Transition-Metal-Catalyzed Reactions of Propargylamine with Carbon Dioxide and Carbon Disulfide

Min Shi* and Yu-Mei Shen

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry,
Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

mshi@pub.sioc.ac.cn

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The reactions of propargylamine derivatives with carbon dioxide and carbon disulfide have been systematically examined in the presence of transition-metal catalysts. $Pd(OAc)_2$ is the best catalyst for the formation of the corresponding oxazolidinones. In addition, we found that, in the reaction of propargylamine with carbon dioxide catalyzed by palladium(0) metal catalyst in toluene, both oxazolidinone **1** and imidazolidinone **2** could be obtained under mild reaction conditions at the same time. The reaction of **1** with primary and secondary amines has been examined. A plausible reaction mechanism for the formation of **2** was proposed. In addition, in this paper, we first disclosed the ligand's effect on this reaction. Using PBu^t_3 as a ligand with $Pd_2(dba)_3$, **1** was exclusively formed in 90% yield.

Carbon dioxide is the earth's most abundant carbon resource and is used by green plants and anaerobic bacteria for chemicals production on a massive scale. In contrast, man's industrial and laboratory utilization of CO_2 as a chemical feedstock is miniscale. During the last two decades of the twentieth century, the chemistry of carbon dioxide has received much attention from the viewpoint of carbon resources and environmental problems.[1] In particular, fixation of CO_2 by transition-metal catalysts has made significant progress. One of the major successes is the utilization of propargylic alcohol derivatives and carbon dioxide as the starting materials to prepare cyclic carbonate in the presence of a metal catalyst such as ruthenium,[2] cobalt,[3] palladium,[4−6] copper,[7−11] or phosphine compounds.[12] This strategy is fundamentally based on the cyclization of the propargylic carbonate species into the corresponding α-alkylidene cyclic carbonate in the presence of metal catalyst. These cyclic carbonates are useful intermediates for the synthesis of functional carbamates, esters, or oxazolidinone compounds and their unsaturated derivatives,[13] such as β-oxopropyl carbonates,[14] furanones,[15] dihydrofuranones,[16] cyclic carbamates,[17] and keto alcohols.[4]

However, until now we only found two reports related with the reaction of N-substituted propargylamines with CO_2 to give oxazolidinones in moderate yields: (1) the reaction of N-substituted propargylamines with carbon dioxide in the presence of a (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium [Ru(COD)(COT)] catalyst and tertiary phosphine;[18] (2) base-catalyzed direct introduction of CO_2 into acetylenic amines.[19] The reaction of N-unsubstituted propargylamine with carbon dioxide has not been investigated so far, although the reaction mechanism should be very similar to that of propargylic alcohol.

Herein, we wish to report an unprecedented Pd(0)-catalyzed reaction of N-unsubstituted and N-substituted propargylamine with carbon dioxide. During our own investigations, we found that both oxazolidinone **1** and imidazolidinone **2** could be obtained in moderate yield (40%) at the same time from the $Pd(PPh_3)_4$ (5 mol %) catalyzed reaction of propargylamine with carbon dioxide under mild reaction conditions (Scheme 1, Table 1, entry 1). The scope and limitations of catalysts and reaction conditions have been carefully examined. Their results are summarized in Table 1. The reaction temperature and time and the pressure of CO_2 are important factors

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* To whom correspondence should be addressed. Fax: 86-21-64166128.

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Scheme 1

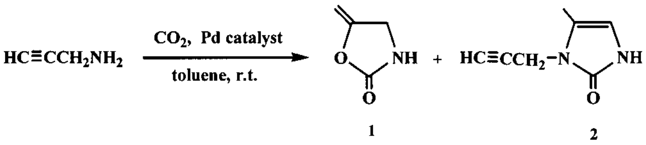
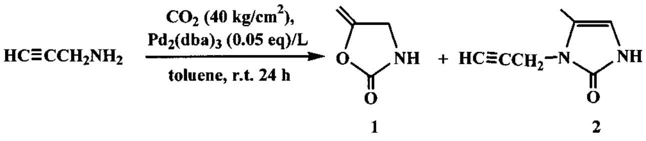


Table 1. Reactions of Proparylamine with Carbon Dioxide in the Presence of Pd Catalyst

entry	catalyst[a]	pressure (kg/cm^2)	T (°C)	time (h)	yield[b] (%) 1	yield[b] (%) 2
1	$Pd(PPh_3)_4$	1	20	60	trace	20
2	$Pd(PPh_3)_4$	40	20	24	35	8
3	$Pd(PPh_3)_4$	40	60	24	7	36
4	$Pd(PPh_3)_4$	40	20	60	8	32
5	$Pd_2(dba)_3$	40	20	24	36	8
6	$Pd(OAc)_2$	40	20	24	85	0
7	$RuH_4(PPh_3)_2$	40	20	24	trace	0
8	$IrCl(CO)(PPh_3)_2$	40	20	24	trace	0
9	$NiBr_2(PPh_3)_2$	40	20	24		0

[a] 0.5 equiv of catalyst. [b] Isolated yield.

