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Palladium-Catalyzed Carbon Dioxide Elimination−Fixation Reaction of 4-Methoxycarbonyloxy-2-buten-1-ols

Masahiro Yoshida,* Yusuke Ohsawa, and Masataka Ihara*

Department of Organic Chemistry, Graduate School of Pharmaceutical Sciences, Tohoku University, Aobayama, Sendai 980-8578, Japan

mihara@mail.pharm.tohoku.ac.jp

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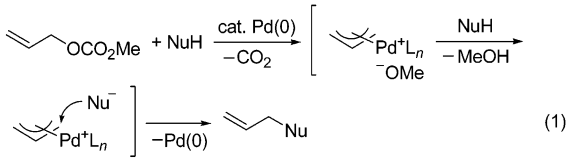
A new type of palladium-catalyzed CO_2 recycling reaction using allylic carbonates is described. Reaction of *trans*-4-methoxycarbonyloxy-2-buten-1-ols in the presence of a palladium catalyst produces cyclic carbonates having a vinyl group via a CO_2 elimination−fixation process. A variety of allylic carbonates participate in the reaction giving cyclic carbonates with high efficiencies. Stereoselective construction of *trans*-cyclic carbonates is achieved by using nonsymmetric substrates. An enantiospecific reaction proceeds to give chiral cyclic carbonate when a chiral methyl-substituted substrate is subjected to the reaction conditions.

Introduction

Palladium-catalyzed allylic substitutions of allylic compounds with soft nucleophiles are an extensively studied research area in organic chemistry, and many examples and their applications have been developed.[1] Among them, reactions of allylic carbonates are one of the most common methods in which various kinds of nucleophiles are substituted at the allylic position via a π-allylpalladium intermediate (eq 1).[1e−k] The reactions can be



(1)

conveniently carried out in neutral conditions because the alkoxide ion formed in situ abstracts the active hydrogen from a protonated nucleophile to generate a reactive anionic nucleophile. In these reactions, CO_2 is invariably produced as a coproduct.

Fixation of carbon dioxide into organic substances represents an attractive area of study in both organic and green chemistry.[2] Palladium-catalyzed reactions are one of the common methods to fix external carbon dioxide into organic compounds.[3,4] Recently, we have developed a novel palladium-catalyzed reaction of propargylic carbonates with phenols, which involves a "recycling of CO_2" process.[5] The reaction proceeds via a carbon dioxide elimination−fixation step and affords phenoxy-substi-

(1) For reviews about palladium-catalyzed reactions of allylic compounds: (a) Tsuji, J. *Acc. Chem. Res.* **1969**, *2*, 144. (b) Tsuji, J. *Pure Appl. Chem.* **1982**, *54*, 197. (c) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 799. (d) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985. (e) Tsuji, J. *J. Organomet. Chem.* **1986**, *300*, 281. (f) Tsuji, J. *Tetrahedron* **1986**, *42*, 4261. (g) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140. (h) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1990. (i) Godleski, S. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Semmelhack, M. F., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 4, p 585. (j) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley and Sons: Chichester, U.K., 1995. (k) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395.

(2) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R. *Chem. Rev.* **2001**, *101*, 953.

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(5) (a) Yoshida, M.; Ihara, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 616. (b) Yoshida, M.; Fujita, M.; Ishii, T.; Ihara, M. *J. Am. Chem. Soc.* **2003**, *125*, 4874.

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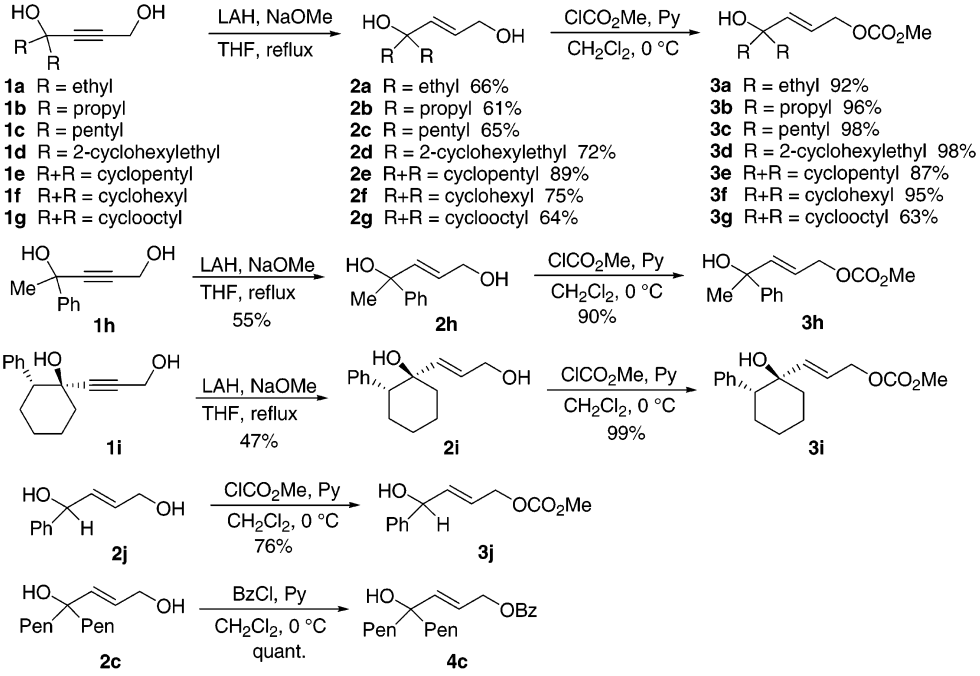
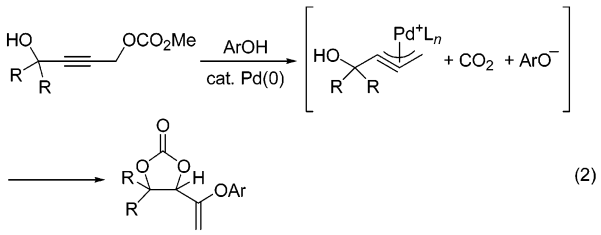
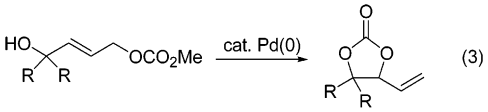
SCHEME 1. Synthesis of Allylic Carbonates



tuted cyclic carbonates (eq 2). We sought to determine



whether a "recycling of CO_2" process could apply for allylic carbonates to yield cyclic carbonates (eq 3). Herein,



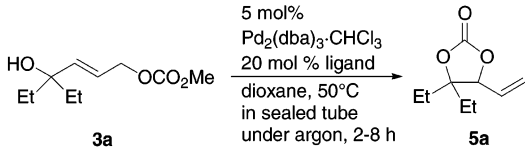
we describe the details of this process.

