JOC Article

Ruthenium-Catalyzed Cyclopropanation of Alkenes Using Propargylic Carboxylates as Precursors of Vinylcarbenoids

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Intermolecular cyclopropanation reactions of various alkenes with propargylic carboxylates **1** are catalyzed by $[RuCl_2(CO)_3]_2$ to give vinylcyclopropanes **2** in good yields. The key intermediate of the reaction is a vinylcarbene complex generated in situ by nucleophilic attack of a carbonyl oxygen of the carboxylates to an internal carbon of the alkyne activated by the ruthenium complex. A variety of transition-metal compounds other than the Ru compound can also be employed in this system. Similar cyclopropanation proceeds with conjugated dienes as well to give *trans-vic*-divinylcyclopropane derivatives and cycloheptadiene derivatives **5**, the latter being thermally derived from the initially formed *cis-vic*-isomers via Cope-type rearrangement. The present reaction is chemically equivalent to the transition metal-catalyzed cyclopropanation reaction using α-diazoketones as carbenoid precursors.

Introduction

The in situ generation of carbenoid species involving transition metals is well-known, and the species has been applied mostly to cyclopropanation and insertion reactions. One of the most versatile methods to generate carbenoids is a decomposition reaction of diazoalkanes by transition metal complexes.[1] This method is quite useful but formidable because of its explosive hazard and a number of unfavorable side reactions such as diazo dimerization and azine formation. To aviod such problems, safe alternatives for diazoalkane handling or special techniques involving slow addition of them are usually required. Recently, much attention has been paid to the activation of alkynes with transition metal complexes as another method to generate carbenoid species. For example, cyclopropylcarbenoids by skeletal reorganization of α,*ω*-enynes,[2,3] dialkylidene ruthenium species from *ω*-diynes,[4] transition metal-containing carbonyl ylides from *o*-ethynylphenylcarbonyl compounds,[5,6] and copper(isoindazolyl)carbene intermediates from (2-ethynylphenyl)triazenes[7] are recognized as new alternatives of carbenoid species in the catalytic process.[8] Most recently, we have reported the synthesis of (2-furyl)-carbene complexes from ene-yne-ketones with group 6 transition metal complexes and their application to catalytic cyclopropanation of alkenes (Scheme 1a).[9] A wide range of transition metal compounds such as Cr-

(1) (a) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*, 2nd ed.; University Science Books: Mill Valley, CA, 1999; p 143. (b) Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911. (c) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223. (d) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091.

(2) Transition metal-catalyzed reorganization reaction of enynes. For example, [Pd] cat.: (a) Trost, B. M.; Tanoury, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 1636. (b) Trost, B. M.; Trost, M. K. *Tetrahedron Lett.* **1991**, *32*, 3647. (c) Trost, B. M.; Trost, M. K. *J. Am. Chem. Soc.* **1991**, *113*, 1850. [Ru] cat.: (d) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049. [Ru] or [Pt] cat.: (e) Chatani, N.; Kataoka, K.; Murai, S.; Furukawa, N.; Seki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9140. (f) Chatani, N.; Inoue, H.; Ikeda, T.; Murai, S. *J. Org. Chem.* **2000**, *65*, 4913. [Pt] cat.: (g) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901. (h) Oi, S.; Tsukamoto, I.; Miyano, S.; Inoue, Y. *Organometallics* **2001**, *20*, 3704. [Ir] cat.: (i) Chatani, N.; Inoue, H.; Morimoto, T.; Muto, T.; Murai, S. *J. Org. Chem.* **2001**, *66*, 4433.

(3) For the reactions of α,*ω*-enynes with dienes via cyclopropylcarbene complexes have been reported: (a) Trost, B. M.; Hashmi, A. S. K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1085. (b) Trost, B. M.; Hashmi, A. S. K. *J. Am. Chem. Soc.* **1994**, *116*, 2183. The reactions of α, *ω*-enynes with alcohols via cyclopropylcarbene complexes, see: (c) Méndez, M.; Muñoz, M. P.; Echavarren, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 11549. (d) Méndez, M.; Muñoz, M. P.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2001**, *123*, 10511. (e) Fernández-Rivas, C.; Méndez, M.; Nieto-Oberhuber, C.; Echavarren, A. M. *J. Org. Chem.* **2002**, *67*, 5197. (f) Martín-Matute, B.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *J. Am. Chem. Soc.* **2003**, *125*, 5757.

(4) Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Kawaguchi, H.; Tatsumi, K.; Itoh, K. *J. Am. Chem. Soc.* **2000**, *122*, 4310.

(5) (a) Iwasawa, N.; Shido, M.; Kusama, H. *J. Am. Chem. Soc.* **2001**, *123*, 5814. For an example of an azomethine ylide, see: (b) Kusama, H.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 11592.

(6) Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12650.

(7) (a) Kimball, D. B.; Herges, R.; Haley, M. M. *J. Am. Chem. Soc.* **2002**, *124*, 1572. (b) Kimball, D. B.; Weakley, T. J. R.; Herges, R.; Haley, M. M. *J. Org. Chem.* **2002**, *67*, 6395. (c) Kimball, D. B.; Weakley, T. J. R.; Herges, R.; Haley, M. M. *J. Am. Chem. Soc.* **2002**, *124*, 13463. (d) Kimball, D. B.; Haley, M. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3339.

(8) There are many reports on generation of carbene complexes such as the Dötz reaction via metathesis between alkynes and carbene complexes. For reviews on enyne metathesis, see: (a) Poulsen, C. S.; Madsen, R. *Synthesis* **2003**, 1 and references therein. (b) Mori, M. *Top. Organomet. Chem.* **1998**, *1*, 133.

(9) (a) Miki, K.; Nishino, F.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 5260. For the synthesis of (2-furyl)carbene complexes, see: (b) Miki, K.; Yokoi, T.; Nishino, F.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **2002**, *645*, 228. Stoichiometric furan formations via the metathesis approach from similar compounds have been reported. See: (c) Jiang, D.; Herndon, J. W. *Org. Lett.* **2000**, *2*, 1267. (d) Ghorai, B. K.; Herndon, J. W.; Lam, Y.-F. *Org. Lett.* **2001**, *3*, 3535. (e) Ghorai, B. K.; Herndon, J. W. *Organometallics* **2003**, ASAP.

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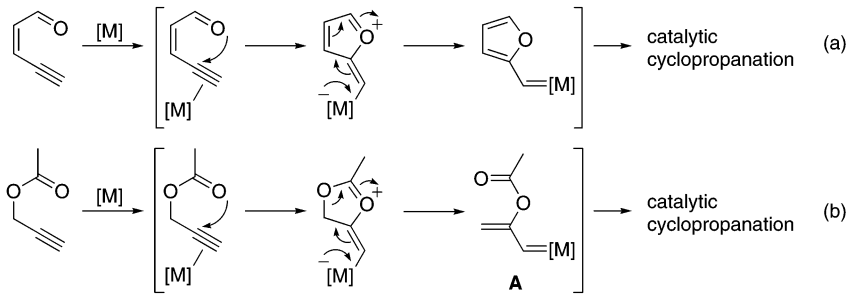
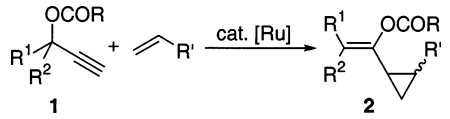
SCHEME 1



SCHEME 2



$(CO)_5(THF)$, $[Rh(OAc)_2]_2$, $[(p\text{-cymene})RuCl_2]_2$, $[RhCl(cod)]_2$, $[RuCl_2(CO)_3]_2$, $PdCl_2$, and $PtCl_2$ were found to be effective catalysts for the cyclopropanation. The key of the reaction is 5-exo-dig cyclization via nucleophilic attack of a carbonyl oxygen to an internal carbon of alkynes activated by transition metal compounds leading to a stable furan structure as a resonance form. This success stimulated us to develop a new method for the preparation of vinylcarbenoid intermediates **A** from propargylic carboxylates, in which nucleophilic attack of a carbonyl oxygen followed by bond cleavage at the propargylic position has been envisioned (Scheme 1b). Although this concept was invalid in most cases due to facile isomerization of propargylic carboxylates into allenyl carboxylates catalyzed by transtion metal compounds,[10] Rautenstrauch first demonstrated the validity of the protocol for a vinylcarbenoid intermediate in palladium-catalyzed inter- and intramolecular carbene transfer reactions using propargylic acetate.[11] Most recently, it was shown that intermediary vinylcarboids were effectively trapped by an alkenyl moiety in the molecule to give carbocyclic compounds in $PtCl_2$-catalyzed cyclization of dienynes.[12] Our continuous investigation for vinylcarbene transfer reactions led us to find an efficient ruthenium-catalyzed intermolecular cyclopropanation of alkenes using propargylic carboxylates (Scheme 2).[13] In this paper, we describe the scope and limitations of the cyclopropanation reaction involving vinylcarbenoids generated in situ from propargylic carboxylates and $[RuCl_2(CO)_3]_2$. The reaction has also been applied to conjugated dienes to construct cycloheptadiene structures, representing a formal [3 + 4] cyclization using the carboxylates as three-carbon components.

