Organometallic Catalysis

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Rhodium-Catalyzed Intramolecular Cyclization of Naphthol- or Phenol-Linked 1,6-Enynes Through the Cleavage and Formation of sp^2 C–O Bonds**

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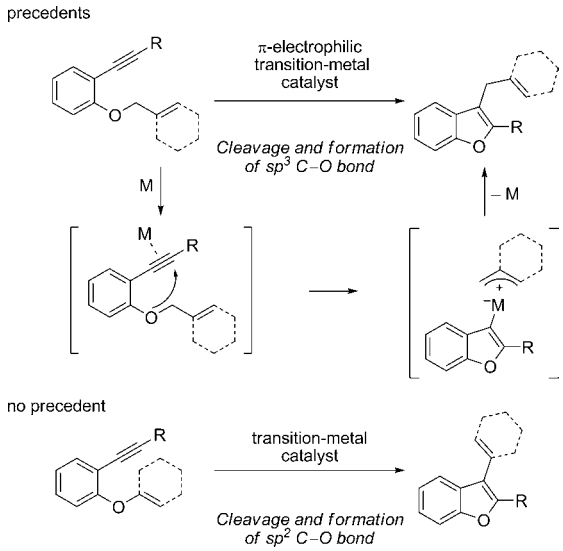
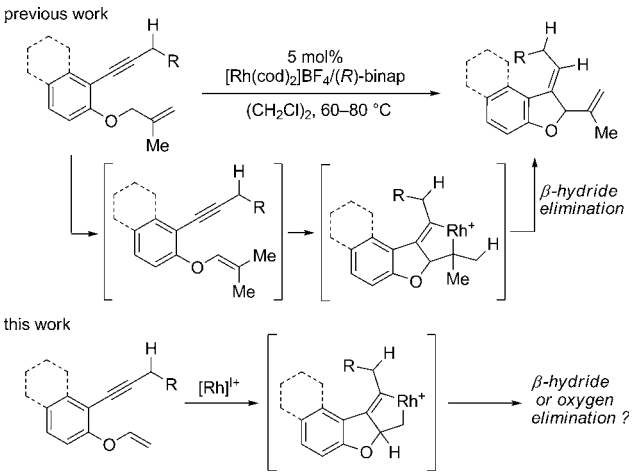
Recently, a number of π-electrophilic transition-metal-catalyzed intramolecular migratory cycloisomerization reactions, which involve sp^3 carbon–heteroatom bond cleavage, have been developed for the synthesis of five-membered heterocycles.[1] In these reactions, copper, silver, gold, palladium, and platinum complexes were frequently employed because of their high catalytic activity for π-bond activation.[2–6] For example, the transition-metal-catalyzed intramolecular cyclization of 2-alkynylphenyl ethers leading to benzofuran derivatives was reported (Scheme 1).[2] In this reaction, the π-electrophilic transition-metal catalyst activates the alkyne π-bond, which generates an (alkenyl)metal intermediate bearing an allyl or benzyl cation fragment.[2] This cation fragment shifts to the most nucleophilic β-position relative to the oxygen atom, which affords the benzofuran derivative and regenerates the transition-metal catalyst.[2] Accordingly, this mode of cyclization is limited to the cleavage and formation of sp^3 C–O bonds by the generation of stabilized cation fragments (Scheme 1).[2] Herein, we disclose the unprecedented transition-metal-catalyzed intramolecular cyclization of naphthol- or phenol-linked 1,6-enynes leading to vinylnaphthofuran or vinylbenzofurans through the cleavage and formation of sp^2 C–O bonds.[7,8]

We recently reported an olefin isomerization/enantioselective intramolecular Alder-ene reaction cascade of phenol- or naphthol-linked 1,7-enynes catalyzed by a cationic rhodium(I)/(*R*)-binap complex (Scheme 2).[9] This cascade reaction proceeds through the formation of phenol- or naphthol-linked 1,6-enynes, which possess an isobutenyl ether moiety, followed by rhodacycle formation and β-hydride elimination.[9] We anticipated that phenol- or naphthol-linked 1,6-enynes possessing a vinyl ether moiety would react with the rhodium(I) complex to generate the corresponding rhodacycles, which would undergo β-hydride or oxygen elimination (Scheme 2).[10–12]