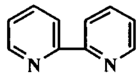
Scheme 2



to affect the selectivity of **1** and **2**. For example, the yield of **2** increased as the reaction temperature rising or if the reaction time was prolonged from 24 to 60 h (Table 1, entries 3 and 4). When the reaction was carried out under high pressure of CO_2 (40 kg/cm^2) for 24 h at room temperature, **1** could be obtained as the major product in 30% yield, along with the formation of 4% of **2**. These results suggested that **2** might be derived from the further reaction of **1** with propargylamine. Using $Pd_2(dba)_3$ (5 mol %) as a catalyst, the similar result was obtained (Table 1, entry 5). However, in the presence of $Pd(OAc)_2$ (5 mol %), **1** was obtained as a sole product in very good yield (Table 1, entry 6). By means of ruthenium [$RuH_4(PPh_3)_2$], Vaska-type complex [$IrCl(CO)(PPh_3)_2$], or nickel catalyst [$NiBr_2(PPh_3)_2$] (Table 1, entries 7–9), oxazolidinone **1** was produced in very low yield under the same reaction conditions. Only Pd catalysts [Pd(0) or Pd(II)] have catalytic activity for the reaction of propargylamine with CO_2. The structures of **1** and **2** were determined by spectroscopic data and microanalyses. Furthermore, the crystal structures of **1** and **2** were unambiguously disclosed by X-ray analyses.

To improve the yields of **1** and **2** and clarify the selectivity of **1** and **2** in the presence of Pd(0) catalyst, we examined the ligand's effect in this reaction. Surprisingly, we found that, using ethylenebis(diphenylphosphine), tributyphosphine, tri(*tert*-butyl)phosphine, or 2,2′-bipyridine (6 mol %) as ligand with $Pd_2(dba)_3$ (5 mol %), the yield of **1** can be significantly improved, along with only a trace amount of **2** (Scheme 2, Table 2, entries 1–4). In particular, when tri(*tert*-butyl)phosphine (PBu^t_3) was used as a ligand, the yield of **1** could reach 90% without formation of **2** (Table 2, entry 4). The combination of $Pd(OAc)_2$ (5 mol %) with tri(*tert*-butyl)phosphine (5 mol %) gave 81% of **1** (Table 2, entry 5). Concerning the tri(*tert*-butyl)phosphine ligand's effect, Fu also reported recently its significant effect in the Suzuki coupling reaction.[20] This is a very novel case in the palladium-catalyzed fixation of CO_2 reaction.

Table 2. Ligand Effects in the Reaction of Propargylamines with Carbon Dioxide

Entry	L	Yield [%][a] 1	Yield [%][a] 2
1		54	trace
2		40	trace
3	PBu_3	60	trace
4	PBu^t_3	90	–
5	$Pd(OAc)_2$ + PBu^t_3	81	–

[a] Isolated yield.

Scheme 3

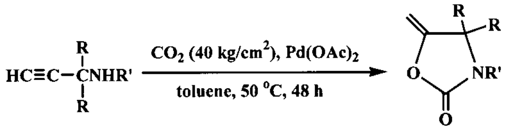
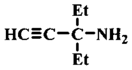
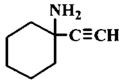


Table 3. Reaction of Propargylamine with CO_2 in the Presence of Pd^{II} Catalyst

Entry	amines	product No.	yield [%][a]
1	 $HC\equiv C-C(Et)_2-NH_2$	3	85
2		4	50
3	$HC\equiv CCH_2NHCH_2Ph$	5	80
4	$HC\equiv CCH_2NH(CH_2)_3Ph$	6	70

[a] Isolated yield.

Scheme 4

$$Ph-C\equiv CCH_2NH_2 \xrightarrow[\text{toluene, r.t. or 50 °C, 36 h}]{CO_2\ (40\ kg/cm_2),\ Pd(OAc)_2\ (0.05\ eq)} \text{complicated products}$$

For other propargylamines including *N*-benzyl-substituted propargylamine, Pd(0) catalyst showed no activity. But when $Pd(OAc)_2$ was used as a catalyst, high yields of cyclic carbamates (**3**–**6**) were obtained as the sole product (Scheme 3, Table 3). The internal alkyne gave many unidentified products under the same conditions (Scheme 4). Thus, we explored a very useful chemical process for the preparation of oxazolidinones from propargylamine derivatives with CO_2 in the presence of Pd catalysts.

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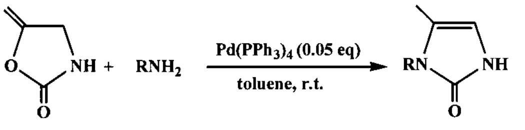
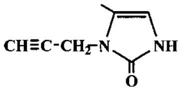
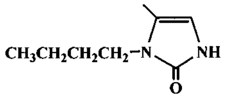
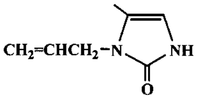
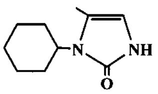
Scheme 5



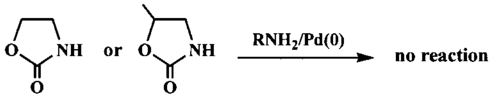
2: R= propargyl; 7: R = butyl; 8: R = propenyl; 9: R = cyclohexyl

Table 4. Preparation of Enol Urethanes from the Reaction of Carbamate 1 with Primary Amines in the Presence of Pd(PPh$_3$)$_4$ (0.1 Equiv) in Toluene at Room Temperature

Entry	amines	product	yield [%][a]
1	propargylamine	 CH≡C-CH$_2$-N NH	70
2	butylamine	 CH$_3$CH$_2$CH$_2$CH$_2$-N NH	60
3	propenylamine	 CH$_2$=CHCH$_2$-N NH	62
4	cyclohexylamine	 N NH	54

[a] Isolated yield.

