Ruthenium-Catalyzed Allylation of Aromatic Compounds and Allylic Ether Formation

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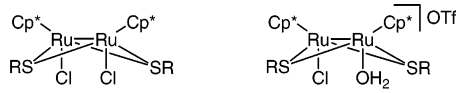
Ruthenium-catalyzed allylation of aromatic compounds such as benzene, toluene, *p*-xylene, anisole, phenol, furans, and thiophenes with allylic alcohol derivatives gives the corresponding allylated products in good to high yields with a high regioselectivity. Only the cationic thiolate-bridged diruthenium(III, III) complexes promote the reaction. Investigation of the allylation pathway in the reaction of cinnamyl alcohol with *p*-xylene has revealed that it proceeds via two ways: a direct allylation with the alcohol itself and an allylation with dicinnamyl ether formed as an intermediate. A new cationic thiolate-bridged diruthenium(III, IV) complex together with allylated cinnamyl chlorides has been formed in the reaction of the diruthenium(III, III) complex with cinnamyl chloride, this new complex being revealed to be effective as an allylation catalyst. The cationic diruthenium(III, III) complexes can also catalyze the allylation of simple alcohols with allylic alcohols to give the corresponding alkyl allylic ethers in high yields with complete regioselectivity. These reactions provide useful methods for allylation of some aromatic compounds and allylic ether formation.

Introduction

We have recently disclosed that the ruthenium-catalyzed propargylation of aromatic compounds with propargylic alcohols bearing not only terminal acetylene but also internal acetylenic units affords the corresponding propargylated products in good yields with complete regioselectivity.[1,2] These reactions are catalyzed only by the neutral and cationic thiolate-bridged diruthenium complexes such as $[Cp^*RuCl(\mu_2\text{-}SR)]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; R = Me (**1a**), ^{n}Pr (**1b**), ^{i}Pr (**1c**))[3] and $[Cp^*RuCl(\mu_2\text{-}SR)_2RuCp^*(OH_2)]OTf$ ($OTf = OSO_2CF_3$; R = Me (**1d**), ^{i}Pr (**1e**))[4] (Chart 1) and not by various mononuclear ruthenium complexes as well as dinuclear ruthenium complexes having no Ru−Ru bond.[1] Here,

Chart 1



it is noteworthy that the use of the cationic thiolate-bridged diruthenium complexes is required to promote the propargylation with propargylic alcohols bearing an internal acetylenic group.[2] These reactions provide a general preparative synthetic method for a variety of propargylated aromatic compounds and meet the requirements of atom economy and environmental friendliness, the only byproduct being water. This finding prompted us to investigate the possibility of the corresponding allylation of aromatic compounds with allylic alcohols using these cationic thiolate-bridged diruthenium complexes as catalyst. We describe here the successful result of the allylation of a variety of aromatic compounds with allylic alcohol derivatives catalyzed by the cationic thiolate-bridged diruthenium complexes in detail.[5]

Results and Discussion

Treatment of (*E*)-cinnamylmethyl carbonate (**2a**) with *p*-xylene in the presence of 5 mol % of **1e** at 140 °C for 2 h under N_2 afforded (*E*)-2-cinnamyl-1,4-dimethylbenzene (**3a**) in 65% GLC yield (Scheme 1, Table 1).

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(1) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 11846.

(2) Nishibayashi, Y.; Inada, Y.; Yoshikawa, M.; Hidai, M.; Uemura, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1495.

(3) (a) The thiolate-bridged diruthenium complexes have been found to provide unique bimetallic reaction sites for activation and transformation of various terminal alkynes, see: Nishibayashi, Y.; Yamanashi, M.; Wakiji, I.; Hidai, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2909, and references therein. (b) The methanethiolate-bridged diruthenium complex $[Cp^*RuCl(\mu_2\text{-}SMe)_2RuCp^*Cl]$ (**1a**) is commercially available from Wako Pure Chemical Industries (Japan) as met-DIRUX (*meth*anethiolate-bridged *diru*thenium comple*x*) (130-14581).

(4) (a) Matsuzaka, H.; Takagi, Y.; Hidai, M. *Organometallics* **1994**, *13*, 13. (b) Matsuzaka, H.; Takagi, Y.; Ishii, Y.; Nishio, M.; Hidai, M. *Organometallics* **1995**, *14*, 2153. (c) Takagi, Y.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *Organometallics* **1997**, *16*, 4445.

(5) A preliminary communication has been reported: Nishibayashi, Y.; Yamanashi, M.; Takagi, Y.; Hidai, M. *Chem. Commun.* **1997**, 859.

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Table 1. Reaction of Cinnamyl Alcohol Derivatives (2) with *p*-Xylene in the Presence of Diruthenium Complex (1e)[a]

run	diruthenium catalyst (mol %)[b]	cinnamyl alcohol derivatives (**2**)	conditions temp. (°C)/time (h)	GLC yield (%) (**3a**)
1	**1e** (5)	**2a**	140/2[c]	65
2	**1e** (5)	**2a**	110/2[c]	56
3	**1e** (5)	**2a**	80/2[c]	0
4	**1e** (5)	**2a**	140/6	>99
5	**1e** (5)	**2b**	140/2	>99
6	**1e** (1)	**2b**	140/2	>99
7	**1e** (0.2)	**2b**	140/2	60
8	**1e** (5)	**2c**	140/2	>99
9	**1e** (1)	**2c**	140/2	30
10	**1e** (5)	**2d**	140/2	17
11	**1e** (5)	**2d**	140/2[d]	0

[a] All the reactions of **2** (0.25 mmol) with *p*-xylene (10 mL) were carried out in the presence of ruthenium catalyst. [b] mol % to **2**. [c] *p*-Xylene (2.5 mL) was used as solvent. [d] Et_3N (0.50 mmol) was added.

Scheme 1

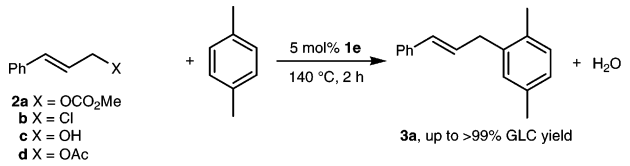
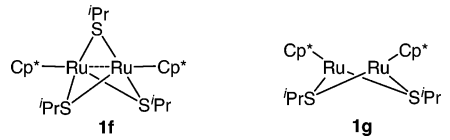