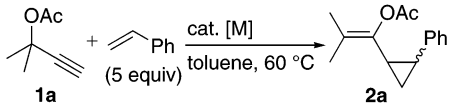
(10) Transition metal-catalyzed isomerization of propargylic acetates has been established as a standard method to prepare allenyl acetates. See: (a) Schlossarczyk, H.; Sieber, W.; Hesse, M.; Hansen, H.-J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 875. (b) Oelberg, D. G.; Schiavelli, M. D. *J. Org. Chem.* **1977**, *42*, 1804. (c) Cookson, R. C.; Cramp, M. C.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1980**, 197 and references therein.

(11) (a) Rautenstrauch, V. *Tetrahedron Lett.* **1984**, *25*, 3845. (b) Rautenstrauch, V. *J. Org. Chem.* **1984**, *49*, 950. Oxidative rearrangement of propargyl esters by palladium catalyst has been reported. See: (c) Kataoka, H.; Watanabe, K.; Goto, K. *Tetrahedron Lett.* **1990**, *31*, 4181.

(12) Mainett, E.; Mouriès, V.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2132.

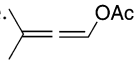
(13) For preliminary communication, see: Miki, K.; Ohe, K.; Uemura, S. *Tetrahedron Lett.* **2003**, *44*, 2019.

TABLE 1. Transition Metal-Catalyzed Cyclopropanation of Styrene with 1a[a]



entry	[M]	time	**2a** (%)[b]	cis/trans[b]	**3** (%)[b]
1	$[RuCl_2(CO)_3]_2$	18 h	86	84:16	5
2	$[RuCl_2(CO)_3]_2$[c]	15 h	90	86:14	0
3	$[Rh(OCOCF_3)_2]_2$	30 min	trace		99
4	$IrCl_3$	24 h	45	72:28	53
5	$[IrCl(cod)]_2$	18 h	37	70:30	7
6	$AuCl_3$[d]	10 min	63	79:21	26
7	$PtCl_2$	1 h	93	78:22	7
8	$GaCl_3$[c,e]	28 h	26	65:35	0

[a] Reaction conditions: **1a** (0.2 mmol), styrene (1.0 mmol), catalyst (0.005 mmol), toluene (1.0 mL), 60 °C. [b] Determined by GLC. [c] 0.01 mmol. [d] $AuCl_3$ (0.002 mmol) was used at room temperature. [e] 1 M solution in methylcyclohexane.

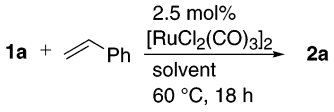


3

Results and Discussion

Effect of Catalyst. At first, the cyclopropanation of styrene with 2-methyl-3-butyn-2-yl acetate (**1a**) in the presence of a transition metal catalyst (2.5−5 mol %), which had been effective for catalytic cyclopropanation via (2-furyl)carbene complexes, was examined.[9a] Results of the catalyst screening are given in Table 1. The reaction of **1a** with styrene in the presence of a catalytic amount of $[RuCl_2(CO)_3]_2$ (2.5 mol %) in toluene at 60 °C for 18 h afforded the cyclopropanated product **2a** in 86% yield (cis/trans = 84:16), along with 5% of allenyl acetate **3**, the isomerization product of **1a** (entry 1). The use of 5 mol % Ru catalyst completely suppressed the formation of **3** (entry 2), and the desired cyclopropane **2a** was produced in 90% yield (cis/trans = 86:14). In contrast, $[Rh(OCOCF_3)_2]_2$, which is known as a good catalyst for carbene transfer reaction, could not catalyze the present cyclopropanation, but it gave only **3** quantitatively (entry 3). $IrCl_3$, $[IrCl(cod)]_2$, and $AuCl_3$ were also found to catalyze the cyclopropanation to give **2a** in 45%, 37%, and 63% yields with 72:28, 70:30, and 79:21 dr, respectively, along with **3** as a byproduct (entries 4, 5, and 6). Particularly, $AuCl_3$ showed a highest activity for both cyclopropanation and allene formation, but it was difficult to control the product selectivity (entry 6). $PtCl_2$, which can act as a good catalyst for intramolecular cyclopropanation (vide supra),[12] catalyzed the present reaction effectively, along with allene formation to some extent (entry 7). $GaCl_3$ was marginally effective in the cyclo-

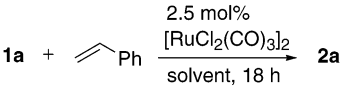
TABLE 2. Effect of Solvent[a]



entry	solvent	conv of **1a** (%)	yield[b] (%) (cis/trans)[c]
1	toluene	100	86 (84:16)
2	DCE	100	95 (79:21)
3[d]	cyclohexane	97	64 (75:25)
4	THF	24	9 (67:33)
5	MeCN	5	2
6	MeOH	18	1

[a] Reaction conditions: **1a** (0.2 mmol), styrene (1.0 mmol), $[RuCl_2(CO)_3]_2$ (0.005 mmol), solvent (1 mL), 60 °C, 18 h. [b] GLC yield. [c] Determined by GLC. [d] 42 h.

TABLE 3. Effect of Temperature[a]



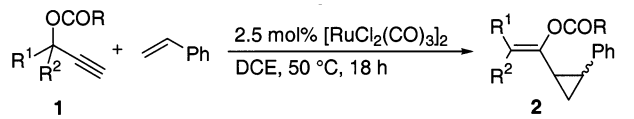
entry	solvent	temp (°C)	yield (%)[b] (cis/trans)[c]
1	toluene	50	75 (87:13)
2	toluene	60	86 (84:16)
3[d]	toluene	80	83 (76:24)
4[e]	DCE	30	83 (93:7)
5	DCE	50	99 (87:13)
6	DCE	60	95 (79:21)
7[d]	DCE	80	83 (77:23)

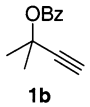
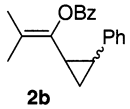
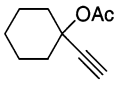
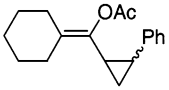
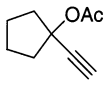
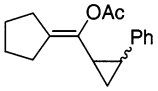
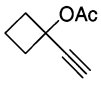
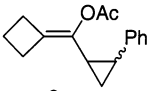
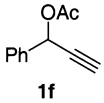
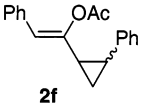
[a] Reaction conditions: **1a** (0.2 mmol), styrene (1.0 mmol), $[RuCl_2(CO)_3]_2$ (0.005 mmol), solvent (1 mL), 18 h. [b] GLC yield. [c] Determined by GLC. [d] 5 h. [e] 17% of **1a** remained unreacted.

propanation to give **2a** in 26% yield with other unidentified products (entry 8). Among other catalysts examined, $Cr(CO)_5(THF)$, $RuCl_3$, $RuCl_3 \cdot 3H_2O$, $[(p\text{-cymene})RuCl_2]_2$, $PdCl_2$, and $PdCl_2(CH_3CN)_2$[11,14] were not effective for the present cyclopropanation.

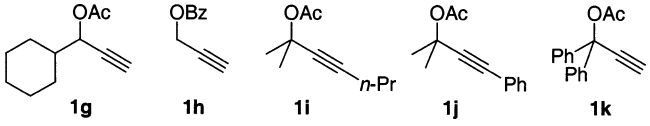
Optimization of Reaction Conditions. Since the cyclopropanation of styrene using propargylic acetate as a vinylcarbenoid precursor was revealed to be efficiently carried out with $[RuCl_2(CO)_3]_2$ as a catalyst, the effects of other parameters such as solvent and reaction temperature on this catalytic reaction were investigated. Ruthenium-catalyzed cyclopropanation in 1,2-dichloroethane (DCE) occurred more efficiently than that in toluene, producing **2a** in 95% yield with 79:21 dr (Table 2, entry 1 vs entry 2).[15] The desired cyclopropanation occurred in cyclohexane as well to give **2a** in 64% yield, but the prolonged time (42 h) was required (entry 3). On the other hand, the reactions conducted in THF, MeCN, and MeOH at 60 °C were very slow, giving only a trace amount of the desired cyclopropanated product in each reaction (entries 4−6). Next, the cyclopropanation using toluene or DCE as effective solvent was carried out by varying the reaction temperature (Table 3). As a consequence, it was found that the cyclopropanation took place with excellent chemical yield and high diastereoselectivity by heating a solution of **1a** and styrene in toluene at 60 °C or in DCE at 50 °C (entries 2 and 5). As optimized reaction conditions for the ruthenium-catalyzed cyclopropanation with a propargylic acetate were finely tuned by employing either DCE or toluene as solvent, the generality of this new reaction was next examined.