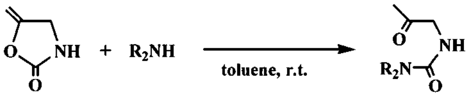
Scheme 6



To the best of our knowledge, the formation of imidazolidinone **2** from the fixation of CO$_2$ with propargylamine has never been reported before. Only Murai reported that palladium-catalyzed reaction of 5-methylene-1,3-dioxolan-2-ones with aromatic isocyanates underwant cycloaddition to give the corresponding oxazolidinones in good yields together with cyclic ureas.[17] To gain more mechanistic insights into this novel reaction, we directly carried out the reaction of **1** with propargylamine or some other amines, such as butylamine, propenylamine, and cyclohexylamine, respectively, in toluene under the same reaction conditions (Scheme 5). We found that the corresponding imidazolidinons **2**, **7**, **8**, and **9** were obtained in moderate yields as well (Table 4). No reactions occurred without Pd(0) catalyst. However, the reaction of **1** with benzylamine (PhCH$_2$NH$_2$) or phenethylamine [PhCH(CH$_3$)NH$_2$] gave very complicated products under the same reaction conditions. On the basis of these results shown in Table 4, it is very clear that the imidazolidinone **2** was in fact formed from the further Pd(0)-catalyzed reaction of **1** with propargylamine, and a novel reaction process for the preparation of imidazolidinones from oxazolidinones **1** has been explored.

It should be emphasized here that, as shown in Scheme 6, for 2-oxazolidione, no reaction occurred with primary amines even in the presence of Pd(0) catalyst. This result suggested that, the olefinic moiety in 2-oxazolidione derivatives must be required for the further reactions of oxazolidinones with primary amines to give the corresponding imidazolidinones.

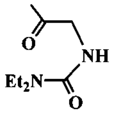
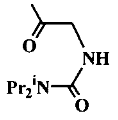
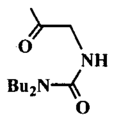
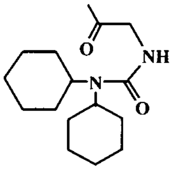
Scheme 7



10-13

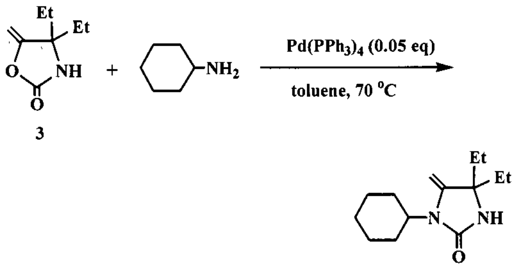
10: R= ethyl; 11: R = isopropyl; 12: R = butyl; 13: R = cyclohexyl

Table 5. Preparation of Urethanes from the Reaction of Carbamate 1 with Secondary Amines in Toluene at Room Temperature

Entry	amines	product	yield [%][a]
1	diethylamine	 NH Et$_2$N	98
2	diisopropylamine	 NH Pr$_2^i$N	98
3	dibutylamine	 NH Bu$_2$N	97
4	dicyclohexylamine	 NH N	96

[a] Isolated yield.

Scheme 8

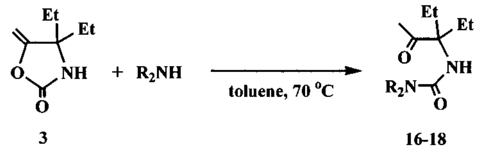


14, 2%

On the other hand, in the reactions of **1** with secondary amines, the ring-opened products **10**−**13** were obtained quantitatively even without palladium catalyst (Scheme 7, Table 5). Using **3** as a substrate in the reaction with primary amine (cyclohexylamine), we found that the corresponding cyclic urethane **14** was obtained in only 2% yield under the same conditions (Scheme 8). In addition, in the reactions of **3** with secondary amines, the ring-opened products **15**−**17** were formed in moderate yields as well (Scheme 9, Table 6).

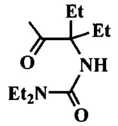
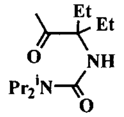
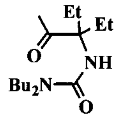
Based on these investigations, we tentatively proposed a plausible mechanism for the formation of **2**, **7**−**9**, and **14** in Scheme 10. The oxazolidinone **1** undergoes a palladium(0)-catalyzed amination reaction of olefin with primary amines to form the intermediate **I**, and then the amine adds to the carbonyl group of intermediate **I** via an intramolecular attacking process giving the intermediate **II**. Dehydration of the intermediate **II** affords the intermediate **III**, which produces the final product by

Scheme 9



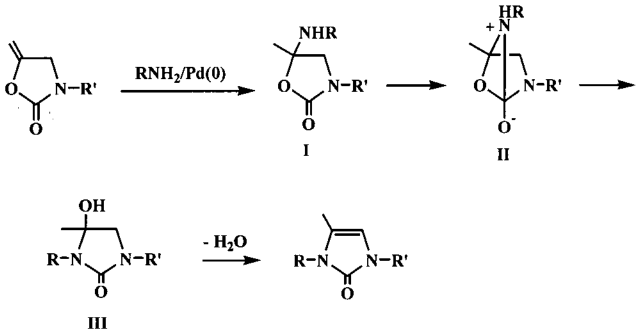
15: R= ethyl; 16: R = isopropyl; 17: R = butyl

Table 6. Preparation of Urethanes from the Reaction of Carbamate 1 with Secondary Amines in Toluene at Room Temperature

Entry	amines	product	yield [%]$^{a)}$
1	diethylamine		70
2	diisopropylamine		76
3	dibutylamine		78

[a] Isolated yield.