We first investigated the reaction of 1-hexynyl-2-naphthyl vinyl ether (**1a**) in the presence of a cationic rhodium(I)/binap complex (10 mol%) at 80°C. We were pleased to find



Scheme 1. Transition-metal-catalyzed intramolecular cyclization of 2-alkynylphenyl ethers leading to benzofuran derivatives.



Scheme 2. Rhodium-catalyzed reactions of phenol- or naphthol-linked 1,7- and 1,6-enynes. Cod = 1,5-cyclooctadiene.

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that intramolecular *trans* carboalkoxylation product **2a** was obtained as the major product along with the minor cycloisomerization product, **3a** (Table 1, entry 1). Screening of biaryl bisphosphine ligands (Figure 1; Table 1, entries 1–6) revealed that the selectivities between **2a** and **3a** depend on the dihedral angles and steric bulk of the biaryl bisphosphine ligands (dihedral angle: H_8-binap > binap > segphos > biphep,[13] **2a**/**3a**: biphep > segphos > binap > H_8-binap; steric bulk: xyl-binap > tol-binap > binap, **2a**/**3a**: xyl-binap > tol-binap > binap). Non-biaryl bisphosphine ligands were also examined and moderate selectivities were observed (Figure 1; Table 1, entries 7 and 8). Although biphep showed the highest selectivity for **2a** over **3a**, binap showed the highest catalytic activity. Thus, reaction conditions were further optimized using binap as a ligand. Gratifyingly, the use of chlorobenzene as a solvent significantly improved the yield of **2a** (entry 9). The catalyst loading could be reduced to 5 mol% (entry 10), and increasing the reaction temperature to 90°C further improved the yield of **2a** (entry 11). Importantly, platinum, gold, and palladium complexes, which are known to catalyze the cyclization of allyl or benzyl 2-alkynylphenyl ethers, failed to catalyze the formation of **2a** and **3a** (entries 12–14).[14]

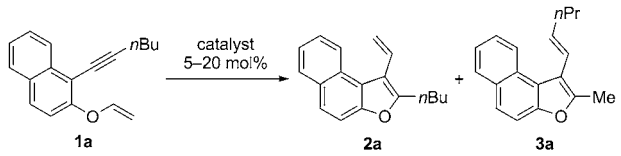
With the optimized reaction conditions in hand, we explored the scope of the cyclization of 1,6-enynes catalyzed by a cationic rhodium(I)/binap complex, as shown in Table 2. With respect to the substituent at the alkyne terminus,[15] not only *n*-butyl (**1a**, entry 1), but also phenylpropyl and chloropropyl substituted alkynes (**1b**,**c**, entries 2 and 3) furnished the desired naphthofurans **2a**–**c** in high yields. Terminal alkyne **1d** (entry 4) could be employed, although the product yield was moderate. Alkenyl- and arylacetylene derivatives (**1e**–**g**, entries 5–7) were also suitable substrates for this process and gave the desired naphthofurans **2e**–**g** in good yields. The 1,6-enynes **1h**–**k**, which possess secondary alkyl groups at the alkyne termini, afforded naphthopyranes **4h**–**k** as major products and naphthofurans **2h**–**k** as minor products (entries 8–11). However, cyclopropylacetylene derivative **1l** (entry 12) afforded naphthofuran **2l** as the sole product. The reaction of racemic 1,6-enyne **1i** using the cationic rhodium(I)/(*R*)-binap catalyst furnished enantioenriched naphthofuran **2i** and racemic naphthopyran **4i** (entry 9). With respect to the aryl ether moiety, the reactions of phenol-linked 1,6-enynes **1m**,**n** afforded benzofurans **2m**,**n**[16] in low yields (entries 13 and 14). Also, phenol-linked 1,6-enyne **1o** afforded benzopyrane **4o** (entry 15), although the yield was lower than for naphthopyrane **4h** (entry 8).

