Regio- and Stereoselective Synthesis of Homoallylic Alcohols Based on the Use of (3-Chloroprop-1-en-1-yl)boronates

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Dedicated to Professor Gianfranco Cainelli on occasion of his 70th birthday

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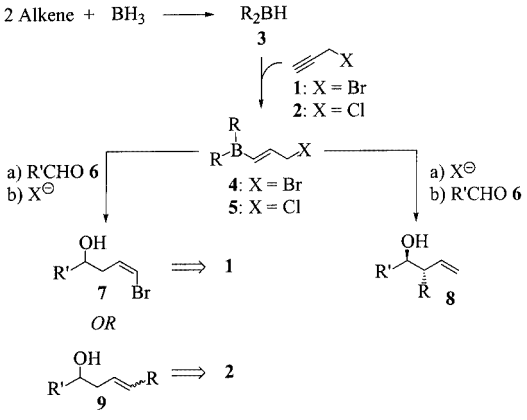
A set of (3-chloroprop-1-en-1-yl)boronates **10** were synthesised, starting from (3-chloroprop-1-en-1-yl)bis(isopinocampheyl)borane. Quaternisation of **10** by Grignard methodology afforded "ate" species **14**, which underwent spontaneous anionotropic rearrangement to give the substituted allylboronates **15**. By a suitable choice of the diol component in **10** and of the reaction temperature, α- or γ-substituted allylboronates **15** or **16** could be selectively produced, offering routes to homoallylic alcohols **9** or *anti*-**8**, respectively, after treatment with an aldehyde.

Introduction

Very recently we reported two simple routes to homoallylic alcohols, consisting of three-component processes involving a dialkylborane, propargyl bromide (**1**)[1,2] or chloride (**2**),[3] and an aldehyde. Sequences of reactions were carried out consecutively in a one-pot fashion, the process beginning with the preparation of a dialkylborane **3** (R_2BH) by hydroboration of an alkene, followed by the hydroboration of **1** or **2** with **3** to give (3-bromoprop-1-en-1-yl)borane **4** or the corresponding 3-chloro analogue **5**, and terminating with the addition of a quaternary ammonium bromide or chloride and of an aldehyde **6**. Investigation of the reaction mechanisms (quaternisation to borate anions, anionotropic rearrangements, 1,3-boratropic shifts and carbonyl additions) allowed us to develop two very efficient synthetic methodologies, differing only in the order of addition of the halide anion and of the aldehyde, but resulting in different homoallylic alcohols.[2,3] Scheme 1 summarises our results; from propargyl bromide (**1**) we have access to (*Z*)-1-bromoalk-1-en-4-ols **7** or *anti*-homoallylic alcohols **8**, while propargyl chloride (**2**) under the same experimental conditions offers a route to (*E*)-homoallylic alcohols **9** or to *anti*-**8**.

The excellent levels of simple diastereoselectivity make our procedures attractive when the R substituent differs from H and CH_3. In fact, it is well known that the milestone in stereocontrolled carbon−carbon bond-forming



Scheme 1

chemistry represented by the allylboration of carbonyl compounds has been almost completely centred on the simple allylation and crotylation process, with exceptional results obtained by the use of chiral boranes and boronates.[4,5] The number of reports related to the synthesis of homoallylic alcohols **8** and **9** with different R groups, however, is very limited.[6−9] If the search for the synthesis of *anti*-homoallylic alcohols **8** is extended to other metals, only a few examples based on the use of substituted allylic chromium(III),[10] triphenoxytitanium(IV)[11,12] or manganate[13] species are available in the literature.

Such divergence between the number of papers dealing with crotylation and those related to variously substituted allylboron derivatives is due on one hand to the huge number of target-oriented research projects aimed at the synthesis of polyketide-derived products, in which crotylation affords the correct pattern of alternate hydroxy and methyl

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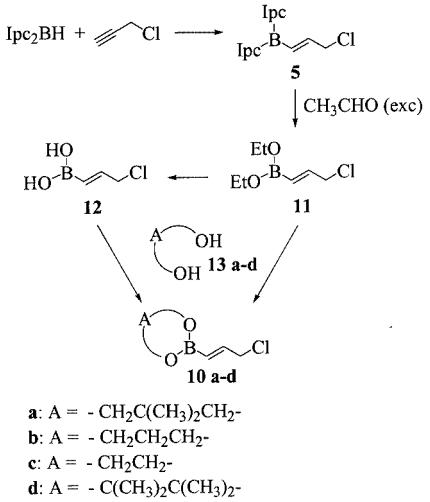
substituents along the carbon chain, and on the other hand to the difficulty associated with the preparation of substituted allylboranes or -boronates. The most widely used route to crotylboranes or -boronates in fact involves metallation of (*E*)- or (*Z*)-2-butene with a Schlosser base, followed by transmetallation; there is no doubt that unsymmetrical alkenes present regio- and stereochemical problems in the metallation step.

Results and Discussion

Synthesis of (3-Chloroprop-1-en-1-yl)boronates

The scopes of our previous procedures were limited by two major drawbacks: (i) the R group in **8** and **9** (Scheme 1) was originally inserted by hydroboration of an olefin, and (ii) it was often not easy to control the hydroboration of an alkene so as to obtain a secondary borane. To overcome these limits and to widen the scope of the reaction to include any R group, we modified our approach, moving from boranes **5** to boronates **10**. Bis(isopinocampheyl)borane chemistry offered an interesting solution, as depicted in Scheme 2. Hydroboration of propargyl chloride with bis(isopinocampheyl)borane (Ipc_2BH) in THF at 0 °C for 1 h afforded (3-chloroprop-1-en-1-yl)bis(isopinocampheyl)borane (**5**) in very good yield. Treatment of **5** with an excess of acetaldehyde proceeded to give α-pinene and diethyl boronate **11** by β-hydride reduction. Conversion of **11** into cyclic boronates **10** could be carried out in a single step by treatment of **11** with an equimolar amount of the selected diol **13a**−**d** (Method A), or alternatively in two steps: hydrolysis of **11** to the boronic acid **12**, followed by esterification with **13a**−**d** (Method B).



Scheme 2

The latter two-step procedure was preferred, since the intermediate boronic acid **12** could be prepared in good yield (up to 80%) on a multigram scale (up to 10 g per batch), could easily be purified by flash chromatography on silica gel, was storable for several weeks at −20 °C under an inert gas, and gave boronates **10** in better yields and higher purity (Table 1).

Table 1. Preparation of boronates **10a-d**

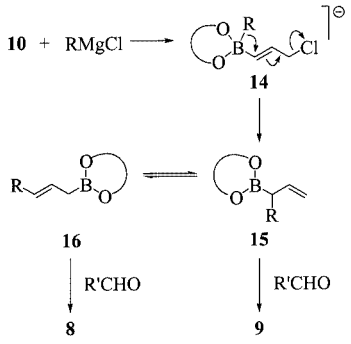
Entry	Product	Method	Yield (%)	Purification
1	**10a**	A	44%[a]	Silica gel chromatography
1	**10a**	B	90%[b]	Silica gel chromatography
2	**10b**	B	59%[b]	Distillation
3	**10c**	B	47%[b]	Distillation
4	**10d**	B	75%[b]	Distillation

[a] Calculated relative to starting Ipc_2BH. [b] Calculated relative to starting boronic acid **12**.

