The Hydroboration of Propargyl Bromide. Simple One-Pot Three-Component Routes to (*Z*)-1-Bromoalk-1-en-4-ols and to *anti*-Homoallylic Alcohols

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The hydroboration of propargyl bromide with dialkylboranes takes place regioselectively to give 3-bromoprop-1-en-1-yl dialkylboranes **13** which, upon quaternization with bromide ion, undergo a series of transformations into a number of allylic boron species. By a suitable choice of the experimental conditions it is possible to trap the reaction intermediates with aldehydes and to steer the process toward either the synthesis of (*Z*)-1-bromoalk-1-en-4-ols **6** or *anti*-homoallylic alcohols **8**. Two one-pot three-component processes were developed based on a sequence of four reactions; preparation of dialkylborane and hydroboration of propargyl bromide are the first steps. Then, quaternization with TEBABr may be carried out either in the presence of the aldehyde when (*Z*)-1-bromoalk-1-en-4-ols **6** are requested, or in the absence of the aldehyde in order to allow the formation of γ-substituted allyl borane **18** which, successively, adds to the aldehyde affording *anti*-homoallylic alcohols **8**.

Introduction

The recourse to one-pot sequential transformations is generally highly desirable in organic synthesis because of the economic and environmental benefits associated to the reduction of the overall number of synthetic steps, such as reduction of cost, time, and waste production.[1] Sequential transformations include the following: (i) domino reactions, also described as cascade or tandem reactions, where a spontaneous sequence of elementary steps occurs, and (ii) consecutive reactions, where a one-pot sequence of transformations is promoted by the sequential addition of reagents, catalysts, etc. Boron chemistry sounds particularly suitable for developing synthetic protocols based on one-pot sequential transformations. Selected examples extracted from the literature include the following: (i) Matteson sequential homologations of boronates with chloromethyllithium,[2] (ii) sequential Diels−Alder/aldehyde allylation reactions starting from 1,3-dien-1-yl boronates,[3] (iii) homologation/aldehyde homoallenylation reactions starting from allenyl boronates,[4] (iv) aldol addition/aldehyde allylation reactions starting from enol borates,[5] (v) and a regio and stereocontrolled protocol for the synthesis of *syn*-aldols developed by our laboratory and based on the 1,4-hydroboration of α,β-unsaturated acyclic enones followed by addition of the intermediate (*Z*)-boron enolate to an aldehyde.[6]

Here we wish to present one-pot synthetic protocols to homoallylic alcohols based on the hydroboration of propargyl bromide as the first step.

The regioselective hydroboration of propargyl chloride by means of dialkylboranes was studied in the early 1970s by Zweifel.[7] He reported that quaternization of the 3-chloroprop-1-en-1-yl boranes **1** with methyllithium brought about the collapse of the intermediate "ate" species **2** to give α-substituted allylboranes **3** (Scheme 1). The latter compound underwent rapid fluxional conversion into the thermodynamically more stable γ-substituted allyl borane **4**. Finally, deuteriolysis of **4** afforded monosubstituted alkenes **5**.

Recently, we found that the hydroboration product of propargyl bromide by means of dialkylboranes may be converted into α or γ-substituted allyl boranes by a catalytic amount of a quaternary ammonium bromide.[8] A deeper insight into the catalytic cycles involved in these reactions, allows us to present now new protocols for the selective synthesis of a variety of substituted homoallylic alcohols of general structure **6**−**8** (Figure 1).

Results and Discussion

At the outset of this work, it was verified that 3-bromoprop-1-en-1-yl dicyclohexylborane (**9**), prepared from a freshly distilled solution of propargyl bromide, could

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(1) (a) Tietze, L. F.; Beifuss, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 131−164. (b) Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115−136. (c) Denmark, S. E.; Thorarensen, A. *Chem. Rev.* **1996**, *96*, 137−166. (d) Winkler, J. D. *Chem. Rev.* **1996**, *96*, 167−176. (e) Ryu, I.; Sonoda, N.; Curran, D. P. *Chem. Rev.* **1996**, *96*, 177−194. (f) Parsons, P. J.; Penkett, C. S.; Shell, A. J. *Chem. Rev.* **1996**, *96*, 195−206. (g) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207−222. (h) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223−270. (i) Harvey, D. F.; Sigano, D. M. *Chem. Rev.* **1996**, *96*, 271−288.

(2) Matteson, D. S.; Singh, R. P.; Schafman, B.; Yang, J.-J. *J. Org. Chem.* **1998**, *63*, 4466. See also: Matteson, D. S. *CHEMTECH* **1999**, 6 and references therein.

(3) Renard, P.-I.; Lallemand, J.-Y. *Tetrahedron*: *Asymm*etry **1996**, *7*, 2523−2524.

(4) Soundararajan, R.; Li, G.; Brown, H. C. *J. Org. Chem.* **1996**, *61*, 100−104.

(5) Hoffmann, R. W.; Froech, S. *Tetrahedron Lett.* **1985**, *26*, 1643−1646.

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(7) Zweifel, G.; Horng, A. *Synthesis* **1973**, 672−674.

(8) Gaddoni, L.; Lombardo, M.; Trombini, C. *Tetrahedron Lett.* **1998**, *39*, 7571−7574.

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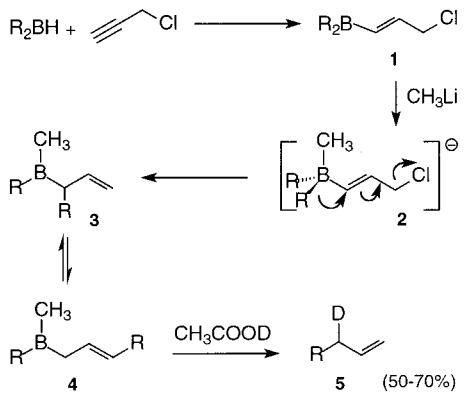
Scheme 1



be stored for a few days under argon at 0 °C without appreciable decomposition, while extensive decomposition occurred within 5−10 h when a yellowish commercial toluene solution of propargyl bromide was used. To shed light into this different behavior, we hydroborated a yellowish old commercial toluene solution of propargyl bromide with dicyclohexylborane and, after 15 h at 20 °C, we quenched two aliquots of the reaction mixture with alkaline hydrogen peroxide and benzaldehyde, respectively. Products **8a** and **11**, reported in Scheme 2, unambiguously revealed that a reaction cascade had to take place, converging into a (*E*)-1-cyclohexylprop-1-en-3-yl borane species **10**.

The *E* geometry of **10** was deduced on the basis of the *E* geometry of the oxidation product **11** and of the anti relative stereochemistry of **8a**, confirmed upon transformation into the 4,5-*trans*-disubstituted 1,3-dioxane **12**.

