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# An Efficient, Stereoselective Approach to *syn*-1,2-Diols Protected as Cyclic Carbonates

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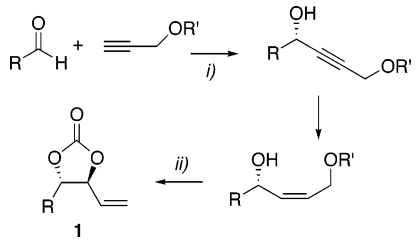
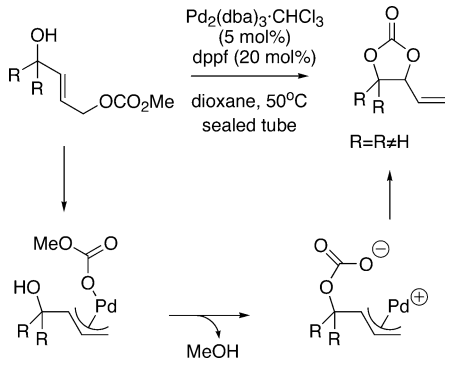
**Abstract:** Enantioenriched 4-hydroxyalk-2-ynyl carbonates (or benzoates) have been prepared by stereoselective zinc-mediated addition of alkyl 2-propynyl carbonates (or their benzoate analogues) to aldehydes. Their partial reduction to *Z*-olefins followed by cyclization under mild Pd-catalyzed conditions allowed a straightforward access to enantioenriched *syn*-1,2-diols protected as cyclic carbonates.

Polyhydroxylated chains are a very common pattern in the structure of many natural products.[1] Although carbohydrates and azasugars are probably the most representative examples, a plethora of naturally occurring compounds, including many polyketide metabolites, possess 1,2-diol or 1,2,3-triol arrays in their framework. As a result, the catalytic stereoselective construction of such substructures has attracted much attention in the literature.[2] For instance, the direct dihydroxylation[2c−e] or epoxidation of allylic alcohols[2f,g] or other olefins[2h−j] are well-established methodologies nowadays. However, very often the corresponding diols and triols need to be protected for additional transformations. Taking advantage of our previous experience in the preparation of enantioenriched propargylic diols[3] and their use in the Pd(0)-catalyzed allylic alkylations,[4] we envisaged a novel approach to the 1,2-diol motif protected as a cyclic carbonate according to the following process (Scheme 1): (i) the zinc-mediated addition of protected 2-alkyn-1-ols to aldehydes[5] and (ii) Pd-catalyzed stereoselective conversion to cyclic carbonates **1**.[6] In addition, the presence of the double bond in the final protected diol makes these compounds amenable to further synthetic transformations.

**SCHEME 1. Synthetic Approach**




**SCHEME 2. Palladium-Catalyzed Formation of Cyclic Carbonates**




In this connection, Ihara et al.[6] very recently reported that the Pd-catalyzed ionization of 4-hydroxybut-2-enyl carbonates affords a $\pi$-allyl intermediate where the vicinal tertiary alcohol[7] can trap $CO_2$ and cyclize to give a cyclic carbonate (Scheme 2). This work prompted us to summarize the results that we have obtained lately. Our findings constitute an alternative, milder version of this reaction with better scope. Thus, we report herein a version of this process that is also valid for secondary alcohols arising from stereoselective addition of propargylic carbonates or benzoates to aldehydes (Scheme 1). Furthermore, transfer of chirality from the chiral carbon to the vicinal carbon was achieved with good levels of stereoselectivity.

To evaluate our approach, we first investigated whether suitable alkyl 2-propynyl carbonates could be added stereoselectively to an aldehyde in good yields (step i in Scheme 1). Among the reported procedures for stereoselective addition of alkynes to aldehydes, the use of Zn-alkynylides generated in situ with $Zn(OTf)_2$ in the

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(1) (a) Omura, S., Ed.; *Macrolide Antibiotics: Chemistry, Biology and Practice*; Academic Press: New York, 2002. (b) Rychnovsky, S. D. *Chem. Rev.* **1995**, *95*, 2021−2040.

