Ruthenium Complex-Catalyzed Carbonylation of Allylic Compounds

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Received July 19, 1994[⊗]

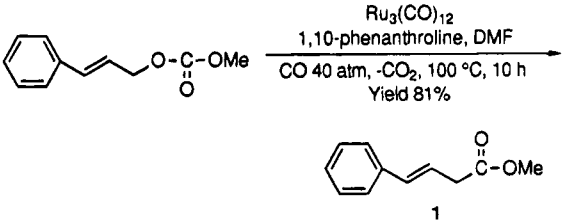
Allylic alkyl carbonates are carbonylated under 40 atm of carbon monoxide at 100–120 °C in the presence of a catalytic amount of $Ru_3(CO)_{12}$/1,10-phenanthroline to give α,β- or β,γ-unsaturated esters in good to high yields. For example, cinnamyl methyl carbonate afforded the corresponding β,γ-unsaturated esters, methyl *trans*-4-phenyl-3-butenoate (**1**) in 93% yield. The regioselectivity in the carbonylation of crotyl methyl carbonate is unusual and it depends on the carbon monoxide pressure. The more sterically hindered carbon (γ-carbon) is predominantly carbonylated at 20–50 atm. When the reaction of cinnamyl methyl carbonate was performed at elevated temperature (150 °C) without 1,10-phenanthroline, the dimer of **1**, dimethyl 3-benzyl-2-(*trans*-2-phenylvinyl)-glutarate, was obtained in 56% yield. In the presence of secondary amines, allylic alkyl carbonates were carbonylated mainly at α-carbon to give α,β- or β,γ-unsaturated amides in high yields.

Introduction

Transition metal-catalyzed carbonylation of allylic compounds attracted much attention for these decades.[1–23] For example, palladium-catalyzed carbonylation of allylic compounds such as halides,[4–12] carbonates,[13] acetates,[4,14–19] phosphates,[19] amines,[20] ethers,[4,21] alcohols,[4,6,22] and carbamates[23] gave the corresponding β,γ-unsaturated carboxylic acid derivatives or cyclocarbonylated products.[14–18] On the other hand, ruthenium complex-catalyzed characteristic reactions of allylic compounds have been reported.[24,25] The products in the ruthenium-catalyzed reactions are often quite different from those in the reactions catalyzed by palladium.[24,25] For catalytic carbonylation reactions of organic compounds, ruthenium complexes have been considered to be less active than Pd, Co, and Rh complexes. No effective ruthenium-catalyzed carbonylation of allylic compounds has been reported.[2,18] This paper deals with the first example of ruthenium complex-catalyzed efficient carbonylation of allylic compounds. In several cases, the regioselectivity was very unusual.

Results and Discussion

Carbonylation of Cinnamyl Methyl Carbonate. Cinnamyl methyl carbonate was carbonylated under 40 atm of carbon monoxide at 100 °C in the presence of 1,10-phenanthroline and a catalytic amount of $Ru_3(CO)_{12}$ in DMF (*N,N*-dimethylformamide) to give the corresponding β,γ-unsaturated ester, methyl *trans*-4-phenyl-3-butenoate (**1**), in high yield (eq 1). The effects of other



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tertiary amines and solvents were examined. Results are summarized in Table 1. The reaction did not proceed without amines as a solvent or as a ligand. The yield of the corresponding β,γ-unsaturated ester markedly increased when 1,10-phenanthroline was used as a ligand, which coordinates to the metal center. A combination of DMF and 1,10-phenanthroline gave the best result.

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

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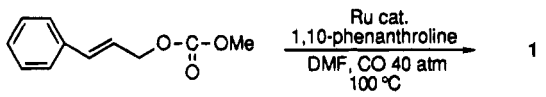
Table 1. Solvent and Ligand Effects on Ruthenium-Catalyzed Carbonylation of Cinnamyl Methyl Carbonate to Methyl 4-Phenyl-3-butenoate (1)[a]

	solvent	ligand	conv[b] (%)	yield of 1 (%)
1	*N*-Methylpiperidine (0.5 mL)	–	100	(42)
2	Et_3N (0.5 mL)	–	78	(24)
3	CH_3OH (1.0 mL)	–	0	0
4	DMF (1.0 mL)	–	60	trace
5	*N*-Methylpiperidine (0.5 mL) CH_3OH (1.0 mL)	–	100	trace
6	–	$Me_2N(CH_2)_4NMe_2$ (1.0 mmol)	100	(35)
7	–	1,10-phenanthroline (1.0 mmol)	100	(54)
8	DMF (1.0 mL)	$Me_2N(CH_2)_4NMe_2$ (1.0 mmol)	100	(45)
9	DMF (1.0 mL)	1,10-phenanthroline (1.0 mmol)	100	72[c] (81)

[a] $Ru_3(CO)_{12}$ (0.025 mmol), cinnamyl methyl carbonate (2.5 mmol), CO (40 atm), 100 °C, 10 h. [b] Conversion of cinnamyl methyl carbonate. [c] Isolated yield. Figures in parentheses are yields determined by GLC.

Table 2. Catalytic Activity of Several Ru Complexes[a]



run	catalyst	conversion[b] (%)	yield of 1[c] (%)
9	$Ru_3(CO)_{12}$	100	72 (81)
10	Ru(cod)(cot)	100	(89)
11	$RuH_2(PPh_3)_4$	90	(26)
12	$RuCl(cod)C_5Me_5$	67	trace
13	$RuCl_2(PPh_3)_3$	0	0
14	$[Ru(CO)_2C_5Me_5]_2$	0	0
15	$RuCl_3{\cdot}3H_2O$	80	(27)
16	$Fe_3(CO)_{12}$	0	0

[a] Ru or Fe-complex (0.075 mmol) as metal atom, cinnamyl methyl carbonate (2.5 mmol), 1,10-phenanthroline (1.0 mmol), DMF (1.0 mL), CO (40 atm), 100 °C, 10 h. [b] Based on the amount of cinnamyl methyl carbonate. [c] Isolated yield. Figures in parentheses are GLC yields.

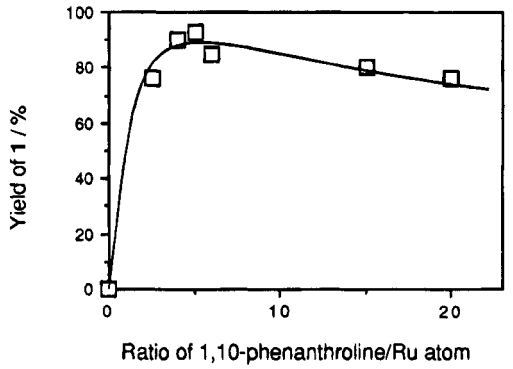


Figure 1. Effect of molar ratio of 1,10-phenanthroline/$Ru_3(CO)_{12}$ on carbonylation of cinnamyl methyl carbonate. Reaction conditions: cinnamyl methyl carbonate (2.5 mmol), $Ru_3(CO)_{12}$ (0.025 mmol), and DMF (1.0 mL) under CO 40 atm at 100 °C for 10 h.