TABLE 4. Ru-Catalyzed Cyclopropanation of Styrene with 1[a]



entry	substrate	product	isolated yield[b]	*cis*:*trans*[b,c]
1	 **1b**	 **2b**	90% (81%)	88:12 (88:12)
2	 **1c**	 **2c**	91% (91%)	88:12 (82:18)
3	 **1d**	 **2d**	97% (69%)	90:10 (89:11)
4	 **1e**	 **2e**	93% (60%)	94:6 (92:8)
5	 **1f**	 **2f**	(77%)	(75:25)

[a] Reaction conditions: **1** (0.2 mmol), styrene (1.0 mmol), $[RuCl_2(CO)_3]_2$ (0.005 mmol), DCE, 60 °C. [b] The values in the parentheses were obtained from reactions in toluene at 60 °C. [c] Diastereomeric ratios were determined by ^1H NMR or GLC.



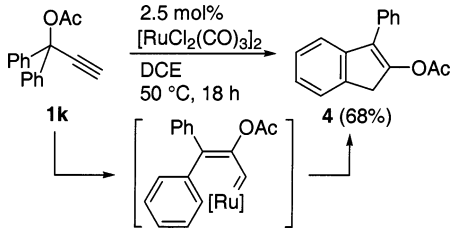
Cyclopropanation Using Various Propargylic Carboxylates and Alkenes. The reactions of styrene with other propargylic carboxylates in the presence of $[RuCl_2(CO)_3]_2$ (2.5 mol %) in DCE at 50 °C or in toluene at 60 °C were examined. Typical results are shown in Table 4.[16] The reaction of propargylic benzoate **1b** with styrene also gave the cyclopropanated product **2b** in 90% yield (cis/trans = 88:12) (entry 1). Cyclic acetates **1c**−**e** reacted with styrene to give the corresponding products **2c**−**e** in 91%, 97%, and 93% yields, respectively (entries 2−4). In the case of tertiary propargylic carboxylates, the reactions conducted in toluene gave the corresponding products with slightly lower yields compared with those in DCE.

(14) Recently, Yamamoto et al. have reported indenol ether formation from arylalkynes via Pd-carbene intermediates. Nakamura, I.; Bajracharya, G. B.; Mizushima, Y.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 4328.

(15) In the $PtCl_2$-catalyzed case, cyclopropanation in DCE resulted in lower yield of **2a** (74%) together with the formation of a substantial amount of allenyl acetate (23%).

(16) Almost all of the cyclopropanes could not be easily separated by column chromatography. Each pure isomer was separated by gel permeation chromatography on $CHCl_3$. Purification details are shown in the Experimental Section.

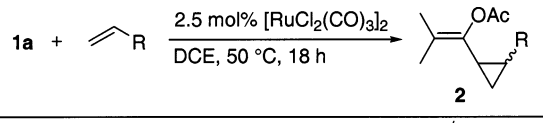
SCHEME 3

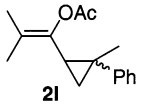
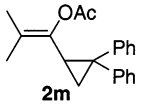
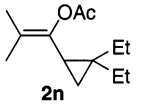
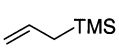
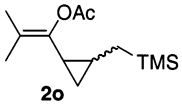
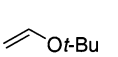
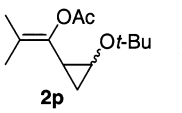
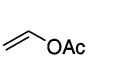
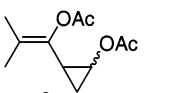


The reaction with secondary propargylic acetate **1f** proceeded smoothly to give **2f** in 77% yield with a 75:25 dr, although the treatment in toluene at 60 °C was essential (entry 5).[17,18] For the secondary propargylic acetate **1g**, having an alkyl group at the propargylic position was less reactive than **1f**, affording a desired product in <30% yield with recovered **1g** even after 48 h. Primary propargylic benzoate **1h** and internal propargylic acetates **1i** and **1j** were less reactive, and cyclopropane formation scarcely occurred even after 48 h. In the case of propargylic acetate **1k**, an indene derivative **4** was mainly obtained together with a small amount of the cyclopropanated product, indicating that another ruthenium-catalyzed reaction competes with the cyclopropanation reaction. In fact, treatment of **1k** in DCE without an alkene in the presence of a catalytic amount of $[RuCl_2(CO)_3]_2$ yielded **4** in 68% yield for 18 h (Scheme 3). The formation of **4** is considered to be attributed to formal insertion of a vinylcarbene intermediate to the C−H bond at the ortho position of a phenyl ring. Next, the reactions of **1a** with several alkenes in the presence of $[RuCl_2(CO)_3]_2$ were examined (Table 5). The reactions of α-methylstyrene and 1,1-diphenylethylene with **1a** proceeded smoothly to give cyclopropane **2l** and **2m** in 91% (dr = 68:32) and 71% yields, respectively (entries 1 and 2). 2-Ethylbut-1-ene and allyltrimethylsilane slowly reacted with **1a** to give **2n** and **2o** in 82% and 72% (cis/trans = 79:21) yields, although the use of 20 equiv of alkenes was required (entries 3 and 4). On the other hand, cyclopropanation of *tert*-butyl vinyl ether and vinyl acetate with **1a** resulted in lower yields of 26% (cis/trans = 38:62) and 24% (cis/trans = 75:25), respectively (entries 5 and 6). The reactions of oct-1-ene and 3,3-dimethylbut-1-ene with **1a** gave the cyclopropanated products in much lower yield (10−20%), along with several unidentified products. Electron-deficient alkenes such as methyl acrylate did not work at all in the present cyclopropanation.

Mechanistic Consideration. The present cyclopropanation can be envisioned to proceed via a vinylcarbenoid intermediate generated in situ from a propargylic carboxylate and a ruthenium complex as shown in Scheme 1b. In the present cyclopropanation, the higher reactivity of electron-rich alkenes can be rationalized in terms of the electrophilic character of the postulated ruthenium vinylcarbenoid intermediate (Figure 1). Takahashi et al. have reported the ruthenium-catalyzed cyclopropanation of norbornene using propargylic alcohols and their ethers via a ruthenacyclopentene intermediate, in which norbornene was the only alkene to react.[19] With this in mind, the reaction of norbornene with propargylic acetate **1a** was carried out in the presence of $[RuCl_2(CO)_3]_2$ catalyst. However, no cyclopropanation of norbornene was observed. Although the difference in alkene reactivity between Takahashi's reaction and our present reaction is obvious and we think that ruthenium vinylcarbenoids are likely as intermediates in our case, it might be meaningful to consider a step containing ruthenacycles. On the basis of the mechanism proposed by Takahashi et al., a plausible reaction course might be outlined in Scheme 4 in the present

TABLE 5. Ru-Catalyzed Cyclopropanation of Various Alkenes with 1a[a]



entry	alkene	product	isolated yield[b]	*cis*:*trans*[b,c]
1		 **2l**	91%	68:32[d]
2		 **2m**	71% (66%)	N.A.[e] N.A.[e]
3[f]		 **2n**	82% (68%)	N.A.[e] N.A.[e]
4[f]		 **2o**	72% (43%)	79:21 (67:33)
5		 **2p**	26% (22%)	38:62 (36:64)
6[f,g]		 **2q**	24% (20%)	75:25 (75:25)

[a] Reaction conditions: **1** (0.2 mmol), styrene (1.0 mmol), $[RuCl_2(CO)_3]_2$ (0.005 mmol), DCE (1.0 mL), 60 °C. [b] The values in the parentheses were obtained from reactions in toluene at 60 °C. [c] Diastereomeric ratios were determined by ^{1}H NMR or GLC. [d] Configuration is not yet known. [e] N.A. = not applicable. [f] Alkene (4.0 mmol) was used. [g] 42 h.

