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Palladium-Catalyzed Carbonylation of Allylamines. Synthesis of β,γ-Unsaturated Amides by One-Carbon Homologation of Allylamines

Shun-Ichi Murahashi,* Yasushi Imada, and Koichi Nishimura

Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama, Toyonaka, Osaka 560, Japan

Abstract: Palladium-catalyzed carbonylation of allylamines under CO (50 atm) at 110 °C proceeds highly efficiently to give the corresponding β,γ-unsaturated amides. The carbonylation occurs at the less substituted carbon of allyl units to give linear amides with high regioselectivity. The reaction can be rationalized by assuming the mechanism which involves oxidative addition of palladium(0) species to allylamines to give π-allylpalladium complexes, insertion of carbon monoxide to give acylpalladium species, and amidation.

INTRODUCTION

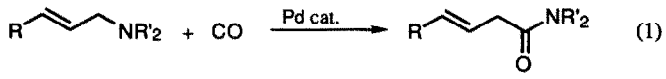
Carbonylation of allylic compounds is a useful process, because introduction of CO into allylic skeletons gives β,γ-unsaturated carbonyl compounds, which are useful precursors for synthesis of natural products[1] and antibiotics.[2] Allylic halides undergo carbonylation with ease by using of nickel,[3] cobalt,[4] and palladium[5,6] complex catalysts. Carbonylations of allylic alcohol derivatives, such as allyl acetates and allyl alkyl ethers, are synthetically more important; however, these require relatively severe reaction conditions.[7,8] Recently, palladium-catalyzed alkoxycarbonylations of allyl phosphates[9] and allyl carbonates[10] were found to proceed under mild reaction conditions. Furthermore, we found that allyl acetates undergo alkoxycarbonylation to give β,γ-unsaturated esters in the presence of bromide ion as co-catalyst under mild reaction conditions.[9] Therefore, we are in a position to be able to achieve alkoxycarbonylation of allylic compounds with oxygen nucleophiles such as alcohols to give β, γ-unsaturated esters.

Azacarbonylation of allylic compounds is quite difficult, because amination of allylic compounds occurs predominantly to give allylamines. The azacarbonylations reported are limited to few reactions. We demonstrated recently that the $Rh_6(CO)_{16}$-catalyzed azacarbonylation of allyl phosphates proceeds under mild reaction conditions.[11] The palladium-catalyzed reaction of ethyl 1-hepten-3-yl carbonate with diethylamine[10a] and the palladium-catalyzed decarboxylation–carbonylations of allyl *N,N*-dialkylcarbamates have been reported.[12]

An alternative method for synthesis of β,γ-unsaturated amides is direct insertion of carbon monoxide into carbon—nitrogen bond of allylamines. Since allylamines are readily available substrates,[13,14] this method seems to be an attractive process for synthesis of β,γ-unsaturated amides. However, incorporation of carbon

monoxide into carbon—nitrogen bond of amine compounds is quite difficult. The reactions reported are limited to the ring-expansion carbonylation reactions of a series of three- or four-membered cyclic amines. The $[Rh(CO)_2Cl]_2$-catalyzed carbonylation of 2-arylaziridines gives β-lactams.[15a] Aziridinones and diaziridines can be carbonylated in the presence of $[Rh(CO)_2Cl]_2$ or $Pd(dba)_2$ catalyst to give azetidin-2,4-diones[15b] and aza-β-lactams,[15c] respectively. Four-membered-ring azetidines are also carbonylated to give pyrrolidines by using $Co_2(CO)_8$ catalyst.[15d] There is no example, to our knowledge, of the direct insertion of carbon monoxide into acyclic amine compounds.

We have found that palladium–phosphine complex catalyzes the carbonylation of allylamines to give the corresponding β,γ-unsaturated amides as depicted in eq 1.[16] The reaction provides a convenient method for the synthesis of β,γ-unsaturated amides,[17] which are useful precursors for various compounds such as homoallylamines. Furthermore, the present reaction is the first demonstration of the insertion of carbon monoxide into carbon—nitrogen bond in acyclic systems. In this paper, full details of the palladium-catalyzed carbonylation of allylamines are described with respects to scope, limitation, and mechanism.[16]

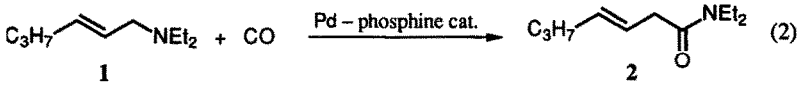


(1)

RESULTS AND DISCUSSION

Carbonylation of Allylamines

The catalytic activity of palladium–phosphine complexes has been examined for the carbonylation of *N,N*-diethyl-2-hexenylamine (**1**) to give *N,N*-diethyl-3-heptenamide (**2**). The reaction was carried out in the presence of 5 mol% of palladium complex and 5 mol% of phosphine ligand under 30 atm of CO at 110 °C (eq 2). As shown in Table 1, the most effective catalyst was found to be a combination of $Pd(OAc)_2$ and dppp



1 2 (2)

(1,3-bis(diphenylphosphino)propane) (entry 8). The carbonylation is strongly affected by the phosphine ligands used. Monodentate phosphines such as PPh_3, PBu_3, PPh_2Et, and $P(o\text{-}Tol)_3$ showed almost no activity (entries 2–5). Dppp was the best ligand, and other bidentate phosphines such as dppm (bis(diphenylphosphino)methane), dppe (1,2-bis(diphenylphosphino)ethane), and dppb (1,4-bis(diphenylphosphino)butane) are not so effective. $Pd(OAc)_2$ showed high catalytic activity, and other palladium complexes such as $PdCl_2(PPh_3)_2$, $PdCl_2(CH_3CN)_2$, $Pd(acac)_2$, and $Pd(dba)_2$ gave low conversions of **1** and poor yields of **2** even in the presence of dppp (entries 10–13). A small amount of hexadiene, which is derived from deamination,[18] was detected among the products.