Chart 2



Although the reaction at 110 °C for 2 h gave **3a** in 56% GLC yield, the reaction at 80 °C did not proceed at all (Table 1, runs 2 and 3). A longer reaction time and more diluted condition improved the yield of **3a** (Table 1, run 4). Other cinnamyl derivatives such as (*E*)-cinnamyl chloride (**2b**) and (*E*)-cinnamyl alcohol (**2c**) were more reactive than **2a**, and the compound **3a** was obtained in almost quantitative yield (Table 1, runs 5 and 8). Among these cinnamyl derivatives, **2b** has the highest reactivity (Table 1, runs 6 and 9), and in fact, even in the presence of 0.2 mol % of **1e**, the allylation proceeded to give **3a** in 60% GLC yield (Table 1, runs 6 and 7). Interestingly, (*E*)-cinnamyl acetate (**2d**) was not available for this allylation, and even in the presence of triethylamine, no allylation proceeded at all (Table 1, runs 10 and 11). We also confirmed separately that no allylation occurred at all in the absence of **1e**. In sharp contrast to the reactivity of the cationic thiolate-bridged diruthenium(III, III) complex (**1e**), the corresponding neutral thiolate-bridged diruthenium(III, III) complexes (**1a**−**1c**) and other diruthenium(II, III) and diruthenium(II, II) complexes[6,7] such as ([Cp*Ru(μ_2-S^{i}Pr)$_3$-RuCp*] (**1f**) and [Cp*Ru(μ_2-S^{i}Pr)$_2$RuCp*] (**1g**)) (Chart 2) were ineffective. Noteworthy is that conventional mono- and polyruthenium complexes such as [Cp*RuCl$_2$]$_2$, [Cp*RuCl]$_4$, [Cp*RuCl(PPh$_3$)$_2$], [CpRuCl(PPh$_3$)$_2$] (Cp = η^5-C$_5$H$_5$), [RuCl$_2$(dppe)$_2$] (dppe = 1,2-bis(diphenylphosphino)ethane), [RuCl$_2$(PPh$_3$)$_3$], [RuCl$_2$(*p*-cymene)]$_2$, and [(η^5-C$_9$H$_7$)RuCl(PPh$_3$)$_2$] did not work at all as catalyst. We do not have any experimental data for explaining the reason that bimetallic complexes bearing a metal−metal bond promote these catalytic reactions. In the catalytic propargylic substitution reaction catalyzed by the thiolate-bridged diruthenium complexes, we considered that one Ru moiety should work as an electron pool or a mobile ligand to another Ru site.[8]

Next, the allylation of various benzene derivatives with (*E*)-cinnamyl alcohol (**2c**) in the presence of a catalytic amount of **1e** was investigated. Typical results are shown in Table 2. The reaction of **2c** with benzene in the presence of 5 mol % of **1e** at reflux temperature (80 °C) for 2 h gave (*E*)-cinnamylbenzene (**3b**) in 27% isolated yield (Table 2, run 1). When the reactions of **2c** with toluene and anisole were carried out, the corresponding allylated products (**3c** and **3d**) were isolated in 52% and 59% isolated yields, respectively, as a mixture of two isomers (Table 2, runs 2 and 3). In the case of toluene, *m*- and *p*-isomers were formed with the ratio of 65:35, while in the case of anisole, *o*- and *p*-isomers were formed with the ratio of 12:88. The reaction of **2c** with 10 equiv of phenol in 1,2-dichloroethane as solvent at reflux temperature (83 °C) for 10 min afforded the cinnamyl phenols (**3e**) in 63% isolated yield as a mixture of *o*- and *p*-isomers with the ratio of 37:63 (Table 2, run 4). In sharp contrast to the reaction of **2c**, the allylation with (*Z*)-cinnamyl alcohol (**2e**) was very sluggish, and even the reaction with *p*-xylene gave **3a** in only 11% GLC yield (Table 2, run 5: compare with run 6) together with the formation of 1-indene in 25% GLC yield. Also, no allylation occurred between 2-cyclohexen-1-ol (one of (*Z*)-allylic alcohols) and *p*-xylene. On the other hand, the allylation of *p*-xylene with allylic alcohols such as (*E*)-crotyl alcohol (**2f**) and 1-phenyl-2-propen-1-ol (**2g**) gave the corresponding allylated products (**3f** and **3a**) in 64% and 85% isolated yields (Table 2, runs 7 and 8). In all cases, the stereochemistry around a double bond in the side chain of the products was trans.

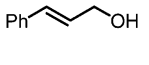
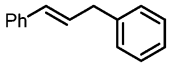
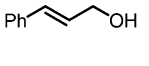
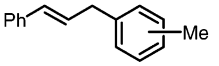
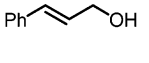
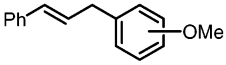
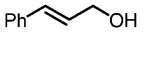
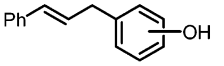
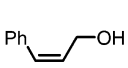
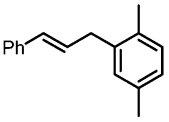
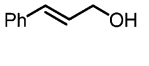
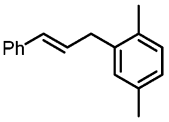
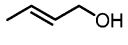
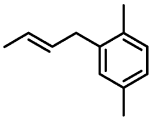
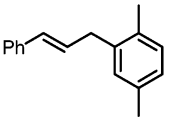
The allylation catalyzed by **1e** could also be applied to heterocyclic compounds as shown in Scheme 2 (Table 3). The reaction of **2c** with 100 equiv of furan in the presence of **1e** in toluene as solvent at 100 °C for 1 h gave the corresponding allylated furans (**4a** and **4a′**) in

(6) (a) Dev, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1990**, *29*, 4797. (b) Matsuzaka, H.; Hirayama, Y.; Nishio, M.; Mizobe, Y.; Hidai, M. *Organometallics* **1993**, *12*, 36. (c) Matsuzaka, H.; Koizumi, H.; Takagi, Y.; Nishio, M.; Hidai, M. *J. Am. Chem. Soc.* **1993**, *115*, 10396.

(7) (a) Takahashi, A.; Mizobe, Y.; Matsuzaka, H.; Dev, S.; Hidai, M. *J. Organomet. Chem.* **1993**, *456*, 243. (b) Nishio, M.; Matsuzaka, H.; Mizobe, Y.; Tanase, T.; Hidai, M. *Organometallics* **1994**, *13*, 4214. (c) Nishio, M.; Matsuzaka, H.; Mizobe, Y.; Hidai, M. *Organometallics* **1996**, *15*, 965.

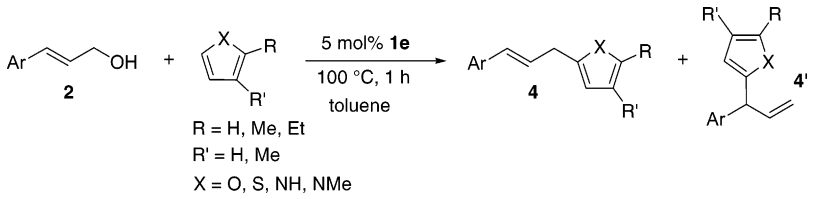
(8) Nishibayashi, Y.; Imajima, H.; Onodera, G.; Hidai, M.; Uemura, S. *Organometallics* **2004**, *23*, 26.

