Rhodium-Catalyzed Formal Hydrocarbamoylation toward an α,β-Unsaturated Carbonyl Compound Using Aryl Isocyanate and Hydrosilane

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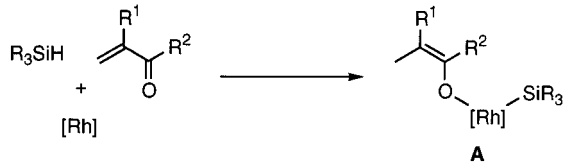
The "hydrocarbamoylation", which introduces a hydrogen and N-substituted carbamoyl group to the olefinic part of an α,β-unsaturated carbonyl compound (**2**), has been accomplished by three-component coupling of an isocyanate (**1**), **2**, and a hydrosilane (**3**) in the presence of the cationic rhodium complex. The regiochemistry of the addition is strictly regulated so that the carbamoyl group links to the α-position of **2**. Many types of aryl isocyanates are suitable for this coupling to form α-carbamoyl esters regardless of the substituent on the phenyl ring, though an alkyl isocyanate shows less reactivity. Isocyanates bearing an electron-withdrawing group are also applicable to this transformation to give α-carbamoyl esters in high yields. This type of three-component coupling can be elucidated by assuming intervention of the rhodium-enolate complex, which becomes a trigger of a nucleophilic attack to an isocyanate.

Introduction

Transition-metal-catalyzed carbon−carbon bond-forming reactions are powerful tools for constructing complicated compounds.[1] Simply mixing the appropriate substrates and a transition metal catalyst can form molecules with more than one functional group.[2] We previously reported some carbon−carbon bond-forming reactions catalyzed by rhodium complexes in which a hydrosilane plays an important role as a trigger of the catalytic cycle.[3] On the basis of a series of reactions, we also proposed the intermediacy of a rhodium enolate species (**A**), the formation of which may involve the consecutive interaction of a hydrosilane and an α,β-unsaturated carbonyl compound with a rhodium complex (Scheme 1). This intermediate seems to possess sufficient nucleophilicity toward both electrophiles such as aldehydes[3o] and allylic esters.[3b]

Scheme 1



On the other hand, isocyanates are used to construct many types of heterocycles due to their high electrophilicity.[4,5] There are also some reports of their reactions with carbon nucleophiles such as carbanions[6−8] and enoxysilanes activated by bases.[9] All of these reactions require more than 1 equiv of base in order to generate nucleophilic species. Accordingly, these transformations are insufficient from the viewpoint of atom economy. In these studies, to the best of our knowledge there has been no reported example of transition-metal-catalyzed homologation to the central carbon of isocyanates.[4b,10]

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(2) For recent reviews, see: (a) Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523. (b) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. (c) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115. (d) Negishi, E.; Copéret, C.; Ma, S.; Lion, S.; Liu, F. *Chem. Rev.* **1996**, *96*, 365. (e) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635.

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(4) For a review, see: (a) Rigby, J. H. *Synlett* **2000**, 1. (b) Braunstein, P.; Nobel, D. *Chem. Rev.* **1989**, *89*, 1927. (c) Ozaki, S. *Chem. Rev.* **1972**, *72*, 457. (d) Trost, B. M.; Fleming, I. In *Comprehensive Organic Synthesis;* Pergamon Press: Oxford, 1991; Vol. 5, pp 102−108. (e) Katrizky, A. R.; Rees, C. W. In *Comprehensive Heterocyclic Chemistry*; Pergamon Press: Oxford, 1984; Parts 2B and 4B.

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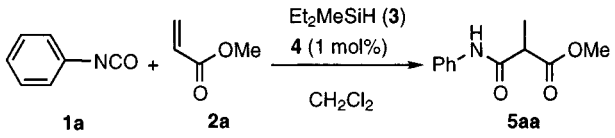
Thus, we focused our attention on the rhodium-catalyzed modification of an isocyanate under neutral conditions. We report here a formal hydrocarbamoylation of alkenes, which is attained by the rhodium-catalyzed three-component coupling of an isocyanate, a hydrosilane, and an α,β-unsaturated carbonyl compound.

Results and Discussion

Three-Component Coupling. Initially, when a CH_2Cl_2 solution of phenyl isocyanate (**1a**) and 2 molar equiv each of methyl acrylate (**2a**) and diethylmethylsilane (**3**) was heated in a sealed tube containing 1 mol % of [Rh(cod){P(OPh)$_3$}$_2$]OTf (**4a**, cod =1,5-cyclooctadiene) for 21 h at 80 °C, **5aa** was isolated in 86% yield as the sole product after chromatographic purification of the reaction mixture (entry 1 in Table 1). The ^{1}H NMR spectrum of **5aa** suggests that **5aa** contains **1a** and **2a** as a composing unit. The precise structure of **5aa** was determined as a methyl 2-carbamoylpropanoate based on its ^{1}H and ^{13}C NMR spectra and combustion analysis. Signals assignable to part of an imidate structure (**6aa**) were observed in the ^{1}H NMR spectrum of the crude product, which was carefully handled under an inert atmosphere {300 MHz in C_6D_6; δ 0.33 (s, 3H, Si−C*H*$_3$), 1.25 (d, J = 6.9 Hz, 3H, C*H*$_3$−CH), 3.29 (s, 3H, OC*H*$_3$), 3.46 (q, J = 6.9 Hz, 1H, C*H*−CH$_3$)}. This implies that **5aa** is produced by the consecutive protodesilylation of **6aa**, which is composed of equivalent moles of **1a**, **2a**, and **3**, as shown in Scheme 2. The overall transformation can be regarded as a formal hydrocarbamoylation toward the olefinic part of **2a**. The regiochemistry of the addition is strictly regulated to the direction that the carbamoyl group links to the α-position of **2a**. Fortunately, the reaction does not need much time (21 h) for completion. This coupling to form **5aa** proceeded sufficiently even under the conditions of refluxing a mixture for 3 h in a flask (bath temp 45 °C, entry 2 in Table 1).

