Ruthenium-Catalyzed Alkenylative Cyclization via Insertion of Alkene into Ruthenacyclopentene

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A novel ruthenium-catalyzed alkenylative cyclization of enyne was developed. When an enyne was reacted with Cp*RuCl(cod) under an atmosphere of ethylene, ethylene was inserted into the ruthenium−sp^2 carbon bond of ruthenacyclopentene derived from enyne and the low-valent ruthenium complex to afford ruthenacycloheptene, and β-hydrogen elimination followed by reductive elimination occurred to give a cyclic compound having a diene moiety. In this reaction, acrylaldehyde could be inserted into ruthenacyclopentene instead of ethylene. Various carbo- and heterocyclic compounds could be obtained in high yields.

Introduction

Ruthenium-catalyzed metathesis reaction is one of the most unique and significant reactions discovered in recent years in synthetic organic chemistry.[1] In 1992, Grubbs discovered olefin metathesis using ruthenium carbene complex **3a** (Figure 1) and synthesized many hetero- and carbocyclic compounds. Then they reported that ruthenium carbene complex **3b** could be used for metathesis reaction.[2] In 1999, the second-generation ruthenium carbene complex **3c**, which has N-heterocyclic carbene (NHC) as a ligand, was developed and was shown to be very effective for metathesis reaction of highly substituted olefins or electron-deficient olefins.[3,4] On the other hand, enyne metathesis is an interesting and unique reaction. The double bond of enyne is cleaved and an alkylidene part is moved onto the alkyne carbon to afford a cyclic compound having a diene moiety. The reaction is also catalyzed by the ruthenium carbene complexes **3a**, **3b**, and **3c**[5] (eq 1).

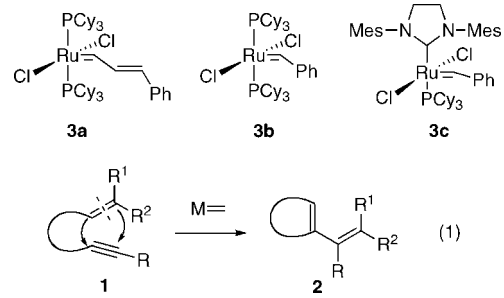

Figure 1

During the course of our reinvestigation of metathesis reaction of enyne having various substituents on the alkene and/or on the alkyne using the second-generation ruthenium carbene complex **3c**,[6,7] we found that the reaction of enyne **1a**, having a nonsubstituted alkene and a terminal alkyne, under argon gas using **3c** gave metathesis product **2a** in low yield. We had found and reported that the use of ethylene gas was effective for enyne metathesis of a substrate having a terminal alkyne using the first-generation ruthenium carbene complex **3b**.[6c] Thus, the reaction of **1a** using **3c** was reinvestigated under ethylene gas. As the result, the yield of **2a** was slightly improved up to 38%;

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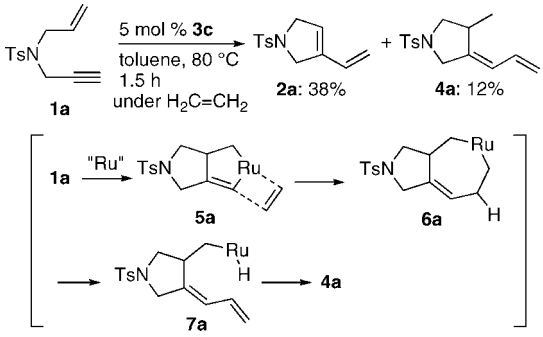
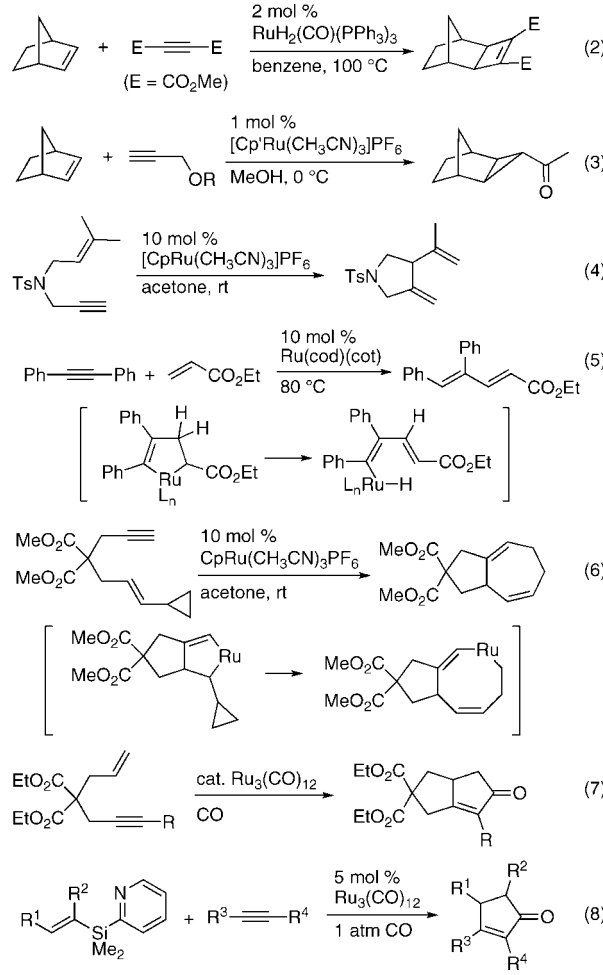
Scheme 1. Reinvestigation of Enyne Metathesis Using 3c



however, cyclic compound **4a**, which has a diene moiety on the pyrrolidine ring, was also obtained in 12% yield (Scheme 1). In the reaction course for formation of **4a**, ruthenacyclopentene **5a** should be formed as an intermediate. Thus, insertion of ethylene into the ruthenium−sp^2 carbon bond of **5a** gives ruthenacycloheptene **6a**, and β-hydrogen elimination from **6a** followed by reductive elimination from **7a** would give **4a**.

Ruthenacyclopentene, derived from enyne and a low-valent ruthenium complex, had been shown to be a useful and important intermediate for several ruthenium-catalyzed reactions in the literature.[8] For instance, intermolecular reaction of norbornene and electron-deficient alkyne has been reported by Mitsudo and co-workers. In this reaction, a cyclobutene derivative would be obtained by reductive elimination from a ruthenacyclopentene intermediate (eq 2).[9a,b] When propargyl alcohol was used as an alkyne in a similar reaction to eq 2, a cyclopropane ring was formed (eq 3).[9c] Trost reported that a five-membered ring compound having 1,4-diene was obtained from enyne through the formation of ruthenacyclopentene followed by β-hydrogen elimination (eq 4).[9d,e] The reaction of diphenylacetylene and ethyl acrylate using the ruthenium catalyst was reported, in which a compound having conjugated diene was produced via β-hydrogen elimination followed by reductive elimination from ruthenacyclopentene (eq 5).[9f] Intramolecular reaction of enyne having a cyclopropane ring on an alkene gave a fused 5,7-membered ring compound (eq 6).[9g] In this reaction, ruthenacyclopentene having a cyclopropane ring was initially formed, which would be in a state of equilibrium with ruthenacyclooctadiene. Reductive elimination from the ruthenacycle intermediate produced a fused 5,7-membered ring compound. Insertion of carbon monoxide into ruthenacyclopentene was also reported, giving cyclopentenone derivatives (eqs 7 and 8).[9h−j]

The reactions shown in eqs 2−8 proceeded via ruthenacyclopentenes formed from the reaction of alkyne, alkene, and a low-valent ruthenium complex, which revealed that ruthenacyclopentenes are key intermediates for the synthesis of various functionalized compounds. The reaction shown in Scheme 1 is different from those because insertion of ethylene into ruthenacyclopentene **5a** would take place and **4a** was formed via β-elimination from **6a**. Thus, it was decided to clarify the



reaction mechanism and to develop this reaction for the synthesis of various carbo- and heterocyclic compounds.[10]

Results and Discussion

As described in the Introduction, we investigated the reactions of enyne **1a** using various ruthenium carbene complexes. The reaction of **1a** using the first-generation ruthenium-carbene complex **3b** in CH_2Cl_2 at room temperature under argon gas produced the usual metathesis product **2a** in 21% yield (Table 1, entry 1). The yield of enyne metathesis product **2a** was increased when the reaction was carried out under ethylene gas (1 atm) (entry 2),[6c] but no ethylenative product **4a** was produced. When a toluene solution of enyne **1a** was warmed at 80 °C in the presence of 5 mol % of the second-generation ruthenium carbene complex **3c** for 1.5 h under argon gas, the usual metathesis product **2a** was obtained in 23% yield (entry 3). On the other hand, the reaction of **1a** with **3c** under ethylene gas

