Addition of Allenylzinc Reagents, Prepared in Situ from Nonracemic Propargylic Mesylates, to Aldehydes. A New Synthesis of Highly Enantioenriched Homopropargylic Alcohols

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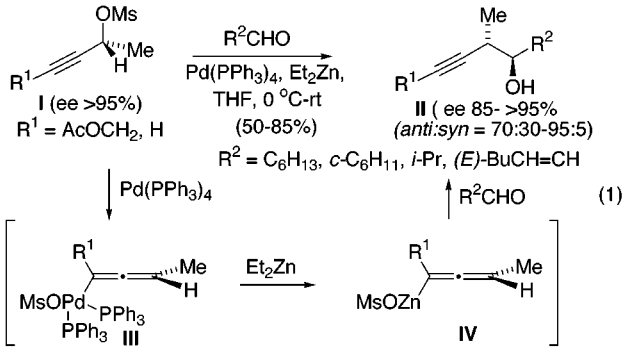
Enantioenriched propargylic mesylates are converted to chiral allenylzinc reagents via transient allenylpalladium species by treatment with a Pd(0)-phosphine catalyst in the presence of excess Et_2Zn. These zinc reagents undergo S_E2' additions to various aldehydes to yield mainly the anti homopropargylic alcohol adducts of high ee. The reaction is most efficient in THF with $Pd(OAc)_2$·PPh_3 as the catalyst precursor. As little as 2.5 mol % of this precursor is effective.

We recently described a method for preparing nonracemic homopropargylic alcohols **II** from propargylic mesylates **I** and aldehydes by metal exchange of a presumed allenylpalladium species with diethylzinc (eq 1).[1] The impetus for these studies came from several



earlier reports by Tamaru and co-workers, who employed racemic allylic and propargylic esters and halides for analogous additions leading to homoallylic and homopropargylic alcohols.[2] Tamaru's studies were carried out on benzaldehyde and achiral or racemic propargylic esters. The homopropargylic adducts derived from 3-butyn-2-yl benzoate, methyl carbonate, bromide, and tosylate were formed as 1:1 mixtures of syn and anti isomers. In contrast, we found that enantioenriched 3-butyn-2-ol mesylates react under the Tamaru conditions with aliphatic aldehydes to form mainly anti adducts of high ee.

The high stereoselectivity of additions to branched aldehydes was of particular interest to us in connection with our work on the synthesis of polypropionate natural products.[3] Our proposed catalytic cycle for the metal exchange process (Figure 1) is based on evidence from the Tamaru group, who isolated the product of β-hydride

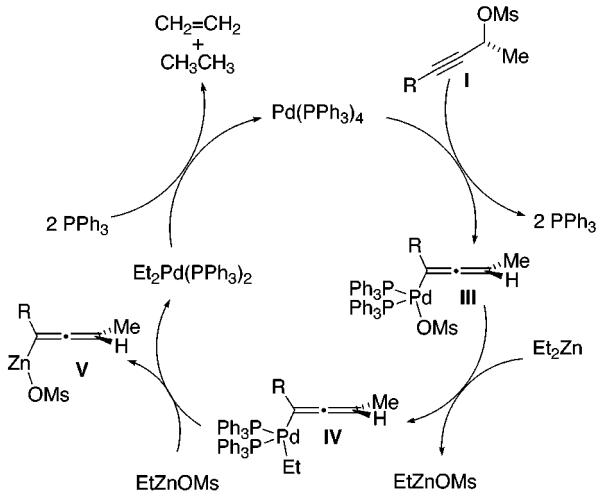


Figure 1. Possible catalytic cycle for Pd(0) catalyzed zincation of propargylic mesylates.

elimination (benzyl acrylate) from reactions in which benzyl β-iodozincopropionate served as the source of zinc.[2d] Additional evidence comes from the work of Knochel and co-workers, who reported the rapid decomposition of Et_2PdLn_2 to ethylene and ethane with regeneration of the Pd(0) catalyst.[4]

