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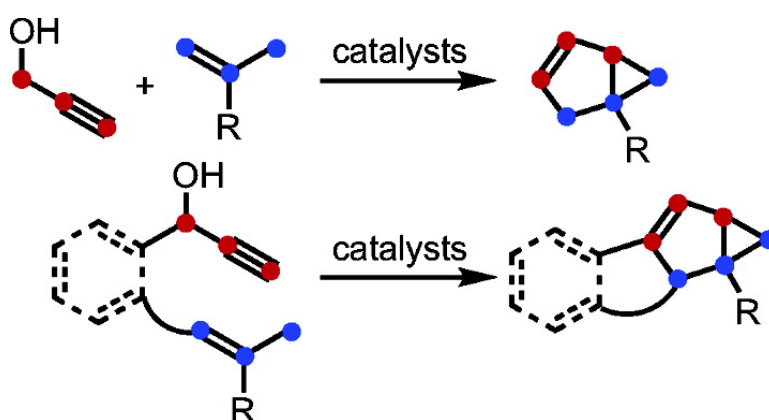
Ruthenium- and Platinum-Catalyzed Sequential Reactions: Selective Synthesis of Fused Polycyclic Compounds from Propargylic Alcohols and Alkenes

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Ruthenium- and Platinum-Catalyzed Sequential Reactions: Selective Synthesis of Fused Polycyclic Compounds from Propargylic Alcohols and Alkenes

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Abstract: A simple method for the preparation of fused polycyclic compounds by an intramolecular cyclization of propargylic alcohols bearing an alkene moiety at a suitable position has been developed, where the presence of both Ru and Pt catalysts promotes a sequence of catalytic cycles in the same medium. This sequential system can be applied to an intermolecular reaction between a propargylic alcohol and an alkene to obtain the corresponding bicyclo[3,1,0]hex-2-ene derivative. These sequential reactions provide a conceptually new type of cycloaddition system between propargylic alcohols and alkenes.

Introduction

Quite recently, we have disclosed that the ruthenium- and platinum-catalyzed sequential reactions of propargylic alcohols with ketones or with both ketones and anilines afforded the corresponding tri- and tetra-substituted furans or pyrroles, respectively, in moderate to good yields with a high regioselectivity.[1] It is noteworthy that, in this catalytic reaction system, both ruthenium and platinum catalysts sequentially promote each catalytic cycle in the same medium. Although some interesting results in which multiple and different transition metal catalysts work in the same medium have already been reported,[2] in most cases, the reaction conditions such as temperature and atmosphere had to be changed on the way, or successive addition of the catalyst was necessary in each reaction step.[3] Our previous

finding[1] prompted us to develop catalytic sequential reactions of such type to synthesize complex organic molecules from simple and readily available starting materials. Toward this end, our attention has been focused on the platinum-catalyzed cycloisomerization of enyne systems,[4] as we have already disclosed the preparative method of some enynes by the ruthenium-catalyzed carbon−carbon bond forming reaction between propargylic alcohols and alkenes.[5] This combination may provide a simple and one-pot synthetic protocol for fused polycyclic compounds directly from propargylic alcohols and alkenes, the first and second steps being propargylic substitution and cycloisomerization, respectively. Although many fused polycyclic compounds especially those containing cyclopropane moiety show biological activity and are widely recognized as potential drug leads,[6] the direct approach to the synthesis of such compounds is yet quite limited.[7] In addition, this sequential

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(2) For recent examples: examples where two catalysts activated different functional groups in the same medium, see: (a) Sawamura, M.; Sudoh, M.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3309. (b) Kamijo, S.; Yamamoto, Y. *J. Org. Chem.* **2003**, *68*, 4764 and references therein. Examples where two different catalytic cycles proceeded in the same medium, see: (c) Barnhart, R. W.; Bazan, G. C.; Mourey, T. *J. Am. Chem. Soc.* **1998**, *120*, 1082. (d) Jeong, N.; Seo, S. D.; Shin, J. Y. *J. Am. Chem. Soc.* **2000**, *122*, 10220. (e) Komon, Z. J. A.; Diamond, G. M.; Leclerc, M. K.; Murphy, V.; Okazaki, M.; Bazan, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 15280.

(3) For recent examples, see: (a) Evans, P. A.; Robinson, J. E. *J. Am. Chem. Soc.* **2001**, *123*, 4609. (b) Choudary, B. M.; Chowdari, N. S.; Madhi, S.; Kantam, M. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 4620. (c) Christopher, J. L.; Bielawski, W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 11312. (d) Shimada, T.; Mukaide, K.; Shinohara, A.; Han, J. W.; Hayashi, T. *J. Am. Chem. Soc.* **2002**, *124*, 1584. (e) Tian, J.; Yamagiwa, N.; Matsunaga, S.; Shibasaki, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3636. (f) Son, S. U.; Park, K. H.; Chung, Y. K. *J. Am. Chem. Soc.* **2002**, *124*, 6838. (g) Trost, B. M.; Machacek, M. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 4693. (h) Sutton, A. E.; Seigal, B. A.; Finnegan, D. F.; Snapper, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 13390. (i) Klapars, A.; Parris, S.; Anderson, K. W.; Buchwald, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 3529.

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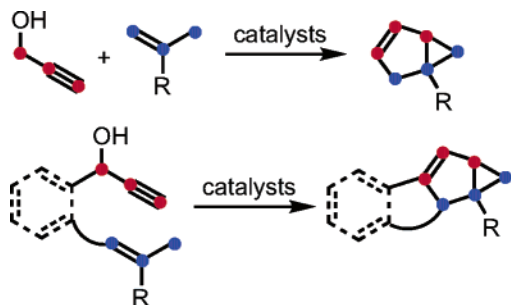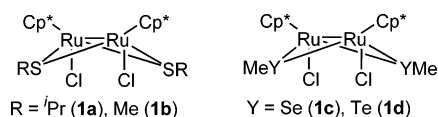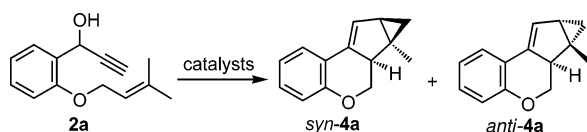
Scheme 1

Chart 1

R = ^{i}Pr (**1a**), Me (**1b**)   Y = Se (**1c**), Te (**1d**)

Scheme 2

Table 1. Reaction of Propargylic Alcohol (**2a**) in the Presence of Chalcogenolate-Bridged Diruthenium Complex (**1**) and Other Catalyst[a]

