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Silver-Catalyzed Carbon Dioxide Incorporation and Rearrangement on Propargylic Derivatives

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A silver/DBU catalyst system was developed for the effective synthesis of cyclic carbonate and oxazolidinone from the reaction of CO_2 with propargylic alcohols and propargylic amines, respectively, in high yields under mild conditions. It was found that the [3,3]-sigmatropic Meyer–Schuster-type rearrangement of the propargylic alcohol was mediated by CO_2 in DMF to afford the corresponding α,β-unsaturated carbonyl compounds in high yields. The silver salt combined with the chiral Schiff base ligand could be applied to enantioselective chemical CO_2 incorporation into various bispropargylic alcohols to produce the corresponding cyclic carbonate in high yields with high enantioselectivity. The absolute configuration was determined by VCD spectroscopy as well as by X-ray analysis. These products were found to be active for the aminolysis reaction to afford the corresponding carbamate derivatives in high yields without any loss of optical purity.

An enormous amount of energy has been generated by the oxidation of hydrocarbons in order to make our life comfortable and convenient while generating an enormous amount of CO_2 worldwide.[1] Because the most oxidized form of the carbon derivatives is much less reactive, its application to organic synthesis has been considered to be one of the most challenging research topics. As well as the chemical fixation of CO_2, much effort has been made to utilize CO_2 as an attractive C1 feedstock for organic synthesis due to its ubiquitous, abundant, and nontoxic properties, however due to its lower reactivity, harsh reaction conditions are required to activate and incorporate CO_2 into organic compounds.[2] It is necessary to develop a mild reaction system including catalysts to efficiently capture CO_2 into a wide variety of substrates, especially fine-chemicals. Various synthetic reactions of CO_2 have been reported. Typically enol derivatives,[3] Grignard reagents,[4] and alkyllithium compounds[5] readily react with CO_2 to afford the corresponding carboxylic acids, though a stoichiometric amount of a strong nucleophile is employed. Transition-metals, such as nickel,[6] rhodium,[7] palladium,[8] copper,[2e,9] and gold,[2e] can catalyze the reaction of CO_2 to produce the corresponding carboxylic acid and lactone derivatives. However, it is required to prepare in advance reactants containing a boron, halogen moiety, etc., and the scope and applicability are limited.

It was recently found that a catalytic amount of a silver salt as a π-Lewis acid to activate an alkyne combined with the use of DBU is an efficient catalyst system for the reaction of CO_2 with propargylic derivatives. We now report that a silver salt/DBU combination catalyzes the reaction of CO_2 with propargylic alcohols[10a] and propargylic amines[10b] to produce the corresponding cyclic carbonates and oxazolidinones in good to excellent yields, respectively. We also describe that a Meyer–Schuster-type rearrangement is mediated by CO_2 in the presence of a catalytic amount of silver methanesulfonate and a base to afford the corresponding enones in high yields.[11] We also describe the asymmetric incorporation of CO_2 into bispropargylic alcohol catalyzed by a chiral silver salt derived from silver acetate and Schiff base ligand to give the corresponding chiral cyclic carbonate in good to excellent yields with high enantioselectivity.[12] The reaction mechanism postulated by a computational approach, the determination of the absolute configuration of the optically active cyclic carbonate using VCD spectroscopy and X-ray analysis, and the application of an optically active cyclic carbonate for aminolysis, is also reported.

Results and Discussion

Reaction of CO_2 with Propargylic Alcohols. Numerous reports[13] have been published for the synthesis of cyclic carbonates from CO_2 with a propargylic alcohol. Although many catalysts including metal salts and phosphines have been developed to demonstrate this reaction, harsh reaction conditions are required to achieve high yields, and terminal

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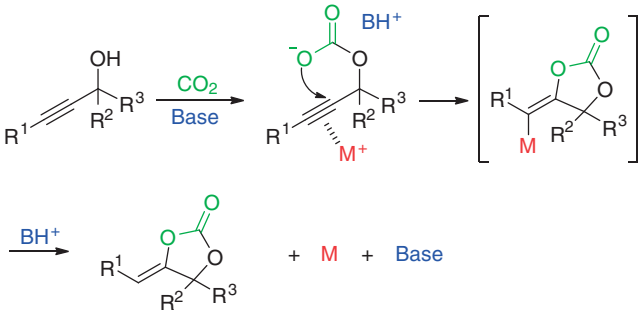


Scheme 1. Proposed mechanism of CO_2 incorporation into propargylic alcohols.

alkynes are the only applicable substrates for these carbonate formations. Supercritical conditions have also been employed for the CO_2 incorporation into propargylic alcohols including internal alkynes in the presence of the phosphine catalyst.[14] However, the applicable substrates are still limited to aryl-substituted propargylic alcohols without any bulky group on the propargylic position.

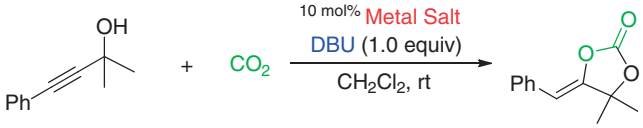
Screening of Metal Salts for a Catalyst: The reaction mechanism of the CO_2 incorporation into propargylic alcohols was assumed to be as follows. The alcohol, activated by the amine base, would react with the CO_2 to generate a carbonate intermediate. An intramolecular ring-closing reaction would then proceed on the alkyne, which would be activated by the metal complex to afford the corresponding cyclic carbonate with the release of the metal complex catalyst (Scheme 1).

The activation of the alkyne by the metal complex catalyst was proposed to be crucial to promote the present reaction. The nucleophilic addition to the acetylenes activated by metal salts is a promising strategy that can be used to obtain various alkenes. For example, it was reported that an intramolecular nucleophilic ring-closing reaction of the carbonate onto the propargylic derivatives activated by a gold(I) catalyst afforded the corresponding cyclic carbonates.[15] We screened various transition-metal salts to activate the C–C triple bond with the use of the phenyl-substituted alkyne **1b** as a model substrate at room temperature under a CO_2 pressure of 2.0 MPa (Table 1). Unfortunately, almost none of the metals, such as rhodium, mercury, platinum, and palladium, that were expected to activate the alkynes, could catalyze the reaction (Entries 1–5). The copper(I) salt produced a trace amount of the cyclic carbonate and gold was inactive for the present reaction (Entries 6 and 7). It was found that by using silver salts as a catalyst in the presence of a stoichiometric amount of DBU, the cyclic carbonate **2b** was quantitatively obtained (Entries 8 and 9).

Next, examination of the counter anion of the silver salt was performed for the reaction of the propargylic alcohol possessing an alkyl-substituted internal alkyne **1g** which had lower reactivity than the phenyl-substituted alkyne **1b** (Table 2). In the presence of 10 mol % silver perchlorate, the reaction smoothly proceeded to afford the cyclic carbonate **2g** with an 83% yield (Entry 7). Other silver salts could catalyze the incorporation reaction (Entries 1–6), but silver cyanide produced a 38% yield and the starting propargyl alcohol was recovered (Entry 1). The most efficient silver salt was found to be silver methanesulfonate or silver acetate. They successfully catalyzed the conversion of **1g** into the corresponding cyclic carbonate **2g** in high yields (Entries 8 and 9). When the reaction was carried out in toluene at a 1.0 MPa CO_2 pressure, the chemical yield improved to 95% (Entry 10).

Application to Various Propargylic Alcohols: The combined catalyst system of silver acetate with a stoichiometric amount of DBU was successfully applied to various propargylic alcohols (Table 3). In the presence of 10 mol % silver acetate and 1.0 equivalent of DBU at room temperature, the terminal alkyne **1a** bearing bulky substituent reacted with CO_2

Table 1. Screening of Various Metals for the Catalytic CO_2 Incorporation Reaction



1b **2b**

Entry[a]	Metal salt	Yield/%[b]
1	$[Rh(acac)_3]$	no reaction
2	$Hg(OTf)_2$	no reaction
3	$PtCl_2$	no reaction
4	$PdCl_2$	no reaction
5	$Pd(OAc)_2$	trace
6	CuCl	trace
7	AuCl	no reaction
8	$AgClO_4$	quant.
9	AgOTs	quant.

a) Reaction conditions: The reaction was carried out in 1.0 mL of dichloromethane using 10 mol % metal salt as catalyst, 0.25 mmol DBU and 0.25 mmol of the substrate **1b** under 2.0 MPa CO_2. b) Isolated yield.

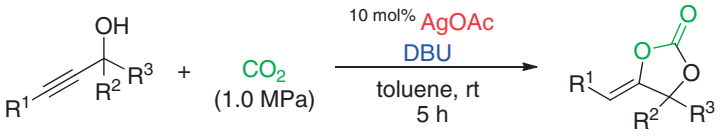
Table 2. Examination of Counter Anion in Silver Salt Catalysts

1g **2g**

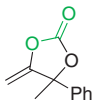
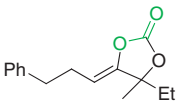
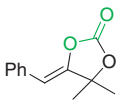
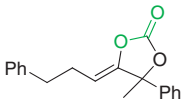
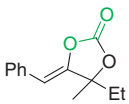
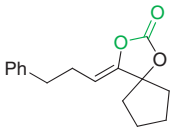
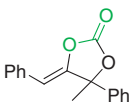
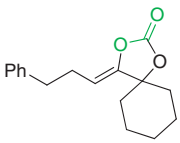
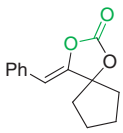
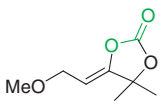
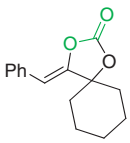
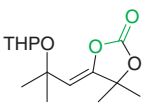
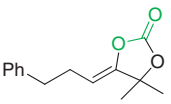
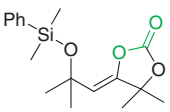
Entry[a]	AgX	Yield/%[b]
1	AgCN	38
2	AgOTf	66
3	Ag_2CO_3	67
4	$AgBF_4$	67
5	AgF	68
6	$AgSbF_6$	77
7	$AgClO_4$	83
8	AgOMs	84
9	AgOAc	84
10[c]	AgOAc	95

a) Reaction conditions: The reaction was carried out in 1.0 mL of dichloromethane using a 10 mol % metal salt as catalyst, 0.25 mmol DBU and 0.25 mmol of the substrate **1g** under 1.0 MPa CO_2. b) Isolated yield. c) The reaction was carried out in toluene.

Table 3. Various Cyclic Carbonates Obtained from Propargylic Alcohols by the Silver-Catalyzed CO_2 Incorporation

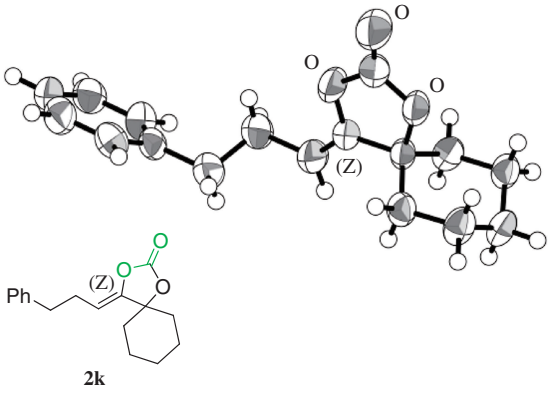


1 **2**

Entry[a]	Carbonate		Yield/%[b]	Entry[a]	Carbonate		Yield/%[b]
1		**2a**	85	13		**2h**	quant.
2 3[c),d)] 4[d),e)]		**2b**	quant. 86 98	14		**2i**	96
5		**2c**	quant.	15		**2j**	95
6		**2d**	95	16		**2k**	96
7[f)] 8		**2e**	80 quant.	17		**21**	76
9[f)] 10		**2f**	84 96	18		**2m**	97
11[f)] 12		**2g**	81 95	19		**2n**	91

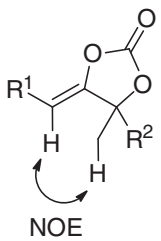
a) Reaction conditions: The reaction was carried out in 1.0 mL of toluene using 10 mol % silver acetate, 0.25 mmol DBU and 0.25 mmol substrate under a 1.0 MPa CO_2 pressure. b) Isolated yield. c) Carried out using 10 mol % of DBU. d) Reaction time: 24 h. e) Carried out using 1.0 mol % silver acetate under a 1.0 MPa CO_2 pressure. f) Carried out under atmospheric CO_2 pressure.