Our initial results, though promising, had several shortcomings. (1) Yields were not uniformly high. (2) A 2-fold excess of the mesylate was required. (3) Low concentrations of reactants (∼0.05 M) were necessary to minimize addition of an ethyl group from the diethylzinc to the aldehyde. In an effort to rectify at least some of these shortcomings, a more systematic study of the reaction was carried out. Several solvents were examined, including benzene, toluene, hexane, CH_2Cl_2, DME, and THF. Of these, THF was clearly superior. No reaction took place in the hydrocarbon solvents, and only slow product formation was observed in CH_2Cl_2 and DME. The use of as much as 10 equiv of Et_2Zn did not increase the yield, and increased concentrations of reactants led to significant amounts (∼50% at 0.1 M) of ethylated aldehyde resulting in reduced yields of propargylic adducts.

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(2) (a) Shimizu, M.; Kimura, M.; Tanaka, S.; Tamaru, Y. *Tetrahedron Lett.* **1998**, *39*, 609. (b) Tamaru, Y.; Goto, S.; Tanaka, A.; Shimizu, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 878. (c) Tamaru, Y.; Tanaka, A.; Yasui, K.; Goto, S.; Tanaka, S. *Angew Chem., Int. Ed. Engl.* **1995**, *34*, 787. (d) Yasui, K.; Goto, Y.; Takafumi, Y.; Taniseki, Y.; Fugami, K.; Tanaka, A.; Tamaru, Y. *Tetrahedron Lett.* **1993**, *34*, 7619.

(3) For a recent application, see: Marshall, J. A.; Johns, B. A. *J. Org. Chem.* **1998**, *63*, 7885.

(4) Stadtmuller, H.; Lentz, R.; Tucker, C. T.; Studmann, T.; Dorner, W.; Knochel, P. *J. Am. Chem. Soc.* **1993**, *115*, 7027.

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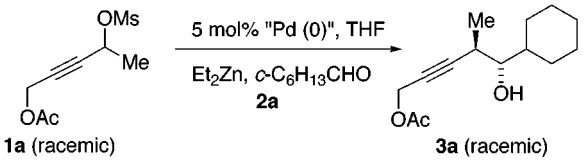
Table 1. Effect of Catalyst on the Allenylozinc Addition



Pd(0)	*t*, h	*T*, °C	**1**, equiv	concn, M	yield,[a] %
Pd $(PPh_3)_4$	3	0	2.0	0.05	51
Pd $(MeCN)_2Cl_2$	2	0	1.5	0.05	dec
Pd(dppf)Cl_2	36	0 to rt	2.0	0.05	37
$Pd(OAc)_2$·PPh_3[b]	12	−20	1.5	0.1	75
$PdCl_2$·$2PPh_3$	2	0	1.5	0.05	74
$Pd(OAc)_2$·$2PPh_3$	2	0 to rt	1.5	0.05	58

[a] ~95:5 anti/syn. [b] 2.5 mol % catalyst.

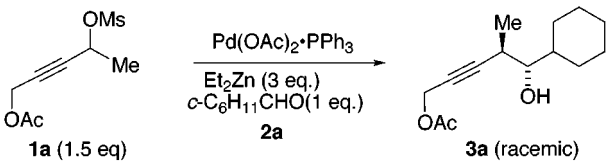
The effect of Pd catalyst was next examined. These studies employed a number of commonly available catalyst precursors[5] with racemic propargylic mesylate **1a** and cyclohexanecarboxaldehyde in THF (Table 1). Additions utilizing $Pd(PPh_3)_4$ as the catalyst produced the anti adduct **3a** in 51% yield with a small amount (<5%) of the syn adduct as a minor product. The use of Pd$(MeCN)_2Cl_2$ caused rapid decomposition of the mesylate. Pd(dppf)Cl_2 was moderately effective but offered no advantages over $Pd(PPh_3)_4$.

