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Cationic Rh(I) Catalyst in Fluorinated Alcohol: Mild Intramolecular Cycloaddition Reactions of Ester-Tethered Unsaturated Compounds

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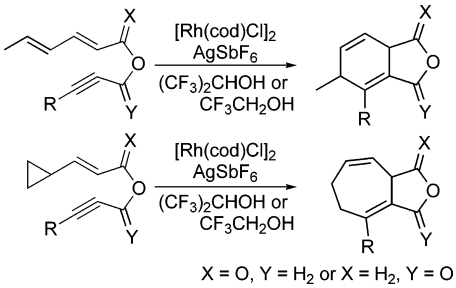
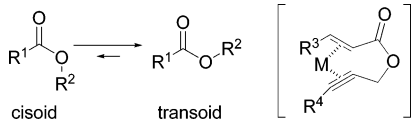


In fluorinated alcohols, the cationic Rh(I) species, which is derived from $[Rh(COD)Cl]_2$ and $AgSbF_6$, efficiently catalyzed intramolecular [4+2] cycloaddition reactions of ester-tethered 1,3-diene-8-yne derivatives. The catalytic system was also effective in intramolecular [5+2] cycloaddition reactions of ester-tethered ω-alkynyl vinylcyclopropane compounds.

Introduction

The intramolecular cycloaddition reaction provides a straightforward procedure for the potentially stereocontrolled construction of bicyclic and polycyclic compounds, and the reaction has been applied to the synthesis of a variety of molecules including natural products.[1] In intramolecular cycloaddition, the reactivity of the substrate and the stereochemical outcome of the product are strongly influenced by the tethering chain which links reaction sites. For example, ester-tethered diene−ene compounds often show low reactivity in the intramolecular Diels−Alder (IMDA) reaction. The reduced reactivity of the ester-tethered compound is due to the difficulty in adopting a cisoid form, in which the diene and the dienophile are in close proximity.[2,3] Such a conformational disadvantage is explained by the steric repulsion between the two substituents (R^1 and R^2) and by the dipole−dipole repulsion between the carbonyl and ethereal oxygen groups (Scheme 1).[4] To overcome this conformational difficulty, the use of a polar solvent[5] or the modification of the tether of the substrates from ester to acetal[6] or to hydroxamate[7] has been reported. These methodologies, however, have drawbacks such as limited availability or requiring laborious synthesis

SCHEME 1



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(2) Reviews on intramolecular Diels−Alder reactions: (a) Ciganek, E. In *Organic Reactions*; Dauben, W. G., Ed.; John Wiley & Sons: New York, 1984; Vol. 32, pp 1−374. (b) Craig, D. *Chem. Soc. Rev.* **1987**, *16*, 187. (c) Roush, W. R. In *Advances in Cycloaddition*; Curran, D. P., Ed.; JAI Press: Greenwich, CT, 1990; Vol. 2, pp 91−146. (d) Roush, W. R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I. Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 5, pp 513−550.

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(4) (a) Cain, D.; Pawar, D. M.; Stewart, M.; Billings, H., Jr.; Noe, E. A. *J. Org. Chem.* **2001**, *66*, 6092. (b) Review on the conformation and stereoelectric effect of ester compounds; see: Deslongchamps, P. in *Stereoelectric Effects in Organic Chemistry*; Pergamon Press: Oxford, 1983; pp 54−100.

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of reactants. It should be mentioned that a Lewis acid, which is effective for intermolecular Diels−Alder reactions, does not necessarily work well in the IMDA reactions of the ester-tethered substrates.[3a,8]

Recently, we reported that a novel bidentate Lewis acid, bisaluminated triflic amide TfN[Al(Me)Cl]2, efficiently promotes the IMDA reaction of 1,7,9-decatrienoate derivatives.[9] This bidentate Lewis acid, however, essentially requires a stoichiometric or a substoichiometric amount for the reaction. We assumed that ester-tethered unsaturated compounds would take a preferable cisoid form through the coordination of transition metal to carbon−carbon unsaturated bonds (Scheme 1), and we reported in a communication that intramolecular [4+2] cycloaddition reactions of ester-tethered 1,3-diene-8-yne compounds can be efficiently catalyzed by the cationic Rh(I) complex in fluorinated alcohols.[10]

Although the usefulness of Rh(I) catalysts has been reported in regard to the formation of medium-sized ring compounds through cycloaddition such as [4+2] cycloadditions of alkyne−diene compounds[11,12] and/or [5+2] cycloadditions of alkyne−vinylcyclopropane compounds,[13] there has been no report about transition-metal-catalyzed intramolecular cycloadditions of ester-tethered alkyne-unsaturated compounds. The efficiency of cationic Rh(I) encouraged us to examine the scope of [4+2] cycloadditions of ester-tethered *ω*-alkynyl dienes as well as the application to [5+2] cycloadditions of ester-tethered *ω*-alkynyl vinylcyclopropane derivatives. In this paper, we describe in detail the mild intramolecular cycloadditions of such ester-tethered substrates catalyzed by cationic Rh(I) in fluorinated alcohol media (Scheme 2).

SCHEME 2

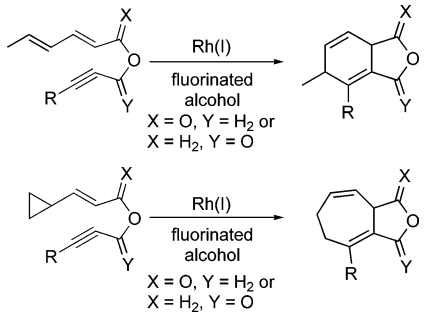
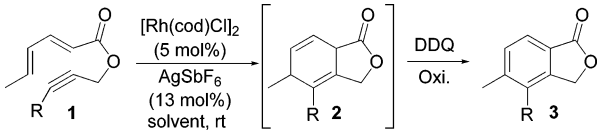


TABLE 1. [4+2] Cycloaddition of Sorbates[a]



entry	**1**	R	solvent	time (h)	**3** (%)[b]
1[c]	**1a**	Me	HFIP	5	**3a** 67
2[c]	**1b**	H	HFIP	1	**3b** 81
3[c]	**1c**	Ph	TFE	27	**3c** 63
4[c,d]	**1d**	*t*BuMe$_2$Si	TFE	48	**3d** 51
5	**1a**	Me	HFIP	2	**3a** 84
6	**1b**	H	HFIP	1	**3b** 81
7	**1c**	Ph	TFE	24	**3c** 77
8[d]	**1d**	*t*BuMe$_2$Si	TFE	24	**3d** 60

[a] Immediately after mixing [Rh(COD)Cl]$_2$ with AgSbF$_6$, **1** was added, unless otherwise noted. [b] Isolated yield. [c] [Rh(COD)Cl]$_2$ was treated with AgSbF$_6$ for 30 min prior to the addition of **1**. [d] Reaction temperature: 50 °C.