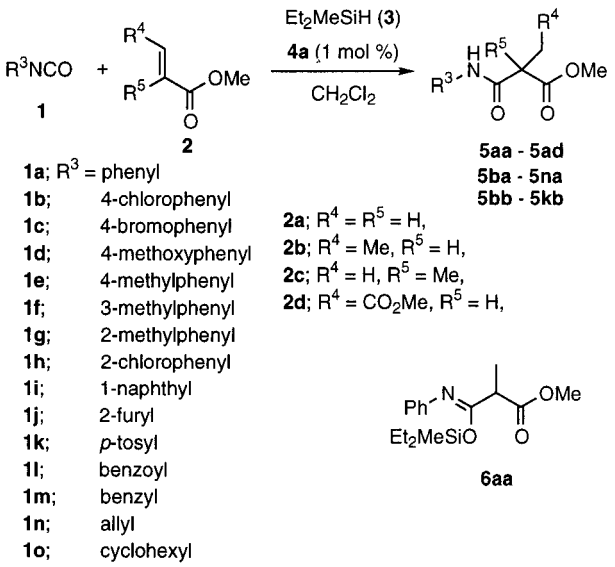
Table 1. Hydrocarbamoylation of 2a with 1a and 3 Catalyzed by 4[a]



entry	rhodium complex (**4**)	reaction time (h)	yield[b] (%)
1	[Rh(cod){P(OPh)$_3$}$_2$]OTf (**4a**)	21[c]	86
2	**4a**	3	90
3	[Rh(cod)(PPh$_3$)$_2$]OTf (**4b**)	14	95
4	[Rh(cod)(PMePh$_2$)$_2$]OTf (**4c**)	10	89
5	[Rh(cod)(dppb)]OTf (**4d**)[d]	47[e]	68
6	$Rh_4(CO)_{12}$ (**4e**)	47[e]	79
7	no catalyst	68	0

[a] A mixture of **1a** (1 mmol), **2a** (2 mmol), and **3** (2 mmol) was added to a solution of **4** (1 mol % for **1a**) in CH_2Cl_2 (6 mL) at 25 °C, and the resulting solution was stirred for a specified period at 45 °C (bath temperature) except entry 1. [b] Isolated yield. [c] The reaction was conducted in a sealed tube at 80 °C. [d] dppb = 1,4-bis(diphenylphosphino)butane. [e] Some **1a** was detected at this stage.

Scheme 2



Other rhodium complexes also worked well as a catalyst for this transformation (entries 3−6 in Table 1). Cationic complexes bearing a monodentate phosphine, PPh_3 or $PMePh_2$ (**4b** and **4c**), were effective for this coupling, although they required a rather longer time than **4a** itself for completion. In contrast, a cationic complex bearing a bidentate ligand such as 1,4-bis(diphenylphosphino)butane (dppb) gave a decreased yield of **5aa** even under analogous conditions (entry 5 in Table 1). This suggests that the phosphine ligand on the rhodium center significantly affects the rate and chemical yield of this transformation. In addition to Rh(I) cationic complexes, $Rh_4(CO)_{12}$ (**4e**) also exhibits catalytic ability for this reaction despite the moderate yield of the desired product (entry 6 in Table 1). This three-component coupling does not proceed at all in the absence of the rhodium complex (entry 7 in Table 1),

(6) Recent examples of the reaction with stabilized carbanion: (a) Mukhopadhyaya, J. K.; Sklenák, S.; Rappoport, Z. *J. Am. Chem. Soc.* **2000**, *122*, 1325. (b) Boiteau, L.; Boivin, J.; Liard, A.; Quiclet-Sire, B.; Zard, S. Z. *Angew. Chem., In. Ed.* **1998**, *37*, 1128. (c) Lee, H. K.; Lee, J. P.; Lee, G. H.; Pak, C. S. *Synlett* **1996**, 1209. (d) Koch, T.; Hesse, M. *Synthesis* **1992**, 931. (e) Rigby, J. H.; Qabar, M. *J. Org. Chem.* **1989**, *54*, 5852. (f) Tay, M. K.; About-Jaudet, E.; Collignon, N.; Savignac, P. *Tetrahedron* **1989**, *45*, 4415. (g) Rigby, J. H.; Burkhardt, F. J. *J. Org. Chem.* **1986**, *51*, 1374. Pioneering work: (h) Dieckmann, W.; Hoppe, J.; Stein, R. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 4627.

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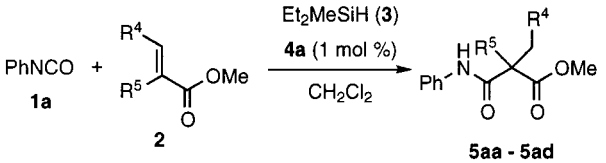
Table 2. Table 2. Hydrocarbamoylation of 2 with 1a and 3 Catalyzed by 4a[a]



entry	2	R^4	R^5	condition	product	yield[b] (%)
1	**2a**	H	H	reflux, 3 h	**5aa**	90
2	**2b**	Me	H	reflux, 13 h	**5ab**	88
3[c]	**2c**	H	Me	80 °C, 24 h	**5ac**	26
4	**2d**	CO_2Me	H	reflux, 14 h	**5ad**	40

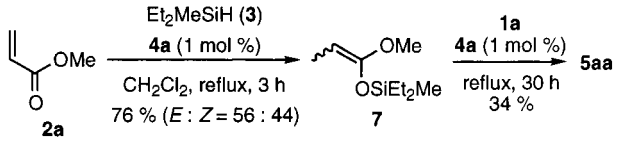
[a] A mixture of **1a** (1 mmol), **2** (2 mmol), and **3** (2 mmol) was added to a solution of **4a** (1 mol % for **1a**) in CH_2Cl_2 at 25 °C, and the mixture was heated under the conditions shown. [b] Isolated yield. [c] The reaction was performed in a sealed tube.

and the presence of any Rh species is crucial for sufficient conversion. On the basis of the reaction time and the yield of **5**, **4a** appears to be the catalyst precursor of choice for the desired reactions. This observation is reminiscent of the Rh-catalyzed hydroallylation of **2a**.[3b]

This type of formal hydrocarbamoylation is suitable for other α,β-unsaturated carbonyl compounds, as cited in Table 2. Methyl crotonate (**2b**) smoothly reacted with **1a** and **3** in the presence of **4a** to give the corresponding product **5ab** in 88% yield, whereas methyl methacrylate (**2c**) gave an unacceptable yield even under severe reaction conditions (80°C, 24 h in a sealed tube, 26% yield, entry 3 in Table 2). These results indicate that the substituent on the α-carbon of **2** has a greater effect on coupling than the substituent on the β-carbon of **2** under these reaction conditions. An electron-withdrawing group on the β-carbon, as exemplified by dimethyl fumarate (**2d**), seems to diminish the yield of this coupling (entry 4 in Table 2). Thus, it is deduced from the above results that unsubstituted methyl 2-alkenoates are available for the present type coupling as a synthetic equivalent of a methyl alkanoate anion under neutral conditions.

On the other hand, a relatively wide variety of isocyanates were suitable for this transformation. Isocyanate reactivity is apparently unaffected by the substituent on the aromatic ring. All of the 4-chloro- (**1b**), 4-bromo- (**1c**), 4-methoxy- (**1d**), 4-methyl- (**1e**), 3-methyl- (**1f**), 2-methyl- (**1g**), and 2-chloro- (**1h**) phenyl isocyanates worked well as the carbamoyl part (entries 3−16 in Table 3). 1-Naphthyl isocyanate (**1i**) was also suitable for formal hydrocarbamoylation toward **2a** or **2b** to give the corresponding product **5ia** or **5ib** in high yields (entries 17 and 18 in Table 3). Other aromatic isocyanates, for example, 2-furyl isocyanate (**1j**), were also appropriate for this reaction to give the coupling product in high yield (entries 19 and 20 in Table 3). Using reaction conditions similar to those for the aromatic isocyanates, the desired products **5ka**, **5kb**, and **5la** were also obtained in good yields from the isocyanates **1k** and **1l**, having a strong electron-attracting group (entries 21−24 in Table 3). In particular, benzoyl isocyanate (**1l**) reacted with **2a** to give the corresponding amide **5la** in a good yield regardless of the reaction temperature (entries 23 and 24 in Table 3).