to afford the corresponding cyclic carbonate **2a** in 85% yield (Entry 1). The internal alkyne **1b** was quantitatively converted into the cyclic product **2b** under 1.0 MPa CO_2 (Entry 2). A catalytic amount of the base effectively promoted the reaction to afford the product in high yield (Entry 3). The lower catalyst loading of 1.0 mol % silver acetate effectively catalyzed the reaction of the alcohol **1b** at 1.0 MPa CO_2 to form the carbonate **2b** in high yield, though a longer time was required to complete the reaction (Entry 4). The more bulky propargylic alcohols **1c** and **1d** were smoothly converted into the corresponding cyclic carbonates **2c** and **2d** in high yields, respectively (Entries 5 and 6). The reaction of the propargylic alcohols having a5-membered ring **1e** or 6-membered ring **1f** smoothly proceeded in excellent yields (Entries 8 and 10). Even under atmospheric CO_2 pressure, the propargylic alcohols **1e**–**1g** could be converted with excellent selectivities (Entries 7, 9, and 11). The alkyl-substituted propargylic alcohols have never been reported for the incorporation reaction of CO_2, whereas in the present catalyst system, they were capable of reacting with CO_2 to afford the cyclic carbonates **2g**–**2k** in high yields (Entries 12–16). It is noted that the propargylic alcohols with ether and acetal functions were smoothly converted into the corresponding products **2l** and **2m** in high yields without any loss of reactivity (Entries 17 and 18). The silyl-protected propargylic alcohol was subjected to the present reaction to afford the cyclic carbonate with the silyl-protected form **2n** in high yield (Entry 19). The geometry of the carbon–carbon double bond in the product **2k** was determined by X-ray analysis and it was revealed that the *Z*-isomer was obtained as the sole product (Figure 1). Product **2b** was also found to have the *Z*-form by comparing the chemical shift of the olefinic proton with the



2k

Figure 1. The structure of the CO_2-incorporated cyclic carbonate **2k**.[10a]



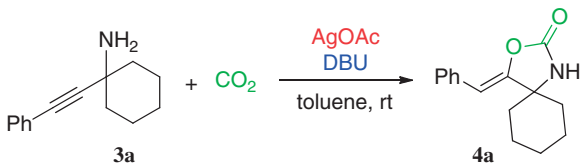
2c : 2.2% **2i** : 2.5%
2d : 1.0% **2j** : 9.0%
2e :14.3% **2l** : 6.0%
2f : 7.1% **2m** : 5.0%
2g : 9.0% **2n** : 1.0%
2h : 3.0%

Figure 2. NOE experiment of the cyclic carbonates **2**.

reported value.[13f] All other cyclic carbonates were obtained as the sole isomer based on NMR spectroscopic analysis, and they were suggested to be the *Z*-isomer by NOE experiments. A correlation between the olefinic proton and the methyl or methylene protons bound to the C-4 carbon on the 5-alkylidene-4,4-disubstituted-1,3-dioxolan-2-one ring of the products **2c**, **2d**, **2e**, **2f**, **2g**, **2h**, **2i**, **2j**, **2l**, **2m**, and **2n** was detected. The intensities (%) of the signals are shown (Figure 2). These observations suggested that a nucleophilic ring-closing step proceeded with activation of the alkyne by the silver catalyst at the anti-position against the carbonate nucleophile.

Application to Propargylic Amines: The present catalytic system could be applied to various propargylic amines to afford the corresponding oxazolidinones. Oxazolidinones have been employed as reliable auxiliaries for various selective synthetic organic reactions. Oxazolidinones have been conventionally prepared from the corresponding 2-aminoalcohols with phosgene,[16] however its high toxicity and environmental burden have been seriously considered. The oxazolidinone preparation from CO_2 is one of the most attractive synthetic methods not using phosgene. Much effort has been made to develop the chemical fixation of CO_2 into propargylic amines to provide oxazolidinone derivatives.[13n,17] In spite of various reports on the incorporation of CO_2 into propargylic amines, practical procedures for the reaction of the propargylic amines with internal alkynes or *N*-unsubstituted amines have never been achieved. Also, it should be pointed out that the applicable substrates are still limited and/or almost all the reported methods required severe reaction conditions, such as high temperature and/or high pressure the same as the reaction of propargylic alcohols.

Table 4. Examination of Various Reaction Conditions



3a **4a**

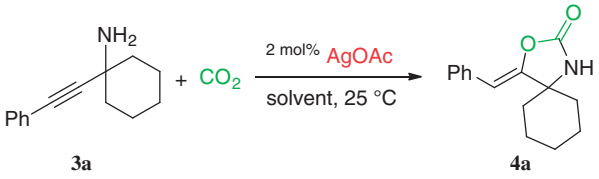
Entry[a)]	CO_2 pressure /MPa	AgOAc /mol %	DBU /mol %	Time /h	Yield /%[b)]
1	1.0	10	100	2	95
2	0.1	10	100	6	95
3	1.0	10	5	23	94
4	1.0	10	0	46	87
5	1.0	3	0	47	93
6[c)]	0.3	2	0	47	91

a) Reaction conditions: The reaction was carried out in 1.0 mL of toluene with 0.25 mmol of substrate at room temperature. b) Isolated yield. c) The reaction was carried out in 1.5 mL of toluene with 0.50 mmol of substrate.

As a model compound of an *N*-unsubstituted propargylic amine with an internal alkyne, 1-(phenylethynyl)cyclohexanamine (**3a**) was first subjected to the standard conditions in the presence of 10 mol % silver acetate and a stoichiometric amount of DBU in toluene at 1.0 MPa CO_2 pressure and room temperature, and the corresponding oxazolidinone **4a** was obtained in 95% yield in 2 h (Table 4, Entry 1). The reaction preceeded so smoothly that milder reaction conditions were examined involving the CO_2 pressure and the amounts of the silver catalyst and DBU in the reaction of **3a** at room temperature (Table 4). Under atmospheric CO_2 pressure, the corresponding product was obtained in an excellent yield (Entry 2). A catalytic amount of the base effectively promotes the reaction to afford the product in excellent yield (Entry 3). It was found that in the absence of DBU, the product was obtained in 87% yield (Entry 4). The mechanism for the present reaction was assumed to be that the carbamate intermediate derived from the propargylic amine with CO_2 successively reacted with the alkyne activated by the silver catalyst to afford the oxazolidinone via an intramolecular ring-closing reaction. Although the DBU base would assist with the carbamate formation, in equilibrium between the corresponding ammonium carbamate and free propargylic amine in a CO_2 atmosphere,[17j] the amine could work as a base to assist with the carbamate formation without DBU. The reaction was also catalyzed by 3 mol % silver acetate to produce an excellent yield (Entry 5). In the reaction with 2 mol % silver acetate under 0.3 MPa CO_2 pressure, the propargylic amine **3a** was completely consumed to afford the product in excellent yield (Entry 6).

Various solvents were screened expecting effective solvation of the carbamate intermediate to accelerate the reaction (Table 5). In MeOH and $CHCl_3$ solvents, the product was obtained in low yields (Entries 1 and 2). In THF, the reaction proceeded as smoothly as in toluene though a longer reaction time was required (Entry 3). When DMF was employed as the solvent, the reaction was dramatically accelerated to afford the product in 98% yield after 4 h (Entry 4). Various aprotic polar solvents then were examined under milder reaction conditions (Entries 5–8). Under atmospheric CO_2 pressure, propargylic

Table 5. Examination of Various Solvents



3a **4a**

Entry[a)]	Solvents	CO_2 pressure/MPa	Time/h	Yield/%[b)]
1	MeOH	0.3	47	19
2	$CHCl_3$	0.3	47	32
3	THF	0.3	47	94
4	DMF	0.3	4	98
5	DMF	0.1	10	97
6	MeCN	0.1	10	91
7	DMA	0.1	10	92
8	DMSO	0.1	10	98

a) Reaction conditions: The reaction was carried out in 1.5 mL of solvent with 0.50 mmol of substrate at 25 °C. b) Isolated yield.

amine **3a** smoothly reacted with CO_2 in aprotic polar solvents, especially in DMSO, and the corresponding oxazolidinone **4a** was obtained in 98% yield after 10 h (Entry 8).

The optimized catalytic system was successfully applied to the reaction of various propargylic amines (Table 6). Propargylic amines with terminal alkyne and primary, secondary, and tertiary *N*-substituted amines were converted into the corresponding oxazolidinones **4b**–**4e** in excellent yields (Entries 1–4). For the less reactive substrates, a 0.4 MPa CO_2 pressure was required to achieve an excellent yield (Entries 3, 4, and 11). Also, the reaction of *N*-unsubstituted propargylic amines with the terminal alkyne **3f** proceeded in high yield (Entry 5). The *N*-substituted internal alkynes, alkyl-substituted alkyne **3g** and **3h** and aryl-substituted alkyne **3i**–**3l**, reacted with CO_2 to afford the corresponding oxazolidinone in high yield (Entries 6–11). It should be pointed out that in the present catalytic system, the *N*-unsubstituted propargylic amines with an internal alkyne, which have never been reported as being involved in a CO_2 incorporation reaction, were smoothly converted into the corresponding cyclic products under mild conditions. The alkyl-substituted (**3m**, Entry 12), aryl-substituted (**3n**–**3t**, Entries 13–20), and heteroaryl-substituted (**3u** and **3v**, Entries 21 and 22) alkynes were converted into the corresponding oxazolidinones in high yield. As for the *exo*-olefin structure, all products were obtained as a sole isomer based on an NMR spectroscopic analysis, and they were suggested to be the *Z*-isomer by NOE experiments. The geometry of the C–C double bond in product **4a** was confirmed to be the *Z*-isomer by X-ray analysis (Figure 3). In the NOE experiments, a correlation between the olefinic proton and the methyl or methylene protons bound to the C-3 or C-4 carbon on the oxazolidinone ring of the products **4a** and **4e**–**4r** was detected, respectively. The intensities (%) of the signals are indicated in Figure 4.

Rearrangement Reaction Mediated by Carbon Dioxide. During the course of examining the reaction conditions for the CO_2 incorporation reaction into propargylic alcohols, the corresponding α,β-unsaturated carbonyl compounds via the Meyer–Schuster-type reaction was detected as a by-product in some polar solvents. In a toluene solution, the silver-catalyzed reaction of propargyl alcohol with CO_2 selectively afforded the corresponding cyclic carbonate, while in dichloromethane and chlorobenzene, the corresponding α,β-unsaturated carbonyl compounds via the Meyer–Schuster-type reaction were obtained along with the cyclic carbonate.

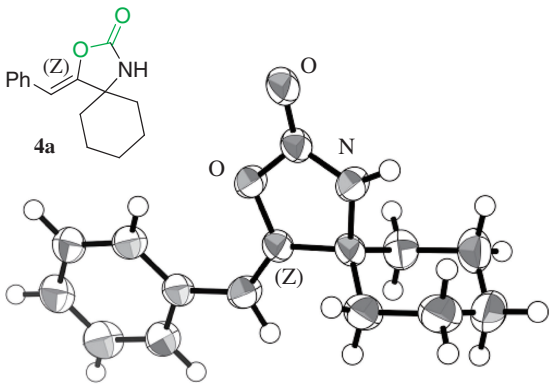
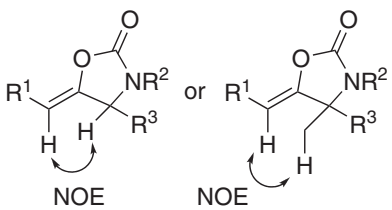


Figure 3. The structure of the CO_2-incorporated oxazolidinone **4a**.[10b]



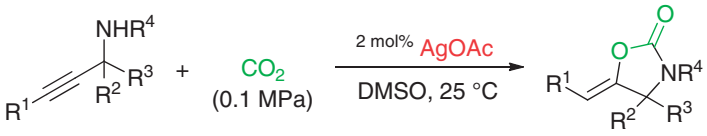
4a : 7.0% **4l** : 3.0%
4e : 4.0% **4m** : 3.0%
4f : 5.0% **4n** : 7.0%
4g : 2.0% **4o** : 4.0%
4h : 4.0% **4p** : 6.0%
4i : 5.0% **4q** : 5.0%
4j : 4.0% **4r** : 6.0%
4k : 3.0%

Figure 4. NOE experiment of the oxazolidinone **4**.