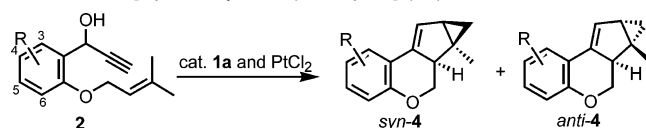| run	catalysts (mol %)	yield of **4a** (%)[b]
1	[Cp*RuCl(μ_2-S^{i}Pr)$_2$Cp*RuCl] (**1a**) (5) and PtCl$_2$ (10)	**4a**, 75 (83)[c,d]
2	[Cp*RuCl(μ_2-S^{i}Pr)$_2$Cp*RuCl] (**1a**) (5) and PtCl$_2$ (5)	**4a** (74)[c]
3	[Cp*RuCl(μ_2-S^{i}Pr)$_2$Cp*RuCl] (**1a**) (5) and PtCl$_4$ (10)	**4a** (28)[c]
4	[Cp*RuCl(μ_2-S^{i}Pr)$_2$Cp*RuCl] (**1a**) (5) and PdCl$_2$ (10)	**4a** (22)[c]
5	[Cp*RuCl(μ_2-S^{i}Pr)$_2$Cp*RuCl] (**1a**) (5) and AuCl$_3$ (10)	**4a** (3)[c,e]
6	[Cp*RuCl(μ_2-S^{i}Pr)$_2$Cp*RuCl] (**1a**) (5) and [Rh(OAc)$_2$]$_2$ (10)	**4a** (0)[c,f]
7	[Cp*RuCl(μ_2-SMe)$_2$Cp*RuCl] (**1b**) (5) and PtCl$_2$ (10)	**4a** (59)[c]
8	[Cp*RuCl(μ_2-SeMe)$_2$Cp*RuCl] (**1c**) (5) and PtCl$_2$ (10)	**4a** (58)[c]
9	[Cp*RuCl(μ_2-TeMe)$_2$Cp*RuCl] (**1d**) and PtCl$_2$ (10)	**4a** (19)[c]

[a] All of the reactions of **2a** (0.30 mmol) were carried out in the presence of catalysts and NH$_4$BF$_4$ (10 mol %) at 60 °C for 24 h. [b] Isolated yield of **4a** as a mixture of *syn-* and *anti*-isomers. [c] GLC yield of **4a** as a mixture of *syn-* and *anti*-isomers. In all cases, the ratio of stereoisomers (*syn-***4**: *anti-***4**) is ca. 9:1. [d] The exact ratio of stereoisomers (*syn-***4**:*anti-***4**) is 92:8. [e] An intermediate *syn-***3** was obtained in 14% GLC yield. [f] An intermediate *syn-***3** was obtained in 95% GLC yield.

system is considered to provide a novel type of cycloaddition reaction between propargylic alcohols and alkenes (Scheme 1). We present here a unique and general method for fused polycyclic compounds having bicyclo[3,1,0]hex-2-ene framework in good to excellent yields with a high selectivity by the ruthenium- and platinum-catalyzed sequential reactions of propargylic alcohols with alkenes.

Results and Discussion

Heating of propargylic alcohols bearing an alkene moiety (**2a**) in 1,2-dichloroethane (ClCH$_2$CH$_2$Cl) at 60 °C for 24 h in the presence of 2-propanethiolate-bridged diruthenium complex [Cp*RuCl(μ_2-S^{i}Pr)$_2$RuCp*Cl][8] (Cp* = η^5-C$_5$Me$_5$) (**1a**; Chart 1) (5 mol %), NH$_4$BF$_4$ (10 mol %), and PtCl$_2$ (10 mol %) afforded a stereoisomeric mixture of the fused tetracyclic compound, *syn-* and *anti*-6b-methyl-6a,6b,7,7a-tetrahydro-6*H*-5-oxacyclopropa[3,4]cyclopenta[1,2-*a*]naphthalene (**4a**), in 83% GLC yield (75% isolated yield: *syn-***4a**:*anti-***4a** = 92:8) (Scheme 2; Table 1, run 1). The reaction proceeded even in the presence of a smaller quantity of **1a** (5 mol %) and PtCl$_2$ (5 mol %) to give **4a** in a similar yield (Table 1, run 2). Other transition metal complexes, such as PtCl$_4$,[9] PdCl$_2$, AuCl$_3$,[10] and [Rh(OAc)$_2$]$_2$, in place of PtCl$_2$ did not work effectively (Table 1, entries 3−6). The complex having a less sterically demanding SMe group

such as [Cp*RuCl(μ_2-SMe)$_2$RuCp*Cl] (**1b**) exhibited a lower catalytic activity (Table 1, run 7). Interestingly, the methaneselenolate-bridged diruthenium complex[11] [Cp*RuCl(μ_2-SeMe)$_2$-RuCp*Cl] (**1c**) worked effectively, while the methanetellurolate-bridged diruthenium complex[11] [Cp*RuCl(μ_2-TeMe)$_2$RuCp*Cl] (**1d**) was not so effective (Table 1, runs 8 and 9). In all cases, **4a** was obtained as a stereoisomeric mixture, *syn*-isomer being rich. The use of other propargylic alcohols having various substituents on the phenyl ring (**2b−2j**) under the conditions of Table 1, run 1, resulted in the formation of a stereoisomeric mixture (ca. 10:1) of the corresponding fused tetracyclic compounds (**4b−4j**) in moderate to high yields. Typical results are shown in Table 2. The introduction of the second halogen atom at position 6 in the phenyl ring decreased the yield of **4** (Table 2, runs 9 and 10).

Next, reactions of other propargylic alcohols bearing various alkene moieties were similarly carried out. Typical results are shown in Table 3. In the use of the propargylic alcohol bearing a geranyl group (**2k**), the catalytic reaction proceeded to form the corresponding fused tetracyclic compound (**4k**) in 86% isolated yield (*syn-***4k**:*anti-***4k** = 77:23) (Table 3, run 1). Formation of the fused pentacyclic compound with naphthalene moiety (**4l**) (*syn-***4l**:*anti-***4l** = 62:38) was observed in the intramolecular cyclization of the propargylic alcohol (**2l**) (Table 3, run 2). Moreover, the use of propargylic alcohols bearing a cyclohexenyl or cycloheptenyl moiety (**2m** and **2n**) resulted in the formation of the corresponding fused pentacyclic compounds (**4m** and **4n**) in 90% and 89% isolated yields, respectively, *syn*-isomer being almost the sole product in both cases (Table 3, runs 3 and 4). The stereochemistry of the fused pentacyclic

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(8) (a) The thiolate-bridged diruthenium complexes have been found to provide unique bimetallic reaction sites for activation and transformation of various terminal alkynes, see: Nishibayashi, Y.; Yamanashi, M.; Wakiji, I.; Hidai, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 2909 and references therein. (b) The methanethiolate-bridged diruthenium complex [Cp*RuCl(μ_2-SMe)$_2$RuCp*Cl] (**1b**) is commercially available from Wako Pure Chemical Industries (Japan) as met-DIRUX (*met*hanethiolate-bridged *diru*thenium comple*x*) (130-14581).

