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3-Bromopropenyl Esters in Organic Synthesis: Indium- and Zinc-Mediated Entries to Alk-1-ene-3,4-diols†

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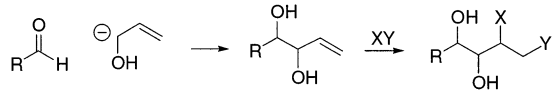
Metallic indium and zinc readily add to 3-bromopropenyl acetate (**5**) and benzoate (**6**) either in THF or in water, affording the corresponding 3-acyloxyallyl organometallic compounds. Nucleophilic addition to aldehydes opens a route to alk-1-ene-3,4-diols **2** in good to excellent yields. Two synthetic protocols were developed, the former involving indium in THF under Grignard conditions and the latter involving zinc in aqueous ammonium chloride under Barbier conditions. The diastereoselectivity, under all the conditions examined, mainly depends on the nature of the carbonyl compound; conjugated aldehydes afford *syn* adducts **2**, while unconjugated aldehydes display the opposite *anti* stereopreference.

Introduction

One of the best strategies for the synthesis of densely functionalized carbon chains involves the addition of synthetic equivalents of the 1-hydroxyallyl anion (**1**) to carbonyl compounds. The α-hydroxyallylation reaction motif, the alk-1-ene-3,4-diol structure **2**, provides a flexible framework useful for further manipulation; for example, **2** can be converted into a variety of tetrafunctional target molecules **3**, as shown in Scheme 1.

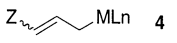
SCHEME 1



1 **2** **3**

X , Y = "O", OH, NH_2

In the last two decades, a number of synthetic equivalents of **1**, with general structure **4** (Figure 1), have been developed and the stereochemical outcome of their addition to carbonyl compounds has been examined, both in terms of simple diastereoselectivity and of facial selectivity, when chiral carbonyl compounds were involved.[1,2]



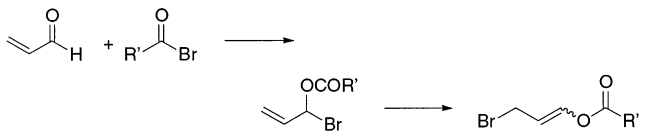
4

FIGURE 1.

Results and Discussion

Preparation of 3-Bromopropenyl Esters. Heterosubstituted allylic complexes **4** are almost invariably prepared by lithiation at low temperature of a protected allylic alcohol followed by transmetalation with the desired metal halide.[1,2] Here, we report an alternative, more practical, and economic route to **4** that involves the oxidative addition of metallic indium and zinc to the carbon−halogen bond of a suitable 3-heterosubstituted allyl bromide, prepared by haloacylation of acrolein.[3,4] When acrolein was reacted with acetyl bromide or benzoyl bromide for 3 days, the 1,2-addition product initially formed slowly rearranged into the more stable 1,4-addition product **5** (*E*/*Z* = 80:20) or pure *E*-**6**. The overall process takes place much more efficiently in a few hours in the presence of a catalytic amount of $ZnCl_2$. By applying this procedure, we synthesized 3-bromopropenyl esters **5** and **6** in multigram scale and 50−60% yield after distillation (**5**) or crystallization (**6**) (Scheme 2). Interestingly, the presence of the Lewis acid strongly affects the C=C bond configuration of 3-bromopropenyl esters **5** and **6**, which are obtained as *E*/*Z* = 35:65 and 50:50 mixtures, respectively.

SCHEME 2



5 : R' = CH_3
6 : R' = C_6H_5

The usefulness of **5**, as precursor of indium and zinc complexes **7** and **8** *via* oxidative addition (Scheme 3), was preliminarily attested by us in two approaches to alk-1-ene-3,4-diols **2**, differing on the metal used and on the protocol adopted.[2,5]

Preparation of Acetoxyallylindium in THF. Despite an extensive interest on indium-mediated organo-

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† In memory of Professor Angelo G. Giumanini.

(1) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207.
(2) Lombardo, M.; Girotti, R.; Morganti, S.; Trombini, C. *Org. Lett.* **2001**, *3*, 2981 and references therein.
(3) Ulich, L. H.; Adams, R. *J. Am. Chem. Soc.* **1921**, *43*, 660.
(4) Neuenschwander, M.; Bigler, P.; Christen, K.; Iseli, R.; Kyburz, R.; Mühle, H. *Helv. Chim. Acta* **1978**, *61*, 2047.

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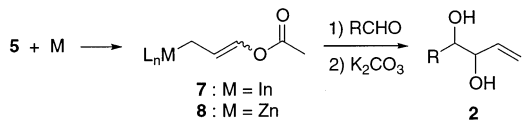
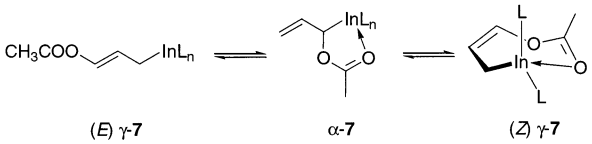
SCHEME 3



metallic reactions,[6] a single NMR study by Chan appeared in the literature affording evidence about the formation of discreet allylindium species, when metallic indium is treated with allyl bromide in water or in aprotic solvents.[7] In analogy to the Chan experiment, we reacted **5** (as a 35:65 *E*/*Z* mixture) with indium in THF-d_8 and followed the reaction by ^{1}H NMR. Despite the complexity of the spectra, clear information could be traced out. The initial enolic proton signals of **5** at 7.43 ppm (dt, J = 1.0/12.2 Hz, *E*-**5**) and 7.19 ppm (dt, J = 0.8/6.2 Hz, *Z*-**5**) begin to disappear and new signals, due to discreet allylic indium intermediates (*E*) γ-7 (at 7.08 ppm, dt, J = 1.4/12.0 Hz), (*Z*) γ-7 (at 6.93 ppm, dt, J = 1.4/6.2 Hz), and α-7 (two multiplets at 5.61−5.96 and 5.03−5.50 ppm), reached a maximum after 0.5 h and then kept almost constant for the following 20 h. The two multiplets due to α-**7** contain contributions of vinylic hydrogens of Wurtz dimerization products, and of H-**2** of (*E*) and (*Z*) γ-**7**. Since the amount of dimerization products was determined to range from 5 to 10% in a series of independent reactions, we could deduce from integral ratios, after subtraction of the known contributions, the following composition: α-**7**/(*Z*) γ-**7**/(*E*) γ-**7** ≈ 50:40:10 (Scheme 4).

SCHEME 4



We are not in the position to assign the observed intermediates to In^I or In^{III} species, however, according to Chan results,[7] intermediates **7** are expected to correspond to In^{III} species, since In^I signals should have been greatly reduced or completely disappeared after 20 h.

Since the same α-**7**/(*Z*) γ-**7**/(*E*) γ-**7** ratio was observed after 3 h using an *E* enriched mixture of **5** (*E*/*Z* = 80:20), the observed composition of allyl indium species is supposed to be the result of a thermodynamic equilibration.

In a further experiment, cyclohexanecarboxaldehyde (0.2 equiv) was added to a solution of **7** in THF-d_8 obtained by reacting indium with **5** for 2 h at 25 °C; after 5 min, both (*E*) γ-**7** and (*Z*) γ-**7** peak intensities decreased with respect to internal TMS and reached the 30:70 relative ratio; then, a further 0.4 equiv of cyclohexanecarboxaldehyde was added and (*E*) γ-**7** and (*Z*) γ-**7** intensities decreased to very low levels and reached a ∼1:1 ratio. The ^{1}H NMR did not give any information about α-**7**, since vinylic protons of adduct **9** (Figure 2) resonate at the same frequencies of vinylic protons of α-**7**.

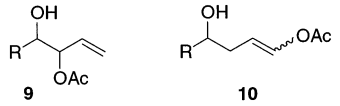


FIGURE 2.

This last experiment told us that (*Z*) γ-**7** is slightly more reactive than (*E*) γ-**7**, and that the kinetic rate constants relative to the addition of (*E*) γ-**7** and (*Z*) γ-**7** to the aldehyde are higher than the (*E*) γ-**7** ⇔ (*Z*) γ-**7** interconversion. Since it is plausible to assume that reactions of **7** with aldehydes occur with allylic inversion via cyclic transition states, we may conclude that α-**7** has no tendency to add to the carbonyl group, since traces of the expected enolacetates **10** (Figure 2) were never detected.

Wurtz-type dimers of **5** were found to be present in 5−10% yield after 4 h at 25 °C, as demonstrated after isolation of hexa-1,5-diene-3,4-diol, upon overnight hydrolysis of the reaction mixture with K_2CO_3 in MeOH/H_2O.

The Reaction of Acyloxyallylindium Reagents with Aldehydes (Grignard Protocol). At the outset of this research, our goal was to exploit zinc in a Grignard-type reaction of **5** (as a 35:65 *E*/*Z* isomer mixture) with aldehydes in THF. When zinc and **5** were stirred for 12 h at 10 °C in THF and cyclohexanecarboxaldehyde was added, **9** (R = cyclohexyl) was isolated in 40% yield as a 12:88 *syn*/*anti* mixture. Quite disappointed by these results, we decided to move to the more expensive but also more reactive indium. Indium immediately revealed much more promising and allowed us to develop a simple synthetic procedure for the synthesis of alk-1-ene-3,4-diols **2**.

In a first set of reactions (Table 1), unless otherwise stated, we preformed the organometallic species in anhydrous THF, by stirring indium powder and **5** or **6** in the 1:1.5 molar ratio, and then an aldehyde (1 equiv) was added.

TABLE 1. Indium-Mediated Grignard Route to Alk-1-ene-3,4-diols 2[a]

entry	substrate (*E*/*Z*)	R-CHO	t_1 (h)	T_2 (°C)	**2** yield[b] (%)	syn/anti
1	**5** (35:65)	Ph	4	0	86	75:25
2	**5** (35:65)	Ph	4	−78	91	85:15
3	**6** (99:1)	Ph	4	0	77	75:25
4	**5** (35:65)	Ph	0	0	80	70:30
5	**5** (75:25)	Ph	0	0	94	70:30
6	**5** (35:65)	cyclohexyl	4	0	90	15:85
7	**5** (35:65)	cyclohexyl	4	−78	70	10:90
8	**6** (50:50)	cyclohexyl	4	0	65	15:85
9	**5** (35:65)	cyclohexyl	0	0	70	10:90
10	**5** (75:25)	cyclohexyl	0	0	88	10:90
11	**5** (35:65)	$(CH_3)_2CH-CH_2-$	4	0	83	35:65
12	**5** (35:65)	$Ph-CH_2-CH_2-$	4	0	95	30:70
13	**5** (35:65)	(*E*)-Ph-CH=CH−	4	0	96	70:30
14	**5** (35:65)	$CH_2=(CH_3)CH-$	4	0	79	85:15
15	**5** (35:65)	2-furyl	4	−78	72	90:10

[a] The following molar ratio was used: indium/**5**/aldehyde = 1:1.5:1. [b] Isolated yields of deprotected diols **2** after overnight treatment of the reaction mixture with K_2CO_3 (3 equiv) in MeOH/H_2O 9:1.