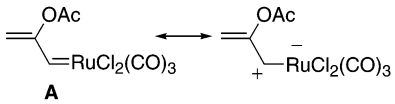


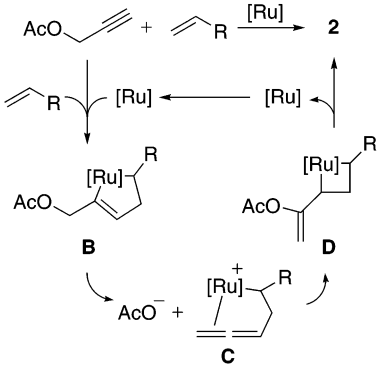
FIGURE 1. Ruthenium vinylcarbenoid as a plausible intermediate.

(17) The geometry of the alkenic part in the major product *cis*-**2f** was assigned to *Z* by X-ray diffraction analysis (see Supporting Information). Since the NMR data of *trans*-**2f** are similar to those of *cis*-**2f** with an exception of cyclopropane ring assignment, we assume that the geometry in *trans*-**2f** would be also *Z*.

(18) The reaction of **1f** with styrene in DCE was not complete even after 36 h.

(19) Takahashi et al. have already reported that cyclopropyl ketones were obtained from propargylic alcohols and norbornene in the presence of $[Cp'Ru(CH_3CN)_3]PF_6$ catalyst. (a) Kikuchi, H.; Uno, M.; Takahashi, S. *Chem. Lett.* **1997**, 1273. (b) Matsushima, Y.; Kikuchi, H.; Uno, M.; Takahashi, S. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2475.

SCHEME 4



reaction. The scheme involves the formation of ruthenacycle **B** from a propargylic compound and an alkene followed by successive formation of an intramolecularly coordinated π-allene complex **C** and a ruthenacyclobutane **D**. Intervention of the π-allene complex **C** via β-elimination of a vicinal acetoxy group implies the possibility of the intermolecular transfer of acetate from one molecule to another. However, such a possibility was excluded by the experimental results of crossover reaction using two types of propargylic carboxylates in the presence of $[RuCl_2(CO)_3]_2$. Thus, when the reaction of styrene with a mixture of an equimolar amount of **1b** and **1c** as competitive reactants was carried out, two cyclopropanated products, **2b** and **2c**, were produced in high yields without any crossover products (Scheme 5). This result, as well as the alkene reactivity, strongly supports that the present cyclopropanation proceeds via a ruthenium vinylcarbenoid (**A**)[20,21] generated by an intramolecular acetoxy migration as shown in Scheme 1b.

Catalytic Cyclopropanation of Dienes. Finally, we examined the cyclopropanation of conjugated dienes with propargylic carboxylates **1a**−**c** in the presence of $[RuCl_2(CO)_3]_2$ as a catalyst. In the reaction of isoprene with **1a**, a more substituted double bond was selectively cyclopropanated to give *trans*-**2r**[22] (46%) together with 1,4-cycloheptadiene **5r** (38%) (Scheme 6). The reaction of 2,3-dimethyl-1,3-butadiene with **1a** also gave similar products, *trans*-**2**[22] (55%) and **5s** (28%). The formation of 1,4-cycloheptadiene **5** in each case can be explained by assuming [3,3]sigmatropic rearrangement of the initially produced cis isomer of **2r** or **2s** (Scheme 7).[23] As shown in Scheme 8, cyclopentadiene also served as a good acceptor of the ruthenium carbenoid intermediate to give mono-cyclopropanated product *syn*(*endo*)-**2t**[24] in 55% yield together with 3-acetoxy-4,4-dimethylbicyclo[3.2.1]-octa-2,6-diene (**5t**) in 15% yield. The cyclopropanated product with anti configuration, *anti*(*exo*)-**2t**, was not obtained at all. Efficient [3,3]sigmatropic isomerization of the isolated bicyclic compound *syn*-**2t** to the rearranged product **5t** was attained by heating a solution of *syn*-**2t** in toluene at 120 °C for 24 h, the yield of **5t** being 90%. Cyclopropanation reactions of cyclopentadiene with **1b** and **1c** followed by thermal rearrangement afforded bicyclo[3.2.1]octadienes **5u** and **5v** in 64% and 76% yields, respectively (Scheme 9). These reactions represent a formal [3 + 4] cycloaddition using propargylic acetates as three-carbon components to produce cycloheptadiene skeletons as shown in Scheme 10.

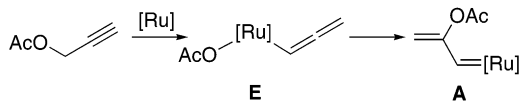
Conclusions

We have developed an effective Ru-catalyzed intermolecular cyclopropanation of various alkenes with propargylic carboxylates via vinylcarbene complexes. Tertiary or secondary propargylic carboxylates can be applied to this procedure with an exception of primary ones. It has also been demonstrated that the vinylcarbenoid intermediates can serve as three-carbon units in a formal [3 + 4] cycloaddition reaction leading to 1,4-cycloheptadiene skeletons. Since the present vinylcarbene transfer reaction is chemically equivalent to the reaction using a combination of α-diazoketone and transition metal compounds, this provides another method for generating carbenoid species from readily available alkynes.

Experimental Section

General Procedures. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. Other solvents were dried by the usual methods and distilled before use. Column chromatographies were performed on silica gel (230−400 mesh). Analytical TLC was performed on ready-made plates coated with silica gel on glass. The NMR spectra were measured for solutions in $CDCl_3$ with Me_4Si as an internal standard (^1H and ^{13}C). The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet.

(20) Oxidative addition of propargylic acetate to a ruthenium complex leading to σ-allenylruthenium acetate **E** followed by transposition of an acetate group from ruthenium to C-2 of the σ-allenyl ligand is another possible route to the vinylcarbenoid. However, experimental results of no formation of crossover products also rule out such a route where the acetoxy group might be liberated in the system.



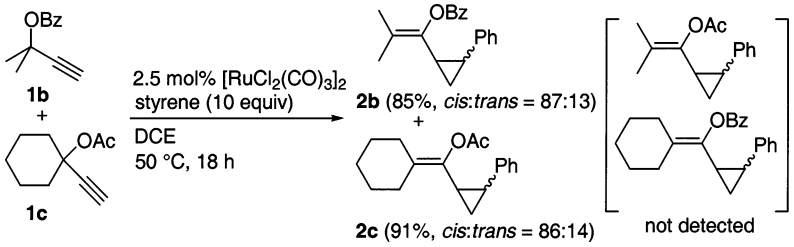
(21) Generation of vinylcarbenoids from propargylic halides, acetates, and alcohols using transition metal hydride complexes has already been reported, and the complexes have been widely applied as metathesis catalysts. The mechanisms of these reactions, however, are apparently different from that of the present hydride-free case. (a) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867. (b) Wolf, J.; Stüer, W.; Grünwald, C.; Gevert, O.; Laubender, M.; Werner, H. *Eur. J. Inorg. Chem*. **1998**, 1827. (c) Hansen, S. M.; Volland, M. A. O.; Rominger, F.; Eisenträger, F.; Hofmann, P. *Angew. Chem., Int. Ed*. **1999**, *38*, 1273. (d) Trost, B. M.; Rudd, M. T. *J. Am. Chem. Soc.* **2001**, *123*, 8862. (e) Volland, M. A. O.; Rominger, F.; Eisenträger, F.; Hofmann, P. *J. Organomet. Chem*. **2002**, *641*, 220.

(22) The reaction of ***trans*-2r** or ***trans*-2s** in toluene at 120 °C did not produce **5r** or **5s** after stirring for 24 h. The results, as well as the ^1H NMR spectrum of **2r** or **2s**, might support the configuration of *trans*-cyclopropane.

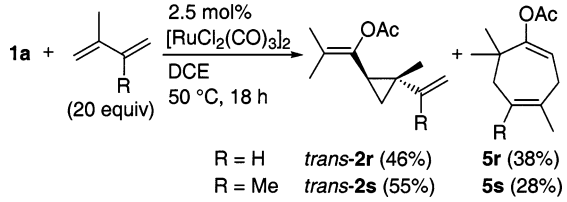
(23) The cascade reaction of carbenoid transfer cyclopropanation and [3, 3]sigmatropy has been developed by using a combination of diazoalkanes and rhodium- and copper-catalysts. For leading references of transition metal-catalyzed reactions, see: (a) Davies, H. M. L. *Advance in Cycloaddit*. **1999**, *5*, 119. (b) Davies, H. M. L.; Stafford, D. G.; Doan, B. D.; Houser, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 3326 and references therein. (c) Davies, H. M. L.; Clark, T. J.; Smith, H. D. *J. Org. Chem*. **1991**, *56*, 3817. For stoichiometric reactions, see: (d) Harvey, D. F.; Sigano, D. M. *Chem. Rev*. **1996**, *96*, 271. (e) Fischer, H.; Froneck, T. *Inorg. Chim. Acta* **1994**, *220*, 327. (f) Barluenga, J.; Tomás, M.; Ballesteros, A.; Santamaría, J.; López-Ortiz, F. *J. Chem. Soc., Chem. Commun*. **1994**, 321. (g) Wulff, W. D.; Bauta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642.

