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Studies on Alkyne-Based Transition Metal-Carbene and -Vinylidene Complexes Aimed at Efficient Catalytic Reactions

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2003

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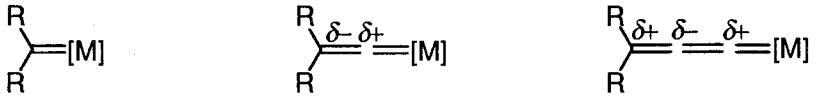
General Introduction

Generation of Carbene, Vinylidene, and Allenylidene Complexes

Carbene complexes, which have formal metal-to-carbon double bonds, are known for metals across the entire transition series (Figure 1).[1] Two extreme types of carbene complexes, $L_nM{=}CR_2$, are represented by (1) Fischer-type carbene complexes which involve low oxidation state late transition metals, π-acceptor ligands, π-donor substituent R on carbene carbon, and $\delta+$ charged electrophilic carbene carbon, (2) Schrock-type carbene complexes which involve high oxidation state early transition metals, non-π-acceptor ligands, non-π-donor R groups, and $\delta-$ charged nucleophilic carbene carbon. The first isolated carbene complexes was characterized by E. O. Fischer in 1964.[2] The first example of Schrock type carbene complex was alkylidene tantalum complexes discovered by R. R. Schrock in 1974.[3] After these landmark discoveries this field has developed very rapidly,

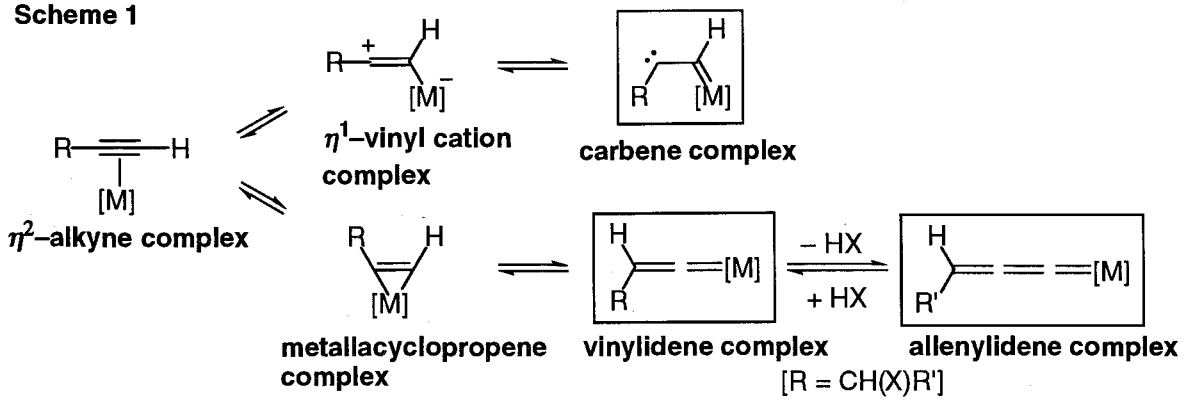


carbene complex **vinylidene complex** **allenylidene complex**

Figure 1. Transition Metal Complexes Having Metal-Carbon Double Bond

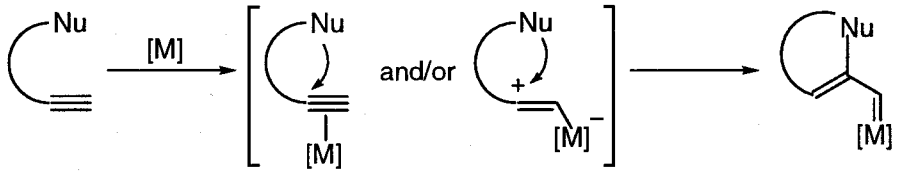
and new varieties of carbene complexes have been widely applied as versatile intermediates or catalysts to a variety of organic unit reactions, total synthesis of natural products, and polymer chemistry.[1] From the 1980s, the *in situ* generation of carbenoid species from diazoalkanes and transition metal complexes has been most widely used for catalytic carbene transfer reactions.[4] Recently, much attention has been paid to activation of alkynes with transition metal complexes as another method to generate carbenoid species. For example, as shown in Scheme 1, it appears reasonable to anticipate that the pre-equilibrium between η^2-alkyne complex and charge sepatrated η^1-vinyl cation complex would be responsible for generation of carbenoid and related species having a metal-carbon double bond from alkynes

Scheme 1



and transition metal compounds. In fact, it has been reported that a reactive carbene complex could be generated via an intramolecular nucleophilic attack of π-electron of alkenes and oxygen or nitrogen atoms to a cationic carbon of η^1-vinyl cation complex and/or an internal carbon of η^2-alkyne complex (Scheme 2).[5-10]

Scheme 2



Vinylidene and allenylidene complexes, in which transition metals stabilize otherwise reactive vinylidene and allenylidene species, are also known for many transition metals (See also Figure 1).[11] The first isolated mononuclear vinylidene-metal complexes were prepared by migration of a chlorine atom from an α-chloroalkenyl ligand with concomitant displacement of carbonyl ligands by a phosphine,[12] although cationic vinylidene intermediates generated by protonation of alkynyl-metal species had so far been proposed.[13] As shown in Scheme 1, the most straightforward route to vinylidene-metal complexes is indebted to 1,2-hydrogen migration from a η^2-alkyne complex[14] or 1,3-shift of a hydride from the metal center to the alkynyl ligand formed by oxidative addition of the alkynyl C-H bond to the metal.[15] A vinylidene complex, which has a suitable functional group for elimination at a propargylic position of the starting alkyne, for example, propargyl alcohol,

could be converted to allenylidene complex.[16] Since facile and useful methods to generate vinylidene and allenylidene complexes from alkynes were discovered, several catalytic reactions via vinylidene and allenylidene species as highly reactive intermediates have been reported to date.[11b,11c,16]

The author focused his attention on the development of new catalytic reactions via transition metal complexes having a metal-carbon double bond (especially carbene and vinylidene complexes) generated from alkynes. The general concept in this thesis is shown in Figure 2: *in situ generation of reactive intermediary carbenoids from alkynes via intramolecular nucleophilic attack of a carbonyl oxygen to the initially formed vinylidene complexes or π-alkyne complexes leading to endo-dig and/or exo-dig cyclizations in which a pair of electrons is accomodated in the cyclic structure through its conjugation.*

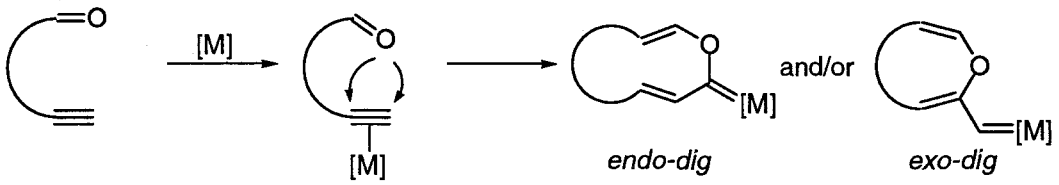
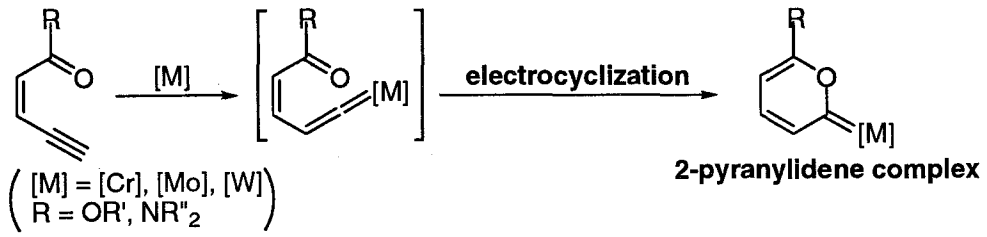


Figure 2. The General Concept for Synthesis of Reactive Intermediary Carbenoids

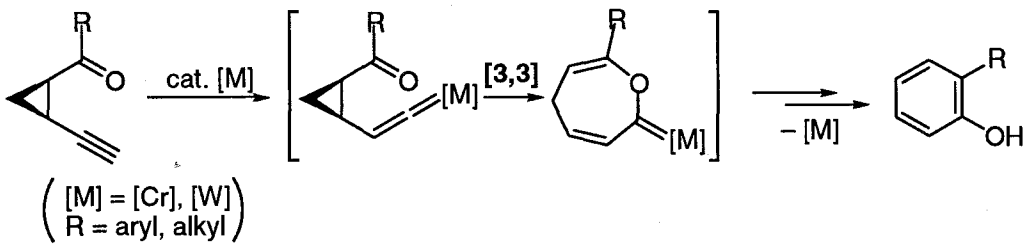
Abstract of This Thesis

This thesis is composed of Parts I-III. Part I, which consists of two chapters, deals with synthesis of 2-pyranylidene complexes via electrocyclization of vinylidene-ene-carbonyl complexes (Chapter 1) (eq 1) and their application to catalytic transformation of ethynylcyclopropanes (Chapter 2) (eq 2). Although many nucleophiles have been known to attack a vinylidene α-carbon in both of stoichiometric and catalytic reactions, few attentions have been paid for carbonyl oxygen as a nucleophile.[11] The author first has demonstrated this concept in preparing cyclic Fischer-type carbene complexes[17] which lead to arene derivatives by further transformation.[18] This success stimulated him to make further efforts to investigate catalytic reactions using cyclic carbene complexes as intermediates. As shown in Chapter 2, the author has described the valence isomerism of 1-acyl-2-

ethynylcyclopropanes via [3,3]sigmatropy of cyclopropanes involving a vinylidene-metal moiety as a vinylogous function.[19]

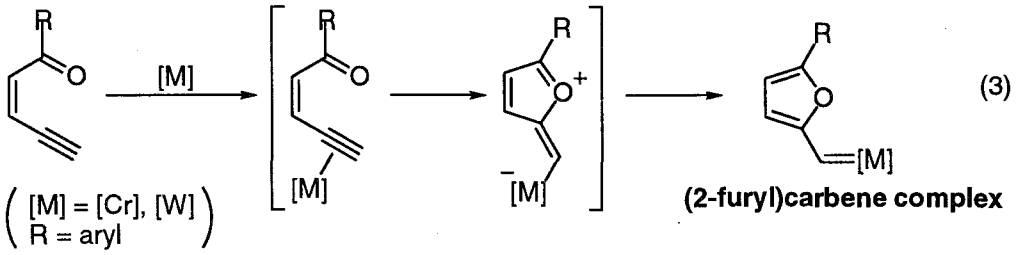


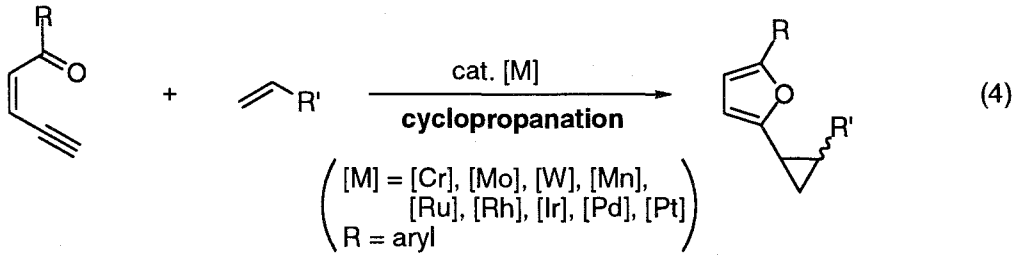
(1)



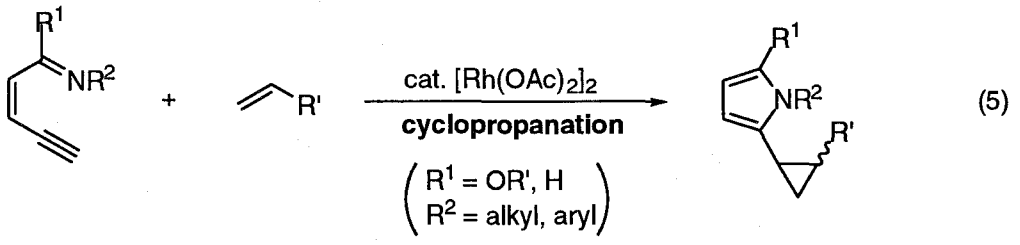
(2)

The author has next described the *in situ* generation of carbene complexes from ene-yne-carbonyl and -imino compounds, and their application to catalytic carbene transfer reactions in Part II which consists of Chapters 3-8. The *in situ* generation of carbenoid species from diazoalkanes with transition metal complexes has been well documented and the species are most applicable to various carbene transfer reactions.[1,20] As mentioned above, activation of alkynes with transition metal complexes to generate carbenoid species is a powerful alternative method for catalytic carbene transfer reactions involving carbenoid intermediates. The author newly disclosed the formation of (2-furyl)carbene complexes generatred *in situ* from ene-yne-ketones by nucleophilic attack of a carbonyl oxygen at an internal alkyne carbon activated by group 6 transition metal complexes (Chapter 3) (eq 3). The generation of (2-furyl)carbenoids led him to find the group 6 transition metal-catalyzed cyclopropanation reaction of alkenes with ene-yne-ketones leading to furylcyclopropanes (Chapter 4) (eq 4). Transition metal compounds which have been widely accepted as effective catalysts for cyclization and skeletal reorganization of 1,6-enynes proved to be effective for the present catalytic cyclopropanation reactions.[5,6]



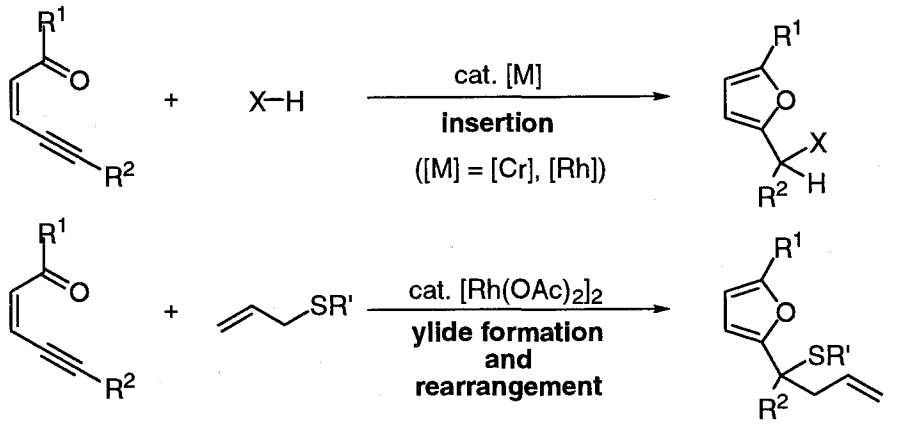


In Chapter 5, the author has described the rhodium-catalyzed cyclopropanation via the formation of (2-pyrrolyl)carbenoid as a nitrogen analogue of (2-furyl)carbenoid (eq 5). The key intermediate of this cyclopropanation is (2-pyrrolyl)carbenoids generated by the nucleophilic attack of an imine nitrogen atom to an internal alkyne carbon activated by the rhodium complex.[8c,9,21,22] Similar cyclopropanation reactions with ene-yne-esters and -amides were unsuccessful (Chapter 1) (eq 1), while the reactions of ene-yne-imino ethers, which are structual isomers of ene-yne-amides, gave 2-pyrrolylcyclopropanes.



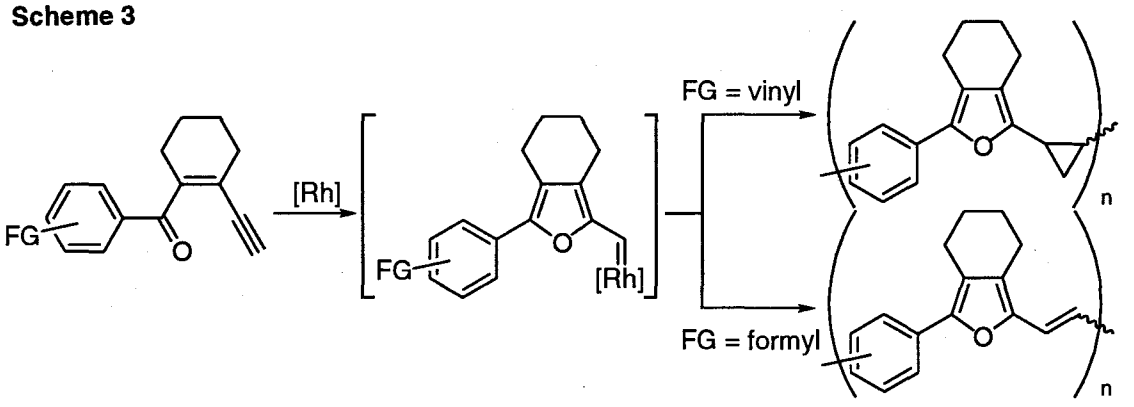
(2-Furyl)carbenoids generated *in situ* from ene-yne-ketones are also useful intermediates for other (2-furyl)carbene transfer reactions, such as σ-bond insertion reactions and ylide formation reactions, as shown in Chapters 6 and 7, respectively.[4] In these cases, ene-yne-carbonyl compounds having an electron-withdrawing group R^2, which could be anticipated to enhance the electrophilicity of intermediary carbenoid species to carbene

acceptors, reacted efficiently rather than ene-yne-ketones having terminal alkynes to give carbenoid-insertion products (eqs 6 and 7).



In Chapter 8, the author has described results of application of the (2-furyl)carbene transfer reactions to polymer synthesis.[23] As shown in Scheme 3, the rhodium-catalyzed polymerizations of ene-yne-ketones having suitable functionalities on phenyl ring as carbene acceptors gave furylcyclopropane- and furfurylidene-containing polymers. Unique structures of alternating copolymers having regularly embedded furylcyclopropanes or furfurylidenes would attract a great deal of interest in polymer chemistry.

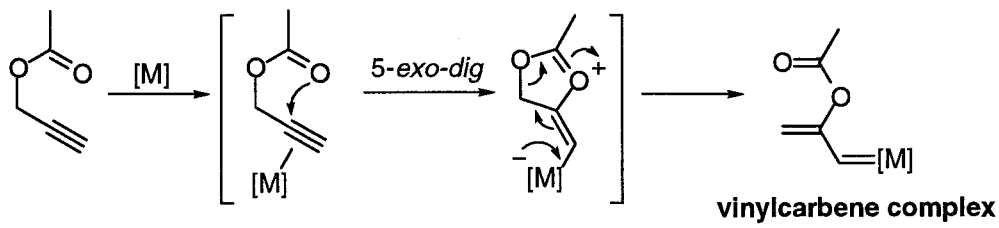
Scheme 3



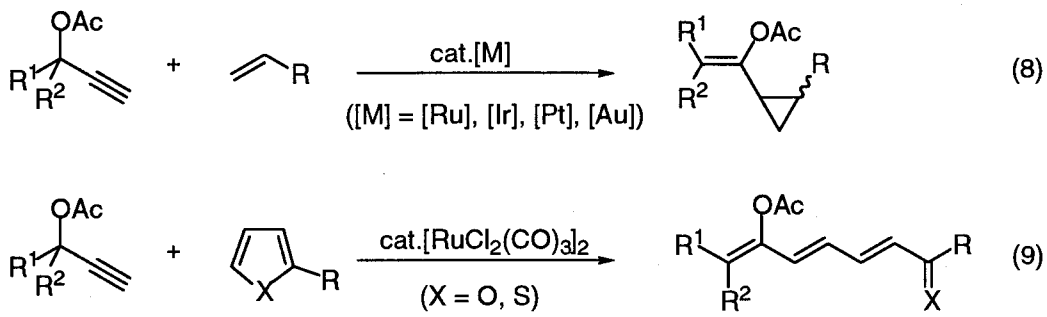
The author has finally described the catalytic reactions using propargylic carboxylates as vinylcarbenoid precursors (Part III). The author extended the principle of 5-*exo-dig*

cyclization mode of yne-carbonyl compounds activated by transition metals to the propargylic carboxylates, and succeeded in generation of vinylcarbenoids (Scheme 4). In Chapter 9, the

Scheme 4



author has demonstrated an efficient intermolecular catalytic cyclopropanation between alkenes and propargylic acetates for the first time (eq 8). In Chapter 10, the catalytic vinylcarbenoid transfer reactions to heteroaromatic compounds has been described (eq 9).[24]



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(23) Ring-opening metathesis polymerization (ROMP) and acyclic-diene metathesis polymerization (ADMET) are quite useful methods for polymerization via carbene intermediates. For recent reviews on ROMP, see: (a) Grubbs, R. H.; Khosravi, E. *Mater. Sci. Technol.* **1999**, *20*, 65. (b) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565.

For recent reports on ADMET, see: (c) Sworen, J. C.; Smith, J. A.; Wagener, K. B.; Baugh, L. S.; Rucker, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 2228. (d) Church, A. C.; Pawlow, J. H.; Wagener, K. B. *Macromolecules* **2002**, *35*, 5746. (e) Lehman, S. E.; Wagener, K. B. *Macromolecules* **2002**, *35*, 48 and references therein.

(24) Similar reactions using diazoalkanes with transition metal complexes as carbenoid precursors have been reported. See: (a) Wenkert, E.; Alonso, M. E.; Gottlieb, H. E.; Sanchez, E. L.; Pellicciari, R.; Cogolli, P. *J. Org. Chem.* **1977**, *42*, 3945. (b) Wenkert, E.; Guo, M.; Lavilla, R.; Porter, B.; Ramachandran, K.; Sheu, J.-H. *J. Org. Chem.* **1990**, *55*, 6203. (c) Wenkert, E.; Khatuya, H. *Helv. Chim. Acta* **1999**, *82*, 551. (d) Shieh, P. C.; Ong, C. W. *Tetrahedron* **2001**, *57*, 7303.

Part I

Generation of Cyclic Fischer-Type Carbene Complexes from Vinylidene Complexes and Their Application to Catalytic Reactions

Chapter 1

Synthesis of 2-Pyranylidene Complexes from Conjugated Ene-Yne-Carbonyl Compounds with Group 6 Transition Metal Complexes

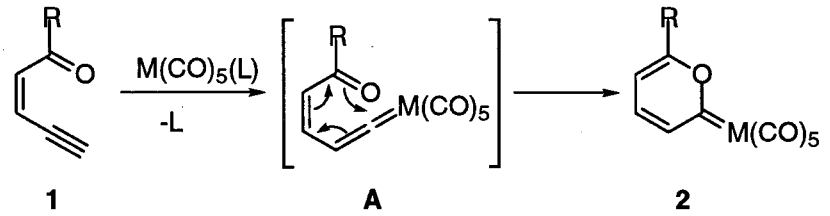
Abstract

The reaction of conjugated ene-yne-carbonyl compounds, such as 1-alkoxycarbonyl or 1-carbamoyl-2-ethynylcycloalkenes, with $Cr(CO)_5(THF)$, $Mo(CO)_5(NEt_3)$, or $W(CO)_5(THF)$ gave the corresponding 6-alkoxy- and 6-amino-2*H*-pyranylidene-chromium, -molybdenum, or -tungsten complex, respectively. A cycloisomerization reaction of the conjugated vinylidene-ene-carbonyl complexes generated from 1-alkoxycarbonyl- or 1-carbamoyl-2-ethynylcycloalkenes and transition metal complexes is a key route to these Fischer-type carbene complexes. The crystal structure of 6-methoxy-2*H*-pyranylidene-tungsten complex **2b** has been determined by X-ray diffraction. New pyranylidene complexes undergo [4 + 2] cycloaddition reaction with acetylenes to give aromatic rings together with the liberation of metal hexacarbonyls.

Introduction

Transition metal carbene complexes, especially Fischer-type carbene complexes, have been widely studied and applied to organic syntheses as versatile organometallic reagents.[1,2] Typical carbene complexes like $(CO)_5M{=}C(OR')R$ are readily prepared by the reaction of the metal hexacarbonyl with a range of organolithium reagents. It has also been demonstrated that nucleophilic addition of an alcoholic O-H bond to the α- and β-carbons of a vinylidene complex ($M{=}C_\alpha{=}C_\beta$, M = Cr, Mo, W) generated from an ω-alkynol provides new access to carbene complexes as intermediates in catalytic reactions and isolable intermediates in stoichiometric reactions.[3-5] The author describes herein a new approach for 2-pyranylidene complex **2** as a group 6 transition metal cyclic carbene compelx via vinylidene-ene-carbonyl complex (**A**) produced from the conjugated compound **1** (Scheme 1).[6,7]

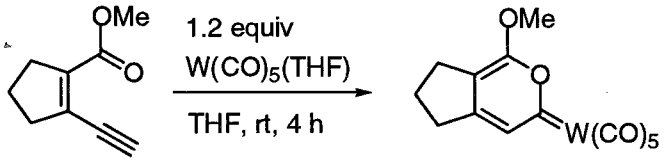
Scheme 1



The structure of **2** represents the α-metalo analogue of α-pyrone.[8] Although the reactivity as well as the structural feature is of much interest, the studies on 2-pyranylidene complexes are still limited.[9,10] Thus, he also describes synthetic application of these 2-pyranylidene compelxes **2** as an enophile to [4 + 2] cycloaddition.

Results and Discussion

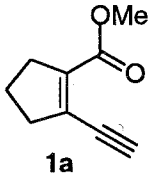
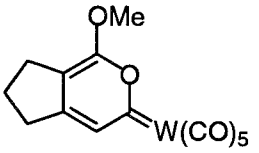
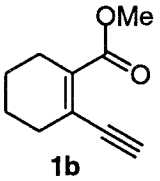
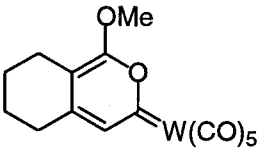
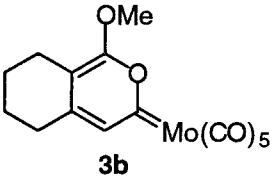
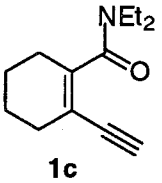
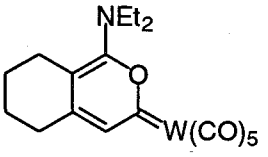
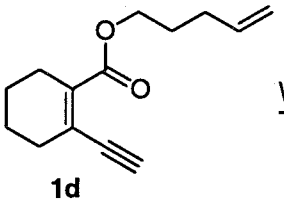
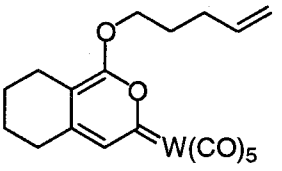
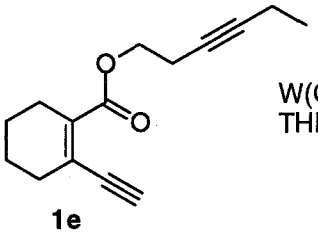
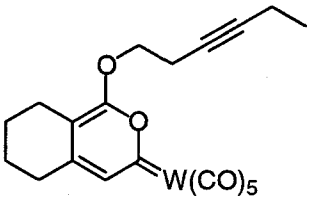
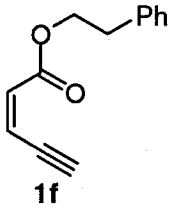
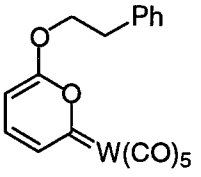
As a first attempt to investigate the idea described above, the author undertook reactions of conjugated ene-yne-carbonyl compounds with group 6 metal complexes, which are capable of the formation of stable Fischer-type carbene complexes. When 2-ethynyl-1-methoxycarbonylcyclopent-1-ene (**1a**) (0.5 mmol) was treated with 1.2 equiv of preformed $W(CO)_5(THF)$[11] at room temperature, the corresponding 2-pyranylidene-tungsten complex **2a** was isolated in 38% yield (eq 1). The compelx **2a** is stable enough to be purified by silica



1a **2a** (38%) (1)

gel column chromatography. The reaction condition was further optimized and the generality of the reaction of ene-yne-carbonyl compounds with group 6 metal carbonyl complexes was examined. Results are shown in Table 1. Reactions of **1a** with an excess amount of $W(CO)_5(THF)$ gave better yields of **2a**, in 51% (2.0 equiv of W) and 75% (3.0 equiv of W), respectively (entries 2 and 3). Although the condition under THF reflux was required, the reaction of 2-ethynyl-1-methoxycarbonylcyclohex-1-ene (**1b**) with $W(CO)_5(THF)$ was complete within 0.5 h to give the corresponding 2-pyranylidene-tungsten complex **2b** in 63% yield as well (entry 4). Similar 2-pyranylidene-molybdenum complex **3b** was obtained in 35% yield from **1b** and preformed $Mo(CO)_5(NEt_3)$[12] (entry 5). An amide compound, 2-ethynyl-1-(*N*,*N*-diethylcarbamoyl)cyclohex-1-ene (**1c**), also reacted with $W(CO)_5(THF)$ at reflux temperature in THF to give 6-(*N*,*N*-diethylamino)pyranylidene complex **2c** in 68% yield (entry 6). The formation of 2-pyranylidene-tungsten complexes, **2d** and **2e** from **1d** and **1e**, demonstrated the tolerance of an ω-alkenyl or an internal alkynyl moiety in the substrate (entries 7 and 8). The simplest substrate, 2-phenylethyl (*Z*)-pent-2-en-4-ynoate (**1f**) was

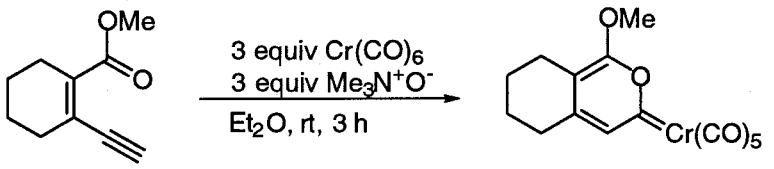
Table 1. Preparation of Pyranylidene-Metal Complexes from Conjugated Ene-Yne-Carbonyl Compounds and Group 6 Metal Complexes.[a]

entry	substrate	conditions[b]	product	isolated yield
1	 **1a**	$W(CO)_5(THF)$ (1.2 equiv) THF, rt, 4 h	 **2a**	38%
2	**1a**	$W(CO)_5(THF)$ (2.0 equiv) THF, rt, 4 h	**2a**	51%
3	**1a**	$W(CO)_5(THF)$ (3.0 equiv) THF, rt, 4 h	**2a**	75%
4	 **1b**	$W(CO)_5(THF)$ (2.0 equiv) THF, reflux, 0.5 h	 **2b**	63%
5	**1b**	$Mo(CO)_5(NEt_3)$ (1.2 equiv) Et_2O, Et_3N, rt, 3 h	 **3b**	35%
6	 **1c**	$W(CO)_5(THF)$ (3.0 equiv) THF, reflux, 0.5 h	 **2c**	68%
7	 **1d**	$W(CO)_5(THF)$ (3.0 equiv) THF, reflux, 0.5 h	 **2d**	55%
8	 **1e**	$W(CO)_5(THF)$ (2.0 equiv) THF, reflux, 0.5 h	 **2e**	71%
9	 **1f**	$W(CO)_5(THF)$ (3.0 equiv) THF, reflux, 0.5 h	 **2f**	58%

[a] Reactions were carried out with **1** (0.2-0.5 mmol) under Ar. [b] The solution of $M(CO)_5(L)$ was prepared by irradiating a THF or Et_2O solution of $M(CO)_6$ for 4 h with a high-pressure Hg lamp (450 W).

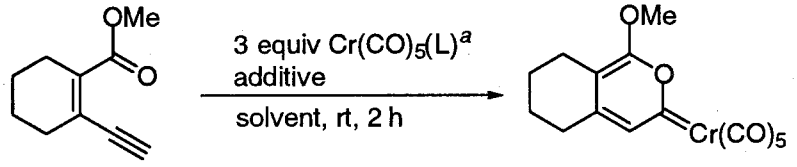
reacted with $W(CO)_5(THF)$ to give 6-(2-phenylethoxy)pyranylidene-tungsten complex **2f** in 58% yield (entry 9).

Next, the author examined the preparation of 2-pyranylidene-chromium complexes from $Cr(CO)_5(L)$ (L = OEt_2, THF), which was prepared by photo-irradiation, but the same procedure using $W(CO)_5(THF)$ was unsuccessful. When the reaction with these chromium complexes was examined in more detail, it was found that the reaction of ene-yne-carbonyl compounds **1b** with $Cr(CO)_5(NMe_3)$, prepared from $Cr(CO)_6$ and $Me_3N^+O^-$, gave 2-pyranylidene-chromium complex **4b** in 9% yield (eq 2). The author considered that trimethylamine, which is generated from the reaction between $Cr(CO)_6$ and $Me_3N^+O^-$, might play some role in the formation of the pyranylidene complex. Then, he tried the reaction using an amine as an additive (Table 2). Although the reaction of **1b** with $Cr(CO)_5(OEt_2)$ in the absence of triethylamine gave none of **4b**, the reaction proceeded in the presence of triethylamine to give the complex **4b** in 27% isolated yield together with the recovered **1b**



1b **4b** (9% yield) (2)

Table 2. Preparation of 2-pyranylidene-chromium Complex **4b**

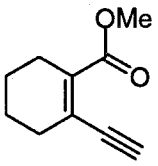
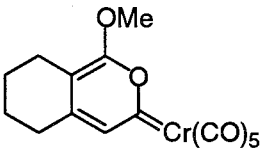
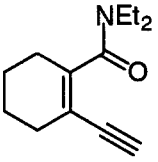
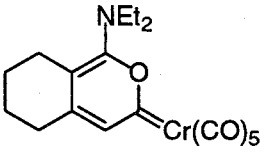
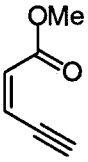
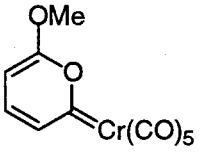
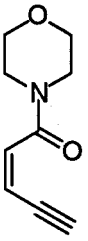
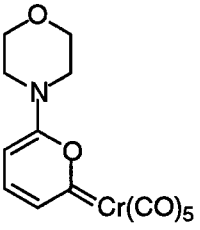
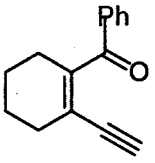
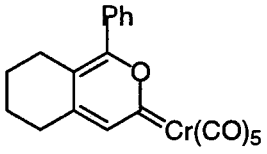


1b (0.2 mmol) **4b**

solvent	additive	isolated yield (%)
Et_2O (30 mL)	—	—
Et_2O (30 mL)	Et_3N (0.1 mL)	27
THF (20 mL)	Et_3N (0.1 mL)	62

[a] The solution of $Cr(CO)_5(L)$ was prepared by irradiating $Cr(CO)_6$ in Et_2O or THF for 4 h with a high-pressure Hg lamp (450 W).

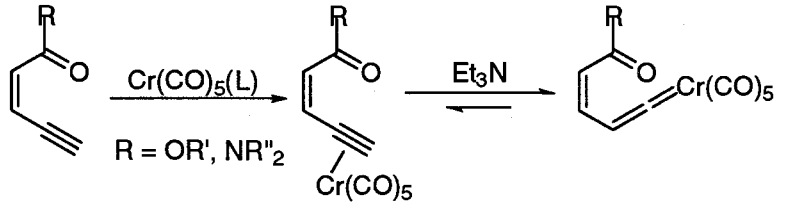
Table 3. Preparation of Pyranylidene-chromium Complexes from Conjugated Ene-yne-carbonyl Compounds and $Cr(CO)_5(L)$[a, b]

entry	1	product	isolatedyield
1[c]	 **1b**	 **4b**	15%
2[d]	**1b**	**4b**	33%
3	**1b**	**4b**	62%
4[e]	 **1c**	 **4c**	68%
5[e]	 **1g**	 **4g**	69%
6[e]	 **1h**	 **4h**	50%
7[e,f]	 **1i**	 **4i**	8%

[a] Reactions were carried out with **1** (0.2 mmol) at room temperature for 2 h under Ar. [b] The solution of $Cr(CO)_5(L)$ was prepared by irradiating a solution of $Cr(CO)_6$ (0.6 mmol) and triethylamine (0.1 mL) in THF (20 mL) for 4 h with a high–pressure Hg lamp (450 W). [c] **1b** (0.5 mmol). [d] **1b** (0.3 mmol). [e] Reaction time was 0.5 h. [f] **1i** (0.6 mmol) and triethylamine (1.0 mL) were used.

(30-50%). The use of THF instead of Et_2O as a solvent gave better yield of **4b**. The reactions of other substrates with $Cr(CO)_5(THF)$ in the presence of triethylamine were next examined. Selected results are shown in Table 3. Reactions of **1b** with a lesser amount of $Cr(CO)_5(THF)$ gave lower yields of **4b** in 15% (1.2 equiv of Cr) and 33% (2.0 equiv of Cr), respectively (entries 1 and 2). The reaction of an amide **1c** with $Cr(CO)_5(THF)$ at room temperature for 0.5 h also gave the corresponding 2-pyranylidene-chromium complex **4c** in 68% yield (entry 4). An ester **1g** and an amide **1h** gave similar complexes **4g** and **4h** in 69% and 50% yields, repectively (entries 5 and 6). However, when the reaction of ene-yne-ketone **1i** instead of ene-yne-ester or -amide with chromium complex was examined in the presence of triethylamine, the corresponding 2-pyranylidene-chromium complex **4i** was obtained in only 8% yield together with many unidentified products (entry 7). This result indicates that ene-yne-ketones are not suitable for synthesis of 2-pyranylidene complexes. [In the case of reactions of ene-yene-ketones without triethylamine, different reaction mode has been found and it will be discussed in Chapter 3.] At present, he assumes that triethylamine facilitates formation of a vinylidene-chromium intermediate from a π-alkyne-chromium complex (Scheme 2).[7b]

Scheme 2



These are all new α,γ-dienyl Fischer-type carbene complexes, the structure of one of them being unambiguously determined by X-ray diffraction. An ORTEP drawing of the complex **2b** is shown in Figure 1. The W(1)-C(1) bond length (2.215(6) Å) is almost similar to the W-C(carbene) bond (2.02-2.22 Å) in typical tungsten-oxacarbene complex.[13] The C(1)-O(1) bond length of 1.430(7) Å indicates the lack of multiple bonding between pyrane

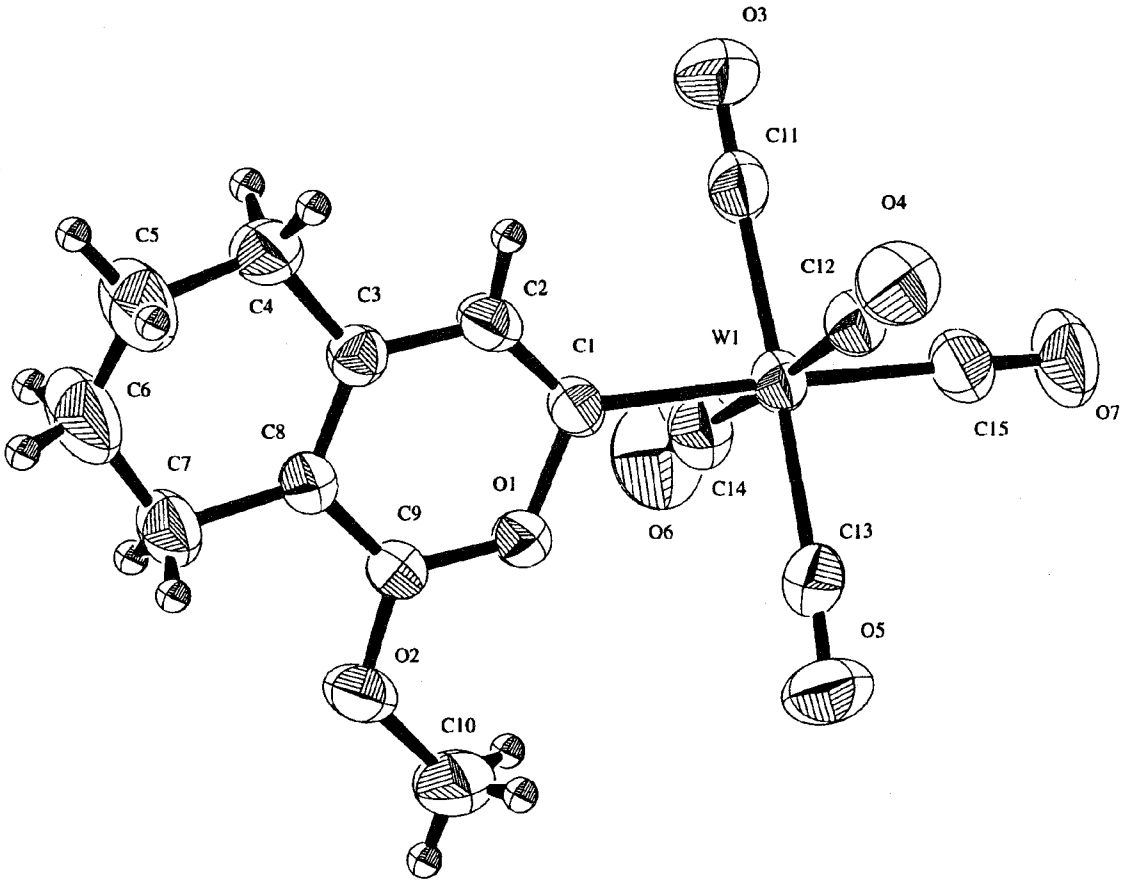
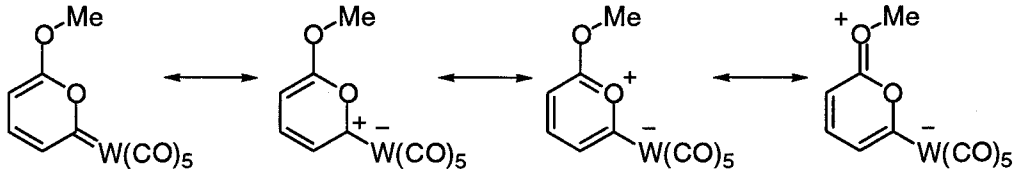


Figure 1. ORTEP drawing of the complex **2b**. Selected bond lengths (Å): W(1)-C(1) = 2.215(6), C(1)-C(2) = 1.362(9), C(1)-O(1) = 1.430(7), C(2)-C(3) = 1.404(8), C(3)-C(8) = 1.383(8), C(8)-C(9) = 1.382(9), C(9)-O(1) = 1.321(7), C(9)-O(2) = 1.316(7).

oxygen and the carbene carbon, otherwise in typical oxacarbene complex C(carbene)-O(1) bond length being in the range of 1.30-1.35 Å.[13,14] The O(1)-C(9) bond length of 1.321(7) Å as well as that of C(9)-O(2) bond of 1.316(7) Å indicates substantial multiple bonding in the complex **2b**. ^{13}C NMR chemical shifts of carbene carbons of the complexes **2** were all observed in the higher-field of 220-236 ppm compared with those observed in 321-347 ppm of typical carbene complex.[13] These data strongly support the contribution of the resonance structures shown in Scheme 3.

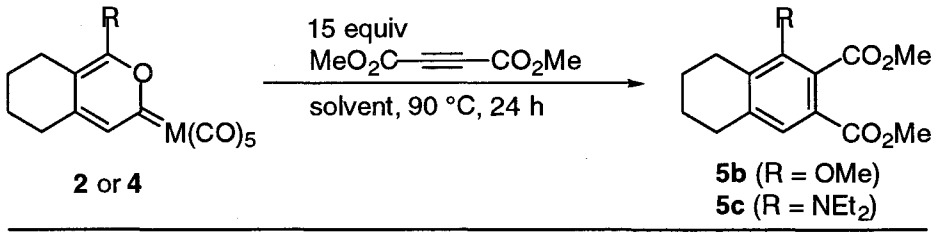
Scheme 3



2

The structure of pyranylidene complexes represents α-metalopyrone. Therefore, the author envisaged cycloaddition reaction of these 2-pyranylidene complexes with dienophiles. The reaction of 2-pyranylidene-tungsten complex **2b** with an excess amount of dimethyl acetylenedicarboxylate (DMAD, 15 equiv) gave the tetralin derivative **5b** in 27% isolated yield (Table 4, entry 1). The complex **2c** also reacted with DMAD to give the corresponding tetralin derivative **5c** in 25% yield (entry 2). The tetralin derivatives **5b** and **5c** were also obtained from similar chromium complexes **4b** and **4c** in 26% and 25% yields, respectively (entries 3 and 4). The use of solvent, such as toluene, did not positively affect the reaction.

Table 4. Reaction of Pyranylidene Complex with Dimethylacetylene Dicarboxylate



2 or **4**

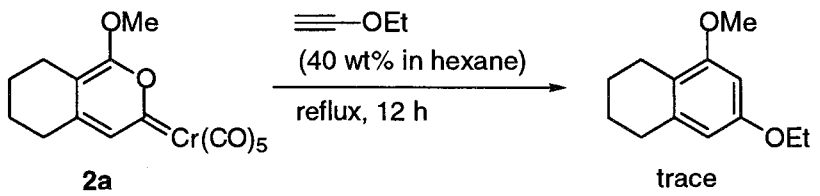
5b (R = OMe)
5c (R = NEt_2)

entry	substrate	solvent	product	yield (%)[a]
1	**2b**	—	**5b**	27
2	**2c**	—	**5c**	25
3	**4b**	—	**5b**	26
4	**4c**	—	**5c**	25
5	**4b**	toluene	**5b**	9
6	**4b**	dioxane	**5b**	0
7	**4b**	DMSO	**5b**	0[b]

[a] Isolated yield. [b] An enyne carbonyl compound **1b** was obtained in 59% yield.

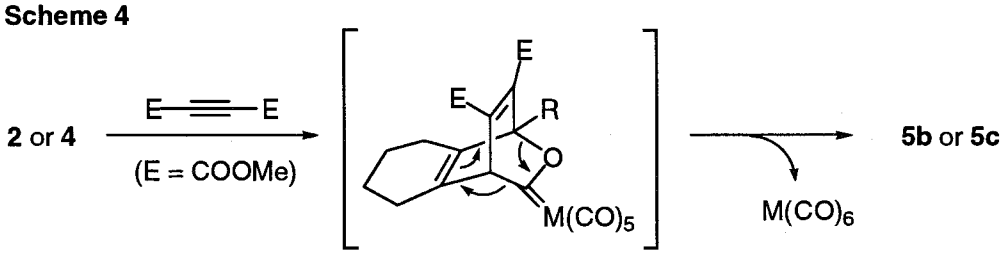
The reaction in DMSO resulted in demetallation leading to the formation of the compound **1b** in 59% yield (entry 7). However, the reaction of **4b** with an electron-rich dienophile, such as ethyl ethynyl ether gave only a trace amount of tetralin derivative as one isomer (eq 3). The transformation was explained by assuming [4 + 2] cycloaddition reaction between 2-pyranylidene complex and the acetylene followed by a pericyclic demetallation of group 6

metal hexacarbonyl (Scheme 4). The demetallation step is quite similar to decarboxylation step in the [4 + 2] cycloaddition of α-pyrone.



(3)

Scheme 4



In conclusion, the author demonstrated that a nucleophilic attack of a carbonyl oxygen to a vinylidene-metal intermediate generated from terminal acetylenes and group 6 metal carbonyl complexes provides new entry to a pyranylidene-metal complex. Further, he disclosed the reactivity of newly prepared 2-pyranylidene complexes in a [4 + 2] cycloaddition. Considering the facile formation of a vinylidene-metal complex from a terminal alkyne and the regeneration of a metal hexacarbonyl with [4 + 2] cycloaddition, this reaction protocol will be applicable to catalytic reactions.

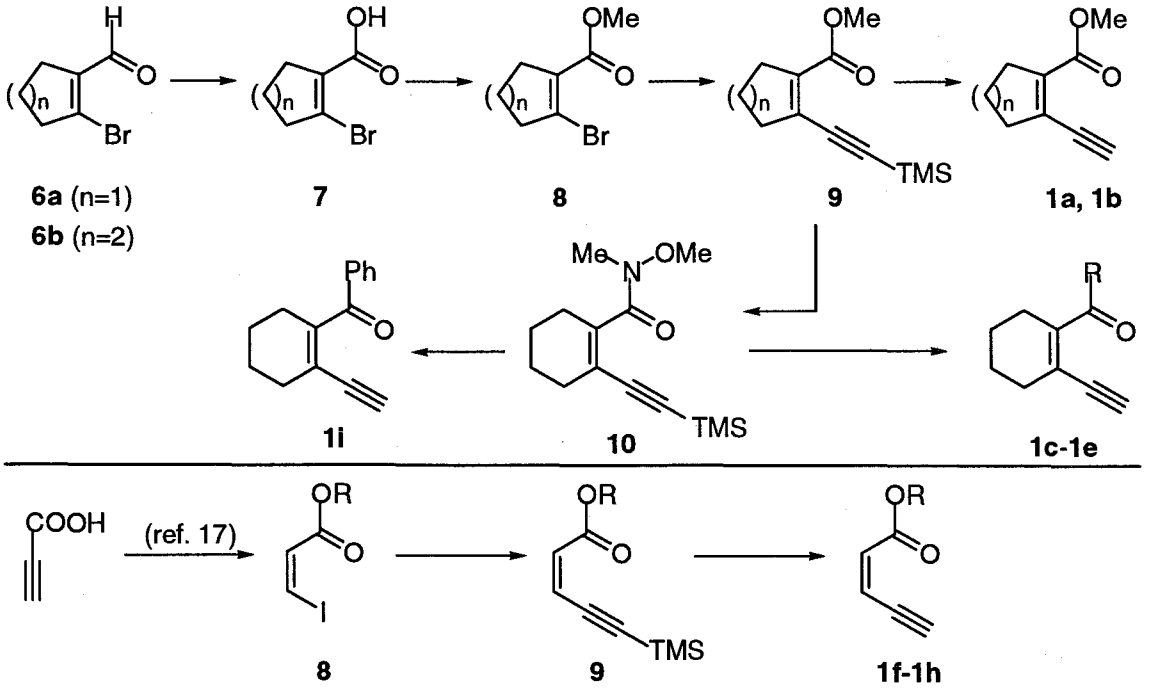
Experimental

General Procedure. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl under argon. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies were performed with Merck silica gel 60. The NMR spectra were measured for solutions in $CDCl_3$ or d_8-THF 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. IR spectra were recorded on an FT-IR spectrometer. Melting points are uncorrected. High-resolution mass spectra (FAB HRMS) and low-resolution mass spectra (FAB LRMS) were obtained with JEOL LMX-SX 102A spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University.

Synthesis of Substrates

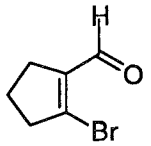
Substrates **1** were prepared by the procedures shown in Scheme 5.

Scheme 5



Typical Procedure for Preparation of Aldehyde 6.[15]

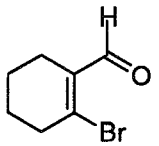
2-Bromo-1-cyclopentenecarbaldehyde (6a).



6a

To a mixture of DMF (50 mL) and $CHCl_3$ (100 mL) was slowly added PBr_3 (11.6 mL, 120 mmol) at 0 °C under N_2. The pale yellow slurry was stirred at room temperature for 2 h. A solution of cyclopentanone (8.8 mL, 100 mmol) in $CHCl_3$ (10 mL) was added dropwise to the above slurry at reflux temperature. The mixture was stirred at this temperature for 2 h, cooled to room temperature, poured into 1 N KOH aqueous solution (100 mL), and extracted with Et_2O (200 mL x 3). The extract was dried over $MgSO_4$. The organic sovlent was removed under reduced pressure, and the residue was subjected to short column chromatography on SiO_2 with hexane/AcOEt (v/v=5/1) to afford **6a** (8.8 g, 50 mmol, 50% yield) as a colorless liquid; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.70-1.74 (m, 4H), 2.41-2.45 (m, 2H), 2.60-2.66 (m, 2H), 10.97 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 21.3, 23.9, 28.6, 38.0, 129.4, 129.6, 172.2.

2-Bromo-1-cyclohexenecarbaldehyde (6b).

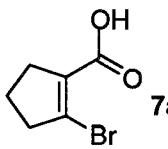


6b

A colorless liquid (45% yield); ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.61-1.82 (m, 4H), 2.24-2.32 (m, 2H), 2.70-2.78 (m, 2H), 10.01 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.1, 24.2, 25.0, 38.8, 135.2, 143.6, 193.7.

Typical Procedure for Preparation of Carboxylic Acid 7.[16]

2-Bromo-1-cyclopentenecarboxylic acid (7a).

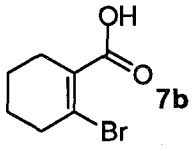


7a

A solution of $NaClO_2$ (80% purity, 3.2 g, 28 mmol) in water (30 mL) was added dropwise to a stirred mixture of **6a** (3.5 g, 20 mmol) in CH_3CN (20 mL), NaH_2PO_4 (0.64 g) in water (10 mL), and 30% aqueous H_2O_2 (2.4 mL), keeping the temperature at 10 °C with water cooling. Oxygen evolved from the solution was monitored until the end of the reaction (about 2 h) with a bubbler connected to the apparatus. The mixture was poured into saturated Na_2CO_3 aqueous solution (50 mL),

and washed with Et_2O (30 mL). The aqueous phase was poured into 1 N HCl solution (200 mL), and extracted with Et_2O (50 mL x 3). The extract was dried over $MgSO_4$. The organic solvent was removed under reduced pressure to afford **7a** (2.9 g, 15 mmol, 76% yield) as a white solid; mp 119.5-120.9 °C; IR (KBr) 1670 (C=C), 1682 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.98 (quint, J = 7.8 Hz, 2H), 2.63-2.70 (m, 2H), 2.81-2.87 (m, 2H), 7.52-10.25 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.6, 32.8, 43.5, 131.4, 135.6, 169.2. Anal. Calcd for $C_6H_7BrO_2$: C, 37.73; H, 3.69. Found: C, 37.46; H, 3.65.

2-Bromo-1-cyclohexenecarboxylic acid (7b).

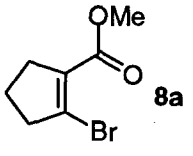


7b

A white solid (92% yield); mp 98.8-100.9 °C; IR (KBr) 1624 (C=C), 1690 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.70-1.74 (m, 4H), 2.41-2.45 (m, 2H), 2.60-2.66 (m, 2H), 10.97 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 21.3, 23.9, 28.6, 38.0, 129.4, 129.6, 172.2. Anal. Calcd for $C_7H_9BrO_2$: C, 41.00; H, 4.42. Found: C, 40.84; H, 4.29.

Typical Procedure for Esterification with Diazomethane. Diazomethane gas, which was generated from *N*-methyl-*N*-nitrosourea, was flowed into an etheral solution of the carboxylic acid. The solvent was removed under reduced pressure to afford a colorless liquid of the methyl ester, quantitatively.

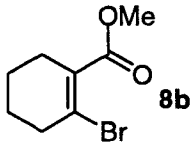
Methyl 2-bromo-1-cyclopentenecarboxylate (8a).



8a

A colorless liquid (100% yield); IR (neat) 1712 (C=C), 1716 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.95 (quint, J = 7.8 Hz, 2H), 2.60-2.65 (m, 2H), 2.77-2.82 (m, 2H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.6, 33.0, 43.0, 51.5, 131.7, 132.5, 164.5. Anal. Calcd for $C_6H_7BrO_2$: C, 41.00; H, 4.42. Found: C, 40.70; H, 4.25.

Methyl 2-bromo-1-cyclohexenecarboxylate (8b).



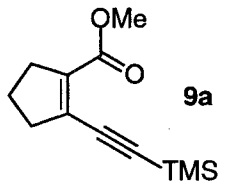
8b

A colorless liquid (100% yield); IR (neat) 1732 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.68-1.72 (m, 4H), 2.32-3.38 (m, 2H), 2.55-2.61

(m, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 21.3, 23.9, 28.7, 37.0, 51.9, 126.0, 130.8, 168.3. Anal. Calcd for $C_8H_{11}BrO_2$: C, 43.86; H, 5.06. Found: C, 43.93; H, 4.98.

Typical Procedure for Coupling Reaction of 8 with Trimethylsilylacetylene.

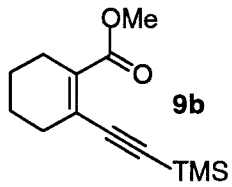
Methyl 2-(trimethylsilylethynyl)-1-cyclopentenecarboxylate (9a).



9a

To a solution of trimethylsilylacetylene (0.50 mL, 3.5 mmol) in benzene (4 mL) were added *n*-$BuNH_2$ (1.7 mL) and **8a** (0.61 g, 3.0 mmol) at room temperature under N_2. To the solution were added CuI (0.10 g, 0.50 mmol) and then $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol). The mixture was stirred at room temperature for 2 h. The organic phase was washed with brine (10 mL), and the aqueous phase was extracted with Et_2O (20 mL x 2). The combined organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=10/1) to afford **9a** (0.49 g, 2.2 mmol, 73% yield) as a colorless liquid; IR (neat) 1705 (C=C), 1726 (C=O), 2144 (C≡C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.21 (s, 9H), 1.89 (quint, J = 7.8 Hz, 2H), 2.60-2.70 (m, 2H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ -0.2, 22.2, 33.3, 39.3, 100.5, 106.0, 134.2, 139.2, 164.8. Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 64.82; H, 8.16. Found: C, 64.71; H, 7.87.

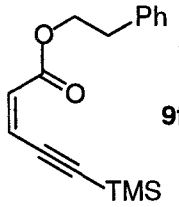
Methyl 2-(trimethylsilylethynyl)-1-cyclohexenecarboxylate (9b).



9b

A colorless liquid (90% yield); IR (neat) 1705 (C=C), 1727 (C=O), 2142 (C≡C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.20 (s, 9H), 1.58-1.63 (m, 4H), 2.32-2.38 (m, 2H), 3.73-3.79 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 0.0, 21.6, 21.8, 26.4, 32.2, 51.5, 101.5, 104.6, 127.9, 135.6, 168.0. Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 66.25; H, 8.80.

2'-Phenylethyl (Z)-5-(trimethylsilyl)pent-2-en-4-ynoate (9f).

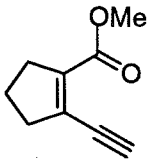


9f

A colorless liquid (52% yield, for three steps); IR (neat) 1712 (C=C), 1728 (C=O), 2152 (C≡C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.24 (s, 9H), 3.00 (t, J = 6.9 Hz, 2H), 4.39 (t, J = 6.9 Hz, 2H), 6.07 (d, J = 11.7 Hz, 1H), 6.15 (d, J = 11.7 Hz, 1H), 7.18-7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ -0.4, 35.1, 65.0, 100.7, 108.4, 122.7, 126.5, 128.5, 128.9, 129.2, 137.7, 164.4. Anal. Calcd for $C_{16}H_{20}O_2Si$: C, 70.54; H, 7.40. Found: C, 70.25; H, 7.38.

Typical Procedure for Preparation of 1.

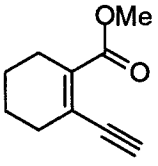
Methyl 2-ethynyl-1-cyclopentenecarboxylate (1a).



1a

To a solution of **9a** (0.89 g, 4.0 mmol) in DMSO (10 mL) was slowly added KF (0.58 g, 10 mmol) at 0 °C. The suspension was stirred at room temperature for 10 min and then the mixture was poured into ice water (50 mL), and extracted with Et_2O (50 mL x 3). The extract was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=10/1) as an eluent to afford **1a** (0.60 g, 4.0 mmol, 100% yield) as a white solid; mp. 47.3-48.0 °C; IR (neat) 1716 (C=O), 2091 (C≡C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.92 (quint, J = 7.8 Hz, 2H), 2.63-2.71 (m, 4H), 3.54 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 22.1, 33.2, 39.1, 51.4, 79.3, 87.5, 133.6, 139.8, 164.6. Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 72.05; H, 6.74.

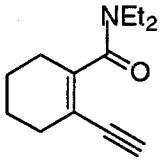
Methyl 2-ethynyl-1-cyclohexenecarboxylate (1b).



1b

A colorless liquid (80% yield); IR (neat) 1716, 1723 (C=O), 2091 (C≡C), 3285 (H–C≡) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.62-1.66 (m, 4H), 2.32-2.38 (m, 4H), 3.37 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.5, 21.6, 26.1, 32.2, 51.6, 83.3, 84.0, 127.6, 136.0, 167.5. HRMS (FAB): calcd for $C_{10}H_{13}O_2$ ($M+H^+$), 165.0916; found, 165.0909.

Preparation of *N,N*-diethyl 2-ethynyl-1-cyclohexenecarboxamide (1c).

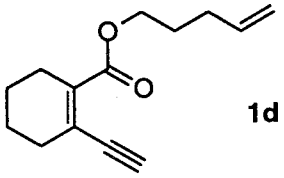


1c

A solution of methyl 2-(trimethylsilyl)-1-cyclohexenecarboxylate (**9b**) (1.0 g, 4.2 mmol) in benzene (4 mL) was added to benzene-hexane solution of Me_2AlNEt_2[19] prepared from a hexane solution of Me_3Al and Et_2NH. The resulting solution was heated under reflux for 44 h, cooled to room temperature, and hydrolyzed by slow and cautious addition of 0.67 M hydrochloric acid (7.0 mL). The upper organic layer was separated, and the aqueous layer was extracted with AcOEt (25 mL x 3). The organic extracts were combined, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure to give the residual liquid, which was subjected to column chromatography on SiO_2 with CH_2Cl_2/AcOEt (v/v=30/1) as an eluent to afford *N,N*-diethyl 2-(trimethylsilyl)-1-cyclohexenecarboxamide (1.1 g, 4.0 mmol, 95% yield) as a pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.06 (s, 9H), 1.11 (t, J = 7.2 Hz, 3H), 1.11 (t, J = 7.2 Hz, 3H), 1.30-1.50 (br m, 4H), 1.80-2.95 (br m, 4H), 3.20-3.65 (br m, 4H).

To a solution of *N,N*-diethyl 2-(trimethylsilyl)-1-cyclohexenecarboxamide (1.1 g, 4.0 mmol) in THF (40 mL) was added tetrabutylammonium fluoride (1.0 M in THF, 4.2 mL) at 0 °C, and the mixture was stirred for 0.5 h. The mixture was poured into saturated NH_4Cl aqueous solution, and extracted with Et_2O (25 mL x 3). The solvent was removed from the extract under reduced pressure. The residual liquid was subjected to column chromatography on SiO_2 with CH_2Cl_2/AcOEt (v/v=30/1) as an eluent to afford **1c** (0.82 g, 4.0 mmol, 99% yield) as a colorless liquid; IR (neat) 1286, 1435, 1620 (C=O), 2092 (C≡C), 3218 (H–C≡) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.17 (q, J = 7.2 Hz, 6H), 1.64-1.70 (m, 4H), 2.15-2.25 (m, 4H), 2.96 (s, 1H), 3.24-3.56 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 12.4, 14.4, 21.4, 21.7, 27.1, 28.9, 38.1, 42.3, 79.7, 82.4, 116.2, 142.8, 170.7. HRMS (FAB): calcd for $C_{13}H_{20}NO$ (M+H$^+$), 206.1545; found, 206.1537.

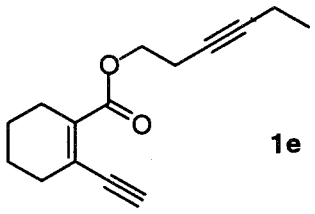
4'-Pentenyl 2-ethynyl-1-cyclohexenecarboxylate (1d).



1d

A colorless liquid (25% yield); IR (neat) 1703 (C=C), 1721 (C=O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.60-1.64 (m, 4H), 1.76 (quint, J = 6.6 Hz, 2H), 2.11-2.19 (dt, J = 6.6, 6.6 Hz, 2H), 2.23-2.41 (m, 4H), 3.33 (s, 1H), 4.17 (t, J = 6.6 Hz, 2H), 4.95-5.05 (m, 2H), 5.72-5.84 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.5, 21.6, 26.2, 27.8, 30.2, 32.3, 64.1, 83.4, 84.0, 115.2, 127.3, 136.2, 137.5, 167.1. HRMS (FAB): calcd for $C_{14}H_{19}O_2$ ($M+H^+$), 219.1385; found, 219.1380.

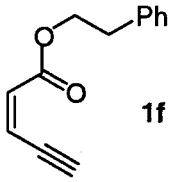
3'-Hexynyl 2-ethynyl-1-cyclopentenecarboxylate (1e).



1e

A colorless liquid (7% yield); IR (neat) 1705 (C=C), 1722 (C=O), 2341, 2360 (C≡C), 3281 (H–C≡) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.08 (t, J = 7.5 Hz, 3H), 1.59-1.63 (m, 4H), 2.08-2.20 (m, 2H), 2.26-2.42 (m, 4H), 2.44-2.55 (m, 2H), 3.34 (s, 1H), 4.21 (t, J = 6.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 12.3, 14.1, 19.2, 21.5, 21.6, 26.1, 31.6, 32.3, 63.0, 74.9, 83.2, 83.4, 84.2, 127.8, 136.0, 166.7. HRMS (FAB): calcd for $C_{15}H_{19}O_2$ ($M+H^+$), 231.1385; found, 231.1381.

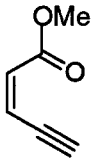
2'-Phenylethyl (*Z*)-pent-2-en-4-ynoate (1f).



1f

A colorless liquid (96% yield); IR (neat) 1716 (C=C), 1727 (C=O), 2098 (C≡C), 3282 (H–C≡) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.99 (t, J = 7.2 Hz, 2H), 3.57 (d, J = 2.1 Hz, 1H), 4.40 (t, J = 7.2 Hz, 2H), 6.12 (d, J = 2.1, 11.4 Hz, 1H), 6.19 (d, J = 11.4 Hz, 1H), 7.20-7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 35.0, 65.1, 79.5, 89.3, 122.1, 126.6, 128.5, 128.9, 130.6, 137.7, 164.2. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.94; H, 6.16.

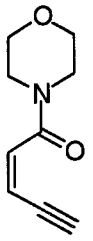
Methyl (*Z*)-pent-2-en-4-ynoate (1g).



1g

A colorless liquid; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 3.60 (d, J = 2.4 Hz, 1H), 3.75 (s, 3H), 6.11 (dd, J = 2.4, 11.4 Hz, 1H), 6.19 (d, J = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 51.5, 79.4, 89.2, 122.1, 130.3, 164.7.

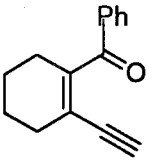
1-Morpholinyl-(*Z*)-pent-2-en-4-yn-1-one (1h).



1h

A colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 3.29 (dd, J = 0.9, 2.4 Hz, 1H), 3.45-3.65 (m, 2H), 3.65-3.80 (m, 6H), 5.85 (dd, J = 2.4, 12.0 Hz, 1H), 6.35 (dd, J = 0.9, 12.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 41.7 (br m), 46.7 (br m), 66.7 (br m), 66.9 (br m), 79.3, 85.5, 115.1, 133.7, 164.9.

2-Ethynyl-1-cyclohexenyl phenyl ketone (1i)



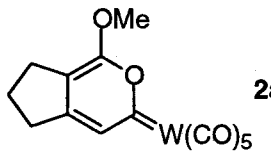
1i

A solution of methyl 2-(trimethylsilylethynyl)-1-cyclohexenecarboxylate (**9b**) (3.6 g, 15 mmol) in benzene (5 mL) was added to benzene (40 mL) and hexane (45 mL) solution of $Me_2AlNMe(OMe)$ prepared from a hexane solution of Me_3Al (45 ml, 45 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (4.4 g, 45 mmol).[18] The resulting solution was heated under reflux for 3 h. The reaction mixture was cooled down to room temperature, and hydrolyzed by slow and cautious addition of 1 N HCl aqueous solution (30 mL). The upper organic layer was separated, and the aqueous layer was extracted with AcOEt (30 mL x 3). The organic extracts were combined, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure to give the residual liquid, which was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=4/1) as an eluent to afford *N*-methyl *N*-methoxy 2-(trimethylsilyl)-1-cyclohexenecarboxamide (**10**) (3.6 g, 14 mmol, 92% yield) as a pale yellow liquid; IR (KBr) 845, 1659 (C=O), 2144 (C≡C) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.12 (s, 9H), 1.57-1.65 (m, 4H), 2.14-2.27 (m, 4H), 3.23 (s, 3H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, -25 °C) δ -0.1 (Si*C*H$_3$), -0.1 (Si*C*H$_3$), 21.5 (*C*H$_2$), 21.5 (*C*H$_2$), 21.8 (*C*H$_2$), 21.9 (*C*H$_2$), 26.5 (*C*H$_2$), 26.7 (*C*H$_2$), 28.8 (*C*H$_2$), 29.5 (*C*H$_2$), 31.8 (N*C*H$_3$), 35.7 (N*C*H$_3$), 60.3 (O*C*H$_3$), 62.0 (O*C*H$_3$), 96.4 (*C*≡), 97.2 (*C*≡), 103.0 (*C*≡), 104.5 (*C*≡), 116.7 (*C*=), 119.4 (*C*=), 140.0 (*C*=), 143.1 (*C*=), 166.4 (*C*=O), 170.8 (*C*=O) as a mixture of rotamers. Anal. Calcd for $C_{14}H_{23}NO_2Si$: C, 63.35; H, 8.73; N, 5.28. Found: C, 63.07; H, 8.47; N, 5.21.