(2) (a) Ojima, I., Ed. *Catalytic Asymmetric Synthesis*; Wiley-VCH: New York, 2000. (b) Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds. *Comprehensive Asymmetric Catalysis*; Springer: Berlin, 1999. (c) Johnson, R. A.; Sharpless, K. B. In ref 2a, Chapter 6D, pp 357−398. (d) Bolm, C.; Hildebrand, J. P.; Muñiz, K. In ref 2a, Chapter 6E, pp 399−428. (e) Markó, I. E.; Svendsen, J. S. In ref 2b, pp 713−790. (f) Johnson, R. A.; Sharpless, K. B. In ref 2a, Chapter 6A, pp 231−280. (g) Katsuki, T. In ref 2b, Chapter 18.1, pp 621−648. (h) Katsuki, T. In ref 2a, Chapter 6B, pp 287−326. (i) Jacobsen, E. N. Wu, M. H. In ref 2b, Chapter 18.2, pp 649−678. (j) Aggarwal, V. K. In ref 2b, Chapter 18.3, pp 679−696.

(3) (a) Amador, M.; Ariza, X.; Garcia, J.; Ortiz, J. *Tetrahedron Lett.* **2002**, *43*, 2691−2694. (b) See also: Diez, R. S.; Adger, B.; Carreira, E. M. *Tetrahedron* **2002**, *58*, 8341−8344.

(4) Amador, M.; Ariza, X.; Garcia, J.; Sevilla, S. *Org. Lett.* **2002**, *4*, 4511−4514.

(5) (a) Frantz, D. E.; Fässler, R.; Tomooka, C. S.; Carreira, E. M. *Acc. Chem. Res.* **2000**, *33*, 373−381. (b) Frantz, D. E.; Fässler, R.; Carreira, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 1806−1807. (c) Anand, N. K.; Carreira, E. M. *J. Am. Chem. Soc.* **2001**, *123*, 9687−9688. (d) El-Sayed, E.; Anand, N. K.; Carreira, E. M. *Org. Lett.* **2001**, *3*, 3017−3020. (e) Boyall, D.; Frantz, D. E.; Carreira, E. M. *Org. Lett.* **2002**, *4*, 2605−2606.

(6) For Pd-catalyzed formation of cyclic carbonates, see: Yoshida, M.; Ohsawa, Y.; Ihara, M. *J. Org. Chem.* **2004**, *69*, 1590−1597 and references therein.

(7) Regarding this cyclization, Ihara et al. indicate that "a tertiary alcohol moiety in the substrate is necessary for the reaction".

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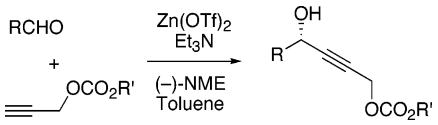
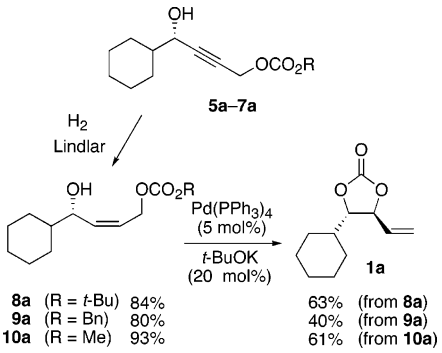
**TABLE 1. Alkyne Addition to Aldehydes**[a]




| entry | R | alkyne (R′) | product | yield (%) | ee[b] (%) |
|---|---|---|---|---|---|
| 1 | cyclohexyl | **2** (*t*-Bu) | **5a** | 91 | 97 |
| 2 | cyclohexyl | **2** (*t*-Bu) | *ent*-**5a**[c] | 92 | 96 |
| 3 | cyclohexyl | **3** (Bn) | **6a** | 93 | 98 |
| 4 | cyclohexyl | **4** (Me) | **7a** | 87 | 96 |
| 5 | isopropyl | **2** (*t*-Bu) | **5b** | 91 | 96 |
| 6 | isobutyl | **2** (*t*-Bu) | **5c** | 58 | 89 |
| 7 | phenyl[d] | **2** (*t*-Bu) | **5d** | 35 | 96 |

[a] Aldehyde (1.2−1.5 equiv), $Et_3N$ (1.2 equiv), $Zn(OTf)_2$ (1.1 equiv), (−)-NME (1.2 equiv), toluene, rt. [b] Determined by HPLC of Mosher's esters. [c] The enantiomer was obtained by performing the reaction with (+)-NME. [d] Aldehyde (5 equiv).