Results and Discussion

[4+2] Cycloaddition Reaction. The cationic Rh(I)-catalyzed [4+2] cycloaddition reactions of sorbates **1a**−**d** are shown in Table 1. In the presence of the cationic Rh(I) catalyst generated in situ by mixing 5 mol % of [Rh(COD)Cl]$_2$ and 13 mol % of AgSbF$_6$ in hexafluoroisopropanol (HFIP) for 30 min, the reaction of **1a** proceeded in HFIP at room temperature for 5 h to give the corresponding cycloadduct **2a**. Because the initially formed **2a** was readily oxidized to benzofuranone **3a** during the workup and was difficult to be separated from **3a**, the crude reaction mixture was directly treated with DDQ. Thus, after the DDQ oxidative workup, **3a** was isolated in 67% yield (entry 1). In addition to the reaction of methyl-substituted **2a**, the formation of hydrogene-substituted **2b** was efficiently achieved in HFIP, and the subsequent DDQ oxidative workup gave **3b** in 81% yield (entry 2). Interestingly, for the reaction of phenyl- or *tert*-butyldimethylsilyl-substituted compound **1c** or **1d**, trifluoroethanol (TFE) was found to be more suitable than HFIP (entries 3 and 4). Furthermore, it turns out that the yield of **3** was improved by the addition of substrate **1** immediately after mixing [Rh(COD)Cl]$_2$ with AgSbF$_6$ (see Experimental Section). A similar observation in regard to the preparation of the cationic Rh catalyst has been reported to provide good results in the cycloisomerization of 1,6-enynes.[14] Thus, **3a** was obtained in 84% yield after the DDQ oxidative workup and **3c** or **3d** was obtained in a good yield (entries 5−8). Because the sole use of a catalytic amount of [Rh(COD)Cl]$_2$ or AgSbF$_6$ did not yield

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SCHEME 3. [4+2] Cycloaddition of Sorbates 1a,b Followed by Silica Gel Workup

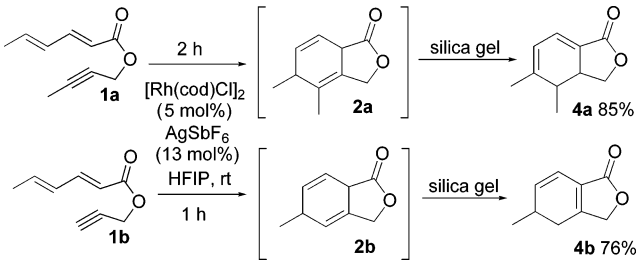
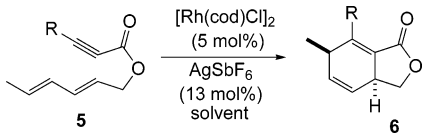


TABLE 2. [4+2] Cycloadditions of Propiolates



entry	5	R	solvent	time (h)	6 (%)[a]
1	**5a**	H	TFE	1	**6a** quant.
2	**5a**	H	HFIP	1	**6a** 11
3	**5a**	H	HFIP−CH_2Cl_2	1	**6a** 73
4	**5b**	Me	TFE	1	**6b** 98
5	**5c**	Ph	TFE	2	**6c** quant.
6[b]	**5a**	H	toluene	12	**6a** 94
7[b,c]	**5b**	Me	xylene	24	**6b** 96
8[b]	**5c**	Ph	xylene	3	**6c** 98

[a] Isolated yield. [b] No catalyst under refluxing conditions. [c] Ref 15a.

2a, the cationic Rh catalyst in the present reaction is suggested to be an active catalyst. It is worth noting that the addition of a phosphine ligand (Ph3P, dppb, or ((CF3)2CHO)3P) to the cationic Rh catalyst or the thermal reaction of **1a** in TFE or HFIP at refluxing temperature without the use of the catalyst did not give a cyclized product.[15]

As shown in the [4+2] cycloaddition reaction of **1a** or **1b** (Scheme 3), the addition of silica gel to the reaction mixture after the consumption of the starting ester (by TLC) gave conjugated dienelactone **4a** or **4b**, which was derived from initially formed **2a** or **2b** through isomerization.

In the [4+2] reaction of propiolate **5**, the cationic Rh(I)−TFE system showed particular efficiency (Table 2). That is, treatment of propiolate **5a** with the cationic Rh(I) catalyst in TFE at room temperature for 1 h afforded the corresponding adduct **6a** in quantitative yield (entry 1). In contrast to the case of sorbate **1**, the use of HFIP solvent lowered the yield of **6a** because of the decomposition of **5a** (entries 2 and 3). In the cases of methyl- and phenyl-substituted compounds **5b** and **5c**, TFE was found to be an efficient solvent, and adducts **6b** and **6c** were obtained in excellent yields, respectively (entries 4 and 5). It should be noted that the thermal IMDA reactions of **5** in the absence of the cationic Rh(I) catalyst showed excellent results for the formation of **6**. It, however, required a higher temperature and longer time to complete the reaction (by TLC) (entries 6−8).[16] In all cases examined, each adduct **6a**−**c** was obtained as a single isomer with illustrated trans stereochemistry.

On the basis of the described procedure, tricyclic lactones **3e** and **6d** were prepared in good yields (Scheme 4). Thus, **3e**

SCHEME 4. Synthesis of Tricyclic Lactone

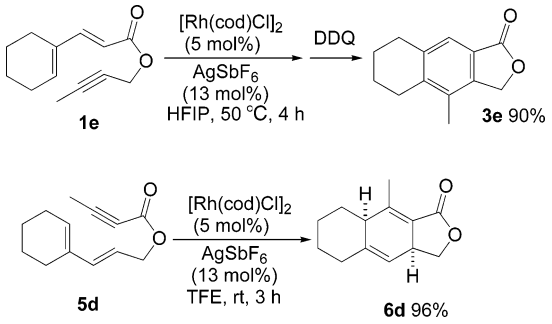
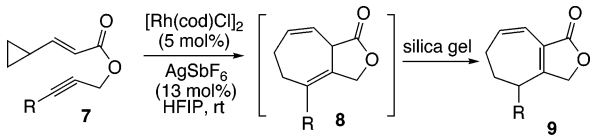