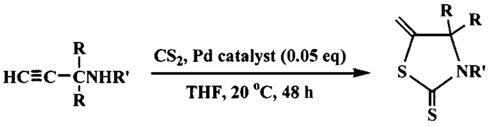
Scheme 10



reductive elimination and regenerate the palladium(0) catalyst. For secondary amines, owing to their high nucleophilicities, the direct attacking to the carbonyl group of **1** can take place to give the corresponding ring-opened product **10**−**13**. In the reaction of oxazolidinone **3** with primary amine, its sterical bulkiness might block out the palladium(0)-catalyzed amination of olefin to give the corresponding imidazolidinone in very low yield. Its sterical bulkiness also caused the relatively low yields of **15**−**17** in the reaction of **3** with secondary amines by comparison of the reactions of **1** with secondary amines (Table 5).

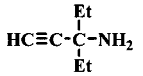
Moreover, we also examined the reaction of propargylamine with carbon disulfide, an analogue of carbon dioxide, under the same reaction conditions. For propargylamine, the reaction proceeded very well in the presence of Pd(0) (5 mol %) catalyst to give **18** in 99% yield at room temperature (Scheme 11, Table 7, entry 1). But for 1,1-diethylpropargylamine and *N*-benzylpropargylamine, the reaction required to be carried out at higher temperature to give **19** and **20** in moderate yields, respectively (Scheme 11).

Scheme 11



18: R= H, R'= H;
19: R= Et, R'= H;
20: R= H, R'= CH_2Ph.

Table 7. Reaction of Propargylamine with CS_2 in the Presence of Pd(0) Catalyst

Entry	amines	Pd catalyst	yield [%]$^{a)}$
1	$HC{\equiv}C{\cdot}CH_2NH_2$	$Pd(PPh_3)_4$	99
2	 $HC{\equiv}C{\cdot}\underset{Et}{\overset{Et}{C}}{-}NH_2$	$Pd(OAc)_2$	40
3	$HC{\equiv}C{-}CH_2{-}NHCH_2Ph$	$Pd(OAc)_2$	25

[a] Isolated yield.

In conclusion, the reactions of propargylamine derivatives with carbon dioxide and carbon disulfide have been systematically examined in the presence of transition metal catalysts. $Pd(OAc)_2$ (5 mol %) is the best catalyst for the formation of the corresponding oxazolidinones. We found that oxazolidinones **1** and imidazolidinones **2** could be obtained from the reaction of propargylamine with carbon dioxide in the presence of a catalytic amount of Pd(0) metal−tertiary phosphine system in toluene. Either **1** or **2** can be obtained as the major product by changing the reaction conditions. A novel transition-metal-catalyzed reaction for the formation of imidazolidinones **2**−**5** was explored from reactions of **1** with proparylamines, butylamine propenylamine, and cyclohexylamines under mild reaction conditions. Efforts are underway to elucidate the mechanistic details of this reaction and to identify systems enabling the similar carboxylation of other substrates and subsequent transformation thereof.

Experimental Section

General Methods. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Coupling constants (*J*) are reported in hertz. Mass spectra were recorded by EI methods, and HRMS was measured on a Finnigan MA+ mass spectrometer. Organic solvents used were dried by standard methods when necessary. All solid compounds reported in this paper gave satisfactory CHN microanalyses. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300−400 mesh silica gel at increased pressure.

General Procedure for the Formation of Oxazolidinones 1 and Imidazolidinones 2. Formation of 1. To a solution of propargylamine (550 mg, 10 mmol) in anhydrous toluene (20 mL) was added a catalytic amount of $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), and the reaction mixture was stirred at room temperature under carbon dioxide atmosphere (40 kg/cm^2) for 24 h. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 1/4) to give **1** as a white solid. This solid was further recrystallized from dichloromethane/petroleum ether = 1/4 to afford a crystal: 350 mg, 35%; mp 50−52 °C; IR ($CHCl_3$) ν 1780 cm^{-1} (C=O); ^1H

NMR (300 MHz, CDCl$_3$, TMS) δ 4.20 (2H, dd, $J = 2.1$ 1.0, CH$_2$), 4.31 (1H, dd, $J = 2.9$ 2.1, CH$_2$), 4.78 (1H, dd, $J = 2.1$ 2.1, CH$_2$), 5.77 (1H, s, NH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ 44.35, 86.86, 151.34, 157.64 (C=O); MS (EI) *m/z* 100 (100) (MH)$^+$, 71 (24.71) (M$^+$ − 28), 43 (66.17) (M$^+$ − 56); HRMS (EI) *m/z* 99.0321, $C_4H_5NO_2$ requires M, 99.0320. Anal. Calcd for $C_4H_5NO_2$: C, 48.48, H, 5.05, N, 14.14. Found: C, 48.39, H, 5.03, N, 14.15.

Formation of 2. This compound was obtained as a white solid in the same manner as that described above using propargylamine (550 mg, 10 mmol) and a catalytic amount of Pd(PPh$_3$)$_4$ (58 mg, 0.05 mmol) at 60 °C: 490 mg, 36%; mp 122−124 °C; IR (CHCl$_3$) ν 1682 cm^{-1} (C=O); ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 2.14 (3H, s, CH$_3$), 2.24 (1H, dd, $J = 2.6$ 2.2, CH), 4.42 (2H, d, $J = 2.6$, CH$_2$), 6.02 (1H, s, CH), 9.90 (1H, s, NH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ 10.22, 29.87, 71.87, 78.26, 104.43, 119.44, 154.33 (C=O); MS (EI) *m/z* 136 (100) (M$^+$), 97 (63.98) (M$^+$ − 39), 42 (28.98) (M$^+$ − 94). Anal. Calcd for $C_7H_8N_2O$: C, 61.76, H, 5.88, N, 20.59. Found: C, 61.66, H, 6.14, N, 20.67.