Results and Discussion

Allylic carbonates for palladium-catalyzed reactions are synthesized as follows (Scheme 1). The propargylic diols having various substituents **1a**−**1g** are selectively reduced to *trans*-allylic diols **2a**−**2g** in 61−89% yields by reactions with LAH in the presence of sodium methoxide. Reactions of **2a**−**2g** with methyl chloroformate in the presence of pyridine afford allylic carbonates **3a**−**3g** in 63−98% yields. Similarly, unsymmetric substrates **3h** and **3i** are prepared from the corresponding propargylic diols **1h** and **1i** in two steps. A substrate **3j** having a secondary alcohol moiety is also synthesized from the corresponding allylic diol **2j**. To perform mechanistic studies on the palladium-catalyzed reaction, allylic benzoate **4c** is prepared from **2c** and benzoyl chloride.

Our initial attempt at palladium-catalyzed reaction of allylic carbonate begins with **3a** (Table 1). When **3a** is

TABLE 1. Formation of Cyclic Carbonate 5a by the Reaction of Propargylic Carbonate 3a

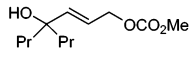
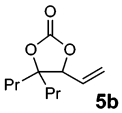
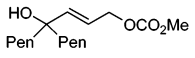
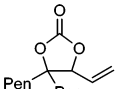
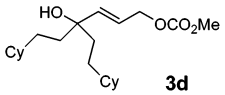
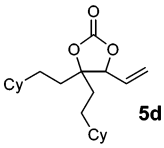
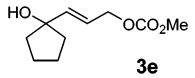
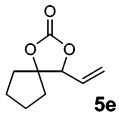
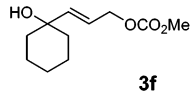
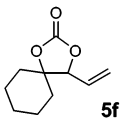
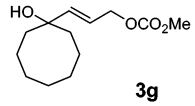
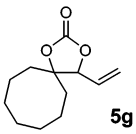


entry	catalyst	time (h)	yield[a] (%)
1	dppe	8	58
2	dppp	8	NR
3	dppb	8	NR
4	dppf	1	79
5[b]	P(*o*-Tol)$_3$	8	NR
6[b]	PPh_3	2	63
7[c]	dppf	4	79
8[d]	dppf	96	57
9[e]	dppf	96	25 (50)

[a] The yield in parentheses is based on recovered starting material. NR stands for no reaction. [b] 40 mol % ligand was used. [c] 2.5 mol % $Pd_2(dba)_3$·$CHCl_3$ and 10 mol % ligand were used. [d] 1 mol % $Pd_2(dba)_3$·$CHCl_3$ and 4 mol % ligand were used. [e] 0.5 mol % $Pd_2(dba)_3$·$CHCl_3$ and 2 mol % ligand were used.

subjected to 5 mol % $Pd_2(dba)_3$·$CHCl_3$ and 20 mol % 1,2-bis(diphenylphosphino)ethane (dppe) in dioxane at 50 °C under an argon atmosphere in a sealed tube, cyclic carbonate **5a**, having a vinyl group, is produced in 58% yield (entry 1). Although no reaction proceeds in the presence of 1,3-bis(diphenylphosphino)propane (dppp), 1,4-bis(diphenylphosphino)butane (dppb), and P(*o*-Tol)$_3$ (entries 2, 3, and 5), the yield is increased to 79% when 1,1′-bis(diphenylphosphino)ferrocene (dppf) is used as a ligand (entry 4). The reaction in the presence of PPh_3 also gives **5a** in 63% yield (entry 6). Although the reason for the observed specificity depending on the ligand is not clear, it is proposed that this CO_2 elimination−fixation process is sensitive for the steric and electronic properties of the phosphine ligand, and dppf is suitable for the

TABLE 2. Reactions of Various Substituted Allylic Carbonates 3b−3g[a]

entry	substrate	product	yield (%)
1	 **3b**	 **5b**	76
2	 **3c**	 **5c**	79
3[b]	 **3d**	 **5d**	68
4	 **3e**	 **5e**	60
5	 **3f**	 **5f**	60
6	 **3g**	 **5g**	77

[a] Reactions were carried out in the presence of 5 mol % $Pd_2(dba)_3{\cdot}CHCl_3$ and 20 mol % dppf in dioxane under an argon atmosphere at 50 °C in a sealed tube for 1−24 h. [b] Dppe was used as a ligand.

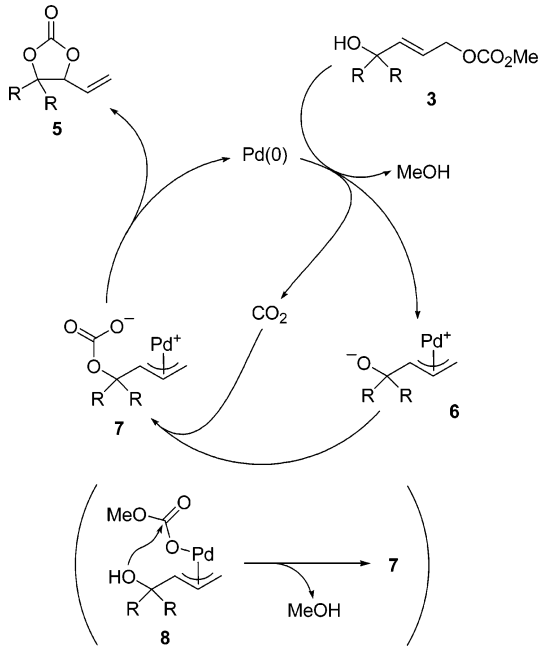
reaction. The reaction exhibits similar reactivity in the presence of 2.5 mol % palladium catalyst (entry 7), but the reactivity has been decreased in the presence of 1 mol % and 0.5 mol % palladium catalyst (entries 8 and 9).

The results of the reactions of allylic carbonates **3b**−**3g**, which contain various substituents, are summarized in Table 2. The corresponding cyclic carbonate **5b** is formed in 76% yield when dipropyl-substituted substrate **3b** is used (entry 1). Substrates **3c** and **3d**, having dipentyl and di-β-cyclohexylethyl groups, are transformed to **5c** and **5d** in 79% and 68% yield, respectively (entries 2 and 3). Reactions of substrates **3e**, **3f**, and **3g** with cycloalkanol moieties of various ring sizes also afford the corresponding products **5e**, **5f**, and **5g** in moderate yields (entries 4, 5, and 6).