Table 2. Reaction of Allylic Alcohols (2) with Benzene Derivatives in the Presence of 1e[a]

run	allylic alcohol		benzene derivative	reaction temp. (°C)	allylated compound		isolated yield (%)
1		**2c**	benzene	80		**3b**	27
2		**2c**	toluene	110		**3c**	52[b]
3		**2c**	anisole	140		**3d**	59[c]
4		**2c**	phenol[d]	83		**3e**	63[e]
5		**2e**	*p*-xylene	140		**3a**	11[f, g]
6		**2c**	*p*-xylene	140		**3a**	78
7		**2f**	*p*-xylene	140[h]		**3f**	64
8		**2g**	*p*-xylene	140		**3a**	85

[a] All the reactions of **2** (0.25 mmol) with benzene derivatives (10 mL) were carried out in the presence of **1e** (0.0125 mmol) for 2 h. [b] Isomer ratio is *o*:*m*:*p* = 0:65:35. [c] Isomer ratio is *o*:*m*:*p* = 12:0:88. [d] The reaction of **2c** with 10 equiv of phenol was carried out in the presence of **1e** (5 mol %) in 1,2-dichloroethane at reflux temperature for 15 min. [e] Isomer ratio is *o*:*m*:*p* = 37:0:63. [f] GLC yield. [g] Indene was formed in 25% GLC yield. [h] For 5 h.

Scheme 2



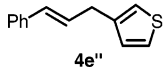
90% isolated yield as a mixture of two regioisomers with the ratio of 96:4. The major and minor products were revealed to be 2-cinnamylfuran (**4a**) and 2-(3-phenyl-2-propenyl)furan (**4a′**), respectively (Table 3, run 1), the ratio of the products (96:4) being determined by ^{1}H NMR. The reactions of **2c** with other substituted furans afforded the corresponding allylated furans in moderate to good yields as a mixture of two regioisomers (Table 3, runs 2−4). Interestingly, the formation of unexpected products was also observed when thiophene derivatives were treated with **2c** in toluene at 100 °C for 1 h (Table 3, runs 5 and 6). Thus, 3-cinnamylthiophene (**4e″**) was formed as a minor allylated product in addition to the formation of the expected 2-cinnamylthiophene (**4e**). A similar phenomenon was observed in the reaction of **2c** with 2-methylthiophene under the same reaction conditions, and 2-methyl-3-cinnamylthiophene (**4f″**) was obtained as a minor product. Unfortunately, no allylation occurred in the reactions of **2c** with pyrrole and *N*-methylpyrrole (Table 3, runs 7 and 8). The allylation of furan with cinnamyl alcohols having a substituent on the benzene ring (**2h**−**2o**) proceeded smoothly in the presence of **1e** in toluene at 100 °C for 1 h. The products were the corresponding substituted 2-cinnamylfurans (**4h**−**4o**) together with a small amount of 2-(3-phenyl-2-propenyl)furans (**4h′**−**4o′**) as minor products (Table 3, runs 9−16). In the reactions with *o*- and *m*-fluoro-substituted cinnamyl alcohols (**2k** and **2l**), the yields of the allylated products were low (Table 3, runs 12 and 13).

To obtain some information of the reaction mechanism, we monitored the reaction of **2c** with *p*-xylene in the presence of **1e** (5 mol %) at 140 °C for 2 h by GLC. The time-profile of the products is shown in Figure 1, which indicates the gradual formation of the allylated product **3a** together with the formation of an intermediate at early stage of the reaction. The intermediate was

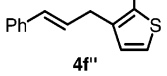
Table 3. Reaction of Cinnamyl Alcohols (2) with Heterocyclic Compounds in the Presence of 1e[a]

run	cinnamyl alcohol	heterocyclic compound	allylated compound	isolated yield (%)	isomer ratio (**4**:**4′**) or (**4**:**4′**:**4″**)
1	Ar = C_6H_5 **2c**	X = O, R = H, R′ = H	**4a** and **4a′**	90	96:4
2	Ar = C_6H_5 **2c**	X = O, R = Me, R′ = H	**4b** and **4b′**	73	77:23
3	Ar = C_6H_5 **2c**	X = O, R = Et, R′ = H	**4c** and **4c′**	72	75:25
4	Ar = C_6H_5 **2c**	X = O, R = Me, R′ = Me	**4d** and **4d′**	38	86:14
5	Ar = C_6H_5 **2c**	X = S, R = H, R′ = H	**4e**, **4e′**, and **4e″**	80	72:2:26
6	Ar = C_6H_5 **2c**	X = S, R = Me, R′ = H	**4f**, **4f′**, and **4f″**	99	72:4:24
7	Ar = C_6H_5 **2c**	X = NH, R = H, R′ = H		0	
8	Ar = C_6H_5 **2c**	X = NMe, R = H, R′ = H		0	
9	Ar = *o*-MeC_6H_4 **2h**	X = O, R = H, R′ = H	**4h** and **4h′**	65	99:1
10	Ar = *m*-MeC_6H_4 **2i**	X = O, R = H, R′ = H	**4i** and **4i′**	75	98:2
11	Ar = *p*-MeC_6H_4 **2j**	X = O, R = H, R′ = H	**4j** and **4j′**	84	99:1
12	Ar = *o*-FC_6H_4 **2k**	X = O, R = H, R′ = H	**4k** and **4k′**	25	97:3
13	Ar = *m*-FC_6H_4 **2l**	X = O, R = H, R′ = H	**4l** and **4l′**	30	96:4
14	Ar = *p*-FC_6H_4 **2m**	X = O, R = H, R′ = H	**4m** and **4m′**	71	98:2
15	Ar = *p*-ClC_6H_4 **2n**	X = O, R = H, R′ = H	**4n** and **4n′**	56	97:3
16	Ar = *p*-$MeOC_6H_4$ **2o**	X = O, R = H, R′ = H	**4o** and **4o′**	52	99:1

[a] All the reactions of **2** (1.00 mmol) with heterocyclic compound (100 mmol) in toluene (10 mL) were carried out in the presence of **1e** (0.05 mmol) for 1 h.



4e″



4f″

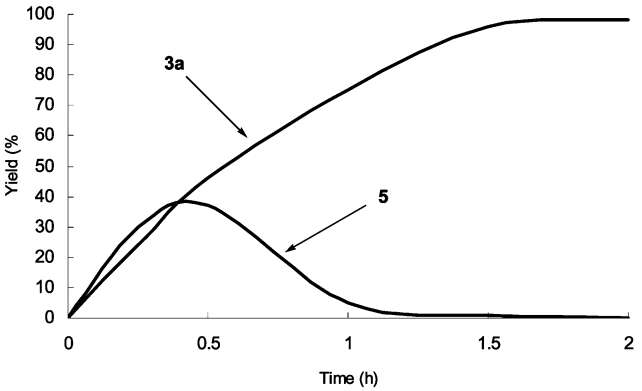


Figure 1. Time-profile of the products (**3a** and **5**) in the reaction of **2c** (0.25 mmol) with *p*-xylene (10 mL) in the presence of **1e** (5 mol %) at 140 °C.

actually isolated in 25% isolated yield in a separate experiment, which was characterized as dicinnamyl ether (**5**).[9] Separately, we confirmed the transformation of **5** into **3a** in the presence of **1e** (5 mol %) in *p*-xylene at 140 °C for 2 h, **3a** being obtained in 78% isolated yield. These results show that the reaction proceeds via both pathways as shown in Scheme 3: namely, a direct allylation with **2c** and an allylation via the intermediate **5**.