The double intramolecular cyclization of **1p** also proceeded to give the corresponding blue-emitting benzene-linked bis(vinylnaphthofuran) **2p** (Scheme 3).[17] This product showed a high quantum yield of 73% in $CHCl_3$ solution and could be employed as a light-emitting polymerization unit.

The transformation of cyclization products was also briefly examined. Diels–Alder reactions between naphthofurans **2a**,**d** and *N*-methylmaleimide (**5**) gave pentacyclic compounds **6a**,**d** in good yields and as single diastereomers (Scheme 4).[18] The Diels–Alder reaction between **5** and naphthopyran **4h** also proceeded to give pentacyclic compound **7** in good yield and as a single diastereomer (Scheme 4).[19] The structure of **7** was unambiguously confirmed by X-ray crystallographic analysis.[20]

A possible mechanism for the rhodium-catalyzed cyclization reactions of 1,6-enynes **1** leading to benzofurans **2** and **3**, and benzopyrans **4** is shown in Scheme 5. The 1,6-enyne **1** reacts with rhodium to generate rhodacyclopentene **A**.[21] Subsequent β-hydride elimination of the propargylic hydrogen affords rhodium hydride **B**. Reductive elimination followed by double bond isomerization[22] affords naphthofuran **3**. Alternatively, a β-oxygen elimination from rhodacyclopentene **A**, followed by aryl–alkenyl single bond rotation

Table 1: Optimization of reaction conditions for the transition-metal-catalyzed cyclization of 1,6-enyne **1a**.[a]



Entry	Catalyst	Solvent	Conditions	Conv. [%]	Yield[%][b] (**2a**/**3a**)[c]
1	$[Rh(cod)_2]BF_4$/binap	$(CH_2Cl)_2$	80°C, 1 h	100	76 (4:1)
2	$[Rh(cod)_2]BF_4$/H_8-binap	$(CH_2Cl)_2$	80°C, 1 h	80	44 (2:1)
3	$[Rh(cod)_2]BF_4$/segphos	$(CH_2Cl)_2$	80°C, 2 h	95	49 (20:1)
4	$[Rh(cod)_2]BF_4$/biphep	$(CH_2Cl)_2$	80°C, 1 h	95	35 (25:1)
5	$[Rh(cod)_2]BF_4$/tol-binap	$(CH_2Cl)_2$	80°C, 3 h	90	58 (5:1)
6	$[Rh(cod)_2]BF_4$/xyl-binap	$(CH_2Cl)_2$	80°C, 3 h	52	18 (8:1)
7	$[Rh(cod)_2]BF_4$/dppb	$(CH_2Cl)_2$	80°C, 3 h	66	22 (5:1)
8	$[Rh(cod)_2]BF_4$/dppf	$(CH_2Cl)_2$	80°C, 3 h	85	41 (5:1)
9	$[Rh(cod)_2]BF_4$/binap	ClC_6H_5	80°C, 1 h	100	88 (25:1)
10[d]	$[Rh(cod)_2]BF_4$/binap	ClC_6H_5	80°C, 1 h	100	86 (25:1)
11[d]	$[Rh(cod)_2]BF_4$/binap	ClC_6H_5	90°C, 1 h	100	88 (>50:1)
12[e]	$PtCl_2$	$(CH_2Cl)_2$	80°C, 16 h	100	0
13[e]	$AuCl(PPh_3)/AgBF_4$	$(CH_2Cl)_2$	80°C, 16 h	100	0
14[e]	$Pd(PPh_3)_4$, K_2CO_3[f]	THF	90°C, 1 h	0	0

[a] Catalyst (0.010 mmol, 10 mol%), **1a** (0.10 mmol), and solvent (1.0 mL) were used. [b] Yield of isolated product. [c] Determined by ^{1}H NMR spectroscopy. [d] Catalyst (0.010 mmol, 5 mol%), **1a** (0.20 mmol), and solvent (3.0 mL) were used. [e] 20 mol% of catalyst was used. [f] 0.50 mmol. Cod = 1,5-cyclooctadiene.