(5) Lombardo, M.; Girotti, R.; Morganti, S.; Trombini, C. *Chem. Commun.* **2001**, 2310.

(6) (a) Cintas, P. *Synlett* **1995**, 1087. (b) Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; Wiley: New York, 1997. (c) Paquette, L. A. In *Green Chemistry: Frontiers in Benign Chemical Synthesis and Processing*; Anastas, P., Williamson, T., Eds.; Oxford University Press: New York, 1998.

(7) Chan, T. H.; Yang, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3228.

TABLE 2. Optimization Studies of the Indium-Mediated Route to Alk-1-ene-3,4-diols 2[a]

entry	R-CHO	T_1(°C)/t_1(min)	cosolvent in step 2	T_2 (°C)/ t_2 (min)	**2** (syn/anti)	**9** (syn/anti)	**12** (syn/anti)	**15** (syn/anti)
1	*c*-C_6H_{11}	0 → 25/240	none	0/240	18 (1:99)	20 (10:90)	25 (4:96)	25 (40:60)
2	C_6H_5	0 → 25/240	none	0/240	33 (45:55)	13 (95:5)	33 (85:15)	13 (99:1)
3	*c*-C_6H_{11}	0 → 25/45	none	25/45	22 (1:99)	10 (5:95)	30 (5:95)	27 (40:60)
4	*c*-C_6H_{11}	0 → 25/45	H_2O[b]	25/45	0	30 (10:90)	0	65 (15:85)
5	*c*-C_6H_{11}	0 → 25/45	H_2O (pH 3)[c]	25/45	0	50 (10:90)	0	45 (20:80)
6	C_6H_5	0 → 25/45	H_2O (pH 3)[c]	25/45	0	50 (65:35)	0	42 (80:20)

[a] All the reactions were carried out on 1 mmol of aldehyde in 2 mL of THF, adopting the same molar ratios reported in Table 1. [b] Water (0.2 mL) was added immediately before the addition of the aldehyde. [c] A pH 3 aq solution (phthalate buffer, 0.2 mL) was added immediately before the addition of the aldehyde.

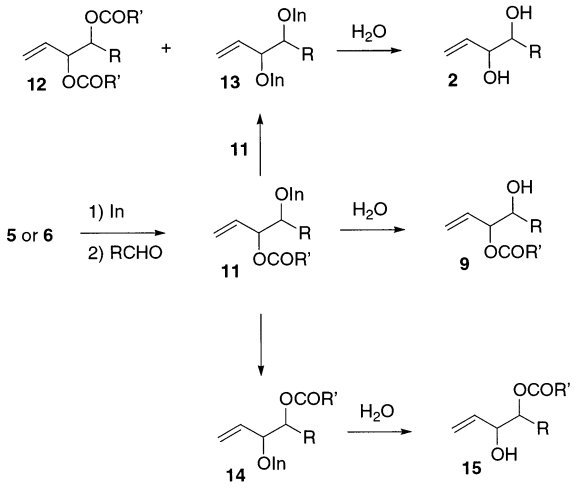
The experimental conditions were fixed as follows:

step 1 (formation of the organometallic species): reaction time (t_1) = 4 h, reaction temperature (T_1) was set at 0 °C for 15 min and then allowed to raise to 25 °C;

step 2 (nucleophilic addition): reaction time (t_2) = 4 h, reaction temperature (T_2) = 0 °C.

A main drawback associated with this procedure is the occurrence of intra- and intermolecular acyl transfer reactions due to nucleophilicity of the intermediate indium alkoxide groups. The overall picture of transesterification reactions occurring downstream the formation of adduct **11** is reported in Scheme 5.

SCHEME 5



To overcome the complexity of the reaction mixture associated to transesterification processes, we directly hydrolyzed the crude reaction mixture containing esters **9**, **12**, and **15** to 1-ene-3,4-diols **2** (K_2CO_3, 3 equiv, methanol/water 9:1). The final *syn*/*anti* ratio of deacylated **2** reflects the original stereopreference of the addition of **7** to the aldehyde, since transesterification reactions do not affect the stereogenic centers formed in the carbonyl addition step.

The most relevant results obtained with indium under Grignard conditions are collected in Table 1.

Isolated chemical yields varied in the range 70−96% yield, and simple diastereoselectivities were found to be dependent on the nature of the aldehyde. In particular, conjugated aldehydes (entries 1−5, 13−15) exhibited *syn* selectivity (*syn*/*anti* = 60/40−90/10), while saturated aldehydes (entries 6−12) clearly showed the inverse *anti* stereopreference (*syn*/*anti* = 35/65−10/90). Such behavior is not common to other heterofunctionalized allylic metal complexes **4**, whose diastereoselectivity is independent of the aldehyde used.

Barbier conditions (t_1 = 0) were also tested (entries 4, 5, 9, and 10), which afforded comparable results in terms of chemical yields but with a slightly lower diastereopreference when benzaldehyde was used.

Furthermore, to check a possible role played by the acyloxy substituent on the stereochemical outcome of the reaction, we carried out two reactions with **6**: the results (Table 1, entries 3 and 8), despite a different distribution of intermediate indium species, revealed an impressive identity in terms of stereochemical results with those obtained with **5** (entries 1 and 6).

Optimization Studies. As previously outlined, the crude reaction mixture contained a group of four products **2**, **12**, **9**, and **15** (Scheme 5). Table 2 collects a few experiments aimed at (i) evaluating the relative amount of each product and their *syn*/*anti* composition, (ii) limiting the occurrence of side reactions, and (iii) optimizing reaction conditions in terms of reaction time and temperature.

Entries 1 and 2 report the product distribution of two model reactions carried out according our previous protocol (Table 1, entries 1 and 6), confirming a high degree of side-transesterification processes. When t_1 was lowered to 45 min and addition to the aldehyde was carried out at T_2 = 25 °C (entry 3), conversion, product distribution, and stereocomposition were almost identical to those obtained in entry 1. What is deduced from entries 1−3 is that *syn* adducts selectively give the intramolecular acyl transfer reaction leading to **15**, as expected by the less congestion of the quasi-eclipsed conformation required for the acyl transfer reaction. On the other hand, *anti* adducts preferentially undergo intermolecular acyl transfer reactions, leading to **2** and **12**.

The subsequent series of experiments (entries 4−6) were designed in order to exploit kinetic advantages offered by water as cosolvent in the carbonyl addition step, both under neutral and acidic pH, as previously reported by Paquette.[8] Besides to affect yield and diastereoselectivity, the hope was to suppress the acetyl scrambling reactions by protonating the intermediate indium alkoxides. Toward this purpose, the organoindium species were preformed, as usual, in anhydrous THF for 45 min, then water (entry 4) or a pH 3 buffered solution (entries 5,6) was added, followed by the addition of the carbonyl compound. Since entry 3 told us that the original reaction times t_1 and t_2 were overestimated and that there was no advantage to carry out the organometallic addition to the aldehyde at 0 °C (entry 3), we set t_1

(8) Paquette, L. A.; Mitzel, T. M. *J. Am. Chem. Soc.* **1996**, *118*, 1931.

and t_2 at 45 min and T_2 at 25 °C. Under these new conditions, intermolecular processes were completely suppressed, but the same did not happen for the intramolecular transesterification, which still was a major side reaction.

Independently of the presence of rearranged adducts **15**, reactions carried out under these new conditions seem to be highly attractive under an overall efficiency point of view, both as refers to chemical yields and to stereoselectivity which seems to increase in absolute terms.

As a further attempt to improve the economy of the reaction, we tested a catalytic version of our protocol in order to reduce the amount of the expensive indium metal, based on the known redox couple formed by indium(III) and cheap commercial manganese powder.[9] Indium powder (0.1 equiv) was added to a stirred mixture of manganese powder (2 equiv), **5** (1.5 equiv), TMSCl (1.1 equiv), and benzaldehyde (1 equiv); adopting the same experimental conditions of Table 1, entry 4 we got the product **2** (R = Ph) in a slightly lower yield (60%) and poorer diastereoselectivity (*syn*/*anti* = 65:35).

The Indium Route to Alk-1-ene-3,4-diols: Simple Diastereoselectivity. Since it is known that the allylmetalation of aldehydes,[10] as well as of imines,[11] is a reversible process, we checked the de values after different time intervals in two reactions, using benzaldehyde and cyclohexancarboxaldehyde, respectively, to ascertain whether the different diastereoselectivities observed with conjugated and unconjugated aldehydes are the result of thermodynamic equilibration. Quenching experiments at different reaction times (5, 10, 30, 60, 120, and 1200 min) following the experimental procedure reported in Table 1 (entries 1 and 6) unambiguously show that there was no change in diastereomeric excess in both cases.

A further experiment to check possible thermodynamic control was designed as follows: two mixtures of monoacetylated products **9** and **15**, deriving from pure *syn*-**2** (R = Ph) and from an anti-enriched mixture of **2** (*syn*/*anti* = 35:65, R = Ph), respectively, were added to a solution of allyliindium derivatives **7**, prepared in THF as previously reported. After stirring at 25 °C for 40 min, quenching, and overnight deacetylation, diol **2** revealed by ^{1}H NMR analysis exactly the same original stereochemical composition. The absence of epimerization under typical reaction conditions confirms that thermodynamic equilibration does not play any role on the final stereochemical outcome.

Thus, the stereochemical outcome of the acetoxyallylation of aldehydes in THF using indium should be controlled by kinetic reasons. On this basis, if both (*E*) γ-**7** and (*Z*) γ-**7** adopted chairlike transition states (TS), according to the classical Zimmermann−Traxler theory, *syn*-**9** should always prevail, (*Z*) γ-**7** being both the more abundant and the more reactive indium intermediate present in solution.

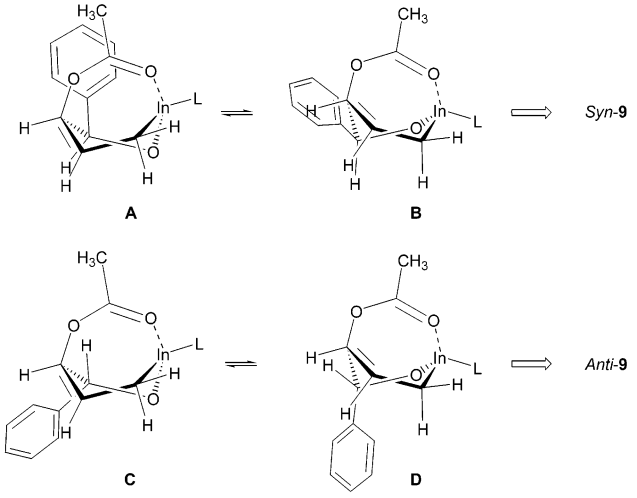


FIGURE 3.