To a solution of **10** (0.47 g, 2.0 mmol) in THF (10 mL) was added preformed phenylmagnesium bromide (4.2 mmol) in THF (15 mL) at 0 °C, and the mixture was stirred at room temperature for 4 h. The reaction mixture was poured into saturated NH_4Cl solution (30 mL), and the aqueous layer was extracted with AcOEt (20 mL x 3). The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and then 1 N KOH solution (2.0 mL) was added to the residue in MeOH (20 mL) at room temperature. After stirring for 0.5 h, this solution was poured into saturated NH_4Cl solution (50 mL). The aqueous layer was extracted with AcOEt (20 mL x 3) and the combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=20/1) as an eluent to afford **1i** (0.22 g, 1.0 mmol, 52% yield) as a colorless liquid; IR (neat) 648, 690, 709, 732, 916, 1662 (C=O), 2093 (C≡C), 3292 (H-C≡) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.71-1.77 (m ,4H), 2.28-2.38 (m, 4H), 2.81 (s, 1H), 7.40-7.48 (m, 2H) 7.50-7.57 (m, 1H), 7.85-7.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.4, 21.8, 27.3, 29.8, 82.2, 82.3, 119.8, 128.5, 129.5, 133.2, 136.0, 145.8, 199.0 (*C*=O). HRMS (FAB): calcd for $C_{15}H_{14}O$ ($M+H^+$), 211.1119; found, 211.1123.

Typical Procedure for Synthesis of 2-Pyranylidene-metal Complex 2.

2-Pyranylidene-tungsten complex 2a.

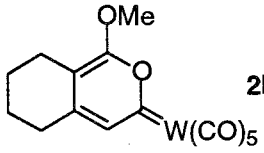


2a

A solution of $W(CO)_6$ (0.21 g, 0.06 mmol) in THF (10 mL) under Ar was irradiated by Hg lamp (450 W, 350 nm) at room temperature for 4 h. To this yellow solution under Ar was added a solution of **1a** (75 mg, 0.5 mmol) in THF (1 mL) by a syringe. The solution was stirred at room temperature for 4 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 10/1) as an eluent to afford **2a** (90 mg, 0.19 mmol, 38% yield) as a yellow solid; mp. 106.1 °C (dec); IR (KBr) 1909, 1957, 2058 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.10 (quint, J = 7.8 Hz,

2H), 2.75 (t, J = 7.8 Hz, 2H), 2.81 (t, J = 7.8 Hz, 2H), 4.30 (s, 3H), 7.61 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 23.8, 27.0, 33.8, 56.9, 114.4, 132.2, 166.0, 170.1, 199.1 (W-CO), 204.0 (W-CO), 235.4 (W=C). Anal. Calcd for $C_{14}H_{10}O_7W$: C, 35.47; H, 2.13. Found: C, 36.39; H, 2.28. HRMS (FAB): calcd for $C_{14}H_{10}O_7W$ (M^+), 473.9933; found, 473.9938.

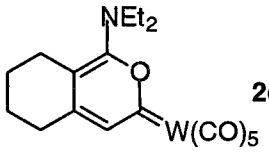
2-Pyranylidene-tungsten complex 2b.



2b

The reaction was carried out in THF at reflux temperature for 0.5 h. A yellow solid (63% yield); mp. 103.8-105.6 °C; IR (KBr) 1882, 1920, 1962, 2059 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.77-1.78 (m, 4H), 2.43-2.50 (m, 2H), 2.55-2.65 (m, 2H), 4.30 (s, 3H), 7.34 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.5, 21.1, 21.3, 29.2, 57.1, 109.3, 135.7, 157.1, 171.1, 199.2 (W-CO), 203.9 (W-CO), 228.1 (W=C). Anal. Calcd for $C_{15}H_{12}O_7W$: C, 36.91; H, 2.48. Found: C, 36.82; H, 2.57.

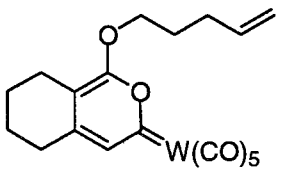
2-Pyranylidene-tungsten complex 2c.



2c

A yellow solid (68% yield); mp. 99.0-101.8 °C; IR (KBr) 1881, 1894, 1922, 1964, 2053 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.35 (t, J = 7.2 Hz, 6H), 1.70-1.77 (m, 4H), 2.45-2.53 (m, 2H), 2.53-2.61 (m, 2H), 3.60 (q, J = 7.2 Hz, 4H), 6.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 13.7, 21.1, 22.6, 25.6, 29.6, 44.9, 109.4, 133.1, 153.1, 169.1, 199.7 (W-CO), 204.3 (W-CO), 220.0 (W=C). Anal. Calcd for $C_{18}H_{19}NO_6W$: C, 40.85; H, 3.62; N, 2.65. Found: C, 41.10; H, 3.70; N, 2.64.

2-Pyranylidene-tungsten complex 2d.

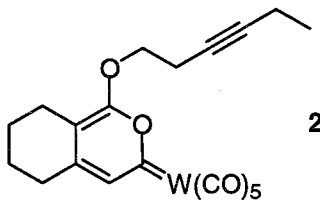


2d

A yellow liquid (55% yield); IR (neat) 1907, 1915, 1965, 2058 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.74-1.80 (m, 4H), 1.99 (quint, J = 6.9 Hz, 2H), 2.20-2.27 (m, 2H), 2.35-2.42 (m, 2H), 2.45-2.55 (m, 2H), 4.65 (t, J = 6.9 Hz, 2H), 5.02-5.09 (m, 2H), 5.75-5.88 (m, 1H), 7.31 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.6, 21.1, 21.3, 27.7, 29.1, 29.7, 70.2, 109.3, 116.1, 135.5, 136.5, 157.1, 170.8, 199.2 (W-CO), 204.0 (W-CO), 227.4 (W=C). Anal. Calcd

for $C_{19}H_{18}O_7W$: C, 42.09; H, 3.35. Found: C, 43.50; H, 3.57. HRMS: (FAB) calcd for $C_{19}H_{18}O_7W$ (M^+), 542.0562; found, 542.0554. (This complex is unstable to air and light to obtain the correct elemental analytical data.)

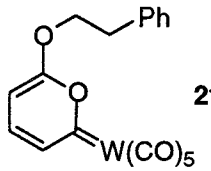
2-Pyranylidene-tungsten complex 2e.



2e

A yellow solid (71% yield); mp. 73.6-75.4 °C (dec); IR (KBr) 1896, 1923, 1976, 2059, 2366 (C≡C) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.10 (t, J = 7.6 Hz, 3H), 1.78-1.79 (m, 4H), 2.15 (qt, J = 2.6, 7.6 Hz, 2H), 2.39-2.53 (m, 2H), 2.53-2.71 (m, 2H), 2.75 (tt, J = 2.6, 6.2 Hz, 2H), 4.69 (t, J = 2.6 Hz, 2H), 7.35 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 12.3, 13.9, 19.6, 20.5, 21.1, 21.3, 29.2, 68.7, 73.5, 84.5, 109.4, 135.8, 157.2, 170.6, 199.7 (W-CO), 203.9 (W-CO), 228.2 (W=C). Anal. Calcd for $C_{20}H_{18}O_7W$: C, 43.34; H, 3.27. Found: C, 43.26; H, 3.18.

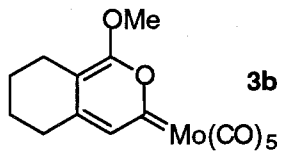
Pyranylidene-tungsten complex 2f.



2f

An orange solid (58% yield); mp. 78.4-79.8 °C; IR (KBr) 1904, 1921, 1939, 1981, 2059 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 3.12 (t, J = 6.8 Hz, 2H), 4.77 (t, J = 6.8 Hz, 2H), 6.14 (d, J = 8.0 Hz, 1H), 7.10-7.30 (m, 6H), 7.56 (d, J = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 35.0, 71.2, 98.5, 127.2, 128.8, 128.9, 135.3, 136.1, 142.4, 173.7, 198.7 (W-CO), 203.0 (W-CO), 242.3 (W=C). Anal. Calcd for $C_{18}H_{12}O_7W$: C, 41.25; H, 2.31. Found: C, 40.76; H, 2.27. HRMS (FAB): calcd for $C_{18}H_{12}O_7W$ (M^+), 524.0096; found, 524.0078.

Synthesis of 2-Pyranylidene-molybdenum Complex 3b.



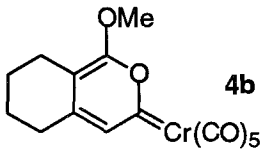
3b

A solution of $Mo(CO)_6$ (82 mg, 0.31 mmol) in Et_2O (25 mL) and Et_3N (4 mL) under Ar was irradiated by Hg lamp (450 W, 350 nm) at room temperature for 1 h. A solution of **1b** (42 mg, 0.26 mmol) in Et_2O (1 mL) was added to this yellow solution. The mixture was stirred at room temperature for 3 h. The solvent was removed under reduced pressure, and the residue was

subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=10/1) as an eluent to afford **3b** (35 mg, 0.09 mmol, 35% yield) as a yellow solid; mp. 89.5-90.8 °C; IR (KBr) 1884, 1927, 1968, 2060 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.76-1.79 (m, 4H), 2.42-2.46 (m, 2H), 2.58-2.62 (m, 2H), 4.31 (s, 3H), 7.30 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.5, 21.2, 21.3, 29.1, 56.9, 109.1, 134.7, 155.8, 171.5, 207.4 (Mo-CO), 213.6 (Mo-CO). Anal. Calcd for $C_{15}H_{12}O_7Mo$: C, 45.02; H, 3.02. Found: C, 44.54; H, 2.87. HRMS (FAB): calcd for $C_{15}H_{12}O_7Mo$ (M^+), 401.9637; found, 401.9644.

Typical Procedure for Synthesis of 2-Pyranylidene-chromium Complex 4.

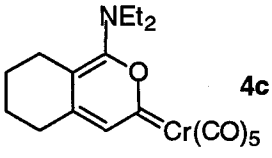
2-Pyranylidene-chromium complex 4b.



4b

A solution of $Cr(CO)_6$ (0.13 g, 0.60 mmol) in THF (20 ml) and Et_3N (0.1 mL) under Ar was irradiated by a Hg lamp (450 W, 350 nm) at room temperature for 4 h. To this orange solution under Ar was added a solution of **1b** (33 mg, 0.20 mmol) in THF (1 mL) by a syringe. The mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=10/1) as an eluent to afford **4b** (44 mg, 62% yield) as an orange solid; mp. 92-94 °C; IR (KBr) 1897, 1935, 1976, 2053 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ = 1.72-1.84 (m, 4H), 2.38-2.49 (m, 2H), 2.55-2.64 (m, 2H), 4.32 (s, 3H), 7.33 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ = 20.4, 21.2, 21.4, 29.0, 56.9, 108.2, 134.7, 154.9, 171.9, 218.6 (Cr-CO), 223.4 (Cr-CO), 251.0 (Cr=C). HRMS (FAB): calcd for $C_{15}H_{12}O_7Cr$ (M^+), 355.9995; found, 355.9988.

2-Pyranylidene-chromium complex 4c

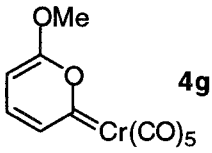


4c

An orange solid (68% yield); mp. 118.4-121.5 °C; IR (KBr) 1888, 1909, 1965, 2045 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.36 (t, J = 6.9 Hz, 6H), 1.69-1.79 (m, 4H), 2.44-2.50 (m, 2H), 2.53-2.60 (m, 2H), 3.63 (q, J = 6.9 Hz, 4H), 6.96 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 13.7, 21.1, 22.6, 25.4, 29.5, 44.7, 108.6, 132.0, 151.2, 170.1, 219.3 (Cr-CO), 223.9 (Cr-CO),

240.7 (Cr=C). Anal. Calcd for $C_{18}H_{19}NO_6Cr$: C, 54.41; H, 4.82; N, 3.53. Found: C, 54.27; H, 5.03; N, 3.40.

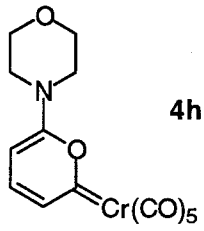
2-Pyranylidene-chromium complex 4g



4g

An orange solid (69% yield); mp. 71.0-73.5 °C; IR (KBr) 1898, 1917, 1976, 2053 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 4.32 (s, 3H), 6.15 (d, J = 8.1 Hz, 1H), 7.15 (dd, J = 8.1, 8.1 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 57.0, 96.9, 134.1, 139.6, 175.0, 217.9 (Cr-CO), 223.4 (Cr-CO), 269.6 (Cr=C). HRMS (FAB): calcd for $C_{11}H_6O_7Cr$ (M^+), 301.9518; found, 301.9519.

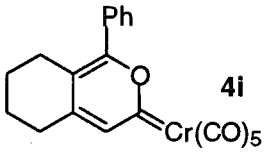
2-Pyranylidene-chromium complex 4h



4h

An orange solid (50% yield); mp. 128.3-129.5 °C; IR (KBr) 1906, 1966, 2052 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 3.75-3.87 (m, 8H), 6.00 (m, 1H), 6.97 (m, 1H), 7.26 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 44.7, 65.9, 95.4, 129.4, 137.6, 169.2, 218.7 (Cr-CO), 223.8 (Cr-CO), 258.1 (Cr=C). HRMS (FAB): calcd for $C_{14}H_{11}NO_7Cr$ (M^+), 356.9934; found, 356.9941.

2-Pyranylidene-chromium complex 4i



4i

The ketone **1i** (0.13 g, 0.61 mmol) and Et_3N (1.0 mL) were used. A red solid (8% yield); mp. 132.0-134.6 °C; IR (KBr) 1918, 1974, 2051 cm^{-1}; ^1H NMR (300 MHz, d_8-THF, 25 °C) δ = 1.78-1.91 (m, 4H), 2.76-2.84 (m, 4H), 7.56-7.62 (m, 3H), 7.79-7.86 (m, 2H), 7.95 (s, 1H); ^{13}C NMR (75 MHz, d_8-THF, 25 °C) δ = 22.0, 23.0, 26.2, 29.6, 124.8, 129.6, 129.7, 132.0, 133.1, 141.0, 150.6, 175.5, 219.2 (Cr-CO), 224.3 (Cr-CO), 268.8 (Cr=C). HRMS (FAB): calcd for $C_{20}H_{14}NO_6Cr$ (M^+), 402.0185; found, 402.0196.

X-ray Crystallography of 2b. Yellow prismatic crystals were obtained from a hexane solution at 23 °C. A crystal of dimensions 0.20 x 0.20 x 0.20 mm was mounted on a glass fiber. Bond lengths and bond angles are given in Table 5. Main features of the refinement appear in Table 6. The intensity data were measured on a Rigaku AFC-7R four-circle

automated diffractometer with Mo-Kα radiation and a graphite monochromator at 23 °C using the ω–2θ scan technique. The structure was solved by Direct Methods (SIR92)[19] and expanded using Fourier techniques. All the calculations were performed using the teXsan crystallographic software package. The final cycle of full-matrix least-squares refinement was based on 3142 observed reflections ($I > 3.00\sigma(I)$) and 220 variable parameters and gave $R = 0.031$ and $R_w = 0.034$. The value of the goodness of fit indicator was 3.07. Lorentz and polarization corrections and secondary extinction were applied for the structure.

Table 2. Selected Interatomic Distances (Å) and Angles (°) for **2b**

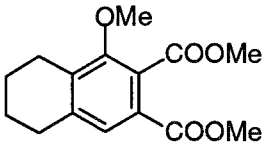
Bond lengths			
W(1)–C(1)	2.215(6)	W(1)–C(11)	2.023(8)
W(1)–C(12)	2.018(8)	W(1)–C(13)	2.042(8)
W(1)–C(14)	2.054(8)	W(1)–C(15)	2.021(7)
O(1)–C(1)	1.430(7)	O(1)–C(9)	1.321(7)
O(2)–C(9)	1.316(7)	O(2)–C(10)	1.448(9)
O(3)–C(11)	1.146(9)	O(4)–C(12)	1.153(9)
O(5)–C(13)	1.138(8)	O(6)–C(14)	1.136(9)
O(7)–C(15)	1.145(8)	C(1)–C(2)	1.362(9)
C(2)–C(3)	1.404(8)	C(3)–C(8)	1.383(8)
C(8)–C(9)	1.382(9)		
Bond angles			
C(1)–W(1)–C(11)	89.4(3)	C(1)–W(1)–C(12)	92.8(3)
C(1)–W(1)–C(13)	88.5(3)	C(1)–W(1)–C(14)	87.8(3)
C(1)–W(1)–C(15)	177.1(3)	C(11)–W(1)–C(12)	86.4(3)
C(11)–W(1)–C(13)	177.9(3)	C(11)–W(1)–C(14)	90.3(3)
C(11)–W(1)–C(15)	92.5(3)	C(12)–W(1)–C(13)	93.3(3)
C(12)–W(1)–C(14)	176.7(3)	C(12)–W(1)–C(15)	89.6(3)
C(14)–W(1)–C(15)	90.0(3)	C(1)–O(1)–C(9)	123.0(5)
C(9)–O(2)–C(10)	119.5(6)	W(1)–C(1)–O(1)	113.8(4)
W(1)–C(1)–C(2)	133.2(5)	O(1)–C(1)–C(2)	112.9(5)
C(1)–C(2)–C(3)	124.5(6)	C(2)–C(3)–C(8)	120.1(6)
C(3)–C(8)–C(9)	115.6(6)	O(1)–C(9)–O(2)	115.8(6)
O(1)–C(9)–C(8)	123.8(5)	O(2)–C(9)–C(8)	120.3(6)
W(1)–C(11)–O(3)	178.1(8)	W(1)–C(12)–O(4)	176.7(6)
W(1)–C(13)–O(5)	177.4(6)	W(1)–C(14)–O(6)	179.3(7)
W(1)–C(15)–O(7)	178.7(7)		

Table 3. Summary of Crystallographic Data of **2b**

empirical formula	$C_{15}H_{12}O_7W$
fw	488.11
crystal syst	monoclinic
space group	$P2_1/n$ (No. 14)
cryst color	yellow
lattice params	
a (Å)	16.141(6)
b (Å)	5.909(6)
c (Å)	18.592(5)
β (Å)	114.17(2)
V (Å^3)	1617(1)
Z	4
D_{calc} (g cm^{-3})	2.004
μ(Mo Kα) (cm^{-1})	71.80
F(000)	928
diffractometer	Rigaku AFC7R
radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated
temp (°C)	23.0
scan type	ω–2θ
Max. 2θ (°)	55
no. of rflns measd	total, 1280; unique, 1239 (R_{int} = 0.045)
no. of observns ($I > 3.00\sigma(I)$)	3142
structure soln	direct methods (SIR92)
refinement	full-matrix least squares
no. of variables	220
reflection/parameter ratio	14.28
residuals: R; R_w	0.031; 0.034
goodness of fit (GOF)	3.07
max shift/error in final cycle	0.03
maximum peak in final diff map (e Å^{-3})	1.21
minimum peak in final diff map (e Å^{-3})	–1.82

Typical Procedure for [4 + 2] Cycloaddition of 2 or 4 with Acetylene.

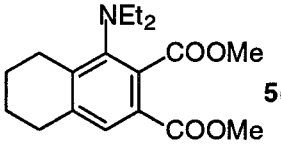
Dimethyl 5,6,7,8-tetrahydro-1-methoxy-2,3-naphthalenedicarboxylate (5b).



5b

A mixture of complex **2b** (0.15 g, 0.30 mmol) and dimethyl acetylenedicarboxylate (0.55 mL, 4.5 mmol) in a sealed tube was stirred at 90 °C for 12 h under N_2. The mixture was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=10/1) as an eluent to afford **5b** (22 mg, 0.080 mmol, 27% yield) as a colorless liquid; IR (neat) 791, 1042, 1146, 1274, 1294, 1328, 1727 (C=O), 1738 (C=O), 2861, 2947, 3430 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.77-1.84 (m, 4H), 2.74-2.82 (m, 4H), 3.79 (s, 3H), 3.86 (s, 3H), 3.94 (s, 3H), 7.52 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 22.2, 22.4, 23.7, 29.3, 52.3, 52.6, 61.7, 125.3, 126.6, 127.2, 136.9, 140.4, 155.0, 165.8, 168.4. Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.79; H, 6.64.

Dimethyl 1-diethylamino-5,6,7,8-tetrahydro-2,3-naphthalenedicarboxylate (5c).



5c

A yellow liquid (25% yield); IR (neat) 1141, 1277, 1731 (C=O), 1738 (C=O), 1916, 2341, 2360, 2859, 2933, 3436 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.00 (t, J = 7.2 Hz, 6H), 1.72-1.82 (m, 4H), 2.65-2.75 (m, 2H), 2.75-2.86 (m, 2H), 2.90-3.12 (m, 4H), 3.85 (s, 3H), 3.89 (s, 3H), 7.57 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 14.4, 22.4, 22.6, 26.6, 29.6, 47.4, 52.1, 52.2, 124.7, 128.1, 134.9, 139.4, 144.2, 146.8, 166.2, 169.8. Anal. Calcd for $C_{18}H_{25}NO_4$: C, 67.69; H, 7.89; N, 4.39. Found: C, 67.67; H, 7.86; N, 4.30.

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Chapter 2

Chromium- and Tungsten-Triggered Valence Isomerism of *cis*-1-Acyl-2-ethynylcyclopropanes via [3,3]Sigmatropy of (2-Acylcyclopropyl)vinylidene-Metal Intermediates

Abstract

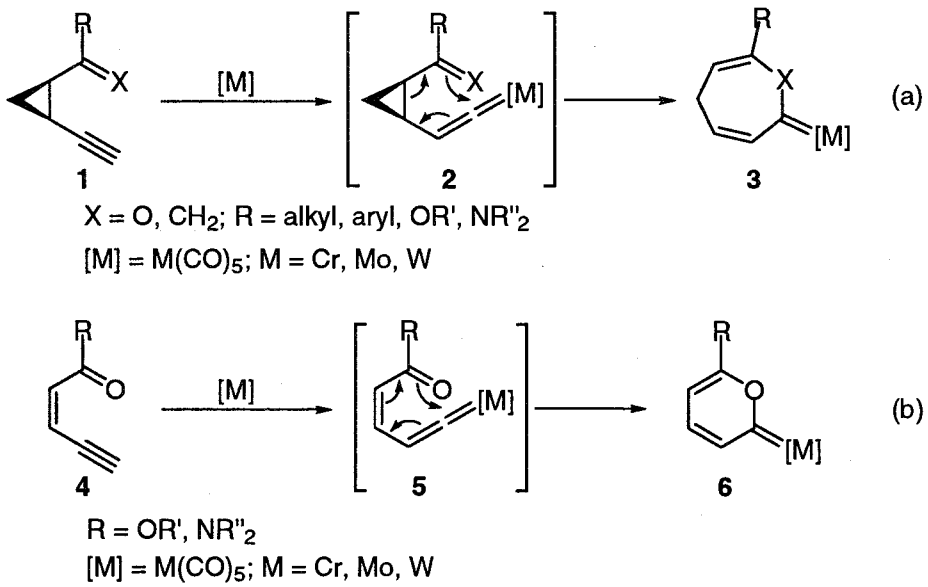
The reaction of *cis*-1-acyl-2-ethynylcyclopropanes in the presence of a catalytic amount of $Cr(CO)_5(THF)$ or $W(CO)_5(THF)$ gave the corresponding phenol derivatives, respectively. A [3,3]sigmatropy of cyclopropanes involving a vinylidene-metal moiety as a vinylogous function is a key step to seven-membered cyclic carbene complex intermediates. Triethylamine as an indispensable additive seems to facilitate the formation of a vinylidene complex from a π-alkyne metal complex. The reaction of *cis*-1-ethynyl-2-vinylcyclopropanes as a carbon analogue of *cis*-1-acyl-2-ethynylcyclopropanes also gave a mixture of two cycloheptatrienes via [1,3]- or [1,5]-hydrogen shifts followed by reductive elimination of $M(CO)_5$ in the seven-membered cyclic carbenoid intermediates.

Introduction

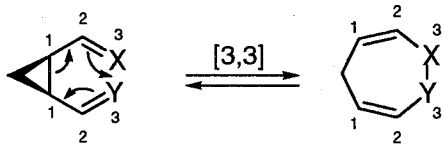
The author describes herein the novel group 6 metal-triggered [3,3]sigmatropy of *cis* vicinal acyl- or vinyl-ethynylcyclopropanes **1** (X = O, CH_2) via cyclopropylvinylidene complexes **2**, as shown in Scheme 1a.

Vinylidene complexes which can be generated directly from terminal alkynes and a variety of transition metal complexes have been identified as particularly versatile synthetic intermediates during the past decade.[1] The author has already found that group 6 transition metal complexes undergo pericyclic or pseudopericyclic reaction of ene-yne-carbonyl compounds **4** via ene-carbonyl-vinylidene complexes **5** to produce 2-pyranylidene complexes **6** (Scheme 1b and see also Chapter 1).[2]

Scheme 1



Scheme 2

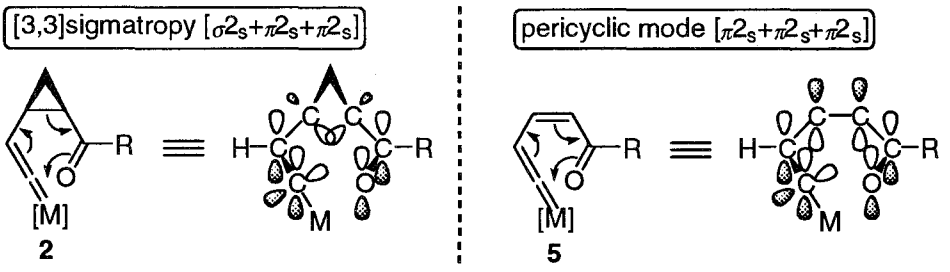


(X, Y) = (CH_2, CH_2), (NR', CH_2), (O, CH_2), ([M], CH_2)

(X, Y) (O, C=[M]), (CH_2, C=[M])

As shown in Scheme 2, [3,3]sigmatropy of vinylcyclopropanes bearing a variety of unsaturated substituents, such as vinyl,[3] iminyl,[3] carbonyl,[3] heterocumulenyl,[3,4] and metal-carbene,[5] heretofore has been well investigated,[6] whereas there has been no report on [3,3]sigmatropy of cyclopropanes involving a vinylidene-metal moiety (Y = C=[M]) as a vinylogous function. The author decided to extend this pericyclic mode to a cyclopropane system having both a vinylidene-metal moiety and an unsaturated side chain, which could exemplify [3,3]sigmatropy represented with a [$\sigma 2_s+\pi 2_s+\pi 2_s$] process (Scheme 3).

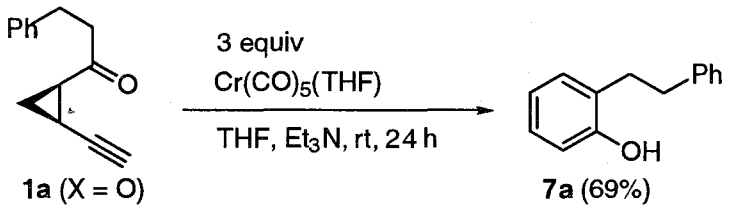
Scheme 3



The author therefore set out to prepare the vicinal carbonyl- or vinyl-substituted ethynylcyclopropanes, and demonstrated the group 6 metal-triggered valence isomerization of *cis* vicinal acyl- or vinyl-ethynylcyclopropanes in stoichiometric and catalytic process. This represents the first example of [3,3]sigmatropy in which a vinylidene-metal works as a function of two-π-electron moiety like a ketene.

Results and Discussion

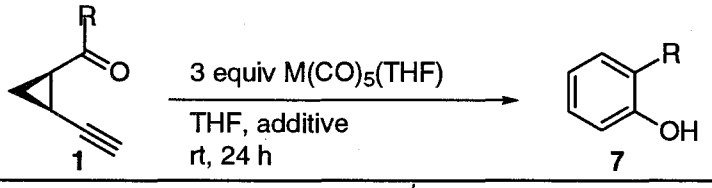
When the reaction of *cis*-vicinal acetylethynylcyclopropane **1a** was carried out under the identical conditions for the synthesis of 2-pyranylidene-chromium complexes **6** employing $Cr(CO)_5(THF)$[10] in the presence of Et_3N at room temperature, an unanticipated product, phenol **7a** was isolated in 69% yield, not a seven-membered Fischer-type carbene complex **3** (eq 1). This result shows that valence isomerization of **1a** was promoted by chromium.



(1)

The author next examined the reaction using other group 6 metal carbonyls and other cyclopropanes having an alkoxycarbonyl or a carbamoyl group (Table 1). The reaction of **1a**

Table 1. Valence Isomerization of **1** (X = O) with $M(CO)_5(THF)$[a]



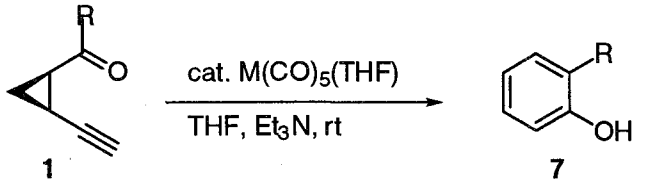
entry	R	M	additive[b]	time (h)	product	yield (%)[c]
1	CH_2CH_2Ph (**1a**)	Cr	Et_3N	24	**7a**	69
2	CH_2CH_2Ph (**1a**)	Cr	—	72	NR[d]	
3	CH_2CH_2Ph (**1a**)	W	Et_3N	24	**7a**	72
4	CH_2CH_2Ph (**1a**)	W	—	72	NR[d]	
5	CH_2CH_2Ph (**1a**)	Mo	Et_3N	72	**7a**	4
6	OCH_2CH_2Ph (**1b**)	Cr	Et_3N	72	NR[d]	
7	morpholino (**1c**)	Cr	Et_3N	72	NR[d]	

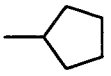
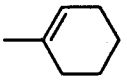
[a] Reactions were carried out at room temperature with **1** (0.2 mmol) and $M(CO)_5(THF)$ prepared by irradiating a solution of $M(CO)_6$ (0.6 mmol) in THF (20 mL). [b] 0.6 mmol. [c] Isolated yield. [d] **1** was completely recovered.

with 3 equiv of $W(CO)_5(THF)$ also gave **7a** in 72 % yield (entry 3), while $Mo(CO)_5(THF)$ was almost ineffective in the reaction (entry 5). Reactions required the addition of Et_3N and no reactions occurred in the absence of it (entries 2 and 4). Triethylamine seems to facilitate the formation of a vinylidene complex.[11] When reactions of other cyclopropanes such as an ester **1b** and an amide **1c** were carried out with 3 equiv of $Cr(CO)_5(THF)$ in the presence of Et_3N, no reactions took place, and both of **1b** and **1c** were recovered intact (entries 6 and 7). The lack of reaction of an ester and an amide is in sharp contrast with pyranylidene-complex formation (see Chapter 1).

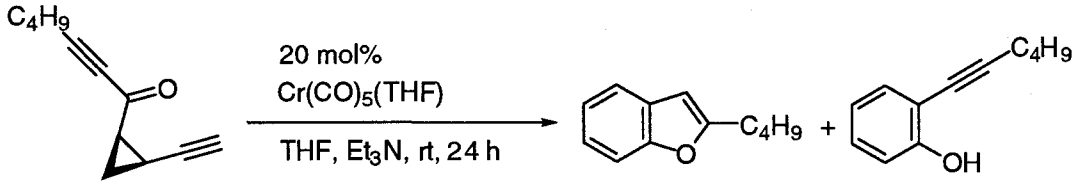
As it was found that the group 6 metals induce valence isomerization of *cis*-1-acyl-2-ethynylcyclopropanes **1** leading to phenols **7**, catalytic reactions of **1** were next examined. Selected results on catalytic reactions are shown in Table 2. Both chromium and tungsten showed the catalytic activity to a similar extent (entries 1 and 2). The use of 5 mol% $Cr(CO)_5(THF)$ is enough to induce catalytic valence isomerization of **1a** to give **7a** quantitatively (entry 3). Reactions of *n*-butyl and cyclopentyl ketones **1d** and **1f** gave **7d** and **7f** in almost quantitative yields, respectively (entries 4 and 6), while the reaction of *tert*-butyl ketone **1e** gave **7e** in moderate yield (entry 5). The reaction of 1-cyclohexyl ketone **1g** as a substrate gave **7g** in good yield (entry 7). Next, reactions of various aromatic ketones were examined. When the reactions of *p*-substituted phenyl ketone **1h-1j** gave **7h-7j** were examined, more electron-donating substituents on a phenyl group (e.g., OCH_3 and CH_3) enhanced the reaction rate (entries 8-10). These results suggest that nucleophilic attack of a carbonyl oxygen to a center carbon of vinylidene plays a pivotal role in this reaction. While the reaction of 1-naphthyl ketone **1k** gave **7k** with much lower yield probably due to the steric hindrance,[12] the reaction of 2-naphthyl ketone **1l** gave the corresponding product **7l** in 92% yield (entries 11 and 12). Heterocycles such as 2-furyl or 2-thienyl tolerated in the reactions (entries 13 and 14), but 2-pyridyl substituent slightly precluded the product formation (entry 15). The reaction of 1-hexyn-1-ylketone **1p** gave benzofuran derivative **8p** in 24% yield together with **7p** as a minor product (eq 2). The formation of **8p** is explained by assuming the formation of **7p** isomerized from **1p** followed by intramolecular addition of a hydroxyl

Table 2. Catalytic Valence Isomerization of **1** (X = O) with $M(CO)_5(THF)$[a]



entry	R	M	mol%[b]	time (h)	product	yield (%)[c]
1	CH_2CH_2Ph (**1a**)	Cr	20	20	**7a**	92
2	CH_2CH_2Ph (**1a**)	W	20	24	**7a**	99
3	CH_2CH_2Ph (**1a**)	Cr	5	24	**7a**	97
4	*n*-Bu (**1d**)	Cr	5	24	**7d**	95
5[d]	*t*-Bu (**1e**)	Cr	30	26	**7e**	41
6	 (**1f**)	Cr	5	20	**7f**	94
7	 (**1g**)	Cr	5	12	**7g**	79
8	$C_6H_4CH_3$-*p* (**1h**)	Cr	5	24	**7h**	95
9	$C_6H_4OCH_3$-*p* (**1i**)	Cr	5	18	**7i**	96
10	$C_6H_4CF_3$-*p* (**1j**)	Cr	5	72	**7j**	72
11[d]	1-naphthyl (**1k**)	Cr	5	24	**7k**	trace
12	2-naphthyl (**1l**)	Cr	5	6	**7l**	92
13	2-furyl (**1m**)	Cr	5	5	**7m**	82
14	2-thienyl (**1n**)	Cr	5	17	**7n**	92
15[d]	2-pyridyl (**1o**)	Cr	5	24	**7o**	42

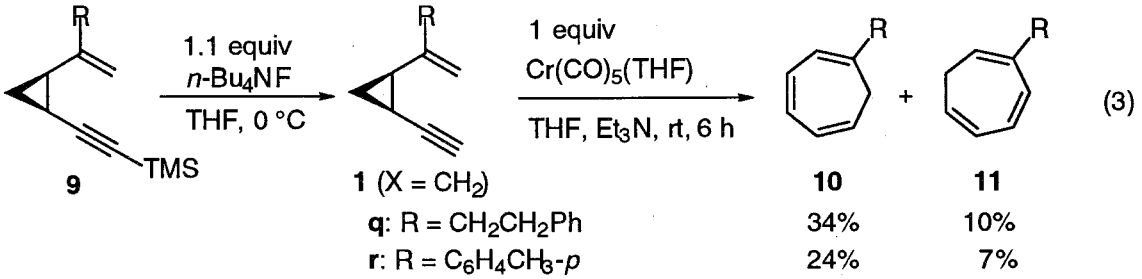
[a] **1** (0.5 mmol), Et_3N (1.5 mmol), and THF (5 mL) at room temperature. [b] Based on the amount of $M(CO)_6$ loaded. [c] Isolated yield. [d] At reflux temperature.



1p **8p** (24%) **7p** (trace) (2)

group to the alkynyl moiety.

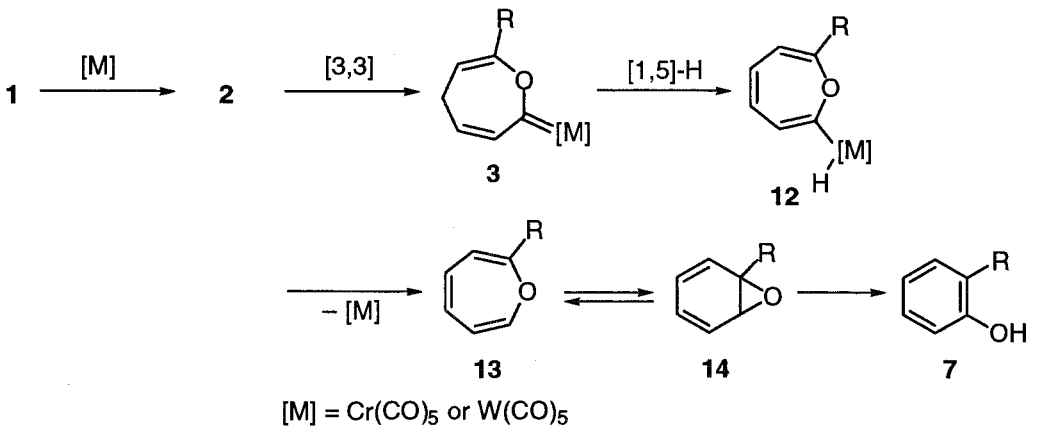
To gain a further insight into a mechanism for the group 6 metal triggering valence isomerism of **1**, two sets of experiments were next carried out. Thus, the author undertook the reaction of *cis*-1-ethynyl-2-vinylcyclopropane as a carbon-analogue, in which a carbonyl oxygen of **1** was replaced with CH_2. The reaction of **1 q** (0.3 mmol) with 1 equiv of $Cr(CO)_5(THF)$ in THF (10 mL) in the presence of Et_3N at room temperature for 6 h gave a mixture of 1- and 2-substituted 1,3,5-cycloheptatrienes **10q** and **11q** in 34 and 10% yields, respectively (eq 3).[13] Reaction of vinylcyclopropane **1r** also gave a mixture of



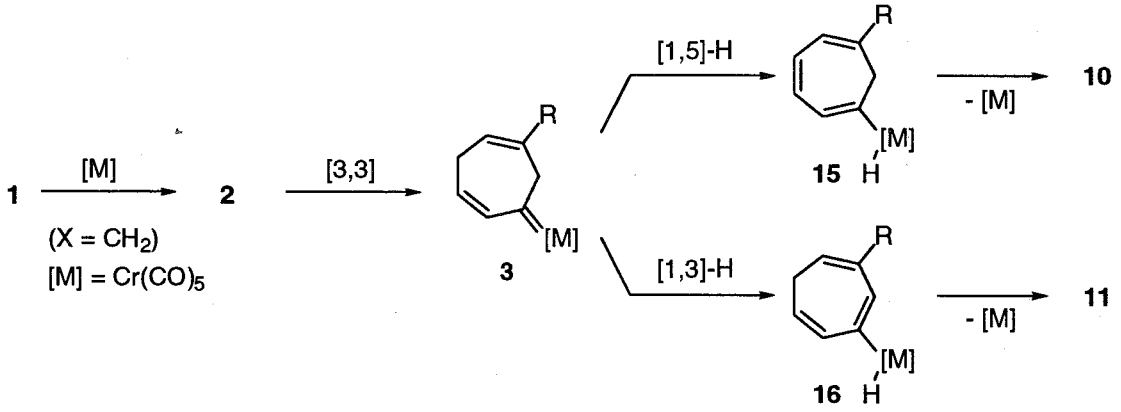
(3)

cycloheptatrienes **10r** (24%) and **11r** (7%). Vinylcyclopropanes **1q** and **1r** were immediately used for the reaction without further purification after desilylation of ethynylcyclopropane **9**,[14] since **1q** and **1r** were labile and gradually decomposed under ambient conditions. The formation of cycloheptatrienes clearly indicates that [3,3]sigmatropy of a vinylcyclopropylvinylidene intermediate **2** (X = CH_2) proceeds to give a seven-membered carbene complex **3** (X = CH_2) as shown in Scheme 1. Formation of two isomeric 1,3,5-cycloheptatrienes **10** and **11** can be explained by assuming the subsequent [1,5]- and [1,3]-hydrogen shifts in the complex **3** (X = CH_2) followed by reductive elimination of pentacarbonylchromium, $Cr(CO)_5$ from hydride complexes **10** and **11**, respectively (Scheme 4). Accordingly, isomerism of *cis*-1-acyl-2-ethynylcyclopropane **1** (X = O) can be also explained by assuming a multistep-pathway as shown in Scheme 5. Thus, [1,5]-H shift from CH_2 in a seven-membered ring of 1-oxa-3,6-cycloheptadien-2-ylidene complex **3** (X = O) to a metal and the subsequent reductive elimination of $M(CO)_5$ from **12** give rise to the formation

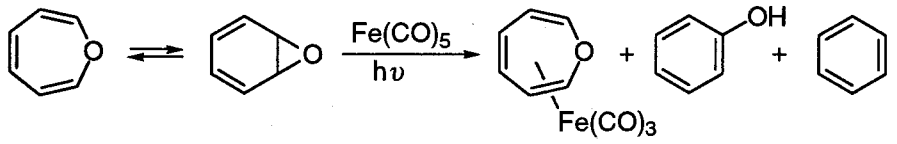
Scheme 4



Scheme 5



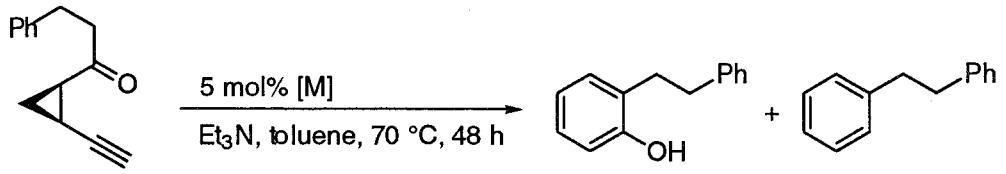
of an oxepin **13** as a primary product. The oxepin **13**, which is in equilibrium with the arene oxide **14**,[15] cannot be isolated, but it is converted into phenol **7** under the present reaction conditions.[16] Aumann *et al.* have reported that the reaction of an equilibrium mixture of an oxepin and a benzene oxide with $Fe(CO)_5$ under irradiation conditions gave benzene and phenol together with an (η^4-oxepin)$Fe(CO)_3$ complex as minor product (eq 4).[17] This strongly supported that phenol **7** as a final product was given with the assistance of $M(CO)_5$ as a Lewis acid under the present reaction conditions.



(4)

Finally, [3,3]sigmatropic rearrangement of acylethynylcyclopropane **1a** using other transition metal complexes was examined. When 2-phenylethyl ketone **1a** was reacted with

5 mol% of $[RuCl_2(CO)_3]_2$ or 5 mol% of $[RhCl(CO)_2]_2$ in toluene at 70 °C in the presence of Et_3N, isomerization occurred to give a mixture of *ortho*-phenylethyl phenol (**7a**) and deoxygenated product **17a** (eq 5). However, the yield of desired phenol **7a** was much lower



(5)

1a **7a** **17a**

[M]	yield[a]	
	7a	**17a**
$[RuCl_2(CO)_3]_2$	5%	trace
$[RhCl(CO)_2]_2$	16%	23%

[a] Determined by ^1H NMR.

in comparison with the case of group 6 metal complexes. The formation of deoxygenated product, i.e. 1,2-diphenylethane (**19a**), is in sharp contrast with reactions using group 6 metal complexes. Further studies are awaited to clarify the precise mechanism using ruthenium or rhodium as a catalyst.

In conclusion, the author has demonstrated the group 6 and other transition metal complexes-triggered valence isomerization of *cis* vicinal acyl- or vinyl-ethynylcyclopropanes in stoichiometric and catalytic processes. Isomerization of *cis* vicinal ethynylvinylcyclopropanes in the presence of group 6 metal complex leading to cycloheptatrienes was also investigated. The isomerism can be explained by [3,3]sigmatropic rearrangement of cyclopropylvinylidene-metal intermediates generated from acyl- or vinylethynylcyclopropanes. This represents the first example of [3,3]sigmatropy in which a vinylidene-metal works as a function of a two-π-electron moiety like a ketene.

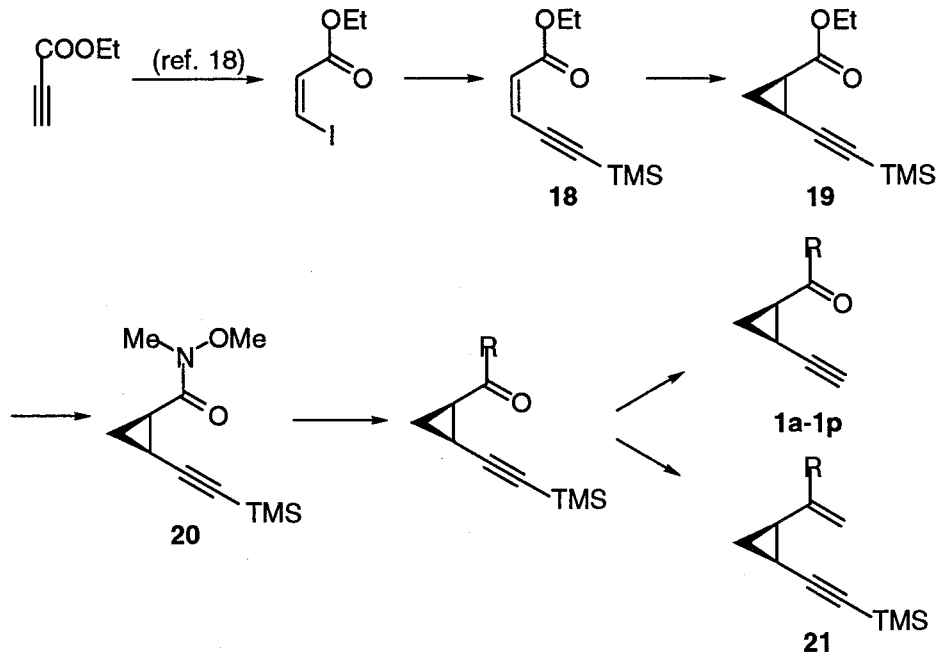
Experimental

General Procedures. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl under argon. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies were performed with Merck silica gel 60. 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, sex: sextet, m: multiplet. IR spectra were recorded on an FT-IR spectrometer. Melting points are uncorrected. High-resolution mass spectra (FAB HRMS) and low-resolution mass spectra (FAB LRMS) were obtained with JEOL LMX-SX 102A spectometer. Elemental analyses were performed at Microanalytical Center of Kyoto University. All new compounds prepared were fully characterized.

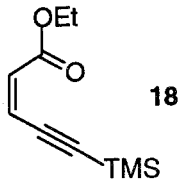
Synthesis of Substrates.

All substrates were prepared by the following procedures (Scheme 6).

Scheme 6



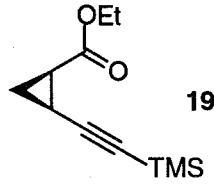
Preparation of (*Z*)-Ethyl 5-Trimethylsilyl-2-penten-4-ynoate (18).



18

To a solution of trimethylsilylacetylene (6.1 mL, 43 mmol), *tert*-butylamine (19 mL, 180 mmol) and (*Z*)-ethyl 3-iodo-2-propenoate[18] (8.1 g, 36 mmol) in benzene (470 mL) were added CuI (1.0 g, 5.3 mmol) and $Pd(PPh_3)_4$ (2.1 g, 1.8 mmol) at 0 °C under N_2. The resulting pale yellow suspension was stirred at room temperature for 1 h. The suspension was washed with saturated NH_4Cl solution (100 mL), and the aqueous layer was extracted with Et_2O (50 mL x 3). The combined organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 10/1) as an eluent to afford **18** (7.0 g, 36 mmol, 99% yield) as a pale yellow liquid; IR (neat) 1713, 1731 (C=O), 2150 (C≡C), 2927, 2961 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.21 (s, 9H), 1.29 (t, J = 7.2 Hz, 3H), 4.22 (q, J = 7.2 Hz, 2H), 6.05 (d, J = 11.4 Hz, 1H), 6.12 (d, J = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ -0.4, 14.2, 60.5, 100.7, 108.0, 122.4, 129.5, 164.6. Anal. Calcd for $C_{10}H_{16}O_2Si$: C, 61.18; H, 8.21. Found: C, 61.41; H, 8.44.

Preparation of *cis*-1-Ethoxycarbonyl-2-(trimethylsilyl)ethynylcyclopropane (19a).

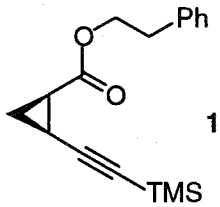


19a

Diazomethane, prepared by the reaction of $CH_3N(NO)CONH_2$ in Et_2O with 30% KOH aqueous solution, was bubbled into a solution of **18** (2.0 g, 10 mmol) and $Pd(OAc)_2$ (67 mg, 0.30 mmol) in *tert*-butyl methyl ether (200 mL). After continuous bubbling of diazomethane for 1 h, the black suspension was filtered with a Celite pad. The oraganic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 30/1) as an eluent to afford **19a** (0.98 g, 4.7 mmol, 47% yield) as a pale yellow liquid; IR (neat) 1731 (C=O), 2171 (C≡C), 2901, 2957 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.11 (s, 9H), 1.16 (ddd, J = 4.5, 8.0, 8.0 Hz, 1H), 1.26 (t, J = 6.9 Hz, 3H), 1.44 (ddd, J = 4.5, 6.3, 6.3 Hz, 1H), 1.79 (ddd, J = 6.3, 8.0, 8.0 Hz, 1H), 1.91 (ddd, J = 6.3, 8.0, 8.0 Hz, 1H), 4.16 (m,

2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 0.0 (Si*C*H$_3$), 10.0 (cyclopropane-*C*H$_2$), 14.3 (CH$_2$*C*H$_3$), 14.4 (*C*H-C≡), 21.8 (*C*H-CO), 60.7 (O*C*H$_2$), 84.0 (≡*C*-Si), 103.6 (C-*C*≡), 169.8 (*C*=O). Anal. Calcd for $C_{11}H_{18}O_2Si$: C, 62.81; H, 8.63. Found: C, 62.55; H, 8.82.

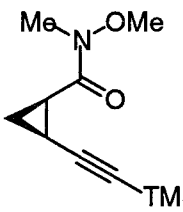
***cis*-1-(2-Phenylethoxycarbonyl)-2-(trimethylsilyl)ethynylcyclopropane (19b).**



19b

(*Z*)-2-Phenylethyl 5-trimethylsilyl-2-penten-4-ynoate[2a] was used as a starting compound. A colorless liquid (50% yield); IR (neat) 700, 760, 843, 1171, 1249, 1737 (C=O), 2171 (C≡C), 2958 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.11 (s, 9H), 1.17 (ddd, J = 5.8, 8.4, 8.4 Hz, 1H), 1.44 (ddd, J = 5.8, 6.4, 6.4 Hz, 1H), 1.82 (ddd, J = 6.4, 8.4, 8.4 Hz, 1H), 1.93 (ddd, J = 6.4, 8.4, 8.4 Hz, 1H), 2.95 (t, J = 7.2 Hz, 2H), 4.26 (dt, J = 5.4, 7.2 Hz, 1H), 4.37 (dt, J = 5.4, 7.2 Hz, 1H), 7.22-7.32 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 0.0 (Si*C*H$_3$), 10.2 (cyclopropane-*C*H$_2$), 14.4 (*C*H-C≡), 21.8 (*C*H-CO), 35.3 (Ph-*C*H$_2$), 65.3 (O*C*H$_2$), 84.2 (≡*C*-Si), 103.6 (C-*C*≡), 126.5 (Ph), 128.5 (Ph), 128.9 (Ph), 137.8 (Ph), 169.8 (*C*=O). Anal. Calcd for $C_{17}H_{22}O_2Si$: C, 71.28; H, 7.74. Found: C, 71.17; H, 7.66.

Preparation of *cis*-1-(*N*-Methoxy-*N*-methyl)carbamoyl-2-(trimethylsilyl)-ethynylcyclopropane (20a).

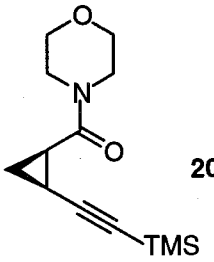


20a

According to the reported method,[19] to a suspension of *N,O*-dimethylhydroxyamine hydrochloride (1.8 g, 18 mmol) in THF (20 mL) was added a solution of $AlMe_3$ in hexane (1.0 M, 18 mL, 18 mmol) at room temperature under N_2. After stirring for 15 min, to the solution was added a solution of **19a** (1.5 g, 7.1 mmol) in THF (2 mL) at room temperature. The resulting brown solution was stirred at reflux temperature for overnight. The reaction mixture was cooled to room temperature, and slowly poured into ice-cooled 0.5 N HCl solution (50 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (20 mL x 3). The combined organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to column

chromatography on SiO_2 with hexane/AcOEt /CH_2Cl_2 (v/v/v = 5/1/1) as an eluent to afford **20a** (1.0 g, 4.4 mmol, 63% yield) as a pale yellow liquid; IR (neat) 641, 759, 843, 1100, 1253, 1424, 1653, 1668 (C=O), 2171 (C≡C), 2359, 2960 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.09 (s, 9H), 1.10 (ddd, J = 4.5, 8.3, 8.3 Hz, 1H), 1.53 (ddd, J = 4.5, 6.3, 6.3 Hz, 1H), 1.78 (ddd, J = 6.3, 8.3, 8.3 Hz, 1H), 2.39 (br m, 1H), 3.23 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, -40 °C) [as a mixture of rotamers] δ -0.4 (Si*C*H_3), 9.0 (cyclopropane-*C*H_2), 9.1 (cyclopropane-*C*H_2), 12.2 (*C*H-C≡), 19.9 (*C*H-CO), 20.0 (*C*H-CO), 32.1 (N*C*H_3), 32.1 (N*C*H_3), 61.4 (O*C*H_3), 83.1 (≡*C*-Si), 104.5 (CH-*C*≡), 168.8 (*C*=O). Anal. Calcd for $C_{11}H_{19}NO_2Si$: C, 58.63; H, 8.50; N, 6.22. Found: C, 58.59; H, 8.28; N, 6.24.

***cis*-1-Morpholinocarbamoyl-2-(trimethylsilyl)ethynylcyclopropane (20b).**

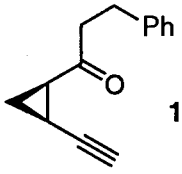


20b

A colorless liquid (86% yield); IR (neat) 638, 760, 844, 859, 1116, 1230, 1249, 1434, 1463, 1651 (C=O), 2169 (C≡C), 2961 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.06 (s, 9H), 1.08 (ddd, J = 5.4, 8.4, 8.4 Hz, 1H), 1.50 (ddd, J = 5.4, 6.0, 6.0 Hz, 1H), 1.73 (ddd, J = 5.4, 8.4, 8.4 Hz, 1H), 1.90 (ddd, J = 6.0, 8.4, 8.4 Hz, 1H), 3.33-3.89 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 0.0 (Si*C*H_3), 8.4 (cyclopropane-*C*H_2), 12.7 (*C*H-C≡), 22.0 (*C*H-CO), 42.9 (N*C*H_2), 45.8 (N*C*H_2), 67.0 (O*C*H_2), 83.4 (≡*C*-Si), 104.3 (C-*C*≡), 166.8 (*C*=O). HRMS (FAB): calcd for $C_{13}H_{21}NO_2Si$ ($M+H^+$), 252.1420; found, 252.1416.

Preparation of *cis*-1-Acyl-2-ethynylcyclopropanes from 20a with Organomagnesium Reagents.

***cis*-1-Ethynyl-2-(3-phenylpropanoyl)cyclopropane (1a).**

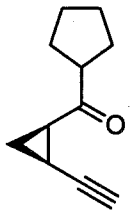


1a

To a solution of **20a** (0.84 g, 3.7 mmol) in THF (5 mL) was added a solution of 2-phenylethylmagnesium bromide (about 2 equiv) in THF (5 mL) at 0 °C under N_2. The mixture was stirred at 0 °C for 0.5 h. The reaction mixture was poured into saturated aqueous NH_4Cl solution (20 mL) and extracted with AcOEt (20 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent

was removed under reduced pressure to leave a brown oil, which was treated with K_2CO_3 (0.77 g, 5.6 mmol) in MeOH (30 mL) at room temperature for 3 h. The obtained brown suspension was poured into saturated NH_4Cl solution (100 mL) and extracted with AcOEt (50 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 8/1) as an eluent to afford **1a** (0.63 g, 3.2 mmol, 85% yield) as a yellow liquid; IR (neat) 669, 1092, 1387, 1705 (C=O), 2121 (C≡C), 2923, 3289 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.17 (ddd, J = 4.8, 8.1, 8.1 Hz, 1H), 1.55 (ddd, J = 4.8, 6.3, 6.3 Hz, 1H), 1.84 (dddd, J = 2.1, 6.3, 8.1, 8.1 Hz, 1H), 1.93 (d, J = 2.1 Hz, 1H), 2.22 (ddd, J = 6.3, 8.1, 8.1 Hz; 1H), 2.89-3.00 (m, 4H), 7.16-7.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.0 (cyclopropane-CH_2), 14.5 (*C*H-C≡), 27.6 (*C*H-CO), 29.6 (CO-CH_2), 45.5 (CH_2-Ph), 68.0 (≡*C*-H), 81.2 (CH-*C*≡), 126.1 (Ph), 128.4 (Ph), 128.4 (Ph), 141.1 (Ph), 204.2 (*C*=O). Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.88; H, 7.02.

***cis*-1-Ethynyl-2-cyclopentylmethanoylcyclopropane (1f).**

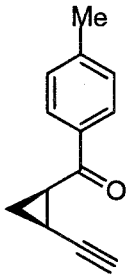


1f

To a solution of **20a** (0.28 g, 1.2 mmol) in THF (5 mL) was added a solution of cyclopentylmagnesium bromide in THF (5 mL) which was prepared from bromocyclopentane (0.36 g, 2.4 mmol) and Mg (58 mg, 2.4 mmol) in THF (3 mL) at 0 °C under N_2. The mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was poured into aqueous 1 N HCl solution (20 mL), and extracted with Et_2O (20 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure to leave a brown oil, which was treated with tetrabutylammonium fluoride (TBAF, 1.0 M in THF, 1.3 mL, 1.3 mmol) in THF (10 mL) at 0 °C for 10 min. The obtained brown solution was poured into saturated NH_4Cl solution (10 mL), and extracted with Et_2O (20 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 8/1) as an eluent to afford **1f** (85 mg, 0.53 mmol, 44% yield) as a colorless oil; IR (neat) 641, 873,

900, 966, 1026, 1058, 1106, 1385, 1431, 1461, 1698, 1703 (C=O), 2122 (C≡C), 2870, 2956, 3268, 3289 (≡C-H) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 1.16 (ddd, J = 4.3, 7.6, 7.6 Hz, 1H), 1.54 (ddd, J = 4.3, 6.2, 6.2 Hz, 1H), 1.56-1.72 (m, 4H), 1.81-1.92 (m, 4H), 1.86 (dddd, J = 2.4, 6.2, 7.6, 7.6 Hz, 1H), 1.94 (d, J = 2.4 Hz, 1H), 2.29 (ddd, J = 6.2, 7.6, 7.6 Hz, 1H), 3.05 (quint, J = 7.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C) δ 11.3 (cyclopropane-CH_2), 14.4 (CH-C≡), 25.9, 26.1, 26.8, 28.1, 28.6, 52.6, 67.7 (≡C-H), 81.5 (CH-C≡), 206.7 (C=O). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.67. Found: C, 81.58; H, 8.74.

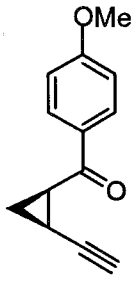
***cis*-1-Ethynyl-2-(*p*-methylbenzoyl)cyclopropane (1h).**



1h

A white solid (82% yield); mp. 58.2-60.1 °C; IR (KBr) 507, 660, 698, 771, 830, 939, 999, 1177, 1229, 1383, 1407, 1605, 1671 (C=O), 2122 (C≡C), 3269 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.30 (ddd, J = 4.2, 7.8, 7.8 Hz, 1H), 1.79 (ddd, J = 4.2, 6.3, 6.3 Hz, 1H), 1.87 (d, J = 2.1 Hz, 1H), 2.04 (dddd, J = 2.1, 6.3, 8.7, 8.7 Hz, 1H), 2.42 (s, 3H), 2.92 (ddd, J = 6.3, 8.7, 8.7 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.6 (cyclopropane-CH_2), 14.1 (CH-C≡), 21.6 (CH-CO), 24.6 (CH_3), 67.8 (≡C-H), 81.2 (CH-C≡), 128.3 (Ph), 129.2 (Ph), 135.4 (Ph), 143.8 (Ph), 194.5 (C=O). Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.56. Found: C, 84.64; H, 6.47.

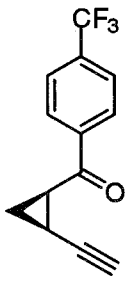
***cis*-1-Ethynyl-2-(*p*-methoxybenzoyl)cyclopropane (1i).**



1i

A white solid (78% yield); mp. 93.5-95.5 °C; IR (KBr) 529, 605, 656, 778, 803, 847, 1028, 1174, 1233, 1259, 1387, 1422, 1601, 1651 (C=O), 2115 (C≡C), 2345, 3274 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.29 (ddd, J = 4.5, 8.4, 8.4 Hz, 1H), 1.78 (ddd, J = 4.5, 6.6, 6.6 Hz, 1H), 1.87 (d, J = 2.1 Hz, 1H), 2.02 (dddd, J = 2.1, 6.6, 8.4, 8.4 Hz, 1H), 2.89 (ddd, J = 6.6, 8.4, 8.4 Hz, 1H), 3.88 (s, 3H), 6.94-6.99 (m, 2H), 8.01-8.06 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.4 (cyclopropane-CH_2), 14.0 (CH-C≡), 24.4 (CH-CO), 25.5 (OCH_3), 67.7 (≡C-H), 81.3 (CH-C≡), 113.7 (Ph), 130.5 (Ph), 130.9 (Ph), 163.4 (Ph), 193.4 (C=O). HRMS (FAB): calcd for $C_{13}H_{13}O_2$ (M^+), 201.0916; found, 201.0915.

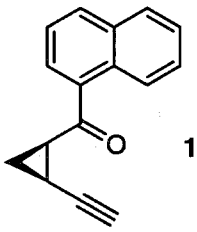
***cis*-1-Ethynyl-2-(*p*-trifluoromethylbenzoyl)cyclopropane (1j).**



1j

A white solid (38% yield); mp. 64.5-66.5 °C; IR (KBr) 677, 705, 855, 997, 1065, 1153, 1222, 1328, 1382, 1413, 1511, 1583, 1676 (C=O), 2119 (C≡C), 3253 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.38 (ddd, J = 4.5, 8.4, 8.4 Hz, 1H), 1.84 (ddd, J = 4.5, 6.6, 6.6 Hz, 1H), 1.90 (d, J = 1.8 Hz, 1H), 2.13 (dddd, J = 1.8, 6.6, 8.4, 8.4 Hz, 1H), 2.94 (ddd, J = 6.6, 8.4, 8.4 Hz, 1H), 7.76 (d, J = 8.1 Hz, 2H), 8.13 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 12.3 (cyclopropane-CH_2), 14.5 (*C*H-C≡), 25.1 (*C*H-CO), 68.2 (≡*C*-H), 80.8 (CH-*C*≡), 121.8 (Ph), 125.4 (Ph), 125.7 (q, $^1J_{C\text{-}F}$ = 3.8 Hz, CF_3), 128.5 (Ph), 134.1 (Ph), 134.5 (Ph), 140.4 (Ph), 194.2 (*C*=O). Anal. Calcd for $C_{13}H_9OF$: C, 65.55; H, 3.81. Found: C, 65.34; H, 3.89.

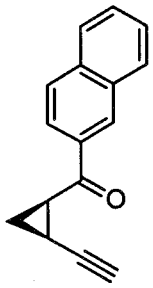
***cis*-1-Ethynyl-2-(1-naphthoyl)cyclopropane (1k).**



1k

A white solid (82% yield); mp. 87.8-90.8 °C; IR (KBr) 684, 778, 793, 992, 1099, 1178, 1231, 1370, 1508, 1664 (C=O), 2113 (C≡C), 2365, 3066, 3249 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.39 (ddd, J = 4.2, 7.5, 7.5 Hz, 1H), 1.93 (ddd, J = 4.2, 6.0, 6.0 Hz, 1H), 1.98 (d, J = 2.4 Hz, 1H), 2.14 (dddd, J = 2.4, 6.0, 7.5, 7.5 Hz, 1H), 2.90 (ddd, J = 6.0, 7.5, 7.5 Hz, 1H), 7.51-7.62 (m, 2H), 7.55 (d, J = 7.8 Hz, 1H), 7.89 (dd, J = 1.8, 7.8 Hz, 1H), 8.00 (d, J = 7.8 Hz, 2H), 8.61 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 12.9 (cyclopropane-CH_2), 15.2 (*C*H-C≡), 28.4 (*C*H-CO), 68.4 (≡*C*-H), 81.1 (CH-*C*≡), 124.5 (naphthyl), 125.8 (naphthyl), 126.5 (naphthyl), 127.7 (naphthyl), 127.8 (naphthyl), 128.4 (naphthyl), 130.1 (naphthyl), 132.4 (naphthyl), 133.9 (naphthyl), 137.1 (naphthyl), 198.4 (*C*=O). Anal. Calcd for $C_{16}H_{12}O$: C, 87.25; H, 5.49. Found: C, 87.07; H, 5.51.

***cis*-1-Ethynyl-2-(2-naphthoyl)cyclopropane (1l).**

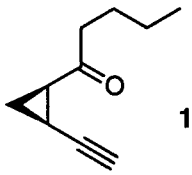


1l

A white solid (82% yield); mp. 101.8-103.4 °C; IR (KBr) 692, 785, 1124, 1171, 1388, 1465, 1668 (C=O), 2116 (C≡C), 3251 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.38 (ddd, J = 4.5, 7.8, 7.8 Hz, 1H), 1.87 (ddd, J = 4.5, 6.6, 6.6 Hz, 1H), 1.89 (d, J = 2.1 Hz, 1H), 2.14 (dddd, J = 2.1, 6.6, 7.8, 7.8 Hz, 1H), 3.11 (ddd, J = 6.6, 7.8, 7.8 Hz, 1H), 7.58 (m, 2H), 7.89 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 8.08 (dd, J = 1.8, 8.4 Hz, 1H), 8.57 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.9 (cyclopropane-CH_2), 14.4 (*C*H-C≡), 24.9 (*C*H-CO), 68.0 (≡*C*-H), 81.2 (CH-*C*≡), 124.0 (naphthyl), 126.8 (naphthyl), 127.8 (naphthyl), 128.4 (naphthyl), 128.4 (naphthyl), 129.6 (naphthyl), 129.9 (naphthyl), 132.5 (naphthyl), 135.2 (naphthyl), 135.2 (naphthyl), 194.9 (*C*=O). Anal. Calcd for $C_{16}H_{12}O$: C, 87.25; H, 5.49. Found: C, 87.19; H, 5.39.

Preparation of *cis*-1-Acyl-2-ethynylcyclopropanes from 20a and Organolithium Reagents.

***cis*-1-Ethynyl-2-pentanoylcyclopropane (1d).**

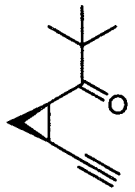


1d

To a solution of **20a** (0.33 g, 1.5 mmol) in THF (20 mL) was added butyllithium in hexane (1.6 M, 2.0 mL, 3.2 mmol) at -20 °C under N_2. After stirring at -20 °C for 40 min, the mixture was poured into saturated NH_4Cl solution (50 mL) and extracted with AcOEt (20 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure to give a brown oil, which was treated with K_2CO_3 (0.30 g, 2.2 mmol) in MeOH (25 mL) at room temperature for 3 h. The resulting brown suspension was poured into saturated NH_4Cl solution (100 mL) and extracted with AcOEt (50 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 15/1) as an eluent to afford **1d** (0.15 g, 1.0 mmol, 69% yield) as a colorless liquid; IR (neat) 1074, 1387, 1705 (C=O), 2876, 2933,

2959, 3289 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.90 (t, J = 7.4 Hz, 3H), 1.13 (ddd, J = 4.4, 7.5, 8.4 Hz, 1H), 1.32 (sex, J = 7.4 Hz, 2H), 1.53 (ddd, J = 4.4, 6.4, 6.4 Hz, 1H), 1.56-1.66 (m, 2H), 1.81 (dddd, J = 2.4, 6.4, 8.4, 8.4 Hz, 1H), 1.90 (d, J = 2.4 Hz, 1H), 2.22 (ddd, J = 6.4, 7.5, 8.4 Hz, 1H), 2.56 (t, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 10.8 (cyclopropane-CH_2), 13.8 (*C*H-C≡), 14.3 (*C*H-CO), 22.4 (butyl), 25.8 (butyl), 27.4 (butyl), 43.8 (butyl), 67.8 (≡*C*-H), 81.3 (CH-*C*≡), 205.4 (*C*=O). Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.57; H, 9.42.