(24) The syn stereochemistry of **2t** was more clearly determined by NOE analysis. Thus, percentage increments (6% and 5%) in the area intensities of vinyl protons on a cyclopentene ring were observed by irradiation at the two methyl groups of an isopropylidene of **2t**, respectively.

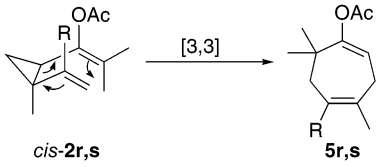
SCHEME 5



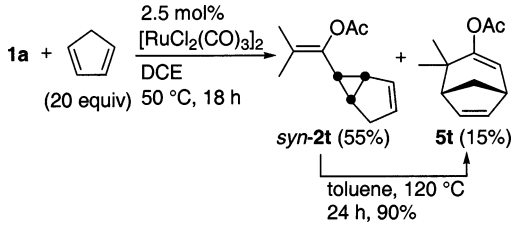
SCHEME 6



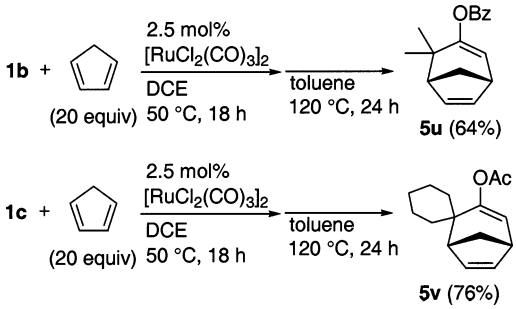
SCHEME 7



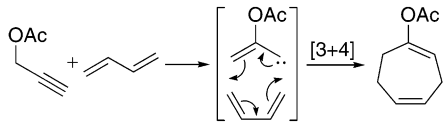
SCHEME 8



SCHEME 9



SCHEME 10



Typical Procedure for Synthesis of Vinylcyclopropane 2. The complex $[RuCl_2(CO)_3]_2$ (2.6 mg, 0.005 mmol) was placed in the flame-dried Schlenk flask under N_2. A solution of substrate **1** (0.20 mmol) and alkene (1.0−4.0 mmol) in solvent (1.0 mL) was added to the flask at room temperature. After the mixture was stirred at the fixed temperature for the appropriate time, it was cooled to room temperature and the amount of products was determined by gas liquid chromatography (GLC) analysis using 2,6-dimethylnaphthalene as an internal standard. All *trans*-cyclopropanes could not be easily separated by column chromatography on SiO_2 (hexane/AcOEt = 15/1). Pure cis isomers of **2a**−**f**, **2o**, **2p**, and major-**2l** were partially separated as a first fraction of column chromatography, whereas trans isomers as minor products were eluted together with their cis isomers. Because of this contamination, GPC on $CHCl_3$ was required to obtain pure trans isomers in each case. The configuration of the cyclopropane ring could be determined by ^{1}H NMR coupling constants between protons in a cyclopropane ring.[25] Generally, coupling constants of J = 7.0−9.0 Hz between two protons in a cyclopropane ring indicate that the configuration is cis, while those of J = 4.0−6.0 Hz correspond to that of trans.

Vinylcyclopropane 2a. Yields and ratios of two isomers were determined by GLC analysis. ***cis*-2a.** A colorless oil. IR (neat) 701, 733, 776, 1113, 1155, 1183, 1218, 1369, 1751 (C=O), 2916 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 1.02 (ddd, J = 5.4, 6.3, 6.3 Hz, 1H), 1.25 (ddd, J = 5.4, 8.9, 8.9 Hz, 1H), 1.41 (s, 3H), 1.47 (s, 3H), 2.04 (s, 3H), 2.20−2.33 (m, 2H), 7.01−7.26 (m, 5H). ^{13}C NMR (67 MHz, $CDCl_3$, 25 °C) δ 11.6, 17.5, 18.6, 20.6, 21.7, 24.2, 123.2, 125.4, 127.2, 127.4, 138.1, 139.1, 169.1. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.49; H, 7.85. ***trans*-2a.** A colorless oil. IR (neat) 698, 760, 1102, 1159, 1196, 1214, 1369, 1749 (C=O), 2917 cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 1.02 (dd, J = 7.3, 7.3 Hz, 2H), 1.57 (s, 3H), 1.79 (s, 3H), 1.94−2.09 (m, 2H), 2.16 (s, 3H), 7.06−7.30 (m, 5H). ^{13}C NMR (67 MHz, $CDCl_3$, 25 °C) δ 14.7, 18.2, 18.8, 20.6, 23.2, 23.5, 120.5, 125.7, 125.8, 128.3, 140.6, 141.9, 169.1. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.96; H, 7.91.

Vinylcyclopropane 2b. A colorless oil (53 mg, 0.18 mmol, 90% yield, cis/trans = 88:12) (a mixture of cis and trans isomers). IR (neat) 702, 709, 771, 1025, 1069, 1091, 1114, 1155, 1177, 1245, 1279, 1451, 1497, 1602, 1728 (C=O), 2915 cm^{-1}. ***cis*-2b.** ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.09 (ddd, J = 5.4, 6.6, 6.6 Hz, 1H), 1.27 (ddd, J = 5.4, 8.7, 8.7 Hz, 1H), 1.47 (s, 3H), 1.63 (s, 3H), 2.27−2.38 (m, 2H), 7.08−7.11 (m, 2H), 7.15−7.27 (m, 3H), 7.38−7.44 (m, 2H), 7.53−7.60 (m, 1H), 7.84−7.88 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.7, 17.6, 18.6, 21.3, 23.7, 123.4, 125.5, 127.5, 127.6, 128.2, 129.7, 129.8, 133.0, 138.5, 139.2, 164.6. ***trans*-2b.** ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.84−0.90 (m, 1H), 1.07−1.13 (m, 1H), 1.82 (s, 3H), 1.85 (s, 3H), 2.06−2.17 (m, 2H), 7.07−7.12 (m, 2H), 7.14−7.27 (m, 3H), 7.36−7.43 (m, 1H), 7.47−7.60 (m, 2H), 8.10−8.14 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 14.1, 18.1, 18.8, 23.3, 23.6, 120.9, 125.7, 125.9, 128.3, 128.5, 129.6, 129.9, 132.8, 133.2, 142.0, 164.7. HRMS (FAB): [M$^+$] calcd for $C_{20}H_{20}O_2$, 292.1463; found, 292.1460.

Vinylcyclopropane 2c. A colorless oil (49 mg, 0.18 mmol, 91% yield, cis/trans = 88:12) (a mixture of cis and trans isomers) (after recrystallization of **2c**, ***cis*-2c** was obtained as colorless crystals, mp 53.4−55.0 °C). ***cis*-2c.** IR (KBr) 701, 774, 1009, 1061, 1073, 1112, 1157, 1178, 1216, 1236, 1256, 1370, 1446, 1745 (C=O), 2852, 2923, 2962 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.38−0.48 (m, 1H), 1.01 (ddd, J = 5.7, 5.7, 5.7 Hz, 1H), 1.04−1.12 (m, 1H), 1.17−1.47 (m, 4H), 1.25 (ddd, J

(25) Breitmaier, E. *Structure Elucidation by NMR in Organic Chemistry* (translated by Wade, J.); John Wiley and Sons: Chichester, 1993; p 42.

= 5.7, 9.0, 9.0 Hz, 1H), 1.71−1.81 (m, 1H), 1.89−2.02 (m, 1H), 2.05−2.15 (m, 1H), 2.09 (s, 3H), 7.02 (d, J = 7.5 Hz, 2H), 7.13 (dd, J = 7.5, 7.5 Hz, 1H), 7.23 (dd, J = 7.5, 7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.5, 20.5, 21.5, 24.5, 26.1, 26.4, 26.5, 27.5, 28.6, 125.5, 127.2, 127.4, 130.4, 135.1, 139.3, 169.4. ***trans*-2c.** IR (neat) 698, 734, 756, 1020, 1068, 1103, 1111, 1161, 1189, 1213, 1237, 1255, 1368, 1448, 1498, 1604, 1755 (C═O), 2853, 2929, 2962 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.13 (dd, J = 7.2, 7.2 Hz, 2H), 1.45−1.60 (m, 6H), 1.96−2.08 (m, 4H), 2.15 (s, 3H), 2.24−2.28 (m, 2H), 7.05−7.09 (m, 2H), 7.11−7.18 (m, 1H), 7.22−7.29 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 14.7, 20.5, 22.8, 23.6, 26.4, 26.9, 27.2, 28.2, 29.0, 125.7, 125.8, 128.2, 128.3, 138.1, 139.3, 142.0, 169.3. Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.69; H, 8.15.