Catalytic activities of various ruthenium complexes were examined in the carbonylation of cinnamyl methyl carbonate using 1,10-phenanthroline as a ligand; results are summarized in Table 2. Among the catalysts examined, zerovalent ruthenium complexes such as $Ru_3(CO)_{12}$ and (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium [Ru(cod)(cot)] showed high catalytic activity. Under carbon monoxide pressure, Ru(cod)(cot) was readily converted into $Ru_3(CO)_{12}$.[26]

Effects of the molar ratio of 1,10-phenanthroline to $Ru_3(CO)_{12}$ on the carbonylation of cinnamyl methyl carbonate is shown in Figure 1. Addition of 5-fold amount of 1,10-phenanthroline to that of Ru atom gave the best result.

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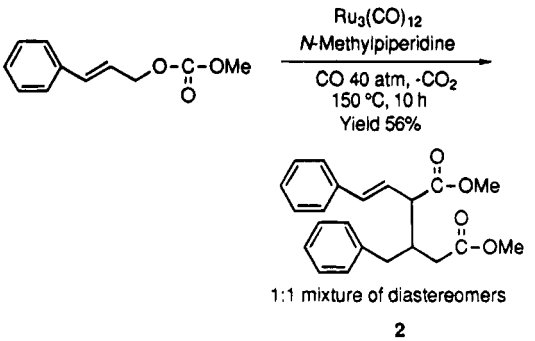
Among cinnamylic compounds, carbonates and phenyl ether reacted. Cinnamyl phenyl ether reacted in the presence of methanol to afford the corresponding β,γ-unsaturated methyl ester **1** in 28% yield. Cinnamyl acetate, alcohol, bromide, and chloride did not react under the reaction conditions.

On the other hand, when the carbonylation of cinnamyl methyl carbonate was performed at the elevated temperature, at 150 °C, in the presence of *N*-methylpiperidine as a solvent and a catalytic amount of $Ru_3(CO)_{12}$ under CO pressure without 1,10-phenanthroline, the dimer of **1, 2,** was formed in 56% yield (eq 2). The dimer



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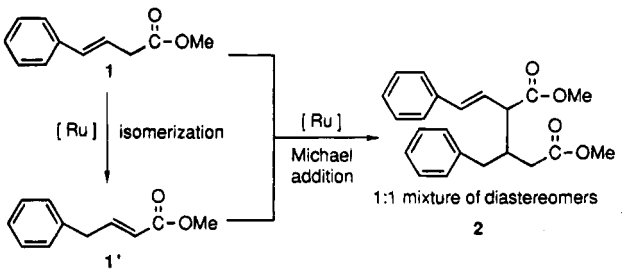
2 was a 1:1 mixture of diastereomers. The formation of **2** can be explained by Michael addition of **1** to the α,β-unsaturated ester **1′** that was formed by the ruthenium-catalyzed isomerization of **1** (Scheme 1). When **1** was treated under the same reaction conditions, **2** was formed in 15% yield. In the presence of 1,10-phenanthroline, cinnamyl methyl carbonate gave only **1** at 150 °C and the formation of the dimer was suppressed; 1,10-phenanthroline disturbed the isomerization of **1** to **1′**.

Scheme 1



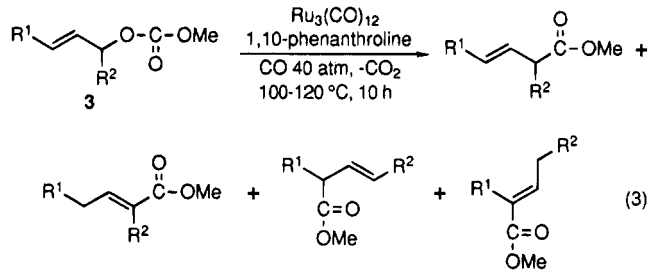
Carbonylation of Various Allylic Carbonates. Various allylic methyl carbonates were carbonylated to give α,β- and β,γ-unsaturated esters in good to high yields in the presence of a catalytic amount of $Ru_3(CO)_{12}$/1,10-

Table 3. Ruthenium-Catalyzed Carbonylation of Various Allylic Carbonates[a]

run	allylic carbonate	products (% yield)	total yields[b] (%)
16[c]	(*E*)-PhCH=CHCH$_2$OCO$_2$CH$_3$ **3a**	(*E*)-PhCH=CHCH$_2$CO$_2$CH$_3$ **1** (93)	(93)
17[c]	CH$_2$=CHCH(Ph)OCO$_2$CH$_3$ **3b**	**1** (66)	66
18	CH$_2$=CHCH$_2$OCO$_2$CH$_3$ **3c**	CH$_2$=CHCH$_2$CO$_2$CH$_3$ **4c** (trace), (*E*)-CH$_3$CH=CHCO$_2$CH$_3$ **4c'** (18)	18
19	(*E*)-CH$_3$CH=CHCH$_2$OCO$_2$CH$_3$ **3d**	(*E*)-CH$_3$CH=CHCH$_2$CO$_2$CH$_3$ **4d** (7), CH$_2$=CHCH(CH$_3$)CO$_2$CH$_3$ **5d** (trace), (*E*)-CH$_3$CH$_2$CH=CHCO$_2$CH$_3$ **4d'** (13), (*E*)-CH$_3$CH=C(CH$_3$)CO$_2$CH$_3$ **5d'** (45)	65
20[d]	**3d**	**4d** (21), **4d'** (7), **5d** (trace), **5d'** (11)	39
21	CH$_2$=CHCH(CH$_3$)OCO$_2$CH$_3$ **3e**	**5d** (trace), **5d'** (7), **4d** (29), **4d'** (42)	78
22	(*E*)-CH$_3$(CH$_2$)$_2$CH=CHCH$_2$OCO$_2$CH$_3$ **3f**	(*E*)-CH$_3$(CH$_2$)$_2$CH=CHCH$_2$CO$_2$CH$_3$ **4f** (16), CH$_2$=CHCH(^{n}C$_3$H$_7$)CO$_2$CH$_3$ **5f** (6), (*E*)-CH$_3$(CH$_2$)$_3$CH=CHCO$_2$CH$_3$ **4f'** (4), (*E*)-CH$_3$CH=C(^{n}C$_3$H$_7$)CO$_2$CH$_3$ **5f'** (14)	40
23[c]	(*E*)-(CH$_3$)$_2$C=CH(CH$_2$)$_2$C(CH$_3$)=CHCH$_2$OCO$_2$CH$_3$ **3g**	(*E*)-(CH$_3$)$_2$C=CH(CH$_2$)$_2$C(CH$_3$)=CHCH$_2$CO$_2$CH$_3$ **4g** (66)	66

