Synthesis of Enantioenriched Homopropargylic Alcohols through Diastereoselective S_E' Additions of Chiral Allenylstannanes to Aldehydes

James A. Marshall* and Xiao-jun Wang

Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, South Carolina 29208

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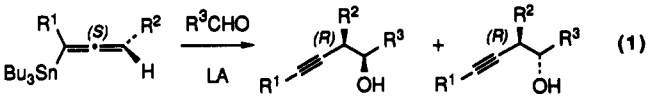
Allenylstannanes (*S*)-**4** and (*R*)-**4**, available in ca. 90% ee from alkynones **1** through reduction with the $LiAlH_4$–Darvon alcohol or -*ent*-Darvon alcohol complex, followed by S_N2' displacement on the derived mesylates (*R*)-**3** or (*S*)-**3** with $Bu_3SnLi{\cdot}CuBr{\cdot}Me_2S$, readily add to various aldehydes under Lewis acid catalysis to afford optically active homopropargylic alcohols with good to excellent syn diastereoselectivity. With 2-(benzyloxy)propanal (**48**), $MgBr_2$-catalyzed reactions are highly stereoselective, affording the syn adduct **49** from the (*S*)-stannane (*S*)-**4** and the anti adduct **52** from the (*R*)-stannane (*R*)-**4**. BF_3-promoted additions give mainly or exclusively the syn adducts **49** and **51**. Additions of (*S*)- and (*R*)-**4** to (*R*)-3-(benzyloxy)-2-methylpropanal (**61**) yield the syn adducts **62** and **64** as major or exclusive products.

We recently found that chiral allenylstannanes undergo stereospecific S_E' additions to aldehydes in the presence of Lewis acids, affording homopropargylic alcohols with good to excellent diastereoselectivity (eq 1).[1,2] The present



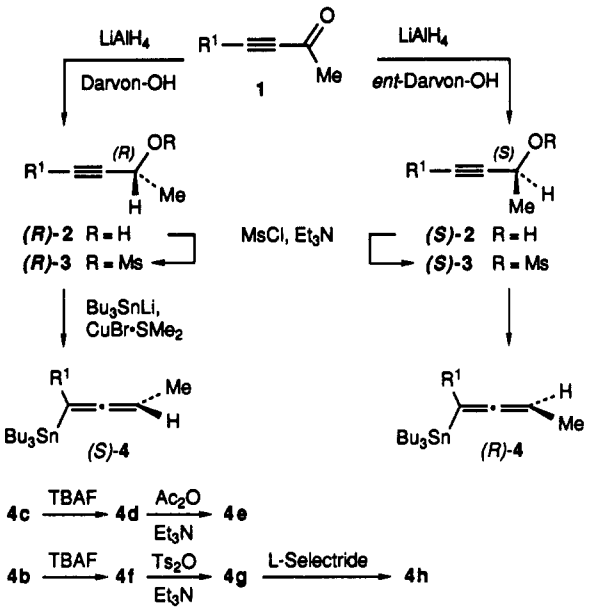
(1)

study was undertaken to examine such additions in more detail with stannanes and aldehydes of appropriate structure for the synthesis of polypropionate and polyether natural products.[3]

The stannanes (*S*)-**4** and (*R*)-**4** were readily prepared by S_N2' displacement on the (*R*)- or (*S*)-propargylic mesylates **3** with the reagent prepared from Bu_3SnLi and $CuBr{\cdot}SMe_2$.[4] The stannanes thus obtained were free of propargylic isomers. The alcohol precursors of mesylates **3** were available in ca. 90% ee through reduction of the acetylenic ketones **1** with the chiral alkoxyalumino hydride complex derived from $LiAlH_4$ and Darvon alcohol or the enantiomer of Darvon alcohol[5] (Scheme I).

The allenylstannanes **4** were found to be stable. No racemization or isomerization was detected upon exposure to excess cuprate or chromatography on silica gel or on storage.[6] Previous studies have shown that S_N2' displacements on propargylic mesylates by stannylcopper reagents proceed by a predominantly anti pathway.[4] As a check on the degree of specificity in the present examples, we prepared allenylstannane **15** by cuprate displacement on mesylate **10** and from ester **12**, the product of orthoester Claisen rearrangement of alcohol **11**.[7] It is

Scheme I



a series, $R^1 = n\text{-}C_7H_{15}$; **b** series, $R^1 = CH_2CH_2OTBS$;
c series, $R^1 = CH_2OTBS$; **d** series, $R^1 = CH_2OH$;
e series, $R^1 = CH_2OAc$; **f** series, $R^1 = CH_2CH_2OH$;
g series, $R^1 = CH_2CH_2OTs$; **h** series, $R^1 = CH_2CH_3$

assumed that the [3,3] rearrangement leading to **12** is concerted and the stereochemistry is assigned accordingly. It is also assumed that the ee of **12** and therefore **15** is equal to that of the alcohol precursor. From alcohol **5** of 82% ee, stannane **15** of $[\alpha]_D$ +77.6° was prepared by the Claisen route whereas material secured from **5** through the cuprate route was found to have $[\alpha]_D$ +76.4°. Thus, the cuprate displacement is highly anti selective (Scheme II).

Allenylstannane (*S*)-**4f**, the precursor of stannane (*S*)-**4h**, was similarly prepared by the [3,3] route from alcohol **20** via ester **21**. An independent synthesis of this alcohol was effected through stannylcopper addition to mesylate **23** followed by TBS ether cleavage. The rotations of material secured by the two routes were in close agreement after correction for the differing ee of the starting alcohols (68.7° from Claisen vs 67.7° from cuprate).

The synthesis of alcohol **20** could, in principle, be achieved more directly by reduction of alkynone **16** to alcohol **19**, thereby circumventing the silylation and desilylation steps. However, reduction of **16** with LAH–

(1) Marshall, J. A.; Wang, X.-j. *J. Org. Chem.* **1991**, *56*, 3212.
(2) Marshall, J. A.; Wang, X.-j. *J. Org. Chem.* **1990**, *55*, 6246.
(3) Cf. Masamune, S.; McCarthy, P. A. *Macrolide Antibiotics; Chemistry Biology and Practice*; Omura, S., Ed.; Academic Press: New York, 1984. Paterson, I.; Mansuri, M. M. *Tetrahedron* **1985**, *41*, 3569. Boeckman, R. K.; Goldstein, S. W. The Total Synthesis of Macrocyclic Lactones in *The Total Synthesis of Natural Products*, Vol. 7; ApSimon, J., Ed.; John Wiley and Sons: New York: 1988, pp 1–139. Westley, J. W., Ed. *Polyether Antibiotics: Naturally Occurring Acid Ionophores*; Marcel Dekker, Inc.: New York, 1982, Vols. I and II.
(4) Cf. Ruitenberg, K.; Westmijze, H.; Meijer, J.; Elsevier, C. J.; Vermeer, P. *J. Organomet. Chem.* **1983**, *241*, 417. Ruitenberg, K.; Westmijze, H.; Kleijn, H.; Vermeer, P. *J. Organomet. Chem.* **1984**, *277*, 227.
(5) Yamaguchi, S.; Mosher, H. S. *J. Org. Chem.* **1973**, *38*, 1870. Marshall, J. A.; Salovich, J. M.; Shearer, B. G. *J. Org. Chem.* **1990**, *55*, 2398. A sample of *ent*-Darvon alcohol was supplied by Eli Lilly and Co., to whom we are grateful.
(6) It has been reported that allenes prepared by S_N2' displacements on propargylic mesylates with organocopper reagents racemize upon prolonged contact (>15 min) with the copper reagent. Olsson, L.; Claesson, A. *Acta Chem. Scand., Ser. B.* **1979**, *33*, 679. Claesson, A.; Olsson, S. *J. Chem. Soc., Chem. Commun.* **1979**, 524.
(7) Cf. Hill, R. K.; Soman, R.; Sawada, S. *J. Org. Chem.* **1973**, *38*, 4218.

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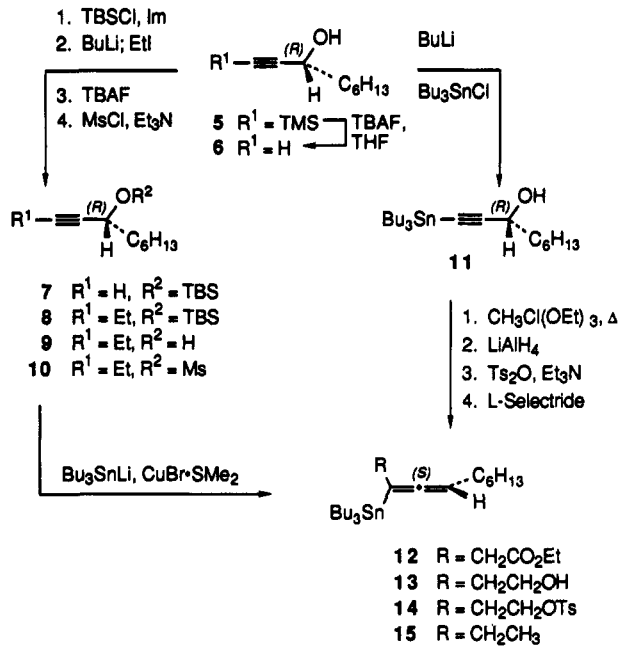
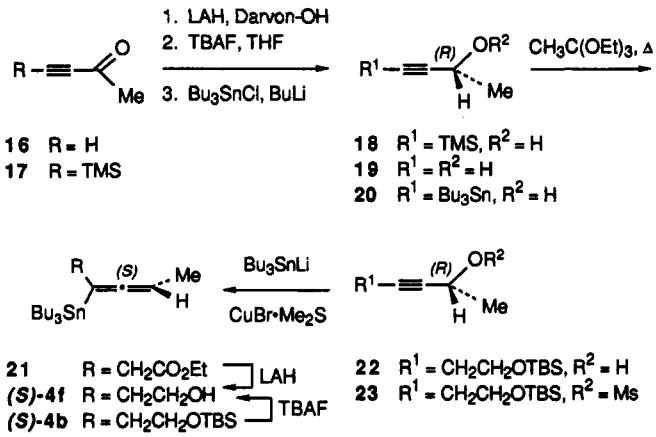
Scheme II



Scheme III

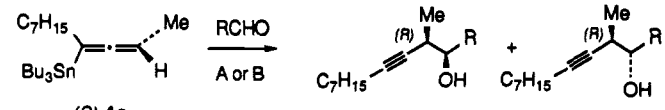


Darvon alcohol gave alcohol **19** of only 40% ee in contrast to the reduction of TMS alkynone **17**, which afforded **18** of 82% ee (Scheme III).

In order to establish intrinsic stereochemical preferences, we examined additions of the allenylstannane (*S*)-**4a** to a number of achiral aldehyde substrates.[8] With *n*-heptanal, BF_3·OEt_2-promoted addition afforded a 39:61 mixture of diastereomeric products in 83% yield. In contrast, $MgBr_2$·OEt_2 led to a nearly opposite ratio of products (66:34) in 56% yield (Table I, entries 1 and 2). The relative stereochemistry of these adducts was established as syn and anti (**24** and **27**), respectively, through degradation to the acetonides **35** and **37**[9] (Scheme IV).

Additions to isobutyraldehyde and pivalic aldehyde were highly syn selective. The BF_3-promoted reactions proceeded readily at −78 °C, affording the adducts **25** and **26** in high yield (Table I, entries 3 and 5). The $MgBr_2$-promoted reactions were considerably slower and somewhat less selective (Table I, entry 4). The relative and absolute stereochemistry of alcohol **25** was established by conversion to the benzyl ether **43** along the lines employed for the analogues **30** and **36**. Ether **43** was independently prepared by addition of isopropylmagnesium bromide to (*R*)-3-(benzyloxy)-2-methylpropanal (**47**) and separation of the

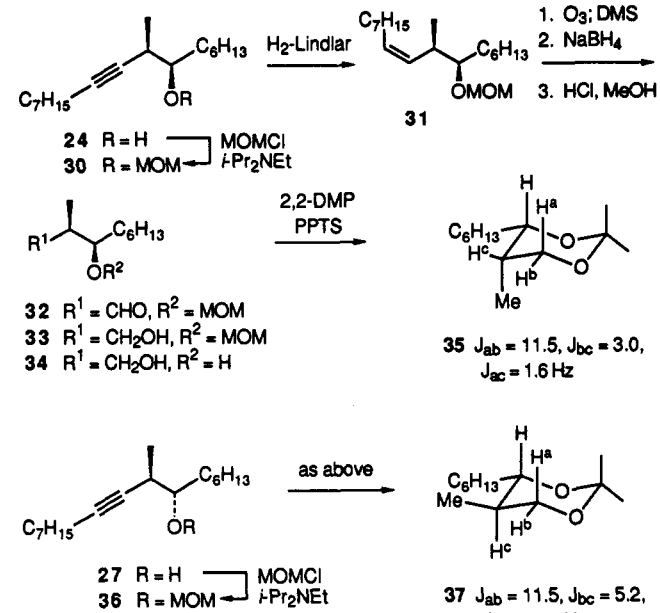
Table I. Additions of Allenylstannane (*S*)-4a to Achiral Aldehydes



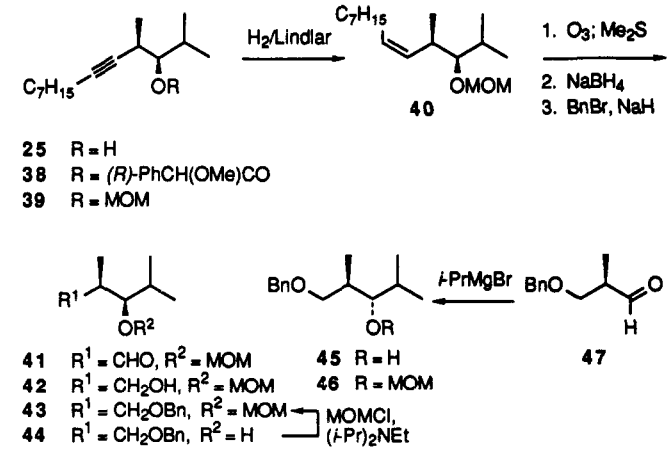
entry	R	condns[a]	yield, %	syn:anti
1[b]	C_6H_{13}	A	83	39:61
2[b]	C_6H_{13}	B	56	66:34
3	*i*-Pr	A	80	99:1
4	*i*-Pr	B	68	88:12
5	*t*-Bu	A	92	99:1

[a] A = BF_3·OEt_2, CH_2Cl_2, −78 °C, 0.5 h; B = $MgBr_2$·OEt_2, CH_2Cl_2, −23 to 0 °C, 24–36 h. [b] Racemic **4a** was employed.