Formation of 3. This compound was obtained as a colorless oil in the same manner as that described above using 1,1-diethylpropargylamine (1.10 g, 10 mmol), but using Pd(OAc)$_2$ (110 mg, 0.05 mmol) as a catalyst: 1.32 g, 85%; IR (CHCl$_3$) ν 1777 cm^{-1} (C=O); ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 0.94 (6H, t, $J = 7.4$ Hz, CH$_3$), 1.50−1.80 (4H, m, CH$_2$), 4.13 (1H, d, $J = 3.3$, CH), 4.76 (1H, d, $J = 3.3$, CH), 5.97 (1H, s, NH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ 7.68, 33.13, 65.95, 84.91, 156.57, 159.01 (C=O); MS (EI) *m/z* 155 (7.8) (M$^+$), 126 (100) (M$^+$ − 29), 112 (9.7) (M$^+$ − 43); HRMS (EI) *m/z* 155.0935, $C_8H_{13}NO_2$ requires M, 155.0946.

Formation of 4. This compound was obtained as a colorless oil in the same manner as that described above using 1-ethynylcyclohexylamine (1.23 g, 10 mmol), but using Pd(OAc)$_2$ (110 mg, 0.05 mmol) as a catalyst: 0.84 g, 50%; IR (CHCl$_3$) ν 1774 cm^{-1} (C=O); ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 1.20−1.40 (2H, m, CH$_2$), 1.40−1.80 (4H, m, CH$_2$), 1.80−2.0 (4H, m, CH$_2$), 4.23 (1H, d, $J = 3.3$, CH), 4.66 (1H, d, $J = 3.3$ Hz, CH), 8.0 (1H, s, NH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ 7.41, 25.45, 26.19, 28.58, 34.10, 52.54, 79.06, 150.23, 162.30 (C=O); MS (EI) *m/z* 167 (58) (M$^+$), 139 (40) (M$^+$ − 28), 124 (100) (M$^+$ − 43); HRMS (EI) *m/z* 167.0944, $C_9H_{13}NO_2$ requires M, 167.0946.

Formation of 5. This compound was obtained as a colorless oil in the same manner as that described above using *N*-benzylpropargylamine (1.45 g, 10 mmol), but using Pd(OAc)$_2$ (110 mg, 0.0 5 mmol) as a catalyst: 1.50 g, 80%; IR (CHCl$_3$) ν 1784 cm^{-1} (C=O); ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 4.02 (2H, t, $J = 2.4$ Hz, CH$_2$), 4.22−4.25 (1H, m, CH), 4.47 (2H, s, CH$_2$), 4.72−4.75 (1H, m, CH), 7.20−7.40 (5H, m, Ar); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ 47.18, 47.78, 86.66, 128.10, 128.18, 128.91, 134.94, 148.94, 155.59 (C=O); MS (EI) *m/z* 189 (13) (M$^+$), 91 (100) (M$^+$ − 98), 65 (12) (M$^+$ − 124); HRMS (EI) *m/z* 189.0789, $C_{11}H_{11}NO_2$ requires M, 187.0790.

Formation of 6. This compound was obtained as a colorless oil in the same manner as that described above using *N*-(3-phenylpropyl)propargylamine (1.73 g, 10 mmol), but using Pd(OAc)$_2$ (110 mg, 0.0 5 mmol) as a catalyst: 1.52 g, 70%; IR (CHCl$_3$) ν 1781 cm^{-1} (C=O); ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 1.88 (2H, quint, $J = 7.6$ Hz, CH$_2$), 2.65 (2H, t, $J = 7.6$ Hz, CH$_2$), 3.33 (2H, t, $J = 7.6$ Hz, CH$_2$), 4.12 (2H, t, $J = 2.7$ Hz, CH$_2$), 4.28 (1H, dd, $J = 4.4$, 2.0 Hz, CH$_2$), 4.72 (1H, dd, $J =$ 4.4, 2.0 Hz, CH$_2$), 7.20−7.40 (5H, m, Ar); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ 28.63, 32.64, 43.22, 47.56, 86.21, 125.94, 128.09, 128.30, 140.68, 148.95, 155.38 (C=O); MS (EI) *m/z* 217 (82) (M$^+$), 174 (23) (M$^+$ − 43), 91 (100) (M$^+$ − 126); HRMS (EI) *m/z* 217.1112, $C_{13}H_{15}NO_2$ requires M, 217.1103.

Formation of 7. To a solution of **1** (100 mg, 1.0 mmol) and Pd(PPh$_3$)$_4$ (5.8 mg, 0.005 mmol) catalyst in anhydrous toluene (10 mL) was added butylamine (79 mg, 1.1 mmol), and the reaction mixture was stirred at room temperature for 24 h. The solution was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc =1/4) to give **7** as a viscous oily product: 93 mg, 60%; IR (CHCl$_3$) ν 1672 cm^{-1} (C=O); ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 0.94 (3H, t, $J = 7.3$, CH$_3$), 1.40−1.26 (2H, m, CH$_2$), 1.56−1.64 (2H, m, CH$_2$), 2.06 (3H, s, CH$_3$), 3.58 (2H, t, $J = 7.3$, CH$_2$), 5.99 (1H, s, CH), 9.98 (1H, s, NH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ 10.37, 13.79, 20.05, 31.87, 40.64, 103.92, 119.52, 154.91 (C=O); MS (EI) *m/z* 154 (51.45) (M$^+$), 98 (64.60) (M$^+$ − 56), 73 (100) (M$^+$ − 81), 44 (89.04) (M$^+$ − 110); HRMS (EI) *m/z* 154.1117, $C_8H_{13}N_2O$ requires M, 154.1106.