Scheme 3



In contrast to the high yields of the reactions with isocyanates bearing an aromatic ring or a strong electron-withdrawing group, the products with alkyl isocyanates were obtained in unacceptable yields. Amides **5ma** and **5na** were formed in moderate yields in the reactions of **1m** and **1n** (entries 25 and 26 in Table 3), whereas the desired product was not detected at all in the reaction of the cyclohexyl isocyanate (**1o**) (entry 27 in Table 3).

These results imply that the electrophilicity of an isocyanate toward the rhodium enolate may control the progress of these couplings. This trend is consistent with the conventional propensity that aromatic isocyanates show higher reactivity than alkyl isocyanates in classical nucleophilic reactions.[4c]

Pathway for the Coupling. Any information on the intermediate or catalytic species has not been obtained in the present three-component coupling. Since oxidative addition of **3** to a low-valence Rh complex is well documented,[11] the formation of a ketene silyl acetal and the subsequent reaction of it with **1** are a probable explanation for the final product. In fact, ketene silyl acetal **7** was isolated in 76% yield (*E*:*Z* = 56:44) as the sole product in a reaction of methyl acrylate **2a** with **3** catalyzed by 1 mol % of **4a** (Scheme 3), although it has been reported that a mixture of ketene silyl acetal similar to **7** and methyl 3-silylpropanoate (**8**)[12] or only **8** as the sole product[13] was formed in a reaction of **2a** with a hydrosilane-catalyzed by $RhCl(PPh_3)_3$. At the subsequent stage, **5aa** was obtained in 34% yield when a CH_2Cl_2 solution of **1a** and **7** was conducted with 1 mol % of **4a** for 30 h at reflux temperature.

This result seems to be consistent with the postulated stepwise pathway as shown in Scheme 3. However, if this is the case, it is difficult to explain the reason the yield of **5aa** is so poor in a direct reaction of **7** with **2a** despite a long reaction time.

This inconsistency between two different procedures to form **5aa** prompts us to postulate the intervention of a Rh-enolate species. Thus, Scheme 4 offers a possible explanation for the catalytic cycle in this coupling. The fundamental pathway is similar to that in aldol-type coupling.[3o] Oxidative addition of the hydrosilane to a low-valence rhodium center **4** would form hydride−rhodium complex **10**. Subsequent conjugative insertion of **2a** into the Rh−H bond could result in the rhodium−enolate intermediate **12a**.[14,15] Coordination of the isocyanate to **12a** followed by intramolecular nucleophilic attack on the central carbon of R^3−N=C=O of **13a** would form **14a**. Reductive elimination of the silyl

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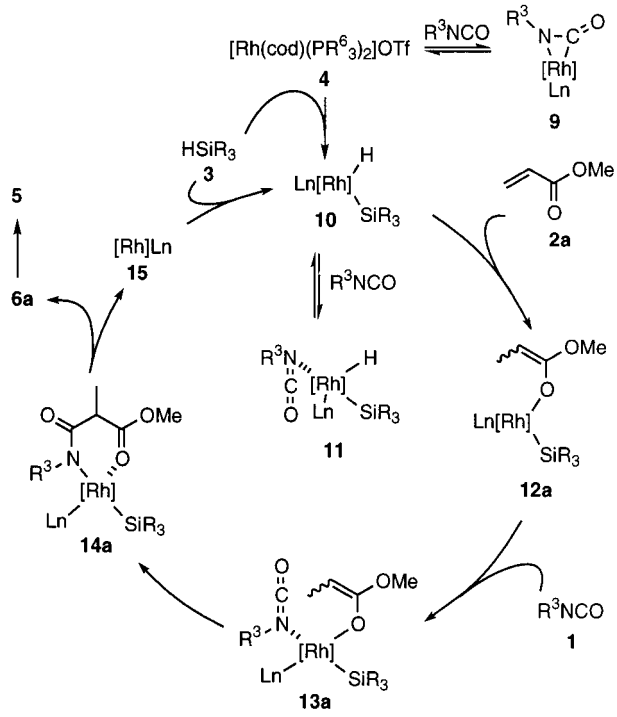
(13) Ojima, I.; Kumagai, M. *J. Organomet. Chem.* **1976**, *111*, 43.

Table 3. Hydrocarbamoylation of 2a or 2b with 1 and 3 Catalyzed by 4a[a]

entry	1	2	conditions °C/h	product (yield[b] (%))	entry	1	2	conditions °C/h	product (yield[b] (%))
1	**1a**	**2a**	45/3	**5aa** (90)	15	**1h**	**2a**	45/12	**5ha** (94)
2		**2b**	45/13	**5ab** (88)					
3	**1b**	**2a**	45/3	**5ba** (93)	16		**2b**	45/5	**5hb** (95)
4		**2b**	45/4	**5bb** (87)	17	**1i**	**2a**	45/6	**5ia** (99)
5	**1c**	**2a**	45/13	**5ca** (96)	18		**2b**	45/15	**5ib** (83)
6		**2b**	45/13	**5cb** (80)	19	**1j**	**2a**	45/4	**5ja** (85)
7	**1d**	**2a**	45/5	**5da** (73)	20		**2b**	45/4	**5jb** (53)
8		**2b**	45/14	**5db** (91)	21	**1k**	**2a**	45/12	**5ka** (82)
9	**1e**	**2a**	45/15	**5ea** (96)	22		**2b**	45/12	**5kb** (61)
10		**2b**	45/12	**5eb** (92)	23	**1l**	**2a**	45/14	**5la** (82)
11	**1f**	**2a**	45/13	**5fa** (96)	24		**2a**	25/15	**5la** (70)
12		**2b**	45/14	**5fb** (95)	25[c]	**1m**	**2a**	80/15	**5ma** (45)
13	**1g**	**2a**	45/13	**5ga** (86)	26[c]	**1n**	**2a**	50/61	**5na** (43)
14		**2b**	45/14	**5gb** (84)	27[c]	**1o**	**2a**	80/24	**5oa** (0)

[a] A mixture of **1** (1 mmol), **2** (2 mmol), and **3** (2 mmol) was added to a solution of **4a** (1 mol% for **1a**) in CH_2Cl_2 at 25 °C and the mixture was heated under the conditions shown. [b] Isolated yield. [c] The reaction was performed in a sealed tube.

Scheme 4



imidate (**6a**) from **14a** would give a low-valence rhodium complex **15**, and oxidative addition of **3** would restart the catalytic cycle. The final product **5** would be derived from **6a** during conventional workup for isolation.

In addition to this principal cycle, either an equilibrium step between **4** and **9** or between **10** and **11** should be considered for a consistent elucidation of our results. The formation of **9** or **11** interferes with the approach of **3** or **2a** to the metal center. This would explain why heating of the reaction system is crucial for smooth coupling, although the electrophilicity of an isocyanate is much higher than that of an aldehyde.

