Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 671–677
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Ruthenium-catalyzed intramolecular cyclization of hetero-functionalized allylbenzenes

Tetsuo Ohta *, Yohei Kataoka, Akio Miyoshi, Yohei Oe, Isao Furukawa, Yoshihiko Ito

Department of Molecular Science and Technology, Faculty of Engineering, Doshisha University, Kyotanabe, Kyoto 610-0394, Japan

Received 1 March 2006; received in revised form 12 May 2006; accepted 17 May 2006
Available online 30 August 2006

Abstract

Intramolecular addition of heterofunctionalities to C=C double bonds without β-hydride elimination was investigated and catalyzed by ruthenium complexes. The combination of $RuCl_3 \cdot nH_2O$ (10 mol%) and 3 equiv. of AgOTf acted as a catalyst for cyclization of 2-allylphenol (**1a**) to 2,3-dihydro-2-methylbenzofuran (**2a**) in good yield in the presence of $Cu(OTf)_2$ as a co-catalyst and PPh_3 as a ligand. This catalyst system also catalyzed the cyclization of 2-allylbenzoic acid to lactone in 91% yield. Then, a new catalyst system $(RuCp^*Cl_2)_2$ (1.0 mol%)/4AgOTf/4PPh_3, was found to be more active even in the absence of $Cu(OTf)_2$. Furthermore, this catalysis was applied to asymmetric reaction of 2-allylphenol (**1a**). When using TolBINAP as a ligand, over 60% e.e. was achieved.

Keywords: Ruthenium; Intramolecular cyclization; Olefin; Heterocycles; Enantioselective reaction; Catalysis

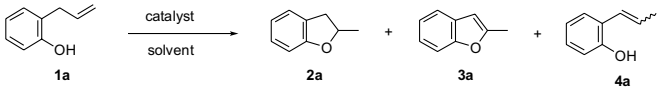
1. Introduction

As olefin is the most accessible raw material in chemical industry, transformation of olefin is a great deal to constructing various materials. Nevertheless, addition of RXH (X = heteroatom) to olefin under neutral conditions has been limited [1–3]. There have been only few examples of intramolecular [4] and intermolecular [5] addition of heteroatom nucleophiles to olefins, except for the amination of olefins [6].

We have already reported the preliminary work of intramolecular addition of phenolic hydroxide to olefin in 2-allylphenol in the presence of a catalytic amount of $RuCl_3 \cdot nH_2O$/3AgOTf and $Cu(OTf)_2$ [7]. This catalysis revealed that ruthenium complex catalyzes the addition of nucleophiles (RXH) to olefins without β-elimination [8–10]. The high loading of catalyst was needed for getting reasonable yield of the product. Then, we have been searching other catalysts for this reaction and found that $(RuCp^*Cl_2)_2$ [11] can act as an effective catalyst for this reaction even without $Cu(OTf)_2$. Herein, we would like to describe the details of the reaction using ruthenium catalysts [12].

2. Results and discussion

2.1. Intramolecular cyclization using $RuCl_3 \cdot nH_2O$/3AgOTf/$Cu(OTf)_2$



Various catalytic systems and reaction conditions were examined for the cyclization of **1a**, and some representative results are listed in Table 1. Ruthenium and iron compounds treated with AgOTf showed some activities for this reaction, while only the ruthenium compound exhibited good catalytic activity with the addition of $Cu(OTf)_2$. Cyclization of **1a** was effectively performed in acetonitrile at 80 °C in the presence of a ruthenium-based catalyst prepared by pre-heating a mixture of $RuCl_3 \cdot nH_2O$ and

* Corresponding author. Fax: +81 774 65 6789.
E-mail address: tota@mail.doshisha.ac.jp (T. Ohta).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.05.059

Table 1
Cyclization of **1a** by transition-metal catalyst[a]

Entry	Catalyst	Additive	Yield[b] (%)		
			2a	**3a**	**4a**
1	$RuCl_3 \cdot nH_2O$/3AgOTf	$Cu(OTf)_2$	51	4	15
2	$RuCl_3 \cdot nH_2O$/3AgOTf	–	4	1	10
3[c]	$PdCl_2$/2AgOTf	$Cu(OTf)_2$	0	4	23
4	$RhCl_3 \cdot 3H_2O$/3AgOTf	$Cu(OTf)_2$	0	Trace	5
5	$FeCl_3 \cdot 6H_2O$/3AgOTf	$Cu(OTf)_2$	4	0	10
6	AgOTf	–	0	0	0
7[d]	–	$Cu(OTf)_2$	0	0	0
8	–	TfOH[e]	0	0	0
9[f]	$RuCl_3 \cdot nH_2O$/3AgOTf	$Cu(OTf)_2$/TfOH	63	0	Trace
10[g]	$RuCl_3 \cdot nH_2O$/3AgOTf	$Cu(OTf)_2/PPh_3$	69	0	2

[a] *Reaction conditions*: **1a** (4.0 mmol), $RuCl_3 \cdot nH_2O$ (0.4 mmol), AgOTf (1.2 mmol), additive (2.0 mmol), CH_3CN (10 mL), 80 °C, 24 h.
[b] Determined by GLC analysis (PEG-20M).
[c] CH_3OH (10 mL) as a solvent.
[d] $Cu(OTf)_2$ (4.0 mmol).
[e] TfOH (1.0 mL, 11 mmol).
[f] TfOH (0.3 mL, 3.4 mmol).
[g] CH_3CN (3 mL), 48 h, PPh_3 (0.8 mmol).