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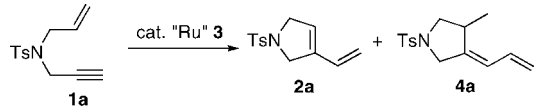
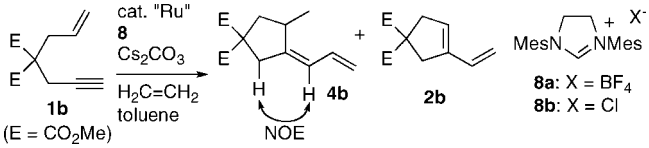
Table 1. Reinvestigation of Enyne Metathesis of 1a



entry	Ru (mol %)	atmosphere	solvent	temp (°C)	time (h)	yield (%) 2a	4a
1	**3b**(1)	argon	CH_2Cl_2	rt	22	21	
2	**3b**(1)	ethylene	CH_2Cl_2	rt	22	90	
3	**3c**(5)	argon	toluene	80	1.5	23	
4	**3c**(5)	ethylene	toluene	80	1.5	38	12

Table 2. Optimization of Reaction Conditions

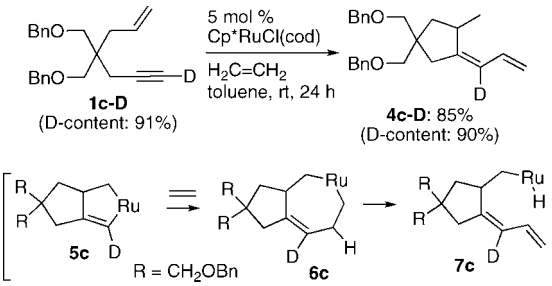


entry	"Ru" (mol %)	**8** (mol %)	temp (°C)	time (h)	yield (%) 4b	2b	1b
1	$[RuCl_2(CO)_3]_2$ (2.5)	**8a** (5)	80	6		10	85
2	$Ru_3(CO)_{12}$ (3.3)	**8a** (10)	80	12			80
3	$[RuCl_2(p\text{-cymene})]_2$ (2.5)	**8a** (5)	80	24	33		
4	$[RuCl_2(p\text{-cymene})]_2$ (5)	**8a** (10)	80	8	31		
5	$[RuCl_2(p\text{-cymene})]_2$ (5)	**8a** (10)	120	6	8		
6	$[RuCl_2(p\text{-cymene})]_2$ (5)	**8a** (10)	60	13	12		40
7	$[RuCl_2(p\text{-cymene})]_2$ (5)	**8b** (10)	80	0.75	24	24	
8	$[RuCl_2(p\text{-cymene})]_2$ (5)		80	16	28		8
9	Cp*RuCl(cod) (10)		80	0.33	71		
10	Cp*RuCl(cod) (10)		60	0.33	76		
11	Cp*RuCl(cod) (10)		40	0.66	81		
12	Cp*RuCl(cod) (10)		rt	1.5	84		
13	Cp*RuCl(cod) (5)		rt	3	85		
14	Cp*RuCl(cod) (1)		rt	23	20		74

(1 atm) produced **4a**, having a diene moiety on the pyrrolidine ring, in 12% yield, whose structure was determined to be **4a** on the basis of various spectral data (entry 4). These results indicated that the ethylene product **4a** was formed when the reaction was carried out using only the second-generation ruthenium carbene complex **3c** under an atmosphere of ethylene.

As shown in Scheme 1, it was thought that the reaction would proceed via ruthenacyclopentene **5a** formed by the reaction of alkyne and alkene parts in the substrate with a low-valent ruthenium complex, which would be generated from the second-generation ruthenium carbene complex **3c**. Thus, the reaction was investigated using various ruthenium complexes. We chose **1b** as a substrate, and the reaction was carried out in the presence or in the absence of NHC ligand because ruthenium carbene complex **3c** has one NHC as a ligand. The use of $[RuCl_2(CO)_3]_2$ and $Ru_3(CO)_4$ in the presence of imidazolinium salt **8a** and Cs_2CO_3[11] (an equimolar amount of **8**) did not afford the desired product **4b** (Table 2, entries 1 and 2). When 5 mol % of $[RuCl_2(p\text{-cymene})]_2$[12] was used in the presence of **8a** and Cs_2CO_3, a relatively large amount of **4b** was obtained (entry 3). However, an increase in the amount of the catalyst did not give a good result (entry 4). A higher or lower reaction temperature decreased the yield of desired product **4b** (entries 5 and 6). It was interesting that metathesis product **2b** was

Scheme 2. Examination of Enyne Having Deuterium on Alkyne



formed in 24% yield in the case of shorter reaction times[13] (entries 4 and 7). In the absence of the NHC ligand, a similar result was obtained (entry 8). On the other hand, the reaction of enyne **1b** with ethylene in the presence of 10 mol % of Cp*RuCl(cod)[14] proceeded smoothly to give cyclized compound **4b** in 71% yield after only 20 min (entry 9). Since the use of Cp*RuCl(cod) gave a good result, the reaction was carried out using this catalyst in the absence of NHC under various conditions. A lower reaction temperature increased the yield of **4b** (entries 9−11), and the reaction proceeded even at room temperature for only 1.5 h (entry 12). A decrease in the amount of the catalyst gave the same result after 3 h (entry 13), but the use of 1 mol % of catalyst did not give a good result, and the starting material was recovered in 74% yield (entry 14). The geometry of the olefin part of **4b** was determined to be the *Z*-form by an NOE experiment.

To confirm the reaction mechanism shown in Scheme 1, enyne **1c-D** was synthesized and the reaction was carried out under standard conditions (Scheme 2). As a result, desired cyclized compound **4c-D**, having a deuterium on the diene moiety, was obtained in high yield, and the D-content was 90%. The result indicates that the reaction proceeded via the proposed mechanism.

Various enynes were used for this reaction under the optimal conditions, and the results are shown in Table 3. A variety of carbo- and heterocyclic compounds **4** having a diene moiety on the five-membered ring were obtained in high yields (entries 1−4). Even in the presence of an amino group in a chain, this cyclization proceeded smoothly, and the desired compound **4f** was obtained in good yield (entry 5). An enyne having an amide or ynamide group could be used as a substrate, and desired cyclized compound **4g** or **4h** was obtained in good to moderate yield (entry 6 or 7).

Furthermore, the effects of substituents on the alkyne of enyne were examined (Table 4). Enynes **1m** and **1n**, having a methyl and a siloxymethyl group on the alkyne, did not give desired cyclized compounds, while the reaction of enyne **1i**, which was a tosylamide analogue of **1n**, proceeded smoothly to afford the corresponding cyclized product **4i** in high yield (entry 1). In this case, the heteroatom in a chain would play an important role, although the reason is not clear. It was interesting that enynes **1j**−**l**, having an ester and a formyl group on the alkyne, afforded the desired compounds **4j**−**l** in high yields (entries 2−4). On the other hand, enynes **1o**−**q**, having an amide or silyl group on the alkyne, did not give a cyclized compound and the staring material was recovered unchanged in each case.

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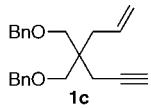
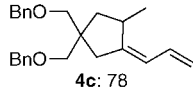
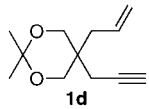
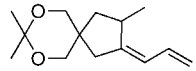
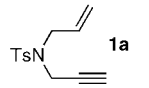
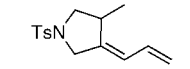
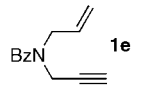
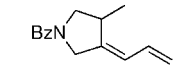
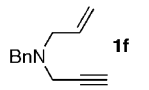
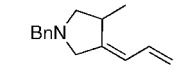
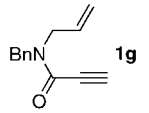
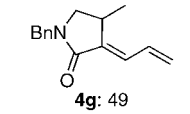
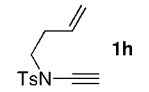
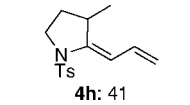
(12) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233.