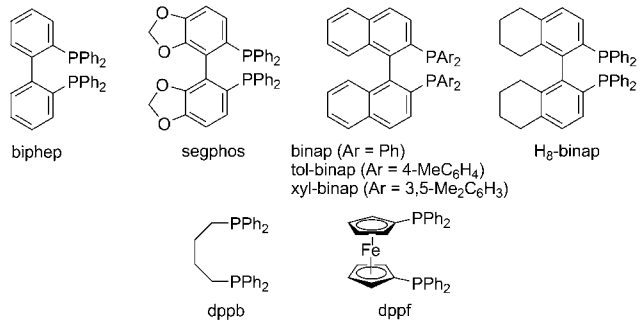
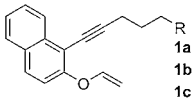
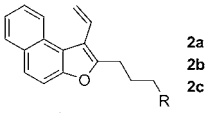
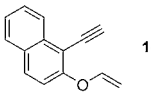
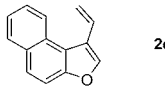
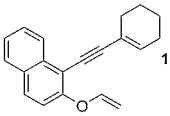
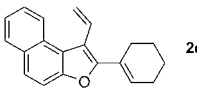
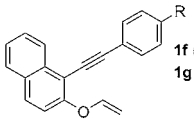
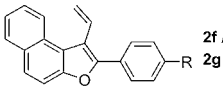
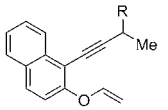
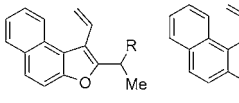
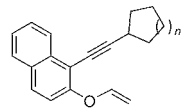
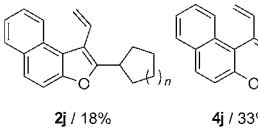
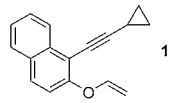
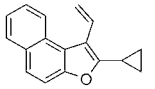
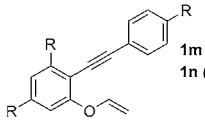
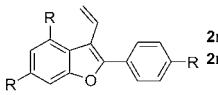
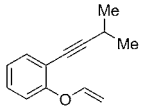
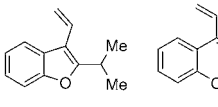


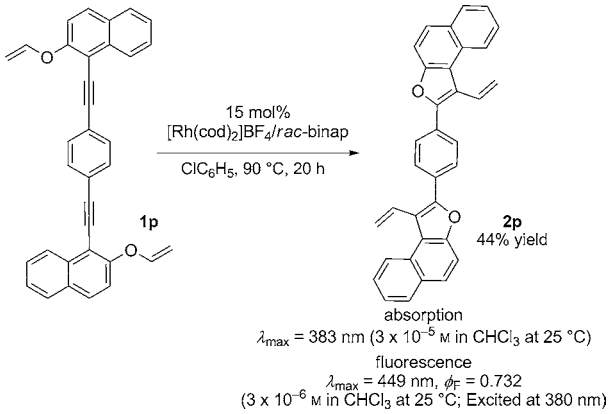
Figure 1. Structures of bisphosphine ligands.

