Scope and Limitations of the Scandium-Catalyzed Enantioselective Addition of Chiral Allylboronates to Aldehydes

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Received 17 December 2003; revised 2 March 2004

Dedicated in memory of Professor Satoru Masamune, a former member of our Department (1964–1978) and a pioneer in the field of stereodirected synthesis with organoboron compounds.

Abstract: Scandium triflate catalyzes the addition of camphor-derived allyl-, methallyl-, and crotylboronates to aldehydes to provide homoallylic alcohols with excellent diastereo- and enantioselectivity. Aromatic, aliphatic, and propargylic aldehydes can be used successfully in this system. Additional advantages of the camphor-diol allylboronates are their ease of synthesis, their availability in both enantiomeric forms, and their stability towards silica gel chromatography. The usefulness of this methodology is further demonstrated by the gram-scale synthesis of various homoallylic alcohols of high enantiomeric excess and by the concise synthesis of the pheromone (4*S*)-2-methyloctan-4-ol.

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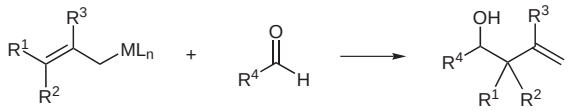
Key words: allylations, chiral auxiliaries, crotylations, Lewis acids, scandium

1 Introduction

Carbonyl allylation chemistry is one of the most useful tools in modern organic synthesis, particularly for the construction of polyacetate and polypropionate natural products.[1] Yet, despite extensive investigations, there is no general method using simple and *stable* allylation reagents for the stereocontrolled formation of a wide variety of homoallylic alcohols (Equation 1).



Equation 1

Whereas many highly enantioselective allylation methods (Equation 1, R^1, R^2, R^3 = H) have been developed,[2–9] few of these procedures have been successfully extended to the enantioselective methallylation (Equation 1, R^1, R^2 = H, R^3 = Me) and crotylation (Equation 1, R^3 = H, R^1, R^2 = H, Me or Me, H) of aldehydes.

In fact, the crotylation of aldehydes with stable reagents to afford either *syn* or *anti* products predictably in a highly enantioselective manner (>95% ee) remains problematic. Indeed, while most crotylation methods using silicon or tin reagents give rise to *syn* products preferentially,[1a,10] methods using chromium, titanium, zirconium, or indium generally provide *anti* products predominantly.[1a] Chiral crotylboron reagents have attracted particular attention in this area, as they can give access to both *syn* and *anti* products in a predictable fashion and in very high diastereoselectivity. A closed chair-like transition state has been postulated to account for the diastereospecificity of these reactions.[11] Examples of chiral crotylboration reagents include Brown's pinene-based **1**,[12] Roush's tartrate-derived **2**,[13] Masamune's borane **3**,[14] and Hoffmann's camphor-derived reagents **4**[15] (Figure 1). Despite their usefulness, methods using these reagents suffer from one or many drawbacks such as air and moisture sensitivity, low enantioselectivities, lengthy preparation of reagents, and poor reactivity.

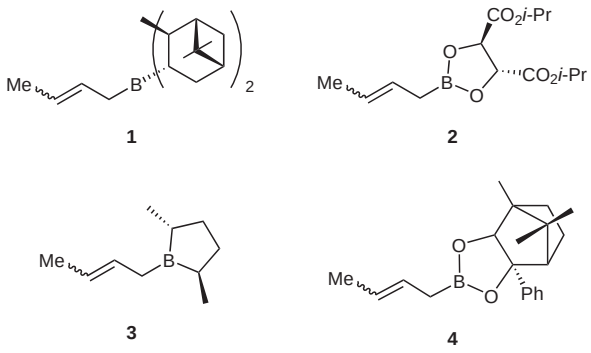


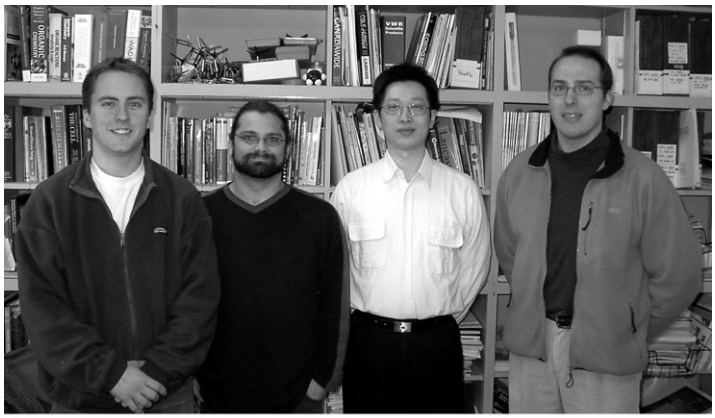
Figure 1 Examples of chiral crotylboration reagents for aldehydes.