(13) Dixneuf reported that the reaction of enyne with $[RuCl_2(p\text{-cymene})]_2$ in the presence of NHC afforded the metathesis product. See: (a) Ackermann, L.; Bruneau, C.; Dixneuf, P. H. *Synlett* **2001**, 397. (b) Sémeril, D.; Bruneau, C.; Dixneuf, P. H. *Adv. Synth. Catal.* **2002**, *344*, 585.

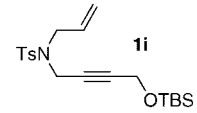
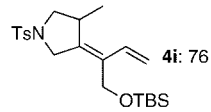
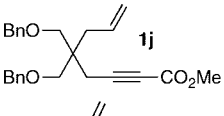
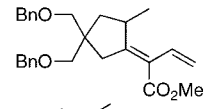
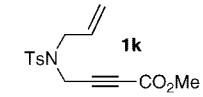
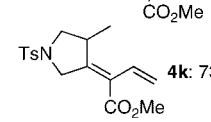
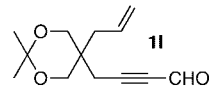
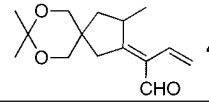
(14) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161.

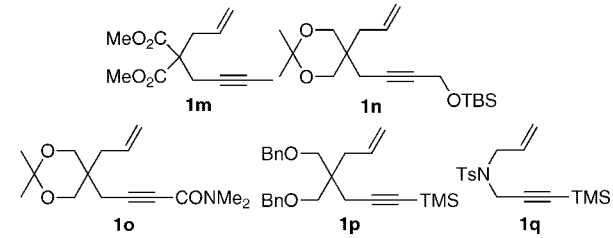
Table 3. Synthesis of Various Five-Membered Ring Compounds[a]

entry	substrate	time (h)	product (%)
1	 **1c**	24	 **4c**: 78
2	 **1d**	22	 **4d**: 90
3	 **1a**	1	 **4a**: 83
4	 **1e**	3	 **4e**: 70
5	 **1f**	18	 **4f**: 74
6	 **1g**	4	 **4g**: 49
7	 **1h**	14	 **4h**: 41

[a] The reaction was carried out in toluene at room temperature in the presence of Cp*RuCl(cod) (5 mol %) under ethylene gas (1 atm).

Table 4. Effects of Substituent on the Alkyne[a]

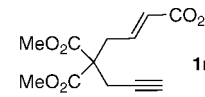
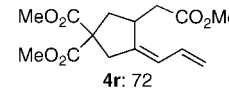
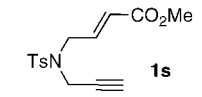
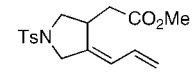
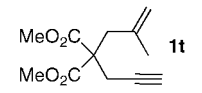
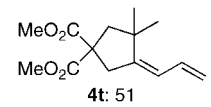
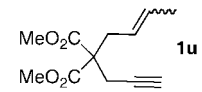
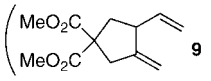
entry	substrate	time (h)	product (%)
1	 **1i**	5	 **4i**: 76
2	 **1j**	8	 **4j**: 89
3	 **1k**	1.5	 **4k**: 73
4	 **1l**	3	 **4l**: 71

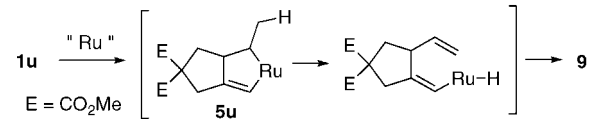


[a] The reaction was carried out in toluene at room temperature in the presence of Cp*RuCl(cod) (5 mol %) under ethylene gas (1 atm).

Next, the effects of substituents on the alkene were examined (Table 5). Enyne **1r**, having an ester group on the alkene, gave the desired compound **4r** in high yield (entry 1), but enyne **1s**, containing nitrogen in a chain, afforded **4s** in low yield (entry 2). Although enyne **1t**, having a 1,1-disubstituted alkene, gave the cyclized compound **4t** in good yield, 1,2-disubstituted alkene **1u** did not give a good result and cyclized compound **9** was obtained in 26% yield (entry 4). Presumably, compound **9** is formed via β-hydrogen elimination from the methyl group on the ruthenacyclopentene **5u**.[15]

Table 5. Effects of Substituents on Alkene[a]

entry	substrate	time (h)	product (%)
1	 **1r**	19	 **4r**: 72
2	 **1s**	3	 **4s**: 18
3	 **1t**	5	 **4t**: 51
4[b]	 **1u**	5	 **9**



[a] The reaction was carried out in toluene at room temperature (entries 1 and 2) or at 60 °C (entries 3 and 4) in the presence of Cp*RuCl(cod) (5 mol %) under ethylene gas (1 atm). [b] **1u** was recovered in 58% yield and **9** was obtained in 26% yield.

Next, we turned our attention to the construction of the six-membered ring (Scheme 3). When a toluene solution of enyne **10a** was refluxed in the presence of 5 mol % of Cp*RuCl(cod) under ethylene gas for 14 h, no product was obtained and a complex mixture was produced. Thus, when the reaction of enyne **10b**, whose alkene and alkyne parts were connected on the aromatic ring, was carried out in a similar manner at room temperature for 3 h, the desired quinoline derivative **11b** was obtained in 46% yield. Lower reaction temperature improved the yield of **11b** to 64%. When enyne **10c** was treated in a similar manner, quinoline derivative **11c** was obtained in 20% yield, and the starting material was recovered in 28% yield.

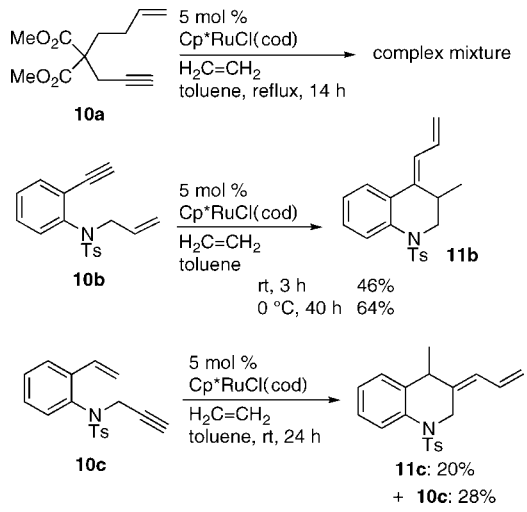
Although various alkenes, including acrylonitrile, acrylaldehyde, allylsilane, and ethyl vinyl ether, were investigated instead of ethylene for introduction into the ruthenacyclopentene, only acrylaldehyde could be introduced to afford cyclized compound **12b** in 27% yield (Scheme 4). Presumably, carbonyl oxygen of acrolein coordinates to the ruthenium metal of ruthenacyclopentene, which might assist an alkene part in insertion into the ruthenacyclopentene **5b** to give cyclized compound **12b**.

As a compound having other multiple bonds, 1,6-hexadiene **13** was examined in this reaction, but the reaction did not proceed and the starting material was recovered unchanged

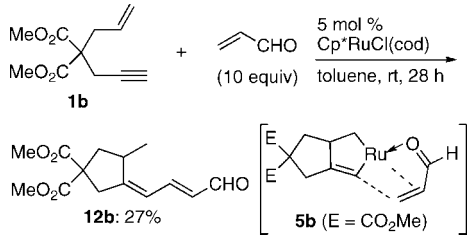
(15) The reaction course is the same as that reported by Trost.[9d,e]

(16) (a) Yi, C. S.; Torres-Lubian, J. R.; Liu, N.; Rheingold, A. L.; Guzei, I. A. *Organometallics* **1998**, *17*, 1257. (b) Kondo, T.; Kaneko, Y.; Tsunawaki, F.; Okada, T.; Shiotsuki, M.; Morisaki, Y.; Mitsudo, T. *Organometallics* **2002**, *21*, 4564. (c) Varela, J. A.; Castedo, L.; Saá, C. *Org. Lett.* **2003**, *5*, 2841. (d) Varela, J. A.; Rubín, S. G.; Castedo, L.; Saá, C. *J. Org. Chem.* **2008**, *73*, 1320. (e) Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Itoh, K. *J. Org. Chem.* **1998**, *63*, 9610.