3 equiv. of AgOTf in the presence of $Cu(OTf)_2$ in CH_3CN to give **2a** in moderate yield. Acetonitrile was solely chosen among the solvents examined. No reaction occurred by the use of $AgBF_4$ instead of AgOTf or by the addition of $CuCl_2$ instead of $Cu(OTf)_2$.

From the reaction, the desired product **2a** was obtained in moderate yield followed by considerable amounts of **3a** and olefin-isomerized product (*E*)- and (*Z*)-2-(1-propenyl)phenol (**4a**). Interestingly, the addition of TfOH or PPh_3 suppressed the formation of **3a** and **4a**. Since TfOH alone was ineffective as a catalyst for this cyclization in acetonitrile, TfOH influenced the catalytic stage mediated by ruthenium.

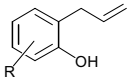
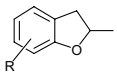
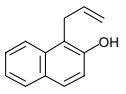
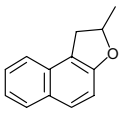
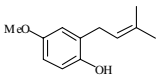
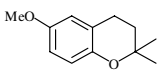
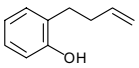
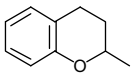
This catalytic cyclization was not influenced by the substituents on the aromatic ring of the substrates (Table 2), and five-membered ring compounds were always formed from allyl derivatives (entries 1–5). In the case of phenol derivative with 3-methyl-2-butenyl substituent **7**, six-membered product **8**, Markovnikov type product, was formed. 2-Homoallylphenol (**9**) was transformed to a six-membered cyclic product, 3,4-dihydro-2*H*-2-methylbenzopyran (**10**), in good yield, while 2-vinylphenol was not converted to the cyclic compound.

Benzoic acids were also used for this catalysis (Table 3). 2-Allylbenzoic acid (**11**) was converted to six-membered lactone **12** in good yield, while five-membered lactone **14** was obtained from the reaction of 2-vinylbenzoic acid (**13**). This catalysis was also applied to aliphatic carboxylic acid, 4-pentenoic acid (**15**), to give γ-valerolactone (**16**) in moderate yield.

2.2. Intramolecular cyclization of 2-allylphenol (*1a*) using $(Cp^*RuCl_2)_2$

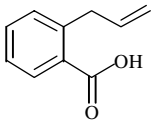
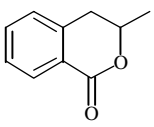
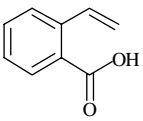
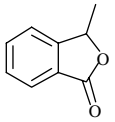
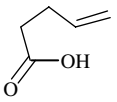
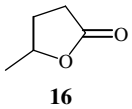
The reaction of 2-allylphenol (**1a**) was performed in the presence of a ruthenium complex derived from 1 mol% of $(Cp^*RuCl_2)_2$, 4 mol% of AgOTf, and PPh_3, in various solvents in the presence of $Cu(OTf)_2$. The representative results are listed in Table 4. The reaction did not proceed

Table 2
Cyclization using $RuCl_3 \cdot nH_2O$/3 AgOTf in the presence of $Cu(OTf)_2$[a]

Entry	Substrate	Product	Yield[b] (%)
			
1	**1a**: R = H	**2a**: R = H	61 (69)[c]
2	**1b**: R = 4-MeO	**2b**: R = 5-MeO	51
3	**1c**: R = 6-MeO	**2c**: R = 7-MeO	53
4	**1d**: R = 6-Me	**2d**: R = 7-Me	65
5	 **5**	 **6**	58
6	 **7**	 **8**	68
7	 **9**	 **10**	72

[a] *Reaction conditions*: substrate (4.0 mmol), $RuCl_3 \cdot nH_2O$ (0.4 mmol), AgOTf (1.2 mmol), $Cu(OTf)_2$ (2.0 mmol), CH_3CN (10 mL), 80 °C, 24 h.
[b] Isolated yield.
[c] The figure in parentheses was determined by GC.

Table 3
Cyclization of carboxylic acid derivatives[a]

Entry	Substrate	Product	Yield[b] (%)
1	 **11**	 **12**	89 (91)
2	 **13**	 **14**	78 (83)
3	 **15**	 **16**	46 (67)

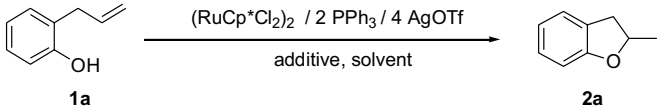
[a] *Reaction conditions*: substrates (4 mmol), $RuCl_3 \cdot H_2O$ (0.4 mmol), AgOTf (1.2 mmol), $Cu(OTf)_2$ (2 mmol), PPh_3 (0.8 mmol), CH_3CN (3 mL), 80 °C, 48 h, under Ar.
[b] Isolated yield of cyclization product. Figures in parentheses show the yield from the reaction for 96 h.