For this study we prepared two 1,3,2-dioxaborinanes (**10a** and **10b**) and two 1,3,2-dioxaborolanes (**10c** and **10d**).

Synthesis of Homoallylic Alcohols

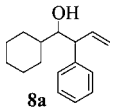
With **10** in hand, a kind of vinylogous Matteson reaction[14] was developed, by use of Grignard methodology. The result was the formation of substituted allylboronates, which could be trapped by aldehydes to give variously substituted homoallylic alcohols (Scheme 3). The "ate" species **14** underwent anionotropic 1,2-shift to give the α-substituted allylboronate **15**, which could undergo boratropic conversion into the thermodynamically more stable (*E*)-**16**.[15] Lastly, allylic intermediates **15** and **16** could be trapped by aldehydes, affording **9** and *anti*-**8**, respectively.

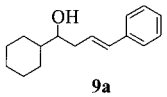


Scheme 3

At first, we focused our attention on factors determining the rearrangement of **15** into **16**. It is known that the energy barrier for the 1,3-boratropic shift is rather higher in allylic boronates than in allylic boranes, and that most crotyl boronates are configurationally stable at 0−20 °C.[4,16] We therefore carried out a series of experiments in which phenylmagnesium chloride was added to **10**, and the reaction mixture was then equilibrated for different times at various temperature (equilibration conditions) in order to allow migration and possible boratropic rearrangement to take place. Lastly, cyclohexanecarboxaldehyde was added, and the reaction mixture was stirred for 24 h at 20 °C and finally quenched (H_2O_2/NaOH), to give homoallylic alcohols **8a** and/or **9a**. Results are collected in Table 2.

Table 2. Treatment of phenylmagnesium chloride with **10**, followed by trapping with cyclohexanecarboxaldehyde, in THF as solvent; synthesis of homoallylic alcohols **8a** and **9a**


8a


9a

Entry	Boronate	Equilibration conditions t [h]	T [°C]	Reaction temperature[a] T [°C]	8a Yield (%)[b] (*anti*/*syn*)	9a Yield (%)[b] (*E*/*Z*)
1	**10a**	24	−78 → 20	20	9 (> 99:1)	39 (98:2)
2	**10a**	0.25	−15	−15 → 20	17 (98:2)	41 (98:2)
3	**10a**	0.5	−15	20	34 (> 99:1)	15 (98:2)
		24	70[c]			
4[d]	**10a**	0.5	−15	20	49 (> 99:1)	traces
		24	120[c]			
5	**10b**	24	−78 → 20	20	8 (> 99:1)	32 (98:2)
6	**10c**	0.75	−15	−15 → 20	21 (> 99:1)	21 (98:2)
7	**10c**	24	−15	20	36 (96:4)	traces
8	**10d**	0.5	−15	−15 → 20	traces	60 (98:2)

[a] Reaction time was always 24 h. [b] Isolated yields. [c] External bath temperature. [d] THF was replaced with toluene after the addition of PhMgCl to **10a**.

When **10a** was used and the equilibration temperature was ≤ 20 °C, a mixture of **8a** and **9a** enriched in **9a** was invariably obtained (Entries 1, 2). An increase in the temperature to 70 °C had the effect of raising the **15** → **16** rearrangement rate (Entry 3). When THF was replaced with toluene and the equilibration temperature was set at 120 °C, **8a** was the only homoallylic alcohol produced (Entry 4). A change from 5,5-dimethyl-1,3,2-dioxaborinane **10a** to the unsubstituted dioxaborinane **10b** had little effect on the **8**/**9** ratio (cf. Entries 1 and 5).

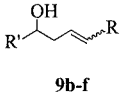
With the five-membered ring boronates **10c** and **10d** a dramatic effect on the fluxional behaviour of the corresponding allylboronates **15** and **16** was apparent, due to the presence of methyl substituents on the 1,3-dioxaborolane ring. When the ethylene glycol derived boronate **10c** was used we observed a greater propensity of **15** to isomerise to the thermodynamically more stable **16** (Entries 6, 7), affording almost pure *anti*-**8a** when a 24 h equilibration was adopted. On the other hand, when the pinacol-derived **10d** was used, the (α-phenylallyl)boronate **15** had virtually no tendency to isomerise to **16**, and **9a** was the sole product.[17]

As a final comment, Entries 4, 7, and 8 look attractive as synthetic procedures for the preparation of homoallylic alcohols *anti*-**8** or **9**.

Aware that a further factor controlling the isomerisation of substituted allylboronates was represented by the sub-

Table 3. Synthesis of homoallylic alcohols **8b**−**f** and **9b**−**f**


8b-f


9b-f

b: R = *i*Pr ; R' = Ph
c: R = *i*Pr ; R' = (*E*)-PhCH=CH-
d: R = Ph ; R' = $BnOCH_2$-
e: R = *n*Bu ; R' = Ph
f: R = Me ; R' = $PhCH_2CH_2$-

Entry	**10**	RMgCl R	Equilibration conditions T [°C]/t [h]	R′CHO R′	Reaction temperature T [°C][a]	**8** Yield (%)[b] *anti*/*syn*	**9** Yield (%),[b] (*E*)/(*Z*)
1	**10a**	*i*Pr	−15/0.25	Ph	−15 → 20	**8b** (13, > 99:1)	**9b** (52, 30:70)
2[c]	**10a**	*i*Pr	−15/0.5 120[d]/20	Ph	20	**8b** (44, > 99:1)	**9b** (traces)
3	**10b**	*i*Pr	−78 → 20/24	Ph	20	**8b** (13, > 99:1)	**9b** (32, 30:70)
4	**10c**	*i*Pr	−15 → 20/24	Ph	20	**8b** (30, 99:1)	**9b** (traces)
5	**10d**	*i*Pr	−15/0.75	Ph	−15 → 20	**8b** (traces)	**9b** (55, 30:70)
6	**10d**	*i*Pr	−15/0.75	(*E*)-PhCH=CH	−15 → 20	**8c** (traces)	**9c** (60, 30:70)
7	**10d**	Ph	−15/0.75	$BnOCH_2$	−15 → 20	**8d** (traces)	**9d** (35, 2:98)
8	**10d**	*n*Bu	−15/0.75	Ph	−15 → 20	**8e** (6, > 99:1)	**9e** (59, 20:80)

[a] Reaction time was always 24 h. [b] Isolated yields. [c] THF was replaced with toluene after addition of *i*PrMgCl to **10a**. [d] External bath temperature.

stituent R in **15**, we planned a new set of experiments with various RMgCl/**10a−d**/aldehyde systems, in order to explore the scope of the proposed procedures (Table 3).