Vinylcyclopropane 2d. A colorless oil (50 mg, 0.19 mmol, 97% yield, cis/trans = 90:10) (a mixture of cis and trans isomers). ***cis*-2d.** IR (neat) 601, 700, 774, 1013, 1031, 1064, 1147, 1157, 1199, 1225, 1247, 1367, 1434, 1452, 1497, 1603, 1748 (C═O), 2867, 2954 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.07 (ddd, J = 5.4, 5.4, 6.6 Hz, 1H), 1.24 (ddd, J = 5.4, 9.0, 9.0 Hz, 1H), 1.29−1.60 (m, 4H), 1.96 (s, 3H), 1.96−2.04 (m, 3H), 2.14−2.32 (m, 3H), 7.06−7.09 (m, 2H), 7.13−7.16 (m, 1H), 7.19−7.24 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 10.8, 20.4, 21.9, 23.4, 25.9, 26.5, 28.9, 29.2, 125.5, 127.5, 127.5, 134.2, 135.8, 139.2, 168.9. ***trans*-2d.** IR (neat) 698, 754, 1030, 1071, 1102, 1148, 1158, 1199, 1228, 1243, 1368, 1435, 1452, 1498, 1604, 1698, 1756 (C═O), 2954 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.08−1.20 (m, 2H), 1.57−1.74 (m, 5H), 1.85−1.94 (m, 1H), 2.04−2.20 (m, 2H), 2.15 (s, 3H), 2.34−2.42 (m, 2H), 7.07−7.10 (m, 2H), 7.13−7.18 (m, 1H), 7.22−7.28 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 13.9, 20.5, 22.5, 24.0, 26.2, 26.8, 29.3, 29.5, 125.7, 125.9, 128.3, 131.4, 137.8, 142.1, 169.0. Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.54; H, 7.86.

Vinylcyclopropane 2e. A colorless oil (45 mg, 0.19 mmol, 93% yield, cis/trans = 94:6) (a mixture of cis and trans isomers). ***cis*-2e.** IR (neat) 699, 774, 1064, 1194, 1226, 1367, 1497, 1604, 1748 (C═O), 2921, 2951, 2983 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.12 (ddd, J = 5.4, 6.3, 6.3 Hz, 1H), 1.20 (ddd, J = 5.4, 9.0, 9.0 Hz, 1H), 1.78−1.90 (m, 2H), 1.85 (s, 3H), 1.95−2.08 (m, 1H), 2.23 (ddd, J = 6.3, 9.0, 9.0 Hz, 1H), 2.33−2.45 (m, 2H), 2.48−2.61 (m, 1H), 2.64−2.75 (m, 1H), 7.12−7.19 (m, 3H), 7.22−7.28 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 9.7, 16.8, 19.8, 20.4, 22.5, 27.8, 27.9, 125.7, 127.7, 128.1, 130.2, 136.4, 138.9, 168.6. ***trans*-2e.** IR (neat) 698, 735, 752, 1030, 1070, 1099, 1197, 1225, 1250, 1368, 1498, 1604, 1759 (C═O), 2920, 2950, 2983 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.06−1.22 (m, 2H), 1.68−1.78 (m, 1H), 1.93−2.10 (m, 3H), 2.12 (s, 3H), 2.53−2.60 (m, 2H), 2.77−2.86 (m, 2H), 7.04−7.09 (m, 2H), 7.12−7.19 (m, 1H), 7.22−7.29 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 13.6, 16.8, 20.5, 22.1, 22.6, 27.6, 27.9, 125.7, 125.9, 128.3, 128.5, 138.2, 141.9, 168.8. Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.05; H, 7.49.

Vinylcyclopropane 2f. A colorless oil (43 mg, 0.16 mmol, 77% yield, cis/trans = 75:25) (a mixture of cis and trans isomers) (after recrystallization of **2f**, ***cis*-2f** was obtained as colorless crystals, mp 71.7−73.5 °C). IR (neat) 698, 720, 752, 776, 832, 835, 925, 953, 1014, 1033, 1064, 1174, 1199, 1373, 1448, 1495, 1601, 1662, 1748 (C═O), 1755, (C═O), 2929, 3025, 3056 cm^{-1}. ***cis*-2f.** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.32 (ddd, J = 6.0, 6.4, 6.4 Hz, 1H), 1.38 (ddd, J = 6.0, 8.8, 8.8 Hz, 1H), 1.99 (s, 3H), 2.32 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.39 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 5.90 (s, 1H), 7.10−7.25 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 11.0, 21.0, 23.6, 23.7, 118.3, 126.0, 126.8, 127.8, 128.1, 128.1, 128.3, 134.2, 137.9, 146.5, 168.5. ***trans*-2f.** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.26 (ddd, J = 5.6, 5.6, 8.8 Hz, 1H), 1.35 (ddd, J = 5.6, 5.6, 8.8 Hz, 1H), 1.97 (ddd, J = 5.6, 5.6, 8.8 Hz, 1H), 2.16−2.28 (m, 4H), 6.09 (s, 1H), 7.10−7.38 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 14.7, 21.1, 24.4, 26.8, 121.5, 125.9, 127.0, 128.0, 128.3, 128.6, 133.3, 134.2, 141.3, 148.6, 168.3. Anal. Calcd for $C_{19}H_{18}O_2$ (a mixture of cis and trans isomers): C, 81.99; H, 6.52. Found: C, 81.72; H, 6.60.

Vinylcyclopropane 2l. A colorless oil (44 mg, 0.18 mmol, 91% yield, dr = 68:32) (a mixture of diastereoisomers). IR (neat) 700, 767, 883, 1031, 1082, 1123, 1181, 1214, 1368, 1445, 1498, 1603, 1754 (C═O), 2920, 2954 cm^{-1}. **Major-2l.** ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.02 (dd, J = 5.1, 9.0 Hz, 1H), 1.20 (dd, J = 5.1, 5.1 Hz, 1H), 1.38 (s, 3H), 1.48 (s, 3H), 1.67 (s, 3H), 1.92 (s, 3H), 2.01−2.07 (m, 1H), 7.13−7.30 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 17.7, 18.4, 18.8, 20.3, 27.2, 27.6, 27.9, 121.6, 125.7, 127.7, 127.8, 139.1, 142.6, 169.1. **Minor-2l.** ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.82 (dd, J = 4.8, 6.3 Hz, 1H), 1.32 (dd, J = 4.8, 9.6 Hz, 1H), 1.35 (s, 3H), 1.64 (s, 3H), 1.78 (s, 3H), 2.05−2.14 (m, 1H), 2.18 (s, 3H), 7.14−7.42 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 17.8, 19.0, 20.1, 20.6, 20.8, 26.7, 27.6, 122.7, 125.7, 126.2, 128.3, 139.8, 146.4, 169.2. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.93; H, 8.24.

Vinylcyclopropane 2m. A white solid (44 mg, 0.14 mmol, 71% yield), mp 76.4−77.6 °C. IR (KBr) 703, 750, 765, 1179, 1220, 1370, 1444, 1497, 1599, 1747 (C═O), 2925 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.46 (s, 3H), 1.46 (dd, J = 4.8, 8.8 Hz, 1H), 1.61 (dd, J = 4.8, 6.4 Hz, 1H), 1.90 (s, 3H), 2.20 (s, 3H), 2.70 (dd, J = 6.4, 8.8 Hz, 1H), 7.13−7.26 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 18.0, 19.1, 19.9, 20.3, 27.7, 36.6, 122.4, 125.9, 126.1, 127.7, 127.7, 128.3, 129.4, 138.6, 141.0, 145.9, 168.9. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.04; H, 7.28.

Vinylcyclopropane 2n. A colorless oil (34 mg, 0.16 mmol, 82% yield). IR (neat) 882, 1063, 1093, 1105, 1122, 1180, 1215, 1258, 1370, 1446, 1460, 1752 (C═O), 2934, 2963 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.34 (dd, J = 8.7, 8.7 Hz, 1H), 0.60 (dd, J = 4.5, 8.7 Hz, 1H), 0.89 (t, J = 6.9 Hz, 6H), 1.08 (q, J = 6.9 Hz, 2H), 1.40−1.57 (q, J = 6.9 Hz, 2H), 1.49−1.62 (m, 1H), 1.57 (s, 3H), 1.76 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 10.4, 10.6, 17.6, 17.8, 18.9, 20.6, 23.7, 24.8, 28.6, 28.6, 121.4, 140.8, 169.2. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.46; H, 10.74.

