavage of the carboxylic acid anhydride C–O bond. The reaction of a terminal γ-alkynyl aldehyde with diethyl pyrocarbonate afforded a cyclic allylic carbonate with a high *ee* value.

Introduction

A number of transition-metal-catalyzed cyclization reactions of γ-alkynyl aldehydes via oxametallacycle intermediates have been developed for the stereoselective synthesis of cyclic allylic alcohol derivatives.[1–6] For example, the titanium-,[3] nickel-,[4] rhodium-,[5] and ruthenium-catalyzed[6] cyclization reactions of γ-alkynyl aldehydes were accomplished by using organozincs,[4a] alkenylzirconiums,[4d] organosilanes,[4b,4c,4e,4h,4i,4k–4m,5a,5b] organoboranes,[4f,4g,4h,4j] dihydrogen,[5c,5d] and formic acid.[6] Recently, our research group reported the cationic rhodium(I)/H_8-binap [H_8-binap = 2,2′-bis(diphenylphosphanyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl] complex catalyzed cyclization reaction of γ-alkynyl aldehydes with heteroatom-substituted acetaldehydes.[7] In this cyclization reaction, the heteroatom-substituted acetaldehyde acts as a reducing agent through cleavage of the aldehyde C–H bond.[7] Subsequently, we extended the above reaction to the cyclization of γ-alkynyl aldehydes with an acyl phosphonate leading to cyclic allylic ester **A** through cleavage of the acyl phosphonate C–P bond via oxarhodacycle intermediate **B** bearing the chelating acyl phosphonate (Scheme 1).[8] We anticipated that the cyclization of the γ-alkynyl aldehyde with a carboxylic acid anhydride would proceed to give cyclic allylic ester **C** through cleavage of the carboxylic acid anhydride C–O bond via rhodacycle intermediate **D** bearing the chelating carboxylic acid anhydride,[9,10] although the chelation mode of the carboxylic acid anhydride to rhodium would be different from that of the acyl phosphonate (six- vs. five-membered chelation, Scheme 1). Unexpectedly, we found that the use of carboxylic acid anhydrides in place of heteroatom-substituted acetaldehydes or acyl phosphonates promoted different modes of cyclization reactions. Herein, we disclose the rhodium-catalyzed cyclization reactions of γ-alkynyl aldehydes with carboxylic acid anhydrides to produce cyclic allylic *gem*-dicarboxylates and cyclic dienyl esters through cleavage of the carboxylic acid anhydride C–O bond.



Scheme 1. Rhodium-catalyzed expected cyclization of γ-alkynyl aldehydes with carboxylic acid anhydrides.

Results and Discussion

We first examined the reaction of tosylamide-linked terminal γ-alkynyl aldehyde **1a** with benzoic anhydride (**2a**) at

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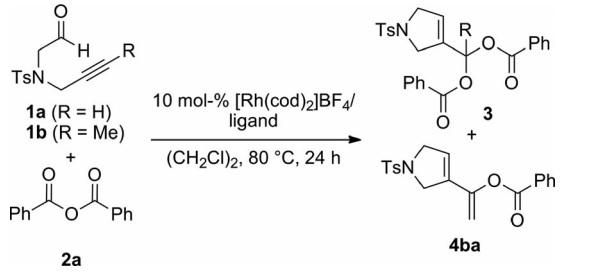
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201300734.

80 °C in the presence of the cationic rhodium(I)/H_8-binap catalyst. Unexpectedly, not cyclic allylic ester **C** but cyclic allylic *gem*-dibenzoate **3aa** was obtained in low yield (Table 1, entry 1). Various biaryl bisphosphane ligands (Figure 1) were then screened, which revealed that decreasing the dihedral angle of biaryl bisphosphane ligands decreased the yield of **3aa** (dihedral angles:[11] H_8-binap > binap > segphos, yield of **3aa**: H_8-binap > binap > segphos; Table 1, entries 1–3). Non-biaryl bisphosphane ligands were also tested, but **3aa** was not obtained at all (Table 1, entries 4 and 5). Increasing the amount of **2a** increased the yield of **3aa** (Table 1, entries 6 and 7). This unexpected structure of **3aa** was unambiguously confirmed by X-ray crystallographic analysis.[12] Next, the reaction of internal γ-alkynyl aldehyde **1b** with **2a** was examined. Interestingly, not cyclic allylic *gem*-dibenzoate **3ba** but cyclic dienyl benzoate **4ba** was obtained in good yield (Table 1, entry 9). Screening of biaryl bisphosphane ligands (Table 1, entries 9–11) revealed that the use of binap furnished **4ba** in the highest yield (Table 1, entry 10). Contrary to the formation of **3aa**, increasing the amount of **2a** decreased the yield of **4ba** (Table 1, entry 12).