Toluene is the best solvent among the solvents examined such as THF and acetonitrile. The carbonylation of **1** in ethanol gave the corresponding β,γ-unsaturated esters. The carbonylation of **1** proceeds smoothly at 110 °C, and that at 80 °C resulted in low conversion of **1**. The reaction at 140 °C gave **2** in relatively low yield, because deamination of **1** occurred mainly at higher temperature.[18] The carbonylation

proceeds selectively under the CO pressure of 50 atm, but that under the pressure below 20 atm gives **2** in low yield. High pressure of CO depressed the deamination of **1** and resulted in giving the product **2** with high selectivity. Thus, the carbonylation of (*E*)-**1** in toluene in the presence of 5 mol% of $Pd(OAc)_2$ and 10 mol% of dppp under CO (50 atm) at 110 °C for 20 h gave **2** in 83% isolated yield. The *E*:*Z* ratio of **2** thus obtained was determined to be 80:20 on the basis of GLC and ^1H NMR analyses.

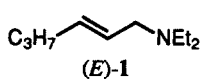
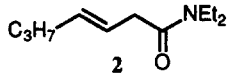
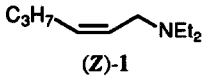
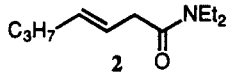
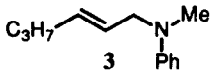
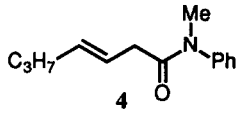
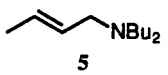
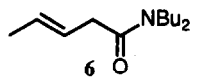
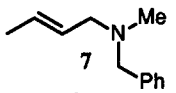
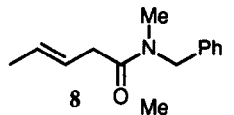
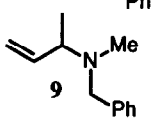
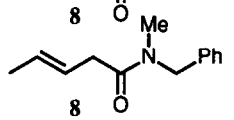
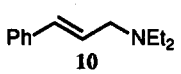
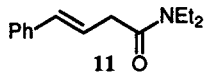
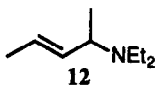
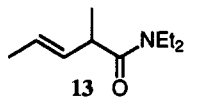
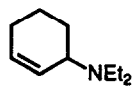
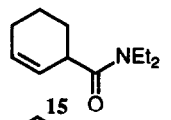
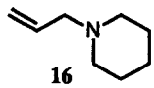
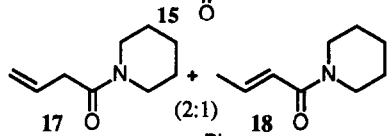
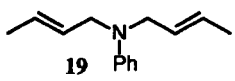
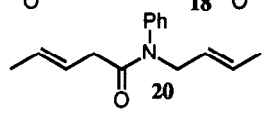
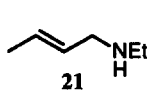
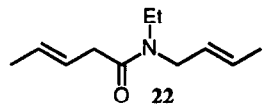
Table 1. Catalytic Activity of Palladium–Phosphine Complexes for Carbonylation of **1**[a]

entry	catalyst	phosphine	convn of **1**, %[b]	yield of **2**, %[b,c]
1	$Pd(OAc)_2$	none	2	-
2	$Pd(OAc)_2$	PPh_3	22	0
3	$Pd(OAc)_2$	PBu_3	1	-
4	$Pd(OAc)_2$	PPh_2Et	19	26
5	$Pd(OAc)_2$	P(*o*-Tol)$_3$	14	0
6	$Pd(OAc)_2$	dppm	35	11
7	$Pd(OAc)_2$	dppe	17	41
8	$Pd(OAc)_2$	dppp	99	78
9	$Pd(OAc)_2$	dppb	61	61
10	$PdCl_2(PPh_3)_2$	dppp	21	29
11	$PdCl_2(CH_3CN)_2$	dppp	19	16
12	$Pd(acac)_2$	dppp	11	0
13	$Pd(dba)_2$	dppp	37	41

[a]Carbonylation of allylamine **1** (1 mmol) was performed by using catalyst (5 mol%), phosphine (5 mol% for bisphosphines, 10 mol% for others) in toluene under the pressure of CO (30 atm) at 110 °C for 20 h. [b]Determined by GLC analysis. [c]Based on consumed **1**.

Generally, the palladium-catalyzed carbonylation of allylamines gives the corresponding β,γ-unsaturated amides in good yields as shown in Table 2. Insertion of CO takes place with high regioselectivity at the less substituted terminal carbon of allyl units to give linear amides rather than branched isomers. Thus, the carbonylations of *N*-benzyl-*N*-methyl-2-buten-1-ylamine (**7**) (entry 5) and *N*-benzyl-*N*-methyl-1-buten-3-ylamine (**9**) (entry 6) gave *N*-benzyl-*N*-methyl-3-pentenamide (**8**) exclusively. (*E*)-β,γ-unsaturated amides have been obtained preferentially irrespective of the stereochemistry of the starting allylamines. The carbonylations of (*E*)- and (*Z*)-**1** (entries 1 and 2) gave **2** with the same *E*:*Z* ratio (*ca.* 8:2). *N*,*N*-Diethylcinnamylamine (**10**) was carbonylated stereoselectively to give (*E*)-*N*,*N*-diethyl-4-phenyl-3-butenamide ((*E*)-**11**) (entry 7). Usually, carbonylations at the secondary allylic carbon is very difficult because of steric effect. However, the carbonylations of *N*,*N*-diethyl-3-penten-2-ylamine (**12**) and *N*,*N*-diethyl-2-cyclohexylamine (**14**) were performed at higher temperature (130 °C) to give the corresponding amides **13** and **15** in 30% and 35% yield, respectively . The reaction of *N*-2-propen-1-ylpiperidine (**16**) gave β,γ-unsaturated amide **17** and α,β-unsaturated isomer **18**, which is derived from isomerization of **17**,[19] in 90% yield in the ratio of **17**:**18** = 2:1 (entry 10). When diallylamine was allowed to carbonylate, insertion of CO took place at one of the allyl