More recently, crotyltrichlorosilane reagents have also been shown to react diastereospecifically, presumably through a cyclic transition state. Despite their high efficiency with aromatic aldehydes, crotylsilylation methods based on chiral phosphoramide[16] or *N*-oxide[17] catalysts are incompatible with aliphatic aldehydes.

Given the importance of the products of allylation, methallylation, and crotylation reactions, we set out to develop the first general, highly enantio- and diastereoselective

SYNTHESIS 2004, No. 8, pp 1290–1302
Advanced online publication: 04.05.2004
DOI: 10.1055/s-2004-822359; Art ID: M05003SS

Biographical Sketches



from left to right: Michel Gravel, Hugo Lachance, Xiaosong Lu, Dennis Hall

Michel Gravel was born in 1973 in Québec, Québec, Canada. After obtaining his B.Sc. (pharmaceutical chemistry) from Université de Sherbrooke in 1997, he enrolled in the Ph.D. program at the University of Alberta, working under the supervision of Prof. Dennis Hall. His research focuses on new allylboration and crotylboration reagents and methodology, as well as the use of boronic acid-diethanolamine adducts in organic synthesis. In 2004, he has moved to the University of Chicago to pursue postdoctoral work under the guidance of Prof. Viresh H. Rawal.

Hugo Lachance was born in 1974 in Québec, Québec, Canada. He obtained his B.Sc. (pharmaceutical chemistry) in 2000 from Université de Sherbrooke. He then worked briefly as a research assistant in medicinal chemistry at Merck Frosst, Montréal, Canada. Since 2001, he has been enrolled in the Ph.D. program at the University of Alberta, working under the supervision of Prof. Dennis Hall. His research focuses on new allylboration and methallylboration reagents and methodology.

Xiaosong Lu was born in 1967 in Beijing, China. He obtained his Ph.D. in 2001 in physical organic chemistry under the direction of Prof. John Warkentin at McMaster University. From 2001 to 2003, he did postdoctoral research in the group of Prof. Dennis Hall at the University of Alberta. His research focused on stereocontrolled crotylboration methodology, and the synthesis of functionalized arylboronic acids for use in solid phase organic synthesis and oligosaccharide recognition. In January 2004, he joined Naeja Pharmaceutical Inc. (Edmonton, Alberta) as a research scientist.

Dennis Hall was born in 1968 in Baie-Comeau, Québec, Canada. He obtained his Ph.D. in 1995, working in synthetic organic chemistry under the direction of Prof. Pierre Deslongchamps at Université de Sherbrooke. From 1995 to 1997 he was an NSERC Postdoctoral Fellow in the bioorganic chemistry laboratory of Prof. Peter G. Schultz in the Department of Chemistry at the University of California, Berkeley. He returned to Canada in August 1997 to take a Faculty position in the Department of Chemistry at the University of Alberta, and he was promoted to Associate level in 2001. The unifying theme of his research program is the development of new synthetic and biological applications of organoboronic acid derivatives. Ongoing projects in his laboratory cover a wide range of topics, including stereocontrolled synthetic methodology, multicomponent reactions, solid-phase organic synthesis, combinatorial chemistry and oligosaccharide recognition. He received a Boehringer Ingelheim Young Investigator Award for Organic Chemistry (1999), a Research Corporation Innovation Award (1999), a Petro-Canada Young Innovator Award (2003), and the AstraZeneca Award in Chemistry (2003). He is currently a member of the Editorial Advisory Board of the Journal of Combinatorial Chemistry (American Chemical Society).

system for the allylation of aldehydes based on a conveniently handled, stable boron-based reagent.[18]

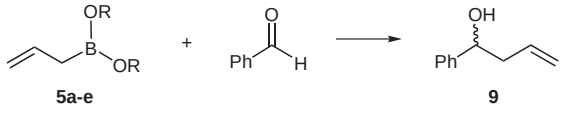
Following the discovery of Lewis acid-catalyzed allylborations by our group[19] and others,[20] we recently reported on the use of chiral allylboronates in highly diastereo- and enantioselective allylation, methallylation, and crotylation reactions.[21] This new approach to the allylation of aldehydes uses Hoffmann's air-stable allylboronates under $Sc(OTf)_3$ catalysis. Hoffmann's boronates were developed over twenty years ago and were the first chiral allylboron reagents ever reported.[7] Significant advantages of these boronates are their stability and the availability of camphor in both enantiomeric forms. Our new Lewis acid-catalyzed procedure provides the benefit of increased reactivity at low temperatures, which significantly improves substrate scope and stereoselectivity. Indeed, a wide variety of aldehydes can be employed successfully, including functionalized aliphatic aldehydes that are useful for the elaboration of complex natural products. Herein, we present the optimization of this methodology, the demonstration of its gram-scale capability, and its application to a concise synthesis of the pheromone (4*S*)-2-methyloctan-4-ol.