The fact that **5** was produced from **2c** under this reaction condition prompted us to investigate an ether formation from allylic alcohols and simple alcohols such as EtOH and PrOH (Scheme 4, Table 4). For example, the reaction of **2c** with 10 equiv of EtOH in 1,2-dichloroethane at reflux temperature for 30 min in the presence of 5 mol % of **1e** gave (*E*)-cinnamyl ethyl ether (**6a**) in >99% GLC yield (85% isolated yield) with complete stereoselectivity (Table 4, run 1). The reaction proceeded even in the presence of 1 mol % of **1e**, but it was sluggish (Table 4, run 2). Other simple alcohols such as ^{n}PrOH, ^{i}PrOH, and benzyl alcohol are available for this ether formation (Table 4, runs 3−5). Interestingly, the reaction of 1-phenyl-2-propen-1-ol (**2g**) with 10 equiv of EtOH afforded **6a** in >99% GLC yield (Table 4, run 6), showing the presence of a common allylic intermediate during the reaction. This reaction seems to provide one of the most reliable preparative methods for allylic ethers.

Similarly to allylic ether formation, both **2c** and **2g** reacted with 2-methylfuran to give the same products (**4b** and **4b′**) in high yield with a similar regioselectivity (Scheme 5), showing also the formation of a common allylic intermediate, probably (π-allyl)diruthenium complex. To prepare this key intermediate, we carried out the reaction of **1e** with 5 equiv of cinnamyl chloride (**2b**) in 1,2-dichloroethane at 80 °C for 2 h, but the expected (π-allyl)diruthenium complex could not be obtained. Instead, unexpectedly, a novel cationic diruthenium(III, IV) complex, $[Cp^*RuCl(\mu_2\text{-}S^iPr)]_2OTf$ (**1h**), was isolated in 29% yield as black crystals together with allylated cinnamyl chlorides (**7**) (Scheme 6). The structure of the paramagnetic complex **1h** was unambiguously clarified by X-ray analysis, and an ORTEP drawing is shown in Figure 2. The Ru−Ru bond distance (2.667(4) Å) of **1h** is shorter than those of the cationic diruthenium(III, III) complexes (ca. 2.80 Å).[10] The paramagnetic nature of **1h** suggests the existence of a bonding interaction between two Ru atoms. Interestingly, when the catalytic reaction of **2c** with *p*-xylene was performed in the presence of **1h**, **3a** was obtained in >99% GLC yield. This result shows that in the present catalytic allylation reaction a diruthenium(III, IV) complex such as **1h** formed in situ may also be considered to be one of the reactive species from which some (π-allyl)diruthenium complexes are derived.

As described above, toluene was mainly allylated at the 3- and 4-positions (Table 2, run 2) and thiophene was allylated at the 2- and 3-positions (Table 3, runs 5 and 6). These results suggest that this allylation did not proceed via classical electrophilic aromatic substitution. Although the reaction mechanism is not yet clear, we assume that the first step involves the formation of a

(9) ^{1}H NMR δ 4.19 (dd, 4H, J = 6.0 and 1.3 Hz), 6.31 (dt, 2H, J = 6.0 and 16.2 Hz), 6.63 (d, 2H, J = 16.2 Hz), 7.20−7.41 (m, 10H): Gómez-Bengoa, E.; Noheda, P.; Echavarren, A. M. *Tetrahedron Lett.* **1994**, *35*, 7097.

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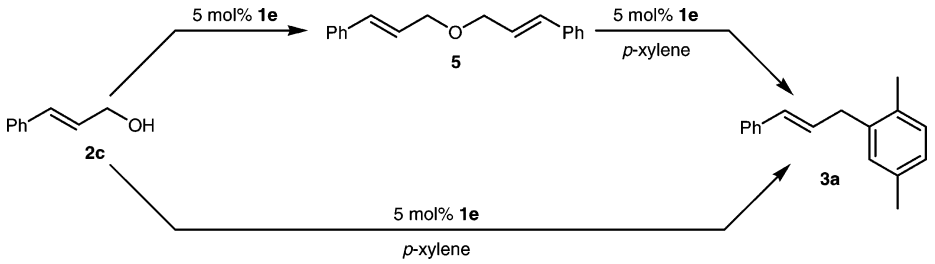
Scheme 3



Scheme 4

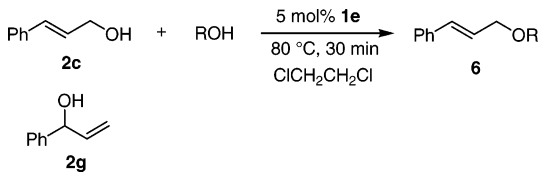


Table 4. Reaction of Allylic Alcohols (2) with Alcohols in the Presence of 1e[a]

run	allylic alcohol	ROH	allylic ether	GLC yield (%)
1	**2c**	EtOH	**6a**	>99 (85)[b]
2[c]	**2c**	EtOH	**6a**	21
3	**2c**	^{n}PrOH	**6b**	97
4	**2c**	^{i}PrOH	**6c**	66
5	**2c**	$PhCH_2OH$	**6d**	98
6	**2g**	EtOH	**6a**	>99

[a] All the reactions of **2** (0.25 mmol) with alcohol (2.50 mmol) in 1,2-dichloroethane (5 mL) were carried out in the presence of **1e** (0.0125 mmol) at reflux temperature for 30 min. [b] Isolated yield. [c] 1 mol % of **1e** was used.

(π-allyl)diruthenium complex, which is followed by the attack of aromatic compounds on the π-allyl moiety. The ambiphilic reactivity of a (π-allyl)monoruthenium complex has been recognized,[11a] where the complex can react with both nucleophile and electrophile to give the corresponding allylated products in high yields. Also, ruthenium-catalyzed nucleophilic and electrophilic allylation of allylic alcohol derivatives has been described in detail.[11a] However, the stoichiometric reaction of (π-allyl)monoruthenium complexes with aromatic compounds as well as any ruthenium-catalyzed allylation of aromatic compounds with allylic alcohol derivatives have not yet been reported until now. To our knowledge,