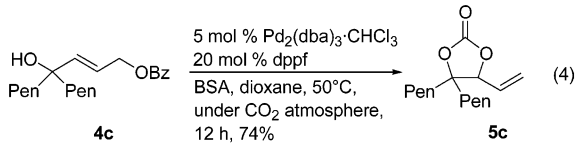
Mechanistic Studies. A proposed mechanism for the formation of cyclic carbonates by the palladium-catalyzed reaction of the allylic carbonates is shown in Scheme 2. A palladium catalyst initially promotes decarboxylation of allylic carbonate to generate a π-allylpalladium complex **6**, MeOH, and CO_2. Fixation of CO_2 by the resulting hydroxyl anion leads to an intermediate **7**, and subsequent cyclization gives a cyclic carbonate **5**. However, as another mechanism, an intramolecular CO_2 transfer pathway via **8**, which involves a chelation of carbonate to palladium without decarboxylation, is also expected.

To examine whether CO_2 dissociates from the substrate in the reaction, several experiments were attempted. We

SCHEME 2. Proposed Reaction Mechanism

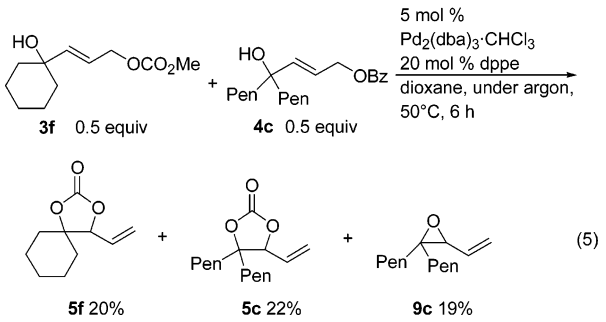


initially examined the reactions of allylic benzoate **4c**, having a non-CO_2 liberating leaving group, in the presence of CO_2. When **4c** is subjected to the palladium catalyst in the presence of *N*,*O*-bis(trimethylsilyl)acetamide (BSA)[6] under an atmosphere of CO_2, the corresponding cyclic carbonate **5c** is produced in 74% yield (eq 4). This result indicates that the product is formed



by a route in which CO_2 is incorporated from an external source.

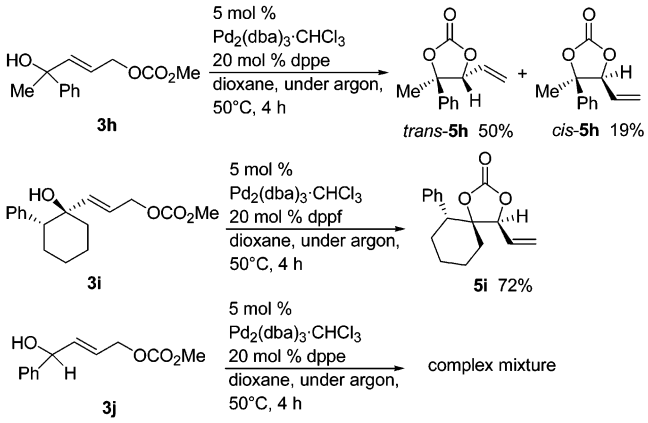
A crossover experiment with allylic carbonate **3f** and allylic benzoate **4c** is next performed (eq 5). Reaction of



an equimolar mixture of **3f** and **4c** under palladium catalysis results in production of cyclic carbonate **5c** in 22% yield, which is derived from **4c**, along with the formation of **3f**-derived cyclic carbonate **5f** and **4c**-derived epoxide **9c** in 20% and 19% yield, respectively. It is clear

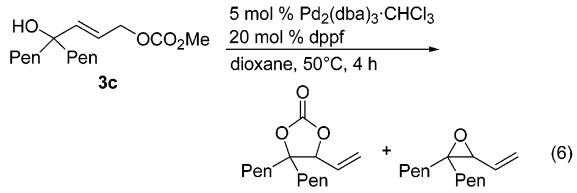
(6) For a review on BSA: El Gihani, M. T.; Heaney, H. *Synthesis* **1998**, 357.

SCHEME 3. Diastereoselective Construction of Cyclic Carbonates



that **5c** arises by reaction of in situ generated CO_2 formed by decarboxylation of **3f**.

We also conducted the reactions in both the presence and the absence of a CO_2 source (eq 6). While the reaction of allylic carbonate **3c** with $Pd_2(dba)_3$·$CHCl_3$ and dppf under an argon atmosphere yields cyclic carbonate **5c** in 79% yield (entry 4 in Table 1), the process carried out under 1 atm of CO_2 leads to an 86% yield of **5c**.



(6)

	5c	**9c**
under CO_2 atmosphere	86%	0%
under bubbling argon	17%	20%

Furthermore, when the reaction is carried out under bubbling argon to remove the resulting CO_2, **5c** is formed in only 17% yield together with epoxide **9c** in 20% yield. It is expected that **9c** would be obtained by direct cyclization from intermediate **6** without fixation of CO_2, and these results support the hypothesis that the process proceeds through a pathway involving decarboxylation−fixation of liberated CO_2.

Stereoselective Construction of Cyclic Carbonate. We also studied the reaction using unsymmetric allylic carbonates (Scheme 3). Substrate **3h**, derived from acetophenone, reacts with the palladium catalyst to afford a mixture of products *trans*- and *cis*-**5h** with *trans*-selectivity (50% yield of *trans*-**5h**, 19% yield of *cis*-**5h**). Furthermore, *trans*-cyclic carbonate **5i** is produced as a sole product in 72% yield when substrate **3i**, having a 2-phenylcyclohexyl group, is subjected to the reaction. On the other hand, a reaction of allylic carbonates **3j** with a secondary alcohol moiety gives a complex mixture, which reveals that a tertiary alcohol moiety in the substrate is necessary for the reaction.[7] The stereochemistries of the obtained products were all determined by NOESY spectra (Figure 1). A proposed rationale for the

(7) Previously, we obtained a similar result in the palladium-catalyzed reaction of propargylic carbonate containing a primary alcohol; see ref 5b.