Scheme IV



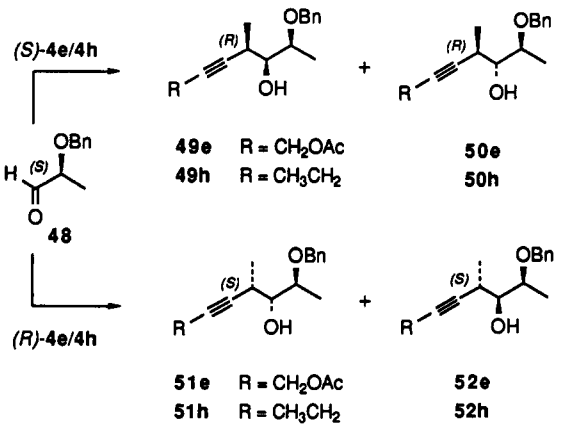
Scheme V



(8) An analogous study involving allenylsilanes has been described. Danheiser, R. L.; Carini, D. J.; Kwasigroch, C. A. *J. Org. Chem.* **1986**, *51*, 3870.

(9) Additions of crotylstannanes to simple branched or unbranched aldehydes in the presence of BF_3·OEt_2 typically afford ca. 90:10 mixtures of syn and anti diastereomers. Yamamoto, Y.; Yatagai, H.; Ishihara, Y.; Maeda, N.; Maruyama, K. *Tetrahedron* **1984**, *40*, 2239. Keck, G. E.; Abbott, D. E.; Boden, E. P.; Enholm, E. J. *Tetrahedron Lett.* **1984**, *25*, 3927.

Table II. Addition of Allenylstannanes (*S*)-4e/4h and (*R*)-4e/4h to Aldehyde 48



entry	stannane	condns[a]	yield, %	product composition[b] 49:50	51:52
1	(*S*)-4e	A	95	68:32	
2	(*S*)-4e	B	97	>99:1	
3	(*R*)-4e	A	97		97:3
4	(*R*)-4e	B	97		1:99
5	(*S*)-4h	A	92	87:13	
6	(*S*)-4h	B	98	>99:1	
7	(*R*)-4h	A	89		>99:1
8	(*R*)-4h	B	95		1:99

[a] A = BF_3·OEt_2, CH_2Cl_2, −78 °C, 2 h (4e) or 0.2 h (4h); B = $MgBr_2$·OEt_2, CH_2Cl_2, −23 °C, 2 h (4e) or 0.5 h (4h). [b] Corrected for ee of starting stannane.

alcohol adducts **44** and **45** (1:5 ratio) and then benzylation of the former. The optical rotation of the two samples thus prepared (−10° for **43** from **47** of 99% ee and −9.5° for **43** from **25** of 92% ee) were in close agreement (Scheme V).

It can thus be concluded that the addition of allenylstannane (*S*)-**4a** to isobutyraldehyde proceeds stereospecifically by an anti S_E' pathway.

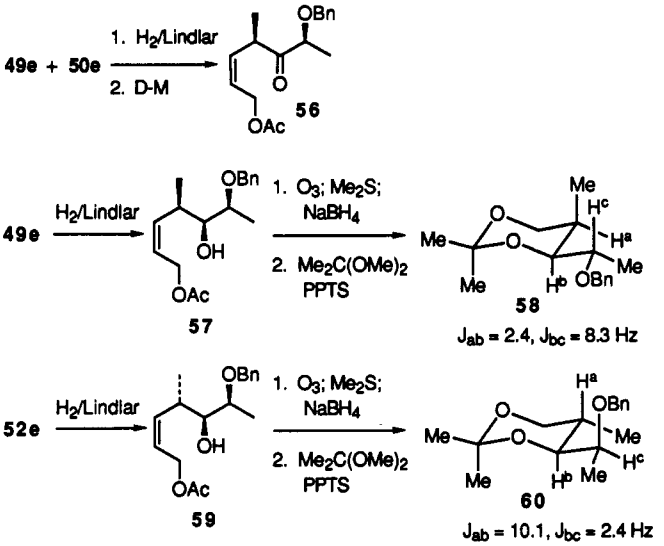
An independent check on the absolute configuration of alcohol **25** came from the ^1H NMR spectrum of the derived (*R*)-*O*-methylmandelate **38**.[10] However, because alcohol **25** was relatively unreactive, partial racemization of the mandelate took place during esterification. Thus, the analysis could not be used to determine the ee of **25**.

We next examined additions of allenylstannanes **4e** and **4h** to chiral aldehydes. The former stannane is of interest as a reagent for chain extensions leading to subunits of polyether and polypropionate natural products. The latter was chosen as a control in the event that the polar and basic acetoxy function of **4e** exhibited unusual behavior with the Lewis acid catalysts. Stannane **4h** also offered the advantage of an established absolute configuration and ee based on comparison of its progenitor **4f** with material derived from the Claisen product **21**.

The BF_3·OEt_2-promoted addition of allenylstannane (*S*)-**4e** to (*S*)-2-(benzyloxy)propanal (**48**) proceeded readily at −78 °C to afford a 68:32 mixture of diastereomeric adducts **49e** and **50e** in 95% yield (Table II, entry 1).[11] The same reaction, but with $MgBr_2$·OEt_2 as catalyst at −23 °C, gave adduct **49e** as the only detectable product in 97% yield (entry 2).[12] The enantiomeric stannane (*R*)-**4e** gave rise to a 97:3 mixture of diastereomeric alcohols **51e** and **52e** in the BF_3 reaction (entry 3).[11] Interestingly, the latter isomer was formed to the virtual exclusion of the former when $MgBr_2$ was employed as the catalyst (entry 4).[12]

The absolute stereochemistry of the carbinyl center in alcohols **49e** and **52e** was deduced through ^1H NMR analysis of the (*S*)-*O*-methylmandelates **53** and **55**.[10] However, as in the case of **25**, the esterification of these alcohols was slow and partial racemization of the mandelic α-position occurred. Partial racemization was also observed in the reaction leading to the (*R*)-mandelate **54**.

Scheme VI



49e R = H
53 R = (*S*)-PhCH(OMe)CO
54 R = (*R*)-PhCH(OMe)CO

52e R = H
55 R = (*S*)-PhCH(OMe)CO

Alcohols **49e** and **50e** were shown to be epimeric at the carbinyl center by Lindlar hydrogenation[13] and then Dess–Martin oxidation[14] to ketone **56**, a single isomer according to the ^1H NMR spectrum. The hydrogenation product **57** of alkynol **49e** was converted to acetonide **58** by sequential ozonolysis–reduction and ketalization. The ^1H NMR coupling constants confirmed the relative stereochemistry, as shown. Alcohol **52e** was similarly converted via **59** to acetonide **60**. Thus, it is established that alcohol **52e** from the $MgBr_2$-promoted addition of (*R*)-**4e** to aldehyde **48** is the anti diastereoisomer. Analogous reactions of crotylstannanes are highly syn selective. Anti products are rarely observed in significant amounts[12] (Scheme VI).

Additions of allenylstannanes (*S*)-**4h** and (*R*)-**4h** to aldehyde **48** proceeded analogously to those of **4e** (Table II, entries 5–8). Thus, BF_3 favored the syn adducts **49h** and **51h**, whereas $MgBr_2$ gave the syn adduct **49h** with (*S*)-**4h**

(10) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. D. *J. Org. Chem.* **1986**, *51*, 2370.

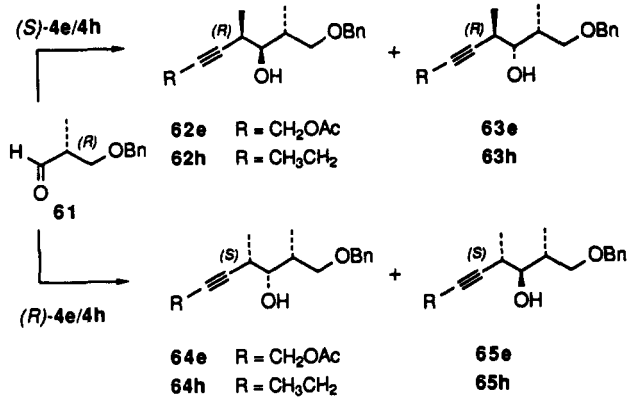
(11) Additions of crotylstannanes to such aldehydes in the presence of BF_3·OEt_2 typically give ca. 90:10 mixtures of syn and anti products mainly through anti-Cram additions (~2:1). Keck, G. E.; Boden, E. P. *Tetrahedron Lett.* **1984**, *25*, 1879.

(12) Additions of crotylstannanes to such aldehydes in the presence of $MgBr_2$ typically give ca. 90:10 mixtures of syn and anti products through chelation-controlled additions (>200:1).[11] Recently α-methylcrotylstannanes have been found to give mainly the anti adduct with racemic **48** under conditions of chelation control. Mikami, K.; Kawamoto, K.; Loh, T.-P.; Nakai, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1161.

(13) Lindlar, H.; Dubuis, R. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol V, p 880.

(14) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4156.

Table III. Addition of Allenylstannanes (*S*)-4e/4h and (*R*)-4e/4h to Aldehyde 61



entry	stannane	condns[a]	yield, %	product composition[b] 62:63	64:65
1	(*S*)-**4e**	A	98	83:17	
2	(*S*)-**4e**	B	95	>99:1	
3	(*R*)-**4e**	A	96		>99:1
4	(*R*)-**4e**	B	96		>99:1
5	(*S*)-**4h**	A	88	84:16	
6	(*S*)-**4h**	B	93	>99:1	
7	(*R*)-**4h**	A	92		>99:1
8	(*R*)-**4h**	B	94		50:50

[a] A = BF_3·OEt_2, CH_2Cl_2, −78 °C, 6 h (**4e**) or 0.1 h (**4h**); B = $MgBr_2$·OEt_2, CH_2Cl_2, −23 °C, 16 h (**4e**) or 0.5 h (**4h**). [b] Corrected for ee of starting stannane.

and the anti adduct **52h** with (*R*)-**4h**.

Additions to (*R*)-3-(benzyloxy)-2-methylpropanal (**61**) were next examined (Table III) as prototypes for the preparation of polypropionate subunits. Reactions involving (*S*)-**4e** proceeded analogously to those involving aldehyde **48**. The syn adduct **62e** was favored in both BF_3 and $MgBr_2$ reactions (entries 1 and 2).[15] This was also found to be the case with (*R*)-**4e** (entry 3). In contrast to the strong anti preference observed in the $MgBr_2$-promoted addition of (*R*)-**4e** to aldehyde **48** (Table II, entry 4), the analogous reaction with aldehyde **61** gave only the syn adduct **64e** (Table III, entry 4).

Stannanes (*S*)-**4h** and (*R*)-**4h** yielded mainly the syn adducts **62h** and **64h** in reactions with aldehyde **61** when BF_3 was employed as the catalyst (Table III, entries 5 and 7). However, the $MgBr_2$-promoted addition of (*R*)-**4h** to **61** led to a 50:50 mixture of syn and anti products **64h** and **65h**, in contrast to the 99:1 preference for the syn adduct **64e** exhibited by (*R*)-**4e** under the same conditions (entry 4 vs 8).

The stereochemistry of adducts **62h–65h** was assigned as follows. Lindlar hydrogenation[13] of the 1:1 mixture of **64h** and **65h** and then oxidation with the Dess–Martin reagent[14] afforded a single ketone **66**, thus establishing the epimeric nature of the two alcohols. Hydrogenation of **62h** over Pd–C effected saturation of the alkyne and cleavage of the benzyl ether. The resulting 1,3-diol was converted to the acetonide **67**. Partial hydrogenation of alkyne **62h** followed by ozonolysis–reduction and acetonide formation led to **68**, thus establishing the relative and absolute stereochemistry of **62h**. Alcohol **64h** was similarly elucidated through conversion to acetonides **69** and **70** (Scheme VII).

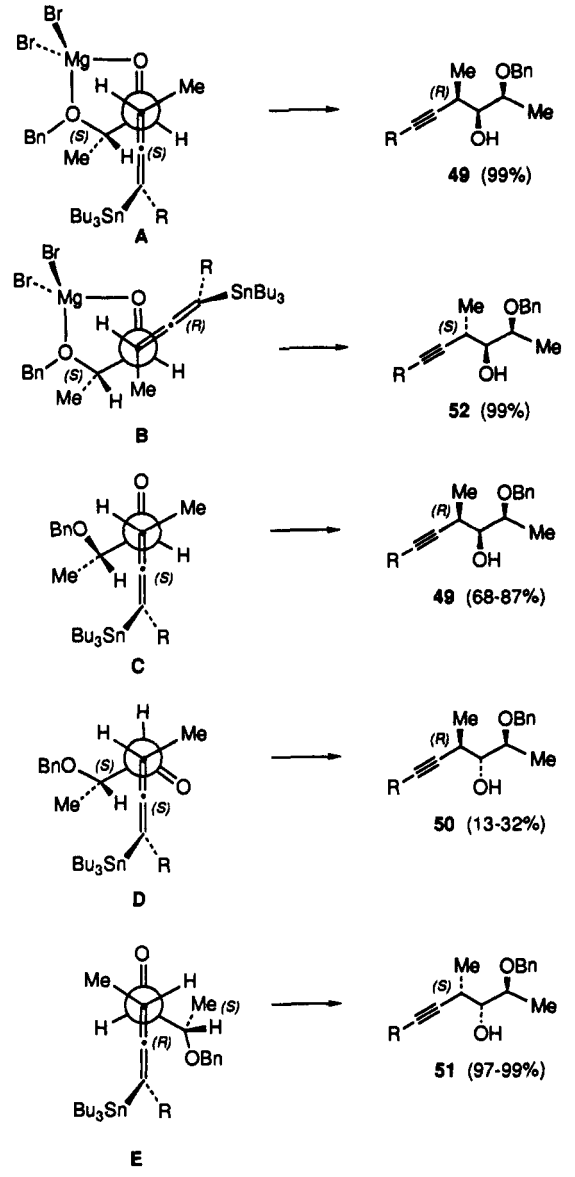


Figure 1. Transition-state geometries for additions of stannanes (*S*)-**4e/4h** and (*R*)-**4e/4h** to aldehyde **48**.