**SCHEME 3. Cyclization of Carbonates 8a−10a**

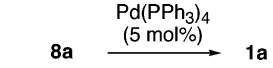



presence of *N*-methylephedrine (NME) and $Et_3N$ in toluene at rt was our first choice.[5] In fact, our previous experience indicated that the parent propargylic benzoates can be efficiently added to aldehydes under such mild conditions.[3] However, the use of the propargylic carbonates instead of benzoates was unprecedented. To our delight, excellent yields and stereoselectivities were obtained in the addition of protected alkynols **2**−**4** to cyclohexanecarbaldehyde to obtain alkynols **5a**−**7a** (Table 1, entries 1−4). When we extended the same protocol to other representative aldehydes (Table 1, entries 5−7), the addition of alkyne **2** to 2-methylpropanal and 3-methylbutanal afforded alkynols **5b** and **5c** in useful yields and selectivities. However, lower yield was noted with benzaldehyde even when an excess of aldehyde was used. This disappointing result was not completely unexpected since it is known that aromatic aldehydes are not good substrates for this kind of additions.[5b,d]

The partial reduction of alkynols **5a**−**7a** to *Z*-olefins **8a**−**10a** was achieved easily by hydrogenation in the presence of Lindlar's catalyst (80−93% yield). Having in hand the required olefins, we next examined the cyclic carbonate formation (step ii in Scheme 1). Our first trials of cyclization were attempted by using $Pd(PPh_3)_4$ (5 mol %) and *t*-BuOK (20 mol %) in THF. As shown in Scheme 3, these preliminary results indicated that the *trans* cyclic carbonate **1a** was readily formed with a remarkable diastereoselectivity (>96:4) but in moderate yields.[8]

(8) (a) Relative stereochemical determinations were derived from NOE experiments. (b) Minor isomer can be separated by column chromatography on silica gel with hexane/$Et_2O$ as eluant.

**TABLE 2. Cyclization to Carbonate 1a**




| entry | solvent | base[a] | yield (%) |
|---|---|---|---|
| 1 | $CH_3CN$ | *t*-BuOK | 55 |
| 2 | toluene | *t*-BuOK | 44 |
| 3 | $CH_2Cl_2$ | *t*-BuOK | 62 |
| 4 | $CH_2Cl_2$ | $Et_3N$ | 88 |
| 5 | $CH_2Cl_2$ | no base | 91 |
| 6 | THF | no base | 81 |

[a] 20 mol % of base.

Indeed, the presence of a small amount of base accelerated the reaction but we also observed that *t*-BuOK caused a competitive decomposition of the starting material. Thus, we undertook a study on the cyclization of **8a** using alternative solvents and bases. We found that among the solvents tested only $CH_2Cl_2$ gave yields comparable to those obtained with THF (Table 2, entries 1−3). On the other hand, when a milder base ($Et_3N$, entry 4) was used the yield increased (88%).

Finally, we observed that minimizing the volume of nitrogen atmosphere was crucial. Thus, yields were remarkably improved when the reaction was performed in a flask sealed with a septum and the solution filled up the flask almost completely.[9] Certainly, under these conditions the base can be omitted without any detrimental effect on the yields (entries 5 and 6).

It is worth noting that the yield decreased when the amount of $Pd(PPh_3)_4$ was reduced to 0.5 mol % (30%). In addition, under these conditions a mixture (1:5) of the *cis* carbonate (*cis*-**1a**) and *trans* carbonate (*trans*-**1a**) was obtained. When the isolated mixture was further treated with $Pd(PPh_3)_4$ (5 mol %), an almost complete isomerization to the *trans* isomer was observed (*trans*-**1a**/*cis*-**1a** dr > 96:4). This result suggested that the reaction was probably controlled under thermodynamic conditions.[10] On the other hand, we also noted that cyclization of the *E*-isomer (i.e., *E*-**8a**), although slightly slower, led to the same *trans* cyclic carbonate (*trans*-**1a**) with identical stereoselectivity (>96:4). Finally, the tandem reduction−cyclization was extended to the rest of monoprotected propargylic 1,4-diols **5b**−**d** to obtain cyclic carbonates **1b**−**d** with excellent yields and stereoselectivities (Scheme 4).[8b,11]

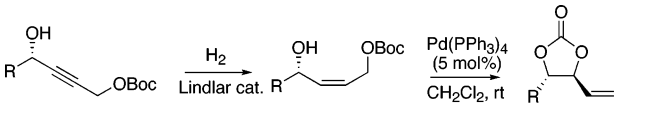
Then, we turned our attention to the obtention of cyclic carbonates **1** bearing a linear R group (as R = *n*-$C_5H_{11}$, **1e**). It is known that the Carreira addition of Zn-alkynylides to α-unbranched aldehydes is not satisfactory,

(9) Presumably, $CO_2$ can be removed or fixed during the $\pi$-allyl formation step (see ref 6). Since the $CO_2$ carbon atom is necessary for the cyclization step, the reduction of the amount of the gas phase might increase the amount of $CO_2$ to be trapped in solution.