[a] Ru$_3$(CO)$_{12}$ (0.050 mmol), allylic methyl carbonate (5.0 mmol), 1,10-phenanthroline (0.66 mmol), CO (40 atm), 120 °C, 10 h. [b] Yield of the mixture of the isomers obtained by column chromatography and Kugelrohr distillation. [c] Ru$_3$(CO)$_{12}$ (0.025 mmol), allylic methyl carbonate (2.5 mmol), 1,10-phenanthroline (0.33 mmol), DMF (1.0 mL), CO (40 atm), 100 °C, 10 h. [d] 2,2'-Bipyridine was used in place of 1,10-phenanthroline. Figures in parentheses are yields determined by GLC.

phenanthroline under CO pressure (eq 3). Results are



summarized in Table 3. 1-Phenylallyl methyl carbonate (**3b**) gave a sole product **1**, the same product in the reaction of cinnamyl methyl carbonate (**3a**). This result strongly suggests that the present reaction proceeds via a (π-allyl)ruthenium intermediate. The reaction of geranyl methyl carbonate (**3g**) selectively gave the corresponding β,γ-unsaturated ester **4g** in 66% yield. On the other hand, the reaction of crotyl methyl carbonate (**3d**) was unusual; the carbonylation predominantly occurred at the more sterically hindered carbon (γ-carbon). The carbonylation of crotyl methyl carbonate (**3d**) using 2,2'-bipyridine as a ligand in place of 1,10-phenanthroline gave the product that carbonylated at the less hindered α-carbon as a major product. These results show that regioselectivity is controlled by the ligands. On the contrary, 1-methylallyl methyl carbonate (**3e**) was carbonylated predominantly at the less sterically hindered carbon. These results suggest that the structures of the (π-allyl)ruthenium intermediates depends on the substrates. 2-Hexenyl methyl carbonate (**3f**) also gave the products that are carbonylated at both α- and γ-carbons. This regioselectivity in catalytic carbonylation of allylic compounds has not been reported previously.

Effects of Carbon Monoxide Pressure on Carbonylation of Crotyl (3d) and 1-Methylallyl Methyl Carbonate (3e). Effects of carbon monoxide pressure on the regioselectivity of the products were very interesting. Results are shown in Figure 2. In the reaction of crotyl methyl carbonate (**3d**) at 10 atm, the selectivity for the product (**5d'**) derived by the γ-carbonylation was 36%. With the increase of the carbon monoxide pressure the selectivity increased; the maximum selectivity was 69% at 40 atm. Further increase of the pressure caused a decrease of the selectivity for **5d'**.

In contrast, in the reaction of 1-methylallyl carbonate,

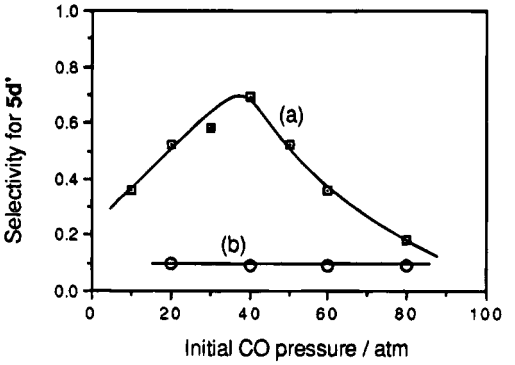
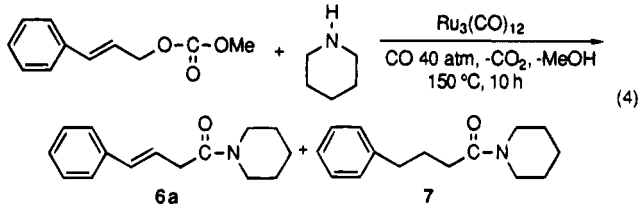


Figure 2. Effects of CO pressure on the formation of methyl tiglate (**5d'**), by the carbonylation of (a) crotyl methyl carbonate (**3d**) and (b) 1-methylallyl methyl carbonate (**3e**). Reaction conditions: allylic methyl carbonate (5.0 mmol), Ru3(CO)12 (0.050 mmol) and 1,10-phenanthroline (0.66 mmol) at 120 °C for 10 h.

selectivity for **5d'** did not depend on the carbon monoxide pressure; the ratio was constant, ca. 10%.

Carbonylation of Cinnamyl Methyl Carbonate in the Presence of Secondary Amines. Cinnamyl methyl carbonate reacted with piperidine in the presence of a catalytic amount of Ru$_3$(CO)$_{12}$ under CO pressure, to give the corresponding β,γ-unsaturated amide **6a** and the saturated amide **7** (eq 4). Effects of solvents and ligands



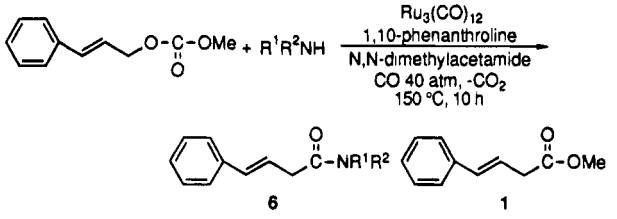
are shown in Table 4. *N*-Methylpiperidine, *N,N,N',N'*-tetramethylbutanediamine, or 1,10-phenanthroline was effective as a ligand. The combination of DMF with 1,10-phenanthroline, which was most effective in the carbonylation of cinnamyl methyl carbonate to **1**, was also effective but the yield of the amide **6a** was 63%. In addition, DMF reacted with cinnamyl methyl carbonate to give *N,N*-dimethyl-4-phenyl-3-butenamide as a byproduct. *N,N*-Dimethylacetamide in place of DMF was employed as a solvent to give selectively the corresponding β,γ-unsaturated amide **6a** in 77% yield. On the other

Table 4. Piperidino Carbonylation of Cinnamyl Methyl Carbonate[a]

run	solvent	ligand	total yield of 6a and 7[b] (%)	6a:7
24	*N*-methylpiperidine (0.5 mL)	–	47	34:13
25	toluene (1.0 mL)	–	(18)	18:0
26	*N*-methylpiperidine (0.5 mL), DMF (1.0 mL)	–	70	60:10
27	*N*-methylpiperidine (0.5 mL), 1,4-dioxane (1.0 mL)	–	(78)	68:10
28	–	$Me_2N(CH_2)_2NMe_2$ (1 mmol)	(45)	39:6
29	–	$Me_2N(CH_2)_3NMe_2$ (1 mmol)	(55)	46:9
30	–	$Me_2N(CH_2)_4NMe_2$ (1 mmol)	(72)	60:12
31	–	$Me_2N(CH_2)_6NMe_2$ (1 mmol)	(39)	33:6
32	–	1,10-phenanthroline (1 mmol)	(60)	54:6
33	DMF (1.0 mL)	1,10-phenanthroline (0.33 mmol)	63	63:trace
34	CH_3CONMe_2 (1.0 mL)	1,10-phenanthroline (0.33 mmol)	77	77:–

[a] $Ru_3(CO)_{12}$ (0.025 mmol), cinnamyl methyl carbonate (2.5 mmol), piperidine (2.5 mmol), 150 °C, 10 h, CO (40 atm). [b] Yield of the mixture of the carbonylation products obtained by Kugelrohr distillation. Figures in parentheses are yields determined by GLC.