In our opinion, a catalytic amount of free bromide ion (X = Br in Scheme 2) was present in the aged sample of propargyl bromide as the result of substrate decomposition, and it was responsible for a reaction cascade involving quaternization of **9** and converging to the γ-substituted allyl borane **10**.

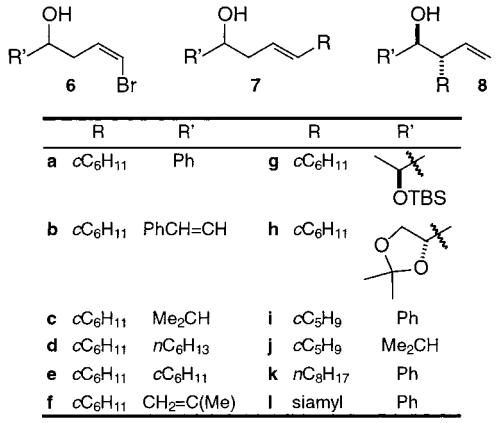
When the same reactions where reproduced using freshly distilled propargyl bromide, we did not detect any trace of **8a** or **11**.

Delighted by the disclosure of a straightforward route to substituted allylic boranes,[9] we carried out further experiments using the system dicyclohexyl borane and freshly distilled propargyl bromide, and studied the effect exerted by a source of bromide ions such as triethylbenzylammonium bromide (TEBABr).

The most significant results are collected in Table 1.

The presence of a catalytic amount (10% mol) of TEBABr speeded up the formation of allylic boranes in 1 h and, depending on the solvent and on the order of addition of TEBABr and benzaldehyde, homoallylic alcohols **6a**, **7a**, or **8a** could be selectively obtained. More in detail, **6a** was produced in major extent when quaternization with TEBABr was carried out in THF in the presence of benzaldehyde (henceforth we refer to this addition order as protocol A) (entry 1); **7a** and **8a** were the prominent products when an equilibration time (t_{eq}) was adopted between the quaternization with TEBABr and the addition of the aldehyde (protocol B), in noncoordinating solvents (entries 5 and 6) or in THF (entries 2−4), respectively.

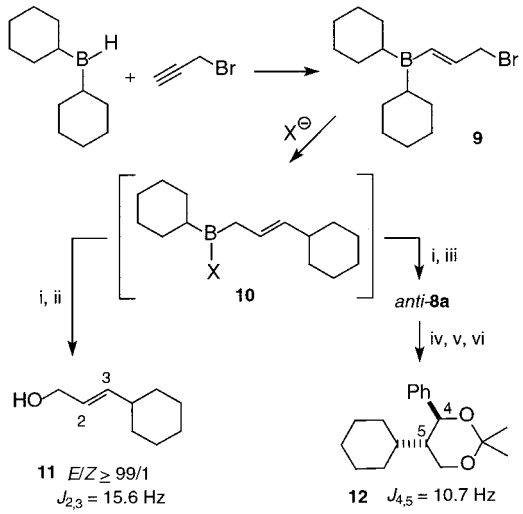
(9) (a) Roush, W. R. In *Comprehensive Organic Synthesis*; Trost B. M., Fleming I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, pp 1−53. (b) Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 489−594.



	R	R'		R	R'
a	*c*C_6H_{11}	Ph	**g**	*c*C_6H_{11}	
b	*c*C_6H_{11}	PhCH=CH	**h**	*c*C_6H_{11}	
c	*c*C_6H_{11}	Me_2CH	**i**	*c*C_5H_9	Ph
d	*c*C_6H_{11}	*n*C_6H_{13}	**j**	*c*C_5H_9	Me_2CH
e	*c*C_6H_{11}	*c*C_6H_{11}	**k**	*n*C_8H_{17}	Ph
f	*c*C_6H_{11}	CH_2=C(Me)	**l**	siamyl	Ph

Figure 1. Structures of homoallylic alcohols **6**−**8**.

Scheme 2[a]



[a] Key: (i) 15 h at 20 °C; (ii) 30% H_2O_2/3 M NaOH; (iii) PhCHO; (iv) O_3; (v) BH_3·THF; (vi) 2,2-dimethoxypropane, H^+.

Entries 2−4, in particular, reveal that **6a** was gradually replaced by **8a** as the major product when either t_{eq} or the equilibration temperature (T_{eq}) were increased.

The results obtained are consistent with the general reaction scheme depicted in Figure 2. Bromide ion adds to **13** to give the "ate" ion **14**, which collapses via anionotropic 1,2-shift of a boron ligand to the migration terminus represented by the 3-bromoprop-1-en-1-yl group. Bromide displays a migratory aptitude higher than cyclohexyl and, consequently, the α-bromoallylborane **15** is the major product (path *A*), when R = *c*-C_6H_{11} and at short reaction time. After a longer equilibration time, α-substituted and γ-substituted allyl boranes **17** and **18** become the dominant products. Disappearance of **15** after t_{eq} = 1 h indicates that two different reaction channels are possible, converging into the α-substituted allyl borane **17**: a direct route due to the alkyl group migration in **14** (path B), and a second involving bromide quaternization of **15** to give the new borate complex **16**, followed by alkyl migration. Once the α-alkyl substituted allyl borane **17** is formed, conversion into the more thermodynamically stable γ-alkyl substituted allyl borane **18** takes place with a rate constant depending on temperature,[9a] solvent and on the R group (*vide infra*).

Unravelling the overall reactions cascade shown in Figure 2, gave us the fundamental background for

Table 1. Quenching Experiments of 9 with Benzaldehyde (3 h at 0 °C) after Equilibration with TEBABr (10% Mol)[a]

entry	solvent	protocol[b]	t_{eq} (h)	T_{eq} (°C)	**6a**[c] (*E*/*Z*) (%)	**7a**[c] (*E*/*Z*) (%)	**8a**[c] (anti/syn) (%)
1	THF	A			65 (15:85)	<3	nd[d]
2	THF	B	1	0	32 (15:85)	nd	33 (>98:2)
3	THF	B	2	0	14 (15:85)	nd	54 (>98:2)
4	THF	B	1	20	nd	nd	68 (>98:2)
5	nC_5H_{12}	B	1	20	5	37 (90:10)	<3
6	nC_5H_{12}/CH_2Cl_2 9:1	B	1	20	11 (18/82)	55 (90:10)	3
7	nC_5H_{12}/THF 3:1	B	1	20	9 (16/84)	4	28 (>98:2)

[a] Freshly distilled propargyl bromide was used for the preparation of **9**. [b] Protocol A: to a THF solution of **9** are added, in turn, the aldehyde and TEBABr. Protocol B: to a THF solution of **9** TEBABr is added, and after equilibration (t_{eq}, T_{eq}) the aldehyde is added. For further details see the Experimental Section. [c] Isolated yields. [d] Not detected.