TABLE 3. [5+2] Cycloadditions of β-Cyclopropylacrylates[a]



			time (h)		
entry	7	R	addition	total	9 (%)[b]
1	**7a**	Me		3	**9a** 84
2[c]	**7a**	Me		3	**9a** 80
3[d,e]	**7a**	Me		5	**9a** 50
4	**7a**	Me		24	**9a** –[f]
5	**7b**	H	1	2	**9b** 73
6	**7c**	CH_2OMe	1	2	**9c** 87
7	**7d**	*n*-Bu	1	3	**9d** 70

[a] Immediately after mixing $[Rh(COD)Cl]_2$ with $AgSbF_6$, **7** was added, unless otherwise noted. [b] Isolated yield. [c] $[Rh(COD)Cl]_2$ was treated with $AgSbF_6$ in the presence of **7**. [d] $[Rh(COD)Cl]_2$ was treated with $AgSbF_6$ for 30 min prior to the addition of **7**. [e] Solvent: TFE. [f] Recovery of **7a**: 23%.

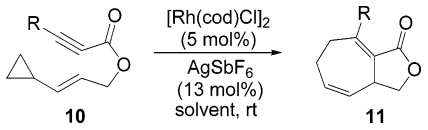
was obtained in 90% yield after the cycloaddition of **1e** in HFIP at 50 °C for 4 h and the subsequent DDQ oxidative workup, and **6d** was obtained in 96% yield in TFE at room temperature for 3 h.

[5+2] Cycloaddition Reaction. The Rh(I)-catalyzed inter- or intramolecular [5+2] cycloaddition reactions of vinylcyclopropane and alkyne compounds have been reported to give seven-membered ring compounds.[13] To our knowledge, however, no successful examples of the intramolecular reaction of the ester-tethered substrates have been reported. The established efficiency of the cationic Rh(I) species in fluorinated alcohol for the [4+2] cycloaddition of ester-tethered diene−yne compounds encouraged us to examine the [5+2] cycloaddition of β-cyclopropylacrylates **7** (Table 3). As expected, the cationic Rh(I) catalyst prepared in situ from $[Rh(COD)Cl]_2$ and $AgSbF_6$ was efficient in bringing about cycloaddition, and lactone **9a** was obtained in 84% yield from **7a** in HFIP at room temperature for 5 h (entry 1). The obtained **9a** would be generated by the isomerization of initially formed [5+2] adduct **8a** during the workup. The premixing of $[Rh(COD)Cl]_2$ and $AgSbF_6$ for 30 min prior to the addition of **2a** decreased the yield of **9a** to 50% (entry 2). The reaction of **7a** in TFE did not give the cyclized product because of alcoholysis of the starting material

(15) Thermal IMDA reactions of sorbate derivatives require a very high temperature (200 °C) to give the products; see: (a) Boeckman, R. K., Jr.; Demko, D. M. *J. Org. Chem.* **1982**, *47*, 1789. (b) Martin, S. F.; Williamson, S. A.; Gist, R. P.; Smith, K. M. *J. Org. Chem.* **1983**, *48*, 5170.

(16) Thermal IMDA reactions of 2,4-pentadienyl propiolates are known; see: (a) White, J. D.; Sheldon, B. G. *J. Org. Chem.* **1981**, *46*, 2273. (b) Birtwhistle, D. H.; Brown, J. M.; Foxton, M. W. *Tetrahedron* **1998**, *44*, 7309. (c) Turner, C. I.; Williamson, R. M.; Paddon-Row, M. N.; Sherburn, M. S. *J. Org. Chem.* **2001**, *66*, 3963. (d) Pradilla, R. F.; Baile, R.; Tortosa, S. *Chem. Commun.* **2003**, 2476.

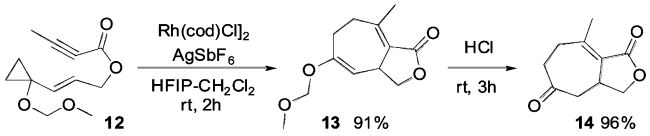
TABLE 4. [5+2] Cycloadditions of Propiolates[a]



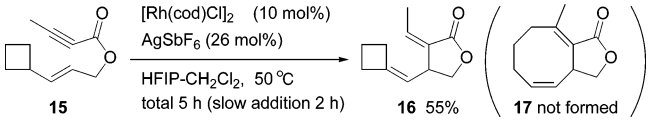
entry	**10**	R	solvent	time (h)	**11** (%)[b]
1[c]	**10a**	H	TFE	2	**11a** 20
2[c]	**10a**	H	HFIP	2	**11a** 23
3[c]	**10a**	H	CH_2Cl_2	4	**11a** 12
4[c]	**10a**	H	HFIP−CH_2Cl_2	2	**11a** 41
5	**10a**	H	HFIP−CH_2Cl_2	1	**11a** 78
6	**10b**	Me	HFIP−CH_2Cl_2	1	**11b** 97
7[d]	**10c**	Ph	HFIP−CH_2Cl_2	3	**11c** 56
8[d]	**10d**	*i*-Pr	HFIP−CH_2Cl_2	3	**11d** 58

[a] Immediately after mixing $[Rh(COD)Cl]_2$ with $AgSbF_6$, **10** was added, unless otherwise noted. [b] Isolated yield. [c] $[Rh(COD)Cl]_2$ was treated with $AgSbF_6$ for 30 min prior to the addition of **10**. [d] Slow addition (1 h) of **10**.

SCHEME 5. [5+2] Cycloaddition of Propiolate 12



SCHEME 6. Cycloisomerization of Propiolate 15



(entry 3). As shown in entries 4−6, the cationic Rh(I)−HFIP system worked well in the reactions of **7b**−**d** to give **9b**−**d**. In particular, the slow addition of **7** (0.5 mmol/2 mL in HFIP, 1 h addition) exerted a preferable effect, and thus terminal alkynyl compound **9b** was obtained in 73% yield at room temperature for 2 h. Likewise, **9c** and **9d** were obtained in good yields (**9c**, 87%; **9d**, 70%).