Considering that (*Z*) γ-**7**, the major reactive allylindium species present in solution, is expected to be the major responsible for the final stereochemical outcome, we suggest that twist-boat transition states (TS), stabilized with respect to chairlike TS by intramolecular chelation, are preferentially adopted. In Figure 3, structures **A** and **B** represent the two possible twisted conformations of hypothetical bicyclo[3.2.2]nonane-type TS, deriving from the approach of benzaldehyde *si* face to the *si* face of (*Z*)-**7**, while **C** and **D** refer to the alternative approach of benzaldehyde *re* face to the *si* face of (*Z*)-**7**.

We believe that a delicate balance of steric, stereoelectronic and dipolar effects are at the basis of stereocrossover in the reaction of (*Z*) γ-**7** with aldehydes. On purely steric grounds, the less hindered location for the aldehyde substituent seems to be found in TS-**C**, thus implying that formation of *anti*-**9** should be favored. On the other hand, if the aldehyde is conjugated, TS-**A** offers the unsaturated group, e.g., the phenyl ring, the opportunity of meeting face to face the acetoxy carbonyl group, thus developing an attractive stabilizing interaction. In our opinion, π-staking[12] can account for the *syn* stereopreference of conjugated aldehydes.

These issues await detailed analysis, but whatever the explanation a clear dependence of the reaction outcome on the nature of the aldehyde has been demonstrated.

Preparation and Reactivity of Acetoxyallylindium and Zinc Species in Water. Within the framework of green chemistry principles,[13] one of the priority research areas deals with design and utilization of alternative solvents, with reduced environmental impact. Significant attention has been devoted in the past decade to replace volatile, dangerous and toxic solvents with water; a major breakthrough is represented by the reaction of indium and zinc allyl complexes with carbonyl compounds in water,[6] which is denoted by high levels of

(9) Augé, J.; Lubin-Germain, N.; Thiaw-Woaye, A. *Tetrahedron Lett.* **1999**, *40*, 9245. See also Steurer, S.; Podlech, J. *Adv. Synth. Catal.* **2001**, *343*, 251.

(10) (a) Jones, P.; Knochel, P. *J. Org. Chem.* **1999**, *64*, 186. (b) Barbot, F.; Miginiac, P. *J. Organomet. Chem.* **1977**, *132*, 445, and ref. therein.

(11) Grilli, S.; Martelli, G.; Savoia, D. *Eur. J. Org. Chem.* **2001**, 2917 and references therein.

(12) As examples of asymmetric induction promoted by π-staking between an ester group and an aromatic ring, see the chemistry of (a) 8-arylmenthol-derived chiral auxiliaries (Jones, G. B.; Chapman, B. J. *Synthesis*, **1995**, 475) and of (b) Diels−Alder catalysts based on 6-naphthylcyclohexyldichloroborane: Hawkins, J. M.; Loren, S.; Nambu, M. *J. Am. Chem. Soc.* **1994**, *116*, 1657.

(13) Tundo, P.; Anastas, P.; Black, D. StC.; Breen, J.; Collins, T.; Memoli, S.; Miyamoto, J.; Polyakoff, M.; Tumas, W. *Pure Appl. Chem.* **2000**, *72*, 1207.

TABLE 3. Synthesis of Monoacetylated Alk-1-ene-3,4-diol Derivatives 9 and 15 in Water under Barbier Conditions[a]

entry	substrate	R-CHO	metal	solvent[b]	T[c] (°C)	**9** + **15** overall yield[d] (%)	syn/anti[e]
1	**5**	Ph	In	H_2O	22[f]	75	70:30
2	**5**	Ph	In	H_2O/THF[g]	22[f]	79	70:30
3	**5**	cyclohexyl	In	H_2O/THF[g]	22[f]	84	20:80
4	**5**	Ph	Zn	H_2O	22	65	65:35
5	**5**	Ph	Zn	NH_4Cl/H_2O	22	90	65:35
6	**5**	Ph	Zn	NH_4Cl/H_2O	4	80	70:30
7	**6**[h]	Ph	Zn	NH_4Cl/H_2O	25	80	55:45
8	**6**[i]	Ph	Zn	NH_4Cl/H_2O	25	86	50:50
9	**5**	2-furyl	Zn	NH_4Cl/H_2O	2	81	80:20
10	**5**	4-tolyl	Zn	NH_4Cl/H_2O	24	60	60:40
11	**5**	4-nitrophenyl	Zn	NH_4Cl/H_2O	22	0	-
12	**5**	4-fluorophenyl	Zn	NH_4Cl/H_2O	24	0	-
13	**5**	4-anisyl	Zn	NH_4Cl/H_2O	24	72	70:30
14	**5**	(*E*)-PhCH=CH	Zn	NH_4Cl/H_2O	20	81	60:40
15	**5**	cyclohexyl	Zn	NH_4Cl/H_2O	22	84	30:70
16	**6**[h]	cyclohexyl	Zn	NH_4Cl/H_2O	22	80	15:85
17	**6**[i]	cyclohexyl	Zn	NH_4Cl/H_2O	25	80	15:85
18	**5**	n-C_6H_{13}	Zn	NH_4Cl/H_2O	22	84	30:70
19	**5**	$PhCH_2CH_2$	Zn	NH_4Cl/H_2O	22	81	30:70
20	**5**	$(CH_3)_2CHCH_2$	Zn	NH_4Cl/H_2O	22	76	30:70

[a] Starting **5** was always used as a 35:65 *E*/*Z* mixture. [b] Unless otherwise stated, saturated aqueous ammonium chloride is used. [c] External bath temperature (±1 °C). [d] Isolated yields. The **9**/**15** ratio ranged from 80:20 to 70:30 when conjugated aldehydes were used and 95:5 to 90:10 in the other cases. [e] Determined on the corresponding alk-1-ene-3,4-diols after hydrolysis of the crude reaction mixture with K_2CO_3. [f] The reaction mixture was stirred for 6 h. [g] A 1:1 v/v mixture was used. [h] Pure (*E*)-**6** was used. [i] A 1:1 *E*/*Z* mixture of **6** was used.

regio- and diastereoselectivity.[14] We decided to explore the reaction of **5** and **6** with indium in water, in the presence of an aldehyde under typical Barbier conditions, even though indium works at acidic pH[15] and the enol-ester functionality of **5** and **6** is sensitive to hydrolysis under these conditions.

We first followed by ^{1}H NMR the reaction of an equimolar amount of **5** and metallic indium in D_2O. After 5 min, two weak doublets were detected at 6.55 ppm (1H, J = 6.0 Hz) and at 1.57 ppm (2H, J = 9.6), assignable to a discreet (*Z*) γ-**7** allylindium species. Since these peaks disappeared within 10 min, they should be assigned to an indium(I) complex according to Chan observation of simple allylindium(I) in D_2O.[7] Addition of cyclohexanecarboxaldehyde after 5 min afforded a mixture of Wurtz products in 50% yield and adducts **9** + **15** (R = cyclohexyl) in 30% overall yield.

Due to the very fast Wurtz dimerization in water, the only chance was to rely on a Barbier protocol; starting bromide **5** or **6** was added to the stirred mixture of the aldehyde and indium powder in water.[16] Very luckily, the interaction of **5** or **6** with the metal was even more rapid than Wurtz dimerization, and good to excellent amounts of adducts **9** and **15** could be isolated after short reaction times. Results of a series of experiments carried out according to this new protocol are collected in Table 3 (entries 1−3). Conversions were good, and interestingly the same stereochemical trend observed in THF under Grignard conditions was confirmed in water under Barbier conditions: benzaldehyde favors the formation of a *syn*-enriched adduct **9**, and cyclohexanecarboxaldehyde favors the *anti* adduct **9**.

Even though these preliminary results were encouraging, economy criteria impelled us to check zinc also, a much less expensive metal, whose chemical reactivity toward allyl halides parallels that of indium. We were delighted by the observation that zinc was even superior to indium in terms of reaction rates and conversions, particularly in saturated ammonium chloride as the reaction medium. Pure water could be used as solvent but results were inferior, as shown by entries 4 and 5.

A number of experiments are collected in Table 3 (entries 5−20) where conjugated and unconjugated aldehydes are used. Again, the general stereochemical trend is preserved even though using **5**, the diastereoselectivity is lower both with respect to the use of indium in water (cfr. entries 1, 2, 4, 5 and 3, 15) and in THF (Table 1). Replacement of the acetoxy for the benzoyloxy group had opposite effects when benzaldehyde or cyclohexanecarboxaldehyde were used: diastereoselectivity was almost completely lost with benzaldehyde (entries 7 and 8), while the latter aldehyde afforded the best excess of *anti* adduct **2** (entries 16 and 17). These experiments also confirm that the final stereochemical results are independent of the geometry of the starting bromide.

Thus, an exceptionally mild and simple Barbier protocol (zinc and ammonium chloride) was developed using **5** or **6**, allowing to isolate monoacetylated products **9** accompanied by lower amount of **15** (5−30%), in very good overall yields. Intramolecular transesterification mainly involves *syn*-**9**, which better accommodates substituents to the C3−C4 bond in the quasi-eclipsed conformation required by the acyl transfer reaction. This also accounts for why compounds **15** are present to a major extent (20−30%) when conjugated aldehydes are used.

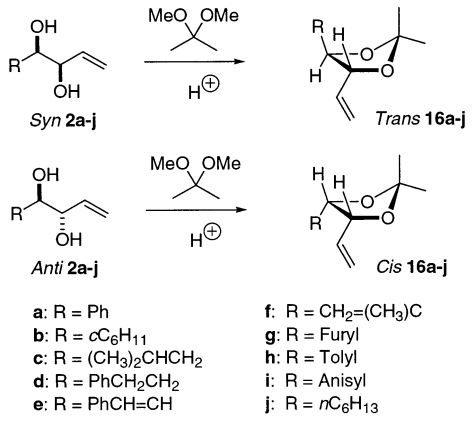
Among aromatic aldehydes, 4-nitro and 4-fluorobenzaldehyde did not afford any adduct, a sticky insoluble material being formed in both cases; no further investigation was done in order to ascertain the fate of these aldehydes in our reaction system.

(14) (a) Isaac, M. B.; Chan, T. H. *Tetrahedron Lett.* **1995**, *36*, 8957. (b) Isaac, M. B.; Chan, T. H. *J. Chem. Soc., Chem.. Commun.* **1995**, 1003. (c) Paquette, L. A.; Mitzel, T. M. *J. Org. Chem.* **1996**, *61*, 8799. (d) Paquette, L. A.; Lobben, P. C. *J. Org. Chem.* **1998**, *63*, 5604.