Formation of 8. This compound was obtained as a colorless oil in the same manner as that described above using **1** (100 mg, 1.0 mmol), propenylamine (63 mg, 1.10 mmol), and Pd(PPh$_3$)$_4$ (5.8 mg, 0.005 mmol): 86 mg, 62%; IR (CHCl$_3$) ν 1714 cm^{-1} (C=O); ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 2.01 (3H, s, CH$_3$), 4.25 (2H, dd, $J = 2.6$ 2.0, CH$_2$), 5.08 (1H, dd, $J = 15.9$ 1.0, CH), 5.17 (1H, d, $J = 10.3$, CH), 5.82−5.95 (1H, m, CH), 6.02 (1H, s, CH), 9.65 (1H, s, NH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ 20.21, 42.69, 103.98, 116.12, 119.90, 133.30, 154.77 (C=O); MS (EI) *m/z* 138 (100) (M$^+$), 97 (69.99) (M$^+$ − 41), 56 (40.14) (M$^+$ − 82), 41 (47.26) (M$^+$ − 97); HRMS (EI) *m/z* 138.0796, $C_7H_{10}N_2O$ requires M, 138.0793.

Formation of 9. This compound was obtained as a white solid in the same manner as that described above using **1** (100 mg, 1.0 mmol), cyclohexylamine (109 mg, 1.10 mmol), and Pd(PPh$_3$)$_4$ (5.8 mg, 0.005 mmol): 97 mg, 54%; mp 100−102 °C; IR (CHCl$_3$) ν 1714 cm^{-1} (C=O); ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 1.28−2.18 (10H, m, cyclohexyl), 2.23 (3H, s, CH$_3$), 3.96−4.04 (1H, m, CH), 6.09(1H, s, CH), 9.58 (1H, s, NH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ 11.96, 25.33, 26.23, 31.10, 53.38, 104.33, 119.62, 156.01 (C=O); MS (EI) *m/z* 180 (19.77) (M$^+$), 98 (85.96) (M$^+$ − 82), 56 (100) (M$^+$ − 124), 43 (88.78) (M$^+$ − 137); HRMS (EI) *m/z* 180.1267, $C_{10}H_{16}N_2O$ requires M, 180.1263.

General Procedure for the Reaction of Oxazolidinones 1 with Secondary Amines. Formation of 10. To a solution of **1** (40 mg, 0.40 mmol) in anhydrous toluene (10 mL) was added diethylamine (32 mg, 0.44 mmol), and the reaction mixture was stirred at room temperature for 24 h. The solution was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/ EtOAc =1/4) to give **10** as a viscous oily compound: 69 mg, 98%; IR (CHCl$_3$) ν 1721 cm^{-1} and 1784 (C=O); ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 1.10 (6H, t, $J = 7.2$ Hz, CH$_3$), 2.16 (3H, s, CH$_3$), 3.25 (4H, q, $J = 7.2$ Hz, CH$_2$), 4.12 (2H, d, $J = 4.4$ Hz, CH$_2$), 5.15 (1H, s, NH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ 13.68, 27.18, 41.53, 51.42, 166.10 (C=O), 204.82 (C=O); MS (EI) *m/z* 172 (4.13) (M$^+$), 129 (46.71) (M$^+$ − 43), 100 (100) (M$^+$ − 72), 72 (65.24) (M$^+$ − 100); HRMS (EI) *m/z* 172.1222, $C_8H_{16}N_2O_2$ requires M, 172.1212.

Formation of 11. This compound was obtained as a viscous oily product in the same manner as that described above using **1** (40 mg, 0.4 mmol) and diisopropylamine (44 mg, 0.44 mmol): 78 mg, 98%; IR (CHCl$_3$) ν 1714 cm^{-1} (C=O); ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 1.24 (12H, d, $J = 7.0$ Hz, CH$_3$), 2.18 (3H, s, CH$_3$), 3.90 (2H, qu, $J = 7.0$ Hz, CH$_2$), 4.18 (2H, d, $J =$ 4.2 Hz, CH$_2$), 5.11 (1H, s, NH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ 20.93, 27.08, 45.56, 51.45, 156.58 (C=O), 204.61 (C=O); MS (EI) *m/z* 200 (15.62) (M$^+$), 185 (42.23) (M$^+$ − 15), 128 (80.54) (M$^+$ − 72), 86 (100) (M$^+$ − 114); HRMS (EI) *m/z* 200.1531, $C_{10}H_{20}N_2O_2$ requires M, 200.1525.

Formation of 12. This compound was obtained as a viscous oily product in the same manner as that described above using **1** (40 mg, 0.4 mmol) and dibutylamine (57 mg, 0.44 mmol): 88 mg, 97%; IR (CHCl$_3$) ν 1721 cm^{-1} (C=O); ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 1.10 (6H, t, $J = 7.2$ Hz, CH$_3$), 1.20−1.35 (2H, m, CH$_2$), 1.40−1.52 (2H, m, CH$_2$), 2.18 (3H, s, CH$_3$), 3.15 (4H, t, $J = 7.2$ Hz, CH$_2$), 4.12 (2H, d, $J = 4.38$, CH$_2$), 5.15 (1H, s, NH); ^{13}C NMR (75 MHz, CDCl$_3$, TMS) δ 13.81, 20.13, 27.11, 30.61, 47.11, 51.43, 157.12 (C=O), 204.51 (C=O); MS (EI) *m/z* 228 (19.32) (M$^+$), 185 (61.88) (M$^+$ − 42), 156 (93.84) (M$^+$ − 71), 86 (100) (M$^+$ − 141); HRMS (EI) *m/z* 228.1800, $C_{12}H_{24}N_2O_2$ requires M, 228.1838.