Conclusion

We have shown that the formal hydrocarbamoylation of alkenes can be achieved by cationic Rh(I)-catalyzed coupling of an isocyanate, a hydrosilane, and an α,β-unsaturated carbonyl compound under almost neutral conditions. The location of the resulting carbamoyl group is strictly controlled at the α-position of α,β-unsaturated carbonyl compounds. This coupling to form an α-carbamoyl ester is very effective for aryl isocyanate regardless of the substituent on the phenyl ring, though alkyl isocyanate shows less reactivity. Both rhodium-enolate and ketene silyl acetal, which are produced in the reaction system, seem to possess sufficient nucleophilicity toward an isocyanate; the former has higher reactivity than the latter.

Experimental Section

General Procedures. All hydrocarbamoylation reactions were carried out in a 20 mL round-bottomed flask under nitrogen atmosphere unless otherwise indicated. Anhydrous solvents were transferred via an oven-dried syringe. CH_2Cl_2 was distilled from CaH_2. Rhodium(I) cation complexes **4a**−**d** were prepared by a procedure similar to that reported for [Rh(cod)$(PPh_3)_2$]BF_4,[16] and the preparation of $Rh_4(CO)_{12}$ (**4e**) was based on a standard literature procedure.[17] Aryl and alkyl isocyanates, **1a**−**o** except **1j** and **1l**, α,β-unsaturated carbonyl compounds **2a**−**d**, and hydrosilane **3** were purchased from Aldrich, Shin-etsu Chemicals, Tokyo Kasei, or Wako Chemicals. They were used as received. 2-Fulyl isocyanate **1j**[18] and benzoyl isocyanate **1l**[19] were prepared by the literature procedure.

All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60 F-254) using UV light as visualizing agent and 7% ethanolic phosphomolybdic acid and heat as developing agent. E. Merck silica gel (60, particle size 0.040−0.063 mm) was used for column chromatography.

Proton nuclear magnetic resonance (^{1}H NMR) data were obtained at 300 MHz on a Varian Mercury 300 spectrometer or at 500 MHz on a Varian INOVA-500 spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) relative to the singlet at 7.26 ppm for chloroform-*d*. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q,

(14) (a) Slough, G. A.; Hayashi, R.; Ashbaugh, J. R.; Shamblin, S. L.; Aukamp, A. M. *Organometallics* **1994**, *13*, 890. (b) Slough, G. A.; Ashbaugh, J. R.; Zannoni, L. A. *Organometallics* **1994**, *13*, 3587. (c) Sato, S.; Matsuda, I.; Izumi, Y. *J. Organomet. Chem.* **1988**, *352*, 223. (d) For an example of a η^1 oxygen-bound rhodium enolate, see: Slough, G. A.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1989**, *111*, 938

(15) A similar sequence is postulated in reactions for constructing aldol-type products from an α,β-enone, a hydrosilane, and an aldehyde.[30] Rhodium enolate complexes are formed by interacting a chlororhodium species with an enolate anion.[14d]

(16) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 2397.

(17) Martinengo, S.; Giordano, G.; Chini, P. *Inorg. Synth.* **1990**, *28*, 242.

(18) Singleton, H. M.; Edwards, Jr. W. R. *J. Am. Chem. Soc.* **1938**, *60*, 540.

(19) Speziale, A. J.; Smith, L. R. *J. Org. Chem.* **1963**, *28*, 1805.

quartet; quint, quintet; m, multiplet; and b, broad. Coupling constants are reported in hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were obtained at 75 MHz on a Varian Mercury 300 spectrometer or at 125.7 MHz on a Varian INOVA-500 and are reported in ppm with the center line of a triplet at 77.00 ppm for chloroform-*d*. Routine ^{13}C spectra were fully decoupled by broad-band decoupling. Infrared data were recorded in 0.2 mm path length sodium chloride cavity cells on a JASCO FT/IR-230 spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Melting points were obtained on a Büchi 510-K apparatus in sealed capillary tubes and are uncorrected. Boiling points are also uncorrected. Elemental analyses were performed by the Microanalytical Center of Kyoto University.

Typical Procedure for Rh-Catalyzed Hydrocarbamoylation of an α,β-Unsaturated Carbonyl Compound with a Hydrosilane and an Aryl or Alkyl Isocyanate. To a solution of [Rh(cod){P(OPh)$_3$}$_2$]OTf (9.9 mg, 0.010 mmol) in CH_2Cl_2 (4 mL) was added a mixture of phenyl isocyanate **1a** (121 mg, 1.0 mmol), methyl methacrylate **2a** (182 mg, 2.1 mmol), and diethylmethylsilane **3** (205 mg, 2.0 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was then refluxed for 3 h under N_2 atmosphere. The solvent was removed under reduced pressure, and the residue was purified by silica gel flash column chromatography (hexane/ethyl acetate = 4:1 as an eluent) to afford **5aa** (188 mg, 0.91 mmol) as a white solid (90%). The reactions of aryl or alkyl isocyanates **1a**−**o** and α,β-unsaturated carbonyl compounds **2a**−**d** were carried out in similar manners. Conditions and yields are summarized in Tables 1−3, respectively.

Property of 5aa: colorless needles (mp 84.5−85.5 °C) from ethyl acetate and hexane. IR (CCl_4): 3349 (N−H), 1720 (C═O), 1688 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.55 (d, *J* = 7.1 Hz, 3H, C*H*$_3$), 3.46 (q, *J* = 7.1 Hz, 1H, C*H*), 3.79 (s, 3H, OC*H*$_3$), 7.12 (t, *J* = 7.4 Hz, 1H, Ph), 7.33 (dd, *J* = 8.1 and 7.4 Hz, 2H, Ph), 7.54 (d, *J* = 8.1 Hz, 2H, Ph), 8.54 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.51 (*C*H$_3$), 47.43 (*C*H), 52.80 (O*C*H$_3$), 119.84 (Ph), 124.43 (Ph), 128.90 (Ph), 137.45 (Ph), 166.58 (NH*C*O), 173.06 (*C*O). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.76; H, 6.32; N, 6.76. Found: C, 63.79; H, 6.34; N, 6.62.

Spectroscopic Confirmation of the Presence of 6aa in the Crude Product. To a solution of [Rh(cod){P(OPh)$_3$}$_2$]OTf (9.4 mg, 0.0096 mmol) in CH_2Cl_2 (4 mL) was added a mixture of phenyl isocyanate **1a** (121 mg, 1.0 mmol), methyl methacrylate **2a** (173 mg, 2.0 mmol), and diethylmethylsilane **3a** (206 mg, 2.0 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was then refluxed for 4 h under N_2 atmosphere. The solvent was removed under reduced pressure, and the residue was dried for 30 min. The crude product was then analyzed by ^{1}H NMR in C_6D_6. The spectral data that are assignable to the apparent peaks are cited in the text.