2 Results and Discussion

2.1 Optimization

In the development of stable boron-based allylation reagents, boronates are preferred because of their superior stability over boranes. When we started this work, however, there were no chiral allylboronic esters known to afford practical levels of enantioselectivity (>95% ee) in additions to achiral aldehydes under typical low-temperature conditions (–78 °C).[1a] On the basis of the potential beneficial effect of a lower reaction temperature and the different mechanistic nature of the Lewis acid-catalyzed manifold on the enantioselectivity, we revisited a number of known chiral diol auxiliaries for boronic acids. In our initial series of experiments, the allylation of benzaldehyde was investigated using various solvents, temperatures, and Lewis acids identified from our previous studies (Equation 2).[19] A small set of allylboronates **5** derived from chiral diol precursors **a**–**e** was compared under a number of different conditions (Figure 2).

Using allylboronate (–)-**5a**, these investigations revealed that $Sc(OTf)_3$ provides the best combination of rate and enantioselectivity in the formation of homoallylic alcohol **9** (Table 1, entries 1–7). A pronounced solvent effect was also observed, with dichloromethane standing out as the most efficient one both in terms of conversion and ee (entries 7–12). Whereas pinanediol-based **5c** and the tartrate-based reagents **5d**[5] and **5e**[22] gave low enantioselectivity (entries 14–16), the Hoffmann camphor-derived allylboronates **5a** and **5b**[7] gave excellent results (entries 7, 13). Further optimization confirmed that the preferred order of addition involves mixing $Sc(OTf)_3$ in CH_2Cl_2 at –78 °C, followed by the aldehyde and a solution of the allylboronate in CH_2Cl_2.



Equation 2

An important feature of Hoffmann's allylboronates is their relative stability. Indeed, they can be purified by chromatography and handled without any special precautions. Moreover, the diol precursor of allylboronate **5a** can be easily synthesized without chromatographic purification in four steps from camphorquinone,[7] which is commercially available in both enantiomeric forms. While the enantioselectivities and the rates originally reported were modest (see entry 1, with no catalyst),[7] the results obtained under our new catalytic manifold are remarkable.

2.2 Substrate Scope

As shown in Table 2, allylations of aromatic, aliphatic, and propargylic aldehydes using boronates **5a**–**8a** (Equation 3) generally proceeded in good yields and with very high ee's.

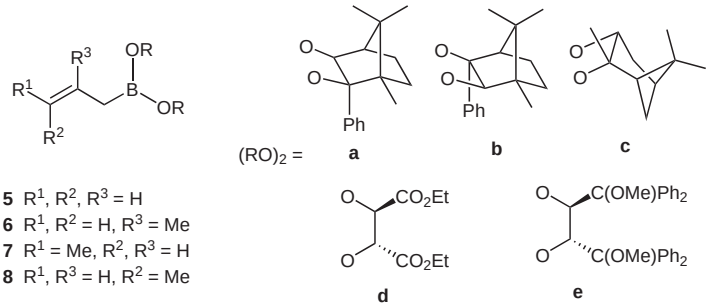
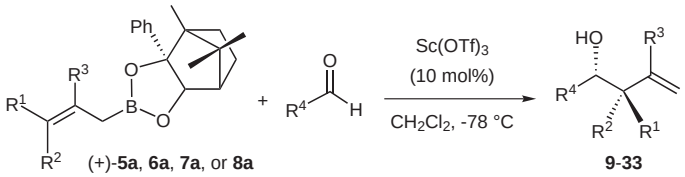


Figure 2 Chiral allylboronates evaluated for enantioselective Lewis acid-catalyzed additions onto benzaldehyde.