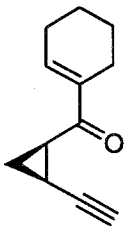
***cis*-(2,2-Dimethylpropanoyl)-1-ethynylcyclopropane (1e).**



1e

To a solution of **20a** (0.34 g, 1.5 mmol) in THF (20 mL) was added *tert*-butyllithium in pentane (1.4 M, 1.6 mL, 2.3 mmol) at -78 °C under N_2. After stirring at -78 °C for 1 h, the mixture was poured into aqueous 1 N HCl solution (20 mL) and extracted with Et_2O (20 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure to give a brown oil, which was treated with TBAF (1.0 M in THF, 1.7 mL, 1.7 mmol) in THF (10 mL) at 0 °C for 15 min. The resulting brown suspension was poured into saturated NH_4Cl solution (20 mL) and extracted with Et_2O (20 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 8/1) as an eluent to afford **1d** (0.13 g, 0.89 mmol, 59% yield) as a white solid; mp. 60.5-61.7 °C; IR (KBr) 843, 1084, 1249, 1367, 1393, 1692 (C=O), 2162 (C≡C), 2346, 2372, 2927, 2960, 3309 (≡C-H), 3400 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.15 (ddd, J = 4.5, 8.1, 8.1 Hz, 1H), 1.22 (s, 9H), 1.55 (ddd, J = 4.5, 6.3, 6.3 Hz, 1H), 1.83 (dddd, J = 2.1, 6.6, 8.1, 8.1 Hz, 1H), 1.89 (d, J = 2.1 Hz, 1H), 2.49 (ddd, J = 6.6, 8.1, 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.3 (cyclopropane-CH_2), 14.0 (*C*H-C≡), 23.3 (*C*H-CO), 26.1 (*C*-CH_3), 44.3 (*C*-CH_3), 67.5 (≡*C*-H), 81.6 (CH-*C*≡), 209.1 (*C*=O). HRMS (FAB): calcd for $C_{10}H_{15}O$ (M^+), 151.1123; found, 151.1128.

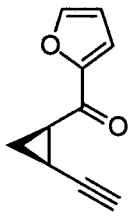
***cis*-1-Cyclohexenyl 2-ethynylcyclopropyl ketone (1g).**



1g

To a solution of **20a** (0.41 g, 1.8 mmol) in THF (dry, 20 mL) was added 1-cyclohexenyllithium in *n*-hexane which was prepared from cyclohexanone *p*-tosylhydrazone (0.96 g, 1.0 mmol), tetramethylethylenediamine (1.3 mL, 8.6 mmol) and *sec*-butyllithium (1.0 M in *n*-hexane and cyclohexane, 2.0 mL, 2.0 mmol) at 0 °C under N_2. After stirring at room temperature for 20 min, the mixture was poured into aqueous 1 N HCl solution (20 mL) and extracted with Et_2O (20 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure to give a brown oil, which was treated with TBAF (1.0 M in THF, 2.0 mL, 2.0 mmol) in THF (18 mL) at 0 °C for 1 h. The resulting brown suspension was poured into saturated NH_4Cl solution (20 mL) and extracted with Et_2O (20 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 8/1) as an eluent to afford **1g** (53 mg, 0.31 mmol, 17% yield) as a white solid; mp. 49.2-50.5 °C; IR (KBr) 509, 688, 845, 898, 998, 1049, 1182, 1208, 1402, 1645 (C=O), 2118 (C≡C), 2346, 2929, 3251 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.16 (ddd, J = 4.2, 7.8, 7.8 Hz, 1H), 1.61 (ddd, J = 4.2, 6.6, 6.6 Hz, 1H), 1.63-1.71 (m, 4H), 1.85 (dddd, J = 2.1, 6.6, 7.8, 7.8 Hz, 1H), 1.90 (d, J = 2.1 Hz, 1H), 2.21-2.40 (m, 4H), 2.62 (ddd, J = 6.6, 7.8, 7.8 Hz, 1H), 7.03 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 10.9 (cyclopropane-CH_2), 13.8 (*C*H-C≡), 21.6 (CH_2), 23.3 (CH_2), 23.3 (*C*H-CO), 26.1 (CH_2), 67.5 (≡*C*-H), 81.7 (CH-*C*≡), 140.1 (vinyl), 140.2 (vinyl), 195.4 (*C*=O). HRMS (FAB): calcd for $C_{12}H_{15}O$ (M^+), 175.1123; found, 175.1122.

***cis*-2-Ethynylcyclopropyl 2-furyl ketone (1m).**[20]

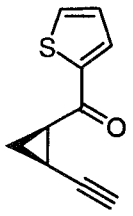


1m

A yellow solid (75% yield); mp. 73.0-73.9 °C; IR (KBr) 616, 657, 800, 881, 908, 1002, 1066, 1264, 1467, 1561, 1656 (C=O), 2166 (C≡C), 3121, 3138, 3292 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.33 (ddd, J = 4.5, 8.4, 8.4 Hz, 1H), 1.75 (ddd, J = 4.5, 6.6, 6.6 Hz, 1H), 1.96 (d,

J = 2.1 Hz, 1H), 2.02 (dddd, J = 2.1, 6.6, 8.4, 8.4 Hz, 1H), 2.92 (ddd, J = 6.6, 8.4, 8.4 Hz, 1H), 6.57 (dd, J = 1.8, 3.6 Hz, 1H), 7.27 (d, J = 3.6 Hz, 1H), 7.61 (d, J = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.9 (cyclopropane-CH_2), 14.4 (CH-C≡), 24.1 (CH-CO), 68.3 (≡C-H), 80.8 (CH-C≡), 112.2 (furyl), 116.8 (furyl), 146.3 (furyl), 153.2 (furyl), 183.5 (C=O). Anal. Calcd for $C_{10}H_8O_2$: C, 74.99; H, 5.03. Found: C, 74.87; H, 5.08.

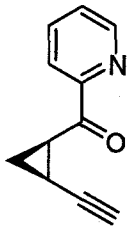
***cis*-2-Ethynylcyclopropyl 2-thienyl ketone (1n).**[21]



1n

A yellow liquid (76% yield); IR (neat) 725, 856, 908, 1064, 1237, 1386, 1417, 1517, 1651 (C=O), 2120 (C≡C), 3292 (≡C-H) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.32 (ddd, J = 4.5, 7.8, 7.8 Hz, 1H), 1.74 (ddd, J = 4.5, 6.6, 6.6 Hz, 1H), 1.93 (d, J = 2.1 Hz, 1H), 2.01 (dddd, J = 2.1, 6.6, 7.8, 7.8 Hz, 1H), 2.83 (ddd, J = 6.6, 7.8, 7.8 Hz, 1H), 7.14 (dd, J = 3.3, 4.8 Hz, 1H), 7.63 (d, J = 4.8 Hz, 1H), 7.80 (d, J = 3.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.9 (cyclopropane-CH_2), 14.6 (CH-C≡), 25.3 (CH-CO), 68.3 (≡C-H), 80.9 (CH-C≡), 128.1 (thienyl), 131.8 (thienyl), 133.5 (thienyl), 144.9 (thienyl), 187.2 (C=O). Anal. Calcd for $C_{10}H_8OS$: C, 68.15; H, 4.58. Found: C, 67.99; H, 4.56.

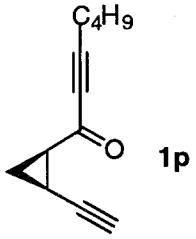
***cis*-2-Ethynylcyclopropyl 2-pyridyl ketone (1o).**



1o

A white solid (47% yield); mp. 73.9-75.3 °C; IR (KBr) 678, 689, 763, 1003, 1218, 1383, 1438, 1582, 1682 (C=O), 2109 (C≡C), 3263 (≡C-H) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.42 (ddd, J = 4.2, 7.8, 7.8 Hz, 1H), 1.75 (ddd, J = 4.2, 6.6, 6.6 Hz, 1H), 1.96 (d, J = 2.1 Hz, 1H), 2.11 (dddd, J = 2.1, 6.6, 7.8, 7.8 Hz, 1H), 3.86 (ddd, J = 6.6, 7.8, 7.8 Hz, 1H), 7.47-7.52 (m, 1H), 7.83-7.89 (m, 1H), 8.10-8.13 (m, 1H), 8.71-8.73 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 13.0 (cyclopropane-CH_2), 16.1 (CH-C≡), 22.9 (CH-CO), 68.2 (≡C-H), 81.5 (CH-C≡), 122.0 (pyridyl), 127.1 (pyridyl), 137.0 (pyridyl), 148.9 (pyridyl), 153.6, (pyridyl), 195.8 (C=O). Anal. Calcd for $C_{11}H_9NO$: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.95; H, 5.39; N, 8.07.

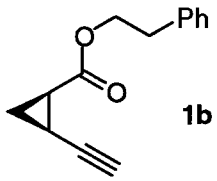
***cis*-2-Ethynylcyclopropyl 1-hex-1-ynyl ketone (1p).**



To a solution of **20a** (0.30 g, 1.3 mmol) in THF (8 mL) was added 1-hexynyllithium (2.0 mmol) which was prepared from 1-hexyne (0.27 g, 3.3 mmol), and *n*-butyllithium (1.6 M in *n*-hexane, 1.6 mL, 2.6 mmol) at room temperature under N_2. After stirring at room temperature for 1 h, the mixture was poured into aqueous 1 N HCl solution (20 mL) and extracted with Et_2O (20 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure to give a brown oil, which was treated with KF (0.19 g, 3.3 mmol) in DMSO (10 mL) at room temperature for 9 h. The resulting purple solution was poured into H_2O (20 mL) and extracted with Et_2O (20 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 8/1) as an eluent to afford **1p** (0.20 g, 1.1 mmol, 86% yield) as a yellow liquid; IR (neat) 642, 926, 1000, 1057, 1121, 1171, 1191, 1265, 1380, 1429, 1652, 1661 (C=O), 2210 (C≡C), 2873, 2934, 2960, 3297 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.97 (t, J = 7.2 Hz, 3H), 1.26 (ddd, J = 4.5, 8.1, 8.1 Hz, 1H), 1.42 (sex, J = 7.2 Hz, 2H), 1.51-1.61 (m, 2H), 1.65 (ddd, J = 4.5, 6.6, 6.6 Hz, 1H), 1.93 (dddd, J = 2.1, 6.6, 8.1, 8.1 Hz, 1H), 1.98 (d, J = 2.1 Hz, 1H), 2.36 (ddd, J = 6.6, 8.1, 8.1 Hz, 1H), 2.37 (t, J = 6.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.3 (cyclopropane-CH_2), 14.0 (*C*H-C≡), 23.3 (*C*H-CO), 26.1 (C-CH_3), 44.3 (*C*-CH_3), 67.5 (≡*C*-H), 81.6 (CH-*C*≡), 209.1 (*C*=O). HRMS (FAB): calcd for $C_{12}H_{14}O$ (M^+), 174.1045; found, 174.1041.

Preparation of 1b and 1c (Deprotection of Trimethylsilyl Group).

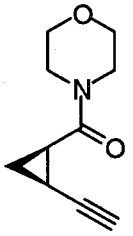
***cis*-2-Ethynyl-1-(2-phenylethoxycarbonyl)cyclopropane (1b).**



To a solution of **19b** (0.29 g, 1.0 mmol) in MeOH (10 mL) was added 1 N KOH aqueous solution (1 mL) at 0 °C. The resulting brown solution was stirred at room temperature for 1 h, poured into saturated

NH_4Cl solution (30 mL), and extracted with AcOEt (10 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 15/1) as an eluent to afford **1b** (0.16 g, 0.76 mmol, 76% yield) as a colorless liquid; IR (neat) 654, 700, 750, 819, 1123, 1174, 1402, 1732 (C=O), 2124 (C≡C), 2956, 3289 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.22 (ddd, J = 5.6, 8.4, 8.4 Hz, 1H), 1.44 (ddd, J = 5.6, 6.3, 6.3 Hz, 1H), 1.81 (dddd, J = 2.1, 6.3, 8.4, 8.4 Hz, 1H), 1.92 (d, J = 2.1 Hz, 1H), 1.94 (ddd, J = 6.3, 8.4, 8.4 Hz, 1H), 2.97 (t, J = 7.2 Hz, 2H), 4.35 (dt, J = 5.1, 7.2 Hz, 2H), 7.23-7.33 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 9.1 (cyclopropane-CH_2), 14.2 (*C*H-C≡), 20.9 (*C*H-CO), 35.1 (Ph-CH_2), 65.3 (OCH_2), 67.7 (≡*C*-H), 81.2 (CH-*C*≡), 126.4 (Ph), 128.4 (Ph), 128.8 (Ph), 137.7 (Ph), 170.0 (*C*=O). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.20; H, 6.63.

***cis*-2-Ethynyl-1-morpholinocarbamoylcyclopropane (1c).**



1c

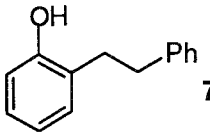
A colorless liquid (81% yield); IR (neat) 845, 1032, 1067, 1114, 1234, 1436, 1471, 1646 (C=O), 2121 (C≡C), 2861, 3284 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.16 (ddd, J = 5.3, 8.5, 8.5 Hz, 1H), 1.60 (ddd, J = 5.3, 6.0, 6.0 Hz, 1H), 1.76 (dddd, J = 2.4, 6.0, 8.5, 8.5 Hz, 1H), 1.90 (d, J = 2.4 Hz, 1H), 1.98 (ddd, J = 6.0, 8.5, 8.5 Hz, 1H), 3.42-3.92 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 7.5 (cyclopropane-CH_2), 12.6 (*C*H-C≡), 21.0 (*C*H-CO), 42.5 (N*C*H_2), 45.9 (N*C*H_2), 67.0 (O*C*H_2), 67.1 (≡*C*-H), 82.0 (CH-*C*≡), 167.1 (*C*=O). HRMS (FAB): calcd for $C_{10}H_{14}NO_2$ ($M+H^+$), 180.1025; found, 180.1020.

Typical Procedure for Chromium-catalyzed Isomerization Reaction of 1.

The complex $Cr(CO)_6$ (5.5 mg, 0.025 mmol) was placed in the flame dried Schlenk flask and dissolved in THF (dry and deoxygenated, 5.0 mL) at room temperature under N_2. This solution was irradiated with high-pressure Hg lamp (450 W, 350 nm) for 2 h at room temperature. Then, N_2 gas was bubbled into the yellow solution for 10 min. To the yellow

solution were added the substrate (0.5 mmol), if necessary with THF (1 mL), and triethylamine (0.2 mL, 1.4 mmol). After the reaction was complete, the organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 10/1 or 8/1) as an eluent to afford **7**.

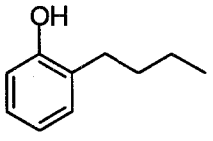
2-(2-Phenylethyl)phenol (7a).



7a

A white solid (97% yield); mp. 81.8-82.8 °C; IR (KBr) 506, 700, 745, 758, 1095, 1142, 1326, 1453, 1501, 1591, 3521 (O-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.92 (m, 4H), 4.59 (br s, 1H), 6.74 (d, J = 9.0 Hz, 1H), 6.85 (dd, J = 9.0, 9.0 Hz, 1H), 7.05-7.11 (m, 2H), 7.17-7.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 32.3, 36.2, 115.4, 120.9, 126.0, 127.3, 127.8, 128.4, 128.5, 130.3, 142.0, 153.5. Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.90; H, 7.42.

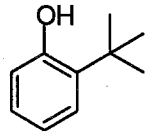
2-(*n*-Butyl)phenol (7d).



7d

A colorless liquid (95% yield); IR (neat) 751, 1115, 1455, 2928, 2957, 3389 (O-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.94 (t, J = 7.2 Hz, 3H), 1.39 (sex, J = 7.2 Hz, 2H), 1.55-1.65 (m, 2H), 2.60 (t, J = 7.2 Hz, 2H), 4.69 (br s, 1H), 6.75 (d, J = 7.5 Hz, 1H), 6.86 (dd, J = 7.5, 7.5 Hz, 1H), 7.07 (dd, J = 7.5, 7.5 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 14.0, 22.6, 29.6, 31.9, 115.2, 120.8, 127.0, 128.5, 130.2, 153.4. Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.17; H, 9.51.

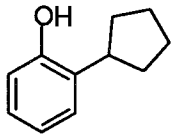
2-(*tert*-Butyl)phenol (7e).



7e

Phenol **7e** is commercially available, and the ^1H NMR spectrum of **7e** which is shown below was the same as the spectrum of an authentic sample. A colorless liquid (95% yield); ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.41 (s, 9H), 4.88 (br s, 1H), 6.67 (d, J = 7.6 Hz, 1H), 6.87 (dd, J = 7.6, 7.6 Hz, 1H), 7.07 (dd, J = 7.6, 7.6 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H).

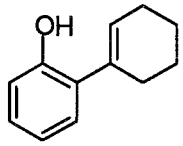
2-Cyclopentylphenol (7f).



7f

A colorless liquid (94% yield); IR (neat) 751, 822, 1043, 1097, 1174, 1237, 1331, 1343, 1492, 1502, 1588, 2868, 2953, 3369 (O-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.61-1.81 (m, 6H), 2.04-2.06 (m, 2H), 3.16-3.27 (m, 1H), 4.78 (s, 1H), 6.75 (d, J = 7.8 Hz, 1H), 6.89 (dd, J = 6.6, 7.8 Hz, 1H), 7.06 (dd, J = 6.6, 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 25.3, 32.8, 39.0, 115.2, 120.8, 126.7, 127.0, 131.9, 153.4. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.51; H, 8.96.

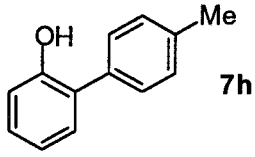
2-(1-Cyclohexenyl)phenol (7g).



7g

A yellow liquid (79% yield); IR (neat) 487, 576, 649, 752, 816, 851, 919, 1179, 1228, 1280, 1447, 1487, 2857, 2930, 3437 (O-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.66-1.74 (m, 2H), 1.76-1.84 (m, 2H), 2.17-2.30 (m, 4H), 5.64 (s, 1H), 5.59-5.89 (m, 1H), 6.84-6.93 (m, 2H), 7.05-7.16 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.9, 23.0, 25.4, 29.8, 115.2, 120.1, 128.0, 128.0, 128.1, 129.8, 134.8, 152.0. HRMS (FAB): calcd for $C_{12}H_{14}O$ (M^+), 174.1045; found, 174.1040.

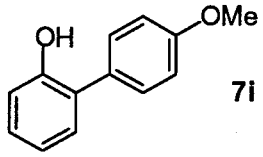
2-(4-Methylphenyl)phenol (7h).



7h

A brown liquid (95% yield); IR (neat) 667, 752, 817, 1108, 1181, 1478, 1482, 1582, 2920, 3418 (O-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.41 (s, 3H), 5.21 (br s, 1H), 6.97 (d, J = 7.2 Hz, 1H), 6.98 (dd, J = 7.2, 7.2 Hz, 1H), 7.21-7.37 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.2, 115.7, 120.8, 128.1, 128.9, 129.0, 130.0, 130.2, 134.0, 137.7, 152.5. Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.54; H, 6.55.

2-(4-Methoxyphenyl)phenol (7i).

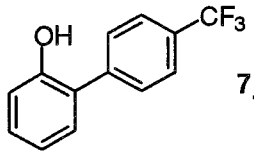


7i

A brown liquid (96% yield); IR (neat) 568, 587, 756, 795, 829, 1045, 1105, 1246, 1274, 1452, 1483, 1516, 1583, 1607, 2836, 3424, 3531 (O-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 3.86 (s, 3H),

5.20 (br s, 1H), 6.95-6.99 (m, 2H), 6.99-7.03 (m, 2H), 7.20-7.26 (m, 2H), 7.37-7.40 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 55.3, 114.7, 115.6, 120.8, 127.8, 128.8, 129.1, 130.2, 130.3, 152.5, 159.3. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.75; H, 6.18.

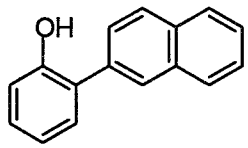
2-(4-Trifluoromethylphenyl)phenol (7j).



7j

Phenol **7j** has already been known,[21] and several spectra of **7j** are shown below. A purple solid (72% yield); mp. 104.7-106.8 °C; IR (neat) 611, 760, 831, 1071, 1104, 1114, 1164, 1328, 1588, 1616, 3524 (O-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 5.16 (s, 1H), 6.93 (d, J = 8.1 Hz, 1H), 6.99-7.04 (m, 1H), 7.22-7.30 (m, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 116.2, 122.3, 125.8 (q, J = 3.7 Hz, CF_3), 126.9, 128.6, 129.0, 129.5, 129.8, 130.4, 141.2, 141.2, 152.3.

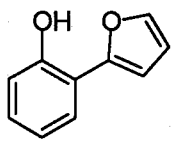
2-(2-Naphthyl)phenol (7l).



7l

A white solid (92% yield); mp. 89.8-91.8 °C; IR (KBr) 484, 756, 815, 830, 899, 1101, 1180, 1277, 1328, 1449, 1500, 3533 (O-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 5.30 (br s, 1H), 7.01-7.06 (m, 2H), 7.25-7.36 (m, 2H), 7.51-7.60 (m, 3H), 7.86-7.98 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 115.9, 120.9, 126.4, 126.6, 127.1, 127.8, 127.8, 128.0, 128.1, 129.1, 129.2, 130.4, 132.7, 133.6, 134.5, 152.6. Anal. Calcd for $C_{16}H_{12}O$: C, 87.25; H, 5.49. Found: C, 87.17; H, 5.54.

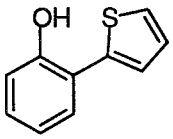
2-(2-Furyl)phenol (7m).



7m

A yellow liquid (82% yield); IR (neat) 754, 820, 904, 1010, 1212, 1297, 1464, 1489, 1509, 1595, 3521 (O-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 6.53 (dd, J = 1.8, 3.6 Hz, 1H), 6.70 (d, J = 3.6 Hz, 1H), 6.91-6.97 (m, 2H), 7.00 (br s, 1H), 7.16-7.22 (m, 1H), 7.50-7.53 (m, 1H), 7.53-7.55 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 106.6, 111.7, 116.4, 117.2, 120.6, 126.2, 129.2, 141.2, 152.4, 152.7. HRMS (FAB): calcd for $C_{10}H_8O_2$ (M^+), 160.0524; found, 160.0527.

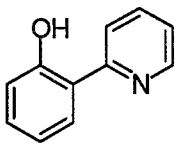
2-(2-Thienyl)phenol (7n).



7n

A brown liquid (92% yield); IR (neat) 669, 715, 748, 832, 856, 1099, 1201, 1286, 1449, 3099, 3289 (O-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 5.52 (br s, 1H), 6.93-6.98 (m, 2H), 7.14 (dd, J = 3.0, 4.5 Hz, 1H), 7.20-7.25 (m, 1H), 7.29 (m, 1H), 7.36-7.44 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 116.1, 120.9, 120.9, 126.0, 126.2, 127.8, 129.3, 130.1, 138.7, 152.4. Anal. Calcd for $C_{10}H_8OS$: C, 68.15; H, 4.58. Found: C, 68.13; H, 4.58.

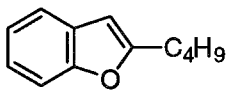
2-(2-Pyridyl)phenol (7o).



7o

A pale yellow liquid (42% yield); IR (neat) 629, 641, 726, 751, 854, 1244, 1270, 1304, 1401, 1478, 1504, 1562, 1594, 2620, 2854, 2932, 3057 (O-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 6.89-6.94 (m, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.25-7.33 (m, 2H), 7.36-7.40 (m, 1H), 7.76 (dd, J = 1.8, 7.8 Hz, 1H), 7.97-8.01 (m, 2H), 8.62 (d, J = 5.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 118.6, 118.7, 118.8, 119.3, 121.5, 126.2, 131.6, 138.0, 145.6, 157.6, 159.9. HRMS (FAB): calcd for $C_{11}H_{10}NO$ ($M+H^+$), 172.0762; found, 172.0760.

2-Butylbenzofuran (8p).



8p

A yellow liquid (24% yield); IR (neat) 669, 740, 750, 795, 945, 1169, 1253, 1455, 1588, 1601, 2861, 2871, 2928, 2957 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.95 (t, J = 7.5 Hz, 3H), 1.42 (sex, J = 7.5 Hz, 2H), 1.75 (quint, J = 7.5 Hz, 2H), 2.76 (t, J = 7.5 Hz, 2H), 6.36 (br s, 1H), 7.13-7.22 (m, 2H), 7.39-7.42 (m, 1H), 7.45-7.48 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 13.8, 22.3, 28.1, 29.8, 101.7, 110.7, 120.1, 122.3, 123.0, 129.0, 154.6, 159.7. HRMS (FAB): calcd for $C_{12}H_{14}O$ (M^+), 174.1045; found, 174.1041.

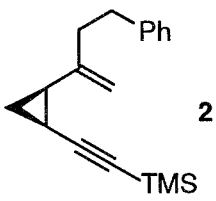
Tungsten-catalyzed Isomerization Reaction of 1a. According to the activation method of $Cr(CO)_6$, a solution of $W(CO)_6$ (35 mg, 0.10 mmol) in THF (dry and deoxygenated, 5 mL) was irradiated at room temperature for 2 h under N_2. To the resulted yellow solution were

added a solution of **1a** (99 mg, 0.5 mmol) in THF(1 mL) and triethylamine (0.2 mL, 1.4 mmol). After stirring for 24 h, the organic solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 10/1) as an eluent to afford **7a** (99% yield).

Preparation of *cis*-1-Vinyl-2-ethynylcyclopropanes from 20a.

cis-1-Vinyl-2-ethynylcyclopropanes were unstable and easily polymerized at room temperature. Therefore, these substrates **1q** and **1r** were used without further purification as soon as possible after protodesilylation of **21q** and **21r** by 1 M solution of TBAF in THF.

***cis*-1-[2-(3-Phenyl-1-butenyl)]-2-(trimethylsilyl)ethynylcyclopropane (21q).**



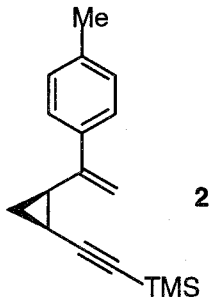
21q

To a solution of **20a** (0.40 g, 1.5 mmol) in THF (5 mL) was added a solution of 2-phenylethylmagnesium bromide (about 2 equiv) in THF (5 mL) at 0 °C under N_2. The mixture was stirred at 0 °C for 0.5 h, poured into saturated NH_4Cl solution (20 mL), and extracted with AcOEt (20 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure to afford crude *cis*-2-(3-phenylpropanoyl)-1-(trimethylsilyl)ethynylcyclopropane as a brown oil.

Then, to a suspension of CH_3PPh_3I (2.5 g, 6.3 mmol) in THF (30 mL) was slowly added *n*-BuLi in hexane (1.6 M, 3.9 mL, 6.2 mmol) at -78 °C under N_2. The resulting yellow solution was stirred for 1 h at 0 °C, and to it was added a solution of the crude *cis*-2-(3-phenylpropanoyl)-1-(trimethylsilyl)ethynylcyclopropane in THF (2 mL) at -78 °C. The color changed from yellow to orange. This orange suspension was stirred at 0 °C for 3.5 h, poured into water (100 mL), and extracted with Et_2O (30 mL x 3). The organic layer was dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 40/1) as an eluent to afford **21q** (0.24 g, 0.94 mmol, 61% yield) as a colorless liquid; IR (neat) 542, 698, 759, 841, 863, 891, 1120, 1249, 1438, 1454, 1496, 1645, 2168 (C≡C), 2958, 3027 cm^{-1}; ^1H NMR (300

MHz, $CDCl_3$, 25 °C) δ 0.12 (s, 9H), 0.97-1.10 (m, 2H), 1.58 (ddd, J = 5.7, 8.4, 8.4 Hz, 1H), 1.68 (ddd, J = 7.5, 8.4, 8.4 Hz, 1H), 2.46 (dd, J = 8.1, 9.0 Hz, 2H), 2.84 (dd, J = 8.1, 9.0 Hz, 2H), 4.81 (br s, 1H), 4.96 (br s, 1H), 7.16-7.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 0.2, 8.7, 13.3, 24.8, 34.3, 38.5, 107.1, 110.7, 125.8, 128.3, 128.4, 132.0, 142.4, 145.2. HRMS (FAB): calcd for $C_{19}H_{24}Si$ (M^+), 268.1647; found, 268.1653.

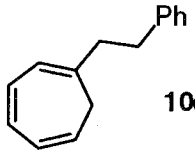
***cis*-1-(1-*p*-Tolylethenyl)-2-(trimethylsilyl)ethynylcyclopropane (21r).**



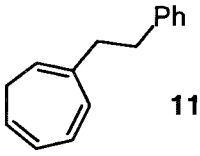
21r

A yellow liquid (81% yield); IR (neat) 759, 825, 841, 871, 1248, 1514, 2166 (C≡C), 2958 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.08 (s, 9H), 1.07-1.22 (m, 2H), 1.78 (ddd, J = 5.7, 8.1, 8.1 Hz, 1H), 2.01 (ddd J = 7.2, 8.1, 8.1 Hz, 1H), 2.34 (s, 3H), 5.00 (br s, 1H), 5.45 (br s, 1H), 7.12 (d, J = 7.8 Hz, 2H), 7.42 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 0.0, 9.8, 13.6, 21.1, 24.3, 83.0, 106.7, 112.3, 126.2, 128.7, 137.0, 138.8, 144.0. HRMS (FAB): calcd for $C_{17}H_{23}Si$ ($M+H^+$), 255.1569; found, 255.1558.

Typical Procedure for Chromium-triggered Isomerization Reaction of 1q or 1r. Cycloheptatrienes 10q and 11q.



10q



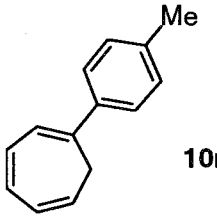
11q

To a solution of **21q** (81 mg, 0.30 mmol) in THF (2 mL) was added 1 M solution of tetrabutylammonium fluoride in THF (0.33 mL, 0.33 mmol) at 0 °C under N_2. After stirring for 15 min, the resulting brown solution was poured into saturated NH_4Cl solution (10 mL), and extracted with Et_2O (10 mL x 3). The organic layer was dried over $MgSO_4$. (The organic solvent was removed under reduced pressure to afford **1q** quantitatively.)

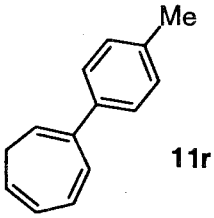
To a yellow solution of $Cr(CO)_5(THF)$ in THF (9 mL) were added a solution of **1q** in THF(1 mL) and triethylamine (0.13 mL, 0.90 mmol). After stirring for 8 h, the organic solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 50:1) as an eluent to afford a mixture of

10q (34% yield) and **11q** (10% yield). The yield of **10q** and **11q** was determined by ^{1}H NMR; IR (neat, a mixture of **10q** and **11q**) 698, 709, 746, 771, 1454, 1496, 1603, 1626, 2854, 2926, 3024, 3062 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) **10q**: δ 2.35 (d, J = 6.9 Hz, 2H), 2.56 (dd, J = 6.9, 9.0 Hz, 2H), 2.79 (dd, J = 6.9, 9.0 Hz, 2H), 5.36 (dt, J = 6.9, 9.0 Hz, 1H), 5.96-5.99 (m, 1H), 6.15 (dt, J = 2.7, 9.0 Hz, 1H), 6.49 (t, J = 2.7 Hz, 2H), 7.17-7.27 (m, 5H); **11q**: δ 2.18 (t, J = 6.9 Hz, 2H), 2.47 (dd, J = 7.2, 8.7 Hz, 2H), 2.70 (dd, J = 7.2, 8.7 Hz, 2H), 5.11 (t, J = 6.9 Hz, 1H), 5.47 (dt, J = 6.9, 9.3 Hz, 1H), 6.12 (dt, J = 2.7, 9.3 Hz, 1H), 6.56 (d, J = 2.7 Hz, 2H), 7.09-7.22(m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) a mixture of **10q** and **11q**: δ 27.5, 32.7, 36.2, 36.7, 38.0, 40.3, 117.8, 120.6, 121.5, 122.6, 125.6, 125.8, 126.0, 126.4, 128.1, 128.2, 128.3, 128.4, 129.0, 130.5, 130.7, 133.1, 136.9, 138.1, 141.6, 141.9. HRMS (FAB): calcd for $C_{15}H_{16}$ (M^+), 196.1252; found, 196.1258.

Cycloheptatrienes 10r and 11r.



10r



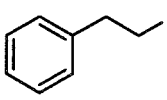
11r

A yellow liquid (**10r**: 24%, **11r**: 7% yield); IR (neat, a mixture of **10r** and **11r**) 447, 651, 702, 716, 737, 779, 816, 1375, 1435, 1509, 2921, 3022 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) **10r**: δ 2.35 (s, 3H), 2.76 (d, J = 5.4 Hz, 2H), 5.45 (dt, J = 5.4, 9.2 Hz, 1H), 6.25 (dd, J = 5.6, 9.2 Hz, 1H), 6.47 (d, J = 5.6 Hz, 1H), 6.58-6.72 (m, 2H), 7.14 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H); **11r**: δ 2.31 (t, J = 7.2 Hz, 2H), 2.38 (s, 3H), 5.54 (dt, J = 7.2, 9.6 Hz, 1H), 5.60 (t, J = 7.2 Hz, 1H), 6.22 (dd, J = 5.6, 9.6 Hz, 1H), 6.75 (dd, J = 5.6, 11.2 Hz, 1H), 6.86 (d, J = 11.2 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) a mixture of **10r** and **11r**: δ 21.1, 21.2, 27.9, 31.7, 117.2, 120.8, 122.0, 122.4, 126.4, 126.9, 127.3, 127.5, 128.8, 129.0, 129.7, 130.8, 131.7, 131.7, 132.4, 132.8, 136.5, 137.0, 138.1, 138.8. HRMS (FAB): calcd for $C_{14}H_{14}$ (M^+), 182.1096; found, 182.1095.

Typical Procedure for Catalytic Isomerization Reaction of 1a Using Other Metal Complexes.

A metal complex (0.010 mmol) was placed in the flame dried Schlenk flask and dissolved in toluene (dry, 4.0 mL) at room temperature under N_2. To this solution was added a solution of **1a** (38 mg, 0.20 mmol) in toluene (1 mL) and triethylamine (75 μL, 0.60 mmol) at room temperature. After stirring at 70 °C for 48 h, the organic solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 8/1) to afford a mixture of **7a** and **17a**.

1,2-Diphenylethane (17a).



17a

The product **17a** is commercially available, and the ^{1}H NMR spectrum of **19a** which is shown below was the same as the spectrum of an authentic sample. ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 2.92 (s, 4H), 7.17-7.31 (m, 10H).

References and Notes

(1) For reviews on vinylidene transition metal complexes, see: (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (c) McDonald, F. E. *Chem. Eur. J.* **1999**, *5*, 3103.

(2) (a) Ohe, K.; Miki, K.; Yokoi, T.; Nishino, F.; Uemura, S. *Organometallics* **2000**, *19*, 5525. For benzopyranylidene complexes, see: (b) Iwasawa, N.; Shido, M.; Maeyama, K.; Kusama, H. *J. Am. Chem. Soc.* **2000**, *122*, 10226. (c) Miura, T.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 518. Electrocyclization of dienynes promoted by ruthenium and tungsten vinylidene complexes have been reported as related reactions. See: (d) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319. (e) Maeyama, K.; Iwasawa, N. *J. Org. Chem.* **1999**, *64*, 1344.

(3) For reviews on [3,3]sigmatropic rearrangement of divinylcyclopropanes and their equivalents, see: (a) Hudlicky, T.; Fan, R. L.; Reed, J. W.; Gadamasetti, K. G. *Org.*

React. **1992**, *41*, 1. (b) Hudlicky, T.; Fan, R. L.; Beckers, D. A.; Kozhushkov, S. I. In *Methods of Organic Chemistry (Houben-Weyl)*, 4th ed.; de Meijere, A., Ed; Thieme: Stuttgart, 1997; Vol. E17c, p 2589.

(4) Böttcher, G.; Reißig, H.-U. *Synlett* **2000**, 725.

(5) (a) Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 6854. (b) Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257 and references therein.

(6) It has been reported that thermal [3,3]sigmatropic rearrangements of 1,2-diethynylcyclopropanes,[7] 1-ethynyl-2-vinylcyclopropane[8], and 1-ethynyl-2-iminyl- or 1-ethynyl-2-formylcyclopropane[9] gave rise to seven-membered diallenic and allenic intermediates. For brevity, limited references are shown below.

(7) (a) D'Amore, M. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1969**, *91*, 5694. (b) Henry, T. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 5103. (c) Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25.

(8) Dolbier, W. R.; Garza, O. T.; Al-Sader, B. H. *J. Am. Chem. Soc.* **1975**, *97*, 5038.

(9) (a) Manisse, N.; Chuche, J. *J. Am. Chem. Soc.* **1977**, *99*, 1272. (b) Bourelle-Wargnier, F.; Vincent, M.; Chuche, J. *J. Chem. Soc., Chem. Commun.* **1979**, 584.

(10) The solution of $Cr(CO)_5(THF)$ (n equiv) used was prepared by irradiating a solution of a THF solution of $Cr(CO)_6$ (n equiv) at room temperature for 4 h with a high-pressure Hg lamp. See Experimental Section.

(11) Similar effects of Et_3N have been proposed, see: (a) Ohe, K.; Kojima, M.; Yonehara, K.; Uemura, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1823. (b) Manabe, T.; Yanagi, S.; Ohe, K.; Uemura, S. *Organometallics* **1998**, *17*, 2942. (c) Miki, K.; Yokoi, T.; Nishino, F.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **2002**, *645*, 228 and see also Chapter 1 of this thesis.

(12) Isomerization of **1f** to *trans*-1-ethynyl-2-(1-naphthoyl)cyclopropane (20%) was observed in this reaction.

(13) Structures of **15** and **16** were confirmed by comparing their NMR spectra in two regions of δ 1.0-2.5 ppm and δ 5.0-7.0 ppm with those of 1- and 2-methyl-1,3,5-

cycloheptatrienes reported. See: Egger, K. W.; Moser, W. R. *J. Phys. Chem.* **1967**, *71*, 3699. See also Experimental Section.

(14) The literature of ref. 9 also describes the reason why the substrate **1q** and **1r** are unstable.

(15) (a) Vogel, E.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 385. (b) Bruice, T. C.; Bruice, P. Y. *Acc. Chem. Res.* **1976**, *9*, 378.

(16) Triethylamine and/or $M(CO)_5$ are presumably responsible for isomerization of **11** to **7**.

(17) Aumann, R.; Averbeck, C.; Kruger, C. *Chem. Ber.* **1975**, *71*, 3669.

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Part II

Generation of (2-Furyl)carbene Complexes from π-Alkyne Complexes and Their Application to Catalytic Carbene Transfer Reactions

Chapter 3

Synthesis of 2-(Furyl)carbene Complexes from Conjugated Ene-Yne-Ketones with Group 6 Transition Metal Complexes

Abstract

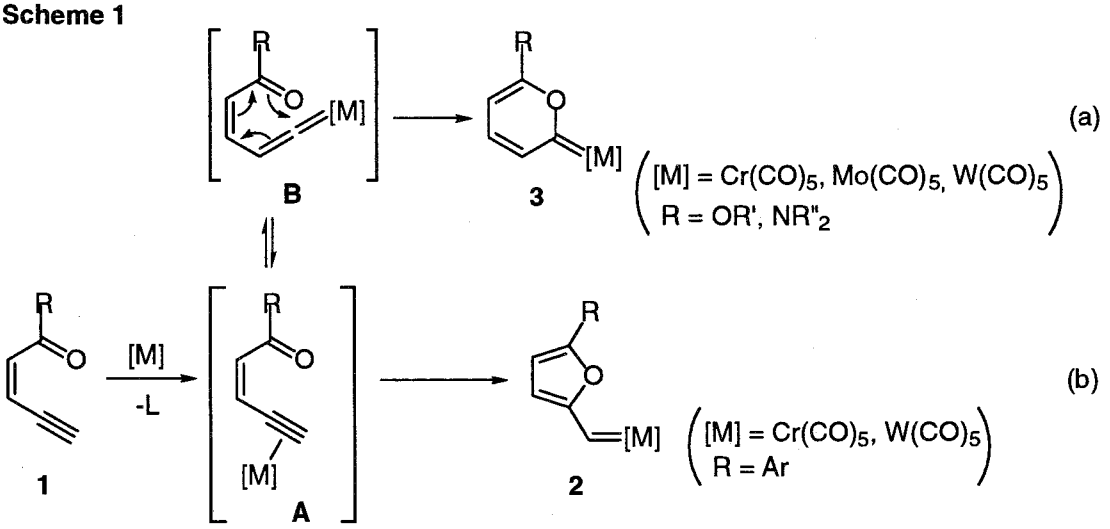
The reaction of conjugated ene-yne-ketones such as 1-phenylcarbonyl-2-ethynylcycloalkenes with $Cr(CO)_5(THF)$ or $W(CO)_5(THF)$ gave the corresponding 5-phenyl-furylcarbene-chromium or -tungsten complex, respectively. A nucleophilic attack at an internal alkyne carbon in π-alkyne or σ-vinyl cationic complexes generated from 1-phenyl-2-ethynylcycloalkenes and transition metal complexes is a key route to these nonheteroatom-stabilized carbene complexes. New (2-furyl)carbene complexes undergo oxidative cleavage reaction under oxygen atmosphere to give furfural derivatives.

Introduction

In Chapter 1, the author has described that the reactions of ene-yne-esters and -amides **1** (R = OR', NR''_2) with group 6 transition metal complexes afforded 2-pyranylidene complexes **3** via the electrocyclization of vinylidene-ene-carbonyl intermediates **A** (Scheme 1, path a).[1,2]

In this chapter, the author describes the preparation of (2-furyl)carbene complexes **2** from ene-yne-ketones **1** (R = Ar) with group 6 transition metal complexes via a nucleophilic attack of a carbonyl oxygen at an internal carbon of alkyne in π-alkyne complex **A** (Scheme 1, path b).

Scheme 1

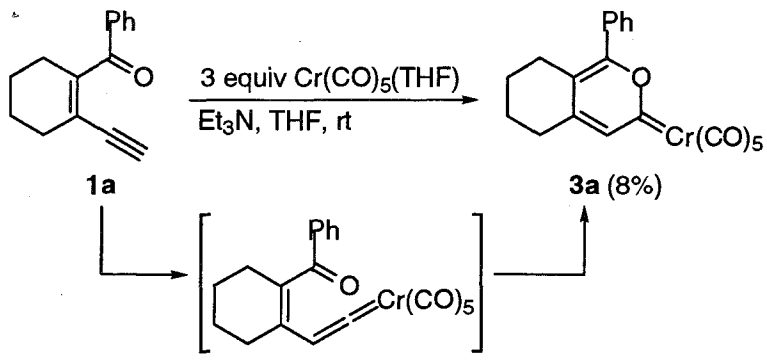


(2-Furyl)carbene complexes are stable enough to be purified with short column chromatography on SiO_2. In a THF solution of these carbene compelxes under oxygen, the corresponding furfurals were obtained in good yields.

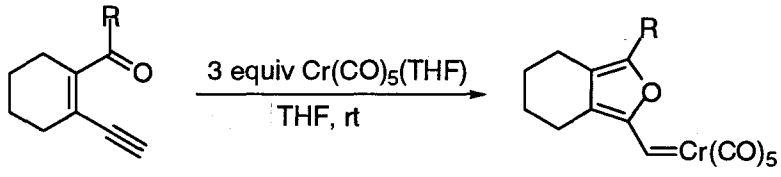
Results and Discussion

At first, the reactions of an ene-yne-ketone with chromium and tungsten carbonyl complexes were examined. When 2-ethynyl-1-cyclohexenyl phenyl ketone (**1a**) was treated with 3 equiv of $Cr(CO)_5(THF)$[4] in the presence of triethylamine, the corresponding 2-pyranylidene-chromium complex **3a** was obtained only in 8% yield together with many unidentified products (Scheme 2). The formation of **3a** can be explained by assuming the electrocyclization of a vinylidene intermediate as described in Chapter 1.

Scheme 2



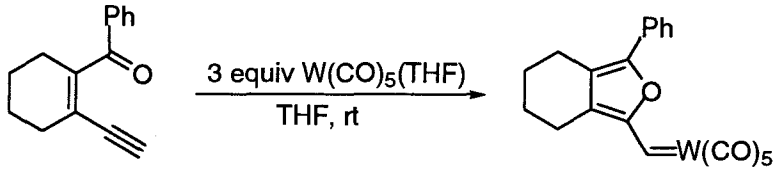
On the other hand, in the absence of triethylamine the reaction of **1a** with 3 equiv of $Cr(CO)_5(THF)$ did not afford **3a**, and instead (2-furyl)carbene-chromium complex **2a** was isolated in 52% yield as a blue solid (eq 1). The complex **2a** is marginally stable during



(1)

1a (R = Ph)
1b (R = 2-thienyl)

2a (52%)
2b (59%)

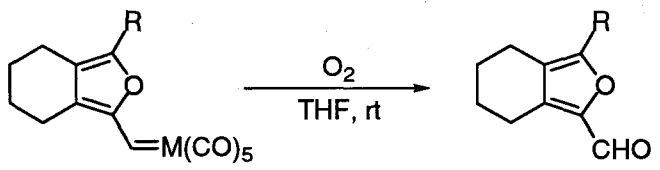


(2)

1a

2c (56%)

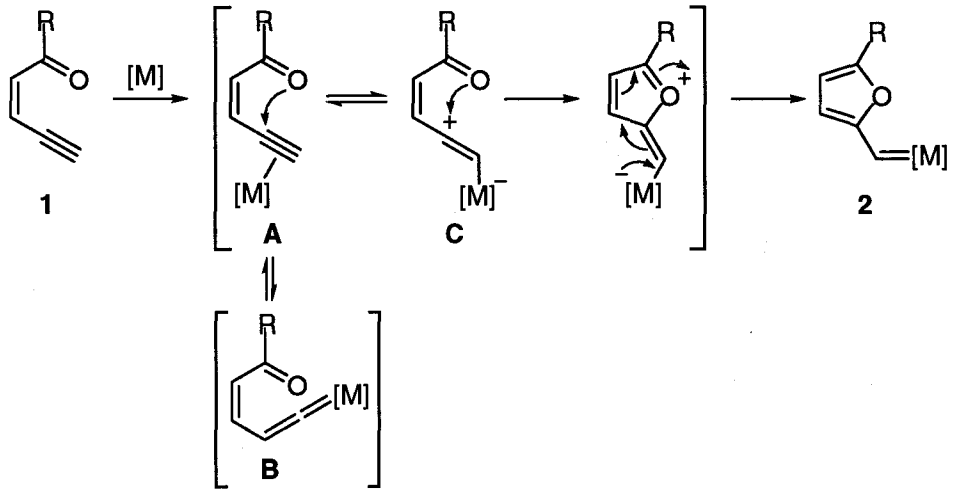
purification with silica gel column chromatography. 2-Thienyl ketone **1b** also gave the corresponding (2-furyl)carbene-chromium complex **2b** in 59% yield. When **1a** was treated with 3 equiv of $W(CO)_5(THF)$[5], (2-furyl)carbene-tungsten complex **2c** was isolated in 56% yield (eq 2).[1] However, in the reaction of an alkyl ketone such as ethyl 2-ethynyl-1-cyclohexenyl ketone (R = Et in **1**) with $Cr(CO)_5(THF)$ and $W(CO)_5(THF)$, the color of the solution changed yellow to blue, which probably indicated the generation of (2-furyl)carbene complexes, isolation of the corresponding (2-furyl)carbene complex failed with decomposition by column chromatography. Isolated complexes **2a**-**2c** could be stored for several days under N_2 atmosphere, but they gradually decomposed in $CDCl_3$ or under oxygen atmosphere. When the isolated carbene complex **2a** was stirred in THF under oxygen atmosphere, furfural derivative **4a** was obtained in 76% yield (eq 3). The displacement of metal carbonyl moiety with the oxygen atom in carbene complex by molecular oxygen is a well-known process.[6] Most plausible pathway from **1** to **2** is shown in Scheme 3. As shown in Scheme 3, 5-*exo-dig* cyclization of ene-yne-ketone **1** via nucleophilic attack of a carbonyl



(3)

2a (R = Ph, M = Cr) **4a** (76%)
2b (R = 2-thienyl, M = Cr) **4b** (76%)
2c (R = Ph, M = W) **4a** (84%)

Scheme 3



oxygen to an internal carbon of an alkyne in π-alkyne complex **A** might be most plausible pathway for generation of (2-furyl)carbene complex **2** (M = $Cr(CO)_5$, $W(CO)_5$). A slipped, polarized η-complex **C** would be an alternatively possible intermediate. The latter reaction pathway will be described in Chapter 4 as well. In the pre-equilibrium between a π-alkyne complex **A** and a vinylidene complex **B** (Scheme 1), 5-*exo-dig* cyclization takes place as a favorable and fast process to give the furylcarbene complex. The presence of triethylamine, which may promote the isomerization of a π-alkyne complex to a vinylidene complex, in fact, precluded the formation of the (2-furyl)carbene complex (eqs 1 and 2 and Scheme 3). The mode of carbene complex formation would be also attributed to the difference in the reactivity of carbonyl functionality of ene-yne-esters, -amides, and -ketones.

In conclusion, the author has demonstrated that the reaction of ene-yne-ketones with $M(CO)_5(THF)$ [M = Cr, W] gave (2-furyl)carbene complexes selectively via a nucleophilic attack of a carbonyl oxygen to a π-alkyne complex. The reactivity of newly prepared (2-furyl)carbene-chromium and tungsten complexes has been clarified in part in the oxidative conversion of them to the corresponding furfurals.

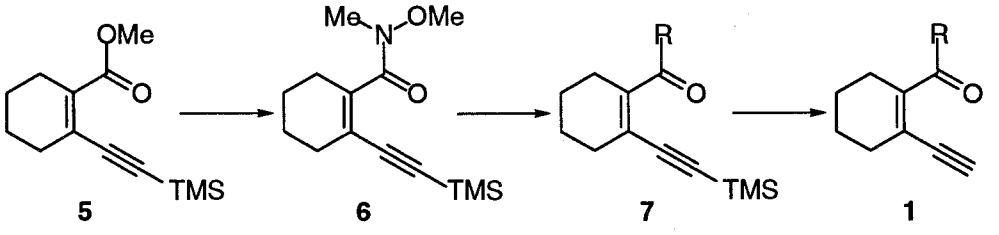
Experimental

General Procedure. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies were performed with Merck silica gel 60. The NMR spectra were measured for solutions in $CDCl_3$ or d_8-THF 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. IR spectra were recorded on an FT-IR spectrometer. Melting points are uncorrected. High-resolution mass spectra (FAB HRMS) and low-resolution mass spectra (FAB LRMS) were obtained with JEOL LMX-SX 102A spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University.

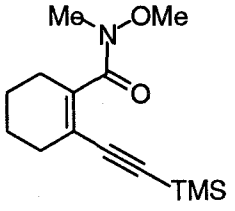
Synthesis of Substrates

Substrates **1a** and **1b** were prepared by the following procedures (Scheme 4, and see Chapter 1 of this thesis).

Scheme 4



N-Methyl *N*-methoxy 2-(trimethylsilylethynyl)-1-cyclohexenecarboxamide (6)[7]



6

Methyl 2-(trimethylsilyl)-1-cyclohexenecarboxylate (**5**) was prepared from cyclohexanone in several steps. See Experimantal Section of Chapter 1.

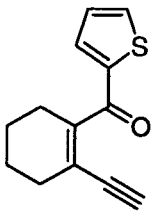
A solution of methyl 2-(trimethylsilylethynyl)-1-cyclohexenecarboxylate (**5**) (3.6 g, 15 mmol) in benzene (5 mL) was added to benzene (40

mL) and hexane (45 mL) solution of $Me_2AlNMe(OMe)$ prepared from a hexane solution of Me_3Al (45 mL, 45 mmol) and *N,O*-dimethylhydroxylamine hydrochloride (4.4 g, 45 mmol). The resulting solution was heated under reflux for 3 h. The reaction mixture was cooled to room temperature, and hydrolyzed by slow and cautious addition of 1.0 N hydrochloric acid (30 mL). The upper organic layer was separated, and the aqueous layer was extracted with AcOEt (30 mL x 3). The combined organic layer was washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure to give the residual liquid, which was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=4/1) as an eluent to afford *N*-methyl *N*-methoxy 2-(trimethylsilylethynyl)-1-cyclohexenecarboxamide (**6**) (3.6 g, 14 mmol, 92% yield) as a pale yellow liquid; IR (KBr) 845, 1659 (C=O), 2144 (C≡C) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 0.12 (s, 9H), 1.57-1.65 (m, 4H), 2.14-2.27 (m, 4H), 3.23 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (CD_2Cl_2, 100 MHz, -25 °C) δ -0.1 (Si*C*H_3), -0.1 (Si*C*H_3), 21.5 (*C*H_2), 21.5 (*C*H_2), 21.8 (*C*H_2), 21.9 (*C*H_2), 26.5 (*C*H_2), 26.7 (*C*H_2), 28.8 (*C*H_2), 29.5 (*C*H_2), 31.8 (N*C*H_3), 35.7 (N*C*H_3), 60.3 (O*C*H_3), 62.0 (O*C*H_3), 96.4 (*C*≡), 97.2 (*C*≡), 103.0 (*C*≡), 104.5 (*C*≡), 116.7 (*C*=), 119.4 (*C*=), 140.0 (*C*=), 143.1 (*C*=), 166.4 (*C*=O), 170.8 (*C*=O) as a mixture of rotamers. Anal. Calcd for $C_{14}H_{23}NO_2Si$: C, 63.35; H, 8.73; N, 5.28. Found: C, 63.07; H, 8.47; N, 5.21.

2-Ethynylcyclohexenyl phenyl ketone (1a)

Spectral data of ketone **1a** has been shown in Chapter 1 of this thesis.

2-Ethynyl-1-cyclohexenyl 2-thienyl ketone (1b)



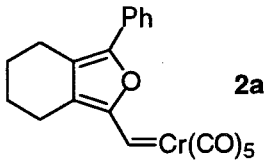
1b

To a solution of thiophene (0.46 mL, 6.0 mmol) in THF (5 mL) was added *n*-BuLi (4 mL, 1.6 M in hexane, 6.4 mmol) at 0 °C under N_2, and the mixture was stirred at room temperature for 2 h. The mixture was added to a solution of **6** (0.80 g, 3.0 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred at room temperature for 10 min. The reaction mixture was poured into saturated

NH_4Cl solution (20 mL), and the aqueous layer was extracted with AcOEt (10 mL x 3). The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and then K_2CO_3 (1.0 g, 7.5 mmol) was added to the residue in MeOH (30 mL) at room temperature. After stirring for 12 h, this solution was poured into saturated NH_4Cl solution (100 mL). The aqueous layer was extracted with AcOEt (30 mL x 3), and the combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=20/1) as an eluent to afford **1b** (0.28 g, 1.3 mmol, 43% yield) as a colorless liquid; IR (neat) 643, 734, 774, 856, 1262, 1285, 1411, 1644 (C=O), 2094 (C≡C), 2935, 3288 (≡C-H) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, 25 °C) δ 1.71-1.77 (m, 4H), 2.28-2.40 (m, 4H), 2.92 (s, 1H), 7.13 (dd, J = 4.2, 4.2 Hz, 1H), 7.68 (d, J = 4.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C) δ 21.4, 21.7, 27.3, 29.7, 82.0, 82.2, 119.4, 128.1, 134.6, 134.7, 143.0, 145.8, 191.2. HRMS (FAB): calcd for $C_{13}H_{12}OS$ ($M+H^+$), 217.0687; found, 217.0685.

Synthesis of Furylcarbene Complexes 2

Chromium complex 2a

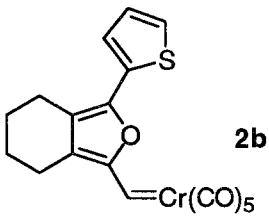


2a

A solution of $Cr(CO)_6$ (0.13 g, 0.60 mmol) in THF (20 mL) under Ar was irradiated by a Hg lamp (450 W, 350 nm) at room temperature for 4 h. To the yellow solution under Ar was added a solution of **4a** (42 mg, 0.20 mmol) in THF (1 mL) by a syringe. The mixture was stirred at room temperature for 0.5 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=10/1) as an eluent to afford **2a** (42 mg, 0.10 mmol, 52% yield) as a blue solid (air stable for a few days under N_2, but gradually decomposed in $CDCl_3$ or under O_2); IR (KBr) 651, 826, 1934, 1994, 2045 cm^{-1}; ^1H NMR (d_8-THF, 300 MHz, 25 °C) δ 1.84-2.00 (m, 4H), 2.75-2.83 (m, 2H), 2.95-3.04 (m, 2H), 7.60-7.69 (m, 3H), 8.16-8.25 (m, 2H), 13.5 (s, 1H); ^{13}C NMR (d_8-THF,

75 MHz, 25 °C) δ 23.0, 24.0, 24.1, 24.4, 127.7, 128.8, 129.9, 130.8, 132.9, 138.4, 168.2, 171.7, 219.6 (Cr-*C*O), 233.9 (Cr-*C*O), 284.4 (Cr=*C*). HRMS (FAB): calcd for $C_{20}H_{14}CrO_6$ (M^+), 402.0219; found, 402.0195.

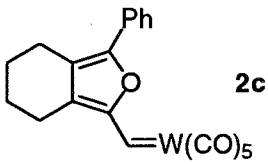
Chromium complex 2b



2b

A blue solid (59% yield: air stable for a few days under N_2, but gradually decomposed in $CDCl_3$ or under O_2). IR (KBr) 1933, 1970, 2041 cm^{-1}. ^1H NMR (d_8-THF, 300 MHz, 25 °C) δ 1.73-1.90 (m, 4H), 2.66 (t, J = 3.9 Hz, 2H), 2.77 (t, J = 3.9 Hz, 2H), 7.27-7.31 (m, 1H), 7.88-7.94 (m, 2H), 13.0 (s, 1H). ^{13}C NMR (d_8-THF, 75 MHz, 25 °C) δ 21.5, 21.6, 22.2, 22.7, 125.3, 129.2, 130.3, 131.5, 132.8, 137.2, 163.3, 169.9, 218.2 (Cr-*C*O), 232.3 (Cr-*C*O), 276.4 (Cr=*C*). HRMS (FAB): calcd for $C_{19}H_{12}CrO_6S$ ($M+H^+$), 407.9760; found, 407.9756.

Tungsten complex 2c

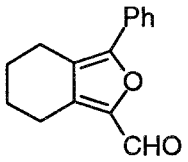


2c

A solution of $W(CO)_6$ (0.21 g, 0.60 mmol) in THF (20 mL) under Ar was irradiated by a Hg lamp (450 W, 350 nm) at room temperature for 4 h. To the yellow solution under Ar was added a solution of **1a** (42 mg, 0.2 mmol) in THF (1 mL) by a syringe. The mixture was stirred at room temperature for 0.5 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=10/1) as an eluent to afford **5c** (60 mg, 0.11 mmol, 56% yield) as a blue solid (air stable for a few days under N_2, but gradually decomposed in $CDCl_3$ or under O_2); IR (KBr) 580, 677, 825, 1920, 1934, 2052 cm^{-1}; ^1H NMR (d_8-THF, 300 MHz, 25 °C) δ 1.94-2.10 (m, 4H), 2.54-2.60 (m, 2H), 3.07-3.13 (m, 2H), 7.64-7.78 (m, 3H), 8.26-8.32 (m, 2H), 13.3 (s, 1H); ^{13}C NMR (d_8-THF, 75 MHz, 25 °C) δ 21.3, 22.5, 22.5, 23.5, 127.4, 127.9, 129.5, 129.8, 131.5, 141.7, 166.5, 171.3, 198.1 (W-*C*O), 210.2 (W-*C*O), 247.8 (W=*C*). HRMS (FAB): calcd for $C_{20}H_{14}WO_6$ (M^+), 534.0286; found, 534.0300.

Synthesis of Furfural Derivatives 4

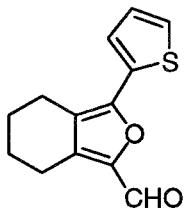
Furfural 4a



4a

A solution of **2a** (22 mg, 0.054 mmol) in THF (5 mL) was stirred at room temperature under O_2 atmosphere for 12 h. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=8:1) as an eluent to afford **4a** (9.2 mg, 0.041 mmol, 76% yield) as a white solid; mp 91.3-94.8 °C; IR (KBr) 696, 773, 828, 1650, 1669 cm^{-1}; ^1H NMR (d_8-THF, 300 MHz, 25 °C) δ 1.73-1.86 (m, 4H), 2.81-2.87 (m, 2H), 2.87-2.93 (m, 2H), 7.31-7.38 (m, 1H), 7.41-7.49 (m, 2H), 7.76-7.81 (m, 2H), 9.73 (s, 1H); ^{13}C NMR (d_8-THF, 75 MHz, 25 °C) δ 22.8, 23.4, 23.9, 24.4, 122.6, 124.7, 127.1, 129.9, 130.2, 132.1, 147.8, 152.9, 178.2 (*C*HO). HRMS (FAB): calcd for $C_{15}H_{14}O_2$ ($M+H^+$), 227.1072; found, 227.1067.

Furfural 4b



4b

A white solid (76% yield); mp 100.5-101.6 °C; IR (KBr) 698, 819, 853, 1445, 1635, 1663 cm^{-1}; ^1H NMR (d_8-THF, 300 MHz, 25 °C) δ 1.75-1.90 (m, 4H), 2.68-2.76 (m, 2H), 2.87-2.94 (m, 2H), 7.14 (dd, J = 3.6, 4.8 Hz, 1H), 7.42 (d, J = 4.8 Hz, 1H), 7.47 (d, J = 3.6 Hz, 1H), 9.69 (s, 1H); ^{13}C NMR (d_8-THF, 75 MHz, 25 °C) δ 22.7, 23.1, 23.5, 24.1, 121.6, 126.6, 128.2, 129.3, 134.0, 136.7, 147.4, 149.6, 177.8 (*C*HO). Anal. Calc. for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.21. Found: C, 66.97; H, 5.17.

References and Notes

(1) For preparation of pyranylidene-metal complexes via vinylidene-metal intermediates, see: (a) Ohe, K.; Miki, K.; Yokoi, T.; Nishino, F.; Uemura, S. *Organometallics* **2000**, *19*, 5525. (b) Iwasawa, N.; Shido, M.; Maeyama, K.; Kusama, H. *J. Am. Chem. Soc.* **2000**, *122*, 10226.

(2) Transformation of vinylidene-metal intermediates in conjugated systems, see: (a) Wang, Y.; Finn, M. G. *J. Am. Chem. Soc.* **1995**, *117*, 8045. (b) Ohe, K.; Kojima, M.; Yonehara, K.; Uemura, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1823. (c) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc.* **1996**, *118*, 11319. (d) Manabe, T.; Yanagi, S.; Ohe, K.; Uemura, S. *Organometallics* **1998**, *17*, 2942. (e) Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928. (f) Maeyama, K.; Iwasawa, N. *J. Org. Chem.* **1999**, *64*, 1344.

(3) (a) Wrighton, M. *Chem. Rev.* **1974**, *74*, 401. (b) McDonald, F. E.; Schultz, C. C. *J. Am. Chem. Soc.* **1994**, *116*, 9363.

(4) Strohmeier, W.; Gerlach, K. *Chem. Ber.* **1961**, *94*, 398.

(5) Chromium moieties of carbene complexes are readily displaced with the oxygen atom by molecular oxygen, see: (a) Silveman, R. B.; Olofson, R. A. *Chem. Commun.* **1968**, 1313. (b) Fischer, E. O.; Riedmüller, S. *Chem. Ber.* **1974**, *107*, 915.

(6) For preparation of ketones, see: (a) Lipton, M. F.; Baska, A.; Weinreb, S. M. *Org. Synth.* **1979**, *59*, 49. (b) Levin, J. I.; Turos, E.; Weinreb, S. M. *Synth. Commun.* **1982**, *12*, 989. (c) Nahm, S.; Weinreb, S. M. *Tetrahedron Lett.* **1981**, *22*, 3815.

Chapter 4

Novel Approach for Catalytic Cyclopropanation of Alkenes via (2-Furyl)carbene Complexes from 1-Benzoyl-*cis*-1-buten-3-yne with Transition Metal Compounds

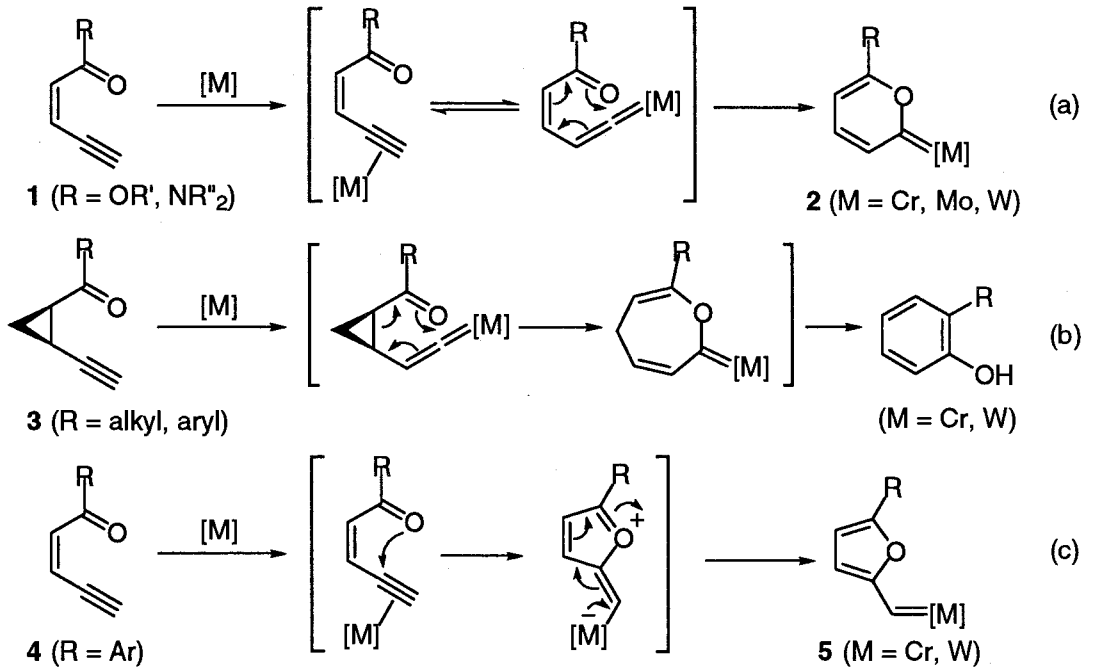
Abstract

The reaction of alkenes with conjugated ene-yne-ketones such as 1-benzoyl-2-ethynylcycloalkenes with a catalytic amount of $Cr(CO)_5(THF)$ gave 5-phenyl-2-furylcyclopropane derivatives in good yields. The key intermediate of this cyclopropanation is a (2-furyl)carbene compelx generated by a nucleophilic attack of a carbonyl oxygen to an internal alkyne carbon in π-alkyne complex or σ-vinyl cationic complex. A wide range of late transition metal compounds such as $[RuCl_2(CO)_3]_2$, $[RhCl(cod)]_2$, $PdCl_2$, and $PtCl_2$ also catalyzes the cyclopropanation of alkenes with ene-yne-ketones effectively. When the reactions were carried out with dienes as a carbene acceptor, more substituted or more electron-rich alkene part was selectively cyclopropanated with the (2-furyl)carbenoid intermediate.

Introduction

The *in situ* generation of carbenoid species from diazoalkanes and transition metal complexes has been most widely used for catalytic cyclopropanation and a wide range of carbene transfer reactions.[1] Diazo decomposition by transition metal complexes is often a useful but formidable task due to explosive hazard and a number of unfavorable side reaction such as diazo dimerization and azine formation. To circumvent such difficulties, safe alternatives to handling diazoalkanes or special techniques involving slow addition of them are required. Recently, much attention has been paid to activation of alkynes with transition metal compounds as a safe and facile alternative to diazo decomposition. Cyclopropylcarbenoid in 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] copper-(isoindazolyl)carbenoids from (2-ethynylphenyl)triazenes,[7] and vinylcarbenoids from propargylic carboxylates[8] have so far been recognized as new entries to metal carbenoids from alkynes. The author has already demonstrated electrocyclization of vinylidene intermediates generated from ene-yne-esters or

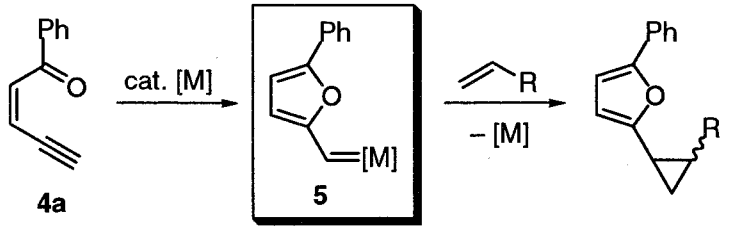
Scheme 1



-amides **1** (R = OR' or R = NR"$_2$) with group 6 transition metal compelxes leading to 2-pyranylidene complexes **2** (Scheme 1a, see also Chapter 1)[9] and valence isomerization of 1-acyl-2-ethynylcyclopropanes **3** via [3,3]sigmatropy of acylcyclopropylvinylidene intermediates catalyzed by group 6 transition metal complexes (Scheme 1b, see also Chapter 2).[10] He also demonstrated the formation of stable (2-furyl)carbene-chromium or -tungsten complexes **5** from ene-yne-ketones **4** (R = Ar) (Scheme 1c, see also Chapter 3).[11] The key of the third reaction is 5-*exo-dig* cyclization via a nucleophilic attack of a carbonyl oxygen to an internal carbon of an alkyne part activated by transition metal complexes. Furylcarbene complexes **5** were somewhat more stable than the corresponding phenylcarbene complexes,[12] which could be stoichiometrically generated and used in cyclopropanation reactions.[13] His continuous work mainly focusing on the catalytic acitivity of **5** led him to find new catalytic cyclopropanation via (2-furyl)carbene complexes without using the corresponding diazoalkane as a precursor. Cyclopropanation using (2-furyl)diazomethane was scarcely investigated due to the instability of the (2-furyl)carbene intermediate.[14]

In this chapter, the author describes the details and the scope of the cyclopropanation reaction involving (2-furyl)carbene complexes **5** directly generated from ene-yne-ketones **4** with a wide range of transition metal compounds (Scheme 2).