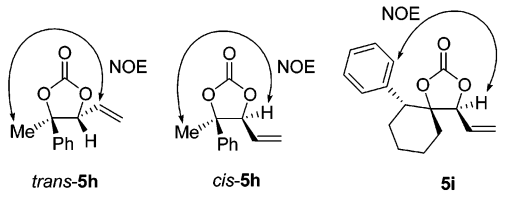
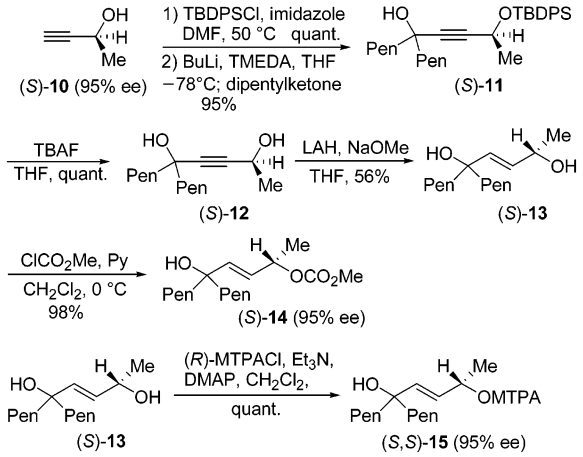
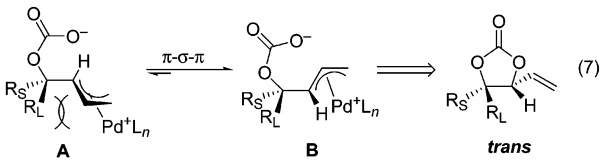


FIGURE 1. NOESY correlations of *trans*- and *cis*-**5h** and **5i**.

SCHEME 4. Synthesis of Chiral Allylic Carbonate (*S*)-14



stereochemical outcome of the process is based on a consideration of the transition state for cyclization of the interconverting, isomeric π-allylpalladium intermediates **A** and **B** (eq 7). Equilibration between **A** and **B** occurs



(7)

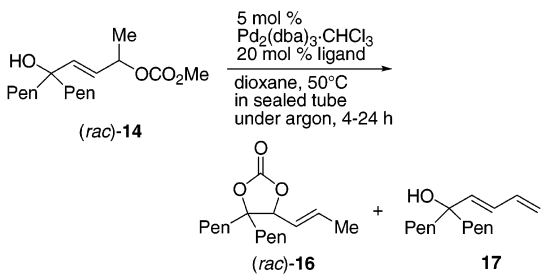
by $\pi-\sigma-\pi$ isomerization. It is expected that the transition state for cyclization **B**, forming the *trans*-product, would be of lower energy because of the absence of the steric repulsion that is present in the transition state derived from **A**.

Enantiospecific Construction of Cyclic Carbonate. It is known that enantiospecific chirality transfer is observed in the palladium-catalyzed reaction of chiral allylic compounds.[8] We sought to apply this property of π-allylpalladium species to our CO_2 recycling process by introducing an asymmetric center at an allylic position.[9] Scheme 4 shows the synthesis of chiral methyl-substituted substrate (*S*)-**14**. Chiral propargylic alcohol (*S*)-**10**, with 95% ee, is protected with the TBDPS group and then treated with BuLi followed by dipentyl ketone to give propargylic alcohol (*S*)-**11** in 95% yield. After the deprotection of the silyl group that leads to diol (*S*)-**12**,

(8) For reviews on stereochemical studies of palladium-catalyzed reactions of allylic compounds: (a) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (b) Consiglio, G.; Waymouth, R. M. *Chem. Rev.* **1989**, *89*, 257. (c) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1173. (d) Heumann, A.; Réglier, M. *Tetrahedron* **1995**, *51*, 975. (e) Trost, B. M.; Vranken, D. L. V. *Chem. Rev.* **1996**, *96*, 395.

(9) Recently, we discovered the reaction of substituted chiral propargylic carbonates with phenols proceeds with transferring chirality: Yoshida, M.; Fujita, M.; Ihara, M. *Org. Lett.* **2003**, *5*, 3325.

TABLE 3. Formation of Cyclic Carbonate 16 by the Reaction of Propargylic Carbonate 14



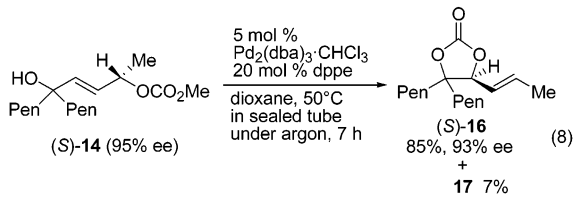
				yield[a,b] (%)	
entry	ligand	atmosphere	time (h)	**16**	**17**
1	dppf	argon	24	13 (15)	45 (53)
2	dppf	CO_2	48	19 (66)	4 (12)
3	dppe	argon	12	85	7
4	dppp	argon	6	15	64
5	dppb	argon	4	64	6
6[c]	PPh_3	argon	4	32	67

[a] Isolated yields. [b] The yields in parentheses are based on recovered starting material. [c] 40 mol % ligand was used.

reduction of the alkyne followed by methyl carbonation of the secondary alcohol affords chiral allylic carbonate (*S*)-**14**. By following the same procedure, racemic allylic carbonate **14** is also synthesized from racemic **10**. The enantiomeric excess of (*S*)-**14** is determined as 95% ee by conversion of diol (*S*)-**13** with 2-methoxy-2-trifluoromethyl-2-phenylacetyl chloride (MTPACl) to MTPA ester (*S*,*S*)-**15**.

We initially attempted the reaction using racemic allylic carbonate **14** (Table 3). Reaction of the substrate in the presence of 5 mol % $Pd_2(dba)_3$·$CHCl_3$ and 20 mol % dppe in dioxane at 50 °C under an argon atmosphere for 24 h produces racemic cyclic carbonate **16**, which has *E* geometry, in 13% yield together with diene **17** in 45% yield and a small amount of recovered starting material. It is presumed that byproduct **17** would be yielded by β-elimination with the terminal methyl hydrogen from the π-allylpalladium intermediate. The production of **17** is suppressed by employing the reaction under a CO_2 atmosphere, but a fair amount of starting material remains (entry 2). Gratifyingly, the desired cyclic carbonate **16** is selectively obtained in 85% yield when the reaction is carried out in the presence of dppe (entry 3). Similar reactivity is observed by the use of dppb (64% yield), while diene **17** is predominantly formed when dppp and PPh_3 are used (entries 4 and 6).