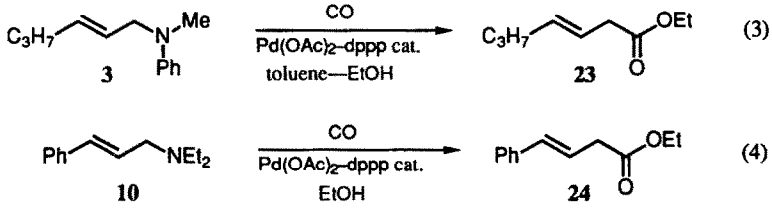
Table 2. Palladium-Catalyzed Carbonylation of Allylamines[a]

entry	allylamine	β,γ-unsaturated amide	yield, %[b]	*E*:*Z* ratio[c]
1	 (*E*)-**1**	 **2**	83	80:20
2	 (*Z*)-**1**	 **2**	57d	78:22
3	 **3**	 **4**	76	78:22
4	 **5**	 **6**	77	73:27
5	 **7**	 **8**	85	75:25
6	 **9**	 **8**	89	70:30
7	 **10**	 **11**	70	100:0
8	 **12**	 **13**	30[e]	83:17
9	 **14**	 **15**	35[e]	–
10	 **16**	 **17** (2:1) **18**	90	–
11	 **19**	 **20**	77	–
12	 **21**	 **22**	29	–

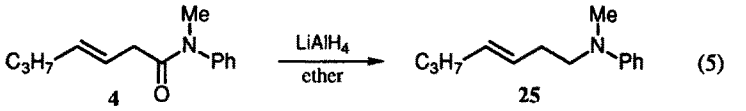
[a]Carbonylation of allylamines was performed by using $Pd(OAc)_2$ (5 mol%) and dppp (10 mol%) in toluene under CO (50 atm) at 110 °C for 20 h. [b]Isolated yield. [c]Determined by ^1H NMR and/or GLC. [d]for 40 h. [e]at 130 °C.

groups. Typically, *N,N*-bis(2-buten-1-yl)aniline (**19**) was converted to *N*-2-buten-1-yl-*N*-phenyl-3-butenamide (**20**) in 77% yield (entry 11). When *N*-ethyl-2-buten-1-ylamine (**21**) was treated under the standard conditions, *N*-ethyl-*N*-2-buten-1-yl-3-pentenamide (**22**) was obtained in 29% yield (entry 12). Amide **22** is formed by palladium-catalyzed amine exchange reaction[20] followed by carbonylation of *N*-ethylbis(2-buten-1-yl)amine.

It is noteworthy that carbonylation of allylamines in the presence of an alcohol gives the corresponding β,γ-unsaturated acid esters. For example, carbonylation of *N*-phenyl-*N*-methyl-2-hexen-1-ylamine (**3**) under the same reaction conditions in the presence of 2 equiv. of ethanol gave a mixture of amide **4** and ethyl 3-heptenoate (**23**) in the ratio of **4**:**23** = 3:1. The oxacarbonylation proceeds efficiently by using excess of alcohols. When **3** was carbonylated in a mixture of toluene and ethanol (1:1), the ester **23** was obtained in 63% yield (eq 3). Furthermore, the carbonylation of *N,N*-diethylcinnamylamine (**10**) in ethanol gave ethyl (*E*)-3-phenyl-2-butenoate (**24**) selectively in 71% yield (eq 4).



The β,γ-unsaturated amides thus obtained are readily converted into the corresponding homoallylamines upon treatment with $LiAlH_4$.[21] Typically, the reduction of β,γ-unsaturated amide **4** with $LiAlH_4$ in ether gave *N*-methyl-*N*-phenyl-3-hepten-1-ylamine (**25**) in 85% yield (eq 5). Since the starting allylamines can be readily prepared by the palladium-catalyzed amination of allyl esters,[13] the present reaction provides a convenient method for the preparation of homoallylic amines, which are synthetically important building blocks.[22]