A first set of experiments (Entries 1−6) was performed with *i*PrMgCl. We were happy to verify that the product distributions were almost the same, the fluxional behaviour of the **15/16** system being independent of the nature of the R substituent (*i*Pr vs. Ph).

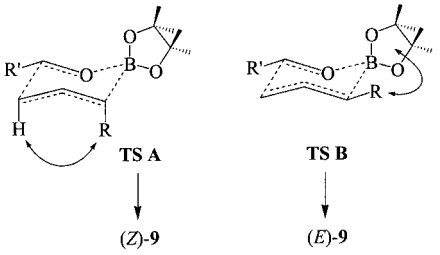
The most interesting features emerging from Tables 2 and 3 are as follows:

(i) Two routes for the synthesis of *anti*-**8** were devised, the first one exploiting the easily accessible and stable 1,3-dioxaborinane **10a** but requiring replacement of THF with toluene, the second route making use of the 1,3-dioxaborolane **10c**, much less stable to hydrolysis and to storage than **10a**, but needing much milder reaction conditions.

(ii) Pinacol-derived **10d**, conversely, was the substrate of choice when the target molecules were the homoallylic alcohols **9**. What we observed was the reversal of the C=C bond configuration in **9** when the migrating group R was an alkyl fragment rather than a phenyl ring. Thus, when the migrating group was phenyl the C=C bond configuration was (*E*), as in **9a** and **9d**, while when the migrating group was a primary or secondary alkyl group, the C=C bond was enriched in the (*Z*) isomer. It was interesting to note that, when homoallylic alcohols **9** had been obtained via RClBCH(R)CH=CH_2, (*E*)-**9** was invariably the major product even though the migrating R substituents were invariably alkyl groups.[3]

In order to shed light on the different (*E*)/(*Z*) compositions of **9** when R was an alkyl group or a phenyl ring, we performed quenching experiments with **10d** (Table 2, Entry 5 and Table 3, Entry 8) with short reaction times (1 h) and low conversion. The isomer distribution observed after 24 h was almost the same, within experimental error (± 5%). We thus ruled out the possibility that addition to the aldehyde was a reversible step and that the final (*E*)/(*Z*) composition was the result of thermodynamic equilibration.

On the other hand, inspection of molecular models of the Zimmerman−Traxler chair-like transitions states (TSs) A and B (Scheme 4) seemed to offer an explanation:

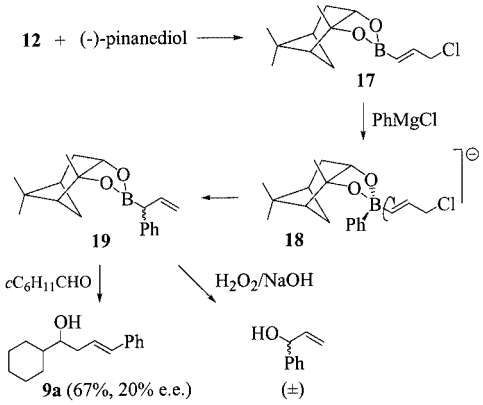


Scheme 4

(i) TS A was favoured when the pseudoaxial R was a bulky alkyl group, 1,3-diaxial interaction being less severe than the steric repulsion present in TS B between equatorial R and methyl groups on the dioxaborolane ring.

(ii) When R was the flat phenyl ring, it was able to adopt the equatorial arrangement (TS B) without suffering from steric compression, while a not negligible 1,3-diaxial interaction was present in TS A, due to the *ortho*-hydrogen atoms of the phenyl ring.

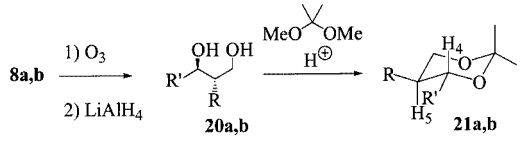
We performed a final experiment with the pinanediol-derived boronate **17** (Scheme 5), better to mimic a vinylogous Matteson reaction.[14] Unfortunately, owing to the free rotation around the B−vinyl bond in **18**, both diastereotopic faces of the sp^2 migration terminus were offered to the migrating group; we in fact isolated 1-phenyl-2-propen-1-ol in racemic form after oxidative quenching of the intermediate **19**. When we added cyclohexanecarboxaldehyde to the equimolar epimer mixture of **19**, the (*E*)-configured homoallylic alcohol **9a** was again obtained in quite good amounts. We also checked the *ee* of **9a** (HPLC, Chiralcel OD column, hexane/2-propanol), which proved to be 20%, thus attesting that the epimeric allylboronates **19**, present in the reaction mixture in equal amount, displayed different levels of facial selectivity.[18]



Scheme 5

Assignment of Stereochemistry to the Homoallylic Alcohols 8 and 9

In order to assign the *anti* stereochemistry to the dominant isomer of **8a** and **8b** (see Tables 2 and 3), we carried out reductive ozonisation of the C=C double bond, followed by protection of the 1,3-diol **20** as the acetonide **21** (Scheme 6). The original *anti* stereorelationship was easily determined from a *trans* H4-H5 coupling constant: $^3J_{H4\text{-}H5}$ = 10.6 Hz (**21a**) and 10.8 Hz (**21b**).



Scheme 6

As regards the (*E*)/(*Z*) configuration of **9**, this was determined when possible on the basis of geminal coupling constants in the ^{1}H NMR spectrum, or, as an alternative, on the basis of the chemical shifts of allylic carbon atoms in the ^{13}C NMR spectrum. It is known that carbon atoms

directly connected to (*Z*)-configured C=C bonds are more shielded than those connected to (*E*)-configured C=C bonds,[19] and, in fact, the chemical shifts of the allylic carbon atoms of (*Z*)-**9** regularly resonated at higher fields (δ = 4−6 ppm) than those in the corresponding (*E*)-**9**.

Conclusions

In conclusion, this study represents the third contribution in a series of papers centred on the development of new procedures for the synthesis of *anti*-homoallylic alcohols of general structure **8** or homoallylic alcohols of general structure **9**. All the solutions we offer to achieve this goal share the same starting point: namely the hydroboration of a propargyl halide that will ultimately furnish the allyl moiety in the target molecule **8** or **9**. While in our previous reports the R group in **8** and **9** invariably came from an alkene through hydroboration, this contribution widens the opportunities for the synthesis of homoallylic alcohols bearing, in principle, any R group, originating from a Grignard reagent.