The reaction using enantiomerically enriched chiral allylic carbonate (*S*)-**14** was next examined (eq 8). When (*S*)-**14** is subjected to the reaction in the presence of palladium catalyst and dppe, chiral cyclic carbonate **16** is produced in 85% yield. The absolute configuration of



(8)

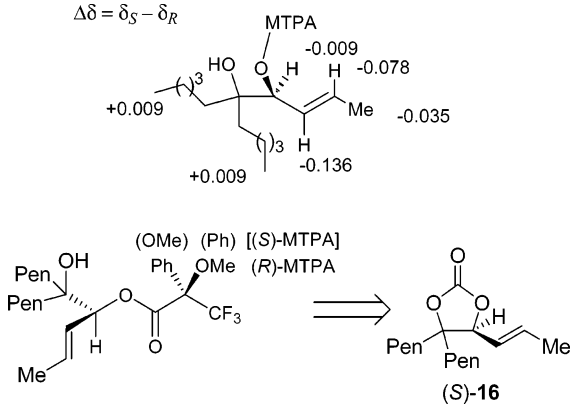
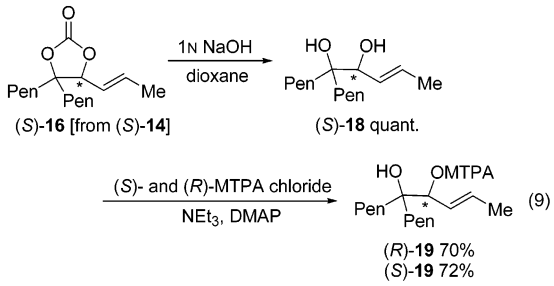


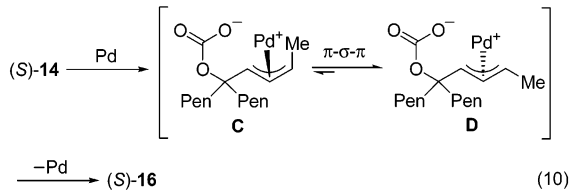
FIGURE 2. Determination of the absolute configuration of **16**.

the product is determined by Kusumi's method[10] after conversion to the MTPA esters. Product (*S*)-**16** is subjected to hydrolysis in the presence of 1 N NaOH to give diol **18**, and then the product is transformed to (*S*)- and (*R*)-MTPA ester (*S*)- and (*R*)-**19** by reaction with (*R*)- and (*S*)-MTPA chloride (eq 9). On the basis of the $\Delta\delta$ values



(9)

($\Delta\delta = \delta_{(S)-\text{ester}} - \delta_{(R)-\text{ester}}$) (Figure 2), the absolute configuration of **16** is determined as *S*. Furthermore, it is noteworthy that the enantiomeric excess of (*S*)-**16** is determined as 93% by ^{1}H NMR integration of (*S*)- and (*R*)-**19**. The result clearly shows that the CO_2 recycling reaction of allylic carbonate occurs with a transfer of chirality. The observed high enantiospecificity is explained as follows (eq 10). The initial attack of the



(10)

palladium complex to (*S*)-**14** would proceed with conversion of the stereochemistry to give π-allylpalladium intermediate **C** and isomer **D**. It is expected that there is equilibrium between **C** and **D**, and the nucleophilic cyclization process would proceed via the more stable intermediate **D** from the back side against the π-allylpalladium species to afford (*S*)-**16** without loss of chirality.

(10) (a) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092. For reviews about the determination of absolute configuration by the use of MTPA esters, see: (b) Seco, J. M.; Quiñoá, E.; Riguera, R. *Tetrahedron: Asymmetry* **2001**, *12*, 2915. (c) Kusumi, T. *J. Synth. Org. Chem., Jpn.* **1993**, *51*, 462.

Conclusion

In conclusion, we have developed a novel type of CO_2 recycling process involving a palladium-catalyzed reaction of 4-methoxycarbonyloxy-2-buten-1-ols. This reaction can create a variety of cyclic carbonates via a CO_2 elimination−fixation process. *trans*-Cyclic carbonates are generated with a high degree of stereochemical control in the reactions of unsymmetric substrates. By the use of chiral methyl-substituted allylic carbonates, an enantiospecific reaction occurs to produce a chiral product with high specificity. The CO_2 fixation processes in the reactions generally proceed with high efficiency. The reaction should not only provide a new possibility of a CO_2 recycling reaction but also gain the attention of scientists searching for new eco-friendly chemical reactions.

Experimental Section

General. Substrates **1a**−**1i** and **2j** were prepared by following the literature.[5b,11,12] Propargylic alcohol (*S*)-**10** was purchased from a commercial supplier. All nonaqueous reactions were carried out under a positive atmosphere of argon or nitrogen in dried glassware unless otherwise indicated. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocols. The phrase "residue upon workup" refers to the residue obtained when the organic layer was separated and dried over anhydrous $MgSO_4$ and the solvent was evaporated under reduced pressure.

General Experimental Procedure for Scheme 1. (a) Synthesis of *trans*-Allylic Alcohol 2a. To a stirred suspension of LAH (1.07 g, 28.2 mmol) and NaOMe (3.05 g, 56.4 mmol) in THF (120 mL) was added dropwise the solution of propargylic diol **1a** (2.00 g, 14.1 mmol) in THF (30 mL) at 0 °C. After refluxing for 3 h, the reaction mixture was treated with the minimum amount of cold water at rt and extracted with AcOEt. The combined extracts were washed with aqueous $NaHCO_3$ and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (60:40 v/v) as eluent to give diol **2a** (1.33 g, 66%) as colorless needles: mp 57−58 °C; IR (KBr) 3344, 2967, 2936 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (6H, t, J = 7.2 Hz), 1.50−1.59 (4H, m), 1.99 (1H, s), 2.69 (1H, s), 4.16 (2H, d, J = 5.6 Hz), 5.66 (1H, d, J = 15.6 Hz), 5.81 (1H, dt, J = 5.6 and 15.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.8, 63.0, 75.1, 127.6, 136.7; MS m/z 115 [$M^+ - 29$ (C_2H_5)]. Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.51; H, 10.91.

(b) Synthesis of Allylic Carbonate 3a. To a stirred solution of diol **2a** (463 mg, 3.2 mol) and pyridine (0.78 mL, 9.6 mmol) in CH_2Cl_2 (35 mL) was added dropwise methyl chloroformate (0.27 mL, 3.52 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (85:15 v/v) as eluent to give allylic carbonate **3a** (595 mg, 92%) as a colorless oil: IR (neat) 3345, 2967, 1732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (6H, t, J = 7.8 Hz), 1.54 (4H, dq, J = 2.1 and 7.8 Hz), 2.01 (1H, s), 3.78 (3H, s), 4.65 (2H, dd, J = 1.2 and 3.6 Hz), 5.77−5.80 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 7.3, 32.4, 54.3, 67.8, 74.8, 121.8, 140.7, 155.5; MS m/z 173 [$M^+ - 29$ (C_2H_5)]. Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.44; H, 8.75.