Table 5. Carbonylation of Cinnamyl Methyl Carbonate in the Presence of Various Secondary Amines[a]



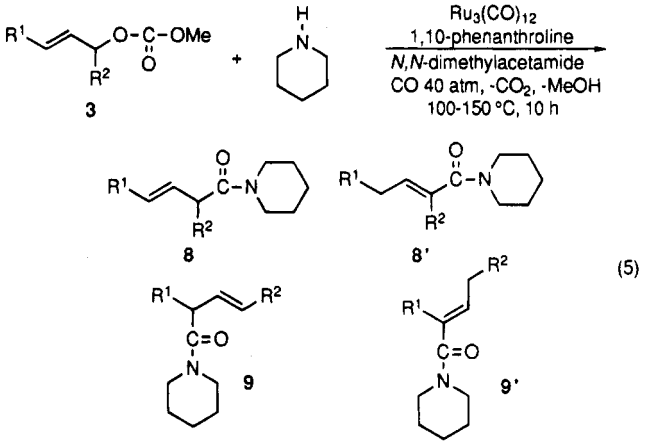
run	secondary amines	yield of 6[b] (%)	yield of 1[b] (%)
34	piperidine	77 (**6a**)	–
35	morpholine	69 (**6b**)	–
36	Et_2NH	56 (**6c**)	29
37	$(i\text{-}Pr)_2NH$	4 (**6d**)	24

[a] $Ru_3(CO)_{12}$ (0.025 mmol), cinnamyl methyl carbonate (2.5 mmol), secondary amine (2.5 mmol), *N,N*-dimethylacetamide (1.0 mL), 1,10-phenanthroline (0.33 mmol), 150 °C, CO (40 atm), 10 h. [b] Isolated yield.

hand, **1** did not react with piperidine under these reaction conditions. *N*-Cinnamylpiperidine was not carbonylated to **6a** under these reaction conditions.

Carbonylation of cinnamyl methyl carbonate in the presence of several secondary amines was examined and results are shown in Table 5. In the presence of piperidine or morpholine the reaction proceeded selectively to give the corresponding β,γ-unsaturated amides in high yields. In the reaction with diethylamine, the corresponding β,γ-unsaturated amide **6c** was obtained as a major product in 56% yield together with 29% of **1**. No saturated amide **7** was obtained. In the reaction with diisopropylamine, **1** was obtained as a major product in 24% yield. On the other hand, the reaction of cinnamyl methyl carbonate with primary amines gave a number of products. Further identification was not attempted.

Carbonylation of Various Allylic Carbonates in the Presence of Piperidine. Allylic methyl carbonates reacted with piperidine to give a mixture of α,β- and β,γ-unsaturated amides in good to high yields (eq 5). Results are summarized in Table 6. Cinnamyl methyl carbonate (**3a**) and 1-phenylallyl methyl carbonate (**3b**) were converted into the same product **6a**. These results also indicate that the present reaction proceeds via a (π-allyl)-ruthenium intermediate. Geranyl methyl carbonate (**3g**) gave the corresponding β,γ-unsaturated amide **8g** in 54% yield. In these reactions, no α,β-unsaturated amide was obtained. In contrast, allyl methyl carbonate gave two products, **8c** and **8c'**; the main product was the isomerized α,β-unsaturated amide. Crotyl methyl carbonate (**3d**) was also carbonylated predominantly at the less sterically hindered carbon (α-carbon) at 100 or 150 °C.



(5)

2-Hexenyl methyl carbonate (**3f**) was also carbonylated predominantly at the α-carbon. Unusual regioselectivity for γ-carbon carbonylation was not observed in the amidation reaction. The present reaction is the first example of the ruthenium-catalyzed amidation reaction, although the formation of amides by carbonylation of allylic compounds in the presence of primary or secondary amines by palladium[13] and rhodium[2] complex catalysts has already been reported briefly.

Mechanism of the Carbonylation. On the basis of the mechanisms proposed for the palladium catalyzed carbonylation,[13,27] the mechanism of the carbonylation of allylic carbonates to esters can be explained as follows (Scheme 2). Allyl methyl carbonate oxidatively adds to a ruthenium–carbonyl species to give a (π-allyl)ruthenium complex (**10**) with an evolution of CO_2.[25d] There are two possible reaction pathways for CO insertion. One is the insertion of CO to the (π-allyl)–ruthenium bond to give two acyl complexes. Another one is the insertion into the ruthenium–methoxy bond to give a (methoxycarbonyl)(π-allyl)ruthenium complex. The reductive elimination takes place to give two β,γ-unsaturated esters. β,γ-Unsaturated esters are isomerized by ruthenium complex to give the corresponding α,β-unsaturated esters, respectively.

The regioselectivity observed in the esterification of crotyl or 1-methyl carbonates mentioned above show that the mechanism of the reaction is very complicated. The effects of the carbon monoxide pressure on the regioselectivity of the products show that at least two different mechanisms compete to determine the product distributions. Attempts to isolate reaction intermediates or to examine the intermediate complexes by spectroscopic

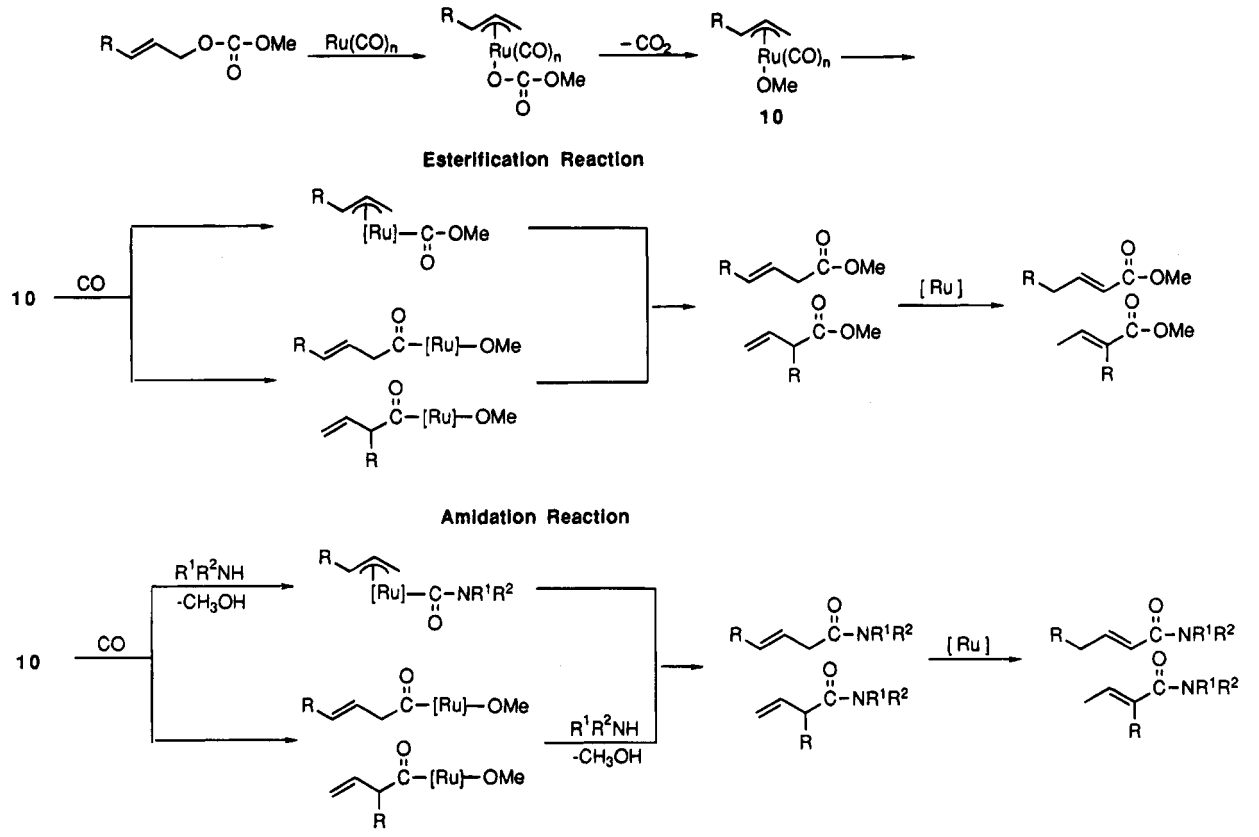
(27) Milstein, D. *Organometallics* **1982**, *1*, 888.