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Table 2. Reaction of Various Propargylic Alcohols (**2**) in the Presence of [Cp*RuCl(μ_2-S^{i}Pr)$_2$RuCp*Cl] (**1a**) and PtCl$_2$[a]
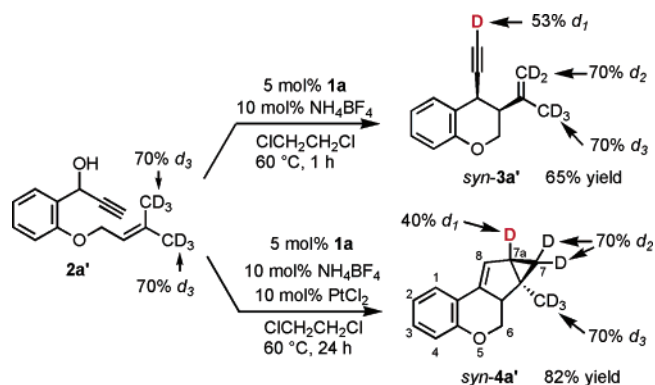

run	propargylic alcohol	yield of **4** (%)[b]	ratio of isomers[c] (syn-**4**:anti-**4**)
1	**2a**, R = H	**4a**, 75	92:8
2	**2b**, R = 4-Me	**4b**, 76	91:9
3	**2c**, R = 4-OMe	**4c**, 66	92:8
4	**2d**, R = 4-Cl	**4d**, 65	94:6
5	**2e**, R = 4-Br	**4e**, 69	93:7
6	**2f**, R = 4-NO$_2$	**4f**, 70	95:5
7	**2g**, R = 6-Me	**4g**, 83	92:8
8	**2h**, R = 6-OMe	**4h**, 81	92:8
9	**2i**, R = 4-Cl, 6-Cl	**4i**, 38	98:2
10	**2j**, R = 4-Br, 6-Br	**4j**, 39	93:7

[a] All of the reactions of **2** (0.30 mmol) were carried out in the presence of **1a** (5 mol %), NH$_4$BF$_4$ (10 mol %), and PtCl$_2$ (10 mol %), at 60 °C for 24 h. [b] Isolated yield of **4** as a mixture of *syn*- and *anti*-isomers. [c] The ratio of two stereoisomers of **4** was determined by ^{1}H NMR.
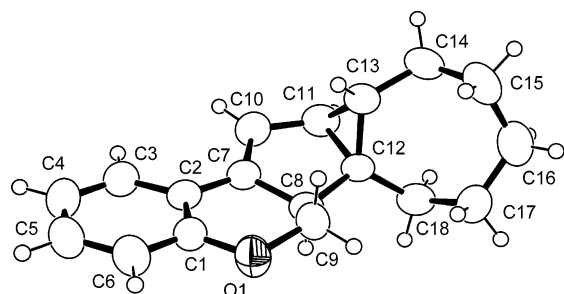
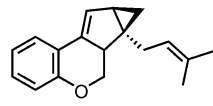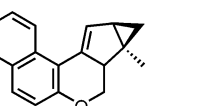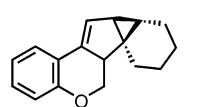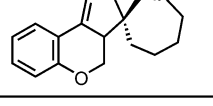**Figure 1.** Crystal structure of *syn*-**4n** with 50% probability ellipsoids.

compound (*syn*-**4n**) was unambiguously confirmed by X-ray analysis, and an ORTEP drawing of *syn*-**4n** is shown in Figure 1.

To obtain more information on the sequential reaction, the following reactions were carried out. A mixture of *syn*-**3a** and *anti*-**3a** with the ratio of 4.6:1 was found when **2a** was heated in the presence of only **1b** at 60 °C for 1 h (Scheme 3). When

Scheme 3

84% yield (*syn*-**3a**: *anti*-**3a** = 4.6 : 1)

Scheme 4

99% yield (**4a**: *anti*-**3a** = 4.4 : 1)
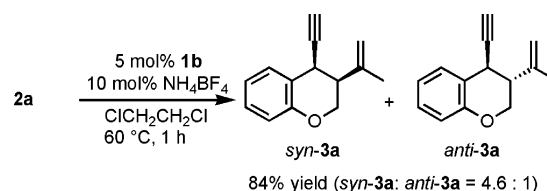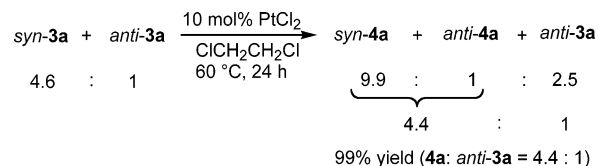
Scheme 5

the obtained mixture of *syn*-**3a** and *anti*-**3a** with the ratio of 4.6:1 was then treated with only PtCl$_2$ (10 mol %) at 60 °C for 24 h, the intramolecular cycloisomerization of *syn*-**3a** occurred to afford *syn*-**4a** and *anti*-**4a**, while all of *anti*-**3a** was recovered intact; the ratio of **4a** and *anti*-**3a** (4.4:1) was nearly the same as that of the starting *syn*-**3a** and *anti*-**3a** (4.6:1) (Scheme 4). This result clearly indicates that only *syn*-**3a** is transformed into the corresponding tetracyclic compound (*syn*-**4a** and *anti*-**4a**) and cycloisomerization of *anti*-**3a** does not proceed at all.

Table 3. Reaction of Various Propargylic Alcohols (**2**) in the Presence of [Cp*RuCl(μ_2-S^{i}Pr)$_2$RuCp*Cl] (**1a**) and PtCl$_2$[a]

run	propargylic alcohol	polycyclic compound (syn-**4**)	yield of **4** (%)[b]	ratio of isomers[c] (syn-**4** : anti-**4**)
1	**2k**		86 (**4k**)	77 : 23
2	**2l**		68 (**4l**)	62 : 38
3	**2m**		90 (**4m**)	>95 : <5
4	**2n**		89 (**4n**)	>95 : <5

[a] All of the reactions of **2** (0.30 mmol) were carried out in the presence of **1a** (5 mol %), NH$_4$BF$_4$ (10 mol %), and PtCl$_2$ (10 mol %), at 60 °C for 24 h. [b] Isolated yield of **4** as a mixture of *syn*- and *anti*-isomers. [c] The ratio of two stereoisomers of **4** was determined by ^{1}H NMR.