Table 4
Ruthenium complex-catalyzed intramolecular cyclization of 2-allylphenol[a]

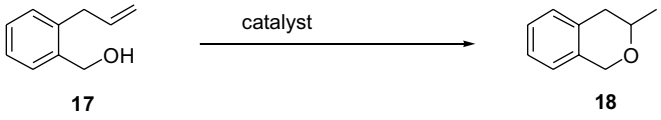
Entry	Reaction condition			Yield[b] of **2a** (%)
	Solvent	Temperature (°C)/time (h)	Additive (mol%)	
1	CH_3CN	80/48	$Cu(OTf)_2$ (50)	0
2	THF	80/48	$Cu(OTf)_2$ (50)	0
3	MeOH	80/48	$Cu(OTf)_2$ (50)	0
4	Benzene	80/48	$Cu(OTf)_2$ (50)	88
5	CH_2Cl_2	Reflux/48	$Cu(OTf)_2$ (50)	72
6	$CHCl_3$	60/48	$Cu(OTf)_2$ (50)	>95
7[c]	$CHCl_3$	60/48	$Cu(OTf)_2$ (50)	>95
8[c]	$CHCl_3$	60/48	$Cu(OTf)_2$ (25)	>94
9[c]	$CHCl_3$	60/48	$Cu(OTf)_2$ (10)	83
10[c]	$CHCl_3$	60/48	$Cu(OTf)_2$ (1)	67
11[c]	$CHCl_3$	60/48	–	21
12[d]	$CHCl_3$	60/48	$Cu(OTf)_2$ (10)	58–68
13[d]	$CHCl_3$	60/48	AgOTf (10)	7
14[d]	$CHCl_3$	60/48	$CuCl_2$ (50)	0
15[d]	$CHCl_3$	60/48	TfOH (20)	45

[a] *Reaction conditions*: **1a** (1.0 mmol), $(Cp^*RuCl_2)_2$ (1 mol%), AgOTf (4 mol%), solvent (3 mL), PPh_3 (2 mol%), under Ar.
[b] Yields were determined by ^1H NMR using internal standard (dibenzyl ether) method.
[c] $(Cp^*RuCl_2)_2$ (0.5 mol%), AgOTf (2 mol%), and PPh_3 (1 mol%) were used.
[d] Without $(Cp^*RuCl_2)_2$ and AgOTf.

in acetonitrile, which was chosen as the solvent for the reaction using $RuCl_3 \cdot nH_2O$/3AgOTf as a catalyst in the previous section. No reaction occurred in THF and methanol. On the other hand, benzene, dichloromethane and chloroform are the choice of solvents for this catalysis to give the cyclic product in good yield (up to >95%). In chloroform, the amount of catalyst was able to be reduced to 0.5 mol% without any loss of the yield (entry 7). The amount of $Cu(OTf)_2$ was also able to be reduced, but use of less than 25 mol% of $Cu(OTf)_2$ slightly decreased the yield of the product. In acetonitrile, $Cu(OTf)_2$ and AgOTf showed no catalytic activities. But interestingly, $Cu(OTf)_2$ was catalytically active in chloroform. Still, AgOTf gave the product in less than catalytic amount yield in chloroform. $CuCl_2$ did not work as a catalyst for cyclization. These metal compounds are going to be demonstrated separately as a catalyst for this reaction. Trifluoromethanesulfonic acid also showed catalytic activity in chloroform.

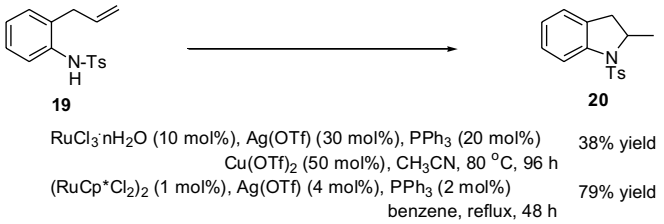


2.3. Other substrates



Alcohols were subjected for this reaction instead of phenols. Using $RuCl_3 \cdot nH_2O + AgOTf$, 2-allylbenzyl alcohol (**17**) reacted to give cyclic product **18** in 15%, while $(Cp^*RuCl_2)_2 + AgOTf$ system showed better catalytic activity even through the yield was low. Acidity of the protic hydrogen might affect the reactivity. Aliphatic alcohol, 5-hexen-1-ol, did not give the cyclic product (see Table 5).

In cases of aniline derivatives, the reaction was strongly dependent of the substituent on nitrogen. In both catalytic systems, 2-allylaniline was not converted at all. When *N*-methyl-2-allylaniline was used, cyclization did not occur, and furthermore, isomerization of olefin proceeded (2-(1-propenyl)-*N*-methylaniline 95% (*cis*/*trans* = 59:36)). This probably is due to the enhanced coordination ability of nitrogen in *N*-methyl-2-allylaniline. 2-Allylacetanilide and 2-allylbenzanilide did not suffer any transformation, while 2-allyl-*N*-tosylaniline (**19**) converted to cyclic product **20** in 38% yield by $RuCl_3 \cdot nH_2O$-based catalyst system and in 79% yield by $(Cp^*RuCl_2)_2$catalyst system. These results suggested that the acidity of the proton on nitrogen of the substrates was very important in this catalysis.



2.4. Attempt for asymmetric reaction

Our preliminary study for asymmetric cyclization of 2-allylphenol demonstrated that the reaction proceeded in an asymmetric fashion using $RuCl_3 \cdot nH_2O$ with BINAP without $Cu(OTf)_2$ in acetonitrile to give the optically active product with about 90% e.e. even in trace yield. On the other hand, the reaction by the same catalyst in the presence of $Cu(OTf)_2$ (50 mol% to substrate) gave racemic product in 48% yield. These observations forced us to find the catalyst system without $Cu(OTf)_2$. The results are listed in Table 6. Using high loading catalyst, higher reaction temperature, and long reaction time gave the product in higher yields (entries 1–5). Using less polar solvent, such as benzene and toluene, exhibited good influence in yield. That is, in benzene and the product was obtained in 95% yield from the reaction at reflux for 48 h (entries 6–8). The use of cyclohexane led to a decrease in the yield of the product (entry 9).