Property of 5ab: colorless needles (mp 76.0−77.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3371 (N−H), 1722 (C═O), 1689 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, *J* = 7.4 Hz, 3H, C*H*$_3$), 2.03 (dq, *J* = 7.4 and 7.3 Hz, 2H, C*H*$_2$), 3.32 (t, *J* = 7.3 Hz, 1H, C*H*), 3.76 (s, 3H, OC*H*$_3$), 7.10 (t, *J* = 7.5 Hz, 1H, Ph), 7.30 (dd, *J* = 8.4 and 7.5 Hz, 2H, Ph), 7.54 (d, *J* = 8.4 Hz, 2H, Ph), 8.74 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.78 (*C*H$_3$), 24.88 (*C*H$_2$), 52.52 (*C*H), 54.86 (O*C*H$_3$), 119.88 (Ph), 124.35 (Ph), 128.78 (Ph), 137.40 (Ph), 166.30 (NH*C*O), 172.68 (*C*O). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.30; H, 6.57; N, 6.28.

Property of 5ac: colorless liquid (bp 160 °C/0.1 Torr), solidifies on storage (mp 76.4−77.4 °C). IR (CCl_4): 3343 (N−H), 1715 (C═O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.56 (s, 6H, C*H*$_3$), 3.79 (s, 3H, OC*H*$_3$), 7.11 (t, *J* = 7.5 Hz, 1H, Ph), 7.32 (dd, *J* = 8.3 and 7.5 Hz, 2H, Ph), 7.53 (d, *J* = 8.3 Hz, 2H, Ph), 8.56 (bs, 1H, N*H*). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 23.85 (*C*H$_3$), 50.41 (*C*H), 52.95 (O*C*H$_3$), 119.90 (Ph), 124.34 (Ph), 128.91 (Ph), 137.71 (Ph), 169.53 (NH*C*O), 175.97 (*C*O). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 64.98; H, 6.82; N, 6.24.

Property of 5ad. IR (neat): 3331 (N−H), 1738 (C═O), 1676 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.09 (d, *J* = 6.9 Hz, 2H, C*H*$_2$), 3.72 (s, 3H, OC*H*$_3$), 3.81 (s, 3H, OC*H*$_3$), 3.85 (t, *J* = 6.9 Hz, 1H, C*H*), 7.12 (t, *J* = 7.3 Hz, 1H, Ph), 7.33 (dd, *J* = 8.4 and 7.3 Hz, 2H, Ph), 7.53 (d, *J* = 8.4 Hz, 2H, Ph), 8.53 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 32.45 (*C*H$_2$), 48.78 (*C*H), 52.19 (O*C*H$_3$), 53.13 (O*C*H$_3$), 119.83 (Ph), 124.54 (Ph), 128.87 (Ph), 137.30 (Ph), 164.39 (NH*C*O), 170.01 (*C*O), 171.97 (*C*O). Anal. Calcd for $C_{13}H_{15}NO_5$: C, 58.86; H, 5.70; N, 5.28. Found: C, 58.65; H, 5.75; N, 5.11.

Property of 5ba: colorless needles (mp 110.0−111.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3342 (N−H), 1720 (C═O), 1698 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.55 (d, *J* = 7.4 Hz, 3H, C*H*$_3$), 3.45 (q, *J* = 7.4 Hz, 1H, C*H*), 3.79 (s, 3H, OC*H*$_3$), 7.26−7.31 (m, 2H, Ph), 7.47−7.52 (m, 2H, Ph), 8.67 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.58 (*C*H$_3$), 47.24 (*C*H), 52.87 (O*C*H$_3$), 121.08 (Ph), 128.90 (Ph), 129.38 (Ph), 136.03 (Ph), 166.64 (NH*C*O), 173.13 (*C*O). Anal. Calcd for $C_{11}H_{12}ClNO_3$: C, 54.67; H, 5.00; N, 5.80. Found: C, 54.65; H, 5.00; N, 5.76.

Property of 5bb: colorless needles (mp 91.5−92.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3350 (N−H), 1721 (C═O), 1693 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (t, *J* = 7.6 Hz, 3H, C*H*$_3$), 2.04 (dq, *J* = 7.6 and 7.2 Hz, 2H, C*H*$_2$), 3.30 (t, *J* = 7.2 Hz, 1H, C*H*), 3.79 (s, 3H, OC*H*$_3$), 7.25−7.30 (m, 2H, Ph), 7.48−7.53 (m, 2H, Ph), 8.80 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.82 (*C*H$_3$), 25.39 (*C*H$_2$), 52.69 (O*C*H$_3$), 54.63 (*C*H), 121.09 (Ph), 128.85 (Ph), 129.30 (Ph), 135.94 (Ph), 166.21 (NH*C*O), 173.10 (*C*O). Anal. Calcd for $C_{12}H_{14}ClNO_3$: C, 56.37; H, 5.52; N, 5.48. Found: C, 56.13; H, 5.48; N, 5.53.

Property of 5ca: colorless needles (mp 101.5−104.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3340 (N−H), 1720 (C═O), 1691 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54 (d, *J* = 7.4 Hz, 3H, C*H*$_3$), 3.44 (q, *J* = 7.4 Hz, 1H, C*H*), 3.78 (s, 3H, OC*H*$_3$), 7.39−7.46 (m, 4H, Ph), 8.70 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.45 (*C*H$_3$), 47.26 (*C*H), 52.84 (O*C*H$_3$), 117.00 (Ph), 121.41 (Ph), 131.81 (Ph), 136.53 (Ph), 166.75 (NH*C*O), 172.94 (*C*O). Anal. Calcd for $C_{11}H_{12}BrNO_3$: C, 46.18; H, 4.23; N, 4.90. Found: C, 46.16; H, 4.32; N, 4.71.

Property of 5cb: colorless needles (mp 99.0−100.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3349 (N−H), 1722 (C═O), 1697 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00 (t, *J* = 7.4 Hz, 3H, C*H*$_3$), 2.03 (dq, *J* = 7.4 and 7.3 Hz, 2H, C*H*$_2$), 3.30 (t, *J* = 7.3 Hz, 1H, C*H*), 3.79 (s, 3H, OC*H*$_3$), 7.40−7.47 (m, 4H, Ph), 8.77 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.80 (*C*H$_3$), 25.33 (*C*H$_2$), 52.67 (O*C*H$_3$), 54.70 (*C*H), 116.97 (Ph), 121.43 (Ph), 131.81 (Ph), 136.50 (Ph), 166.18 (NH*C*O), 173.05 (*C*O). Anal. Calcd for $C_{12}H_{14}BrNO_3$: C, 48.02; H, 4.70; N, 4.67. Found: C, 47.84; H, 4.60; N, 4.64.