Table 1. Optimization of reaction conditions for the rhodium-catalyzed cyclization of **1a** and **1b** with **2a**.[a]



Entry	**1**	Ligand	**2a** [equiv.]	Yield [%][b] **3**	**4ba**
1	**1a**	H_8-binap	1.1	**3aa** / 36	–
2	**1a**	binap	1.1	**3aa** / 33	–
3	**1a**	segphos	1.1	**3aa** / 11	–
4	**1a**	dppb	1.1	**3aa** / 0	–
5[c]	**1a**	dppe	1.1	**3aa** / 0	–
6	**1a**	H_8-binap	2.0	**3aa** / 42	–
7	**1a**	H_8-binap	3.0	**3aa** / 59	–
8	**1a**	H_8-binap	5.0	**3aa** / 37	–
9	**1b**	H_8-binap	1.1	**3ab** / 0	67
10	**1b**	binap	1.1	**3ab** / 0	73
11	**1b**	segphos	1.1	**3ab** / 0	41
12	**1b**	binap	2.0	**3ab** / 0	66

[a] Reaction conditions: $[Rh(cod)_2]BF_4$ (0.010 mmol, cod = 1,5-cyclooctadiene), ligand (0.010 mmol), **1** (0.10 mmol), **2a** (0.11–0.30 mmol), and $(CH_2Cl)_2$ (2.0 mL). [b] Isolated yield. [c] $[Rh(nbd)_2]BF_4$ was used (nbd = 2,5-norbornadiene).

Thus, we explored the scope of the cyclic allylic *gem*-dicarboxylate synthesis[13] by using the cationic rhodium(I)/H_8-binap catalyst at 80 °C (Table 2, entries 1–6). Not only a tosylamide-linked terminal γ-alkynyl aldehyde (i.e., **1a**; Table 2, entry 1) but also a readily removable nosylamide-linked[14] one (i.e., **1c**; Table 2, entry 2) could participate in this reaction. However, the reaction of phenyl-substituted

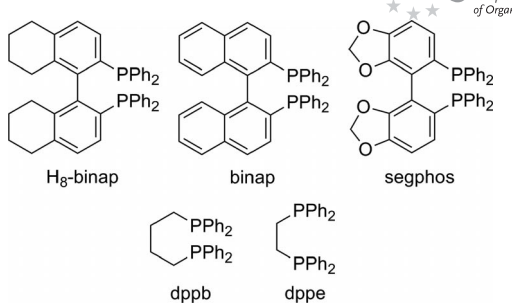
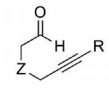
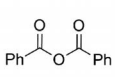
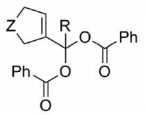
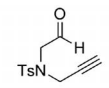
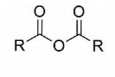
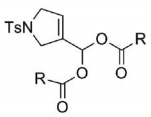
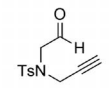
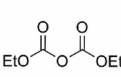
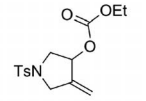
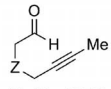
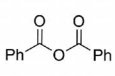
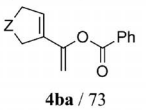
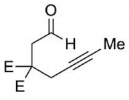
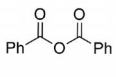
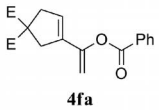
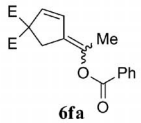
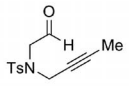
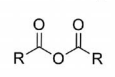
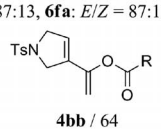
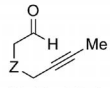
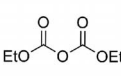
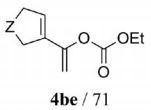
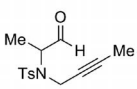
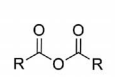
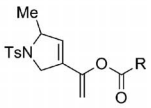
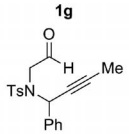
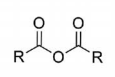
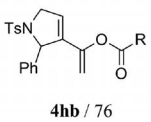
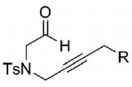
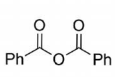
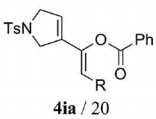