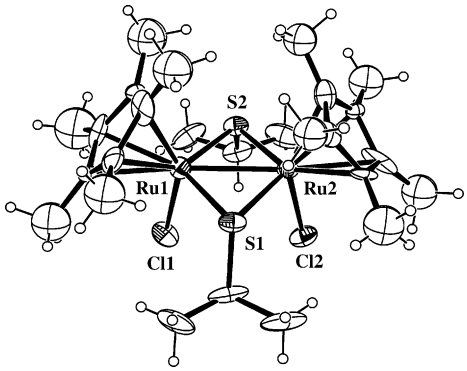


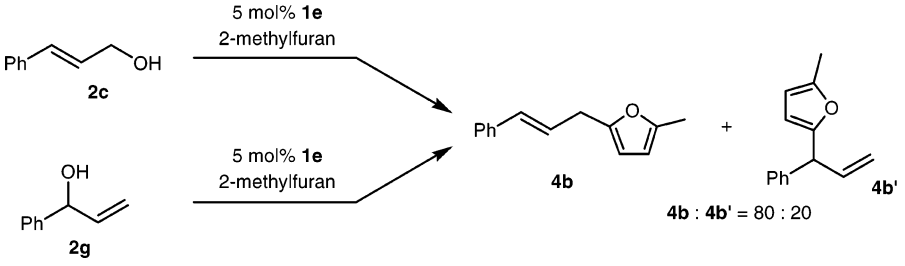
Figure 2. Crystal structure of **1h**·CH_2Cl_2. OTf anion and solvent are omitted for clarity.

the direct allylation of aromatic compounds with allylic alcohols is still limited only to the recent molybdenum- and tungsten-catalyzed reactions,[12−14] where the stereochemistry of the allylic moiety in allylated products was retained in contrast to the Lewis acid-catalyzed allylation reactions of aromatic compounds.[15] The catalytic activity of thiolate-bridged diruthenium complexes presented here is much better than that of molybdenum and tungsten complexes[13] for the allylation of aromatic compounds with allylic alcohols.

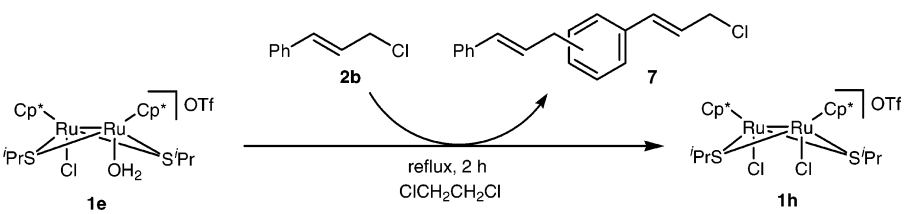
Conclusion

Cationic thiolate-bridged diruthenium(III, III) complexes worked as good catalysts for the allylation of aromatic compounds with allylic alcohol derivatives. Not only benzene derivatives such as benzene, toluene, *p*-xylene, anisole, and phenol but also heterocyclic compounds such as furans and thiophenes were avail-

Scheme 5



Scheme 6



able for this allylation. The formation of the same products from the reaction with either cinnamyl alcohol or 1-phenyl-2-propen-1-ol suggested the existence of a common (π-allyl)diruthenium complex as an intermediate, though it was neither observed nor isolated. Aromatic compounds may attack directly on the π-allyl moiety of the complex. These complexes also work as good catalysts for alkyl allylic ether formation by the reaction between allylic alcohol and alkanol. New catalytic reactions presented in this article may provide a useful synthetic methodology using the thiolate-bridged diruthenium complexes.[16]

Experimental Section

Synthesis of Substrates. Thiolate-bridged diruthenium complexes (**1**) were prepared according to our previous procedures.[4] All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use. Substituted cinnamyl alcohols were prepared according to the previous procedure.[17]

General Procedure for Allylation of Benzene Derivatives with Allylic Alcohols (2) Catalyzed by [Cp*RuCl(μ_2-S^{i}Pr)$_2$RuCp*(OH$_2$)]OTf (1e). A typical experimental procedure for allylation of anisole with cinnamyl alcohol (**2c**) catalyzed by **1e** is as follows. In a 50 mL flask was placed **1e** (19.8 mg, 0.0240 mmol). Cinnamyl alcohol **2c** (66.4 mg, 0.495 mmol) and anhydrous anisole (20 mL) were added under N_2. The reaction flask was kept at 140 °C for 2 h. After cooling, the solvent was concentrated in vacuo, and then the residue was purified by TLC (SiO_2) with EtOAc/*n*-hexane (3/7) to give **3d**[18] as a yellow oil (66.0 mg, 0.294 mmol, 59% yield). The ratio of isomers was determined by ^{1}H NMR. Other allylated products such as **3a**,[19] **3b**,[20] **3c**,[20] **3e**,[15b] and **3f**[21] are also known compounds.

General Procedure for Allylation of Heterocyclic Compounds with Allylic Alcohols (2) Catalyzed by [Cp*RuCl(μ_2-S^{i}Pr)$_2$RuCp*(OH$_2$)]OTf (1e). A typical experimental procedure for allylation of 2-methylfuran with cinnamyl alcohol (**2c**) catalyzed by **1e** is as follows. In a 20 mL flask was placed **1e** (42.9 mg, 0.0520 mmol). Anhydrous toluene (10 mL) was added under N_2, and then the mixture was magnetically stirred at room temperature. After the addition of **2c** (135.1 mg, 1.01 mmol) and 2-methylfuran (8.22 g, 0.100 mol), the reaction flask was kept at 100 °C for 1 h. After cooling, the solvent was concentrated in vacuo, and then the residue was purified by column chromatography on SiO_2 with *n*-hexane as eluent to give the corresponding allylated products as a mixture of two isomers with the ratio of 77:23 (**4b** and **4b′**) (146 mg, 0.736 mmol, 73% yield). The ratio of isomers was determined by ^{1}H NMR.

(*E*)-3-(5-Methylfuran-2-yl)-1-phenyl-1-propene (4b) and 3-(5-Methylfuran-2-yl)-3-phenyl-1-propene (4b′). Isomer ratio: 77:23. A pale yellow oil. ^{1}H NMR δ **4b**: 2.26 (s, 3H), 3.49 (d, 2H, J = 6.8 Hz), 5.87 (d, 1H, J = 2.9 Hz), 5.93 (d, 1H, J = 2.9 Hz), 6.29 (dt, 1H, J = 15.8 and 6.8 Hz), 6.48 (d, 1H, J = 15.8 Hz), 7.18−7.38 (m, 5H); **4b′**: 2.24 (s, 3H), 4.67 (d, 1H, J = 7.2 Hz), 5.04 (d, 1H, J = 17.1 Hz), 5.18 (d, 1H, J = 10.1 Hz), 5.90 (d, 1H, J = 2.9 Hz), 6.19 (ddd, 1H, J = 17.1, 10.1, and 7.2 Hz). ^{13}C NMR δ **4b**: 13.5, 31.8, 106.0, 106.2, 126.2, 127.2, 128.2, 128.5, 131.7, 137.3, 150.8, 152.0; **4b′**: 13.6, 49.2. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.58; H, 7.19.

Spectroscopic data and isolated yields of other products are as follows. The ratio of isomers was determined by ^{1}H NMR.