The cationic Rh(I)-catalyzed [5+2] cycloaddition of propiolates **10** and **12** in an analogous method to **7** was also examined (Table 4 and Scheme 5). In the reaction of **10a** in TFE, which was a suitable solvent in the [4+2] cycloaddition of propiolate **5**, an incomplete reaction took place (by TLC analysis), and [5+2] adduct **11a** was obtained in 20% yield together with the recovered **10a** (Table 4, entry 1). Because the use of HFIP as a solvent lead to the decomposition of **10a**, the reaction in HFIP scarcely provided an improved result even in the absence of a catalyst (entry 2). However, the addition of a solution of **10a** in CH_2Cl_2 to the cationic Rh(I) catalyst prepared in HFIP increased the yield of **11a** up to 41% (entry 4). A better yield of **11a** (78%) was obtained with the addition of a solution of **10a** in CH_2Cl_2 to the catalyst solution immediately after the preparation of the cationic Rh(I) catalyst (entry 5). The reaction of Me-substituted **10b** also proceeded smoothly under similar conditions to **10a** giving rise to the corresponding adduct **11b** quantitatively (entry 6). In the cases of Ph-substituted **10c** and *i*-Pr-substituted **10d**, by the slow addition of a substrate (0.5 mmol/2 mL in CH_2Cl_2, 1 h addition), **11c** and **11d** were obtained in 56 and 58% yields, respectively (entries 8 and 9). The [5+2] cycloaddition of propiolate **12** with a MOM−oxy-substituted cyclopropane ring gave the corresponding adduct **13** in 91% yield, and the product was converted to ketone **14** quantitatively (Scheme 5).[13c,d]

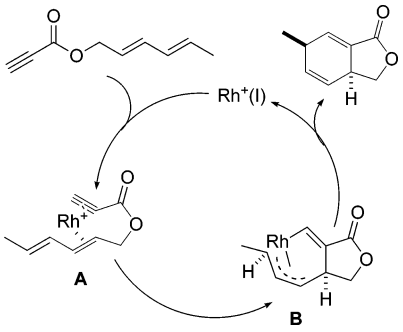


FIGURE 1. Catalytic cycle of [4+2] cycloaddition.

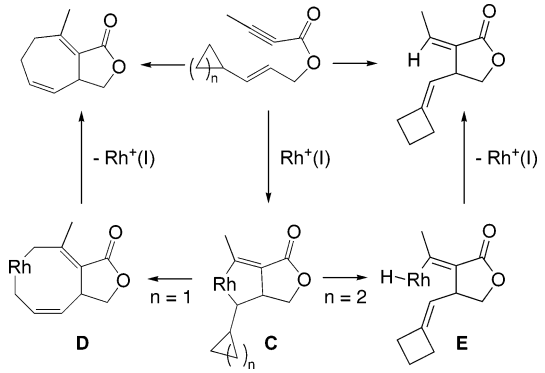


FIGURE 2. Catalytic cycle of [5+2] cycloaddition.

The formation of eight-membered ring-fused lactones by the [6+2] cycloaddition of propiolate **15** under the present conditions could be considered to be difficult to take place according to Wender et al.'s observations.[17] Thus, an attempted reaction of **15**, by means of the slow addition of a substrate for 2 h at 50 °C and the further stirring for 3 h, did not yield the bicyclic lactone **17** but afforded the 1,4-dienelactone **16** in 55% yield as a major product (Scheme 6).

Catalytic Cycles. On the basis of previous reports about the transition-metal-catalyzed [4+2] cycloadditions of alkyne−diene compounds[12,13] and [5+2] cycloadditions of alkene−vinylcyclopropane compounds,[14] plausible catalytic cycles for the cationic Rh(I)-catalyzed [4+2] and [5+2] reactions of the present ester-tethered substrates are shown in Figures 1 and 2, respectively. Thus, in the [4+2] reaction of the ester-tethered ω-alkynyl diene derivatives (Figure 1), the formation of metallacyclic intermediate **B** and the reductive elimination of Rh(I) gave cycloadducts. As shown in the [5+2] reaction of the ester-tethered ω-alkynyl vinylcyclopropanes ($n = 1$, Figure 2), metallacycle **C** was converted to metallacycle **D** through a cyclopropane ring opening, and bicyclic lactones were obtained by the reductive elimination of Rh(I). In the case of ω-alkynyl vinylcyclobutane ($n = 2$, Figure 2), because of the difficulty of the cyclobutane ring opening in intermediate **C**, β-hydrogen elimination and subsequent reductive elimination of Rh(I) in rhodium hydride **E** occurred to give 1,4-dienelactone. A similar result was observed in the Ru-catalyzed cycloisomerization of the alkyne−vinylcyclobutane compound, in which an analogous catalytic cycle has been proposed.[18]

(17) As far as we know, the [6+2] cycloaddition with simple vinylcyclobutane has never been successful; see: Wender, P. A.; Correa, A. G.; Sato, Y.; Sun, R. *J. Am. Chem. Soc.* **2000**, *122*, 7815.

(18) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **2002**, *124*, 5025.

Although the significant effect of the fluorinated alcohols in our case is quite notable, no evident advantage to the use of TFE has been reported in cationic Rh(I)-catalyzed cyclizations of 1,3-diene-8-yne derivatives.[11c] At present, we believe that fluorinated alcohols might increase the cisoid conformation of an ester-tethered substrate by the polar effect[5] and/or accelerate in the generation and reactivity of the cationic Rh(I) catalyst, which coordinates to unsaturated bonds.[19] Thus, the adverse effect caused by the addition of phosphine ligands would be a result of a decrease in the electrophilicity of the cationic Rh(I) by coordination of the added phosphine ligand to the cationic metal center.

Conclusion

For the purpose of the mild intramolecular [4+2] cycloaddition reaction of ester-tethered alkyne−diene compounds, which usually requires high temperatures and long reaction times in the thermal Diels−Alder reactions, the cationic Rh(I) catalyst in fluorinated alcohols was found to be very efficient. The cationic Rh(I) was generated in situ from $[Rh(COD)Cl]_2$ and $AgSbF_6$ in fluorinated alcohols. The cationic Rh(I)-fluorinated alcohol system was applied to the [5+2] cycloaddition of ester-tethered substrates giving seven-membered ring fused lactones. We believe that the present reactions of ester compounds provide an attractive procedure for the formation of medium-sized ring fused five-membered lactones under mild conditions. Further studies on the reaction of ester-tethered enyne compounds and application to the synthesis of natural products are under way.

Experimental Section

General Information. For details, see Supporting Information.