(10) *cis*-**1a** can be converted to *trans*-**1a** by Pd-catalyzed ionization, $\pi-\sigma-\pi$ interconversion of the $\pi$-allyl intermediate and cyclization.

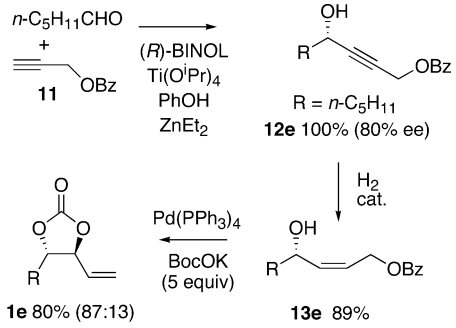
(11) Cyclic carbonates **1** were hydrolyzed under basic conditions (NaOH/dioxane) to afford the corresponding 1,2-diols. Comparison of their spectroscopic data with those reported in the literature allowed the stereochemical assignment of **1**. (a) For **1a** and **1c**, see: Lombardo, M.; Morganti, S.; Trombini, C. *J. Org. Chem.* **2003**, *68*, 997−1006. (b) For **1b**, see: Adam, W.; Díaz, M. T.; Saha-Möller, C. R. *Tetrahedron: Asymmetry* **1998**, *9*, 589−598. (c) For **1d**, see: Lombardo, M.; Licciulli, S.; Tromboni, C. *Tetrahedron: Asymmetry* **2004**, *15*, 285−292. (d) For **1e**, see: Matsumoto, T.; Kitano, Y.; Sato, F. *Tetrahedron Lett.* **1988**, *29*, 5685−5688.

**SCHEME 4. Formation of Cyclic Carbonates 1b−d**




| | | | | |
|---|---|---|---|---|
| **5b** | (R = *i*-Pr) | **8b** | 83% | **1b** 87% (dr > 96:4) |
| **5c** | (R = *i*-Bu) | **8c** | 83% | **1c** 92% (dr 90:10) |
| **5d** | (R = Ph) | **8d** | 90% | **1d** 83% (dr 90:10) |

**SCHEME 5. Preparation of Carbonate 1e from Hexanal**

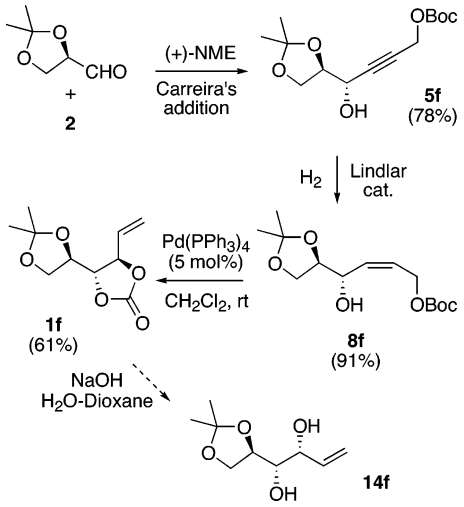



resulting in low yields and/or selectivities. Thus, we attempted the Zn-mediated addition of alkynes **2**−**4** to hexanal in the presence of $Ti(O^iPr)_4$ and BINOL following a reported protocol,[12] but complex crude mixtures were obtained (<30%yield). In sharp contrast, the related 2-propynyl benzoate **11** readily gave alkynol **12e** (quantitative yield, 80%ee) under such conditions (Scheme 5). As usual, *Z*-olefin **13e** was obtained by partial hydrogenation. The formation of the 1,3-dioxolan-2-one **1e** was first tried without success by saturating a THF solution of the olefin **13e** with $CO_2$ and adding a catalytic amount of $Pd(PPh_3)_4$. Fortunately, a much better result was obtained using BocOK as an external source of $CO_2$ to give **1e** in 80%yield.[8b,13]

Then, we turned our attention to the obtention of the protected tetraol **1f** where1,2- and 3,4-diols are blocked by an acid-labile and a base-labile protecting group, respectively (Scheme 6). Very interestingly, addition of **2** to D-glyceraldehyde was completely stereoselective, and the configuration of the new created stereocenter in **5f** was controlled by the ephedrine used. Reduction to alkenol **8f** and cyclization allowed the obtention of dioxolane **1f**. We confirmed the stereochemistry of **1f** by hydrolyzing the carbonate under basic conditions to give the known diol **14f**.