Table 6. Ruthenium-Catalyzed Carbonylation of Various Allylic Carbonates in the Presence of Piperidine[a]

run	allylic carbonate	products (% yield)	total yields[b] (%)
34	(*E*)-PhCH=CHCH$_2$OCO$_2$CH$_3$ **3a**	(*E*)-PhCH=CHCH$_2$CONC$_5$H$_{10}$ **6a** (77)	77
38	CH$_2$=CHCH(Ph)OCO$_2$CH$_3$ **3b**	(*E*)-PhCH=CHCH$_2$CONC$_5$H$_{10}$ **6a** (57)	57
39	CH$_2$=CHCH$_2$OCO$_2$CH$_3$ **3c**	CH$_2$=CHCH$_2$CONC$_5$H$_{10}$ **8c** (3), (*E*)-CH$_3$CH=CHCONC$_5$H$_{10}$ **8c'** (64)	67
40	(*E*)-CH$_3$CH=CHCH$_2$OCO$_2$CH$_3$ **3d**	(*E*)-CH$_3$CH=CHCH$_2$CONC$_5$H$_{10}$ **8d** (21), CH$_2$=CHCH(CH$_3$)CONC$_5$H$_{10}$ **9d** (3), (*E*)-CH$_3$CH$_2$CH=CHCONC$_5$H$_{10}$ **8d'** (10), (*E*)-CH$_3$CH=C(CH$_3$)CONC$_5$H$_{10}$ **9d'** (trace)	34
41[c]	**3d**	**8d** (26), **8d'** (10), **9d** (6), **9d'** (trace)	32
42	(*E*)-CH$_3$(CH$_2$)$_2$CH=CHCH$_2$OCO$_2$CH$_3$ **3f**	(*E*)-CH$_3$(CH$_2$)$_2$CH=CHCH$_2$CONC$_5$H$_{10}$ **8f** (27), CH$_2$=CHCH(^{n}C$_3$H$_7$)CONC$_5$H$_{10}$ **9f** (2), (*E*)-CH$_3$(CH$_2$)$_3$CH=CHCONC$_5$H$_{10}$ **8f'** (7), (*E*)-CH$_3$CH=C(^{n}C$_3$H$_7$)CONC$_5$H$_{10}$ **9f'** (trace)	36
43	(*E*)-(CH$_3$)$_2$C=CH(CH$_2$)$_2$C(CH$_3$)=CHCH$_2$OCO$_2$CH$_3$ **3g**	(*E*)-(CH$_3$)$_2$C=CH(CH$_2$)$_2$C(CH$_3$)=CHCH$_2$CONC$_5$H$_{10}$ **8g** (54)	54

[a] Ru$_3$(CO)$_{12}$ (0.025 mmol), allylic methyl carbonate (2.5 mmol), 1,10-phenanthroline (0.33 mmol), piperidine (2.5 mmol), *N,N*-dimethylacetamide (1.0 mL), CO (40 atm), 150 °C, 10 h. [b] Yield of the mixture of the isomers obtained by column chromatography and Kugelrohr distillation. [c] Reaction was carried out at 100 °C.

Scheme 2



method are so far unsuccessful. To explain these complicated results, further investigations on the intermediate complexes are required.

The carbonylation of allylic carbonates to amides can be similarly explained by the following mechanism (Scheme 2). After formation of the (π-allyl)ruthenium complex (**10**), there are two possible reaction pathways. One is the insertion of CO to the (π-allyl)-ruthenium bond to give two acyl complexes. Then the nucleophilic attack of amines to the carbonyl carbons of two acyl moieties takes place with methanol leaving. Another one is the nucleophilic attack of amines to carbon monoxide ligand on ruthenium to give a (π-allyl)(carbamoyl)ruthenium complex, and the subsequent reductive elimination proceeded. As mentioned above, two β,γ-unsaturated amides are formed and α,β-unsaturated amides are obtained by subsequent isomerization of them. The difference of the regioselectivity between the methoxycarbonylation and amidation reaction and the ligand control of the regioselectivity mentioned above strongly suggest that the mechanism of the regiocontrolling step is different for the two reactions. Quite recently, in the stoichiometric acylation of π-allyliron complexes, the π-allyliron complex was acetylated at the more hindered carbon. While π-cinnamyliron complex was acetylated at the less hindered carbon. Futhermore, the regioselectivity in the acetylation of π-crotyl complex was controlled by solvents.[28] Further investigation on the π-allyl methoxy ruthenium or π-allyl carbamoyl ruthenium complexes are required to get a clear-cut explanation.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL GSX270 spectrometer in $CDCl_3$ solution. IR

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spectra were obtained on a Shimadzu FTIR-8100 spectrometer. $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ were purchased from Strem Chemicals and used without further purification. $RuCl_3 \cdot 3H_2O$ were purchased from Wako Pure Chemical Industries and used without further purification. Ru(cod)(cot),[29] $RuH_2(PPh_3)_4$,[30] $RuCl(cod)C_5Me_5$,[31] $RuCl_2(PPh_3)_3$,[32] and $[Ru(CO)_2C_5Me_5]_2$[33] were prepared by literature methods. Allyl carbonates were prepared from the corresponding alcohols and methyl chloroformate according to the reported procedure.[13] The known products are shown by the reference, however, since the high resolution ^1H NMR (270 MHz) and ^{13}C NMR spectral data were not reported, they are shown below.