Figure 1. Structures of bisphosphane ligands.

γ-alkynyl aldehyde **1d** with **2a** led to a complex mixture of products (Table 2, entry 3). The use of substituted benzoic anhydrides was also examined. The reactions of sterically less-demanding anhydrides **2b** and **2c** with **1a** proceeded in significantly higher yields (Table 2, entries 4 and 5) than sterically demanding anhydride **2d** (Table 2, entry 6). Interestingly, the reaction of **1a** with diethyl pyrocarbonate (**2e**) did not afford the expected cyclic allylic *gem*-dicarbonates but instead unexpected cyclic allylic carbonate **5ae** with a high *ee* value (Table 2, entry 7). We subsequently explored the scope of the cyclic dienyl ester synthesis by using the cationic rhodium(I)/binap catalyst at 80 °C (Table 2, entries 8–20). Tosylamide- (i.e., **1b**; Table 2, entry 8), nosylamide- (i.e., **1e**; Table 2, entry 9), and malonate-linked (i.e., **1f**; Table 2, entry 10) methyl-substituted γ-alkynyl aldehydes participated in this reaction. In the reaction of **1f** with **2a**, olefin isomerization product **6fa** was generated along with **4fa** (Table 2, entry 10). The use of substituted benzoic anhydrides was also examined. Their electronic and steric nature appeared to have a small impact on the product yields (Table 2, entries 11–14). The reactions of **2e** with **1b** and **1e** afforded expected cyclic dienyl carbonates **4be** and **4ee** in good yields (Table 2, entries 15 and 16). The use of substituted γ-alkynyl aldehydes was next examined. The reactions of α-methyl and γ-phenyl-substituted γ-alkynyl aldehydes **1g** and **1h** with **2b** proceeded in high yields (Table 2, entries 17 and 18). Ethyl- and butyl-substituted γ-alkynyl aldehydes **1i** and **1j** reacted with **2a** to give the corresponding cyclic dienyl benzoates **4ia** and **4ja**, respectively, with complete stereoselectivity, although their yields were low (Table 2, entries 19 and 20).