Then, we tested the asymmetric reaction using various optically active phosphine ligands without $Cu(OTf)_2$, and the results are summarized in Table 7. At first, (*S*)-BINAP was used as a ligand for determining a standard condition (entries 1–4). Toluene was a choice of solvent, and long reaction time did not affect enantiomeric excess. Lower reaction temperature made e.e. better as 48% even through the yield became low (entry 4). As a result, the reaction was

Table 5
Intramolecular cyclization of 2-allylbenzyl alcohol (**17**) using $(Cp^*RuCl_2)_2$[a]

Entry	Reaction condition				Yield[b] of **18** (%)
	Catalyst (mol%)	Solvent	Temperature (°C)/time (h)	$Cu(OTf)_2$ (mol%)	
1	$RuCl_3 \cdot nH_2O$ (10) + AgOTf (30)	CH_3CN	80/48	50	15
2	$(Cp^*RuCl_2)_2$ (1) + AgOTf (4)	Toluene	Reflux/48	0	12
3	$(Cp^*RuCl_2)_2$ (1) + AgOTf (4)	Benzene	Reflux/48	0	24

[a] *Reaction conditions*: **17** (1.0 mmol), catalyst, solvent (3 mL), PPh_3 (20 mol% for $RuCl_3 \cdot nH_2O$, 2 mol% for $(Cp^*RuCl_2)_2$), under Ar.
[b] Yields were determined by ^1H NMR using internal standard (bibenzyl) method.

Table 6
Intramolecular cyclization of 2-allylphenol (**1a**) using $(Cp^*RuCl_2)_2$[a]

Entry	Solvent	Temperature (°C)/time (h)	Yield[b] of **2a** (%)
1[c]	$CHCl_3$	60/48	21
2	$CHCl_3$	60/48	26
3	$CHCl_3$	Reflux/24	39
4	$CHCl_3$	Reflux/48	64
5	$CHCl_3$	Reflux/72	64
6	Benzene	Reflux/24	75
7	Benzene	Reflux/48	95
8	Toluene	Reflux/48	85
9	Cyclohexane	Reflux/48	56

[a] *Reaction conditions*: **1a** (1.0 mmol), $(Cp^*RuCl_2)_2$ (1.0 mol%), AgOTf (4.0 mol%), PPh_3 (2.0 mol%), a solvent (3 mL), under Ar.
[b] Yields were determined by ^1H NMR using internal standard (dibenzyl ether) method.
[c] $(Cp^*RuCl_2)_2$ (0.5 mol%), AgOTf (2.0 mol%), PPh_3 (1.0 mol%).

Table 7
Asymmetric intramolecular cyclization of 2-allylphenol (**1a**) using $(Cp^*RuCl_2)_2$[a]

Entry	Ligand	Yield of **2** (%)[b]	% e.e.[c] of **2**
1[d]	(*S*)-BINAP	63	17
2	(*S*)-BINAP	74	28
3[e]	(*S*)-BINAP	50	7
4[f]	(*S*)-BINAP	28	48
5	(*S*)-TolBINAP	80	33
6[f]	(*S*)-TolBINAP	37	65
7[g]	(*S*)-TolBINAP	2	13
8	(*S*,*S*)-BPPM	0(100)	–
9	(*S*,*R*)-BPPFA	0(100)	–
10	(*R*,*R*)-Me-DuPHOS	90	2
11	(*R*,*R*)-DIOP	33 (60)	37
12[f]	(*R*,*R*)-DIOP	75	15
13	(*R*,*S*)-JOSIPHOS	10 (78)	69
14[f]	(*R*,*S*)-JOSIPHOS	41	47
15	(*R*,*R*)-CHIRAPHOS	57	3
16	(*R*)-PROPHOS	78	14
17	(*R*,*R*)-NORPHOS	73	4

[a] *Reaction conditions*: 2-allylphenol (1.0 mmol), $(Cp^*RuCl_2)_2$ (1 mol%), AgOTf (4 mol%), ligand (2 mol%), toluene (3 mL), reflux, 48 h, argon atmosphere.
[b] Yields were determined by ^1H NMR using internal standard (dibenzyl ether) method, and figures in parentheses are recovered substrate **1a**.
[c] Determined by chiral HPLC (column packing: Daicel Chiralcel OJ-R; eluent: $MeOH/H_2O = 3/2$; detector: UV254 nm; flow rate 0.3 mL/min).
[d] In benzene.
[e] In cyclohexane.
[f] At 50 °C for 96 h.
[g] At 30 °C for 150 h.

performed in toluene at reflux temperature using various optically active ligands. Using (*S*)-TolBINAP showed higher catalytic activity and moderate selectivity (entry 5). BPPM and BPPFA did not promote the reaction at all (entries 10 and 11). DIOP and JOSIPHOS showed moderate enantiomeric excesses as 37% and 69%, respectively, even through a considerable amount of substrates remained unchanged (entries 11 and 13). Lowering the temperature led to an increase in the enantiomeric the use of (*S*)-TolBINAP, while the enantiomeric excess with became lower in cases of DIOP and JOSIPHOS (entries 6, 12, and 14).