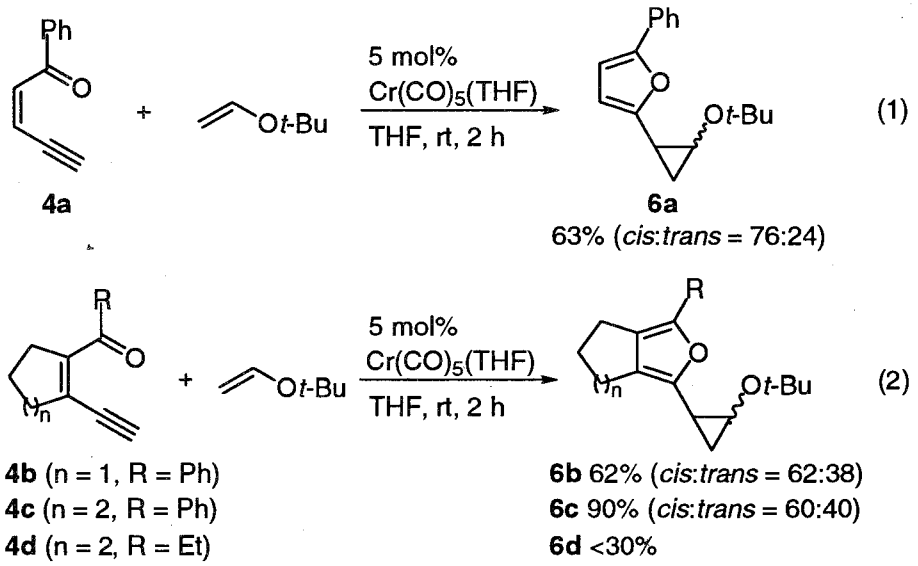
Scheme 2



Results and Discussion

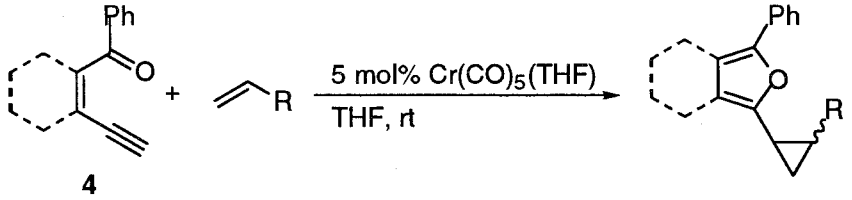
Chromium-Catalyzed Cyclopropanation of Alkenes.

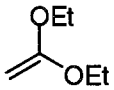
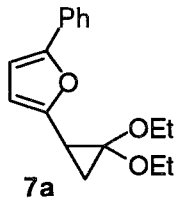
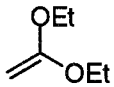
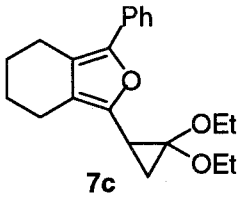
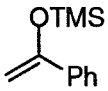
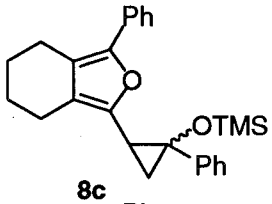
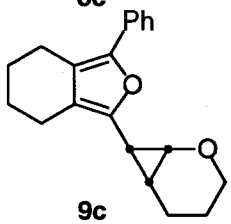
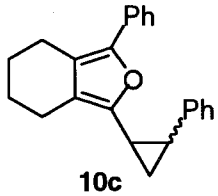
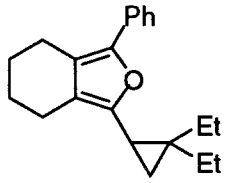
At first, the reaction of **4a** with 2 equiv of *tert*-butyl vinyl ether was carried out in the presence of 5 mol% of $Cr(CO)_5(THF)$ at room temperature (eq 1). The color of the reaction



mixture gradually changed from deep blue to yellow as the reaction proceeded.[15] After 2 h, 1-*tert*-butoxy-2-[(5-phenyl)fur-2-yl]cyclopropane (**6a**) was isolated in 63% yield as a mixture of *cis* and *trans* isomers (*cis*:*trans* = 76:24). As shown in eq 2, similar ene-yne-ketones **4b** and **4c** also afforded the corresponding cyclopropanated products **6b** (62% yield, *cis*:*trans* = 62:38) and **6c** (90% yield, *cis*:*trans* = 60:40), respectively. The reaction of ethyl ketone **4d** with *tert*-butyl vinyl ether was quite complex and many unidentified products were formed, reducing the yield of cyclopropanated product **6d** to 20-30%. To the best of his knowledge, examples of chromium-catalyzed cyclopropanation had been thus far limited to papers reported by Dötz *et al.*[16] Since the chromium-catalyzed cyclopropanation using ene-yne-ketones as carbenoid precursors was effectively delineated, cyclopropanations of several alkenes with **4a** and **4c** were next examined. Typical results are given in Table 1. Reactions of **4a** and **4c** with ketene diethyl acetal proceeded quite smoothly to give furylcyclopropanes

Table 1. Chromium-Catalyzed Cyclopropanation of Alkenes with **4**[a]

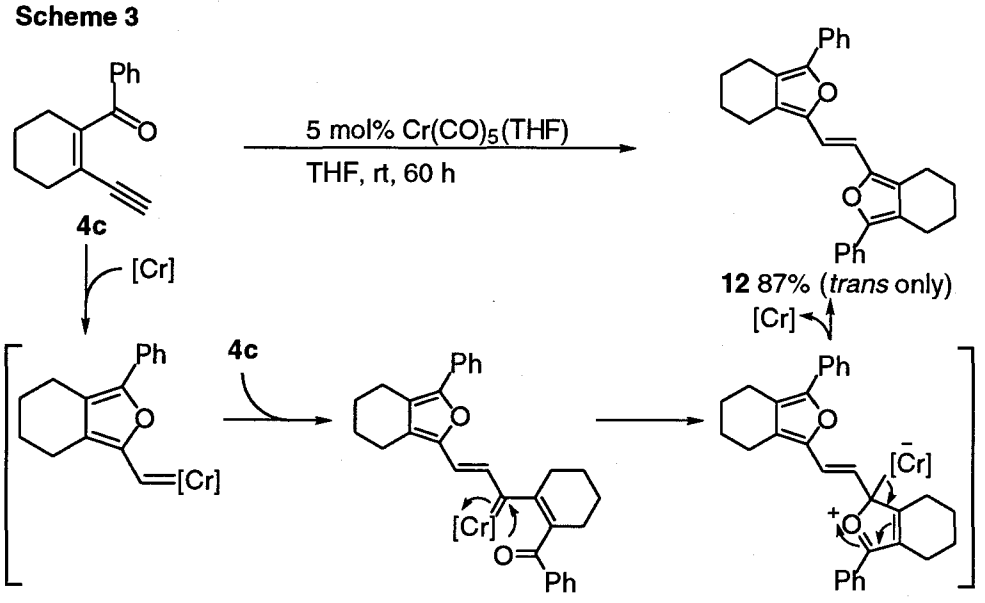


entry	4	alkene	time (h)	product	isolated yield	*cis*:*trans*[b]
1	**a**		1.5	 **7a**	82%	N.A.[c]
2	**c**		2	 **7c**	99%	N.A.[c]
3	**c**		4	 **8c**	83%	66:34[d]
4	**c**		22	 **9c**	90%	endo only
5[e]	**c**		14	 **10c**	85%	74:26
6[f]	**c**		96	 **11c**	52%	N.A.[c]

[a] Reactions were carried out at room temperature with **4** (0.5 mmol), alkene (1.0 mmol), and $Cr(CO)_5(THF)$ prepared *in situ* by irradiating a solution of $Cr(CO)_6$ (0.025 mmol) in THF (2 mL) unless otherwise noted. [b] Determined by ^1H NMR. [c] N.A. = not applicable. [d] Configuration is not yet clear. [e] Alkene (10 mmol). [f] 2-Ethylbut-1-ene (7.5 mmol).

7a (82%) and **7c** (99%), respectively (entries 1 and 2). Ene-yne-ketone **4c** also reacted with enol silyl ether to give **8c** in 83% yield with 66:34 diastereomeric ratio (entry 3). Interestingly, the reaction of **4c** with 3,4-dihydro-2*H*-pyran as a cyclic vinyl ether exclusively gave *endo* cyclopropanated product **9c** in 90% yield (entry 4).[17] Styrene reacted slowly with **4c** to give **10c** (85%, *cis*:*trans* = 74:26), although the reaction required 20 equiv of styrene (entry 5). In the cyclopropanation of 2-ethylbut-1-ene with **4c**, both prolonged reaction time (96 h) and excess use of alkenes (12.5 eqiuv to **4c**) were requisite, the product **11c** being produced in 52% yield (entry 6). On the other hand, cyclopropanation of vinyl acetate and 1-octene with **4c** was sluggish, the yields of the corresponding cyclopropanated products being 22% (6 days) and 19% (10 days), respectively. Here, the complete consumption of the starting ene-yne-ketone **4c** was observed, indicating that other reactions catalyzed by chromium compete with the cyclopropanation reaction. In fact, treatment of **4c** in THF without an alkene in the presence of a catalytic amount of $Cr(CO)_5(THF)$ for 60 h yielded 1,2-difurylethene **12** in 87% yield with high *trans* stereoselectivity. The plausible mechanism giving **12** is considered to be similar to the one proposed by Herndon *et al.* (Scheme 3).[18] Since the side reaction occurs more slowly compared with the desired cyclopropanation, the slow addition of **4** is not always required in the present cyclopropanation reaction.

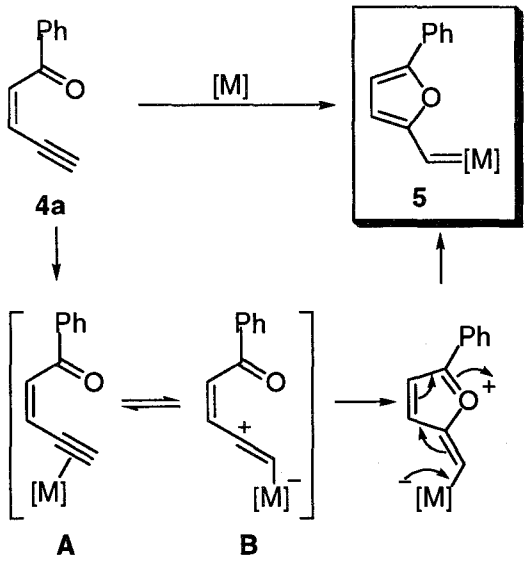
Scheme 3



Other Transition Metal-Catalyzed Cyclopropanation of Alkenes.

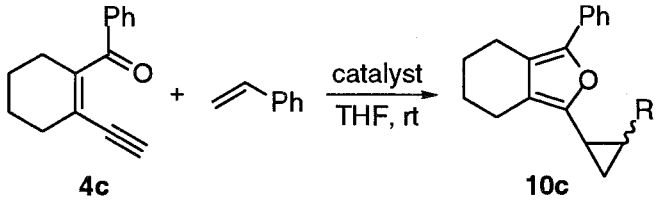
As shown in Scheme 4, 5-*exo-dig* cyclization of ene-yne-ketone **4**[10] via a nucleophilic attack of a carbonyl oxygen to an internal carbon of an alkyne in π-alkyne complex **A** might be the most plausible pathway for generation of (2-furyl)carbene-chromium complex **5** (M =

Scheme 4



$Cr(CO)_5$). A slipped, polarized η^1-complex **B** would be an alternatively possible intermediate. It is well known that **A** is prone to isomerize to **B**, which has been widely accepted for an intermediate for cyclization and skeletal reorganization of 1,6-enynes using a diversity of metal complexes.[2,3] Considering the possibility of the intervention of **B**, we examined cyclopropanation of styrene with **4c** in the presence of other transition metal compounds as catalysts (Table 2). Other group 6 metal complexes such as $Mo(CO)_5(THF)$ and $W(CO)_5(THF)$ were found to catalyze the cyclopropanation to give **10c** in 23% and 54% yields with 54:46 and 70:30 *cis* and *trans* ratios, respectively (entries 1 and 2). $Mn(CO)_5Br$ of group 7 triad was marginally effective in the cyclopropanation reaction (entry 3). Of group 8 triad metals, ruthenium complexes such as $[(p\text{-cymeme})RuCl_2]_2$ and $[RuCl_2(CO)_3]_2$ were effective to give **10c** in 85% (*cis*:*trans* = 33:67) and 42% (*cis*:*trans* = 12:88) yields, respectively (entries 4 and 5).[19] Rhodium and iridium complexes of group 9 triad exhibited

Table 2. Catalytic Cyclopropanation of styrene using **4c**[a]

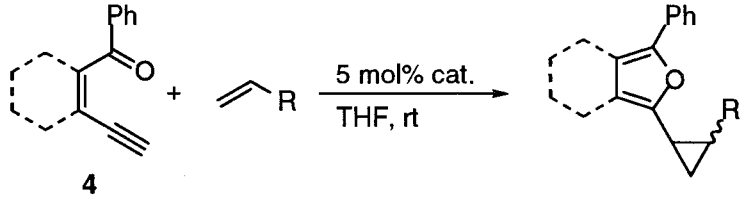


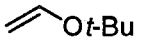
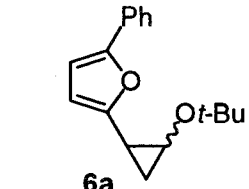
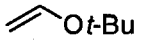
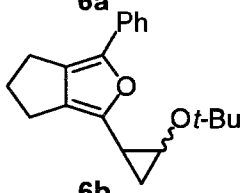
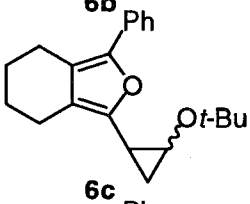
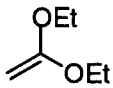
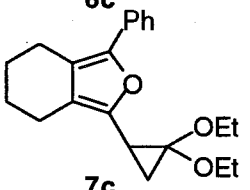
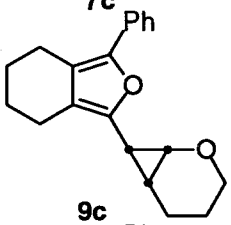
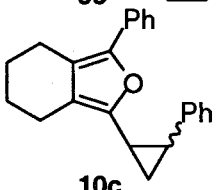
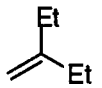
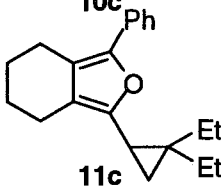
entry	catalyst	time (h)	yield (%)[b]	*cis*:*trans*[c]
1	$Mo(CO)_5(THF)$[d]	2	23	54:46
2	$W(CO)_5(THF)$[d]	2	54	70:30
3	$Mn(CO)_5Br$	24	21	9:91
4	$[(p\text{-cymene})RuCl_2]_2$[e]	2	85	33:67
5	$[RuCl_2(CO)_3]_2$[e]	24	42	12:88
6	$[Rh(OAc)_2]_2$[e,f]	1	93	8:92
7	$[RhCl(cod)]_2$[e]	2	69	56:44
8	$[IrCl(cod)]_2$[e]	2	92	57:43
9	$PdCl_2$	2	79	21:79
10	$PtCl_2$	1	81	23:77

[a] Reactions were carried out at room temperature with **4c** (0.20 mmol), styrene (4.0 mmol), and a catalyst (0.010 mmol) in THF (2 mL) unless otherwise noted. [b] Determined by ^1H NMR. [c] Prepared *in situ* by irradiating a solution of $M(CO)_6$ in THF. [d] 0.005 mmol. [e] Styrene (0.40 mmol).

the high catalytic efficiency in the present reaction (entries 6-8). In particular, $[Rh(OAc)_2]_2$ catalyzed the cyclopropanation of 2 equiv of styrene using **4c** to give **10c** for 1 h with exquisite efficiency (93% yield) and selectivity (*cis*:*trans* = 8:92) (entry 6). $PdCl_2$ and $PtCl_2$ of group 10 triad effectively catalyzed the cyclopropanation of styrene to give **10c** in 79% (21:79 ratio) and 81% yields (23:77 ratio), respectively (entries 9 and 10). Other metal compounds such as Cp_2Ti(isobutylene), $Mn(acac)_2$, $NiCl_2$, $CuOTf(1/2C_6H_6)$, $Cu(OTf)_2$, and $AuCl_3$ were not effective as catalysts in the present cyclopropanation. Variable stereoselectivity obtained in these reactions indicates that cyclopropanation proceeds in a different manner depending on each catalyst. The stereochemistry of the present cyclopropanation reaction will be argued in the last section (vide infra). In order to compare

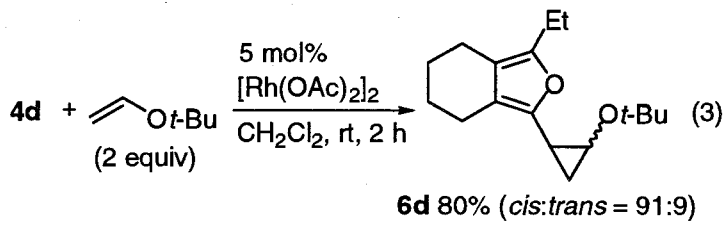
Table 3. Rh- or Pt-Catalyzed Cyclopropanation of Alkenes with **4**[a]



entry	4	alkene	cat.[b]	product	isolated yield	*cis*:*trans*[c]
1	a		[Rh]	 **6a**	99%	85:15
2	a		[Pt]		89%	32:68
3	b		[Rh]	 **6b**	92%	85:15
4	c		[Rh]	 **6c**	99%	90:10
5	c		[Pt]		68%	27:73
6	c		[Rh]	 **7c**	96%	N.A.[d]
7	c		[Pt]		56%	N.A.[d]
8	c		[Rh]	 **9c**	75%	endo only
9	c		[Pt]		60%	endo only
10	c		[Rh]	 **10c**	81%	24:76
11[e]	c		[Pt]		82%	14:86
12	c		[Rh]	 **11c**	67%	N.A.[d]
13[f]	c		[Pt]		18%	N.A.[d]

[a] Reactions were carried out at room temperature with **4** (0.2 mmol), alkene (0.4 mmol), and $[Rh(OAc)_2]_2$ (0.005 mmol) or $PtCl_2$ (0.01 mmol) in THF (2 mL) for 1 h unless otherwise noted. [b] [Rh] = $[Rh(OAc)_2]_2$, [Pt] = $PtCl_2$. [c] Determined by ^{1}H NMR. [d] N.A. = not applicable. [e] Styrene (4.0 mmol). [f] 3 h.

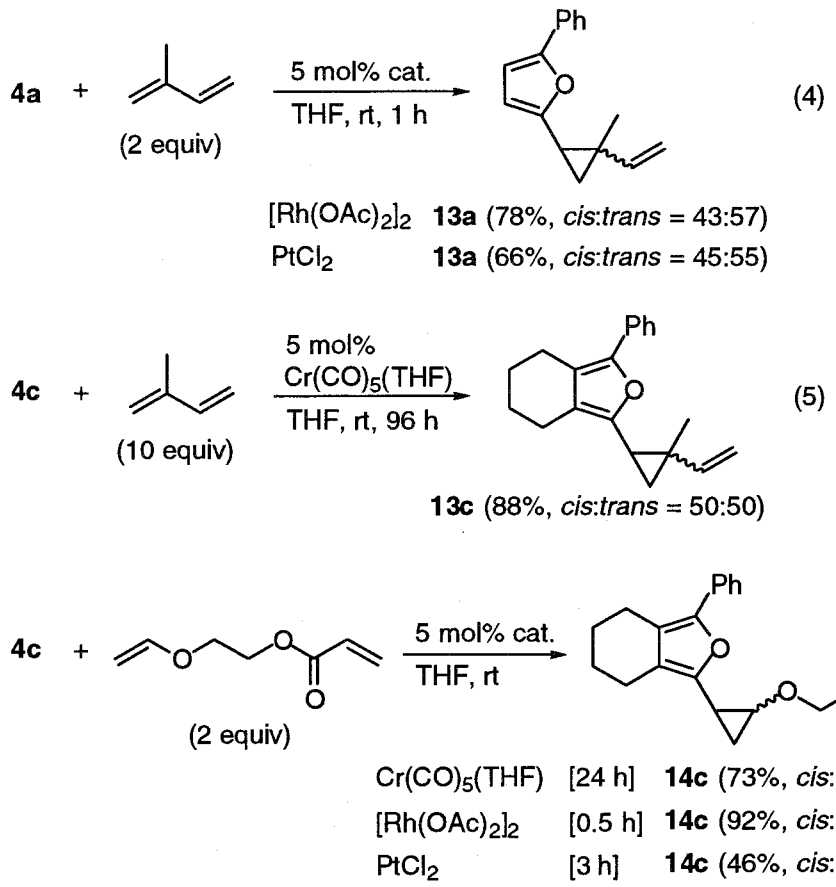
the chromium catalysis with other transition metal catalysis, we next examined cyclopropanation of several alkenes with ene-yne-ketones **4a-c** in the presence of $[Rh(OAc)_2]_2$ and $PtCl_2$ as selected catalysts. These results are summarized in Table 3. The reactions of **4a-c** with *tert*-butyl vinyl ether, ketene diethyl acetal, cyclic vinyl ether, and styrene proceeded quite smoothly to give the cyclopropanated products **6a-c**, **7c**, **9c**, and **10c** in good yields, respectively (entries 1-11). In the presence of $[Rh(OAc)_2]_2$ as a catalyst, the cyclopropanation of 2-ethylbut-1-ene with **4c** gave **11c** in 67% yield (entry 12), while a similar reaction with $PtCl_2$ catalyst gave **11c** in only 18% yield together with other unidentified products (entry 13). $[Rh(OAc)_2]_2$ can act as an effective catalyst in cyclopropanation of *tert*-butyl vinyl ether using ethyl ketone **4d** (eq 3), which led to lower yield of cyclopropanated product in chromium catalysis (see eq 2).



Regioselectivity and Chemoselectivity in Catalytic Cyclopropanation.

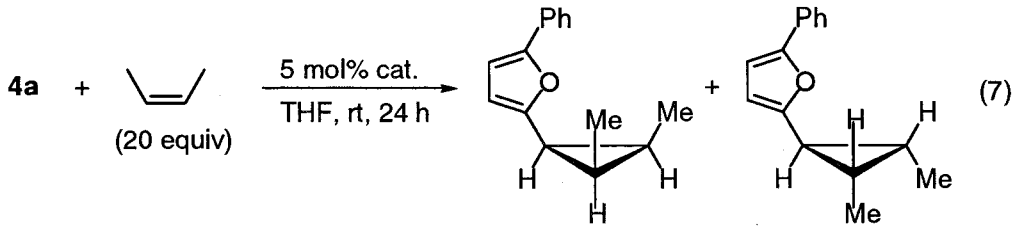
The pronounced preference for the cyclopropanation reaction to take place at electron-rich C=C bonds was verified by chromium-, rhodium-, and platinum-catalyzed reaction of **4** with isoprene and 2-vinyloxyethyl acrylate as shown in eqs 4-6. In each reaction of isoprene with **4a** and **4c**, a more substituted double bond was selectively cyclopropanated to give **13a** and **13c** in good yields with nondiastereoselective manner, respectively (eqs 4 and 5). As shown in eq 6, a more electron-rich C=C double bond of 2-vinyloxyethyl acrylate was selectively cyclopropanated to give **14c** (73% with [Cr], 92% with [Rh], and 46% with [Pt]) as a mixture of diastereoisomers (67:33 to 90:10), respectively. A higher reactivity of electron-rich alkenes and preferential formation of *cis*-cyclopropanes in this reaction indicate

that the cyclopropanation proceeds through the formation of an electrophilic (2-furyl)carbenoid intermediate like phenylcarbene-tungsten and -iron complexes.[12,13]



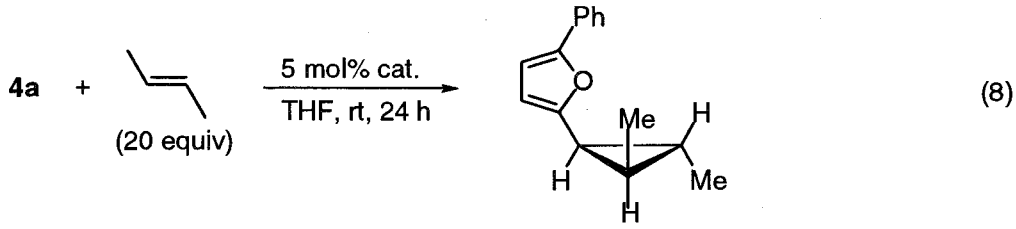
Plausible Reaction Pathway.

In order to elucidate the reaction pathway, cyclopropanation of stereodefined *cis*- and *trans*-but-2-ene was examined. In the presence of $Cr(CO)_5(THF)$ and $PtCl_2$ as selected catalysts, cyclopropanation reaction of *cis*- and *trans*-but-2-ene with an ene-yne-ketone **4a** proceeded stereospecifically to give only the cyclopropanated products with retention of configuration of alkenes, **15a** (14%, *syn*:*anti* = 91:9 with [Cr]; 26%, *syn*:*anti* = 75:25 with [Pt]) and **16a** (7% with [Cr]; 23% with [Pt]), respectively (eqs 7 and 8). The outcomes of the stereochemistry show that the most plausible pathway for cyclopropanation of an alkene with an ene-yne-ketone **4** is that illustrated in Scheme 5. The ene-yne-ketone **4** reacts with a transition metal complex to give a (2-furyl)carbene complex **5** as shown in Scheme 4.



$Cr(CO)_5(THF)$ **15a** (14%, *syn*:*anti* = 91:9)

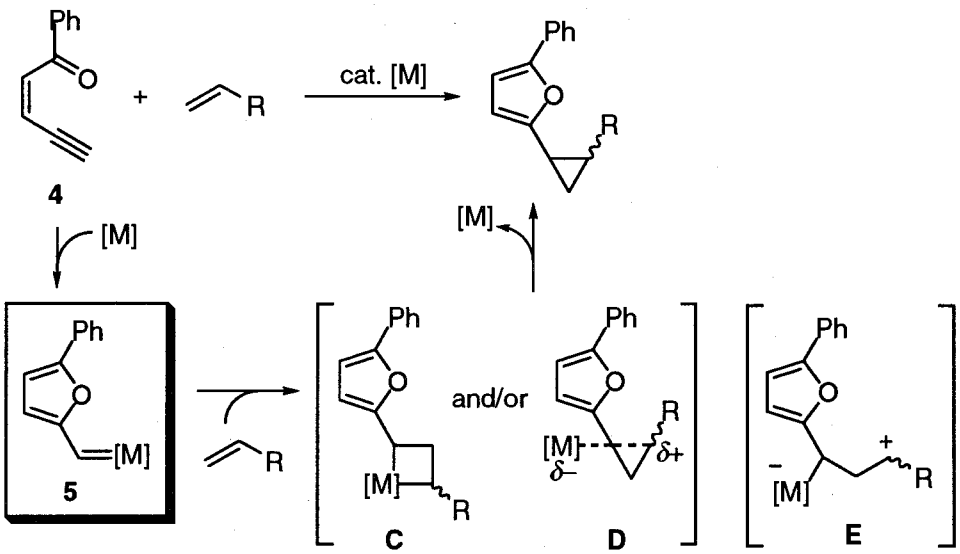
$PtCl_2$ **15a** (26%, *syn*:*anti* = 75:25)



$Cr(CO)_5(THF)$ **16a** (7%)

$PtCl_2$ **16a** (23%)

Scheme 5



Subsequently, the complex **5** reacts with an alkene to give the cyclopropanated product through a metallacyclobutane **C** or a charge-developed intermediate **D**.[12a,c,h,13] The preference for the *cis* cyclopropane isomer is a characteristic feature of the electrophilic metal-carbenoid having the same or similar steric environment ($Cr(CO)_5$ or $[Rh(OAc)_2]_2$ in octahedral geometry) except for the styrene case using $[Rh(OAc)_2]_2$.[20] In the case of the late

transition metals having the square planar geometry, the diastereoselectivity considerably depends on the structure of alkenes and the stability of metallacycles. The logical contention remains, but at least the intervention of a carbocationic intermediate **E** can be presumably excluded in the present reaction.

The author has demonstrated new catalytic cyclopropanation of alkenes on the basis of the generation of (2-furyl)carbene complexes from conjugated ene-yne-ketones. This catalytic system has wide applicability to a diversity of transition metal complexes as well as a variety of ene-yne-ketones, and indeed finds some applications in other catalytic 2-furfurylidene transfer reactions such as Doyle-Kirmse reaction (see Chapter 8). This reaction represents new protocol to generate carbenoid species via activation of alkynes with transition metal complexes.

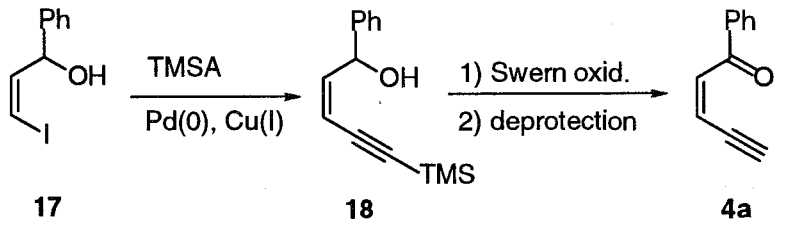
Experimental

General Procedure. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies were performed with Merck silica gel 60. The NMR spectra were measured for solutions in $CDCl_3$ or in d_8-THF 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. IR spectra were recorded on an FT-IR spectrometer. Melting points are uncorrected. High-resolution mass spectra (FAB HRMS) and low-resolution mass spectra (FAB LRMS) were obtained with JEOL JMX-SX 102A spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University.

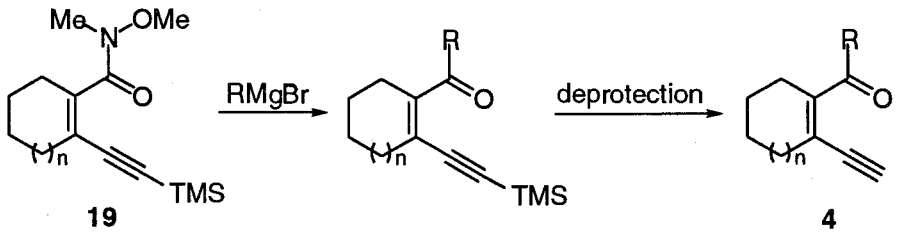
Synthesis of Substrates.

Substrate **4c**[11] was prepared as shown in Chapter 3. Substrate **4a** was prepared as shown in Scheme 6. Substrates **4b** and **4d** were prepared from ene-yne-carbonyl compound **19**[11] as shown in Scheme 7.

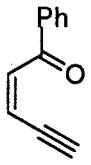
Scheme 6



Scheme 7



1-Phenyl-*cis*-pent-2-en-4-yn-1-one 4a.



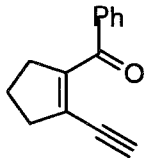
4a

To a solution of trimethylsilylacetylene (3.4 mL, 24 mmol) in benzene (200 mL) were added *t*-$BuNH_2$ (10 mL) and then benzyl alcohol **17**[21] (5.2 g, 20 mmol) at 0 °C under N_2. To the solution were added CuI (0.56 g, 3.0 mmol) and then $Pd(PPh_3)_4$ (1.16 g, 1.0 mmol) at 0 °C. The mixture was stirred at room temperature for 2 h. The solution was washed with saturated aqueous NH_4Cl solution (50 mL), and the aqueous phase was extracted with AcOEt (50 mL x 2). The combined organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v=8:1) to afford the coupling product **18** (4.6 g, quant.) as a pale yellow liquid; IR (neat) 640, 698, 745, 760, 844, 977, 1024, 1036, 1251, 1452, 1493, 2148 (C≡C), 2960, 3347 (OH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.23 (s, 9H), 2.17 (br s, 1H), 5.60 (d, J = 10.8 Hz, 1H), 5.81 (d, J = 8.8 Hz, 1H), 6.11 (dd, J = 8.8, 10.8 Hz, 1H), 7.28 (dd, J = 7.2, 7.2 Hz, 1H), 7.36 (dd, J = 7.2, 7.2 Hz,

2H), 7.44 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ -0.1, 72.0, 100.9, 101.0, 109.8, 125.7, 127.6, 128.5, 142.3, 145.4. Anal. Calcd for $C_{14}H_{18}OSi$: C, 72.99; H, 7.88. Found: C, 72.80; H, 7.83.

The compound **18** was oxidized by Swern oxidation method[22] (a ketone was obtained in 66% yield). To a solution of a crude ketone in DMSO (0.1 M) was added KF (2 equiv) at 0 °C. After stirring at room temperature for 2 h, the suspension was diluted with Et_2O (0.1M) and the organic layer was washed with water. The organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 30:1) to afford a pale yellow liquid **4a** (39% yield for two steps); IR (neat) 691, 751, 954, 1011, 1234, 1449, 1584, 1598, 1667 (CO), 2092 (C≡C), 3290 (≡C-H) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 3.51 (d, J = 2.7 Hz, 1H), 6.20 (dd, J = 2.7, 11.4 Hz, 1H), 7.20 (d, J = 11.4 Hz, 1H), 7.48 (dd, J = 7.5, 7.5 Hz, 1H), 7.58 (dd, J = 7.5, 7.5 Hz, 2H), 7.96 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 80.6, 88.1, 120.1, 128.5, 128.6, 133.2, 135.2, 137.1, 189.0. HRMS (FAB): calcd for $C_{11}H_9O$ (M^+), 157.0653; found, 157.0652.

1-Ethynyl-2-benzoylcyclopent-1-ene 4b.

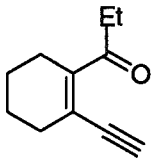


4b

To a solution of **17** (1.2 g, 4.4 mmol) in THF (10 mL) was added EtMgBr (9 mL, 9.0 mmol, 1.0 M in THF) at 0 °C. The mixture was stirred at room temperature for 30 min. The mixture was washed with saturated NH_4Cl solution (10 mL) and the aqueous phase was extracted with AcOEt (10 mL x 3). The combined organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 10/1) as an eluent to afford the crude ene-yne-ketone (0.56 g, 2.4 mmol, 54%) as a pale yellow oil. To a solution of this crude ene-yne-ketone in MeOH (20 mL) was added K_2CO_3 (0.66 g, 4.8 mmol) at room temperature. After stirring for 30 min, the suspension was poured into a mixture of saturated aqueous NH_4Cl solution (30 mL) and Et_2O (30 mL), and the aqueous phase was extracted with Et_2O (10 mL x 3). The combined

organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 15/1) as an eluent to afford ene-yne-ketone **4b** (0.35 g, 2.2 mmol, 64% yield for 2 steps) as a pale yellow oil; IR (neat) 680, 695, 720, 800, 883, 1338, 1448, 1576, 1595, 1639 (C=O), 2087 (C≡C), 2950, 2968, 3242 (≡C-H) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.03 (quint, J = 7.6 Hz, 2H), 2.74 (tt, J = 2.0, 7.6 Hz, 2H), 2.87 (tt, J = 2.0, 7.6 Hz , 2H), 3.03 (s, 1H), 7.43 (dd, J = 7.6, 7.6 Hz, 2H), 7.54 (dd, J = 7.6, 7.6 Hz, 1H), 7.83 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 22.5, 35.4, 39.2, 79.0, 86.4, 128.1, 129.3, 129.5, 132.7, 137.3, 148.4, 194.9. Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.38; H, 6.04. HRMS (FAB): calcd for $C_{14}H_{13}O$ ($M+H^+$), 197.0966; found, 197.0965.

1-Ethynyl-2-propionylcyclohex-1-ene 4d.



4d

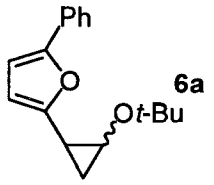
Substrate **4d** was prepared by a similar procedure of **4b**. A colorless oil (47% yield for 2 steps); IR (neat) 637, 1215, 1363, 1433, 1450, 1662 (C=O), 2088 (C≡C), 2861, 2936, 3256 (≡C-H) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.10 (t, J = 7.2 Hz, 3H), 1.58-1.72 (m, 4H), 2.26-2.40 (m, 4H), 2.87 (q, J = 7.2 Hz , 2H), 3.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 8.1, 21.6, 21.8, 26.1, 31.7, 34.9, 84.0, 100.5, 122.5, 145.7, 205.3. Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 80.56; H, 8.84. HRMS (FAB): calcd for $C_{11}H_{15}O$ ($M+H^+$), 163.1123; found, 163.1120.

Typical Procedure for Chromium-Catalyzed Cyclopropanation Reactions. The complex $Cr(CO)_6$ (5.5 mg, 0.025 mmol) was placed in the flame dried Schlenk flask and dissolved in dry and deoxygenated THF (2.0 mL) at room temperature under N_2. This solution was irradiated with high-pressure Hg lamp (450 W, 350 nm) for 2 h at room temperature. Then, N_2 gas was bubbled into the yellow solution for 5 min. To this yellow solution were added a solution of **4** (0.5 mmol) and an alkene in THF (2 mL). After the reaction was complete (the color of the solution changed from blue to yellow), the organic solvent was removed under

reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt as an eluent to afford cyclopropanes.

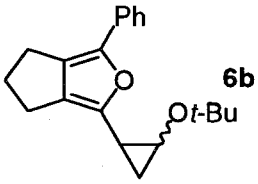
Typical Procedure for Other Transition Metal-Catalyzed Cyclopropanation Reaction of Styrene with 4b. To a solution of **4** (0.20 mmol) and alkene (0.4-4.0 mmol) in THF (2 mL) was added a transition metal complex (0.010 mmol) at room temperature under N_2. After the reaction was complete, the reaction mixture was filtered through Florisil®. The organic solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt as an eluent to afford the corresponding cyclopropanes.

Cyclopropane 6a.



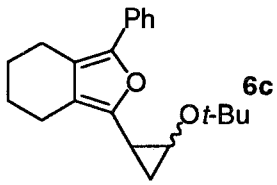
A pale yellow oil (63% yield, *cis/trans* = 76/24); IR (neat) 692, 758, 784, 885, 972, 1014, 1025, 1190, 1365, 1390, 1487, 1549, 1595, 2975 cm^{-1}; ^1H NMR (300 MHz, d_8-THF, 25 °C): *cis* isomer, δ 0.95 (ddd, J = 4.0, 6.4, 6.8 Hz, 1H), 1.09 (s, 9H), 1.13 (ddd, J = 6.4, 6.8, 9.6 Hz, 1H), 1.95 (ddd, J = 6.4, 6.4, 9.6 Hz, 1H), 3.51 (ddd, J = 4.0, 6.4, 6.4 Hz, 1H), 6.04 (d, J = 3.6 Hz, 1H), 6.62 (d, J = 3.6 Hz, 1H), 7.15 (dd, J = 7.6, 7.6 Hz, 1H), 7.30 (dd, J = 7.6, 7.6 Hz, 2H), 7.60 (d, J = 7.6 Hz, 2H); *trans* isomer, δ 1.07-1.13 (m, 2H), 1.25 (s, 9H), 1.94-1.99 (m, 1H), 3.36 (ddd, J = 2.8, 2.8, 8.0 Hz, 1H), 6.01 (d, J = 3.6 Hz, 1H), 6.60 (d, J = 3.6 Hz, 1H), 7.14 (dd, J = 7.6, 7.6 Hz, 1H), 7.30 (dd, J = 7.6, 7.6 Hz, 2H), 7.58 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C): *cis* isomer, δ 12.9, 17.3, 28.2, 52.4, 75.0, 106.6, 107.7, 123.7, 127.0, 129.2, 132.3, 152.5, 154.6; *trans* isomer, δ 14.1, 19.1, 28.6, 54.2, 75.4, 106.5, 106.6, 123.8, 127.3, 129.2, 132.1, 152.8, 155.9. HRMS (FAB): calcd for $C_{17}H_{20}O_2$ (a mixture of *cis* and *trans* isomers) (M^+), 256.1463; found, 256.1463. Anal. Calcd for $C_{17}H_{20}O_2$ (a mixture of *cis* and *trans* isomers): C, 79.65; H, 7.86. Found: C, 79.75; H, 8.01.

Cyclopropane 6b.



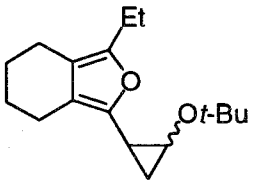
A colorless oil (92%, *cis/trans* = 85/15); IR (neat) 692, 761, 894, 922, 1010, 1024, 1190, 1363, 1389, 1494, 1604, 2973 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) *cis* isomer: δ 0.96-1.10 (m, 2H), 1.08 (s, 9H), 1.89 (ddd, J = 6.4, 6.4, 10.0 Hz, 1H), 2.30-2.40 (m, 2H), 2.51-2.67 (m, 2H), 2.75-2.79 (m, 2H), 3.48 (ddd, J = 4.4, 6.4, 6.4 Hz, 1H), 7.07 (dd, J = 7.6, 7.6 Hz, 1H), 7.28 (dd, J = 7.6, 7.6 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) *cis* isomer:δ 10.6, 16.5, 24.1, 25.0, 27.4, 32.1, 51.6, 74.0, 122.8, 125.0, 128.2, 129.3, 130.2, 132.2, 141.2, 142.4. Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.95; H, 8.27. HRMS (FAB): calcd for $C_{20}H_{24}O_2$ (a mixture of *cis* and *trans* isomers) (M^+), 296.1776; found, 296.1782.

Cyclopropane 6c.



A pale yellow oil (90% yield, *cis/trans* = 60/40); IR (neat) 693, 762, 1048, 1153, 1191, 1364, 1440, 1493, 1600, 2931, 2974 cm^{-1}; ^1H NMR (300 MHz, d_8-THF, 25 °C): *cis* isomer, δ 1.01-1.09 (m, 1H), 1.08 (s, 9H), 1.26-1.31 (m, 1H), 1.66-1.73 (m, 4H), 1.84 (ddd, J = 6.3, 6.3, 9.9 Hz, 1H), 2.44-2.64 (m, 2H), 2.73-2.78 (m, 2H), 3.49 (ddd, J = 4.2, 6.3, 6.3 Hz, 1H), 7.08 (dd, J = 7.8, 7.8 Hz, 1H), 7.29 (dd, J = 7.8, 7.8 Hz, 2H), 7.51 (d, J = 7.8 Hz, 2H); *trans* isomer, δ 1.04-1.11 (m, 1H), 1.19 (ddd, J = 6.3, 6.3, 6.3 Hz, 1H), 1.26 (s, 9H), 1.68-1.76 (m, 4H), 1.90 (ddd, J = 3.0, 6.3, 9.6 Hz, 1H), 2.52-2.67 (m, 2H), 2.70-2.76 (m, 2H), 3.48 (ddd, J = 3.0, 6.3, 6.3 Hz, 1H), 7.10 (dd, J = 7.8, 7.8 Hz, 1H), 7.30 (dd, J = 7.8, 7.8 Hz, 2H), 7.49 (d, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, d_8-THF, 25 °C): *cis* isomer, δ 11.0, 16.7, 22.0, 24.0, 24.1, 24.5, 28.2, 52.3, 74.8, 119.8, 120.1, 124.4, 125.9, 129.1, 133.6, 144.9, 146.6; *trans* isomer, δ 13.9, 18.0, 21.4, 23.9, 23.9, 24.4, 28.5, 53.4, 75.2, 118.7, 120.1, 124.4, 126.2, 129.1, 133.3, 144.8, 147.9. HRMS (FAB): calcd for $C_{21}H_{26}O_2$ (a mixture of *cis* and *trans* isomers) (M^+), 310.1933; found, 310.1935. Anal. Calcd for $C_{21}H_{26}O_2$ (a mixture of *cis* and *trans* isomers): C, 81.25; H, 8.44. Found: C, 80.97; H, 8.52.

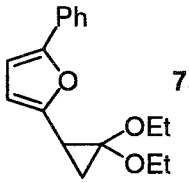
Cyclopropane 6d.



6d

A pale yellow oil (80% yield, cis/trans = 91/9); IR (neat) 893, 1000, 1039, 1062, 1150, 1192, 1238, 1259, 1364, 1388, 1444, 1593, 2855, 2932, 2973 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) *cis* isomer: δ 1.03 (ddd, J = 5.6, 6.8, 10.0 Hz, 1H), 1.01 (s ,9H), 1.06 (t, J = 7.6 Hz, 3H), 1.07 (ddd, J = 4.0, 5.6, 7.2 Hz, 1H), 1.52-1.61 (m, 4H), 1.66 (ddd, J = 6.0, 7.2, 10.0 Hz, 1H), 2.30-2.51 (m, 4H), 2.41 (q, J = 7.6 Hz, 2H), 3.33 (ddd, J = 4.0, 6.0, 6.8 Hz, 1H); ^{13}C NMR (75 MHz, d_8-THF, 25 °C) *cis* isomer:δ 9.4, 12.6, 15.9, 19.6, 20.6, 21.2, 23.8, 23.8, 27.4, 51.0, 73.7, 115.2, 116.5, 143.1, 147.1. HRMS (FAB): calcd for $C_{17}H_{27}O_2$ (a mixture of *cis* and *trans* isomers) ($M+H^+$), 263.2011; found, 263.2006.

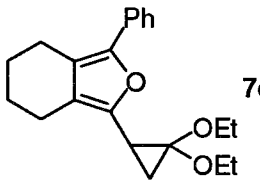
Cyclopropane 7a.



7a

A pale yellow oil (82% yield); IR (neat) 691, 759, 1023, 1056, 1117, 1212, 1285, 1443, 1487, 1548, 1595, 2884, 2929, 2975 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) δ 0.99 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.2 Hz, 3H), 1.31 (dd, J = 6.0, 6.8 Hz, 1H), 1.41 (dd, J = 6.0, 10.4 Hz, 1H), 2.37 (dd, J = 6.8, 10.4 Hz, 1H), 3.38-3.51 (m, 1H), 3.58-3.75 (m, 3H), 6.09 (d, J = 3.6 Hz, 1H), 6.62 (d, J = 3.6 Hz, 1H), 7.15 (dd, J = 7.6, 7.6 Hz, 1H), 7.30 (dd, J = 7.6, 7.6 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) δ 15.6, 15.8, 19.2, 24.5, 62.3, 62.8, 92.3, 106.7, 108.1, 123.9, 127.3, 129.2, 132.1, 153.0, 153.4. Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.90; H, 7.37. HRMS (FAB): calcd for $C_{17}H_{20}O_3$ (M^+), 272.1412; found, 272.1407.

Cyclopropane 7c.

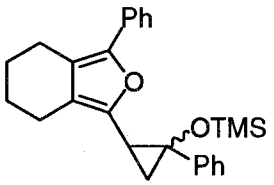


7c

A pale yellow oil (99% yield); IR (neat) 693, 762, 983, 1054, 1070, 1118, 1201, 1269, 1441, 1493, 1561, 1601, 2929, 2974 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) δ 0.99 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H), 1.35 (dd, J = 5.2, 10.4 Hz, 1H), 1.57 (dd, J = 5.2, 6.8 Hz, 1H), 1.65-1.78 (m, 4H), 2.26 (dd, J = 6.8, 10.4 Hz, 1H), 2.50-2.58 (m, 2H), 2.71-2.78 (m, 2H), 3.42-3.50 (m, 1H), 3.57-3.73 (m, 3H), 7.09 (dd, J = 7.6, 7.6 Hz, 1H), 7.29 (dd, J = 7.6, 7.6 Hz, 2H), 7.54 (d,

J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) δ 15.8, 15.8, 17.8, 21.8, 23.7, 24.0, 24.0, 24.5, 62.2, 62.8, 92.3, 120.0, 120.2, 124.4, 126.1, 129.0, 133.3, 144.9, 145.1. HRMS (FAB): calcd for $C_{21}H_{26}O_3$ (M^+), 326.1882; found, 326.1884.

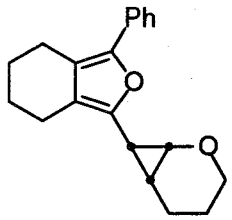
Cyclopropane 8c.



8c

A colorless oil (83% yield, as a mixture of *cis* and *trans* isomers); IR (neat) 695, 760, 843, 1203, 1250, 1447, 1494, 1601, 2933 cm^{-1}; ^{1}H NMR (400 MHz, d_8-THF, 25 °C) δ -0.18 (s, 9H), -0.01 (s, 9H), 1.54-1.66 (m, 4H), 1.62 (dd, J = 6.0, 10.0 Hz, 1H), 1.66-1.80 (m, 4H), 1.74 (dd, J = 6.4, 10.0 Hz, 1H), 1.96 (dd, J = 6.4, 7.2 Hz, 1H), 2.00 (dd, J = 6.0, 7.2 Hz, 1H), 2.16 (dd, J = 7.2, 10.0 Hz, 1H), 2.38-2.42 (m, 2H), 2.47-2.66 (m, 4H), 2.49 (dd, J = 7.2, 10.0 Hz, 1H), 2.71-2.75 (m, 2H), 7.02-7.36 (m, 16H), 7.40 (d, J = 7.6 Hz, 2H), 7.60 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) δ -0.4, -0.4, 17.5, 18.1, 20.0, 20.3, 22.1, 22.3, 22.4, 22.4, 22.8, 23.0, 24.3, 24.6, 61.7, 62.8, 118.0, 118.6, 119.2, 119.9, 122.9, 122.9, 124.4, 124.5, 124.8, 124.8, 125.7, 126.1, 126.6, 127.2, 127.3, 127.4, 131.5, 131.8, 139.4, 139.4, 143.4, 143.4, 143.7, 143.8. HRMS (FAB): calcd for $C_{26}H_{30}O_2Si$ (a mixture of *cis* and *trans* isomers) (M^+), 402.2015; found, 402.2018.

Cyclopropane 9c.



9c

A pale yellow solid (90% yield); mp. 87.0-88.8 °C; IR (KBr) 698, 766, 1041, 1105, 1142, 1236, 1245, 1438, 1447, 1599, 2854, 2929, 2939, 2953 cm^{-1}; ^{1}H NMR (400 MHz, d_8-THF, 25 °C) δ 0.64-0.76 (m, 1H), 1.07-1.20 (m, 1H), 1.33 (ddd, J = 6.8, 6.8, 6.8 Hz, 1H), 1.64-1.77 (m, 5H), 1.93 (dddd, J = 6.8, 6.8, 12.0, 14.0 Hz, 1H), 2.25 (dd, J = 4.2, 14.0 Hz, 1H), 2.43-2.51 (m, 1H), 2.69-2.78 (m, 3H), 3.16-3.23 (m, 1H), 3.35-3.40 (m, 1H), 3.78 (dd, J = 6.8, 6.8 Hz, 1H), 7.12 (dd, J = 7.2, 7.2 Hz, 1H), 7.32 (dd, J = 7.2, 7.2 Hz, 2H), 7.57 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) δ 14.9, 17.1, 19.0, 21.8, 23.4, 24.0, 24.0, 24.6, 54.9, 64.8, 119.9, 122.3, 124.5, 126.1, 129.1, 133.5, 145.8, 145.8. Anal. Calcd for

$C_{20}H_{22}O_2$: C, 81.60; H, 7.53. Found: C, 80.84; H, 7.53. HRMS (FAB): calcd for $C_{20}H_{22}O_2$ (M^+), 294.1620; found, 294.1619.

X-ray Crystallographic Studies of 9c. Yellow crystals of **9c** suitable for X-ray analysis were obtained by recrystallization from hexane. The single crystal was sealed in a Pyrex glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation. Details of crystal and data collection parameters are summarized in Table 4. The positions of non-hydrogen atoms were determined by direct methods (SIR92)[23] and subsequent Fourier syntheses (DIRDIF PATTY). An ORTEP drawing of **9c** is shown in Figure 1.

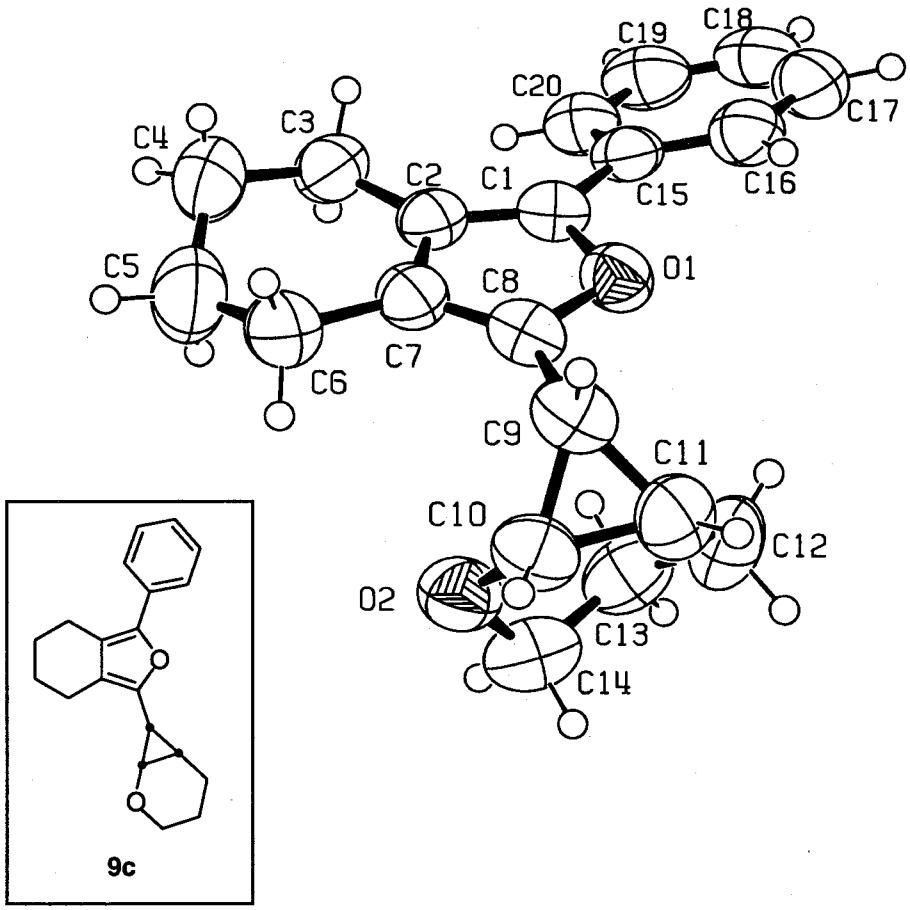
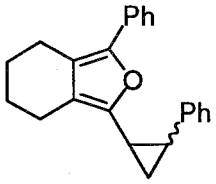


Figure 1. Crystal structure of **9c**

Table 4. Summary of Crystallographic Data of **9c**

empirical formula	$C_{20}H_{22}O_2$
fw	294.39
crystal syst	orthorhombic
space group	$Pca2_1$ (No. 29)
cryst color	colorless, needle
lattice params	
a (Å)	15.972(1)
b (Å)	8.803(9)
c (Å)	11.400(4)
V (Å^3)	1603.0(9)
Z	4
D_{calc} (g cm^{-3})	1.220
μ(Mo Kα) (cm^{-1})	0.77
F(000)	632
diffractometer	Rigaku RAXIS-RAPID
radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated
temp (°C)	23.0
scan type	ω–2θ
Max. 2θ (°)	54.9
no. of rflns measd	total, 1922
no. of observns ($I > 3.00\sigma(I)$)	1356
structure soln	direct methods (SIR92)
refinement	full-matrix least-squares on F
no. of variables	199
reflection/parameter ratio	6.81
residuals: R; R_w	0.070; 0.081
goodness of fit (GOF)	0.95
max shift/error in final cycle	0.00
maximum peak in final diff map (e Å^{-3})	0.22
minimum peak in final diff map (e Å^{-3})	–0.36

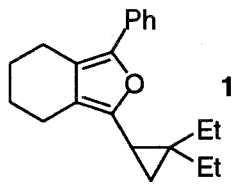
Cyclopropane 10c.



10c

A colorless oil (85% yield, *cis/trans* = 74/26); IR (neat) 693, 762, 906, 1029, 1072, 1439, 1494, 1560, 1601, 2855, 2929 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C): *cis* isomer, δ 1.45 (ddd, J = 5.2, 8.8, 8.8 Hz, 1H), 1.53-1.70 (m, 4H), 1.61 (ddd, J = 5.2, 6.4, 6.4 Hz, 1H), 2.19-2.45 (m, 2H), 2.30 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.42 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.58-2.68 (m, 2H), 7.02-7.16 (m, 6H), 7.24-7.37 (m, 4H); *trans* isomer, δ 1.39 (ddd, J = 4.8, 6.0, 8.8 Hz, 1H), 1.65 (ddd, J = 4.8, 6.0, 8.8 Hz, 1H), 1.66-1.76 (m, 4H), 2.09 (ddd, J = 4.8, 6.0, 8.8 Hz, 1H), 2.44 (ddd, J = 4.8, 6.0, 8.8 Hz, 1H), 2.54 (t, J = 6.0 Hz, 2H), 2.76 (t, J = 6.0 Hz, 2H), 7.12-7.21 (m, 4H), 7.29 (dd, J = 7.8, 7.8 Hz, 2H), 7.35 (dd, J = 7.8, 7.8 Hz, 2H), 7.56 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *cis* isomer, δ 10.7, 16.7, 20.7, 22.8, 22.9, 23.4, 23.6, 119.2, 121.1, 125.4, 125.4, 125.8, 127.6, 128.1, 128.4, 132.3, 138.9, 144.3, 145.2; *trans* isomer, δ 15.8, 20.3, 20.7, 23.0, 23.1, 23.5, 24.8, 118.5, 119.6, 123.8, 125.6, 125.7, 125.8, 128.3, 128.4, 132.1, 142.0, 143.9, 147.3. Anal. Calcd for $C_{23}H_{22}O$ (a mixture of *cis* and *trans* isomers): C, 87.86; H, 7.05. Found: C, 87.99; H, 7.20. HRMS (FAB): calcd for $C_{23}H_{22}O$ (a mixture of *cis* and *trans* isomers) (M^+), 314.1671; found, 314.1671.

Cyclopropane 11c.

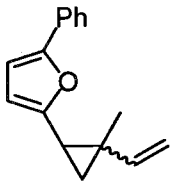


11c

A colorless oil (52% yield) ; IR (neat) 691, 760, 1034, 1441, 1458, 1493, 1560, 1601, 2932, 2961 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.80 (dd, J = 4.4, 8.8 Hz, 1H), 0.84 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H), 1.02 (dd, J = 4.4, 5.2Hz, 1H), 1.13 (qd, J = 7.2, 14.4 Hz, 1H), 1.27 (qd, J = 7.2, 14.4 Hz, 1H), 1.35 (qd, J = 7.2, 14.4 Hz, 1H), 1.50 (qd, J = 7.2, 14.4 Hz, 1H), 1.64 (dd, J = 5.2, 8.8 Hz, 1H), 1.67-1.79 (m, 4H), 2.45-2.53 (m, 2H), 2.72-2.79 (m, 2H), 7.14 (dd, J = 7.6, 7.6 Hz, 1H), 7.34 (dd, J = 7.6, 7.6 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 10.7, 10.8, 17.4, 20.8, 21.2, 23.1, 23.2, 23.3, 23.6, 28.8, 29.6, 119.5, 119.8, 123.7, 125.3, 128.3, 132.4, 143.7, 147.3. Anal. Calcd for

$C_{21}H_{26}O$: C, 85.67; H, 8.90. Found: C, 85.42; H, 9.16. HRMS (FAB): calcd for $C_{21}H_{26}O$ (M^+), 294.1984; found, 294.1976.

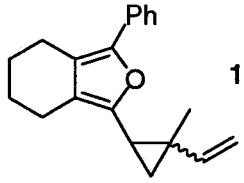
Cyclopropane 13a.



13a

A colorless oil (78% yield, *cis/trans* = 43/57); IR (neat) 691, 758, 786, 898, 1019, 1487, 1548, 1595, 1636, 2929, 2956, 3002 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.10 (s, 3H), 1.15-1.22 (m, 4H), 1.32 (s, 3H), 2.08 (dd, J = 6.4, 8.8 Hz, 1H), 2.12 (dd, J = 6.4, 8.8 Hz, 1H), 4.94 (dd, J = 1.2, 10.4 Hz, 1H), 4.98 (dd, J = 0.8, 10.8 Hz, 1H), 5.04 (dd, J = 0.8, 17.2 Hz, 1H), 5.05 (dd, J = 1.2, 17.6 Hz, 1H), 5.54 (dd, J = 10.8, 17.2 Hz, 1H), 5.56 (dd, J = 10.4, 17.6 Hz, 1H), 6.07 (d, J = 3.2 Hz, 1H), 6.09 (d, J = 3.2 Hz, 1H), 6.54 (d, J = 3.2 Hz, 1H), 6.56 (d, J = 3.2 Hz, 1H), 7.20 (dd, J = 7.6, 7.6 Hz, 1H), 7.20 (dd, J = 7.6, 7.6 Hz, 1H), 7.34 (dd, J = 7.6, 7.6 Hz, 2H), 7.34 (dd, J = 7.6, 7.6 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 15.8, 19.6, 20.2, 21.8, 24.1, 25.1, 26.1, 26.2, 105.7, 105.7, 108.3, 108.7, 110.6, 112.4, 123.3, 123.3, 126.7, 126.7, 128.5, 128.5, 131.0, 131.0, 140.9, 145.1, 152.2, 152.4, 153.6, 153.9. Anal. Calcd for $C_{16}H_{16}O$ (a mixture of *cis* and *trans* isomers): C, 85.68; H, 7.19. Found: C, 85.66; H, 7.36. HRMS (FAB): calcd for $C_{16}H_{16}O$ (a mixture of *cis* and *trans* isomers) (M^+), 224.1201; found, 224.1202.

Cyclopropane 13c.

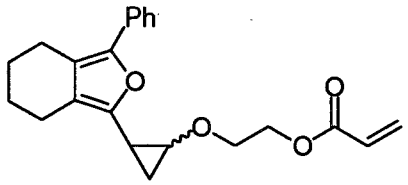


13c

A colorless oil (88% yield, *cis/trans* = 50/50); IR (neat) 692, 760, 896, 995, 1030, 1071, 1441, 1493, 1558, 1601, 1633, 2857, 2930 cm^{-1}; ^1H NMR (400 MHz, d_8-THF, 25 °C) δ 1.09 (s, 3H), 1.15 (dd, J = 4.4, 8.8 Hz, 1H), 1.18 (dd, J = 4.8, 9.2 Hz, 1H), 1.31 (s, 3H), 1.34 (dd, J = 4.8, 6.4 Hz, 1H), 1.44 (dd, J = 4.8, 6.4 Hz, 1H), 1.64-1.80 (m, 8H), 1.98 (dd, J = 6.4, 9.2 Hz, 1H), 2.03 (dd, J = 6.4, 8.8 Hz, 1H), 2.45-2.55 (m, 4H), 2.70-2.80 (m, 4H), 4.86 (dd, J = 1.2, 10.8 Hz, 1H), 4.91 (dd, J = 1.2, 10.8 Hz, 1H), 5.00 (dd, J = 1.2, 17.6 Hz, 1H), 5.01 (dd, J = 1.2, 17.6 Hz, 1H), 5.53 (dd, J = 10.8, 17.6 Hz, 1H), 5.60 (dd, J = 10.8, 17.6 Hz, 1H), 7.11 (dd, J = 7.6, 7.6 Hz, 1H), 7.12 (dd, J = 7.6, 7.6 Hz, 1H), 7.31 (dd, J = 7.6, 7.6 Hz, 2H), 7.31 (dd, J = 7.6, 7.6 Hz,

2H), 7.53 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, d_8-THF, 25 °C) δ 16.2, 19.2, 20.2, 20.9, 21.0, 21.7, 23.0, 23.0, 23.1, 23.1, 23.1, 23.5, 23.5, 24.1, 25.7, 25.9, 110.1, 111.8, 119.5, 120.6, 120.7, 123.8, 123.8, 124.2, 125.5, 125.5, 128.4, 128.4, 132.2, 132.2, 141.7, 144.2, 144.3, 145.5, 145.7, 146.1. HRMS (FAB): calcd for $C_{20}H_{22}O$ (a mixture of *cis* and *trans* isomers) (M^+), 278.1671; found, 278.1668.

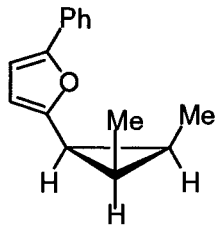
Cyclopropane 14c.



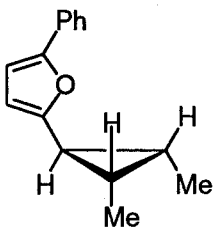
14c

A pale yellow oil (92% yield, *cis/trans* = 90/10); IR (neat) 694, 764, 810, 986, 1071, 1098, 1192, 1271, 1296, 1406, 1440, 1493, 1600, 1725 (C=O), 2858, 2931 cm^{-1}; ^{1}H NMR (400 MHz, d_8-THF, 25 °C) *cis* isomer: δ 1.03 (ddd, J = 6.4, 6.4, 9.6 Hz, 1H), 1.33-1.37 (m, 1H), 1.62-1.73 (m, 4H), 1.85 (ddd, J = 6.4, 6.4, 9.6 Hz, 1H), 2.48-2.51 (m, 2H), 2.67-2.70 (m, 2H), 3.47-3.53 (m, 2H), 3.57-3.62 (m, 1H), 3.99-4.03 (m, 2H), 5.59 (d, J = 10.0 Hz, 1H), 5.88 (dd, J = 10.0, 16.4 Hz, 1H), 6.16 (d, J = 16.4 Hz, 1H), 7.05 (dd, J = 7.6, 7.6 Hz, 1H), 7.25 (dd, J = 7.6, 7.6 Hz, 2H), 7.50 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, d_8-THF, 25 °C) *cis* isomer:δ 14.9, 21.0, 23.1, 24.1, 24.3, 24.7, 57.7, 63.1, 68.4, 119.1, 119.8, 123.6, 125.2, 128.1, 128.4, 129.4, 132.4, 144.3, 144.3, 164.9. HRMS (FAB): calcd for $C_{22}H_{24}O_4$ (a mixture of *cis* and *trans* isomers) (M^+), 352.1675; found, 352.1674.

Cyclopropane 15a.



syn-**15a**

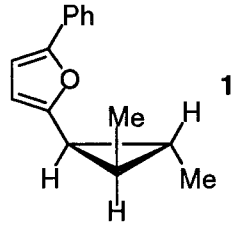


anti-**15a**

A colorless oil (26% yield, *syn/anti* = 75/25); IR (neat) 691, 758, 786, 1020, 1070, 1385, 1449, 1487, 1548, 1594, 2875, 2953, 3008 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) *syn* isomer:δ 1.07 (s, 3H), 1.09 (s, 3H), 1.24-1.31 (m, 2H), 1.94 (t, J = 8.7 Hz, 1H), 6.11 (d, J = 3.3 Hz, 1H), 6.56 (d, J = 3.3 Hz, 1H), 7.20 (dd, J = 7.5, 7.5 Hz, 1H), 7.35 (dd, J = 7.5, 7.5 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H); *anti* isomer: 1.15 (s, 3H), 1.17 (s, 3H), 1.24-1.31 (m, 2H), 1.91-1.97 (m, 1H), 5.95 (d, J = 3.3 Hz, 1H), 6.51 (d, J = 3.3 Hz, 1H), 7.15-7.20 (m ,1H), 7.30-7.36 (m, 2H), 7.58 (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) *syn*

isomer: δ 8.9, 12.2, 15.3, 16.9, 20.0, 105.6, 109.5, 123.3, 126.6, 128.6, 131.2, 152.2, 153.5; *anti* isomer: δ 8.9, 12.2, 15.2, 19.9, 24.9, 104.6, 105.9, 123.1, 126.5, 128.5, 131.2, 151.3, 157.5. HRMS (FAB): calcd for $C_{15}H_{16}O$ (a mixture of *cis* and *trans* isomers) (M^+), 212.1201; found, 212.1209.

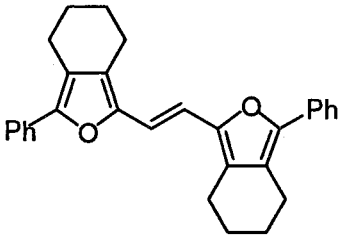
Cyclopropane 16a.



16a

A colorless oil (23% yield); IR (neat) 691, 758, 783, 1020, 1062, 1383, 1449, 1487, 1548, 1595, 2867, 2953, 3004 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.90-0.96 (m, 1H), 1.00 (d, J = 5.6 Hz, 3H), 1.00-1.07 (m, 1H), 1.19 (d, J = 5.6 Hz, 3H), 1.70 (dd, J = 4.8, 8.4 Hz, 1H), 6.03 (d, J = 3.6 Hz, 1H), 6.55 (d, J = 3.6 Hz, 1H), 7.19 (dd, J = 7.6, 7.6 Hz, 1H), 7.34 (dd, J = 7.6, 7.6 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 13.3, 18.5, 20.6, 22.3, 22.7, 105.7, 108.0, 123.2, 126.5, 128.5, 131.2, 151.8, 154.9. HRMS (FAB): calcd for $C_{15}H_{16}O$ (a mixture of *cis* and *trans* isomers) (M^+), 212.1201; found, 212.1207.

Chromium-Catalyzed Synthesis of Bisfurfurylidene 12.



12

Bisfurfurylidene **12** was obtained by chromium-catalyzed cyclopropanation without alkenes.