Property of 5da: colorless needles (mp 118.0−119.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3356 (N−H), 1718 (C═O), 1693 (C═O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.53 (d, *J* = 7.4 Hz, 3H, C*H*$_3$), 3.44 (q, *J* = 7.4 Hz, 1H, C*H*), 3.77 (s, 3H, OC*H*$_3$), 3.78 (s, 3H, OC*H*$_3$), 6.83−6.86 (m, 2H, Ph), 7.41−7.45 (m, 2H, Ph), 8.46 (bs, 1H, N*H*). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 15.31 (*C*H$_3$), 47.15 (*C*H), 52.67 (O*C*H$_3$), 55.41 (O*C*H$_3$), 114.04 (Ph), 121.70 (Ph), 130.65 (Ph), 156.47 (Ph), 166.73 (NH*C*O), 173.10 (*C*O). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.48; H, 6.43; N, 5.80.

Property of 5db: colorless needles (mp 102.0−103.5 °C) from ethyl acetate and hexane. IR (CCl_4): 3350 (N−H), 1722 (C═O), 1684 (C═O) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.99 (t, *J* = 7.3 Hz, 3H, C*H*$_3$), 2.03 (dq, *J* = 7.4 and 7.3 Hz, 2H, C*H*$_2$), 3.29 (t, *J* = 7.4 Hz, 1H, C*H*), 3.77 (s, 3H, OC*H*$_3$), 3.78 (s, 3H, OC*H*$_3$), 6.83−6.86 (m, 2H, Ph), 7.42−7.45 (m, 2H, Ph), 8.56 (bs, 1H, N*H*). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ 11.70 (*C*H$_3$), 24.98 (*C*H$_2$), 52.49 (O*C*H$_3$), 54.65 (*C*H), 55.41 (O*C*H$_3$), 114.03 (Ph), 121.70 (Ph), 130.63 (Ph), 156.44 (Ph), 166.15 (NH*C*O),

173.07 (*C*O). Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.31; H, 6.99; N, 5.54.

Property of 5ea: colorless needles (mp 102.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3353 (N−H), 1722 (C═O), 1693 (C═O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.51 (d, J = 7.3 Hz, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.45 (q, J = 7.3 Hz, 1H, C*H*), 3.76 (s, 3H, OCH_3), 7.10 (d, J = 8.6 Hz, 2H, Ph), 7.41 (d, J = 8.6 Hz, 2H, Ph), 8.57 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.18 (*C*H_3), 20.87 (*C*H_3), 47.32 (*C*H), 52.63 (O*C*H_3), 119.93 (Ph), 129.25 (Ph), 133.96 (Ph), 134.88 (Ph), 166.78 (NH*C*O), 172.63 (*C*O). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 64.97; H, 6.68; N, 6.28.

Property of 5eb: colorless needles (mp 95.0−96.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3355 (N−H), 1722 (C═O), 1691 (C═O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.00 (t, J = 7.4 Hz, 3H, CH_3), 2.04 (dq, J = 7.4 and 7.4 Hz, 2H, CH_2), 2.31 (s, 3H, CH_3), 3.30 (t, J = 7.4 Hz, 1H, C*H*), 3.78 (s, 3H, OCH_3), 7.12 (d, J = 8.4 Hz, 2H, Ph), 7.42 (d, J = 8.4 Hz, 2H, Ph), 8.57 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.83 (*C*H_3), 20.93 (*C*H_3), 25.17 (*C*H_2), 52.55 (O*C*H_3), 54.89 (*C*H), 119.93 (Ph), 129.33 (Ph), 134.00 (Ph), 134.87 (Ph), 165.96 (NH*C*O), 172.98 (*C*O). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.29; H, 7.25; N, 6.05.

Property of 5fa: colorless needles (mp 65.5−66.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3353 (N−H), 1720 (C═O), 1690 (C═O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.54 (d, J = 7.3 Hz, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.45 (q, J = 7.3 Hz, 1H, C*H*), 3.78 (s, 3H, OCH_3), 6.93 (d, J = 7.8 Hz, 1H, Ph), 7.20 (dd, J = 7.8 and 7.8 Hz, 1H, Ph), 7.32 (d, J = 7.8 Hz, 1H, Ph), 7.39 (s, 1H, Ph), 8.50 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.43 (*C*H_3), 21.53 (*C*H_3), 47.43 (*C*H), 52.77 (O*C*H_3), 116.88 (Ph), 120.45 (Ph), 125.20 (Ph), 128.68 (Ph), 137.32 (Ph), 138.79 (Ph), 166.60 (NH*C*O), 172.95 (*C*O). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.26; H, 6.90; N, 6.26.

Property of 5fb: colorless needles (mp 52.0−55.0 °C) from ethyl acetate and hexane. IR ($CHCl_3$): 3345 (N−H), 1719 (C═O), 1686 (C═O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.00 (t, J = 7.4 Hz, 3H, CH_3), 2.04 (dq, J = 7.4 and 7.4 Hz, 2H, CH_2), 2.32 (s, 3H, CH_3), 3.30 (t, J = 7.4 Hz, 1H, C*H*), 3.78 (s, 3H, OCH_3), 6.93 (d, J = 7.7 Hz, 1H, Ph), 7.19 (dd, J = 7.9 and 7.7 Hz, 1H, Ph), 7.33 (d, J = 7.9 Hz, 1H, Ph), 7.40 (s, 1H, Ph), 8.63 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.82 (*C*H_3), 21.49 (*C*H_3), 25.09 (*C*H_2), 52.56 (O*C*H_3), 54.89 (*C*H), 116.91 (Ph), 120.46 (Ph), 125.16 (Ph), 128.64 (Ph), 137.29 (Ph), 138.74 (Ph), 166.12 (NH*C*O), 172.85 (*C*O). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.17; H, 7.32; N, 6.12.

Property of 5ga: colorless needles (mp 112.0−113.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3357 (N−H), 1720 (C═O), 1689 (C═O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.59 (d, J = 7.3 Hz, 3H, CH_3), 2.30 (s, 3H, CH_3), 3.50 (q, J = 7.3 Hz, 1H, C*H*), 3.81 (s, 3H, OCH_3), 7.07 (dd, J = 7.5 and 7.1 Hz, 1H, Ph), 7.19 (d, J = 7.5 Hz, 1H, Ph), 7.21 (dd, J = 8.0 and 7.1 Hz, 1H, Ph), 7.93 (d, J = 8.0 Hz, 1H, Ph), 8.61 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.99 (*C*H_3), 17.80 (*C*H_3), 47.23 (*C*H), 52.82 (O*C*H_3), 122.14 (Ph), 124.89 (Ph), 126.66 (Ph), 128.40 (Ph), 130.32 (Ph), 135.49 (Ph), 166.59 (NH*C*O), 173.60 (*C*O). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.08; H, 7.01; N, 6.26.