Scheme 6
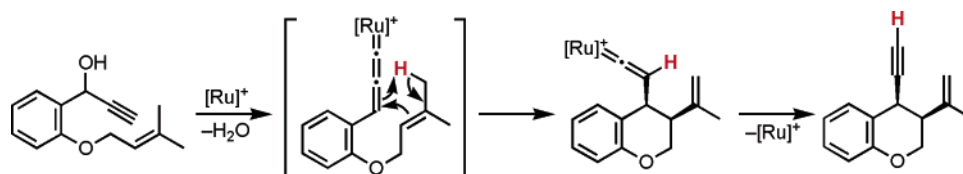
Scheme 7
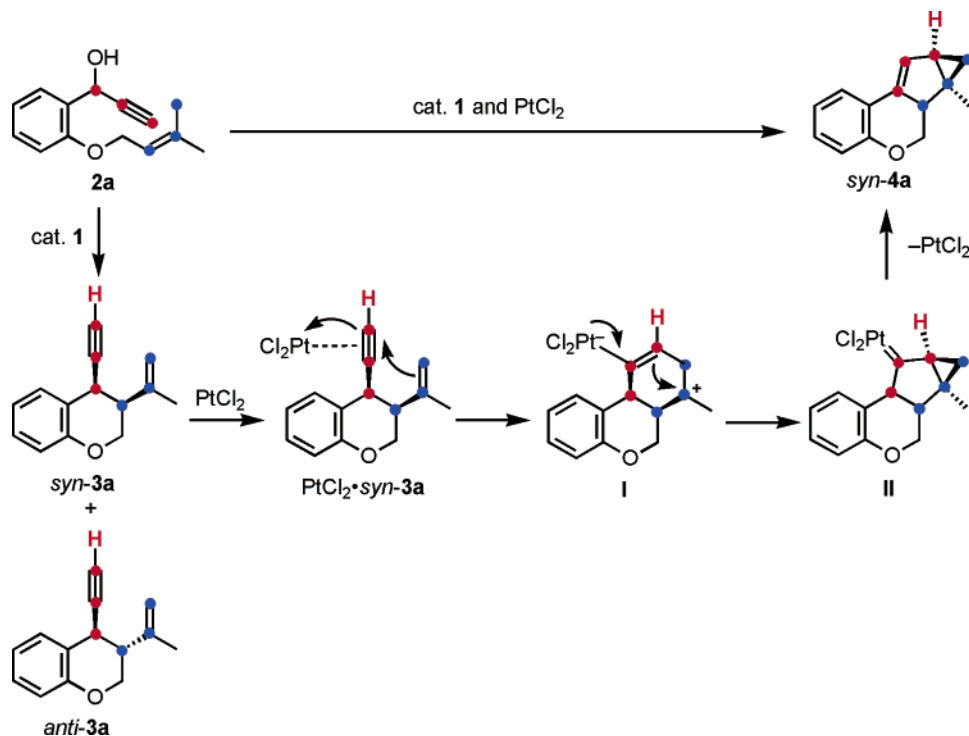
Next, the catalytic transformation of propargylic alcohol bearing the deuterium-substituted group (**2a′**) was investigated (Scheme 5). Intramolecular cyclization of **2a′** in the presence of only **1a** afforded *syn*-**3a′** in 65% yield with a high deuterium incorporation (53% by ^{1}H NMR) at the alkyne terminal position. This finding supports our previous reaction pathway as shown in Scheme 6.[5] On the other hand, bimetallic sequential reaction of **2a′** in the presence of both **1a** and PtCl₂ gave *syn*-**4a′** in 82% isolated yield with the deuterium incorporation (40%) at C-7a position. These results indicate that the deuterium incorporation at C-7a position of *syn*-**4a′** surely comes from the alkyne terminal position of *syn*-**3a′**.

On the basis of these findings, a pathway for this sequential reaction is proposed in Scheme 7. At first, **2a** was transformed rapidly into *syn*-**3a** and *anti*-**3a** in the presence of ruthenium catalyst **1a**. In the next step, platinum-catalyzed cycloisomerization proceeded only with *syn*-**3a** via the intermediates such as **I** and **II**, to afford the product *syn*-**4a**.[4] As has been pointed out by Fürstner[4c−e] and Echavarren,[4f−i] we should also consider the scheme for this cycloisomerization involving a nonclassical carbocation as the reactive intermediate.

This sequential catalytic system can be applied to an intermolecular reaction as well (Scheme 8). Treatment of 1-phenyl-2-propyn-1-ol (**5**) with α-methylstyrene in the presence of **1b** (5 mol %) and PtCl₂ (10 mol %) in ClCH₂CH₂Cl at 60 °C for 24 h gave 3,5-diphenylbicyclo[3,1,0]hex-2-ene (**7**) in 13% yield. When **1a** was used as a catalyst, the yield of **7** was

Scheme 8
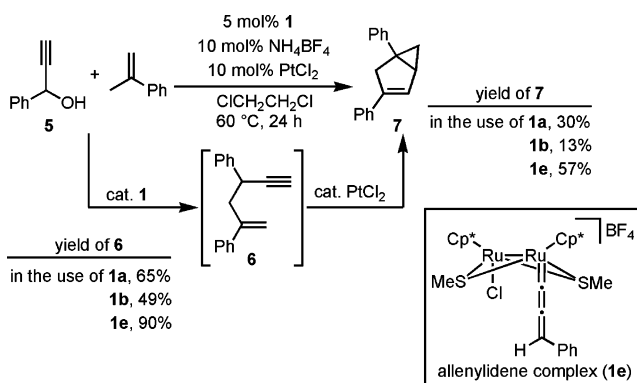
improved to 30% yield. Heating of the 1,5-enyne **6**, prepared separately by the **1a**-catalyzed reaction between **5** and α-methylstyrene,[5] in 1,2-dichloroethane at 60 °C for 24 h in the presence of 10 mol % of PtCl₂ gave **7** in 85% isolated yield, clearly showing that the Pt-catalyzed cycloisomerization step is involved in this sequential reaction. It was further disclosed that an allenylidene complex [Cp*RuCl(SMe)₂Cp*Ru(=C= C=CHPh)]BF₄ (**1e**),[12] which can be prepared by the reaction of **1b** with 1 equiv of **5** in the presence of NH₄BF₄ in tetrahydrofuran (THF) at room temperature for 30 min, worked more effectively. Thus, reaction of **5** with α-methylstyrene in the presence of **1e** (5 mol %) and PtCl₂ (10 mol %) gave **7** in 57% isolated yield with a complete selectivity. This is due to

the fact that **1e** works more effectively than others in the first propargylic substitution step as shown in Scheme 8.