General Procedure for the [4+2] Cycloaddition of Sorbate 1 Followed by DDQ Oxidation (Table 1): 4,5-Dimethylisobenzofuran-1(3*H*)-one (3a). Under an argon atmosphere, immediately after treatment of a solution of bis(1,5-cyclooctadiene)-μ,μ'-dichloro dimmer (12.4 mg, 25 μmol) in HFIP (3 mL) with silver hexafluoroantimonate (0.25 M in a CH_2Cl_2 solution, 0.26 mL, 65 μmol) at room temperature, **1a** (82 mg, 0.5 mmol) in HFIP (2 mL) was added. After being stirred for 2 h at the same temperature, the reaction mixture was diluted with ether and filtered through a Celite pad. After concentration of the filtrate to dryness, to a solution of the residue in toluene (5 mL) was added 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (113 mg, 0.5 mmol). After being stirred at room temperature for 1 h, the reaction mixture was quenched by saturated $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with brine and dried over $MgSO_4$, and subsequent purification by silica gel column chromatography (hexane/AcOEt = 6:1) gave **3a** (60.0 mg, 84% yield) as a white solid. Mp 126−128 °C. IR (neat) ν cm^{-1}: 1758. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.15 (s, 3H), 2.32 (s, 3H), 5.13 (s, 2H), 7.23 (d, 1H, J = 7.7 Hz), 7.53 (d, 1H, J = 7.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.5, 19.6, 69.0, 122.6, 122.9, 130.5, 130.8, 143.4, 145.8, 171.5. FAB-LM *m*/*z*: 163 (M^+ + H). FAB-HM calcd for $C_{10}H_{11}O_2$, 163.0761; found, 163.0759. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.09; H, 6.21.

5-Methylisobenzofuran-1(3*H*)-one (3b). White solid. Mp 104−106 °C. IR (neat) ν cm^{-1}: 1716. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.50 (s, 3H), 5.27 (s, 2H), 7.29 (s, 1H), 7.33 (d, 1H, J = 7.7 Hz), 7.79 (d, 1H, J = 7.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.1, 69.4, 122.4, 123.1, 125.4, 130.2, 145.3, 147.1, 171.2. FAB-LM *m*/*z*: 149 (M^+ + H). FAB-HM Calcd for $C_9H_9O_2$, 149.0585; found, 149.0620. Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 72.79; H, 5.55.

5-Methyl-4-phenylisobenzofuran-1(3*H*)-one (3c). White solid. Mp 111−112 °C. IR (neat) ν cm^{-1}; 1760. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.30 (s, 3H), 5.04 (s, 2H), 7.28−7.27 (m, 2H), 7.40−7.51 (m, 4H), 7.81 (d, 1H, J = 7.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.2, 69.2, 123.4, 124.3, 128.1, 128.3, 128.9, 131.4, 136.4, 136.5, 142.8, 146.0, 171.3. FAB-LM *m*/*z*: 225 (M^+ + H). FAB-HM Calcd for $C_{15}H_{13}O_2$, 225.0915; found, 225.0915. Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.44; H, 5.46.

4-(*tert*-Butyldimethylsilyl)-5-methylisobenzofuran-1(3*H*)-one (3d). White solid. Mp 135−137 °C. IR (neat) ν cm^{-1}: 1706. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.42 (s, 6H), 0.91 (s, 9H), 2.58 (s, 3H), 5.31 (s, 2H), 7.31 (d, 1H, J = 7.8 Hz), 7.89 (d, 1H, J = 7.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: −1.1, 19.4, 25.4, 26.8, 72.0, 122.5, 126.2, 130.8, 131.8, 152.0, 153.9, 171.4. FAB-LM *m*/*z*: 263 (M^+ + H). FAB-HM Calcd for $C_{15}H_{23}O_2Si$, 263.1483; found, 263.1467.

General Procedure for the [4+2] Cycloaddition of Sorbate 1 Followed by Treatment with Silica Gel (Scheme 3): 4,5-Dihydro-5-methylisobenzofuran-1(3*H*)-one (4a). Under an argon atmosphere, immediately after treatment of a solution of bis(1,5-cyclooctadiene)-μ,μ'-dichloro dimmer (12.4 mg, 25 μmol) in HFIP (3 mL) with silver hexafluoroantimonate (0.25 M in CH_2Cl_2 solution, 0.26 mL, 65 μmol) at room temperature, **1a** (82 mg, 0.5 mmol) in HFIP (2 mL) was added. After being stirred for 2 h at the same temperature, the reaction mixture was treated with silica gel (2 g) for 1 h. After filtration of the silica gel and concentration of the filtrate to dryness, the residue was purified by silica gel column chromatography (hexane/AcOEt = 6:1) to give **4a** (70.3 mg, 75% yield) as a white solid. Mp 44−45 °C. IR (neat) ν cm^{-1}: 1751. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.28 (d, 3H, J = 7.5 Hz), 2.22 (s, 3H), 2.91−2.96 (m, 1H), 3.44−3.54 (m, 1H), 3.77 (dd, 1H, J = 8.2, 10.8 Hz), 4.52 (dd, 1H, J = 8.2, 8.2 Hz), 5.66 (d, 1H, J = 9.8 Hz), 5.74 (d, 1H, J = 9.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.6, 18.3, 36.5, 38.8, 69.6, 119.9, 122.1, 133.7, 150.4, 169.2. FAB-LM *m*/*z*: 165 (M^+ + H). FAB-HM Calcd for $C_{10}H_{13}O_2$, 165.0923; found, 165.0915. Anal. Calcd for $C_{10}H_{12}O_2$: C, 71.98; H, 6.71. Found: C, 71.72; H, 6.73.

3*a*,4-Dihydro-4,5-dimethylisobenzofuran-1(3*H*)-one (4b). White solid. Mp 41−42 °C. IR (neat) ν cm^{-1}: 1720. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.31 (d, 3H, J = 7.2 Hz), 2.28−2.36 (m, 1H), 2.63−2.71 (m, 2H), 4.75 (d, 1H, J = 18.0 Hz), 4.84 (d, 1H, J = 18.0 Hz), 5.83 (dd, 1H, J = 2.8, 9.6 Hz), 6.15 (d, 1H, J = 9.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.3, 28.5, 29.4, 71.4, 115.5, 124.1, 135.1, 158.3, 171.6. FAB-LM *m*/*z*: 151 (M^+ + H). FAB-HM Calcd for $C_9H_{11}O_2$, 151.0750; found, 151.0759. Anal. Calcd for $C_9H_{10}O_2$: C, 73.15; H, 7.37. Found: C, 73.13; H, 7.43.