(*E*)-3-(Furan-2-yl)-1-phenyl-1-propene (4a) and 3-(Furan-2-yl)-3-phenyl-1-propene (4a′). Yield: 90%. Isomer ratio: 96:4. A pale yellow oil. ^{1}H NMR δ **4a**: 3.55 (d, 2H, J = 6.6 Hz), 6.07 (dd, 1H, J = 0.9 and 3.0 Hz), 6.31 (dt, 1H, J = 15.8 and 6.6 Hz), 6.31 (d, 1H, J = 3.0 Hz), 6.49 (d, 1H, J = 15.8 Hz), 7.21−7.38 (m, 6H); **4a′**: 4.73 (d, 1H, J = 6.9 Hz), 5.05 (d, 1H, J = 17.1 Hz), 5.21 (d, 1H, J = 10.2 Hz). ^{13}C NMR δ **4a**: 31.7, 105.6, 110.3, 125.6, 126.2, 127.3, 128.5, 132.0, 137.2, 141.3, 153.9. Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.64; H, 6.79.

(*E*)-3-(5-Ethylfuran-2-yl)-1-phenyl-1-propene (4c) and 3-(5-Ethylfuran-2-yl)-3-phenyl-1-propene (4c′). Yield: 72%. Isomer ratio: 75:25. A pale yellow oil. ^{1}H NMR δ **4c**: 1.22 (t, 3H, J = 7.5 Hz), 2.62 (q, 2H, J = 7.5 Hz), 3.50 (d, 2H, J = 6.7 Hz), 5.88 (d, 1H, J = 3.0 Hz), 5.94 (d, 1H, J = 3.0 Hz), 6.30 (dt, 1H, J = 15.8 and 6.7 Hz), 6.48 (d, 1H, J = 15.8 Hz), 7.19−7.37 (m, 5H); **4c′**: 1.19 (t, 3H, J = 7.5 Hz), 2.59 (q, 2H, J = 7.5 Hz), 4.68 (d, 1H, J = 7.1 Hz), 5.03 (d, 1H, J = 17.1 Hz), 5.18 (d, 1H, J = 10.1 Hz), 6.19 (ddd, 1H, J = 17.1, 10.1, and 7.1 Hz). ^{13}C NMR δ **4c**: 12.2, 21.4, 31.8, 106.0, 107.1, 126.2, 127.2, 128.4, 128.5, 131.7, 137.4, 151.9, 156.7; **4c′**: 12.1, 21.3, 49.2. Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.91; H, 7.65.

(*E*)-3-(4,5-Dimethylfuran-2-yl)-1-phenyl-1-propene (4d) and 3-(4,5-Dimethylfuran-2-yl)-3-phenyl-1-propene (4d′). Yield: 38%. Isomer ratio: 86:14. A pale yellow oil. ^{1}H NMR δ **4d**: 1.90 (s, 3H), 2.17 (s, 3H), 3.46 (d, 2H, J = 6.7 Hz), 5.84 (s, 1H), 6.28 (dt, 1H, J = 15.8 and 6.7 Hz), 6.48 (d, 1H, J = 15.8 Hz), 7.20−7.38 (m, 5H); **4d′**: 1.90 (s, 3H), 2.15 (s, 3H), 4.63 (d, 1H, J = 7.2 Hz), 5.04 (ddd, 1H, J = 17.1, 1.5, and 1.5 Hz), 5.17 (ddd, 1H, J = 10.1, 1.5, and 1.5 Hz), 5.80 (s, 1H), 6.18 (ddd, 1H, J = 17.1, 10.1, and 7.2 Hz). ^{13}C NMR δ **4d**: 10.0, 11.3, 31.9, 108.8, 114.4, 126.1, 127.1, 128.1, 128.4, 131.5, 150.6, 156.7; **4d′**: 49.2. HRMS: Calcd for $C_{15}H_{16}O$ [M] 211.1123, found 211.1121.

(*E*)-1-Phenyl-3-(thiophen-2-yl)-1-propene (4e), 3-Phenyl-3-(thiophen-2-yl)-1-propene (4e′), and (*E*)-1-Phenyl-3-(thiophen-3-yl)-1-propene (4e″). Yield: 80%. Isomer ratio: 72:2:26. A pale yellow oil. ^{1}H NMR δ **4e**: 3.73 (d, 2H, J = 6.6 Hz), 6.36 (dt, 1H, J = 15.8 and 6.6 Hz), 6.51 (d, 1H, J = 15.8 Hz), 6.84−6.87 (m, 1H), 6.95 (dd, 1H, J = 5.3 and 3.5 Hz), 7.14−7.39 (m, 6H); **4e′**: 4.90 (d, 1H, J = 7.6 Hz), 5.09 (ddd, 1H, J = 17.0, 1.4, and 1.4 Hz), 5.21 (ddd, 1H, J = 10.3, 1.4, and 1.4 Hz); **4e″**: 3.55 (d, 2H, J = 6.3 Hz), 6.35 (dt, 1H, J = 15.7 and 6.3 Hz), 6.46 (d, 1H, J = 15.7 Hz), 6.97−7.02 (m, 2H). ^{13}C NMR δ **4e**: 33.4, 123.7, 124.6, 126.1, 126.8, 127.2, 128.1,

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128.4, 130.9, 131.3, 137.1; **4e″**: 33.9. Anal. Calcd for $C_{13}H_{12}S$: C, 77.95; H, 6.04. Found: C, 78.09; H, 6.01.

(*E*)-3-(5-Methylthiophen-2-yl)-1-phenyl-1-propene (4f), 3-(5-Methylthiophen-2-yl)-3-phenyl-1-propene (4f′), and (*E*)-3-(2-Methylthiophen-3-yl)-1-phenyl-1-propene (4f″). Yield: 99%. Isomer ratio: 72:4:24. A pale yellow oil. ^{1}H NMR δ **4f**: 2.43 (s, 3H), 3.65 (d, 2H, J = 7.0 Hz), 6.34 (dt, 1H, J = 15.6 and 7.0 Hz), 6.49 (d, 1H, J = 15.6 Hz), 6.58 (d, 1H, J = 2.8 Hz), 6.62 (d, 1H, J = 2.8 Hz), 7.19−7.37 (m, 5H); **4f′**: 4.82 (d, 1H, J = 7.2 Hz), 5.09 (d, 1H, J = 17.2 Hz), 5.19 (d, 1H, J = 10.0 Hz); **4f″**: 2.40 (s, 3H), 3.44 (d, 2H, J = 6.0 Hz), 6.85 (d, 1H, J = 5.2 Hz), 7.02 (d, 1H, J = 5.2 Hz). ^{13}C NMR δ **4f**: 15.3, 33.5, 124.4, 124.8, 126.2, 127.2, 128.4, 128.5, 130.4, 131.1, 137.3, 140.7; **4f″**: 12.9, 31.8. Anal. Calcd for $C_{14}H_{14}S$: C, 78.45; H, 6.58. Found: C, 78.49; H, 6.59.