Conclusion

In summary, a novel sequential catalytic system providing a simple and efficient one-pot synthetic method for a new type of skeleton of fused polycyclic compounds with a potential of biological activity is presented. In this system, thiolate-bridged diruthenium complexes promote catalytic propargylic substitution reaction between propargylic alcohols and alkenes in the first step, while PtCl$_2$ catalyzes cycloisomerization of the produced enynes in the same medium in the second step. The reaction proceeds intermolecularly as well as intramolecularly. These sequential reactions provide a conceptually new type of cycloaddition system between propargylic alcohols and alkenes.[13]

Experimental Section

General Method. ^{1}H NMR (400, 300, and 270 MHz) and ^{13}C NMR (100, 75, and 67.8 MHz) spectra were recorded using CDCl$_3$ as solvent. Quantitative GLC analyses were performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector using a 25 m × 0.25 mm CBP10 fused silica capillary column. GC-MS analyses were carried out on a Shimadzu GC-MS QP-5000 spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Mass spectra were measured on a JEOL JMS600H mass spectrometer. All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried by the usual methods and distilled before use.

Materials. The chalcogenolate-bridged diruthenium complexes[8,11] (**1**) and the allenylidene complex[12] (**1e**) were prepared according to our previous procedures. Propargylic alcohol (**2a**) was a commercial product. Other propargylic alcohols were prepared according to literature procedures.[5,14]

Selective Synthesis of Fused Polycyclic Compounds from Propargylic Alcohols Bearing an Alkene Moiety. A typical experimental procedure for the reaction of 1-[2-(3-methyl-2-butenyloxy)phenyl]prop-2-yn-1-ol (**2a**) catalyzed by [Cp*RuCl(μ_2-S^{i}Pr)$_2$RuCp*Cl] (**1a**) and PtCl$_2$ is described below. In a 50 mL flask were placed **1a** (10.4 mg, 0.015 mmol), NH$_4$BF$_4$ (3.1 mg, 0.03 mmol), and PtCl$_2$ (8.0 mg, 0.03 mmol) under N$_2$. Anhydrous ClCH$_2$CH$_2$Cl (27 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **2a** (64.9 mg, 0.30 mmol), the reaction mixture was heated at 60 °C for 24 h. The solvent was removed under reduced pressure by an aspirator, and then the residue was purified by TLC (SiO$_2$) with *n*-hexane as an eluent to give 6b-methyl-6a,6b,7,7a-tetrahydro-6*H*-5-oxacyclopropa[3,4]cyclopenta[1,2-*a*]naphthalene (**4a**) as a colorless oil (44.6 mg, 0.225 mmol, 75% yield). Two stereoisomers with the ratio

(12) (a) Nishibayashi, Y.; Wakiji, I.; Hidai, M. *J. Am. Chem. Soc.* **2000**, *122*, 11019. (b) Nishibayashi, Y.; Wakiji, I.; Ishii, Y.; Uemura, S.; Hidai, M. *J. Am. Chem. Soc.* **2001**, *123*, 3393. (c) Nishibayashi, Y.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 7900. (d) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 11846. (e) Nishibayashi, Y.; Onodera, G.; Inada, Y.; Hidai, M.; Uemura, S. *Organometallics* **2003**, *22*, 873. (f) Nishibayashi, Y.; Yoshikawa, M.; Inada, Y.; Hidai, M.; Uemura, S. *J. Org. Chem.* **2004**, *69*, 3408. (g) Nishibayashi, Y.; Milton, M. D.; Inada, Y.; Yoshikawa, M.; Wakiji, I.; Hidai, M.; Uemura, S. *Chem. Eur. J.*, in press.
(13) After the submission of our manuscript, a similar example of the reaction of propargylic alcohol with alkene catalyzed by rhenium and gold complexes was reported by Toste and co-workers.[4m] In this sequential reaction, however, the reaction conditions have to be changed on the way, and the successive addition of gold complex is necessary after the reaction of propargylic alcohol with allylsilane in the presence of rhenium complex. In contrast, it is noteworthy that, in our catalytic reaction system, both ruthenium and platinum catalysts sequentially promote each catalytic cycle in the same medium without changing the reaction conditions.
(14) Mann, A.; Muller, C.; Tyrrell, E. *J. Chem. Soc.*, *Perkin Trans. 1* **1998**, 1427.

of 92:8. ^{1}H NMR: δ 0.33 (t, 1H, J = 4.2 Hz), 0.62 (dd, 1H, J = 4.2 and 7.2 Hz), 1.36 (s, 3H), 1.64 (d, 1H, J = 7.2 Hz), 3.30 (dd, 1H, J = 5.1 and 12.1 Hz), 3.74 (dd, 1H, J = 10.2 and 12.1 Hz), 4.64 (dd, 1H, J = 5.1 and 10.2 Hz), 6.15 (s, 1H), 6.79−6.85 (m, 2H), 7.06 (dt, 1H, J = 4.8 and 15.5 Hz), 7.35 (dd, 1H, J = 1.4 and 7.7 Hz). ^{13}C NMR: δ 19.0, 20.9, 21.4, 29.3, 48.3, 71.0, 116.9, 120.6, 121.0, 124.6, 126.2, 128.4, 134.0, 153.6. Anal. Calcd for C$_{14}$H$_{14}$O: C, 84.81; H, 7.12. Found: C, 84.82; H, 7.32.