Property of 5gb: colorless needles (mp 103.5−103.8 °C) from ethyl acetate and hexane. IR (CCl_4): 3352 (N−H), 1722 (C═O), 1693 (C═O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.03 (t, J = 7.4 Hz, 3H, CH_3), 2.08 (dq, J = 7.4 and 7.3 Hz, 2H, CH_2), 2.30 (s, 3H, CH_3), 3.36 (t, J = 7.3 Hz, 1H, C*H*), 3.81 (s, 3H, OCH_3), 7.06 (dd, J = 7.7 and 7.6 Hz, 1H, Ph), 7.19 (d, J = 7.7 Hz, 1H, Ph), 7.21 (dd, J = 7.8 and 7.6 Hz, 1H, Ph), 7.94 (d, J = 7.8 Hz, 1H, Ph), 8.72 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.86 (*C*H_3), 17.84 (*C*H_3), 25.81 (*C*H_2), 52.64 (O*C*H_3), 54.68 (*C*H), 122.09 (Ph), 124.83 (Ph), 126.63 (Ph), 128.36 (Ph), 130.31 (Ph), 135.50 (Ph), 166.09 (NH*C*O), 173.62 (*C*O). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.07; H, 7.25; N, 5.93.

Property of 5ha: colorless needles (mp 96.0−97.0 °C) from ethyl acetate and hexane. IR ($CHCl_3$): 3371 (N−H), 1720 (C═O), 1691 (C═O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.57 (d, J = 7.3 Hz, 3H, CH_3), 3.53 (q, J = 7.3 Hz, 1H, C*H*), 3.82 (s, 3H, OCH_3), 7.05 (ddd, J = 8.0, 7.6 and 1.6 Hz, 1H, Ph), 7.27 (ddd, J = 8.3, 7.6 and 1.5 Hz, 1H, Ph), 7.38 (dd, J = 8.0 and 1.5 Hz, 1H, Ph), 8.36 (dd, J = 8.3 and 1.6 Hz, 1H, Ph), 9.04 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.27 (*C*H_3), 47.64 (*C*H), 52.93 (O*C*H_3), 121.54 (Ph), 123.06 (Ph), 124.76 (Ph), 127.56 (Ph), 128.98 (Ph), 134.35 (Ph), 166.63 (NH*C*O), 172.38 (*C*O). Anal. Calcd for $C_{11}H_{12}ClNO_3$: C, 54.67; H, 5.00; N, 5.80. Found: C, 54.58; H, 4.85; N, 5.59.

Property of 5hb: colorless needles (mp 78.0−78.5 °C) from ethyl acetate and hexane. IR ($CHCl_3$): 3321 (N−H), 1720 (C═O), 1693 (C═O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.03 (t, J = 7.4 Hz, 3H, CH_3), 2.08 (dq, J = 7.4 and 7.3 Hz, 2H, CH_2), 3.37 (t, J = 7.3 Hz, 1H, C*H*), 3.81 (s, 3H, OCH_3), 7.05 (ddd, J = 8.0, 7.5 and 1.5 Hz, 1H, Ph), 7.27 (ddd, J = 8.3, 7.5 and 1.5 Hz, 1H, Ph), 7.38 (dd, J = 8.0 and 1.5 Hz, 1H, Ph), 8.36 (dd, J = 8.3 and 1.5 Hz, 1H, Ph), 9.15 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.87 (*C*H_3), 25.27 (*C*H_2), 52.74 (O*C*H_3), 55.18 (*C*H), 121.62 (Ph), 123.19 (Ph), 124.77 (Ph), 127.50 (Ph), 128.99 (Ph), 134.35 (Ph), 166.24 (NH*C*O), 172.50 (*C*O). Anal. Calcd for $C_{12}H_{14}ClNO_3$: C, 56.37; H, 5.52; N, 5.48. Found: C, 56.60; H, 5.40; N, 5.46.

Property of 5ia: colorless needles (mp 143.0−144.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3247 (N−H), 1718 (C═O), 1693 (C═O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.66 (d, J = 7.0 Hz, 3H, CH_3), 3.61 (q, J = 7.0 Hz, 1H, C*H*), 3.87 (s, 3H, OCH_3), 7.45−7.59 (m, 3 H, naphth), 7.68 (d, J = 8.1 Hz, 1H, naphth), 7.87 (d, J = 7.7 Hz, 1H, naphth), 7.94 (d, J = 8.6 Hz, 1H, naphth), 8.08 (d, J = 7.1 Hz, 1H, naphth), 9.33 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.10 (*C*H_3), 47.25 (*C*H), 52.92 (O*C*H_3), 119.60 (naphth), 120.33 (naphth), 125.38 (naphth), 125.64 (naphth), 125.86 (naphth), 126.33 (naphth), 126.49 (naphth), 128.66 (naphth), 132.11 (naphth), 133.97 (naphth), 167.06 (NH*C*O), 173.92 (*C*O). Anal. Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 69.79; H, 5.99; N, 5.21.

Property of 5ib: colorless needles (mp 104.0−106.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3357 (N−H), 1720 (C═O), 1697 (C═O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.09 (t, J = 7.4 Hz, 3H, CH_3), 2.16 (dq, J = 7.4 and 7.3 Hz, 2H, CH_2), 3.45 (t, J = 7.3 Hz, 1H, C*H*), 3.86 (s, 3H, OCH_3), 7.45−7.59 (m, 3H, naphth), 7.68 (d, J = 8.4 Hz, 1H, naphth), 7.87 (d, J = 7.8 Hz, 1H, naphth), 7.95 (d, 8.1 Hz, 1H, naphth), 8.10 (d, J = 7.5 Hz, 1H, naphth), 9.45 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.86 (*C*H_3), 25.90 (*C*H_2), 52.72 (O*C*H_3), 54.63 (*C*H), 119.43 (naphth), 120.31 (naphth), 125.27 (naphth), 125.64 (naphth), 125.84 (naphth), 126.31 (naphth), 126.47 (naphth), 128.62 (naphth), 132.09 (naphth), 133.94 (naphth), 166.54 (NH*C*O), 173.89 (*C*O). Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 70.70; H, 6.27; N, 4.86.

Property of 5ja: colorless needles (mp 76.0−78.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3507 (N−H), 1737 (C═O), 1704 (C═O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.53 (d, J = 7.4 Hz, 3H, CH_3), 3.47 (q, J = 7.4 Hz, 1H, C*H*), 3.79 (s, 3H, OCH_3), 6.32 (d, J = 3.3 Hz, 1H, furyl), 6.36 (dd, J = 3.3 and 1.4 Hz, 1H, furyl), 7.05 (d, J = 1.4 Hz, 1H, furyl), 9.07 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.30 (*C*H_3), 46.45 (*C*H), 52.91 (O*C*H_3), 95.25 (furyl), 111.39 (furyl), 135.31 (furyl), 144.75 (furyl), 164.74 (NH*C*O), 172.61 (*C*O). Anal. Calcd for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.70; H, 5.70; N, 7.25.