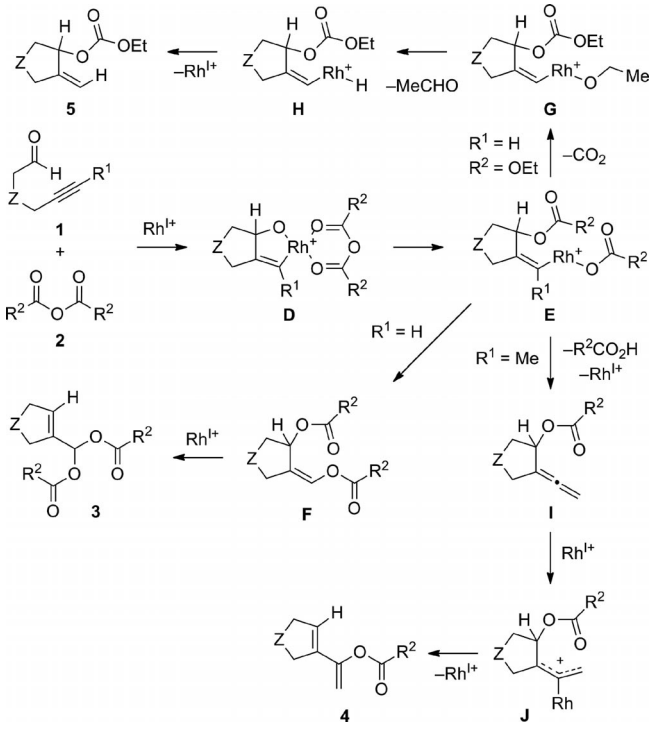
Scheme 2 depicts a possible mechanism for the formation of **3**, **4**, and **5**, although this proposal is speculative and a precise mechanism cannot be concluded at the present stage.[15] γ-Alkynyl aldehyde **1** reacts with the rhodium(I) catalyst to afford oxarhodacyclopentene **D** with chelating acid anhydride **2**. σ-Bond metathesis between the C–O and Rh–O bonds affords intermediate **E**.[16] In the case of a terminal γ-alkynyl aldehyde (R^1 = H), reductive elimination proceeds to afford diester **F**, which undergoes rhodium-catalyzed acyloxy migration to afford cyclic allylic *gem*-dicarboxylate **3**. In contrast, if diethyl pyrocarbonate (**2e**) is employed, decarboxylation[17] from intermediate **E** proceeds to afford intermediate **G**. β-Hydride elimination affords rhodium hydride **H**, and subsequent reductive elimination affords cyclic allylic carbonate **5**. In the case of an internal

Table 2. Rhodium-catalyzed cyclization reactions of γ-alkynyl aldehydes **1a**–**j** with carboxylic acid anhydrides **2a**–**f**.[a]

Entry	1	2 (equiv.)	Product / yield [%][b]
			
1	**1a** (Z = NTs, R = H)	**2a** (3)	**3aa** / 59
2	**1c** (Z = NNs[c], R = H)	**2a** (3)	**3ca** / 54
3	**1d** (Z = NTs, R = Ph)	**2a** (3)	**3da** / 0
			
4	**1a**	**2b** (R = 4-MeOC$_6$H$_4$, 3)	**3ab** / 54
5	**1a**	**2c** (R = 3-MeC$_6$H$_4$, 3)	**3ac** / 60
6	**1a**	**2d** (R = 2-MeC$_6$H$_4$, 3)	**3ad** / 34
			
7	**1a**	**2e** (3)	(+)-**5ae** / 36, 97 % *ee*
			
8	**1b** (Z = NTs)	**2a** (1.1)	**4ba** / 73
9	**1e** (Z = NNs[c])	**2a** (1.1)	**4ea** / 54
			 
10[d]	**1f** (E = CO_2Bn)	**2a** (1.1)	**4fa** / **6fa** 67 (**4fa**/**6fa** = 87:13, **6fa**: *E*/*Z* = 87:13)
			
11	**1b**	**2b** (R = 4-MeOC$_6$H$_4$, 1.1)	**4bb** / 64
12	**1b**	**2c** (R = 3-MeC$_6$H$_4$, 1.1)	**4bc** / 65
13	**1b**	**2d** (R = 2-MeC$_6$H$_4$, 1.1)	**4bd** / 56
14	**1b**	**2f** (R = 4-F$_3$CC$_6$H$_4$, 1.1)	**4bf** / 59
			
15	**1b** (Z = NTs)	**2e** (2)	**4be** / 71
16	**1e** (Z = NNs[c])	**2e** (2)	**4ee** / 61
			
17	**1g**	**2b** (R = 4-MeOC$_6$H$_4$, 1.1)	**4gb** / 81
			
18	**1h**	**2b** (R = 4-MeOC$_6$H$_4$, 1.1)	**4hb** / 76
			
19[e]	**1i** (R = Me)	**2a** (1.1)	**4ia** / 20
20[e]	**1j** (R = *n*Pr)	**2a** (1.1)	**4ja** / 22