Table 2: Cyclization of 1,6-enynes **1a–o** catalyzed by a cationic Rh^{I}/binap complex.[a]

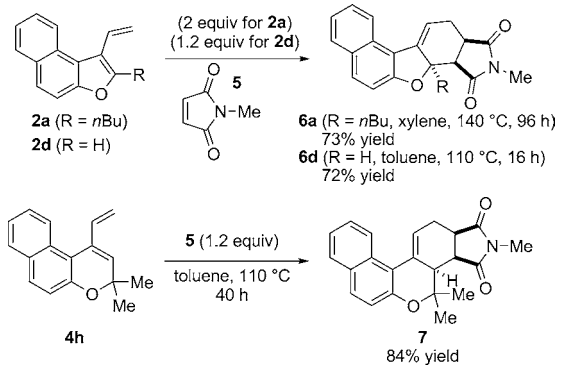
Entry	Substrate	Product / Yield[b]
1	 **1a** (R = Me)	 **2a** / 88%
2	**1b** (R = Ph)	**2b** / 81%
3	**1c** (R = Cl)	**2c** / 74%
4[c,d]	 **1d**	 **2d** / 54%
5[c,e]	 **1e**	 **2e** / 52%
6	 **1f** (R = H)	 **2f** / 71%
7	**1g** (R = OMe)	**2g** / 66%
8[c,d,e]	 **1h** (R = Me)	 **2h** / <5% **4h** / 51%
9[c,d,f]	**1i** (R = Ph, racemic)	(+)-**2i** / 20% (39% *ee*) **4i** / 51% (<1% *ee*)
10[c,d,e]	 **1j** (n = 2)	 **2j** / 18% **4j** / 33%
11[c,d,e]	**1k** (n = 1)	**2k** / 21% **4k** / 28%
12[c]	 **1l**	 **2l** / 34%
13	 **1m** (R = H)	 **2m** / 16%
14	**1n** (R = OMe)	**2n** / 15%
15[c,d,e]	 **1o**	 **2o** / <5% **4o** / 32%

[a] Reactions were conducted using $[Rh(cod)_2]BF_4$/*rac*-binap (0.010 mmol, 5 mol%), and **1** (0.20 mmol) in ClC_6H_5 (3.0 mL) at 90°C for 1–24 h. [b] Yield of isolated product. [c] Reaction conducted at 80°C. [d] ClC_6H_5 (8.0 mL) was used. [e] $[Rh(cod)_2]BF_4$/*rac*-binap (0.020 mmol, 10 mol%) was used. [f] Catalyst: $[Rh(cod)_2]BF_4$/(*R*)-binap (0.020 mmol, 10 mol%). Cod = 1,5-cyclooctadiene.

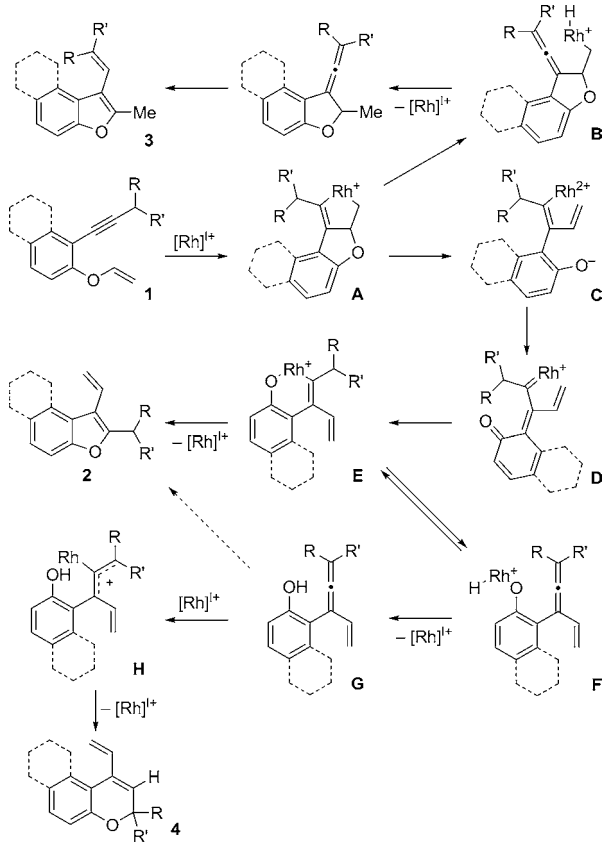
in zwitterionic intermediate **C** and cyclization of rhodium carbene **D** affords oxarhodacycle **E**, whereupon reductive elimination of rhodium affords benzofuran **2**. When the 1,6-enyne possesses an alkyl group at the alkyne terminus, β-hydride elimination from intermediate **E** would instead afford intermediate **F**. We believe that, as the formation of oxarhodacycle **E** and rhodium hydride **F** is reversible, 1,6-enynes **1h–k**, which possess secondary alkyl groups at the alkyne termini, would favor the formation of thermodynamically stable tetrasubstituted allene intermediate **F**. Elimina-