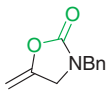
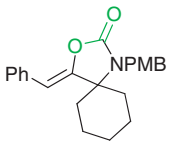
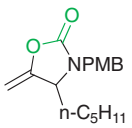
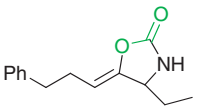
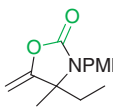
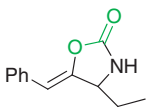
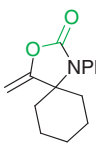
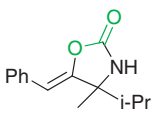
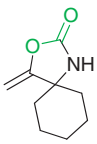
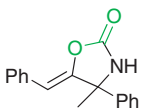
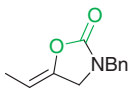
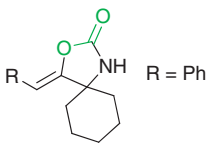
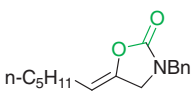
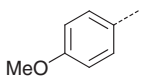
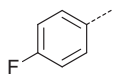
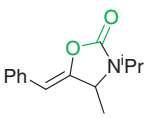
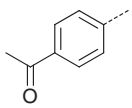
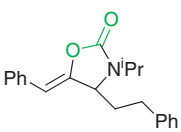
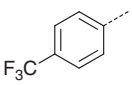
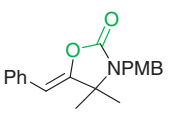
The Meyer–Schuster rearrangement[18] reaction reported in 1922[19] is the rearrangement of propargylic alcohol into the corresponding α,β-unsaturated carbonyl compounds. This reaction consists of two key steps: (1) effective enhancement of the leaving ability of the hydroxy group to generate the carbocation intermediate, and (2) nucleophilic addition of the hydroxide equivalent to the activated alkyne to afford the resulting enone. For a tertiary propargylic alcohol, a protic acid was used as a simple reagent to drive this reaction though the Rupe rearrangement via the enyne intermediate to afford the undesired α,β-unsaturated carbonyl compounds as by-products. In order to suppress the side reactions in this textbook reaction,[20] oxo-metallic reagents[21,22] have been examined to concomitantly remove the hydroxy group with the [3,3]-sigmatropic rearrangement involving the nucleophilic addition to an alkyne, but a high reaction temperature is required to almost complete these reactions.[23] The high affinity of the late transition-metals, such as gold,[24] to the acetylenic π-bond was used to activate the propargylic alcohols under the mild conditions. The ruthenium complex catalyst[25] was employed for the activation of the alkyne via the vinylidene–ruthenium intermediate derived from the terminal alkynes.

Screening of Metal Salt Catalysts: Several metal salts were screened as a catalyst. Rhodium, palladium, iridium, and copper(I) were not active for the reaction, whereas platinum, mercury, and gold could catalyze the reaction to afford the

Table 6. Various Propargylic Amines

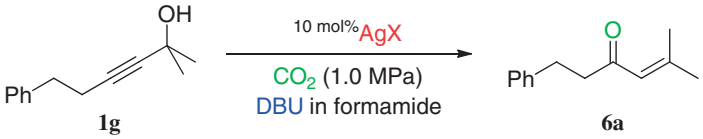


3 **4**

Entry[a]	Oxazolidinone		Time/h	Yield/%[b]	Entry[a]	Oxazolidinone		Time/h	Yield/%[b]
1		**4b**	7.0	95	11[c),d)]		**4l**	24	98
2		**4c**	7.0	97	12		**4m**	7.0	77
3[c),d)]		**4d**	32	99	13		**4n**	5.0	97
4[c),d)]		**4e**	72	83	14		**4o**	3.0	99
5		**4f**	4.0	95	15		**4p**	4.0	quant.
6		**4g**	3.0	99	16		**4a**	10	98
7		**4h**	1.5	95	17	R = 	**4q**	2.5	94
					18	R = 	**4r**	3.0	99
8		**4i**	2.0	99	19	R = 	**4s**	7.0	94
9		**4j**	1.5	99	20	R = 	**4t**	2.5	quant.
10		**4k**	3.0	97	21	R = 	**4u**	3.0	97
					22	R = 	**4v**	7.0	89

a) Reaction conditions: The reaction was carried out in 1.5 mL of DMSO with 2 mol % silver acetate and 0.50 mmol of substrate under 0.1 MPa CO_2 pressure at 25 °C. b) Isolated yield. c) PMB: *p*-Methoxybenzyl. d) 0.4 MPa of CO_2 pressure.

Table 7. Examination of Various Silver Salts



1g **6a**

Entry[a]	AgX	Time/h	Yield/%[b]	Entry[a]	AgX	Time/h	Yield/%[b]
1	AgCl	10	trace	7	AgOTf	20	76
2	AgI	8	trace	8	Ag_2O	12	78
3	AgF	12	68	9	$AgOCOCF_3$	11	79
4	$AgSbF_6$	12	73	10	$AgNO_3$	12	80
5	AgOTs	12	74	11	$AgBF_4$	11	85
6	AgOAc	12	76	12	AgOMs	8	89

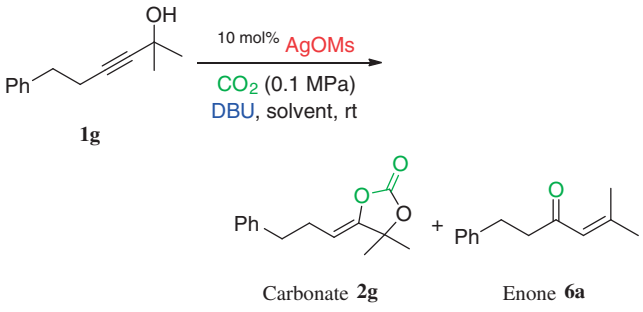
a) Reaction conditions: The reaction was carried out in 0.5 mL of formamide with 10 mol % silver salt, 0.25 mmol of substrate and 0.2 equiv of DBU at 60 °C under 1.0 MPa CO_2 pressure. b) Isolated yield.

corresponding α,β-unsaturated carbonyl compounds. A silver salt was found to be the best catalyst for this reaction among them. Various silver salts were next examined for the reaction of propargylic alcohol **1g** in formamide under CO_2 pressure (1.0 MPa). Among the silver halides examined, only silver fluoride affected the reaction to afford the corresponding enone **6a** in 68% yield (Table 7, Entries 1–3). Almost all the cationic silver salts which were investigated catalyzed the synthesis of the α,β-unsaturated carbonyl compounds in good yields (Entries 4–11). It was found that silver methanesulfonate was the best catalyst for the Meyer–Schuster-type rearrangement mediated by CO_2 to produce the corresponding α,β-unsaturated carbonyl compound in high yield (Entry 12).

Examination of Reaction Solvents: The optimization of several solvents for the Meyer–Schuster-type rearrangement mediated by CO_2 was performed (Table 8). In a toluene solution, the silver-catalyzed reaction of propargylic alcohol with CO_2 selectively afforded the corresponding cyclic carbonate (Entry 3), while in dichloromethane and chlorobenzene, the corresponding α,β-unsaturated carbonyl compounds via the Meyer–Schuster-type reaction was obtained along with the cyclic carbonate (Entries 1 and 2). The polar solvents, such as DMF and DMA, improved the selectivity toward the enone (Entries 4–7). Finally, it was found that formamide was the best solvent to selectively obtain the corresponding enone (Entry 8).

Various Propargylic Alcohols: The optimized system was successfully applied to various propargylic alcohols (Table 9). In the presence of 10 mol % silver methanesulfonate and 0.2 equivalent DBU under 1.0 MPa CO_2 at 60 °C, the alkyl-substituted tertiary propargylic alcohols **1g** and **5b** were smoothly converted into the corresponding α,β-unsaturated ketones **6a** and **6b** in high yield (Entries 1 and 2). The propargylic alcohol **5c** possessing bulky substituents was also converted into the corresponding enone **6c** in high yield (Entry 3) when a 3.0 equivalents DBU was employed at 60 °C. For the propargylic alcohols **1j**, **1k**, and **5f** with a five-to-seven-membered ring, the reactions smoothly proceeded under mild conditions using a 1.0 equivalent diisopropylethylamine to afford the rearranged products **6d**–**6f** with the cycloalkylidene groups in 93%, 90%, and 94% yields, respectively, without any isomerization of the C–C double bond. The propargylic alcohols **1i** and **5h** with a phenyl group at the propargylic

Table 8. Examination of Various Solvents



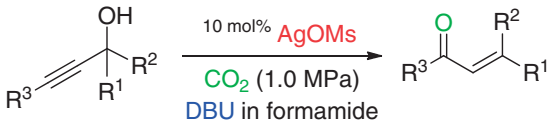
1g Carbonate **2g** Enone **6a**

Entry[a]	Solvent	Time/h	Yield/%[b]	
			Carbonate **2g**	Enone **6a**
1	CH_2Cl_2	24	45	39
2	PhCl	24	79	11
3	toluene	24	74	trace
4[c]	2-propanol	48	trace	51
5	DMF	72	trace	39
6[d]	DMF	12	7	73
7[d]	DMA	12	16	63
8[d]	formamide	12	6	86

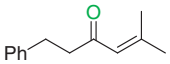
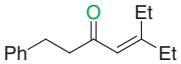
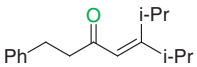
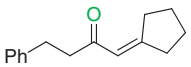
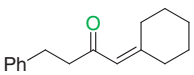
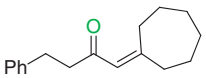
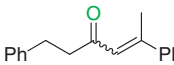
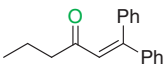
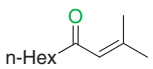
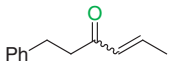
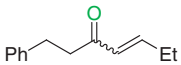
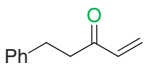
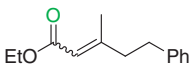
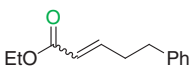
a) Reaction conditions: The reaction was carried out in 0.5 mL of solvent using 10 mol % silver methanesulfonate, 0.25 mmol of substrate and 0.25 mmol of DBU at room temperature under atmospheric CO_2 pressure. b) Isolated yield. c) Carried out at 50 °C. d) Carried out under 1.0 MPa CO_2 pressure.

position were capable of reacting with CO_2 to afford the corresponding enones **6g** in 98% yield (Entry 7) and **6h** in 80% yield in DMF (Entry 8). The present catalytic system could be applied to various tertiary as well as secondary propargylic alcohols to afford the products **6j** and **6k** in high yield at room temperature (Entries 10 and 11), although it has been reported that the secondary propargylic alcohols were difficult to convert into the corresponding α,β-unsaturated ketones under mild conditions. However, the propargylic alcohol **5l** was less reactive and the corresponding monosubstituted enone **6l** was obtained in 29% yield (Entry 12). The ethoxy-substituted propargylic alcohols **5m** and **5n** were good substrates that afforded the corresponding ethyl esters of the α,β-unsaturated carboxylic acids **6m** and **6n** in high yields (Entries 13 and 14).

Table 9. Transformation of Various Propargyl Alcohols into the Enones

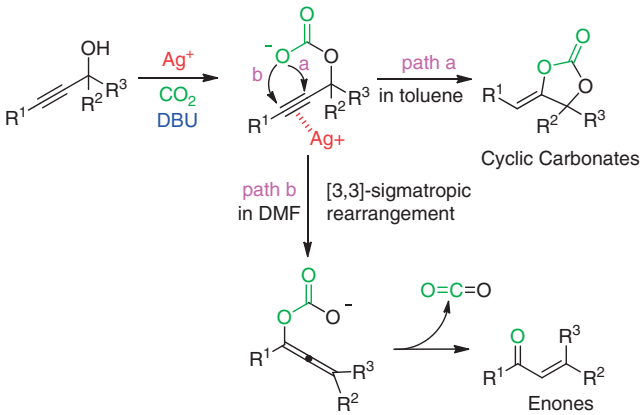


1 and **5** **6**

Entry[a]	Enone		Time/h	Yield/%[b] (E/Z)[c]
1[d]		**6a**	8	89
2[d]		**6b**	24	74
3[e]		**6c**	25	70
4[f]		**6d**	24	93
5[f]		**6e**	48	90
6[f]		**6f**	40	94
7[f]		**6g**	47	98 (46/54)
8[g]		**6h**	96	80
9[g]		**6i**	19	84
10		**6j**	48	93 (75/25)
11		**6k**	48	84 (76/24)
12		**6l**	72	29
13[f]		**6m**	19	87 (46/54)
14[f]		**6n**	54	70 (79/21)

a) Reaction conditions: The reaction was carried out in 0.5 mL of formamide with 10 mol% silver methanesulfonate, 0.25 mmol of substrate and 1.0 equiv of DBU at rt under 1.0 MPa CO_2 pressure. b) Isolated yield. c) E/Z ratio is shown in parenthesis. d) 0.2 equiv of DBU was used at 60 °C. e) 3.0 equiv of DBU was used at 60 °C. f) i-Pr_2NEt was used as a base. g) The reaction was carried out in DMF.