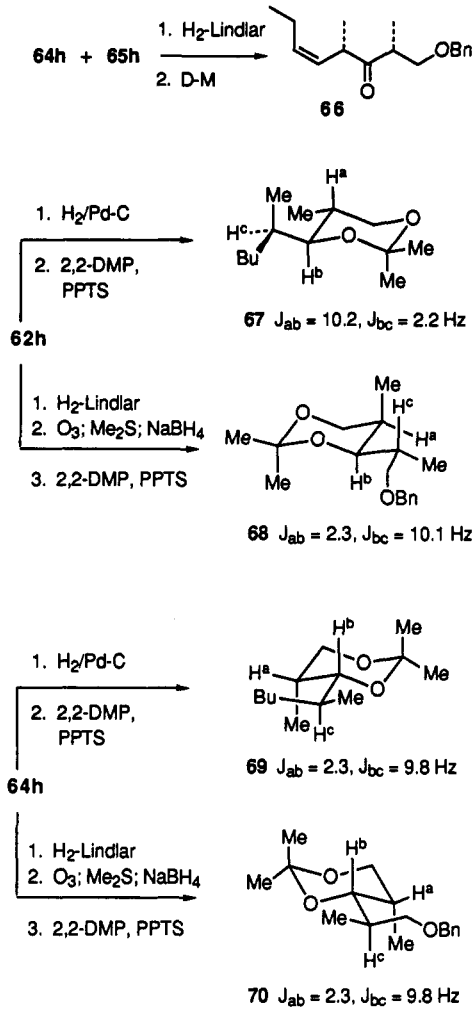
Possible transition states for additions to (*S*)-2-(benzyloxy)propanal (**48**) are depicted in Figure 1 (**A–E**). The observed configurational relationship between the allene reactant and the propargylic stereocenter in the product requires an anti-S_E' pathway for all the additions as has been found for allylic stannanes and allenylsilanes.[16] In the $MgBr_2$-promoted reactions, attack of (*S*)-**4** on the chelated aldehyde as in **A** leads to the adduct **49**. Transition state **A** has minimal steric interactions and possibly benefits electronically from an anti arrangement of the carbonyl and allenyl system, as suggested by Yamamoto for allylstannane S_E' additions.[17] Attack of (*R*)-**4** on the chelated aldehyde leads to the anti product **52** by presumed transition state **B**. Here the antiperiplanar C=C/C=O arrangement would lead to steric interactions involving the allenyl CH_3 (*si* attack) or the aldehyde CH_3 (*re* attack), so the synclinal orientation is adopted. As **52** is produced nearly quantitatively, the advantages of antiperiplanar vs synclinal alignment is insufficient to overcome unfavorable steric interactions.

(15) Additions of crotylstannane to aldehyde **61** in the presence of $MgBr_2$ affords a 91:9 mixture of syn and anti adducts with an 88:12 preference for chelation-controlled addition. Keck, G. E.; Abbott, D. E. *Tetrahedron Lett.* **1984**, *25*, 1883.

(16) Marshall, J. A.; Gung, W. Y. *Tetrahedron* **1989**, *45*, 1043. Marshall, J. A.; Luke, G. P. *J. Org. Chem.* **1991**, *56*, 483.

(17) Yamamoto, Y.; Yatagi, H.; Ishikara, Y.; Maeda, M.; Maruyama, K. *Tetrahedron* **1984**, *40*, 2239.

Scheme VII



An analysis of the BF_3-promoted additions of allenylstannanes **4e/4h** to aldehyde **48** is complicated by the conformational mobility of the aldehyde. The (*R*)-allenylstannaes exhibit significantly higher diastereoselectivity (97:3 for **4e** and >99:1 for **4h**) than the *S* enantiomers (68:32 for **4e** and 87:13 for **4h**). In the former case transition state **E**, in which the aldehyde adopts the Cornforth orientation,[18] serves to minimize steric interactions between the allenyl CH_3 and the aldehyde substituents and allows an antiperiplanar arrangement of the CO and C=C. The α-X carbonyl Felkin–Ahn orientation[19] (OBn > Me) would also account for the preferred formation of **51**. Attack of the (*S*)-allenylstannane on the Cornforth orientation of **48**, as in **D** or the closely related α-X carbonyl Felkin–Ahn conformer (OBn > Me),[19] requires a synclinal arrangement of C=O and C=C. The alternative Felkin–Ahn conformer (Me > OBn) as in **C** minimizes steric interactions, permits antiperiplanar alignment of C=O and C=C, and accounts for the major product **49** of the mismatching pairing.

Additions of allenylstannanes **4e/4h** to aldehyde **61** show comparable trends to those involving aldehyde **48** save for the $MgBr_2$-promoted addition of (*R*)-**4h**. Stannanes (*R*)-**4e/4h** are matched and (*S*)-**4e/4h** are mismatched in the BF_3 additions to **61**. Transition state **I** with aldehyde **61** in the Felkin–Ahn arrangement (CH_2OBn > Me) and with antiperiplanar orientations both for C=C/C=O and allenyl Me/aldehyde substituents accounts for the highly favored formation of syn adduct **64** (Figure 2). Transition state **F**, only slightly less favored than **I**, accounts for the major product **62** of the *S* stannanes. **G** benefits from the lower energy Felkin–Ahn orientation (CH_2OBn > Me) of the aldehyde but suffers from a synclinal C=O/C=C alignment.

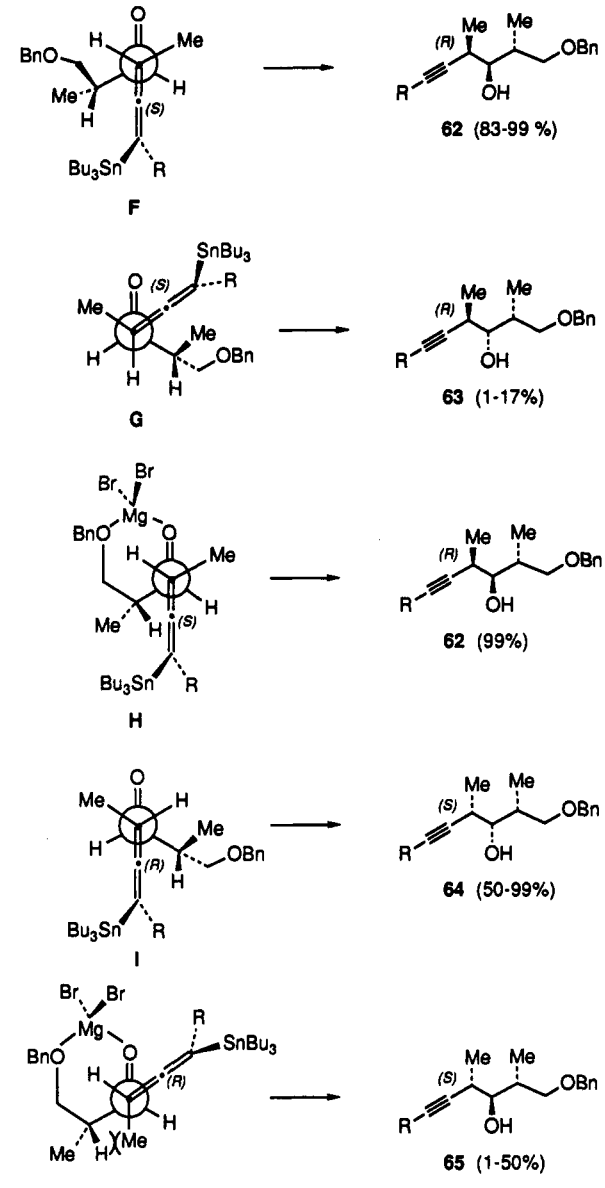


Figure 2. Transition-state geometries for additions of stannanes (*S*)-**4e/4h** and (*R*)-**4e/4h** to aldehyde **61**.

The $MgBr_2$-promoted addition of (*S*)-**4e/4h** to aldehyde **61**, affording the syn adduct **62**, may be explained by the chelated transition state **H** or the Felkin–Ahn arrangement as in **F**. The analogous chelated transition state **J** for (*R*)-**4e/4h** would lead to the anti product **65**. However, (*R*)-**4e** gives only the syn product **64e** as expected for transition state **I** and (*R*)-**4h** affords a 1:1 mixture of syn and anti adducts **64h** and **65h**. Assuming **65h** arises from the chelated transition state **J**, the differing behavior of (*R*)-**4e** and (*R*)-**4h** may stem from coordination of $MgBr_2$ to the acetate grouping of (*R*)-**4e**, thus disfavoring chelation. Such coordination would also decrease the nucleophilicity of the allenylstannane with a corresponding increase in selectivity. With stannane (*R*)-**4h**, increased availability of $MgBr_2$ would result in more product formation through **J**, assuming a comparable transition-state

(18) Conforth, J. W.; Cornforth, R. H.; Mathew, K. K. *J. Chem. Soc.* **1959**, 112.
(19) Chêrest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199. Ahn, N. T.; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61.

energy for **I** and **J**. In the case of (*S*)-**4e**/**4h** the favored chelated and nonchelated transition states **H** and **F** both lead to the same product so chelation is not a major consideration.

From a practical standpoint, these findings show that additions of chiral allenylstannanes to α-branched achiral and α-chiral aldehydes allow efficient access to homopropargylic alcohols of high ee with excellent diastereoselectivity. These alcohols are of interest as potential subunits of polypropionate and ionophore natural products.

Experimental Section

(*R*)-(+)-3-Undecyn-2-ol (2a). To a suspension of 3.1 mL (3.1 mmol) of 1 M $LiAlH_4$ in 75 mL of ether was added dropwise a solution of 1.95 g (6.9 mmol) of (*R*)-Chirald in 15 mL of ether at 0 °C. The mixture was cooled to −78 °C. A solution of 424 mg (2.6 mmol) of 3-undecyn-2-one (**1a**) in 15 mL of ether was added to the mixture over 2 h. The resulting mixture was stirred at −78 °C for 5 h and quenched with 10% HCl. The layers were separated and the aqueous layer was extracted with ether. The combined extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and concentrated. The residue was then chromatographed on silica gel (hexane/ether, 4:1) to afford 417 mg (97%) of (*R*)-3-undecyn-2-ol (**2a**): $[\alpha]_D$ +18.7° ($CHCl_3$, *c* 2.37); IR (film) ν 3363 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.50–4.46 (m, 1 H, $HOCHCH_3$), 2.16 (dt, *J* = 1.9, 7.1 Hz, 2 H, propargylic CH_2), 1.82–1.80 (m, 1 H, OH), 1.49–1.38 (m, 2 H, H-6), 1.40 (d, *J* = 6.5 Hz, 3 H, $OCHCH_3$), 1.33–1.25 (m, 8 H, $(CH_2)_4$), 0.86 (t, *J* = 6.7 Hz, 3 H, CH_2CH_3); MS *m*/*e* (rel intensity) 167 (2, M − H), 151 (19), 109 (70), 95 (100). The ee of this alcohol was found to be 92% by ^1H NMR analysis of the (*R*)-*O*-methylmandelate derivative.

(*S*)-(+)-4-(Tributylstannyl)-2,3-undecadiene (4a). To a mixture of 79 mg (0.47 mmol) of alcohol (*R*)-**2a** and 0.13 mL (0.94 mmol) of Et_3N in 3 mL of CH_2Cl_2 was added 0.06 mL (0.71 mmol) of methansulfonyl chloride at −78 °C. The resulting mixture was stirred at −78 °C for 1 h, then quenched with saturated $NaHCO_3$, and extracted with ether. The ether layer was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure yielded the crude mesylate **3a**, which was dried in vacuo and directly used for the next reaction without further purification.

To a solution of 0.09 mL (0.65 mmol) of diisopropylamine in 3 mL of HMPA–THF (1:1) was added dropwise 0.24 mL (0.61 mmol) of 2.5 M *n*-BuLi at 0 °C. After 30 min, 0.16 mL (0.60 mmol) of Bu_3SnH was added to the mixture. The resulting mixture was stirred at 0 °C for 15 min; then 150 mg (0.47 mmol) of mesylate **3a** in 3 mL of THF was added dropwise during 10 min. The reaction mixture was quenched with saturated $NaHCO_3$ and extracted with ether. The extracts were dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane) to yield 188 mg (91%) of allenylstannane **4a**: $[\alpha]_D$ +88.2° ($CHCl_3$, *c* 0.90); IR (film) ν 1932 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.54 (m, 1 H, vinyl H), 2.02 (m, 2 H, vinyl CH_2), 1.57 (d, *J* = 6.8 Hz, 3 H, vinyl CH_3), 1.52–0.85 (m, 40 H, $(CH_2)_5CH_3$ and Bu_3Sn); HRMS, calcd for $C_{23}H_{46}Sn$ 438.2617, found 438.2618. Anal. Calcd for $C_{23}H_{46}Sn$: C 62.60; H 10.51. Found: C 62.73, H 10.45.