Scheme 3. Double cyclization of **1p**.



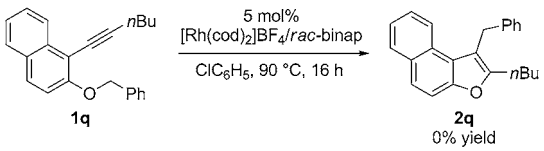
Scheme 4. Diels–Alder reactions.



Scheme 5. Possible reaction mechanism.

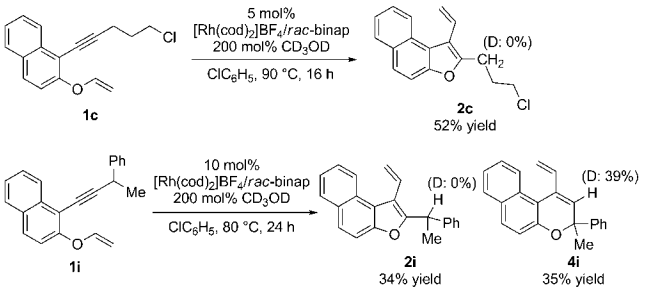
tion of rhodium leads to allenyl phenol **G**, followed by 6-endo cyclization to afford benzopyran **4**. Alternatively, 5-exo cyclization of intermediate **G** would afford benzofuran **2**. The higher yields of the cyclization products from naphthol-linked 1,6-enynes than those from phenol-linked ones might be attributed to the higher reactivity of an oxa-*ortho*-quinodimethane version of intermediate **D**, generated from the phenol-linked 1,6-enyne, versus a 1-methylenenaphthalen-2(1*H*)-one version of intermediate **D**, generated from the naphthol-linked 1,6-enyne. Indeed, the reactions of **1m–o** afforded complex mixtures of products other than the desired products (Table 2, entries 13–15).[23]

The following mechanistic studies were performed to discard mechanistic alternatives. The reaction of benzyl 1-hexynyl-2-naphthyl ether (**1q**) failed to furnish naphthofuran **2q**, which excludes a π-bond activation mechanism with the cationic rhodium(I) complex (Scheme 6).[24]



Scheme 6. Reaction of **1q** with a cationic Rh^{I}/binap catalyst.

No deuterium incorporation was observed for naphthofuran **2c** in the presence of an external deuterium source (CD_3OD) (Scheme 7). This result excludes the formation of **2c** from intermediate **G**. On the other hand, partially deuterated naphthopyran **4i** was generated in the presence of an external deuterium source (CD_3OD), and no deuterium incorporation was observed for naphthofuran **2i** (Scheme 7). This result is consistent with the formation of **4i** from intermediate **G** and **2i** from intermediate **E**.



Scheme 7. Rhodium-catalyzed reactions in the presence of CD_3OD.

As shown in entry 9 of Table 2, the reaction of racemic **1i** using the cationic rhodium(I)/(*R*)-binap catalyst furnished enentioenriched naphthofuran **2i**, while naphthopyran **4i** was obtained as a racemate. Therefore, a kinetic resolution occurs in the reductive elimination and β-hydride elimination steps from oxarhodacycle **E**, which affords enantioenriched **2i** and allene **G** (R = Ph, R′ = Me). However, the 6-endo cyclization of enantioenriched **G** might proceed via planar allyl cation-like intermediate **H**, which is stabilized by the vinyl substituent, resulting in loss of configuration.[25] Thus, the axial chirality of **G** would not be transferred into the central chirality of **4i**.