Proposed Mechanism: The reaction mechanism of the reaction of CO_2 with propargylic alcohol is proposed as follows: the carbonate intermediate would be generated from propargylic alcohol and CO_2 and then intramolecular ring-closing would proceed at the α-carbon of the propargylic alcohol, which is activated by the silver salt, to afford the cyclic carbonate (Scheme 2, path a). The β-carbon of the propargylic alcohol would be alternatively attacked to promote the



Scheme 2. Reaction mechanism of propargylic alcohol with CO_2.

[3,3]-sigmatropic rearrangement into the allene-enolate. The α,β-unsaturated carbonyl compounds resulted from releasing CO_2 (Scheme 2, path b). It is reasonable to assume that the polarized structure with the elongated C–O bond in the carbonate intermediate would be stabilized in a polar solvent to enhance the attack on the β-carbon of the activated propargylic alcohol.

The reaction of the propargylic alcohol **1a** with CO_2 was monitored by time-resolved FT-IR spectroscopy in the presence of 10 mol% AgOAc and one equivalent of DBU. Two experiments were performed; one of the reaction systems was that substrate, DBU, and CO_2 (0.1 MPa) were placed in the reaction vessel and then AgOAc was added. For the other, DBU was added last. In each experiment, the specific absorptions of the product immediately appeared at ca. 1810 (C=O stretching vibration) and 1700 cm^{-1} (C=C stretching vibration) after the addition of AgOAc and DBU (the red line in the Figures 5 and 6). These observations suggested that the all reaction components (silver salt and DBU as a base) were required to allow this reaction. It was assumed that the cyclization step would be very fast to afford the corresponding cyclic carbonate **2a**, which would support the proposed mechanism for the cyclic carbonate and oxazolidinone as shown in Scheme 2.

The proposed mechanism for the α,β-unsaturated carbonyl compound was also supported by an isotopic experiment using $C^{18}O_2$. The reaction was carried out under a CO_2 atmosphere to afford the α,β-unsaturated ketone with MW: 188, whereas the α,β-unsaturated ketone with MW: 190 was obtained from $C^{18}O_2$. As shown in Figure 7, no crossed product with ^{16}O could be detected at all by GC-MS analysis. Under a nitrogen atmosphere, no reaction proceeded. These observations suggested that the present reaction should be promoted by CO_2 and that the rearrangement step should proceed in an intramolecular [3,3]-sigmatropic manner, not by the intermolecular addition of H_2O or the carbonate anion.

The computational approach for the reaction mechanism was performed using the Gaussian 03 program[26] with the B3LYP/6-31+G*//B3LYP/6-31+G* method and basis set (The 3-21G* basis set was employed instead of 6-31+G* for the Ag atom.) and Gaussian 09 program[27] for the single-point energy including the SCRF/PCM approach. As a model substrate, 2-methyl-3-pentyn-2-ol was adopted for the repre-

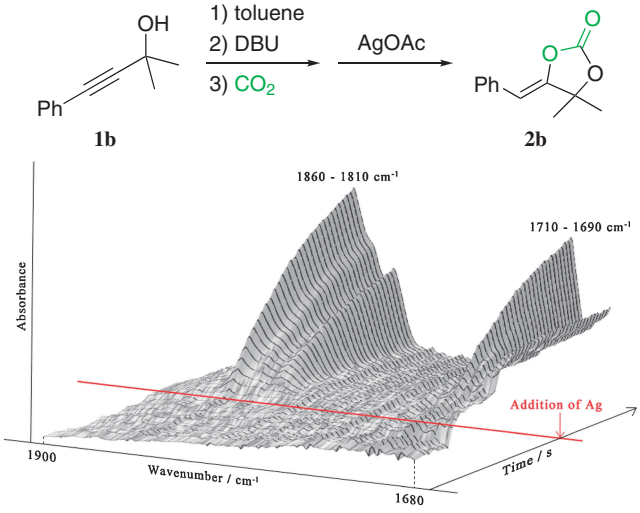


Figure 5. Time-resolved FT-IR measurement for the reaction of propargylic alcohol **1b**.

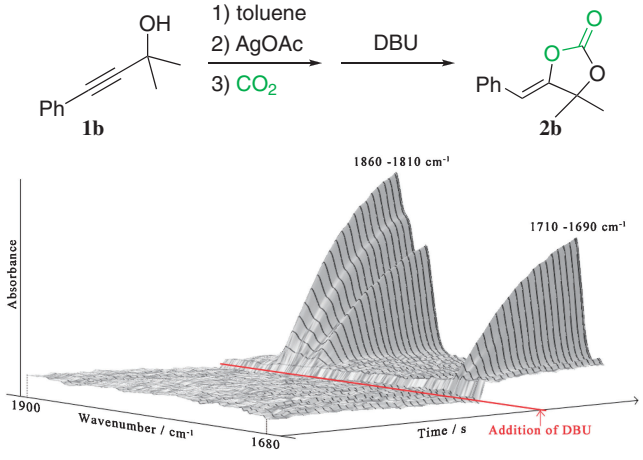


Figure 6. Time-resolved FT-IR measurement for the reaction of propargylic alcohol **1b**.

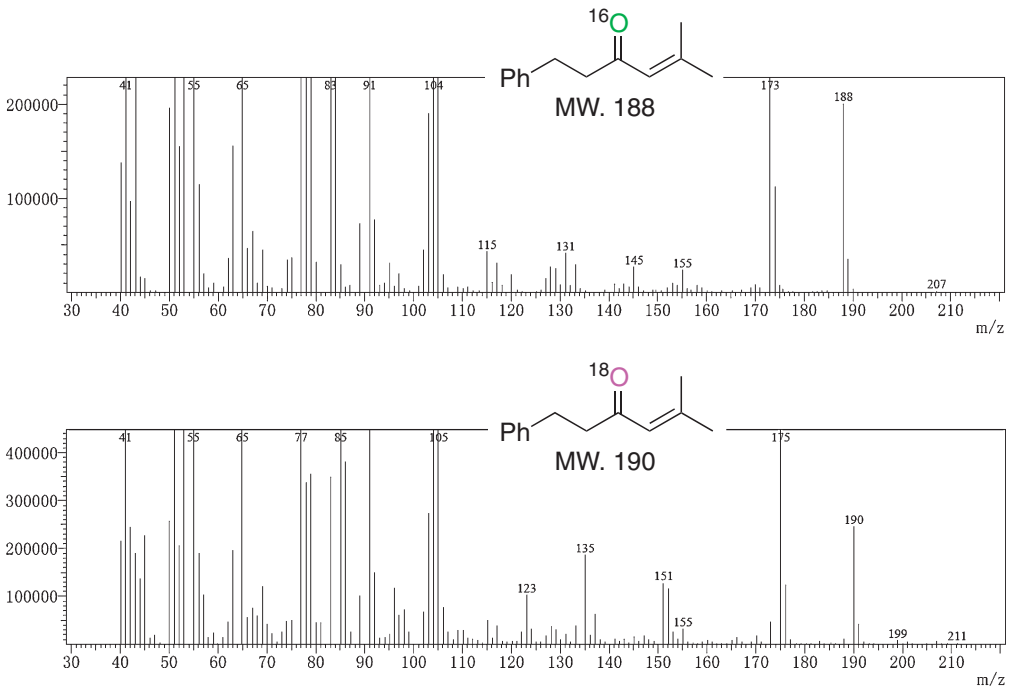


Figure 7. MS spectrum of the enone obtained from CO_2 and the ^{18}O-labeled CO_2.

sentative of propargylic alcohol, and 1-methyl-1,4,5,6-tetrahydropyrimidine for the DBU base. As shown in Figure 8, the anion **7a** derived from the alcohol with the amine base reacted with CO_2 to produce compound **7b** which was more stable than the starting alcohol **7a** in ca. 25.1 kcal mol^{-1} (ZPE: −25.1 kcal mol^{-1}) (Relative energy was established as 0.0 kcal mol^{-1} including the zero point revision. After this, we indicated the energy including zero point revision.). Compound **7b** was coordinated by the silver ion in ca. 160 kcal mol^{-1} as the coordination energy (compounds **7c**–**7e**; **7c** (ZPE: −182.5 kcal mol^{-1}), **7d** (ZPE: −182.6 kcal mol^{-1}), **7e** (ZPE: −180.0 kcal mol^{-1})). Two possible structures were obtained for the coordination of the silver ion versus the carbonate; it coordinates on the carbonate in compounds **7d** and **7e** or the alkyne in compound **7c**. The DBU coordination to compound **7c** afforded the structure **7f** in ca. 30 kcal mol^{-1} as the coordination energy to afford compound **7f** (ZPE: −216.3 kcal mol^{-1}) or the structure **7g** (ZPE: −215.2 kcal mol^{-1}). The silver ion would then coordinate on the alkyne versus the carbonate which would be coordinated by the DBU ammonium salt. This would be attributed to the most anionic carbonate and the repulsion between the silver and DBU ammonium ions.

These calculations suggested that compound **7f** would be formed as an active species, although the reaction pathway was not clear. We then analyzed the cyclization mechanism from the active species **7f**.

The energy of the 5-membered TS **7h** (ZPE: −190.3 kcal mol^{-1}) and the energy of the 6-membered TS **7i** (ZPE:

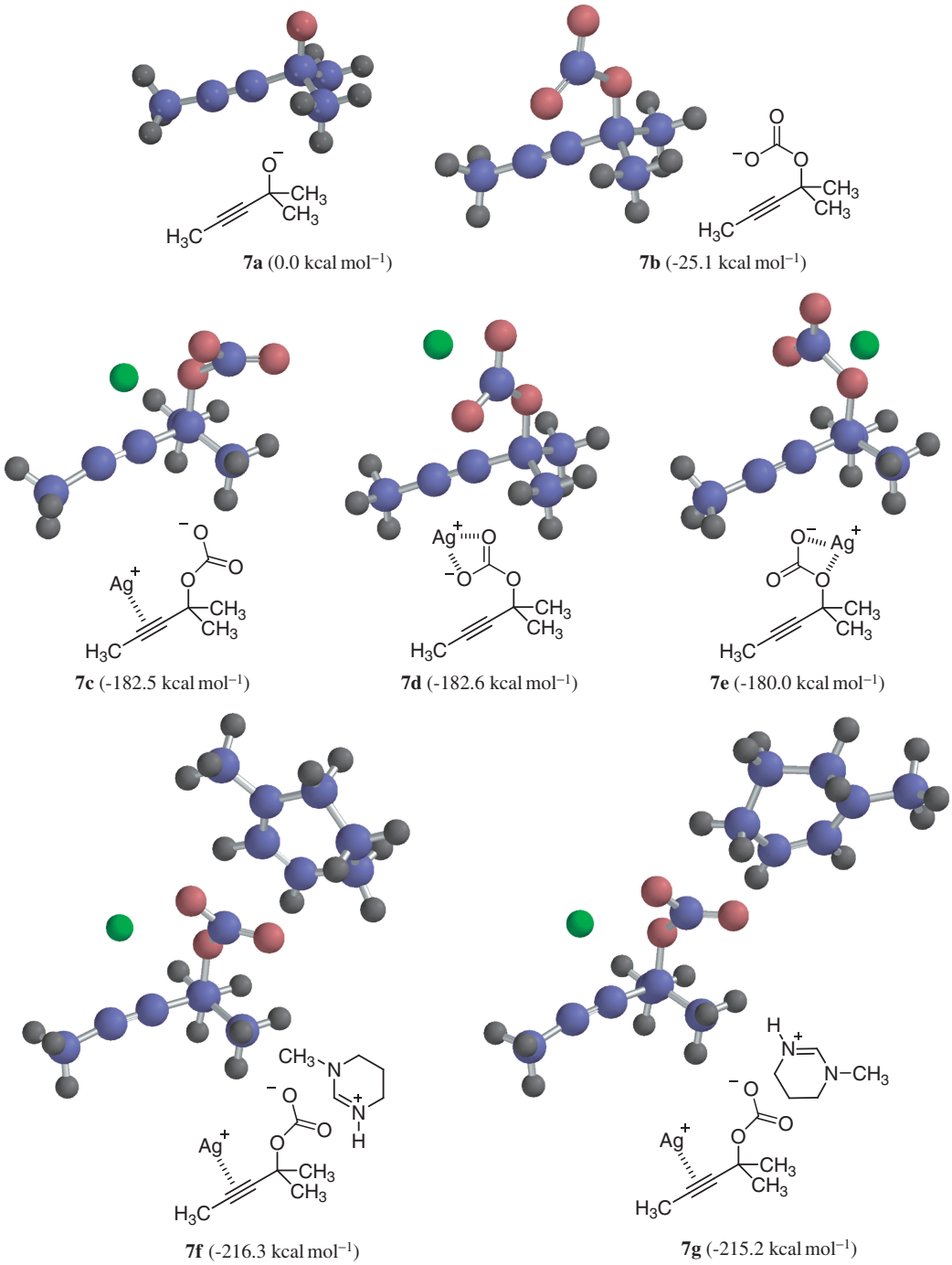


Figure 8. 2-Methyl-3-pentyn-2-ol as a model substrate for the cross section.