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

2-Methyl-6b-methyl-6a,6b,7,7a-tetrahydro-6*H*-5-oxacyclopropa[3,4]cyclopenta[1,2-*a*]naphthalene (4b). Yield 76%. A colorless oil. Two stereoisomers with the ratio of 91:9. ^{1}H NMR: δ 0.31 (t, 1H, J = 4.2 Hz), 0.60 (dd, 1H, J = 4.2 Hz and J = 7.5 Hz), 1.35 (s, 3H), 1.62 (d, 1H, J = 7.5 Hz), 2.23 (s, 3H), 3.29 (dd, 1H, J = 5.1 and 12.2 Hz), 3.70 (dd, 1H, J = 10.2 and 12.2 Hz), 4.60 (dd, 1H, J = 5.1 and 10.2 Hz), 6.12 (s, 1H), 6.70 (d, 1H, J = 8.3 Hz), 6.87 (d, 1H, J = 8.3 Hz), 7.15 (s, 1H). ^{13}C NMR: δ 19.0, 20.5, 20.8, 21.4, 29.3, 48.4, 71.0, 116.6, 120.6, 124.7, 125.8, 129.2, 129.7, 134.2, 151.5. Anal. Calcd for C$_{15}$H$_{16}$O: C, 84.87; H, 7.60. Found: C, 84.82; H, 7.74.

2-Methoxy-6b-methyl-6a,6b,7,7a-tetrahydro-6*H*-5-oxacyclopropa[3,4]cyclopenta[1,2-*a*]naphthalene (4c). Yield 66%. A pale yellow oil. Two stereoisomers with the ratio of 92:8. ^{1}H NMR: δ 0.32 (t, 1H, J = 4.2 Hz), 0.62 (dd, 1H, J = 4.2 and 7.3 Hz), 1.36 (s, 3H), 1.64 (d, 1H, J = 7.3 Hz), 3.29 (dd, 1H, J = 5.0 and 12.1 Hz), 3.69 (dd, 1H, J = 10.1 and 12.1 Hz), 3.74 (s, 3H), 4.59 (dd, 1H, J = 5.0 and 10.1 Hz), 6.14 (s, 1H), 6.64−6.78 (m, 2H), 6.86 (s, 1H). ^{13}C NMR: δ 19.0, 20.8, 21.4, 29.3, 48.4, 55.7, 71.0, 108.4, 115.2, 117.6, 121.2, 126.5, 134.3, 147.9, 153.5. HRMS (FAB) calcd for C$_{15}$H$_{16}$O$_2$ [M], 228.1150; found, 228.1146.

2-Chloro-6b-methyl-6a,6b,7,7a-tetrahydro-6*H*-5-oxacyclopropa[3,4]cyclopenta[1,2-*a*]naphthalene (4d). Yield 65%. A pale yellow oil. Two stereoisomers with the ratio of 94:6. ^{1}H NMR: δ 0.31 (t, 1H, J = 4.0 Hz), 0.63 (dd, 1H, J = 4.0 and 7.2 Hz), 1.35 (s, 3H), 1.65 (d, 1H, J = 7.2 Hz), 3.26 (dd, 1H, J = 4.9 and 12.7 Hz), 3.69 (dd, 1H, J = 10.3 and 12.7 Hz), 4.62 (dd, 1H, J = 4.9 and 10.3 Hz), 6.16 (s, 1H), 6.73 (d, 1H, J = 8.8 Hz), 6.99 (d, 1H, J = 8.8 Hz), 7.29 (s, 1H). ^{13}C NMR: δ 19.0, 20.8, 21.5, 29.4, 48.0, 71.1, 118.2, 122.3, 124.1, 125.4, 127.6, 128.0, 132.9, 152.0. Anal. Calcd for C$_{14}$H$_{13}$ClO: C, 72.26; H, 5.63. Found: C, 72.24; H, 5.68.

2-Bromo-6b-methyl-6a,6b,7,7a-tetrahydro-6*H*-5-oxacyclopropa[3,4]cyclopenta[1,2-*a*]naphthalene (4e). Yield 69%. A pale yellow oil. Two stereoisomers with the ratio of 93:7. ^{1}H NMR: δ 0.31 (t, 1H, J = 4.4 Hz), 0.63 (dd, 1H, J = 4.4 and 7.4 Hz), 1.35 (s, 3H), 1.65 (d, 1H, J = 7.2 Hz), 3.25 (dd, 1H, J = 5.1 and 12.1 Hz), 3.69 (dd, 1H, J = 10.2 and 12.1 Hz), 4.63 (dd, 1H, J = 5.1 and 10.2 Hz), 6.16 (s, 1H), 6.68 (d, 1H, J = 8.9 Hz), 7.13 (d, 1H, J = 8.9 Hz), 7.44 (s, 1H). ^{13}C NMR: δ 19.0, 20.8, 21.5, 29.4, 47.9, 71.1, 112.9, 118.7, 122.9, 127.1, 127.4, 131.0, 132.8, 152.6. Anal. Calcd for C$_{14}$H$_{13}$BrO: C, 60.67; H, 4.73. Found: C, 60.57; H, 4.75.

6b-Methyl-2-nitro-6a,6b,7,7a-tetrahydro-6*H*-5-oxacyclopropa[3,4]cyclopenta[1,2-*a*]naphthalene (4f). Yield 70%. Yellow crystals. Mp. 97.5−98.4 °C. Two stereoisomers with the ratio of 95:5. ^{1}H NMR: δ 0.35 (t, 1H, J = 4.3 Hz), 0.70 (dd, 1H, J = 4.3 and 7.4 Hz), 1.38 (s, 3H), 1.73 (m, 1H), 3.29 (dd, 1H, J = 5.3 and 12.1 Hz), 3.79 (dd, 1H, J = 10.3 and 12.1 Hz), 4.76 (dd, 1H, J = 5.3 and 10.3 Hz), 6.35 (s, 1H), 6.86 (d, 1H, J = 9.1 Hz), 7.93 (dd, 1H, J = 2.7 and 9.1 Hz), 8.22 (d, 1H, J = 2.7 Hz). ^{13}C NMR: δ 19.0, 20.8, 21.8, 29.6, 47.5, 71.7, 117.3, 120.7, 121.2, 123.7, 129.6, 131.7, 141.3, 158.4. Anal. Calcd for C$_{14}$H$_{13}$NO$_3$: C, 69.12; H, 5.39; N, 5.76. Found: C, 69.13; H, 5.44; N, 5.65.

4-Methyl-6b-methyl-6a,6b,7,7a-tetrahydro-6*H*-5-oxacyclopropa[3,4]cyclopenta[1,2-*a*]naphthalene (4g). Yield 83%. A colorless oil. Two stereoisomers with the ratio of 92:8. ^{1}H NMR: δ 0.32 (t, 1H, J = 4.1 Hz), 0.60 (dd, 1H, J = 4.1 and 7.2 Hz), 1.35 (s, 3H), 1.62 (d, 1H, J = 7.2 Hz), 2.16 (s, 3H), 3.28 (dd, 1H, J = 5.1 and 12.1 Hz),

3.72 (dd, 1H, $J = 10.1$ and 12.1 Hz), 4.68 (dd, 1H, $J = 5.1$ and 10.1 Hz), 6.11 (s, 1H), 6.67–6.75 (m, 1H), 6.93 (d, 1H, $J = 7.8$ Hz), 7.20 (d, 1H, $J = 7.8$ Hz). ^{13}C NMR: δ 16.2, 18.9, 20.9, 21.4, 29.4, 48.3, 70.9, 120.0, 120.4, 122.2, 125.9, 126.1, 129.6, 134.5, 151.9. Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 85.17; H, 7.80.