Ruthenium-Catalyzed Carbonylation of Cinnamyl Methyl Carbonate. In a 50 mL stainless autoclave were placed $Ru_3(CO)_{12}$ (0.017 g, 0.027 mmol), 1,10-phenanthroline (0.18 g, 1.00 mmol), cinnamyl methyl carbonate (0.480 g, 2.50 mmol), and *N,N*-dimethylformamide (1.0 mL). After CO was introduced to 40 atm at 25 °C, the mixture was magnetically stirred at 100 °C for 10 h. Kugelrohr distillation of the reaction mixture gave methyl 4-phenyl-3-butenoate (**1**) (0.32 g, 72%) as a colorless oil: bp 115–120 °C (0.5 mmHg); IR (neat) 1740 (C=O) 1256 (C–O) cm^{-1} ; ^1H NMR (270 MHz) δ 3.24 (d, J = 6.8 Hz, 2H), 3.69 (s, 3H), 6.30 (dt, J = 6.8 and 16.1 Hz, 1H), 6.48 (d, J = 16.1 Hz, 1H), 7.21–7.38 (m, 5H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 38.1, 51.8, 121.5, 126.2, 127.5, 128.4, 128.6, 128.7, 133.4, 136.7, 171.9 (C=O); MS m/z 176 (M^+). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.23; H, 6.80.

Ruthenium-Catalyzed Carbonylation of Geranyl Methyl Carbonate. In a 50 ml stainless autoclave were placed $Ru_3(CO)_{12}$ (0.017 g, 0.027 mmol), 1,10-phenanthroline (0.060 g, 0.33 mmol), geranyl methyl carbonate (0.530 g, 2.5 mmol), and *N,N*-dimethylformamide (1.0 mL). After CO was introduced to 40 atm, the mixture was stirred at 100 °C for 10 h. Kugelrohr distillation of the reaction mixture gave methyl 4,8-dimethyl-3,7-nonadienoate (**3g**) (0.32 g, 66%) as a colorless oil: bp 115–120 °C (0.5 mmHg); IR (neat) 1744 (C=O) 1262 (C–O) cm^{-1} ; ^1H NMR (270 MHz) δ 1.61 (s, 3H), 1.63 (s, 3H), 1.68 (s, 3H), 2.06 (m, 4H), 3.06 (d, J = 7.2 Hz, 2H), 3.68 (s, 3H), 5.10 (m, 1H), 5.33 (t, J = 6.6, 1H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 15.8, 17.1, 25.1, 25.8, 32.9, 39.0, 51.1, 115.3, 123.5, 131.0, 138.4, 172.3 (C=O). MS m/z 196 (M^+). Anal. Calcd for $C_{11}H_{20}O_2$: C, 73.43; H, 10.26. Found: C, 73.37; H, 10.38.

General Procedure for Ruthenium-Catalyzed Carbonylation of Allylic Methyl Carbonate. In a 50 mL stainless autoclave were placed $Ru_3(CO)_{12}$ (0.034 g, 0.053 mmol), 1,10-phenanthroline (120.0 mg, 0.66 mmol), and allylic methyl carbonate (5.0 mmol). After CO was introduced at 40 atm, the mixture was stirred at 120 °C for 10 h. After cooling, the products were isolated by column chromatograpy (Florisil, 20 mm × 150 mm; eluent, diethyl ether). Ratio of the isomers was determined by ^1H NMR spectra.

Methyl 2-Butenoate (4c'). Colorless liquid: bp 80–90 °C (Kugelrohr); ^1H NMR (270 MHz) δ 1.88 (d, J = 6.8 Hz, 3H), 3.72 (s, 3H), 5.85 (d, J = 15.4 Hz, 1H), 6.91–7.05 (m, 1H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 17.8, 51.3, 122.3, 144.7, 166.9 (C=O); MS m/z 100 (M^+).

Mixture of 4d, 4d', and 5d'. Colorless liquid: bp 95–100 °C (Kugelrohr). Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 62.89; H, 8.97.

Methyl 3-pentenoate (4d): ^1H NMR (270 MHz) δ 1.69 (d, J = 4.9 Hz, 3H), 3.02 (d, J = 5.9 Hz, 2H), 3.67 (s, 3H), 5.53–5.59 (m, 2H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 17.5, 37.5, 51.1, 122.5, 128.9, 172.1 (C=O); MS m/z 114 (M^+).

Methyl 2-pentenoate (4d'): ^1H NMR (270 MHz) δ 1.07 (t, J = 7.4 Hz, 3H), 2.01–2.28 (m, 2H), 3.68 (s, 3H), 5.81 (d, J = 15.6 Hz, 1H), 7.02 (dt, J = 7.4 and 15.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 11.8, 24.9, 51.2, 121.5, 150.5, 166.8 (C=O); MS m/z 114 (M^+).

Methyl 2-methyl-2-butenoate (5d'): ^1H NMR (270 MHz) δ 1.79 (d, J = 6.8 Hz, 3H), 1.83 (s, 3H), 3.72 (s, 3H), 6.85 (q, J = 6.8 Hz, 1H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 11.6, 13.9, 51.3, 128.2, 136.8, 168.2 (C=O); MS m/z 114 (M^+).

Mixture of 4f, 4f', 5f, and 5f'. Colorless liquid: bp 115–120 °C (Kugelrohr). Anal. Calcd for $C_8H_{14}O_2$: C, 67.58; H, 9.92. Found: C, 67.43; H, 9.98.

Methyl 3-heptenoate (4f): ^1H NMR (270 MHz) δ 0.89–0.93 (m, 3H), 1.33–1.47 (m, 2H), 1.94–2.02 (m, 2H), 3.03 (d, J = 4.4 Hz, 2H), 3.68 (s, 3H), 5.52–5.57 (m, 2H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 13.9, 22.5, 34.8, 38.2, 52.0, 121.8, 135.0, 173.0 (C=O); MS m/z 142 (M^+).

Methyl 2-heptenoate (4f'): ^1H NMR (270 MHz) δ 0.89–0.93 (m, 3H), 1.33–1.47 (m, 4H), 2.17–2.22 (m, 2H), 3.72 (s, 3H), 5.82 (d, J = 15.6 Hz, 1H), 6.95–7.01 (m, 1H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 13.6, 22.2, 22.4, 32.2, 51.5, 121.1, 150.1, 172.5 (C=O); MS m/z 142 (M^+).

Methyl 2-propyl-3-butenoate (5f): ^1H NMR (270 MHz) δ 0.89–0.93 (m, 3H), 1.33–1.47 (m, 4H), 3.67 (s, 3H), 3.81–3.85 (m, 1H), 5.10 (d, J = 10.7 Hz, 1H), 5.11 (d, J = 16.6 Hz, 1H), 5.74–5.88 (m, 1H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 14.2, 22.2, 22.4, 32.8, 50.0, 117.0, 136.1, 167.2 (C=O); MS m/z 142 (M^+).

Methyl 2-propyl-2-butenoate (5f'): ^1H NMR (270 MHz) δ 0.89–0.93 (m, 3H), 1.33–1.47 (m, 2H), 1.80 (d, J = 7.3 Hz, 3H), 2.29 (t, J = 7.6 Hz, 2H), 3.78 (s, 3H), 6.86 (q, J = 7.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 14.1, 14.5, 22.5, 28.6, 51.9, 133.1, 137.8, 168.8 (C=O); MS m/z 142 (M^+).