$-187.8\,kcal\,mol^{-1}$) were determined (Figure 9). The activation energies were 26.0 and $28.5\,kcal\,mol^{-1}$, respectively. An IRC (intrinsic reaction coordinate) analysis showed that the Z-5-membered cyclic carbonate was obtained from the intermediate **7j** via the 5-membered TS **7h**, and the 6-membered intermediate **7k** was produced via the 6-membered TS **7i**. The activation energy of the 6-membered intermediate **7k** was $13.0\,kcal\,mol^{-1}$ and the decarbonation reaction of the intermediate **7k** proceeded to afford the corresponding enone via TS **7l** and the intermediate **7m**. This observation suggested that the formation pathway of the enone consisted of two steps, but it was thought that the Z-5-membered cyclic carbonate was predominantly obtained in the gas phase, since the rate-determining step was the 6-membered TS **7i**.

As indicated in Table 8, the carbonate was predominantly obtained in toluene and PhCl, while the enone was preferentially produced in DMF and formamide. We next tried the single-point calculation including the solvent effect with the PCM model (Table 10). As a result, it was found that the activation energy between the 5-membered TS **7h** and the 6-membered TS **7i** tended to become close depending on the increase in the polarity of the solvent in the order of toluene, CH_2Cl_2, DMF, and formamide. Although the activation energy

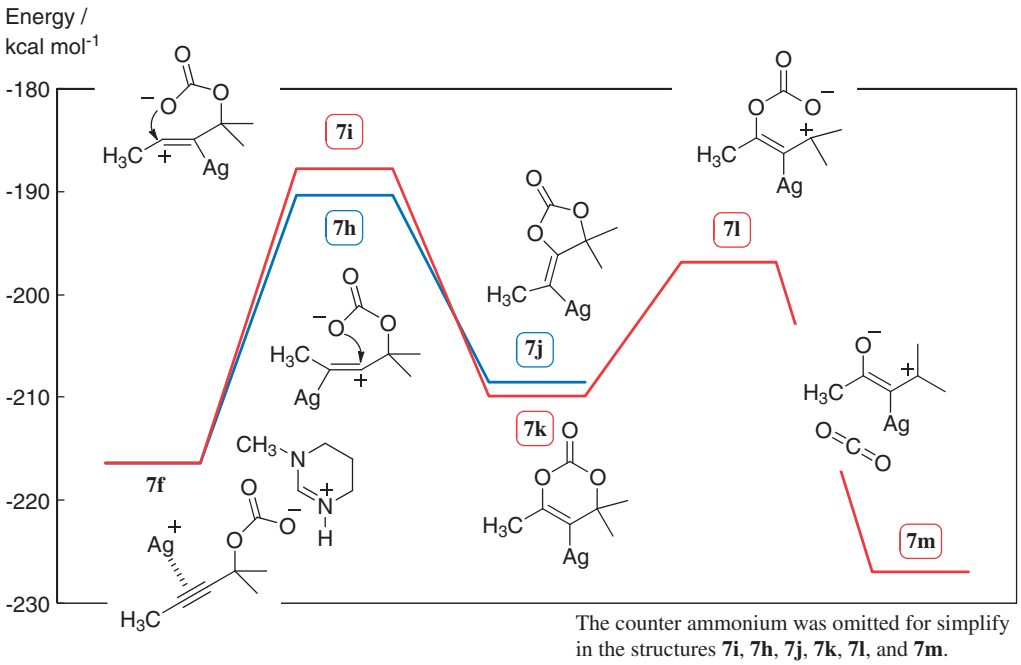
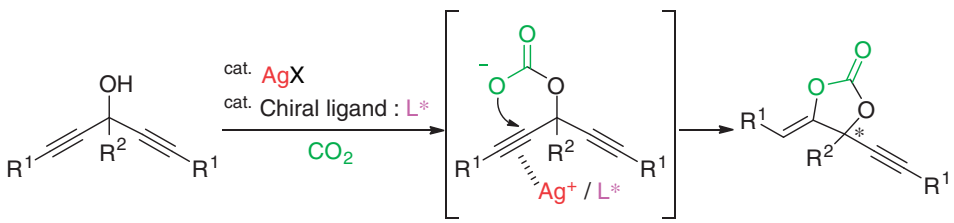


Figure 9. The energy diagram for cyclic carbonate and enone preparations.

Table 10. The Acitivation Energy[a)] and Selectivity in Several Solvents

Entry	Solvent	Calculated			Experimental	
		Activation energy with ZPE/kcal mol^{-1}		ΔE	Yield/%	
		5-Membered TS (**7h**)	6-Membered TS (**7i**)		Carbonate **2g**	Enone **6a**
1	toluene	20.547	22.396	1.85	74	trace
2	CH_2Cl_2	16.993	18.306	1.31	45	39
3	DMF	16.186	16.717	0.53	7	73
4	formamide	16.221	16.680	0.46	6	86

a) PCM-B3LYP/6-31+G*//PCM-B3LYP/6-31+G*.



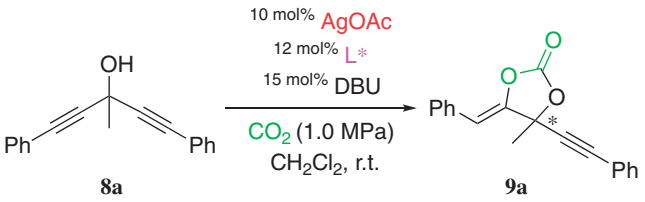
Scheme 3. Enantioselective chemical incorporation of CO_2 into bispropargylic alcohols.

between the two pathways did not reverse in the calculation of the model substrate, this observation shows that the polarity of the solvent was crucial for the ratio between the cyclic carbonate and the enone, and this tendency was consistent with the fact that the carbonate was preferentially obtained in the nonpolar solvent, while the enone was predominantly formed in the polar solvent.

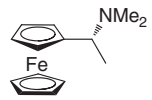
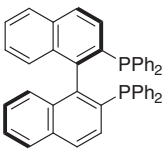
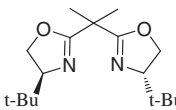
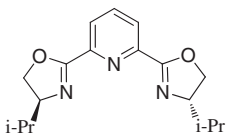
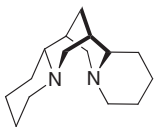
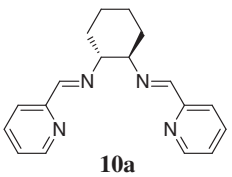
Enantioselective Version of CO_2 Incorporation into Bispropargylic Alcohols. Based on the reaction mechanism in the silver-catalyzed CO_2 incorporation reaction into the propargylic alcohols, supported by the computational approach, the silver catalysts effectively activated the C–C triple bond as a π-Lewis acid on the side opposite the carbonate anion, and then the intramolecular cyclization proceeded to selectively afford the corresponding cyclic product with the (*Z*)-*exo*-alkene, the corresponding optically active cyclic carbonates would be obtained by using an optically active silver catalyst, which is in rapid equilibrium between the two alkynes in the bispropargylic alcohols, and a nucleophilic attack selectively proceeds on one of the C–C triple bonds with asymmetric desymmetrization (Scheme 3).

Screening of Optically Active Ligands: Various optically active ligands were first examined, such as ferrocene derivatives, BINAP, BOX, and Py-BOX (Table 11). In the presence of 10 mol % silver acetate with the ligand, model compound **8a** was treated with 15 mol % of DBU in CH_2Cl_2 under 1.0 MPa CO_2 pressure at room temperature. Although all the reactions proceeded to afford the corresponding cyclic carbonates, the corresponding products were obtained without any enantioselectivity (Entries 1–4 and 6). It was assumed that the DBU

Table 11. Examination of Various Chiral Ligands with DBU



8a **9a**

Entry[a]	L*	Time/h	Yield/%[b]	Ee/%[c]
1		2.5	61	0
2		6	25	4
3		2.5	82	2
4		1	70	3
5[d]		2	94	26
6		0.3	93	5
7[d]		2	96	40

10a

a) Reaction conditions: The reaction was carried out in 1.5 mL of CH_2Cl_2 with 0.25 mmol of substrate under 1.0 MPa CO_2 pressure. b) Isolated yield. c) Enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H. d) Reaction was carried out without DBU.

could strongly coordinate the silver catalyst to block the coordination by the chiral ligand, while (−)-sparteine was employed as a chiral ligand without DBU to afford the corresponding cyclic product with a 26% ee (Entry 5). Without DBU, several chiral ligands were then screened and the product was obtained with 40% ee using the chiral Schiff base ligand **10a**[28] derived from 1,2-diaminocyclohexane and 2-pyridinecarbaldehyde (Entry 7).

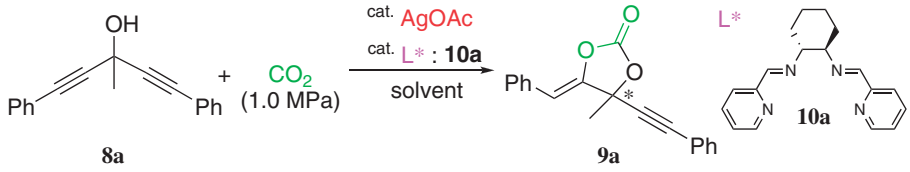
Various reaction conditions involving the solvent, catalyst loading, and temperature were examined in the presence of the ligand **10a** (Table 12). In the DMF and THF solvents, the product was obtained in moderate yield and ee (Entries 1 and 2). In toluene, the selectivity was improved to afford the product with a 71% ee, however, the reactivity was low (Entry 3). When CH_2Cl_2 and $CHCl_3$ were employed as the solvents, the reaction proceeded to afford the cyclic carbonate in 96% yield with 40% ee and in 92% yield with 70% ee, respectively (Entries 4 and 5). In the presence of 5 mol % silver acetate with a 6 mol % chiral ligand at 5 °C, the enantiomeric excess was slightly improved (Entry 6), while the product was obtained in low yield with 82% ee at −10 °C (Entry 7). It was found that in the presence of excess amounts of silver acetate with respect to the chiral ligand, the enantiomeric excess was slightly improved (Entry 8) and the product was obtained with 83% ee at 5 °C (Entry 9).

Under these reaction conditions, various chiral Schiff base ligands were then screened (Table 13). By using the ligand possessing a phenyl (Entry 1) or sterically bulky substituent (Entries 2 and 3), the reaction proceeded, but a low enantiomeric excess was observed. The selectivity was also moderate when an unsymmetrical chiral ligand derived from L-valine amide (Entry 4) or a ligand possessing a five-membered ring backbone (Entries 5 and 6). The effect of side chains were examined using the silver complexes possessing a cyclohexyl backbone (Entries 7–14). Only a trace amount of product was obtained with the pyrrole or 4-pyridyl side chain (Entries 7 and 9). The ligands possessing a quinoline (Entry 10) or substituted-pyridine group (Entries 11–14) on the side chain afforded the corresponding cyclic carbonate with a good enantiomeric excess, while the ligands with thiazole on the side chains gave moderate results (Entry 8). It was eventually found that the chiral ketimine ligand **10b** was the best ligand for both the reactivity and the selectivity. By using the ligand **10b**, the bispropargylic alcohol **8a** was completely consumed to afford the corresponding product in excellent yield with a high enantiomeric excess (Entry 15).

For the reaction with over 2 equivalents of AgOAc versus the chiral ligand **10b**, almost the same enantiomeric excess was observed (Table 14, Entries 3–8 and 10–12). This observation was confirmed by the ^{1}H NMR spectroscopic titration of the silver acetate and chiral ketimine ligand **10b**; the chemical shifts of H_a, H_b, and H_c of ligand **10b** gradually shifted to low field when the ratio of AgOAc to ligand **10b** increased, while using over 2 equivalents of AgOAc versus the chiral ligand **10b**, these chemical shifts became constant. That is, it suggested that the silver acetate and chiral ketimine ligand **10b** would form the corresponding 2:1 complex (Figure 10). After examination of the loading ratio of the ligand/silver, a combination of 3 mol % silver acetate and 1 mol % of **10b** was found to be the best conditions to realize high selectivity (Table 14, Entry 5). When the reaction was carried out at 0 °C, the CO_2-incorporated carbonate was obtained up to 92% ee (Table 14, Entry 13).