(15) Indium salts formed during the reaction undergo acidic hydrolysis which lowers the pH up to 3.

(16) We found that it was sufficient to add **5** and **6** to the stirred mixture of the metal in water to avoid any hydrolysis of the starting material.

SCHEME 6



a: R = Ph
b: R = *c*C_6H_{11}
c: R = $(CH_3)_2CHCH_2$
d: R = $PhCH_2CH_2$
e: R = PhCH=CH
f: R = $CH_2=(CH_3)C$
g: R = Furyl
h: R = Tolyl
i: R = Anisyl
j: R = *n*C_6H_{13}

Assignment of *Syn*/*Anti* Stereochemistry to Adducts 2. As a general strategy to assign relative *syn*/*anti* stereochemistry to adducts **2**, we converted them into acetonides **16** and studied NOEs in both stereoisomers (Scheme 6).

While performing these transformations, a few regularities came out, which may be useful to chemists working on this field.

(i) We confirmed a previous observation by Jiang et al.[17] on alk-1-ene-3,4-diols **2**. Invariably, the chemical shift of the homoallylic proton (H-4) in *syn*-**2** resonates at 0.1−0.3 ppm upfield from that of *anti*-**2**.

(ii) The chemical shift difference of the methyl groups in position 2 is always greater in *cis*-**16** (0.12−0.14 ppm) than in *trans*-**16** (0.01−0.04 ppm).

(iii) GC retention times of *trans*-**16** are always shorter than those of *cis*-**16** (HP-5 cross linked 5% Me Ph silicone).

Conclusions

The usefulness of 3-bromopropenyl esters **5** and **6** as formal precursors of the α-hydroxyallyl anion **1** has been demonstrated. In summary:

(i) 3-bromopropenyl esters are prepared in multigram scale and in good yield by simply mixing acrolein and acetyl bromide or benzoyl bromide; when $ZnCl_2$ was present, the reaction rate remarkably increased and stereoselectivity changed, favoring the formation of the *Z* isomers.

(ii) 3-Bromopropenyl esters easily undergo oxidative addition by zinc and indium in a variety of reaction conditions. The tolerability of a wide range of experimental parameters (solvents, temperature, experimental procedures, etc.) is useful in terms of optimization purposes, for example, when substrates other than aldehydes are examined. A very recent example was reported by Petrini *et al.*,[18] who opened a new route to *anti*-4-aminoalk-1-en-3-ols using α-amidoalkylphenyl sulfones as electrophiles. The best conditions involved the use of zinc and **5** in THF for 24 h at room temperature.

(iii) The use of ester functionality as the Z group in the heterosubstituted allylic species **4** determined an unprecedented stereochemical consequence: simple diastereoselectivity mainly depends on the nature of the carbonyl compound, rather than on the geometry of the double bond of the allylic organometal.

Experimental Section

General Methods. ^1H and ^{13}C NMR were recorded at 300 and 75 MHz, respectively, using tetramethylsilane as an internal standard. Melting points are uncorrected. All reagents were commercially available and were used without further purification, unless otherwise stated.

3-Bromopropenyl Acetate (5). Procedure A. Flame-dried $ZnCl_2$ (0.068 g, 0.5 mmol) was added at −20 °C to a mixture of freshly distilled acrolein (3.32 mL, 50 mmol) and acetyl bromide (3.73 mL, 50 mmol) in anhydrous CH_2Cl_2 (40 mL). The reaction was stirred for 2 h at 0 °C and quenched at 0 °C by addition of aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, the combined organic phases were dried (Na_2SO_4), and CH_2Cl_2 was removed by distillation at atmospheric pressure. Further purification of the residue by distillation (bp = 69−71 °C, P = 22 Torr) afforded 5.44 g (30.5 mmol, 61%) of **5** as a 35:65 mixture of *E*/*Z* isomers. **Procedure B.** Acetyl bromide (1.49 mL, 20 mmol) was added at 0 °C to freshly distilled acrolein (1.33 mL, 20 mmol) in anhydrous CH_2Cl_2 (20 mL). The ice bath was removed, and the reaction was stirred for 72 h at rt. The reaction was quenched at 0 °C by addition of aqueous $NaHCO_3$, the aqueous layer was extracted with CH_2Cl_2, the combined organic phases were dried (Na_2SO_4), and CH_2Cl_2 was removed by distillation at atmospheric pressure. Further purification of the residue by distillation (bp = 69−71 °C, P = 22 Torr) afforded 2.51 g (14 mmol, 70%) of **5** as a 75:25 mixture of *E*/*Z* isomers. (*Z*)-**5**: ^1H NMR (300 MHz, $CDCl_3$) δ 2.22 (s, 3H), 4.09 (dd, J = 0.3/8.1 Hz, 2H), 5.24 (dt, J = 6.3/8.1 Hz, 1H), 7.19 (dt, J = 0.3/6.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5, 23.5, 109.3, 136.9, 166.9. (*E*)-**5**: ^1H NMR (300 MHz, $CDCl_3$) δ 2.16 (s, 3H), 3.99 (dd, J = 0.3/8.1 Hz, 2H), 5.70 (dt, J = 8.1/12.3 Hz, 1H), 7.19 (dt, J = 0.3/12.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5, 28.4, 111.1, 139.0, 167.2. Anal. Calcd for $C_5H_7BrO_2$: C, 33.55; H, 3.94; Br, 44.64. Found: C, 33.48; H, 4.01; Br, 44.72.

3-Bromopropenyl Benzoate (6). Procedure A. Using the same procedure described for **5**, 3-bromopropenyl benzoate **6** was obtained in 54% yield as a 45:55 mixture of *E*/*Z* isomers after purification by flash chromatography on silica (cyclohexane/ethyl acetate = 90/10). **Procedure B.** Using the same procedure B described for **5**, 3-bromopropenyl benzoate **6** was obtained in 77% yield as pure *E* isomers after recrystallization from pentane. (*Z*)-**6**: ^1H NMR (200 MHz, $CDCl_3$) δ 2.22 (s, 3H), 4.09 (dd, J = 0.3/8.1 Hz, 2H), 5.24 (dt, J = 6.3/8.1 Hz, 1H), 7.19 (dt, J = 0.3/6.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.5, 110.0, 128.6, 130.0, 133.9, 137.5, 160.2, 162.6. (*E*)-**6**: mp = 74−76 °C (pentane); ^1H NMR (300 MHz, $CDCl_3$) δ 4.08 (dd, J = 0.9/8.4 Hz, 2H), 5.91 (dt, J = 8.4/12.3 Hz, 1H), 7.46−7.53 (m, 2H), 7.60−7.66 (m, 1H), 7.69 (dt, J = 1.1/12.3 Hz, 1H), 8.08−8.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.5, 111.8, 128.5, 130.0, 133.8, 139.4, 160.2, 163.1. Anal. Calcd for $C_{10}H_9BrO_2$: C, 49.82; H, 3.76; Br, 33.14. Found: C, 49.89; H, 3.71; Br, 33.10.

Hydroxyallylation Reactions Using Indium in THF. Typical Procedure (A). 3-Bromopropenyl acetate **5** (0.175 mL, 1.5 mmol) was added at 0 °C to a suspension of indium powder (0.115 g, 1 mmol) in THF (2 mL). The heterogeneous mixture was stirred for 30 min at 0 °C, the ice bath was removed, and stirring was continued for 3.5 h at rt. Benzaldehyde (0.105 mL, 1 mmol) was added at 0 °C, and the reaction mixture was stirred for 4 h at 0 °C. Water was added (0.5 mL), and the reaction mixture was stirred for 5 min and filtered (Celite). The aqueous layer was extracted with ether, and the combined organic layers were dried (Na_2SO_4) and evaporated at reduce pressure. Purification by flash chromatography on SiO_2 (cyclohexane/ethyl acetate 9:1) afforded 0.082 g of **12a** (0.33 mmol, 33%, *anti*/*syn* = 15:85), 0.054 g of a 1/1 mixture of **9a** (0.13 mmol, 13%, *anti*/*syn* = 5:95) and **15a** (0.13 mmol,

(17) Jiang, S.; Agoston, G. E.; Chen, T.; Cabal, M. P.; Turos, E. *Organometallics* **1995**, *14*, 4697.
(18) Petrini, M.; Profeta, R.; Righi, P. *J. Org. Chem.* **2002**, *67*, 4530.

13%, *anti*/*syn* = 1:99), and 0.054 g of **2a** (0.33 mmol, 33%, *anti*/*syn* = 55:45).

***syn*-3,4-Diacetoxy-4-phenylbut-1-ene (*syn*-12a):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.00 (s, 3H), 2.02 (s, 3H), 5.07−5.14 (m, 1H), 5.18−5.23 (m, 1H), 5.43−5.64 (m, 2H), 5.79 (d, J = 5.6 Hz, 1H), 7.29−7.40 (m, 5H). The following signal in the previous NMR spectra is assigned to the *anti* isomer: ^{1}H NMR δ 5.90 (d, J = 4.7 Hz, 1H).

***syn*-4-Phenyl-4-acetoxybut-1-en-3-ol (*syn*-15a):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.14 (s, 3H), 4.45 (ddt, J = 1.6/5.4/6.8 Hz, 1H), 5.19−5.28 (m, 2H), 5.69 (d, J = 6.8 Hz, 1H), 5.63−5.73 (m, 1H), 5.29−5.40 (m, 5H).

***anti*-1-Phenyl-2-acetoxybut-3-en-1-ol (*anti*-9a):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.08 (s, 3H), 4.90 (d, J = 4.4 Hz, 1H), 5.28 (dt, J = 1.5/17.0 Hz, 1H), 5.29 (dt, J = 1.3/10.8 Hz, 1H), 5.48 (ddt, J = 1.2/4.4/6.8 Hz, 1H), 5.82 (ddd, J = 6.8/10.8/17.0 Hz, 1H), 7.28−7.43 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 75.1, 78.1, 119.6, 126.6, 128.0, 128.3, 131.6, 139.5, 170.0. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.95; H, 6.79.

***syn*-1-Phenyl-2-acetoxybut-3-en-1-ol (*syn*-9a):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.12 (s, 3H), 4.76 (d, J = 6.5 Hz, 1H), 5.13−5.36 (m, 2H), 5.42−5.52 (m, 1H), 5.60−5.75 (m, 1H), 7.30−7.41 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.1, 75.0, 78.0, 119.5, 126.5, 127.9, 128.3, 131.5, 139.3, 169.9. Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.97; H, 6.85.

By applying the same experimental procedure to cyclohexanecarboxaldehyde (0.120 mL, 1 mmol), purification by flash-chromatography on SiO_2 (cyclohexane/ethyl acetate 9:1) afforded 0.064 g of **12b** (0.25 mmol, 25%, *anti*/*syn* = 96:4), 0.042 g of **9b** (0.20 mmol, 20%, *anti*/*syn* = 90:10), 0.053 g of **15b** (0.25 mmol, 25%, *anti*/*syn* = 60:40), and 0.031 g of **2b** (0.18 mmol, 18%, *anti*/*syn* = 99:1).