Experimental Section

General Remarks: All reactions were performed in oven-dried glassware under dry argon. NMR: Varian Gemini 300 (300 and 75 MHz, for ^1H and ^{13}C, respectively) and Varian Gemini 200 (200 and 50 MHz, for ^1H and ^{13}C, respectively); $CHCl_3$ at $\delta_H = 7.27$ and $CDCl_3$ at $\delta_C = 77.0$ as internal standards. GC-MS: HP 5890 II instrument connected to an HP 5970 quadrupole mass detector. CC: Merck 60 Kieselgel. TLC: Merck silica gel plates (60F-254). Bulb-to-bulb distillations were performed with a Büchi GKR-50 apparatus. FT-IR: Nicolet 210 spectrometer.

(*E*)-(3-Chloroprop-1-en-1-yl)boronic Acid (12): $BH_3{\cdot}SMe_2$ (5 mL, 50 mmol) was slowly added at 0 °C to a solution of α-pinene (16 mL, 100 mmol) in THF (40 mL), and the solution was stirred for about 12 h while being allowed to come to room temp. The reaction mixture was cooled to 0 °C, freshly distilled propargyl chloride (4 mL, 55 mmol) was added, and the solution was stirred for 2 h at 0 °C. Acetaldehyde (11 mL, 200 mmol) was added at 0 °C and the reaction mixture was stirred for 12 h, while being allowed to come to room temp. The solution was transferred by cannula into a flask filled with water (30 mL) and stirred for 30 min. The aqueous layer was extracted with ether (3 × 50 mL), the combined organic layers were dried (Na_2SO_4) and filtered, and the solvents were evaporated at reduced pressure. The product was obtained by flash chromatography on SiO_2 (cyclohexane/ether, 8:2) as a variable mixture of boronic acid **12** and its trimer, 2,4,6-tris(3-chloropropenyl)cyclotriboroxane (**12a**), with the same R_f values on silica. Yield: 4.51 g (75%). **12:** $R_f = 0.48$ (cyclohexane/ether, 3:7). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.20 (dd, *J* = 1.2/5.8 Hz, 2 H, CH_2Cl), 5.85 (dt, *J* = 1.2/17.2 Hz, 1 H, BC*H*=CH), 6.99 (dt, *J* = 5.8/17.2 Hz, 1 H, BCH=C*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 47.0 (*C*H_2Cl), 128.2 (B*C*H=CH), 143.4 (BCH=*C*H) ppm. **12a:** $R_f = 0.48$ (cyclohexane/ether, 3:7). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.14 (dd, *J* = 0.9/5.7 Hz, 2 H, CH_2Cl), 5.73 (dt, *J* = 0.9/17.6 Hz, 1 H, BC*H*=CH), 6.57 (dt, *J* = 5.7/17.6 Hz, 1 H, BCH=C*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 47.0 (*C*H_2Cl), 128.2 (B*C*H=CH), 143.4 (BCH=*C*H) ppm.

2-[(*E*)-3-Chloroprop-1-en-1-yl]-5,5-dimethyl-1,3,2-dioxaborinane (10a): Compound **12** (1.2 g, 10 mmol) was added to a solution of 2,2-dimethylpropane-1,3-diol (**13a**, 1.04 g, 10 mmol) in pentane (5 mL). THF was added drop by drop until the solution became clear. The solution was stirred for 12 h, $MgSO_4$ was added, and the reaction mixture was stirred for 1 h. The solution was filtered (Celite®) and the solvents were evaporated to dryness. Pure **10a** was obtained as a clear oil by flash chromatography on SiO_2 (cyclohexane/ether, 9:1). Yield: 1.70 g (90%). $R_f = 0.38$ (cyclohexane/ether, 7:3). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.98 (s, 6 H, CH_3), 3.65 (s, 4 H, OCH_2CH_2O), 4.10 (dd, *J* = 1.2/6.0 Hz, 2 H, CH_2Cl), 5.65 (dt, *J* = 1.2/17.4 Hz, 1 H, BC*H*=CH), 6.56 (dt, *J* = 6.0/17.4 Hz, 1 H, BC*H*=CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (*C*Me_2), 31.6 (C*Me*$_2$), 46.0 (*C*H_2Cl), 71.9 (*C*H_2O), 124.1 (broad, B*C*H=CH), 144.0 (BCH=*C*H) ppm. $C_8H_{14}BClO_2$ (188.08): calcd. C 50.98, H 7.49; found C 50.95, H 7.53.

2-[(*E*)-3-Chloroprop-1-en-1-yl]-1,3,2-dioxaborinane (10b): By the same procedure as described for **10a**, pure **10b** was obtained as a clear oil by distillation (b.p. = 110 °C, *p* = 0.27 Torr). Yield: 0.95 g (59%). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.98 (dt, *J* = 5.1/6.0 Hz, 2 H, OCH$_2$CH_2CH$_2$O), 4.02−4.07 (m, 4 H, OCH_2CH$_2$CH_2O), 4.08−4.10 (m, 2 H, CH_2Cl), 5.62 (dt, *J* = 1.5/17.7 Hz, 1 H, BC*H*=CH), 6.52 (dt, *J* = 6.3/17.7 Hz, 1 H, BCH=C*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 27.3 (OCH$_2$*C*H$_2$CH$_2$O), 46.1 (*C*H_2Cl), 61.7 (OCH_2CH$_2$CH_2O), 125.9 (broad, B*C*H=CH), 143.7 (BCH=*C*H) ppm. $C_6H_{10}BClO_2$ (160.05): calcd. C 44.93, H 6.28; found C 44.97, H 6.25.

2-[(*E*)-3-Chloroprop-1-en-1-yl]-1,3,2-dioxaborolane (10c): By the same procedure as described for **10a**, pure **10c** was obtained as a clear oil by distillation (b.p. = 90 °C, *p* = 0.7 Torr). Yield: 0.69 g (47%). ^1H NMR (200 MHz, $CDCl_3$): δ = 4.12 (dd, *J* = 1.4/6.2 Hz, 2 H, CH_2Cl), 4.60 (s, 4 H, OCH_2CH_2O), 5.79 (dt, *J* = 1.4/17.4 Hz, 1 H, BC*H*=CH), 6.68 (dt, *J* = 6.2/17.4 Hz, 1 H, BCH=C*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 45.9 (*C*H_2Cl), 65.6 (O*C*H$_2$-*C*H$_2$O), 122.7 (broad, B*C*H=CH), 147.1 (BCH=*C*H) ppm. $C_5H_8BClO_2$ (146.03): calcd. C 41.03, H 5.51; found C 41.09, H 5.53.

2-[(*E*)-3-Chloroprop-1-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10d): By the same procedure as described for **10a**, pure **10d** was obtained as a clear oil by distillation (b.p. = 90 °C, *p* = 0.5 Torr). Yield: 1.52 g (75%). ^1H NMR (200 MHz, $CDCl_3$): δ = 1.28 (s, 12 H, *Me*$_2$C−C*Me*$_2$), 4.11 (dd, *J* = 1.4/6.2 Hz, 2 H, CH_2Cl), 5.75 (dt, *J* = 1.4/17.6 Hz, 1 H, BC*H*=CH), 6.64 (dt, *J* = 6.2/17.6 Hz, 1 H, BCH=C*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7 (CH_3), 31.7 (*C*Me_2), 46.1 (*C*H_2Cl), 72.0 (O*C*-*C*O), 126.3 (broad, B*C*H=CH), 144.0 (BCH=*C*H) ppm. $C_9H_{16}BClO_2$ (202.09): calcd. C 53.38, H 7.96; found C 53.32, H 7.93.