General Procedure for Ruthenium-Catalyzed Carbonylation of Allylic Methyl Carbonate in the Presence of Secondary Amine. In a 50 mL stainless autoclave were placed $Ru_3(CO)_{12}$ (0.017 g, 0.027 mmol), 1,10-phenanthroline (60.0 mg, 0.33 mmol), allylic methyl carbonate (2.5 mmol), secondary amine (2.5 mmol), and dimethylacetamide (1.0 mL). After CO was introduced at 40 atm, the mixture was stirred at 150 °C for 10 h. Products were isolated by Kugelrohr distillation.

4-Phenyl-1-piperidino-3-buten-1-one (6a). Pale orange oil: bp 190–195 °C (0.4 mmHg, Kugelrohr); IR (neat) 1634 (C=O) cm^{-1}; ^1H NMR (270 MHz) δ 1.57 (br s, 6H), 3.30 (d, J = 6.5 Hz, 2H), 3.44 (t, J = 4.4 Hz, 2H), 3.58 (t, J = 4.9 Hz, 2H), 6.34 (dt, J = 6.4 and 16.1 Hz, 1H), 6.58 (d, J = 16.1 Hz, 1H), 7.18–7.38 (m, 5H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 24.4, 25.5, 26.5, 38.1, 42.8, 47.0, 123.0, 123.4, 126.2, 126.5, 127.3, 128.5, 132.5, 135.9, 169.1 (C=O); MS m/z 229 (M^+). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.48; H, 8.29; N, 5.85.

4-Phenyl-1-morpholino-3-buten-1-one (6b). Pale orange oil: bp 190–195 °C (0.5 mmHg, Kugelrohr); IR (neat) 1643 (C=O) cm^{-1}; ^1H NMR (270 MHz) δ 3.28 (d, J = 5.9 Hz, 2H), 3.47 (t, J = 4.7 Hz, 2H), 3.62 (br s, 6H), 6.30 (dt, J = 5.9 and 16.1 Hz, 1H), 6.47 (d, J = 16.1 Hz, 1H), 7.19–7.37 (m, 5H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 37.4, 41.8, 46.0, 66.4, 66.6, 122.5, 126.0, 127.3, 128.1, 128.3, 132.7, 136.6, 144.9, 169.5 (C=O); MS m/z 231 (M^+). Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.40; N, 6.06. Found: C 72.47; H 7.50; N; 5.91.

***N,N*-Diethyl-4-phenyl-3-butenamide (6c).** Pale orange oil: bp 160–165 °C (0.25 mmHg, Kugelrohr); IR (neat) 1651 (C=O) cm^{-1}; ^1H NMR (270 MHz) δ 1.14 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H), 3.28 (d, J = 5.4, 2H), 3.30–3.43 (m, 4H), 6.38 (dt, J = 5.4 and 16.1, 1H), 6.47 (d, J = 16.1, 1H), 7.20–7.38 (m, 5H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 13.1, 14.3, 37.8, 40.1, 42.1, 121.7, 123.7, 126.1, 127.2, 128.7, 132.2, 137.0, 143.4, 170.0 (C=O); MS m/z 217 (M^+). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.05; H, 8.73; N, 6.13.

***N,N*-Diisopropyl-4-phenyl-3-butenamide (6d).** Pale orange oil: bp 200–205 °C (0.5 mmHg, Kugelrohr); IR (neat) 1640 (C=O) cm^{-1}; ^1H NMR (270 MHz) δ 1.20 (d, J = 6.8 Hz, 6H), 1.41 (d, J = 6.8 Hz, 6H), 3.26 (d, J = 5.4 Hz, 2H), 3.50 (m, J = 6.8 Hz, 1H), 4.00 (m, J = 6.8 Hz, 1H), 6.35 (dt, J = 5.4 and 16.1 Hz, 1H), 6.46 (d, J =16.1 Hz, 1H), 7.17–7.38 (m, 5H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 20.6, 20.9, 39.9, 45.7, 48.8, 123.9, 126.1, 127.2, 128.4, 128.7, 132.1, 137.1, 142.2, 169.7 (C=O); MS m/z 245 (M^+). Anal. Calcd for $C_{16}H_{23}NO$: C, 78.33; H, 9.44; N, 5.71. Found: C, 78.25; H, 9.56; N, 5.37.

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Mixture of 8c and 8c'. Yellow oil: bp 80–90 °C (0.5 mmHg, Kugelrohr). Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.86; N, 9.14. Found: C, 70.57; H, 9.95; N, 8.96.

1-Piperidino-3-buten-1-one (8c): ^{1}H NMR (270 MHz) δ 1.53–1.59 (m, 4H), 1.63–1.68 (m, 2H), 3.09–3.16 (m, 2H), 3.68 (br s, 2H), 3.71 (br s, 2H), 5.08–5.19 (m, 2H), 5.85–6.01 (m, 1H); ^{13}C{^{1}H} NMR (68 MHz) δ 15.2, 35.9, 36.6, 38.9, 42.1, 47.3, 117.5, 123.6, 165.4 (C=O); MS m/z 133 (M^+).

1-Piperidino-2-buten-1-one (8c'): ^{1}H NMR (270 MHz) δ 1.53–1.59 (m, 4H), 1.63–1.68 (m, 2H), 1.87 (d, J = 6.8 Hz, 3H), 3.48 (br s, 2H), 3.59 (br s, 2H), 6.27 (d, J = 15.1 Hz, 1H), 6.83 (dq, J = 6.8 and 15.1 Hz, 1H); ^{13}C{^{1}H} NMR (68 MHz) δ 18.2, 24.6, 25.5, 26.6, 43.0, 46.8, 122.0, 140.7, 165.5 (C=O); MS m/z 133 (M^+).

Mixture of 8d, 8d', and 9d. Yellow oil: bp 100–110 °C (0.5 mmHg, Kugelrohr). Anal. Calcd for $C_{10}H_{17}NO$: C, 71.82; H, 10.24; N, 8.38. Found: C, 71.40; H, 10.17; N, 8.05.

1-Piperidino-3-penten-1-one (8d): ^{1}H NMR (270 MHz) δ 1.54–1.56 (m, 4H), 1.61–1.67 (m, 2H), 1.70 (d, J = 3.4 Hz, 3H), 3.07 (d, J = 3.9 Hz, 2H), 3.39 (t, J = 5.4 Hz, 2H), 3.54 (t, J = 5.3 Hz, 2H), 5.51–5.64 (m, 2H); ^{13}C{^{1}H} NMR (68 MHz) δ 17.6, 24.3, 25.2, 26.3, 40.2, 42.4, 46.5, 123.8, 127.8, 169.4 (C=O); MS m/z 147 (M^+).