4-Methoxy-6b-methyl-6a,6b,7,7a-tetrahydro-6*H*-5-oxacyclopropa-[3,4]cyclopenta[1,2-*a*]naphthalene (4h). Yield 81%. A colorless oil. Two stereoisomers with the ratio of 92:8. ^{1}H NMR: δ 0.34 (t, 1H, $J = 4.1$ Hz), 0.62 (dd, 1H, $J = 4.1$ and 7.2 Hz), 1.36 (s, 3H), 1.64 (d, 1H, $J = 7.2$ Hz), 3.31 (dd, 1H, $J = 5.2$ and 12.2 Hz), 3.77 (dd, 1H, $J = 10.1$ and 12.2 Hz), 3.84 (s, 3H), 4.78 (dd, 1H, $J = 5.2$ and 10.1 Hz), 6.15 (s, 1H), 6.68 (dd, 1H, $J = 1.5$ and 8.1 Hz), 6.77 (t, 1H, $J = 7.8$ Hz), 6.98 (dd, 1H, $J = 1.5$ and 7.8 Hz). ^{13}C NMR: δ 18.9, 20.8, 21.4, 29.3, 48.0, 55.8, 71.5, 110.0, 116.6, 120.1, 121.6, 126.8, 133.7, 142.9, 148.6. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.82; H, 7.18.

2,4-Dichloro-6b-methyl-6a,6b,7,7a-tetrahydro-6*H*-5-oxacyclopropa-[3,4]cyclopenta[1,2-*a*]naphthalene (4i). Yield 38%. A colorless oil. Two stereoisomers with the ratio of 98:2. ^{1}H NMR: δ 0.32 (t, 1H, $J = 4.3$ Hz), 0.67 (dd, 1H, $J = 4.3$ and 7.4 Hz), 1.36 (s, 3H), 1.68 (d, 1H, $J = 7.4$ Hz), 3.28 (dd, 1H, $J = 5.0$ and 12.0 Hz), 3.75 (dd, 1H, $J = 10.2$ and 12.0 Hz), 4.78 (dd, 1H, $J = 5.0$ and 10.2 Hz), 6.21 (s, 1H), 7.12 (d, 1H, $J = 2.3$ Hz), 7.21 (d, 1H, $J = 2.3$ Hz). ^{13}C NMR: δ 19.0, 20.7, 21.6, 29.5, 47.7, 71.7, 122.4, 122.5, 123.3, 125.0, 128.0, 129.2, 132.0, 147.8. Anal. Calcd for $C_{14}H_{12}Cl_2O$: C, 62.94; H, 4.53. Found: C, 62.79; H, 4.57.

2,4-Dibromo-6b-methyl-6a,6b,7,7a-tetrahydro-6*H*-5-oxacyclopropa-[3,4]cyclopenta[1,2-*a*]naphthalene (4j). Yield 39%. A colorless oil. Two stereoisomers with the ratio of 93:7. ^{1}H NMR: δ 0.32 (t, 1H, $J = 4.3$ Hz), 0.67 (dd, 1H, $J = 4.3$ and 7.4 Hz), 1.36 (s, 3H), 1.64–1.71 (m, 1H), 3.28 (dd, 1H, $J = 5.2$ and 12.2 Hz), 3.76 (dd, 1H, $J = 10.2$ and 12.2 Hz), 4.78 (dd, 1H, $J = 5.2$ and 10.2 Hz), 6.21 (s, 1H), 7.40 (d, 1H, $J = 2.4$ Hz), 7.42 (d, 1H, $J = 2.4$ Hz). ^{13}C NMR: δ 19.0, 20.9, 21.4, 29.3, 48.3, 71.0, 111.8, 112.5, 123.7, 126.2, 129.2, 131.9, 133.4, 149.2. Anal. Calcd for $C_{14}H_{12}Br_2O$: C, 47.23; H, 3.40. Found: C, 47.23; H, 3.39.

6b-(4-Methylpent-3-enyl)-6a,6b,7,7a-tetrahydro-6*H*-5-oxacyclopropa[3,4]cyclopenta[1,2-*a*]naphthalene (4k). Yield 86%. A colorless oil. Two stereoisomers with the ratio of 77:23. ^{1}H NMR: δ 0.38 (t, 1H, $J = 4.2$ Hz), 0.67 (dd, 1H, $J = 4.3$ and $J = 7.3$ Hz), 1.62 (s, 3H), 1.69 (s, 3H), 1.80 (m, 1H), 2.01–2.13 (m, 2H), 3.40 (dd, 1H, $J = 5.0$ and 11.9 Hz), 3.76 (dd, 1H, $J = 10.3$ and 11.9 Hz), 4.67 (dd, 1H, $J = 5.0$ and 10.3 Hz), 5.10–5.15 (m, 1H), 6.13 (s, 1H), 6.79–6.84 (m, 2H), 7.03–7.09 (m, 1H), 7.34 (d, 1H, $J = 7.7$ Hz). ^{13}C NMR: δ 17.7, 18.3, 25.7, 26.2, 26.3, 28.3, 35.9, 46.5, 71.6, 116.6, 120.5, 120.9, 123.9, 124.5, 125.7, 128.2, 131.6, 134.1, 153.3. Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.45; H, 8.41.