[3a*R*-(3aα,4β,6β,7aα)]-2-[(*E*)-3-Chloroprop-1-en-1-yl]-hexahydro-3a,5,5-trimethyl-4,6-methano-1,3,2-benzodioxaborole (10e): By the same procedure as described for **10a**, pure **10e** was obtained as a clear oil by flash chromatography on SiO_2 (cyclohexane/ether, 7:3). Yield: 2.47 g (97%). $[\alpha]_{20}^{D} = -18.3$ (*c* = 1.12, $CHCl_3$). R_f = 0.41 (cyclohexane/ether, 7:3). GC-MS (70 eV): *m*/*z* (%) = 55 (74), 67 (100), 93 (28), 105 (18), 109 (19), 119 (19), 134 (16), 158 (53), 171 (25), 185 (71), 198 (16), 213 (21), 239 (25), 254 (5). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.86 (s, 3 H, OCCH_3), 1.14 (d, *J* = 11.0 Hz, 1 H), 1.30 (s, 3 H, CCH_3), 1.41 (s, 3 H, CCH_3), 1.81−1.99 (m, 2 H), 2.07 (t, *J* = 5.5 Hz, 1 H), 2.15−2.45 (m, 2 H), 4.12 (dd, *J* = 1.5/5.9 Hz, 2 H, CH_2Cl), 4.33 (dd, *J* = 1.5/8.8 Hz, 1 H, C*H*OB), 5.77 (dt, *J* = 1.5/17.6 Hz, 1 H, BC*H*=CH), 6.65 (dt, *J* = 5.9/17.6 Hz, 1 H, BCH=C*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$):

δ = 23.9 (OC*C*H$_3$), 26.3 (C*C*H$_3$), 27.0 (C*C*H$_3$), 28.5, 35.3, 38.1 (*C*Me$_2$), 39.4, 46.0, 51.2, 77.8 (*C*HOB), 85.8 (Me*C*O), 121.6 (broad, B*C*H=CH), 146.3 (BCH=*C*H) ppm. $C_{13}H_{20}BClO_2$ (254.12): calcd. C 61.34, H 7.92; found C 61.39, H 7.97.

Synthesis of *anti*-1-Cyclohexyl-2-phenylbut-3-en-1-ol (8a) and (*E*)-1-Cyclohexyl-4-phenylbut-3-en-1-ol (9a, Table 2, Entry 2). Typical Procedure: Phenylmagnesium chloride (710 μL, 1.8 M solution in THF, 1.28 mmol) was slowly added at −15 °C to a solution of boronate **10a** (1.28 mmol) in anhydrous THF (2 mL), and the reaction mixture was stirred at −15 °C for 15 min. Cyclohexanecarbaldehyde (155 μL, 1.28 mmol) was added at −15 °C, and the reaction mixture was stirred at 20 °C for 24 h. The solution was cooled to 0 °C, quenched with NaOH (1 mL, 1 M solution in water) and H_2O_2 (1 mL, 30% v/v) and stirred at 0 °C for 15 min. The solution was filtered (Celite®), the aqueous layer was extracted with ether (3 × 5 mL), the combined organic layers were dried (Na_2SO_4), and the solvents were evaporated at reduced pressure. The products were separated and purified by flash chromatography on SiO_2 (cyclohexane/ether, 95:5). **8a:** 0.05 g, 17%; R_f = 0.48 (cyclohexane/ether, 7:3). GC-MS (70 eV): *m*/*z* (%) = 55 (10), 67 (7), 91 (11), 95 (25), 115 (14), 118 (100), 119 (13), 128 (1). IR (neat): ṽ [cm^{-1}] = 3462 (broad, OH), 3108, 3062, 2925, 2852, 1637, 1600, 1493, 1450, 1388, 1308, 1085, 1040, 988, 917, 758, 701. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.15−1.85 (m, 11 H), 3.50 (dd, *J* = 7.2/8.6 Hz, 1 H, C*H*Ph), 3.56−3.66 (m, 1 H, C*H*OH), 5.18−5.28 (m, 2 H, CH=C*H*$_2$), 6.18 (ddd, *J* = 9.2/10.8/17.2 Hz, 1 H, C*H*=CH$_2$), 7.23−7.39 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.0, 26.4, 26.5, 26.6, 30.2, 39.6, 53.6 (*C*HPh), 78.1 (*C*HOH), 117.5 (CH=*C*H$_2$), 126.4 (*C*H=CH$_2$), 127.8, 128.6, 138.3, 142.0 ppm. $C_{16}H_{22}O$ (230.17): calcd. C 83.43, H 9.63; found C 83.49, H 9.57. **9a:** 0.121 g, 41%; R_f = 0.38 (cyclohexane/ether, 7:3). M.p. 71−72 °C (cyclohexane). GC-MS (70 eV): *m*/*z* (%) = 55 (12), 67 (8), 91 (13), 95 (42), 115 (14), 118 (100), 119 (12), 128 (2). IR (film): ṽ [cm^{-1}] = 3301 (broad, OH), 2925, 2851, 1449, 1344, 1061, 1035, 968, 742, 693. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05−1.92 (m, 11 H), 2.26−2.36 (m, 1 H, C*H*$_2$CH=), 2.46−2.53 (m, 1 H, C*H*$_2$CH=), 3.42−3.58 (m, 1 H, C*H*OH), 6.26 (ddd, *J* = 1.5/8.1/15.9 Hz, 1 H, C*H*=CHPh), 6.50 (d, *J* = 15.9 Hz, 1 H, CH=C*H*Ph), 7.23−7.39 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.1, 26.3, 28.1, 29.1, 37.9, 43.1, 77.7 (*C*HOH), 125.9 (*C*H=CHPh), 126.9, 127.0, 128.4, 132.7 (CH=*C*HPh), 137.2 ppm. $C_{16}H_{22}O$ (230.17): calcd. C 83.43, H 9.63; found C 83.35, H 9.55.

All the experiments reported in Table 2 (with the exception of Entry 4) and in Table 3 (with the exception of Entry 2) were carried out using the same molar scale, molar ratios, dilution and quenching conditions as reported in the above procedure. Experimental modifications, listed in the Tables, only refer to temperature and reaction time.