***anti*-3,4-Diacetoxy-4-cyclohexylbut-1-ene (*anti*-12b):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92−1.32 (m, 6H), 1.42−1.82 (m, 5H), 2.03 (s, 3H), 2.08 (s, 3H), 4.96 (dd, J = 4.0/8.0 Hz, 1H), 5.32 (dt, J = 1.4/10.4 Hz, 1H), 5.32 (dt, J = 1.4/10.4 Hz, 1H), 5.36 (dt, J = 1.4/17.3 Hz, 1H), 5.43 (broad dd, $J \approx$ 4.2/7.7 Hz, 1H), 5.85 (ddd, J = 7.7/10.4/17.4 Hz, 1H).

***anti*-4-Cyclohexyl-4-acetoxybut-1-en-3-ol (*anti*-15b):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.99−1.31 (m, 6H), 1.61−1.84 (m, 5H), 2.09 (s, 3H), 4.25−4.36 (m, 1H), 4.80 (dd, J = 4.4/7.0 Hz, 1H), 5.24 (dt, J = 1.3/10.5 Hz, 1H), 5.33 (dt, J = 1.1/17.0 Hz, 1H), 5.89 (ddd, J = 7.0/10.5/17.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.1, 25.8, 26.0, 26.2, 28.0, 29.6, 38.5, 72.8, 80.3, 117.7, 136.3, 171.7.

***anti*-1-Cyclohexyl-2-acetoxybut-3-en-1-ol (*anti*-9b):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94−1.47 (m, 6H), 1.61−1.84 (m, 4H), 1.93−2.03 (m, 1H), 2.11 (s, 3H), 3.46−3.53 (m, 1H), 5.33−5.43 (m, 3H), 5.92 (ddd, J = 7.0/10.7/17.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.2, 25.7, 25.8, 28.3, 28.9, 39.6, 75.6, 76.4, 119.5, 131.7, 169.7. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.83; H, 9.54.

Hydroxyallylation Reaction Using Indium in THF/H_2O (pH = 3). Typical Procedure (B). 3-Bromopropenyl acetate **5** (0.175 mL, 1.5 mmol) was added at 0 °C to a suspension of indium powder (0.115 g, 1 mmol) in THF (2 mL). The heterogeneous mixture was stirred for 5 min at 0 °C, the ice bath was removed, and stirring was continued for 40 min at rt. Phthalate buffer (pH = 3, 0.200 mL) was added at rt followed by benzaldehyde (0.105 mL, 1 mmol) and the reaction mixture was stirred for 45 min. Water was added (0.5 mL), and the reaction mixture was stirred for 5 min and filtered (Celite). The aqueous layer was extracted with ether, and the combined organic layers were dried (Na_2SO_4) and evaporated at reduced pressure. Purification by flash chromatography on SiO_2 (cyclohexane/ethyl acetate 9:1) afforded 0.033 g of *anti*-**9a** (0.16 mmol, 16%) and 0.156 g of a 8:36:56 mixture of *anti*-**9a** (0.012 g, 0.06 mmol, 6%), *syn*-**9a** (0.057 g, 0.28 mmol, 28%), and *syn*-**15a** (0.087 g, 0.42 mmol, 42%). The overall isolated yield was 92%.

By applying the same experimental procedure to cyclohexanecarboxaldehyde (0.120 mL, 1 mmol), 0.106 g of **9b** (0.5 mmol, 50%, *anti*/*syn* = 90:10) and 0.096 g of **15b** (0.45 mmol, 45%, *anti*/*syn* = 80:20) were obtained after purification by flash chromatography on SiO_2 (cyclohexane/ethyl acetate 9:1).

Synthesis of 1-Phenylbut-3-ene-1,2-diol (2a). Typical Procedure. The crude reaction mixture obtained by procedure A or B was dissolved in MeOH/H_2O (5 mL, 9:1 v/v), K_2CO_3 (0.415 g, 3 mmol) was added, and the reaction mixture was stirred at rt overnight. MeOH was removed at reduced pressure, and the aqueous layer was extracted with ether. The combined organic layers were dried (Na_2SO_4) and evaporated at reduce pressure. Purification by flash chromatography on SiO_2 (cyclohexane/ethyl acetate 8:2) afforded 0.105 g of *syn*-**2a** (0.64 mmol, 64%) and 0.035 g of *anti*-**2a** (0.21 mmol, 21%).

***syn*-1-Phenylbut-3-ene-1,2-diol (*syn*-2a):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (d, J = 1.8 Hz, 1H), 2.78 (d, J = 1.2 Hz, 1H), 4.19−4.30 (m, 1H), 4.52 (dd, J = 1.8/6.9 Hz, 1H), 5.17 (dt, J = 1.5/10.5 Hz, 1H), 5.28 (dt, J = 1.5/16.8 Hz, 1H), 5.75 (ddd, J = 5.1/10.5/16.8 Hz, 1H), 7.28−7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 76.8, 77.5, 116.8, 127.0, 127.9, 128.2, 136.1, 140.1. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.21; H, 7.38.

***anti*-1-Phenyl-but-3-ene-1,2-diol (*anti*-2a):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (d, J = 3.9 Hz, 1H), 2.40 (d, J = 2.0 Hz, 1H), 4.30−4.39 (m, 1H), 4.78 (t, J = 3.9 Hz, 1H), 5.24 (dt, J = 1.4/10.5 Hz, 1H), 5.30 (dt, J = 1.4/17.5 Hz, 1H), 5.75 (ddd, J = 6.3/10.5/17.5 Hz, 1H), 7.27−7.40 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 76.3, 76.5, 117.5, 126.5, 127.6, 128.1, 135.4, 139.7. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.19; H, 7.69.

***syn*-1-Cyclohexylbut-3-ene-1,2-diol (*syn*-2b):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95−1.48 (m, 5H), 1.56−1.88 (m, 4H), 1.89−2.18 (m, 2H), 3.21−3.28 (m, 1H), 4.15−4.21 (m, 1H), 5.26 (dt, J = 1.3/10.5 Hz, 1H), 5.37 (dt, J = 1.3/17.5 Hz, 1H), 5.90 (ddd, J = 6.3/10.5/17.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.0, 26.2, 26.3, 27.1, 29.6, 29.9, 39.4, 73.0, 78.3. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.61; H, 10.72.

***anti*-1-Cyclohexylbut-3-ene-1,2-diol (*anti*-2b):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93−1.48 (m, 5H), 1.58−1.86 (m, 4H), 1.88−2.20 (m, 2H), 3.39−3.48 (m, 1H), 4.20−4.29 (m, 1H), 5.31 (dt, J = 1.4/10.5 Hz, 1H), 5.38 (dt, J = 1.4/17.5 Hz, 1H), 5.99 (ddd, J = 6.6/10.5/17.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 25.8, 26.3, 28.7, 29.0, 39.7, 73.3, 78.0. Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.58; H, 10.61.

***syn*-6-Methylhept-1-ene-3,4-diol (*syn*-2c):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (d, J = 6.6 Hz, 3H), 0.96 (d, J = 7.2 Hz, 3H), 1.12−1.37 (m, 2H), 1.72−1.95 (m, 1H), 2.14 (d, J = 3.6 Hz, 1H), 2.23 (d, J = 3.6 Hz, 1H), 5.20−5.43 (m, 2H), 5.88 (ddd, J = 6.0/10.5/17.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.5, 23.7, 24.4, 41.8, 72.4, 76.7, 117.0, 137.5. Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.55; H, 11.12.

***anti*-6-Methylhept-1-ene-3,4-diol (*anti*-2c):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (d, J = 7.2 Hz, 3H), 0.95 (d, J = 7.0 Hz, 3H), 1.36−1.53 (m, 2H), 1.75−1.91 (m, 1H), 1.90 (d, J = 6.0 Hz, 1H), 2.07 (d, J = 5.0 Hz, 1H), 5.23−5.41 (m, 2H), 5.93 (ddd, J = 6.4/10.5/17.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.8, 23.5, 24.4, 40.7, 72.1, 76.2, 117.2, 135.9. Anal. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.57; H, 11.25.

***syn*-6-Phenylhex-1-ene-3,4-diol (*syn*-2d):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.73−1.86 (m, 2H), 2.08−2.17 (broad s, 1H), 2.19−2.27 (broad s, 1H), 2.62−2.70 (m, 1H), 2.80−2.89 (m, 1H), 3.41−3.54 (m, 1H), 3.90−3.99 (m, 1H), 5.23 (dt, J = 1.5/10.5 Hz, 1H), 5.34 (dt, J = 1.5/17.5 Hz, 1H), 5.83 (ddd, J = 6.3/10.5/17.5 Hz, 1H), 7.28−7.40 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 31.8, 34.5, 73.6, 76.4, 117.5, 125.7, 128.2, 128.3, 137.3, 141.7. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.93; H, 8.44.

***anti*-6-Phenylhex-1-ene-3,4-diol (*anti*-2d):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67−1.80 (m, 2H), 1.92−2.03 (broad s, 2H), 2.60−2.75 (m, 1H), 2.79−2.91 (m, 1H), 3.65−3.75 (m, 1H), 4.04−4.14 (m, 1H), 5.26 (m, 1H), 5.32 (dt, J = 1.5/17.5 Hz,

1H), 5.90 (ddd, J = 6.3/10.5/17.5 Hz, 1H), 7.28−7.42 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 32.1, 33.6, 73.3, 76.0, 117.5, 128.8, 128.2, 128.3, 135.8, 141.8. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.06; H, 8.46.

***syn*-(*E*)-1-Phenylhexa-1,5-diene-3,4-diol (*syn*-2e):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.18 (d, J = 3.0 Hz, 1H), 2.21 (d, J = 3.0 Hz, 1H), 4.04−4.08 (m, 1H), 4.09−4.12 (m, 1H), 5.28 (dt, J = 1.5/10.5 Hz, 1H), 5.42 (dt, J = 1.5/17.5 Hz, 1H), 5.94 (ddd, J = 5.7/10.5/17.5 Hz, 1H), 6.21 (dd, J = 6.3/15.9 Hz, 1H), 6.70 (d, J = 15.9 Hz, 1H), 7.21−7.42 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 75.6, 75.9, 117.4, 126.5, 127.9, 128.3, 132.6, 135.9, 136.5. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.83; H, 7.47.