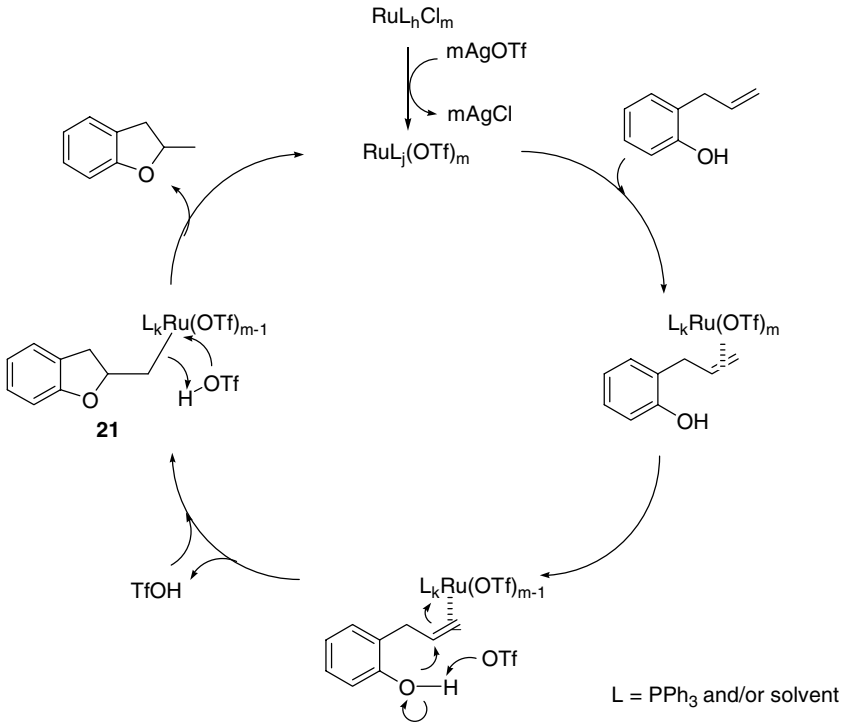
2.5. Reaction mechanism

Now, we have no evidence about the reaction mechanism. Nevertheless, plausible mechanism is shown in Scheme 1. First, ruthenium precursor reacts with AgOTf to give a cationic ruthenium species. This cationic Ru(III) species has some TfO^-, ligand, and/or solvent molecules. The C=C double bond of 2-allylphenol coordinates to this cationic ruthenium to give a Ru–olefin complex, which allowed to react with phenolic oxygen in a nucleophilic fashion intramolecularly to give cyclized intermediate. At this stage, the counter anion holds the phenolic proton, and the resulting TfOH reacts with carbon–ruthenium σ-bond by protonolysis to give the desired product and active ruthenium intermediate. Hosokawa et al. also suggested a similar intermediate in the reaction of **1a** catalyzed by a Pd compound [8b]. Product **2a** could be obtained from **21** by protonolysis, and by-product **3a** could be formed from the same intermediate **21** by β-hydride elimination. No formation of **3a** by addition of TfOH indicates that the protonolysis of **21** proceeds smoothly by adding TfOH. The formation of olefinic by-product **4a** was also suppressed by adding TfOH or PPh_3, suggesting that **4a** was formed from common olefin–ruthenium intermediate via hydrogen migration proposed in the literature [12].

3. Experimental

3.1. General

Proton nuclear magnetic resonance (^1H NMR) spectra were measured using a JEOL JNM A-400 (400 MHz) spectrometer using tetramethylsilane as the internal standard.



Scheme 1. Possible mechanism for the intramolecular cyclization of 2-allylphenol catalyzed by ruthenium complex.

IR spectra were measured on a Shimadzu IR-408 spectrometer. Mass spectral (GC–MS) data were recorded on a Shimadzu QP2000A instrument. HPLC analysis was done by Shimadzu LC-10A with chiral column (Daicel CHIRALCEL OJ-R, 0.3 mL/min, detector UV254 nm). Optical rotation was measured by Horiba Sepa-200 instrument. The substrates purchased were used without further purification. The solvents were purified according to the literature method, and stored under argon.

2-Allyl-4-methoxyphenol (**1b**) [13], 1-allyl-2-naphthol (**5**) [14], 2-(3-methyl-2-butenyl)-4-methoxyphenol (**7**) [15], 2-(3-butenyl)phenol (**9**) [16], 2-allylbenzoic acid (**11**) [17], 2-vinylbenzoic acid (**13**) [18], 2-allylbenzyl alcohol (**17**) [19], 2-allylaniline [20], 2-allyl-*N*-methylaniline [21], *N*-(2-allylphenyl)acetamide [22], 2-allyl-*N*-benzanilide [23], 2-allyl-*N*-tosylaniline (**19**) [24], and dichloropentamethylcyclopentadienylruthenium dimer $[Cp^*RuCl_2]_2$ [11] were prepared according to the literature method.

3.2. Intramolecular cyclization of 2-allylphenol (*1a*)

3.2.1. Typical reaction procedure 1

Into a 30 mL three-necked flask were added $RuCl_3 \cdot nH_2O$ (0.10 g, 0.4 mmol), acetonitrile (3.0 mL), and AgOTf (0.32 g, 1.2 mmol), and then the mixture was heated at 80 °C for 2 h. After cooling, 2-allylphenol (4.0 mmol), PPh_3 (0.21 g, 0.8 mmol), and $Cu(OTf)_2$ (0.72 g, 2.0 mmol) were added to the mixture, and the mixture was stirred at 80 °C for 48 h. After the reaction, solid materials were removed through a Celite pad, and then the eluent was concentrated. To the residue were added water and ether, and the organic materials were extracted by ether. After removal of the solvent, the products were isolated by column chromatography (silica gel, hexane–ethyl acetate) and identified by ^{1}H NMR, GC–MS, and/or IR.