(*S*)-(+)-2-(Tributylstannyl)-2,3-pentadien-1-ol [(*S*)-4d]. To a solution of 250 mg (0.53 mmol) of TBS ether (*S*)-**4c** in 5 mL of aqueous THF was added 1.58 mL (1.58 mmol) of 1.0 M Bu_4NF in THF. The resulting mixture was stirred at room temperature overnight; then it was quenched with water and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 4:1) to yield 162 mg (82%) of alcohol (*S*)-**4d**: $[\alpha]_D$ +64.6° ($CHCl_3$, *c* 0.93); IR (film) ν 3408, 1936 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.86–4.82 (m, 1 H, vinyl H), 4.12 (dq, *J* = 1.3, 5.8 Hz, 2 H, $HOCH_2$), 1.63 (d, *J* = 6.9 Hz, 3 H, vinyl CH_3), 1.60 (t, *J* = 5.8 Hz, 1 H, OH), 1.54–0.84 (m, 27 H, Bu_3Sn); HRMS, calcd for $C_{17}H_{34}OSn$ 370.1627, found 370.1631. Anal. Calcd for $C_{17}H_{34}OSn$: C, 54.72; H, 9.18. Found: C, 54.99; H, 9.13.

(*R*)-(−)-2-(Tributylstannyl)-2,3-pentadien-1-ol [(*R*)-4d]. The above-described cleavage was conducted on the enantiomeric TBS ether (*R*)-**4d**. The spectral properties of this alcohol were identical with those described above for (*S*)-**4d**: yield 82%; $[\alpha]_D$ −65.3° ($CHCl_3$, *c* 0.72).

(*S*)-(+)-1-Acetoxy-2-(tributylstannyl)-2,3-pentadiene [(*S*)-4e]. To a mixture of 112 mg (0.30 mmol) of alcohol (*S*)-**4d** and 0.08 mL (0.60 mmol) of Et_3N in 3 mL of CH_2Cl_2 was added 0.04 mL (0.45 mmol) of acetic anhydride. The resulting mixture was stirred at room temperature for 24 h; then it was quenched with aqueous $NaHCO_3$ and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 10:1) to yield 122 mg (95%) of ester (*S*)-**4e**: $[\alpha]_D$ +57.3° ($CHCl_3$, *c* 0.89); IR (film) ν 1937, 1748, 1227 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.74–4.71 (m, 1 H, vinyl H), 4.62 (m, 2 H, $AcOCH_2$), 2.04 (s, 3 H, CH_3CO), 1.60 (d, *J* = 6.9 Hz, 3 H, vinyl CH_3), 1.55–0.85 (m, 27 H, Bu_3Sn); HRMS, calcd for $C_{15}H_{27}O_2Sn$ 355.1028, found 355.1033. Anal. Calcd for $C_{19}H_{36}O_2Sn$: C, 54.97; H, 8.74. Found: C, 55.22; H, 8.73.

(*R*)-(−)-1-Acetoxy-2-(tributylstannyl)-2,3-pentadiene [(*R*)-4e]. The above-described acetylation was carried out on the enantiomeric alcohol (*R*)-**4d**. The spectral properties of this acetate were identical with those described above for (*S*)-**4e**: yield 93%; $[\alpha]_D$ +58.8° ($CHCl_3$, *c* 0.81).

(*S*)-(+)-3-(Tributylstannyl)-3,4-hexadien-1-ol [(*S*)-4f]. A. From Silyl Ether 4b. To a solution of 1.99 g (3.97 mmol) of TBS ether (*S*)-**4b** in 20 mL of aqueous THF was added 11.9 mL (11.91 mmol) of 1.0 M Bu_4NF in THF. The resulting mixture was stirred at room temperature overnight; then it was quenched with water and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 4:1) to yield 1.18 g (77%) of alcohol (*S*)-**4f**: $[\alpha]_D$ +56.9° ($CHCl_3$, *c* 1.11); IR (film) ν 3338, 1930 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.64 (m, 1 H, vinyl H), 3.70 (q, *J* = 6.1 Hz, 2 H, $HOCH_2$), 2.29 (dt, *J* = 2.9, 6.1 Hz, 2 H, $HOCH_2CH_2$), 1.72 (t, *J* = 6.1 Hz, 1 H, OH), 1.60 (d, *J* = 6.9 Hz, 3 H, vinyl CH_3), 1.60 (t, *J* = 5.8 Hz, 1 H, OH), 1.54–0.84 (m, 27 H, Bu_3Sn); HRMS, calcd for $C_{14}H_{27}OSn$ (M − Bu) 327.1079, found 327.1076. Anal. Calcd for $C_{18}H_{36}OSn$: C, 55.84; H, 9.37. Found: C, 55.94; H, 9.40.

B. From Ester 21. To a solution of 68 mg (0.16 mmol) of ester **21** in 3 mL of ether was added 0.16 mL (0.16 mmol) of 1.0 M $LiAlH_4$ in THF at 0 °C. The mixture was quenched with 3 N NaOH 10 min later and extracted with ether. The extracts were dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 4:1) to afford 55 mg (89%) of alcohol (*S*)-**4f**: $[\alpha]_D$ +52.9 ($CHCl_3$, *c* 0.93). The spectral properties of this alcohol were identical with those of (*S*)-**4f** prepared from TBS ether (*S*)-**4b**.

(*R*)-(−)-2-(Tributylstannyl)-2,3-pentadien-1-ol [(*R*)-4f]. The above-described cleavage was conducted on the enantiomeric TBS ether (*R*)-**4b**. The spectral properties of this alcohol were identical with those described above for (*S*)-**4f**: yield 80%; $[\alpha]_D$ −59.0° ($CHCl_3$, *c* 1.30).

(*S*)-(+)-3-(Tributylstannyl)-3,4-hexadiene [(*S*)-4h]. To a solution of 300 mg (0.77 mmol) of (*S*)-**4f** and 0.16 mL (1.16 mmol) of Et_3N in 5 mL of CH_2Cl_2 was added 329 mg (1.01 mmol) of Ts_2O at 0 °C. The mixture was stirred at 0 °C for 1 h; then it was quenched with saturated $NaHCO_3$ and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 8:1) to yield 371 mg (89%) of tosylate (*S*)-**4g**: $[\alpha]_D$ +34.8° ($CHCl_3$, *c* 1.13); IR (film) ν 1930 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.78, 7.32 (AB q, *J* = 8.3 Hz, 4 H, Ar H), 4.57–4.52 (m, 1 H, vinyl H), 4.07 (t, *J* = 7.6 Hz, 2 H, CH_2OTs), 2.43 (s, 3 H, CH_3), 2.33 (dq, *J* = 2.9, 7.6 Hz, 2 H, CH_2CH_2OTs), 1.52 (d, *J* = 6.9 Hz, 3 H, vinyl CH_3), 1.53–0.84 (m, 27 H, Bu_3Sn).

To a solution of 371 mg (0.69 mmol) of tosylate (*S*)-**4g** in 5 mL of THF was added 1.03 mL (1.03 mmol) of 1.0 M L-Selectride (Aldrich) in THF. The resulting mixture was stirred at room temperature for 30 min; then it was treated with 0.5 mL of 3 N NaOH, followed by 0.5 mL of 30% H_2O_2. After 30 min, the mixture was extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane) to yield 231 mg (91%) of allenylstannane (*S*)-**4h**: $[\alpha]_D$ +64.5° ($CHCl_3$, *c* 0.93); IR (film) ν 1930 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.59–4.56 (m, 1 H, vinyl H), 2.04 (dq, *J* = 3.0, 7.3 Hz, 2 H, vinyl CH_2), 1.58 (d, *J* = 6.8

Hz, 3 H, vinyl CH_3), 1.00 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 1.53–0.84 (m, 27 H, Bu_3Sn); HRMS, Calcd for $C_{14}H_{27}Sn$ (M – Bu) 311.1130, found 311.1117. Anal. Calcd for $C_{18}H_{36}Sn$: C, 58.25; H, 9.78. Found: C, 58.13; H, 9.73.

(*R*)-(–)-3-(Tributylstannyl)-3,4-hexadiene [(*R*)-4h]. The above-described tosylation and reduction were conducted on the enantiomeric alcohol (*R*)-**4f**. The spectral properties of this allenylstannane (*R*)-**4h** were identical with those described above for (*S*)-**4h**: yield 81%; $[\alpha]_D$ –64.2° ($CHCl_3$, *c* 0.86).

(*R*)-1-Nonyn-3-ol (6). To a solution of 0.72 mL (5.09 mmol) of (trimethylsilyl)acetylene in 10 mL of THF was slowly added 1.90 mL (5.60 mmol) of 2.90 M *n*-BuLi at –78 °C. The resulting mixture was stirred for 1 h. To the mixture was added 0.75 mL (5.60 mmol) of heptanal. The resulting mixture was warmed to room temperature and stirred for another 1 h and then neutralized with dilute HCl and extracted with ether. The organic layer was washed with saturated aqueous $NaHCO_3$ and brine and then dried over $MgSO_4$. After removal of solvent, the residue was chromatographed on silica gel (hexane/ether, 4:1) to give 926 mg (86%) of racemic 1-(trimethylsilyl)-1-nonyn-3-ol.

A solution of 700 mg (3.30 mmol) of the above racemic alcohol and 1.42 g (6.59 mmol) of PCC in 15 mL of methylene chloride was stirred at room temperature for 18 h; then 5 g of Florisil was added to the reaction mixture. The mixture was stirred for 15 min and filtered through silica gel, eluting with ether. Evaporation of the solvent gave a yellow oil, which was purified by chromatography on silica gel (hexane/ether, 6:1) to afford 566 mg (82%) of 1-(trimethylsilyl)-1-nonyn-3-one as a colorless oil: IR (film) ν 1679 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.53 (t, J = 7.5 Hz, 2 H, $COCH_2$), 1.64 (m, 2 H, C-5), 1.26 (m, 6 H, $(CH_2)_3$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3), 0.22 (s, 9 H, $(CH_3)_3Si$).

The procedure described for alcohol **2a** was employed with 800 mg (3.80 mmol) of the foregoing ketone to afford 767 mg (95%) of (*R*)-1-(trimethylsilyl)-1-nonyn-3-ol (**5**): $[\alpha]_D$ 0° ($CHCl_3$, *c* 1.23); IR (film) ν 3348, 2171 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.36–4.30 (m, 1 H, $HOCHCH_2$), 2.16 (dt, J = 1.9, 7.1 Hz, 2 H, propargylic H), 1.69 (d, J = 5.6 Hz, 1 H, OH), 1.68–1.64 (m, 2 H, H-4), 1.40–1.27 (m, 8 H, $(CH_2)_4$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3), 0.15 (s, 9 H, $(CH_3)_3Si$). The ee of this alcohol was found to be 82% by ^1H NMR analysis of the (*R*)-*O*-methylmandelate derivative.

A mixture of 1.51 g (7.11 mmol) of the above alcohol and 1.47 g (10.66 mmol) of K_2CO_3 in 10 mL of CH_3OH was stirred at room temperature for 6 h; then it was quenched with water and extracted with ether. The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 4:1) to afford 937 mg (94%) of alcohol **6**: $[\alpha]_D$ +3.8° ($CHCl_3$, *c* 0.71); IR (film) ν 3340, 3312, 2115 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$), δ 4.30 (m, 1 H, $HOCHCH_2$), 2.38 (d, J = 2.0 Hz, 1 H, H-1), 1.77–1.68 (m, 2 H, H-4), 1.45–1.27 (m, 8 H, $(CH_2)_4$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3).

(*R*)-3-Undecyn-5-ol (9). A mixture of 141 mg (1.01 mmol) of alcohol (*R*)-**6**, 228 mg (1.51 mmol) of TBSCl, and 136 mg (2.00 mmol) of imidazole in 5 mL of CH_2Cl_2 was stirred at room temperature for 1 h; then it was quenched with dilute HCl and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 10:1) to yield 246 mg (96%) of silyl ether **7**: $[\alpha]_D$ +33.4° ($CHCl_3$, *c* 0.79); IR (film) ν 3313 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.31 (dt, J = 2.1, 6.8 Hz, 1 H, $TBSOCHCH_2$), 2.35 (d, J = 2.1 Hz, 1 H, H-1), 1.67–1.61 (m, 2 H, H-4), 1.41–1.27 (m, 8 H, $(CH_2)_4$), 0.87 (s, 9 H, Bu^t), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3), 0.11 (s, 3 H, CH_3Si), 0.09 (s, 3 H, CH_3Si); HRMS, calcd for $C_{15}H_{30}OSi$ 254.2066, found 254.2055.

To a solution of 235 mg (0.92 mmol) of the above alkyne **7** in 5 mL of THF was added 0.39 mL (0.93 mmol) of 2.42 M *m*-BuLi in hexane at –78 °C. After 1 h, 0.15 mL (1.84 mmol) of iodoethane was added. The mixture was allowed to warm to room temperature and stirred overnight; then it was quenched with dilute HCl and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The crude silyl ether **8** was used for the next reaction without purification.

The above crude silyl ether **8** was dissolved in 5 mL of THF and treated with 2.76 mL (2.76 mmol) of 1.0 M Bu_4NF in THF, followed by 0.5 mL of AcOH. The mixture was allowed to warm to room temperature and stirred overnight; then it was quenched with saturated $NaHCO_3$ and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 4:1) to give 114 mg (74%) of alcohol (*R*)-**9**: $[\alpha]_D$ +1.1° ($CHCl_3$, *c* 1.64); IR (film) ν 3362, 2235 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.32 (m, 1 H, $HOCHCH_2$), 2.20 (dq, J = 2.0, 7.5 Hz, 2 H, propargylic CH_2), 1.68–1.60 (m, 2 H, $CH(OH)CH_2$), 1.40–1.28 (m, 8 H, $(CH_2)_4$), 1.12 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 0.87 (t, J = 6.9 Hz, 3 H, $(CH_2)_4CH_3$); HRMS, calcd for $C_{11}H_{19}O$ (M – H) 167.1436, found 167.1440.

(*R*)-1-(Tributylstannyl)-1-nonyn-3-ol (11). To a solution of 367 mg (2.62 mmol) of alcohol (*R*)-**6** in 10 mL of THF was added 2.27 mL (5.50 mmol) of 2.42 M *n*-BuLi in hexane at –78 °C. After 1 h, 0.71 mL (2.62 mmol) of Bu_3SnCl was added. The mixture was allowed to warm to room temperature and stirred for 1 h; then it was quenched with saturated $NaHCO_3$ and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 4:1) to yield 1.03 g (92%) of alcohol (*R*)-**11**: $[\alpha]_D$ 0° ($CHCl_3$, *c* 0.78); IR (film) ν 3357, 2147 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.34 (q, J = 5.5 Hz, 1 H, $HOCHCH_2$), 1.68 (d, J = 5.5 Hz, 1 H, OH), 1.68–0.86 (m, 40 H, Bu_3Sn and $(CH_2)_5CH_3$); HRMS, calcd for $C_{17}H_{33}OSn$ (M – Bu) 369.1549, found 369.1540.