A report by Oppolzer on the use of $Pd(OAc)_2$·PBu_3 for an intramolecular metalloene reaction involving an allylic Pd−Zn metathesis prompted our interest in this catalyst precursor.[6] However, we experienced difficulties obtaining Bu_3P of sufficient purity. For this reason, we decided to substitute Ph_3P.[7] This combination showed a marked improvement over the previously examined catalysts. The reaction proceeded in 75% yield, and it could be carried out at −20 °C with only a 30% excess of mesylate. Moreover, a reactant concentration of 0.1 M did not lead to ethylated aldehyde, and as little as 2.5 mol % of catalyst was effective. We also found that $PdCl_2$·$2PPh_3$ could be employed with comparable results. Surprisingly, $Pd(OAc)_2$·$2PPh_3$ was significantly less effective than the analogous chloride or the 1:1 complex. Control experiments in which the Pd(0) catalyst or the Et_2Zn were omitted from the reaction afforded only recovered starting materials. None of the adduct **3a** was detected.

A more systematic examination of reaction concentration and temperature was conducted with $Pd(OAc)_2$·PPh_3 (Table 2). At −78 °C, no products were observed within a reasonable time. However, at −20 to −30 °C, adduct formation was relatively efficient and higher concentrations of reactants could be employed with minimal production of byproducts.

We detected small amounts of ethylated allenic byproduct in the reactions of Table 1, especially with $Pd(PPh_3)_4$ as the catalyst. In addition, a trace amount of at least one other allenic byproduct was produced in quantities too small for characterization. We suspected this to be an allenic dimer formed by coupling of the transient allenylzinc intermediate **V** with the initially formed allenylpalladium species **III** (Figure 1). This suspicion was confirmed upon treatment of the racemic propargylic mesylate **4** with $Pd(PPh_3)_4$ and Et_2Zn in THF without added aldehyde (eq 2). This reaction proceeded significantly slower at −20 °C than those in which aldehyde was present. However, at room temperature, a mixture of the ethylated allene **5** (33%) and the diallene **6** (10%), a 1:1 mixture of diastereomers, was produced in 2 h. Negligible amounts of these materials were formed in reactions employing $Pd(OAc)_2$·PPh_3.

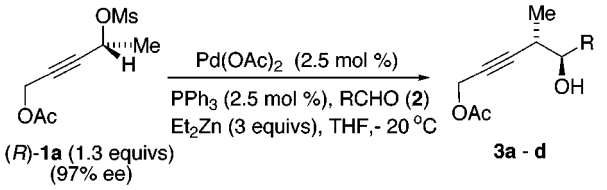
Table 2. Effect of Temperature and Concentration on the Allenylzinc Additiont



concn, M	*T*, °C	*t*, h	yield,[a,b] %
0.1	−78	4	0
0.2	−78	4	0
0.1	−50	36	36
0.2	−30	1.5	50
0.1	−20	12	75

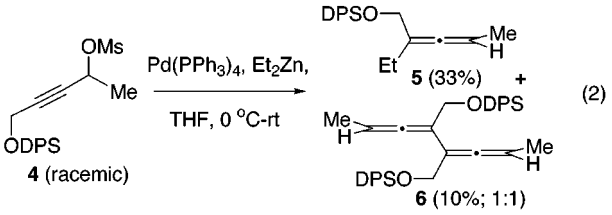
[a] The product is racemic. [b] A 95:5 mixture of anti and syn adducts.

Table 3. Additions of the Allenylzinc Reagent Derived from Mesylate (*R*)-1a to Achiral Aldehydes



R	yield,[a] %	anti/syn	ee,[b] %
c-C_6H_{11} (**2a**)	75 (51)	95:5	90 (**3a**)
C_6H_{13} (**2b**)	74 (57)	88:12	86 (**3b**)
i-Pr (**2c**)	75 (47)	95:5	92 (**3c**)
(*E*)-BuCH=CH (**2d**)	65 (57)	72:28	nd (**3d**)[c]

[a] Yields in parentheses are for reactions in which 5 mol % $Pd(PPh_3)_4$ was employed as the catalyst. [b] For the anti isomer.[c] Not determined.