Synthesis of *anti*-1-Cyclohexyl-2-phenylbut-3-en-1-ol (8a). Alternative Procedure (Table 2, Entry 4): Phenylmagnesium chloride (710 μL, 1.8 M solution in THF, 1.28 mmol) was slowly added at −15 °C to a solution of boronate **10a** (1.28 mmol) in anhydrous THF (2 mL). After stirring at −15 °C for 30 min, the reaction mixture was allowed to come to room temperature and THF was removed at reduced pressure. The residue was dissolved in anhydrous toluene (5 mL) and the resulting solution was heated under reflux for 24 h at 120 °C. The solution was allowed to cool to room temperature, cyclohexanecarboxaldehyde (155 μL, 1.28 mmol) was added, and the reaction mixture was stirred at 20 °C for 24 h. The solution was cooled to 0 °C, quenched with NaOH (1 mL, 1 M solution in water) and H_2O_2 (1 mL, 30% v/v) and stirred at 0 °C for 15 min. The solution was filtered (Celite®), the aqueous layer was extracted with ether (3 × 5 mL), the combined organic layers were dried (Na_2SO_4), and the solvents were evaporated at reduced pressure. Title compound **8a** (0.144 g, 49%) was obtained after purification by flash chromatography on SiO_2 (cyclohexane/ether, 95:5).

***anti*-1-Cyclohexyl-2-phenylpropane-1,3-diol (20a):** A solution of *anti*-1-cyclohexyl-2-phenyl-but-3-en-1-ol (**8a**, 0.163 g, 0.71 mmol) in CH_2Cl_2 (25 mL) was ozonised for 15 min at −78 °C. The solution was allowed to come to room temp. and the solvent was evaporated at reduced pressure. The residue was dissolved in anhydrous THF (10 mL) and a suspension of $LiAlH_4$ (0.08 g, 2.10 mmol) in THF (5 mL) was slowly added at 0 °C. The reaction mixture was stirred at 0 °C for 2 h, quenched by consecutive addition of H_2O (0.4 mL) and NaOH (1 M, 0.1 mL) and stirred at room temperature for a further 30 min. The solution was filtered (Celite®), the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL), the combined organic layers were dried (Na_2SO_4), and the solvents were evaporated at reduced pressure. The title product was obtained as an oil (0.108 g, 65%) by flash chromatography on SiO_2 (cyclohexane/ether, 90:10 v/v). R_f = 0.42 (cyclohexane/ether, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05−1.78 (m, 11 H), 3.03 (ddd, *J* = 4.8/7.8/12.6 Hz, 1 H, C*H*Ph), 3.85−3.90 (m, 2 H, C*H*$_2$OH + C*H*OH), 4.07 (dd, *J* = 7.8/11.1 Hz, 1 H, C*H*$_2$OH), 7.17−7.36 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.2, 26.0, 26.3, 26.4, 30.4, 40.3 (CH$_2$*C*HCH$_2$), 50.0 (Ph*C*H), 67.3 (*C*H$_2$OH), 80.7 (*C*HOH), 126.9, 128.2, 128.8, 140.3 ppm. $C_{15}H_{22}O_2$ (234.16): calcd. C 76.88, H 9.46; found C 76.95, H 9.41.

***trans*-4-Cyclohexyl-2,2-dimethyl-5-phenyl-1,3-dioxane (21a):** A catalytic amount of Amberlyst® 15H (10 mg) was added at room temperature to a solution of freshly distilled 2,2-dimethoxypropane (0.088 mL, 0.72 mmol) and *anti*-1-cyclohexyl-2-phenylpropane-1,3-diol (**20a**, 0.085 g, 0.36 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred at room temperature for 1 h and filtered (Celite®), and the solvent was removed at reduced pressure. The title compound was obtained as an oil (0.097 g, 98%) by flash chromatography on SiO_2 (cyclohexane). R_f = 0.80 (cyclohexane/ether, 6:4). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.05−1.80 (m, 11 H), 3.00 (dt, *J* = 5.6/10.6 Hz, 1 H, C*H*Ph), 3.81 (dd, *J* = 5.6/11.4 Hz, 1 H, C*H*$_2$OH), 4.07 (broad t, *J* ≈ 11.0 Hz, 2 H, C*H*$_2$OH + C*H*OH), 7.18−7.37 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.5, 25.7, 26.4, 26.6, 26.7, 29.7, 30.1, 39.3 (CH$_2$*C*HCH$_2$), 43.8 (Ph*C*H), 66.1 (*C*H$_2$O), 77.1 (*C*HO), 98.3 (*C*Me$_2$), 126.9, 128.2, 128.7, 139.5 ppm. $C_{18}H_{26}O_2$ (274.19): calcd. C 78.79, H 9.55; found C 78.86, H 9.57.

***anti*-2-Isopropyl-1-phenylbut-3-en-1-ol (8b):** R_f = 0.51 (cyclohexane/ether, 7:3). GC-MS (70 eV): *m*/*z* (%) = 51 (7), 55 (5), 77 (34), 79 (57), 105 (9), 107 (100), 129 (4). IR (neat): ṽ [cm^{-1}] = 3420 (broad, OH), 3066, 3029, 2959, 2927, 2871, 1637, 1455, 1386, 1196, 1028, 1001, 914, 763, 700. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.83 (d, *J* = 5.1 Hz, 3 H, C*H*$_3$), 0.87 (d, *J* = 5.1 Hz, 3 H, C*H*$_3$), 1.40−1.53 (m, 1 H, C*H*Me$_2$), 2.09 (br. s, 1 H, O*H*), 2.11−2.25 (m, 1 H, C*H*CH=CH$_2$), 4.63 (d, *J* = 8.8 Hz, 1 H, C*H*OH), 5.18 (dd, *J* = 2.2/16.8 Hz, 1 H, CH=C*H*$_2$), 5.33 (dd, *J* = 2.2/10.3 Hz, 1 H, CH=C*H*$_2$), 5.83 (dt, *J* = 10.3/16.8 Hz, 1 H, C*H*=CH$_2$), 7.23−7.39 (m, 5 H, ArH) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.3 (*C*H$_3$), 22.0 (*C*H$_3$), 27.6 (*C*HMe$_2$), 58.8 (*C*HCH=CH$_2$), 74.7 (*C*HOH), 120.1 (CH=*C*H$_2$), 126.8, 127.6, 128.2, 135.6 (*C*H=CH$_2$), 142.7 ppm. $C_{13}H_{18}O$ (190.14): calcd. C 82.06, H 9.53; found C 82.12, H 9.48. The following signals in the previous ^{1}H NMR spectra are due to the *syn* isomer. δ = 2.38−2.45 (m, 1 H, C*H*CH=CH$_2$), 4.86 (dd, *J* = 2.1/17.0 Hz, 1 H, CH=C*H*$_2$), 5.02 (dd, *J* = 2.1/10.6 Hz, 1 H, CH=C*H*$_2$), 5.50 (dt, *J* = 10.6/17.0 Hz, 1 H, C*H*=CH$_2$) ppm.