Vinylcyclopropane 2o. A colorless oil (35 mg, 0.14 mmol, 72% yield, cis/trans = 79:21) (a mixture of cis and trans isomers). ***cis*-2o.** IR (neat) 694, 841, 862, 1085, 1105, 1212, 1248, 1368, 1446, 1758 (C═O), 2918, 2954 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ −0.02−0.12 (m, 2H), 0.02 (s, 9H), 0.75−0.81 (m, 1H), 0.85 (ddd, J = 4.5, 9.0, 9.0 Hz, 1H), 0.92−1.05 (m, 1H), 1.60 (s, 3H), 1.67−1.74 (m, 1H), 1.77 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ −1.5, 11.9, 14.3, 16.3, 17.1, 17.7, 18.6, 20.6, 121.7, 140.4, 141.8, 169.2. ***trans*-2o.** IR (neat) 695, 843, 861, 1116, 1210, 1248, 1368, 1448, 1759 (C═O), 2896, 2917, 2953 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.01 (s, 9H), 0.34−0.43 (m, 2H), 0.62−0.85 (m, 3H), 1.36 (ddd, J = 4.5, 4.5, 9.0 Hz, 1H), 1.51 (s, 3H), 1.79 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ −1.5, 13.8, 14.3, 18.1, 18.6, 20.3, 20.4, 21.7, 118.8, 141.8, 169.1. Anal. Calcd for $C_{13}H_{24}O_2Si$: C, 64.95; H, 10.06. Found: C, 65.22; H, 9.93.

Vinylcyclopropane 2p. A colorless oil (12 mg, 0.05 mmol, 26% yield, cis/trans = 38:62) (a mixture of cis and trans isomers). IR (neat) 1047, 1116, 1150, 1206, 1217, 1365, 1444, 1472, 1755 (C═O), 2933, 2976 cm^{-1}. ***cis*-2p.** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.55 (ddd, J = 4.0, 6.0, 6.8 Hz, 1H), 0.77 (ddd, J = 6.0, 6.0, 9.6 Hz, 1H), 1.14 (s, 9H), 1.50 (s, 3H), 1.55−1.65 (m, 1H), 1.71 (s, 3H), 2.02 (s, 3H), 3.27 (ddd, J = 4.0, 6.0, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 12.1, 17.1, 18.3, 18.9, 20.9, 28.1, 51.2, 74.8, 121.1, 138.9, 168.7. ***trans*-2p.** ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.64 (ddd, J = 6.4, 6.4, 6.4 Hz, 1H), 0.81 (ddd, J = 4.0, 6.4, 9.6 Hz, 1H), 1.15 (s, 9H), 1.44 (s, 3H), 1.69−1.74 (m, 4H, including δ 1.73, s, 3H), 1.71 (s, 3H), 3.12 (ddd, J = 3.2, 4.0, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 13.1, 18.2, 18.5, 20.2, 20.6, 28.2, 51.4, 75.0, 119.6, 140.3, 169.0. HRMS (FAB): [M + H$^+$] calcd for $C_{13}H_{23}O_3$ (a mixture of cis and trans isomers), 227.1647; found, 227.1643.

Vinylcyclopropane 2q. A colorless oil (10 mg, 0.05 mmol, 24% yield, cis/trans = 75:25) (a mixture of cis and trans isomers, these two isomers could not be separated by column chromatography on SiO_2 or GPC on $CHCl_3$ as eluent). IR (neat) 606, 889, 1019, 1048, 1115, 1139, 1160, 1213, 1238, 1371, 1443, 1748 (C=O), 1754 (C=O), 2919, 2994 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.87−0.98 (m, 2H (1H from ***cis*-2q** and 1H from ***trans*-2q**)), 1.04−1.16 (m, 2H (1H from ***cis*-2q** and 1H from ***trans*-2q**)), 1.55 (d, J = 0.9 Hz, 3H, ***trans*-2q**), 1.58 (d, J = 1.5 Hz, 3H, ***cis*-2q**), 1.78 (s, 3H, ***cis*-2q**), 1.80 (s, 3H, ***trans*-2q**), 2.03 (s, 6H (3H from ***cis*-2q** and 3H from ***trans*-2q**)), 2.12 (s, 3H, ***cis*-2q**), 2.15 (s, 3H, ***trans*-2q**), 4.15 (ddd, J = 3.0, 3.9, 6.9 Hz, 1H, ***trans*-2q**), 4.29 (ddd, J = 3.6, 6.6, 6.6 Hz, 1H, ***cis*-2q**). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 10.3 (***cis*-2q**), 12.8 (***trans*-2q**), 17.3 (***cis*-2q**), 17.9 (***trans*-2q**), 17.9 (***cis*-2q**), 18.4 (***trans*-2q**), 18.7 (***trans*-2q**), 18.7 (***cis*-2q**), 20.4 (***trans*-2q**), 20.5 (***cis*-2q**), 20.8 (***trans*-2q**), 20.8 (***cis*-2q**), 52.4 (***trans*-2q**), 53.4 (***cis*-2q**), 122.0 (***trans*-2q**), 123.6 (***cis*-2q**), 136.9 (***cis*-2q**), 138.5 (***trans*-2q**), 169.0 (***cis*-2q**), 169.3 (***trans*-2q**), 171.3 (***trans*-2q**), 171.6 (***cis*-2q**). HRMS (FAB): [M + H^+] calcd for $C_{11}H_{17}O_4$ (a mixture of cis and trans isomers), 213.1127; found, 213.1129.

Typical Procedure for Cyclopropanation of Dienes. The complex $[RuCl_2(CO)_3]_2$ (6.4 mg, 0.013 mmol) was placed in the flame-dried Schlenk flask under N_2. A solution of substrate **1** (0.50 mmol) and diene (10 mmol) in $ClCH_2CH_2Cl$ (2.5 mL) was added to the flask at room temperature. After the solution was stirred at 50 °C for 18 h, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 15/1) as an eluent to afford a vinylcyclopropane ***trans*-2** and a seven-membered compound **5**.

Vinylcyclopropane *trans*-2r. A colorless oil (18 mg, 0.09 mmol, 46% yield). IR (neat) 758, 894, 1069, 1090, 1121, 1180, 1215, 1369, 1445, 1634, 1754 (C=O), 2917 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.66 (dd, J = 6.3, 8.1 Hz, 1H), 0.94 (dd, J = 4.8, 6.3 Hz, 1H), 1.09 (s, 3H), 1.61 (s, 3H), 1.70 (s, 3H), 1.78−1.89 (m, 1H), 2.13 (s, 3H), 4.92 (d, J = 10.5 Hz, 1H), 4.97 (d, J = 17.4 Hz, 1H), 5.52 (dd, J = 10.5, 17.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 16.3, 17.6, 18.7, 19.5, 20.5, 25.3, 27.0, 110.2, 122.7, 139.2, 145.2, 169.2. HRMS (FAB): [M^+] calcd for $C_{12}H_{18}O_2$, 194.1307; found, 194.1312.

Cycloheptadiene 5r. A colorless oil (14 mg, 0.07 mmol, 38% yield). IR (neat) 595, 813, 833, 871, 912, 1063, 1093, 1210, 1368, 1452, 1759 (C=O), 2928, 2966 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.02 (s, 6H), 1.77 (s, 3H), 2.12 (s, 3H), 2.15 (d, J = 7.2 Hz, 2H), 2.72 (d, J = 6.4 Hz, 2H), 5.22 (t, J = 6.4 Hz, 1H), 5.54 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 21.1, 24.7, 26.8, 27.0, 29.4, 38.6, 38.9, 114.5, 122.3, 140.4, 154.4, 169.7. HRMS (FAB): [M^+] calcd for $C_{12}H_{18}O_2$, 194.1307; found, 194.1313.

Vinylcyclopropane *trans*-2s. A colorless oil (23 mg, 0.11 mmol, 55% yield). IR (neat) 606, 1019, 1048, 1114, 1160, 1211, 1237, 1370, 1441, 1750 (C=O), 2919, 2934 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.52 (dd, J = 4.8, 6.0 Hz, 1H), 1.05 (dd, J = 4.8, 9.3 Hz, 1H), 1.11 (s, 3H), 1.61 (d, J = 1.5 Hz, 3H), 1.71 (s, 3H), 1.76 (s, 3H), 1.86−1.96 (m, 1H), 2.14 (s, 3H), 4.72−4.76 (m, 1H), 4.76−4.79 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 17.7, 18.2, 18.7, 18.8, 20.1, 20.5, 24.7, 28.3, 109.4, 122.2, 139.9, 148.8, 169.2. HRMS (FAB): [M^+] calcd for $C_{13}H_{20}O_2$, 208.1463; found, 208.1468.