As a first test of the improved allenylzinc methodology, we performed additions of the reagent derived from enantioenriched mesylate (*R*)-**1a** to representative achiral aldehydes **2a**−**d** with 3 equiv of Et_2Zn (Table 3). The results of these additions parallel our previous findings with the $Pd(PPh_3)_4$ catalyst, but the yields of adducts are significantly higher.[1] These higher yields are realized with considerably less chiral mesylate than previously employed. The diastereoselectivity and product ee are comparable.

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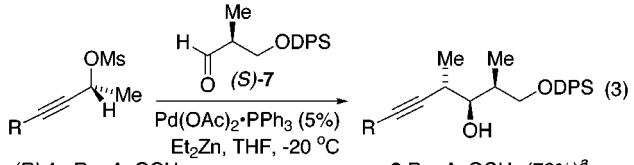
(6) Oppolzer, W.; Flachsmann, F. *Tetrahedron Lett.* **1998**, *39*, 5019. Mandai, T.; Matsumoto, T.; Tsuji, J.; Saito, S. *Tetrahedron Lett.* **1993**, *34*, 2513.

(7) This combination has not previously been utilized. For a discussion of possible catalytically active species, see ref 5, p 2, and the following cited reference: Amatore, C.; Jutand, A.; M'Barki, M. A. *Organometallics* **1992**, *11*, 3009.

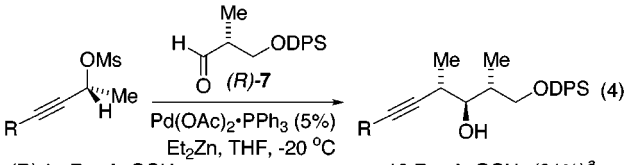
We next examined additions of the reagents derived from the enantioenriched mesylates (*R*)-**1a** and (*R*)-**1b**[1] (>95% ee) to the α-methyl-*β*-ODPS aldehydes (*S*)- and (*R*)-**7** (eqs 3 and 4).[9] The anti,syn adducts **8** and **9** were obtained in 72 and 70% yield from the former aldehyde (eq 3), and the anti,anti adducts **10** and **11** were produced in comparable yield from the latter (eq 4).[10]



(3)

(*R*)-**1a** R = $AcOCH_2$
(*R*)-**1b** R = H

8 R = $AcOCH_2$ (72%)[a]
9 R = H (70%)[a]



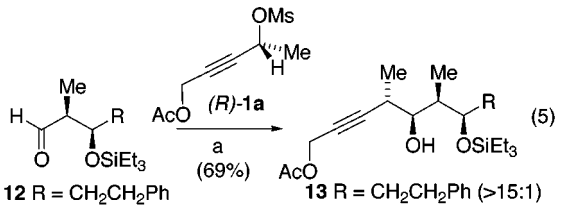
(4)

(*R*)-**1a** R = $AcOCH_2$
(*R*)-**1b** R = H

10 R = $AcOCH_2$ (81%)[a]
11 R = H (75%)[a]

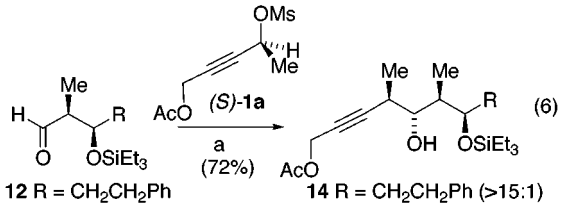
[a] A trace of a diastereomeric product was formed

A further test of double diastereoselection is provided by the reaction of aldehyde **12**[10] and the allenylzinc reagents from mesylates (*R*)-**1a** and (*S*)-**1a** (eqs 5 and 6).