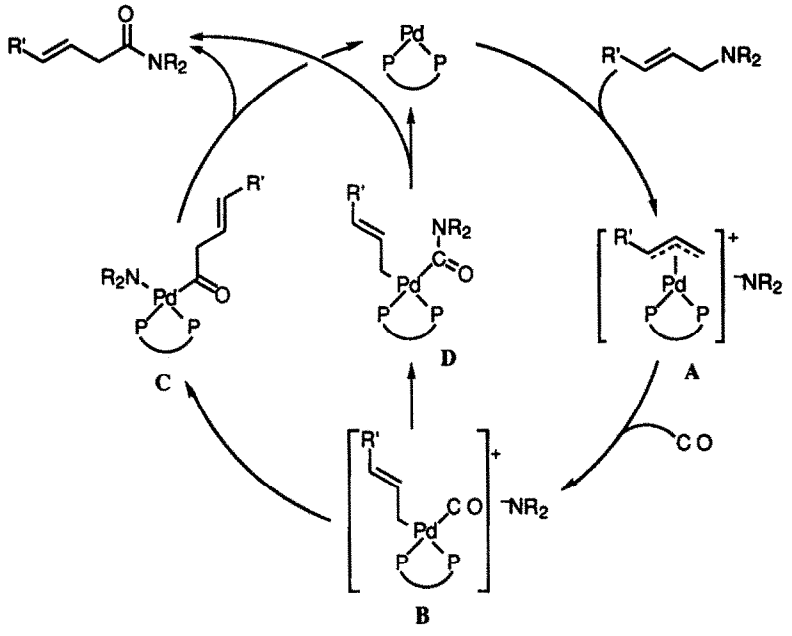
Mechanistic Aspects

Exclusive formation of *N*-benzyl-*N*-methyl-3-pentenamide (**8**) from the reactions of *N*-benzyl-*N*-methyl-2-buten-1-ylamine (**7**) and *N*-benzyl-*N*-methyl-1-buten-3-ylamine (**9**) indicates the intermediacy of π-allyl complexes. The present reaction can be rationalized by assuming the mechanism as depicted by Scheme I. Oxidative addition of allylamine to palladium species gives cationic π-allylpalladium complex **A**. Subsequent insertion of carbon monoxide gives acylpalladium complex **C**[23] through σ-allylpalladium intermediate **B**. Reductive elimination of complex **C** gives the corresponding β,γ-unsaturated amide and palladium-phosphine species to complete the catalytic cycle. An alternative pathway which involves the formation of (carbamoyl)(σ-allyl)palladium complex **D**, derived from direct nucleophilic attack of amide to the co-ordinated CO of **B**, and reductive coupling of **D** cannot be excluded.

Although allylammonium salts undergo oxidative addition to palladium(0) species to form π-allylpalladium complexes readily, the oxidative addition to allylamines is difficult.[24] Palladium-catalyzed alkylation[25] and deamination[18a] of allylamines occur via quaternary allylammonium salts under mild reaction

conditions. Furthermore, allylamines undergo deamination in the presence of acetic acid under mild reaction conditions.[18a] We demonstrated that palladium-catalyzed rearrangement of *N*-allylenamines proceeds readily to give δ,ε-unsaturated imines.[26] In this reaction, addition of a catalytic amount of trifluoroacetic acid accelerates the reaction dramatically. These results show that formation of ammonium salts accelerates the insertion of palladium into carbon—nitrogen bond to give π-allylpalladium complexes.[27] However, the addition of a catalytic amount of an acid such as trifluoroacetic acid (5 mol%) to the carbonylation of allylamine **1** resulted in low conversion of **1** (70%) and low yield of **2** (58%).

Scheme I



The double bond integrity of the products was determined with the carbonylations of (*E*)- and (*Z*)-allylamines **1** precisely. As shown in Table 3, allylamines (*E*)- and (*Z*)-**1** were treated under the optimized conditions, and the stereoisomeric ratios of allylamine **1** and amide **2** were determined based on GLC analyses. Although allylamines (*E*)- and (*Z*)-**1** were converted to the amide **2** with the same stereoisomeric ratio (*ca.* 8:2), their reactivities were quite different. That is, the conversions of (*E*)-**1** after 5 h was 73%, while that of (*Z*)-**1** was 16%. Isomerization of the starting amines, (*E*)- and (*Z*)-**1**; however, could not be detected during the reactions. The *E*:*Z* ratio of 84:16 obtained for the reaction of **1** (entry 2) is not due to the isomerization of the double bond but due to the selective consumption of more reactive (*E*)-isomer. Oxidative addition of allylamines (*E*)- and (*Z*)-**1** to palladium(0) species gives *syn*- and *anti*-π-allylpalladium complexes (**A**), respectively, as shown in Scheme II. Loss of the stereochemistry seems to occur by the π–σ–π-isomerization between *syn*- and *anti*-π-allylpalladium complexes **A**.[28] Thermodynamically stable (*E*)-isomers are obtained preferentially, irrespective of the stereochemistry of the starting allylamines. Quite different reactivity between (*E*)- and (*Z*)-**1** can be rationalized by assuming the mechanism shown in Scheme II. Of two geometrical

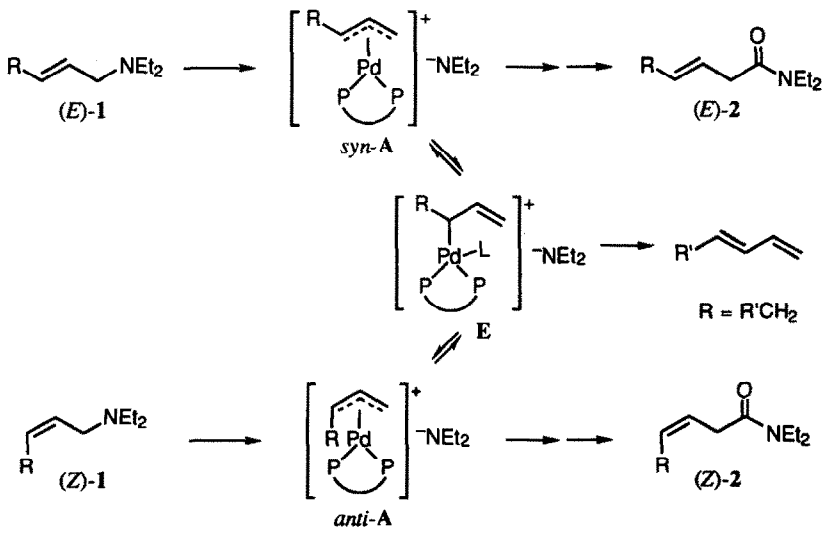
Table 3. Carbonylation of Allylamines (*E*)- and (*Z*)-1[a]

entry	allylamine	time, h	convn of 1, %[b] (*E*:*Z*)[b,c]	yield of 2, %[b] (*E*:*Z*)[b]
1	(*E*)-1	1	16 (96:4)	81 (75:25)
2	(*E*)-1	5	73 (84:16)	76 (77:23)
3	(*E*)-1	20	100 (—)	83 (80:20)
4	(*Z*)-1	5	16 (3:97)	50 (74:26)
5	(*Z*)-1	15	43 (4:96)	60 (76:24)
6	(*Z*)-1	40	100 (—)	57 (78:22)