In conclusion, we have established a new procedure that allows the stereoselective preparation of enantioenriched *syn*-1,2-diols protected as 1,3-dioxolona-2-ones **1** from an aldehyde and an alkyne by a three-step process: addition of the alkyne to the aldehyde, reduction to an alkene, and cyclization by trapping $CO_2$. For α- or *β*-branched aldehydes, Carreira's addition was very

**SCHEME 6. Preparation of Protected Tetraol 1f**




convenient; however, for linear aldehydes the method was more efficient through a BINOL/$Ti(O^iPr)_4$-mediated addition. Two new stereocenters were created: the stereochemistry of the first one was controlled by a chiral ligand (ephedrine or BINOL) and the second one was controlled by a chirality transfer of the first one based on the fact that *trans*-1,3-dioxolan-2-ones are thermodynamically more stable than their *cis* isomers.

## Experimental Section

**General Procedure for the Synthesis of Alkyl 4-Hydroxybut-2-ynyl Carbonates.** $Zn(OTf)_2$ was activated by heating under vacuum. NME was added, and the flask was purged with $N_2$. Anhydrous toluene and $Et_3N$ were added, and the mixture was vigorously stirred at rt or 50 °C for 2 h. A solution of the alkyl 2-propynyl carbonate in toluene was added and stirred for 30−60 min, aldehyde was added, and the reaction mixture was stirred until TLC showed any significant change. The reaction was quenched with satd $NH_4Cl$. The organic layer was washed with HCl (2 N), satd $NaHCO_3$, and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The mixture was purified by flash chromatography on silica gel to give the alcohol.

***tert*-Butyl (*S*)-4-Cyclohexyl-4-hydroxybut-2-ynyl Carbonate (5a).** The general procedure was followed for $Zn(OTf)_2$ (200 mg, 0.55 mmol), (−)-NME (108 mg, 0.60 mmol), toluene (1 mL), and $Et_3N$ (84 μL, 0.60 mmol) at rt for 3 h; alkyne **2** (78.8 mg, 0.5 mmol), toluene (0.5 mL) at rt for 30 min; cyclohexanecarbaldehyde (73 μL, 0.60 mmol) for 4 h. Purification by flash chromatography ($CH_2Cl_2$/MeOH 99/1) gave **5a** (123.0 mg, 91%) as a colorless oil: $[\alpha]^{25}_D$ +1.86 (*c* 1.05, $CHCl_3$) for 97% ee;[14] IR (film) 3425, 2929, 1746, 1453, 1370, 1277 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) *δ* 4.70 (2H, d, *J* = 1.7 Hz), 4.18 (1H, dt, *J* = 6.1, 1.7 Hz), 1.85−1.50 (7H, m), 1.49 (9H, s), 1.32−0.99 (5H, m); $^{13}C$ NMR (50 MHz, $CDCl_3$) *δ* 152.7, 87.2, 82.9, 79.4, 67.1, 54.7, 43.9, 28.4, 28.1, 27.7, 26.3, 25.8, 25.8; HRMS(ESI) calcd for $C_{15}H_{24}NaO_4$ ($M + Na^+$) 291.1572, found 291.1561.

***tert*-Butyl (*S*)-4-Hydroxy-5-methylhex-2-ynyl Carbonate (5b).** The general procedure was followed for $Zn(OTf)_2$ (200 mg, 0.55 mmol), (−)-NME (108 mg, 0.60 mmol), toluene (1 mL), and $Et_3N$ (84 μL, 0.60 mmol) at rt for 2 h; alkyne **2** (77.1 mg, 0.5 mmol), toluene (0.5 mL) at rt for 30 min; 2-methylpropionaldehyde (55 μL, 0.60 mmol) for 4 h. Purification by flash chromatography ($CH_2Cl_2$/MeOH 99/1) gave **5b** (102.8 mg, 91%) as a colorless oil: $[\alpha]^{25}_D$ −1.31 (*c* 1.05, $CHCl_3$) for 96% ee;[14] IR (film) 3469, 2967, 1748, 1459, 1370, 1277 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) *δ* 4.71 (2H, d, *J* = 1.7 Hz), 4.21 (1H, dt, *J* = 5.6, 1.7 Hz), 1.87 (1H, hpd, *J* = 6.6, 5.6 Hz), 1.78 (1H, bs), 1.49 (9H, s), 1.00

(12) (a) Lu, G.; Li, X.-S.; Chen, G.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2003**, *14*, 449−452. (b) Gao, G.; Moore, D.; Xie, R.-G.; Pu, L. *Org. Lett.* **2002**, *4*, 4143−4146. (c) For another Ti-catalyzed addition: Li, Z.-B.; Pu, L. *Org. Lett.* **2004**, *6*, 1065−8.