(c) Synthesis of Allylic Benzoate 4c. To a stirred solution of diol **2c** (151 mg, 0.66 mmol) and Et_3N (0.18 mL, 1.32 mmol) and a catalytic amount of DMAP in CH_2Cl_2 (10 mL) was added dropwise benzoyl chloride (84 μL, 0.73 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (80:20 v/v) as eluent to give allylic benzoate **4c** (219 mg, quantitative yield) as a colorless oil: IR (neat) 2860, 1697, 1452 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (6H, t, J = 6.6 Hz), 1.21−1.31 (12H, m), 1.39 (1H, s), 1.46−1.56 (4H, m), 4.84 (2H, d, J = 4.9 Hz), 5.80−5.91 (2H, m), 7.43 (2H, dd, J = 7.8 and 7.8 Hz), 7.55 (1H, dd, J = 7.8 and 7.8 Hz), 8.04 (2H, d, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 22.4, 22.9, 32.1, 40.7, 65.0, 74.9, 122.1, 128.3, 129.6, 130.3, 132.9, 144.1, 166.4; MS m/z 314 [$M^+ - 18$ (H_2O)]. Anal. Calcd for $C_{21}H_{32}O_2$: C, 75.86; H, 9.70. Found: C, 75.70; H, 9.41.

General Procedure for the Palladium-Catalyzed Reaction of *trans*-4-Methoxycarbonyloxy-2-buten-1-ols. Synthesis of Cyclic Carbonate 5a (Entry 4 in Table 1). To a stirred solution of allylic carbonate **3a** (56.0 mg, 0.28 mmol) in dioxane (2.8 mL) were added $Pd_2(dba)_3{\cdot}CHCl_3$ (14.5 mg, 14.0 μmol) and dppf (31.0 mg, 56.0 μmol) in a sealed tube at rt. After stirring was continued for 1 h at 50 °C, the reaction mixture was concentrated and the residue was chromatographed on silica gel with hexane−AcOEt (80:20 v/v) as eluent to give cyclic carbonate **5a** (37.6 mg, 79%) as a colorless oil: IR (neat) 3645, 2885, 1790, 1028 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.97 (3H, t, J = 7.8 Hz), 0.99 (3H, t, J = 7.8 Hz), 1.56−1.88 (4H, m), 4.82 (1H, dt, J = 6.9 and 1.2 Hz), 5.45 (1H, dt, J = 10.5 and 1.2 Hz), 5.51 (1H, dt, J = 18.3 and 1.2 Hz), 5.88 (1H, ddd, J = 18.3, 10.5, and 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 6.8, 7.0, 25.5, 28.3, 84.0, 88.3, 121.0, 130.0, 154.0; MS m/z 170 (M^+). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.69; H, 8.18.

Procedure for the Palladium-Catalyzed Reaction of Allylic Benzoate under CO_2 Atmosphere (Eq 4). To a stirred solution of allylic benzoate **4c** (46.5 mg, 0.14 mmol) in dioxane (1.4 mL) were added $Pd_2(dba)_3{\cdot}CHCl_3$ (7.2 mg, 7.0 μmol), dppf (15.2 mg, 28.0 μmol), and BSA (50 μL, 0.21 mmol) in a sealed tube at rt. After stirring was continued under CO_2 atmosphere for 12 h at 50 °C, the reaction mixture was concentrated and the residue was chromatographed on silica gel with hexane−AcOEt (90:10 v/v) as eluent to give cyclic carbonate **5c** (26.3 mg, 74%) as a colorless oil.

Crossover Experiment Using Allylic Carbonate 3f and Allylic Benzoate 4c (Eq 5). To a stirred solution of equimolar amounts of allylic carbonate **3f** (57.1 mg, 0.27 mmol) and allylic benzoate **4a** (89.7 mg, 0.27 mmol) in dioxane (2.7 mL) were added $Pd_2(dba)_3{\cdot}CHCl_3$ (27.9 mg, 27.0 μmol), dppe (43.0 mg, 0.11 mmol), and BSA (0.10 mL, 0.41 mmol) in a sealed tube at rt. After stirring was continued for 12 h at 50 °C, the reaction mixture was concentrated and the residue was chromatographed on silica gel with hexane−AcOEt (90:10 v/v) as eluent to give a 1:1.1 mixture of cyclic carbonates **5f** and **5c** (52.9 mg, 20% **5f** and 22% **5c**) and epoxide **9c** (21.2 mg, 19%) as a colorless oil.

General Procedure for the Diastereoselective Synthesis of Cyclic Carbonates (Scheme 3). Synthesis of *trans*- and *cis*-5h. To a stirred solution of allylic carbonate **3h** (50.0 mg, 0.21 mmol) in dioxane (2 mL) were added $Pd_2(dba)_3{\cdot}CHCl_3$ (10.9 mg, 10.5 μmol) and dppf (22.9 mg, 42.0 mmol) in a sealed tube at rt. After stirring was continued for 4 h at 50 °C, the reaction mixture was concentrated and the residue was chromatographed on silica gel with hexane−AcOEt (95:5 v/v) as eluent to give cyclic carbonate *trans*-**5h** (21.1 mg, 50%) as yellow needles and *cis*-**5h** (8.4 mg, 19%) as a colorless oil.

Experimental Procedure for Scheme 4. (a) (*S*)-(*tert*-Butyldiphenylsiloxy)-1,1-dipentyl-2-pentyn-1-ol [(*S*)-11].

(11) Shigemasa, Y.; Oikawa, H.; Ohrai, S.; Sashiya, H.; Saimoto, H. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2594.

(12) Bates, R. W.; Díez-Martín, D.; Kerr, W. J.; Knight, J. G.; Ley, S. V.; Sakellaridis, A. *Tetrahedron* **1990**, *46*, 4063.

To a stirred solution of (*S*)-3-butyn-2-ol (*S*)-**10** (696 mg, 9.93 mmol, 95% ee) and imidazole (1.35 g, 19.9 mmol) in DMF (14 mL) was added TBDPSCl (5.17 mL, 19.9 mmol) at rt, and stirring was continued for 1 h at 50 °C. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated aqueous NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (95:5 v/v) as eluent to give TBDPS ether (3.06 g, quantitative yield) as a colorless oil. To a stirred solution of the product (2.31 g, 7.7 mmol) and TMEDA (1 mL, 7.5 mmol) in THF (80 mL) was added dropwise 1.60 M BuLi in THF (4.7 mL, 7.5 mmol) at −78 °C. After stirring was continued for 2 h at −78 °C, a solution of 6-undecanone (1.02 mL, 5.0 mmol) in THF (20 mL) was added dropwise to this solution, and stirring was continued for 4 h at the same temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (90:10 v/v) as eluent to give propargylic alcohol (*S*)-**11** (2.27 g, 95%) as a colorless oil: $[\alpha]_D^{25} = -5.99$ (*c* 10.2 in $CDCl_3$); IR (neat) 3543, 3071, 2932, 2859 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (6H, t, *J* = 6.3 Hz), 1.06 (9H, s), 1.23−1.37 (12H, m), 1.41 (3H, d, *J* = 6.6 Hz), 1.45−1.57 (6H, m), 7.34−7.43 (6H, m), 7.68−7.77 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 19.2, 22.7, 23.8, 23.9, 25.4, 26.9, 32.0, 41.8, 59.9, 70.9, 86.4, 127.3, 127.5, 129.5, 129.6, 133.7, 133.9, 135.7, 135.9; MS *m*/*z* 421 [$M^+ - 57$ (C_4H_9)]; HRMS *m*/*z* calcd for $C_{27}H_{37}O_2Si$ 421.2562 ($M^+ - 57$), found 421.2549.