[a]Carbonylation of allylamine 1 (1 mmol) was performed by $Pd(OAc)_2$ (5 mol%), dppp (10 mol%) in toluene under the pressure of CO (50 atm) at 110 °C. [b]Determined by GLC analysis. [c]Stereoisomeric ratio of recovered 1.

isomeric complexes A, the *anti*-A is unfavorable because of the steric effect of anti alkyl group. It is noteworthy that isomerization of carbon—carbon double bonds of allylamines did not occur under the present reaction conditions. Since π–σ–π-isomerization of A occurs faster than CO insertion, scrambling of the stereochemistry of the starting allylamine should be observed, if the oxidative addition to form A is reversible. These results show that the initial step (oxidative addition) is irreversible under the present reaction conditions. Small amount of deamination products, that is dienes, were detected among the products. These products is formed from β-hydride elimination of σ-allylpalladium complex E.[29] When 1,3-hexadiene was subjected to the present carbonylation reaction conditions, amide 2 was not formed. Therefore, dienes are not intermediates in the present carbonylation.

Scheme II



Recently, K. Yamamoto reported the palladium-catalyzed carbonylation of allyl carbamates.[12] Carbonylation of allyl carbamates in the presence of $Pd_2(dba)_3$•$CHCl_3$ and PPh_3 catalyst under CO (80 atm) at 100 °C for 60–70 h gave β,γ-unsaturated amides in 50–70% yield. The reaction is rationalized by assuming oxidative addition of palladium(0) species to allyl carbamates, decarboxylation to give π-allylpalladium intermediate,[30,31] insertion of CO, and amidation. This is closely related to the mechanism shown in Scheme I.

EXPERIMENTAL SECTION

General. IR spectra were recorded on a Hitachi 215 and Shimadzu FTIR-4100 spectrometers; data are given in cm^{-1}, only important diagnostic bands being reported. NMR spectra were obtained on JEOL JNM-PMX-60-SI (^1H at 60 MHz), JEOL JNM-FX-100 (^1H at 100 MHz, ^{13}C at 25 MHz), and JEOL JNM-GSX-270 (^1H at 270 MHz, ^{13}C at 68 MHz) spectrometers in $CDCl_3$. Analytical GLC evaluations of the product mixtures were carried out on Shimadzu GC-9A flame ionization gas chromatography by using a 1-m x 4-mm column (10% SE-30 on 80-120 mesh Uniport HP) and Shimadzu GC-mini 2 by using a 25-m x 0-25 mm chemical bonded glass capillary column (OV-1 or PEG 20M). Mass spectra were obtained with a JEOL JMS-DX303 mass spectrometer. Elemental analyses were performed on a Yanagimoto MT-3 CHN instrument.

Materials. $Pd(OAc)_2$ was prepared according to the reported method.[32] 1,3-Bis(diphenylphosphino)-propane (dppp) was purchased from Aldrich Chemical Company Inc. (*Z*)-2-Hexenylamine ((*Z*)-**1**) was prepared according to the reported procedure,[33] and other allylamines were prepared by palladium(0)-catalyzed amination of allylic acetates or allylic phosphates.[13]

(E)-N,N-diethyl-2-hexenylamine ((E)-1). (*E*/*Z* = 97:3): IR (neat) 1460 (NC–H), 970 (CH=CH) cm^{-1}; ^1H NMR (60 MHz) δ 1.00 (t, *J* = 7 Hz, 6 H), 0.60–1.77 (m, 5 H), 1.80–2.23 (m, 2 H), 2.50 (q, *J* = 7 Hz, 4 H), 3.03 (d, *J* = 5 Hz, 2 H), 5.13–5.87 (m, 2 H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 11.5 (CH_3), 13.4 (C-6), 34.4 (C-5), 46.3 (NCH_2), 55.1 (C-4), 127.0, 133.4. Anal. Calcd for $C_{10}H_{21}N$: C, 77.35; H, 13.62; N, 9.02. Found: C, 77.07; H, 13.72; N, 8.88.

(Z)-N,N-Diethyl-2-hexenylamine ((Z)-1). (*E*/*Z* = 0:100): IR (neat) 1660 (C=C), 1460 CH-N) cm^{-1}; ^1H NMR (270 MHz) δ 0.91 (t, *J* = 7.3 Hz, 3 H), 1.04 (t, *J* = 7.1 Hz, 6 H), 1.39 (tq, *J* = 7.3 and 7.3 Hz, 2 H), 2.05 (ddt, *J* = 1.5, 5.5, and 7.3 Hz, 2 H), 2.52 (q, *J* = 7.1 Hz, 4 H), 3.11 (dd, *J* = 1.5 and 6.0 Hz, 2 H), 5.48 (dtt, *J* = 11.0, 1.5, and 5.5 Hz, 1 H), 5.52 (dtt, *J* = 11.0, 1.5, and 6.0 Hz, 1 H); $^{13}C\{^1H\}$ NMR (68 MHz) δ 11.7 (CH_3), 13.6 (C-6), 22.7 (C-5), 29.4 (C-4), 46.6 (NCH_2), 49.5 (C-1), 127.0 (C-2), 132.0 (C-3).