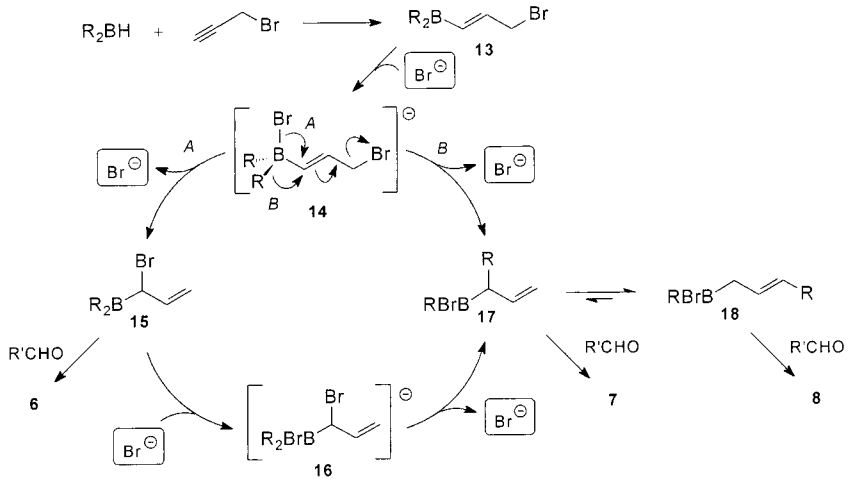


Figure 2. Overall mechanistic scheme for the bromide-catalyzed reaction cascade of **13**.

developing two selective one-pot protocols for the synthesis of homoallylic alcohols **6** and **8** in THF, respectively.

Thus, synthesis of **6** can be achieved if dicyclohexylborane is used and if protocol A is adopted, allowing the intermediate α-bromoallylborane **15** to be trapped by the aldehyde before it undergoes further quaternization to **16**[10] and final conversion to **17**. In all of our experiments we never detected products due to fluxional equilibration of **15**; these results seems to be not in agreement with observations by Oehlschlager et al. who studied the behavior of the chloro analogous of **15**.[11] It is known that metalation of allyl chloride with hindered lithium dialkylamides[12] affords configurationally stable α-chloroallyllithium which may be trapped by R_2BOR' to give α-chloroallyl boronates (R = alkoxy)[13] or α-chloroallyl boranes (R = alkyl),[12] respectively. The latter derivatives, prepared in diethyl ether at −95 °C in the presence of BF_3, according to the Oehlschlager procedure, proved to undergo rapid haptotropic rearrangement, as a consequence of the presence of the Lewis acid. In our procedure, additional Lewis acids are absent and **15** displays constitutional stability.

Table 2. Synthesis of (*Z*)-1-Bromoalk-1-en-4-ols 6 by Adopting Protocol A, in THF at 0 °C and Using Dicyclohexylborane

entry	RCHO	yield[a] (%)	*E*/*Z*	other products (%)
1	PhCHO	**6a** (56)	15:85	**7a** (<3)
2	PhCH=CHCHO	**6b** (65)	18:82	**7b** (5), **8b** (10)
3	$(CH_3)_2CHCHO$	**6c** (46)	16:84	**7c** (2), **8c** (2)
4	$CH_3(CH_2)_5CHO$	**6d** (55)	12:88	**7d** + **8d** (7)
5	$cC_6H_{11}CHO$	**6e** (63)	14:86	**7e** + **8e** (11)

[a] Isolated yields.

Table 2 collects a few examples of syntheses of (*Z*)-1-bromoalk-1-en-4-ols **6**.

Our stereochemical results are in agreement with observations by Hoffmann on the addition of allylboronates carrying a halogen atom or other electronegative substituents in the α position to aldehydes which leads to (*Z*)-homoallylic alcohols.[14] The usefulness of **6** is enhanced by possibility to apply on it palladium-catalyzed cross coupling reactions leading to (*Z*)-configurated γ-alkyl substituted homoallylic alcohols.

The second synthetic procedure we developed leads to *anti*-homoallylic alcohols **8**.

The synthesis of *anti*-**8** requires complete disappearance of **15** and complete conversion of **17** into **18**.[15] This is simply achieved by adopting protocol B and using THF as solvent. Results collected in Table 3 show that THF favors the complete conversion of **17** into **18** if a t_{eq} = 1

(10) For a phenylselenium equivalent of **16**, see: Yamamoto, Y.; Saito, Y.; Maruyama, K. *J. Org. Chem.* **1983**, *48*, 5408−5409.

(11) (a) Jayaraman, S.; Hu, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1995**, *36*, 4765−4768. (b) Hu, S.; Jayaraman, S.; Oehlschlager, A. C. *J. Org. Chem.* **1996**, *61*, 7513−7520. (c) Hu, S.; Jayaraman, S.; Oehlschlager, A. C. *J. Org. Chem.* **1998**, *63*, 8843−8849. (d) Hu, S.; Jayaraman, S.; Oehlschlager, A. C. *J. Org. Chem.* **1999**, *64*, 3719−3721.

(12) MacDonald, T. L.; Narayanan, B. A.; O'Dell, D. E. *J. Org. Chem.* **1981**, *46*, 1504−1506.

(13) (a) Brown, H. C.; Rangaishenvi, M. V. *Tetrahedron Lett.* **1990**, *31*, 7113−7114. (b) Brown, H. C.; Rangaishenvi, M. V. *Tetrahedron Lett.* **1990**, *31*, 7115−7118. The same α-chloroallyl boronates may be prepared by anionotropic shift in borate species carrying a vinylic and a chloromethyl substituent: (c) Matteson, D. S.; Ray, R.; Rocks, R. R.; Tsay, D. J. *Organometallics* **1983**, *2*, 1536. (d) Hoffmann, R. W.; Landmann, B. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 437.

(14) (a) Hoffmann, R. W.; Landmann, B. *Chem. Ber.* **1986**, *119*, 2013−2024. (b) Hoffmann, R. W.; Landmann, B. *Chem. Ber.* **1986**, *119*, 1039−1053. (c) Hoffmann, R. W.; Landmann, B. *Tetrahedron Lett.* **1983**, 3209−3212.