Table 1 Lewis Acid-Catalyzed Allylboration of Benzaldehyde[a]

Entry	Boronate	Acid	Solvent	Temp. (°C)	Conv.[b] (%)	ee[c] (%)
1[d]	**5a**	none	CH_2Cl_2	25	50	11
2	**5a**	$AlCl_3$	CH_2Cl_2	–78	14	63
3	**5a**	$TiCl_4$	CH_2Cl_2	–78	22	78
4	**5a**	TfOH	CH_2Cl_2	–78	72	84
5	**5a**	$Cu(OTf)_2$	CH_2Cl_2	–40	4	52
6	**5a**	$Yb(OTf)_3$	CH_2Cl_2	–40	4	38
7	**5a**	$Sc(OTf)_3$	CH_2Cl_2	–78	90	92
8[e]	**5a**	$Sc(OTf)_3$	CH_2Cl_2	–78	72	93
9	**5a**	$Sc(OTf)_3$	toluene	–78	30	46
10	**5a**	$Sc(OTf)_3$	hexanes	–78	20	8
11	**5a**	$Sc(OTf)_3$	Et_2O	–78	4	–
12	**5a**	$Sc(OTf)_3$	THF	–78	0	–
13	**5b**	$Sc(OTf)_3$	CH_2Cl_2	–78	62	84[f]
14	**5c**	$Sc(OTf)_3$	CH_2Cl_2	–78	100	9
15	**5d**	$Sc(OTf)_3$	CH_2Cl_2	–78	100	7
16	**5e**	$Sc(OTf)_3$	CH_2Cl_2	0	0	–

[a] Typical reaction conditions: 0.44 mmol of (–)-**5**, 0.40 mmol of benzaldehyde, 0.04 mmol of Lewis acid, 1 mL of solvent, –78 °C, 2 h reaction time.
[b] Measured by integration of benzyl alcohol vs. benzaldehyde ^{1}H NMR signals after work-up (see experimental section).
[c] Measured by chiral HPLC (see experimental section).
[d] 72 h reaction time.
[e] 4 Å molecular sieves (10 mg) were added.
[f] The opposite enantiomer is predominant.



Equation 3

The simple allylation using **5a** (entries 1–8) smoothly provides homoallylic alcohols **9**–**16** and is usually complete within 4 hours, with the exception of α-branched aldehydes (entry 8). Although the lower ee obtained with benzyl-protected hydroxyacetaldehyde is disappointing (entry 4), its TBDMS-protected equivalent provides satisfactory results (entry 5). Methallylation using **6a** also constitutes a very efficient process (entries 9–15), providing products **17**–**23**. In fact, this method represents one of the most efficient enantioselective methallylations of aldehydes to date, combining both substrate generality and high enantioselectivities.[1a] Most significantly, the (*E*)- and (*Z*)-crotylboronates **7a** and **8a** provide the respective *anti* and *syn* products **24**–**33** in good yields and high enantioselectivity (entries 16–25). Moreover, the diastereoselectivity observed in reactions using crotylboronates **7a** and **8a** is consistently very high (>95% de). Interestingly, the ee obtained for the crotylation of benzaldehyde using **8a** is much lower than any other observed in this study (entry 21). We believe that the increased steric bulk of benzaldehyde may distort the chair-like transition state in order to alleviate a *syn*-pentane interaction, leading to reduced selectivity (Figure 3).

Table 2 Substrate Scope for the $Sc(OTf)_3$-Catalyzed Addition of Allylboronates **5a**–**8a** to Aldehydes[a]

Entry	Boronate (R^1, R^2, R^3)	Aldehyde (R^4)	Product[b]	Yield[c] (%)	ee[d] (%)
1	**5a** (H, H, H)	Ph	**9**	85	92
2	**5a**	$PhCH_2CH_2$	**10**	64	97
3	**5a**	$TBDPSO(CH_2)_2$	**11**	86	93
4	**5a**	$BnOCH_2$	**12**	62	77
5	**5a**	$TBDMSOCH_2$	**13**	76	90
6	**5a**	$TBDPSOCH_2$	**14**	61	90
7	**5a**	$H_{11}C_5CC$	**15**	87	95
8	**5a**	C_6H_{11}	**16**	53	92
9	**6a** (H, H, Me)	Ph	**17**	64	98
10	**6a**	$PhCH_2CH_2$	**18**	76	97
11	**6a**	$TBDPSO(CH_2)_2$	**19**	77	97
12	**6a**	$BnOCH_2$	**20**	70	97
13	**6a**	$TBDMSOCH_2$	**21**	88	95
14[e]	**6a**	$H_{11}C_5CC$	**22**	95	97
15	**6a**	C_6H_{11}	**23**	63	92
16	**7a** (Me, H, H)	Ph	**24**	60	97
17	**7a**	$PhCH_2CH_2$	**25**	71	96
18	**7a**	$TBDPSO(CH_2)_2$	**26**	63	94
19	**7a**	$TBDMSOCH_2$	**27**	63	96
20	**7a**	$H_{11}C_5CC$	**28**	78	97
21	**8a** (H, Me, H)	Ph	**29**	53	59
22	**8a**	$PhCH_2CH_2$	**30**	52	96
23	**8a**	$TBDPSO(CH_2)_2$	**31**	57	96
24	**8a**	$TBDMSOCH_2$	**32**	57	98
25	**8a**	$H_{11}C_5CC$	**33**	61	95
26[f]	**8a**	$PhCH_2CH_2$	**30**	65	90
27[g]	**8a**	$PhCH_2CH_2$	**30**	48	–[i]
28[h]	**8a**	$PhCH_2CH_2$	**30**	<10	–[i]