(*E*)-3-(Furan-2-yl)-1-(2-methylphenyl)-1-propene (4h) and 3-(Furan-2-yl)-3-(2-methylphenyl)-1-propene (4h′). Yield: 65%. Isomer ratio: 99:1. A pale yellow oil. ^{1}H NMR δ **4h**: 2.33 (s, 3H), 3.57 (d, 2H, J = 6.9 Hz), 6.07 (dd, 1H, J = 0.9 and 3.2 Hz), 6.18 (dt, 1H, J = 15.5 and 6.9 Hz), 6.31 (dd, 1H, J = 1.8 and 3.2 Hz), 6.70 (d, 1H, J = 15.5 Hz), 7.13−7.16 (m, 3H), 7.34 (dd, 1H, J = 0.9 and 1.8 Hz), 7.42−7.44 (m, 1H); **4h′**: 5.22 (d, 1H, J = 10.2 Hz). ^{13}C NMR δ **4h**: 19.9, 32.1, 105.5, 110.2, 125.6, 126.0, 126.7, 127.1, 129.8, 130.1, 135.1, 136.3, 141.2, 153.9. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 85.08; H, 7.06.

(*E*)-3-(Furan-2-yl)-1-(3-methylphenyl)-1-propene (4i) and 3-(Furan-2-yl)-3-(3-methylphenyl)-1-propene (4i′). Yield: 75%. Isomer ratio: 98:2. A pale yellow oil. ^{1}H NMR δ **4i**: 2.33 (s, 3H), 3.54 (d, 2H, J = 6.6 Hz), 6.06 (dd, 1H, J = 0.8 and 3.2 Hz), 6.29 (dt, 1H, J = 15.6 and 6.6 Hz), 6.31 (dd, 1H, J = 2.0 and 3.2 Hz), 6.46 (d, 1H, J = 15.6 Hz), 7.02−7.04 (m, 1H), 7.17−7.19 (m, 3H), 7.34 (dd, 1H, J = 0.8 and 2.0 Hz); **4i′**: 4.69 (d, 1H, J = 6.6 Hz), 5.06 (d, 1H, J = 16.8 Hz), 5.19 (d, 1H, J = 10.2 Hz). ^{13}C NMR δ **4i**: 21.4, 31.8, 105.5, 110.2, 123.3, 125.3, 126.8, 128.0, 128.3, 132.0, 137.1, 137.9, 141.2, 153.8. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 85.07; H, 7.03.

(*E*)-3-(Furan-2-yl)-1-(4-methylphenyl)-1-propene (4j) and 3-(Furan-2-yl)-3-(4-methylphenyl)-1-propene (4j′). Yield: 84%. Isomer ratio: 99:1. A pale yellow oil. ^{1}H NMR δ **4j**: 2.32 (s, 3H), 3.53 (d, 2H, J = 6.6 Hz), 6.06 (d, 1H, J = 2.9 Hz), 6.25 (dt, 1H, J = 15.6 and 6.6 Hz), 6.30 (dd, 1H, J = 1.5 and 2.9 Hz), 6.46 (d, 1H, J = 15.6 Hz), 7.10 (d, 2H, J = 7.8 Hz), 7.26 (d, 2H, J = 7.8 Hz), 7.33 (d, 1H, J = 1.5 Hz); **4j′**: 4.69 (d, 1H, J = 6.6 Hz), 5.04 (d, 1H, J = 17.1 Hz), 5.19 (d, 1H, J = 10.2 Hz). ^{13}C NMR δ **4j**: 21.1, 31.7, 105.5, 110.3, 124.5, 126.1, 129.2, 131.8, 134.4, 137.0, 141.3, 154.1. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.95; H, 7.34.

(*E*)-1-(2-Fluorophenyl)-3-(furan-2-yl)-1-propene (4k) and 3-(2-Fluorophenyl)-3-(furan-2-yl)-1-propene (4k′). Yield: 25%. Isomer ratio: 97:3. A pale yellow oil. ^{1}H NMR δ **4k**: 3.58 (d, 2H, J = 6.9 Hz), 6.08 (dd, 1H, J = 0.8 and 3.1 Hz), 6.31 (dd, 1H, J = 1.5 and 3.1 Hz), 6.39 (dt, 1H, J = 15.9 and 6.9 Hz), 6.65 (d, 1H, J = 15.9 Hz), 6.98−7.10 (m, 2H), 7.14−7.22 (m, 1H), 7.34 (dd, 1H, J = 0.8 and 1.5 Hz), 7.41−7.46 (m, 1H); **4k′**: 5.23 (d, 1H, J = 9.9 Hz). ^{13}C NMR δ **4k**: 32.1, 105.7, 110.3, 115.6 (d, J_{C-F} = 21.6 Hz), 124.0 (d, J_{C-F} = 3.1 Hz), 124.4 (d, J_{C-F} = 3.2 Hz), 124.9 (d, J_{C-F} = 12.4 Hz), 127.3 (d, J_{C-F} = 4.3 Hz), 128.3 (d, J_{C-F} = 5.0 Hz), 128.5 (d, J_{C-F} = 8.7 Hz), 141.4, 153.6, 160.1 (d, J_{C-F} = 246.7 Hz). Anal. Calcd for $C_{13}H_{11}FO$: C, 77.21; H, 5.48. Found: C, 77.18; H, 5.40.

(*E*)-1-(3-Fluorophenyl)-3-(furan-2-yl)-1-propene (4l) and 3-(3-Fluorophenyl)-3-(furan-2-yl)-1-propene (4l′). Yield: 30%. Isomer ratio: 96:4. A pale yellow oil. ^{1}H NMR δ **4l**: 3.55 (d, 2H, J = 6.8 Hz), 6.07 (d, 1H, J = 3.1 Hz), 6.31 (dd, 1H, J = 1.6 and 3.1 Hz), 6.31 (dt, 1H, J = 15.7 and 6.8 Hz), 6.45 (d, 1H, J = 15.7 Hz), 6.86−6.93 (m, 1H), 7.03−7.12 (m, 2H), 7.20−7.28 (m, 1H), 7.34 (d, 1H, J = 1.6 Hz); **4l′**: 4.73 (d, 1H, J = 7.3 Hz), 5.06 (d, 1H, J = 17.0 Hz), 5.23 (d, 1H, J = 10.0 Hz). ^{13}C NMR δ **4l**: 31.7, 105.8, 110.3, 112.6 (d, J_{C-F} = 21.7 Hz), 114.0 (d, J_{C-F} = 21.7 Hz), 122.0 (d, J_{C-F} = 2.8 Hz), 127.0, 129.8 (d, J_{C-F} = 8.9 Hz), 130.8 (d, J_{C-F} = 2.8 Hz), 139.5 (d, J_{C-F} = 7.8 Hz), 141.4, 153.3, 163.0 (d, J_{C-F} = 243.8 Hz). Anal. Calcd for $C_{13}H_{11}FO$: C, 77.21; H, 5.48. Found: C, 77.27; H, 5.44.