3.2.2. Typical reaction procedure 2

Into a 20 mL Schlenk tube under argon were added $(Cp^*RuCl_2)_2$ (6.2 mg, 0.01 mmol), benzene (3.0 mL), and AgOTf (10.3 mg, 0.06 mmol), and then the mixture was heated at reflux for 3 h. After cooling, 2-allylphenol (1.0 mmol) and PPh_3 (0.02 mmol) were added and the mixture was stirred at reflux for 48 h. The solvent was removed, water and dibenzyl ether (48.5 mg, 0.25 mmol) were added, and then the organic materials were extracted with chloroform. The obtained organic mixture was analyzed by ^{1}H NMR, and the yield of 2,3-dihydro-2-methylbenzofuran was determined by its area compared to that of the internal standard (dibenzyl ether). The product was isolated by column chromatography (silica gel, hexane:AcOEt = 10:1). When chiral phosphine was used, the enantiomeric excess was determined using chiral HPLC analysis (column packing: Daicel Chiral OJ-R; eluent: $MeOH/H_2O = 3/2$; detector: UV254 nm; flow rate 0.3 mL/min).

3.3. 2,3-Dihydro-2-methylbenzofuran (*2a*)

^{1}H NMR($CDCl_3$) δ 1.46 (3H, d, $J = 6.4$, CH_3), 2.81 (1H, dd, $J = 14.4$, 7.2, CH_2), 3.30 (1H, dd, $J = 14.4$, 7.2, CH_2), 4.88–4.94 (1H, m, CH), 6.75 (1H, d, $J = 7.6$, Ar), 6.82 (1H, t, $J = 7.6$, Ar), 7.10 (1H, t, $J = 7.6$, Ar), 7.15 (1H, d, $J = 7.6$, Ar). GC–MS (m/z) 134.

3.4. 2,3-Dihydro-5-methoxy-2-methylbenzofuran (**2b**)

^{1}H NMR($CDCl_3$) δ 1.43 (3H, d, $J = 6.79$, CH_3), 2.77 (1H, dd, $J = 15.2$, 7.6, CH_2), 3.25 (1H, dd, $J = 15.2$, 7.6, CH_2), 3.73 (3H, s, OCH_3), 4.83–4.91 (1H, m, CH), 6.61–6.67 (2H, m, *Ar*), 6.73 (1H, d, $J = 2.4$, *Ar*). GC–MS (*m*/*z*) 164.

3.5. 2,3-Dihydro-7-methoxy-2-methylbenzofuran (**2c**)

^{1}H NMR($CDCl_3$) δ 1.51 (3H d, $J = 6.0$, CH_3), 2.84 (1H, dd, $J = 15.2$, 7.6, CH_2), 3.32 (1H, dd, $J = 15.2$, 7.6, CH_2), 3.87 (3H, s, OCH_3), 4.93–5.02 (1H, m, CH), 6.72–6.81 (3H, m, Ar). GC–MS (*m*/*z*) 164.

3.6. 2,3-Dihydro-2,7-dimethylbenzofuran (**2d**)

^{1}H NMR($CDCl_3$) δ 1.47 (3H, d, $J = 6.4$, CH_3), 2.20 (3H, s, CH_3), 2.81 (1H, dd, $J = 15.2$, 7.6, CH_2), 3.30 (1H, dd, $J = 15.2$, 7.6, CH_2), 4.86–4.94 (1H, m, CH), 6.73 (1H, d, $J = 7.6$, Ar), 6.92 (1H, d, $J = 7.6$, Ar), 6.98 (1H, d, $J = 7.6$, Ar). GC–MS (*m*/*z*) 148.

3.7. 2,3-Dihydro-2-methylnaphtho[3,2-b]furan (**6**)

^{1}H NMR($CDCl_3$) δ 1.54 (3H, d, $J = 6.4$, CH_3), 3.07 (1H, dd, $J = 15.2$, 7.6, CHH), 3.60 (1H, dd, $J = 15.2$, 7.6, CHH), 5.08–5.17 (1H, m, CH), 7.08 (1H, d, $J = 8.8$, Ar), 7.27–7.31 (1H, m, Ar), 7.43–7.47 (1H, m, Ar), 7.56 (1H, d, $J = 8.8$, Ar), 7.67 (1H, d, $J = 8.8$, Ar), 7.79 (1H, d, $J = 8.8$). GC–MS (*m*/*z*) 185 (MH+).

3.8. 6-Methoxy-2,2-dimethylchroman (**8**)

^{1}H NMR($CDCl_3$) δ 1.31 (6H, s, $2CH_3$), 1.78 (2H, t, $J = 6.8$, $ArCH_2CH_2$), 2.75 (2H, t, $J = 6.8$, $ArCH_2$), 3.74 (3H, s, OCH_3), 6.61 (1H, d, $J = 2.4$, Ar), 6.66–6.72 (2H, m, Ar). GC–MS (*m*/*z*) 192.