(5)

12 R = CH_2CH_2Ph **13** R = CH_2CH_2Ph (>15:1)



(6)

12 R = CH_2CH_2Ph **14** R = CH_2CH_2Ph (>15:1)

a. $Pd(OAc)_2$•PPh_3 (5%) Et_2Zn, THF, -20 °C

These additions both proceeded in ca. 70% yield. Adduct **13** was produced as the major isomer of a separable mixture (>15:1) of stereoisomers. Adduct **14** was formed as a similar mixture. The structures of these adducts are assigned by analogy. In the latter reaction, the minor product was adduct **13**, which most likely arises as a consequence of partial racemization of the allenylpalladium precursor of the allenylzinc reagent.[12] The minor product accompanying adduct **13** in eq 5 was not isolated in quantities sufficient for structure determination.

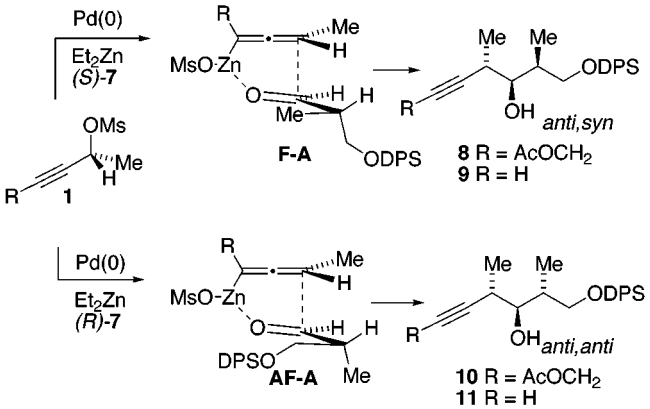


Figure 2. Possible cyclic transition states for allenylzinc additions to aldehydes (*S*)-**7** and (*R*)-**7**.

The formation of mainly anti adducts is suggestive of a cyclic transition state for the additions. One possible scenario is depicted in Figure 2 in which adducts **8** and **9** arise via a Felkin−Ahn orientation (**F**−**A**), whereas **10** and **11** are formed through an anti Felkin−Ahn (**AF**−**A**), or less likely, a chelation-controlled arrangement.[9,13] The trace amounts of inseparable isomeric products detected in these reactions are presumed to be syn adducts. The reactions leading to adducts **13** and **14** can be viewed in a similar light.

To illustrate a possible application of this methodology, we converted the homopropargylic alcohols **9** and **11** to the unsaturated lactones (pentenolides) **17** and **20** through carboxylation of the lithiated alkynes with CO_2 followed by partial hydrogenation of the triple bond[14] and thermal lactonization (eq 7). The 4-alkylpentenolide moiety of **17** and **20** is found in a number of biologically active polypropionate natural products.[15]

The present modifications represent significant improvements in the additions of in situ generated chiral allenylzinc reagents to aldehydes. The high degree of reagent control in additions to aldehydes **7** and **12** is especially noteworthy. In view of the ready availability of the precursor propargylic alcohols,[16] and given the ease of performing the addition reactions, the methodology should find widespread applications for the synthesis of highly enantioenriched homopropargylic alcohols.[3]