(*S*)-(+)-Ethyl 3-(Tributylstannyl)-3,4-undecadienecarboxylate (12). A solution of 357 mg (0.83 mmol) of alcohol **11** in 2 mL of triethyl orthoacetate was heated at 110 °C for 48 h; then it was directly chromatographed on silica gel (hexane) to afford 124 mg (32%) of allenylstannane **12**: $[\alpha]_D$ +59.5° ($CHCl_3$, *c* 0.98); IR (film) ν 1931, 1733 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.68 (m, 1 H, vinyl H), 4.11 (q, J = 9.9 Hz, 2 H, $CO_2CH_2CH_3$), 3.07 (d, J = 2.6 Hz, 2 H, CH_2CO_2Et), 1.93–1.88 (m, 2 H, vinyl CH_2), 1.53–0.84 (m, 41 H, Bu_3Sn, $CO_2CH_2CH_3$ and $(CH_2)_4CH_3$); HRMS, calcd for $C_{21}H_{39}O_2Sn$ (M – Bu) 439.1967, found 439.1971.

(*S*)-(+)-1-[(*p*-Toluenesulfonyl)oxy]-3-(tributylstannyl)-3,4-undecadiene (14). To a solution of 118 mg (0.25 mmol) of ester **12** in 5 mL of ether was added 0.38 mL (0.38 mmol) of 1.0 M $LiAlH_4$ in THF at 0 °C. After 10 min, the mixture was quenched with 0.2 mL of 6 N NaOH and filtered. The filtrate was dried over $MgSO_4$ and concentrated to give crude alcohol **13**, which was used for the next reaction without purification.

To a solution of the above alcohol **13** and 0.07 mL of Et_3N in 5 mL of CH_2Cl_2 was added 122 mg (0.38 mmol) of Ts_2O at 0 °C. The mixture was stirred at 0 °C for 1 h; then it was quenched with saturated $NaHCO_3$ and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 8:1) to yield 108 mg (71%) of (*S*)-tosylate **14**: $[\alpha]_D$ +41.5° ($CHCl_3$, *c* 0.72); IR (film) ν 1932 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.58 (m, 1 H, vinyl H), 4.07 (t, J = 7.6 Hz, 2 H, CH_2OTs), 2.43 (s, 3 H, CH_3), 2.33 (dq, J = 3.0, 7.6 Hz, 2 H, CH_2CH_2OTs), 1.83 (m, 2 H, vinyl CH_2), 1.53–0.84 (m, 38 H, Bu_3Sn and $(CH_2)_4CH_3$); HRMS, calcd for $C_{30}H_{52}O_3Sn$ 608.2655, found 608.2650.

(*S*)-(+)-3-(Tributylstannyl)-3,4-undecadiene (15). A. From Mesylate (*R*)-10. To a mixture of 110 mg (0.65 mmol) of alcohol (*R*)-**9** and 0.18 mL (1.30 mmol) of Et_3N in 5 mL of CH_2Cl_2 was added 0.08 mL (0.98 mmol) of methansulfonyl chloride at –78 °C. The resulting mixture was stirred at –78 °C for 1 h, then quenched with saturated $NaHCO_3$, and extracted with ether. The ether layer was washed with brine and dried over $MgSO_4$. Concentration yielded crude mesylate (*R*)-**10**, which was dried in vacuo and directly used for the next reaction without further purification.

To a solution of 0.20 mL (1.36 mmol) of diisopropylamine in 4 mL of THF was added 0.54 mL (1.30 mmol) of 2.42 M *n*-BuLi in hexane at 0 °C. After 30 min, 0.33 mL (1.23 mmol) of Bu_3SnH was added. After being stirred for 20 min, the mixture was cooled to –50 °C and 253 mg (1.23 mmol) of $CuBr{\cdot}SMe_2$ was added in one portion. The above mesylate in 3 mL of THF was added 30 min later. The resulting mixture was stirred for 30 min with warming from –50 °C to –20 °C; then it was poured into aqueous NaCN solution and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane) to yield 275 mg (97%) of allenylstannane (*S*)-**15**: $[\alpha]_D$ +76.4° ($CHCl_3$, *c* 0.95); IR (film) ν 1932 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.65–4.60

(m, 1 H, vinyl H), 2.05 (dq, J = 3.0, 7.3 Hz, 2 H, vinyl CH_2CH_3), 1.95–1.89 (m, 2 H, vinyl CH_2), 1.01 (t, J = 7.3 Hz, 3 H, vinyl CH_2CH_3), 1.52–0.84 (m, 38 H, Bu_3Sn and $(CH_2)_4CH_3$); HRMS, calcd for $C_{23}H_{46}Sn$ 438.2617, found, 438.2602. Anal. Calcd for $C_{23}H_{46}Sn$: C, 62.60; H, 10.51. Found: C, 62.54; H, 10.53.

B. From Tosylate (*S*)-14. The procedure described for (*S*)-**4h** was employed with 105 mg (0.17 mmol) of tosylate (*S*)-**14** to yield 69 mg (91%) of allenylstannane (*S*)-**15**: $[\alpha]_D$ +77.6° ($CHCl_3$, *c* 0.90). The spectral properties were identical with those of (*S*)-**15** prepared from mesylate (*R*)-**10**.

(*R*)-1-(Tributylstannyl)-1-butyn-3-ol (20). The procedure described for alcohol **11** was followed starting with 280 mg (4.00 mmol) of alcohol (*R*)-**19** (ee 77%). The product was chromatographed on silica gel (hexane/ether, 4:1) to yield 1.19 g (83%) of alcohol (*R*)-**20**: $[\alpha]_D$ +11.0° ($CHCl_3$, *c* 0.69); IR (film) ν 3346, 2137 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.52–4.48 (m, 1 H, HO*CH*CH_3), 1.74 (d, J = 5.2 Hz, 1 H, OH), 1.42 (d, J = 6.6 Hz, 3 H, CH_3), 1.68–0.86 (m, 27 H, Bu_3Sn); MS *m/e* (rel intensity) 359 (10, M^+), 303 (100), 247 (40), 171 (45), 137 (65).

(*S*)-(+)-Ethyl 3-(Tributylstannyl)-3,4-hexadienecarboxylate (21). The procedure described for ester **12** was employed with 273 mg (0.76 mmol) of alcohol **20** to afford 87 mg (27%) of allenylstannane **21**: $[\alpha]_D$ +40.2° ($CHCl_3$, *c* 0.60); IR (film) ν 1939, 1732 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.68–4.60 (m, 1 H, vinyl H), 4.12 (q, J = 7.1 Hz, 2 H, $CO_2CH_2CH_3$), 3.07 (d, J = 2.5 Hz, 2 H, CH_2CO_2Et), 1.59 (d, J = 7.0 Hz, 3 H, vinyl CH_3), 1.53–0.84 (m, 30 H, Bu_3Sn, $CO_2CH_2CH_3$); HRMS, calcd for $C_{21}H_{39}O_2Sn$ (M – Bu) 370.1028, found 370.1035.

8-Methyl-9-heptadecyn-7-ol (24 and 27) (Procedure A). To a solution of 0.04 mL (0.27 mmol) of $BF_3{\cdot}Et_2O$ in 3 mL of CH_2Cl_2 was added dropwise a mixture of 40 mg (0.090 mmol) of racemic **4a** and 20 mg (0.18 mmol) of heptaldehyde in 3 mL of CH_2Cl_2 at –78 °C. The mixture was stirred at –78 °C for 30 min, then quenched with saturated $NaHCO_3$, and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 4:1) to yield 20 mg (83%) of alcohols **24** and **27** as a 39:61 mixture according to GC analysis: IR (film) ν 3480 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.32 (m, 1 H, HO*CH*), 2.48 (m, 1 H, propargylic CH), 2.14 (m, 2 H, propargylic CH_2), 1.65 (d, J = 6.8 Hz, 1 H, OH), 1.47–1.27 (m, 10 H, $(CH_2)_5$), 1.16 (d, J = 7.0 Hz, 3 H, C≡CCH*CH*$_3$), 0.86 (t, J = 6.7 Hz, 3 H, CH_2CH_3); minor peaks could be seen at δ 3.48 (m, 1 H, HO*CH*), 1.73 (d, J = 6.8 Hz, 1 H, OH), 1.11 (d, J = 7.0 Hz, 3 H, C≡CCH*CH*$_3$); HRMS, calcd for $C_{18}H_{34}O$ 266.2610, found 266.2611.

(3*R*,4*R*)-2,4-Dimethyl-5-tridecyn-3-ol (25). The above procedure was employed with 180 mg (0.40 mmol) of allenylstannane (*S*)-**4a** and 0.10 mL (1.12 mmol) of isobutyraldehyde in 3 mL of CH_2Cl_2 at –78 °C to yield 72 mg (80%) of alcohol **25** as a single isomer: $[\alpha]_D$ +3.2° ($CHCl_3$, *c* 1.05); IR (film) ν 3442 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.25 (m, J = 4.3 Hz, 1 H, HO*CH*), 2.56 (m, 1 H, propargylic CH), 2.13 (dt, J = 2.3, 7.1 Hz, 2 H, propargylic CH_2), 1.95 (m, 1 H, *CH*$(CH_3)_2$), 1.68 (d, J = 4.1 Hz, 1 H, OH), 1.46–1.26 (m, 10 H, $(CH_2)_5$), 1.13 (d, J = 6.9 Hz, 3 H, C≡CCH*CH*$_3$), 0.94 (d, J = 6.7 Hz, 3 H, CH(*CH*$_3$)$_2$), 0.89 (d, J = 6.7 Hz, 3 H, CH(*CH*$_3$)$_2$), 0.87 (t, J = 7.0 Hz, 3 H, CH_2CH_3). Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.20; H, 12.54.

(3*S*,4*R*)-2,2,4-Trimethyl-5-tridecyn-3-ol (26). Procedure A was employed with 42 mg (0.10 mmol) of allenylstannane **4a** and 17 mg (0.20 mmol) of trimethylacetaldehyde in 1 mL of CH_2Cl_2 at –78 °C to yield 21 mg (92%) of alcohol **26** as a single isomer: $[\alpha]_D$ –10.8° ($CHCl_3$, *c* 1.25); IR (film) ν 3500 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.33 (t, J = 4.3 Hz, 1 H, H-3), 2.64 (m, 1 H, H-4), 2.12 (dt, J = 2.3, 7.1 Hz, 2 H, propargylic CH_2), 1.72 (d, J = 4.3 Hz, 1 H, OH), 1.45–1.27 (m, 10 H, $(CH_2)_5$), 1.18 (d, J = 6.9 Hz, 3 H, CH*CH*$_3$), 0.97 (s, 9 H, $(CH_3)_3$), 0.86 (t, J = 6.9 Hz, 3 H, CH_2CH_3). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.54, H, 12.58.

***rel*-(7*R*,8*R*)-7-[(Methoxymethyl)oxy]-8-methyl-9-heptadecyne (30).** To a mixture of 72 mg (0.27 mmol) of alcohol **24** and 0.23 mL (1.35 mmol) of $(i\text{-}Pr)_2NEt$ in 20 mL of CH_2Cl_2 was added 0.72 mL (9.48 mmol) of MOMCl. The mixture was stirred at room temperature for 12 h; then it was quenched with saturated $NaHCO_3$ and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 10:1) to afford 81 mg (97%) of ether **30**: ^1H NMR (500 MHz, $CDCl_3$) δ 4.72, 4.65 (AB q, J = 6.9 Hz, 2 H, CH_3OCH_2O), 3.39 (s, 3 H, CH_3O), 3.37 (m, 1 H, MOMOCH), 2.66 (m, 1 H, CH_3CH), 2.13 (dt, J = 2.4, 6.9 Hz, 2 H, propargylic CH_2), 1.54–1.27 (m, 20 H, 2 $(CH_2)_5$), 1.12 (d, J = 7.0 Hz, 3 H, CH_3), 0.87 (t, J = 6.8 Hz, 6 H, 2 CH_2CH_3); HRMS, calcd for $C_{20}H_{38}O_2$ 310.2872, found 310.2869.

***rel*-(2*R*,3*R*)-2-Methyl-3-[(methoxymethyl)oxy]nonan-1-ol (33).** A mixture of 41 mg (0.13 mmol) of alkyne **30** and 10 mg of Lindlar's catalyst in 1 mL of dry benzene was stirred at room temperature under H_2 for 1 h; then it was filtered through a pad of Celite. The filtrate was concentrated to afford 41 mg (99%) of alkene **31**: IR (film) ν 2928 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.37–5.22 (m, 2 H, 2 vinyl H), 4.64 (s, 2 H, CH_3OCH_2O), 3.37 (s, 3 H, CH_3O), 3.37–3.33 (m, 1 H, MOMOCH), 2.67 (m, 1 H, CH_3CH), 2.00 (m, 2 H, vinyl CH_2), 1.53–1.25 (m, 20 H, 2 $(CH_2)_5$), 0.95 (d, J = 6.8 Hz, 3 H, CH_3), 0.86 (t, J = 6.7 Hz, 6 H, 2 CH_2CH_3).