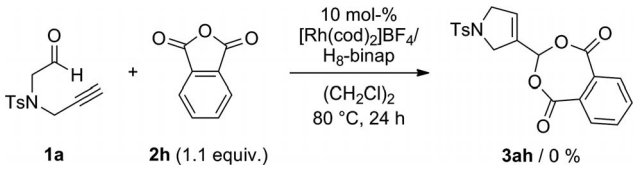
[a] Reactions were conducted with [Rh(cod)$_2$]BF$_4$ (0.010 mmol), H$_8$-binap (entries 1–7) or binap (entries 8–20) (0.010 mmol), **1** (0.10 mmol), **2** (0.11–0.30 mmol), and $(CH_2Cl)_2$ (2.0 mL) at 80 °C for 24 h. [b] Isolated yield. [c] Ns = SO$_2$(2-NO$_2$C$_6$H$_4$). [d] At 60 °C for 40 h. [e] γ-Alkynyl aldehyde **1** (0.20 mmol) and **2a** (0.22 mmol) were used.

γ-alkynyl aldehyde (R^1 = Me), β-hydride elimination from intermediate **E** proceeds to afford allene **I**, which undergoes acyloxy migration to afford cyclic dienyl ester **4**. This migration step might also be catalyzed by the cationic rhodium through activation of the allene moiety, as shown in intermediate **J**.[18]



Scheme 2. Possible reaction mechanism.

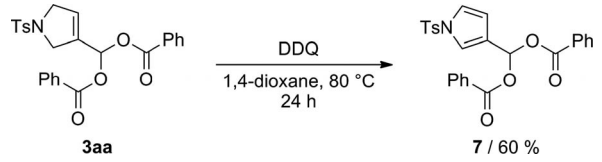
In the mechanism shown in Scheme 2, the chelation of the acid anhydride to the cationic rhodium may be necessary to promote the reactions. Indeed, the reaction of **1a** with nonchelating cyclic carboxylic acid anhydride **2h** did not afford cross-reaction products including cyclic allylic *gem*-dicarboxylate **3ah** (Scheme 3).



Scheme 3. Rhodium-catalyzed reaction of **1a** with cyclic carboxylic acid anhydride **2h**.

Transformations of the cyclization products were briefly examined. 2,5-Dihydropyrrole **3aa** could be readily aromatized by treatment with DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) to give corresponding pyrrole **7** possessing the *gem*-dicarboxylate moiety (Scheme 4).[19]

Annulated heterocycle libraries, structures of which are shown in Figure 2, includes antimigratory agents.[20] We were pleased to find that the rhodium-catalyzed cyclization



Scheme 4. Aromatization of cyclization product **3aa**.

reaction of **1b** with **2b** leading to diene **4bb** and the Diels–Alder reaction of **4bb** with *N*-phenylmaleimide (**8**) and tetracyanoethylene (**9**) proceeded in one-pot to give analogous annulated heterocycles **10bb** and **11bb** in moderate yields (Scheme 5). An aliphatic carboxylic acid anhydride [heptanoic anhydride (**2g**)] could also be employed for the present cyclization reaction, while the products **4** could not be isolated in a pure form due to partial hydrolysis during isolation on a silica gel.[21] Pleasingly, the one-pot reaction involving **2g** proceeded to give the corresponding stable annulated heterocycle **10bg** in moderate yield (Scheme 5).