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(10) Aldehyde **12** was first prepared by Brian Johns in our laboratory through condensation of hydrocinnamaldehyde with the Evans propionyl oxazolidinone derived from norephedrine.[11] Full details are provided in the Supporting Information.
(11) Evans, D. A.; Mathre, D. J.; Scott, W. L. *J. Org. Chem.* **1985**, *50*, 1830. *Cf.* Brimble, M. A. *Aust. J. Chem.* **1990**, *43*, 1035.
(12) Marshall, J. A.; Wolf, M. A. *J. Org. Chem.* **1996**, *61*, 3238.
(13) The transition states depicted in Figure 2 are illustrative only. It is possible that Et_2Zn complexes may also participate as shown by Noyori and others in amine-catalyzed additions of dialkylzinc compounds to aldehydes. Cf. Noyori, R.; Kitamura, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 49. Soai, K.; Niwa, S. *Chem. Rev.* **1992**, *92*, 833. Rijenberg, E.; Neldes, J. H.; Kleij, A. W.; Jastrzebski, J. T. B. H.; Boersma, J.; Janssen, M. D.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 2847. Allylic zinc halides add without catalysis to aldehydes with allylic inversion as expected for S_E2' additions. Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 7. On the basis of other allenylmetal additions, we believe that the allyl analogy is appropriate. However, it should be noted that, under Barbier conditions, crotylzinc halides afford nearly 1:1 mixtures of anti and syn adducts, implying a rather loose transition state.
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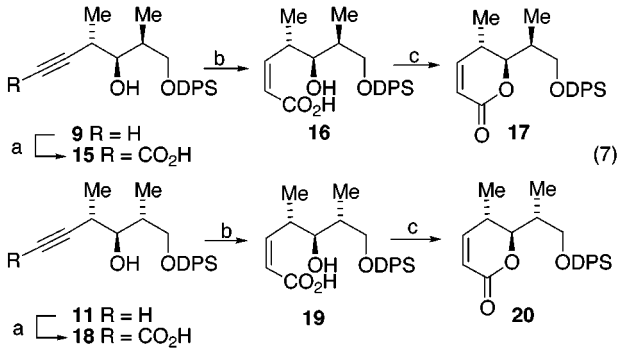

a) BuLi, -40° C; CO_2; b) H_2/5 % Pd-$BaSO_4$, quinoline, EtOH; c) C_6H_6, reflux (**17**, 65% overall; **20**, 63% overall)

Experimental Section

anti*-5-Acetoxy-1-cyclohexyl-3-pentyn-1-ol (3a).** To a solution of $Pd(OAc)_2$ (1.5 mg, 0.007 mmol) in THF (1.8 mL) at −78 °C were added PPh_3 (1.8 mg, 0.007 mmol), mesylate **1a** (88 mg, 0.40 mmol), and freshly distilled cyclohexanecarboxaldehyde (**2a**, 30 mg, 0.27 mmol) followed by dropwise addition of diethylzinc (0.8 mL, 1 M in hexane, 0.8 mmol). The mixture was immediately warmed to −20 °C. After 12 h, the reaction mixture was quenched by dropwise addition of 10% HCl ***(Caution: evolution of gaseous ethane) and diluted with Et_2O. After the mixture was warmed to room temperature, the layers were separated and the ether layer was washed with saturated brine. The aqueous layer was extracted with Et_2O, and the combined extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel (9:1 hexanes/EtOAc) to give 48 mg (75%) of alcohol **3a** and its syn diastereomer as a 95:5 inseparable mixture.[1]

(1*R*,2*S*)-(−)-5-Acetoxy-1-cyclohexyl-3-pentyn-1-ol[1] (3a). The standard procedure was employed with $Pd(OAc)_2$ (4.0 mg, 0.018 mmol), PPh_3 (4.7 mg, 0.018 mmol), mesylate (*R*)-**1a** (204 mg, 0.93 mmol), freshly distilled cyclohexanecarboxaldehyde (**2a**, 80 mg, 0.71 mmol), and diethylzinc (2.1 mL, 1 M in hexane, 2.1 mmol) in THF (7 mL) at −20 °C for 24 h to give 123 mg (72%) of alcohol **3a** and its syn diastereomer as a 95:5 inseparable mixture: $[\alpha]^{20}_D$ −4.8 (*c* 0.65, $CHCl_3$); IR (film) ν 3487, 2239, 1743 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.66 (d, J = 1.9 Hz, 2H), 3.07 (m, 1H), 2.74 (m, 1H), 2.07 (s, 3H), 1.92 (d, J = 12.3 Hz, 1H), 1.81−1.36 (m, 5H), 1.34−0.92 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 87.9, 78.6, 76.8, 52.7, 41.7, 30.0, 29.6, 28.1, 26.3, 26.2, 25.9, 20.7, 17.9.