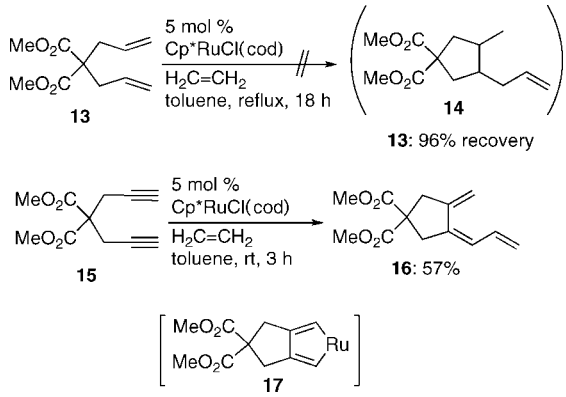
Scheme 3. Examination of the Formation of a Six-Membered Ring



Scheme 4. Insertion of Other Alkenes



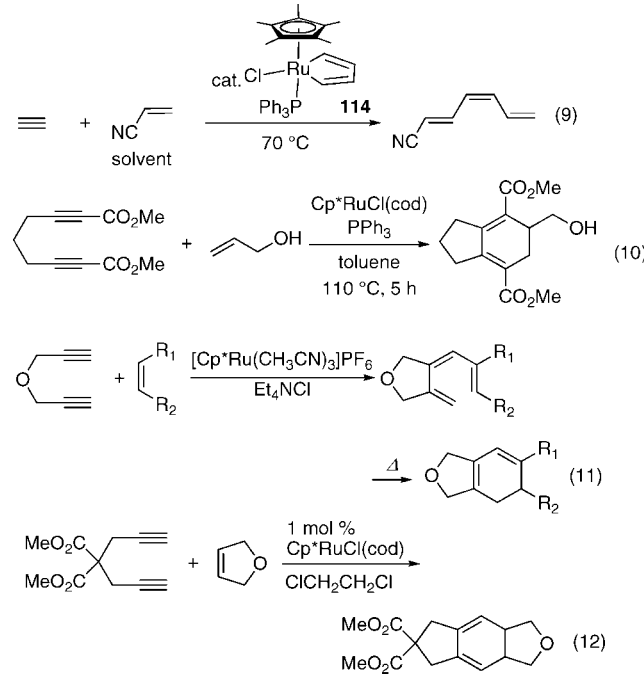
Scheme 5. Reaction of Diene and Diyne with Cp*RuCl(cod)



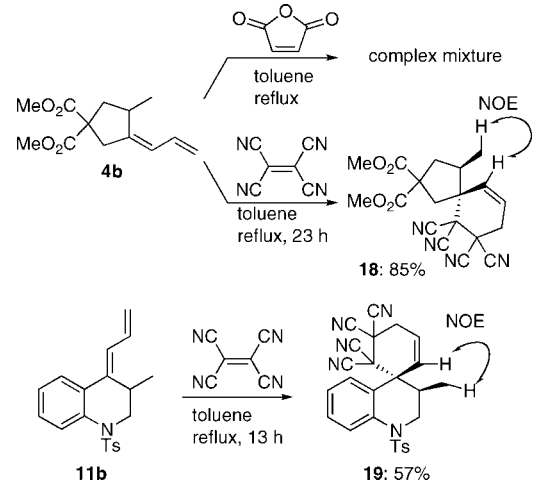
(Scheme 5). On the other hand, when 1,6-hexadiyne **15** was used for this reaction, desired compound **16**, having a triene moiety, was obtained in 57% yield, which means that insertion of ethylene into ruthenacyclopentadiene **17** formed from **15** took place.

There are few reports of insertion of an alkene into ruthenacyclopentadiene. Yi reported that the reaction of acetylene and acrylonitrile afforded a compound having a triene moiety (eq 9).[16a] Mitsudo found that diyne having an ester group on each alkyne reacted with allyl alcohol to give a fused 5,6-membered compound (eq 10).[16b] Recently, a similar reaction in which tetrahydroisobenzofuran was obtained was reported by Saá (eq 11).[16c,d] Itoh and Yamamoto investigated the ruthenium-catalyzed cocyclization of diyne and dihydrofuran, and they obtained a tetrahydroisobenzofuran derivative in high yield by cocyclization of diyne and alkene (eq 12).[16e]

The present alkenylative cyclization products have a diene moiety on the five-membered ring. Thus, as a utilization of these compounds for organic synthesis, a Diels−Alder reaction was



Scheme 6. Diels−Alder Reaction of Cyclized Compound



carried out (Scheme 6). A toluene solution of compound **4b** and maleic anhydride was refluxed overnight, but the desired compound was not obtained and a complex mixture was formed. However, when tetracyanoethylene was used as a dienophile, spiro compound **18**, the stereochemistry of which was determined by an NOE experiment, was obtained in 85% yield. Probably, the dienophile would be attacked from the backside of the methyl group of **4b**. Furthermore, quinoline derivative **11b** was reacted with tetracyanoethylene to afford spiro compound **19** in 57% yield.

Conclusions

The novel ruthenium-catalyzed alkenylative cyclization of enynes using Cp*RuCl(cod) was developed. When the reaction of enyne having an alkyl, an ester, or a formyl group was carried out in the presence of Cp*RuCl(cod) under ethylene gas, ethylene was inserted into the ruthenacyclopentene to give ruthenacycloheptene, from which β-hydrogen elimination followed by reductive elimination occurred to give a cyclic compound having a diene moiety. In this reaction, acrylaldehyde could be used instead of ethylene. Various carbo- and hetero-

cyclic compounds could be synthesized under mild reaction conditions. The quinoline derivatives could be synthesized using this method when the enyne part was connected to the aromatic ring. The diene moiety on the five-membered ring of the cyclized compound reacted with the dienophile to give the spiro compound.

Experimental Section

General Procedure for Cyclization of Enyne under Ethylene Gas. A toluene solution of enyne and a catalytic amount of Cp*RuCl(cod) was stirred at room temperature or 60 °C under ethylene gas (1 atm). After removal of the solvent, the residue was purified by column chromatography on silica gel.

(*E*)-3-Allylidene-4-methyl-1-tosylpyrrolidine (4a). According to the general procedure, a crude product, which was obtained from **1a** (74.8 mg, 0.30 mmol) and Cp*RuCl(cod) (5.7 mg, 0.015 mmol) in toluene (10 mL) at room temperature for 1 h, was purified by column chromatography on silica gel (hexane/AcOEt, 3/1) to give **4a** (69.2 mg, 83%) as a colorless oil: IR (film, $CHCl_3$) 1654, 1597, 1346, 1164 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.11 (d, J = 7.0 Hz, 3 H), 2.43 (s, 3 H), 2.98−3.03 (m, 1 H), 3.13 (dd, J = 6.2, 9.2 Hz, 1 H), 3.22 (dd, J = 2.2, 9.2 Hz, 1 H), 3.61 (d, J = 14.9 Hz, 1 H), 4.05 (d, J = 14.9 Hz, 1 H), 5.01 (d, J = 10.5 Hz, 1 H), 5.07 (d, J = 16.8 Hz, 1 H), 5.84 (d, J = 10.5 Hz, 1 H), 6.35 (ddd, J = 16.8, 10.5, 10.5 Hz, 1 H), 7.33 (d, J = 8.4 Hz, 2 H), 7.70 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 19.8, 21.4, 35.0, 51.7, 55.2, 117.2, 122.3, 127.8, 129.6,132.3, 132.3, 142.9, 143.6; LRMS (EI) m/z 277 (M^+), 262, 155, 122, 91; HRMS (EI) calcd for $C_{15}H_{19}NO_2S$ 277.1136, found 277.1146.

Dimethyl (*Z*)-3-allylidene-4-methylcyclopentane-1,1-dicarboxylate (4b) (Table 2, entry 13). According to the general procedure, a crude product, which was obtained from **1b** (63.1 mg, 0.30 mmol) and Cp*RuCl(cod) (5.7 mg, 0.015 mmol) in toluene (10 mL) at room temperature for 3 h, was purified by column chromatography on silica gel (hexane/Et_2O, 10/1) to give **4b** (61.1 mg, 85%) as a colorless oil: IR (neat) 1736, 1656, 1601 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, J = 6.4 Hz, 3 H), 1.86 (dd, J = 13.3, 6.5 Hz, 1 H), 2.73 (dd, J = 13.6, 8.4 Hz, 1 H), 2.83 (d, J = 16.2 Hz, 1 H), 2.94−3.03 (m, 1 H), 3.14 (d, J = 16.3 Hz, 1 H), 3.70 (s, 3 H), 3.75 (s, 3 H), 5.01 (d, J = 10.5 Hz, 1 H), 5.07 (d, J = 16.8 Hz, 1 H), 5.93 (d, J = 10.5 Hz, 1 H), 6.44 (ddd, J = 16.8, 10.5, 10.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 34.3, 41.6, 42.1, 52.7, 59.1, 115.4, 122.9, 133.0, 147.0, 171.7, 172.0; LRMS (EI) m/z 238 (M^+), 207, 178, 163, 119, 91; HRMS (EI) calcd for $C_{13}H_{18}O_4$ 238.1205, found 238.1204.