8b-Methyl-8a,8b,9,9a-tetrahydro-8*H*-7-oxacyclopropa[3,4]cyclopenta[1,2-*c*]phenanthrene (4l). Yield 68%. A pale yellow oil. Two stereoisomers with the ratio of 62:38. ^{1}H NMR: δ 0.38 (t, 1H, $J = 3.9$ Hz, *anti* isomer), 0.50 (t, 1H, $J = 3.6$ Hz, *syn* isomer), 0.64 (dd, 1H, $J = 3.6$ and 7.5 Hz, *syn* isomer), 0.84 (dd, 1H, $J = 3.9$ and 7.8 Hz, *anti* isomer), 1.40 (s, 3H, *anti* isomer), 1.35 (s, 3H, *syn* isomer), 1.58–1.64 (m, 1H, *anti* isomer), 1.84 (dt, 1H, $J = 2.4$ and 7.5 Hz, *syn* isomer), 3.11 (d, 1H, $J = 16.2$ Hz, *anti* isomer), 3.40–3.45 (m, 1H, *syn* isomer), 3.93 (dd, 1H, $J = 10.2$ and 12.0 Hz, *syn* isomer), 4.76 (dd, 1H, $J = 5.6$ and 10.2 Hz, *syn* isomer), 4.90–5.07 (m, 2H, *anti* isomer), 6.52 (s, 1H, *syn* isomer), 6.99–7.73 (m, 13H), 8.12 (d, 1H, $J = 8.4$ Hz, *anti* isomer), 8.28 (d, 1H, $J = 8.7$ Hz). HRMS (FAB) calcd for $C_{18}H_{16}O$ [M], 248.1201; found, 248.1203.

6a,7,8,9,10,10a,10b-Heptahydro-6*H*-5-oxacyclohexa[2′,3′]cyclopropa[1′,2′:3,4]cyclopenta[1,2-*a*]naphthalene (4m). Yield 90%. A pale yellow oil. Only one isomer was observed. ^{1}H NMR: δ 0.73 (d, 1H, $J = 3.6$ Hz), 1.22–1.44 (m, 3H), 1.50–1.65 (m, 2H), 1.78–2.06 (m, 4H), 3.28 (dd, 1H, $J = 5.1$ and 12.0 Hz), 3.77 (dd, 1H, $J = 10.0$ and 12.0 Hz), 4.61 (dd, 1H, $J = 5.1$ and 10.0 Hz), 6.15 (s, 1H), 6.79–

Table 4. Crystallographic Data for *syn*-**4n**

formula	$C_{18}H_{20}O$
formula weight	252.36
cryst size (mm^3)	$0.80 \times 0.60 \times 0.10$
cryst system	monoclinic
space group	$P2_1/n$ (No. 14)
cryst color	colorless
a (Å)	12.576(7)
b (Å)	13.2311(6)
c (Å)	17.2462(8)
β (deg)	101.968(1)
V (Å^3)	2807.5(2)
Z	8
d_{calc} (g cm^{-3})	1.194
F (000)	1088.00
μ_{calc} (cm^{-1})	0.72
no. of unique data	6415
no. of observations	4933
no. of params refined	383
R_1	0.046
wR_2	0.100
goodness of fit indicator	1.019
maximum residuals (e Å^{-3})	0.38

6.84 (m, 2H), 7.02–7.09 (m, 1H), 7.34–7.37 (m, 1H). ^{13}C NMR: δ 22.2, 22.5, 24.2, 24.6, 25.9, 27.8, 33.8, 49.7, 70.7, 116.8, 120.5, 121.1, 124.6, 125.9, 128.2, 132.6, 153.5. Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.43; H, 7.62.

6a,7,8,9,10,11,11a,11b-Octahydro-6*H*-5-oxacyclohepta[2′,3′]cyclopropa[1′,2′:3,4]cyclopenta[1,2-*a*]naphthalene (4n). Yield 89%. Colorless crystals. Mp 54.0–55.0 °C. Only one isomer was observed. ^{1}H NMR: δ 0.69 (ddd, 1H, $J = 2.6$, 5.8, and 10.4 Hz), 0.96 (m, 1H), 1.16–1.44 (m, 3H), 1.58–1.85 (m, 5H), 2.13–2.23 (m, 2H), 3.33 (dd, 1H, $J = 5.1$ and 12.1 Hz), 3.85 (dd, 1H, $J = 10.0$ and 12.1 Hz), 4.74 (dd, 1H, $J = 5.1$ and 10.0 Hz), 6.12 (s, 1H), 6.77–6.83 (m, 2H), 7.04 (m, 1H), 7.33 (dd, 1H, $J = 1.7$ and 8.0 Hz). ^{13}C NMR: δ 14.1, 28.9, 29.4, 29.7, 31.2, 32.2, 35.2, 38.7, 51.1, 71.3, 116.6, 120.4, 120.9, 124.4, 125.3, 128.1, 133.3, 153.1. HRMS (FAB) calcd for $C_{18}H_{20}O$ [M], 252.1514; found, 252.1515.

Selective Synthesis of Fused Polycyclic Compounds from 1-Phenyl-2-propyn-1-ol with α-Methylstyrene. A typical experimental procedure for the reaction of 1-phenyl-2-propyn-1-ol (**5**) with α-methylstyrene catalyzed by [Cp*RuCl(SMe)$_2$Cp*Ru(=C=C=CHPh)]BF$_4$ (**1e**) and PtCl$_2$ is described below. In a 50 mL flask were placed **1e** (12.0 mg, 0.015 mmol) and PtCl$_2$ (8.0 mg, 0.03 mmol) under N$_2$. Anhydrous ClCH$_2$CH$_2$Cl (27 mL) was added, and then the mixture was magnetically stirred at room temperature. After the addition of **5** (39.7 mg, 0.30 mmol) and α-methylstyrene (709.1 mg, 6.00 mmol), the reaction mixture was heated at 60 °C for 24 h. The solvent was removed under reduced pressure by an aspirator, and then the residue was purified by TLC (SiO$_2$) with *n*-hexane as an eluent to give 3,5-diphenylbicyclo[3,1,0]hex-2-ene (**7**) as a white solid (39.7 mg, 0.171 mmol, 57% yield). ^{1}H NMR: δ 0.72 (t, 1H, $J = 3.8$ Hz), 1.42 (dd, 1H, $J = 3.8$ and 7.6 Hz), 2.28 (m, 1H), 3.14 (d, 1H, $J = 16.9$ Hz), 3.32 (d, 1H, $J = 16.9$ Hz), 6.50 (d, 1H, $J = 2.0$ Hz), 7.17–7.41 (m, 10H). ^{13}C NMR: δ 27.1, 31.5, 32.8, 42.0, 124.9, 125.5, 126.7, 126.8, 128.2, 129.1, 136.1, 140.1, 144.6. Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.25; H, 6.93.

X-ray Crystallographic Studies of 4n. Colorless crystals of *syn*-**4n** suitable for X-ray analysis were obtained by recrystallization from CH$_2$Cl$_2$–*n*-hexane. A single crystal was sealed in a Pyrex glass capillary under N$_2$ atm and was 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 (SIR88) and subsequent Fourier syntheses (DIRDIF99).

Supporting Information Available: Crystallographic data of *syn*-**4n** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

JA045532K