In conclusion, we have established that a cationic rhodium(I)/binap complex catalyzes the intramolecular cyclization reactions of naphthol- or phenol-linked 1,6-enynes to produce vinylnaphtho- or vinylbenzofurans and vinylnaphtho- or vinylbenzopyrans through cleavage and formation of sp^2 C–O bonds. Mechanistic studies imply that the present cyclization reactions proceed by β-oxygen elimination from the rhodacyclopentene intermediate. Future work will focus on further development of novel rhodium catalyzed reactions involving β-heteroatom elimination.

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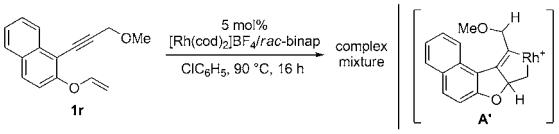
[14] In entries 12 and 13 of Table 1, 2-butylnaphtho[2,1-*b*]furan was generated in ca. 50% yields, presumably through hydrolysis of **1a** to form 2-hexynyl-1-naphthol followed by cyclization. Aside from this benzofuran product, a complex mixture of by-products was generated.

[15] The reaction of enyne **1r** with a cationic rhodium(I) catalyst led to a complex mixture of products. This may be because the expected intermediate, rhodacycle **A′**, possesses two possible β-oxygen or hydride elimination sites.



1r A′

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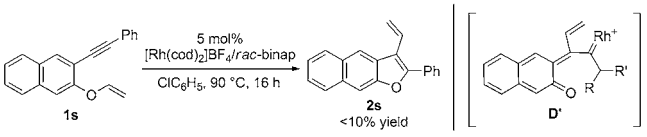
[20] CCDC 865637 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[21] Shibata and co-workers reported the cationic rhodium(I)/tol-binap complex-catalyzed [2+2+2] cycloaddition of 1,6-enynes with 1,4-dimethoxy-2-butyne through rhodacyclopentene intermediates; see: T. Shibata, Y. Arai, Y. Tahara, *Org. Lett.* **2005**, *7*, 4955. Indeed, the reaction of 1,6-enyne **1a** with 1,4-dimethoxy-2-butyne in the presence of the cationic rhodium(I)/binap catalyst (20 mol%) proceeded at 40°C to give the corresponding [2+2+2] cycloaddition product in 27% yield.

[22] We previously reported the rhodium-catalyzed cycloisomerization of 1,6- and 1,7-diynes leading to trienes. In this cycloisomerization, isomerized triene products were obtained instead of allene products; see: K. Tanaka, Y. Otake, M. Hirano, *Org. Lett.* **2007**, *9*, 3953. Furthermore, we have recently demonstrated that the isomerization of 3-alkylidene-1,2-dihydrobenzofuran to benzofuran is rapid at 80°C; see Ref. [9].

[23] The reaction of 2,3-naphthol derivative **1s** was also examined, but the desired naphthofuran **2s** was obtained in very low yield along with a complex mixture of by-products. This result might also be attributed to the high reactivity of oxa-*ortho*-quinodimethane type intermediate **D′**.



1s 2s <10% yield D′

[24] For examples of the π-electrophilic transition-metal-catalyzed intramolecular cyclization of 2-alkynylphenyl benzyl ethers leading to benzofuran derivatives, see Ref. [2e].

[25] Toste and co-workers reported the gold-catalyzed dynamic kinetic asymmetric cyclization of propargyl esters to produce benzopyrans. They proposed that the oxygen substituent of an allene intermediate stabilizes a gold-coordinated planar allyl cation-like intermediate, resulting in the loss of configuration; see: Y.-M. Wang, C. N. Kuzniewski, V. Rauniyar, C. Hoong, F. D. Toste, *J. Am. Chem. Soc.* **2011**, *133*, 12972.

