

## Silver-Catalyzed Enantioselective Carbon Dioxide Incorporation into Bispropargylic Alcohols

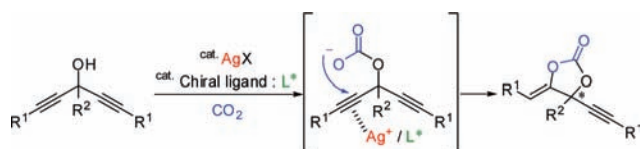
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Since carbon dioxide is expected to be an ubiquitous and abundant C1 feedstock from industrial wastes, much effort has been made to develop effective processes for various chemicals from carbon dioxide.<sup>1</sup> Because of its thermodynamic stability, however, high pressure and/or high temperature are required to react carbon dioxide and transform it into various chemicals. Especially, for the enantioselective synthesis using carbon dioxide, mild reaction conditions and efficient catalytic systems should be applied, though few examples of enantioselective CO<sub>2</sub> fixation reactions have been proposed. It has been reported that the enantioselective CO<sub>2</sub> incorporation into epoxides proceeded with kinetic resolution to afford the corresponding optically active cyclic carbonates or polycarbonates along with unreacted epoxides using optically active salen-cobalt complexes<sup>2</sup> or ketoiminatocobalt complexes<sup>3</sup> as catalysts. Another example is the asymmetric alternating copolymerization of the *meso*-epoxide, such as cyclohexeneoxide, and carbon dioxide using optically active zinc-based complex catalysts.<sup>4</sup> It was also reported that a nickel-catalyzed enantioselective carboxylative cyclization of bis-1,3-dienes proceeded to afford the corresponding cyclic products with high selectivity using CO<sub>2</sub> as a reactant.<sup>5</sup> Although these catalyst systems exhibited a high activity and enantioselectivity, the enantioselective CO<sub>2</sub> incorporation still remains a challenging area.

### Scheme 1. Enantioselective Chemical Incorporation of CO<sub>2</sub> into Bispropargylic Alcohols



In a previous communication, we reported that the combined use of a catalytic amount of silver salt and DBU efficiently catalyzed the incorporation of CO<sub>2</sub> under mild reaction conditions into a wide range of propargylic alcohols to afford the corresponding cyclic carbonates in high-to-excellent yields.<sup>6</sup> In this reaction, it was assumed that the silver catalysts effectively activated the C–C triple bond as a  $\pi$ -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. Based on these observations, the corresponding optically active cyclic carbonates were obtained by using an optically active silver catalyst, which is in rapid equilibrium between the two alkynes in bispropargylic alcohols, and a nucleophilic attack selectively proceeds to one of the C–C triple bonds, with asymmetric desymmetrization. In this communication, we report that the combined catalyst system of silver acetate with a chiral Schiff base ligand achieved the asymmetric carbon dioxide incorporation into bispropargylic alcohols with desymmetrization to afford the cor-

Table 1. Examination of Various Reaction Conditions

entry <sup>a</sup>	L*	AgOAc (mol %)	L* (mol %)	temp (°C)	time (h)	yield <sup>b</sup> (%)	ee <sup>c</sup> (%)
1 <sup>d</sup>	<b>3a</b>	10	12	r.t.	2	96	40
2		10	12	r.t.	5	92	70
3		5	1	20	20	90	75
4		5	1	5	96	91	83
5	<b>3b</b>	2	1	5	22	92	88
6		3	1	5	22	97	90
7		5	2	5	12	90	89
8		3	1	0	48	98	92

<sup>a</sup> Reaction conditions: The reaction was carried out in 1.5 mL of CHCl<sub>3</sub> with 0.25 mmol of substrate under 1.0 MPa of CO<sub>2</sub> pressure. <sup>b</sup> Isolated yield. <sup>c</sup> Enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H. <sup>d</sup> Carried out in CH<sub>2</sub>Cl<sub>2</sub>.

responding cyclic carbonates with good-to-excellent enantiomeric excesses (Scheme 1).

Various optically active ligands were first examined, such as ferrocene derivatives, BINAP, BOX, and Py-BOX. In the presence of 10 mol % of silver acetate with the ligand, a model compound **1a** was treated with a stoichiometric amount of DBU in CH<sub>2</sub>Cl<sub>2</sub> under 1.0 MPa of CO<sub>2</sub> pressure at room temperature. Although all reactions proceeded to afford the corresponding cyclic carbonates, the corresponding products were obtained without any enantioselectivity. It was assumed that the 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 26% ee. Without DBU, various chiral ligands were then screened and the product was obtained with 40% ee by using the chiral Schiff base ligand **3a**<sup>7</sup> derived from 1,2-diaminocyclohexane and 2-pyridinecarboxaldehyde (Table 1, entry 1). Various reaction conditions involving the solvent, catalyst loading, and temperature were examined in the presence of the ligand **3a** (entries 2–4). When CHCl<sub>3</sub> was employed as the solvent, the selectivity was dramatically improved to afford the cyclic product in 92% yield with 70% ee (entry 2). In the presence of excess amounts of silver acetate with respect to the chiral ligand, the enantiomeric excess was slightly improved (entry 3) and the product was obtained with 83% ee at 5 °C (entry 4). It was eventually found that the chiral ketimine ligand **3b** was better than the ligand **3a** for both reactivity and selectivity (entries 5–8). By using the ligand **3b**, the bispropargylic alcohol **1a** was