1-Piperidino-2-penten-1-one (8d'). ^{1}H NMR (270 MHz) δ 1.07 (t, J = 7.3 Hz, 3H), 1.54–1.56 (m, 4H), 1.61–1.67 (m, 2H), 2.17–2.25 (m, 2H), 3.39 (t, J = 5.4 Hz, 2H), 3.54 (t, J = 5.3 Hz, 2H), 6.25 (d, J = 15.2 Hz, 1H), 6.86 (dt, J = 6.6 and 15.2 Hz, 1H); ^{13}C{^{1}H} NMR (68 MHz) δ 12.3, 24.3, 25.2, 26.1, 26.3, 42.7, 46.2, 119.2, 146.7, 169.4 (C=O); MS m/z 147 (M^+).

1-Methyl-1-piperidino-3-buten-1-one (9d): ^{1}H NMR (270 MHz) δ 1.24 (d, J = 6.8 Hz, 3H), 1.54–1.56 (m, 4H), 1.61–1.67 (m, 2H), 3.38–3.42 (m, 1H), 3.39 (t, J = 5.4 Hz, 2H), 3.54 (t, J = 5.3 Hz, 2H), 5.04–5.10 (m, 2H), 5.77–5.96 (m, 1H); ^{13}C{^{1}H} NMR (68 MHz) δ 17.5, 24.3, 25.2, 26.3, 32.2, 42.6, 46.2, 114.7, 124.3, 169.4 (C=O); MS m/z 147 (M^+).

Mixture of 8f, 8f', and 9f. Yellow oil: bp 130–140 °C (0.5 mmHg, Kugelrohr). Anal. Calcd for $C_{12}H_{21}NO$: C, 73.80; H, 10.83; N, 7.17. Found: C, 73.68; H, 10.88; N, 7.10.

1-Piperidino-3-hepten-1-one (8f): ^{1}H NMR (270 MHz) δ 0.89 (t, J = 7.3 Hz, 3H), 1.32–1.46 (m, 2H), 1.54 (br s, 4H), 1.60–1.64 (m, 2H), 1.98–2.02 (m, 2H), 3.08 (d, J = 3.0 Hz, 2H), 3.40 (t, J = 4.9 Hz, 2H), 3.54 (t, J = 4.9 Hz, 2H), 5.52–5.55 (m, 2H); ^{13}C{^{1}H} NMR (68 MHz) δ 13.3, 22.1, 24.2, 25.2, 26.2, 34.3, 37.6, 42.3, 46.6, 122.8, 133.2, 169.4 (C=O); MS m/z 185 (M^+).

1-Piperidino-2-hepten-1-one (8f'): ^{1}H NMR (270 MHz) δ 0.91 (t, J = 6.8 Hz, 3H), 1.32–1.46 (m, 2H), 1.54 (br s, 4H), 1.60–1.64 (m, 4H), 2.17–2.24 (m, 2H), 3.40 (t, J = 4.9 Hz, 2H), 3.54 (t, J = 4.9 Hz, 2H), 6.25 (d, J = 15.1 Hz, 1H), 6.83 (dt, J = 6.8 and 15.1 Hz, 1H); ^{13}C{^{1}H} NMR (68 MHz) δ 13.5, 21.9, 24.2, 24.3, 25.4, 26.2, 31.9, 42.4, 46.1, 120.0, 145.5, 165.2 (C=O); MS m/z 185 (M^+).

1-Piperidino-1-propyl-3-buten-1-one (9f): ^{1}H NMR (270 MHz) δ 0.90 (m, 3H), 1.32–1.46 (m, 2H), 1.54 (br s, 4H), 1.60–1.64 (m, 4H), 3.39–3.54 (m, 1H), 3.40 (t, J = 4.9 Hz, 2H), 3.54 (t, J = 4.9 Hz, 2H), 5.05–5.08 (m, 2H), 5.81–5.93 (m, 1H); ^{13}C{^{1}H} NMR (68 MHz) δ 13.5, 20.1, 22.1, 25.2, 26.2, 26.3, 32.6, 42.6, 46.3, 115.5, 122.2, 169.4 (C=O); MS m/z 185 (M^+).

4,8-Dimethyl-1-piperidino-3,7-nonadien-1-one (8g). Yellow oil: bp 160–165 °C (0.4 mmHg, Kugelrohr); IR (neat) 1653 (C=O) cm^{-1}; ^{1}H NMR (270 MHz) δ 1.45 (br s, 6H), 1.54 (s, 3H), 1.60 (s, 3H), 1.67 (s, 3H), 1.99 (br s, 4H), 3.00 (d, J = 7.0 Hz, 2H), 3.30 (t, J = 5.2 Hz, 2H), 3.46 (t, J = 5.2 Hz, 2H), 5.02 (br s, 1H), 5.24 (t, J = 7.0 Hz, 1H); ^{13}C{^{1}H} NMR (68 MHz) δ 17.7, 23.4, 24.6, 25.6, 25.7, 26.3, 26.6, 32.3, 33.4, 42.8, 46.9, 118.0, 124.1, 131.8, 137.9, 170.2 (C=O); MS m/z 249 (M^+). Anal. Calcd for $C_{16}H_{27}NO$: C, 77.06; H, 10.91; N, 5.62. Found: C, 77.35; H, 10.91; N, 5.55.

Dimethyl 3-benzyl-2-(*trans*-2-phenylvinyl)glutarate (2). In a 50 mL stainless autoclave were placed $Ru_3(CO)_{12}$ (0.017 g, 0.027 mmol), cinnamyl methyl carbonate (0.480 g, 2.5 mmol), and *N*-methylpiperidine (0.5 mL). After CO was introduced at 40 atm at 25 °C, the mixture was magnetically stirred at 150 °C for 10 h. Kugelrohr distillation of the reaction mixture gave dimethyl 3-benzyl-2-(*trans*-2-phenylvinyl)glutarate **(2)** (1:1 mixture of diastereomers, 0.25 g, 56%) as a colorless oil: bp 180–190 °C (0.5 mmHg); ^{1}H NMR (270 MHz) δ 2.28–2.86 (m, 10H), 3.26 (dd, J = 7.3 and 9.2 Hz, 1H), 3.40 (d, J = 7.3 and 9.2 Hz, 1H), 3.50 (s, 3H), 3.60 (s, 3H), 3.71 (s, 3H), 3.74 (s, 3H), 6.19 (dd, J = 9.2 and 15.9 Hz, 1H), 6.26 (dd, J = 9.2 and 15.9 Hz, 1H), 6.47 (d, J = 15.9 Hz, 2H), 7.17–7.37 (m, 20H); ^{13}C{^{1}H} NMR (68 MHz) δ 34.3, 36.4, 37.5, 38.3, 38.9, 50.4, 50.5, 50.9, 52.0, 123.8, 124.0, 125.3, 125.4, 126.8, 127.3, 127.4, 127.5, 127.6, 128.2, 128.3, 128.4, 133.3, 133.4, 135.4, 135.5, 138.0, 138.3, 171.9 (C=O), 172.4 (C=O), 172.6 (C=O); MS m/z 352 (M^+). Anal. Calcd for $C_{22}H_{24}O_4$: C, 74.98; H, 6.86. Found: C, 75.24; H, 6.80.