***anti*-2-Isopropyl-1-phenylpropane-1,3-diol (20b):** By the same procedure as described for **8a**, *anti*-2-isopropyl-1-phenylpropane-1,3-diol was obtained from **8b** in 60% yield after purification by flash chromatography on silica (cyclohexane/ether, 90:10 v/v). R_f = 0.23 (cyclohexane/ether, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.9, 3 H, C*H*$_3$), 1.03 (d, *J* = 6.9 Hz, 3 H, C*H*$_3$), 1.57−1.67 (m, 1 H, Me$_2$C*H*), 1.68−1.80 (m, 1 H, HOCH$_2$C*H*), 3.79−3.83 (m, 2 H, C*H*$_2$OH), 4.93 (d, *J* = 7.2 Hz, 1 H, C*H*OH), 7.29−7.45 (m, 5 H, Ar*H*) ppm.

***trans*-5-Isopropyl-2,2-dimethyl-4-phenyl-1,3-dioxane (21b):** By the same procedure as described for **21a**, 5-isopropyl-2,2-dimethyl-4-phenyl-1,3-dioxane was obtained from **20b** in 98% yield after purification by flash chromatography on silica (cyclohexane). R_f = 0.80 (cyclohexane/ether, 6:4). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81 (d, *J* = 6.9 Hz, 3 H, CHC*H*$_3$), 0.87 (d, *J* = 6.9 Hz, 3 H, CHC*H*$_3$), 1.46−1.54 (m, 1 H, OCH$_2$C*H*), 1.47 (s, 3 H, OCC*H*$_3$), 1.56 (s, 3 H, OCC*H*$_3$), 1.82−1.98 (m, 1 H, Me$_2$C*H*), 3.90 (dd, *J* = 5.4/11.7 Hz, 1 H, C*H*$_2$O), 3.97 (t, *J* ≈ 11.2 Hz, 1 H, C*H*$_2$O), 4.77 (d, *J* = 10.8 Hz, 1 H, PhC*H*), 7.26−7.36 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.8, 19.5, 21.0, 25.6, 29.7, 45.8 (OCH$_2$*C*H), 60.4 (O*C*H$_2$CH), 75.5 (Ph*C*H), 98.7 (*C*Me$_2$), 125.4, 127.6, 128.4, 144.8 ppm. $C_{15}H_{22}O_2$ (234.16): calcd. C 76.88, H 9.46; found C 76.79, H 9.51. The following spectroscopic data for the *cis* isomer were obtained from an enriched chromatographic fraction. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.68 (d, *J* = 6.9 Hz, 3 H, CHC*H*$_3$), 1.06 (d, *J* = 6.9 Hz, 3 H, CHC*H*$_3$), 1.42−1.50 (m, 1 H, OCH$_2$C*H*), 1.51 (s, 3 H, OCC*H*$_3$), 1.55 (s, 3 H, OCC*H*$_3$), 1.52−1.62 (m, 1 H, Me$_2$C*H*), 4.06 (dd, *J* = 1.8/12.3 Hz, 1 H, C*H*$_2$O), 4.19 (dd, *J* = 3.9/12.3 Hz, 1 H, C*H*$_2$O), 5.29 (d, *J* = 3.6 Hz, 1 H, PhC*H*), 7.23−7.36 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.1, 20.4, 22.9, 25.3, 29.4, 43.5 (OCH$_2$*C*H), 61.0 (O*C*H$_2$CH), 73.7 (Ph*C*H), 98.7 (*C*Me$_2$), 125.4, 126.7, 128.0, 141.1 ppm.

(*Z*)-5-Methyl-1-phenylhex-3-en-1-ol (9b): The title compound could not be separated from the minor (*E*) isomer by flash chromatography. The following data were obtained from an enriched mixture. R_f = 0.46 (cyclohexane/ether, 7:3). GC-MS (70 eV): *m*/*z* (%) = 51 (7), 55 (5), 69 (8), 77 (32), 79 (56), 91 (3), 105 (6), 107 (100), 128 (1). IR (neat): ṽ [cm^{-1}] = 3380 (broad, OH), 3062, 3029, 2928, 2852, 1701, 1603, 1493, 1454, 1380, 1305, 1079, 1048, 972, 912, 758, 702. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.6 Hz, 3 H, C*H*$_3$), 0.95 (d, *J* = 6.6 Hz, 3 H, C*H*$_3$), 2.01 (d, *J* = 2.4 Hz, 1 H, CHO*H*), 2.37−2.69 (m, 3 H, C*H*Me$_2$ + C*H*$_2$CH=CH*i*Pr), 4.64−4.78 (m, 1 H, C*H*OH), 5.26−5.36 (m, 1 H, C*H*=CH*i*Pr), 5.43 (br. d, *J* = 8.2 Hz, 1 H, CH=C*H*i*Pr), 7.30−7.38 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.97 (*C*H$_3$), 23.08 (*C*H$_3$), 26.7 (*C*Me$_2$), 37.4 (*C*H$_2$CH=CH*i*Pr), 73.9 (*C*HOH), 122.1 (*C*H=CH*i*Pr), 125.8, 127.4, 128.2, 141.0 (CH=*C*H*i*Pr), 144.0 ppm. $C_{13}H_{18}O$ (190.14): calcd. C 82.06, H 9.53; found C 81.98, H 9.59. **(*E*) Isomer:** The following signals in the previous NMR spectra can easily be assigned to the (*E*) isomer. ^{1}H NMR: δ = 5.57 (dd, *J* = 6.4/15.6 Hz, 1 H, CH=C*H*i*Pr) ppm. ^{13}C NMR: δ = 22.53 (*C*H$_3$), 22.54 (*C*H$_3$), 31.1 (*C*Me$_2$), 42.7 (*C*H$_2$CH=CH*i*Pr), 73.5 (*C*HOH), 122.3 (*C*H=CH*i*Pr), 125.8, 127.3, 128.2, 142.1 (CH=*C*H*i*Pr), 144.1 ppm.