General Procedure for the [4+2] Cycloaddition Reaction of Propiolate 6 (Table 2): (3a*S,6*R**)-3,3*a*-Dihydro-6-methylisobenzofuran-1(6*H*)-one (6a).** Under an argon atmosphere, immediately after treatment of a solution of bis(1,5-cyclooctadiene)-μ,μ'-dichloro dimmer (12.4 mg, 25 μmol) in TFE (3 mL) with silver hexafluoroantimonate (0.25 M in CH_2Cl_2 solution, 0.26 mL, 65 μmol) at room temperature, **5a** (75 mg, 0.5 mmol) in TFE (2 mL) was added. After being stirred for 1 h at the same temperature, the reaction mixture was diluted with ether and filtered through a Celite pad. Concentration of the filtrate to dryness and subsequent purification by silica gel column chromatography (hexane/AcOEt = 6:1) gave **6a** (75.0 mg, quant.) as a colorless oil. IR (neat) ν cm^{-1}: 1760. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.26 (d, 3H, J = 7.7 Hz), 2.99−3.06 (m, 1H), 3.48−3.54 (m, 1H), 3.84 (dd, 1H, J = 8.8, 10.3 Hz), 4.65 (dd, 1H, J = 8.8, 8.8 Hz), 5.64−5.73 (m, 2H), 6.61 (br. s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.4, 32.1, 37.1, 70.7, 121.8, 127.5, 133.1, 138.6, 169.5. FAB-LM *m*/*z*: 151 (M^+ + H). FAB-HM Calcd for $C_9H_{11}O_2$, 151.0781; found, 151.0759. Anal. Calcd for $C_9H_{10}O_2$: C, 71.97; H, 6.71. Found: C, 71.66; H, 6.71.

(19) A rhodium chloride complex such as Willkinson's catalyst accelerates the [4+2] cycloaddition of 1,3-diene-8-yne or 1,3,8-triene derivatives in TFE. It has been suggested that TFE enhances the polarizability of the Rh−Cl bond. See, refs 11a and 11d.

(3a*S,6*R**)-3,3*a*-Dihydro-6,7-dimethylisobenzofuran-1(6*H*)-one (6b).** The ^{1}H NMR spectra of **7b** were identical to those reported in the literature.[15a]

(3a*S,6*R**)-3,3*a*-Dihydro-6-methyl-7-phenylisobenzofuran-1(6*H*)-one (6c).** White solid. Mp 95−97 °C. IR (neat) ν cm^{-1}: 1756. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.96 (d, 3H, J = 7.5 Hz), 3.26−3.37 (m, 1H), 3.60−3.67 (m, 1H), 3.88 (dd, 1H, J = 8.0, 10.8 Hz), 4.56 (dd, 1H, J = 8.0, 8.0 Hz), 5.80 (s, 2H), 7.01−7.12 (m, 2H), 7.30−7.36 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 19.5, 36.0, 39.1, 69.3, 121.4, 121.8, 127.1, 127.7, 127.9, 133.8, 136.5, 150.9, 167.7. FAB-LM *m*/*z*: 227 (M^+ + H). FAB-HM Calcd for $C_{15}H_{15}O_2$, 227.1065; found, 227.1072.

Synthesis of Tricyclic Lactone (Scheme 4): Preparations of 3-Cyclohex-1-enyl-acrylic Acid But-2-ynyl Ester (1e) and (2*E*)-3-Cyclohexenylallyl But-2-ynoate (5d). For details, see Supporting Information.

Preparation of 2,3,5,6,7,8-Hexahydro-1*H*-cyclopenta[*b*]naphthalen-1-one (3e). In a manner similar to **3a**, the [4+2] cycloaddition of **1e** (102 mg, 0.5 mmol) was carried out at 50 °C for 4 h. After the usual workup, to a solution of the obtained residue in toluene (5 mL) was added 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (113 mg, 0.5 mmol). After being stirred at room temperature for 1 h, the reaction mixture was quenched by saturated $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with brine and dried over $MgSO_4$, and subsequent purification by silica gel column chromatography (hexane/AcOEt = 6:1) gave **3e** (93 mg, 90%) as a white solid. Mp 138−140 °C. IR (neat) ν cm^{-1}: 1752. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.68−1.88 (m, 4H), 2.89 (s, 3H), 2.65 (t, 2H, J = 6.1 Hz), 2.71 (t, 2H, J = 6.1 Hz), 5.20 (s, 2H), 7.48 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.5, 22.4, 22.8, 27.1, 30.3, 69.1, 122.2, 123.4, 130.3, 138.8, 142.6, 142.8, 171.9. FAB-LM *m*/*z*: 203 (M^+ + H). FAB-HM Calcd for $C_{13}H_{15}O_2$, 203.1064; found, 203.1072. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.32; H, 7.08.

Preparation of 9-Methyl-3*a*,5,6,7,8,8*a*-hexahydro-3*H*-naphtho[2,3-*c*]furan-1-one (6d). In a manner similar to **6a**, the [4+2] cycloaddition of **1e** (102 mg, 0.5 mmol) and subsequent usual workup gave **6d** (98 mg, 96%) as a white solid. Mp 41−43 °C. IR (neat) ν cm^{-1}: 1756. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.01 (m, 1H), 1.24 (m, 1H), 1.49 (m, 1H), 1.74−2.17 (m, 3H), 2.32 (s, 3H), 2.32−2.38 (m, 2H), 2.68−2.73 (m, 1H), 3.47−3.56 (m, 1H), 3.73 (dd, 1H, J = 7.8, 11.2 Hz), 4.46 (dd, 1H, J = 7.8, 7.8 Hz), 5.40 (q, 1H, J = 1.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 14.5, 26.4, 26.9, 32.0, 35.5, 38.9, 43.5, 70.4, 114.2, 119.6, 140.8, 148.1, 170.0. FAB-LM *m*/*z*: 205 (M^+ + H). FAB-HM Calcd for $C_{13}H_{17}O_2$, 205.1233; found, 205.1229.