[a] Typical reaction conditions: 0.4 mmol of aldehyde in CH_2Cl_2 (0.5 M) with 10 mol% $Sc(OTf)_3$ at –78 °C followed by addition of allylboronate (entries 1–15: 1.1 equiv, entries 16–20: 1.5 equiv). Entries 21–28 are with 1.5 equiv of aldehyde. Reaction time: 12–24 h.
[b] The diastereomeric ratio for entries 16–28 was always over 50:1 (determined by ^1H NMR).
[c] Yields of pure products isolated after flash chromatography.
[d] Measured by chiral HPLC on the free alcohol or a derivative thereof, or through NMR analysis of Mosher esters (see experimental section). The absolute configuration was determined by comparison of optical rotation with known compounds.
[e] Reaction performed on a 6 mmol scale.
[f] Trifluoroacetic acid (10 mol%) was used instead of $Sc(OTf)_3$.
[g] $TiCl_4$ (10 mol%) was used instead of $Sc(OTf)_3$.
[h] $AlCl_3$ (10 mol%) was used instead of $Sc(OTf)_3$.
[i] Not measured.

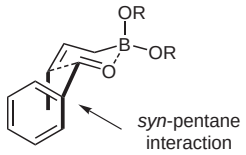


Figure 3 Increased steric bulk in the transition state for the reaction between **8a** and benzaldehyde.

Although crotylborations using **7a** and **8a** are slower than allylations using **5a** or methallylations using **6a**, good yields can be obtained by simply using a small excess of either the boronate or the aldehyde. Other attempts to improve the yields of crotylborations by using different acids (entries 26–28), or by increasing the catalyst loading, the concentration, or the reaction times have not given better results yet. We are presently exploring the use of more Lewis acidic Sc(III) sources to increase the rate of these crotylboration reactions.

Since our first report, we have found that α-branched aldehydes can undergo allylation with **5a** and **6a**, albeit at a slower rate (entries 8, 15). Additionally, we have discovered that propargylic aldehydes are very suitable substrates for allylations using **5a**–**8a**. The application of our methodology to this class of substrates represents a complementary approach to the enantioselective addition of terminal alkynes to aldehydes, for which unstable β,γ-unsaturated aldehydes would be required.[23] Of particular significance is the use of crotylboration reagents **7a** and **8a** in this process. To the best of our knowledge, no other method has been reported for the direct and highly enantioselective crotylation of propargylic aldehydes.[24–26] Interestingly, we noticed that the scandium catalyst exhibits very poor solubility in these reactions, suggesting the possibility of using a reduced catalyst loading, especially for reactions on a larger scale (*vide infra*). The absolute configuration of alcohols **24**–**26**, **29** and **31** was assigned by comparison of the sign of their optical rotation to that of known samples. The absolute configuration of all the other products was assigned by analogy.

In our original procedure, a DIBAL-H quench of the reaction mixture was followed by the addition of dilute acid. This standard workup procedure is required to eliminate any unreacted aldehyde, and to hydrolyze the borate product initially formed in the reaction. Unfortunately, this procedure allowed the recovery of only small amounts of the diol auxiliary (20–30%). We have since found that a simple basic workup following the DIBAL-H quench leads to a much improved recovery of the diol auxiliary. In a typical experiment, the reaction mixture is quenched by the addition of two equivalents of DIBAL-H and stirred at –78 °C for one hour. A 1 M aqueous solution of NaOH is then carefully added and a liquid-liquid extraction provides a crude mixture containing both the homoallylic alcohol and the diol auxiliary. In this way, the diol auxiliary is cleanly cleaved from the borate product and does not tend to decompose as is the case with our original acidic workup. Additionally, any unreacted allylboronate can easily be oxidized and hydrolyzed to maximize the recovery of the diol.[27] It is noteworthy that only one equivalent of diol auxiliary is generated from the reaction, simplifying the subsequent purification compared to other popular allylboron reagents.[2]