(b) (*S*)-4-Hydroxy-1,1-dipentyl-2-pentyn-1-ol [(*S*)-12]. To a stirred solution of propargylic alcohol (*S*)-**11** (1.48 g, 3.1 mmol) in THF (30 mL) was added dropwise a 1.0 M solution of TBAF in THF (6.2 mL, 6.20 mmol) at rt. After stirring was continued for 1 h at the same temperature, the reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (60:40 v/v) as eluent to give diol (*S*)-**12** (745 mg, quantitative yield) as colorless needles: mp 35−38 °C; $[\alpha]_D^{29} = -14.97$ (*c* 10.5 in $CDCl_3$); IR (neat) 3335, 2934, 2862 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (6H, t, *J* = 6.8 Hz), 1.26−1.38 (8H, m), 1.42−1.51 (8H, m), 1.56−1.65 (3H, m), 1.98 (2H, s), 4.56 (1H, d, *J* = 3.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 23.9, 24.5, 31.9, 41.8, 58.3, 71.1, 86.0, 87.0; MS *m*/*z* 387 [$M^+ - 71$ (C_5H_{11})]; HRMS *m*/*z* calcd for $C_{20}H_{26}O_4F_3$ 387.1783 ($M^+ - 71$), found 387.1776.

(c) (*E*,*S*)-4-Hydroxy-1,1-dipentyl-2-penten-1-ol [(*S*)-13]. To a stirred suspension of LAH (190 mg, 5.0 mmol) and NaOMe (546 mg, 10.0 mmol) in THF (40.0 mL) was added dropwise the solution of propargylic diol (*S*)-**12** (600 mg, 2.50 mmol) in THF (10.0 mL) at 0 °C. After the reaction mixture was refluxed for 3 h, it was treated with the minimum amount of cold water and extracted with AcOEt. The combined extracts were washed with aqueous $NaHCO_3$ and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (60:40 v/v) as eluent to give diol (*S*)-**13** (339 mg, 56%) as a colorless oil: $[\alpha]_D^{29} = +0.20$ (*c* 10.0 in $CDCl_3$); IR (neat) 3366, 3225, 2858 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (6H, t, *J* = 6.4 Hz), 1.27−1.33 (16H, m), 1.40 (1H, s), 1.47−1.52 (3H, m), 1.66 (1H, s), 4.35 (1H, m), 5.63 (1H, d, *J* = 15.6 Hz), 5.71 (1H, dd, *J* = 6.0 and 15.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 22.7, 23.2, 23.8, 32.3, 40.9, 41.0, 68.5, 74.7, 132.0, 135.8; MS *m*/*z* 171 [$M^+ - 71$ (C_5H_{11})]; HRMS *m*/*z* calcd for $C_{10}H_{19}O_2$ 171.1385 ($M^+ - 71$), found 171.1385.

(d) (*E*,*S*)-1,1-Dipentyl-4-methoxycarbonyloxy-2-penten-1-ol [(*S*)-14]. To a stirred solution of diol (*S*)-**13** (115 mg, 0.47 mmol) and pyridine (0.11 mL, 1.41 mmol) in CH_2Cl_2 (10 mL) was added dropwise methyl chloroformate (40.0 μL, 0.52 mmol) at 0 °C, and stirring was continued for 1 h at the same temperature. The reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (60:40 v/v) as eluent to give allylic carbonate (*S*)-**14** (140 mg, 98%) as a colorless oil: $[\alpha]_D^{29} = -42.97$ (*c* 10.0 in $CDCl_3$); IR (neat) 3499, 2930, 2860, 1732 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (6H, t, *J* = 7.2 Hz), 1.28−1.34 (12H, m), 1.38 (4H, d, *J* = 7.2 Hz), 1.45−1.52 (3H, m), 1.56 (1H, s), 3.76 (3H, s), 5.19−5.25 (1H, m), 5.66 (1H, dd, *J* = 16.0 and 5.6 Hz), 5.72 (1H, d, *J* = 16.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 20.5, 22.4, 22.9, 32.1, 40.8, 74.8, 74.9, 127.5, 139.0, 155.2; MS *m*/*z* 197 [$M^+ - 103$ ($CHCH_3OCO_2CH_3$)]; HRMS *m*/*z* calcd for $C_{13}H_{25}O$ 197.1906 ($M^+ - 103$), found 197.1893.

Procedure for the Synthesis of MTPA Ester (*S*,*S*)-15. (*E*,*S*)-1,1-Dipentyl-4-[(*S*)-2-methoxy-2-trifluoromethyl-2-phenylacetyl]oxy-2-penten-1-ol [(*S*,*S*)-15]. To a stirred solution of allylic diol (*S*)-**13** (19.9 mg, 82 μmol) and NEt_3 (57.0 μL, 0.41 mmol) and a catalytic amount of DMAP in CH_2Cl_2 (5.0 mL) was added dropwise (*R*)-MTPA chloride (17.0 μL, 90.0 μmol) at 0 °C, and stirring was continued for 2 h at the same temperature. The reaction mixture was diluted with water and extracted with Et_2O. The combined extracts were washed with 1 N HCl, aqueous $NaHCO_3$, and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (80:20 v/v) as eluent to give MTPA ester (*S*,*S*)-**15** (36.3 mg, quantitative yield, 95% ee) as a colorless oil: $[\alpha]_D^{25} = -42.51$ (*c* 5.1 in $CDCl_3$); IR (neat) 3439, 2936, 2862, 1751 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.840.88 (6H, m), 1.23−1.31 (12H, m), 1.36 (3H, d, *J* = 6.2 Hz), 1.43−1.53 (4H, m), 3.54 (3H, s), 5.60−5.64 (1H, m), 5.68−5.72 (1H, m), 5.78 (1H, d, *J* = 15.5 Hz), 7.37−7.42 (3H, m), 7.52 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.1, 20.4, 22.6, 22.6, 23.1, 32.2, 41.0, 41.1, 55.3, 73.7, 74.8, 126.2, 127.2, 127.3, 128.2, 129.4, 132.3, 140.2, 165.5; MS *m*/*z* 189 ($M^+ - 269$); HRMS *m*/*z* calcd for $C_9H_8F_3O$ 189.0527 ($M^+ - 269$), found 189.0497.