completely consumed to afford the corresponding product in excellent yield with a high enantiomeric excess (entries 5–7). For the reaction with over 2 equiv of AgOAc versus the chiral ligand **3b**, almost the same enantiomeric excess was observed. The  $^1\text{H}$  NMR spectroscopic analysis suggested that the silver acetate and chiral ketimine ligand **3b** would form the corresponding 2:1 complex. After examination of the loading ratio of the ligand/silver,<sup>8</sup> a combination of 3 mol % of silver acetate and 1 mol % of **3b** was found to be optimum to realize a high selectivity (entry 7). When the reaction was carried out at 0 °C, the CO<sub>2</sub>-incorporated carbonate was obtained at up to 92% ee. The absolute configuration of carbonate **2a** was determined by VCD measurement in combination with the corresponding spectra predicted by DFT calculations.<sup>9</sup> As a result, it was found that (*S*)-**2a** was obtained in the reaction catalyzed by the complex with (*R,R*)-**3b**.<sup>8</sup>

**Table 2.** Enantioselective Carbon Dioxide Incorporation into Various Bispropargylic Alcohols

entry <sup>a</sup>	R <sup>1</sup>	R <sup>2</sup>		time (h)	yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
1 <sup>d</sup>	Ph	Me	<b>2a</b>	48	98	92
2 <sup>d</sup>		Et	<b>2b</b>	44	98	93
3 <sup>e</sup>		CH <sub>2</sub> F	<b>2c</b>	40	93	91
4 <sup>f</sup>		CH <sub>2</sub> CH <sub>2</sub> Ph	<b>2d</b>	140	91	90
5 <sup>e</sup>		<i>i</i> -Pr	<b>2e</b>	44	94	90
6 <sup>g</sup>		<i>t</i> -Bu	<b>2f</b>	168	58	82
7 <sup>d</sup>	4-Me-C <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> F	<b>2g</b>	46	99	90
8 <sup>d</sup>	3-MeO-C <sub>6</sub> H <sub>4</sub>	Me	<b>2h</b>	46	97	87
9 <sup>e</sup>	4-CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	Me	<b>2i</b>	78	96	79
10 <sup>h</sup>	4-Br-C <sub>6</sub> H <sub>4</sub>	Me	<b>2j</b>	168	90	79
11 <sup>f</sup>	C(CH <sub>3</sub> )=CH <sub>2</sub>	Me	<b>2k</b>	120	91	80
12 <sup>f</sup>	CH <sub>2</sub> OBn	Me	<b>2l</b>	46	97	47

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

The optimized catalytic system was successfully applied to various bispropargylic alcohols (Table 2). In the presence of 3 mol % of silver acetate and 1 mol % of ligand **3b** under 1.0 MPa of CO<sub>2</sub> pressure at 0 °C, the phenyl-substituted bispropargylic alcohols **1a** and **1b** were converted into the corresponding cyclic carbonates **2a** and **2b** in excellent yield with 92% ee and 93% ee, respectively (entries 1–2). The reaction of the fluoromethyl substituted propargylic alcohol **1c** also proceeded in high yield with a high ee (entry 3). Though the bispropargylic alcohol with a homobenzyl substituent **1d** was less reactive than the other phenyl-substituted alcohols, the cyclic product **2d** was obtained without affecting the enantioselectivity (entry 4). The isopropyl substituted alkyne **1e** reacted with CO<sub>2</sub> to afford the corresponding carbonate **2e** in high yield with high ee (entry 5). Due to the steric bulkiness, the alkyne **1f** was

less reactive and the corresponding product **2f** was obtained in 58% yield with 82% ee (entry 6). Bispropargylic alcohols with a substituted phenyl **1g–1j** were also good substrates that afforded the corresponding cyclic carbonates **2g–2j** 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 **2k** was also obtained in high yield with 80% ee (entry 11). The alkyl-substituted alkynes with a protective group in the molecule **1l** was converted into the corresponding cyclic product **2l** 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 an NMR spectroscopic analysis, and they were suggested to be the *Z* isomer by NOE experiments. The optically active cyclic carbonate was readily hydrolyzed in the presence of aqueous NaOH to afford the corresponding  $\alpha$ -hydroxyketone in high yield without any loss of optical purity.<sup>8</sup>

It is noted that enantioselective chemical CO<sub>2</sub> incorporation into various bispropargylic alcohols was achieved by the combined use of a catalytic amount of silver acetate and chiral Schiff base ligand. Further investigations involving the mechanistic study and transformation of the chiral cyclic carbonates are now under way.

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**Supporting Information Available:** Experimental procedure and spectra data of the new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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