2.3 Synthetic Applications

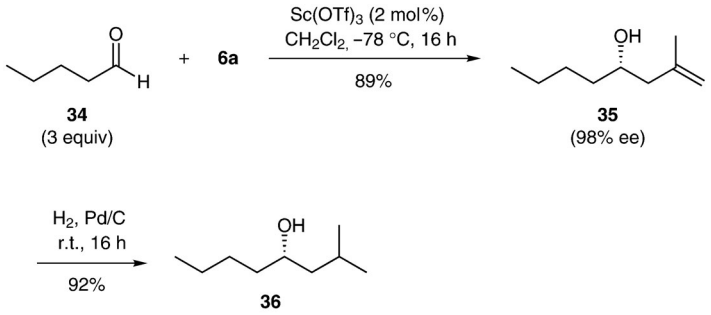
In order to test the practical potential of this system, we performed selected examples of allyl-, methallyl- and crotylborations on a gram-scale. As can be seen from Table 3, reagents **5a**–**8a** all give satisfactory results on a preparative scale. Importantly, the diol auxiliary can be recovered in good yield in all cases where the new basic workup was performed (entries 1, 2, 4–6). These results point to the potential application of this methodology in natural product synthesis.

Table 3 Gram-Scale Addition of Allylboronates **5a**–**8a** to Aldehydes, According to Equation 3[a]

Entry	Boronate	Product	Yield (%)		ee[d] (%)
			Product[b]	Diol[c]	
1	**5a**	**11**	65	78	97
2	**5a**	**15**	60	80	98
3	**6a**	**19**	71	–[e]	96
4	**6a**	**22**	95	65	97
5	**7a**	**28**	75	75	96
6	**8a**	**33**	72	75	95

[a] See experimental section for reaction conditions.
[b] Yields of pure homoallylic alcohol products isolated after flash chromatography.
[c] Combined recovery yield of diol from the allylboration and the oxidation/hydrolysis of unreacted allylboronate.
[d] Measured by NMR analysis of the Mosher ester derivatives.
[e] The original acidic workup was used and no diol isolation was achieved.

Accordingly, the usefulness of our methodology was tested towards a concise synthesis of (*S*)-(+)-2-methyl-4-octanol (**36**), the volatile male-produced aggregation pheromone of *Metamasius hemipterus* (Scheme 1).[28] Allylation of pentanal (**34**) using boronate **6a** proceeded as expected, providing the homoallylic alcohol **35** in excellent yield (89%) and enantioselectivity (98% ee). In fact, the reaction proceeded smoothly with the use of only 2 mol% catalyst, a loading level at which the catalyst is still mostly insoluble. Standard hydrogenation of the olefin in **35** gave access to the naturally occurring enantiomer of the pheromone in only two steps. This sequence represents the shortest enantioselective synthesis of (4*S*)-2-methyloctan-4-ol (**36**) to date,[29] and demonstrates the usefulness of boronates **5a**–**8a** for accessing aliphatic secondary alcohols that are difficult to synthesize through asymmetric reduction of the corresponding ketone.



Scheme 1 Asymmetric synthesis of (4*S*)-2-methyloctan-4-ol (**36**).

2.4 Mechanistic Considerations

On the basis of preliminary arguments presented earlier[19] and the fact that the crotylation reactions proceed diastereospecifically, these allylboration reactions are thought to proceed through the usual closed chair-like transition state. Indeed, our recent mechanistic studies provided substantial evidence for a closed bimolecular transition structure involving activation of the boronate via coordination of the scandium to one of the two exocyclic oxygen atoms.[30] This coordination should increase the electrophilicity of the boron atom, a factor that was shown to be determinant in the reactivity of allylboron reagents.[31] These results also allowed us to develop a possible interpretation to explain the enantioselectivity of the current allylation system. From the accepted stereoinduction model based on a π_{phenyl}-$\pi^*_{C=O}$ attraction,[7,32] the proposed transition structure (Figure 4) implicates coordination of Sc(III) to the least hindered lone pair (*syn* to H) of the pseudo-equatorial oxygen, thereby suppressing n_O-p_B conjugation and maximizing boron-carbonyl bonding.

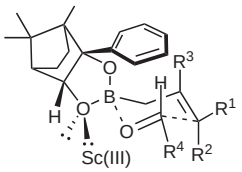


Figure 4 Proposed transition structure with $Sc(OTf)_3$ activation.