(*Z*)-1,1-Bis(benzyloxymethyl)-3-allylidene-4-methylcyclopentane (4c). According to the general procedure, a crude product, which was obtained from **1c** (100 mg, 0.3 mmol) and Cp*RuCl(cod) (5.7 mg, 0.015 mmol) in toluene (10 mL) at room temperature for 24 h, was purified by column chromatography on silica gel (hexane/benzene, 1/1) to give **4c** (85.0 mg, 78%) as a colorless oil: IR (film, $CHCl_3$) 1654, 1600, 1101 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.12 (d, J = 7.2 Hz, 3 H), 1.29 (dd, J = 6.8, 13.2 Hz, 1 H), 1.99 (dd, J = 8.8, 13.2 Hz, 1 H), 2.55 (d, J = 16 Hz, 1 H), 2.41 (d, J = 16 Hz, 1 H), 2.81−2.87 (m, 1 H), 3.27 (s, 2 H), 3.45 (d, J = 8.8 Hz, 1 H), 3.48 (d, J = 8.8 Hz, 1 H), 4.47 (s, 2 H), 4.52 (s, 2 H), 4.95 (d, J = 10.0 Hz, 1 H), 5.03 (d, J = 16.8 Hz, 1 H), 5.88 (d, J = 10.8 Hz, 1 H), 6.49 (ddd, J = 10.0, 16.8, 10.8 Hz, 1 H), 7.23−7.34 (m, 10 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 22.9, 34.2, 40.8, 47.5, 72.7, 73.6, 73.7, 75.2, 114.5, 122.8, 127.8, 127.8, 128.7, 134.2, 139.4, 151.8; LRMS (EI) m/z 362 (M^+), 271, 254, 241, 91; HRMS (EI) calcd for $C_{25}H_{30}O_2$ 362.2246, found 362.2240. Anal. Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.78; H, 8.31.

(*Z*)-2-Allylidene-3,8,8-trimethyl-7,9-dioxaspiro[4.5]decane (4d). According to the general procedure, a crude product, which was obtained from **1d** (67.7 mg, 0.35 mmol) and Cp*RuCl(cod) (6.6 mg, 0.017 mmol) in toluene (12 mL) at room temperature for 22 h, was purified by column chromatography on silica gel (hexane/AcOEt, 30/1) to give **4d** (70.5 mg, 90%) as a colorless oil: IR (neat) 1654, 1600, 1067 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.10−1.17 (m, 4 H), 1.40 (s, 3 H), 1.42 (s, 3 H), 1.98 (dd, J = 13.5, 8.6 Hz, 1 H), 2.24−2.47 (m, 2 H), 2.83−2.91 (m, 1 H), 3.45−3.75 (m, 4 H), 4.98 (d, J = 10.5 Hz, 1 H), 5.08 (d, J = 17.0 Hz, 1 H), 5.94 (d, J = 10.5 Hz, 1 H), 6.49 (ddd, J = 17.0, 10.5, 10.5 Hz, 1 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 22.4, 22.5, 33.4, 40.8, 41.2, 41.3, 67.6, 69.7, 97.8, 114.7, 123.2, 133.4, 149.7; LRMS (EI) m/z 222 (M^+), 207, 164, 147, 133, 91; HRMS (EI) calcd for $C_{14}H_{22}O_2$ 222.1620, found 222.1631.

(*E*)-3-Allylidene-1-benzoyl-4-methylpyrrolidine (4e). According to the general procedure, a crude product, which was obtained from **1e** (100.8 mg, 0.51 mmol) and Cp*RuCl(cod) (9.6 mg, 0.025 mmol) in toluene (17 mL) at room temperature for 3 h, was purified by column chromatography on silica gel (CH_2Cl_2/AcOEt, 20/1) to give **4e** (81.5 mg, 70%) as a colorless oil: IR (neat) 1624, 1576 cm^{-1}; ^1H NMR (270 MHz, DMSO, 100 °C) δ 1.10 (d, J = 6.8 Hz, 3 H), 3.16 (d, J = 11.1 Hz, 1 H), 3.38 (d, J = 11.1 Hz, 1 H), 3.66 (dd, J = 11.1, 6.8 Hz, 1 H), 4.04 (d, J = 16.7 Hz, 1 H), 4.34 (d, J = 16.7 Hz, 1 H), 5.10 (d, J = 11.1 Hz, 1 H), 5.15 (d, J = 17.8 Hz, 1 H), 5.98 (d, J = 10.8 Hz, 1 H), 6.50 (ddd, J = 17.8, 11.1, 10.8 Hz, 1 H), 7.42−7.49 (m, 5 H); LRMS (EI) m/z 227 (M^+), 212, 198, 149, 134, 122, 105; HRMS (EI) calcd for $C_{15}H_{17}NO$ 227.1310, found 227.1315.

(*E*)-3-Allylidene-1-benzyl-4-methylpyrrolidine (4f). According to the general procedure, a crude product, which was obtained from **1f** (97.1 mg, 0.52 mmol) and Cp*RuCl(cod) (10.0 mg, 0.026 mmol) in toluene (17 mL) at room temperature for 18 h, was purified by column chromatography on silica gel (hexane/AcOEt, 15/1) to give **4f** (81.6 mg, 74%) as a colorless oil: IR (neat) 1663, 1602, 1122 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.20 (d, J = 7.0 Hz, 3 H), 2.39 (dd, J = 8.6, 4.1 Hz, 1 H), 2.78 (dd, J = 8.6, 7.0 Hz, 1 H), 2.92−3.00 (m, 1 H), 3.07 (d, J = 13.5 Hz, 1 H), 3.32 (d, J = 13.5 Hz, 1 H), 3.60 (s, 2 H), 5.04 (d, J = 9.7 Hz, 1 H), 5.06 (d, J = 18.4 Hz, 1 H), 5.89 (d, J = 11.1 Hz, 1 H), 6.48 (ddd, J = 18.4, 11.1, 9.7 Hz, 1 H), 7.24−7.33 (m, 5 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 20.4, 35.3, 59.8, 60.4, 62.3, 114.9, 120.7, 126.7, 127.9, 128.4, 133.2, 138.7, 147.8; LRMS (EI) m/z 213 (M^+), 198, 184, 170, 91; HRMS (EI) calcd for $C_{15}H_{19}N$ 213.1517, found 213.1509.

(*E*)-3-Allylidene-1-benzyl-4-methylpyrrolidin-2-one (4g). According to the general procedure, a crude product, which was obtained from **1g** (85.6 mg, 0.43 mmol) and Cp*RuCl(cod) (8.2 mg, 0.022 mmol) in toluene (14 mL) at room temperature for 4 h, was purified by column chromatography on silica gel (hexane/AcOEt, 4/1) to give **4g** (47.8 mg, 49%) as a colorless oil: IR (film, $CHCl_3$) 1683, 1604 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.19 (d, J = 5.9 Hz, 3 H), 2.83 (dd, J = 10.0, 1.6 Hz, 1 H), 3.09−3.15 (m, 1 H), 3.45 (dd, J = 10.0, 7.6 Hz, 1 H), 4.52 (d, J = 14.6 Hz, 1 H), 4.60 (d, J = 14.6 Hz, 1 H), 5.44 (d, J = 11.9 Hz, 1 H), 5.56 (d, J = 16.5 Hz, 1 H), 6.55 (ddd, J = 16.5, 11.9, 11.6 Hz, 1 H), 6.94 (d, J = 11.6 Hz, 1 H), 7.23−7.36 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 29.1, 47.1, 52.2, 123.3, 127.3, 127.9, 128.4, 130.0, 131.5, 136.1, 137.7, 167.8; LRMS (EI) m/z 227 (M^+), 212, 91; HRMS (EI) calcd for $C_{15}H_{17}NO$ 227.1310, found 227.1307.