General Procedure for the [5+2] Cycloaddition of β-Cyclopropylacrylate 7 (Table 3): 5,6-Dihydro-4-methyl-3*H*-cyclohepta[*c*]furan-1(4*H*)-one (9a). Under an argon atmosphere, immediately after treatment of a solution of bis(1,5-cyclooctadiene)-μ,μ'-dichloro dimmer (12.4 mg, 25 μmol) in HFIP (3 mL) with silver hexafluoroantimonate (0.25 M in CH_2Cl_2 solution, 0.26 mL, 65 μmol) at room temperature, **7a** (82 mg, 0.5 mmol) in HFIP (2 mL) was added. After being stirred for 3 h at the same temperature, the reaction mixture was treated with silica gel (2 g) for 1 h. Filtration of silica gel, concentration of the filtrate to dryness, and subsequent purification by silica gel column chromatography (hexane/AcOEt = 6:1) gave **9a** (68.9 mg, 84%) as a colorless oil. IR (neat) ν cm^{-1}: 1718. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.12 (d, 3H, J = 7.2 Hz), 1.51 (m, 2H), 1.76−1.87 (m, 2H), 2.39−2.43 (m, 1H), 4.55 (d, 1H, J = 17.6 Hz), 4.75 (d, 1H, J = 17.6 Hz), 6.03 (dt, 1H, J = 11.4, 5.3 Hz), 6.13 (d, 1H, J = 11.4 Hz).^{13}C NMR (75 MHz, $CDCl_3$) δ: 19.3, 27.6, 30.1, 34.3, 70.8, 118.0, 122.3, 136.8, 164.3, 174.2. FAB-LM *m*/*z*: 165 (M^+ + H). FAB-HM Calcd for $C_{10}H_{13}O_2$,165.0919; found, 165.0916. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.93; H, 7.35.

5,6-Dihydro-3*H*-cyclohepta[*c*]furan-1(4*H*)-one (9b). Colorless oil. IR (neat) ν cm^{-1}: 1741. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.92−2.00 (m, 2H), 2.48−2.51 (m, 2H), 2.51−2.63 (m, 2H), 4.68 (s, 2H), 6.07 (d, 1H, J = 11.7 Hz), 6.16 (dt, 1H, J = 11.7, 5.3 Hz).^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.4, 29.8, 31.0, 71.8, 118.0, 123.6, 160.6, 174.1. FAB-LM *m*/*z*: 151 (M^+ + H). FAB-HM Calcd for $C_9H_{11}O_2$, 151.0746; found, 151.0801. Anal. Calcd for $C_{10}H_{12}O_2$: C, 71.98; H, 6.71. Found: C, 71.69; H, 6.81.

5,6-Dihydro-4-(methoxymethyl)-3*H*-cyclohepta[*c*]furan-1(4*H*)-one (9c). Colorless oil. IR (neat) ν cm^{-1}: 1754. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.80−1.90 (m, 1H), 1.95−2.05 (m, 1H), 2.43−2.50 (m, 2H), 2.92−3.01 (m, 1H), 3.35 (s, 3H), 3.41 (dd, 1H, J = 9.0, 7.9 Hz), 3.48 (dd, 1H, J = 9.0, 5.5 Hz), 4.72 (d, 1H, J = 18.3 Hz), 4.89 (d, 1H, J = 18.3 Hz), 6.09 (dt, 1H, J = 11.5, 5.5 Hz), 6.22 (d, 1H, J = 11.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.7, 28.2, 40.3, 58.9, 71.8, 74.8, 118.0, 123.3, 136.6, 161.7, 174.1. FAB-LM *m*/*z*: 195 (M^+ + H). FAB-HM Calcd for $C_{11}H_{15}O_3$, 195.1038; found, 195.1021.

4-Butyl-5,6-dihydro-3*H*-cyclohepta[*c*]furan-1(4*H*)-one (9d). Colorless oil. IR (neat) ν cm^{-1}: 1724. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.91 (t, 3H, J = 7.0 Hz), 1.20−1.59 (m, 6H), 1.76−1.83 (m, 1H), 1.92−2.04 (m, 1H), 2.46−2.47 (m, 2H), 2.61−2.70 (m, 1H), 4.65 (d, 1H, J = 17.6 Hz), 4.83 (d, 1H, J = 17.6 Hz), 6.08 (dd, 1H, J = 11.5, 5.4 Hz), 6.19 (d, 1H, J = 11.5 Hz).^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.9, 22.6, 26.1, 27.3, 28.8, 32.4, 38.8, 71.2, 117.8, 122.5, 136.7, 164.4, 174.2. FAB-LM *m*/*z*: 207 (M^+ + H). FAB-HM Calcd for $C_{13}H_{19}O_2$, 207.1397; found 207.1353. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.80; H, 8.66.

General Procedure for the [5+2] Cycloaddition of Propiolate 10 or 12 (Table 4 and Scheme 5): 3,3*a*,6,7-Tetrahydrocyclohepta[*c*]furan-1-one (11a). Under an argon atmosphere, immediately after treatment of a solution of bis(1,5-cyclooctadiene)-μ,μ'-dichloro dimmer (12.4 mg, 25 μmol) in HFIP (3 mL) with silver hexafluoroantimonate (0.25 M in CH_2Cl_2 solution, 0.26 mL, 65 μmol) at room temperature, **10a** (75 mg, 0.5 mmol) in CH_2Cl_2 (2 mL) was added. After being stirred for 1 h at the same temperature, the reaction mixture was diluted with ether and filtered through a Celite pad. Concentration of the filtrate to dryness and subsequent purification by silica gel column chromatography (hexane/AcOEt = 6:1) gave **11a** (58.2 mg, 84%) as a white solid. Mp 51−54 °C. IR (neat) ν cm^{-1}: 1741. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.09−2.33 (m, 2H), 2.40−2.53 (m, 2H), 3.89 (dd, 1H, J = 8.8, 8.8 Hz), 4.04−4.22 (m, 1H), 4.52 (dd, 1H, J = 8.8, 8.8 Hz), 5.53 (dt, 1H, J = 10.3, 2.2 Hz), 5.83−5.92 (m, 1H), 6.89 (dd, 1H, J = 8.8, 3.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 24.8, 26.2, 37.1, 70.5, 128.6, 129.9, 132.2, 140.8, 170.9. FAB-LM *m*/*z*: 151 (M^+ + H). FAB-HM Calcd for $C_9H_{11}O_2$, 151.0766; found, 151.0719. Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.79; H, 6.81.

3,3*a*,6,7-Tetrahydro-8-methylcyclohepta[*c*]furan-1-one (11b). IR (neat) ν cm^{-1}: 1743. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.09−2.39 (m, 2H), 2.27 (s, 3H), 2.68−2.78 (m, 1H), 3.85 (dd, 1H, J = 8.8, 8.8 Hz), 4.11 (m, 1H), 4.48 (dd, 1H, J = 8.8, 8.8 Hz), 5.53 (ddd, 1H, J = 11.0, 3.7, 1.5 Hz), 5.67−5.75 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 19.8, 24.8, 35.4, 37.8, 70.4, 123.3, 128.3, 130.7, 156.1, 170.1. FAB-LM *m*/*z*: 165 (M^+ + H). FAB−HM Calcd for $C_{10}H_{13}O_2$, 165.0915; found, 165.0916. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.29; H, 7.30.