Procedure for the Enantiospecific Reaction of (*S*)-14 (Eq 8). To a stirred solution of allylic carbonate (*S*)-**14** (28.2 mg, 94.0 μmol) in dioxane (2 mL) were added $Pd_2(dba)_3{\cdot}CHCl_3$ (4.9 mg, 4.7 μmol) and dppe (7.5 mg, 18.8 μmol) in a sealed tube at rt. After stirring was continued for 7 h at 50 °C, the reaction mixture was concentrated and the residue was chromatographed on silica gel with hexane−AcOEt (90:10 v/v) as eluent to give cyclic carbonate (*S*)-**16** (21.8 mg, 85%) and diene **17** (1.5 mg, 7%) as colorless oils.

(a) (*E*,*S*)-1,2-Dihydroxy-1,1-dipentyl-3-pentene [(*S*)-18]. To a stirred solution of cyclic carbonate (*S*)-**16** (18.0 mg, 67.0 μmol) in dioxane (2.0 mL) was added 1 N NaOH (2.0 mL) at rt. After stirring had been continued for 1 h at the same temperature, the reaction mixture was diluted with water and extracted with AcOEt. The combined extracts were washed with aqueous NH_4Cl and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (90:10 v/v) as eluent to give chiral diol **18** (16.2 mg, quantitative yield) as a colorless oil: $[\alpha]_D^{26} = -3.44$ (*c* 1.6 in $CDCl_3$); IR (neat) 3418, 2932, 2955, 2680 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (6H, dt, *J* = 1.5 and 7.2 Hz), 1.26−1.58 (16H, m), 1.74 (3H, dd, *J* = 6.4 and 1.5 Hz), 1.83 (2H, brs), 3.94 (1H, d, *J* = 7.5 Hz), 5.59 (1H, ddq, *J* = 15.3, 7.5, and 1.5 Hz), 5.74 (1H, dd, *J* = 15.3 and 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.5, 23.8, 24.4, 31.9, 41.8, 58.2, 71.1, 86.0, 86.9; MS *m*/*z* 171 [$M^+ - 71$ (C_5H_{11})]; HRMS *m*/*z* calcd for $C_{10}H_{17}O_2$ 171.1749 ($M^+ - 71$), found 171.1724.

(b) (*E*,*S*)-1,1-Dipentyl-2-[(*R*)-2-methoxy-2-trifluoromethyl-2-phenylacetyl]oxy-3-penten-1-ol [(*S*,*R*)-19]. To a stirred solution of chiral diol (*S*)-**18** (4.0 mg, 16.5 μmol) and NEt_3 (11 μL, 82.3 μmol) and a catalytic amount of DMAP in CH_2Cl_2 (2 mL) was added dropwise (*S*)-MTPA chloride (3.5 μL, 18.2 μmol) at 0 °C, and stirring was continued for 2 h at the same temperature. The reaction mixture was diluted with water and extracted with Et_2O. The combined extracts were washed with 1 N HCl, aqueous $NaHCO_3$, and saturated NaCl. The residue upon workup was chromatographed on silica gel with hexane−AcOEt (85:15 v/v) as eluent to give MTPA ester

(*S*,*R*)-**19** (5.1 mg, 70%) as a colorless oil: $[\alpha]_D^{26} = +12.53$ (*c* 1.5 in $CDCl_3$); IR (neat) 3537, 2928, 2856, 1732 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.87 (6H, t, $J = 7.2$ Hz), 1.14−1.45 (16H, m), 1.76 (3H, d, $J = 6.5$ Hz), 3.55 (3H, s), 5.33 (1H, d, $J = 9.0$ Hz), 5.60 (1H, qt, $J = 1.7$, 9.0, and 15.5 Hz), 5.93−5.99 (1H, m), 7.36−7.41 (3H, m), 7.51−7.54 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 14.0, 18.1, 19.2, 22.3, 22.5, 22.8, 30.5, 31.9, 32.2, 32.3, 34.2, 35.6, 55.5, 65.5, 75.3, 81.8, 124.2, 127.0, 128.2, 128.7, 129.4, 130.7, 132.1, 134.5, 165.4; MS *m*/*z* 458 (M^+); HRMS *m*/*z* calcd for $C_{25}H_{37}O_4F_3$ 458.2644 (M^+), found 458.2648.

(c) (*E*,*S*)-1,1-Dipentyl-2-[(*S*)-2-methoxy-2-trifluoromethyl-2-phenylacetyl]oxy-3-penten-1-ol [(*S*,*S*)-19]. By following the same procedure described for (*S*,*R*)-**19**, MTPA ester (*S*,*S*)-**19** was prepared from allylic diol **18** and (*R*)-MTPA chloride in 72% yield as a colorless oil: $[\alpha]_D^{25} = -17.40$ (*c* 1.0 in $CDCl_3$); IR (neat) 3351, 2932, 2850, 1746 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.88 (6H, t, $J = 7.2$ Hz), 1.23−1.49 (16H, m), 1.73 (3H, d, $J = 6.4$ Hz), 3.51 (3H, s), 5.33 (1H, d, $J = 5.7$ Hz), 5.46 (1H, qd, $J = 10.3$, 5.7, and 2.7 Hz), 5.85−5.91 (1H, m), 7.38−7.41 (3H, m), 7.49−7.54 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 14.0, 18.0, 19.2, 22.4, 22.5, 22.8, 30.6, 32.4, 34.5, 36.1, 55.4, 65.6, 82.1, 124.2, 127.7, 128.4, 128.9, 129.6, 131.0, 132.1, 133.9, 165.7; MS *m*/*z* 458 (M^+); HRMS *m*/*z* calcd for $C_{25}H_{37}O_4F_3$ 458.2644 (M^+), found 458.2617.

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Supporting Information Available: Spectral data of **2b**−**2i**, **3b**−**3j**, **5b**−**5i**, **9c**, (*S*)-**16**, and **17**, ^1H NMR and ^{13}C NMR spectra for **2d**, **2f**−**2i**, **3c**, **3d**, **3f**, **3g**, **5b**, **5d**−**5g**, **9c**, *cis*-**5h**, and **11**−**19**, and NOESY spectra for *trans*- and *cis*-**5h** and **5i**. This material is available free of charge via the Internet at http://pubs.acs.org.

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