Property of 5jb: colorless needles (mp 46.0−48.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3333 (N−H), 1724 (C═O), 1704 (C═O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.99 (t, J = 7.4 Hz, 3H, CH_3), 2.03 (dq, J = 7.4 and 7.3 Hz, 2H, CH_2), 3.34 (t, J = 7.3 Hz, 1H, C*H*), 3.78 (s, 3H, OCH_3), 6.32 (d, J = 3.0

Hz, 1H, furyl), 6.36 (dd, J = 3.0 and 1.9 Hz, 1H, furyl), 7.05 (d, J = 1.9 Hz, 1H, furyl), 9.15 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.74 (*C*H_3), 25.15 (*C*H_2), 52.73 (O*C*H_3), 53.83 (*C*H), 95.23 (furyl), 111.38 (furyl), 135.28 (furyl), 144.75 (furyl), 164.28 (NH*C*O), 172.64 (*C*O). Anal. Calcd for $C_{10}H_{13}NO_4$, C, 56.86; H, 6.20; N, 6.63. Found: C, 56.72; H, 6.37; N, 6.56.

Property of 5ka: colorless liquid (bp 230−240 °C/0.25 Torr). IR (neat): 3245 (N−H), 1724 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.39 (d, J = 7.2 Hz, 3H, C*H*$_3$), 2.43 (s, 3H, C*H*$_3$), 3.34 (q, J = 7.2 Hz, 1H, C*H*), 3.72 (s, 3H, OC*H*$_3$), 7.32−7.34 (m, 2H, Ph), 7.92−7.97 (m, 2H, Ph), 9.51 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.10 (*C*H_3), 21.76 (*C*H_3), 46.83 (*C*H), 53.10 (O*C*H_3), 128.39 (Ph), 129.43 (Ph), 135.18 (Ph), 145.05 (Ph), 166.39 (NH*C*O), 171.28 (*C*O). Anal. Calcd for $C_{12}H_{15}NO_5S$: C, 50.52; H, 5.30; N, 4.91. Found: C, 50.23; H, 5.31; N, 4.92.

Property of 5kb: colorless needles (mp 85.5−87.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3259 (N−H), 1727 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, J = 7.4 Hz, 3H, C*H*$_3$), 1.88 (dq, J = 7.4 and 7.0 Hz, 2H, C*H*$_2$), 2.43 (s, 3H, C*H*$_3$), 3.18 (t, J = 7.0 Hz, 1H, C*H*), 3.73 (s, 3H, OC*H*$_3$), 7.31−7.34 (m, 2H, Ph), 7.93−7.96 (m, 2H, Ph), 9.53 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.42 (*C*H_3), 21.78 (*C*H_3), 24.73 (*C*H_2), 52.94 (O*C*H_3), 54.01 (*C*H), 128.39 (Ph), 129.41 (Ph), 135.26 (Ph), 145.01 (Ph), 165.97 (NH*C*O), 171.65 (*C*O). Anal. Calcd for $C_{13}H_{17}NO_5S$: C, 52.16; H, 5.72; N, 4.68. Found: C, 51.94; H, 5.64; N, 4.64

Property of 5la: colorless needles (mp 104.5−105.0 °C) from ethyl acetate and hexane. IR ($CHCl_3$): 3403 (N−H), 1721 (C═O), 1698 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 (d, J = 7.4 Hz, 3H, C*H*$_3$), 3.74 (s, 3H, OC*H*$_3$), 4.34 (q, J = 7.4 Hz, 1H, C*H*), 7.46−7.53 (m, 2H, Ph), 7.57−7.62 (m, 1H, Ph), 7.90−7.93 (m, 2H, Ph), 9.60 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.63 (*C*H_3), 47.82 (*C*H), 52.59 (O*C*H_3), 127.76 (Ph), 128.77 (Ph), 132.12 (Ph), 133.23 (Ph), 165.42 (NH*C*O), 171.17 (*C*O), 171.70 (*C*O). Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95. Found: C, 61.10; H, 5.48; N, 5.78.

Property of 5ma: colorless needles (mp 77.0−79.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3384 (N−H), 1725 (C═O), 1687 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.46 (d, J = 7.4 Hz, 3H, C*H*$_3$), 3.34 (q, J = 7.4 Hz, 1H, C*H*), 3.72 (s, 3H, OC*H*$_3$), 4.41 (dd, J = 14.9 and 5.9 Hz, 1H, PhC*H*), 4.47 (dd, J = 14.9 and 5.9 Hz, 1H, PhC*H*), 6.80 (bs, 1H, N*H*), 7.24−7.35 (m, 5H, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.14 (*C*H_3), 43.72 (*C*H_2), 46.75 (*C*H), 52.51 (O*C*H_3), 127.38 (Ph), 127.48 (Ph), 128.58 (Ph), 137.83 (Ph), 168.59 (NH*C*O), 172.51 (*C*O). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.18; H, 6.88; N, 6.32.

Property of 5na: colorless needles (mp 43.0−44.0 °C) from ethyl acetate and hexane. IR (CCl_4): 3386 (N−H), 1725 (C═O), 1687 (C═O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.47 (d, J = 7.4 Hz, 3H, C*H*$_3$), 3.33 (q, J = 7.4 Hz, 1H, C*H*), 3.75 (s, 3H, OC*H*$_3$), 3.90 (t, J = 5.5 Hz, 2H, NHC*H*$_2$), 5.15 (dd, J = 8.6 and 1.5 Hz, 1H, C*H*═CHCH$_2$), 5.19 (dd, J = 16.5 and 1.5 Hz, 1H, C*H*═CHCH$_2$), 5.84 (ddt, J = 16.5 and 8.6 and 5.5 Hz, 1H, CH$_2$═C*H*CH$_2$), 6.55 (bs, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.13 (*C*H_3), 41.96 (*C*H_2), 46.68 (*C*H), 52.49 (O*C*H_3), 116.14 (*C*H$_2$═CH), 133.67 (CH$_2$═*C*H), 168.56 (NH*C*O), 172.53 (*C*O). Anal. Calcd for $C_8H_{13}NO_3$: C, 56.13; H, 7.65; N, 8.18. Found: C, 55.87; H, 7.86; N, 8.20.

Hydrosilylation of 2a with 3 Catalyzed by 4a. To a solution of [Rh(cod){P(OPh)$_3$}$_2$]OTf (93 mg, 0.095 mmol) in CH_2Cl_2 (4 mL) was added a mixture of methyl acrylate **2a** (861 mg, 10.0 mmol) and diethylmethylsilane **3** (1.04 g, 10.2 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was then refluxed for 3 h under N_2 atmosphere. The solvent was distilled under atmospheric pressure, and the residue was distilled under reduced pressure to give **7** (1.43 g, 7.57 mmol) in 76% yield as a colorless liquid (116−118 °C/90 Torr) and as a mixture of two stereoisomers.

Spectral Data for 7. ^{1}H NMR (300 MHz, $CDCl_3$): for *Z* isomer; δ 0.01 (s, 3H, Si−C*H*$_3$), 1.18 (d, J = 7.1 Hz, 3H, C*H*$_3$), 2.13 (q, J = 7.1 Hz, 1H, C*H*), 3.63 (s, 3H, OC*H*$_3$). for *E* isomer; δ 0.00 (s, 3H, Si−C*H*$_3$), 1.16 (d, J = 7.7 Hz, 3H, C*H*$_3$), 2.33 (q, J = 7.7 Hz, 1H, C*H*), 3.67 (s, 3H, OC*H*$_3$).

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