Palladium-Catalyzed Carbonylation of* N,N-*Diethyl-2-hexenylamine (1). (A) Catalytic Activity of Palladium Complexes. In a 10-mL stainless-steal autoclave were placed palladium complex (0.05 mmol), phosphine (0.05 mmol for bidentate phosphines, 0.10 mmol for others), allylamine **1** (1.0 mmol), and dry toluene (2.0 mL). Then CO was introduced up to 30 atm, and the mixture was stirred at 110 °C for 20 h. The conversion of allylamine **1** and the yield of *N,N*-diethyl-3-heptenamide (**2**) based on consumed **1** were determined by GLC analysis using dodecane as an internal standard. These results are listed in Table 1 and the spectral data of **2** are shown below. ***(B) Influence of CO Pressure.*** A solution of $Pd(OAc)_2$ (0.05 mmol), **1** (1.0 mmol), and dppp (0.05 mmol) in toluene (2 mL) was stirred under CO at 110 °C for 20 h. The conversion of **1** and the yield of **2** based on consumed **1** are as follows: P_{CO} 10 (87%, 41%), 20 (94%, 64%), 30 (99%, 78%), 50 (99%, 90%) atm. ***(C) Temperature Dependency.*** A solution of $Pd(OAc)_2$ (0.05 mmol), **1** (1.0

mmol), and dppp (0.05 mmol) in toluene (2 mL) was stirred under CO (30 atm) at constant temperature for 20 h. The conversion of **1** and the yield of **2** based on consumed **1** are as follows: *T* 50 (10%, 0%), 80 (31%, 32%), 110 (99%, 78%), 140 (99%, 64%) °C. ***(D) Influence of Solvent.*** A solution of $Pd(OAc)_2$ (0.05 mmol), **1** (1.0 mmol), and dppp (0.10 mmol) in solvent (2 mL) was stirred under CO (50 atm) at 110 °C for 5 h. The conversion of **1** and the yield of **2** based on consumed **1** are as follows: Solvent toluene (91%, 84%), CH_3CN (53%, 28%), THF (11%, 45%), ethanol (86%, 0%), none (47%, 19%). When ethanol was used as a solvent, ethyl 3-heptenoate was obtained in 53% yield, and the reaction in the presence of CF_3CO_2H (0.05 mmol) afforded **2** in 58% yield (70% converion).

General Procedure for the Carbonylation of Allylamines. In a 10-mL stainless-steel autoclave were placed $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), allylamine (1.0 mmol), dppp (41.2 mg, 0.10 mmol), and dry toluene (2 mL). Then CO was introduced up to 50 atm, and the mixture was stirred at 110 °C for 20 h. After cooling to room temperature, the reaction mixture was diluted with ether (10 mL) and washed with 2 M HCl (10 mL x 3), saturated aqueous $NaHCO_3$ (10 mL), and brine (10 mL). The organic layer was dried ($MgSO_4$) and the filtrate was evaporated. The residue was purified by using silica gel column chromatography or preparative TLC to give β,γ-unsaturated amide. The stereoisomeric ratio of *E*:*Z* was determined on the basis of ^1H and ^{13}C NMR and/or capillary GLC analyses. These results for the carbonylation of various allylamines are listed in Table 2.

N,N-*Diethyl-3-heptenamide (2)*: IR (neat) 1640 (C=O), 970 (CH=CH) cm^{-1}; ^1H NMR (270 MHz) δ 0.89 (t, *J* = 7.3 Hz, 3 H, H-7), 1.11 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.18 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.25–1.48 (m, 2 H, H-6), 2.02 (dt, *J* = 5.2, 6.8 Hz, 2 H, H-5), 3.06 (d, *J* = 5.1 Hz, 2 H, H-2), 3.32 (q, *J* = 7.1 Hz, 2 H, NCH_2), 3.37 (q, *J* = 7.1 Hz, 2 H, NCH_2), 5.50 (dt, *J* = 15.3, 5.2 Hz, 1 H, H-4), 5.59 (dt, *J* = 15.3, 5.2 Hz, 1 H, H-3) for (*E*)-**2**; 3.10 (d, *J* = 4.9 Hz, 2 H, H-2) for (*Z*)-**2**; $^{13}C\{^1H\}$ NMR (68 MHz) δ 13.0 (CH_3), 13.6 (C-7), 14.4 (CH_3), 22.4 (C-6), 34.7 (C-5), 37.7 (C-2), 40.1 (NCH_2), 42.2 (NCH_2), 123.5 (C-3), 133.5 (C-4), 170.9 (C=O) for (*E*)-**2**; 29.7 (C-5), 32.6 (C-2), 122.8 (C-3), 132.2 (C-4) for (*Z*)-**2**; Mass spectrum, *m/e* (relative intensity) 183 (M^+, 28), 168 (13), 154 (25), 111 (13), 83 (M^+–C(O)NEt_2, 100). Anal. Calcd for $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64. Found: C, 71.98; H, 11.60; N, 7.62.

N-*Methyl*-N-*phenyl-3-heptenamide (4)*: IR (neat) 1660 (C=O), 1600 (C=C), 970 (CH=CH) cm^{-1}; ^1H NMR (60 MHz) δ 0.85 (t, *J* = 6.0 Hz, 3 H, H-7), 1.03–1.73 (m, 2 H, H-6), 1.73-2.33 (m, 2 H, H-5), 2.83 (d, *J* = 5.0 Hz, 2 H, H-2), 3.27 (s, 3 H, NCH_3), 5.20 (dt, *J* = 15.0 and 5.0 Hz, 1 H, H-4), 5.53 (dt, *J* = 15.0 and 5.0 Hz, 1 H, H-3), 6.97–7.66 (m, 5 H, Ph); HRMS for $C_{14}H_{19}NO$, Calcd 217.1467, Found 217.1469.