3 Conclusion

In conclusion, we have developed a remarkably general method for the enantioselective allylation, methallylation, and crotylation of aldehydes using Lewis acid catalysis. Of particular importance is the fact that this method uses stable, chiral allylboronates to give access to a wide range of homoallylic alcohols in very high diastereo- and enantioselectivity. We are currently exploring other synthetic applications of this methodology, and progress in this area will be reported in due course.

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. Toluene, hexanes and CH_2Cl_2 were distilled over CaH_2. THF and Et_2O were distilled over sodium/benzophenone ketyl. All aldehydes were purified by bulb-to-bulb distillation prior to use. Boronates **5a**, **6a**, **7a**, and **8a** were used within 24 hours after their purification. Thin layer chromatography (TLC) was performed on Merck Silica Gel 60 F_{254} plates and were visualized with UV light and 5% phosphomolybdic acid/EtOH (PMA). NMR spectra were recorded on Bruker AM 300, Bruker AM 200, Varian INOVA-300, INOVA-400 or INOVA-500 instruments. The residual solvent protons (^{1}H) or the solvent carbons (^{13}C) were used as internal standards for chemical shifts. Boron NMR spectra were referenced to external $BF_3{\cdot}OEt_2$; ^{19}F spectra were referenced to external $CFCl_3$. High resolution mass spectra were recorded by the University of Alberta Mass Spectrometry Services Laboratory using either electron impact (EI) or electrospray (ES) ionization techniques. Infrared spectra were obtained on a Nicolet Magna-IR 750 instrument. Optical rotations were recorded using Perkin-Elmer PE-241. Elemental analyses were performed on a Carlo Erba CHNS-O EA1108 system. The enantiomeric excess for compounds **13**, **15**, **16**, **19**, **21**–**23**, **28**, **33**, and **35** was determined using integration of the ^{19}F NMR signals of the corresponding Mosher ester derivatives.[33] The enantiomeric excess for compounds **9**–**12**, **14**, **17, 18**, **20**, **24**–**27**, and **29**–**32** was determined using an Agilent 1100 HPLC system. The enantiomeric excess for compounds **27** and **32** was determined on the corresponding phenylisocyanate adduct using an Agilent 1100 HPLC system. Chiralcel AD-RH, Chiralcel OD-RH, Chiralcel OD, and Chiralcel AD columns were purchased from Chiral Technologies Inc. Racemic homoallylic alcohols were prepared in the same manner using the pinacol boronate derivatives. The absolute stereochemistry for compounds **24**–**26**, **29**, and **31** was determined by comparison of the sign of optical rotation with reported literature values. The absolute stereochemistry for all other homoallylic alcohols was assigned by analogy.

(1*R*,2*S*,3*R*,4*S*)-2,3-*O*-[Allylboryl]-2-phenyl-1,7,7-trimethylbornanediol (5a)[7]

To a solution of triisopropylborate (1.30 mL, 5.71 mmol) in Et_2O (12 mL) at –78 °C was added a solution of allylmagnesium bromide (1.02 M in Et_2O, 5.00 mL, 5.10 mmol) dropwise and the resulting mixture was stirred at –78 °C for 4 h. The resulting suspension was poured onto an ice-cold mixture of 1 N HCl (50 mL), Et_2O (50 mL), and (1*R*,2*S*,3*R*,4*S*)-2-phenyl-1,7,7-trimethylbornanediol (**a**)[7] (980 mg, 3.98 mmol). The resulting mixture was stirred at ambient temperature for 30 min, then extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography (10% EtOAc–hexanes) yielded a colorless oil (1.104 g, 93%).

TLC (15% EtOAc–hexanes, PMA): 0.70.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.25 (m, 5 H), 5.91–5.77 (m, 1 H), 4.98–4.88 (m, 2 H), 5.11 (d, 1 H, *J* = 10.0 Hz), 4.73 (s, 1 H), 2.15 (d, 2 H, *J* = 5.2 Hz), 1.88–1.81 (m, 1 H), 1.71 (d, 2 H, *J* = 7.5

Hz), 1.23 (s, 3 H), 1.19–1.14 (m, 2 H), 1.08–1.01 (m, 2 H), 0.97 (s, 3 H), 0.94 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.8, 134.0, 127.5, 127.3, 126.8, 114.8, 95.8, 88.7, 52.1, 50.3, 48.9, 29.7, 24.8, 23.6, 20.8, 9.4.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 33.7.