Determination of Absolute Configuration: Although we tried to determine the absolute configuration of the carbonate **9a** by X-ray analysis, an appropriate single crystal for X-ray analysis could not be obtained. The absolute configuration was then determined by VCD measurements combined with the corresponding spectra predicted by the DFT calculations.[29] VCD (vibrational circular dichroism) has received much attention in recent years to nonempirically determine absolute configuration. The VCD spectra were obtained using a JASCO FVS-6000 spectrometer at the resolution of 4 cm^{-1} using a $CDCl_3$ solution in a 50 μm BaF_2 cell. The concentrations were 0.115 M and the baselines for the spectra were the VCD spectra

Table 12. Examination of Various Reaction Conditions



Entry[a)]	Solvent	AgOAc/mol %	L*/mol %	Temp/°C	Time/h	Yield/%[b)]	Ee/%[c)]
1	DMF	10	12	rt	18	63	6
2	THF	10	12	rt	21	40	56
3	toluene	10	12	rt	21	27	71
4	CH_2Cl_2	10	12	rt	2	96	40
5	$CHCl_3$	10	12	rt	5	92	70
6	$CHCl_3$	5	6	5	48	92	75
7	$CHCl_3$	5	6	−10	168	11	82
8	$CHCl_3$	5	1	20	20	90	75
9	$CHCl_3$	5	1	5	96	91	83

a) Reaction conditions: The reaction was carried out in 1.5 mL of solvent with 0.25 mmol of substrate under 1.0 MPa CO_2 pressure. b) Isolated yield. c) Enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H.

of $CDCl_3$. Products **9a** obtained with (*R*,*R*)- and (*S*,*S*)-**10b** were recrystallized over *n*-hexane to prepare >99% ee cyclic carbonates for the VCD measurement. The absolute configuration of **9a** was determined by comparison of the experimental and calculated VCD spectra. The IR and VCD spectra of **9a** were theoretically calculated based on the density functional theory at the B3LYP/6-31G(d,p) level (blue line in Figures 11 and 12). The scaling factor of 0.97 was employed.[30] A conformational analysis provided only one stable conformer for **9a**. All of the calculations were conducted using the Gaussian 03[31] program code. The observed VCD spectrum of **9a** obtained with (*S*,*S*)-**10b** (green line in Figure 12) was identical to the calculated spectrum of (*R*)-**9a** (blue line in Figure 12). Therefore, it was concluded that (*R*)-**9a** was obtained from the reaction catalyzed by the silver complex with a chiral ligand (*S*,*S*)-**10b**.

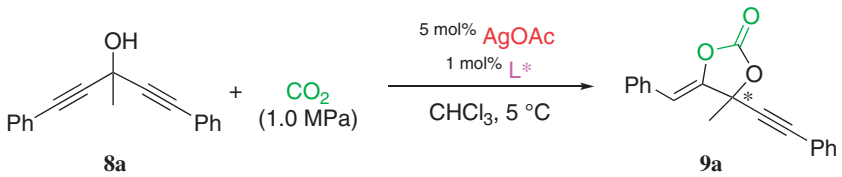
The absolute configuration of the carbonate **9a** was also confirmed by an X-ray analysis of the **9a**–cobalt carbonyl complex (Figure 13). The product **9a** obtained with (*R*,*R*)-**10b** was recrystallized over *n*-hexane to prepare the >99% ee cyclic carbonate. The obtained enantiomerically pure **9a** was treated with $[Co_2(CO)_8]$ in heptane to afford the corresponding **9a**–cobalt carbonyl complex (Scheme 4).[32] The result of the X-ray analysis revealed that the (*S*)-**9a** was obtained as the *Z*-isomer in the reaction catalyzed by the complex with (*R*,*R*)-**10b**.

Various Bispropargylic Alcohols: The optimized catalytic system was successfully applied to various bispropargylic alcohols (Table 15). In the presence of 3 mol % silver acetate and 1 mol % ligand **10b** under a 1.0 MPa CO_2 pressure at 0 °C, the phenyl-substituted bispropargylic alcohols **8a** and **8b** were converted into the corresponding cyclic carbonates **9a** and **9b** in the excellent yields with 92% ee and 93% ee, respectively (Entries 1 and 2). The reaction of the fluoromethyl-substituted propargylic alcohol **8c** also proceeded in high yield with a high ee (Entry 3). Though the bispropargylic alcohol with a homobenzyl substituent **8d** was less reactive than the other phenyl-substituted alcohols, the cyclic product **9d** was obtained without affecting the enantioselectivity (Entry 4). The isopropyl-substituted alkyne **8e** reacted with CO_2 to afford the corresponding carbonate **9e** in high yield with a high ee (Entry 5). Due to the steric bulkiness, the alkyne **8f** was less reactive and the corresponding product **9f** was obtained in 58% yield with an 82% ee (Entry 6). Bispropargylic alcohols with a substituted phenyl **8g**–**8j** were also good substrates that afforded the corresponding cyclic carbonates **9g**–**9j** in excellent yields with good to high enantiomeric excesses regardless of the electron-donating and -withdrawing substituents (Entries 7–10). The enantiomer-enriched conjugated cyclic carbonate **9k** was also obtained in high yield with an 80% ee (Entry 11). The alkyl-substituted alkyne with a protective group in the molecule **8l** was converted into the corresponding cyclic product **9l** in excellent yield with a moderate enantioselectivity (Entry 12). As for the *exo* olefin structure, all products were obtained as the sole isomer based on NMR spectroscopic analysis, and they were suggested to be the *Z*-isomer based on the NOE experiments.

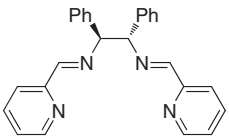
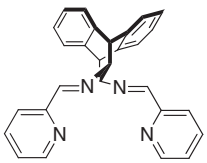
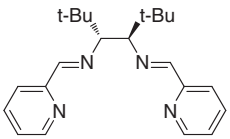
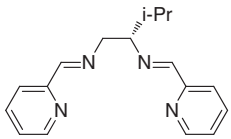
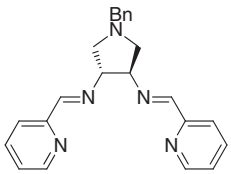
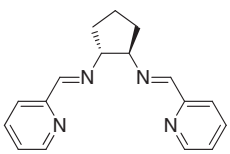
The Application for Aminolysis Reaction: The obtained optically active cyclic carbonate was found to afford the corresponding carbamates via the aminolysis reaction without any loss of enantioselectivity. Although a protocol to produce the carbamate was recently reported involving the reaction of an amine, internal propargylic alcohol and CO_2,[33] a high reaction temperature was required within the limitation of the secondary amines. Milder reaction conditions should be developed for the stereoselective aminolysis of a wide variety of amines.

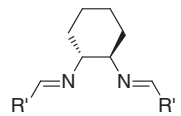
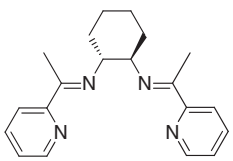
The reactions of the obtained optically active cyclic carbonate **9a** with various amines were carried out in THF at 5 °C (Table 16). Secondary amines, such as diethylamine, pyrrolidine, and morpholine, produced the corresponding carbamate **11a**–**11c** in high to excellent yields while maintaining the enantioselectivity, however the reaction of diethylamine required 24 h to consume the optically active cyclic carbonate **9a** (Entries 1–3). The reaction of aliphatic primary amines, such as *tert*-butylamine, *iso*-propylamine, and propylamine, also proceeded to afford the corresponding products **11d**–**11f** in

Table 13. Examination of Various Chiral Schiff Base Ligands



8a **9a**

Entry[a]	L*	Time/h	Yield/%[b]	Ee/%[c]
1		96	89	4
2		64	87	27[d]
3		42	96	3
4		94	90	37[d]
5		86	93	30
6		96	70	58

Entry[a]	L*	Time/h	Yield/%[b]	Ee/%[c]
	 R′ =			
7	2-pyrrolyl	40	trace	
8	2-thiazolyl	136	67	53
9	4-pyridyl	48	trace	
10	2-quinolyl	92	76	80
11	2-pyridyl	82	91	82
12	2-(3,5-di-Me-pyridyl)	92	92	72
13	2-(6-Me-pyridyl)	42	84	83
14	2-(4-Me_2N-pyridyl)	42	91	76
15	 **10b**	22	97	89

a) Reaction conditions: The reaction was carried out in 1.5 mL of $CHCl_3$ with 0.25 mmol of substrate under 1.0 MPa CO_2 pressure. b) Isolated yield. c) Enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H. d) Major isomers were different form other entries.

excellent yields without any loss of enantioselectivity although their reactivities were lower than the secondary amines (Entries 4–6). An allylamine was also found to be an appropriate amine for the reaction to produce the corresponding carbamate **11g** in 96% yield with the same enantioselectivity (Entry 7).

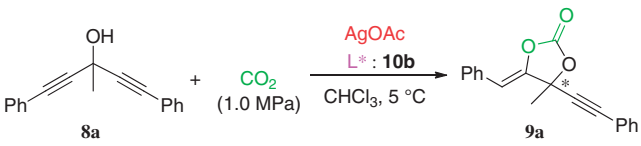
Conclusion

It is noted that the silver catalyst system could be used for various CO_2 incorporation reactions; in the presence of DBU, the cyclization of CO_2 with propargylic alcohols and propargylic amines stereoselectively proceeded to afford the corresponding cyclic carbonate derivatives and oxazolidinone derivatives, respectively, as a *Z*-isomer in high chemical yields under mild reaction conditions. By using the present catalyst system, the [3,3]-sigmatropic Meyer–Schuster-type reaction of various tertiary and secondary propargyl alcohols were efficiently promoted by CO_2 to afford the corresponding α,β-unsaturated carbonyl compounds in high yield. The former reaction selectively proceeded in toluene, whereas the latter in polar solvents, such as DMF. It was found that the enantioselective chemical CO_2 incorporation into various bispropargylic alcohols was achieved by the combined use of a catalytic amount of silver acetate and chiral Schiff base ligand. These products were active for the aminolysis reaction to afford the corresponding carbamate derivatives in high yields without any loss of enantioselectivity.

Experimental

General. The ^1H and ^{13}C NMR spectra were recorded with a JOEL model AL-400 or α-400 spectrometer using $CDCl_3$ as

Table 14. The Effect of AgOAc/L*10b Ratio



Entry[a]	AgOAc /mol %	L* /mol %	AgOAc /L*	Time /h	Yield /%[b]	Ee /%[c]
1	1	1	1/1	22	94	81
2	1.5	1	1.5/1	20	98	84
3	2	1	2/1	22	92	88
4	2.5	1	2.5/1	24	92	88
5	3	1	3/1	22	97	90
6	4	1	4/1	22	92	89
7	5	1	5/1	22	97	89
8	7	1	7/1	22	87	88
9	2	4	1/2	12	90	84
10	4	2	2/1	11	98	88
11	5	2	2.5/1	12	90	89
12	6	2	3/1	11	96	89
13[d]	3	1	3/1	48	98	92

a) Reaction conditions: The reaction was carried out in 1.5 mL of $CHCl_3$ with 0.25 mmol of substrate under 1.0 MPa CO_2 pressure at 5 °C. b) Isolated yield. c) Enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H. d) Carried out at 0 °C.

the solvent. The IR spectra were measured with a Thermo Electron Corporation model NICOLET 6700 FT-IR spectrometer. The melting points were measured with a Stanford Research Systems MPA100. The gas chromatograph mass spectra were obtained using a Shimadzu model GCMS-QP5000 spectrometer equipped with a DB-1 (Agilent Technologies, Inc.) GC column. The ESI high-resolution mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. Column chromatography was conducted on silica gel (Kanto 60 N). The dehydrated THF was purchased from Kanto Chemical Co., Inc., and used without further purification. Diethylamine, pyrrolidine, morpholine, *tert*-butylamine, *iso*-propylamine, propylamine, and allylamine were distilled before use. The HPLC analyses were performed using a Shimadzu LC-6A and/or LC-10A chromatograph equipped with a chiral column (Daicel Chiralcel OD-H, Daicel Chiralcel OZ-H, or Chiralpak IA); the peak areas were obtained with a Shimadzu SPD-M10AVP diode array detector/Shimadzu Class-VP or JASCO MD-2010 plus multiwavelength detector/ChromNAV. The optical rotations were recorded with JASCO P-2200 digital polarimaters. The VCD spectra were measured with a JASCO FVS-6000 spectrometer at a resolution of 4 cm^{-1} using a $CDCl_3$ solution in a 50 μm BaF_2 cell with an MCT detector. The React IR™ 4000 system (Mettler-Toledo International, Inc.) equipped with a SiComp ATR probe was used for the time-resolved FT-IR measurements. The analysis software for the React IR™ 4000 system was iC IR™ (Ver. 4.0). The data of compounds **2**,[10a] **4**,[10b] **6**,[11] and **9**[12] had been already reported in previous papers, respectively. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-635752, -734834, and -773512 for compound **2k**, **4a**, and **9a**–cobalt complex, respectively.