(13) The same strategy was applied to obtain **1d** (R = Ph) without success. Although **11** was readily added to benzaldehyde (quantitative yield, 90% ee), the cyclization step failed.

(14) Determined by HPLC of the corresponding Mosher's esters.

(15) Determined by $^1H$ and $^{19}F$ NMR of the corresponding Mosher's esters.

(3H, d, $J$ = 6.6 Hz), 0.98 (3H, d, $J$ = 6.6 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 152.8, 86.9, 82.9, 79.4, 67.8, 54.7, 34.3, 27.7, 18.0, 17.4.

***tert*-Butyl (*S*)-4-Hydroxy-6-methylhept-2-ynyl Carbonate (5c).** The general procedure was followed for $Zn(OTf)_2$ (246 mg, 0.67 mmol), (−)-NME (120 mg, 0.67 mmol), toluene (1 mL), and $Et_3N$ (112 $\mu$L, 0.73 mmol) at 50 °C for 2 h; alkyne **2** (116 mg, 0.74 mmol) for 1 h at rt; 3-methylbutanal (273 mg, 3.17 mmol) for 3 h. Direct purification by flash chromatography on silica gel (EtOAc/hexane 1/9) gave **5c** as a colorless oil (105 mg, 58%): $[\alpha]^{25}_D$ −11.7 (*c* 0.73, $CHCl_3$) for 89% ee;[14] IR (film) 3445, 2959, 1748, 1369, 1279, 1153 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.70 (2H, d, $J$ = 1.8 Hz), 4.45 (1H, qt, $J$ = 6.6, 1.8 Hz), 1.89 (1H, bd, $J$ = 5.5 Hz), 1.84 (1H, hp, $J$ = 6.7 Hz), 1.67−1.52 (2H, m), 1.49 (9H, s), 0.94 (3H, d, $J$ = 6.6 Hz), 0.92 (3H, d, $J$ = 6.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 152.8, 88.4, 82.9, 78.5, 60.9, 54.7, 46.5, 27.7, 24.6, 22.5, 22.4; HRMS(ESI) calcd for $C_{13}H_{22}NaO_4$ (M + $Na^+$) 265.1416, found 265.1410.

***tert*-Butyl (*S*)-4-Hydroxy-4-phenylbut-2-ynyl Carbonate (5d).** The general procedure was followed for $Zn(OTf)_2$ (246 mg, 0.67 mmol), (−)-NME (120 mg, 0.67 mmol), toluene (1 mL), and $Et_3N$ (112 $\mu$L, 0.73 mmol) at 50 °C for 2 h; Alkyne **2** (95 mg, 0.61 mmol) for 1 h at rt; benzaldehyde (63 $\mu$L, 0.91 mmol) for 3 h. Purification by flash chromatography on silica gel ($Et_2O$/hexane 3/7) gave **5d** as a colorless oil (56 mg, 35%): $[\alpha]^{25}_D$ −1.5 (*c* 1.05, $CHCl_3$) for >96% ee;[15] IR (film) 3436, 3033, 2983, 2936, 1746, 1256, 1161 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.53−7.51 (2H, m), 7.37−7.33 (3H, m), 5.49 (1H, s), 4.74 (2H, d, $J$ = 1.8 Hz), 2.57 (1H, bs), 1.49 (9H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 152.8, 140.0, 128.6, 128.4, 126.6, 86.8, 83.0, 80.3, 64.4, 54.7, 27.7; HRMS(ESI) calcd for $C_{15}H_{18}NaO_4$ (M + $Na^+$) 285.1103, found 285.1118.