To a solution of above olefin **31** in 1 mL of methanol was bubbled O_3 at –78 °C until a blue color appeared. The excess O_3 was bubbled off by N_2 and 0.25 mL of Me_2S was added. The mixture was allowed to warm to room temperature and stirred for 10 min; then 12 mg (0.32 mmol) of $NaBH_4$ was added. After 10 min, the mixture was quenched with saturated $NaHCO_3$ and extracted with ether. The extracts were dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 2:1) to yield 24 mg (85%) of alcohol **33**: IR (film) ν 3429 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.65 (s, 2 H, CH_3OCH_2O), 3.65 (m, 1 H, MOMOC*H*), 3.61–3.50 (m, 2 H, HOCH_2), 3.40 (s, 3 H, CH_3O), 2.70 (dd, J = 4.9, 7.5 Hz, 1 H, OH), 1.91 (m, H, CH_3CH), 1.56–1.26 (m, 10 H, $(CH_2)_5$), 0.87 (t, J = 6.8 Hz, 3 H, CH_2CH_3), 0.81 (d, J = 7.0 Hz, 3 H, CH_3); HRMS, calcd for $C_{11}H_{23}O_2$ (M – OCH_3) 187.1698, found 187.1703. Anal. Calcd for $C_{12}H_{26}O_3$: C, 66.01; H, 12.00. Found: C, 66.03; H, 12.00.

***rel*-(2*R*,3*R*)-2-Methylnonane-1,3-diol (34).** To a solution of 66 mg (0.30 mmol) of ether **33** in 1 mL of methanol was added a few drops of 12 N HCl. The mixture was stirred at room temperature for 3 h; then it was quenched with saturated $NaHCO_3$ and extracted with ether. The extracts were dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 4:1) to yield 25 mg (44%) of 2-methyl-1,3-(methylenedioxy)nonane: ^1H NMR (300 MHz, $CDCl_3$) δ 5.03, 4.63 (AB q, J = 6.1 Hz, 2 H, OCH_2O), 3.93 (dd, J = 4.7, 11.2 Hz, 1 H, H-3), 1.79–1.62 (m, 1 H, H-2), 1.60–1.27 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.7 Hz, 3 H, CH_2CH_3), 0.70 (d, J = 6.7 Hz, 3 H, CH_3); HRMS, calcd for $C_{11}H_{22}O$ 186.1620, found 186.1614. Anal. Calcd for $C_{11}H_{22}O$: C, 70.92; H, 11.90. Found: C, 71.00; H, 11.86.

Continued elution (hexane/ether, 1:1) afforded 25 mg (47%) of diol **34**: IR (film) ν 3354 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.75 (dd, A of ABX, J – 3.7, 10.8 Hz, 1 H, HOCH_2), 3.61 (dd, B of ABX, J = 4.9, 10.8 Hz, 1 H, HOCH_2), 3.55–3.51 (m, 1 H, H-3), 2.60 (bs, 2 H, 2 HO), 1.74–1.68 (m, X of ABX, 1 H, CH_3CH), 1.47–1.28 (m, 10 H, $(CH_2)_5$), 0.88 (d, J = 7.0 Hz, 3 H, CH_3), 0.86 (t, J = 6.8 Hz, 3 H, CH_3CH_2); HRMS, calcd for $C_{10}H_{23}O_2$ 175.1698, found 175.1706.

***rel*-(2*R*,3*R*)-2-Methyl-1,3-(isopropylidenedioxy)nonane (35).** A mixture of 25 mg (0.14 mmol) of diol **34** and a catalytic amount of PPTS in 1 mL of DMP was stirred at room temperature overnight; then it was filtered through a short column. The filtrate was concentrated to afford acetonide **35** quantitatively: ^1H NMR (300 MHz, $CDCl_3$) δ 4.07 (dd, A of ABX, J = 3.0, 11.5 Hz, HOCH_2), 3.88 (m, 1 H, H-3), 3.57 (dd, B of ABX, J = 1.6, 11.5 Hz, 1 H, HOCH_2), 1.50 (m, X of ABX, 1 H, CH_3CH), 1.40–1.26 (m, 10 H, $(CH_2)_5$), 1.41 (s, 3 H, $C(CH_3)_2$), 1.36 (s, 3 H, $C(CH_3)_2$), 1.03 (d, J = 6.9 Hz, 3 H, CH_3), 0.86 (t, J = 6.8 Hz, 3 H, CH_3CH_2); HRMS, calcd for $C_{12}H_{23}O_2$ (M – CH_3) 199.1698, found 199.1698.

(3*R*,4*R*)-(+)-2,4-Dimethyl-3-[(methoxymethyl)oxy]-5-tridecene (39). The procedure described for ether **30** was employed with 85 mg (0.38 mmol) of alcohol **25** to afford 99.5 mg (95%) of ether **39**: $[\alpha]_D$ +18.6° ($CHCl_3$, *c* 0.87); ^1H NMR (500 MHz, $CDCl_3$) δ 4.76, 4.66 (AB q, J = 6.3 Hz, 2 H, CH_3OCH_2), 3.40 (s, 3 H, CH_3O), 3.18 (dd, J = 4.3, 6.9 Hz, 1 H, MOMOC*H*), 2.62–2.57 (m, 2 H, CH_3CH), 2.11 (dt, J = 2.3, 7.1 Hz, 2 H, propargylic CH_2), 2.10–2.03 (m, 1 H, $CH(CH_3)_2$), 1.45–1.26 (m, 10 H, $(CH_2)_5$), 1.16 (d, J = 6.9 Hz, 3 H, CH_3), 0.94 (d, J = 6.9 Hz, 6 H, CH(*CH*$_3$)$_2$), 0.86 (t, J = 6.7 Hz, 3 H, CH_2CH_3); HRMS, calcd for $C_{17}H_{32}O_2$ (M + 1) 269.2481, found, 269.2486. Anal. Calcd for $C_{17}H_{32}O_2$: C,

76.06; H, 12.01. Found: C, 75.98; H, 12.00.

(2*R*,3*R*)-(-)-2,4-Dimethyl-3-[(methoxymethyl)oxy]pentan-1-ol (42). The procedure described for alcohol **33** was employed with 58 mg (0.22 mmol) of alkyne **39** to afford 44 mg (78%) of alkene **40**: $[\alpha]_D$ +7.8° ($CHCl_3$, *c* 0.50); ^1H NMR (300 MHz, $CDCl_3$) δ 5.31–5.18 (m, 2 H, 2 vinyl H), 4.65 (s, 2 H, CH_3OCH_2O), 3.40 (s, 3 H, CH_3O), 3.02 (dd, *J* = 4.0, 7.3 Hz, 1 H, MOMOCH), 2.68–2.64 (m, 1 H, CH_3CH), 2.00 (m, 2 H, vinyl CH_2), 1.80 (m, 1 H, $CH(CH_3)_2$), 1.41–1.25 (m, 10 H, $(CH_2)_5$), 0.97 (d, *J* = 6.7 Hz, CH_3), 0.93 (d, *J* = 6.9 Hz, $CH(CH_3)_2$), 0.87 (d, *J* = 6.8 Hz, $CH(CH_3)_2$), 0.86 (t, *J* = 7.0 Hz, 3 H, CH_2CH_3); HRMS, calcd for $C_{16}H_{31}O$ (M - OCH_3) 239.2375, found 239.2368.

A 40-mg (0.15 mmol) sample of olefin **40** was ozonized and reduced as described for **31** to yield 22 mg (84%) of alcohol **42**: $[\alpha]_D$ -110.3° ($CHCl_3$, *c* 0.76); IR (film) ν 3425 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.69, 4.66 (AB q, *J* = 6.7 Hz, 2 H, CH_3OCH_2O), 3.50 (dd, *J* = 1.6, 6.8 Hz, 1 H, $HOCH_2$), 3.47 (d, *J* = 6.8 Hz, 1 H, $HOCH_2$), 3.42 (s, 3 H, CH_3O), 3.30 (dd, *J* = 2.6, 9.0 Hz, 1 H, MOMOCH), 3.08 (t, *J* = 6.8 Hz, 1 H, OH), 1.99–1.79 (m, 2 H, CH_3CH and $CH(CH_3)_2$), 0.97 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.85 (d, *J* = 6.8 Hz, 3 H, $CH(CH_3)_2$), 0.77 (d, *J* = 6.9 Hz, 3 H, $CH(CH_3)_2$); HRMS, calcd for $C_8H_{17}O_2$ (M - OCH_3) 145.1229, found 145.1226.

(2*R*,3*R*)-(-)-1-(Benzyloxy)-2,4-dimethyl-3-[(methoxymethyl)oxy]pentane (43). A. From Alcohol 42. To a suspension of 15 mg (0.62 mmol) of NaH in 2 mL of THF was added 73 mg (0.41 mmol) of alcohol **42** in 1 mL of THF. After 30 min, 0.08 mL (0.62 mmol) of benzyl bromide was added. The resulting mixture was stirred at room temperature for 12 h; then it was quenched with dilute HCl and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 4:1) to give 101 mg (93%) of ether **43**: $[\alpha]_D$ -9.5° ($CHCl_3$, *c* 1.47); ^1H NMR (300 MHz, $CDCl_3$) δ 7.33–7.24 (m, 5 H, Ar H), 4.64, 4.59 (AB q, *J* = 6.8 Hz, 2 H, $PhCH_2O$), 4.51, 4.45 (AB q, *J* = 12.0 Hz, 2 H, CH_3OCH_2O), 3.41 (dd, A of ABX, *J* = 6.2, 7.6 Hz, 1 H, $BnOCH_2$), 3.35 (s, 3 H, CH_3O), 3.32 (d, B of ABX, *J* = 6.8 Hz, 1 H, $BnOCH_2$), 3.28 (m, 1 H, MOMOCH), 2.05 (m, X of ABX, 1 H, CH_3CH), 1.80 (m, 1 H, $CH(CH_3)_2$), 0.94 (d, *J* = 6.7 Hz, 3 H, CH_3), 0.89 (d, *J* = 6.9 Hz, 3 H, $CH(CH_3)_2$), 0.88 (d, *J* = 6.9 Hz, 3 H, $CH(CH_3)_2$). Anal. Calcd for $C_9H_{20}O_3$: C, 72.14; H, 9.84. Found: C, 72.03; H, 9.79.

B. From Alcohol 44. The procedure described for ether **30** was employed with 22 mg (0.099 mmol) of alcohol **44** to afford 26 mg (99%) of ether **43**: $[\alpha]_D$ -10.0° ($CHCl_3$, *c* 1.00). The spectral properties of this benzyl ether were identical with those of **43** prepared from alcohol **42**.

(2*R*,3*R*)-(-)-1-(Benzyloxy)-2,4-dimethylpentan-3-ol (44). To a mixture of 51 mg (2.22 mmol) of Mg powder and a catalytic amount of I_2 in 2 mL of ether was slowly added 205 mg (1.67 mmol) of isopropyl bromide in 5 mL of ether. After 10 min, 200 mg (1.10 mmol) of (*R*)-2-methyl-3-(benzyloxy)propanal in 5 mL of ether was added at 0 °C. The reaction mixture was quenched with dilute HCl 5 min later and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 2:1) to afford 156 mg (73%) of alcohol **45**: IR (film) ν 3493 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33–7.24 (m, 5 H, Ar H), 4.50 (s, 2 H, $PhCH_2O$), 3.61 (dd, A of ABX, *J* = 4.1, 9.0 Hz, 1 H, $BnOCH_2$), 3.48 (dd, B of ABX, *J* = 7.2, 9.1 Hz, 1 H, $BnOCH_2$), 3.26 (m, 2 H, OH and HOCH), 1.92 (m, X of ABX, 1 H, CH_3CH), 1.75 (m, 1 H, $CH(CH_3)_2$), 0.95 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.89 (d, *J* = 6.9 Hz, 3 H, $CH(CH_3)_2$), 0.88 (d, *J* = 6.9 Hz, 3 H, $CH(CH_3)_2$). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.65; H, 9.94. Continued elution yielded 36 mg (15%) of alcohol **44**: $[\alpha]_D$ -22.9° ($CHCl_3$, *c* 0.82); IR (film) ν 3400 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33–7.24 (m, 5 H, Ar H), 4.53, 4.48 (AB q, *J* = 12.1 Hz, 2 H, $PhCH_2O$), 3.53 (d, *J* = 4.8 Hz, 2 H, $BnOCH_2$), 3.39–3.35 (m, 1 H, HOCH), 2.50 (d, *J* = 3.3 Hz, 1 H, OH), 1.96–1.90 (m, 1 H, CH_3CH), 1.73–1.61 (m, 1 H, $CH(CH_3)_2$), 0.99 (d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_2$), 0.85 (d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_2$), 0.83 (d, *J* = 6.7 Hz, 3 H, CH_3). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.53; H, 9.96.

(2*S*,3*S*,4*R*)-(+)-2-(Benzyloxy)-4-methyl-5-octyn-3-ol (49h). A. $MgBr_2$·OEt_2-Promoted Addition (Procedure B). To a solution of 46 mg (0.28 mmol) of (*S*)-α-(benzyloxy)propanal (**48**) in 3 mL of CH_2Cl_2 was added 155 mg (0.60 mmol) of $MgBr_2$·OEt_2 in one portion at -23 °C. After 5 min, 112 mg (0.30 mmol) of allenylstannane (*S*)-**4h** (ee 84%) in 2 mL of CH_2Cl_2 was added. The resulting mixture was stirred at -23 °C for 30 min; then it was quenched with water and extracted with ether. The combined extracts were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 2:1) to afford 67 mg (98%) of alcohol **49h** admixed with 7% of **52h** arising from the 8% (*R*)-**4h** present in the sample of allenylstannane employed in this experiment: $[\alpha]_D$ +106.8° ($CHCl_3$, *c* 0.96); IR (film) ν 3456 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35–7.26 (m, 5 H, Ar H), 4.65, 4.49 (AB q, *J* = 11.4 Hz, 2 H, $ArCH_2O$), 3.97 (dq, *J* = 2.5, 6.3 Hz, 1 H, BnOCH), 3.15 (dt, *J* = 2.5, 8.8 Hz, 1 H, HOCH), 2.64–2.59 (m, 1 H, propargylic CH), 2.13 (dq, *J* = 2.3, 7.5 Hz, 2 H, propargylic CH_2), 2.07 (d, *J* = 9.0 Hz, 1 H, OH), 1.26 (d, *J* = 6.3 Hz, 3 H, CH_3CHOBn), 1.22 (d, *J* = 6.9 Hz, 3 H, $CHCH_3$), 1.07 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.10; H, 8.97.