A yellow solid (87% yield); mp. 213.5-216.4 °C; IR (KBr) 692, 761, 944, 1033, 1246, 1352, 1437, 1491, 1596, 2858, 2938 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.72-1.80 (m, 8H), 2.59-2.65 (m, 4H), 2.72-2.78 (m, 4H), 6.75 (s, 2H, vinyl), 7.13 (dd, J = 7.6, 7.6 Hz, 2H), 7.32 (dd, J = 7.6, 7.6 Hz, 4H), 7.63 (d, J = 7.6 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.0, 22.7, 22.9, 23.4, 111.2, 120.7, 122.8, 124.1, 126.1, 128.3, 131.7, 146.0, 146.8. HRMS (FAB): calcd for $C_{30}H_{28}O_2$ (*trans* isomer) (M^+), 420.2089; found, 420.2080.

X-ray Crystallographic Studies of 12. Yellow crystals of **12** suitable for X-ray analysis were obtained by recrystallization from hexane. The single crystal was sealed in a Pyrex

glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation. Details of crystal and data collection parameters are summarized in Table 5. The positions of non-hydrogen atoms were determined by direct methods (SIR92)[23] and subsequent Fourier syntheses (DIRDIF PATTY). An ORTEP drawing of **12** is shown in Figure 2.

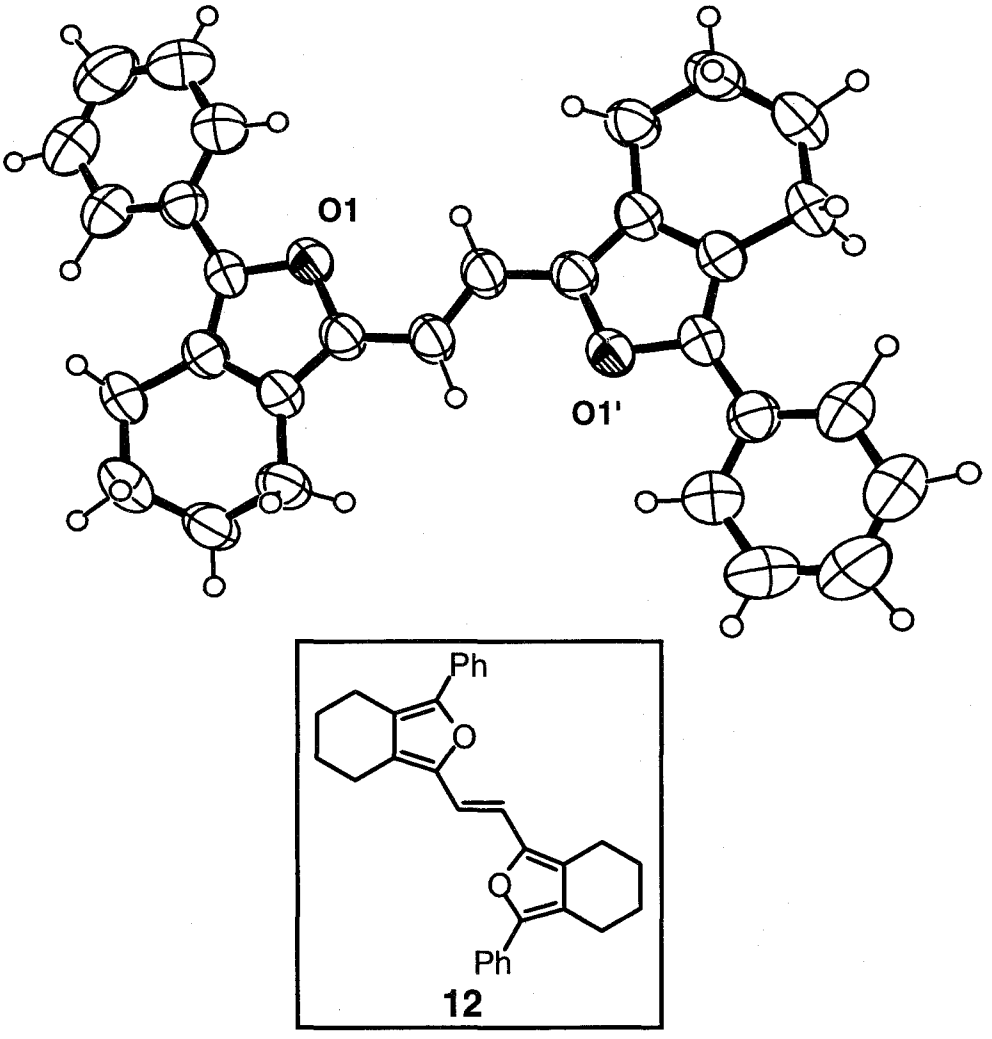


Figure 2. Crystal structure of **12**

Table 5. Summary of Crystallographic Data of **12**

empirical formula	$C_{30}H_{28}O_2$
fw	420.55
crystal syst	monoclinic
space group	$P2_1/c$ (No. 14)
cryst color	yellow, block
lattice params	
a (Å)	8.8511(7)
b (Å)	14.341(1)
c (Å)	9.5857(8)
β (Å)	107.198(3)
V (Å^3)	1162.4(2)
Z	2
D_{calc} (g cm^{-3})	1.201
μ(Mo Kα) (cm^{-1})	0.73
F(000)	448
diffractometer	Rigaku RAXIS-RAPID
radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated
temp (°C)	23.0
scan type	ω–2θ
Max. 2θ (°)	54.9
no. of rflns measd	total, 9452
no. of observns ($I > 3.00\sigma(I)$)	2631
structure soln	direct methods (SIR92)
refinement	full-matrix least-squares on F
no. of variables	203
reflection/parameter ratio	5.97
residuals: R; R_w	0.044; 0.040
goodness of fit (GOF)	1.47
max shift/error in final cycle	0.26
maximum peak in final diff map (e Å^{-3})	0.14
minimum peak in final diff map (e Å^{-3})	–0.15

References and Notes

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(15) The blue color indicates the generation of a (2-furyl)carbene chromium complex. Thus, consumption of the starting material **4** could be visibly monitored.

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(17) The structure was unambiguously determined by X-ray diffraction analysis of **9c**. See Experimental Section.

(18) Furan ring construction from enyne-aldehyde derivatives with a stoichiometric amount of Fischer carbene complexes has been demonstrated. See: (a) Herndon, J. W.; Wang,

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(19) In the case of [(*p*-cymene)RuCl]$_2$, a remarkable solvent effect was observed. Thus, the use of $ClCH_2CH_2Cl$ in place of THF as solvent led to the rapid formation of the cyclopropanated product **10c** in 96% yield from styrene with **4c** at room temperature for 1 h with a high trans selectivity (*cis*:*trans* = 11:89).

(20) *Cis* preference was observed in the cyclopropanation of styrene using $PhCHN_2$ as a carbenoid precursor, the ratio of *cis*:*trans* being 77:23. See: Doyle, M. P.; Griffin, J. H.; Bagheri, V.; Dorow, R. L. *Organometallics* **1984**, *3*, 53.

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Chapter 5

Rhodium-Catalyzed Cyclopropanation Using Ene-Yne-Imino Ethers as Precursors of (2-Pyrrolyl)carbenoids

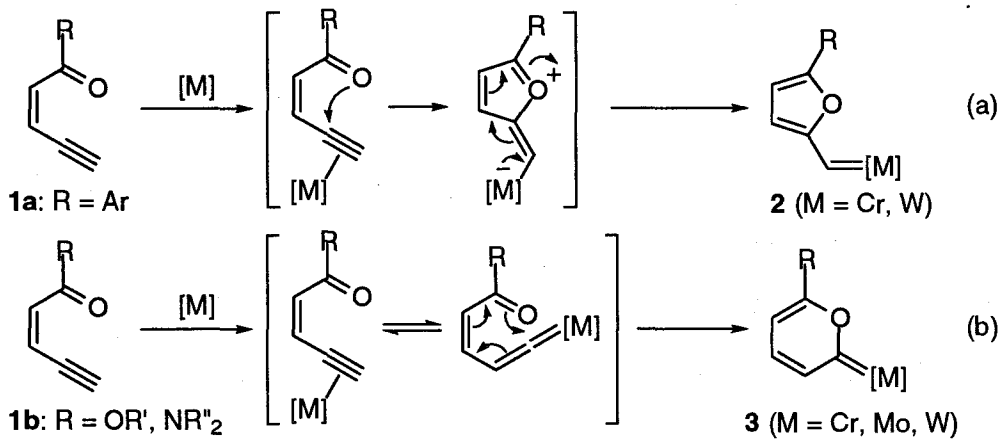
Abstract

The reaction of alkenes with the conjugated ene-yne-imino ethers and an ene-yne-aldimine in the presence of a catalytic amount of $[Rh(OAc)_2]_2$ gives 2-pyrrolylcyclopropanes in good yields. The key intermediate of this cyclopropanation is (2-pyrrolyl)carbenoids generated by a nucleophilic attack of an imine nitrogen atom to an internal alkyne carbon activated by the rhodium complex. The obtained 2-pyrrolylcyclopropanes are easily converted to pyrrolin-2-ones upon treatment with 1 N HCl solution. The reaction of alkenes with ene-yne-imino ethers having acceptors for carbenoid intermediates is revealed to afford polycyclic compounds as the result of intramolecular cyclopropanation or C-H insertion reaction.

Introduction

The author has previously reported the formation of (2-furyl)carbene complexes **2** from ene-yne-ketones **1a** promoted by group 6 transition metal complexes,[1] and their application to catalytic cyclopropanation of alkenes using **1a** as (2-furyl)carbenoid precursors[2] (Scheme 1a, and also see Chapters 3 and 4). However, similar cyclopropanation reactions with ene-yne-esters and -amides **1b** were unsuccessful due to the fact that group 6 transition metals undergo pericyclic or pseudopericyclic reactions of vinylidene intermediates generated from **1b** to produce stable 2-pyranylidene-complexes **3** (Scheme 1b, and also see Chapter 1).[3] For

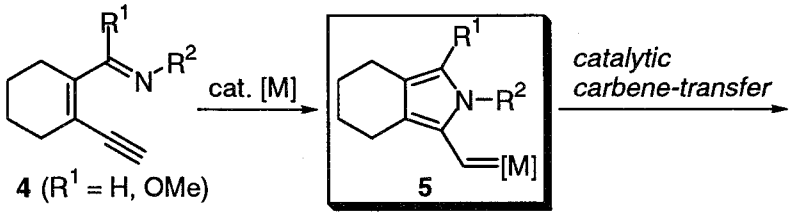
Scheme 1



searching the new reactivity of these π-conjugated system with transition metal complexes, the author next attempted to elucidate the reactivity of nitrogen analogues **4**, such as ene-yne-imino ethers (R^1 = OR) and an ene-yne-imine (R^1 = H) toward transition metal complexes (Scheme 2). These scenarios led us to find novel rhodium-catalyzed cyclopropanation via the formation of (2-pyrrolyl)carbenoid **5** as a nitrogen analogue of (2-furyl)carbenoid **2**. Since pyrroles are found in naturally occurring and biologically important molecules,[4,5] and a major class of heterocycles broadly used in organic synthesis and material science, this approach also provides an additional leverage to introduce a diverse array of pyrrole structure into organic molecules. Here, the author wishes to describe the new entry to pyrrole ring

construction from ene-yne-imino compounds **4** via transition metal-induced 5-*exo-dig* cyclization, followed by catalytic cyclopropanation of alkenes leading to 2-pyrrolylcyclopropanes.[6-9]

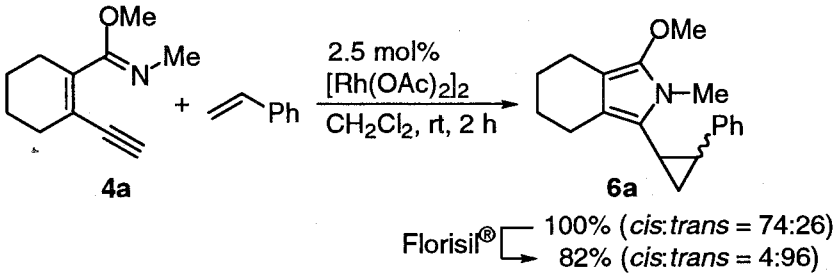
Scheme 2



Results and Discussion

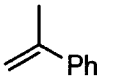
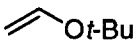
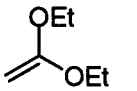
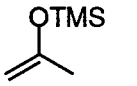
At first, when the reaction of ene-yne-imino ether **4a** with styrene was carried out in the presence of $[Rh(OAc)_2]_2$ (2.5 mol%) in CH_2Cl_2 at room temperature for 2 h, 1-phenyl-2-pyrrolylcyclopropane **6a** was obtained quantitatively as a mixture of *cis* and *trans* isomers (*cis*:*trans* = 74:26) (Scheme 3).[10] The product is somewhat labile in silica gel column

Scheme 3



chromatography which causes its decomposition, while it is isolable by short Florisil® column chromatography with some isomerization of *cis* to *trans* isomer [from 100% yield (*cis*:*trans* = 74:26) to 82% yield (*cis*:*trans* = 4:96)].[11] Next, the author examined cyclopropanation of

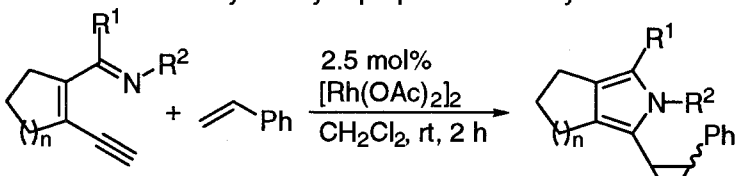
Table 1. Rh-Catalyzed Cyclopropanation of Alkenes with **4a**[a]

entry	alkene	product	yield (%)[b]	d.r.[b,c]
1		**7a**	98 (88)	59:41 (12:88)
2		**8a**	90 (47)	10:90 (25:75)
3		**9a**	100	N. A.[d]
4		**10a**	88	76:24

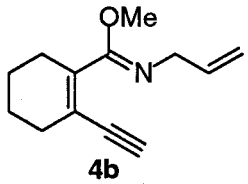
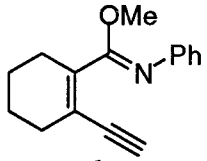
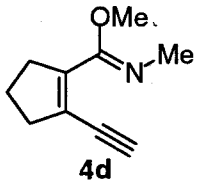
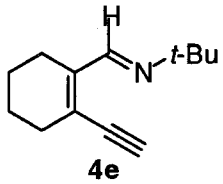
[a] Reactions of **4a** (0.20 mmol) with alkene (0.40 mmol) in CH_2Cl_2 (2.0 mL) were carried out in the presence of $[Rh(OAc)_2]_2$ (0.005 mmol) at room temperature under N_2. [b] Without purification. Values in parentheses after purification with Florisil®. [c] Configuration is not yet clear. [d] N. A. = not applicable.

several alkenes with ene-yne-imino ether **4a** in the presence of $[Rh(OAc)_2]_2$ as a catalyst. These results are summarized in Table 1. The reaction of **4a** with α-methylstyrene also gave the cyclopropanated product **7a** in 98% yield with a 59:41 diastereomeric ratio (entry 1). Reactions of **4a** with *tert*-butyl vinyl ether and ketene diethyl acetal proceeded quite smoothly to give cyclopropanes **8a** (90%, *cis*:*trans* = 10:90) and **9a** (100%), respectively (entries 2 and 3). Enol silyl ether was also reacted with **4a** to give the corresponding product **10a** in 88% yield with a 76:24 diastereomeric ratio (entry 4). After purification with Florisil® column, a

Table 2. Rh-Catalyzed Cyclopropanation of Styrene with **4**[a]



4 (n = 1 or 2) **6**

entry	substrate	product	yield (%)[b]	*cis*:*trans*[b]
1	 **4b**	**6b**	99 (88)	64:36 (3:97)
2	 **4c**	**6c**	99 (81)[c]	55:45[d] (27:73)[c,d]
3	 **4d**	**6d**	93 (47)	93:7 (45:55)
4	 **4e**	**6e**	18[c]	–[d]

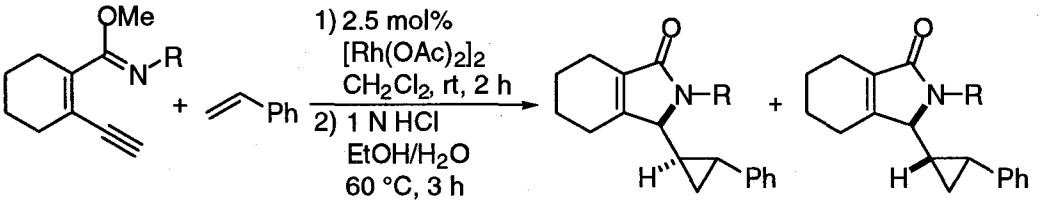
[a] Reactions of **4** (0.20 mmol) with alkene (0.40 mmol) in CH_2Cl_2 (2.0 mL) were carried out in the presence of $[Rh(OAc)_2]_2$ (0.005 mmol) at room temperature under N_2. [b] Without purification. Values in parentheses after purification with Florisil®. [c] After purification with column chromatography. [d] Configuration is not yet clear.

major component of **7a** or **8a** was a *trans* isomer (Refer to values in parentheses in Table 1).

The author then examined cyclopropanation of styrene with other ene-yne-imino ethers **4** in the presence of rhodium catalyst (Table 2). An ene-yne-imino ether **4b** bearing an allyl group on nitrogen reacted with styrene to give the cyclopropanated product **6b** in 99% yield (*cis*:*trans* = 64:36) (entry 1). The reaction of **4c** having a phenyl group proceeded quite smoothly to give the corresponding product **6c** in 99% yield (d.r. = 55:45) (entry 2). A cyclopentenyl imino ether **4d** reacted with styrene to give cyclopropane **6d** (93%, *cis*:*trans* = 93:7) (entry 3). A *trans* isomer of cyclopropanes was a major product after purification with Florisil® in each case. Cyclopropanation between an aldimine **4e** and styrene also gave the cyclopropanated product **6e**, although its yield was lower (18%) (entry 4). These results show that both ene-yne-imino ethers **4** (R^1 = OMe) and an aldimine **4e** (R^1 = H) are amenable to (2-pyrrolyl)carbenoid formation like ene-yne-ketones **1a** leading to (2-furyl)carbenoids.

Pyrrolin-2-ones as well as pyrroles are pharmacologically active materials, and more importantly pyrrolinones are synthons for γ-amino acid,[12] various alkaloids,[13] and natural products.[14] Then, the author attempted the conversion of 2-methoxypyrroles obtained by the present method to pyrrolin-2-ones. Thus, when crude products obtained by cyclopropanation reactions of styrene with **4a**, **4b**, and **4c** were directly treated with 1 N HCl solution in EtOH/H_2O at 60 °C for 3 h,[15] the corresponding pyrrolin-2-ones **11a**, **11b**, and **11c** were produced in 81%, 87%, and 96% yields, respectively (Scheme 4). All pyrrolinones obtained could be purified by column chromatography on silica gel without decomposition.

Scheme 4



4a: R = Me
4b: R = allyl
4c: R = Ph

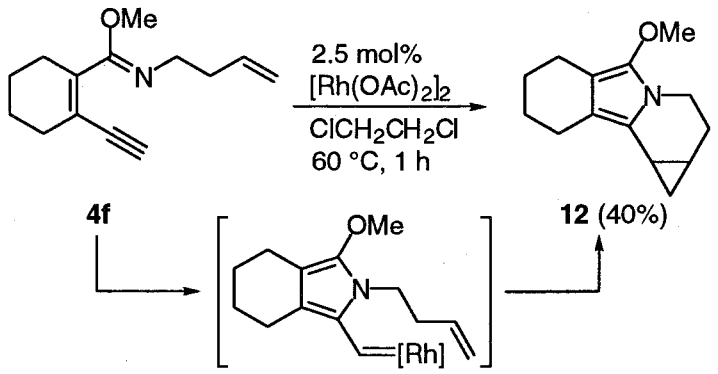
11a: 81% (d.r. = 46:54)
11b: 87% (d.r. = 50:50)
11c: 96% (—)[a]

[a] The diastereomeric ratio is not determined.

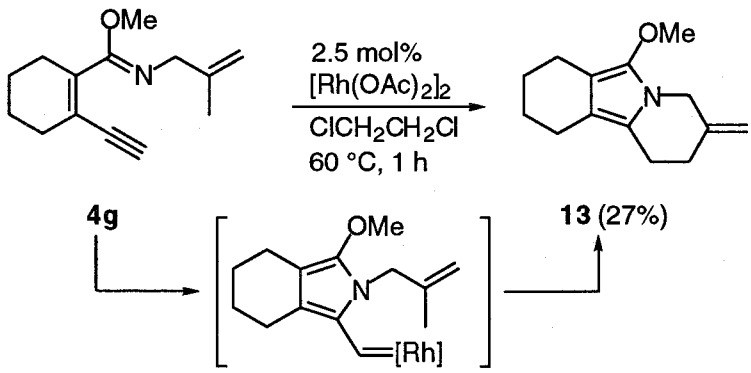
In these cases, the configurations at constructed cyclopropyl rings are only *trans*, and therefore the diastereomeric ratios of **11a** and **11b** would be attributed to the relative configuration between C-1' of cyclopropane ring and C-5 of pyrrolin-2-one.

Finally, the author decided to investigate intramolecular reactions of ene-yne-imino ether having acceptors for a carbenoid intermediate. Treatment of an ene-yne-imino ether **4f** having a homoallyl group on nitrogen in the presence of $[Rh(OAc)_2]_2$ (2.5 mol%) for 1 h afforded the tetracyclic product **12** in 40% yield, although higher reaction temperature (60 °C) and diluted conditions (0.01 M) in $ClCH_2CH_2Cl$ were required (Scheme 5). Formation of **12**

Scheme 5



Scheme 6



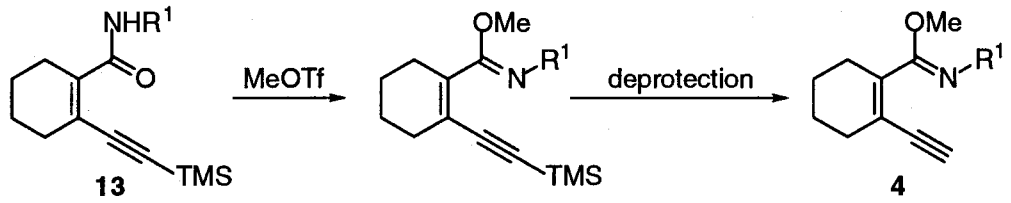
can be explained by assuming the intramolecular cyclopropanation of a (2-pyrrolyl)carbene-rhodium intermediate. Interestingly, the reaction of **4g** having a methallyl group on nitrogen under the identical conditions gave the tricyclic compound **13** rather than a cyclopropanated product (Scheme 6). The formation of this tricyclic structure can be attributed to an intramolecular C-H insertion reaction in a (2-pyrrolyl)carbene-rhodium complex.

In conclusion, the author has developed a new rhodium-catalyzed inter- and intra-molecular carbene transfer reactions on the basis of the generation of (2-pyrrolyl)carbenoids from the conjugated ene-yne-imino compounds. Both ene-yne-imino ethers (R^1 = OMe) and an aldimine (R^1 = H) are applicable to the present reaction. These studies have demonstrated the cyclization mode of ene-yne-imino compounds in 5-*exo-dig* manner like the corresponding ketone leading to (2-furyl)carbenoid, providing the new synthetic method for pyrrole and pyrrolinone structures.

Experimental

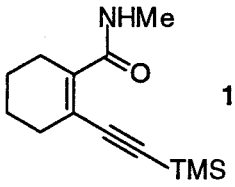
General Procedures. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates or silica gel FL 100DX Fuji Silysia Chemical NH plates. Column chromatographies were performed with Merck silica gel 60, Fuji Silysia Chemical silica gel FL 100DX, or Floridin Co. Florisil® (150-250 μm, 60-100 mesh). The NMR spectra were measured for solutions in $CDCl_3$ with Me_4Si as an internal standard or CD_2Cl_2 (^1H and ^{13}C): the following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. IR spectra were recorded on an FT-IR spectrometer. Melting points are uncorrected. High-resolution mass spectra (FAB HRMS) and low-resolution mass spectra (FAB LRMS) were obtained with JEOL JMX-SX 102A spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University. Solvents were dried by the usual methods and distilled before use.

Typical Procedure for Synthesis of Ene-yne-imino Ether 4.



To a solution of an amide **13** (5.0 mmol), which was prepared by our reported procedure,[3a,16] in dichloromethane (50 mL) was added MeOTf (0.58 mL, 5.0 mmol) under N_2, and the solution was stirred at room temperature for 96–144 h.[17] The reaction mixture was washed with 1 N NaOH solution (25 mL) and then the organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 20/1) to afford the corresponding imino ether as a pale yellow oil. To a solution of the imino ether (1.0 mmol) in MeOH (10 mL) was added K_2CO_3 (0.21 g, 1.5 mmol), and the solution was stirred at room temperature for 30 min. The reaction mixture was poured into water, and the aqueous phase was extracted with Et_2O (20 mL x 3). The combined organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 20/1) as an eluent to afford the compound **4** as a pale yellow oil.

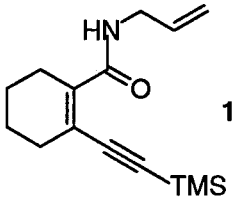
Ene-yne-carbonyl compound 13a.



13a

A white solid (85% yield); mp. 73.8–75.5 °C; IR (KBr) 699, 761, 855, 888, 1043, 1249, 1551, 1605, 1641 (C=O), 2142 (C≡C), 2927, 3322 (N-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.18 (s, 9H), 1.55–1.64 (m, 4H), 2.21–2.28 (m, 2H), 2.37–2.44 (m, 2H), 2.85 (d, J = 3.0 Hz, 3H), 7.00 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ –0.2, 21.6, 21.7, 25.8, 26.2, 31.2, 101.2, 104.5, 120.6, 140.8, 168.5. Anal. Calcd for $C_{13}H_{21}NOSi$: C, 66.33; H, 8.99; N, 5.95. Found: C, 66.24; H, 8.82; N, 5.96.

Ene-yne-carbonyl compound 13b.

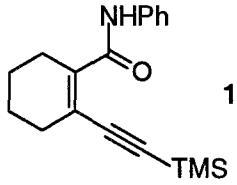


13b

A pale yellow oil (92% yield); IR (neat) 698, 760, 845, 886, 1250, 1285, 1527, 1650 (C=O), 2140 (C≡C), 2936, 3307 (N-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.18 (s, 9H), 1.59–1.63 (m, 4H), 2.26–2.30 (m, 2H), 2.40–2.44 (m, 2H), 3.97 (dd, J = 5.2, 5.7 Hz, 2H), 5.13 (dd, J = 1.5, 10.5 Hz, 1H), 5.25 (dd, J = 1.5, 16.5 Hz, 1H), 5.88 (ddd, J = 5.7, 10.5, 16.5 Hz, 1H), 7.23 (br s,

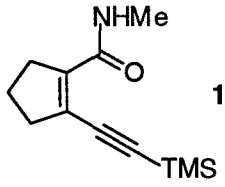
1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ –0.2, 21.7, 21.8, 26.3, 31.6, 42.1, 102.1, 104.4, 116.5, 121.1, 134.2, 140.1, 167.4. Anal. Calcd for $C_{15}H_{23}NOSi$: C, 68.91; H, 8.87; N, 5.36. Found: C, 68.51; H, 8.82; N, 5.27.

Ene-yne-carbonyl compound 13c.



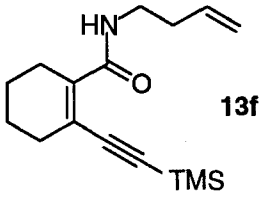
13c A pale yellow solid (91% yield); mp. 100.8–102.5 °C; IR (KBr) 696, 758, 845, 876, 910, 1248, 1321, 1442, 1548, 1599, 1649 (C=O), 2144 (C≡C), 2941, 3288 (N-H) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.15 (s, 9H), 1.63–1.68 (m, 4H), 2.33–2.38 (m, 2H), 2.47–2.53 (m, 2H), 7.10 (dd, J = 7.5, 7.5 Hz, 1H), 7.33 (dd, J = 7.5, 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 8.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ –0.2, 21.6, 21.8, 26.2, 31.7, 103.4, 103.8, 119.7, 121.9, 124.1, 128.9, 137.9, 140.7, 165.7. Anal. Calcd for $C_{18}H_{23}NOSi$: C, 72.68; H, 7.79; N, 4.71. Found: C, 72.59; H, 7.64; N, 4.61.

Ene-yne-carbonyl compound 13d.



13d A pale yellow solid (82% yield); mp. 54.1–55.2 °C; IR (KBr) 618, 760, 846, 1249, 1401, 1597, 1641 (C=O), 2141 (C≡C), 2961, 3368 (N-H) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.24 (s, 9H), 1.86 (quint, J = 7.6 Hz, 2H), 2.65 (tt, J = 7.6, 2.2 Hz, 2H), 2.76 (tt, J = 7.6, 2.2 Hz, 2H), 2.88 (d, J = 5.1 Hz, 3H), 7.29 (br s, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ –0.2, 21.8, 25.9, 33.9, 38.9, 101.2, 105.7, 125.1, 145.0, 164.6. Anal. Calcd for $C_{12}H_{19}NOSi$: C, 65.11; H, 8.65; N, 6.33. Found: C, 64.85; H, 8.64; N, 6.20.

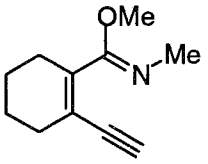
Ene-yne-carbonyl compound 13f.



13f A white solid (77% yield); mp. 46.2–47.8 °C; IR (KBr) 693, 757, 840, 890, 1129, 1248, 1290, 1520, 1638 (C=O), 2140 (C≡C), 2940, 3383 (N-H) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.18 (s, 9H), 1.57–1.61 (m, 4H), 2.23–2.28 (m, 2H), 2.29 (dt, J = 6.9, 6.9 Hz, 2H), 2.36–2.40 (m, 2H), 3.39 (dt, J = 6.0, 6.9 Hz, 2H), 5.05 (dd, J = 1.2, 10.2 Hz, 1H), 5.09 (dd, J = 1.2, 17.1 Hz, 1H), 5.79 (ddt, J = 10.2, 17.1, 6.9 Hz, 1H), 7.03 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ –0.2,

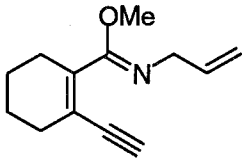
21.6, 21.8, 26.2, 31.5, 33.7, 38.8, 101.4, 104.4, 116.9, 120.6, 135.3, 140.4, 167.8. Anal. Calcd for $C_{16}H_{25}NOSi$: C, 69.76; H, 9.15; N, 5.08. Found: C, 69.78; H, 8.96; N, 5.06.

Ene-yne-imino ether 4a.



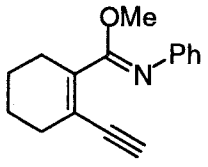
4a A pale yellow oil (72% yield for two steps); IR (neat) 694, 823, 1028, 1080, 1254, 1281, 1435, 1629, 1678 (C=N), 2094 (C≡C), 2360, 2940, 3286 (≡C-H) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 1.65–1.70 (m, 4H), 2.14–2.20 (m, 2H), 2.22–2.28 (m, 2H), 2.96 (s, 1H), 3.03 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ 21.4, 21.8, 27.2, 29.2, 36.0, 52.8, 79.2, 82.6, 119.5, 138.6, 163.0. HRMS (FAB): calcd for $C_{11}H_{16}NO$ ($M+H^+$), 178.1232; found, 178.1234.

Ene-yne-imino ether 4b.



4b A pale yellow oil (76% yield for two steps); IR (neat) 639, 915, 1032, 1075, 1197, 1254, 1280, 1358, 1434, 1627, 1674 (C=N), 2091 (C≡C), 2940, 3289 (≡C-H) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 1.62–1.68 (m, 4H), 2.12–2.18 (m, 2H), 2.20–2.28 (m, 2H), 2.96 (s, 1H), 3.74 (s, 3H), 3.90 (d, J = 5.4 Hz, 2H), 5.05 (dd, J = 1.6, 10.5 Hz, 1H), 5.20 (dd, J = 1.6, 17.0 Hz, 1H), 5.97 (ddd, J = 5.4, 10.5, 17.0 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ 21.1, 21.8, 27.5, 29.1, 51.6, 53.0, 79.6, 82.5, 114.2, 119.4, 137.2, 138.8, 162.5. HRMS (FAB): calcd for $C_{13}H_{18}NO$ ($M+H^+$), 204.1388; found, 204.1391.

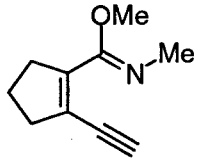
Ene-yne-imino ether 4c.



4c A pale yellow oil (46% yield for two steps); IR (neat) 640, 697, 763, 891, 1047, 1072, 1180, 1258, 1289, 1359, 1434, 1600, 1624, 1661 (C=N), 2096 (C≡C), 2371, 2941, 3286 (≡C-H) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.36–1.46 (m, 4H), 1.88–1.96 (m, 2H), 2.08–2.15 (m, 2H), 3.10 (s, 1H), 3.88 (s, 3H), 6.88 (d, J = 7.2 Hz, 2H), 7.01 (dd, J = 7.2, 7.2 Hz, 1H), 7.23 (dd, J = 7.2, 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.1, 21.4, 27.4, 29.1, 53.8, 80.2, 83.1,

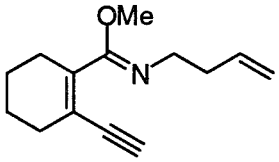
121.4, 123.0, 128.4, 128.8, 139.6, 147.6, 162.2. HRMS (FAB): calcd for $C_{16}H_{18}NO$ ($M+H^+$), 240.1388; found, 240.1378.

Ene-yne-imino ether 4d.



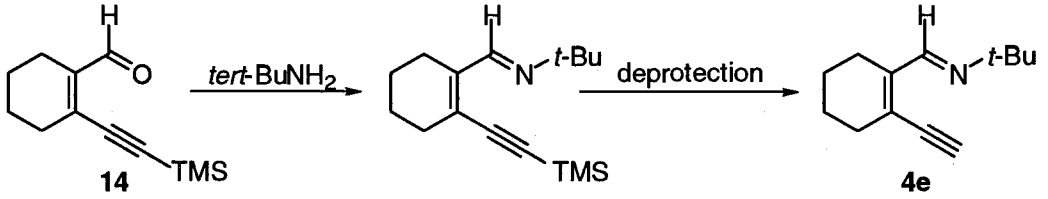
4d A pale yellow oil (40% yield for two steps); IR (neat) 668, 922, 1012, 1097, 1216, 1263, 1435, 1621, 1674 (C=N), 2096 (C≡C), 2359, 2945, 3289 (≡C-H) cm^{-1}; ^1H NMR (270 MHz, CD_2Cl_2, 25 °C) δ 1.96 (quint, J = 7.6 Hz, 2H), 2.59 (t, J = 7.6 Hz, 2H), 2.59 (t, J = 7.6 Hz, 2H), 3.04 (s, 3H), 3.23 (s, 1H), 3.63 (s, 3H); ^{13}C NMR (67.8 MHz, CD_2Cl_2, 25 °C) δ 23.1, 35.7, 36.7, 37.5, 52.7, 79.7, 83.2, 124.6, 142.0, 159.5. HRMS (FAB): calcd for $C_{10}H_{14}NO$ ($M+H^+$), 164.1075; found, 164.1073.

Ene-yne-imino ether 4f.



4f A pale yellow oil (50% yield for two steps); IR (neat) 642, 668, 913, 1038, 1083, 1197, 1252, 1280, 1434, 1640, 1674 (C=N), 2095 (C≡C), 2360, 2940, 3291 (≡C-H) cm^{-1}; ^1H NMR (270 MHz, CD_2Cl_2, 25 °C) δ 1.62–1.66 (m, 4H), 2.12–2.16 (m, 2H), 2.20–2.24 (m, 2H), 2.28 (dddt, J = 1.4, 1.4, 7.0, 7.3 Hz, 2H), 2.99 (s, 1H), 3.26 (t, J = 7.3 Hz, 2H), 3.63 (s, 3H), 4.97 (ddt, J = 0.5, 10.0, 1.4 Hz, 1H), 5.05 (ddt, J = 0.5, 17.3, 1.4 Hz, 1H), 5.86 (ddt, J = 10.0, 17.3, 7.0 Hz, 1H); ^{13}C NMR (67.8 MHz, CD_2Cl_2, 25 °C) δ 21.7, 22.2, 28.0, 29.6, 36.6, 49.2, 52.9, 79.3, 83.2, 115.3, 119.3, 137.6, 139.5, 161.6. HRMS (FAB): calcd for $C_{14}H_{20}NO$ ($M+H^+$), 218.1545; found, 218.1543.

Synthesis of ene-yne-imino compound 4e.



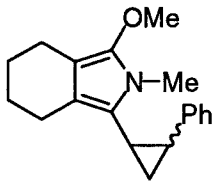
To a solution of the compound **14**[1a] (0.21 g, 1.0 mmol) in dichloromethane (10 mL) were added Na_2SO_4 (1.14 g, 8.0 mmol) and *tert*-$BuNH_2$ (0.32 mL, 3.0 mmol) under N_2, and

the solution was stirred at room temperature for 40 h. The reaction mixture was filtered, and the organic solvent was removed under reduced pressure to afford the corresponding imine as a yellow oil. To a solution of the obtained imine in MeOH (10 mL) was added K_2CO_3 (0.21 g, 1.5 mmol), and the solution was stirred at room temperature for 30 min. The reaction mixture was poured into water, and the aqueous phase was extracted with Et_2O (20 mL x 3). The combined organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure to afford the compound **4e** (0.15 g, 0.78 mmol, 78% yield) as a pale yellow oil; IR (neat) 696, 735, 1077, 1210, 1365, 1435, 1629, 1677 (C=N), 2094 (C≡C), 2360, 2925, 3286 (≡C-H) cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 1.19 (s, 9H), 1.62–1.68 (m, 4H), 2.30–2.34 (m, 4H), 3.35 (s, 1H), 8.54 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C) δ 22.1, 22.7, 24.7, 29.9, 31.7, 57.5, 82.7, 83.4, 125.9, 144.4, 156.1. HRMS (FAB): calcd for $C_{13}H_{20}N$ ($M+H^+$), 190.1596; found, 190.1595.

Typical Procedure for Rhodium-Catalyzed Cyclopropanations of Alkenes.

$[Rh(OAc)_2]_2$ (2.2 mg, 0.005 mmol) was placed in the flame dried Schlenk flask and dissolved in dry and deoxygenated CH_2Cl_2 (1.0 mL). To the solution were added an alkene (0.40 mmol) and a solution of **4** (0.20 mmol) in CH_2Cl_2 (1.0 mL) at room temperature under N_2. After the reaction was complete, the organic solvent and an excess alkene were removed under reduced pressure, and the residue was filtered with short Florisil® column or subjected to column chromatography on Fuji Silysia Chemical silica gel FL 100DX with hexane /AcOEt (v/v = 50/1) as an eluent to afford the cyclopropanes.

Cyclopropane 6a.

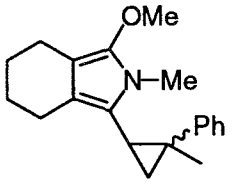


6a

A yellow oil (82% yield, *cis/trans* = 4/96); IR (neat) 698, 750, 944, 1040, 1218, 1385, 1446, 1544, 1602, 1705, 2359, 2852, 2928, 3400 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C): *cis* isomer, δ 1.26 (ddd, J = 5.6, 6.4, 6.4 Hz, 1H), 1.49 (ddd, J = 5.6, 8.8, 8.8 Hz, 1H), 1.56–1.62 (m, 4H), 1.80 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.17 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.52–2.58 (m, 4H), 2.88

(s, 3H), 3.60 (s, 3H), 6.76, (d, J = 7.6 Hz, 2H), 7.03–7.31 (m, 3H); *trans* isomer, δ 1.29 (ddd, J = 5.2, 6.0, 8.8 Hz, 1H), 1.36 (ddd, J = 5.2, 6.0, 8.8 Hz, 1H), 1.65–1.73 (m, 4H), 1.84 (ddd, J = 5.2, 5.2, 8.8 Hz, 1H), 2.07 (ddd, J = 5.2, 5.2, 8.8 Hz, 1H), 2.54–2.60 (m, 4H), 3.36 (s, 3H), 3.82 (s, 3H), 7.14–7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *cis* isomer, δ 13.7, 16.7, 20.9, 22.2, 23.0, 24.1, 24.3, 28.0, 61.0, 99.4, 116.4, 125.1, 125.6, 126.3, 127.5, 128.3, 140.1; *trans* isomer, δ 15.8, 18.7, 21.0, 22.5, 23.8, 23.9, 24.1, 28.6, 60.9, 99.2, 114.3, 118.1, 125.5, 125.6, 128.3, 140.6, 142.5. HRMS (FAB): calcd for $C_{19}H_{23}NO$ (a mixture of *cis* and *trans* isomers) (M^+), 281.1780; found, 281.1778.

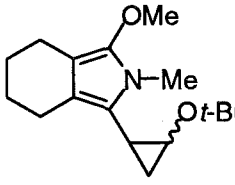
Cyclopropane 7a.



7a

A yellow oil (88% yield, d.r. = 88/12, as a mixture of *cis* and *trans* isomers); IR (neat) 700, 763, 1029, 1070, 1244, 1264, 1382, 1397, 1445, 1600, 1705, 2360, 2932, 3392 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 1.19 (s, 3H), 1.22–1.27 (m, 1H), 1.24–1.26 (m, 1H), 1.47–1.53 (m, 1H), 1.47–1.53 (m, 1H), 1.60 (s, 3H), 1.65–1.70 (m, 4H), 1.70–1.78 (m, 4H), 1.91–1.96 (m, 1H), 1.91–1.96 (m, 1H), 2.36–2.42 (m, 4H), 2.50–2.62 (m, 4H), 2.95 (s, 3H), 3.28 (s, 3H), 3.57 (s, 3H), 3.78 (s, 3H), 6.98–7.13 (m, 6H), 7.27–7.34 (m, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C) δ 20.2, 20.7, 20.9, 21.2, 21.4, 23.3, 23.4, 24.4, 24.7, 24.8, 24.8, 24.9, 25.0, 25.0, 25.5, 25.7, 28.4, 28.8, 61.1, 61.2, 99.4, 99.6, 115.3, 115.5, 115.5, 116.4, 125.2, 125.6, 126.0, 126.6, 127.5, 128.6, 140.8, 143.0, 147.3, 151.5. HRMS (FAB): calcd for $C_{20}H_{25}NO$ (a mixture of *cis* and *trans* isomers) (M^+), 295.1936; found, 295.1943.

Cyclopropane 8a.

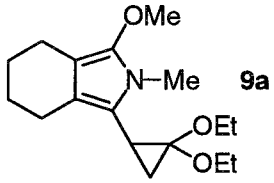


8a

A yellow oil (90% yield, *cis*/*trans* = 10/90); IR (neat) 1032, 1192, 1241, 1363, 1434, 1599, 1682, 1712, 2390, 2858, 2932, 3400 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): *cis* isomer, δ 0.76–0.80 (m, 1H), 0.98 (ddd, J = 4.0, 5.2, 8.4 Hz, 1H), 1.28 (s, 9H), 1.48–1.54 (m, 1H), 1.60–1.72 (m, 4H), 2.48–2.55 (m, 4H), 3.36 (s, 3H), 3.37–3.41 (m, 1H), 3.76 (s, 3H) ; *trans* isomer, δ 0.79 (ddd, J = 4.0, 5.6, 7.2 Hz, 1H), 1.03 (ddd, J = 5.6, 6.0, 9.6 Hz, 1H), 1.24 (s, 9H), 1.51 (ddd, J

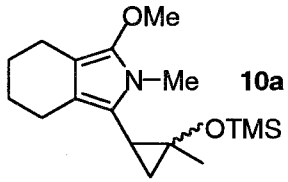
= 4.0, 4.0, 9.6 Hz, 1H), 1.60–1.72 (m, 4H), 2.48–2.55 (m, 4H), 3.37 (s, 3H), 3.38 (ddd, J = 4.0, 6.0, 7.2 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): *cis* isomer, δ 14.0, 15.8, 21.3, 22.9, 24.3, 24.6, 28.4, 28.5, 52.2, 61.2, 74.9, 99.5, 114.0, 117.0, 140.7; *trans* isomer, δ 11.2, 13.4, 21.4, 22.9, 24.5, 24.7, 28.2, 28.6, 50.0, 61.3, 74.9, 99.7, 115.3, 115.8, 140.6. HRMS (FAB): calcd for $C_{17}H_{27}NO_2$ (a mixture of *cis* and *trans* isomers) (M^+), 277.2042; found, 277.2040.

Cyclopropane 9a.



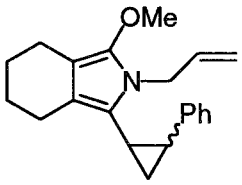
A yellow oil (100% yield); IR (neat) 694, 754, 955, 989, 1052, 1379, 1435, 1542, 1598, 1705, 2360, 2859, 2929, 3445 cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2, 25 °C) δ 1.14 (t, J = 7.3 Hz, 3H), 1.19 (dd, J = 5.1, 7.0 Hz, 1H), 1.21 (t, J = 7.3 Hz, 3H), 1.31 (dd, J = 5.1, 10.3 Hz, 1H), 1.56–1.67 (m, 4H), 1.98 (dd, J = 7.0, 10.3 Hz, 1H), 2.48–2.53 (m, 4H), 3.37 (s, 3H), 3.46–3.58 (m, 2H), 3.63–3.73 (m, 2H), 3.76 (s, 3H); ^{13}C NMR (67.8 MHz, CD_2Cl_2, 25 °C) δ 15.6, 15.6, 18.7, 21.3, 21.6, 23.0, 24.3, 24.6, 28.7, 61.3, 61.5, 62.4, 91.4, 99.9, 114.3, 115.7, 140.7. HRMS (FAB): calcd for $C_{17}H_{27}NO_3$ (M^+), 293.1991; found, 293.1992.

Cyclopropane 10a.



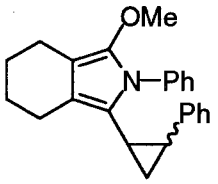
A yellow oil (88% yield, d.r. = 76/24, as a mixture of *cis* and *trans* isomers); IR (neat) 754, 845, 1035, 1050, 1253, 1379, 1435, 1597, 1707, 2360, 2859, 2935, 3400 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ –0.04 (s, 9H), 0.15 (s, 9H), 0.86 (dd, J = 5.2, 6.8 Hz, 1H), 0.93 (dd, J = 5.2, 9.6 Hz, 1H), 1.12 (dd, J = 5.2, 6.4 Hz, 1H), 1.23 (dd, J = 5.2, 9.6 Hz, 1H), 1.37–1.41 (m, 1H), 1.37–1.41 (m, 1H), 1.47 (s, 3H), 1.53 (s, 3H), 1.54–1.58 (m, 4H), 1.65–1.70 (m, 4H), 2.42–2.53 (m, 4H), 2.42–2.53 (m, 4H), 3.32 (s, 3H), 3.35 (s, 3H), 3.73 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C) δ 1.1, 1.5, 19.4, 19.7, 20.4, 21.3, 21.4, 21.8, 22.1, 23.0, 23.2, 24.4, 24.6, 24.7, 24.8, 26.7, 28.6, 28.8, 56.8, 58.0, 61.1, 61.3, 99.5, 99.6, 115.3, 116.0, 121.7, 122.5, 140.5, 146.6. HRMS (FAB): calcd for $C_{17}H_{29}NO_2Si$ (a mixture of *cis* and *trans* isomers) (M^+), 307.1968; found, 307.1967.

Cyclopropane 6b.



6b A yellow oil (88% yield, *cis/trans* = 3/97); IR (neat) 639, 915, 1032, 1075, 1197, 1254, 1280, 1434, 1627, 1673, 2860, 2940, 3289 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): *cis* isomer, δ 1.30 (ddd, J = 4.8, 6.4, 6.4 Hz, 1H), 1.47 (ddd, J = 4.8, 8.8, 8.8 Hz, 1H), 1.74–1.85 (m, 4H), 2.10 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.18 (ddd, J = 6.4, 8.8, 8.8 Hz, 1H), 2.45–2.57 (m, 4H), 3.59 (s, 3H), 3.83–3.99 (m, 2H), 4.85 (dd, J = 1.6, 17.2 Hz, 1H), 5.00 (dd, J = 1.6, 10.4 Hz, 1H), 5.68 (ddt, J = 10.4, 17.2, 5.6 Hz, 1H), 6.81 (d, J = 6.8 Hz, 2H), 7.06–7.13 (m, 3H); *trans* isomer, δ 1.27 (ddd, J = 4.8, 5.6, 8.4 Hz, 1H), 1.36 (ddd, J = 4.8, 5.6, 8.4 Hz, 1H), 1.63–1.75 (m, 4H), 1.82 (ddd, J = 4.8, 4.8, 8.4 Hz, 1H), 2.05 (ddd, J = 4.8, 4.8, 8.4 Hz, 1H), 2.52–2.65 (m, 4H), 3.79 (s, 3H), 4.37–4.39 (m, 2H), 4.77 (ddd, J = 1.6, 3.6, 16.8 Hz, 1H), 5.05 (ddd, J = 1.6, 3.6, 10.4 Hz, 1H), 5.87 (ddt, J = 10.4, 16.8, 5.2 Hz, 1H), 7.14–7.21 (m, 3H), 7.28–7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *cis* isomer, δ 13.7, 17.2, 21.3, 22.5, 23.5, 24.4, 24.7, 44.1, 61.4, 99.8, 113.8, 115.0, 117.0, 125.4, 126.9, 127.7, 136.0, 140.5, 140.6; *trans* isomer, δ 16.1, 19.3, 21.4, 23.1, 24.0, 24.3, 24.6, 44.5, 61.4, 99.7, 114.9, 115.4, 117.8, 125.8, 128.6, 128.8, 136.0, 140.7, 143.1. HRMS (FAB): calcd for $C_{21}H_{25}NO$ (a mixture of *cis* and *trans* isomers) (M^+), 307.1936; found, 307.1931.

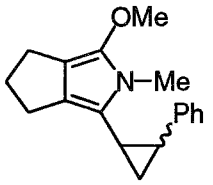
Cyclopropane 6c.



6c A white solid (81% yield, *cis/trans* = 27/73); mp. 102.8–104.2 °C; IR (KBr) 698, 754, 988, 1029, 1071, 1244, 1379, 1454, 1501, 1547, 1599, 1705, 2855, 2931, 3391 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): *cis* isomer, δ 1.21–1.24 (m, 1H), 1.33 (ddd, J = 5.2, 8.8, 8.8 Hz, 1H), 1.68–1.77 (m, 4H), 1.73–1.82 (m, 1H), 2.17–2.23 (m, 1H), 2.52–2.67 (m, 4H), 3.46 (s, 3H), 6.42–6.44 (m, 2H), 6.69–6.73, (m, 2H), 6.96–7.02 (m, 3H), 7.18–7.23 (m, 3H); *trans* isomer, δ 1.05–1.09 (m, 2H), 1.68–1.77 (m, 4H), 1.73–1.82 (m, 2H), 2.52–2.67 (m, 4H), 3.59 (s, 3H), 6.74–6.76 (m, 2H), 7.05–7.15 (m, 3H), 7.20–7.33 (m, 5H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): *cis* isomer, δ 14.4, 18.0, 21.2, 22.9, 23.4, 24.3, 24.6, 61.2, 101.0, 115.4, 118.6, 125.1,

126.1, 126.7, 127.5, 127.7, 128.2, 137.6, 140.4, 142.7; *trans* isomer, δ 16.3, 20.0, 21.3, 23.0, 24.3, 24.6, 25.0, 61.3, 101.0, 116.2, 119.5, 125.5, 125.8, 126.7, 127.9, 128.1, 128.8, 137.9, 140.9, 142.6. HRMS (FAB): calcd for $C_{24}H_{25}NO$ (a mixture of *cis* and *trans* isomers) (M^+), 343.1936; found, 343.1932.

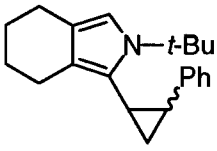
Cyclopropane 6d.



6d

A yellow oil (93% yield, *cis/trans* = 45/55); IR (neat) 698, 799, 1042, 1074, 1261, 1354, 1403, 1461, 1573, 1619, 1715, 2850, 2946, 3400 cm^{-1}; ^1H NMR (270 MHz, CD_2Cl_2, 25 °C): *cis* isomer, δ 1.27 (ddd, J = 5.1, 5.9, 5.9 Hz, 1H), 1.39 (ddd, J = 5.1, 8.6, 8.6 Hz, 1H), 2.09–2.28 (m, 4H), 2.49–2.56 (m, 2H), 2.63 (t, J = 7.3 Hz, 2H), 2.69 (s, 3H), 3.70 (s, 3H), 6.87 (dd, J = 1.6, 7.6 Hz, 2H), 7.04–7.12 (m, 3H); *trans* isomer, δ 1.22–1.36 (m, 2H), 1.84 (ddd, J = 5.4, 8.9, 8.9 Hz, 1H), 1.99 (ddd, J = 5.4, 8.9, 8.9 Hz, 1H), 2.09–2.28 (m, 2H), 2.44–2.56 (m, 2H), 2.63 (t, J = 7.3 Hz, 2H), 3.29 (s, 3H), 3.84 (s, 3H), 7.06–7.19 (m, 3H), 7.25–7.31 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$, 25 °C): *cis* isomer, δ 11.7, 17.9, 23.4, 25.6, 25.8, 28.7, 32.1, 58.6, 103.7, 111.3, 125.4, 127.2, 127.3, 127.7, 138.3, 140.0; *trans* isomer, δ 15.6, 20.1, 24.8, 25.4, 25.5, 29.1, 32.0, 58.7, 104.0, 115.6, 124.4, 125.7, 125.8, 128.5, 138.5, 143.0. HRMS (FAB): calcd for $C_{18}H_{21}NO$ (a mixture of *cis* and *trans* isomers) (M^+), 267.1623; found, 267.1620.

Cyclopropane 6e.



6e

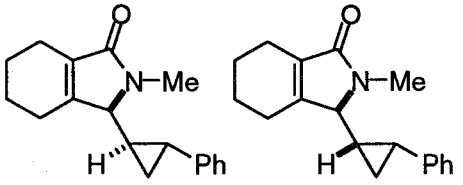
A yellow oil (18% yield, as a mixture of *cis* and *trans* isomers); IR (neat) 696, 735, 772, 1077, 1187, 1224, 1300, 1365, 1459, 1497, 1677, 2851, 2926, 2977, 3245, 3299 cm^{-1}; ^1H NMR (270 MHz, CD_2Cl_2, 25 °C) δ 1.32 (s, 9H), 1.55 (s, 9H), 1.52–1.62 (m, 8H), 1.62–1.70 (m, 4H), 1.77–1.96 (m, 2H), 2.13 (ddd, J = 5.9, 8.6, 8.6 Hz, 1H), 2.23 (ddd, J = 5.9, 5.9, 8.6 Hz, 1H), 2.40–2.61 (m, 8H), 6.44 (s, 1H), 6.51 (s, 1H), 6.82–6.85 (m, 3H), 7.00–7.19 (m, 5H), 7.26–7.31 (m, 2H); ^{13}C NMR (67.8 MHz, CD_2Cl_2, 25 °C) δ 17.0, 19.2, 22.1, 22.6, 22.7, 23.1, 24.5, 24.5, 24.7, 25.1, 25.2, 25.2, 25.4, 26.2, 31.5, 31.6, 56.2, 56.3, 114.3, 115.2, 117.2, 120.9, 121.9, 122.2,

125.3, 125.3, 125.7, 125.8, 127.1, 127.8, 128.6, 129.8, 141.3, 143.1. HRMS (FAB): calcd for $C_{21}H_{27}N$ (a mixture of *cis* and *trans* isomers) (M^+), 293.2144; found, 293.2144.

Synthesis of Pyrrolin-2-one Derivatives 11.

$[Rh(OAc)_2]_2$ (2.2 mg, 0.005 mmol) was placed in the flame dried Schlenk flask and dissolved in dry and deoxygenated CH_2Cl_2 (1.0 mL). To this solution were added an alkene (0.40 mmol) and a solution of **4** (0.20 mmol) in CH_2Cl_2 (1.0 mL) at room temperature under N_2. After the reaction was complete, the organic solvent and excess alkene were removed under reduced pressure to afford the compound **6** as a yellow oil. To a solution of the crude compound **6** in EtOH/H_2O was added 1 N HCl solution (3 drops), and the solution was stirred at 60 °C for 3 h. The reaction mixture was poured into water and the aqueous phase was extracted with EtOAc (20 mL x 3). The combined organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with CH_2Cl_2/AcOEt (v/v = 10/1) as an eluent to afford the compound **11** as a pale yellow oil.

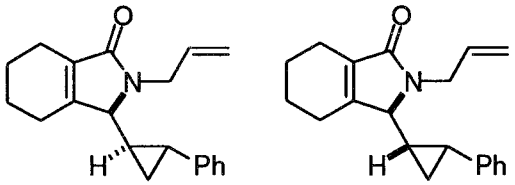
Pyrrolin-2-one derivative 11a.



11a

A pale yellow oil (81% yield, as a mixture of two diastereoisomers); IR (neat) 698, 751, 1036, 1256, 1399, 1428, 1680 (C=O), 2930, 3364 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.81–0.89 (m, 2H), 1.02 (ddd, J = 5.2, 5.2, 8.8 Hz, 1H), 1.06–1.13 (m, 2H), 1.18 (ddd, J = 5.2, 5.2, 8.8 Hz, 1H), 1.59–1.77 (m, 8H), 1.87 (ddd, J = 5.2, 5.2, 8.8 Hz, 1H), 1.95 (ddd, J = 5.2, 5.2, 8.8 Hz, 1H), 2.15–2.34 (m, 8H), 3.01 (s, 3H), 3.04–3.07 (m, 2H), 3.07 (s, 3H), 7.04–7.06 (m, 4H), 7.15–7.20 (m, 2H), 7.24–7.30 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 11.5, 14.5, 18.8, 20.2, 20.3, 21.7, 21.8, 21.9, 22.2, 22.3, 23.5, 23.6, 23.7, 23.9, 27.4, 27.4, 68.9, 68.9, 125.5, 125.5, 125.8, 125.9, 128.4, 128.4, 131.3, 131.4, 141.1, 141.2, 152.8, 152.9, 171.0, 171.0. HRMS (FAB): calcd for $C_{18}H_{22}NO$ (a mixture of *cis* and *trans* isomers) ($M+H^+$), 268.1701; found, 268.1696.

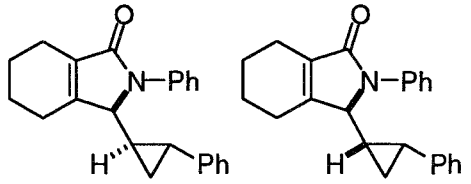
Pyrrolin-2-one derivative 11b.



11b

A pale yellow oil (87% yield, as a mixture of two diastereoisomers); IR (neat) 698, 752, 1409, 1434, 1682 (C=O), 2928, 3417 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.81–0.90 (m, 2H), 0.98–1.07 (m, 2H), 1.07–1.16 (m, 2H), 1.58–1.80 (m, 8H), 1.86 (ddd, J = 5.2, 5.2, 8.8 Hz, 1H), 1.92 (ddd, J = 5.2, 5.2, 8.8 Hz, 1H), 2.15–2.30 (m, 8H), 3.20 (d, J = 9.2 Hz, 1H), 3.22 (d, J = 9.2 Hz, 1H), 3.65 (dd, J = 8.0, 16.0 Hz, 1H), 3.88 (dd, J = 8.0, 16.0 Hz, 1H), 4.49–4.62 (m, 2H), 5.12–5.18 (m, 4H), 5.68–5.83 (m, 2H), 7.02–7.05 (m, 4H), 7.14–7.20 (m, 2H), 7.25–7.29 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 12.1, 14.7, 19.3, 20.3, 20.3, 21.5, 21.8, 22.0, 22.3, 22.3, 23.7, 23.8, 23.8, 23.8, 42.3, 42.6, 66.2, 66.4, 116.5, 116.6, 125.4, 125.5, 125.9, 125.9, 128.4, 128.4, 131.0, 131.2, 134.4, 134.4, 141.3, 141.3, 153.5, 153.6, 170.7, 170.7. HRMS (FAB): calcd for $C_{20}H_{24}NO$ (a mixture of *cis* and *trans* isomers) ($M+H^+$), 294.1858; found, 294.1854.

Pyrrolin-2-one derivative 11c.



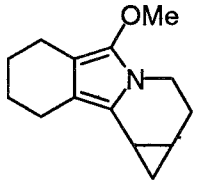
11c

A pale yellow oil (96% yield, as a mixture of two diastereoisomers); IR (neat) 698, 753, 1090, 1409, 1434, 1682 (C=O), 2929, 3399 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.72–0.92 (m, 3H), 0.95-1.18 (m, 3H), 1.53–1.89 (m, 9H), 1.92–2.04 (m, 1H), 2.13–2.37 (m, 8H), 3.88–3.96 (m, 2H), 6.65–6.73 (m, 4H), 7.06–7.20 (m, 8H), 7.22–7.47 (m, 8H); ^{13}C NMR (67.8 MHz, $CDCl_3$, 25 °C) δ 6.8, 8.4, 19.0, 20.0, 20.4, 20.5, 21.8, 21.9, 22.3, 22.5, 22.8, 23.2, 23.8, 24.6, 61.6, 63.2, 125.6, 125.7, 125.9, 126.0, 126.0, 126.2, 127.7, 127.9, 128.0, 128.2, 128.6, 128.8, 130.6, 131.4, 137.0, 137.1, 137.9, 137.9, 154.7, 154.7, 170.2, 170.2. HRMS (FAB): calcd for $C_{23}H_{24}NO$ (a mixture of *cis* and *trans* isomers) ($M+H^+$), 330.1858; found, 330.1855.

Typical Procedure of Rhodium-Catalyzed Intramolecular Carbene Transfer Reactions.

$[Rh(OAc)_2]_2$ (2.2 mg, 0.005 mmol) was placed in the flame dried Schlenk flask and dissolved in dry and deoxygenated $ClCH_2CH_2Cl$ (15 mL) at room temperature under N_2. To this solution was added a solution of **4f** or **4g** (0.20 mmol) in $ClCH_2CH_2Cl$ (5.0 mL) at 60 °C for 1 h. After the reaction was complete, the organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on Fuji Silysia Chemical silica gel FL 100DX with hexane /AcOEt (v/v = 50/1) as an eluent to afford the compound **12** or **13** as a yellow oil, respectively;

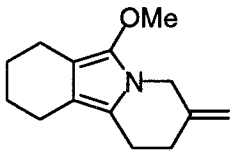
Tetracyclic Compound 12.



12

A yellow oil (40% yield); IR (neat) 740, 829, 917, 995, 1057, 1227, 1335, 1386, 1445, 1585, 1710, 2853, 2927, 3400 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 0.61 (ddd, J = 4.8, 4.8, 5.2 Hz, 1H), 0.80 (ddd, J = 5.2, 8.4, 8.4 Hz, 1H), 1.38–1.45 (m, 1H), 1.60–1.70 (m, 4H), 1.59 (ddd, J = 4.8, 8.4, 8.4 Hz, 1H), 1.92–2.07 (m, 2H), 2.45–2.55 (m, 4H), 3.17 (ddd, J = 4.8, 12.4, 12.4 Hz, 1H), 3.72 (s, 3H), 3.80–3.85 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C) δ 8.3, 8.5, 11.1, 21.2, 21.6, 22.6, 24.6, 24.6, 35.8, 61.5, 99.7, 111.5, 115.9, 139.1. HRMS (FAB): calcd for $C_{14}H_{20}NO$ ($M+H^+$), 218.1545; found, 218.1543.

Tricyclic Compound 13.



13

A yellow oil (27% yield); IR (neat) 715, 894, 1039, 1067, 1240, 1341, 1378, 1406, 1444, 1542, 1601, 2851, 2924, 3410 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 1.60–1.70 (m, 8H), 2.15–2.25 (m, 2H), 2.45–2.55 (m, 2H), 3.70 (s, 3H), 4.00 (s, 2H), 4.17 (br s, 1H), 4.70 (br s, 1H); ^{13}C NMR (75.5 MHz, CD_2Cl_2, 25 °C) δ 20.2, 20.8, 21.3, 21.9, 24.5, 24.7, 46.9, 61.6, 99.6, 109.0, 114.1, 115.2, 141.3, 143.8. HRMS (FAB): calcd for $C_{14}H_{20}NO$ ($M+H^+$), 218.1545; found, 218.1545.

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(10) Purity of **6a** (>90%) was confirmed by ^{1}H and ^{13}C NMR spectra.

(11) Florisil® (150-250 μm, 60-100 mesh) was purchased from Wako Chemicals USA, Inc. This isomerism is presumably attributed to the basic nature of Florisil®.

(12) (a) Jouin, P.; Castro, B. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1177. (b) Ma, D.; Ma, J.; Ding, W.; Dai, L. *Tetrahedron: Asymmetry* **1996**, *7*, 2365.

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Chapter 6

Chromium- and Rhodium-Catalyzed Insertion Reactions Using Ene-Yne-Carbonyl Compounds as Precursors of (2-Furyl)carbenoids

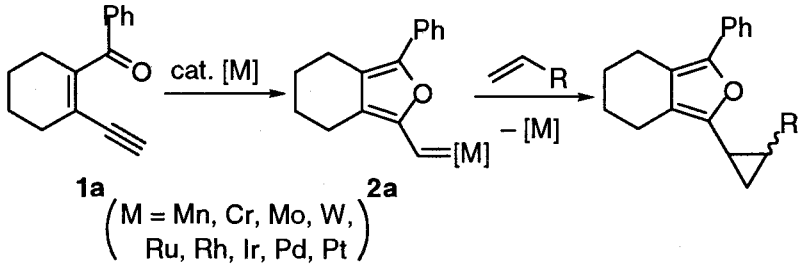
Abstract

The reaction of methanol with conjugate ene-yne-ketones in the presence of a catalytic amount of $Cr(CO)_5(THF)$ gives bicyclic acetals in good yields. The key intermediates of this insertion reaction are (2-furyl)carbene compelxes generated by a nucleophilic attack of a carbonyl oxygen to an internal alkyne carbon of ene-yne-ketones. In contrast, $[Rh(OAc)_2]_2$-catalyzed insertion reaction of methanol with ene-yne-ketones selectively affords furfuryl ethers in good yields. These selectivities may be caused by the difference of carbenoid characters between chromium and rhodium intermediates.

Introduction

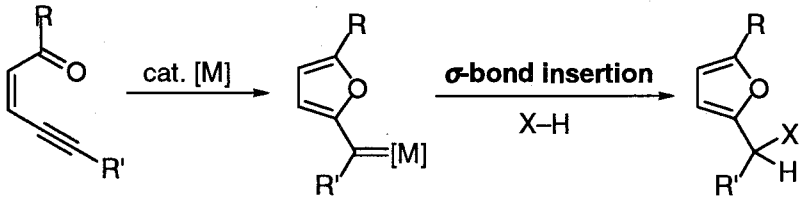
The reactions of transient electrophilic carbenoids with either activated or unactivated σ-bond-containing reagents were found to serve as one of the most powerful σ-bond construction reations.[1] Electrophilic carbenoids generated *in situ* from α-diazocarbonyl compounds and transition metal complexes have been known as effective intermediates in various inter- or intramolecular σ-bond insertion reactions.[2] On the other hand, much attention has been paid to activation of alkynes with transition metal complexes as a new entry to generate carbenoid species.[3-8] The author has already demonstrated the *in situ* generation of furylcarbenoids from ene-yne-ketones and their application to catalytic cyclopropanation reaction (Scheme 1, see also Chapters 3 and 4). Further investigation based

Scheme 1



on the generation of (2-furyl)carbenoid species led him to find the chromium- and rhodium-catalyzed insertion reaction with methanol and triethylsilane as carbenoid acceptors (Scheme 2).