(2*S*,3*S*,4*S*)-(+)-1-[(*tert*-Butyldiphenylsilyl)oxy]-2,4-dimethyl-5-hexyn-3-ol (9). The standard procedure was employed with $Pd(OAc)_2$ (2.7 mg, 0.012 mmol), PPh_3 (3.1 mg, 0.012 mmol), mesylate (*R*)-**1b** (62 mg, 0.42 mmol), aldehyde *(S)*-**7** (80 mg, 0.24 mmol), and diethylzinc (0.74 mL, 1 M in hexane, 0.74 mmol) in THF (1.7 mL) at −20 °C for 24 h. Purification by flash chromatography (19:1 hexanes/EtOAc) gave 65 mg (70%) of alcohol **9** as a clear oil: $[\alpha]^{20}_D$ +3.5 (*c* 1.01, $CHCl_3$); IR (film) ν 3483, 3306 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75−7.63 (m, 4H), 7.49−7.34 (m, 6H), 3.80−3.61 (m, 3H), 2.68 (m, 1H), 2.44 (bs, 1H), 2.00 (m, 1H), 1.87 (m, 1H), 1.21 (d, J = 6.9 Hz, 3H), 1.09 (s, 9H), 0.99 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 133.4, 129.7, 127.7, 86.2, 75.6, 70.4, 67.4, 37.9, 30.5, 26.9, 19.2, 17.7, 10.6. Anal. Calcd for $C_{24}H_{32}O_2Si$: C, 75.74; H, 8.47. Found: C, 75.48; H, 8.41.

(2*R*,3*S*,4*S*)-(−)-1-[(*tert*-Butyldiphenylsilyl)oxy]-2,4-dimethyl-7-acetoxy-5-heptyn-3-ol[9] (10). The standard procedure was employed with $Pd(OAc)_2$ (2.7 mg, 0.012 mmol), PPh_3 (3.1 mg, 0.012 mmol), mesylate (*R*)-**1a** (193 mg, 0.42 mmol), aldehyde *(R)*-**7** (80 mg, 0.24 mmol), and diethylzinc (0.74 mL, 1 M in hexane, 0.74 mmol) in THF (1.7 mL) at −20 °C for 24 h. Purification by flash chromatography (9:1 hexanes/EtOAc) gave 90 mg (81%) of alcohol **10** as a clear oil: $[\alpha]^{20}_D$ −16.8 (*c* 1.17, $CHCl_3$); IR (film) ν 3491, 2240, 1747 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.71−7.64 (m, 4H), 7.48−7.36 (m, 6H), 4.69 (d, J = 1.8 Hz, 2H), 3.80−3.66 (m, 2H), 3.43 (m, 2H), 2.74 (m, 1H), 2.08 (s, 3H), 2.01 (m, 1H), 1.30 (d, J = 6.9 Hz, 3H), 1.06 (s, 9H), 0.83 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 135.5, 132.9, 129.8, 127.7, 87.8, 78.1, 76.1, 68.3, 52.7, 38.9, 30.4, 26.7, 20.7, 19.0, 17.6, 13.5. Anal. Calcd for $C_{27}H_{36}O_4Si$: C, 71.64; H, 8.02. Found: C, 71.41; H, 8.05.