***tert*-Butyl (*R*,*R*)-4-(2,2-Dimethyl-1,3-dioxolan-4-yl)-4-hydroxybut-2-ynyl Carbonate (5f).** The general procedure was followed for $Zn(OTf)_2$ (246 mg, 0.67 mmol), (+)-NME (120 mg, 0.67 mmol), toluene (1 mL), and $Et_3N$ (112 $\mu$L, 0.73 mmol) at 50 °C for 2 h; alkyne **2** (118 mg, 0.75 mmol) for 45 min at rt; (+)-2,3-*O*-isopropylidene-D-glyceraldehyde (415 mg, 3.20 mmol) for 30 min. Direct purification by flash chromatography on silica gel (EtOAc/hexane 3/7) gave **5f** as a colorless oil (170 mg, 78%) as the *anti* isomer: $[\alpha]^{25}_D$ +17.7 (*c* 0.93, $CHCl_3$); IR (film) 3440, 2987, 2939, 1748, 1480, 1457, 1374, 1279, 1256 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 4.70 (2H, d, $J$ = 1.8 Hz), 4.50 (1H, dt, $J$ = 4.5, 1.8 Hz), 4.23 (1H, ddd, $J$ = 6.5, 6.1, 4.5 Hz), 4.08 (1H, dd, $J$ = 8.6, 6.5 Hz), 4.03 (1H, dd, $J$ = 8.6, 6.1 Hz), 1.49 (9H, s), 1.46 (3H, s), 1.37 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 152.4, 109.8, 84.0, 82.7, 79.8, 76.4, 65.0, 62.3, 54.2, 27.3, 26.0, 24.8; HRMS-(ESI) calcd for $C_{14}H_{22}NaO_6$ (M + $Na^+$) 309.1314, found 309.1340.

**General Procedure for Cyclizations.** A solution of $Pd(PPh_3)_4$ in $CH_2Cl_2$ was added to a flask (sealed with a septum) that contained the alkenol under $N_2$. The size of the flask should be appropriated to the volume of solvent added, trying to minimize the nitrogen atmosphere. The mixture was stirred at rt until TLC showed complete disappearance of the starting material. The solvent was removed in vacuo, and the crude mixture was purified by flash chromatography on silica gel.

**(*S*,*S*)-4-Cyclohexyl-5-vinyl-1,3-dioxolan-2-one (1a).** The general procedure was followed for alkenol **8a** (42.6 mg, 0.18 mmol) and $Pd(PPh_3)_4$ (10.4 mg, 0.009 mmol) in $CH_2Cl_2$ (1.8 mL) for 15 min. Purification by flash chromatography ($CH_2Cl_2$/hexane 1/1) afforded **1a** (28.2 mg, 91%, dr 96:4) as a colorless oil: $[\alpha]^{25}_D$ −44.8 (*c* 1.13, $CHCl_3$); IR (film) 2931, 1804, 1451, 1362, 1275 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.86 (1H, ddd, $J$ = 17.2, 10.3, 6.8 Hz), 5.48 (1H, bd, $J$ = 17.2 Hz), 5.40 (1H, bd, $J$ = 10.3 Hz), 4.79 (1H, t, $J$ = 6.8 Hz), 4.09 (1H, t, $J$ = 6.8 Hz), 1.92−1.63 (5H, m), 1.35−1.00 (6H, m); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 154.4, 133.1, 120.6, 85.4, 80.3, 41.0, 27.7, 27.6, 25.9 25.4, 25.2; HRMS-(ESI) calcd for $C_{11}H_{16}NaO_3$ (M + $Na^+$) 219.0997, found 219.1001.

**(*S*,*S*)-4-Isopropyl-5-vinyl-1,3-dioxolan-2-one (1b).** The general procedure was followed for alkenol **8b** (34.7 mg, 0.15 mmol) and $Pd(PPh_3)_4$ (8.0 mg, 0.007 mmol) in $CH_2Cl_2$ (1.8 mL) for 15 min. Purification by flash chromatography ($CH_2Cl_2$/hexane 1/1) afforded **1b** (20.6 mg, 87%, dr > 96:4) as a colorless oil: $[\alpha]^{25}_D$ −59.4 (*c* 1.05, $CHCl_3$); IR (film) 2970, 1804, 1364, 1162, 1045 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.88 (1H, ddd, $J$ = 17.0, 10.3, 7.0 Hz), 5.49 (1H, dt, $J$ = 17.0, 0.9 Hz), 5.42 (1H, dt, $J$ = 10.3, 0.9 Hz), 4.76 (1H, ddt, $J$ = 7.0, 6.6, 0.9 Hz), 4.09 (1H, t, $J$ = 6.7 Hz), 1.97 (1H, oct, $J$ = 6.8 Hz), 1.05 (3H, d, $J$ = 6.8 Hz), 0.99 (3H, d, $J$ = 6.8 Hz); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 154.2, 133.1, 120.7, 86.1, 80.3, 31.5, 17.4, 17.3; HRMS(EI) calcd for $C_8H_{12}O_3$ ($M^+$) 156.0786, found 156.0780.