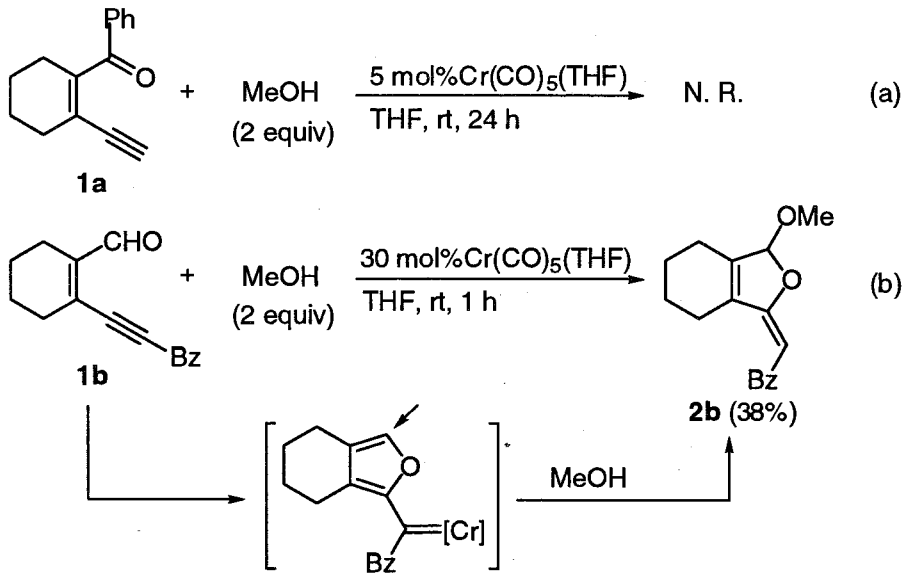
Scheme 2



Results and Discussion

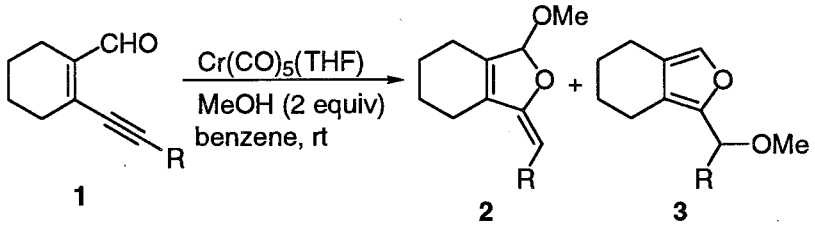
At first, the reaction of **1a** with MeOH (2 equiv) in THF was carried out in the presence of 5 mol% of $Cr(CO)_5(THF)$ at room temperature (Scheme 3a). The color of the reaction

Scheme 3



mixture gradually changed from yellowish brown to deep blue indicating the generation of (2-furyl)carbene-chromium complex.[9] After 24 h, however, no desired products were obtained. On the other hand, the reaction of MeOH with ene-yne-carbonyl compound **1b** having an electron-withdrawing benzoyl group, which could be expected to enhance the electrophilicity of intermediary carbenoid species to an O-H bond, afforded the insertion product **2b** in 38% yield (Scheme 3b).[10] When other solvents to be used for the chromium-mediated insertion reaction were examined, benzene was revealed to be the solvent of choice. Thus, reactions of ene-yne-carbonyl compounds **1b** and **1c** having an acyl group at an yne-terminus in benzene were next exmained, and these results are shown in Table 1. When the reaction of **1b** with MeOH in benzene was carried out in the presence of $Cr(CO)_5(THF)$ (120 mol%) at room temperature for 0.5 h, the insertion product **2b** was obtained in 72% yield (entry 1). The same product was also obtained in nearly the same yield even with 30 mol% of

Table 1. Cr-Mediated O-H bond insertion reaction[a,b]

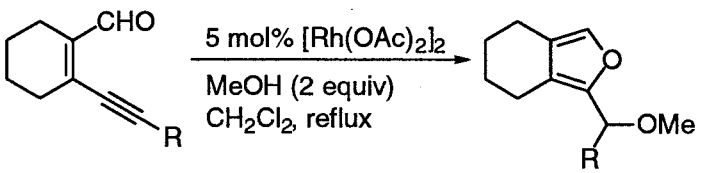


entry	[Cr] (mol%)	R in **1**	time (h)	**2** (%)	**3** (%)
1	120	Bz (**1b**)	0.5	72 (**2b**)	0
2	30	Bz (**1b**)	1.5	69 (**2b**)	0
3	120	Ac (**1c**)	2	8 (**2c**)	55 (**3c**)

[a] Reactions were carried out with **1** (0.25 mmol) under Ar.
[b] The solution of $Cr(CO)_5(L)$ was prepared by irradiating a benzene (10 mL) solution of $Cr(CO)_6$ (66 mg, 0.30 mmol) and THF (24 μL, 0.30 mmol) for 4 h with a high-pressure Hg lamp (450 W).

$Cr(CO)_5(THF)$ (entry 2). When ene-yne-carbonyl compound **1c** having an acetyl group at the terminal position of alkyne was treated with 120 mol% of $Cr(CO)_5(THF)$, the corresponding product **2c** was obtained only in 8% yield, and instead **3c** as a MeOH insertion product at a carbene carbon was obtained in 55% yield. Different selectivity between reactions of **1b** and **1c** may be probably due to the sterical factor. Next, the reaction of **1b** with MeOH in the presence of $[Rh(OAc)_2]_2$ catalyst, which efficiently catalyzes the cyclopropanation of ene-yne-keto and -imino compounds, was examined.[9] Results are shown in Scheme 4. Ene-yne-carbonyl compounds **1b** and **1c** afforded the insertion products **3b** (65% yield) and **3c** (74% yield), respectively. The reaction of ene-yne-carbonyl compound **1d** having a methoxycarbonyl group with MeOH was quite complex and many

Scheme 4

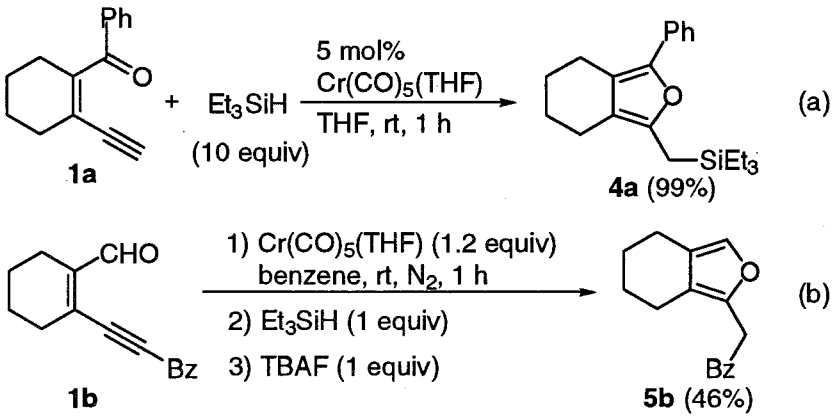


1b (R = Bz) **3b** 65% (8 h)
1c (R = Ac) **3c** 74% (5 h)
1d (R = CO_2Me) **3d** 20% (6 h)

unidentified products were formed reducing the yield of product **3d** to 20%. The fact that the rhodium-catalyzed insertion reaction of MeOH with ene-yne-carbonyl compounds **1** proceeded at the carbene carbon may point out that the rhodium carbenoids would be more electrophilic than the chromium analogues.

Next, the author examined the Si-H insertion reaction of a (2-furyl)carbenoid intermediate. When the reaction of **1a** with triethylsilane was carried out in the presence of a catalytic amount of $Cr(CO)_5(THF)$, the insertion product **4a** was obtained in 99% yield (Scheme 5a). On the other hand, the reaction of **1b** with 1.2 equiv of chromium complex was

Scheme 5



quite complex because of the decomposition of the corresponding Si-H insertion product **4b**.[11] Thus, when we treated the resulting reaction mixture with tetra-*n*-butylammonium fluoride (TBAF) after the reaction was complete, **5b** as a protodesilylated product was obtained in 46% yield (Scheme 5b).

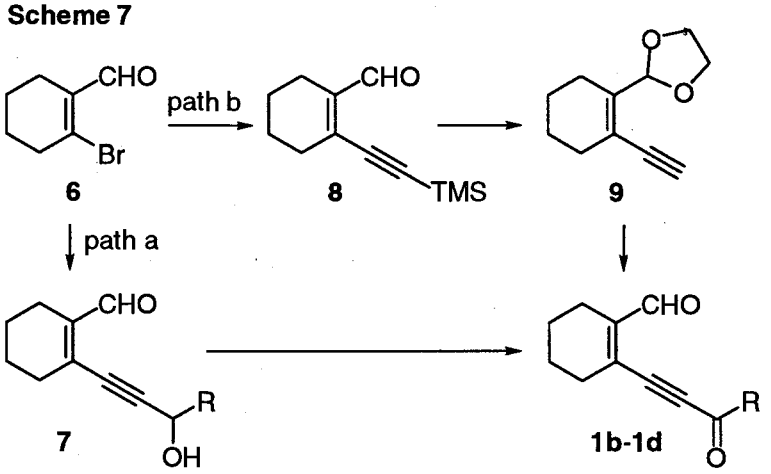
Experimental

General Procedure. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. Benzene was distilled from calcium hydride under nitrogen. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies were performed with Merck silica gel 60. The NMR spectra were measured for solutions in $CDCl_3$ or d_8-THF with Me_4Si as an internal standard (^1H and ^{13}C): the following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. IR spectra were recorded with an FT-IR spectrometer. Melting points are uncorrected. Elemental analyses were performed at Microanalytical Center of Kyoto University.

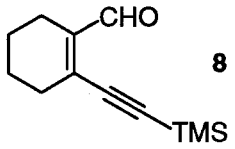
Synthesis of Substrates.

The substrates were prepared by following procedures (Scheme 7). 2-Bromo-1-cyclohexenecarboxaldehyde **(6)**[3b,12,13] and the substrate **1a**[3b] were prepared by the reported methods.

Scheme 7



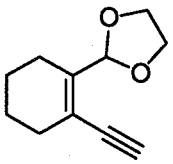
Ene-yne-carbonyl compound 8.



To a solution of trimethylsilylacetylene (2.4 mL, 18 mmol), **6** (2.8 g, 15 mmol), and triethylamine (10 mL, 75 mmol) in benzene (15 mL)

were added CuI (0.21 g, 7.5 mol%) and $Pd(PPh_3)_4$ (0.43 g, 2.5 mol%) at 0 °C under N_2. After stirring at room temperature for 10 min, the resulting black solution was washed with saturated aqueous NH_4Cl solution (30 mL) and the aqueous phase was extracted with AcOEt (10 mL x 3). The organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 20/1) as an eluent to afford ene-yne-carbonyl compound **8** (3.0 g, 15 mmol, 98% yield) as a pale yellow oil; IR (neat) 675, 760, 844, 878, 894, 1146, 1226, 1250, 1363, 1599, 1677 (C=O), 2140 (C≡C), 2834, 2862, 2939 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.19 (s, 9H), 1.60–1.63 (m, 4H), 2.22–2.24 (m, 2H), 2.35–2.38 (m, 2H), 10.1 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 0.4, 21.6, 22.4, 22.6, 32.8, 102.1, 105.3, 140.4, 144.2, 193.7. HRMS (FAB): calcd for $C_{12}H_{19}OSi$ ($M+H^+$), 207.1205; found, 207.1207.

Ene-yne compound 9.

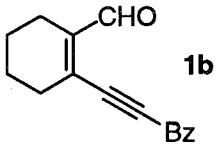


9

To a solution of **8** (3.0 g, 15 mmol) and ethylene glycol (2.5 mL, 45 mmol) in benzene (10 mL) was added *p*-toluenesulfonic acid monohydrate (43 mg, 5 mol%) at room temperature. After stirring for 2 h at reflux temperature using Dean-Stark apparatus, the solution was washed with saturated aqueous $NaHCO_3$ solution and the aqueous phase was extracted with Et_2O (10 mL x 3). The combined organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure. To a solution of the residue in DMSO (20 mL) was added KF (1.28 g, 22 mmol) at room temperature. After stirring for 1 h, the resulting brown solution was poured into water/Et_2O mixture (50 mL, v/v = 1/1). The aqueous phase was extracted with Et_2O (10 mL x 3) and the combined organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 15/1) to afford ene-yne compound **9** (1.8 g, 10 mmol, 67% yield for 2 steps) as a white solid (gradually decomposed at room temperature); mp. 32.0–32.3 °C; IR (KBr) 659, 949, 987, 1070, 1075, 1101, 1142, 1227, 1387, 2080 (C≡C),

2892, 2935, 3258 (≡C-H) cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 1.58–1.65 (m, 4H), 2.08–2.09 (m, 2H), 2.17–2.19 (m, 2H), 3.15 (s, 1H), 3.84–4.00 (m, 4H), 5.79 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C) δ 21.9, 22.1, 22.5, 30.8, 65.9, 81.2, 82.2, 102.9, 120.9, 143.1. HRMS (FAB): calcd for $C_{11}H_{15}O_2$ ($M+H^+$), 179.1072; found, 179.1074.

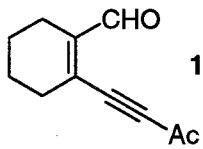
Ene-yne-carbonyl compound 1b (path a).



1b

To a solution of 1-phenyl-2-propyn-1-ol (2.5 mL, 10 mmol), **6** (2.5 g, 13 mmol), and triethylamine (7.0 mL, 50 mmol) in benzene (10 mL) were added CuI (0.15 g, 7.5 mol%) and $Pd(PPh_3)_4$ (0.29 g, 2.5 mol%) at 0 °C under N_2. After stirring at room temperature for 1 h, the resulting black solution was washed with saturated aqueous NH_4Cl solution (20 mL) and the aqueous phase was extracted with AcOEt (20 mL x 3). The organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to short column chromatography on SiO_2 with hexane/AcOEt (v/v = 40/1) as an eluent to afford crude propargylic alcohol as a pale brown oil. This crude alcohol was oxidized by Swern method to give ene-yne-carbonyl compound **1b** (0.8 g, 3.4 mmol, 34% yield for 2 steps) as a colorless solid; mp. 82.8–84.6 °C; IR (KBr) 638, 707, 993, 1003, 1159, 1219, 1265, 1283, 1311, 1448, 1578, 1595, 1639 (C=O), 1675 (C=O), 2184 (C≡C), 2859, 2913, 2936, 2958 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.70–1.79 (m, 4H), 2.33–2.39 (m, 2H), 2.54–2.60 (m, 2H), 7.52 (dd, J = 7.2, 7.2 Hz, 2H), 7.65 (dd, J = 7.2, 7.2 Hz, 1H), 8.12 (d, J = 7.2 Hz, 2H), 10.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 20.7, 21.7, 22.4, 31.6, 88.2, 94.1, 128.7, 129.3, 134.4, 136.3, 136.4, 147.3, 177.1, 191.2. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.36; H, 5.92.

Ene-yne-carbonyl compound 1c (path a).

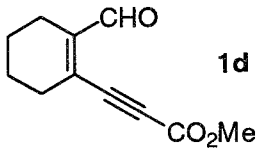


1c

Ene-yne-carbonyl compound **1c** was obtained by the same procedure for the synthesis of **1b**; A yellow oil (34% yield for 2 steps); IR (neat) 608, 706, 1214, 1246, 1364, 1428, 1680 (C=O), 2183 (C≡C), 2860, 2934 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.65–1.71 (m, 4H), 2.28–2.35 (m, 2H), 2.42

(s, 3H), 2.45–2.50 (m, 2H), 10.15 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.7, 21.6, 22.4, 31.4, 32.8, 85.6, 95.2, 136.0, 147.1, 183.5, 191.2. HRMS (FAB): calcd for $C_{11}H_{13}O_2$ ($M+H^+$), 177.0916; found, 177.0916.

Ene-yne-carbonyl compound 1d (path b).

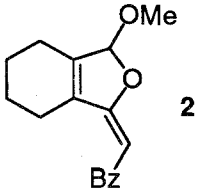


To a solution of *i*-Pr_2NH (0.64 mL, 4.5 mmol) in THF (50 mL) was slowly added *n*-BuLi (2.8 mL, 4.5 mmol, 1.6 M in hexane) at -78 °C under N_2. After stirring at -78 °C for 10 min, a THF (5 mL) solution of **9** (0.53 g, 3.0 mmol) was added dropwise to this pale yellow solution at -78 °C. After stirring for 30 min at -78 °C, to this solution was added dropwise chloroformate (0.70 mL, 9.0 mmol) at -78 °C, and then the resulting solution was gradually warmed up to room temperature. After an additional stirring for 30 min, the solution was washed with saturated aqueous NH_4Cl solution (50 mL), and the aqueous phase was extracted with AcOEt (20 mL x 3). The combined organic phase was dried over $MgSO_4$. The organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 10/1) as an eluent to afford ene-yne-carbonyl compound **1d** (0.41 g, 2.1 mmol, 71% yield) as a colorless oil; IR (neat) 733, 747, 1147, 1221, 1261, 1281, 1433, 1681 (C=O), 1716 (C=O), 2210 (C≡C), 2863, 2943 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 1.63–1.75 (m, 4H), 2.29–2.33 (m, 2H), 2.42–2.45 (m, 2H), 3.82 (s, 3H), 10.13 (s, 1H); ^{13}C NMR (67.5 MHz, $CDCl_3$, 25 °C) δ 20.7, 21.6, 22.3, 31.2, 53.0, 82.2, 87.9, 135.5, 147.7, 153.5, 191.2. HRMS (FAB): calcd for $C_{11}H_{13}O_3$ ($M+H^+$), 193.0865; found, 193.0865.

Typical Procedure for Insertion Reaction of (2-Furyl)carbene Complexes. A solution of $Cr(CO)_6$ (66 mg, 0.30 mmol) and THF (24 μL, 0.30 mmol) in benzene (10 mL) in flame-dried Schlenk tube under N_2 was irradiated by Hg lamp (450 W, 350 nm) at room temperature for 2 h. To this yellow solution was added substrate (0.25 mmol) and reagents at room temperature. The color of the reaction mixture gradually changed from deep blue to yellowish brown as the reaction proceeded. The solvent was removed under reduced

pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt as an eluent.

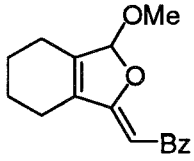
Cyclic acetal 2b.



2b

A white solid (72% yield); mp. 68.3-69.8 °C; IR (KBr) 706, 937, 965, 1069, 1081, 1207, 1391, 1573, 1591, 1651 (C=O), 2933 cm^{-1}; ^1H NMR (400 MHz, C_4D_8O, 25 °C) δ 1.60-1.75 (m, 4H), 2.20-2.28 (m, 2H), 2.47-2.60 (m, 1H), 2.62-2.75 (m, 1H), 3.39 (s, 3H), 5.75 (s, 1H), 6.47 (s, 1H), 7.41 (dd, J = 7.2, 7.2 Hz, 2H), 7.47 (dd, J = 7.2, 7.2 Hz, 2H), 7.94 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, C_4D_8O, 25 °C) δ 21.3, 22.5, 22.6, 24.0, 53.8, 96.6, 107.9, 127.8, 128.0, 131.5, 133.8, 139.7, 149.3, 170.4, 187.3. HRMS (FAB) calcd for $C_{17}H_{19}O_3$ ($M+H^+$): 271.1334; found, 271.1327.

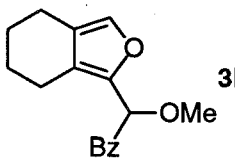
Cyclic acetal 2b'.



2b'

A white solid; mp. 82.7-83.4 °C; IR (KBr) 629, 705, 715, 772, 854, 935, 1004, 1218, 1317, 1569, 1600, 1650 (C=O), 2860, 2930 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.63-1.78 (m, 4H), 2.20-2.25 (m, 4H), 3.55 (s, 3H), 5.91 (s, 1H), 5.94 (s, 1H), 7.41-7.52 (m, 3H), 7.92 (d, J = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, C_4D_8O, 25 °C) δ 20.2, 21.5, 21.6, 22.0, 55.9, 92.0, 111.1, 127.8, 128.2, 131.6, 134.7, 139.9, 146.9, 168.5, 189.1.

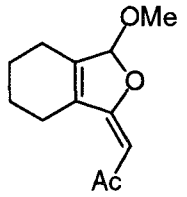
Furfuryl methyl ether 3b.



3b

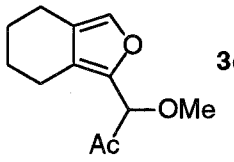
A colorless oil (65% yield); IR (neat) 596, 620, 690, 753, 852, 938, 1027, 1094, 1384, 1446, 1592, 1650, 1694 (C=O), 2852, 2928, 3411 cm^{-1}; ^1H NMR (300 MHz, C_4D_8O, 25 °C) δ 1.48-1.54 (m, 4H), 2.24-2.39 (m, 4H), 3.21 (s, 3H), 5.47 (s, 1H), 6.47 (s, 1H), 7.02 (s, 1H), 7.27 (dd, J = 7.2, 7.2 Hz, 2H), 7.38 (dd, J = 7.2, 7.2 Hz, 2H), 7.85 (d, J = 7.2 Hz, 1H); ^{13}C NMR (75 MHz, C_4D_8O, 25 °C) δ 20.4, 20.7, 23.5, 23.6, 56.4, 79.6, 122.0, 122.9, 128.6, 129.0, 133.1, 136.2, 138.0, 143.4, 193.2.

Cyclic acetal 2c.



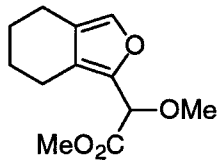
2c A colorless oil (8% yield); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.69-1.74 (m, 4H), 2.10-2.18 (m, 2H), 2.24-2.32 (m, 2H), 2.43 (s, 3H), 3.51 (s, 3H), 5.11 (s, 1H), 5.88 (s, 1H).

Furfuryl methyl ether 3c.



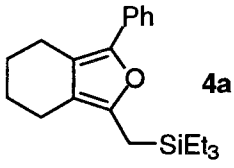
3c A pale yellow oil (74% yield); IR (neat) 563, 617, 776, 849, 918, 954, 1093, 1168, 1187, 1354, 1442, 1644, 1731 (C=O), 2856, 2933, 3431 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.68-1.70 (m, 4H), 2.19 (s, 3H), 2.47-2.53 (m, 4H), 3.22 (s, 3H), 4.69 (s, 1H), 7.14 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 19.9, 20.1, 22.9, 26.3, 56.6, 81.2, 122.4, 122.4, 137.8, 141.7, 204.0.

Furfuryl methyl ether 3d.



3d A colorless oil (20% yield); IR (neat) 602, 763, 850, 920, 947, 1009, 1109, 1194, 1270, 1335, 1439, 1581, 1758 (C=O), 2850, 2932, 3437 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.68-1.70 (m, 4H), 2.52-2.55 (m, 4H), 3.37 (s, 3H), 3.79 (s, 3H), 4.84 (s, 1H), 7.12 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 20.1, 20.1, 23.0, 23.0, 52.5, 57.0, 74.5, 121.8, 122.3, 137.6, 141.8, 169.1. Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 63.99; H, 7.23.

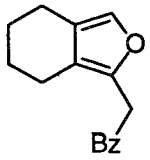
Silane 4a.



4a A solution of $Cr(CO)_6$ (2.8 mg, 0.013 mmol) in THF (1.0 mL) was irradiated by Hg lamp (450 W, 350 nm) at room temperature for 2 h. To this yellow solution were added substrate **1a** (53 mg, 0.25 mmol) and triethylsilane (0.40 mL, 2.5 mmol) at room temperature. The color of the reaction mixture gradually changed from deep blue to yellowish brown as the reaction proceeded. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 30/1) as an eluent to afford a colorless liquid **4a** (99% yield). IR (neat) 691, 730, 748, 759, 1018, 1068, 1240, 1493, 1600, 2913,

2935, 2951 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 0.63 (q, J = 7.6 Hz, 6H), 0.99 (t, J = 7.6 Hz, 9H), 1.68-1.81 (m, 4H), 2.05 (s, 2H), 2.42 (t, J = 5.6 Hz, 2H), 2.78 (t, J = 6.0 Hz, 2H), 7.15 (dd, J = 7.2, 7.2 Hz, 2H), 7.37 (dd, J = 7.2, 7.2 Hz, 2H), 7.57 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 4.4, 7.6, 11.8, 21.9, 23.9, 24.1, 24.5, 117.0, 119.8, 123.9, 125.7, 128.9, 133.4, 144.7, 148.0. HRMS (FAB) calcd for $C_{21}H_{30}OSi$ (M^+): 326.2066; found, 326.2067.

Tetrahydroisobenzofuran derivative 5b.



5b A colorless liquid (46% yield); IR (neat) 690, 752, 1179, 1209, 1252, 1276, 1448, 1580, 1597, 1687 (C=O), 2855, 2930 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.60-1.74 (m, 4H), 2.41-2.55 (m, 4H), 4.18 (s, 2H), 7.08 (s, 1H), 7.45 (dd, J = 7.2, 7.2 Hz, 2H), 7.55 (dd, J = 7.2, 7.2 Hz, 2H), 8.01 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 20.2, 20.3, 23.1, 23.2, 37.5, 119.0, 122.4, 128.5, 128.5, 133.1, 136.2, 136.3, 141.5, 194.9. HRMS (FAB) calcd for $C_{16}H_{17}O_2$ ($M+H^+$): 241.1229; found, 241.1225.

X-ray Crystallographic Studies of 2b and 2b'. Colorless crystals of **2b** and **2b'** suitable for X-ray analysis were obtained by recrystallization from AcOEt-hexane. Both of the single crystals were sealed in a Pyrex glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation. Details of crystal and data collection parameters are summarized in Tables 1 and 2. The positions of non-hydrogen atoms were determined by direst methods (SIR92) and subsequent Fourier syntheses (DIRDIF PATTY).[14] An ORTEP drawing of **2b** and **2b'** is shown in Figures 1 and 2, respectively.

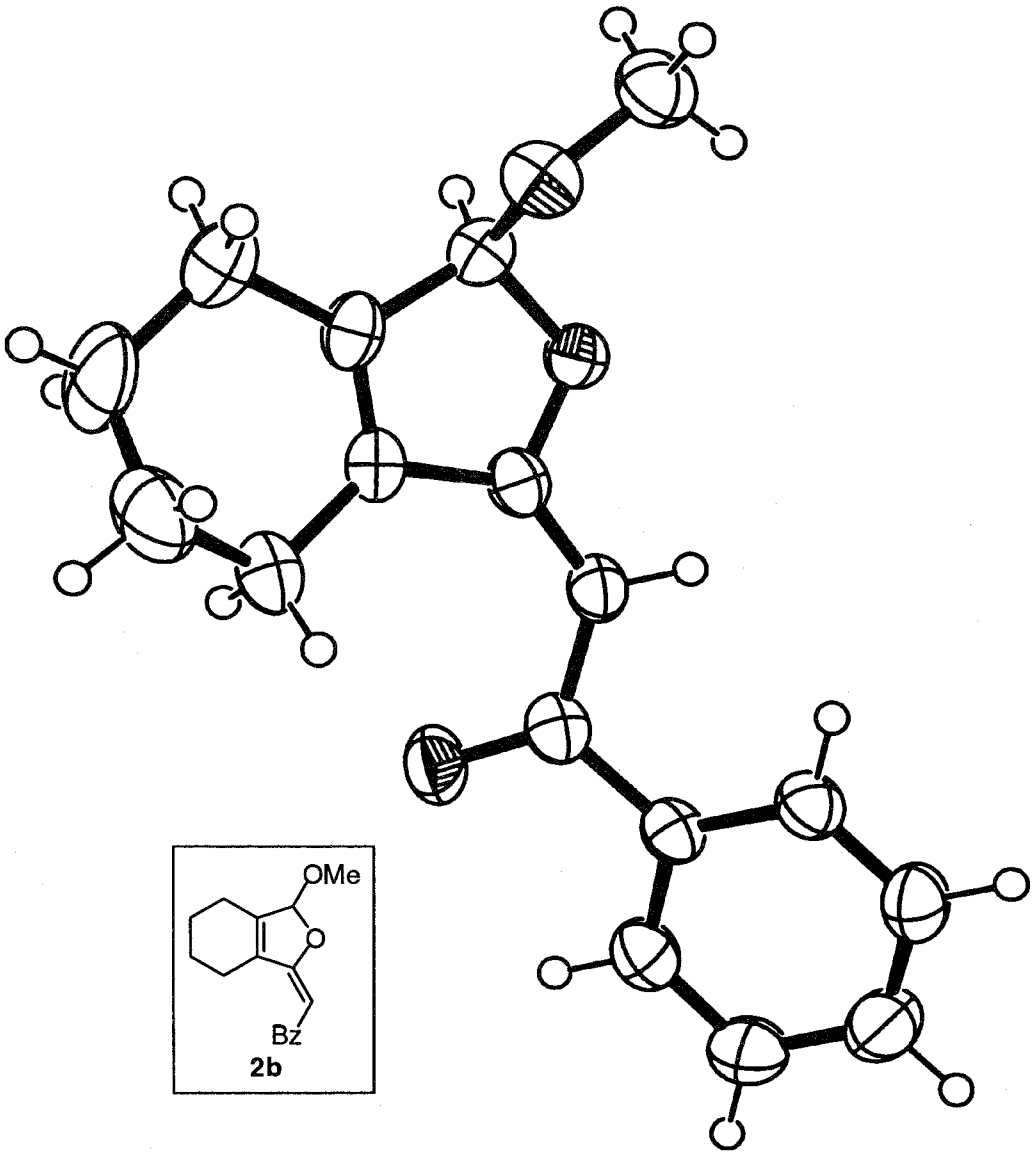


Figure 1. Crystal structure of **2b**

Table 1. Summary of Crystallographic Data of **2b**

empirical formula	$C_{17}H_{18}O_3$
fw	270.33
crystal syst	triclinic
space group	*P*-1 (No. 2)
cryst color	colorless, block
lattice params	
a (Å)	7.743(8)
b (Å)	14.067(2)
c (Å)	13.234(1)
β(Å)	100.795(1)
V (Å^3)	1416.(1)
Z	4
D_{calc} (g cm^{-3})	1.268
μ(Mo Kα) (cm^{-1})	0.86
F(000)	576
diffractometer	Rigaku RAXIS-RAPID
radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated
temp (°C)	23.0
scan type	ω–2θ
Max. 2θ (°)	55
no. of rflns measd	total, 12751
no. of observns ($I > 3.00\sigma(I)$)	1581
structure soln	direct methods (SIR92)
refinement	full-matrix least-squares on F
no. of variables	199
reflection/parameter ratio	7.94
residuals: R; R_W	0.055; 0.053
goodness of fit (GOF)	2.36
max shift/error in final cycle	0.03
maximum peak in final diff map (e Å^{-3})	1.80
minimum peak in final diff map (e Å^{-3})	–3.42

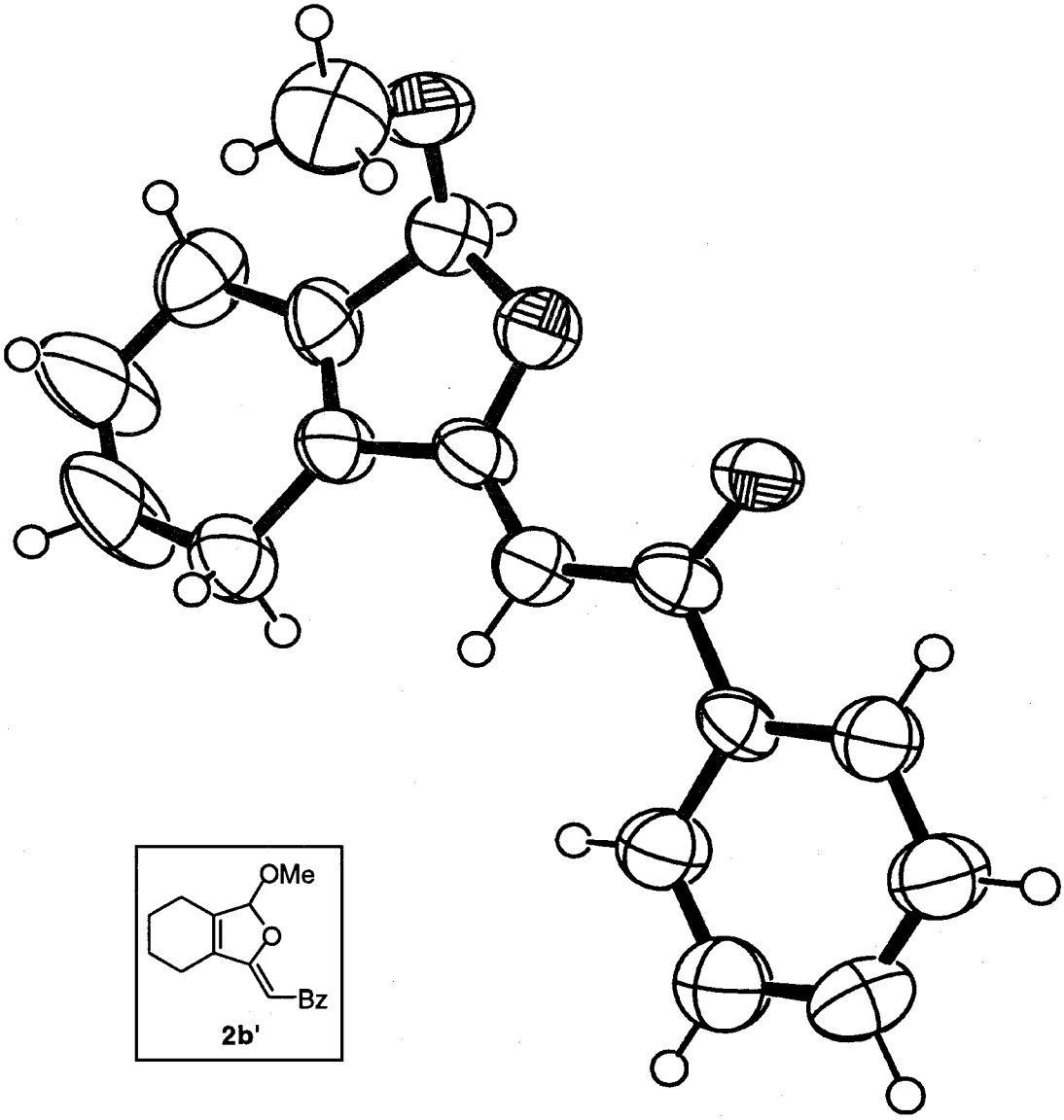


Figure 2. Crystal structure of **2b'**

Table 2. Summary of Crystallographic Data of **2b'**

empirical formula	$C_{17}H_{18}O_3$
fw	270.33
crystal syst	triclinic
space group	*P*-1 (No. 2)
cryst color	colorless, block
lattice params	
a (Å)	8.033(7)
b (Å)	11.412(1)
c (Å)	15.858(1)
α (Å)	89.969(3)
β (Å)	95.727(4)
γ (Å)	90.112(4)
V (Å^3)	1446.(6)
Z	4
D_{calc} (g cm^{-3})	1.241
μ(Mo Kα) (cm^{-1})	0.84
F(000)	576
diffractometer	Rigaku RAXIS-RAPID
radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated
temp (°C)	23.0
scan type	ω–2θ
Max. 2θ (°)	55
no. of rflns measd	total, 10124
no. of observns ($I > 3.00\sigma(I)$)	2162
structure soln	direct methods (SIR92)
refinement	full-matrix least-squares on F
no. of variables	392
reflection/parameter ratio	5.52
residuals: R; R_W	0.103; 0.104
goodness of fit (GOF)	0.29
max shift/error in final cycle	0.01
maximum peak in final diff map (e Å^{-3})	0.36
minimum peak in final diff map (e Å^{-3})	–0.40

References and Notes

(1) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules, 2nd Ed.*; University Science Books: Mill Valley, CA, 1999; p 143.

(2) For selected references, see: (a) Doyle, M. P.; McKervey, M. A.; Ye, T. *In Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley-Interscience: New York, 1998. (b) Ye, T.; McKervey, M. A. *Chem. Rev.* **1994**, *94*, 1091.

(3) 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.

(4) The reactions of α,ω-enynes with dienes via cyclopropylcarbene complexes have been reported. See: (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. For 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.

(5) (a) Yamamoto, Y.; Kitahara, H.; Ogawa, R.; Kawaguchi, H.; Tatsumi, K.; Itoh, K. *J. Am. Chem. Soc.* **2000**, *122*, 4310. (b) Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143.

(6) (a) Iwasawa, N.; Shido, M.; Kusama, H. *J. Am. Chem. Soc.* **2001**, *123*, 5814. For example of azomethine ylide, see: (b) Kusama, H.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 11592. Also see: (c) Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12650.

(7) Copper-(isoindazolyl)carbenoids from (2-ethynylphenyl)triazenes, see: (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.

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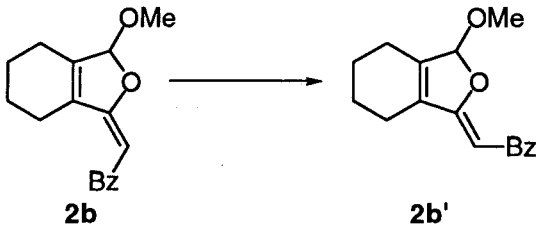
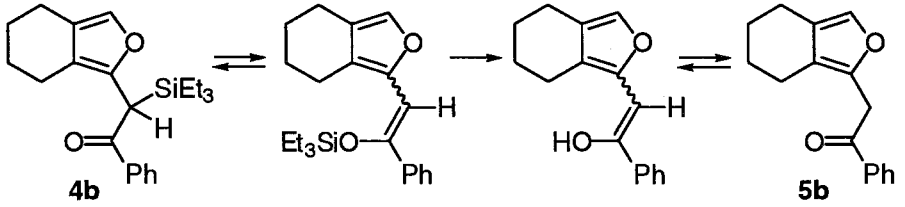
(9) (a) Ohe, K.; Miki, K.; Yokoi, T.; Nishino, F.; Uemura, S. *J. Organomet. Chem.* **2002**, *645*, 228. (b) Miki, K.; Nishino, F.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 5260.

(10) Product **2b** was gradually transformed into thermodynamically stable **2b'** at room temperature (*vide infra*). Both structures of **2b** and **2b'** were determined by X-ray diffraction analyses (see Experimental Section).



(11) The Si-H insertion product **4b** as an α-silylcarbonyl compound is labile due to the equilibrium with silyl enolate isomer yielding a mixture of the silylated and protodesilylated products.



(12) (a) Ohe, K.; Miki, K.; Yokoi, T.; Nishino, F.; Uemura, S. *Organometallics* **2000**, *19*, 5525. Also see: (b) Herndon, J. W.; Wang, H. *J. Org. Chem.* **1998**, *63*, 4564.

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(14) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

Chapter 7

Doyle-Kirmse Reaction of Allylic Sulfides with Diazoalkane-Free (2-Furyl)carbenoid Transfer

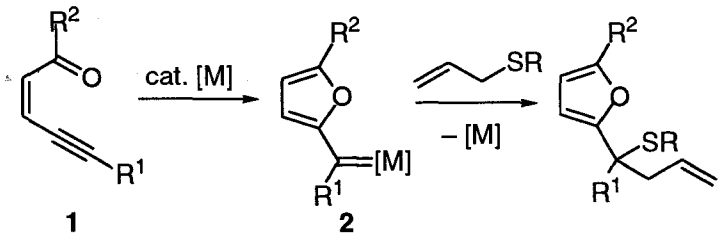
Abstract

In the presence of rhodium catalyst, conjugated ene-yne-carbonyl compounds **1** react with allylic sulfides to produce furan containing sulfides in good yields. The key intermediate of this reaction is a (2-furyl)carbenoid generated *in situ* by a nucleophilic attack of a carbonyl oxygen atom to an internal alkyne carbon of **1** activated by rhodium complex. The [2,3]sigmatropic rearrangement of the resulting sulfur ylides generated by the (2-furyl)carbenoid transfer to allylic sulifides leads to the products. When diallyl sulfide is employed, heteroatom (O and S) containing polycyclic compounds are obtained by sequential intramolecular Diels-Alder cyclization reaction with a constructed furan ring as an enophile.

Introduction

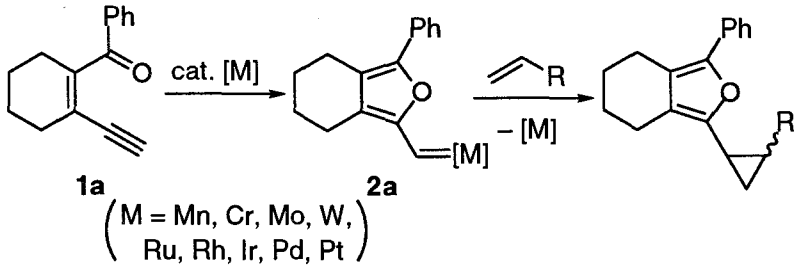
The Doyle-Kirmse reaction of allylic sulfides and diazo compounds ([2,3]sigmatropic rearrangement of sulfur ylides) is a powerful synthetic method for creating new C-C bonds, presumably involving carbenoid complexes as intermediates.[1,2] The author describes herein the rhodium(II)-catalyzed Doyle-Kirmse type reaction using (2-furyl)carbenoid precursors **1** without involving the corresponding diazoalkanes as shown in Scheme 1. The author has

Scheme 1



already reported the cyclopropanation of alkenes via (2-furyl)carbenoid complexes **2a** generated from **1a**, which can be catalyzed by a wide range of transition metal complexes (Scheme 2, and also see Chapter 4).[3,4] A further investigation on the reactivity of such

Scheme 2

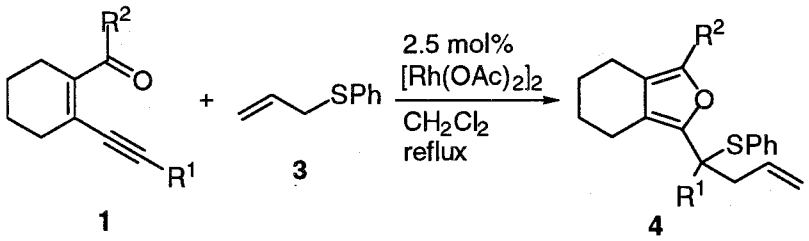


carbenoids demonstrated that $[Rh(OAc)_2]_2$ worked efficiently as a catalyst for the Doyle-Kirmse reaction between allylic sulifides and ene-yne-carbonyl compounds **1** having electron-withdrawing groups at an alkyne terminus.

Results and Discussion

First, the reactions of **1** with allyl phenyl sulfide **3** as a carbenoid acceptor were examined. Results are shown in Table 1. The reaction of **1a** with **3** in the presence of 2.5

Table 1. Rh-catalyzed Carbene Transfer Reaction with Sulfide **3**[a]

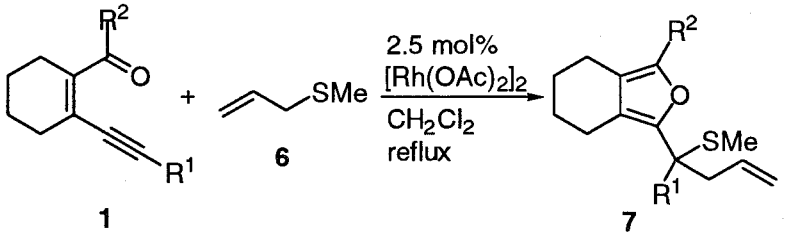


entry	1	R^1	R^2	time (h)	isolated yield
1	**1a**	H	Ph	4	complex mixture
2	**1b**	Bz	H	10	98%
3	**1c**	Ac	H	7	94%
4	**1d**	CO_2Me	H	12	83%

[a] Reaction conditions: **1** (0.2 mmol), sulfide (2.0 mmol), $[Rh(OAc)_2]_2$ (0.005 mmol) in CH_2Cl_2 (1 mL).

mol% of $[Rh(OAc)_2]_2$ at room temperature or at reflux temperature gave a complex mixture, but none of the desired product was obtained (entry 1). On the other hand, the reaction of **3** with ene-yne-carbonyl compounds **1b-d** having an electron-withdrawing group R^1, which could be expected to enhance the electrophilicity of intermediary carbenoid species to sulfur atom afforded the expected compound **4**. Thus, the reaction of benzoyl group-containing ene-yne-carbonyl compound **1b** with **3** gave **4b** quantitatively (entry 2). Ene-yne-carbonyl compounds, **1c** and **1d**, having acetyl or methoxycarbonyl moiety also reacted with **3** to give **4c** and **4d**[5] in good yields (entries 3 and 4). Since slow addition of diazoalkane is necessary in most cases of Doyle-Kirmse reaction using diazoalkanes,[2] it is noted that slow addition of **1** is not required in the present diazoalkane-free reaction. Diazoalkane-free carbenoid transfer reaction using **1** was also effective for more nucleophilic allyl methyl sulfide **6**.[2b,f] These results are summarized in Table 2. The reaction of **1a** with **6**, which gave

Table 2. Rh-catalyzed Carbene Transfer Reaction with Sulfide **6**[a]



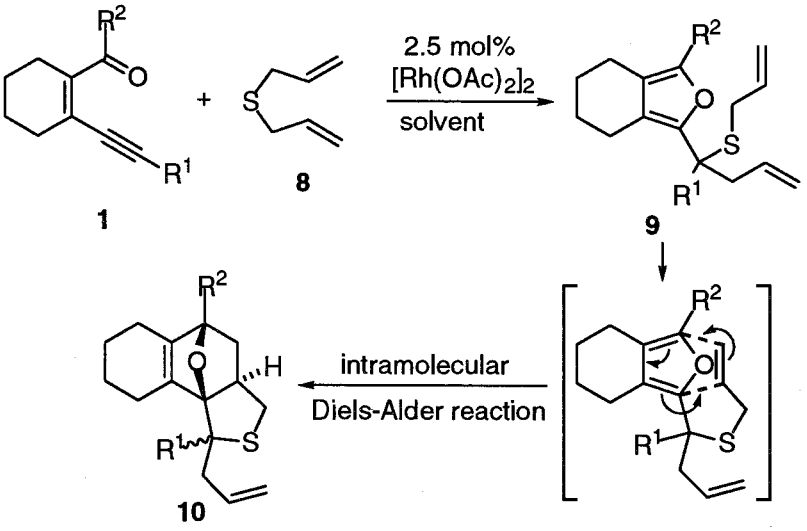
entry	1	R^1	R^2	time (h)	isolated yield
1	**1a**	H	Ph	7	60%
2	**1b**	Bz	H	120	77%[b]
3	**1c**	Ac	H	48	72%
4	**1d**	CO_2Me	H	48	91%

[a] Reaction conditions: **1** (0.2 mmol), sulfide (2.0 mmol), $[Rh(OAc)_2]_2$ (0.005 mmol) in CH_2Cl_2 (1 mL). [b] **1b** (11%) was recovered.

unsatisfactory result with **3**, afforded the corresponding expected product **7a** in 60% yield (entry1). Reactions of **1b-d** with sulfide **6** also gave products **7b-d** in fair to good yields, respectively, although prolonged reaction time (48-120 h) was required for each reaction (entries 2-4).

Next, we carried out the rhodium-catalyzed reaction of **1** with diallyl sulfide **8**. Results are shown in Table 3. The reaction of **1a** with **8** in CH_2Cl_2 at reflux temperature gave the product **9a**, in which the reaction occurred at one end of two allylic moieties (entry 1). On the other hand, the reaction using **1b** for prolonged reaction time produced **9b** in 32% yield together with tetracyclic product **10b** in 43% yield as a mixture of two isomers (ratio = 79/21)[6] (entry 2). The latter product **10b** was considered to be formed by the subsequent intramolecular Diels-Alder product from an initially produced **9b**. The reaction time did not affect the product ratio of **9b/10b**, but higher reaction temperature at 80 °C in 1,2-dichloroethane (DCE) considerably afforded only the Diels-Alder adduct **10b** (entry 3). The absence of Diels-Alder adduct **10a** in the reaction using **1a** might be attributed to the lack of the sterically demanding R^1 group. In reactions of **1c** and **1d** with **8**, only Diels-Alder adducts **10c** and **10d** were also obtained, respectively (entries 4 and 5). Notably, in the reaction using **1d**, reflux temperature in CH_2Cl_2 was sufficient for the Doyle-Kirmse type

Table 3. Rh-catalyzed Carbene Transfer Reaction with Sulfide **8** and Sequential Intramolecular Diels-Alder Cyclization[a]



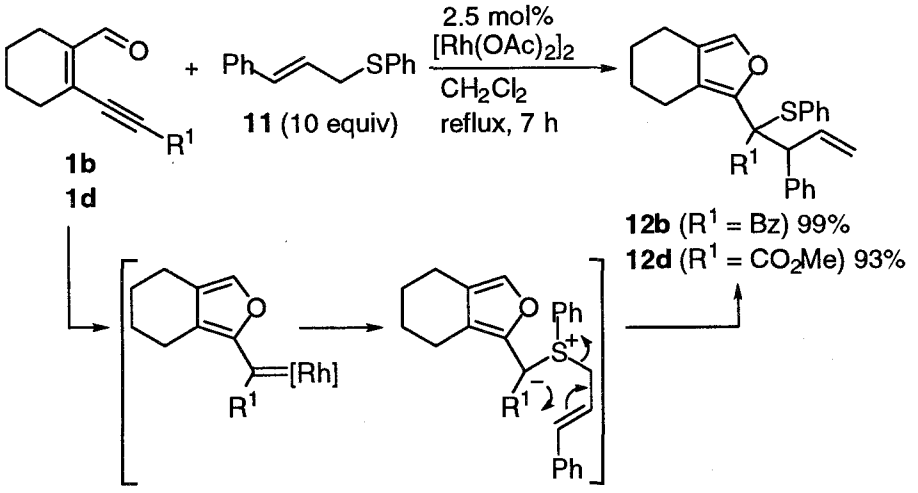
entry	1	R^1	R^2	solvent	temp.	time	isolated yield	
							9	10[b]
1	**1a**	H	Ph	CH_2Cl_2	reflux	7 h	43%	–
2[c]	**1b**	Bz	H	CH_2Cl_2	reflux	120 h	32%	43% (79/21)
3	**1b**	Bz	H	DCE[d]	80 °C	72 h	–	92% (79/21)
4	**1c**	Ac	H	DCE[d]	80 °C	54 h	–	80% (67/33)
5	**1d**	CO_2Me	H	CH_2Cl_2	reflux	120 h	trace	90% (73/27)

[a] Reaction conditions: **1** (0.2 mmol), sulfide (2.0 mmol), $[Rh(OAc)_2]_2$ (0.005 mmol) in CH_2Cl_2 (1 mL). [b] The values in the parentheses indicate diastereomeric ratio determined by ^1H NMR. [c] **1b** (9%) was recovered. [d] DCE = $ClCH_2CH_2Cl$.

reaction and subsequent intramolecular Diels-Alder reaction. This clearly shows that introduction of an electron-withdrawing methoxycarbonyl moiety into **1** prominently facilitates ylide formation by carbenoid transfer as well as intramolecular Diels-Alder reaction.

Finally, the reaction with cinnamyl phenyl sulfide **11** using **1** as a carbenoid source was examined in order to elucidate the reaction pathway. In the presence of 2.5 mol% $[Rh(OAc)_2]_2$, the reactions of **1b** and **1d** with **11** gave **12b** and **12d** as a single diastereomer, in 99% and 93% yields, respectively (Scheme 3). These results clearly indicate that the rearrangement of sulfur ylides generated by (2-furyl)carbenoid transfer proceeds via [2,3]sigmatropy as accepted for Doyle-Kirmse reaction.

Scheme 3



In summary, the author has demonstrated catalytic carbene transfer reactions with allylic sulfides leading to ylide formation on the basis of the *in situ* generation of (2-furyl)carbenoids from conjugated ene-yne-ketones. The resulting sulfur ylides efficiently undergo [2,3]sigmatropic rearrangement to give furan-containing sulfides. Reaction cascade of [2,3]sigmatropy followed by intramolecular Diels-Alder reaction employing diallyl sulfide allows the one-pot synthesis of polycyclic heterocycles.

Experimental

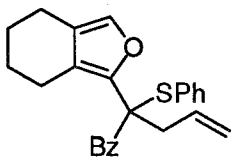
General Procedures. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies were performed with Merck silica gel 60. NMR spectra were measured for solutions in $CDCl_3$ with Me_4Si as an internal standard or CD_2Cl_2 (^1H and ^{13}C): the following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. IR spectra were recorded on an FT-IR spectrometer. Melting points are uncorrected. High-resolution mass spectra (FAB HRMS) and low-resolution mass spectra (FAB LRMS) were obtained with JEOL JMX-SX 102A spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University.

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon, and other solvents were dried by the usual methods and distilled before use.

Typical Procedure for Catalytic Carbene Transfer Reaction with 1.

To a solution of **1** (0.25 mmol) and sulfide (10 equiv) placed in the flame dried Schlenk flask and dissolved in dry and deoxygenated CH_2Cl_2 or $ClCH_2CH_2Cl$ (1.0 mL) was added $[Rh(OAc)_2]_2$ (2.7 mg, 0.006 mmol) at room temperature. After the reaction was complete, the organic solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 20/1) as an eluent to afford the corresponding products **4**, **7**, **9**, **10**, and **12**.

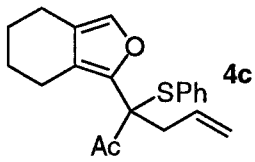
Sulfide 4b.



4b

A colorless oil (98% yield); IR (neat) 693, 749, 919, 1123, 1182, 1213, 1229, 1255, 1439, 1446, 1473, 1579, 1595, 1679 (C=O), 2855, 2931, 3073 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 1.49–1.60 (m, 4H), 1.80–1.89 (m, 1H), 2.34–2.43 (m, 1H), 2.45–2.53 (m, 2H), 2.90 (d, J = 6.8 Hz, 2H), 4.78 (d, J = 17.2 Hz, 1H), 5.03 (d, J = 10.0 Hz, 1H), 5.94 (tdd, J = 6.8, 10.0, 17.2 Hz, 1H), 7.09 (s, 1H), 7.13 (d, J = 7.2 Hz, 2H), 7.22 (dd, J = 7.2, 7.2 Hz, 2H), 7.28–7.36 (m, 3H), 7.45 (dd, J = 7.2, 7.2 Hz, 1H), 7.58 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C) δ 19.5, 20.5, 22.3, 22.4, 37.9, 67.0, 116.8, 119.3, 122.5, 127.2, 127.5, 128.2, 128.2, 130.5, 131.4, 132.0, 135.0, 135.4, 136.7, 143.3, 192.4. HRMS (FAB): calcd for $C_{25}H_{25}O_2S$ ($M+H^+$), 389.1575; found, 389.1570.

Sulfide 4c.

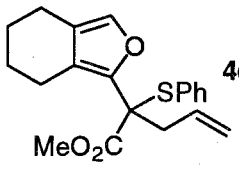


4c

A colorless oil (94% yield); IR (neat) 693, 748, 917, 1180, 1350, 1440, 1715 (C=O), 2935 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 1.58–1.65 (m, 4H), 2.04–2.08 (m, 1H), 2.16 (s, 3H), 2.43–2.50 (m, 3H), 2.74 (d, J = 6.9 Hz, 2H), 5.09 (d, J = 17.1 Hz, 1H), 5.13 (d, J = 9.6 Hz, 1H), 5.93 (tdd, J = 6.9, 9.6, 17.1 Hz, 1H), 7.08 (s, 1H), 7.15 (d, J = 7.8 Hz, 2H), 7.23 (dd, J = 7.8, 7.8 Hz, 2H),

7.33 (dd, J = 7.8, 7.8 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ 20.3, 21.3, 22.7, 23.1, 26.3, 37.0, 68.1, 118.4, 120.7, 122.9, 128.5, 129.2, 130.5, 132.7, 136.5, 137.1, 143.4, 202.3. HRMS (FAB): calcd for $C_{20}H_{22}O_2S$ ($M+H^+$), 327.1419; found, 327.1418.

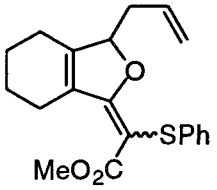
Sulfide 4d.



4d

A colorless oil (83% yield); IR (neat) 692, 730, 953, 990, 1053, 1216, 1315, 1437, 1612, 1705 (C=O), 2941, 3431 cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 1.27–1.63 (m, 4H), 1.78 (td, J = 6.6, 16.2 Hz, 1H), 2.20 (td, J = 6.6, 16.2 Hz, 1H), 2.45–2.47 (m, 2H), 2.87 (m, 2H), 3.72, (s, 3H), 5.15 (d, J = 16.8 Hz, 1H), 5.16 (d, J = 10.2 Hz, 1H), 5.98 (tdd, J = 6.6, 10.2, 16.8 Hz, 1H), 7.04 (s, 1H), 7.12 (d, J = 7.2 Hz, 2H), 7.22 (dd, J = 7.2, 7.2 Hz, 2H), 7.34 (dd, J = 7.2, 7.2 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ 20.6, 21.3, 23.0, 23.4, 39.7, 53.0, 62.9, 119.0, 120.7, 123.1, 128.6, 129.6, 131.1, 133.2, 136.1, 137.9, 144.4, 170.5. HRMS (FAB): calcd for $C_{20}H_{22}O_3S$ (M^+), 342.1290; found, 342.1288.

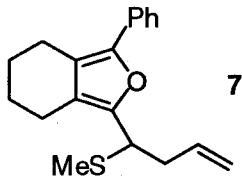
Sulfide 5d.



5d

A colorless oil (85% yield); IR (neat) 690, 739, 1024, 1255, 1438, 1478, 1741 (C=O), 2934 cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2, 25 °C) δ 1.52–1.68 (m, 4H), 2.30–2.47 (m, 4H), 2.49–2.73 (m, 2H), 3.57, (s, 3H), 3.67 (t, J = 6.8 Hz, 1H), 4.90 (d, J = 10.0 Hz, 1H), 4.96 (d, J = 17.0 Hz, 1H), 5.62 (tdd, J = 6.8, 10.0, 17.0 Hz, 1H), 6.95 (d, J = 7.3 Hz, 2H), 7.04 (dd, J = 7.3, 7.3 Hz, 1H), 7.14 (dd, J = 7.3, 7.3 Hz, 2H); ^{13}C NMR (67.5 MHz, CD_2Cl_2, 25 °C) δ 20.7, 21.6, 23.1, 23.3, 34.4, 44.4, 52.4, 117.1, 121.0, 125.9, 126.6, 126.7, 129.1, 132.2, 135.1, 137.5, 148.8, 171.3. HRMS (FAB): calcd for $C_{20}H_{22}O_3S$ (M^+), 342.1290; found, 342.1292.

Sulfide 7a.

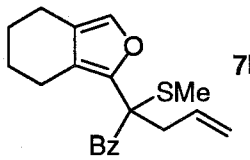


7a

A yellow oil [purified by column chromatography on SiO_2 with hexane/AcOEt (v/v = 300/1), 60% yield]; IR (neat) 691, 763, 912, 1067, 1440, 1495, 1596, 2935, 3403 cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2, 25 °C) δ 1.66–1.73 (m, 4H), 1.99 (s, 3H), 2.48–2.50 (m, 2H), 2.60–2.85 (m, 4H),

3.87 (dd, J = 6.8, 8.6 Hz, 1H), 4.98 (d, J = 10.3 Hz, 1H), 5.07 (d, J = 17.0 Hz, 1H), 5.78 (tdd, J = 6.8, 10.3, 17.0 Hz, 1H), 7.16 (dd, J = 7.6, 7.6 Hz, 1H), 7.34 (dd, J = 7.6, 7.6 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H); ^{13}C NMR (67.5 MHz, CD_2Cl_2, 25 °C) δ 14.2, 21.1, 23.2, 23.3, 23.8, 37.7, 42.5, 116.7, 119.4, 120.8, 124.2, 126.2, 128.7, 132.2, 135.8, 145.5, 146.6. HRMS (FAB): calcd for $C_{19}H_{22}OS$ (M^+), 298.1391; found, 298.1389.

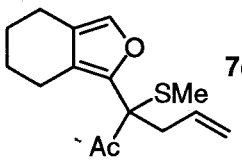
Sulfide 7b.



7b

A colorless oil (77% yield); IR (neat) 695, 915, 1231, 1446, 1595, 1681 (C=O), 1769, 2937, 3071, 3470 cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2, 25 °C) δ 1.45–1.52 (m, 4H), 1.74 (s, 3H), 2.22–2.31 (m, 2H), 2.32–2.43 (m, 2H), 2.89 (d, J = 6.6 Hz, 2H), 4.84 (d, J = 17.3 Hz, 1H), 4.90 (d, J = 10.0 Hz, 1H), 5.64 (tdd, J = 6.6, 10.0, 17.3 Hz, 1H), 7.03 (s, 1H), 7.18 (dd, J = 7.3, 7.3 Hz, 2H), 7.33 (dd, J = 7.3, 7.3 Hz, 1H), 7.52 (d, J = 7.3 Hz, 2H); ^{13}C NMR (67.5 MHz, CD_2Cl_2, 25 °C) δ 11.4, 20.6, 21.7, 23.3, 23.5, 37.9, 61.1, 118.0, 119.7, 123.7, 128.1, 129.3, 132.3, 133.0, 135.8, 136.3, 144.3, 194.1. HRMS (FAB): calcd for $C_{20}H_{23}O_2S$ ($M+H^+$), 327.1419; found, 327.1418.

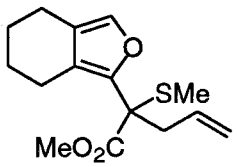
Sulfide 7c.



7c

A colorless oil (72% yield); IR (neat) 914, 1129, 1352, 1437, 1597, 1702 (C=O), 1769, 2937, 3380 cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2, 25 °C) δ 1.63–1.69 (m, 4H), 1.80 (s, 3H), 2.06 (s, 3H), 2.45–2.52 (m, 4H), 2.78 (d, J = 7.0 Hz, 2H), 5.04 (d, J = 17.0 Hz, 1H), 5.06 (d, J = 10.0 Hz, 1H), 5.68 (tdd, J = 7.0, 10.0, 17.0 Hz, 1H), 7.10 (s, 1H); ^{13}C NMR (67.5 MHz, CD_2Cl_2, 25 °C) δ 11.4, 20.7, 22.1, 23.3, 23.7, 25.7, 36.2, 62.6, 117.7, 120.1, 123.3, 133.5, 136.6, 143.9, 201.1. HRMS (FAB): calcd for $C_{15}H_{21}O_2S$ ($M+H^+$), 265.1262; found, 265.1263.

Sulfide 7d.

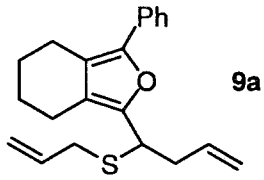


7d

A colorless oil (91% yield); IR (neat) 609, 755, 917, 1128, 1211, 1435, 1737 (C=O), 2930, 3450 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 1.49–1.58 (m, 4H), 1.81 (s, 3H), 2.27–2.31 (m, 1H), 2.40–2.43

(m, 3H), 2.86 (d, J = 7.2 Hz, 2H), 3.65 (s, 3H), 4.97 (d, J = 10.0 Hz, 1H), 5.01 (d, J = 16.8 Hz, 1H), 5.69 (tdd, J = 7.2, 10.0, 16.8 Hz, 1H), 7.00 (s, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C) δ 12.9, 20.6, 21.7, 23.2, 23.6, 39.9, 52.9, 57.4, 118.5, 119.4, 123.1, 133.2, 136.1, 144.6, 170.8. HRMS (FAB): calcd for $C_{15}H_{20}O_3S$ (M^+), 280.1133; found, 280.1136.

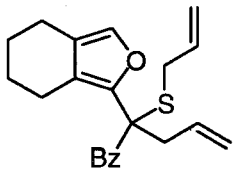
Sulfide 9a.



9a

A yellow oil [purified by column chromatography on SiO_2 with hexane/AcOEt (v/v = 300/1), 43% yield]; IR (neat) 692, 762, 916, 989, 1070, 1438, 1492, 1600, 2360, 2925, 3077 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ1.66–1.75 (m, 4H), 2.47 (dd, J = 6.0, 6.0 Hz, 2H), 2.54–2.59 (m, 1H), 2.72–2.76 (m, 3H), 3.06 (dd, J = 6.0, 6.0 Hz, 2H), 3.93 (dd, J = 6.8, 9.2 Hz, 1H), 4.96–5.10 (m, 4H), 5.72–5.81 (m, 2H), 7.10 (dd, J = 7.6, 7.6 Hz, 1H), 7.28 (dd, J = 7.6, 7.6 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C) δ21.2, 23.2, 23.3, 23.8, 34.4, 38.2, 40.6, 116.8, 119.5, 120.9, 124.3, 126.2, 128.6, 128.7, 132.3, 135.0, 135.7, 145.5, 146.7. HRMS (FAB): calcd for $C_{21}H_{25}OS$ ($M+H^+$), 325.1626; found, 325.1629.

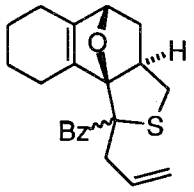
Sulfide 9b.



9b

A colorless oil [purified by column chromatography on SiO_2 with hexane/AcOEt (v/v = 30/1 to 20/1), 32% yield]; IR (neat) 696, 919, 1020, 1230, 1260, 1446, 1673 (C=O), 1769, 2934, 3075, 3435 cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ1.31–1.67 (m, 4H), 2.29–2.48 (m, 4H), 2.97 (d, J = 6.9 Hz, 2H), 3.04 (d, J = 6.9 Hz, 2H), 4.88–5.13 (m, 4H), 5.62–5.83 (m, 2H), 7.14 (s, 1H), 7.29 (dd, J = 7.5, 7.5 Hz, 2H), 7.45 (dd, J = 7.5, 7.5 Hz, 1H), 7.60 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ20.5, 21.7, 23.2, 23.4, 31.9, 39.2, 62.5, 117.8, 118.4, 120.1, 123.9, 128.3, 129.4, 132.5, 133.1, 133.9, 135.9, 136.4, 144.4, 194.8. HRMS (FAB): calcd for $C_{22}H_{24}O_2S$ (M^+), 352.1497; found, 352.1495.

Sulfide 10b.



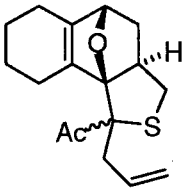
10b

After the reaction of **1b** at 80 °C was complete, **10b** was obtained as a mixture of diastereoisomers (92% yield, d.r. = 79:21). These isomers could be separated by column chromatography on SiO_2 with hexane/AcOEt (v/v = 20/1 to 4/1) as an eluent.

10b (major); a colorless oil; IR (neat) 646, 697, 767, 923, 1000, 1294, 1443, 1669 (C=O), 2359, 2932, 3507 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 1.30–1.49 (m, 2H), 1.58–1.69 (m, 2H), 1.71–2.12 (m, 5H), 2.21–2.28 (m, 1H), 2.68 (dd, J = 5.4, 10.8 Hz, 1H), 2.84–3.02 (m, 3H), 3.14 (dd, J = 9.5, 10.8 Hz, 1H), 4.28 (d, J = 17.0 Hz, 1H), 4.63 (s, 1H), 4.65 (d, J = 10.3 Hz, 1H), 5.47 (tdd, J = 7.6, 10.3, 17.0 Hz, 1H), 7.40 (dd, J = 7.5, 7.5 Hz, 2H), 7.50 (dd, J = 7.5, 7.5 Hz, 1H), 7.82 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ 22.5, 22.8, 23.2, 25.3, 36.2, 38.3, 38.9, 49.7, 64.1, 78.8, 103.7, 118.5, 128.2, 128.9, 131.5, 133.1, 138.6, 139.8, 143.4, 198.3. HRMS (FAB): calcd for $C_{22}H_{25}O_2S$ ($M+H^+$), 353.1575; found, 353.1575.

10b (minor); a yellow oil; IR (neat) 639, 696, 921, 1003, 1230, 1445, 1597, 1667 (C=O), 2923, 3422 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 1.48–1.64 (m, 4H), 1.74–1.77 (m, 2H), 1.87–2.00 (m, 1H), 2.17–2.31 (m, 2H), 2.48–2.55 (m, 2H), 2.66–2.76 (m, 2H), 3.14 (dd, J = 8.4, 10.8 Hz, 1H), 3.45 (dd, J = 7.2, 13.2 Hz, 1H), 4.69 (d, J = 3.9 Hz, 1H), 5.03 (d, J = 17.1 Hz, 1H), 5.07 (d, J = 10.2 Hz, 1H), 5.76 (tdd, J = 6.9, 10.2, 17.1 Hz, 1H), 7.34 (dd, J = 7.2, 7.2 Hz, 2H), 7.43 (dd, J = 7.2, 7.2 Hz, 1H), 7.66 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ 22.3, 22.9, 23.6, 24.4, 36.2, 37.7, 43.2, 49.6, 71.8, 80.8, 104.6, 119.3, 127.7, 128.6, 131.1, 133.8, 138.5, 140.1, 144.5, 201.7. HRMS (FAB): calcd for $C_{22}H_{25}O_2S$ ($M+H^+$), 353.1575; found, 353.1573.

Sulfide 10c.



10c

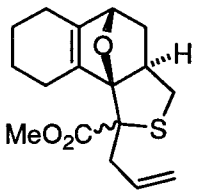
After the reaction of **1c** at 80 °C was complete, **10c** was obtained as a mixture of diastereoisomers (80% yield, d.r. = 67:33). These isomers could be separated by column chromatography on SiO_2 with

hexane/AcOEt (v/v = 20/1 to 4/1) as an eluent.

10c (major); A yellow oil; IR (neat) 843, 920, 1185, 1360, 1440, 1675, 1690 (C=O), 2856, 2925, 3414 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 1.33–1.48 (m, 2H), 1.62–1.70 (m, 2H), 1.73–1.78 (m, 2H), 1.81–1.88 (m, 2H), 1.93–1.98 (m, 1H), 2.15-2.28 (m, 1H), 2.32 (s, 3H), 2.64–2.72 (m, 2H), 2.78 (tdd, J = 5.4, 6.9, 9.3 Hz, 1H), 2.93 (dd, J = 5.4, 14.4 Hz, 1H), 3.11 (dd, J = 9.3, 10.2 Hz, 1H), 4.71 (d, J = 4.5 Hz, 1H), 5.00 (d, J = 10.2 Hz, 1H), 5.12 (d, J = 17.1 Hz, 1H), 5.87 (tdd, J = 7.2, 10.2, 17.1 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ 22.4, 22.8, 23.1, 25.1, 25.8, 35.8, 37.3, 39.1, 49.5, 65.8, 78.7, 102.4, 118.4, 134.3, 139.3, 143.8, 202.0. HRMS (FAB): calcd for $C_{17}H_{22}O_2S$ (M^+), 290.1341; found, 290.1339.

10c (minor); A white solid; mp. 87.2-89.0 °C; IR (KBr) 649, 668, 678, 871, 924, 1071, 1123, 1450, 1535, 1635 (C=O), 2341, 2360, 2929, 3443 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 1.41–1.62 (m, 4H), 1.71–1.76 (m, 3H), 1.86–1.90 (m, 1H), 2.11–2.16 (m, 1H), 2. 23 (s, 3H), 2.42–2.55 (m, 3H), 2.70 (dd, J = 7.5, 10.8 Hz, 1H), 3.16 (dd, J = 8.4, 10.8 Hz, 1H), 3.29 (dd, J = 6.9, 13.5 Hz, 1H), 4.66 (d, J = 3.6 Hz, 1H), 5.09 (d, J = 10.5 Hz, 1H), 5.13 (d, J = 17.1 Hz, 1H), 5.75 (tdd, J = 6.9, 10.5, 17.1 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ 22.2, 22.8, 23.5, 24.4, 29.7, 35.6, 38.1, 41.7, 48.6, 72.0, 80.4, 104.0, 118.8, 134.0, 137.6, 145.4, 206.0. HRMS (FAB): calcd for $C_{17}H_{22}O_2S$ (M^+), 290.1341; found, 290.1340.