(*E*)-1-(4-Fluorophenyl)-3-(furan-2-yl)-1-propene (4m) and 3-(4-Fluorophenyl)-3-(furan-2-yl)-1-propene (4m′). Yield: 71%. Isomer ratio: 98:2. A pale yellow oil. ^{1}H NMR δ **4m**: 3.54 (d, 2H, J = 6.8 Hz), 6.06 (d, 1H, J = 3.2 Hz), 6.22 (dt, 1H, J = 16.0 and 6.8 Hz), 6.31 (dd, 1H, J = 2.2 and 3.2 Hz), 6.45 (d, 1H, J = 16.0 Hz), 6.96−7.00 (m, 2H), 7.30−7.34 (m, 3H); **4m′**: 4.72 (d, 1H, J = 6.0 Hz), 5.03 (d, 1H, J = 17.2 Hz), 5.21 (d, 1H, J = 10.4 Hz). ^{13}C NMR δ **4m**: 31.7, 105.6, 110.3, 115.3 (d, J_{C-F} = 21.5 Hz), 125.3, 127.6 (d, J_{C-F} = 8.3 Hz), 130.7, 133.3 (d, J_{C-F} = 3.3 Hz), 141.3, 153.6, 162.0 (d, J_{C-F} = 244.2 Hz). Anal. Calcd for $C_{13}H_{11}FO$: C, 77.21; H, 5.48. Found: C, 77.22; H, 5.76.

(*E*)-1-(4-Chlorophenyl)-3-(furan-2-yl)-1-propene (4n) and 3-(4-Chlorophenyl)-3-(furan-2-yl)-1-propene (4n′). Yield: 56%. Isomer ratio: 97:3. A pale yellow oil. ^{1}H NMR δ **4n**: 3.55 (d, 2H, J = 6.7 Hz), 6.07 (d, 1H, J = 2.8 Hz), 6.28 (dt, 1H, J = 15.6 and 6.7 Hz), 6.31 (dd, 1H, J = 1.6 and 2.8 Hz), 6.44 (d, 1H, J = 15.6 Hz), 7.25−7.30 (m, 4H), 7.35 (d, 1H, J = 1.6 Hz); **4n′**: 4.71 (d, 1H, J = 6.8 Hz), 5.03 (d, 1H, J = 18.0 Hz), 5.22 (d, 1H, J = 10.4 Hz). ^{13}C NMR δ **4n**: 31.7, 105.7, 110.3, 126.3, 127.3, 128.6, 130.7, 132.8, 135.6, 141.3, 153.4. Anal. Calcd for $C_{13}H_{11}ClO$: C, 71.40; H, 5.07. Found: C, 71.38; H, 5.21.

(*E*)-3-(Furan-2-yl)-1-(4-methoxyphenyl)-1-propene (4o) and 3-(Furan-2-yl)-3-(4-methoxyphenyl)-1-propene (4o′). Yield: 52%. Isomer ratio: 99:1. A pale yellow oil. ^{1}H NMR δ **4o**: 3.53 (d, 2H, J = 6.8 Hz), 3.13 (s, 3H), 6.06 (dd, 1H, J = 0.8 and 3.1 Hz), 6.16 (dt, 1H, J = 15.7 and 6.8 Hz), 6.30 (dd, 1H, J = 1.9 and 3.1 Hz), 6.44 (d, 1H, J = 15.7 Hz), 6.84 (d, 2H, J = 8.8 Hz), 7.29 (d, 2H, J = 8.8 Hz), 7.33 (dd, 1H, J = 0.8 and 1.9 Hz); **4o′**: 4.69 (d, 1H, J = 7.0 Hz), 5.03 (d, 1H, J = 17.3 Hz), 5.19 (d, 1H, J = 10.3 Hz). ^{13}C NMR δ **4o**: 31.8, 55.3, 105.4, 110.2, 113.8, 123.3, 127.2, 129.9, 131.2, 141.2, 154.0, 158.8. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.78; H, 6.70.

General Procedure for Allylation of Simple Alcohols with Allylic Alcohols (2) Catalyzed by [Cp*RuCl(μ_2-S^{i}Pr)$_2$RuCp*(OH$_2$)]OTf (1e). A typical experimental procedure for allylation of ethanol with cinnamyl alcohol (**2c**) catalyzed by **1e** is as follows. In a 50 mL flask was placed **1e** (10.3 mg, 0.0125 mmol). Cinnamyl alcohol **2c** (33.5 mg, 0.25 mmol) and ethanol (115.2 mg, 2.50 mmol) with anhydrous 1,2-dichloroethane (5 mL) were added under N_2. The reaction flask was kept at 78 °C for 2 h. After cooling, the solvent was concentrated in vacuo, and then the residure was purified by column chromatography on SiO_2 with EtOAc/*n*-hexane (1:9) as eluent followed by preparative HPLC to give **6a**[22] as a colorless oil. Other cinnamyl ethers such as **6b**,[23] **6c**,[24] and **6d**[24] are also known compounds.

Preparation of [Cp*RuCl(μ_2-S^{i}Pr)]$_2$OTf (Cp* = η^5-C$_5$Me$_5$; OTf = OSO$_2$CF$_3$) (1h). In a 50 mL flask was placed **1e** (825 mg, 1.00 mmol) under N_2. Anhydrous 1,2-dichloroethane (20 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2b** (763 mg, 5.00 mmol), the reaction flask was kept at reflux temperature for 2 h. After cooling, the solvent was removed under reduced pressure, and the residue was recrystallized from CH_2Cl_2/*n*-hexane to give black crystals of **1h**·CH_2Cl_2 (269 mg, 0.29 mmol, 29%). Anal. Calcd for $C_{27}H_{44}Cl_2F_3O_3Ru_2S_3$·$CH_2Cl_2$: C, 36.25; H, 5.00. Found: C, 36.10; H, 4.92.

7. Isolated yield: 35% (as a mixture of isomers). A colorless oil. ^{1}H NMR δ a major isomer: 3.60 (d, 2H, J = 7.0 Hz), 4.25 (d, 2H, J = 7.0 Hz), 6.30 (dt, 1H, J = 15.6 and 7.0 Hz), 6.33

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(dt, 1H, J = 15.6 and 7.0 Hz), 6.64 (d, 1H, J = 15.6 Hz), 6.66 (d, 1H, J = 15.6 Hz), 7.23−7.44 (m, 9H). GCMS (m/z) 268 (M^+).

X-ray Crystallographic Studies. Suitable black crystals of **1h**·CH_2Cl_2 for X-ray analysis were obtained by recrystallization from CH_2Cl_2/*n*-hexane. A single crystal was sealed in a Pyrex glass capillary tube under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation and a rotating anode generator. Details of crystal and data collection parameters are shown in the Supporting Information. The positions of non-hydrogen atoms were determined by heavy-atom Patterson methods and subsequent Fourier syntheses (DIRDIF94).

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Supporting Information Available: Crystallographic data of **1h**; crystallographic data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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