3,3*a*,6,7-Tetrahydro-8-phenylcyclohepta[*c*]furan-1-one (11c). Colorless oil. IR (neat) ν cm^{-1}: 1745. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.28−2.47 (m, 3H), 2.29−3.08 (m, 1H), 3.90 (dd, 1H, J = 8.1, 8.1 Hz), 4.21 (m, 1H), 4.50 (dd, 1H, J = 8.1, 8.1 Hz), 5.40 (ddd, 1H, J = 11.0, 3.7, 2.2 Hz), 5.74−5.78 (m, 1H), 7.16−7.32 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 25.4, 36.2, 38.3, 70.2, 125.1, 127.5, 127.8, 127.9, 128.2, 131.1, 139.8, 156.2, 168.5. FAB-LM *m*/*z*: 227 (M^+ + H). FAB-HM Calcd for $C_{15}H_{15}O_2$, 227.1069; found, 227.1084. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.73; H, 6.38.

3,3*a*,6,7-Tetrahydro-8-isopropylcyclohepta[*c*]furan-1-one (11d). Colorless oil. IR (neat) ν cm^{-1}: 1743. ^{1}H NMR (300 MHz, $CDCl_3$)

δ: 1.00 (d, 3H, J = 6.8 Hz), 1.05 (d, 3H, J = 6.8 Hz), 2.06−2.18 (m, 1H), 2.31−2.59 (m, 2H), 3.88 (dd, 1H, J = 8.5, 8.5 Hz), 4.40 (seotet, 1H, J = *n*6.8 Hz), 5.30 (ddd, 1H, J = 11.4, 4.2, 2.0 Hz), 5.62−5.7 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 19.6, 20.2, 26.6, 27.1, 27.8, 38.1, 70.6, 123.3, 127.4, 130.6, 165.4, 169.6. FAB-LM *m*/*z*: 193 (M^+ + H). FAB-HM Calcd for $C_{12}H_{17}O_2$, 193.1240; found, 193.1229. Anal. Calcd for $C_{12}H_{17}O_2$: C, 74.97; H, 8.39. Found: C, 74.75; H, 8.44.

3,3*a*,6,7-Tetrahydro-5-(methoxymethoxy)cyclohepta[*c*]furan-1-one (13). Colorless oil. IR (neat) ν cm^{-1}: 1743. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.17−2.33 (m, H), 2.26 (s, 3H), 2.46−2.62 (m, 2H), 3.39 (s, 3H), 3.85 (dd, 1H, J = 8.2, 8.2 Hz), 3.91−4.05 (m, 1H), 4.51 (dd, 1H, J = 8.2, 8.2 Hz), 4.73 (br.s, 1H), 4.84 (d, 1H, J = 6.6 Hz), 4.92 (d, 1H, J = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 19.8, 28.5, 33.9, 35.3, 56.0, 71.0, 93.6, 100.5, 123.7, 154.6, 155.8, 170.2. FAB-LM *m*/*z*: 225 (M^+ + H). FAB-HM Calcd for $C_{12}H_{17}O_4$, 225.1114; found, 225.1161.

Preparation of 3*a*,4,6,7-Tetrahydro-8-methyl-3*H*-cyclohepta-[*c*]furan-1,5-dione (14). To a solution of lactone **13** (38 mg, 16.8 mmol) in EtOH (3 mL) was added 10% HCl−MeOH (0.3 mL) at room temperature. After being stirred for 3 h at the same temperature, concentration of the reaction mixture to dryness and subsequent purification by silica gel column chromatography (hexane/AcOEt = 1:1) gave **11a** (29 mg, 96%) as a colorless oil. IR (neat) ν cm^{-1}: 1743, 1708. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.32 (d, 3H, J = 2.2 Hz), 2.42−2.48 (m, 1H), 2.54−2.66 (m, 4H), 2.89−2.98 (m, 1H), 3.50−3.55 (m, 1H), 3.77 (dd, 1H, J = 8.9, 8.9 Hz), 4.47 (dd, 1H, J = 8.9, 8.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.4, 33.9, 35.0, 40.9, 46.8, 69.1, 123.6, 154.4, 169.9, 208.4. FAB-LM *m*/*z*: 181 (M^+ + H). FAB-HM Calcd for $C_{10}H_{13}O_3$, 181.0866; found, 181.0865.

Cycloisomerization of Propiolate 15 (Scheme 6): (3*Z*)-4-(Cyclobutylidenemethyl)-3-ethylidenedihydrofuran-2(3*H*)-one (16). Under an argon atmosphere, immediately after treatment of a solution of bis(1,5-cyclooctadiene)-μ,μ'-dichloro dimmer (12.4 mg, 25 μmol) in HFIP (3 mL) with silver hexafluoroantimonate (0.25 M in CH_2Cl_2 solution, 0.26 mL, 65 μmol) at room temperature, **15** (44.5 mg, 0.25 mmol) in CH_2Cl_2 (2 mL) was slowly added for 2 h at 50 °C. After being stirred for 3 h at the same temperature, the reaction mixture was diluted with ether and filtered through a Celite pad. Concentration of the filtrate to dryness and subsequent purification by silica gel column chromatography (hexane/AcOEt = 6:1) gave **16** (24.5 mg, 55%) as a colorless oil. IR (neat) ν cm^{-1}: 1716. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.99 (dddd, 2H, J = 8.0, 8.0, 8.0, 8.0 Hz), 2.42 (dd, 3H, J = 7.4, 2.8 Hz), 2.65−2.73 (m, 4H), 3.60−3.65 (m, 1H), 4.83 (dd, 1H, J = 8.7, 8.7 Hz), 4.39 (dd, 1H, J = 8.7, 8.7 Hz), 4.93 (m, 1H), 6.13 (qd, 1H, J = 2.7, 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.8, 16.9, 29.3, 30.9, 40.4. 70.2, 117.7, 128.4, 139.1, 145.5, 170.2. FAB-LM *m*/*z*: 179 (M^+ + H). FAB−HM Calcd for $C_{11}H_{15}O_2$, 179.1060; found, 179.1072.

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Supporting Information Available: Physical data of **1**, **3**, **5**, **7**, **10**, **12**, and **15** and stereochemical determination of **7a** and **7c**. ^{1}H/^{13}C NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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