Formation of 13. This compound was obtained as a white solid in the same manner as that described above using **1** (40 mg, 0.4 mmol) and dicyclohexylamine (80 mg, 0.44 mmol): mp 104−106 °C; 110 mg, 98%; IR (CHCl$_3$) ν 1714 cm^{-1} (C=O); ^{1}H NMR (300 MHz, CDCl$_3$, TMS) δ 0.95−1.53 (8H, m, CH$_2$), 1.50−

2.0 (12H, m, CH_2), 2.20 (3H, s, CH_3), 3.38−3.52 (2H, m, CH_2), 4.16 (2H, d, $J = 4.2$ Hz, CH_2), 5.16 (1H, s, NH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 25.54, 26.46, 27.22, 31.64, 51.58, 55.15, 156.89 (C═O), 204.75 (C═O); MS (EI) m/z 280 (60.61) (M^+), 223 (83.37) ($M^+ - 57$), 138 (100) ($M^+ - 108$); HRMS (EI) m/z 280.2147, $C_{16}H_{28}N_2O_2$ requires M, 280.2152.

Formation of 14. This compound was obtained as a viscous oily product in the same manner as that described above using **3** (62 mg, 0.4 mmol), cyclohexylamine (44 mg, 0.44 mmol), and $Pd(PPh_3)_4$ (23 mg, 0.02 mmol): 2.0 mg, 2%; IR ($CHCl_3$) ν 1788 cm^{-1} (C═O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.83 (6H, t, $J = 7.4$ Hz, CH_3), 1.0−1.40 (6H, m, CH_2), 1.50−1.75 (4H, m, CH_2), 1.76−1.90 (2H, m, CH_3), 2.0−2.20 (2H, m, CH_2), 3.60−3.80 (1H, m, CH), 3.84 (1H, d, $J = 2.4$ Hz, CH), 4.25 (1H, d, $J = 2.4$ Hz, CH), 4.43 (1H, s, NH); MS (EI) m/z 236 (7.56) (M^+), 207 (59.33) ($M^+ - 29$), 125 (100) ($M^+ - 111$); HRMS (EI) m/z 236.1909, $C_{14}H_{24}N_2O$ requires M, 236.1899.

Formation of 15. This compound was obtained as a colorless oil in the same manner as that described above using **3** (62 mg, 0.4 mmol) and diethylamine (32 mg, 0.44 mmol): 64 mg, 70%; IR ($CHCl_3$) ν 1638 and 1707 cm^{-1} (C═O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.65 (6H, t, $J = 7.5$ Hz, CH_3), 1.14 (6H, t, $J = 7.5$ Hz, CH_3), 1.66 (1H, q, $J = 7.5$ Hz, CH_2), 1.68 (1H, q, $J = 7.5$ Hz, CH_2), 2.14 (3H, s, CH_3), 2.53 (1H, q, $J = 7.5$ Hz, CH_2), 2.56 (1H, q, $J = 7.5$ Hz, CH_2), 3.26 (4H, q, $J = 7.5$ Hz, CH_2), 5.73 (1H, s, NH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 8.15, 13.91, 23.28, 27.69, 41.26, 69.79, 155.37 (C═O), 209.83 (C═O); MS (EI) m/z 229 (29.70) (MH^+), 211 (27.6) ($M^+ - 18$), 185 (38.7) ($M^+ - 43$), 100 (100) ($M^+ - 128$); HRMS (EI) m/z 228.1829, $C_{14}H_{24}N_2O$ requires M, 228.1838.

Formation of 16. This compound was obtained as a colorless oil in the same manner as that described above using **3** (62 mg, 0.4 mmol) and diisopropylamine (44 mg, 0.44 mmol): 78 mg, 76%; IR ($CHCl_3$) ν 1700 and 1785 cm^{-1} (C═O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.67 (6H, t, $J = 7.5$ Hz, CH_3), 1.24 (12H, d, $J = 7.0$ Hz, CH_3), 1.60−1.80 (2H, m, CH_2), 2.15 (3H, s, CH_3), 2.50−2.65 (2H, m, CH_2), 4.03 (2H, quintet, $J = 7.0$ Hz, CH), 5.65 (1H, s, NH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 8.24, 13.91, 21.22, 27.78, 33.18, 44.16, 70.36, 155.09 (C═O), 210.04 (C═O); MS (EI) m/z 257 (23.3) (MH^+), 213 (34.3) ($M^+ - 44$), 128 (64.2) ($M^+ - 128$), 86 (100) ($M^+ - 179$); HRMS (EI) m/z 256.2146, $C_{14}H_{28}N_2O_2$ requires M, 256.2151.

Formation of 17. This compound was obtained as a colorless oil in the same manner as that described above using **3** (62 mg, 0.4 mmol) and dibutylamine (57 mg, 0.44 mmol): 89 mg, 78%; IR ($CHCl_3$) ν 1638 and 1707 cm^{-1} (C═O); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 0.67 (6H, t, $J = 7.5$ Hz, CH_3), 0.94 (6H, t, $J = 7.5$ Hz, CH_3), 1.25−1.50 (4H, m, CH_2), 1.50−1.62 (4H, m, CH_2), 1.60−1.80 (2H, m, CH_2), 2.16 (3H, s, CH_3), 2.50−2.65 (2H, m, CH_2), 3.20 (4H, t, $J = 7.5$ Hz, CH_2), 5.75 (1H, s, NH); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 8.18, 13.91, 20.22, 23.28, 27.74, 30.82, 47.17, 69.87, 155.71 (C═O), 209.89 (C═O); MS (EI) m/z 285 (22.6) (MH^+), 241 (48.9) ($M^+ - 44$), 156 (100) ($M^+ - 128$), 57 (58.1) ($M^+ - 227$); HRMS (EI) m/z 282.2466, $C_{16}H_{32}N_2O_2$ requires M, 284.2464.