***anti,anti,syn*-Alcohol 14.** The standard procedure was employed with $Pd(OAc)_2$ (2.7 mg, 0.012 mmol), PPh_3 (3.1 mg, 0.012 mmol), mesylate (*S*)-**1a** (81 mg, 0.37 mmol), aldehyde **12** (75 mg, 0.24 mmol), and diethylzinc (0.74 mL, 1 M in hexane, 0.74 mmol) in THF (1.8 mL) at −20 °C for 22 h. Purification by flash chromatography (9:1 hexanes/EtOAc) gave 77 mg (72%) of alcohol **14** as a clear oil: $[\alpha]^{20}_D$ 3.0 (*c* 0.64, $CHCl_3$); IR (film) ν 3473, 1748 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30−7.15 (m, 5H), 4.68 (d, J = 2.1 Hz, 2H), 4.37 (apparent s, 1H), 3.89 (dt, J = 9.0, 3.0 Hz, 1H), 3.48 (m, 1H), 2.87 (ddd, J = 13.2, 5.4, 1.8 Hz, 1H), 2.61 (m, 1H), 2.49 (m, 1H), 2.08 (m, 1H), 2.07 (s, 3H), 1.97−1.74 (m, 2H), 1.28 (d, J = 7.2 Hz, 3H), 1.01 (t, J = 7.5 Hz, 9H), 0.80 (d, J = 6.9 Hz, 3H), 0.71 (q, J = 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 142.0, 128.3, 128.2, 125.8, 87.8, 77.5, 75.9, 52.8, 41.5, 33.6, 33.2, 31.7, 30.5, 20.7, 17.4, 13.4, 6.8, 4.9. Anal. Calcd for $C_{25}H_{40}O_4Si$: C, 69.40; H, 9.32. Found: C, 69.57; H, 9.35.

Lactone 17. To solution of alkyne **9** (290 mg, 0.76 mmol) in THF (30 mL) at −78 °C was added dropwise *n*-BuLi (0.70 mL, 2.5 M in hexane, 1.75 mmol). The reaction mixture was allowed to warm to −40 °C and stirred for 1 h. Carbon dioxide was then bubbled through the solution for 15 min. The reaction mixture was poured onto crushed dry ice, diluted with Et_2O, and acidified by dropwise addition of 10% HCl ***(Caution: evolution of gaseous butane).*** The biphasic mixture was allowed to warm to room temperature. The layers were separated, and the aqueous layer was extracted twice with Et_2O. The combined Et_2O layers were dried over $MgSO_4$ and concentrated under reduced pressure to give acid **15** (400 mg, contaminated with pentanoic acid), which was used immediately without purification.

To a solution of acid **15** (400 mg, contaminated with pentanoic acid) in EtOH (15 mL) were added 5% $Pd/BaSO_4$ (48 mg) and quinoline (24 mg, 0.19 mmol). The resultant suspension was stirred vigorously for 1 h under a balloon atmosphere of H_2. After filtration through Celite with Et_2O, the solvents were removed under reduced pressure. The residue was resubjected to the above conditions for 1 h to give alkene **13** (400 mg, contaminated with pentanoic acid), which was used immediately without purification.

A solution of alkene **16** (400 mg, contaminated with pentanoic acid) in benzene (10 mL) was heated to reflux. After 4 h, the benzene was removed under reduced pressure, and the residue was chromatographed on silica gel (9:1 hexanes/EtOAc) to give 203 mg (65%) of lactone **17** as a white powder: $[\alpha]^{20}_D$ −31.5 (*c* 1.63, $CHCl_3$); mp 70−71 °C; IR (film) ν 1726 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.77−7.61 (m, 4H), 7.51−7.35 (m, 6H), 6.66 (d, J = 10.0 Hz, 1H), 5.96 (d, J = 10.0 Hz, 1H), 4.43 (d, J = 10.8 Hz, 1H), 3.84 (apparent t, J = 9.6 Hz, 1H), 3.62 (dd, J = 10.0, 5.3 Hz, 1H), 2.65 (m, 1H), 2.03 (m, 1H), 1.10 (d, $J \approx 7$ Hz, 3H), 1.07 (s, 9H), 0.90 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 152.1, 135.4, 133.3, 129.6, 127.6, 120.0, 82.2, 64.9, 36.8, 30.4, 26.8, 19.1, 15.9, 9.7. Anal. Calcd for $C_{25}H_{32}O_3Si$: C, 73.49; H, 7.89. Found: C, 73.31; H, 7.99.

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Supporting Information Available: Experimental procedures for **3a**−**d**, **5**, **6**, **8**, **11**−**13**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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