Table 3. Synthesis of *anti*-8 Adopting Protocol B (THF, t_{eq} = 1 h, T_{eq} = 0 °C → 20 °C)

run	R in R_2BH	R′CHO	yield[a] (%)	anti/syn	other products (%)
1	cyclohexyl	PhCHO	**8a** (68)	>98:2	nd[b]
2	cyclohexyl	$(CH_3)_2CHCHO$	**8c** (72)	>98:2	nd
3	cyclohexyl	$CH_3(CH_2)_5CHO$	**8d** (82)	>98:2	nd
4	cyclohexyl	$CH_2{=}C(CH_3)CHO$	**8f** (84)	>98:2	nd
5	cyclohexyl	*O*-TBDMS-L-lactaldehyde	**8g** (80)	*c*	nd
6	cyclohexyl	2,3-*O*-isopropylidene-D-glyceraldehyde	**8h** (40)	*d*	nd
7	cyclopentyl	PhCHO	**8i** (45)	>98:2	nd
8	cyclopentyl	$(CH_3)_2CHCHO$	**8j** (60)	>98:2	nd
9	*n*-octyl[e]	PhCHO	**8k** (40)	>98:2	nd
10	siamyl	PhCHO	**8l** (13)	>98:2	**7l** (50%)
11	siamyl[f]	PhCHO	**8l** (38)	>98:2	**7l** (28%)

[a] Isolated yields. [b] Not detected. [c] No facial selectivity was observed. [d] Facial diastereoselectivity (de) was 70%. [e] Thexyl octylborane was formally used. See Experimental. [f] t_{eq} = 15 h.

h at 20 °C is adopted when cyclohexyl, cyclopentyl, or a primary alkyl migrating group are used (entries 1−9).

Besides solvent and temperature, the haptotropic rearrangement in substituted allylic boranes also depends on the nature of the alkyl substituent on the allyl fragment. In fact, a very slow rearrangement at room temperature in THF was observed in the case of the siamyl subsituent, as demonstrated by the results of entries 10 and 11, where the **8l**/**7l** ratio increased from 0.3 to 1.3 when t_{eq} was increased from 1 to 15 h.

Chemical yields reported in Tables 1−3 deserve a comment: they refer to pure isolated products and generally lie in the 40−80% range. By a synthetic point of view they can be considered acceptable values since they correspond to the overall yield of a one-pot multistep sequence which requires 7 h for its completion, starting from the preparation of the dialkylborane up to the final workup of the condensation reaction.

A main limit of the scope of the proposed synthetic protocols is represented by the limited number of dialkylboranes which may be directly produced by hydroboration of two equivalents of an alkene.[16] Indirect routes to dialkylboranes, such as hydroboration of two equivalents of an alkene with chloroborane or bromoborane followed by reduction with aluminum hydrides[17] are less practical and leave acidic species into the reaction mixture which may affect the haptotropic rearrangement. Since both the hydroboration of terminal alkynes and that of terminal alkenes are very fast, we developed the following solution for the preparation of **13** carrying an octyl group on boron. We envisaged in thexylborane a good regioselective hydroborating agent and treated it with an equimolar solution of 1-octene and propargyl bromide at −20 °C, then leaving the temperature to raise to 20 °C. Final yield of **8k** (40%, Table 3, entry 9) is acceptable, considering that nine elementary steps are involved in this one-pot sequence.

Coming back to entries 5 and 6 of Table 1, homoallylic alcohols **7** are also, in principle, accessible via protocol **B** by a simple change of the experimental conditions, namely a solvent change from THF to less polar media. Under these conditions the equilibration time was required to allow the conversion of **13** into **17** in acceptable amount, but the fluxional transformation of **17** into the thermodynamically more stable γ-substituted isomer **18** appeared to be much slower than the addition to the aldehyde, thus favoring **7** as major product. A general and practical synthetic protocol leading to **7** is under development and will be published in due course.

Conclusions

A mechanistic study of the reaction of 3-bromoprop-1-en-1-yl dialkyl boranes **13** with bromide ion is presented. A reaction cascade made of anionotropic migrations, quaternization reactions and haptotropic rearrangements takes place affording three types of allylic boranes, namely α-bromoallylborane **15**, α-alkylallylborane **17** and γ-alkylallylborane **18**. By a careful choice of the experimental parameters, conditions can be found in which each single borane prevails. Interesting observations were done on the borotropic shift converting **17** into **18**. It does strongly depend on the solvent polarity, reaction rate being very high in THF and quite lower in pentane; at the best of our knowledge a careful study of the kinetics of borotropic rearrangements in crotyl boranes and boronates in different solvents is still lacking and could be highly desirable. Furthermore, steric bulk of the alkyl substituent of the allylic moiety in substituted allyl boranes does considerably affect the haptotropic rearrangement.

The overall mechanistic picture allowed us to develop two one-pot three-component protocols leading to (*Z*)-1-bromo-alk-1-en-4-ols **6** or to *anti*-homoallylic alcohols **8**. In particular, we wish to emphasize that very few studies are available in the literature relative to the preparation of *anti*-**8** using substituted allyl organometallic reagents with R ≠ Me,[18] in comparison with the terrific amount of papers which dealt in the last two decades with the synthesis of their crotyl analogues.[9,19]

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were recorded at 300 or 200 MHz and 75 or 50 MHz, respectively, in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm (δ) downfield from TMS. GC-MS

(15) The 1,3-borotropic shift in allylic boranes has been widely studied by dynamic NMR experiments and in terms of stereochemical outcome of the process. See, for example: (a) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem*. **1977**, *132*, 9−27. (b) Brown, H. C.; Jadhav, P. K.; Bhat, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 2564−2565. (c) Bubnov, Y. N.; Gurskii, M. F.; Gridnev, I. D.; Ignatenko, A. V.; Ustynyuk, Y. A.; Mstislavsky, V. I. *J. Organomet. Chem*. **1992**, *424*, 127−132. (d) Hoffmann, R. W.; Polachowski, A. *Chem. Eur. J*. **1998**, *4*, 1724−1730.

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(18) (a) Fürstner, A. *Chem. Rev.* **1999**, *99*, 991−1045. (b) Salmon, A.; Carboni, B. *J. Organomet. Chem*. **1998**, *567*, 31−38. (c) Takeda, T.; Miura, I.; Horikawa, Y.; Fujiwara, T. *Tetrahedron Lett.* **1995**, *36*, 1495−1498.

(19) Bloch, R. *Chem. Rev.* **1998**, *98*, 1407−1438.

analyses (70 eV) were performed with a quadrupole instrument. Solvents were dried using standard methods: THF was distilled from lithium aluminum hydride (LAH) and pentane from sodium benzophenone immediately prior to use. All reactions were carried out in oven-dried glassware under an atmosphere of dry argon. All reagents were commercially available (Fluka, Aldrich) and were used without further purification, unless otherwise stated.

Materials. Propargyl bromide was distilled immediately prior the use. Triethylbenzylammonium bromide (TEBABr) was dried and stored under argon in a vacuum desiccator in the presence of P_2O_5. A 2M solution of $BH_3{\cdot}SMe_2$ in THF (Fluka) was handled using Schlenk techniques. Stocks of dicyclohexyl borane have been also prepared, stored under argon at −10 °C, and used for about two weeks.