3.9. 3,4-Dihydro-2-methyl-2H-1-benzopyran (**10**)

^{1}H NMR ($CDCl_3$) δ 1.39 (3H, d, $J = 6.0$, CH_3), 1.65–1.48 (1H, m, CH_2CH_2CH), 1.94–2.00 (1H, m, CH_2CH_2CH), 2.70–2.76 (1H, ddd, $J = 16.4$, 3.2, CH_2CH_2CH), 2.81–2.90 (1H, ddd, $J = 16.4$, 6.4, 3.2, CH_2CH_2CH), 4.08–4.18 (1H, m, CH), 6.78–6.83 (2H, m, *Ar*), 7.02–7.09 (2H, m, *Ar*). GC–MS (*m*/*z*) 148.

3.10. 3,4-Dihydro-3-methyl-1-oxoisocoumarine (**12**)

^{1}H NMR ($CDCl_3$) δ 1.53 (3H, d, $J = 6.0$, CH_3), 2.90–3.02 (2H, m, CH_2), 4.65–4.73 (1H, m, CH), 7.24 (1H, d, $J = 7.2$, *Ar*), 7.39 (1H, t, $J = 7.6$, *Ar*), 7.54 (1H, t, $J = 7.6$, *Ar*), 8.09 (1H, d, $J = 6.4$, *Ar*). GC–MS (*m*/*z*) 162.

3.11. 3-Methylphthalide (**14**)

^{1}H NMR ($CDCl_3$) δ 1.64 (3H, d, $J = 6.4$, CH_3), 5.57 (1H, q, $J = 6.5$, CH), 7.46 (1H, t, $J = 7.6$, *Ar*), 7.53 (1H, d, $J = 7.6$, *Ar*), 7.68 (1H, t, $J = 7.3$, *Ar*), 7.89 (1H, d, $J = 7.6$, *Ar*). GC–MS (*m*/*z*) 169.

3.12. γ-Methylbutyrolactone (**16**)

^{1}H NMR ($CDCl_3$) δ 1.38 (2H, d, $J = 6.1$, CH_3), 1.77–1.85 (1H, m, $COCH_2CH_2$), 2.03–2.37 (1H, m, $COCH_2CH_2$), 2.50–2.54 (2H, m, $COCH_2$), 4.57–4.65 (1H, m, CH). GC–MS (*m*/*z*) 100.

3.13. 3-Methylisochroman (**18**)

^{1}H NMR ($CDCl_3$) δ 1.35 (3H, d, $J = 6.0$, CH_3), 2.71 (2H, d, $J = 6.8$, $ArCH_2CH$), 3.82 (1H, m, CH), 4.83 (2H, s, $ArCH_2O$), 6.99–7.36 (4H, m, *Ar*).

3.14. 2-Methyl-N-tosylindoline (**20**)

^{1}H NMR ($CDCl_3$) δ 1.46 (3H, d, $J = 6.4$, $CHCH_3$), 2.38 (3H, s, $ArCH_3$), 2.46 (1H, dd, $J = 6.4$, 3.2, CH_2), 4.34–4.42 (1H, m, CH), 7.03–7.09 (2H, m, *Ar*), 7.18–7.26 (3H, m, *Ar*), 7.58 (2H, d, $J = 8.4$, *Ar*),7.69 (1H,d, $J = 8.0$, *Ar*). GC–MS (*m*/*z*) 287.

Acknowledgements

This work was partially supported by Doshisha University's Research Promotion Fund, and a grant to RCAST at Doshisha University from the Ministry of Education, Culture, Sports, Science and Technology, Japan. This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 16033259, "Reaction Control of Dynamic Complexes") from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] (a) Wacker-type reactions see: L. Hintermann, second ed., in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, vol. 2, Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim, 2004, pp. 379–388;
(b) T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105 (2005) 2329–2363;
(c) J.M. Takacs, X-t Jiang, Curr. Org. Chem. 7 (2003) 369–396;
(d) R. Jira, second ed., in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, Wiley–VCH Verlag GmbH, Weinheim, 2002, pp. 386–405.

[2] (a) Acidic conditions see: D. Barton, W.D. Ollis, J.F. Stoddart (Eds.), Comprehensive Organic Chemistry, vol. I, Pergamon, Oxford, 1979;
(b) J. March, Advanced Organic Chemistry, Reactions, Mechanisms, and Structure, fourth ed., John Wiley & Sons, New York, 1992 (Chapter 15);
(c) J. Meinwald, J. Am. Chem. Soc. 77 (1955) 1617;
(d) P.E. Peterson, E.V.P. Tao, J. Org. Chem. 29 (1964) 2322;
(e) A.O. Fitton, R.K. Smalley, Practical Heterocyclic Chemistry, Academic Press, New York, 1968, p. 16;
(f) C.D. Hurd, W.A. Hoffman, J. Org. Chem. 5 (1940) 212;
(g) A.B. Sen, R.P. Rastogi, J. Indian Chem. Soc. 30 (1953) 355;
(h) C.M. Evans, A.J. Kirby, J. Chem. Soc. Perkin Trans. 2 (1984) 1259.