(*E*)-2-Allylidene-3-methyl-1-tosylpyrrolidine (4h). According to the general procedure, a crude product, which was obtained from **1h** (56.9 mg, 0.23 mmol) and Cp*RuCl(cod) (4.3 mg, 0.011 mmol) in toluene (7.5 mL) at room temperature for 14 h, was purified by column chromatography on silica gel (hexane/Et_2O, 2/1) to give **4h** (26.2 mg, 41%) as a colorless solid: mp 118−122 °C (recrystallized from AcOEt/hexane); IR (film, $CHCl_3$) 1644, 1599, 1348, 1163 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 0.56 (d, J = 7.0 Hz, 3 H), 1.47 (dd, J = 6.2, 12.2 Hz, 1 H), 1.90 (dddd, J = 7.0, 10.3, 12.2, 14.9 Hz, 1 H), 2.42 (s, 3 H), 3.04 (ddd, J = 7.0, 7.0, 14.9 Hz, 1 H), 3.46 (dt, J = 6.2, 7.0 Hz, 1 H), 3.85 (dd, J = 7.0, 10.3 Hz, 1

H), 4.94 (dd, J = 2.2, 10.0 Hz, 1 H), 5.16 (dd, J = 2.2, 15.7 Hz, 1 H), 6.31 (ddd, J = 10.0, 11.3, 15.7 Hz, 1 H), 6.42 (d, J = 11.3 Hz, 1 H), 7.29 (d, J = 8.4 Hz, 2 H), 7.72 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 21.8, 29.0, 35.4, 49.0, 108.6, 114.1, 127.2, 129.2, 132.8, 133.8, 143.7, 145.0; LRMS (EI) m/z 277 (M^+), 212, 198, 122, 80; HRMS (EI) calcd for $C_{15}H_{19}NO_2S$ 277.1136, found 277.1135.

(*Z*)-3-[1-(*tert*-Butyldimethylsilyloxy)but-3-en-2-ylidene]-4-methyl-1-tosylpyrrolidine (4i). According to the general procedure, a crude product, which was obtained from **1i** (94.6 mg, 0.24 mmol) and Cp*RuCl(cod) (4.6 mg, 0.012 mmol) in toluene (8 mL) at room temperature for 5 h, was purified by column chromatography on silica gel (hexane/AcOEt, 10/1) to give **4i** (77.1 mg, 76%) as a colorless oil: IR (neat) 1599, 1350, 1162 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.06 (s, 6 H), 0.88 (s, 9 H), 1.14 (d, J = 7.0 Hz, 3 H), 2.42 (s, 3 H), 2.95−3.06 (m, 1 H), 2.99 (d, J = 8.1 Hz, 1 H), 3.29 (d, J = 8.1 Hz, 1 H), 3.71 (d, J = 15.7 Hz, 1 H), 4.18 (s, 1 H), 4.21 (s, 1 H), 4.22 (d, J = 15.7 Hz, 1 H), 5.09 (d, J = 10.3 Hz, 1 H), 5.28 (d, J = 17.0 Hz, 1 H), 6.39 (dd, J = 10.3, 17.0 Hz, 1 H), 7.31 (d, J = 8.1 Hz, 2 H), 7.70 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.1, −5.0, 18.5, 20.1, 21.6, 26.1, 35.7, 50.2, 54.7, 60.3, 113.9, 127.7, 128.6, 129.4, 131.8, 132.4, 142.2, 143.3; LRMS (EI) m/z 421 (M^+), 406, 364, 289, 274, 91, 75; HRMS (EI) calcd for $C_{22}H_{35}NO_3SiS$ 421.2107, found 421.2119.

(*E*)-1,1-Bis(benzyloxymethyl)-3-(1-methoxycarbonylprop-2-en-1-ylidene)-4-methylcyclopentane (4j). According to the general procedure, a crude product, which was obtained from **1j** (69.9 mg, 0.18 mmol) and Cp*RuCl(cod) (3.4 mg, 0.008 mmol) in toluene (6 mL) at room temperature for 8 h, was purified by column chromatography on silica gel (benzene) to give **4j** (67.3 mg, 89%) as a colorless oil: IR (neat) 1723, 1636, 1098 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (d, J = 7.0 Hz, 3 H), 1.36 (dd, J = 6.8, 13.5 Hz, 1 H), 2.02 (dd, J = 8.6, 13.5 Hz, 1 H), 2.52 (s, 2 H), 2.90−3.00 (m, 1 H), 3.24 (s, 2 H), 3.46 (s, 2 H), 3.74 (s, 3 H), 4.45 (s, 2 H), 4.51 (s, 2 H), 5.16 (d, J = 11.2 Hz, 1 H), 5.20 (d, J = 17.2 Hz, 1 H), 6.44 (dd, J = 11.2, 17.2 Hz, 1 H), 7.23−7.34 (m, 10 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.9, 35.3, 39.2, 39.3, 47.4, 51.5, 72.5, 73.2, 73.3, 74.4, 115.3, 126.2, 127.3, 127.3, 127.4, 128.2, 130.8, 138.7, 157.1, 169.0; LRMS (EI) m/z 420 (M^+), 388, 312, 191, 91; HRMS (EI) calcd for $C_{27}H_{32}O_4$ 420.2300, found 420.2312. Anal. Calcd for $C_{27}H_{32}O_4$: C, 77.11; H, 7.67. Found: C, 77.04; H, 7.87.

(*Z*)-3-(1-Methoxycarbonylprop-2-en-1-ylidene)-4-methyl-1-tosylpyrrolidine (4k). According to the general procedure, a crude product, which was obtained from **1k** (56.0 mg, 0.18 mmol) and Cp*RuCl(cod) (3.5 mg, 0.009 mmol) in toluene (6 mL) at room temperature for 1.5 h, was purified by column chromatography on silica gel (hexane/AcOEt, 10/1) to give **4k** (44.0 mg, 73%) as a colorless oil: IR (neat) 1164, 1217, 1348, 1598, 1715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (d, J = 7.2 Hz, 3 H), 2.43 (s, 3 H), 3.01−3.12 (m, 1 H), 3.04 (d, J = 8.4 Hz, 1 H), 3.29 (d, J = 8.4 Hz, 1 H), 3.77 (s, 3 H), 3.85 (d, J = 17.6 Hz, 1 H), 4.37 (d, J = 17.6 Hz, 1 H), 5.29 (d, J = 11.6 Hz, 1 H), 5.44 (d, J = 17.6 Hz, 1 H), 6.31 (dd, J = 11.6, 17.6 Hz, 1 H), 7.34 (d, J = 8.4 Hz, 2 H), 7.71 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 21.7, 37.0, 51.8, 52.1, 54.1, 118.5, 124.3, 127.7, 129.5, 129.5, 131.8, 143.5, 152.8, 166.4; LRMS (EI) m/z 335 (M^+), 304, 276, 260, 180, 148, 120; HRMS (EI) calcd for $C_{17}H_{21}NO_4S$ 335.1191, found 335.1189.

(*E*)-2-(1-Formylprop-2-en-1-ylidene)-3,8,8-trimethyl-7,9-dioxaspiro[4.5]decane (4l). According to the general procedure, a crude product, which was obtained from **1l** (83.3 mg, 0.37 mmol) and Cp*RuCl(cod) (7.1 mg, 0.019 mmol) in toluene (12.5 mL) at room temperature for 3 h, was purified by column chromatography on silica gel (hexane/AcOEt, 4/1) to give **4l** (66.2 mg, 71%) as a colorless oil: IR (neat) 1682, 1120 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (d, J = 7.2 Hz, 3 H), 1.26 (dd, J = 6.4, 13.6 Hz, 1 H), 1.42 (s, 3 H), 1.44 (s, 3 H), 2.02 (dd, J = 8.4, 13.6 Hz, 1 H), 2.61 (d, J = 18.0 Hz, 1 H), 3.11 (ddq, J = 6.4, 8.4, 7.2 Hz, 1 H), 3.25 (d, J = 18.0 Hz, 1 H), 3.45 (dd, J = 1.2, 11.2 Hz, 1 H), 3.56 (d, J = 11.2 Hz, 1 H), 3.73 (dd, J = 1.2, 11.2 Hz, 1 H), 3.80 (d, J = 11.2 Hz, 1 H), 5.35 (d, J = 11.6 Hz, 1 H), 5.79 (d, J = 17.6 Hz, 1 H), 6.36 (dd, J = 11.6, 17.6 Hz, 1 H), 10.03 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 22.5, 25.2, 36.9, 37.9, 39.5, 41.8, 67.7, 69.4, 97.9, 118.3, 129.2, 130.4, 169.0, 191.1; LRMS (EI) m/z 250 (M^+), 235, 192, 174, 162; HRMS (EI) calcd for $C_{15}H_{22}O_3$ 250.1569, found 250.1560.