(*E*)-3-Cyclohexylprop-2-en-1-ol (11). A 2M solution of $BH_3{\cdot}SMe_2$ in THF (2 mL, 4 mmol) was added at 0 °C to a solution of cyclohexene (0.8 mL, 8 mmol) in THF (8 mL), and the reaction mixture was vigorously stirred at 0 °C for 2 h. Aged propargyl bromide (0.4 mL, 4 mmol) was added, and the mixture was stirred for 15 h at 20 °C. Oxidative quenching (H_2O_2/NaOH), followed by extraction with ether and purification by flash-chromatography (SiO_2, cyclohexane) afforded 0.47 g (3.36 mmol, 84%) of **11**. ^{1}H NMR (300 MHz): δ 1.06−1.43 (m, 5H), 1.63−1.75 (m, 5H), 1.90−2.05 (m, 1H), 4.09 (d, J = 5.4 Hz, 2H), 5.58 (dd, J = 5.4/15.6 Hz, 1H), 5.66 (dd, J = 5.4, 15.6 Hz, 1H). ^{13}C NMR (75 MHz): δ 25.9, 26.1, 32.7, 40.2, 63.6, 126.3, 138.8. MS (EI): m/z 122 ([M$^+$ − 18], 30), 109 (34), 99 (70), 81 (100), 67 (98), 55 (54). Anal. Calcd for $C_9H_{16}O$ (140.23): C, 77.09; H, 11.50. Found: C, 77.14; H, 11.45.

General Procedure for the Synthesis of (*Z*)-1-Bromoalk-1-en-4-ols (6). Protocol A (Table 2, Entry 1). A 2 M solution of $BH_3{\cdot}SMe_2$ in THF (0.5 mL, 1 mmol) was added at 0 °C to a solution of cyclohexene (0.2 mL, 2 mmol) in THF (2 mL), and the reaction mixture was vigorously stirred at 0 °C for 1 h. Propargyl bromide (0.1 mL, 1 mmol) was added, and the mixture was stirred for an additional hour, until the white precipitate of dicyclohexyl borane dissolved. Benzaldehyde (0.1 mL, 1 mmol) was added followed by TEBABr (0.013 g), and the temperature was allowed to raise to 20 °C under stirring for 3 h. The reaction was quenched at 0 °C by consecutive addition of 3 N NaOH and 30% H_2O_2 followed by stirring for 30 min. The aqueous layer was extracted with ether (3 × 5 mL), and the combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure to afford a 15:85 mixture of (*E*)- and (*Z*)-diastereoisomers. The diastereomeric ratio was determined by GC−MS and ^{1}H NMR analyses of the crude reaction mixture. Purification of the residue by careful flash-chromatography (SiO_2, cyclohexane/ether 95:5) afforded 0.05 g of analytically pure (*Z*)-**6a** (0.22 mmol, 22%) and 0.08 g (0.80 mmol, 34%) of a 25:75 mixture of (*E*)- and (*Z*)-**6a**. Spectral data of the major pure diastereoisomer are reported, while only ^{13}C NMR and GC-MS spectra are reported for (*E*)-**6a**. ^{1}H NMR coupling constants allowed us to assign the stereochemistry of major (*Z*)-**6a**, re-enforced by ^{13}C NMR chemical shifts of both (*E*)- and (*Z*)-**6a**, on the basis of comparison with literature data.[14a,20]

(*Z*)-1-Phenyl-4-bromobut-3-en-1-ol (6a). ^{1}H NMR (300 MHz): δ 2.66 (dd, J = 6.3/14.5 Hz, 1H), 2.75 (dd, J = 7.8/14.5 Hz, 1H), 4.85 (br t, J ∼ 6.6 Hz, 1H), 6.19 (q, J = 6.9 Hz, 1H), 6.29 (d, J = 6.9 Hz, 1H), 7.28−7.42 (m, 5H). ^{13}C NMR (75 MHz): δ 39.2, 72.9, 109.9, 125.7, 127.7, 128.4, 130.7, 143.4. MS (EI): m/z 128 (2), 108 (8), 107 (100), 105 (8), 79 (85), 77 (53), 51 (19). Anal. Calcd for $C_{10}H_{11}BrO$ (227.10): C, 52.89; H, 4.88. Found: C, 52.81; H, 4.84.

(*E*)-1-Phenyl-4-bromobut-3-en-1-ol (6a). ^{13}C NMR (75 MHz): δ = 42.3, 73.0, 107.1, 125.6, 127.7, 128.3, 133.7, 143.2. MS (EI): m/z 128 (2), 108 (8), 107 (100), 105 (8), 79 (80), 77 (55), 51 (20).

General Procedure for the Synthesis of *anti*-Homoallylic Alcohols 8 Starting from Propargyl Bromide. Protocol B (Table 3, Entry 1). A 2 M solution of $BH_3{\cdot}SMe_2$ in THF (0.5 mL, 1 mmol) was added at 0 °C to a solution of cyclohexene (0.2 mL, 2 mmol) in THF (2 mL), and the reaction mixture was vigorously stirred at 0 °C for 1 h. Propargyl bromide (0.1 mL, 1 mmol) was added, and the mixture was stirred for an additional 1 h, until the white precipitate of dicyclohexyl borane dissolved. TEBABr (0.013 g) was added, and the reaction mixture was equilibrated with stirring for 1 h while the temperature was allowed to raise to 20 °C. Benzaldehyde (0.1 mL, 1 mmol) was added, and the mixture was stirred at 20 °C for 3 h. The reaction was quenched at 0 °C by the consecutive addition of 3 N NaOH and 30% H_2O_2 followed by stirring for 30 min. The aqueous layer was extracted with ether (3 × 5 mL), and the combined organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. Purification of the residue by flash-chromatography (SiO_2, cyclohexane/ether 95:5) afforded 0.16 g (0.68 mmol, 68%) of *anti*-**8a**. Signals due to *syn*-**8a** in the crude ^{1}H NMR spectra were close to the detection limit or absent.

***anti*-1-Phenyl-2-cyclohexylbut-3-en-1-ol (8a).** ^{1}H NMR (300 MHz): δ 0.95−1.32 (m, 6H), 1.58−1.82 (m, 5H), 2.14 (br dt, J ∼ 3.9/9.0 Hz, 1H), 4.70 (d, J = 8.1 Hz, 1H), 5.10 (dd, J = 2.1/17.1 Hz, 1H), 5.26 (dd, J = 2.1/10.1 Hz, 1H), 5.83 (dt, J = 10.1/17.1 Hz, 1H), 7.27−7.40 (m, 5H). ^{13}C NMR (75 MHz): δ 26.3, 26.4, 26.5, 28.6, 37.8, 58.6, 73.8, 119.3, 126.7, 127.4, 128.1, 136.6, 143.0. MS (EI): m/z 124 (33), 107 (100), 82 (13), 81 (11), 79 (32), 77 (16), 67 (7). Anal. Calcd for $C_{16}H_{22}O$ (230.35): C, 83.43; H, 9.63. Found: C, 83.35; H, 9.68.