Cycloheptadiene 5s. A colorless oil (12 mg, 0.06 mmol, 28% yield). IR (neat) 1070, 1209, 1368, 1384, 1758 (C=O), 2924, 2964 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.02 (s, 6H), 1.73−1.77 (m, 6H), 2.11 (s, 3H), 2.24 (s, 2H), 2.70 (d, J = 6.3 Hz, 2H), 5.25 (t, J = 6.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.6, 21.0, 21.7, 26.8, 26.8, 30.8, 38.5, 46.0, 115.2, 128.4, 132.0, 154.0, 169.8. HRMS (FAB): [M^+] calcd for $C_{13}H_{20}O_2$, 208.1463; found, 208.1459.

Typical Procedure for Cyclopropanation of Cyclopentadiene and the Product Rearrangement. The complex $[RuCl_2(CO)_3]_2$ (6.4 mg, 0.013 mmol) was placed in a flame-dried Schlenk flask under N_2. A solution of substrate **1** (0.50 mmol) and cyclopentadiene (10 mmol) in $ClCH_2CH_2Cl$ (2.5 mL) was added to the flask at room temperature. After the solution was stirred at 50 °C for 18 h, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue, which contains **2** and **5**, was dissolved in toluene (2.5 mL), and the mixture was stirred at 120 °C for 24 h. The resulting mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 15/1) as an eluent to afford a bicyclic compound **5**.

Bicyclic Compound *syn*(*endo*)-2t. Before the rearrangement reaction in toluene, this compound was obtained as a colorless oil by using column chromatography on SiO_2 with hexane/AcOEt (v/v = 15/1) in 55% yield (21 mg, 0.11 mmol). IR (neat) 678, 702, 1013, 1092, 1111, 1221, 1262, 1369, 1435, 1747 (C=O), 2915 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.53 (s, 3H), 1.74 (s, 3H), 1.86 (ddd, J = 6.8, 6.8, 7.2 Hz, 1H), 1.95−1.99 (m, 1H), 2.11 (s, 3H), 2.13−2.19 (m, 1H), 2.21−2.26 (m, 1H), 2.51 (dd, J = 6.8, 18.0 Hz, 1H), 5.44−5.47 (m, 1H), 5.67 (dd, J = 1.6, 5.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 17.3 (*C*H_3), 18.6 (*C*H_3), 20.8 (*C*H_3), 22.8 (cyclopropane-*C*H), 23.3 (cyclopropane-*C*H), 30.3 (cyclopropane-*C*H), 33.0 (*C*H_2), 123.1 (*C*), 129.2 (*C*H=CH), 129.6 (CH=*C*H), 138.7 (*C*), 169.1 (*C*=O). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.81; H, 8.54.

Bicyclic Compound 5t. A colorless oil (25 mg, 0.13 mmol, 65% yield). IR (neat) 557, 736, 841, 908, 936, 1021, 1036, 1095, 1113, 1212, 1369, 1471, 1653, 1755 (C=O), 2941, 2967 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.91 (s, 3H), 1.16 (s, 3H), 1.84 (ddd, J = 4.8, 4.8, 9.6 Hz, 1H), 1.97 (d, J = 9.6 Hz, 1H), 2.10 (s, 3H), 2.48 (dd, J = 3.2, 4.8 Hz, 1H), 2.79 (ddd, J = 3.2, 4.8, 7.2 Hz, 1H), 5.71 (d, J = 7.2 Hz, 1H), 5.84 (dd, J = 3.2, 6.0 Hz, 1H), 6.36 (dd, J = 3.2, 6.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.1 (*C*H_3), 21.5 (*C*H_3), 27.4 (C(O)*C*H_3), 38.3 (*C*H), 39.1 (*C*), 40.3 (*C*H_2), 51.2 (*C*H), 119.9 (*C*H=CO), 131.1 (*C*H=CH), 140.1 (CH=*C*H), 150.8 (CH=*C*O), 169.5 (*C*=O). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.01; H, 8.34.

Bicyclic Compound 5u. A colorless oil (33 mg, 0.13 mmol, 64% yield). IR (neat) 623, 707, 736, 935, 1026, 1061, 1098, 1118, 1176, 1228, 1247, 1271, 1280, 1451, 1738 (C=O), 2941, 2966 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.01 (s, 3H), 1.26 (s, 3H), 1.90 (ddd, J = 4.4, 4.4, 9.6 Hz, 1H), 2.06 (d, J = 9.6 Hz, 1H), 2.54 (dd, J = 2.8, 4.4 Hz, 1H), 2.79 (ddd, J = 2.8, 4.4, 6.8 Hz, 1H), 5.89 (d, J = 6.8 Hz, 1H), 5.90 (dd, J = 2.8, 6.0 Hz, 1H), 6.42 (dd, J = 2.8, 6.0 Hz, 1H), 7.45 (dd, J = 7.6, 7.6 Hz, 2H), 7.57 (dd, J = 7.6, 7.6 Hz, 1H), 8.06 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 21.7 (*C*H_3), 27.6 (*C*H_3), 38.4 (*C*H), 39.4 (*C*), 40.3 (*C*H_2), 51.4 (*C*H), 120.1 (*C*H=CO), 128.3 (Ar), 129.7 (Ar), 129.8 (Ar), 131.2 (*C*H=CH), 133.0 (Ar), 140.9 (CH=*C*H), 151.0 (CH=*C*O), 165.1 (*C*=O). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.05; H, 7.28.

Tricyclic Compound 5v. A colorless oil (35 mg, 0.15 mmol, 76% yield). IR (neat) 733, 841, 894, 905, 915, 1015, 1096, 1112, 1136, 1187, 1201, 1214, 1368, 1454, 1651, 1763 (C=O), 2863, 2934 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.10−1.27 (m, 2H), 1.38−1.63 (m, 6H), 1.63−1.73 (m, 2H), 1.84 (ddd, J = 4.4, 4.4, 9.6 Hz, 1H), 1.89 (d, J = 9.6 Hz, 1H), 2.11 (s, 3H), 2.77 (ddd, J = 2.8, 4.4, 6.8 Hz, 1H), 3.12 (dd, J = 2.8, 4.4 Hz, 1H), 5.74 (d, J = 6.8 Hz, 1H), 5.80 (dd, J = 2.8, 6.0 Hz, 1H), 6.36 (dd, J = 2.8, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 21.2 (*C*H_2), 21.2 (*C*H_2), 21.2 (*C*H_2), 25.8 (*C*H_2), 28.4 (*C*H_3), 32.4 (*C*H_2), 38.1 (*C*H), 39.6 (*C*), 42.4 (*C*H or *C*H_2), 42.7 (*C*H or *C*H_2), 121.1 (*C*H=CO), 130.6 (*C*H=CH), 141.0 (CH=*C*H), 150.4 (CH=*C*O), 169.6 (*C*=O). HRMS (FAB): [M^+] calcd for $C_{15}H_{20}O_2$, 232.1463; found, 232.1460.

Ruthenium-Catalyzed Synthesis of Indene 4. The complex $[RuCl_2(CO)_3]_2$ (2.6 mg, 0.005 mmol) was placed in a flame-dried Schlenk flask under N_2. A solution of substrate **1k** (0.20 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was added to the flask at room temperature. After the mixture was stirred at 50 °C for 18 h, the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 15/1) as an eluent to afford indene **4** as a pale-yellow solid (34 mg, 0.14 mmol, 68% yield), mp 69.0−71.8 °C. IR (KBr) 700, 721, 755, 772, 858, 1012, 1184, 1208, 1236, 1369, 1461, 1494, 1600, 1766 (C=O), 3025, 3056 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.19 (s, 3H), 3.78 (s, 2H), 7.09−7.12 (m, 1H), 7.19−7.33 (m, 3H), 7.34−7.51 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 21.0, 37.4, 114.9, 120.1, 123.7, 124.9, 126.4, 127.6, 128.1, 128.4, 128.5, 138.2, 142.4. 150.7, 168.8. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.28; H, 5.48.

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Supporting Information Available: The X-ray diffraction analyses of ***cis*-2c** and ***cis*-2f** are described. The ^1H and ^{13}C NMR spectra of compounds **2a**−**f**, **2l**−**t**, and **5r**−**5v** are also shown in PDF. This material is available free of charge via the Internet at http://pubs.acs.org.

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