***anti*-(*E*)-1-Phenylhexa-1,5-diene-3,4-diol (*anti*-2e):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.07 (d, J = 3.2 Hz, 1H), 2.10 (d, J = 3.0 Hz, 1H), 4.12−4.16 (m, 1H), 4.18−4.21 (m, 1H), 5.31 (dt, J = 1.5/10.5 Hz, 1H), 5.40 (dt, J = 1.5/17.5 Hz, 1H), 5.95 (ddd, J = 6.3/10.5/17.5 Hz, 1H), 6.24 (dd, J = 6.3/15.9 Hz, 1H), 6.68 (d, J = 15.9 Hz, 1H), 7.20−7.40 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 75.3, 75.7, 117.7, 126.9, 127.3, 127.5, 132.8, 135.6, 136.3. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.71; H, 7.38.

***syn*-2-Methyl-hexa-1,5-diene-3,4-diol (*syn*-2f):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.78 (s, 3H), 2.25 (d, J = 3.1 Hz, 1H), 2.34 (d, J = 3.1 Hz, 1H), 3.91−3.99 (m, 1H), 4.10−4.21 (m, 1H), 4.99−5.05 (m, 1H), 5.06−5.07 (m, 1H), 5.25 (dt, J = 1.4/10.5 Hz, 1H), 5.39 (dq, J = 1.4/17.1 Hz, 1H), 5.87 (ddd, J = 5.7/10.5/17.1 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.6, 73.7, 78.4, 113.8, 116.8, 136.7, 143.7. Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.68; H, 9.40.

***anti*-2-Methylhexa-1,5-diene-3,4-diol (*anti*-2f):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.63 (s, 3H), 2.05 (d, J = 5.1 Hz, 1H), 2.09 (d, J = 5.1 Hz, 1H), 4.01−4.05 (m, 1H), 4.18−4.27 (m, 1H), 5.29 (dt, J = 1.7/10.5 Hz, 1H), 5.40 (dt, J = 1.7/17.5 Hz, 1H), 5.91 (ddd, J = 6.0/10.5/17.5 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.8, 76.4, 77.8, 113.0, 117.6, 135.9, 143.6. Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.54; H, 9.38.

***syn*-1-(2-Furyl)but-3-ene-1,2-diol (*syn*-2g):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.54 (s, 1H), 2.75 (s, 1H), 4.43−4.51 (m, 1H), 4.56 (dd, J = 5.0/7.0 Hz, 1H), 5.22 (dt, J = 1.8/10.5 Hz, 1H), 5.35 (dt, J = 1.8/17.2 Hz, 1H), 5.80 (ddd, J = 5.2/10.5/17.2 Hz, 1H), 6.33−6.39 (m, 2H), 7.40−7.43 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 70.9, 74.5, 108.0, 110.1, 117.1, 135.8, 142.1, 153.0. Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.39; H, 6.47.

***anti*-1-(2-Furyl)but-3-ene-1,2-diol (*anti*-2g):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.40−4.46 (m, 1H), 4.75 (t, J = 5.4 Hz, 1H), 5.23 (dt, J = 1.4/10.5 Hz, 1H), 5.39 (dt, J = 1.4/17.2 Hz, 1H), 5.87 (ddd, J = 5.6/10.5/17.2 Hz, 1H), 6.32−6.39 (m, 2H), 7.40−7.42 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 70.7, 74.7, 107.7, 110.1, 117.4, 135.6, 117.4, 135.6, 141.9, 153.0. Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.36; H, 6.59.

***syn*-1-(4-Methylphenyl)but-3-ene-1,2-diol (*syn*-2h):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 4.24 (ddt, J = 1.5/5.4/6.9 Hz, 1H), 4.49 (d, J = 6.9 Hz, 1H), 5.16 (dt, J = 1.6/10.6 Hz, 1H), 5.28 (dt, J = 1.6/17.4 Hz, 1H), 5.75 (ddd, J = 5.4/10.6/17.4 Hz, 1H), 7.14−7.21 (m, 2H), 7.22−7.29 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 77.0, 77.6, 116.9, 127.1, 129.1, 136.6, 137.5, 137.8. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.18; H, 7.96.

***anti*-1-(4-Methylphenyl)but-3-ene-1,2-diol (*anti*-2h):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 4.32 (ddt, J = 1.3/5.1/6.2 Hz, 1H), 4.72 (d, J = 5.1 Hz, 1H), 5.25 (dt, J = 1.4/10.4 Hz, 1H), 5.32 (dt, J = 1.4/17.1 Hz, 1H), 5.84 (ddd, J = 6.2/10.4/17.1 Hz, 1H), 7.15−7.21 (m, 2H), 7.22−7.30 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.8, 76.5, 76.8, 117.7, 126.8, 129.0, 136.1, 137.0, 137.6. Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.06; H, 7.98.

***syn*-1-(4-Methoxyphenyl)but-3-ene-1,2-diol (*syn*-2i):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.40 (d, J = 3.4 Hz, 1H), 2.59 (d, J = 2.6 Hz, 1H), 3.82 (s, 3H), 4.20−4.29 (m, 1H), 4.48 (dd, J = 2.6/7.3 Hz, 1H), 5.16 (dt, J = 1.4/10.5 Hz, 1H), 5.27 (ddd, J = 1.5/17.2 Hz, 1H), 5.74 (ddd, J = 5.5/10.5/17.2 Hz, 1H), 6.85−6.95 (m, 2H), 7.25−7.34 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 55.8, 77.6, 77.8, 114.3, 117.6, 128.8, 132.9, 136.9, 159.8. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.08; H, 7.34.

***anti*-1-(4-Methoxyphenyl)but-3-ene-1,2-diol (*anti*-2i):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.92 (d, J = 4.7 Hz, 1H), 2.27 (d, J = 3.7 Hz, 1H), 3.82 (s, 3H), 4.21−4.28 (m, 1H), 4.70 (broad t, $J \sim$ 3.4 Hz, 1H), 5.25 (dt, J = 1.4/10.5 Hz, 1H), 5.27 (ddd, J = 1.5/17.2 Hz, 1H), 5.85 (ddd, J = 6.2/10.5/17.2 Hz, 1H), 6.83−6.95 (m, 2H), 7.24−7.34 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 55.8, 77.7, 78.3, 114.3, 118.2, 128.5, 132.5, 136.6, 159.7. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.11; H, 7.21.

***syn*-Dec-1-ene-3,4-diol (*syn*-2j):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (broad t, $J \sim$ 7.2 Hz, 3H), 1.24−1.37 (m, 7H), 1.37−1.57 (m, 3H), 2.17 (broad s, 1H), 2.22 (broad s, 1H), 3.43−3.54 (m, 1H), 3.90−3.98 (m, 1H), 5.26 (dt, J = 1.3/10.7 Hz, 1H), 5.32 (dt, J = 1.4/17.0 Hz, 1H), 5.88 (ddd, J = 6.4/10.7/17.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 25.5, 29.7, 31.7, 32.9, 74.4, 76.2, 117.3, 137.8. Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.66; H, 11.74.

***anti*-Dec-1-ene-3,4-diol (*anti*-2j):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (broad t, J = 7.2 Hz, 3H), 1.24−1.37 (m, 7H), 1.37−1.57 (m, 3H), 1.94 (broad s, 1H), 2.07 (broad s, 1H), 3.64−3.76 (m, 1H), 4.05−4.16 (m, 1H), 5.29 (dt, J = 1.5/10.6 Hz, 1H), 5.35 (dt, J = 1.4/17.0 Hz, 1H), 5.94 (ddd, J = 6.3/10.6/17.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 22.6, 25.8, 29.3, 31.7, 32.1, 71.1, 76.0, 117.6, 136.1. Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.78; H, 11.77.

Synthesis of 2,2-Dimethyl-4-phenyl-5-ethenyl-1,3-dioxolane 16a. Typical Procedure. A catalytic amount of Amberlyst-15H (10 mg) was added to a solution of freshly distilled 2,2-dimethoxypropane (0.210 mL, 1.72 mmol) and 1-phenylbut-3-ene-1,2-diol **2a** (0.141 g, 0.86 mmol, *anti*/*syn* = 25:75) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at rt overnight and filtered (Celite), and the organic layer was evaporated at reduced pressure. Purification by flash-chromatography on SiO_2 (cyclohexane/ethyl ether 98:2) afforded 0.129 g of *trans*-**16a** (0.63 mmol, 73%) and 0.043 g of *cis*-**16a** (0.21 mmol, 24%).

4,5-*trans*-2,2-Dimethyl-4-phenyl-5-ethenyl-1,3-dioxolane (*trans*-16a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.55 (s, 3H), 1.60 (s, 3H), 4.19 (t, J = 8.4 Hz, 1H), 4.67 (d, J = 8.4 Hz, 1H), 5.21−5.24 (m, 1H), 5.29−5.31 (m, 1H), 5.89 (ddd, J = 6.8/9.8/17.6 Hz, 1H), 7.25−7.42 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.08, 27.13, 82.9, 84.7, 109.2, 119.3, 126.4, 128.1, 128.4, 133.8, 137.1. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.48; H, 7.86.

4,5-*cis*-2,2-Dimethyl-4-phenyl-5-ethenyl-1,3-dioxolane (*cis*-16a): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.53 (s, 3H), 1.70 (s, 3H), 4.83 (t, J = 7.0 Hz, 1H), 5.00 (dd, J = 2.2/7.0 Hz, 1H), 5.22−5.25 (m, 1H), 5.28−5.34 (m, 1H), 5.89 (ddd, J = 6.8/9.9/17.1 Hz, 1H), 7.25−7.40 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.1, 27.4, 80.2, 80.7, 108.8, 117.8, 126.8, 128.0, 128.1, 134.9, 137.3. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.43; H, 7.94.

4,5-*trans*-2,2-Dimethyl-4-ethenyl-5-cyclohexyl-1,3-dioxolane (*trans*-16b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80−1.80 (m, 10H), 1.41 (broad s, 6H), 1.82−1.92 (m, 1H), 3.52 (dd, J = 6.0/7.4 Hz, 1H), 4.19 (t, J = 7.4 Hz, 1H), 5.24 (dt, J = 1.2/10.2, 1H), 5.37 (dt, J = 1.2/16.5, 1H), 5.88 (ddd, J = 7.5/10.2/16.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.0, 26.2, 27.2, 27.4, 29.3, 29.7, 30.0, 40.6, 80.6, 85.1, 108.8, 118.6, 136.9. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.28; H, 10.51.

4,5-*cis*-2,2-Dimethyl-4-ethenyl-5-cyclohexyl-1,3-dioxolane (*cis*-16b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80−1.80 (m, 10H), 1.35 (s, 3H), 1.45 (s, 3H), 1.95−2.02 (m, 1H), 3.79 (dd, J = 5.7/8.8 Hz, 1H), 4.41 (dd, J = 5.4/8.8 Hz, 1H), 5.20−5.32 (m, 1H), 5.28−5.34 (m, 1H), 5.88 (ddd, J = 8.4/10.2/18.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.77, 25.80, 26.0, 26.7, 28.6,

29.0, 30.6, 37.4, 80.0, 82.7, 108.1, 118.4, 135.0. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.29; H, 10.58.