N-*Benzyl*-N-*methyl-3-heptenamide (6)*: IR (neat) 1640 (C=O), 1600 (C=C), 980 (CH=CH) cm^{-1}; ^1H NMR (270 MHz) δ 0.89 (t, *J* = 7.3 Hz, 3 H, H-7), 1.33–1.44 (m, 2 H, H-6), 1.98–2.07 (m, 2 H, H-5), 2.91 (s, 3 H x 0.6, *anti*-NCH_3), 2.92 (s, 3 H x 0.4, *syn*-NCH_3), 3.14 (d, *J* = 5.0 Hz, 2 H, H-2), 4.53 (s, 2 H x 0.4, *anti*-NCH_2Ph), 4.58 (s, 2 H x 0.6, *syn*-NCH_2Ph), 5.53–5.60 (m, 2 H, H-3 and H-4), 7.12–7.38 (m, 5 H, Ph) for (*E*)-**6**; 0.88 (t, *J* = 7.3 Hz, 3 H, H-7), 3.18 (d, *J* = 5.0 Hz, 2 H, H-2) for (*Z*)-**6**; HRMS for $C_{15}H_{21}NO$, Calcd 231.1623, Found 231.1620.

N,N-*Dibutyl-3-pentenamide (8)*: IR (neat) 1640 (C=O), 970 (CH=CH), cm^{-1}; ^1H NMR (270 MHz) δ 0.85 (t, *J* = 7.3 Hz, 3 H, CH_3), 0.88 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.24 (tq, *J* = 7.0 and 7.3 Hz, 4 H), 1.38–1.54 (m, 4 H), 1.62 (d, *J* = 5.0 Hz, 2 H, H-5), 2.97 (d, *J* = 6.0 Hz, 2 H, H-2), 3.10–3.25 (m, 4 H, NCH_2), 5.37–5.60 (m, 2 H, H-3 and H-4) for (*E*)-**8**; 1.58 (d, *J* = 5.0 Hz, 3 H, H-5), 3.03 (d, *J* = 4.5 Hz, 2 H, H-2) for (*Z*)-**8**; HRMS for $C_{13}H_{25}NO$, Calcd 211.1936, Found 211.1943.

***(E)*-N,N-*Diethyl-4-phenyl-3-butenamide (11)*:** IR (neat) 1640 (C=O), 970 (CH=CH) cm^{-1}; ^1H NMR (270 MHz) δ 1.14 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.20 (t, *J* = 7.1 Hz, 3 H, CH_3), 3.28 (d, *J* = 5.4 Hz, 2 H, H-2), 3.35 (q, *J* = 7.1 Hz, 2 H, NCH_2), 3.40 (q, *J* = 7.1 Hz, 2 H, NCH_2), 6.37 (dt, *J* = 16.1 and 5.6 Hz, 1 H, H-3), 6.41 (d, *J* = 16.1 Hz, 1 H, H-4), 7.15–7.38 (m, 5 H, Ph); $^{13}C\{^1H\}$ NMR (68 MHz) δ 13.0 (CH_3), 14.4 (CH_3), 37.8 (NCH_2), 40.2 (C-2), 42.2 (NCH_2), 123.8, 126.2, 127.3, 128.5, 132.4 137.1 (*i*), 170.1 (C=O). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.10; H, 9.00; N, 6.35.

N,N-*Diethyl-2-methyl-3-pentenamide (13)*: IR (neat) 1640 (C=O), 970 (CH=CH) cm^{-1}; ^1H NMR (60 MHz) δ 0.83–1.40 (m, 9 H), 1.66 (d, *J* = 5.0 Hz, 3 H, H-5), 2.96–3.73 (m, 5 H, NCH_2 and H-2), 5.10–5.77 (m, 2 H, H-3 and H-4). HRMS for $C_{10}H_{19}NO$, Calcd 169.1467, Found 169.1443.

N,N-*Diethyl-2-cyclohexene-1-carboxyamide (15)*: IR (neat) 1640 (C=O), 720 (CH=CH) cm^{-1}; ^1H NMR (60 MHz) δ 0.67–1.50 (m, 6 H, CH_3), 1.43-2.50 (m, 6 H), 2.77–3.87 (m, 5 H, NCH_2 and H-1), 5.20–6.20 (m, 2 H, H-2 and H-3).

***Carbonylation of* N-*Allylpiperidine (16)*.** Carbonylation of **16** according to the general procedure afforded a mixture of *N*-3-butenoylpiperidine (**17**) and *N*-2-butenoylpiperidine (**18**) in 90% yield in the ratio of **17**:**18** = 2:1: IR (neat) 1650 (C=O) cm^{-1}; ^1H NMR (60 MHz) δ 1.67–2.20 (m, 6 H), 3.00 (dt, *J* = 6.0 and 1.0 Hz, 2 H, H-2), 3.02–3.67 (m, 4 H, NCH_2), 5.00 (br-d, *J* = 18.0 Hz, 1 H, H-4), 5.03 (br-d, *J* = 9.0 Hz, 1 H, H-4), 5.79 (ddt, *J* = 9.0, 18.0, and 6.0 Hz, 1 H, H-3) for **17**; 1.77 (dd, *J* = 1.0 and 6.0 Hz, 3 H, H-3), 6.18 (br-d, *J* = 13.0 Hz, 1 H, H-2), 6.67 (dq, *J* = 13.0 and 6.0 Hz, 1 H, H-3) for **18**.

N-*Phenyl*-N-*2'-butenyl-3-pentenamide (20)*: IR (neat) 1640 (C=O), 1590 (C=C), 960 (CH=CH) cm^{-1}; ^1H NMR (100 MHz) δ 1.46 (dd, *J* = 2.4 and 6.8 Hz, 3 H, H-5), 1.52 (dd, *J* = 2.4 and 8.4 Hz, 3 H, H-4'), 2.56–3.00 (m, 2 H, H-2), 4.24 (dd, *J* = 2.4 and 8.4 Hz, 2 H, H-1'), 5.04–5.72 (m, 4 H), 6.92–7.48 (m, 5 H, Ph). Anal Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N 6.45. Found: C, 77.26; H, 8.90; N, 6.40.