Sulfide 10d.



10d

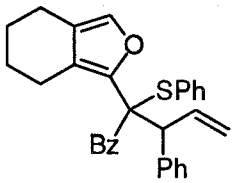
After the reaction of **1d** at reflux temperature of CH_2Cl_2 was complete, **10d** was obtained as a mixture of diastereoisomers (90% yield, d.r. = 73:27). These isomers could be separated by column chromatography on SiO_2 with hexane/AcOEt (v/v = 10/1 to 4/1) as an eluent.

10d(major); A colorless oil; IR (neat) 698, 917, 976, 1003, 1130, 1219, 1436, 1731 (C=O), 2938, 3443 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 1.37–1.53 (m, 2H), 1.59–1.99 (m, 7H), 2.17–2.28 (m, 1H), 2.70–2.75 (m, 3H), 2.83–2.91 (m, 1H), 3.31 (dd, J = 9.6, 9.6 Hz, 1H), 3.73 (s, 3H), 4.71 (d, J = 4.5 Hz, 1H), 5.00 (d, J = 10.2 Hz, 1H), 5.12 (d, J =

17.1 Hz, 1H), 5.87 (tdd, J = 7.2, 10.2, 17.1 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ 22.3, 22.6, 22.9, 23.1, 36.6, 37.4, 38.7, 50.0, 52.3, 59.7, 79.4, 102.6, 118.2, 134.8, 138.3, 144.3, 173.2. HRMS (FAB): calcd for $C_{17}H_{22}O_3S$ (M^+), 306.1290; found, 306.1290.

10d(minor); A yellow oil; IR (neat) 917, 992, 1126, 1226, 1267, 1433, 1731 (C=O), 2934, 3478 cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 1.43–1.77 (m, 7H), 2.03–2.16 (m, 1H), 2.18–2.29 (m, 1H), 2.37–2.48 (m, 1H), 2.52 (dd, J = 6.3, 13.2 Hz, 2H), 2.66 (dd, J = 6.3, 11.1 Hz, 1H), 3.15 (dd, J = 9.0, 11.1 Hz, 1H), 3.23 (dd, J = 7.5, 13.2 Hz, 1H), 3.65 (s, 3H), 4.65 (d, J = 4.2 Hz, 1H), 5.12 (d, J = 10.2 Hz, 1H), 5.15 (d, J = 17.1 Hz, 1H), 5.87 (tdd, J = 6.3, 10.2, 17.1 Hz, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ 22.3, 22.7, 23.4, 24.1, 34.7, 38.8, 41.9, 47.7, 52.7, 67.2, 80.0, 103.6, 118.8, 133.9, 138.1, 144.4, 171.1. HRMS (FAB): calcd for $C_{17}H_{22}O_3S$ (M^+), 306.1290; found, 306.1293.

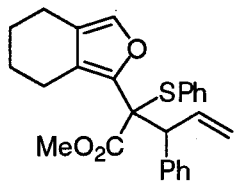
Sulfide 12b.



12b

A colorless oil [purified by column chromatography on SiO_2 with hexane/AcOEt (v/v = 30/1), 99% yield]; IR (neat) 700, 747, 918, 971, 1024, 1182, 1226, 1446, 1595, 1673 (C=O), 2853, 2934, 3052 cm^{-1}; ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 1.14–1.23 (m, 1H), 1.38–1.51 (m, 3H), 1.76–1.83 (m, 1H), 2.24–2.33 (m, 1H), 2.45–2.53 (m, 2H), 4.47 (d, J = 7.2 Hz, 1H), 4.80 (d, J = 16.8 Hz, 1H), 4.92 (d, J = 10.2 Hz, 1H), 6.16 (ddd, J = 7.2, 10.2, 16.8 Hz, 1H), 6.97 (s, 1H), 7.16–7.38 (m, 13H), 7.72 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ 19.3, 21.8, 22.1, 22.3, 55.1, 64.6, 115.5, 120.9, 122.3, 125.7, 126.5, 126.7, 127.6, 128.4, 128.8, 130.1, 130.3, 130.8, 135.7, 135.9, 136.5, 138.8, 139.3, 142.7, 190.7. HRMS (FAB): calcd for $C_{31}H_{29}O_2S$ ($M+H^+$), 465.1888; found, 465.1887.

Sulfide 12d.



12d

A colorless oil [purified by column chromatography on SiO_2 with hexane/AcOEt (v/v = 25/1), 93% yield]; IR (neat) 700, 753, 919, 1025, 1065, 1233, 1437, 1600, 1731 (C=O), 2926, 3076 cm^{-1}; ^{1}H NMR (270 MHz, CD_2Cl_2, 25 °C) δ 1.19–1.38 (m, 2H), 1.40–1.49 (m, 2H), 1.56–1.67 (m,

1H), 1.86–1.94 (m, 1H), 2.38–2.42 (m, 2H), 3.36 (s, 3H), 4.35 (d, J = 8.9 Hz, 1H), 5.07 (d, J = 18.1 Hz, 1H), 5.09 (d, J = 10.0 Hz, 1H), 6.35 (ddd, J = 8.9, 10.0, 18.1 Hz, 1H), 6.90 (s, 1H), 7.07–7.23 (m, 10H); ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C) δ 20.7, 22.7, 23.1, 23.6, 52.2, 57.9, 65.5, 118.0, 122.6, 123.2, 127.2, 127.8, 128.5, 129.2, 130.0, 132.1, 135.7, 136.5, 137.9, 139.8, 143.1, 169.1. HRMS (FAB): calcd for $C_{26}H_{27}O_3S$ ($M+H^+$), 419.1681; found, 419.1676.

References and Notes

(1) For reviews, see: (a) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*: John Wiley & Sons: New York, 1998. (b) Li, A.–H.; Dai, L.-X.; Aggarwal, V. K. *Chem. Rev.* **1997**, *97*, 2341. (c) Doyle, M. P. In *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon: Oxford, 1995; Vol. 12, pp 421-468.

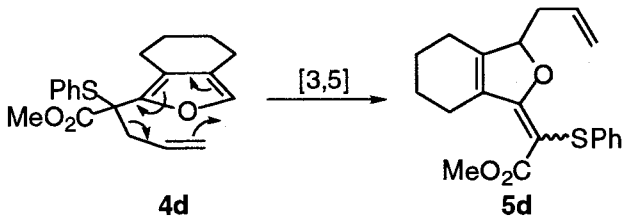
(2) For leading references, see: (a) Zhang, X.; Qu, Z.; Ma, Z.; Shi, W.; Jin, X.; Wang, J. *J. Org. Chem.* **2002**, *67*, 5621. (b) Simonneaux, G.; Galardon, E.; Paul-Roth, C.; Gulea, M.; Masson, S. *J. Organomet. Chem.* **2001**, *617-618*, 360. (c) Carter, D. S.; Van Vranken, D. L. *Org. Lett.* **2000**, *2*, 1303. (d) Carter, D. S.; Van Vranken, D. L. *Tetrahedron Lett.* **1999**, *40*, 1617. (e) Aggarwal, V. K.; Ferrara, M.; Hainz, R.; Spey, S. E. *Tetrahedron Lett.* **1999**, *40*, 8923. (f) Gulea, M.; Marchand, P.; Masson, S.; Saquet, M.; Collignon, N. *Synthesis* **1998**, 1635. (g) Meyer, O.; Cagle, P. C.; Weickhardt, K.; Vichard, D.; Gladysz, J. A. *Pure Appl. Chem.* **1996**, *68*, 79. (h) Cagle, P. C.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 3655. (i) Doyle, M. P.; Tamblyn, W. H.; Bagheri, V. *J. Org. Chem.* **1981**, *46*, 5094. (j) Kirmse, W.; Kapps, M. *Chem. Ber.* **1968**, *101*, 994.

(3) (a) Miki, K.; Nishino, F.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 5260. For isolation of chromium (2-furyl)carbenoid, see: (b) Miki, K.; Yokoi, T.; Nishino, F.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **2002**, *645*, 228. For vinylcarbenoids as

related carbenoid species, see: (c) Miki, K.; Ohe, K.; Uemura, S. *Tetrahedron Lett.* **2003**, *44*, 2019.

(4) For rhodium-catalyzed (2-pyrrolyl)carbenoid transferred cyclopropanation using ene-yne-imino ethers. Nishino, F.; Miki K.; Kato, Y.; Ohe, K.; Uemura, S. *Org. Lett.* **2003**, *5*, 2615. Also see Chapter 5.

(5) The isolated product **4d** was thermally labile, which gradually isomerized to another structural form **5d** at ambient temperature. Although the precise isomerism of **4d** is not clear at present, [3,5]sigmatropic rearrangement of an allylic moiety is a likely process for the isomerization. For precedents of [3,5]sigmatropic rearrangement, see: Battye, P. J.; Jones, D. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1807 and references therein.



(6) Two isomers stemed from epimers at quaternary carbon having R^1 and allyl groups of tetrahydrothiophene, although configuration is not yet clear. The intramolecular Diels-Alder reaction involving furan moieties as enophiles might take place via *exo*-cyclization. Similar stereochemical outcomes in the intramolecular Diels-Alder reactions have already been reported: Klein, L. L. *J. Am. Chem. Soc.* **1985**, *107*, 2573; Klein, L. L.; Shanklin, M. S. *J. Org. Chem.* **1988**, *53*, 5202; Sternbach, D. D.; Rossana, D. M. *J. Am. Chem. Soc.* **1982**, 104, 5853.

Chapter 8

Polyaddition and Polycondensation Reactions of (2-Furyl)carbenoid as Step-Growth Polymerization Strategies: Synthesis of Furylcyclopropane- and Furfurylidene-Containing Polymers

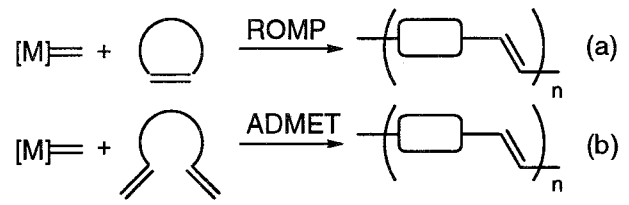
Abstract

As shown in Chapters 4, 6, and 7, (2-furyl)carbenoids generated *in situ* from ene-yne-ketones are versatile and reactive intermediates for several catalytic carbene transfer reactions. In this chapter, the results of application of these carbene transfer reaetions to polyaddition and polycondensation reactions of ene-yne-ketones are summarized. Ene-yne-ketones having suitable functionalities as carbene acceptors afford furylcyclopropane- and furfurylidene-containing polymers in good yields in the presence of $[Rh(OAc)_2]_2$ as catalyst. The key intermediate of these polymerizations is (2-furyl)carbene compelx generated by a nucleophilic attack of a carbonyl oxygen to an internal alkyne carbon in π-alkyne complex or σ-vinyl cationic complex. The number-average molecular weight (M_n) of both polymers is measured in a range of 6000-7000. The fluorescence emission of furfurylidene-containing polymers indicates the extension of π-conjugation caused by elongation of furfurylidene units.

Introduction

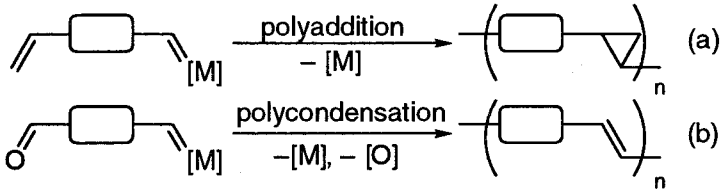
Transition metal carbene complex-catalyzed polymerizations, such as ring-opening-metathesis polymerization (ROMP, Scheme 1a)[1] and acyclic-diene-metathesis polymerization (ADMET, Scheme 1b),[2] have generated great excitement in recent years as to their wide applicability to the synthesis of various alkene-containing polymers. These polymerizations

Scheme 1



are exemplified by the mechanistic feature of chain-growth and step-growth metathesis polymerizations, respectively, and both of which require the involvement of carbenoid species as a catalyst. In this chapter, the author demonstrated transition metal-catalyzed polyaddition (Scheme 2a) and polycondensation (Scheme 2b) as a new step-growth polymerization strategy without involving metathesis catalysts, in which the intermediate is, instead, a metal carbenoid generated from a carbenoid trigger embeded in monomers. This method using

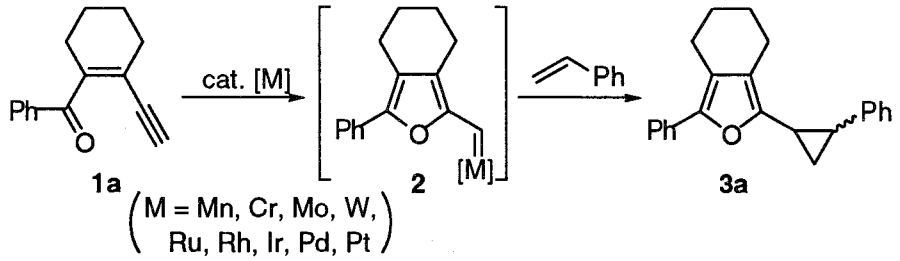
Scheme 2



a new class of monomers having both carbenoid donor and acceptor provides new alternating copolymers containing cyclopropanes or alkenes. The author has already reported the formation of (2-furyl)carbenoid **2** from ene-yne-ketone **1a** with group 6 transition metal complexes (Chapter 3),[3] and their application to catalytic cyclopropanation of various alkenes

leading to (2-furyl)cyclopropanes (Scheme 3, Chapter 4).[4] His continuous study mainly focusing on the catalytic reactions involving (2-furyl)carbenoids led him to find new carbene transfer polymerizations of ene-yne-ketones having suitable functionalities as carbenoid acceptors.

Scheme 3



Results and Discussion

At the outset of the studies, the author examined the synthesis of furylcyclopropane-containing polymer using catalytic cyclopropanation reaction. When ene-yne-ketone **1b** having a vinyl group at *ortho* position of a phenyl ring was treated in CH_2Cl_2 in the presence of a catalytic amount of $[Rh(OAc)_2]_2$ at room temperature, the reaction was immediately complete to afford (2-furyl)cyclopropane-containing polymer **3b** quantitatively as a yellow powder (85% yield after purification with gel permeation chromatography (GPC) in $CHCl_3$ eluent) (Scheme 4). *Meta*- and *para*-substituted ene-yne-ketones **1c** and **1d** also reacted to give the corresponding polymers **3c** and **3d** in 78% and 92% yield, respectively. The molecular weight measurements of polymers **3b-d** were performed by GPC in $CHCl_3$ eluent using a calibration curve of polystyrene standards (Table 1). The number-average molecular weight (M_n) of **3 b-d** was in a range of 6300-6900, which corresponds to a degree of polymerization of 27-29 with M_w/M_n of 1.1. The molecular weights (M_n and M_w) of **3d** obtained without any purification were diminished to 6100 and 6800, respectively, due to contamination of low-molecular weight oligomers. Optical properties of model compound

Scheme 4

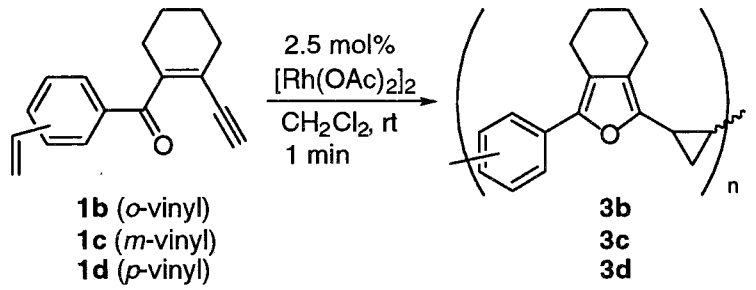


Table 1. Properties of **3a** and polymers **3b-3d**[a]

1	3	yield[b]	M_n[c]	M_w[c]	M_w/M_n[c]	UV λ_{max}[d]
1a	**3a**	—	—	—	—	316 nm
1b	**3b**	85%	6400	6800	1.1	317 nm
1c	**3c**	78%	6300	6800	1.1	323 nm
1d	**3d**	92%	6900	7600	1.1	327 nm

[a] Reaction conditions: a mixture of **1** (0.20 mmol) and $[Rh(OAc)_2]_2$ (0.0050 mmol) in CH_2Cl_2 (2 mL) were stirred at room temperature under N_2 for 1 min. [b] Isolated yield after purification with GPC ($CHCl_3$). [c] Determined by GPC ($CHCl_3$) with polystyrene standard. [d] Absorption spectra were recorded in dilute $CHCl_3$ solutions at room temperature.

3a and polymers **3b-d** are also listed in Table 1. The UV-vis spectra of **3a-d** in a dilute $CHCl_3$ solution at room temperature exhibited absorption maxima near 320 nm. Although there is no obvious difference in absorption maxima between model compound **3a** and polymers **3b-d**, unique structures of alternating copolymers having regularly embedded cyclopropane units would attract a great deal of interest in polymer chemistry.

Since the extension of π-conjugation was anticipated by introducing a C=C bond instead of a cyclopropane ring in **3b-d**, the author next investigated the synthesis of furfurylidene-containing polymer **4** by using a carbene transfer reaction (Scheme 2b). Prior to examine polycondensation reactions, the synthesis of furfurylidene-containing compound **4a** was attempted as a model compound. When the reaction of **1a** with 1.2 equiv of benzaldehyde and 1.2 equiv of triphenylphosphine was carried out in $ClCH_2CH_2Cl$ in the presence of 2.5 mol% of $[Rh(OAc)_2]_2$ at 70 °C for 1 h, 2-benzylidenefuran **4a** was obtained in 77% yield (*cis*:*trans* = 10:90) (Scheme 5). In the absence of triphenylphosphine, **4a** was not obtained at all.[5] Therefore, the formation of **4a** can be rationalized by intervention of (2-

furyl)phosphorus ylide **5** generated from (2-furyl)carbenoid **2** and triphenylphosphine followed by Wittig-type condensation of the ylide with benzaldehyde.[6,7] Thus, he extended this condensation protocol to polymer synthesis. The polycondensation reaction of ene-yne-ketones, **1e** and **1f**, as monomers having a formyl functionality on phenyl ring afforded the

Scheme 5

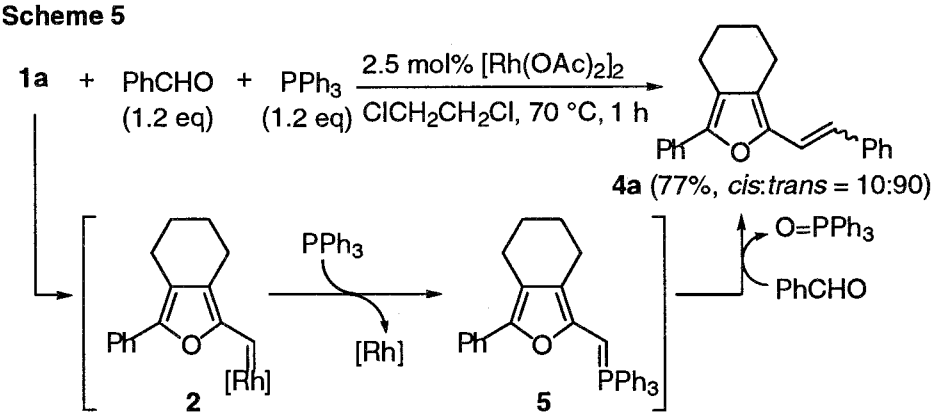
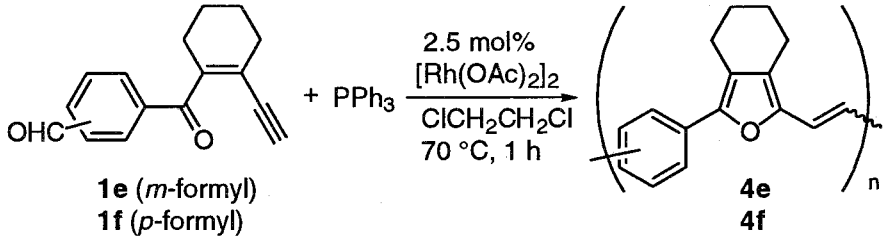


Table 2. Properties of **4a** and polymers **4e** and **4f**[a]



1	4	yield[b]	M_n[c]	M_w[c]	M_w/M_n[c]	UV λ_{max}[d]	PL λ_{max}[d,e]
1a	**4a**	77%	—	—	—	372 nm	433 nm
1e	**4e**	51%	6000	6500	1.1	380 nm	461 nm
1f	**4f**	58%	6200	6900	1.1	457 nm	559 nm

[a] Reaction conditions: a mixture of **1** (0.20 mmol), triphenylphosphine (0.48 mmol) and $[Rh(OAc)_2]_2$ (0.0050 mmol) in $ClCH_2CH_2Cl$ (2 mL) were stirred at 70 °C under N_2 for 1 h. [b] Isolated yield after purification with GPC ($CHCl_3$). [c] Determined by GPC ($CHCl_3$) with polystyrene standard. [d] Absorption and emission spectra were recorded in dilute $CHCl_3$ solutions at room temperature. [e] Solutions (2.0×10^{-4} M) were excited at 380 nm (**4a** and **4e**) or 440 nm (**4f**).

corresponding polymers **4e** and **4f** in 51% and 58% yields, respectively. The number-average molecular weights (M_n) of **4e** and **4f** are 6000 and 6200, which corresponded to a degree of polymerization of 27 and 28, respectively. Optical properties of model compound

4a and polymers **4e** and **4f** are summarized in Table 2. The UV-vis spectra of model compound **4a** and polymer **4e** exhibited absorption maxima at near 380 nm, while the spectra of **4f** (λ_{max} = 457 nm) showed a red shift of 85 nm relative to **4a** (λ_{max} = 372 nm) under the identical condition. This result indicates the effective extension of π-conjugation caused by elongation of 5-aryl-2-furfurylidene units in **4f**. The fluorescence emission spectra of the solutions of **4a**, **4e**, and **4f** in $CHCl_3$ (2.0 x 10^{-4} M) at room temperature were also measured on excitation at 380 nm (**4a** and **4e**) or 440 nm (**4f**). The emission peaks were observed at 433 nm, 461 nm, and 559 nm, respectively. In the case of polymer **4f**, the dependence of the spectra on its concentration was also observed (Figure 1). These findings suggest that the emission peak at 559 nm in concentrated solution may be the result of intermolecular excimer formation.[8] On the other hand, the formation of excimer in the solid film resulted in a decrease of luminescence yield, the weak emission λ_{max} of **4f** being observed at 618 nm.

In conclusion, the author has developed the polymerization of ene-yne-ketones to give furylcyclopropane-containing polymer **3** and furfurylidene-containing polymer **4** using (2-furyl)carbene Rh-complexes generated *in situ*. The present new methodology may find a wide applicability to polymer synthesis and some applications in other polymerization.

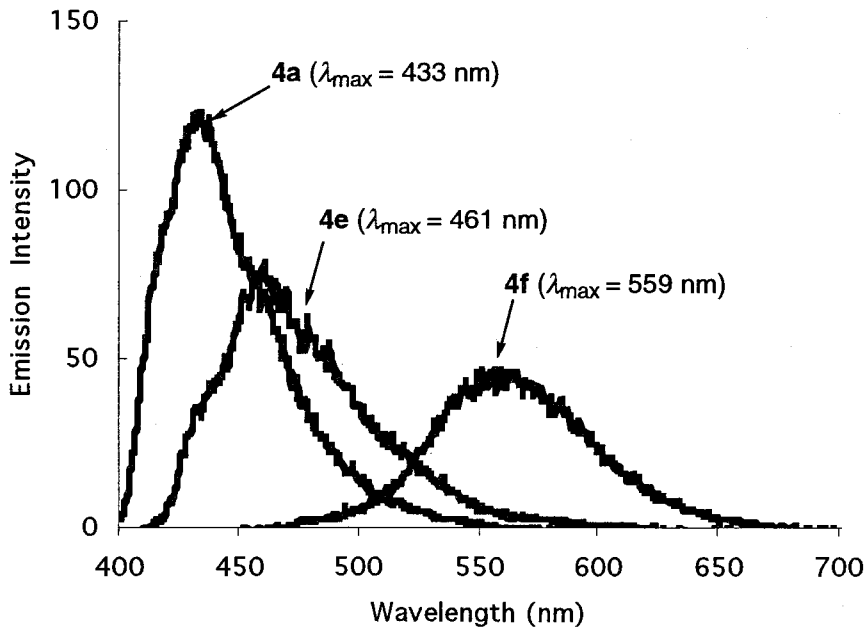


Figure 1. Comparison of fluorescence spectra of **4a**, **4e**, and **4f** in $CHCl_3$ solution (2.0 x 10^{-4} M). Solutions were excited at 380 nm (**4a** and **4e**) or 440 nm (**4f**).

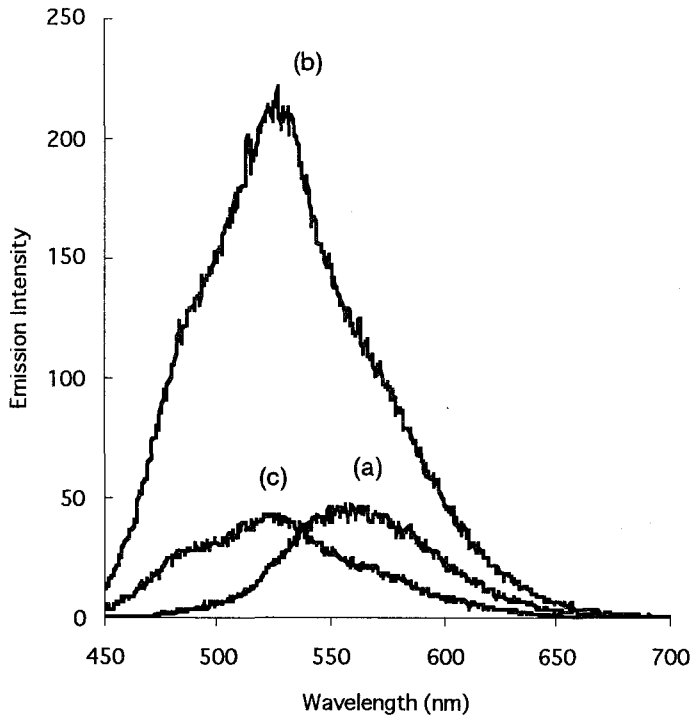


Figure 2. Dependence of fluorescence spectra of polymer **4f** on its concentration in $CHCl_3$ solution (excitation wavelength at 440 nm). (a) 2.0×10^{-4} M (λ_{max} = 559 nm), (b) 2.0×10^{-5} M (λ_{max} = 527 nm), (c) 2.0×10^{-6} M (λ_{max} = 522 nm).

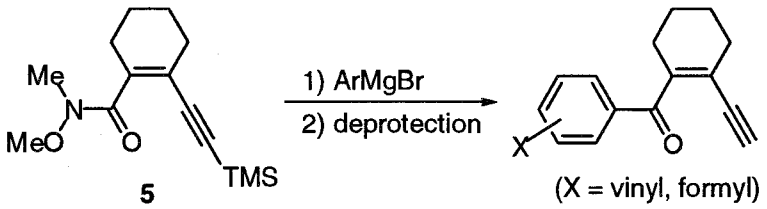
Experimental

General Procedure. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies were performed with Merck silica gel 60. 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, m: multiplet. IR spectra were recorded on an FT-IR spectrometer. UV-visible spectra were recorded on SHIMADZU MultiSpec-1500 spectrometer. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. Melting points are uncorrected. High-resolution mass spectra (FAB HRMS) and low-resolution mass spectra (FAB LRMS) were obtained with JEOL JMX-SX 102A spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University.

Synthesis of Substrates.

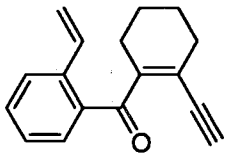
Substrates were prepared as shown in Scheme 6. Substrate **1a** and amide **5** were prepared by our reported procedure.[3,4]

Scheme 6



Typical Procedue for Synthesis of Ene-Yne-Carbonyl Compounds 1b-1d.

Ene-yne-carbonyl compound 1b.



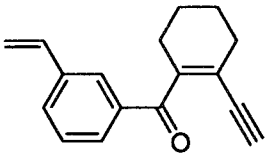
1b

To a suspension of Mg (99 mg, 4.0 mmol) in THF (5 mL) was dropwise added *o*-bromostyrene (0.73 g, 4.0 mmol) at 0 °C under N_2. The suspension was stirred for 1 h at room temperature, and the resulting mixture was slowly added to a solution of **5** (0.54 g, 2.0 mmol) in THF (15 mL) at -78 °C. After stirring for 48 h at room temperature, the mixture was washed with saturated aqueous NH_4Cl solution (20 mL x 2), and the aqueous phase was extracted with Et_2O (20 mL x 2). The combined organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 30/1) as an eluent to afford crude ene-yne-ketone (62 mg, 0.20 mmol) as a yellow oil.

The crude product was dissolved in MeOH (2 mL) and to this solution was added K_2CO_3 (69 mg, 0.50 mmol) at room temperature. After stirring for 30 min, the suspension was poured into Et_2O/H_2O (20 mL/20 mL), and the aqueous phase was extracted with Et_2O (10 mL x 2). The combined organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 30/1) as an eluent to afford crude ene-yne-ketone **1b** (43 mg, 0.18 mmol, 9% yield) as a yellow oil; IR (neat) 636, 670, 726, 766, 917, 1245, 1292, 1596,

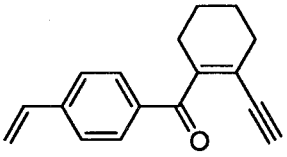
1650 (C=O), 2090 (C≡C), 2859, 2933, 3290 (≡C-H) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 1.66-1.74 (m, 4H), 2.28-2.36 (m, 2H), 2.38-2.46 (m, 2H), 2.86 (s, 1H), 5.30 (d, J = 11.1 Hz, 1H), 5.64 (d, J = 17.6 Hz, 1H), 7.03 (dd, J = 11.1, 17.6 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.38-7.47 (m, 2H), 7.53 (d, J = 7.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C) δ 21.6, 21.8, 26.8, 31.5, 82.0, 84.3, 116.1, 125.4, 126.3, 127.1, 129.2, 130.9, 135.1, 137.7, 138.2, 145.8, 199.5. HRMS (FAB): calcd for $C_{17}H_{17}O$ ($M+H^+$), 237.1279; found, 237.1275.

Ene-yne-carbonyl compound 1c.



1c A yellow solid (46% yield for 2 steps); mp. 40.5-42.5 °C; IR (KBr) 685, 706, 748, 767, 807, 915, 997, 1162, 1266, 1463, 1595, 1664 (C=O), 2091 (C≡C), 2856, 2931, 3239 (≡C-H) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.70-1.82 (m, 4H), 2.35-2.37 (m, 4H), 2.85 (s, 1H), 5.33 (d, J = 11.2 Hz, 1H), 5.82 (d, J = 17.6 Hz, 1H), 6.76 (dd, J = 11.2, 17.6 Hz, 1H), 7.41 (d, J = 7.6, 8.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.6, 1H), 7.93 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 21.5, 21.9, 27.4, 29.9, 82.3, 82.3, 115.1, 119.9, 127.0, 128.6, 129.1, 130.6, 135.4, 136.2, 137.9, 145.7, 198.7. HRMS (FAB): calcd for $C_{17}H_{17}O$ ($M+H^+$), 237.1279; found, 237.1281.

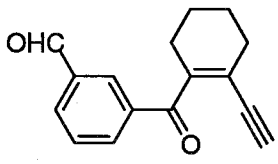
Ene-yne-carbonyl compound 1d.



1d A yellow solid (38% yield for 2 steps); mp. 40.0-41.2 °C; IR (KBr) 617, 648, 710, 768, 851, 921, 990, 1183, 1258, 1279, 1601, 1660 (C=O), 2092 (C≡C), 2859, 2933, 3290 (≡C-H) cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 1.73-1.78 (m, 4H), 2.33-2.36 (m, 4H), 2.84 (s, 1H), 5.40 (d, J = 11.3 Hz, 1H), 5.88 (d, J = 17.3 Hz, 1H), 6.76 (dd, J = 11.3, 17.3 Hz, 1H), 7.48 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.5 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C) δ 21.5, 21.9, 27.4, 29.8, 82.2, 82.4, 116.6, 119.5, 126.2, 129.9, 135.0, 136.0, 142.1, 145.8, 198.2. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.17; H, 6.80.

Typical Procedue for Synthesis of Ene-Yne-Carbonyl Compounds 1e and 1f.

Ene-yne-carbonyl compond 1e.



1e

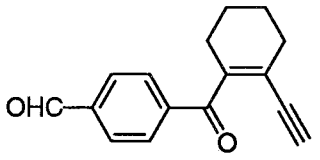
To a suspension of Mg (0.24 g, 10 mmol) in THF (20 mL) was dropwise added *m*-bromobenzaldehyde dimethylacetal (1.3 g, 10 mmol) at 0 °C under N_2. The suspension was stirred for 1 h at room temperature, and the resulting mixture was slowly added to a solution of **5** (1.3 g, 5.0 mmol) in THF (1 mL) at -78 °C. After stirring for 2 h at room temperature, the mixture was washed with saturated aqueous NH_4Cl solution (25 mL x 2), and the aqueous phase was extracted with Et_2O (20 mL x 2). The combined organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 10/1) as an eluent to afford crude ene-yne-ketone (0.32 g, 0.89 mmol) as a yellow oil.

The crude product was dissolved in CH_2Cl_2/acetone (not dried, 20 mL/15 mL), and to this solution was added Montmorillonite K-10 (0.50 g, purchased from Aldrich) at room temperature. After stirring for 30 min, the suspension was filtered, and the solvents were removed under reduced pressure. The residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 10/1) as an eluent to afford crude ene-yne-ketone (0.28 g, 0.89 mmol) as a yellow oil.

The crude product was dissolved in DMSO (5 mL) and to this solution was added KF (0.40 g, 6.9 mmol) at room temperature. After stirring for 10 min, the suspension was poured into Et_2O/H_2O (20 mL/20 mL), and the aqueous phase was extracted with Et_2O (10 mL x 2). The combined organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 10/1) as an eluent to afford crude ene-yne-ketone **1e** (0.15 g, 0.65 mmol, 13% yield) as an orange oil; IR (KBr) 648, 677, 696, 737, 795, 810, 954, 1107, 1154, 1199, 1261, 1281, 1296, 1355, 1382, 1434, 1599, 1667 (C=O), 1702 (C=O), 2094 (C≡C), 2081, 2936, 3270 (≡C-H) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.75-1.82 (m, 4H),

2.32-2.44 (m, 4H), 2.84 (s, 1H), 7.65 (dd, J = 7.6, 7.6 Hz, 1H), 8.09 (d. J = 7.6 Hz, 1H), 8.16 (d, J = 7.6, 1H), 8.35 (s, 1H), 10.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 21.4, 21.8, 27.1, 30.1, 82.2, 83.5, 121.7, 129.3, 130.9, 133.1, 134.9, 136.5, 137.2, 144.7, 191.3, 197.6. HRMS (FAB): calcd for $C_{16}H_{15}O_2$ ($M+H^+$), 239.1072; found, 239.1070.

Ene-yne-carbonyl compound 1f.



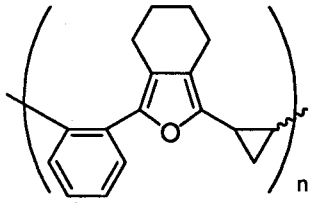
1f

A red solid (52% yield for 2 steps); mp. 47.5-49.0 °C; IR (KBr) 751, 796, 847, 1206, 1253, 1278, 1301, 1654 (C=O), 1697 (C=O), 2096 (C≡C), 2840, 2859, 2937, 3257(≡C-H) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 1.72-1.84 (m, 4H), 2.30-2.46 (m, 4H), 2.84 (s, 1H), 7.95 (d, J = 8.4 Hz, 2H), 8.02 (d. J = 8.4 Hz, 2H), 10.10 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C) δ 21.5, 21.8, 27.1, 30.2, 82.2, 83.7, 122.0, 129.6, 129.8, 138.8, 141.0, 144.8, 191.5, 197.9. Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.37; H, 6.13.

Typical Procedue for Rhodium-Catalyzed Polymerization Using Sequential Cyclopropanation.

To a solution of ene-yne-carbonyl compound **1** (0.20 mmol) in CH_2Cl_2 (2 mL) was added $[Rh(OAc)_2]_2$ (2.2 mg, 0.0050 mmol) at room temperature under N_2. After stirring for 1 min, the rhodium catalyst was removed by centrifugal separator. The solvent was removed under reduced pressure to afford cyclopropane-containing polymer **3** as a yellow powder. Model compound **3a** was prepared by our reported method.[4]

Polymer 3b.

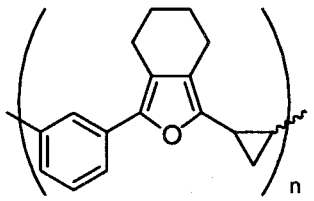


3b

A yellow powder (85% yield); IR (KBr) 759, 848, 907, 1246, 1445, 1600, 1669, 1725, 2856, 2929, 3060 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.12-1.86 (br m, 6H), 1.86-2.89 (br m, 6H), 6.57-7.85 (br m, 4H) [the following peaks are not attributed to polymer unit, and therefore they would indicate that there are terminal or internal alkene parts in this polymer **3b**, the values of protons being relative ratios compared

with unit protons; δ 4.94-5.39 (m, 0.2H), 5.39-5.75 (br m, 0.2H), 6.28-6.57 (m, 0.2H)]; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 11.0, 14.1, 20.3-20.7 (br), 22.0-23.0 (br), 28.9, 29.7, 30.4, 34.1, 38.7, 68.1, 113.7, 119.2-119.4 (br), 120.7, 125.1-130.9 (br), 132.4, 135.4, 136.2, 137.2, 137.3, 145.4-145.5 (br), 167.8. UV/vis ($CHCl_3$): λ_{max} (ε), 317 (3845).

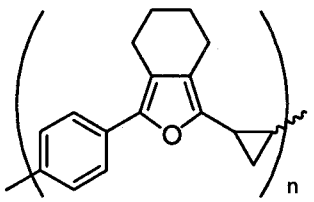
Polymer 3c.



3c

A yellow powder (78% yield); IR (KBr) 697, 797, 907, 1029, 1082, 1257, 1277, 1445, 1602, 1668, 2856, 2930 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.98-1.86 (br m, 6H), 1.86-2.97 (br m, 6H), 6.85-7.87 (br m, 4H) [the following peaks are not attributed to polymer unit, and therefore they would indicate that there are terminal or internal alkene parts in this polymer **3c**, the values of protons being relative ratios compared with unit protons; δ 5.10-5.40 (br m, 0.3H), 5.56-5.96 (br m, 0.3H), 6.60-6.85 (br m, 0.3H)]; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 10.8-10.9 (br), 14.0, 16.6, 20.7, 22.3-23.5 (br), 25.8, 29.7, 29.8, 30.0, 30.9, 34.1, 36.2, 44.6, 113.6-111.7, 119.3, 121.4-121.9 (br), 123.4, 123.7-123.8 (br), 124.2, 124.9, 125.4, 126.1, 126.7, 127.3, 127.4-127.8 (br), 128.3-128.6 (br), 131.3, 132.4, 134.6, 137.1-137.5 (br), 137.5, 144.6, 145.3, 155.1. UV/vis ($CHCl_3$): λ_{max} (ε), 323 (2490).

Polymer 3d.



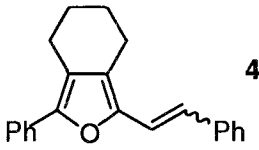
3d

A yellow powder (92% yield); IR (KBr) 697, 797, 907, 1029, 1082, 1257, 1277, 1445, 1602, 1668, 2856, 2930 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.06-1.92 (br m, 6H), 1.93-3.07 (br m, 6H), 6.81-8.76 (br m, 4H) [the following peaks are not attributed to polymer unit, and therefore they would indicate that there are terminal or internal alkene parts in this polymer **3d**, the values of protons being relative ratios compared with unit protons; δ 5.07-5.54 (m, 0.2H), 5.54-6.06 (m, 0.2H), 6.50-6.80 (m, 0.2H)]; ^{13}C NMR (68 MHz, $CDCl_3$, 25 °C) δ 10.9, 14.0, 20.7, 22.3-23.7 (br), 112.7, 118.2-

118.4 (br), 119.6, 121.1, 123.2-123.8 (br), 126.2, 127.8-128.1 (br), 128.8, 129.7-129.9 (br), 136.3-136.6 (br), 144.2, 144.7, 145.5. UV/vis ($CHCl_3$): λ_{max} (ε), 327 (3735).

Rhodium-Catalyzed Carbene Transfer Reaction to Phosphine Atom and Sequential Wittig-Type Condensation of Resulting Phosphorus Ylide.

Model compound 4a.



4a

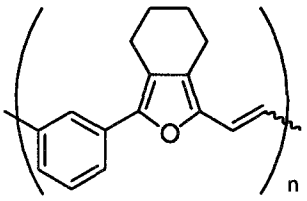
To a solution of ene-yne-ketone **1a** (42 mg, 0.20 mmol), benzaldehyde (24 μL, 0.24 mmol), and triphenylphosphine (68 mg, 0.24 mmol) in 1,2-dichloroethane (2 mL) was added $[Rh(OAc)_2]_2$ (2.2 mg, 0.0050 mmol) at room temperature under N_2. After stirring at 70 °C for 1 h, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane/AcOEt (v/v = 60/1) as an eluent to afford **4a** (46 mg, 0.15 mmol, 77% yield determined by ^1H NMR) as a yellow oil (After recrystallization of **4a**, *trans*-**4a** was obtained as a yellow solid); *trans* isomer: mp. 60.5-63.5 °C; IR (KBr) 542, 694, 723, 752, 763, 1028, 1071, 1120, 1176, 1258, 1438, 1448, 1491, 1597, 1665, 2858, 2932 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.80 (m, 4H), 2.60-2.72 (m, 2H), 2.76-2.84 (m, 2H), 6.89 (d, J = 16.2 Hz, 1H), 7.02 (d, J = 16.2 Hz, 1H), 7.32-7.51 (m, 8H), 7.70 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 21.1, 22.7, 23.0, 23.3, 115.0, 120.7, 123.4, 124.4, 125.0, 126.0, 126.2, 127.0, 128.5, 128.6, 131.3, 137.6, 146.1, 146.2. UV/vis $CHCl_3$: λ_{max} (ε), 372 (6867). HRMS (FAB): calcd for $C_{22}H_{20}O$ (a mixture of *cis* and *trans* isomers) (M^+), 300.1514; found, 300.1502.

Typical Procedure for Rhodium-Catalyzed Polymerization Using Wittig-Type Condensation of Phosphorus Ylide.

To a solution of ene-yne-carbonyl compound **1** (0.20 mmol) and triphenylphosphine (0.13 g, 0.50 mmol) in 1,2-dichloroethane (2 mL) was added $[Rh(OAc)_2]_2$ (2.2 mg, 0.0050 mmol) at room temperature under N_2. After stirring at 70 °C for 1 h, the solvent was

removed under reduced pressure to give crude polymer **4** containing phosphine compounds, which could be removed by GPC system with $CHCl_3$ as an eluent.

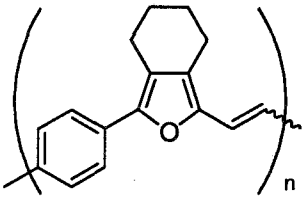
Polymer 4e.



4e

An orange powder (51% yield); IR (KBr) 687, 698, 788, 795, 949, 1030, 1084, 1164, 1188, 1384, 1437, 1598, 1630, 1680, 2855, 2929, 3446 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.31-2.00 (br m, 4H), 2.20-2.97 (br m, 4H), 6.81-7.24 (br m, 1H), 7.20-8.25 (br m, 5H) [δ 10.00 (br s, 0.3H)]; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 14.0, 21.0, 21.1, 22.3-23.2 (br), 29.7, 34.1, 115.1, 121.0-137.9 (br), 144.9-147.0 (br), 192.3. UV/vis ($CHCl_3$): λ_{max} (ε), 380 (17665).

Polymer 4f.



4f

A red powder (58% yield); IR (KBr) 1083, 1438, 1598, 2857, 2928, 3427 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.37-2.14 (br m, 4H), 2.23-3.08 (br m, 4H), 6.69-7.18 (m, 1H), 7.11-8.20 (br m, 5H) [δ 9.95 (br s, 0.3H)]; ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.1-21.2 (br), 22.3-22.5 (br), 23.0-23.2 (br), 123.5-125.5 (br), 126.0-126.5 (br), 128.1, 128.2, 128.4, 128.6, 130.1-130.3 (br), 132.0-132.2 (br), 133.8, 134.0, 134.7, 135.1, 137.0, 191.6. UV/vis ($CHCl_3$): λ_{max} (ε), 457 (16672).

Acknowledgment

The author thanks Professor Yoshiki Chujo, Dr. Kensuke Naka, and Mr. Tomokazu Umeyama for their helpful discussion and assistance with GPC and fluorescence spectroscopy as well as helpful discussion.

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(1) For recent reviews on ROMP, see: (a) Grubbs, R. H.; Khosravi, E. *Mater. Sci. Technol.* **1999**, *20*, 65. (b) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565.

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(3) Miki, K.; Yokoi, T.; Nishino, F.; Ohe, K.; Uemura, S. *J. Organomet. Chem.* **2002**, *645*, 228.

(4) Miki, K.; Nishino, F.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 5260.

(5) Phosphine-mediated generation of (2-furyl)phosphorus ylides followed by sequential Wittig-type condensation with aldehydes has already been reported. Kuroda, H.; Hanaki, E.; Kawakami, M. *Tetrahedron Lett.* **1999**, *40*, 3753. However, the reaction shown in Scheme 5 did not proceed smoothly to give **4a** in the absence of $[Rh(OAc)_2]_2$ (<20% even after 24 h).

(6) For recent reports on transition metal-catalyzed olefination of aldehydes using diazoalkanes and phosphine compounds, see: (a) Mirafzal, G. A.; Cheng, G.; Woo, L. K. *J. Am. Chem. Soc.* **2002**, *124*, 176. (b) Cheng, G.; Mirafzal, G. A.; Woo, L. K. *Organometallics* **2003**, *22*, 1468 and references therein. (c) Aggarwal, V. K.; Fulton, J. R.; Sheldon, C. G.; de Vicente, J. *J. Am. Chem. Soc.* **2003**, *125*, 6034.

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(8) For a review on excimer formation and luminescence in conjugated polymers, see: (a) Conwell, E. *Trends Polym. Sci.* **1997**, *5*, 218. For leading references in this area, see: (b) Li, H.; Powell, D. R.; Hayashi, R. K.; West, R. *Macromolecules* **1998**, *31*, 52. (c) Cornil, J.; dos Santos, D. A.; Crispin, X.; Silbey, R.; Bredas, J. l. *J. Am. Chem. Soc.*

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Part III

Transition Metal-Catalyzed Carbene Transfer Reactions Using Propargylic Carboxylates as Precursors of Vinylcarbenoids

Chapter 9

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

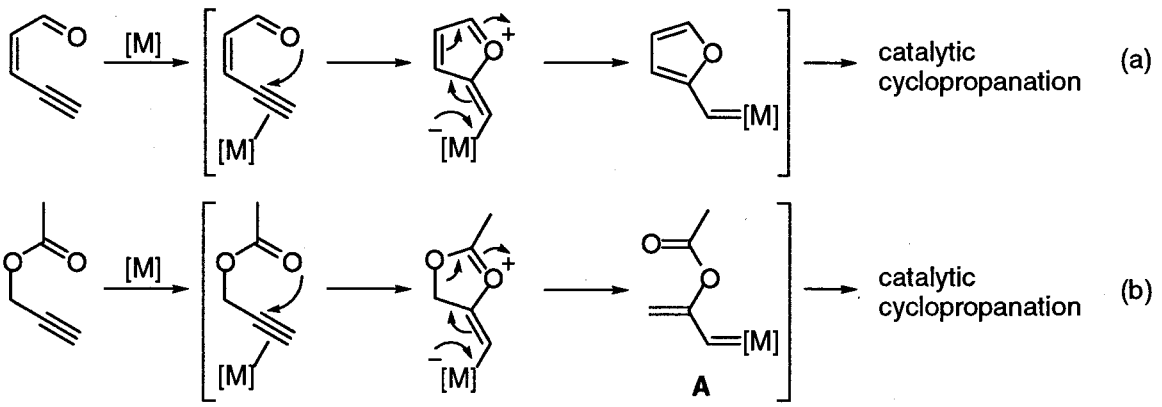
Abstract

Intermolecular cyclopropanation reactions of various alkenes with propargylic carboxylates are catalyzed by $[RuCl_2(CO)_3]_2$ to give vinylcyclopropanes 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 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, the latter being thermally derived from the initially formed *cis-vic*-isomers via Cope-type rearrangement. The present reaction is chemically equivalent to transition metal-catalyzed cyclopropanation reaction using α-diazoketones as carbenoid precursors.

Introduction

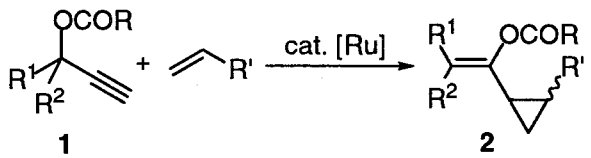
The *in situ* generation of carbenoid species involving transition metal compounds is well-known and the species has been applied mostly to cyclopropanation and insertion reactions. One of the most versatile methods to generate carbenoids is a decomposition reaction of diazoalkanes by transition metal 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 catalytic process.[8] Most recently, the author has 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 $Cr(CO)_5(THF)$, $[Rh(OAc)_2]_2$, $[(p\text{-cymene})RuCl_2]_2$,

Scheme 1



$[RhCl(cod)]_2$, $[RuCl_2(CO)_3]_2$, $PdCl_2$ 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 him to develop a new method for the preparation of vinylcarbenoid intermediate **A** from propargylic carboxylates, in which the nucleophilic attack of a carbonyl oxygen followed by bond cleavage at 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 vinylcarbenoids were effectively trapped by an alkenyl moiety in the molecule to give carbocyclic compounds in $PtCl_2$-catalyzed cyclization of dienynes.[12] His continuous investigation for vinylcarbene transfer reactions led him to find an efficient ruthenium-catalyzed intermolecular cyclopropanation of alkenes using propargylic carboxylates (Scheme 2).[13] In this chapter, the author described the scope and limitations of

Scheme 2



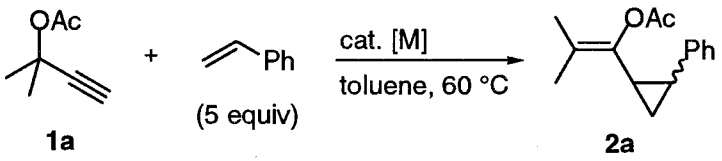
the cyclopropanation reaction involving vinylcarbenoids generated *in situ* from propargylic carboxylates and $[RuCl_2(CO)_3]_2$. The reaction has also been applied to conjugated dienes to construct cycloheptadiene structures, representing a formal [3+4] cyclization using the carboxylates as three-carbons components.

Results and Discussion

1. Effect of Catalyst

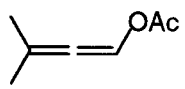
At first, the cyclopropanation of styrene with 2-methyl-3-butyn-2-yl acetate (**1a**) in the presence of a transition metal catalyst (2.5-5 mol%), which had been effective for catalytic cyclopropanation via (2-furyl)carbene complexes, was examined.[9a] Results of catalyst-screening are given in Table 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

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



entry	[M]	time	**2a** (%)[b]	*cis*:*trans*[b]	allene (%)[b]
1	$[RuCl_2(CO)_3]_2$	18 h	86	80:20	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

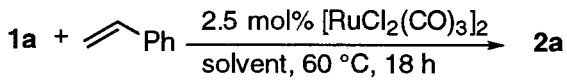
90% yield (*cis*:*trans* = 86:14). In contrast, $[Rh(OCOCF_3)_2]_2$, which is known as a good catalyst for carbene transfer reaction, could not catalyze the present cyclopropanation, but it gave only allene **3** quantitatively (entry 3). $IrCl_3$, $[IrCl(cod)]_2$, and $AuCl_3$ were also found to catalyze the cyclopropanation to give **2a** in 45%, 37% and 63% yields with 72:28, 70:30, and 79:21 diastereomeric ratios, respectively, along with **3** as a byproduct (entries 4, 5 and 6). Particularly, $AuCl_3$ showed a highest activity for both of 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 cyclopropanation 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.

2. 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 in toluene, producing **2a** in 95% yield with 79:21 diastereomeric ratio (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 desired cyclopropanated product in each reaction (entries 4-6). Next, the cyclopropanation using toluene or DCE as effective solvents were 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 the 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.

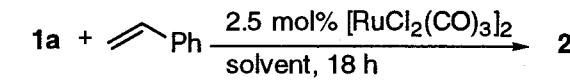
Table 2. Effect of Solvent.[a]



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]



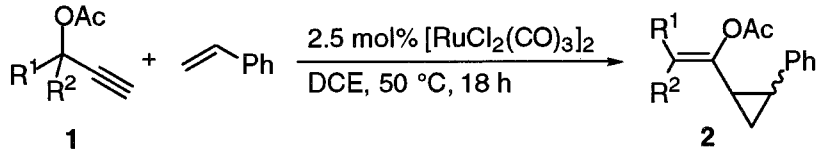
entry	solvent	temp.	yield[b] (*cis*:*trans*)[c]
1	toluene	50 °C	75% (87:13)
2	toluene	60 °C	86% (84:16)
3[d]	toluene	80 °C	83% (76:24)
4[e]	DCE	30 °C	83% (93:7)
5	DCE	50 °C	99% (87:13)
6	DCE	60 °C	95% (79:21)
7[d]	DCE	80 °C	83% (77:23)

[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** was recovered.

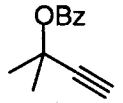
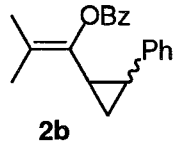
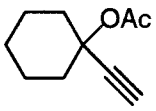
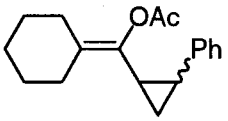
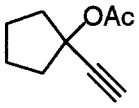
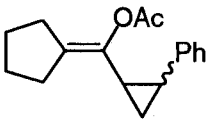
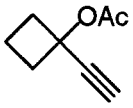
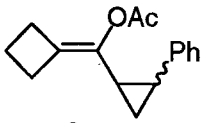
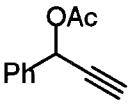
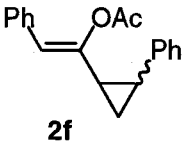
3. Cyclopropanation Using Various Propargylic Carboxylates and Alkenes

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

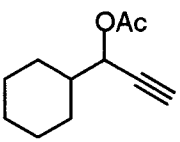
Table 4. Ru-Catalyzed Cyclopropanation of Styrene with **1**[a]



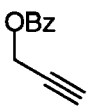
1 **2**

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)

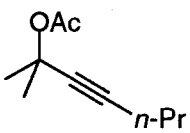
[a] Reaction conditions: **1** (0.2 mmol), styrene (1.0 mmol), $[RuCl_2(CO)_3]_2$ (0.005 mmol), DCE (1.0 mL), 50 °C. [b] The values in the parentheses were obtained from the reactions in toluene at 60 °C. [c] Diastereomeric ratios were determined by ^{1}H NMR or GLC.



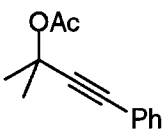
1g



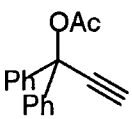
1h



1i



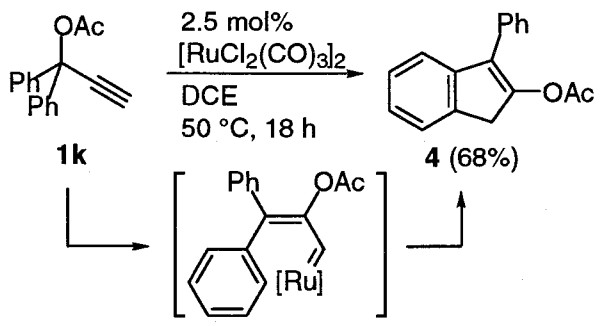
1j



1k

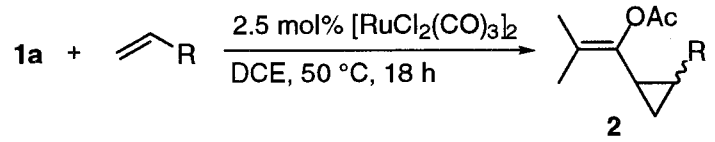
gave the cyclopropanated product **2b** in 90% yield (*cis*:*trans* = 88:12) (entry 1). Cyclic acetates **1c**, **1d**, and **1e** reacted with styrene to give the corresponding products **2c**, **2d**, and **2e** in 91%, 97%, and 93% yield, respectively (entries 2, 3 and 4). In the case of tertiary propargylic carboxylates, the reactions conducted in toluene gave the corresponding products with slightly lower yields compared with those in DCE. The reaction with secondary propargylic acetate **1f** proceeded smoothly to give **2f** in 77% yield with a 75:25 diastereomeric ratio, although the treatment in toluene at 60 °C was essential (entry 5).[17,18] Secondary propargylic acetate **1g** having an alkyl group at 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 other 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).

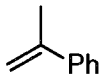
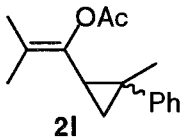
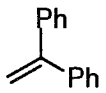
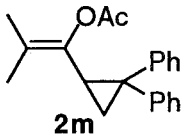
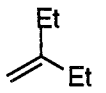
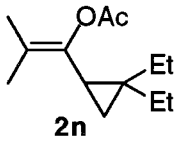
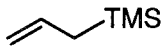
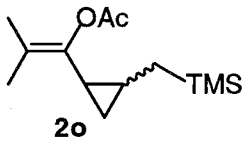
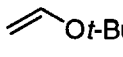
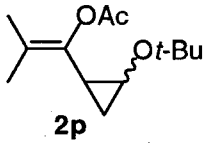
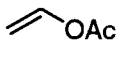
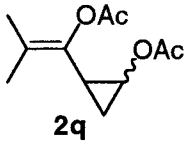
Scheme 3



The formation of **4** is considered to be attributed to formal insertion of vinylcarbenoid to C-H bond at *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 cyclopropanes **2l** and **2m** in 91% (d.r. = 68:32) and 71% yields, respectively (entries 1 and 2). 2-Ethylbut-1-ene and

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), 50 °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.

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 were 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 reaction of oct-1-ene or 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.

4. 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 Ru-vinylcarbenoid intermediate (Figure 1). Takahashi *et al.* have reported the ruthenium-

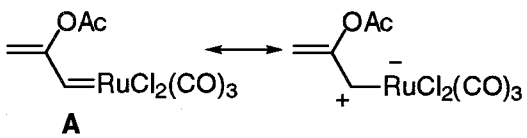
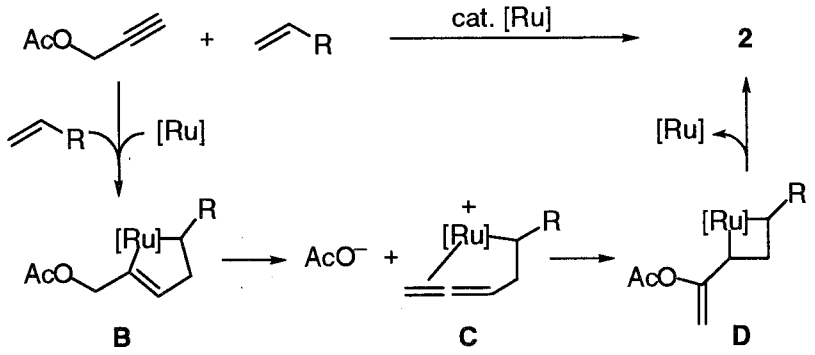


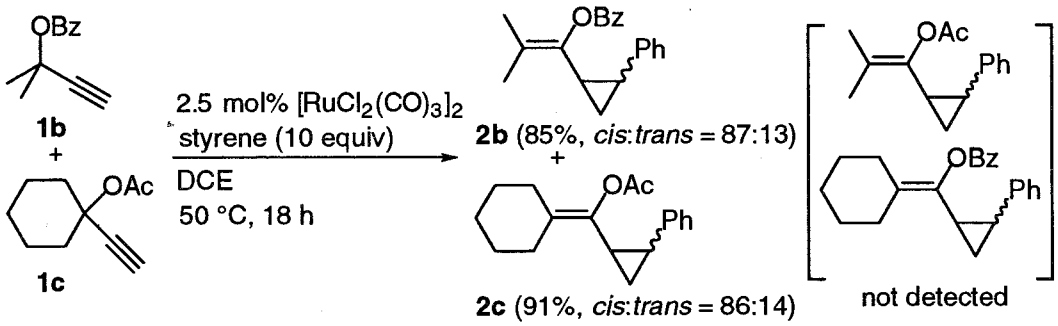
Fig. 1 Ruthenium Vinylcarbenoid as a Plausible Intermediate

catalyzed cyclopropanation of norbornene using propargylic alcohols and their ethers via a ruthenacyclopentene intermediate, in which norbornene was the only alkene to react.[19] Keeping 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 the author thinks that Ru-vinylcarbenoids are likely as intermediates in our case, it might be meaningful to consider a step containing ruthenacycles. On the basis of mechanism proposed by Takahashi *et al.*, a plausible reaction course might be outlined in Scheme 4 in the present 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 implys the possibility of the intermolecular transfer of acetate from one molecule to another. However, such possibility was excluded by the experimental results of crossover reaction

Scheme 4



Scheme 5

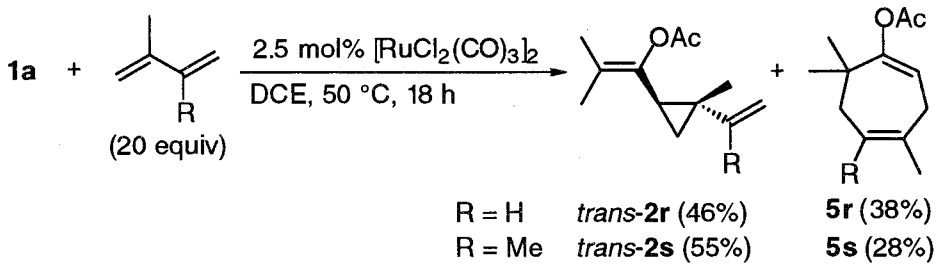


using two types of propargylic carboxylates in the presence of $[RuCl_2(CO)_3]_2$. Thus, when the reaction of styrene with a mixture of an equimolar amount of **1b** and **1c** as competitive reactants was carried out, two cyclopropanated products **2b** and **2c** were produced in high yields without any crossover products (Scheme 5). This result as well as the alkene reactivity strongly supports that the present cyclopropanation proceeds via a Ru-vinylcarbenoid (**A**)[20,21] generated by an intramolecular acetoxy migration as shown in Scheme 1b.

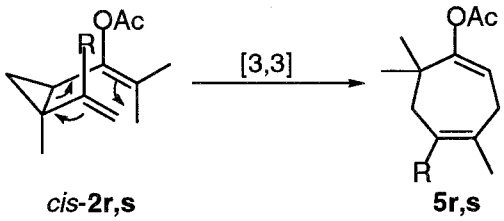
5. Catalytic Cyclopropanation of Dienes

Finally, the author examined the cyclopropanation of conjugated dienes with propargylic carboxylates **1a**, **1b**, and **1c** 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%) with 1,4-cycloheptadiene **5r** (38%) (Scheme 6). The reaction of 2,3-dimethyl-1,3-butadiene with **1a** also gave similar products, *trans*-**2s**[22] (55%) and **5s** (28%). The formation of 1,4-cycloheptadiene **5** in each case can be explained

Scheme 6

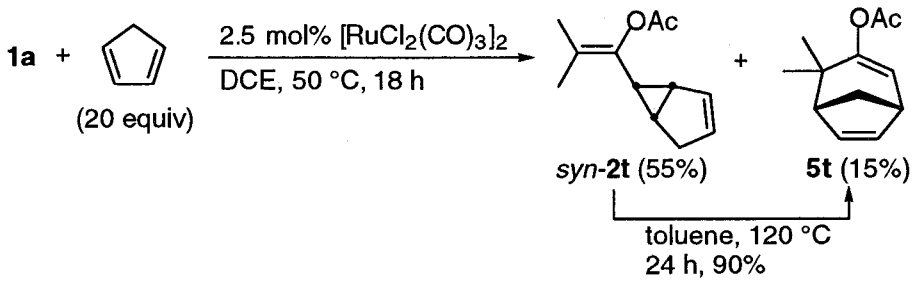


Scheme 7

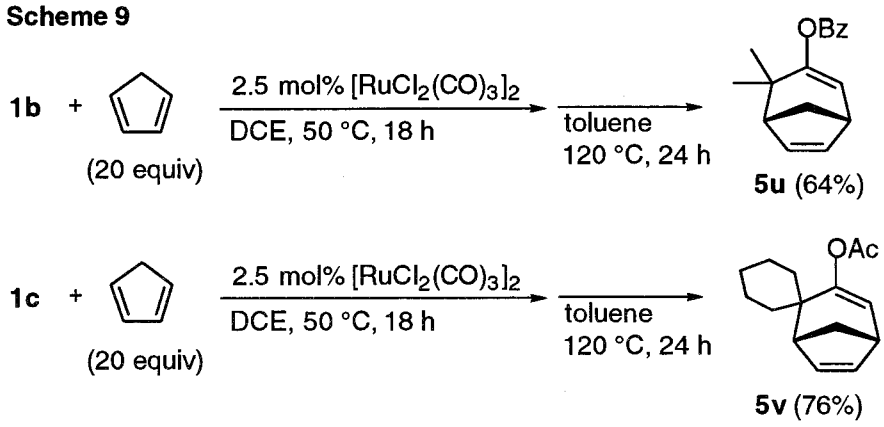


by assuming [3,3]sigmatropic rearrangement of the initially produced *cis*-isomer **2r** or **2s** (Scheme 7).[23] As shown in Scheme 8, cyclopentadiene also served as a good acceptor of Ru-carbenoid intermediate to give mono-cyclopropanated product *syn(endo)*-**2t**[24] in 55% yield together with 3-acetoxy-4,4-dimethylbicyclo[3.2.1]octa-2,6-diene (**5t**) in 15% yield. 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-carbons components to produce cycloheptadiene skeletons as shown in Scheme 10.

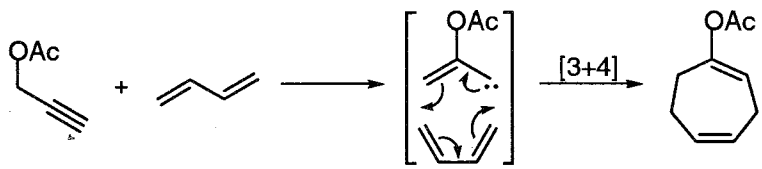
Scheme 8



Scheme 9



Scheme 10



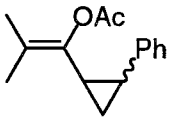
In conclusion, the author has developed an effective Ru-catalyzed intermolecular cyclopropanation of various alkenes with propargylic carboxylates via vinylcarbene complexes. Tertiary or secondary propargylic carboxylates can be applied to this procedure with an exception of primary ones. It has also been demonstrated that the vinylcarbenoid intermediates can serve as three-carbons unit in a formal [3+4] cycloaddition reaction leading to 1,4-cycloheptadiene skeletons. Since the present vinylcarbenoid 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

General Procedures. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. Other solvents were dried by the usual methods and distilled before use. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies were performed with Merck silica gel 60. 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. IR spectra were recorded with an FT-IR spectrometer. Melting points are uncorrected. High-resolution mass spectra (FAB HRMS) and low-resolution mass spectra (FAB LRMS) were obtained with JEOL JMX-SX 102A spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University.

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 stirring at the fixed temperature for appropriate time, the mixture was cooled to room temperature, and the amount of products was determined by 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 cyclopropane ring could be determined by ^1H NMR coupling constants between protons in a cyclopropane ring.[25] Generally, coupling constanes of J = 7.0-9.0 Hz between 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*.

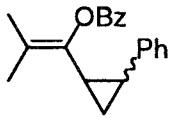
Vinylcyclopropane 2a.



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}; ^1H 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}; ^1H 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.

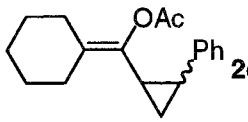
Vinylcyclopropane 2b.



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**: ^1H 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); ^{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, 128.3, 129.7, 129.8, 133.0, 138.5, 139.2, 164.6. ***trans*-2b**: ^1H 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, 23.7, 120.9, 125.7, 125.9, 128.3, 128.5, 129.6, 129.9, 132.8, 133.2, 142.0, 164.7. HRMS (FAB): calcd for $C_{20}H_{20}O_2$ (M^+), 292.1463; found, 292.1460.

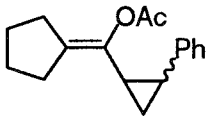
Vinylcyclopropane 2c.



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}; ^1H 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 = 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}; ^1H 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), 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.

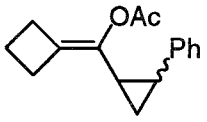


2d

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}; ^1H 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), 2.32-2.42 (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.

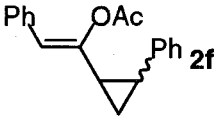
Vinylcyclopropane 2e.



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.

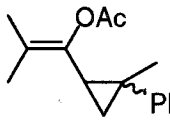


2f

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.