Dimethyl (*Z*)-3-allylidene-4-(methoxycarbonylmethyl)cyclopentane-1,1-dicarboxylate (4r). According to the general procedure, a crude product, which was obtained from **1r** (66.1 mg, 0.25 mmol) and Cp*RuCl(cod) (4.7 mg, 0.012 mmol) in toluene (8 mL) at room temperature for 19 h, was purified by column chromatography on silica gel (hexane/AcOEt, 5/1) to give **4r** (52.3 mg, 72%) as a colorless oil.: IR (neat) 1734, 1654, 1601 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.04 (dd, J = 14.0, 5.7 Hz, 1 H), 2.33 (dd, J = 15.7, 10.5 Hz, 1 H), 2.61 (dd, J = 15.7, 4.6 Hz, 1 H), 2.79 (dd, J = 14.0, 8.6 Hz, 1 H), 2.86 (d, J = 16.5 Hz, 1 H), 3.13 (d, J = 16.5 Hz, 1 H), 3.31−3.40 (m, 1 H), 3.68 (s, 3 H), 3.71 (s, 3 H), 3.74 (s, 3 H), 5.06 (d, J = 10.3 Hz, 1 H), 5.12 (d, J = 17.3 Hz, 1 H), 5.99 (d, J = 11.3 Hz, 1 H), 6.39 (ddd, J = 17.3, 11.3, 10.3 Hz, 1 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 36.2, 39.7, 39.9, 41.4, 51.6, 52.8, 58.8, 116.8, 124.1, 132.5, 143.9, 171.6, 171.9, 172.3; LRMS (EI) m/z 296 (M^+), 265, 236, 204, 176, 117; HRMS (EI) calcd for $C_{15}H_{20}O_6$ 296.1260, found 296.1255.

(*E*)-3-Allylidene-4-(methoxycarbonylmethyl)-1-tosylpyrrolidine (4s). According to the general procedure, a crude product, which was obtained from **1s** (85.2 mg, 0.28 mmol) and Cp*RuCl(cod) (5.3 mg, 0.014 mmol) in toluene (9 mL) at room temperature for 3 h, was purified by column chromatography on silica gel (hexane/AcOEt, 5/1) to give **4s** (16.7 mg, 18%) as a colorless oil: IR (neat) 1736, 1598, 1348, 1165 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.38−2.52 (m, 2 H), 2.44 (s, 3 H), 3.07 (dd, J = 9.5, 5.9 Hz, 1 H), 3.29−3.40 (m, 1 H), 3.45 (d, J = 9.5 Hz, 1 H), 3.55 (d, J = 14.9 Hz, 1 H), 3.68 (s, 3 H), 4.08 (d, J = 14.9 Hz, 1 H), 5.12 (d, J = 8.9 Hz, 1 H), 5.16 (d, J = 13.0 Hz, 1 H), 5.91 (d, J = 10.5 Hz, 1 H), 6.29 (ddd, J = 13.0, 10.5, 8.9 Hz, 1 H), 7.33 (d, J = 8.1 Hz, 2 H), 7.70 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.5, 36.9, 37.7, 51.6, 51.9, 53.4, 118.5, 123.8, 127.9, 129.7, 131.9, 132.0, 139.6, 143.9, 172.1; LRMS (EI) m/z 335 (M^+), 304, 262, 180, 155, 120, 91; HRMS (EI) calcd for $C_{17}H_{21}NO_4S$ 335.1191, found 335.1189.

Dimethyl (*Z*)-4-allylidene-3,3-dimethylcyclopentane-1,1-dicarboxylate (4t). According to the general procedure, a crude product, which was obtained from **1t** (67.3 mg, 0.30 mmol) and Cp*RuCl(cod) (11.4 mg, 0.03 mmol) in toluene (10 mL) at 60 °C for 5 h, was purified by column chromatography on silica gel (hexane/Et_2O, 10/1) to give **4t** (38.6 mg, 51%) as a colorless oil: IR (neat) 1737, 1648, 1595 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 6 H), 2.06 (s, 2 H), 2.36 (s, 2 H), 3.72 (s, 6 H), 5.01 (d, J = 9.1 Hz, 1 H), 5.04 (d, J = 15.8 Hz, 1 H), 5.89 (d, J = 11.4 Hz, 1 H), 6.66 (ddd, J = 15.8, 11.4, 9.1 Hz, 1 H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 29.5, 41.5, 43.6, 51.2, 52.7, 58.0, 116.0, 122.9 132.6, 149.7, 172.2; LRMS (EI) m/z 252 (M^+), 221, 192, 177, 160, 133; HRMS (EI) calcd for $C_{14}H_{20}O_4$ 252.1361, found 252.1350. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.80; H, 8.17.

Dimethyl 3-Methylene-4-vinylcyclopentane-1,1-dicarboxylate (9) [Registry No. 109433-02-5]. According to the general procedure, a crude product, which was obtained from **1u** (67.3 mg, 0.30 mmol) and Cp*RuCl(cod) (5.7 mg, 0.015 mmol) in toluene (10 mL) at 60 °C for 5 h, was purified by column chromatography on silica gel (hexane/Et_2O, 10/1) to give an inseparable mixture of **1u** and **9** (56.9 mg, 84% in a ratio of 2.2 to 1). The ratio was determined by ^{1}H NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (m, 1 H), 2.58 (ddd, J = 13.0, 7.7, 1.2 Hz, 1 H), 2.95 (dddd,

J = 17.2, 2.3, 2.3, 2.3 Hz, 1 H), 3.08 (brd, J = 17.2 Hz, 1 H), 3.16 (m, 1 H), 3.73 (s, 3 H), 3.75 (s, 3 H), 4.82 (m, 1 H), 4.90−5.25 (m, 3 H), 5.65 (m, 1 H).

(*E*)-4-Allylidene-3-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (11b). According to the general procedure, a crude product, which was obtained from **10b** (76.4 mg, 0.25 mmol) and Cp*RuCl(cod) (4.7 mg, 0.012 mmol) in toluene (8 mL) at 0 °C for 40 h, was purified by column chromatography on silica gel (hexane/AcOEt, 5/1) to give **11b** (53.9 mg, 64%) as a colorless oil: IR (neat) 733, 1165, 1350, 1598, 1654 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.02 (d, J = 6.8 Hz, 3 H), 2.29 (s, 3 H), 3.12 (qdd, J = 6.8, 6.4, 8.4 Hz, 1 H), 3.37 (dd, J = 8.4, 13.6 Hz, 1 H), 4.11 (dd, J = 6.4, 13.6 Hz, 1 H), 5.12 (d, J = 10.4 Hz, 1 H), 5.17 (d, J = 16.8 Hz, 1 H), 5.99 (d, J = 11.2 Hz, 1 H), 6.33 (ddd, J = 10.4, 11.2, 16.8 Hz, 1 H), 7.09 (d, J = 8.4 Hz, 2 H), 7.15 (ddd, J = 1.2, 8.0, 8.0 Hz, 1 H), 7.23 (ddd, J = 1.6, 8.0, 8.0 Hz, 1 H), 7.38 (dd, J = 1.6, 8.0 Hz, 1 H), 7.45 (d, J = 8.4 Hz, 2 H), 7.55 (dd, J = 1.2, 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 21.5, 31.7, 52.3, 117.9, 124.6, 124.8, 125.8, 125.9, 126.9, 127.7, 129.3, 131.6, 132.1, 136.4, 136.5, 136.8, 143.3; LRMS (EI) m/z 339 (M^+), 274, 184, 168, 154; HRMS (EI) calcd for $C_{20}H_{21}NO_2S$ 339.1293, found 339.1293.

(*Z*)-3-Allylidene-4-methyl-1-tosyl-1,2,3,4-tetrahydroquinoline (11c). According to the general procedure, a crude product, which was obtained from **10c** (80.8 mg, 0.26 mmol) and Cp*RuCl(cod) (4.9 mg, 0.013 mmol) in toluene (8.5 mL) at room temperature for 24 h, was purified by column chromatography on silica gel (hexane/AcOEt, 5/1) to give **11c** (17.8 mg, 20%) as a colorless oil: IR (neat) 1599, 1350, 1164 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.19 (d, J = 7.6 Hz, 3 H), 2.28 (s, 3 H), 3.31 (qd, J = 7.6 Hz, 1 H), 4.04 (d, J = 15.1 Hz, 1 H), 4.52 (d, J = 15.1 Hz, 1 H), 5.10 (d, J = 10.3 Hz, 1 H), 5.15 (d, J = 17.0 Hz, 1 H), 5.75 (d, J = 11.1 Hz, 1 H), 6.21 (ddd, J = 10.3, 11.1, 17.0 Hz, 1 H), 6.99−7.80 (m, 8 H); LRMS (EI) m/z 339 (M^+), 279, 212, 184, 168, 149, 91; HRMS (EI) calcd for $C_{20}H_{21}NO_2S$ 339.1293, found 339.1302.