4,5-*trans*-2,2-Dimethyl-4-ethenyl-5-(2′-methylpropyl)-1,3-dioxolane (*trans*-16c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (d, J = 6.6 Hz, 6H), 1.25−1.60 (m, 2H), 1.44 (broad s, 6H), 1.65−1.85 (m, 1H), 3.76 (dt, J = 3.9/8.3 Hz, 1H), 3.96 (t, J = 8.3 Hz, 1H), 5.22−5.30 (m, 1H), 5.33−5.44 (m, 1H), 5.80 (ddd, J = 8.3/10.2/17.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.2, 25.4, 27.0, 27.4, 28.4, 29.7, 40.9, 78.9, 83.2, 108.4, 118.6, 135.3. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.66; H, 10.97.

4,5-*cis*-2,2-Dimethyl-4-ethenyl-5-(2′-methylpropyl)-1,3-dioxolane (*cis*-16c): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.96 (d, J = 6.6 Hz, 6H), 1.09−1.32 (m, 1H), 1.40 (s, 3H), 1.45−1.56 (m, 1H), 1.51 (s, 3H), 1.65−1.87 (m, 1H), 4.26 (ddd, J = 4.3/6.2/9.6 Hz, 1H), 4.49 (dd, J = 6.2/7.3 Hz, 1H), 5.20−5.27 (m, 1H), 5.28−5.36 (m, 1H), 5.84 (ddd, J = 7.3/10.0/17.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.0, 23.5, 25.1, 25.8, 28.4, 39.1, 76.3, 80.0, 107.9, 117.9, 134.6. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.77; H, 10.97.

4,5-*trans*-2,2-Dimethyl-4-ethenyl-5-(2′-phenylethyl)-1,3-dioxolane (*trans*-16d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 3H), 1.46 (s, 3H), 1.82−1.96 (m, 2H), 2.62−2.75 (m, 1H), 2.78−2.84 (m, 1H), 3.72 (dt, J = 5.7/8.0 Hz, 1H), 4.07 (t, J = 8.0 Hz, 1H), 5.25 (dt, J = 1.1/10.4 Hz, 1H), 5.35 (dt, J = 1.1/17.0 Hz, 1H), 5.80 (ddd, J = 7.3/10.4/17.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.0, 27.3, 32.3, 33.6, 79.9, 82.7, 108.6, 118.9, 125.8, 128.3, 128.4, 135.3, 141.7. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.50; H, 8.63.

4,5-*Cis*-2,2-Dimethyl-4-ethenyl-5-(2′-phenylethyl)-1,3-dioxolane (*cis*-16d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (s, 3H), 1.53 (s, 3H), 1.63−1.75 (m, 1H), 1.76−1.92 (m, 1H), 2.65 (ddd, J = 6.9/9.8/13.7 Hz, 1H), 2.82 (ddd, J = 5.2/10.1/13.7 Hz, 1H), 4.16 (ddd, J = 4.6/6.3/10.7 Hz, 1H), 4.50 (t, J = 6.3 Hz, 1H), 5.23 (ddd, J = 0.8/1.6/10.3 Hz, 1H), 5.31 (dt, J = 1.5/17.1 Hz, 1H), 5.83 (ddd, J = 7.8/10.3/17.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 28.3, 32.4 (2C), 77.4, 79.7, 108.2, 118.2, 125.8, 128.3, 128.4, 134.3, 141.6. Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.61; H, 8.74.

4,5-*trans*-2,2-Dimethyl-4-(2′-phenylethenyl)-5-ethenyl-1,3-dioxolane (*trans*-16e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (s, 3H), 1.50 (s, 3H), 4.18 (t, J = 6.9 Hz, 1H), 4.27 (dd, J = 6.9/7.1 Hz, 1H), 5.27 (dd, J = 1.1/10.1 Hz, 1H), 5.38 (dd, J = 1.1/17.2 Hz, 1H), 5.85 (ddd, J = 6.9/10.1/17.2 Hz, 1H), 6.15 (dd, J = 7.1/15.6 Hz, 1H), 6.67 (d, J = 15.6 Hz, 1H), 7.21−7.44 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.07, 27.11, 82.1, 82.4, 109.2, 118.9, 125.0, 126.6, 127.9, 128.5, 133.9, 134.0, 136.2. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.28; H, 7.81.

4,5-*cis*-2,2-Dimethyl-4-(2′-phenylethenyl)-5-ethenyl-1,3-dioxolane (*cis*-16e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.44 (s, 3H), 1.58 (s, 3H), 4.67 (ddt, J = 1.1/6.5/7.2 Hz, 1H), 4.79 (ddd, J = 0.9/6.5/7.7 Hz, 1H), 5.23 (ddd, J = 0.8/1.7/10.5 Hz, 1H), 5.34 (dd, J = 1.1/1.7/17.0 Hz, 1H), 5.81 (ddd, J = 7.2/10.5/17.0 Hz, 1H), 6.11 (dd, J = 7.7/16.0 Hz, 1H), 6.62 (d, J = 16.0 Hz, 1H), 7.21−7.44 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.6, 28.1, 79.6, 80.1, 108.9, 118.2, 125.5, 126.6, 127.8, 128.5, 133.2, 134.3, 136.4. Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.25; H, 7.83.

4,5-*trans*-2,2-Dimethyl-4-(1′-methylethenyl)-5-ethenyl-1,3-dioxolane (*trans*-16f): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.46 (s, 3H), 1.47 (s, 3H), 1.78 (t, J = 0.8 Hz, 3H), 4.08−4.22 (m, 2H), 4.95−4.99 (m, 1H), 5.04−5.09 (m, 1H), 5.23−5.30 (m, 1H), 5.31−5.42 (m, 1H), 5.84 (ddd, J = 5.9/10.3/17.3 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.8, 26.9, 27.1, 81.0, 84.5, 109.0, 113.8, 118.8, 134.9, 140.7. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.46; H, 9.53.

4,5-*cis*-2,2-Dimethyl-4-(1′-methylethenyl)-5-ethenyl-1,3-dioxolane (*cis*-16f): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.42 (s, 3H), 1.56 (s, 3H), 1.67 (t, J = 1.2 Hz, 3H), 4.58−4.67 (m, 2H), 4.91−4.96 (m, 1H), 5.06−5.12 (m, 1H), 5.15−5.23 (m, 1H), 5.28−5.34 (m, 1H), 5.84 (ddd, J = 5.8/10.1/17.0 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.3, 25.2, 27.5, 65.8, 79.6, 108.6, 112.0, 117.9, 134.3, 140.6. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.45; H, 9.64.

4,5-*trans*-2,2-Dimethyl-4-furyl-5-ethenyl-1,3-dioxolane (*trans*-16g): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.51 (s, 3H), 1.55 (s, 3H), 4.59−4.72 (m, 2H), 5.26 (ddd, J = 1.4/10.3 Hz, 1H), 5.34 (ddd, J = 1.4/17.2 Hz, 1H), 5.87 (ddd, J = 6.0/10.3/17.2 Hz, 1H), 6.34−6.41 (m, 2H), 7.45 (d, J = 1.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.7, 27.0, 76.3, 80.5, 109.2, 109.6, 110.2, 119.0, 133.8, 143.2, 150.0. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 68.06; H, 7.21.

4,5-*cis*-2,2-Dimethyl-4-furyl-5-ethenyl-1,3-dioxolane (*cis*-16g): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.47 (s, 3H), 1.64 (s, 3H), 4.62 (d, J = 6.7 Hz, 1H), 4.77 (t, J = 6.7 Hz, 1H), 5.15 (ddd, J = 1.8/10.3 Hz, 1H), 5.31 (ddd, J = 1.8/17.2 Hz, 1H), 5.82−5.86 (m, 1H), 6.26−6.35 (m, 2H), 7.40 (d, J = 1.8 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.3, 27.2, 74.6, 80.0, 108.6, 109.4, 110.0, 118.0, 133.3, 142.4, 149.8. Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.94; H, 7.31.

4,5-*trans*-2,2-Dimethyl-4-(4-methylphenyl)-5-ethenyl-1,3-dioxolane (*trans*-16h): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.56 (s, 3H), 1.61 (s, 3H), 2.37 (s, 3H), 4.20 (broad t, J = 7.5 Hz, 1H), 4.65 (d, J = 8.3 Hz, 1H), 5.19−5.35 (m, 2H), 5.90 (ddd, J = 7.1/10.1/17.6 Hz, 1H), 7.14−7.23 (m, 2H), 7.24−7.32 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.2, 27.1, 82.8, 84.6, 109.1, 119.0, 126.4, 129.0, 133.9, 135.0, 137.8. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.13; H, 8.38.

4,5-*cis*-2,2-Dimethyl-(4-methylphenyl)-5-ethenyl-1,3-dioxolane (*cis*-16h): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.53 (s, 3H), 1.69 (s, 3H), 2.36 (s, 3H), 4.81 (broad t, $J \sim$ 7.1 Hz, 1H), 4.65 (broad dd, J = 1.0/2.5/6.8 Hz, 1H), 5.20−5.35 (m, 2H), 5.87 (ddd, J = 7.1/10.3/17.2 Hz, 1H), 7.16−7.23 (m, 2H), 7.24−7.30 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.0, 27.5, 80.1, 80.7, 108.6, 117.7, 126.7, 128.7, 134.0, 134.3, 138.0. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.09; H, 8.25.

4,5-*trans*-2,2-Dimethyl-4-(4-methoxyphenyl)-5-ethenyl-1,3-dioxolane (*trans*-16i): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.55 (s, 3H), 1.60 (s, 3H), 3.82 (s, 3H), 4.19 (broad t, $J \sim$ 8.2 Hz, 1H), 4.63 (d, J = 8.2 Hz, 1H), 5.21−5.30 (m, 2H), 5.88 (ddd, J = 7.1/10.3/17.4 Hz, 1H), 6.92 (d, J = 9.4, 2H), 7.31 (d, J = 9.4, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.1, 55.2, 82.7, 84.5, 109.0, 113.8, 119.0, 127.7, 129.0, 133.9, 159.8. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.77; H, 7.74.

4,5-*cis*-2,2-Dimethyl-4-(4-methoxyphenyl)-5-ethenyl-1,3-dioxolane (*cis*-16i): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.51 (s, 3H), 1.68 (s, 3H), 3.83 (s, 3H), 4.79 (broad t, $J \sim$ 7.6 Hz, 1H), 5.02 (d, J = 7.6 Hz, 1H), 5.19−5.28 (m, 2H), 5.87 (ddd, J = 6.8/10.2/17.3 Hz, 1H), 6.88 (d, J = 9.4, 2H), 7.21 (d, J = 9.4, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 29.8, 55.2, 79.9, 80.6, 108.6, 113.7, 117.7, 128.0, 130.8, 135.0, 160.0. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.77; H, 7.74.