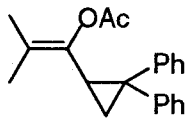
Vinylcyclopropane 2l.



2l

A colorless oil (44 mg, 0.18 mmol, 91% yield, d.r. = 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.

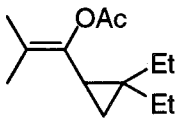


2m

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.

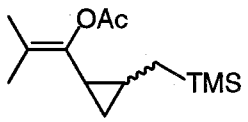
Vinylcyclopropane 2n.



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}; ^1H 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.

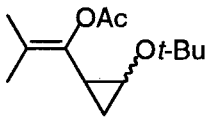
Vinylcyclopropane 2o.



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}; ^1H 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}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.01 (s, 18H), 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, 141.9, 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.

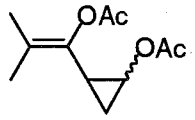


2p

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**: ^1H 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**: ^1H 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): calcd for $C_{13}H_{23}O_3$ (a mixture of *cis* and *trans* isomers) ($M+H^+$), 227.1647; found, 227.1643.

Vinylcyclopropane 2q.

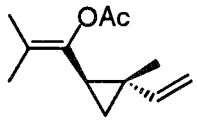


2q

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, 1019, 1048, 1114, 1160, 1211, 1237, 1370, 1441, 1750 (C=O), 2919, 2934 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 0.87-0.98 (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**), 18.5 (***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): calcd for $C_{11}H_{17}O_4$ (a mixture of *cis* and *trans* isomers) ($M+H^+$), 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 stirring 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**.

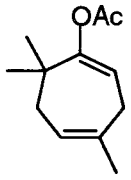
Vinylcyclopropane *trans*-2r.



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, 6.3Hz, 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): calcd for $C_{12}H_{18}O_2$ (M^+), 194.1307; found, 194.1312.

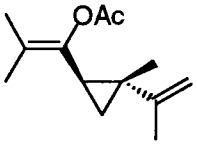
Cycloheptadiene 5r.



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): calcd for $C_{12}H_{18}O_2$ (M^+), 194.1307; found, 194.1313.

Vinylcyclopropane *trans*-2s.

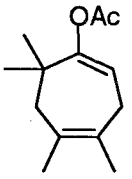


trans-**2s**

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): calcd for $C_{13}H_{20}O_2$ (M^+), 208.1463; found, 208.1468.

Cycloheptadiene 5s.

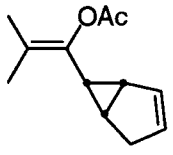


5s

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): calcd for $C_{13}H_{20}O_2$ (M^+), 208.1463; found, 208.1459.

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 cyclopentadiene (10 mmol) in $ClCH_2CH_2Cl$ (2.5 mL) was added to the flask at room temperature. After stirring 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.

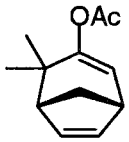


syn-**2t**

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) as an eluent 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}; ^{1}H 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, 18.6, 20.8, 22.8, 23.3, 30.3, 33.0, 123.1, 129.2, 129.6, 138.7, 169.1. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.81; H, 8.54.

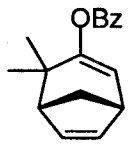
Bicyclic compound 5t.



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}; ^{1}H 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, 21.5, 27.4, 38.3, 39.1, 40.3, 51.2, 119.9, 131.1, 140.1, 150.8, 169.5. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.01; H, 8.34.

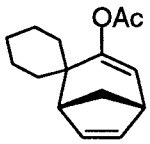
Bicyclic compound 5u.



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}; ^{1}H 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, 27.6, 38.4, 39.4, 40.3, 51.4, 120.1, 128.3, 129.7, 129.8, 131.2, 133.0, 140.9, 151.0, 165.1. 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.

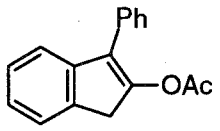


5v

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, 21.2, 21.2, 25.8, 28.4, 32.4, 38.1, 39.6, 42.4, 42.7, 121.1, 130.6, 141.0, 150.4, 169.6. HRMS (FAB): calcd for $C_{15}H_{20}O_2$ (M^+), 232.1463; found, 232.1460.

Ruthenium-Catalyzed Synthesis of Indene 4.



4

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 **1k** (0.20 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was added to the flask at room temperature. After stirring 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.

X-ray Crystallographic Studies of *cis*-2c and *cis*-2f. White crystals of ***cis*-2c** and ***cis*-2f** suitable for X-ray analysis were obtained by recrystallization from hexane and AcOEt, respectively. Both of the single crystals were sealed in a Pyrex glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation. Details of

crystal and data collection parameters are summarized in Tables 6 and 7. The positions of non-hydrogen atoms were determined by direct methods (SIR92)[21] and subsequent Fourier syntheses (DIRDIF PATTY). An ORTEP drawing of ***cis*-2c** and ***cis*-2f** is shown in Figures 2 and 3, respectively.

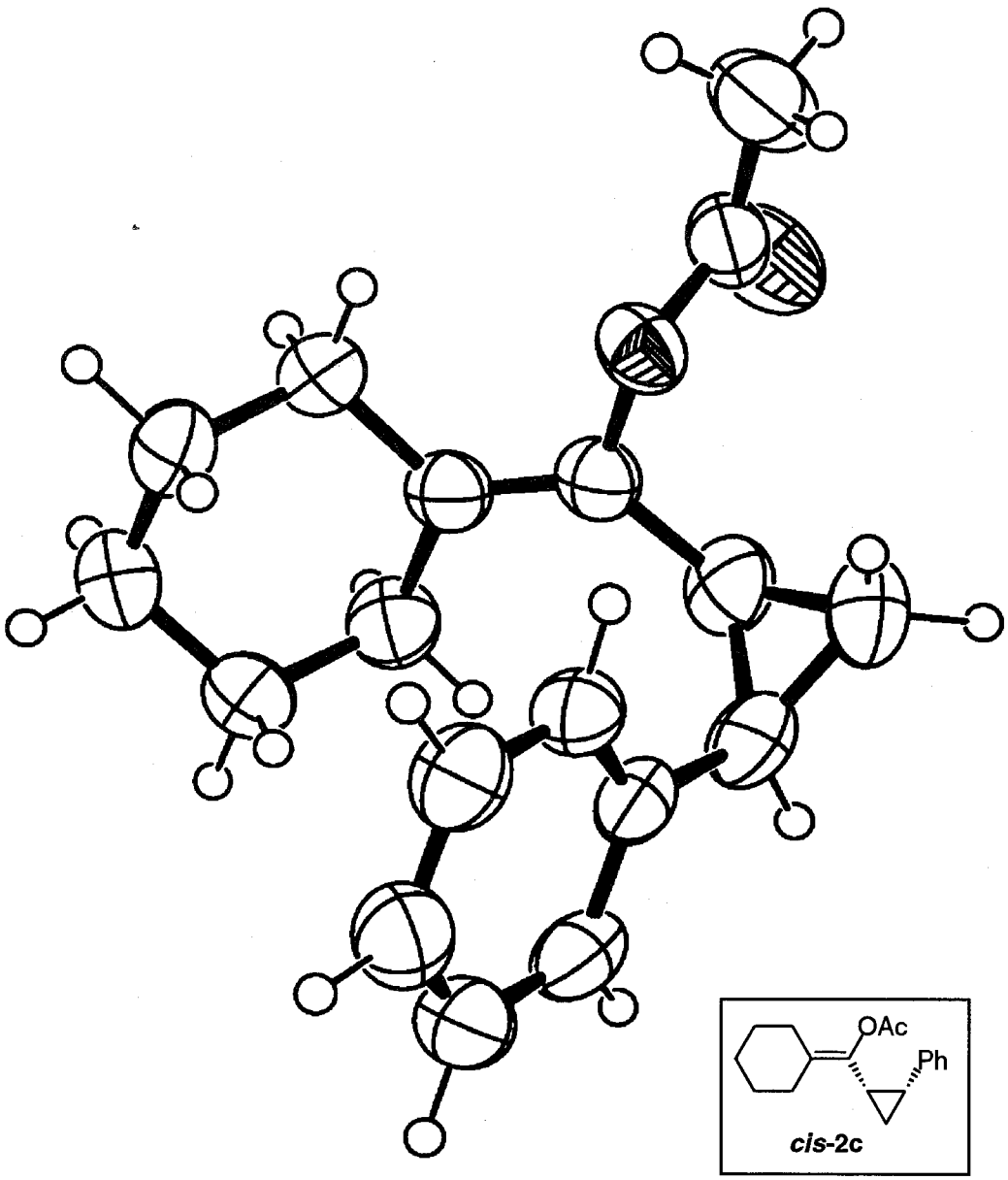


Figure 2. Crystal structure of ***cis*-2c**

Table 6. Summary of Crystallographic Data of ***cis*-2c**

empirical formula	$C_{18}H_{22}O_2$
fw	270.37
crystal syst	monoclinic
space group	$P2_1/n$ (No. 14)
cryst color	colorless
lattice params	
a (Å)	15.625(0)
b (Å)	5.935(4)
c (Å)	17.382(1)
β (Å)	106.92(9)
V (Å^3)	1542.(2)
Z	4
D_{calc} (g cm^{-3})	1.164
μ(Mo Kα) (cm^{-1})	0.74
F(000)	584
diffractometer	Rigaku RAXIS-RAPID
radiation	MoKα (λ = 0.71069 Å) graphite monochromated
temp (°C)	23.0
scan type	ω–2θ
Max. 2θ (°)	55
no. of rflns measd	total, 127980; unique, 3275 (R_{int} = 0.025)
no. of observns ($I > 3.00\sigma(I)$)	2004
structure soln	direct methods (SIR92)
refinement	full-matrix least squares
no. of variables	260
reflection/parameter ratio	7.71
residuals: R ; R_w	0.046; 0.043
goodness of fit (GOF)	1.72
max shift/error in final cycle	0.09
maximum peak in final diff map (e Å^{-3})	0.18
minimum peak in final diff map (e Å^{-3})	–0.15

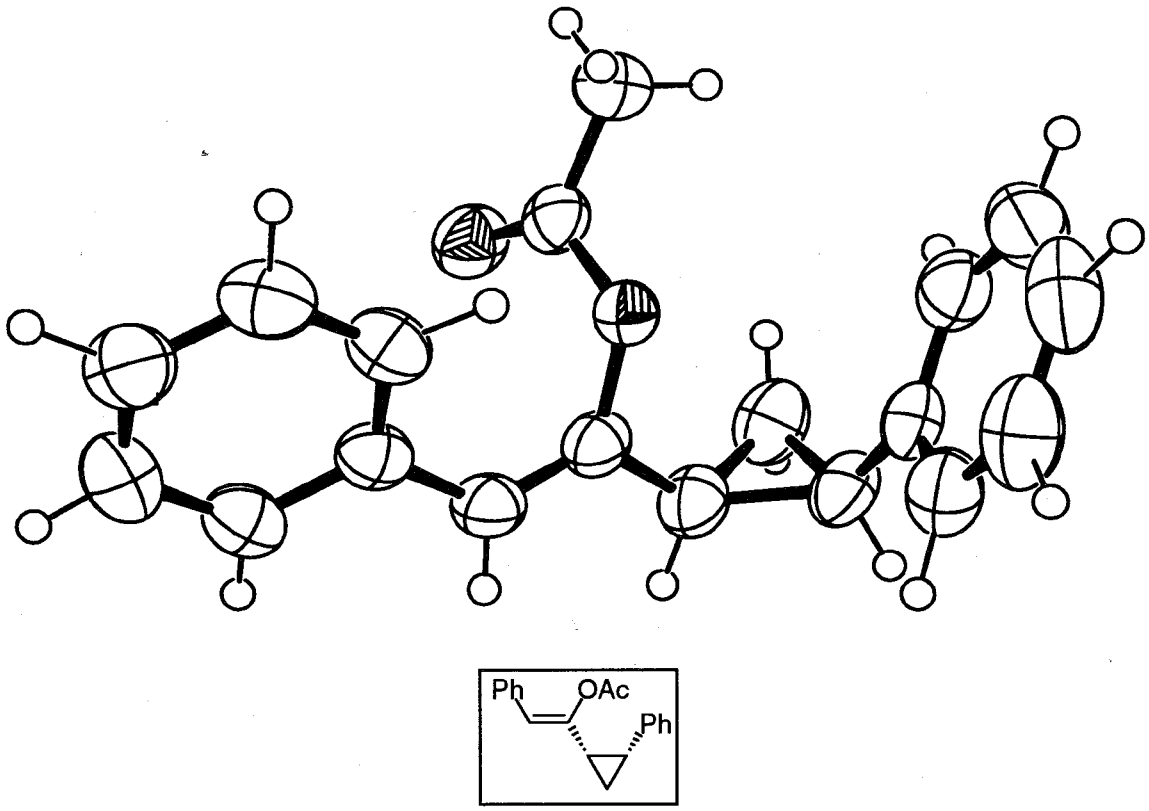


Figure 3. Crystal structure of ***cis*-2f**

Table 7. Summary of Crystallographic Data of ***cis*-2f**

empirical formula	$C_{19}H_{18}O_2$
fw	278.35
crystal syst	monoclinic
space group	$P2_1$ (No. 4)
cryst color	colorless
lattice params	
a (Å)	8.115(9)
b (Å)	9.330(1)
c (Å)	10.366(1)
β (Å)	97.600(8)
V (Å^3)	778.(0)
Z	2
D_{calc} (g cm^{-3})	1.188
μ(Mo Kα) (cm^{-1})	0.76
F(000)	296
diffractometer	Rigaku RAXIS-RAPID
radiation	MoKα (λ = 0.71069 Å) graphite monochromated
temp (°C)	23.0
scan type	ω–2θ
Max. 2θ (°)	54.7
no. of rflns measd	total, 6774; unique, 1863 (R_{int} = 0.022)
no. of observns ($I > 3.00\sigma(I)$)	1649
structure soln	direct methods (SIR92)
refinement	full-matrix least squares
no. of variables	253
reflection/parameter ratio	6.52
residuals: R ; R_w	0.042; 0.048
goodness of fit (GOF)	3.43
max shift/error in final cycle	0.08
maximum peak in final diff map (e Å^{-3})	0.15
minimum peak in final diff map (e Å^{-3})	–0.16

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

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

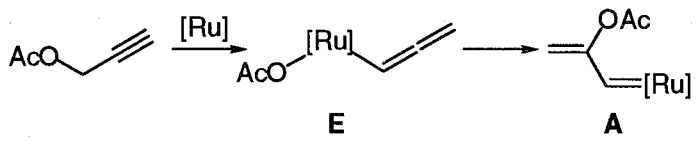
(17) Geometry of an alkenic part in the major product *cis*-**2f** was assigned to *Z* by X-ray diffraction analysis (see Experimental Section). Since the NMR data of *trans*-**2f** are similar to that of *cis*-**2f** with an exception of cyclopropane ring assignment, we assume that the geometry in *trans*-**2f** 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 cyclopropylketones 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.

(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 σ-allenyl ligand is another possible route to the vinylcarbenoid. However, experimental results of no formation of crossover products also rule out such route where the acetoxy group might liberate in the system.



(21) Generation of vinylcarbene complexes 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 mechanism of these reactions, however, is apparently different from 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 ^{1}H NMR spectrum of **2r** or **2s** might support the configuration of *trans*-cyclopropane.

(23) 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 Cycloaddition* **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.;

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(24) *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 cyclopropane ring were observed by irradiation at two methyl groups of an isopropylidene of **2t**, respectively.

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

Chapter 10

Ruthenium-Catalyzed Ring-Opening Reactions of Heteroaromatic Compounds Using Propargylic Carboxylates as Precursors of Vinylcarbenoids

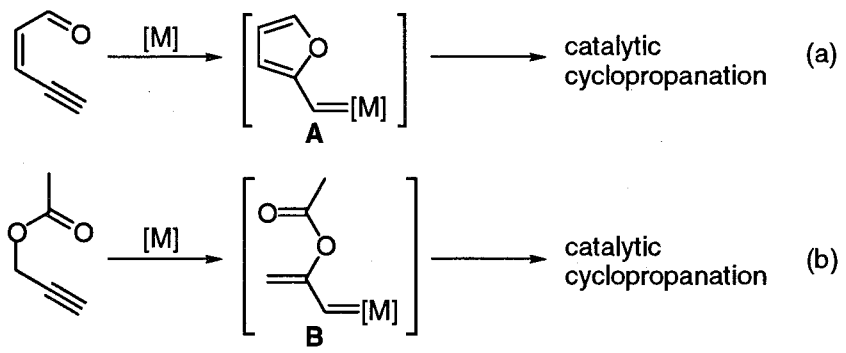
Abstract

The reaction of heteroaromatic compounds with propargylic acetates in the presence of a catalytic amount of $[RuCl_2(CO)_3]_2$ gives trienes in good yields. The key intermediate of this reaction is (1-acetoxyvinyl)carbene complex generated by the nucleophilic attack of a carbonyl oxygen to an internal alkyne carbon of the activated propargylic acetates. The reaction of benzofuran with the acetates produces cyclopropanated products and formal insertion products instead of trienes. Trienes and formal insertion products would be produced through an electrophilic attack of the charge separated ruthenium carbenoid species.

Introduction

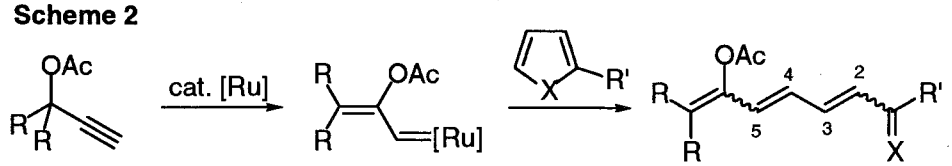
Rhodium(II) acetate which is one of superior catalysts for the *in situ* generation of transient electrophilic carbenoids from α-diazocarbonyl compounds effectively catalyzes various inter- or intramolecular carbenoid transfer reactions.[1] The reactions of transient electrophilic carbenoids with furan and 2-alkylfuran have been found to serve as one of the most convenient routes to 1,6-dioxo-2,4-diene derivatives,[2] which have been applied to the synthesis of a number of natural products[3] and heterocyclic systems.[4] Recently, much attention has been paid to activation of alkynes with transition metal complexes as an alternative route to generate carbenoid species.[5-10] The author has already demonstrated the *in situ* generation of furylcarbenoids **A** from ene-yne-ketones (Scheme 1a, Chapter 3) and vinylcarbenoids **B** from propargylic carboxylates (Scheme 1b, Chapter 9), and their

Scheme 1



application to catalytic carbene transfer reactions.[11] Further investigation based on the generation of vinylcarbenoids **B** led him to find the catalytic ring-opening reaction of heteroaromatic compounds as carbenoid acceptors (Scheme 2).

Scheme 2



Results and Discussion

At first, when the reaction of 2-methyl-3-butyn-2-yl acetate (**1a**) with 5 equiv of furan in dichloroethane (DCE) was carried out in the presence of $[RuCl_2(CO)_3]_2$ (2.5 mol%) under the effective conditions for catalytic cyclopropanation[11] via vinylcarbene complexes, triene (2*E*, 4*E*)-**2a** was obtained in 62% yield (eq 1). Next, the author examined carefully the

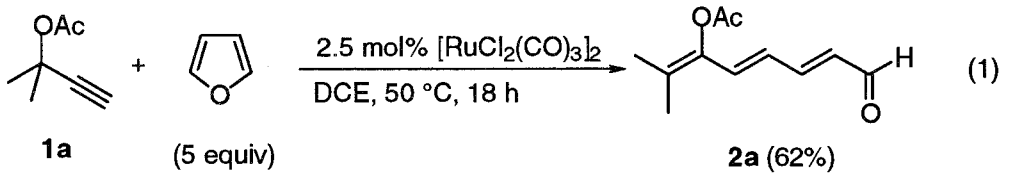
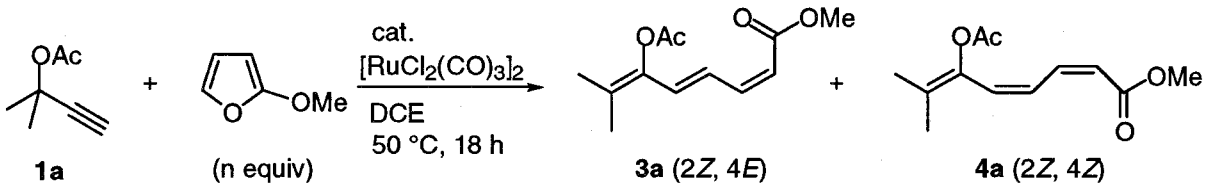


Table 1. Optimization of Ru-Catalyzed Ring-Opening Reaction of 2-Methoxyfuran[a]



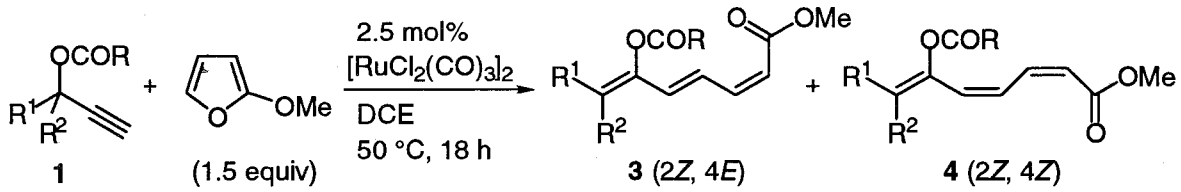
entry	cat. (mol%)	n (equiv)	DCE (mL)	isolated yield	ratio (**3a**:**4a**)
1	2.5	5.0	2.5	82%	38:62
2	2.5	2.0	2.5	85%	41:59
3	2.5	1.5	2.5	86%	42:58
4	2.5	1.2	2.5	80%	44:56
5	1.0	1.5	2.5	62%	38:62
6	2.5	1.5	1.0	84%	41:59

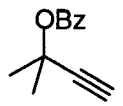
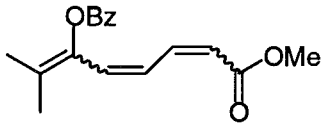
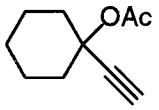
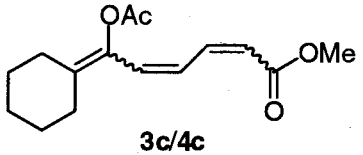
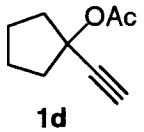
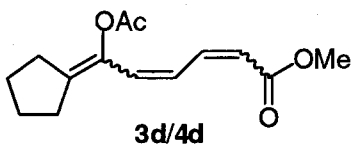
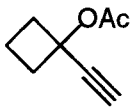
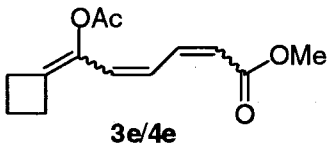
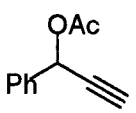
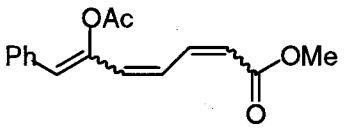
[a] The reaction of propargylic acetate **1a** (0.5 mmol) with 2-methoxyfuran (0.6-2.5 mmol) in DCE was carried out under N_2 in the presence of a catalytic amount of $[RuCl_2(CO)_3]_2$.

reaction of 2-methoxyfuran with propargylic acetate **1a** in order to find optimized reaction conditions. The results are summarized in Table 1. In contrast with the reaction of furan shown in eq 1, the reaction of 2-methoxyfuran gave a mixture of trienes (2*Z*, 4*E*)-**3a** and (2*Z*, 4*Z*)-**4a** (entry 1). It was found that the ring-opening reaction took place with good chemical yield by heating a solution of **1a** and 2-methoxyfuran (1.5 equiv) in DCE (2.5 mL) at 50 °C in the presence of 2.5 mol% ruthenium catalyst (entry 3). Under this condition, the reactions of

2-methoxyfuran with other propargylic carboxylates were next examined, and the results are summarized in Table 2. The reaction of propargylic benzoate **1b** with 2-methoxyfuran also gave a mixture of trienes (2*Z*, 4*E*)-**3b** and (2*Z*, 4*Z*)-**4b** in 86% total yield (**3b**:**4b** = 43:57) (entry 1). From cyclic acetates **1c**, **1d**, and **1e**, the corresponding products **3c/4c**, **3d/4d**, and **3e/4e** were obtained in 83%, 86%, and 89% total yields, respectively (entries 2, 3 and 4). In the case of the reaction of secondary propargylic acetate **1f**, a mixture of **3f** and **4f** was obtained in 44% total yield with 57:43 diastereomeric ratio. Primary propargylic benzoate

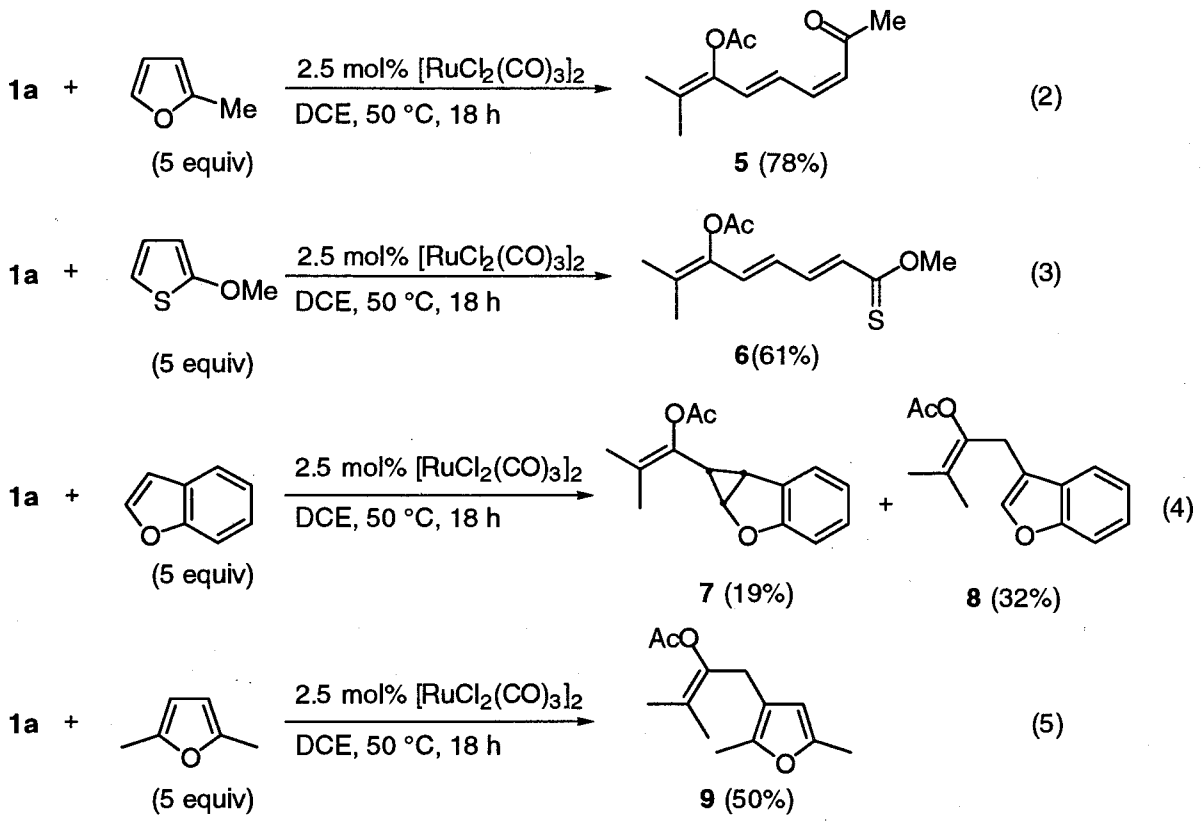
Table 2. Ru-Catalyzed Ring-Opening Reaction of 2-Methoxyfuran with Propargylic Carboxylates[a]



entry	1	product	isolated yield	ratio (3:4)
1	 **1b**	 **3b/4b**	86%	43:57
2	 **1c**	 **3c/4c**	83%	39:61
3	 **1d**	 **3d/4d**	86%	62:38
4	 **1e**	 **3e/4e**	89%	50:50
5	 **1f**	 **3f/4f**	44%	57:43

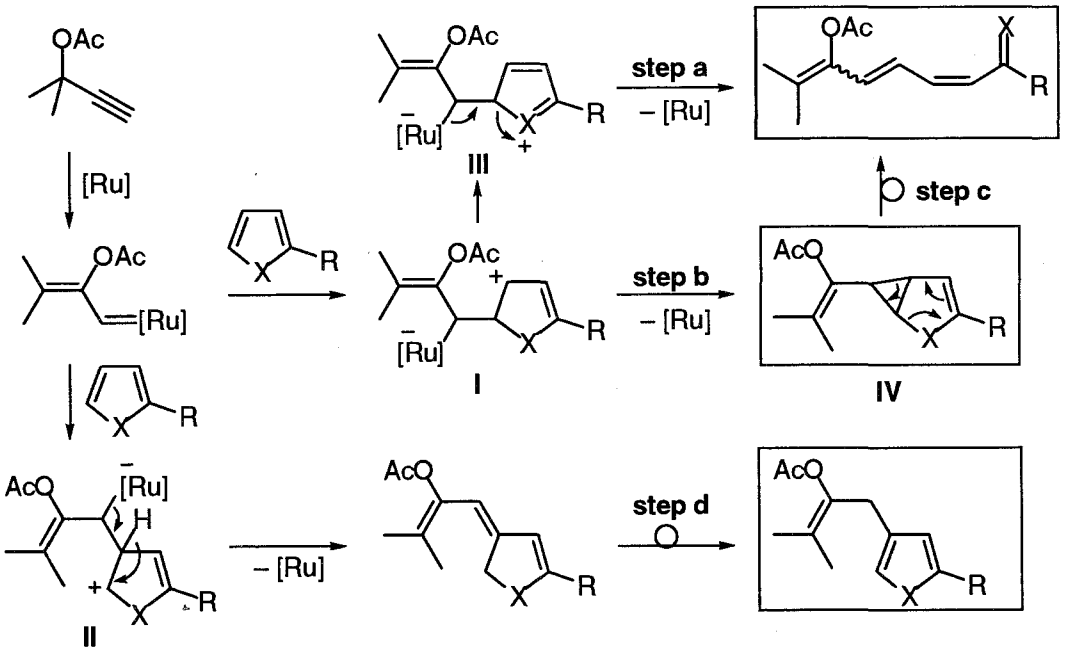
[a] The reaction of propargylic carboxylate **1** (0.5 mmol) with 2-methoxyfuran (0.75 mmol) in DCE was carried out under N_2 in the presence of a catalytic amount of $[RuCl_2(CO)_3]_2$.

was less reactive and the formation of the corresponding product was scarcely detected even after 48 h. The recation of **1a** with 2-methylfuran gave triene (2*Z*, 4*E*)-**5** exclusively in 78% yield (eq 2). The reaction of 2-methoxythiophene gave triene (2*E*, 4*E*)-**6** in 61% yield (eq 3). From benzofuran, tricyclic cyclopropane **7** and 3-substituted benzofuran derivative **8** were obtained in 19% and 32% yields, respectively, and the triene was not obtained at all in this case (eq 4). The reaction of **1a** with 2,5-dimethylfuran gave 3-substituted-2,5-dimethylfuran **9** selectively in 50% yield (eq 5).



The plausible reaction pathway to account for the formation of these products involving trienes, cyclopropanes, and substituted products is shown in Scheme 3. A ruthenium-carbenoid formation is the first step which is followed by nucleophilic attack of a double bond in a heteroaromatic compound to the carbenoid carbon. In the latter step, two pathways for carbon-carbon bond formation with the carbenoid species would be anticipated. The bond formation at 2- or 3-position of a heteroaromatic compound gives cationic intermediates **I** and

Scheme 3



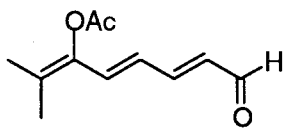
II, respectively. The charge-separated intermediate **I** successively undergoes ring-opening (step **a**) and cyclopropanation (step **b**) leading to trienes and cyclopropanes **IV**, respectively. Sigmatropic rearrangement of cyclopropanes **IV** (step **c**) may also be responsible to the triene formation.[12] The charge-separated intermediate **II** allows mainly hydride shift and aromatization (step **d**) to produce 3-substituted products. Reactions of benzofuran and 2,5-dimethylfuran favor the intermediary of **II** probably due to the stability of the carbocation and the sterical preference. It appears reasonable to attribute the configuration of triene double bonds to their thermodynamic stability, whereas *Z* configuraion of 2-position stems from the possible bond cleavage in a five-membered cyclic structure such as an intermediate **III** or an initially formed cyclopropane **IV**.

Experimental

General Procedure. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies were performed with Merck silica gel 60. 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, m: multiplet. IR spectra were recorded on an FT-IR spectrometer. Melting points are uncorrected. High-resolution mass spectra (FAB HRMS) and low-resolution mass spectra (FAB LRMS) were obtained with JEOL JMX-SX 102A spectrometer. Elemental analyses were performed at Microanalytical Center of Kyoto University. All new compounds prepared were fully characterized.

Typical Procedure for Ruthenium-Catalyzed Ring-Opening Reactions of Heteroaromatics. The complex $[RuCl_2(CO)_3]_2$ (2.6 mg, 0.010 mmol) was placed in the flame dried Schlenk flask under N_2. A solution of substrate **1** (0.20 mmol) and heteroaromatic compound (0.24-1.0 mmol) in DCE (1.0 mL) was added to the flask at room temperature. After stirring at 50 °C, the solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 (hexane/AcOEt = 15/1 – 4/1).

Triene (2*E*, 4*E*)-2a.

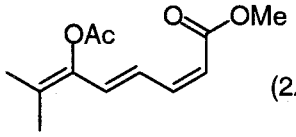


(2*E*, 4*E*)-**2a**

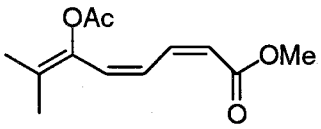
A colorless solid (62% yield); mp. 103.0-103.8 °C; IR (KBr) 532, 594, 878, 948, 987, 1013, 1115, 1167, 1183, 1202, 1215, 1371, 1443, 1604, 1679, 1743 (C=O), 2916 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.74 (s, 3H), 1.97 (s, 3H), 2.29 (s, 3H), 6.17 (dd, J = 7.6, 15.2 Hz, 1H), 6.26 (dd, J = 11.2, 15.2 Hz, 1H), 6.91 (d, J = 15.2 Hz, 1H), 7.17 (dd, J = 11.2, 15.2 Hz, 1H), 9.56 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 19.3, 19.3, 20.5, 124.3, 131.6, 132.0, 132.2, 140.4, 151.4, 193.2. Anal. Calcd for $C_{11}H_{14}O_3$:

C, 68.02; H, 7.27. Found: C, 67.87; H, 7.37.

Trienes (2*Z*,4*E*)-3a and (2*Z*,4*Z*)-4a.



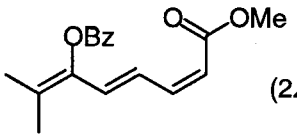
(2*Z*, 4*E*)-**3a**



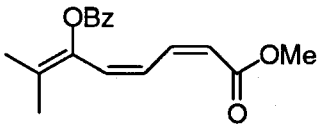
(2*Z*, 4*Z*)-**4a**

(2*Z*, 4*E*)-**3a**: A white solid; mp. 83.0-85.0 °C; IR (KBr) 821, 962, 1003, 1021, 1177, 1196, 1218, 1234, 1377, 1412, 1439, 1577, 1609, 1715 (C=O), 1748 (C=O), 2950 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.73 (s, 3H), 1.93 (s, 3H), 2.31 (s, 3H), 3.72 (s, 3H), 5.66 (d, J = 11.6 Hz, 1H), 6.64 (dd, J = 11.6, 11.6 Hz, 1H), 6.70 (d, J = 15.2 Hz, 1H), 7.42 (dd, J = 11.6, 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 19.1, 19.2, 20.6, 51.1, 117.0, 123.2, 129.8, 130.9, 140.7, 144.2, 166.6, 168.8. (2*Z*, 4*Z*)-**4a**: A colorless oil; IR (neat) 684, 756, 817, 888, 1011, 1099, 1109, 1177, 1195, 1209, 1370, 1441, 1611, 1716 (C=O), 1759 (C=O), 2951 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.69 (s, 3H), 1.82 (s, 3H), 2.18 (s, 3H), 3.73 (s, 3H), 5.73 (d, J = 11.6 Hz, 1H), 6.36 (d, J = 11.6 Hz, 1H), 7.13 (dd, J = 11.6, 12.0 Hz, 1H), 7.27 (dd, J = 11.6, 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 18.5, 19.7, 20.7, 51.2, 118.5, 124.3, 127.9, 128.5, 139.7, 139.9, 166.4, 168.4. HRMS (FAB): calcd for $C_{12}H_{17}O_4$ (a mixture of **3a** and **4a**) ($M+H^+$), 225.1127; found, 225.1124.

Trienes (2*Z*,4*E*)-3b and (2*Z*,4*Z*)-4b.



(2*Z*, 4*E*)-**3b**

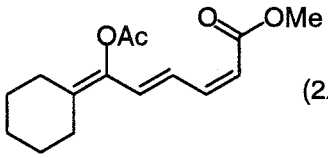


(2*Z*, 4*Z*)-**4b**

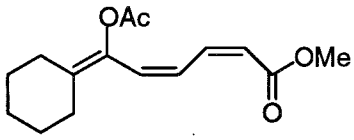
(2*Z*, 4*E*)-**3b**: A pale yellow oil; IR (neat) 711, 820, 1065, 1092, 1176, 1195, 1247, 1288, 1438, 1451, 1613, 1713 (C=O), 1732 (C=O), 2949 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.77 (s, 3H), 2.00 (s, 3H), 3.48 (s, 3H), 5.62 (d, J = 11.4 Hz, 1H), 6.65 (dd, J = 11.4, 11.4 Hz, 1H), 6.80 (d, J = 15.0 Hz, 1H), 7.39 (dd, J = 11.4, 15.0 Hz, 1H), 7.51 (dd, J = 8.1, 8.1 Hz, 2H), 7.60-7.66 (m, 1H), 8.20-8.23 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 19.2, 19.2, 50.8, 117.5, 123.5, 128.6, 129.3, 130.1, 130.1, 131.0, 133.4, 140.8, 143.8, 164.4, 166.6. (2*Z*, 4*Z*)-**4b**: A colorless oil; IR (neat) 710, 802, 1024, 1068, 1086, 1108, 1159, 1175, 1194, 1244,

1273, 1451, 1609, 1716 (C=O), 1737 (C=O), 2949 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.74 (s, 3H), 1.89 (s, 3H), 3.69 (s, 3H), 5.58 (d, J = 11.7 Hz, 1H), 6.46 (d, J = 11.7 Hz, 1H), 7.15 (dd, J = 11.7, 11.7 Hz, 1H), 7.32 (dd, J = 11.7, 11.7 Hz, 1H), 7.46-7.51 (m, 2H), 7.59-7.65 (m, 1H), 8.12-8.15 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 18.5, 19.7, 51.1, 118.6, 124.5, 127.8, 128.6, 128.8, 129.3, 129.9, 133.5, 139.9, 139.9, 164.2, 166.5. Anal. Calcd for $C_{17}H_{18}O_4$ (a mixture of **3b** and **4b**): C, 71.31; H, 6.34. Found: C, 71.28; H, 6.45.

Trienes (2*Z*,4*E*)-3c and (2*Z*,4*Z*)-4c.



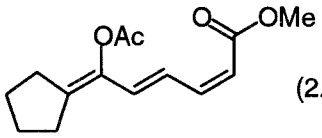
(2*Z*, 4*E*)-**3c**



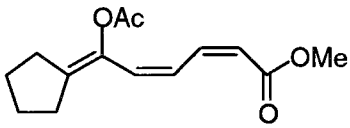
(2*Z*, 4*Z*)-**4c**

(2*Z*, 4*E*)-**3c**: A pale yellow oil; IR (neat) 820, 1017, 1209, 1371, 1439, 1610, 1713 (C=O), 1759 (C=O), 2855, 2933 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.56-1.69 (m, 6H), 2.12-2.17 (m, 2H), 2.31 (s, 3H), 2.36-2.41 (m, 2H), 3.72 (s, 3H), 5.65 (d, J = 11.4 Hz, 1H), 6.64 (dd, J = 11.4, 11.4 Hz, 1H), 6.75 (d, J = 15.0 Hz, 1H), 7.45 (dd, J = 11.4, 15.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.5, 26.2, 27.1, 27.6, 29.1, 29.5, 51.1, 116.9, 123.5, 130.7, 137.6, 137.9, 144.4, 166.7, 169.1. (2*Z*, 4*Z*)-**4c**: A white solid; mp. 73.6-75.3 °C; IR (KBr) 824, 1160, 1178, 1206, 1239, 1371, 1443, 1597, 1712 (C=O), 1760 (C=O), 2935 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.54-1.69 (m, 6H), 2.10-2.18 (m, 2H), 2.17 (s, 3H), 2.19-2.25 (m, 2H), 3.72 (s, 3H), 5.72 (d, J = 11.4 Hz, 1H), 6.35 (d, J = 11.4 Hz, 1H), 7.15 (dd, J = 11.4, 11.4 Hz, 1H), 7.32 (dd, J = 11.4, 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.7, 26.1, 27.0, 27.3, 28.2, 29.8, 51.2, 118.4, 125.0, 128.0, 135.6, 136.5, 140.2, 166.6, 168.7. Anal. Calcd for $C_{15}H_{20}O_4$ (a mixture of **3c** and **4c**): C, 68.16; H, 7.63. Found: C, 67.98; H, 7.53.

Trienes (2*Z*,4*E*)-3d and (2*Z*,4*Z*)-4d.



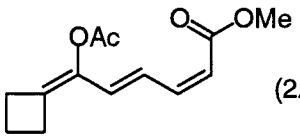
(2*Z*, 4*E*)-**3d**



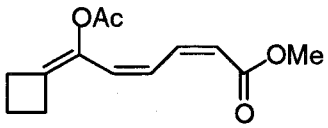
(2*Z*, 4*Z*)-**4d**

(2*Z*, 4*E*)-**3d**: A colorless oil; IR (neat) 820, 1018, 1028, 1159, 1174, 1199, 1268, 1371, 1437, 1611, 1713 (C=O), 1759 (C=O), 2871, 2952 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.64-1.82 (m, 4H), 2.24-2.34 (m, 2H), 2.28 (s, 3H), 2.45-2.55 (m, 2H), 3.72 (s, 3H), 5.65 (d, J = 11.4 Hz, 1H), 6.52 (d, J = 15.3 Hz, 1H), 6.63 (dd, J = 11.4, 11.4 Hz, 1H), 7.39 (dd, J = 11.4, 15.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.5, 25.9, 26.7, 29.9, 30.5, 51.1, 116.9, 122.3, 132.6, 138.2, 142.3, 144.3, 166.8, 168.7. (2*Z*, 4*Z*)-**4d**: A white solid; mp. 58.0-60.5 °C; IR (KBr) 809, 1008, 1148, 1174, 1193, 1205, 1222, 1378, 1444, 1608, 1714 (C=O), 1741 (C=O), 2956 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.64-1.79 (m, 4H), 2.19 (s, 3H), 2.23-2.30 (m, 2H), 2.41-2.47 (m, 2H), 3.72 (s, 3H), 5.66-5.75 (m, 1H), 6.22-6.32 (m, 1H), 7.15-7.25 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.8, 25.9, 26.7, 30.2, 30.4, 51.2, 118.3, 122.4, 128.4, 138.2, 139.8, 142.4, 166.6, 168.2. Anal. Calcd for $C_{14}H_{18}O_4$ (a mixture of **3d** and **4d**): C, 67.18; H, 7.25. Found: C, 66.92; H, 7.21.

Trienes (2*Z*,4*E*)-3e and (2*Z*,4*Z*)-4e.



(2*Z*, 4*E*)-**3e**

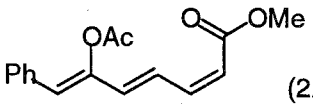


(2*Z*, 4*Z*)-**4e**

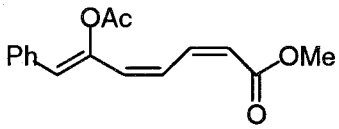
(2*Z*, 4*E*)-**3e**: A pale yellow oil; IR (neat) 820, 1000, 1027, 1174, 1198, 1229, 1370, 1439, 1613, 1713 (C=O), 1760 (C=O), 2952 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.07 (tt, J = 8.4, 8.4 Hz, 2H), 2.26 (s, 3H), 2.67-2.74 (m, 2H), 2.89-2.95 (m, 2H), 3.72 (s, 3H), 5.65 (d, J = 11.4 Hz, 1H), 6.30 (d, J = 15.0 Hz, 1H), 6.60 (dd, J = 11.4, 11.4 Hz, 1H), 7.38 (dd, J = 11.4, 15.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 16.6, 20.5, 28.4, 28.7, 51.1, 117.0, 122.0, 131.0, 138.2, 139.9, 144.2, 166.8, 168.4. (2*Z*, 4*Z*)-**4e**: A pale yellow oil; IR (neat) 813, 1001, 1025, 1056, 1114, 1173, 1190, 1215, 1370, 1446, 1608, 1715 (C=O), 1760 (C=O), 2952 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.04 (tt, J = 8.4, 8.4 Hz, 2H), 2.18 (s, 3H),

2.64-2.70 (m, 2H), 2.81-2.88 (m, 2H), 3.72 (s, 3H), 5.65-5.75 (m, 1H), 6.00-6.09 (m, 1H), 7.13-7.23 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 16.4, 20.8, 28.6, 28.9, 51.2, 118.2, 122.2, 126.6, 138.4, 139.7, 140.1, 166.6, 167.9. Anal. Calcd for $C_{13}H_{16}O_4$ (a mixture of **3e** and **4e**): C, 66.09; H, 6.83. Found: C, 65.70; H, 6.82.

Trienes (2*Z*,4*E*)-3f and (2*Z*,4*Z*)-4f.



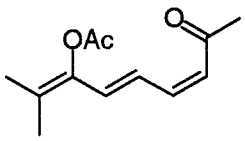
(2*Z*, 4*E*)-**3f**



(2*Z*, 4*Z*)-**4f**

(2*Z*, 4*E*)-**3f**: A white solid; mp. 95.7-97.2 °C; IR (KBr) 692, 758, 819, 1013 1176, 1199, 1211, 1442, 1610, 1628, 1713 (C=O), 1762 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.38 (s, 3H), 3.73 (s, 3H), 5.73 (d, J = 11.4 Hz, 1H), 6.38 (s, 1H), 6.49 (d, J = 15.3 Hz, 1H), 6.65 (dd, J = 11.4, 11.4 Hz, 1H), 7.24-7.37 (m, 3H), 7.47 (d, J = 7.2 Hz, 2H), 7.62 (dd, J = 11.4, 15.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 20.9, 51.2, 118.2, 124.2, 125.3, 128.4, 128.7, 129.0, 133.8, 135.6, 143.3, 145.6, 166.6, 168.1. (2*Z*, 4*Z*)-**4f**: A pale yellow solid; mp. 72.8-75.5 °C; IR (KBr) 692, 758, 818, 998, 1012, 1176, 1199, 1211, 1442, 1610, 1627, 1712 (C=O), 1761 (C=O) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 2.25 (s, 3H), 3.74 (s, 3H), 5.79 (d, J = 11.1 Hz, 1H), 6.25-6.28 (m, 1H), 6.32 (s, 1H), 7.24-7.39 (m, 5H), 7.42-7.47 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 21.2, 51.3, 119.6, 124.6, 125.7, 128.4, 128.6, 128.9, 131.4, 133.7, 138.9, 145.3, 166.5, 167.7. Anal. Calcd for $C_{16}H_{16}O_4$ (a mixture of **3f** and **4f**): C, 70.57; H, 5.92. Found: C, 70.28; H, 5.88.

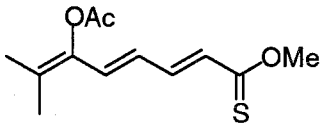
Triene (2*Z*, 4*E*)-5.



(2*Z*, 4*E*)-**5**

A white solid; mp. 53.4-55.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 1.72 (s, 3H), 1.95 (s, 3H), 2.27 (s, 3H), 2.27 (s, 3H), 6.15 (dd, J = 11.1, 15.0 Hz, 1H), 6.16 (d, J = 15.3 Hz, 1H), 6.85 (d, J = 15.0 Hz, 1H), 7.19 (dd, J = 11.1, 15.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C) δ 19.1, 19.1, 20.4, 27.3, 105.8, 124.8, 130.5, 131.2, 140.5, 142.9, 168.6, 198.2. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.01; H, 7.59.

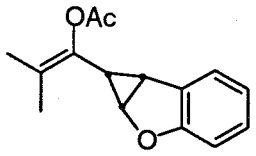
Triene (2*E*, 4*E*)-6.



(2*E*, 4*E*)-**6**

An orange solid; mp. 94.3-95.0 °C; IR (KBr) 514, 603, 746, 881, 946, 981, 1004, 1015, 1133, 1164, 1181, 1199, 1212, 1227, 1273, 1333, 1377, 1433, 1581, 1597, 1757 (C=O), 2941, 2993 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.70 (s, 3H), 1.92 (s, 3H), 2.26 (s, 3H), 4.12 (s, 3H), 6.14 (dd, J = 11.2, 15.2 Hz, 1H), 6.47 (d, J = 15.2 Hz, 1H), 6.86 (d, J = 15.2 Hz, 1H), 7.40 (dd, J = 11.2, 15.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 19.1, 19.2 ,20.4, 58.3, 124.8, 124.8, 130.1, 131.2, 131.7, 140.7, 168.3, 210.3. Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71. Found: C, 59.71; H, 6.60.

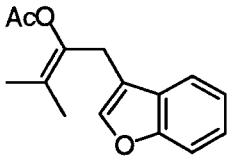
Cyclopropane 7.



7

A colorless oil; IR (neat) 749, 830, 1001, 1015, 1046, 1103, 1118, 1218, 1229, 1262, 1367, 1464, 1477, 1745 (C=O), 2917 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.34 (d, J = 1.6 Hz, 3H), 1.75 (s, 3H), 2.02 (s, 3H), 2.04-2.11 (m, 1H), 2.97 (dd, J = 5.2, 9.2 Hz, 1H), 4.89 (dd, J = 5.2, 5.2 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 6.86 (dd, J = 7.6, 7.6 Hz, 1H), 7.09 (dd, J = 7.6, 7.6 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 17.3, 17.4, 18.8, 20.7, 26.6, 65.5, 109.3, 120.4, 124.5, 125.0, 127.0, 127.1, 135.0, 159.9, 169.3. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.85; H, 6.66.

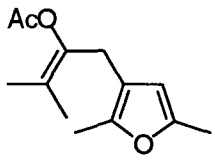
3-Substituted benzofuran 8.



8

A colorless oil; IR (neat) 751, 1011, 1102, 1144, 1168, 1215, 1255, 1369, 1455, 1587, 1601, 1755 (C=O), 2920 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.64 (s, 3H), 1.83 (s, 3H), 2.09 (s, 3H), 3.76 (s, 2H), 6.45 (s, 1H), 7.15-7.24 (m, 2H), 7.41 (d, J = 8.4 Hz, 1H), 7.46-7.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 17.9, 18.9, 20.7, 29.6, 103.3, 110.8, 120.3, 121.8, 122.4, 123.3, 128.6, 137.7, 154.8, 154.9, 169.2. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.70; H, 6.63.

3-Substituted-2,5-dimethylfuran 9.



9 A colorless oil; IR (neat) 791, 925, 1010, 1077, 1120, 1142, 1217, 1254, 1369, 1435, 1583, 1748 (C=O), 2921 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, 25 °C) δ 1.57 (s, 3H), 1.79 (s, 3H), 2.08 (s, 3H), 2.15 (s, 3H), 2.20 (s, 3H), 3.25 (s, 2H), 5.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 11.3, 13.5, 17.7, 18.7, 20.7, 25.5, 107.4, 115.6, 118.9, 141.1, 145.7, 149.2, 169.1. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.11; H, 8.18.

X-ray Crystallographic Studies of (2*Z*, 4*E*)-3a and (2*E*, 4*E*)-6. Colorless crystals of (2*Z*, 4*E*)-**3a** and (2*E*, 4*E*)-**6** suitable for X-ray analysis were obtained by recrystallization from AcOEt-hexane. Both of the single crystals were sealed in a Pyrex glass capillary under N_2 atmosphere and used for data collection. All measurements were made on a Rigaku RAXIS imaging plate area detector with graphite monochromated Mo-Kα radiation. Details of crystal and data collection parameters are summarized in Tables 1 and 2. The positions of non-hydrogen atoms were determined by direct methods (SIR92) and subsequent Fourier syntheses (DIRDIF PATTY).[13] An ORTEP drawing of (2*Z*, 4*E*)-**3a** and (2*E*, 4*E*)-**6** is shown in Figures 1 and 2.

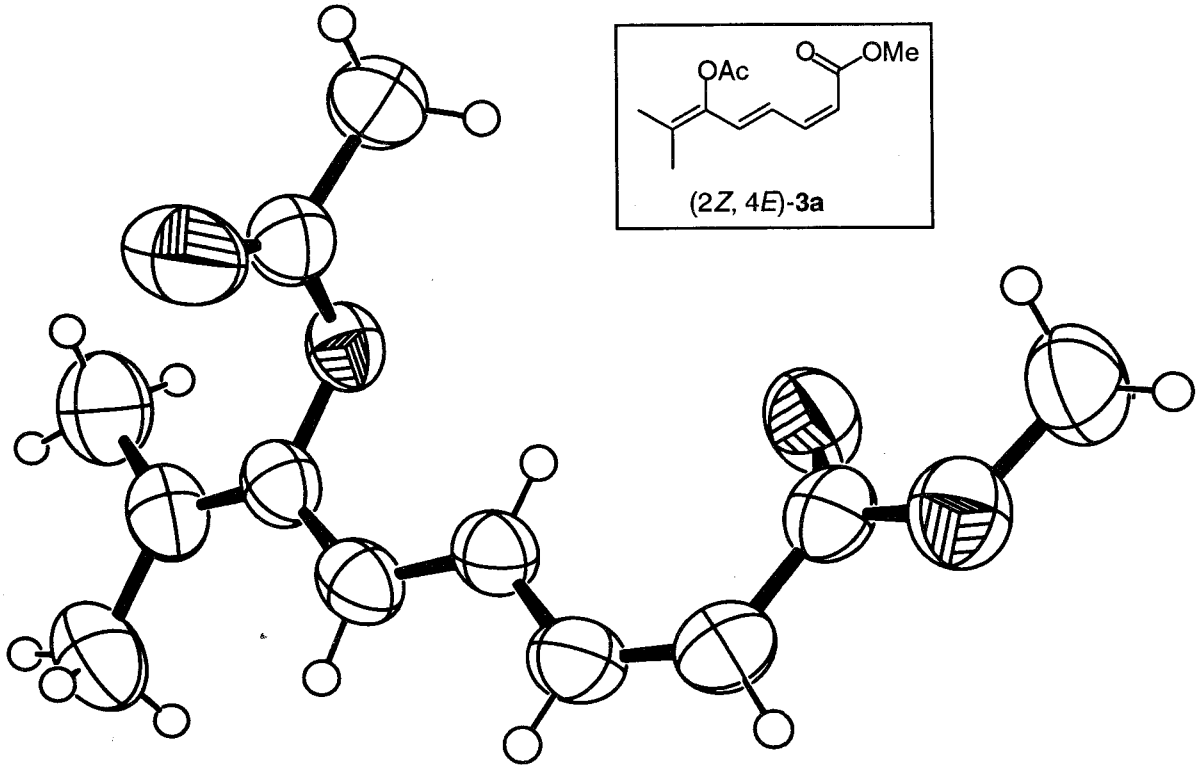


Figure 1. Crystal structure of **(2Z, 4*E*)-3a**

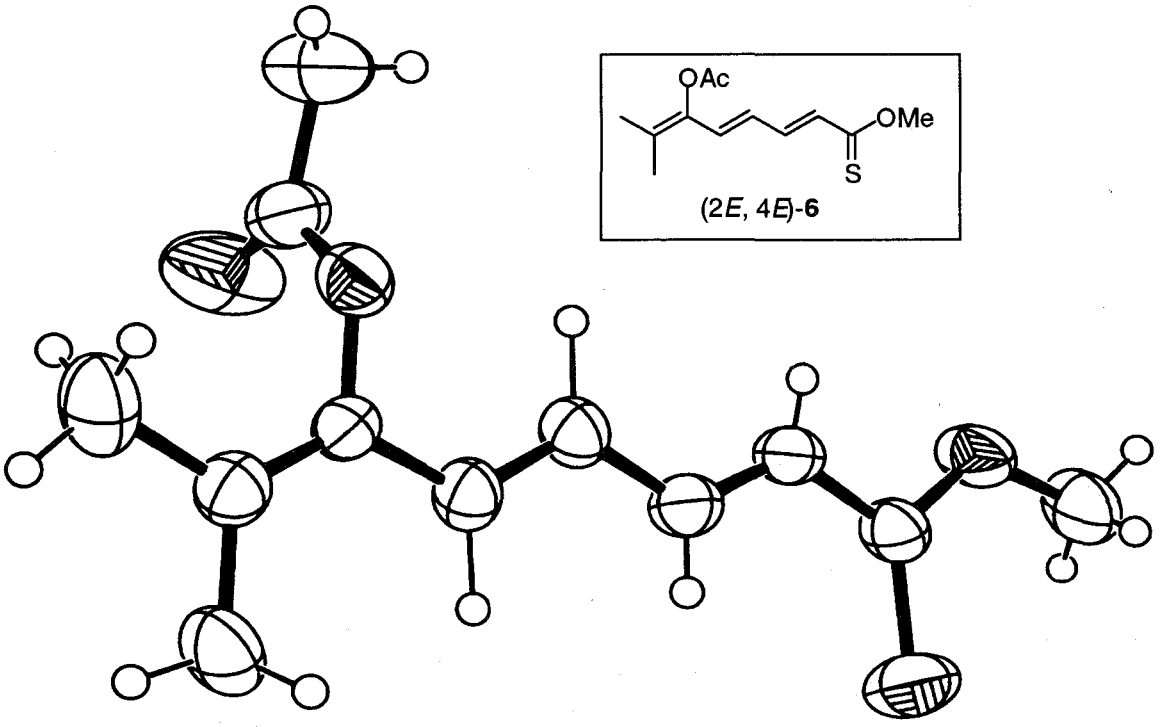


Figure 2. Crystal structure of (2*E*, 4*E*)-**6**

Table 1. Summary of Crystallographic Data of (2*Z*, 4*E*)-**3a**

empirical formula	$C_{12}H_{16}O_4$
fw	224.26
crystal syst	triclinic
space group	*P*-1 (No. 2)
cryst color	colorless, platelet
lattice params	
a (Å)	9.864(1)
b (Å)	10.025(1)
c (Å)	14.013(1)
α(Å)	76.782(3)
β (Å)	75.253(8)
γ (Å)	80.105(6)
V (Å^3)	1294.(9)
Z	4
D_{calc} (g cm^{-3})	1.150
μ(Mo Kα) (cm^{-1})	0.86
F(000)	480
diffractometer	Rigaku RAXIS-RAPID
radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated
temp (°C)	23.0
scan type	ω–2θ
Max. 2θ (°)	55
no. of rflns measd	total, 9138
no. of observns ($I > 3.00\sigma(I)$)	2830
structure soln	direct methods (SIR92)
refinement	full-matrix least-squares on F
no. of variables	345
reflection/parameter ratio	8.20
residuals: R; R_w	0.066; 0.070
goodness of fit (GOF)	0.28
max shift/error in final cycle	0.36
maximum peak in final diff map (e Å^{-3})	0.26
minimum peak in final diff map (e Å^{-3})	–0.23

Table 2. Summary of Crystallographic Data of (2*E*, 4*E*)-**6**

empirical formula	$C_{12}H_{16}O_3S$
fw	240.32
crystal syst	triclinic
space group	*P*-1 (No. 2)
cryst color	orange, platelet
lattice params	
a (Å)	5.787(4)
b (Å)	8.636(0)
c (Å)	13.477(2)
α (Å)	93.18(1)
β (Å)	95.00(1)
γ (Å)	94.36(3)
V (Å^3)	667.(7)
Z	2
D_{calc} (g cm^{-3})	1.195
μ(Mo Kα) (cm^{-1})	2.33
F(000)	256
diffractometer	Rigaku RAXIS-RAPID
radiation	MoKα (λ = 0.71069 Å)
	graphite monochromated
temp (°C)	23.0
scan type	ω–2θ
Max. 2θ (°)	55
no. of rflns measd	total, 4547
no. of observns ($I > 3.00\sigma(I)$)	1806
structure soln	direct methods (SIR92)
refinement	full-matrix least-squares on F
no. of variables	191
reflection/parameter ratio	9.46
residuals: R; R_w	0.103; 0.111
goodness of fit (GOF)	5.43
max shift/error in final cycle	0.02
maximum peak in final diff map (e Å^{-3})	0.46
minimum peak in final diff map (e Å^{-3})	–0.46

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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.

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General Conclusion

In this thesis, new effficient catalytic reactions using alkyne-based transition metal-carbene and -vinylidene complexes have been studied. The results mentioned in three parts (ten chapters) of this thesis are summarized as follows.

In Part 1, which consists of two chapters, synthesis of 2-pyranylidene complexes via electrocyclization of vinylidene-ene-carbonyl complexes (Chapter 1) and their application to catalytic transformation of ethynylcyclopropanes (Chapter 2) have been described. The catalytic valence isomerization reaction smoothly gave phenol derivatives in high yields under mild conditions. Seven-membered cyclic Fischer-type carbene complexes generated via vinylidene intermediates are proposed as plausible intermediates for the valence isomerism.

In Part 2, which consists of six chapters, synthesis and efficient application of (2-furyl) and (2-pyrrolyl)carbene complexes generated from ene-yne-ketones and ene-yne-imino compounds with various transition metal compounds have been described. Chapter 3 dealt with the stoichiometric synthesis of (2-furyl)carbene complexes from ene-yne-ketones with group 6 metal carbonyls. The key step of this carbenoid formation is 5-*exo-dig* cyclization caused by nucleophilic attack of a carbonyl oxygen at an internal alkyne carbon activated by group 6 traisition metal compounds. In Chapter 4, group 6 transition metal-catalyzed cyclopropanation reaction of alkenes with ene-yne-ketones leading to furylcyclopropanes has been described. Various transition metal compounds have been proved to be effective for the catalytic cyclopropanation reactions. In Chapter 5, the rhodium-catalyzed cyclopropanation via the formation of (2-pyrrolyl)carbenoid as a nitrogen analogue of (2-furyl)carbenoid has been summarized. (2-Furyl)carbenoids generated *in situ* from ene-yne-ketones are also useful intermediates for other (2-furyl)carbene transfer reactions, such as σ-bond insertion reactions and ylide formation reactions, as shown in Chapters 6 and 7, respectively. Ene-yne-carbonyl compounds having an electron-withdrawing substituent at an alkyne terminus, which could be expected to enhance the electrophilicity of intermediary carbenoid species to

carbene acceptors, reacted efficiently rather than those having terminal alkynes to give carbenoid-insertion products. In Chapter 8, the results of application of the (2-furyl)carbene transfer reactions to polymer synthesis have been shown. The rhodium-catalyzed polymerizations of ene-yne-ketones having suitable functionalities as carbene acceptors gave furylcyclopropane- and furfurylidene-containing polymers. Unique structures of alternating copolymers having regularly embedded furylcyclopropanes or furfurylidenes would attract a great deal of interest in polymer chemistry.

In Part 3, which consists of two chapters, the catalytic reactions using propargylic carboxylates as vinylcarbenoid precursors have been summarized where the principle of 5-*exo-dig* cyclization mode of ene-yne-carbonyl compounds was extended successfully to the propargylic carboxylates to generate vinylcarbenoids. In Chapter 9, the efficient intermolecular catalytic cyclopropanation between alkenes and propargylic carboxylates has been described for the first time. In Chapter 10, the catalytic vinylcarbenoid transfer reactions to heteroaromatic compounds for the synthesis of functionalized trienes or alkylated heteroaromatics has been described.

The present studies on the *in situ* generation of carbenoid species from alkynes activated by transition metal compounds provide a variety of efficient carbene transfer reactions, and shall contribute to the development of organic synthesis as well as organometallic chemistry.

List of Publications

Part I **Generation of Cyclic Fischer-Type Carbene Complexes from Vinylidene Complexes and Their Application to Catalytic Reactions**

Chapter 1 "Novel Pyranylidene-Complexes from Group 6 Transition Metals and β-Ethynyl α,β-Unsaturated Carbonyl Compounds"
Kouichi Ohe, Koji Miki, Tomomi Yokoi, Fumiaki Nishino, Sakae Uemura
Organometallics **2000**, *19*, 5525.

Chapter 2 "Chromium- and Tungsten-Triggered Valence Isomerism of *cis*-1-Acyl-2-ethynylcyclopropanes via [3,3]Sigmatropy of (2-Acylcyclopropyl)vinylidene-metal Intermediates"
Kouichi Ohe, Tomomi Yokoi, Koji Miki, Fumiaki Nishino, Sakae Uemura
J. Am. Chem. Soc. **2002**, *124*, 526.

Part II **Generation of (2-Furyl)carbene Complexes from π-Alkyne Complexes and Their Application to Catalytic Carbene Transfer Reactions**

Chapter 3 "Synthesis of 2-Pyranylidene or (2-Furyl)carbene-Chromium Complexes from Conjugated Enyne Carbonyl Compounds with $Cr(CO)_5(THF)$"
Koji Miki, Tomomi Yokoi, Fumiaki Nishino, Kouichi Ohe, Sakae Uemura
J. Organomet. Chem. **2002**, *645*, 228.

Chapter 4 "Novel Approach for Catalytic Cyclopropanation of Alkenes via (2-Furyl)carbene Complexes from 1-Benzoyl-*cis*-1-buten-3-yne"
Koji Miki, Fumiaki Nishino, Kouichi Ohe, Sakae Uemura
J. Am. Chem. Soc. **2002**, *124*, 5260.

"Catalytic Cyclopropanation of Alkenes via (2-Furyl)carbene Complexes from 1-Benzoyl-*cis*-1-buten-3-yne with Transition Metal Compounds"

Koji Miki, Tomomi Yokoi, Fumiaki Nishino, Yumiko Kato, Yosuke Washitake, Kouichi Ohe, Sakae Uemura

Submitted to *J. Org. Chem.*

Chapter 5 "Rhodium-Catalyzed Cyclopropanation with Ene-yne-imino Ether Compounds as Precursors of (2-Pyrrolyl)carbenoids"

Fumiaki Nishino, Koji Miki, Yumiko Kato, Kouichi Ohe, Sakae Uemura

Org. Lett. **2003**, *5*, 2615.

Chapter 6 Chromium- and Rhodium-Catalyzed Insertion Reactions Using Ene-Yne-Carbonyl Compounds as Precursors of (2-Furyl)carbenoids

Yumiko Kato, Koji Miki, Fumiaki Nishino, Kouichi Ohe, Sakae Uemura

In preparation.

Chapter 7 "Doyle-Kirmse Reaction of Allylic Sulfides with Diazoalkane-Free (2-Furyl)carbenoid Transfer"

Yumiko Kato, Koji Miki, Fumiaki Nishino, Kouichi Ohe, Sakae Uemura

Org. Lett. **2003**, *5*, 2619.

Chapter 8 "Polyaddition and Polycondensation Reactions of (2-Furyl)carbenoid as Step-Growth Polymerization Strategies: Synthesis of Furylcyclopropane- and Furfurylidene-Containing Polymers"

Koji Miki, Yosuke Washitake, Kouichi Ohe, Sakae Uemura

Submitted to *Angew. Chem. Int. Ed.*

Part III **Transition Metal-Catalyzed Carbene Transfer Reactions Using Propargylic Carboxylates as Precursors of Vinylcarbenoids**

Chapter 9 "A New Ruthenium-Catalyzed Cyclopropanation of Alkenes Using Propargylic Acetates as a Precursor of Vinylcarbenoids"
Koji Miki, Kouichi Ohe, Sakae Uemura
Tetrahedron Lett. **2003**, *44*, 2019.

"Ruthenium-Catalyzed Cyclopropanation of Alkenes Using Propargylic Acetates as Precursors of Vinylcarbenoids"
Koji Miki, Kouichi Ohe, Sakae Uemura
J. Org. Chem. in press.

Chapter 10 "Ruthenium-Catalyzed Ring-Opening Reactions of Heteroaromatic Compounds Using Propargylic Carboxylates as Precursors of Vinylcarbenoids"
Koji Miki, Michinobu Fujita, Kouichi Ohe, Sakae Uemura
In preparation.

Other Publications

The following publications are not included in this dissertation.

"Selective Conjugate Addition to Zerumbone and Transannular Cyclization of Its Derivatives"

Kouichi Ohe, Koji Miki, Shin-ichi Yanagi, Takumi Tanaka, Seiji Sawada, Sakae Uemura

J. Chem. Soc., Perkin Trans 1 **2000**, *21*, 3627.

"Catalytic Reactions via Carbene, Vinylidene, and Allenylidene Complexes through Activation of Alkynes with Transition Metal Complexes"

Kouichi Ohe, Koji Miki, Sakae Uemura

J. Synth. Org. Chem., Jpn (Yuki Gosei Kagaku Kyokaishi)

In preparation.

"Direct Generation of Alkylidene and Vinylidene Complexes from Alkynes as a New Tool for Catalytic Reactions"

Kouichi Ohe, Koji Miki, Sakae Uemura

Synlett

In preparation.

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