(1*E*,5*Z*)-7-Methyl-1-phenylocta-1,5-dien-3-ol (9c): The title compound could not be separated from the minor (5*E*) isomer by flash chromatography. The following data were obtained from an enriched mixture. R_f = 0.46 (cyclohexane/ether, 7:3). GC-MS (70 eV): *m*/*z* (%) =55 (40), 77 (19), 91 (6), 102 (8), 115 (24), 133 (100). IR (neat): ṽ [cm^{-1}] = 3429 (broad, OH), 3060, 3027, 2957, 2852, 1716, 1601, 1495, 1450, 1362, 1174, 1070, 969, 749, 697. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.0 (d, *J* = 4.0 Hz, 3 H, C*H*$_3$), 1.04 (d, *J* = 4.0 Hz, 3 H, C*H*$_3$), 1.81 (d, *J* = 4.2 Hz, 1 H, O*H*), 2.26−2.52 (m, 3 H, C*H*Me$_2$ + C*H*$_2$CH=CH*i*Pr), 4.29−4.45 (m, 1 H, C*H*OH), 5.34−5.44 (m, 1 H, C*H*=CH*i*Pr), 5.49 (br. d, *J* = 9.4 Hz, 1 H, CH=C*H*i*Pr), 6.29 (dd, *J* = 6.2/15.8 Hz, 1 H, PhCH=C*H*), 6.65 (d, *J* = 15.8 Hz, 1 H, PhC*H*=CH), 7.30−7.45 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.1 (*C*H$_3$), 26.6 (*C*Me$_2$), 35.5 (*C*H$_2$CH=CH*i*Pr), 72.2 (*C*HOH), 121.7 (Ph*C*H=CH), 126.3 (*C*H=CH*i*Pr), 127.4, 128.4, 130.1 (PhCH=*C*H), 131.7, 136.6, 140.9 (CH=*C*H*i*Pr) ppm. $C_{15}H_{20}O$ (216.15): calcd. C 83.29, H 9.32; found C 83.35, H 9.38. **(1*E*,5*E*) Isomer:** The following signals in the previous NMR spectra are due to the (5*E*) isomer. ^{1}H NMR: δ = 5.63 (dd, *J* = 6.4/15.8 Hz, 1 H, CH=C*H*i*Pr) ppm. ^{13}C NMR: δ = 22.6 (*C*H$_3$), 31.1 (*C*Me$_2$), 40.8 (*C*H$_2$CH=CH*i*Pr), 71.9 (*C*HOH), 121.8 (Ph*C*H=CH), 126.3 (*C*H=CH*i*Pr), 127.4, 128.4, 129.9 (PhCH=*C*H), 131.6, 136.7, 142.1 (CH=*C*H*i*Pr) ppm.

(*E*)-1-Benzyloxy-5-phenylpent-4-en-2-ol (9d): R_f = 0.45 (cyclohexane/ether, 7:3). IR (neat): ṽ [cm^{-1}] = 3433 (broad, OH), 3059, 3026, 2930, 2830, 1637, 1598, 1495, 1451, 1362, 1305, 1096, 1027, 967, 739, 695. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.37−2.50 (m, 2 H, C*H*$_2$CH=CHPh), 3.45 (dd, *J* = 7.2/9.4 Hz, 1 H, C*H*$_2$OBn), 3.58 (dd, *J* = 3.6/9.4 Hz, 1 H, C*H*$_2$OBn), 3.90−4.05 (m, 1 H, C*H*OH), 4.59 (s, 2 H, C*H*$_2$Ph), 6.16−6.31 (dt, *J* = 7.0/15.8 Hz, 1 H, C*H*=CHPh), 6.44−6.52 (d, *J* = 15.8 Hz, 1 H, CH=C*H*Ph), 7.22−7.39 (m, 10 H, Ar*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 37.1 (*C*H$_2$CH=CHPh), 70.0 (*C*HOH), 73.3 (*C*H$_2$Ph), 73.8 (*C*H$_2$OBn), 125.7 (*C*H=CHPh), 126.0, 127.0, 127.62, 128.3, 132.5 (CH=*C*HPh), 137.1, 137.8 ppm. $C_{18}H_{20}O_2$ (268.15): calcd. C 80.56, H 7.51; found C 80.48, H 7.58.

(*Z*)-1-Phenyloct-3-en-1-ol (9e): The title compound could not be separated from the minor (*E*) isomer by flash chromatography. The following data were obtained from an enriched mixture. R_f = 0.42 (cyclohexane/ether, 8:2). IR (neat): ṽ [cm^{-1}] = 3381 (broad, OH), 3063, 3028, 2955, 2860, 1693, 1603, 1493, 1453, 1378, 1307, 1198, 1048, 971, 912, 758, 700. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 5.8 Hz, 3 H, C*H*$_3$), 1.15−1.38 (m, 4 H, CH$_3$C*H*$_2$C*H*$_2$), 1.96−2.10 (m, 2 H, C*H*$_2$CH=CH), 2.16 (br. s, 1 H, O*H*), 2.39−2.67 (m, 2 H, CH=CHC*H*$_2$), 4.70 (dd, *J* = 6.0/7.0 Hz, 1 H, C*H*OH), 5.34−5.66 (m, 2 H, C*H*=C*H*), 7.23−7.39 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 14.0 (CH$_3$), 22.3, 27.1, 31.7, 37.2 (CH=CH*C*H$_2$), 73.8 (*C*HOH), 126.8 (CH$_2$*C*H=CH), 127.4, 127.8, 128.2, 133.4 (CH=*C*HCH$_2$), 139.2 ppm. $C_{14}H_{20}O$ (204.15): calcd. C 82.30, H 9.87; found C 82.34, H 9.93. The following signals in the previous ^{13}C NMR spectra are due to the (*E*) isomer. δ = 22.1 (*C*H$_3$), 29.3, 30.1, 32.3, 42.7 (CH=CH*C*H$_2$), 73.4 (*C*HOH), 124.5 (CH$_2$*C*H=CH), 127.2, 127.8, 128.2, 134.9 (CH=*C*HCH$_2$), 138.2 ppm.

(*Z*)-1-Phenylhept-5-en-3-ol (9f): The title compound could not be separated from the minor (*E*) isomer by flash chromatography. The following data were obtained from an enriched mixture: R_f = 0.42 (cyclohexane/ether, 6:4). GC-MS (70 eV): *m*/*z* (%) = 51 (6), 65 (15), 77 (7), 91 (100), 92 (28), 118 (17), 134 (20), 135 (8). IR (neat): ṽ [cm^{-1}] = 3380 (broad, OH), 3061, 3024, 2931, 2859, 1653, 1603, 1495, 1454, 1048, 968, 747, 704. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.70 (br. d, *J* = 6.8 Hz, 3 H, C*H*$_3$), 1.78−1.92 (m, 2 H, PhCH$_2$C*H*$_2$), 2.31 (br. t, *J* = 6.8 Hz, 2 H, C*H*$_2$CH=CH), 2.63−2.97 (m, 2 H, PhC*H*$_2$), 3.61−3.80 (m, 1 H, C*H*OH), 5.38−5.61 (m, 1 H, CH=C*H*CH$_3$), 5.62−5.81 (m, 1 H, C*H*=CHCH$_3$), 7.20−7.38 (m, 5 H, Ar*H*) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.1 (*C*H$_3$), 32.1 (*C*H$_2$CH=CH), 35.1 (Ph*C*H$_2$), 38.4 (PhCH$_2$*C*H$_2$), 70.7 (*C*HOH), 125.7 (CH=*C*HCH$_3$), 125.8, 127.3, 128.26, 128.32 (*C*H=CHCH$_3$), 142.0 ppm. $C_{13}H_{18}O$ (190.14): calcd. C 82.06, H 9.53; found C 82.13, H 9.49. The following sig-

nals in the previous ^{13}C NMR spectra are due to the (*E*) isomer. δ = 18.1 (CH_3), 40.8 ($CH_2CH{=}CH$), 70.1 (*C*HOH) ppm.[20]

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