***trans*-2,2-Dimethyl-4-phenyl-5-cyclohexyl-1,3-dioxane (12).** A solution of **8a** (0.23 g, 1 mmol) in CH_2Cl_2 (20 mL) was ozonized for 30 min at −78 °C. The reaction mixture was quenched at −78 °C with $BH_3{\cdot}SMe_2$ (∼10M, 0.4 mL, 4 mmol) and allowed to reach 20 °C. The reaction mixture was quenched with 3N HCl and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried (Na_2SO_4), concentrated at reduced pressure and the residue was purified by flash-chromatography (SiO_2, cyclohexane:acetate 80:20) to afford 0.182 g (0.78 mmol, 78%) of 1-phenyl-2-cyclohexylpropan-1,3-diol. ^{1}H NMR (300 MHz): δ 0.80−1.90 (m, 11H), 1.96−2.15 (m, 2H), 3.74−3.82 (m, 2H), 5.03 (d, J = 9.3 Hz, 1H), 7.20−7.45 (m, 5H). ^{13}C NMR (75 MHz): δ 26.5, 26.6, 26.9, 29.4, 31.6, 35.9, 51.7, 61.9, 76.6, 126.0, 127.2, 128.2, 144.0. Anal. Calcd for $C_{15}H_{22}O_2$ (234.34): C, 76.88; H, 9.46. Found: C, 76.95; H, 9.43.

To a solution of the diol (0.165 g, 0.7 mmol) in CH_2Cl_2 (2 mL) were added 2,2-dimethoxypropane (0.18 mL, 1.4 mmol) and a catalytic amount of Amberlyst 15H, and the reaction mixture was stirred at 20 °C for 1 h. The solution was filtered (Celite) and evaporated to dryness. Purification of the residue by flash chromatography (SiO_2, cyclohexane/acetate 90:10) afforded 0.178 g (0.65 mmol, 83%) of title compound **12** as a white solid. Mp: 77−78 °C. ^{1}H NMR (300 MHz): δ 0.75−1.98 (m, 8H), 1.46 (s, 3H), 1.55 (s, 3H), 1.55−1.80 (m, 3H), 1.81−1.86 (m, 1H), 3.84−4.05 (m, 2H), 4.82 (d, J = 10.7 Hz, 1H), 7.20−7.42 (m, 5H). ^{13}C NMR (75 MHz): δ 26.5, 26.7, 26.8, 28.0, 29.7, 31.4, 36.5, 46.0, 61.3, 75.0, 98.5, 127.5, 127.9, 128.3, 140.6. MS (EI): m/z 259 ([M$^+$ − 15], 2), 117 (25), 110 (100), 107 (46), 95 (14), 91 (11), 81(50), 67 (16), 55 (7). Anal. Calcd for $C_{18}H_{26}O_2$ (274.40): C, 78.79; H, 9.55. Found: C, 78.82; H, 9.49.

(Table 3, Entry 5): 2-*tert*-Butyldimethylsilyloxy-4-cyclohexylhex-5-en-3-ol (8g). By applying protocol B to *O*−*t*butyldimethylsilyl-L-lactaldehyde, the title product was obtained in overall 83% yield as a 50/50 mixture of (2*S*,3*S*,4*R*)-**8g** and (2*S*,3*R*,4*S*)-**8g**; the diastereomeric ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. Assignment of stereochemical relationships was made by converting homoallylic alcohols into their corresponding 1,3-dioxolane-2-ones (Scheme 3). ^{13}C NMR chemical shifts of carbons directly connected to the cyclic framework allowed us to assign the relative cis/trans stereochemistry. In the case of cis substitu-

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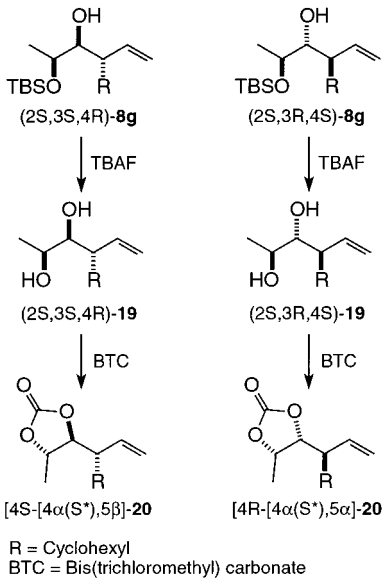
Scheme 3



tion, a marked γ-gauche effect results in a upfield shift of both resonance lines of 3−5 ppm with respect to the trans isomer.[20,21]

(2*S*,3*S*,4*R*)-8g. *Y* = 42%. R_f = 0.37 (cyclohexane/ethyl acetate 95:5). $[\alpha]^{20}_D$ = +8.6 (*c* = 1.50, $CHCl_3$). ^{1}H NMR (300 MHz): δ 0.09 (s, 6H), 0.90 (s, 9H), 0.72−1.01 (m, 2H), 1.08 (d, *J* = 6.1 Hz, 3H), 1.12−1.34 (m, 4H), 1.41−1.81 (m, 5H), 1.82−1.95 (m, 1H), 3.46 (dd, *J* = 3.2/7.5 Hz, 1H), 3.70 (dq, *J* = 6.4/7.5 Hz, 1H), 4.90 (dd, *J* = 2.4/17.3 Hz, 1H), 5.09 (dd, *J* = 2.4/10.2 Hz, 1H), 5.78 (dt, *J* = 10.2/17.3 Hz, 1H). ^{13}C NMR (75 MHz): δ −4.8, −4.0, 18.0, 19.4, 25.8, 26.5, 26.7, 31.1, 31.2, 37.9, 51.8, 70.8, 75.0, 116.7, 137.3. MS (EI): *m*/*z* 255 ([M^+ − 57], 1), 189 (4), 173 (15), 163 (10), 159 (34), 131 (34), 119 (100), 103 (13), 95 (8), 82 (36), 75 (62), 73 (50), 67 (10), 55(15). Anal. Calcd for $C_{18}H_{36}O_2Si$ (312.57): C, 69.17; H, 11.61. Found: C, 69.23; H, 11.68.