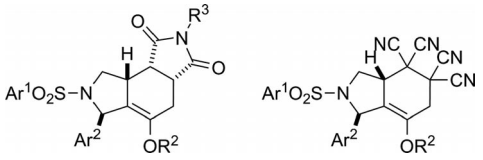
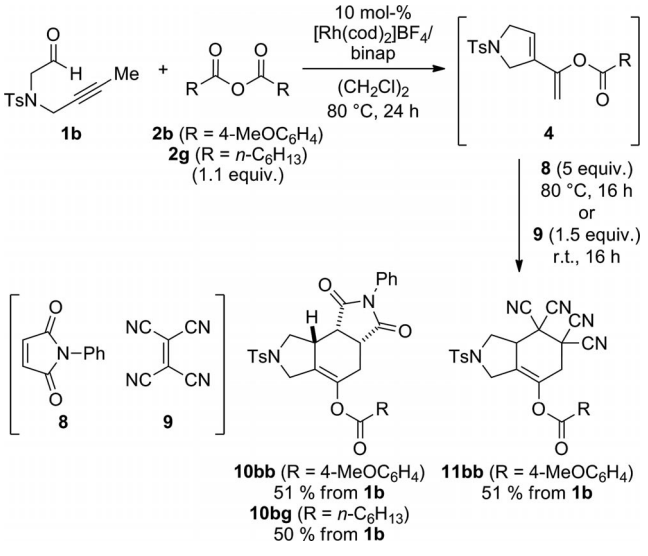
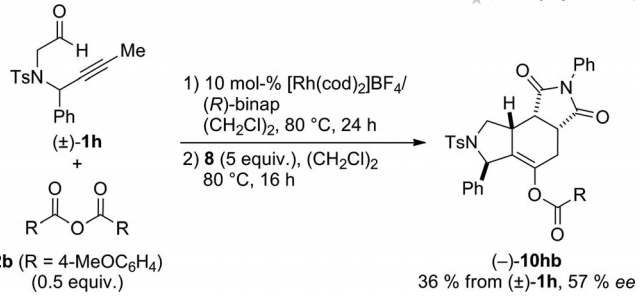


Figure 2. Annulated heterocycle libraries including antimigratory agents.



Scheme 5. One-pot rhodium-catalyzed cyclization and Diels–Alder reaction.

Finally, kinetic resolution of racemic γ-substituted alkynal **1h** with **2b** followed by a Diels–Alder reaction with **8** proceeded by using the $[Rh(cod)_2]BF_4$/(*R*)-binap catalyst to give corresponding enantioenriched annulated heterocycle (–)-**10hb** with a moderate *ee* value (Scheme 6).



Scheme 6. One-pot reaction of (±)-**1h** with **2b** through kinetic resolution.

Conclusions

In conclusion, we have established that a cationic rhodium(I)/H_8-binap or binap complex catalyzes two different modes of cyclization of γ-alkynyl aldehydes with carboxylic acid anhydrides to give cyclic allylic *gem*-dicarboxylates and cyclic dienyl esters through cleavage of the carboxylic acid anhydride C–O bond. In contrast, the reaction of a terminal γ-alkynyl aldehyde with diethyl pyrocarbonate afforded a cyclic allylic carbonate with a high *ee* value. Future studies will focus on further utilization of chelating carbonyl compounds for this process.

Experimental Section

Representative Procedure for the Rh-Catalyzed Cyclization Reactions of Terminal γ-Alkynyl Aldehydes with Carboxylic Acid Anhydrides: H_8-binap (6.3 mg, 0.010 mmol) and $[Rh(cod)_2]BF_4$ (4.1 mg, 0.010 mmol) were dissolved in CH_2Cl_2 (2.0 mL), and the mixture was stirred at room temperature for 10 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 45 min, the resulting mixture was concentrated to dryness. To a solution of the residue in $(CH_2Cl)_2$ (0.5 mL) was added a solution of **1a** (25.1 mg, 0.100 mmol) and **2a** (67.9 mg, 0.300 mmol) in $(CH_2Cl)_2$ (1.5 mL). The mixture was stirred at 80 °C for 24 h. The resulting solution was concentrated and purified by preparative TLC (hexane/EtOAc/toluene = 6:1:2), which furnished **3aa** (28.2 mg, 0.0591 mmol, 59% yield; Table 2, entry 1) as a colorless oil.

Representative Procedure for the Rh-Catalyzed Cyclization Reactions of Internal γ-Alkynyl Aldehydes with Carboxylic Acid Anhydrides: The binap ligand (6.2 mg, 0.010 mmol) and $[Rh(cod)_2]BF_4$ (4.1 mg, 0.010 mmol) were dissolved in CH_2Cl_2 (2.0 mL), and the mixture was stirred at room temperature for 10 min. H_2 was introduced to the resulting solution in a Schlenk tube. After stirring at room temperature for 45 min, the resulting mixture was concentrated to dryness. To a solution of the residue in $(CH_2Cl)_2$ (0.5 mL) was added a solution of **1b** (26.5 mg, 0.100 mmol) and **2a** (24.9 mg, 0.110 mmol) in $(CH_2Cl)_2$ (1.5 mL). The mixture was stirred at 80 °C for 24 h. The resulting solution was concentrated and purified by preparative TLC (EtOAc/toluene = 1:5), which furnished **4ba** (28.7 mg, 0.0733 mmol, 73% yield; Table 2, entry 8) as a colorless oil.