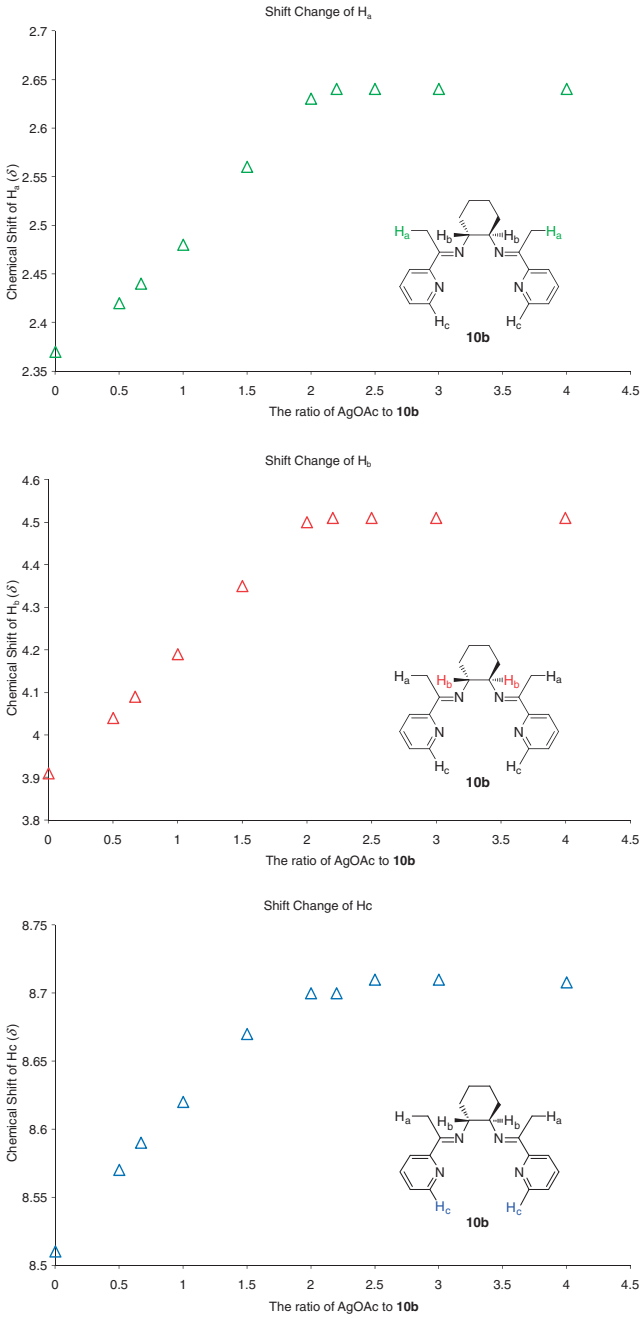
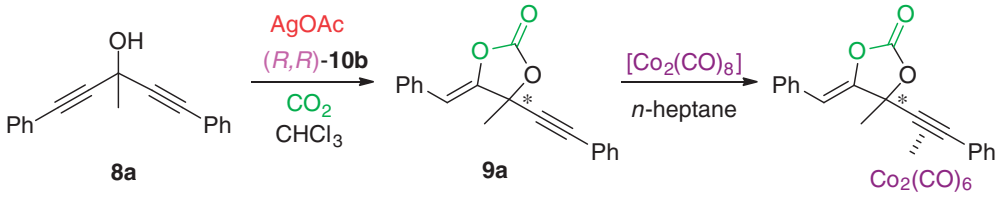


Figure 10. Changes in chemical shift with AgOAc/**10b** ratio.

Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

General Procedure for the Synthesis of Cyclic Carbonate. To a solution of propargylic alcohol **1** (0.25 mmol) in toluene (1.0 mL) was added AgOAc (4.1 mg, 0.025 mmol) and DBU (38.0 mg, 0.25 mmol). The reaction mixture was stirred under 1.0 MPa CO_2 pressure at room temperature. After the reaction was complete, the product was purified by silica gel column chromatography to afford the corresponding carbonate **2**.



Scheme 4. Synthesis of **9a**–cobalt complex.

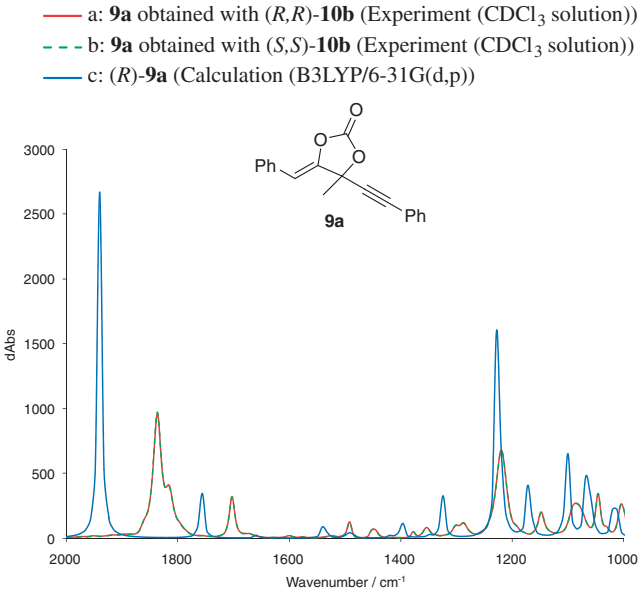


Figure 11. Calculated and experimental IR spectra.

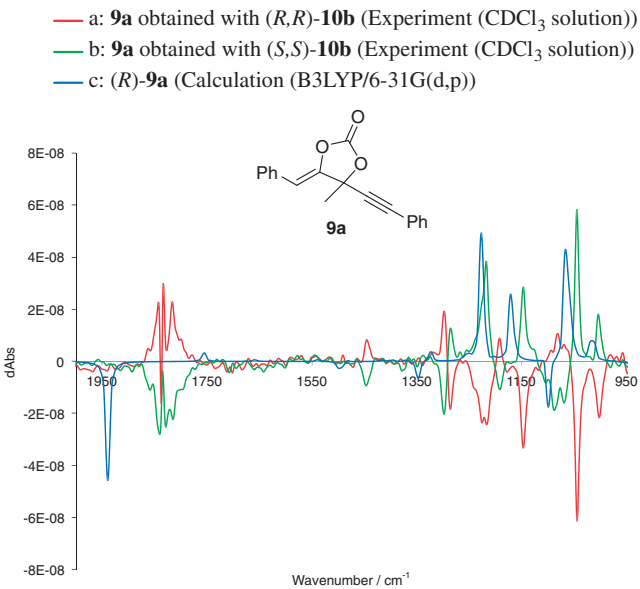


Figure 12. Calculated and experimental VCD spectra.

General Procedure for the Synthesis of Oxazolidinone. To a solution of propargylic amine **3** (0.50 mmol) in DMSO (1.5 mL) was added AgOAc (1.7 mg, 0.01 mmol). The reaction mixture was stirred at 25 °C under atmospheric CO_2 pressure. After the reaction was complete, purification by silica gel column chromatography gave the corresponding oxazolidinone **4**.

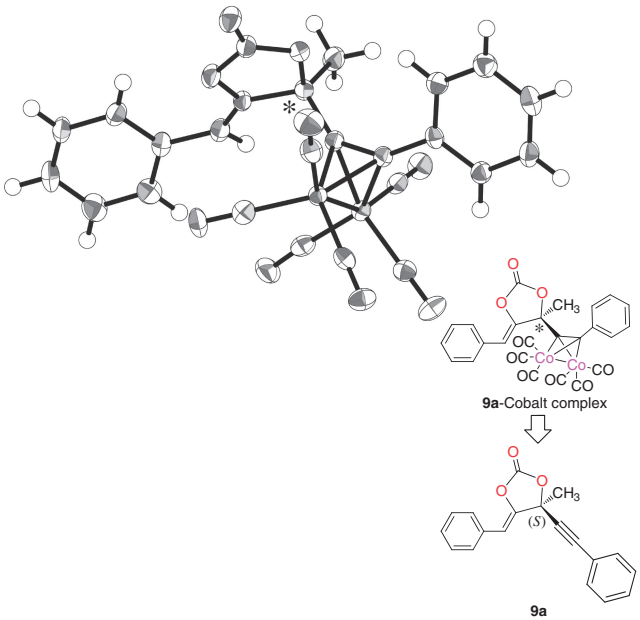


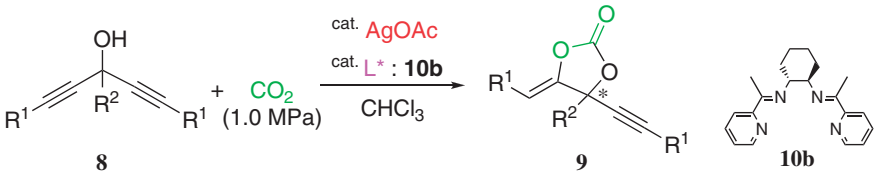
Figure 13. The absolute configuration of **9a**–cobalt complex.

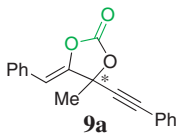
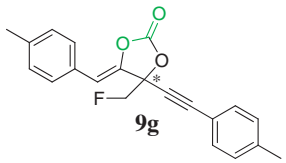
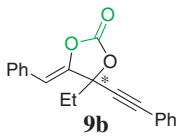
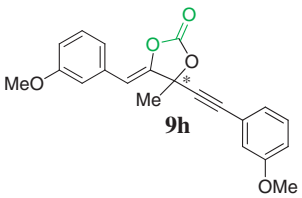
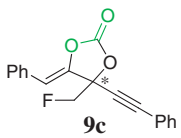
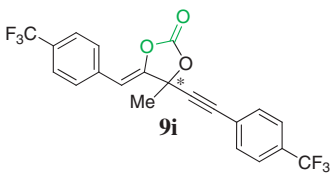
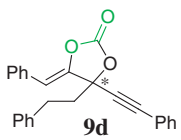
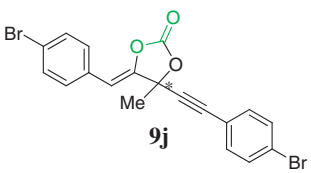
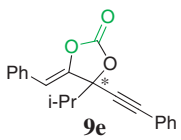
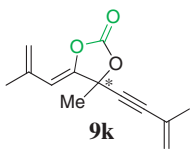
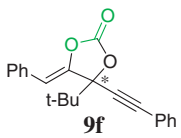
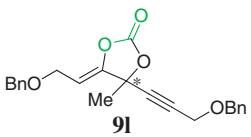
General Procedure for the Meyer–Schuster-Type Rearrangement Mediated by CO_2. To a solution of propargyl alcohol **1** (or **5**) (0.25 mmol) in formamide (0.5 mL) was added silver methanesulfonate (5.1 mg, 0.025 mmol) and DBU (7.5 mg, 0.050 mmol). The reaction mixture was stirred at 60 °C under 1.0 MPa CO_2 pressure. After the reaction was complete, purification by silica gel column chromatography gave the corresponding enone **6**.

The Procedure for the Isotopic Experiment Using $C^{18}O_2$. To a solution of propargyl alcohol **1g** (41.7 mg, 0.25 mmol) in DMF (0.5 mL) was added silver methanesulfonate (5.1 mg, 0.025 mmol) and DBU (37.5 mg, 0.25 mmol). The reaction mixture was stirred at room temperature under atmospheric $C^{18}O_2$ pressure for 3 days. After the reaction mixture was analyzed by GC-MS, purification by silica gel column chromatography (EtOAc/hexane, 1:50) gave the corresponding enone-^{18}O **6a** in 38% yield.

General Procedure for the Reaction of Bispropargylic Alcohol with CO_2. A mixture of AgOAc (1.3 mg, 7.5 µmol) and **10b** (0.8 mg, 2.5 µmol) in $CHCl_3$ (0.5 mL) was stirred for 30 min in the dark under air. To this mixture was added bispropargylic alcohol **8** (0.25 mmol) in $CHCl_3$ (1.0 mL). The reaction mixture was pressurized to 1.0 MPa in an autoclave after the vessel was purged three times with carbon dioxide, which was then stirred at 0 °C. After the reaction was complete, purification by silica gel column chromatography gave the corresponding cyclic carbonate **9**.