(2*S*,3*R*,4*S*)-8g. *Y* = 41%. R_f = 0.18 (cyclohexane/ethyl acetate 95:5). $[\alpha]^{20}_D$ = +6.7 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz): δ 0.08 (s, 3H), 0.09 (s, 3H), 0.90 (s, 9H), 0.92−1.44 (m, 6H), 1.13 (d, *J* = 6.2 Hz, 3H), 1.51−1.80 (m, 5H), 2.01 (br dt, *J* ∼ 6.1/9.6 Hz, 1H), 3.63 (dd, *J* = 4.5/6.6 Hz, 1H), 3.86 (dq, *J* = 4.5/6.2 Hz, 1H), 5.04 (dd, *J* = 2.2/17.2 Hz, 1H), 5.17 (dd, *J* = 2.2/10.3 Hz, 1H), 5.76 (dt, *J* = 10.3/17.2 Hz, 1H). ^{13}C NMR (75 MHz): δ −4.8, −4.2, 17.4, 18.1, 25.8, 26.6, 29.2, 31.7, 38.2, 51.3, 69.6, 74.7, 117.4, 137.1. MS (EI): *m*/*z* 255 ([M^+- 57], 1), 189 (2), 173 (8), 163 (8), 159 (57), 131 (28), 119 (100), 115 (13), 103 (19), 95 (7), 81 (51), 75 (60), 73 (60), 67 (15), 55(16). Anal. Calcd for $C_{18}H_{36}O_2Si$ (312.57): C, 69.17; H, 11.61. Found: C, 69.14; H, 11.65.

(2*S*,3*S*,4*R*)-4-Cyclohexylhex-5-ene-2,3-diol 19. A 1 M solution of tetrabutylammonium fluoride in THF (0.76 mL, 0.76 mmol) was added to a solution of (2*S*,3*S*,4*R*)-**8g** (0.2 g, 0.64 mmol) in THF (2 mL), and the reaction mixture was stirred at 20 °C for 4 h. The reaction was quenched with water, and the aqueous layer was extracted twice with ether. The combined organic layers were dried (Na_2SO_4) and evaporated at reduced pressure. The residue was purified by flash chromatography (SiO_2, cyclohexane/ethyl acetate 70:30) to afford 0.116 g (0.56 mmol, 92%) of (2*S*,3*S*,4*R*)-**19**. $[\alpha]^{20}_D$ = −11.7 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (300 MHz): δ 0.79−1.08 (m, 2H), 1.18 (d, *J* = 6.3 Hz, 3H), 1.18−1.38 (m, 3H), 1.55−1.80 (m, 6H), 1.80−1.90 (m, 1H), 2.05 (d, *J* = 5.1 Hz, 1H), 2.13 (d, *J* = 4.1 Hz, 1H), 3.51 (dt, *J* = 4.1/6.3 Hz, 1H), 3.73 (dquintet, *J* = 5.1/6.3 Hz, 1H), 5.02 (dd, *J* = 2.2/17.3 Hz, 1H), 5.18 (dd, *J* = 2.2/10.3 Hz, 1H), 5.78 (dt, *J* = 10.3/17.3 Hz, 1H). ^{13}C NMR (75 MHz): δ 19.1, 26.4, 26.5, 30.8, 31.1, 37.3, 52.5, 69.2, 74.8, 117.7, 136.9. Anal. Calcd for $C_{12}H_{22}O_2$ (198.31): C, 72.68; H, 11.18. Found: C, 72.73; H, 11.23.

(2*S*,3*R*,4*S*)-4-Cyclohexylhex-5-ene-2,3-diol 19. Applying the same procedure reported above to (2*S*,3*R*,4*S*)-**8g**, (2*S*,3*R*,4*S*)-**19** was obtained in 94% overall yield. $[\alpha]^{20}_D$ = +6.7 (*c* = 1.1, $CHCl_3$). ^{1}H NMR (300 MHz): δ 0.80−1.48 (m, 6H), 1.22 (d, *J* = 6.4 Hz, 3H), 1.52−1.79 (m, 6H), 1.84 (d, *J* = 7.8 Hz, 1H), 1.99 (dt, *J* = 6.0/9.9 Hz, 1H), 3.68 (dt, *J* = 4.9/6.0 Hz, 1H), 3.83 (ddq, *J* = 4.9/6.4/7.8 Hz, 1H), 5.12 (dd, *J* = 2.1/17.1 Hz, 1H), 5.23 (dd, *J* = 2.1/9.9 Hz, 1H), 5.80 (dt, *J* = 9.9/17.1 Hz, 1H); ^{13}C NMR (75 MHz): δ = 17.8, 25.6, 26.5 (2C), 29.4, 31.7, 37.6, 52.4, 68.9, 73.8, 118.5, 137.3. Anal. Calcd for $C_{12}H_{22}O_2$ (198.31): C, 72.68; H, 11.18. Found: C, 72.75; H, 11.14.

[4*S*-[4α(*S),5*β*]-4-(1-Cyclohexyl-2-propenyl)-5-methyl-1,3-dioxolan-2-one 20.** Bis(trichloromethyl) carbonate (0.058 g, 0.19 mmol) and triethylamine (0.055 mL, 0.39 mmol) were added to a solution of (2*S*,3*S*,4*R*)-**19** (0.035 g, 0.18 mmol) in CH_2Cl_2 (1 mL). After 1 h, the reaction was quenched with water, and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by flash chromatography (SiO_2, cyclohexane/ethyl acetate 90:10) affording 0.038 g (0.17 mmol, 94%) of trans cyclic carbonate **20**. $[\alpha]^{20}_D$ = −19.0 (*c* = 1.64, $CHCl_3$). ^{1}H NMR (300 MHz): δ 0.81−1.47 (m, 6H), 1.44 (d, *J* = 6.4 Hz, 3H), 1.45−1.89 (m, 6H), 4.42 (dd, *J* = 2.6/7.0 Hz, 1H), 4.51 (br quintet, *J* = 7.0 Hz, 1H), 5.11 (dd, *J* = 1.8/17.1 Hz, 1H), 5.30 (dd, *J* = 1.8/10.3 Hz, 1H), 5.68 (dt, *J* = 10.3/17.1 Hz, 1H). ^{13}C NMR (75 MHz): δ 19.1, 26.1 (2C), 26.2, 30.7, 30.8, 38.5, 52.7, 76.4, 83.0, 120.5, 133.4, 154.6. MS (EI): *m*/*z* 142 (66), 123 (13), 98 (62), 83 (36), 81 (99), 80 (78), 79 (75), 69 (17), 67 (57), 55 (100). Anal. Calcd for $C_{13}H_{20}O_3$ (224.30): C, 69.61; H, 8.99. Found: C, 69.55; H, 9.05.

[4*R*-[4α(*S),5*β*]-4-(1-Cyclohexyl-2-propenyl)-5-methyl-1,3-dioxolan-2-one 20.** Applying the same procedure reported above to (2*S*,3*R*,4*S*)-**19**, cis cyclic carbonate **20** was obtained in 90% overall yield. $[\alpha]^{20}_D$ = +8.0 (*c* = 2.80, $CHCl_3$). ^{1}H NMR (300 MHz): δ = 0.84−1.40 (m, 6H), 1.43 (d, *J* = 6.5 Hz, 3H), 1.51−1.81 (m, 5H), 2.17−2.24 (m, 1H), 4.76 (dd, *J* = 6.0/6.7 Hz, 1H), 4.85 (br quintet, *J* = 6.7 Hz, 1H), 5.14 (dd, *J* = 1.7/17.2 Hz, 1H), 5.27 (dd, *J* = 1.7/10.4 Hz, 1H), 5.74 (dt, *J* = 10.4/17.2 Hz, 1H). ^{13}C NMR (75 MHz): δ = 14.3, 26.2, 26.3, 26.4, 29.0, 31.3, 39.6, 49.0, 76.6, 79.9, 119.7, 133.7, 154.6. MS (EI): *m*/*z* 142 (80), 123 (19), 99 (10), 98 (51), 83 (36), 81 (100), 80 (60), 79 (55), 69 (13), 67 (40), 55 (53). Anal. Calcd for $C_{13}H_{20}O_3$ (224.30): C, 69.61; H, 8.99. Found: C, 69.53; H, 8.94.