[3] Photocatalytic, see: G. Fráter, H. Schmid, Helv. Chim. Acta 50 (1967) 255.
[4] (a) C.-G. Yang, N.W. Reich, Z. Shi, C. He, Org. Lett. 7 (2005) 4553–4556;
(b) J.-S. Ryu, T.J. Marks, F.E. McDonald, J. Org. Chem. 69 (2004) 1038–1052;
(c) H. Qian, X. Han, R.A. Windenhoefer, J. Am. Chem. Soc. 126 (2004) 9536;
(d) S. Geresh, O. Levy, Y. Markovits, A. Shani, Tetrahedron 31 (1975) 2803–2807;
(e) M.F. Grundon, D. Stewart, W.E. Watts, J. Chem. Soc. Chem. Commun. (1973) 573–574.
[5] (a) C.-G. Yang, C. He, J. Am. Chem. Soc. 127 (2005) 6966–6967;
(b) M. Beller, J. Seayad, A. Tillack, H. Jiao, Angew. Chem., Int. Ed. 43 (2004) 3368–3398;
(c) T. Yoshida, T. Matsuda, T. Okano, T. Kitani, S. Otsuka, J. Am. Chem. Soc. 101 (1979) 2027;
(d) H.E. Bryndza, J.C. Calabrese, S.S. Wreford, Organometallics 3 (1984) 1603;
(e) C.M. Jensen, W.C. Trogler, Science 233 (1986) 1069.
[6] (a) J. Zhang, C.G. Yang, C. He, J. Am. Chem. Soc. 128 (2006) 1798–1799, and references are cited therein;
(b) A.M. Johns, M. Utsunomiya, C.D. Incarvito, J.F. Hartwig, J. Am. Chem. Soc. 128 (2006) 1828–1839;
(c) J.F. Hartwig, Pure Appl. Chem. 76 (2004) 507–516.
[7] K. Hori, H. Kitagawa, A. Miyoshi, T. Ohta, I. Furukawa, Chem. Lett. (1998) 1083–1084.
[8] (a) Wacker-type cyclization of 2-allylphenol, see: K.F. McDaniel, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, 1995, p. 601;
(b) T. Hosokawa, K. Maeda, K. Koga, I. Moritani, Tetrahedron Lett. (1973) 739;
(c) T. Hosokawa, H. Ohkata, I. Moritani, Bull. Chem. Soc. Jpn. 48 (1975) 1533;
(d) T. Hosokawa, S. Miyagi, S.-I. Murahashi, A. Sonoda, J. Chem. Soc. Chem. Commun. (1978) 687;
(e) T. Hosokawa, T. Uno, S.-I. Murahashi, J. Chem. Soc. Chem. Commun. (1979) 475;
(f) T. Hosokawa, M. Hirata, S.-I. Murahashi, A. Sonoda, Tetrahedron Lett. (1976) 1821;
(g) T. Hosokawa, T. Kono, T. Uno, S.-I. Murahashi, Bull. Chem. Soc. Jpn. 59 (1986) 2191;
(h) M.F. Semmelhack, C.R. Kim, W. Dobler, M. Meier, Tetrahedron Lett. 30 (1989) 4925;
(i) S. Saito, T. Hara, N. Takahashi, M. Hirai, T. Morikawa, Synlett (1992) 237.
[9] (a) Intramolecular cyclization of amino-olefins with β-hydride elimination, see: L.S. Hegedus, G.F. Allen, E.L. Waterman, J. Am. Chem. Soc. 98 (1976) 2674;
(b) L.S. Hegedus, G.F. Allen, J.J. Bozell, E.L. Waterman, J. Am. Chem. Soc. 100 (1978) 5800;
(c) L.S. Hegedus, J.M. McKearin, J. Am. Chem. Soc. 104 (1982) 2444;
(d) P.J. Harrington, L.S. Hegedus, J. Org. Chem. 49 (1984) 2657.
[10] B. Pugin, L.M. Venanzi, J. Organomet. Chem. 214 (1981) 125.
[11] N. Oshima, H. Suzuki, Y. Morooka, Chem. Lett. (1984) 1161.
[12] (a) Our intermolecular addition to olefins, see: Y. Oe, T. Ohta, Y. Ito, Chem. Commun. (2004) 1620–1621;
(b) Y. Oe, T. Ohta, Y. Ito, Synlett (2005) 179–181.
[13] D.E. Nichols, A.J. Hoffman, R.A. Oberlender, R.M. Riggs, J. Med. Chem. 29 (1986) 302–304.
[14] F.C. Gozzo, S.A. Fernandes, D.C. Rodrigues, M.N. Eberlin, A.J. Marsaioli, J. Org. Chem. 68 (2003) 5493–5499.
[15] V. De Felice, A. De Renzi, M. Funicello, A. Panunzi, A. Saporito, Gazz. Chim. Ital. 115 (1985) 13–15.
[16] P. Yates, T.S. Macas, Can. J. Chem. 66 (1988) 1–10.
[17] S. Ozaki, M. Adachi, S. Sekiya, R. Kamikawa, J. Org. Chem. 68 (2003) 4586–4589.
[18] S. Chamoin, S. Houldsworth, V. Snieckus, Tetrahedron Lett. 39 (1998) 4175–4178.
[19] C.F.H. Allen, J.W. Gates, Org. Synth., Coll. III (1991) 198.
[20] N. Takamatsu, S. Inoue, Y. Kishi, Tetrahedron Lett. (1971) 4661–4664.
[21] L.G. Beholz, J.R. Stille, J. Org. Chem. 58 (1993) 5095–5100.
[22] S. Jolidon, H.-J. Hansen, Helv. Chem. Acta 101 (1977) 978–1032.
[23] J.P. Marino Jr., M.H. Osterhout, A.T. Price, S.M. Sheehan, A. Padwa, Tetrahedron Lett. 35 (1994) 849–852.
[24] M. Muehlstadt, K. Hollmann, R. Widera, Zeits. Chem. 28 (1988) 436.