**(*S*,*S*)-4-Isobutyl-5-vinyl-1,3-dioxolan-2-one (1c).** The general procedure was followed for alkenol **8c** (26.0 mg, 0.11 mmol) and $Pd(PPh_3)_4$ (6.2 mg, 0.005 mmol) in $CH_2Cl_2$ (1.8 mL) for 30 min. Purification by flash chromatography ($CH_2Cl_2$/hexane 1/1) afforded **1c** (16.6 mg, 92%, dr 90:10) as a colorless oil: $[\alpha]^{25}_D$ −51.6 (*c* 0.94, $CHCl_3$); IR (film) 2962, 1806, 1470, 1368, 1260 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.87 (1H, ddd, $J$ = 17.1, 10.4, 7.2 Hz), 5.49 (1H, dt, $J$ = 17.1, 1.0 Hz), 5.43 (1H, dt, $J$ = 10.4, 0.9 Hz), 4.59 (1H, ddt, $J$ = 7.7, 7.2, 1.0 Hz), 4.36 (1H, ddd, $J$ = 9.0, 7.7, 4.0 Hz), 1.90−1.69 (2H, m), 1.49 (1H, ddd, $J$ = 14.1, 7.9, 4.0 Hz), 0.98 (3H, d, $J$ = 6.6 Hz), 0.97 (3H, d, $J$ = 6.6 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 154.3, 131.9, 121.4, 83.1, 80.6, 41.9, 24.8, 22.8, 21.9.

**(*S*,*S*)-4-Phenyl-5-vinyl-1,3-dioxolan-2-one (1d).** The general procedure was followed for alkenol **8d** (33.0 mg, 0.13 mmol) and $Pd(PPh_3)_4$ (8.5 mg, 0.007 mmol) in $CH_2Cl_2$ (1.8 mL) for 1 h. Purification by flash chromatography ($CH_2Cl_2$/hexane 1/1) afforded **1d** (19.6 mg, 83%, dr 90:10) as a colorless oil: $[\alpha]^{25}_D$ +3.74 (*c* 0.6, $CHCl_3$); IR (film) 2923, 1802, 1654 cm$^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.46−7.35 (5H, m), 5.99 (1H, ddd, $J$ = 17.0, 10.5, 7.1 Hz), 5.48 (1H, dt, $J$ = 10.5, 0.9 Hz), 5.46 (1H, dt, $J$ = 17.0, 1.0 Hz), 5.28 (1H, d, $J$ = 8.1 Hz), 4.88 (1H, ddt, $J$ = 8.1, 7.1, 1.0 Hz); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 154.0, 134.7, 131.2, 129.7, 129.2, 125.8, 122.1, 84.7, 83.0; HRMS(ESI) calcd for $C_{11}H_{10}NaO_3$ (M + $Na^+$) 213.0528, found 213.0556.

**(4*S*,4′*R*,5*S*)-4-(2,2-Dimethyl-1,3-dioxolanyl)-5-vinyl-1,3-dioxolan-2-one (1f).** The general procedure was followed for alkenol **8f** (41.0 mg, 0.14 mmol) and, $Pd(PPh_3)_4$ (8.2 mg, 0.007 mmol) in $CH_2Cl_2$ (1.8 mL) for 1 h. Purification by flash chromatography on silica gel ($CH_2Cl_2$) afforded **1f** (18.5 mg, 61%) as a colorless oil: $[\alpha]^{25}_D$ +20.3 (*c* 0.65, $CHCl_3$); IR (film) 2925, 1802, 1456, 1374 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.91 (1H, ddd, $J$ = 17.1, 10.5, 6.4 Hz), 5.52 (1H, bd, $J$ = 17.1 Hz), 5.41 (1H, bd, $J$ = 10.5 Hz), 5.04 (1H, ddt, $J$ = 6.4, 5.3, 1.2 Hz), 4.28−4.13 (3H, m), 3.94 (1H, dd, $J$ = 9.2, 3.7 Hz), 1.43 (3H, s), 1.36 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 153.7, 132.8, 120.0, 110.6, 80.6, 79.3, 74.9, 66.2, 26.7, 24.7; HRMS(ESI) calcd for $C_{10}H_{14}NaO_5$ (M + $Na^+$) 237.0739, found 237.0744.

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**Supporting Information Available:** Experimental procedures and characterization data of compounds **1e**, **6a**, **7a**, *E*-**8a**, **8a**−**d**, **8f**, **9a**, **10a**, **12e**, **13e**, and **14f**. $^1$H and $^{13}$C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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