(Table 3, Entry 6): 2,2-Dimethyl-α-(1-cyclohexyl-2-propenyl)-1,3-dioxolane-4-methanol (8h). By applying protocol B to D-glyceraldehyde acetonide, the title product was obtained in overall 40% yield as a 85/15 mixture of [4*R*-[4*R**-[*R**(*R**)]]]-**8h** and [4*R*-[4*R**[*S**(*S**)]]]-**8h**; the diastereomeric ratio was determined by ^{1}H NMR on the crude reaction mixture. We assigned the anti-anti stereorelationship to the most abundant isomer on the basis of the well-known intrinsic diastereofacial preference of glyceraldehyde acetonide observed in the addition of allyl organometallic species,[22] allylic boronates,[23] and borolanes.[24]

[4*R*-[4*R[*S**(*S**)]]]-8h.** *Y* = 6%. R_f = 0.30 (cyclohexane/ethyl acetate 90:10). $[\alpha]^{20}_D$ = +1.0 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (300 MHz): δ 0.72−1.42 (m, 6H), 1.36 (s, 3H), 1.43 (s, 3H), 1.45−1.78 (m, 5H), 1.78−1.92 (m, 1H), 3.59 (dd, *J* = 6.7/8.0 Hz, 1H), 3.72 (dd, *J* = 2.6/7.9 Hz, 1H), 3.99 (dd, *J* = 6.4/8.0 Hz, 1H), 4.08 (dt, *J* = 6.7/7.9 Hz, 1H), 4.91 (dd, *J* = 2.2/17.2 Hz, 1H), 5.13 (dd, *J* = 2.2/10.3 Hz, 1H), 5.81 (dt, *J* = 10.3/17.2

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Hz, 1H). ^{13}C NMR (75 MHz): δ 25.5, 26.4, 26.6, 26.9, 31.08, 31.14, 37.4, 52.9, 65.8, 72.3, 78.3, 109.4, 117.3, 136.9. MS (EI): *m*/*z* 239 ([M$^+$ − 15], 6), 153(4), 131 (100), 124 (6), 101 (51), 95 (7), 83 (16), 81 (13), 59 (35), 55 (17). Anal. Calcd for $C_{15}H_{26}O_3$ (254.37): C, 70.83; H, 10.30. Found: C, 70.92; H, 10.35.

[4*R*-[4*R[*R**(*R**)]]]-8h.** *Y* = 34%. R_f = 0.15 (cyclohexane/ethyl acetate 90:10). $[\alpha]^{20}_D$ = +3.0 (*c* = 1.40, $CHCl_3$). ^{1}H NMR (300 MHz): δ = 0.82−1.29 (m, 5H), 1.36 (s, 3H), 1.42 (s, 3H), 1.32−1.53 (m, 1H), 1.58−1.82 (m, 5H), 1.95 (ddd, *J* = 3.5/7.5/10.3 Hz, 1H), 3.90−4.07 (m, 4H), 5.08 (dd, *J* = 2.2/17.1 Hz, 1H), 5.18 (dd, *J* = 2.2/10.3 Hz, 1H), 5.74 (dt, *J* = 10.3/17.1 Hz, 1H). ^{13}C NMR (75 MHz): δ = 25.3, 26.37, 26.40, 26.5, 26.7, 30.7, 31.1, 37.8, 52.2, 65.6, 71.0, 77.8, 108.3, 118.2, 136.5. MS (EI): *m*/*z* 239 ([M$^+$ − 15], 12), 153 (9), 131 (46), 124 (15), 101 (100), 95 (12), 83 (25), 81 (24), 59 (43), 55 (22). Anal. Calcd for $C_{15}H_{26}O_3$ (254.37): C, 70.83; H, 10.30. Found: C, 70.77; H, 10.26.

(Table 3, Entry 9): *anti*-1-Phenyl-2-ethenyldecan-1-ol (8k). To a stirred THF solution (3 mL) of 2,3-dimethyl-2-butene (0.24 mL, 2 mmol) was added BH_3·SMe_2 (2 M solution in THF, 1 mL, 2 mmol) at −20 °C. After 2 h at −20 °C, a solution of propargyl bromide (0.2 mL, 2 mmol) and 1-octene (0.32 mL, 2 mmol) in THF (1 mL) was added, and the solution was allowed to reach 20 °C in 2 h under stirring. TEBABr (0.055 g) was added, and the heterogeneous mixture was equilibrated at 20 °C for 1 h. Benzaldehyde (0.2 mL, 2 mmol) was added, and the reaction mixture was stirred at 20 °C for 3 h. Oxidative workup (H_2O_2/NaOH) followed by extraction with ether (3 × 5 mL) and purification by flash chromatography (SiO_2, cyclohexane/ethyl acetate 95:5) afforded 0.21 g (0.8 mmol, 40%) of the title compound. ^{1}H NMR (300 MHz): δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.02−1.35 (m, 14H), 2.30 (br quintet, *J* ∼ 7.5 Hz, 1H), 4.39 (d, *J* = 7.8 Hz, 1H), 5.20 (ddd, *J* = 0.6/2.1/17.1 Hz, 1H), 5.27 (dd, *J* = 2.1/10.2 Hz, 1H), 5.67 (ddd, *J* = 9.0/10.2/17.1 Hz, 1H), 7.22−7.41 (m, 5H). ^{13}C NMR (50 MHz): δ 14.1, 22.6, 27.1, 29.2, 29.4 (2C), 30.3, 31.8, 52.5, 76.5, 118.3, 126.8, 127.3, 128.0, 139.2, 142.4. MS (EI): *m*/*z* 154 (2), 129 (2), 115 (1), 107 (100), 91 (3), 79 (33), 77 (17), 55 (5). Anal. Calcd for $C_{18}H_{28}O$ (260.42): C, 83.02; H, 10.84. Found: C, 83.09; H, 10.80.

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Supporting Information Available: Spectral and analytical data for compounds **6b**−**e**, **7l**, **8c**,**d**,**f**,**i**,**j**,**l**. This material is available free of charge via the Internet at http://pubs.acs.org.

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