Table 15. Enantioselective Carbon Dioxide Incorporation into Various Bispropargylic Alcohols



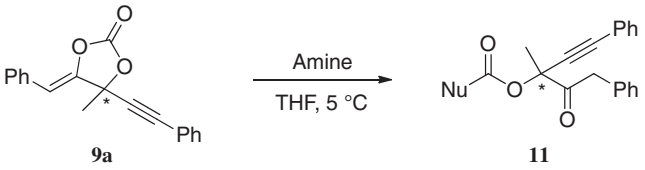
Entry[a]	Products	Time/h	Yield/%[b]	Ee/%[c]	Entry[a]	Products	Time/h	Yield/%[b]	Ee/%[c]
1[d]	 **9a**	48	98	92	7[d]	 **9g**	46	99	90
2[d]	 **9b**	44	98	93	8[d]	 **9h**	46	97	87
3[e]	 **9c**	40	93	91	9[e]	 **9i**	78	96	79
4[f]	 **9d**	140	91	90	10[h]	 **9j**	168	90	79
5[e]	 **9e**	44	94	90	11[f]	 **9k**	120	91	80
6[g]	 **9f**	168	58	82	12[f]	 **9l**	46	97	47

a) Reaction conditions: The reaction was carried out in 1.5 mL of $CHCl_3$ with 0.25 mmol of substrate under 1.0 MPa CO_2 pressure. b) Isolated yield. c) Enantiomeric excess was determined by HPLC analysis using chiral column (Daicel Chiralcel OD-H or Chiralpak IB). d) Using 3 mol % of silver acetate and 1 mol % **10b** at 0 °C. e) Using 3 mol % of silver acetate and 1 mol % **10b** at 5 °C. f) Using 5 mol % of silver acetate and 2 mol % **10b** at 5 °C. g) Using 7.5 mol % of silver acetate and 3 mol % **10b** at 5 °C. h) Using 12 mol % of silver acetate and 5 mol % **10b** in 2.5 mL of $CHCl_3$ at 5 °C.

General Procedure for Aminolysis of Optically Active Cyclic Carbonate 9a. To a solution of the cyclic carbonate **9a** (0.125 mmol) in THF (0.5 mL) was slowly added a THF (0.5 mL) solution of an amine at 5 °C. After the carbonate **9a** was completely consumed, the mixture was evaporated to remove THF. Purification by silica gel column chromatography gave the corresponding carbamate **11**.

3-Methyl-4-oxo-1,5-diphenylpent-1-yn-3-yl Diethylcarbamate (11a): Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.15 (t, 3H, $J = 8.0$ Hz), 1.20 (t, 3H, $J = 8.0$ Hz), 1.73 (s, 3H), 3.24–3.39 (m, 4H), 4.21 (d, 2H, $J = 17.6$ Hz), 7.20–7.38 (m, 8H), 7.44–7.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.5, 14.1, 25.2, 41.7, 42.0, 44.4, 76.9, 87.1, 87.2, 122.0, 126.7, 128.3, 128.4, 128.8, 129.8, 131.8, 134.2, 154.1, 201.9. IR (KBr): 2973, 2936, 1701, 1474, 1430, 1381, 1277, 1169, 975, 757, 719, 696. HRMS(ESI): Calcd for $C_{23}H_{26}NO_3$: $[M + H]^+$: 364.1913. Found: m/z 364.1912. HPLC: Daicel chiralcel OZ-H (0.3% EtOH in hexane; flow rate = 1.0 mL min^{-1}), 10.7 min (major), 15.0 min (minor). $[\alpha]_D^{31}$ +81.5° ($c = 0.22$ in $CHCl_3$).

Table 16. Aminolyis Reaction of Optically Cyclic Carbonate **9a**



9a **11**

Entry[a]	Amine	Equiv	Time/h	**11**	Yield/%[b]	Ee/%[c]	
						9a	**11**
1	Et_2NH	2.0	24	**11a**	99	93	93
2	NH	1.5	3	**11b**	98	89	89
3	O NH	1.5	4	**11c**	>99	94	94
4	NH_2	3.0	72	**11d**	95	94	94
5	NH_2	1.5	5	**11e**	>99	93	93
6	NH_2	1.2	5.5	**11f**	>99	89	89
7	NH_2	1.5	3	**11g**	96	94	94

a) Reaction conditions: The reaction was carried out in 1.0 mL of THF with 0.125 mmol of substrate. b) Isolated yield. c) Enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H for **9a**, Daicel Chiralcel OZ-H for **11a**–**11c**, and Daicel Chiralpak IA for **11d**–**11g**.

3-Methyl-4-oxo-1,5-diphenylpent-1-yn-3-yl Pyrrolidine-1-carboxylate (11b): Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.73 (s, 3H), 1.82–1.95 (m, 4H), 3.39–3.47 (m, 4H), 4.23 (d, 1H, $J = 16.8$ Hz), 4.26 (d, 1H, $J = 16.8$ Hz), 7.21–7.37 (m, 8H), 7.50–7.53 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.9, 25.4, 25.7, 44.6, 46.1, 76.6, 87.1, 87.3, 122.0, 126.7, 128.3, 128.8, 129.8, 131.88, 131.92, 134.1, 153.1, 202.2. IR (KBr): 3033, 2982, 2872, 1701, 1498, 1417, 1277, 1229, 1073, 1063, 1037, 754, 719, 699. HRMS(ESI): Calcd for $C_{23}H_{24}NO_3$: $[M + H]^+$: 362.1756. Found: m/z 362.1753. HPLC: Daicel chiralcel OZ-H (2% EtOH in hexane; flow rate = 1.0 mL min^{-1}), 13.5 min (major), 19.9 min (minor). $[\alpha]_D^{28}$ +75.0° ($c = 0.21$ in $CHCl_3$).

3-Methyl-4-oxo-1,5-diphenylpent-1-yn-3-yl Morpholine-4-carboxylate (11c): Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.73 (s, 3H), 3.48 (s, 2H), 3.55 (s, 2H), 3.69 (t, 4H, $J = 4.4$ Hz), 4.23 (d, 2H, $J = 16.4$ Hz), 7.23–7.39 (m, 8H), 7.46–7.53 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.3, 44.6, 66.5, 77.1, 86.8, 87.5, 121.8, 126.9, 128.3, 128.4, 129.0, 129.8, 131.9, 133.8, 153.5, 201.8. IR (KBr): 2920, 1735, 1541, 1417, 1225, 1084, 1026, 765, 729, 696. HRMS(ESI): Calcd for $C_{23}H_{24}NO_4$: $[M + H]^+$: 378.1705. Found: m/z 378.1710. HPLC: Daicel chiralcel OZ-H (2.0% EtOH in hexane; flow rate = 1.0 mL min^{-1}), 17.9 min (major), 25.8 min (minor). $[\alpha]_D^{30}$ +54.3° ($c = 0.24$ in $CHCl_3$).

3-Methyl-4-oxo-1,5-diphenylpent-1-yn-3-yl *tert*-Butylcarbamate (11d): Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.34 (s, 9H), 1.71 (s, 3H), 4.14 (d, 1H, $J = 16.8$ Hz), 4.20 (d, 1H, $J = 16.8$ Hz), 4.89 (s, 1H), 7.22–7.37 (m, 8H), 7.42–7.48 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.8, 28.8, 43.9, 50.8, 76.8, 86.7, 87.3, 121.9, 126.8, 128.27, 128.3, 128.9, 129.8, 131.8, 134.1, 152.8, 201.7. IR (KBr): 3368, 2984, 1701, 1517, 1506, 1460, 1260, 1205, 1088, 762, 756, 720, 706, 691. HRMS(ESI): Calcd for $C_{23}H_{26}NO_3$: $[M + H]^+$: 364.1913. Found: m/z 364.1930. HPLC: Daicel chiralpak IA (0.5% EtOH in hexane; flow rate = 1.0 mL min^{-1}), 9.0 min (minor), 10.3 (major). $[\alpha]_D^{29}$ +96.2° ($c = 0.20$ in $CHCl_3$).

3-Methyl-4-oxo-1,5-diphenylpent-1-yn-3-yl Isopropylcarbamate (11e): Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.16–1.17 (m, 6H), 1.72 (s, 3H), 3.77–3.85 (m, 1H), 4.19 (d, 1H, $J = 16$ Hz), 4.23 (d, 1H, $J = 16$ Hz), 4.78 (d, 1H, $J = 7.6$ Hz), 7.21–7.38 (m, 8H), 7.44–7.49 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.9, 25.1, 86.7, 87.3, 121.8, 126.8, 128.27, 128.3, 128.9, 129.8, 131.8, 134.0, 153.7, 201.8. IR (KBr): 3390, 3057, 2989, 2235, 1958, 1887, 1712, 1598, 1489, 1443, 1258, 1092, 1015. HRMS(ESI): Calcd for $C_{22}H_{24}NO_3$: $[M + H]^+$: 350.1756. Found: m/z 350.1758. HPLC: Daicel chiralpak IA (2.0% THF in hexane; flow rate = 1.0 mL min^{-1}), 14.0 min (minor), 19.7 min (major). $[\alpha]_D^{30}$ +92.3° ($c = 0.22$ in $CHCl_3$).

3-Methyl-4-oxo-1,5-diphenylpent-1-yn-3-yl Propylcarbamate (11f): Colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.93 (t, 3H, $J = 7.6$ Hz), 1.52–1.57 (m, 2H), 1.72 (s, 3H), 3.13–3.20 (m, 2H), 4.21 (s, 2H), 4.88 (s, 1H), 7.12–7.38 (m, 8H), 7.45–7.50 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.1, 23.1, 25.1, 42.8, 44.3, 76.9, 86.7, 87.4, 121.8, 126.8, 128.28, 128.35, 128.9, 129.8, 131.9, 134.0, 154.5, 201.9. IR (KBr): 3374, 3032, 2966, 2877, 1733, 1541, 1520, 1454, 1252, 1132, 764, 719, 689. HRMS(ESI): Calcd for $C_{22}H_{24}NO_3$: $[M + H]^+$: 350.1756. Found: m/z 350.1758. HPLC: Daicel chiralpak IA (2% THF in hexane; flow rate = 1.0 mL min^{-1}), 7.4 min (minor), 11.5 min (major); $[\alpha]_D^{30}$ +98.2° ($c = 0.20$ in $CHCl_3$).

3-Methyl-4-oxo-1,5-diphenylpent-1-yn-3-yl Allylcarbamate (11g): Pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.73 (s, 3H), 3.83 (s, 2H), 4.22 (s, 2H), 4.96 (s, 1H), 5.15 (d, 1H, $J = 10.8$ Hz), 5.23 (d, 1H, $J = 17.2$ Hz), 5.81–5.90 (m, 1H), 7.24–7.38 (m, 8H), 7.45–7.51 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.1, 43.4, 44.3, 86.5, 87.5, 116.3, 121.7, 126.8, 128.3, 128.4, 128.9, 129.8, 131.8, 133.9, 154.4, 201.8. IR (KBr): 3364, 3064, 3029, 2930, 1716, 1646, 1602, 1543, 1508, 1455, 1244, 1091, 1063, 1030, 992, 915, 763, 718, 690. HRMS(ESI): Calcd for $C_{22}H_{22}NO_3$: $[M + H]^+$: 348.1600. Found: m/z 348.1601; HPLC Daicel chiralpak IA (10% THF in hexane; flow rate = 1.0 mL min^{-1}), 16.4 min (minor), 41.4 min (major). $[\alpha]_D^{29}$ +79.8° ($c = 0.19$ in $CHCl_3$).

Computational Methods. The Gaussian 03 program was used for the full geometry optimizations with the B3LYP/6-31+G*//B3LYP/6-31+G* method and basis set (The 3-21G* basis set was substituted for 6-31+G* in the case of the Ag atom.). 5d functions were used for the d orbital. Calculations were performed without assuming symmetry. Frequency calculations were performed for all of the obtained structures at the same level. It was confirmed that all the frequencies were real for the ground states and one imaginary frequency existed for the transition state (TS). Vectors of the imaginary frequencies directed the reaction mode, and intrinsic reaction coordinate calculations were further performed to confirm that the obtained TSs were on the saddle points of the energy surface between the reactant and the product. The

single-point energy including the SCRF/PCM approach was calculated using the Gaussian 09 program.

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Supporting Information

X-ray analysis of **2k**, **4a**, and **9a**–cobalt complex. NMR and HPLC data of the compounds **11a**–**11g**. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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