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.

Acknowledgments

This work was supported partly by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan through Grants-in-Aid for Scientific Research (grant numbers 25105714, 23105512, and 20675002) and by the Japan Science and Technology Agency (JST), Japan through ACT-C. The authors are grateful to Takasago International Corporation for the gift of H_8-binap and segphos and to Umicore for generous support in supplying the rhodium complexes.

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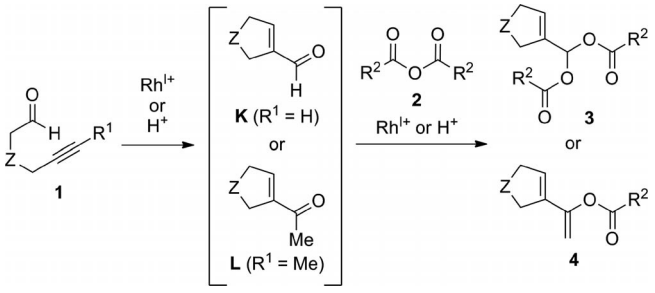
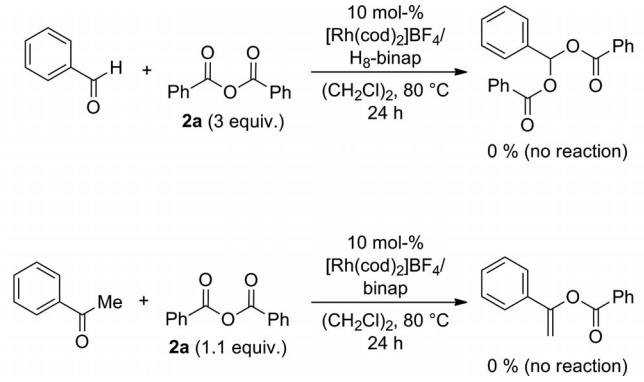


Furthermore, the reactions of benzaldehyde and acetophenone with **2a** in the presence of the cationic rhodium(I)/H_8-binap or binap catalyst at 80 °C for 24 h did not afford the correspond-

ing *gem*-dicarboxylate and enol ester at all. (The Lewis acid mediated *gem*-dicarboxylate synthesis from aldehydes was reported, see: K. S. Kochhar, B. S. Bal, R. P. Deshpande, S. N. Rajadhyaksha, H. W. Pinnick, *J. Org. Chem.* **1983**, *48*, 1765).



The marked ligand effects (Table 1) and enantioinduction (Table 2, entry 7; Scheme 6) also excluded the mechanism via cyclic enal **K** and enone **L**.

[16] In the nickel-catalyzed cyclization with the use of organosilanes, Montgomery proposed that the reaction proceeds through σ-bond metathesis of the organosilane Si–H bond and the Ni–O bond of the oxanickelacyclopentene intermediate; see ref.[4k] In the rhodium-catalyzed cyclization with the use of dihydrogen, Krische proposed that the reaction proceeds through σ-bond metathesis of the dihydrogen H–H bond and the Rh–O bond of the oxarhodacyclopentene intermediate, see ref.[5c]

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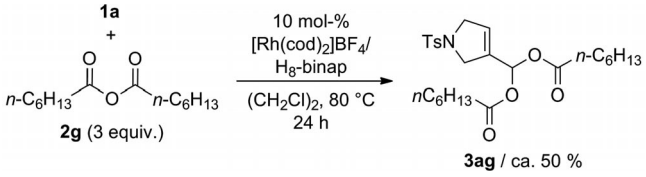

[21] The reaction of **1a** with **2g** afforded cyclic allylic *gem*-dibenzoate **3ag**, although this product could not be isolated in a pure form.

Received: May 18, 2013
Published Online: July 12, 2013