***Carbonylation of* N-*Ethyl-2-buten-1-ylamine (21)*.** Carbonylation of **21** according to the general procedure afforded *N*-2-butenyl-*N*-ethyl-3-pentenamide (**22**) in 29% yield: IR (neat) 1640 (C=O), 970 (CH=CH) cm^{-1}; ^1H NMR (60 MHz) δ 1.08 (t, *J* = 7 Hz, 3 H x 0.5, *anti*-CH_3), 1.12 (t, *J* = 7 H, 3 H x 0.5, *syn*-CH_3), 1.50–1.85 (m, 6 H, H-5 and H-4'), 2.90–3.16 (m, 2 H, H-2), 3.33 (q, *J* = 7 Hz, 2 H x 0.5, *anti*-NCH_2), 3.40 (q, *J* = 7 Hz, 2 H x 0.5, *syn*-NCH_2), 3.67–4.30 (m, 2 H, H-1'), 5.01–6.00 (m, 4 H). Anal Calcd for $C_{14}H_{19}NO$: C, 70.96; H, 11.31; N 8.27. Found: C, 70.86; H, 8.92; N, 6.40.

***Carbonylation of Allylamines in Ethanol*.** Carbonylation of allylamine **3** (1 mmol) according to the general procedure in toluene—ethanol (1:1) gave ethyl 3-heptenoate (**23**) in 63% isolated yield (*E*:*Z* = 81:19). The reaction of **3** (1 mmol) in the presence of ethanol (2 mmol) gave a mixture of **4** and **23** in the ratio of 3:1: ^1H NMR (270 MHz) δ 0.89 (t, *J* = 7.2 Hz, 3 H, H-7), 1.26 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.39 (tq, *J* = 7.3 and 7.2 Hz, 2 H, H-6), 1.95–2.10 (m, 2 H, H-5), 3.02 (d, *J* = 5.0 Hz, 2 H, H-2), 4.14 (q, *J* = 7.2 Hz, 2 H, OCH_2), 5.44–5.64 (m, 2 H, H-3 and H-4) for (*E*)-**23**; 0.91 (t, *J* = 7.2 Hz, 3 H, H-7), 3.08 (d, *J* = 5.0 Hz, 2 H, H-2) for (*Z*)-**23**.

***(E)-Ethyl 4-phenyl-3-butenoate (24)*.** Carbonylation of **10** (1 mmol) according to the general procedure in ethanol in place of toluene afforded **24** in 71% yield (*E*:Z = 100:0): R_f = 0.20 (SiO_2, CH_2Cl_2—hexane = 3:7); bp 75–80 °C (0.2 mmHg) (Kugelrohr); IR (neat) 1735 (C=O), 1650 (C=C), 1250 (C–O) cm^{-1}; ^1H NMR (270 MHz) δ 1.26 (t, *J* = 7.2 Hz, 3 H), 3.21 (dd, *J* = 1.3 and 7.0 Hz, 2 H, H-2), 4.15 (q, *J* = 7.2 Hz, 2 H), 6.28 (dt, *J* = 16 and 7.0 Hz, 1 H, H-3), 6.48 (dt, *J* = 16 and 1.3 Hz, 1 H, H-4), 7.10–7.40 (m, 5 H, Ph); $^{13}C\{^1H\}$ NMR (25 MHz) δ 14.2, 38.3 (C-2), 60.6, 122.0 (C-4), 126.3, 127.5, 128.5, 133.2, 136.9 (*i*),171.2 (C=O). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.51; H, 7.45.

***Preparation of* N-*Methyl*-N-*3-hepten-1-ylaniline (25)*.** To a suspension of $LiAlH_4$ (0.057 g,1.50 mmol) in dry ether (1 mL), a solution of *N*-phenyl-*N*-methyl-3-heptenamide (**4**) (0.217 g, 1.00 mmol) in ether (1.5 mL) was added dropwise at room temperature. After the mixture was stirred at room temperature for 1 h, water (1 mL) was added The product was extracted with 2 M HCl. The combined acidic layers were neutralized and reextracted with ether. The extracts were washed with brine and dried (Na_2SO_4). The filtrate was evaporated to give homoallylamine **25** (0.172 g, 85%): IR (neat) 1600 (C=C), 970 (CH=CH) cm^{-1}; ^1H NMR (100 MHz) δ 0.88 (t, *J* = 4.0 Hz, 3 H, H-7), 1.12–1.54 (m, 2 H, H-6), 1 .67–2.06 (m, 2 H, H-5), 2.06–2.46 (m, 2 H, H-2), 2.73 (s, 3 H, NCH_3), 3.30 (t, *J* = 4.5 Hz, 2 H, H-1), 5.31 (dt, *J* = 18.3 and 6.8 Hz, 1 H, H-4), 5.48 (dt, *J* = 18,3 and 6.8 Hz, 1 H, H-3), 6.52–6.76 (m, 3 H, Ph), 7.00–7.28 (m, 2 H, Ph). Anal. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.77; H, 10.47; N, 6.85.

***Carbonylation of Allylamines (E)- and (Z)-1*.** A solution of $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), dppp (41.2 mg, 0.10 mmol), allylamine **1** (1.0 mmol) in toluene (2.0 mL) was stirred under CO (50 atm) at 110 °C. The conversion of allylamine **1** and the yield of **2** based on the consumed **1** were determined by GLC analysis using dodecane as an internal standard. Stereoisomeric ratios of **1** and **2** were determined by GLC analysis using capillary column. These results are listed in Table 3.

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