Dimethyl (*Z*)-3-methyl-4-[(*E*)-4-oxobut-2-enylidene]cyclopentane-1,1-dicarboxylate (12b). A solution of **1b** (38.0 mg, 0.18 mmol), acrylaldehyde (0.12 mL, 1.8 mmol), and Cp*RuCl(cod) (3.4 mg, 0.008 mmol) in toluene (6 mL) was stirred at room temperature for 28 h under Ar (1 atm). After removal of the volatiles, a crude product was purified by column chromatography on silica gel (hexane/AcOEt, 2/1) to give **12b** (12.9 mg, 27%) as a colorless oil: IR (neat) 1265, 1638, 1679, 1734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (d, J = 7.2 Hz, 3 H), 1.97 (dd, J = 6.4, 13.6 Hz, 1 H), 2.79 (dd, J = 9.2, 13.6 Hz, 1 H), 2.96 (d, J = 17.6 Hz, 1 H), 3.11−3.20 (m, 1 H), 3.27 (d, J = 17.6 Hz, 1 H), 3.72 (s, 3 H), 3.76 (s, 3 H), 6.05 (dd, J = 8.0, 15.2 Hz, 1 H), 6.22 (d, J = 12.0 Hz, 1 H), 7.25 (dd, J = 12.0, 15.2 Hz, 1 H), 9.56 (d, J = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 35.4, 41.9, 42.5, 53.0, 59.0, 120.8, 130.3, 147.4, 159.9, 171.2, 171.3, 193.2; LRMS (EI) m/z 266 (M^+), 235, 206, 174, 145; HRMS (EI) calcd for $C_{14}H_{18}O_5$ 266.1154, found 266.1159.

Dimethyl (*Z*)-3-allylidene-4-methylenecyclopentane-1,1-dicarboxylate (16). According to the general procedure, a crude product, which was obtained from **15** (70.9 mg, 0.34 mmol) and Cp*RuCl(cod) (6.5 mg, 0.017 mmol) in toluene (11 mL) at room temperature for 3 h, was purified by column chromatography on silica gel (hexane/AcOEt, 10/1) to give **16** (46.1 mg, 57%) as a colorless oil: IR (neat) 1737, 1642, 1610 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 3.06 (s, 2 H), 3.07 (s, 2 H), 3.73 (s, 6 H), 5.15 (d, J = 10.3 Hz, 1 H), 5.21 (s, 1 H), 5.26 (d, J = 17.0 Hz, 1 H), 5.37 (s, 1 H), 6.11 (d, J = 11.3 Hz, 1 H), 6.89 (ddd, J = 17.0, 11.3, 10.3 Hz, 1 H); ^{13}C NMR (67.8 MHz, C_6D_6) δ 42.9, 43.1, 52.3, 57.6, 112.1, 118.6, 126.5, 133.5, 137.6, 144.5, 171.4; LRMS (EI) m/z 236 (M^+), 176, 117; HRMS (EI) calcd for $C_{13}H_{16}O_4$ 236.1048, found 236.1049.

(4*R,5*R**)-9,9,10,10-Tetracyano-2,2-bis(methoxycarbonyl)-4-methylspiro[4.5]dec-6-ene (18).** A solution of **4b** (47.2 mg, 0.20 mmol) and tetracyanoethylene (128 mg, 1.0 mmol) in toluene (6.5 mL) was refluxed for 23 h. After removal of the solvent, a residue was purified by column chromatography on silica gel (hexane/AcOEt, 3/1) to give **18** (62.3 mg, 85%) as a colorless solid: mp 135−137 °C (recrystallized from AcOEt); IR (film, $CHCl_3$) 2306, 1735, 1266 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (d, J = 6.5 Hz, 3 H), 1.88 (dd, J = 11.6, 13.2 Hz, 1 H), 2.68 (qdd, J = 6.5, 6.8, 11.6 Hz, 1 H), 2.81 (dd, J = 6.8, 13.2 Hz, 1 H), 2.97 (d, J = 16.2 Hz, 1 H), 3.15 (s, 2 H), 3.23 (d, J = 16.2 Hz, 1 H), 3.76 (s, 3 H), 3.79 (s, 3 H), 5.85 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1, 32.4, 38.0, 41.6, 42.9, 45.8, 47.7, 51.4, 53.4, 57.9, 110.0, 110.5, 110.9, 111.1, 117.4, 129.7, 170.4, 170.7; LRMS (EI) m/z 366 (M^+), 335, 307, 275, 172; HRMS (EI) calcd for $C_{19}H_{18}N_4O_4$ 366.1328, found 366.1319.

(1*R,3′*R**)-5,5,6,6,-Tetracyano-3′-methyl-1′-tosyl-2′,3′-dihydro-1′*H*-spiro[cyclohex[2]ene-1,4′-quinoline] (19).** Similar to the synthesis of **18** from **4b**, a crude product, which was obtained from **11b** (26.3 mg, 0.08 mmol) and tetracyanoethylene (49.6 mg, 0.39 mmol) in toluene (2.6 mL) at 110 °C for 13 h, was purified by column chromatography on silica gel (hexane/AcOEt, 1/1) to give **19** (20.7 mg, 57%) as a colorless solid: mp 206−210 °C (recrystallized from AcOEt); IR (film, $CHCl_3$) 2255, 1355, 1168 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (d, J = 7.2 Hz, 3 H), 2.42 (s, 3 H), 2.89 (br, 1 H), 3.19 (d, J = 18.0 Hz, 1 H), 3.27 (d, J = 18.0 Hz, 1 H), 4.15 (d, J = 13.6 Hz, 1 H), 4.41 (d, J = 13.6 Hz, 1 H), 5.98 (d, J = 10.8 Hz, 1 H), 6.18−6.22 (m, 1 H), 7.01 (t, J = 7.6 Hz, 1 H), 7.30−7.38 (m, 4 H), 7.75 (d, J = 8.4 Hz, 1 H), 7.86 (d, J = 8.4 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.8, 21.6, 31.2, 36.4, 38.7, 48.9, 49.3, 49.4, 110.1, 110.2, 110.8, 111.8, 118.3, 121.6, 122.3, 127.2, 130.1, 130.8, 131.3, 132.9, 136.4, 137.0, 144.7; LRMS (EI) m/z 467 (M^+), 339, 312, 184, 168, 91; HRMS (EI) calcd for $C_{26}H_{21}N_5O_2S$ 467.1416, found 467.1414.

Dimethyl (*Z*)-1,1-bis(benzyloxymethyl)-3-methyl-4-(2-propenylidene-1-d)cyclopentane dicarboxylate (4c-D) (Scheme 2). According to the general procedure, a crude product, which was obtained from **1c-D** (100.6 mg, 0.3 mmol) and Cp*RuCl(cod) (5.7 mg, 0.015 mmol) in toluene (10 mL) at room temperature for 24 h, was purified by column chromatography on silica gel (hexane/benzene, 1/1) to give **4c-D** (93.0 mg, 85%) as a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.12 (d, J = 7.2 Hz, 3 H), 1.29 (dd, J = 6.8, 13.6 Hz, 1 H), 1.99 (dd, J = 8.4, 13.6 Hz, 1 H), 2.55 (d, J = 15.6 Hz, 1 H), 2.41 (d, J = 15.6 Hz, 1 H), 2.80−2.89 (m, 1 H), 3.27 (s, 2 H), 3.45 (d, J = 8.8 Hz, 1 H), 3.48 (d, J = 8.8 Hz, 1 H), 4.47 (s, 2 H), 4.52 (s, 2 H), 4.95 (d, J = 10.0 Hz, 1 H), 5.03 (d, J = 16.8 Hz, 1 H), 6.48 (dd, J = 10.0, 16.8 Hz, 1 H), 7.23−7.34 (m, 10 H).

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Supporting Information Available: General information, experimental procedure for the preparation of substrates, and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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