B. BF_3·OEt_2-Promoted Addition. Procedure A was employed with 106 mg (0.29 mmol) of allenylstannane (*S*)-**4h** (ee 84%) and 43 mg (0.26 mmol) of (*S*)-α-(benzyloxy)propanal (**48**) with stirring at -78 °C for 10 min. The product was chromatographed on silica gel (hexane/ether, 2:1) to afford 59 mg (92%) of alcohols **49h**, **50h**, and **51h** (from (*R*)-**4h**) as a 81:12:8 mixture. The diastereomers **50h** and **51h** were assigned according to the ^1H NMR spectra of the analogous **50e** and **51e**.

(2*S*,3*R*,4*S*)-(+)-2-(Benzyloxy)-4-methyl-5-octyn-3-ol (51h). BF_3·OEt_2-Promoted Addition. Procedure A was employed with 86 mg (0.27 mmol) of allenylstannane (*R*)-**4h** (ee 84%) and 35 mg (0.21 mmol) of (*S*)-α-(benzyloxy)propanal (**48**) to afford 46 mg (89%) of alcohols **51h** and **49h** (from (*S*)-**4h**) as a 94:6 mixture: $[\alpha]_D$ +27.6° ($CHCl_3$, *c* 0.94); IR (film) ν 3460 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.26 (m, 5 H, Ar H), 4.59, 4.51 (AB q, *J* = 11.7 Hz, 2 H, $ArCH_2O$), 3.87–3.81 (m, 1 H, BnOCH), 3.67–3.63 (m, 1 H, HOCH), 2.48–2.43 (m, 1 H, propargylic CH), 2.20 (d, *J* = 2.1 Hz, 1 H, OH), 2.11 (dq, *J* = 2.3, 7.5 Hz, 2 H, propargylic CH_2), 1.21 (d, *J* = 6.2 Hz, 3 H, CH_3CHOBn), 1.19 (d, *J* = 6.2 Hz, 3 H, $CHCH_3$), 1.08 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3); HRMS, calcd for $C_{16}H_{21}O$ (M - OH) 229.1592, found 229.1593. Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 69.98; H, 9.06.

(2*S*,3*S*,4*S*)(+)-2-(Benzyloxy)-4-methyl-5-octyn-3-ol (52h). $MgBr_2$·OEt_2-Promoted Addition. Procedure B was followed with 38 mg (0.23 mmol) of (*S*)-α-(benzyloxy)propanal (**48**) and 94 mg (0.25 mmol) of allenylstannane (*R*)-**4h** (ee 84%) to afford 54 mg (95%) of alcohols **52h** and **49h** as a 93:7 (from (*S*)-**4h**) mixture: $[\alpha]_D$ +54.9° ($CHCl_3$, *c* 0.97); IR (film) ν 3560 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.26 (m, 5 H, Ar H), 4.67, 4.46 (AB q, *J* = 11.5 Hz, 2 H, $ArCH_2O$), 3.65 (m, 1 H, BnOCH), 3.30–3.25 (m, 1 H, HOCH), 2.66 (d, *J* = 3.1 Hz, 1 H, OH), 2.65 (m, 1 H, propargylic CH), 2.14 (dq, *J* = 2.3, 7.5 Hz, 2 H, propargylic CH_2), 1.21 (d, *J* = 6.2 Hz, 3 H, CH_3CHOBn), 1.19 (d, *J* = 7.1 Hz, 3 H, $CHCH_3$), 1.08 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3); HRMS, calcd for $C_{16}H_{21}O_2$ (M - H) 245.1542, found 245.1543. Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00 Found: C, 70.14; H, 9.01.

(2*R*,4*R*)-(*Z*)-2-(Benzyloxy)-4-methyl-7-acetoxy-5-penten-3-one (56). A mixture of 30 mg (0.10 mmol) of a 65:35 mixture of alcohols **49e** and **50e** and 10 mg of Lindlar's catalyst in 2 mL of C_6H_6 was stirred at room temperature under H_2 for 1 h; then it was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure to afford the (*Z*)-alcohols **57** and **59** quantitatively.

To a solution of the above alcohol in 3 mL of CH_2Cl_2 was added 59 mg (0.14 mmol) of Dess–Martin reagent.[14] After being stirred at room temperature for 10 min, the mixture was directly submitted to column chromatographed on silica gel (hexane/ether, 4:1) to give 26 mg (86%) of a single ketone (**56**): IR (film) ν 3030, 1738, 1719 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.27 (m, 5 H, Ar H), 5.67–5.54 (m, 2 H, vinyl H), 4.66–4.48 (m, 2 H, $AcOCH_2$), 4.54, 4.44 (AB q, *J* = 11.8 Hz, 2 H, $ArCH_2O$), 4.04–4.00 (m, 1 H, allylic CH), 4.00 (t, *J* = 6.8 Hz, BnOCH), 2.00 (s, 3 H, AcO), 1.33 (d, *J* = 7.0 Hz, 3 H, $BnOCHCH_3$), 1.15 (d, *J* = 6.9 Hz, 3 H, $CHCH_3$); HRMS, calcd for $C_{17}H_{23}O_4$ (M + H) 291.1596, found 291.1598.

(2*R*,3*S*,4*S*)-2-Methyl-4-(benzyloxy)-1,3-(isopropylidenedioxy)pentane (58). The procedure described for alcohol **33** was employed with 67 mg (0.23 mmol) of alcohol **49e** to afford alcohol **57** quantitatively: ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.27 (m, 5 H, Ar H), 5.57–5.49 (m, 2 H, vinyl H), 4.63–4.56 (m, 2 H,

$AcOCH_2$), 4.63, 4.38 (AB q, J = 11.3 Hz, 2 H, $ArCH_2O$), 3.58–3.54 (m, 1 H, BnOCH), 3.20–3.14 (m, 1 H, HOC*H*), 2.73 (m, 1 H, allylic CH), 2.27 (d, J = 7.1 Hz, 1 H, OH), 2.01 (s, 3 H, AcO), 1.24 (d, J = 6.2 Hz, 3 H, CH_3CHOBn), 1.02 (d, J = 6.8 Hz, 3 H, CHCH_3).

A 65-mg (0.22 mmol) sample of alkene **57** was ozonized and reduced as described for **31**. The crude diol was used for the next reaction without purification.

A mixture of the above diol and a catalytic amount of *p*-TsOH in 2 mL of 2,2-dimethoxypropane was stirred at room temperature overnight; then it was directly chromatographed on silica gel (hexane/ether, 4:1) to yield acetonide **58** quantitatively: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.25 (m, 5 H, Ar H), 4.73, 4.60 (AB q, J = 11.9 Hz, 2 H, $ArCH_2O$), 4.11 (d, J = 2.7, 11.5 Hz, 1 H, OCH_2), 3.88 (dd, J = 2.4, 8.3 Hz, 1 H, OCH), 3.56 (dd, J = 1.6, 11.5 Hz, 1 H, OCH_2), 3.48 (dq, J = 6.4, 8.3 Hz, 1 H, BnOCH), 1.46 (m, 1 H, CH_3CH), 1.46 (s, 3 H, $(CH_3)_2C$), 1.42 (s, 3 H, $(CH_3)_2C$), 1.09 (d, J = 6.4 Hz, 3 H, BnOCHCH_3), 1.05 (d, J = 6.8 Hz, 3 H, CHCH_3); HRMS, calcd for $C_{16}H_{23}O_3$ (M − H) 263.1647, found 263.1645.

(2*S*,3*S*,4*R*)-2-Methyl-4-(benzyloxy)-1,3-(isopropylidenedioxy)pentane (60). The procedure described for alcohol **33** was employed with 56 mg (0.19 mmol) of alcohol **20** to afford alcohol **59** quantitatively: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34–7.27 (m, 5 H, Ar H), 5.72–5.54 (m, 2 H, vinyl H), 4.61–4.57 (m, 2 H, $AcOCH_2$), 4.64, 4.38 (AB q, J = 11.5 Hz, 2 H, $ArCH_2O$), 3.43–3.39 (m, 1 H, BnOCH), 3.29 (m, 1 H, HOC*H*), 2.65 (m, 1 H, allylic CH), 2.59 (d, J = 3.2 Hz, 1 H, OH), 2.04 (s, 3 H, AcO), 1.17 (d, J = 6.1 Hz, 3 H, CH_3CHOBn), 1.02 (d, J = 6.9 Hz, 3 H, CHCH_3). A 56-mg (0.19 mmol) sample of alkene **59** was ozonized and reduced as described for **31**. The crude diol was used for the next reaction without purification.

A mixture of the above diol and a catalytic amount of PPTS in 2 mL of 2,2-dimethoxypropane was stirred at room temperature overnight; then it was directly chromatographed on silica gel (hexane/ether, 4:1) to yield acetonide **60** quantitatively: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45–7.26 (m, 5 H, Ar H), 4.68, 4.42 (AB q, J = 12.1 Hz, 2 H, $ArCH_2O$), 3.68 (dd, J = 5.2, 11.5 Hz, 1 H, OCH_2), 3.61 (dq, J = 2.4, 6.4 Hz, 1 H, BnOCH), 3.47 (dd, J = 11.2, 11.5 Hz, 1 H, OCH_2), 3.43 (dd, J = 2.4, 10.1 Hz, 1 H, OCH), 2.12–2.01 (m, 1 H, CH_3CH), 1.40 (s, 3 H, $(CH_3)_2C$), 1.39 (s, 3 H, $(CH_3)_2C$), 1.22 (d, J = 6.4 Hz, 3 H, BnOCHCH_3), 0.62 (d, J = 6.7 Hz, 3 H, CHCH_3). Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.63; H, 7.14.

(2*R*,3*S*,4*R*)-(+)-1-(Benzyloxy)-2,4-dimethyl-7-acetoxy-5-heptyn-3-ol (62e). A. $MgBr_2$·OEt_2-Promoted Addition. Procedure B was followed with 47 mg (0.26 mmol) of (*R*)-3-(benzyloxy)-2-methylpropanal (**61**) and 100 mg (0.24 mmol) of allenylstannane (*S*)-**4e** (ee 90%) at −23 °C for 12 h to afford 68 mg (95%) of alcohols **62e** and **64e** (from (*R*)-**4e**) as a 95:5 mixture: $[\alpha]_D$ +20.8° ($CHCl_3$, *c* 1.48); IR (film) ν 3492 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.26 (m, 5 H, Ar H), 4.64 (d, J = 2.0 Hz, 2 H, $AcOCH_2$), 4.49 (s, 2 H, $ArCH_2O$), 3.73 (dd, A of ABX, J = 3.9, 9.2 Hz, 1 H, $BnOCH_2$), 3.50 (dd, B of ABX, J = 4.9, 9.2 Hz, 1 H, $BnOCH_2$), 3.48–3.42 (m, 1 H, HOC*H*), 3.25 (d, J = 6.1 Hz, 1 H, OH), 2.59 (m, 1 H, propargylic CH), 2.08 (m, X of ABX, $BnOCH_2CH$), 2.06 (s, 3 H, AcO), 1.23 (d, J = 6.9 Hz, 3 H, CH_3CHCH_2OBn), 1.03 (d, J = 7.1 Hz, 3 H, CHCH_3); HRMS, calcd for $C_{18}H_{24}O_4$ (M + H) 305.1753, found 305.1743.

B. BF_3·OEt_2-Promoted Addition. Procedure A was followed with 70 mg (0.17 mmol) of allenylstannane (*S*)-**4e** (ee 90%) and 36 mg (0.20 mmol) of (*R*)-3-(benzyloxy)-2-methylpropanal (**61**) at −78 °C for 4 h. The product was chromatographed on silica gel (hexane/ether, 1:1) to afford 42 mg (82%) of alcohol **62e** admixed with 4% of the diastereomer **64e** (from (*R*)-**4e**): $[\alpha]_D$ +20.8° ($CHCl_3$, *c* 0.93).

Continued elution afforded 8 mg (16%) of alcohol **63e**: IR (film) ν 3400 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.26 (m, 5 H, Ar H), 4.65 (d, J = 2.0 Hz, 2 H, $AcOCH_2$), 4.49 (s, 2 H, $ArCH_2O$), 3.56–3.43 (m, 3 H, HOC*H* and CH_2OBn), 2.67 (m, 1 H, propargylic CH), 2.38 (d, J = 5.1 Hz, 1 H, OH), 2.06 (s, 3 H, AcO), 1.95 (m, 1 H, $CHCH_2OBn$), 1.17 (d, J = 7.0 Hz, 3 H, CH_3CHCH_2OBn), 0.96 (d, J = 7.0 Hz, 3 H, CHCH_3); HRMS, calcd for $C_{18}H_{24}O_4$ 304.1675, found 304.1675.

(2*R*,3*R*,4*S*)-(+)-1-(Benzyloxy)-2,4-diethyl-7-acetoxy-5-heptyn-3-ol (64e). A. BF_3·OEt_2-Promoted Addition. Procedure A was followed with 70 mg (0.17 mmol) of allenylstannane (*R*)-**4e** (ee 90%) and 36 mg (0.20 mmol) of (*R*)-3-(benzyloxy)-2-methylpropanal (**61**) at −78 °C for 4 h. The product was chromatographed on silica gel (hexane/ether, 1:1) to afford 49 mg (96%) of alcohol **64e**: $[\alpha]_D$ +3.7° ($CHCl_3$, *c* 2.14); IR (film) ν 3486 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.26 (m, 5 H, Ar H), 4.62 (d, J = 2.0 Hz, 2 H, $AcOCH_2$), 4.53, 4.47 (AB q, J = 11.9 Hz, 2 H, $ArCH_2O$), 3.66 (m, 1 H, HOC*H*), 3.61 (dd, A of ABX, J = 3.8, 9.0 Hz, 1 H, $BnOCH_2$), 3.53 (dd, B of ABX, J = 4.8, 9.0 Hz, 1 H, $BnOCH_2$), 2.91 (d, J = 2.7 Hz, 1 H, OH), 2.57–2.52 (m, 1 H, propargylic OH), 2.23 (m, X of ABX, 1 H, $CHCH_2OBn$), 2.06 (s, 3 H, AcO), 1.25 (d, J = 6.8 Hz, 3 H, CH_3CHCH_2OBn), 1.01 (d, J = 7.1 Hz, 3 H, CHCH_3); HRMS, calcd for $C_{18}H_{24}O_4$ 304.1675, found 304.1670.