Formation of 18. To a solution of propargylamine (500 mg, 9.1 mmol) and carbon disulfide (800 mg, 10.5 mmol) in anhydrous toluene (15 mL) was added a catalytic amount of $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol) and triphenylphosphine (PPh_3) (5.24 mg, 0.02 mmol), and the reaction mixture was stirred at room temperature for 24 h. The solution was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc= 1/4) to give **18** as a white solid: 1.2 g, 99%; mp 120−121 °C; IR ($CHCl_3$) ν 1626, 1490, 902 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 4.67 (2H, t, $J = 2.7$ Hz, CH_2), 5.14 (1H, dd, $J = 5.4$, 2.7 Hz, CH_2), 5.24 (1H, dd, $J = 4.8$, 2.4 Hz, CH_2), 7.96 (1H, s, NH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 57.05, 105.67, 141.13, 199.11 (C═S); MS (EI) m/z 131 (M^+), HRMS (EI) m/z 131.9954, $C_4H_6NS_2$ requires M, 131.9942.

Formation of 19. This compound was prepared in the same manner as that described above, but using 1,1-diethylpropargylamine (1.01 g, 9.1 mmol), carbon disulfide (800 mg, 10.5 mmol) and $Pd(OAc)_2$ (102 mg, 0.5 mmol) as a catalyst, to give a white solid: 680 mg, 40%; mp 102−104 °C; IR ($CHCl_3$) ν 1618, 1518, 1062 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.02 (6H, t, $J = 7.4$ Hz, CH_3), 1.70−1.90 (4H, m, CH_2), 5.05 (1H, d, $J = 2.6$ Hz, CH), 5.23 (1H, d, $J = 2.6$ Hz, CH), 7.96 (1H, s, NH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 7.81, 34.60, 79.18, 103.48, 148.27, 195.79 (C═S); MS (EI) m/z 187 (M^+). Anal. Calcd for $C_8H_{13}NS_2$: C, 51.29, H, 6.99, N, 7.48. Found: C, 51.37, H, 6.81, N, 7.46.

Formation of 20. This compound was prepared in the same manner as that described above, but using *N*-benzylpropargylamine (1.32 g, 9.1 mmol), carbon disulfide (800 mg, 10.5 mmol), and $Pd(OAc)_2$ (102 mg, 0.5 mmol) as a catalyst, to give a colorless oil: 503 mg, 25%; IR ($CHCl_3$) ν 1624, 1481, 1079 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 4.57 (2H, t, $J = 2.7$ Hz, CH_2), 5.02 (2H, s, CH_2), 5.08 (1H, dd, $J = 4.9$, 2.8 Hz, CH), 5.13 (1H, dd, $J = 4.9$, 2.8 Hz, CH), 7.30−7.45 (5H, m, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 51.91, 61.17, 104.82, 128.24, 128.34, 129.0, 134.54, 136.08, 194.45 (C═S); MS (EI) m/z 221 (M^+); HRMS (EI) m/z 221.0326, $C_{11}H_{21}NS_2$ requires M, 221.0333.

General Procedure for the Formation of Oxazolidinones 1 and Imidazolidinones 2 under High Pressure of CO_2. Propargylamine (550 mg, 10 mmol), $Pd(PPh_3)_4$ (45 mg, 0.05 mmol), PPh_3 (13 mg, 0.05 mmol), and anhydrous toluene 20 mL and a magnetic stir bar were placed in the 50 mL glass liner of a stainless steel autoclave under a nitrogen purge. The autoclave was purged several times with CO_2 (40 kg/cm^2), sealed, and stirred at room temperature for 24 h. After release of the pressure, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatograph (eluent: petroleum ether/EtOAc = 1/4) to give **1** and **2** as a white solid.

Crystal data of 1: empirical formula, $C_4H_5NO_2$; formula weight, 99.09; crystal color, habit, colorless, column; crystal dimensions, 0.28 × 0.30 × 0.25 mm; crystal system; monoclinic; lattice type, primitive; lattice parameters, $a = 10.776(2)$ Å, $b = 4.552(2)$ Å, $c = 10.073(2)$ Å, $\beta = 109.44^o$, $V = 465.9(2)$ Å^3; space group $P2_1/c$(#14); $Z_{value} = 4$; $D_{calcd} = 1.413$ g/cm^3; $F_{000} = 208.00$; μ(Mo Kα) = 1.15 cm^{-1}; residuals: R; $R_w = 0.068$; 0.138. Its structure has been deposited at the Cambridge Crystallographic Data Centre and has been allocated the deposition no. CCDC 164437.

Crystal data of 2: empirical formula, $C_7H_8N_2O$; formula weight, 136.15; crystal color, habit, colorless, prismatic; crystal dimensions, 0.20 × 0.20 × 0.30 mm; crystal system; monoclinic; lattice type, primitive; lattice parameters, $a = 4.385(4)$ Å, $b = 17.655(4)$ Å, $c = 9.622(3)$ Å, $\beta = 101.26(4)^o$, $V = 730.6(8)$ Å^3; space group $P2_1/c$(#14); $Z_{value} = 4$; $D_{calcd} = 1.238$ g/cm^3; $F_{000} = 288.00$; μ(Mo Kα) = 0.86 cm^{-1}; residuals: R; $R_w = 0.046$; 0.053. Its structure has been deposited at the Cambridge Crystallographic Data Centre and has been allocated the deposition no. CCDC 164438.

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Supporting Information Available: ^{13}C NMR spectra of **1**−**20**; ORTEP diagrams of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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