4,5-*trans*-2,2-Dimethyl-4-hexyl-5-ethenyl-1,3-dioxolane (*trans*-16j): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (broad t, $J \sim$ 6.7 Hz, 3H), 1.24−1.62 (m, 10H), 1.43 (s, 3H), 1.44 (s, 3H), 4.15 (dt, J = 6.2/8.0 Hz, 1H), 4.49 (broad t, $J \sim$ 6.6 Hz, 1H), 5.26 (ddd, J = 0.77/1.8/10.3 Hz, 1H), 5.38 (ddd, J = 0.77/1.5/17.2 Hz, 1H), 5.83 (ddd, J = 7.3/10.3/17.2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 22.7, 26.0, 26.9, 27.4, 80.7, 82.8, 108.3, 118.6, 135.5. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.59; H, 11.46.

4,5-*cis*-2,2-Dimethyl-4-hexyl-5-ethenyl-1,3-dioxolane (*cis*-16j): ^{1}H NMR (200 MHz, $CDCl_3$) δ; ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.91 (broad t, $J \sim$ 6.7 Hz, 3H), 1.24−1.60 (m, 10H), 1.39 (s, 3H), 1.51 (s, 3H), 3.69 (dt, J = 5.8/8.5 Hz, 1H), 4.00 (broad t, $J \sim$ 8.2 Hz, 1H), 5.24 (ddd, J = 0.77/1.9/10.2 Hz, 1H), 5.31 (ddd, J = 0.77/1.8/17.2 Hz, 1H), 5.84 (ddd, J = 7.8/10.2/17.2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 22.7, 25.7, 26.2, 28.3, 29.4, 30.4, 31.8, 78.3, 79.9, 107.9, 118.0, 134.6. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.48; H, 11.45.

Hydroxyallylation Reaction Using Zn in Aqueous NH_4Cl. Typical Procedure. Benzaldheyde (0.105 mL, 1

mmol), 3-bromopropenyl acetate **5** (0.175 mL, 1.5 mmol), and zinc powder (0.98 g, 1.5 mmol) were subsequently added at rt to a saturated aqueous solution of NH_4Cl (5 mL). The reaction was quite exothermic, so temperature was controlled with a water bath. Zinc powder almost completely dissolved in 2 min. The reaction was checked after 15 min, the aqueous layer was extracted with ether after 30 min. The combined organic layers were dried (Na_2SO_4) and evaporated at reduced pressure. Purification by flash chromatography on SiO_2 (cyclohexane/ethyl acetate 9:1) afforded 0.186 g of a 70:30 mixture of **9a** and **15a**.

***anti*-3-Acetoxy-6-methylhept-1-en-4-ol (*anti*-9c):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.92 (d, J = 6.7 Hz, 3H), 0.96 (d, J = 6.7 Hz, 3H), 1.25 (dd, J = 3.8/9.1 Hz, 1H), 1.36 (dd, J = 5.1/9.4 Hz, 1H), 1.74−1.89 (m, 1H), 2.12 (s, 3H), 3.79−3.92 (m, 1H), 5.13−5.43 (m, 3H), 5.87 (ddd, J = 6.8/10.2/17.2 Hz, 1H). The following signals in the NMR spectra of crude reaction mixture are assigned to **15c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.07−4.27 (m, 1H, *syn* + *anti*), 4.95−5.10 (m, 1H, syn + anti).; ^{13}C NMR (200 MHz, $CDCl_3$) δ 21.2, 21.7, 23.5, 24.3, 41.2, 70.7, 78.3, 129.3, 130.8, 170.1. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.41; H, 9.81.

***anti*-3-Acetoxy-6-phenylhexen-1-en-4-ol (*anti*-9d):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.73−1.87 (m, 1H), 1.90−2.02 (m, 1H), 2.13 (s, 3H), 2.61−2.79 (m, 1H), 2.82−2.99 (m, 1H), 3.73−3.87 (m, 1H), 5.18−5.47 (m, 3H), 5.88 (ddd, J = 10.0/10.3/17.3 Hz, 1H), 7.16−7.39 (m, 5H). The following signals in the NMR spectra of crude reaction mixture are assigned to **15d**: ^{1}H NMR (200 MHz, $CDCl_3$) _4.17−4.32 (m, 1H), 4.93−5.05 (m, 1H).; ^{13}C NMR (200 MHz, $CDCl_3$) δ 21.4, 32.1, 34.2, 72.1, 78.2, 119.7, 126.1, 128.5, 132.1, 141.8, 170.4. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.84; H, 7.79.

***syn*-(*E*)-1-Phenyl-4-acetoxy-hexa-1,5-dien-3-ol (*syn*-9e).** ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.14 (s, 3H), 4.26−4.52 (m, 1H), 5.28−5.48 (m, 3H), 5.77−6.01 (m, 1H), 6.19 (dd, J = 6.2/15.8 Hz, 1H), 6.7 (d, J = 15.8 Hz, 1H), 7.23−7.45 (m, 5H). The following signals in the NMR spectra of crude reaction mixture are assigned to **15e**: (200 MHz, $CDCl_3$) _3.75−3.79 (m, 1H), 5.23−5.27 (m, 1H).; ^{13}C NMR (200 MHz, $CDCl_3$) δ 21.1, 73.4, 73.9, 118.9, 119.2, 123.7, 126.4, 128.2, 131.9, 132.6, 134.5, 170.2. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.31; H, 6.87.

2-Methyl-4-acetoxyhexa-1,5-dien-3-ol (9f): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.80 (s, 3H), 2.12 (s, 3H), 4.15−4.36 (m, 1H), 4.95−5.14 (m, 2H), 5.18−5.46 (m, 3H), 5.72−5.96 (m, 1H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 18.0, 21.1, 72.8, 73.8, 114.6, 119.0, 132.7, 135.8, 144.0, 170.2. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.58; H, 8.34.

***syn*-1-Furyl-2-acetoxybut-3-en-1-ol (*syn*-9g):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.09 (s, 3H), 2.41 (d, J = 5.9 Hz, 1H), 4.86 (broad t, $J \sim$ 5.3 Hz, 1H), 5.34 (dt, J = 1.4/10.4 Hz, 1H), 5.38 (dt, J = 1.4/17.4 Hz, 1H), 5.60 (ddt, J = 1.2/4.8/6.3 Hz, 1H), 5.89 (ddd, J = 6.3/10.4/17.4 Hz, 1H), 6.30−6.40 (m, 2H), 7.37−7.43 (m, 1H). The following signals in the NMR spectra of crude reaction mixture are assigned to **15g**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.57−4.70 (m, 1H), 5.78 (d, J = 7.3 Hz, 1H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 21.1, 69.5, 76.0, 107.7, 110.2, 119.6, 131.7, 142.3, 152.4, 169.9. Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16. Found: C, 61.28; H, 6.22.

***syn*-1-(4-Methylphenyl)-2-acetoxybut-3-en-1-ol (*syn*-9h):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.08 (s, 3H), 2.35 (s, 3H), 4.86 (t, J = 4.1 Hz, 1H), 5.28 (dt, J = 1.4/17.4 Hz, 1H), 5.29 (dt, J = 1.5/9.9 Hz, 1H), 5.46 (ddt, J = 1.2/4.5/6.2 Hz, 1H), 5.82 (ddd, J = 6.2/9.9/17.4 Hz, 1H), 7.16 (br d, J = 7.7 Hz, 2H), 7.27 (br d, J = 7.7 Hz, 2H). The following signals in the NMR spectra of crude reaction mixture are assigned to **15h**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.36−4.50 (m, 1H), 5.65 (d, J = 6.8 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 21.5, 77.3, 77.9, 117.2, 127.4, 129.4, 136.9, 137.7, 138.1. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.97; H, 7.41.

***syn*-1-(4-Methoxyphenyl)-2-acetoxybut-3-en-1-ol (*syn*-9i):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.07 (s, 3H), 3.82 (s, 3H), 4.83 (d, J = 4.8 Hz, 1H), 5.28 (dt, J = 1.1/16.5 Hz, 1H), 5.29 (dt, J = 1.1/10.3 Hz, 1H), 5.43 (ddt, J = 1.1/4.8/6.6 Hz, 1H), 5.83 (ddd, J = 6.6/10.3/16.5 Hz, 1H), 6.89 (br d, J = 8.7 Hz, 2H), 7.30 (br d, J = 8.7 Hz, 2H). The following signals in the NMR spectra of crude reaction mixture are assigned to **15i**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.35−4.48 (m, 1H), 5.63 (d, J = 7.5 Hz, 1H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 21.2, 55.5, 74.7, 78.1, 113.3, 119.6, 127.8, 131.5, 131.8, 159.2, 169.9. Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 66.15; H, 6.76.

***anti*-3-Acetoxydec-1-en-4-ol (*anti*-9j):** ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (broad t, $J \sim$ 7.3 Hz, 3H), 1.21−1.35 (m, 7H), 1.36−1.53 (m, 3H), 2.10 (s, 3H), 3.68−3.81 (m, 1H), 5.15−5.35 (m, 2H), 5.33−5.40 (m, 1H), 5.86 (ddd, J = 7.0/10.3/17.5 Hz, 1H). The following signals in the NMR spectra of crude reaction mixture are assigned to **15j**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.08−4.25 (m, 1H), 4.82−5.02 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 21.2, 22.6, 25.6, 29.2, 31.7, 32.3, 72.6, 77.9, 119.3, 131.8, 170.1. Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.26; H, 10.35. Found: C, 67.33; H, 10.29.

Equilibration Experiments. A 1:1 mixture of *syn*-**9a** and *syn*-**15a** (0.145 g, 0.7 mmol) was added at 25 °C to a solution of **7** (1 mmol), prepared according to typical procedure A. After the mixture was stirred at 25 °C for 40 min, water was added (0.5 mL), and the reaction mixture was stirred for 5 min and filtered (Celite). The aqueous layer was extracted with ether, and the combined organic layers were dried (Na_2SO_4) and evaporated at reduce pressure. The crude reaction mixture was dissolved in MeOH/H_2O (5 mL, 9:1 v/v), K_2CO_3 (0.415 g, 3 mmol) was added, and the reaction mixture was stirred at rt overnight. MeOH was removed at reduced pressure and the aqueous layer was extracted with ether. The combined organic layers were dried (Na_2SO_4) and evaporated at reduce pressure. ^{1}H NMR analysis of the crude reaction mixture revealed the presence of pure *syn*-**2a**.

A second experiment was carried out with an *anti*-enriched 1:1 mixture of **9a** and **15a** (190 mg, 0.9 mmol, *syn*/*anti* = 33:67). Again, ^{1}H NMR analysis of the crude reaction mixture revealed that **2a** had preserved the same original 33:67 *syn*/*anti* ratio.

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Note Added After ASAP Posting.

The Table of Contents graphic had an incorrect structure in the version posted January 9, 2003; the correct version was posted January 10, 2003.

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