B. $MgBr_2$·OEt_2-Promoted Addition. Procedure B was followed with 41 mg (0.23 mmol) of (*R*)-3-(benzyloxy)-2-methylpropanal (**61**) and 80 mg (0.19 mmol) of allenylstannane (*R*)-**4e** (ee 90%) at −23 °C for 12 h. The product was chromatographed on silica gel (hexane/ether, 2:1) to afford 56 mg (95%) of alcohol **64e**: $[\alpha]_D$ +3.4° ($CHCl_3$, *c* 1.34).

(2*R*,4*S*)-(*Z*)-1-(Benzyloxy)-2,4-diethyl-5-octen-3-one (66). A mixture of 38 mg (0.14 mmol) of a 50:50 mixture of alcohols **64h** and **65h** and 10 mg of Lindlar's catalyst in 2 mL of C_6H_6 was stirred at room temperature under H_2 for 1 h; then it was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure to afford the (*Z*)-alcohols quantitatively.

To a solution of the above alcohol in 3 mL of CH_2Cl_2 was added 68 mg (0.16 mmol) of Dess–Martin reagent.[14] After being stirred at room temperature for 10 min, the mixture was directly submitted to column chromatographed on silica gel (hexane/ether, 4:1) to give 34 mg (91%) of ketone **66**: IR (film) ν 1714 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.24 (m, 5 H, Ar H), 5.50–5.25 (m, 2 H, vinyl H), 4.44 (s, 2 H, $ArCH_2O$), 3.63 (dd, A of ABX, J = 7.5, 9.1 Hz, 1 H, CH_2OBn), 3.60 (m, 1 H, allylic CH), 3.36 (dd, B of ABX, J = 6.1, 9.1 Hz, 1 H, CH_2OBn), 3.04 (m, 1 H, $COCHCH_3$), 2.07 (m, 2 H, CH_3CH_2), 1.12 (d, J = 6.8 Hz, 3 H, $BnOCHCH_2CH_3$), 1.05 (d, J = 7.1 Hz, 3 H, CHCH_3), 0.96 (t, J = 7.5 Hz, 3 H, CH_3CH_2); HRMS, calcd for $C_{17}H_{24}O_2$ 260.1776, found 260.1764.

(2*R*,3*S*,4*R*)-2,4-Dimethyl-1,3-(isopropylidenedioxy)octane (67). A mixture of 27 mg (0.10 mmol) of alcohol **62h** and 80 mg of 10% paladium on carbon in 2 mL of C_6H_6 was stirred at room temperature under H_2 for 1 h; then it was filtered through a pad of Celite. The filtrate was concentrated to afford (2*R*,3*R*,4*R*)-2,4-dimethyloctane-1,3-diol quantitatively.

A mixture of the above diol and a catalytic amount of PPTS in 1 mL of 2,2-dimethoxypropane was stirred at room temperature overnight; then it was directly chromatographed on silica gel (hexane/ether, 4:1) to yield 21 mg (95%) of acetonide **67**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 (dd, J = 5.0, 11.4 Hz, 1 H, OCH_2), 3.48 (dd, J = 11.1, 11.4 Hz, 1 H, OCH_2), 3.40 (dd, J = 2.2, 10.2 Hz, 1 H, OCH), 1.80 (m, 1 H, H-2), 1.60 (m, 1 H, H-4), 1.38 (s, 3 H, $(CH_3)_2C$), 1.33 (s, 3 H, $(CH_3)_2C$), 1.33–1.25 (m, 6 H, $(CH_2)_3$), 0.87 (t, J = 6.9 Hz, 3 H, CH_2CH_3), 0.83 (d, J = 6.8 Hz, 3 H, CHCH_3), 0.68 (d, J = 6.7 Hz, 3 H, CHCH_3); HRMS, calcd for $C_{13}H_{26}O_2$ 214.1933, found 214.1938.

(2*R*,3*R*,4*R*)-2,4-Dimethyl-5-(benzyloxy)-1,3-(isopropylidenedioxy)pentane (68). The hydrogenation–ozonolysis–reduction sequence (see **30** → **35**) was employed with 58 mg (0.19 mmol) of alcohol **62h** to yield 45 mg (86%) of acetonide **68**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.26 (m, 5 H, Ar H), 4.52, 4.44 (AB q, J = 12.0 Hz, 2 H, $ArCH_2O$), 4.08 (dd, J = 2.8, 11.4 Hz, 1 H, OCH_2), 3.75 (dd, J = 2.3, 10.1 Hz, 1 H, OCH), 3.59 (dd, J = 1.7, 11.4 Hz, 1 H, OCH_2), 3.51 (dd, J = 3.0, 8.8 Hz, 1 H, $BnOCH_2$), 3.43 (dd, J = 5.9, 8.8 Hz, $BnOCH_2$), 1.78 (m, 1 H, H-2), 1.53 (m, 1 H, H-4), 1.47 (s, 3 H, $(CH_3)_2C$), 1.35 (s, 3 H, $(CH_3)_2C$), 1.04 (d, J = 6.9 Hz, 3 H, $BnOCHCH_2CH_3$), 0.92 (d, J = 6.9 Hz, 3 H, CHCH_3); HRMS, calcd for $C_{17}H_{26}O_3$ 278.1882, found, 278.1882.

(2*R*,3*R*,4*S*)-2,4-Dimethyl-1,3-(isopropylidenedioxy)octane (69). A mixture of 26 mg (0.10 mmol) of alcohol **64h** and 80 mg of 10% paladium on carbon in 2 mL of C_6H_6 was stirred at room temperature under H_2 for 1 h; then it was filtered through a pad of Celite. The filtrate was concentrated to afford (2*R*,3*S*,4*S*)-2,4-dimethyloctane-1,3-diol quantitatively.

A mixture of the above diol and a catalytic amount of PPTS in 1 mL of 2,2-dimethoxypropane was stirred at room temperature

overnight; then it was directly chromatographed on silica gel (hexane/ether, 4:1) to yield 19 mg (88%) of acetonide **69**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (dd, J = 2.8, 11.4 Hz, 1 H, OCH_2), 3.58 (dd, J = 1.7, 11.4 Hz, 1 H, OCH_2), 3.44 (dd, J = 2.3, 9.8 Hz, 1 H, OCH), 1.60–1.40 (m, 2 H, H-2 and H-4), 1.39 (s, 3 H, $(CH_3)_2C$), 1.38 (s, 3 H, $(CH_3)_2C$), 1.38–1.25 (m, 6 H, $(CH_2)_3$), 1.03 (d, J = 6.9 Hz, 3 H, $CHCH_3$), 0.89 (d, J = 6.4 Hz, 3 H, $CHCH_3$), 0.87 (t, J = 6.9 Hz, 3 H, CH_2CH_3). Anal. Calcd for $C_{13}H_{26}O_2$: C, 72.84; H, 12.23. Found: C, 72.70; H, 12.17.

(2*S*,3*S*,4*R*)-2,4-Dimethyl-5-(benzyloxy)-1,3-(isopropylidenedioxy)pentane (70). The sequence described for **30** → **35** was employed with 52 mg (0.17 mmol) of alcohol **64h**. **70**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.26 (m, 5 H, Ar H), 4.52, 4.44 (AB q, J = 12.0 Hz, 2 H, $ArCH_2O$), 4.05 (dd, J = 2.7, 11.4 Hz, 1 H, OCH_2), 3.71 (dd, J = 2.3, 9.6 Hz, 1 H, OCH), 3.53 (dd, J = 1.7, 11.4 Hz, 1 H, OCH_2), 3.35 (dd, J = 4.2, 9.3 Hz, 1 H, $BnOCH_2$), 3.30 (dd, J = 5.2, 9.3 Hz, $BnOCH_2$), 1.80 (m, 1 H, H-2), 1.50 (m, 1 H, H-4), 1.40 (s, 3 H, $(CH_3)_2C$), 1.38 (s, 3 H, $(CH_3)_2C$), 1.04 (d, J = 6.9 Hz, 3 H, $BnOCHCH_2CH_3$), 1.02 (d, J = 6.7 Hz, 3 H, $CHCH_3$); HRMS, calcd for $C_{17}H_{26}O_3$ 278.1882, found, 278.1884. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 73.42; H, 9.44.

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Registry No. **1a**, 62967-60-6; **1b**, 96429-42-4; **1c**, 81535-82-2; (*R*)-**2a**, 124126-37-0; (*R*)-**2b**, 137920-03-7; (*S*)-**2b**, 137920-04-8; (*R*)-**2c**, 133910-77-7; (*S*)-**2c**, 133910-89-1; (*S*)-**4a**, 138124-08-0; (±)-**4a**, 131043-65-7; (*S*)-**4b**, 137920-05-9; (*R*)-**4b**, 137920-30-0; (*S*)-**4c**, 133930-05-9; (*R*)-**4c**, 133930-07-1; (*S*)-**4d**, 133910-78-8; (*R*)-**4d**, 133910-90-4; (*S*)-**4e**, 133910-79-9; (*R*)-**4e**, 133910-91-5; (*S*)-**4f**, 137920-06-0; (*R*)-**4f**, 137920-07-1; (*S*)-**4g**, 137920-08-2; (*S*)-**4h**, 137920-09-3; (*R*)-**4h**, 137920-10-6; **5**, 133910-80-2; **6**, 73501-37-8; **7**, 137920-11-7; **9**, 133910-81-3; **10**, 133910-82-4; **11**, 133910-83-5; **12**, 133910-85-7; **14**, 133930-06-0; **15**, 133910-84-6; **19**, 42969-65-3; **20**, 137920-12-8; **21**, 137920-13-9; **24**, 131043-68-0; **25**, 138124-09-1; **26**, 138124-10-4; **27**, 131043-71-5; **30**, 137920-14-0; **31**, 137920-15-1; **33**, 137920-16-2; **34**, 137920-17-3; **35**, 137920-18-4; **37**, 137920-19-5; **39**, 131043-72-6; **40**, 131043-73-7; **42**, 131043-75-9; **43**, 137920-20-8; **44**, 137920-21-9; **45**, 137920-22-0; **47**, 79026-61-2; **48**, 81445-44-5; **49e**, 133910-87-9; **49h**, 137920-23-1; **50e**, 133964-09-7; **50h**, 138050-84-7; **51e**, 133964-10-0; **51h**, 138050-85-8; **52e**, 133964-11-1; **52h**, 138050-86-9; **56**, 137920-24-2; **57**, 137920-25-3; **58**, 137943-34-1; **59**, 138124-11-5; **60**, 137920-26-4; **61**, 79026-61-2; **62e**, 137920-27-5; **62h**, 137943-35-2; **63e**, 138124-12-6; **63h**, 138124-46-6; **64e**, 138124-13-7; **64h**, 138124-47-7; **65h**, 138124-48-8; **66**, 137943-36-3; **67**, 137920-28-6; **68**, 138124-14-8; **69**, 137943-37-4; **70**, 98102-72-8; (trimethylsilyl)acetylene, 1066-54-2; heptanol, 111-71-7; *rac*-1-(trimethylsilyl)-1-nonyn-3-ol, 135501-86-9; 1-(trimethylsilyl)-1-nonyn-3-one, 97367-36-7; 2-methyl-1,3-(methylenedioxy)nonane, 137920-29-7; trimethylacetaldehyde, 630-19-3.

Supplementary Material Available: Experimental procedures for *R* and *S* isomers of **2b–c**, **4b–c**, **49e**, **51e**, **52e**, **62h**, and **64h** and ^{1}H NMR spectra for **6**, **9**, **11**, **12**, **14**, **20**, **21**, **23**, **24**, **30**, **34**, **35**, **42**, **56**, **58**, **62e**, **63e**, **66**, **67**, **68**, **62h**, and **64h** (27 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

N-Nitrososulfamates: Sources of Carbonium Ions in Aqueous Media and Substrates in Solid-State Decompositions[1]

Emil H. White,* Min Li, and Shanzheng Lu

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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Potassium *N*-nitrososulfamates of benzylamine, 2-phenylethylamine, and cyclohexylamine **2a–c** were synthesized and examined as sources of carbonium ions in aqueous media. The nitrososulfamates are crystalline compounds which decompose readily at low pHs (~2) under conditions where the parent amines are relatively stable to nitrous acid. In water solutions they produce the corresponding alcohols, principally, along with small percentages of the corresponding esters of potassium bisulfate. The decomposition of the benzyl analogue **2b** in the presence of sodium thiocyanate produced, principally, benzyl alcohol, but also benzyl thiocyanate and benzyl isothiocyanate in a ratio of 4.4/1, indicating a muted role for nucleophilicity in this carbonium ion reaction. In sulfate buffers they decompose by psuedo-first-order kinetics (rate constants are reported). In acetic acid they produce principally the corresponding acetate esters. A reaction mechanism is proposed in which the slow step involves the production of a diazohydroxide rather than a direct formation of a carbonium ion. The benzyl analogue **2b** is an inhibitor of the enzyme pepsin; it also undergoes a photoelimination reaction on irradiation. The nitrososulfamates are perfectly stable when dry, but they undergo a relatively rapid solid-state decomposition ($T_{1/2} \approx$ 2–5 days) when exposed to normal atmospheric humidity; surprisingly, the external appearance of the crystals does not change during the decompositions. The products are, principally, the esters of sulfuric acid and potassium bisulfate.

The deamination of aliphatic amines in organic solvents can be achieved through use of *N*-nitrosoamides,[2] *N*-nitroamides, and the acylation of nitroamine salts,[3] *N*-nitrosohydroxylamines,[4] triazenes,[5] sydnones,[6] and related compounds,[7] and through the reactions of amines with

(1) Paper 46 in a series on alkyl diazonium ion pairs and deamination. Paper 45: White, E. H.; DePinto, J. T.; Polito, A. J.; Bauer, I.; Roswell, D. F. The Preparation of Carbonium Ions and Other High-Energy Alkylating Agents Under Mild Conditions. *J. Am. Chem. Soc.* **1988**, *110*, 3708.

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