(1*R*,2*S*,3*R*,4*S*)-2,3-*O*-[2-Methylallylboryl]-2-phenyl-1,7,7-trimethylbornanediol (6a)

To a solution of triisopropylborate (1.50 mL, 6.60 mmol) in Et_2O (12 mL) was added (1*R*,2*S*,3*R*,4*S*)-2-phenyl-1,7,7-trimethylbornanediol (**a**)[7] (1.48 g, 6.00 mmol). The mixture was stirred at ambient temperature for 30 min, then concentrated under reduced pressure and co-evaporated with CH_2Cl_2 (3 × 5 mL). The remaining colorless oil was dissolved in Et_2O (12 mL) and cooled to –78 °C. To this solution was added a solution of 2-methylallylmagnesium chloride (0.5 M in THF, 12.6 mL, 6.3 mmol). The resulting suspension was stirred at –78 °C for 4 h, then poured onto an ice-cold mixture of 1 N HCl (50 mL) and Et_2O (50 mL). The resulting mixture was stirred at ambient temperature for 30 min, then extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Flash chromatography (10% EtOAc–hexanes, SiO_2 pre-treated with 5% Et_3N–hexanes) yielded a colorless oil (1.31 g, 70%).

TLC (15% EtOAc–hexanes, PMA): 0.60.

$[\alpha]^{25}_D$ +24.3 (*c* = 2.16, $CHCl_3$).

IR (CH_2Cl_2 cast): 3072, 2957, 1646, 1445, 1338, 1034 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 2 H), 7.37–7.25 (m, 3 H), 4.73 (s, 1 H), 4.62 (dd, 1 H, *J* = 1.9, 1.4 Hz), 4.57 (d, 1 H, *J* = 0.8 Hz), 2.15 (d, 1 H, *J* = 4.1 Hz), 1.88–1.76 (m, 1 H), 1.75 (dd, 3 H, *J* = 1.4, 0.8 Hz), 1.71 (s, 2 H), 1.24 (s, 3 H), 1.27–1.14 (m, 2 H), 1.08–0.98 (m, 1 H), 0.96 (s, 3 H), 0.94 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.8, 141.8, 127.5, 127.3, 126.8, 124.8, 110.0, 100.5, 95.8, 88.7, 52.0, 50.2, 48.9, 29.6, 24.8, 24.4, 23.6, 20.9, 9.4.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 33.6.

HRMS (EI): *m*/*z* calcd for $C_{20}H_{27}O_2B$: 310.21042; found: 310.21114.

Anal. Calcd for $C_{20}H_{27}O_2B$: C, 77.43; H, 8.77. Found: C, 77.40; H, 8.85.

(1*R*,2*S*,3*R*,4*S*)-2,3-*O*-[(*E*)-2-Butenylboryl]-2-phenyl-1,7,7-trimethylbornanediol (7a)

A 200-mL three-neck round-bottom flask equipped with a magnetic stir bar and a thermometer was charged with THF (110 mL) and KO*t*-Bu (4.65 g, 41.5 mmol). This mixture was cooled to –78 °C, and *trans*-2-butene (2.46 g, 43.9 mmol) was added via cannula. *n*-BuLi (1.43 M in hexane, 29 mL, 41.5 mmol) was then added dropwise over 1 h using a syringe pump, so that the internal temperature did not rise above –73 °C. After completion of the addition, the reaction mixture was allowed to warm until the internal temperature reached –50 °C. The solution was maintained at –50 °C for 15 min, then cooled back to –78 °C. Triisopropylborate (10.5 mL, 45.6 mmol) was then added dropwise over 30 min through a syringe pump. The resulting solution was maintained at –78 °C for 2 h, then sealed with Ar and stored at –20 °C for a few weeks without any noticeable change of its quality. To this solution (10 mL, approx. 2.7 mmol) was added 1 N HCl (15 mL), and the resulting biphasic mixture was extracted with Et_2O (3 × 25 mL). To the combined organic layers was added (1*R*,2*S*,3*R*,4*S*)-2-phenyl-1,7,7-trimethylbornanediol (**a**)[7] (220 mg, 0.89 mmol) and $MgSO_4$ (approx. 500 mg). The resulting mixture was stirred at ambient temperature for 45 min, filtered, and concentrated under reduced pressure. Flash chromatography (5% EtOAc–hexanes, SiO_2 pre-treated with 5% Et_3N–hexanes) yielded a colorless oil (277 mg, 99%).

$[\alpha]^{25}_D$ +10.5 (*c* = 1.84, $CHCl_3$).

IR (CH_2Cl_2 cast): 3001, 2957, 1348, 1319, 1265, 1011 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42–7.41 (m, 2 H), 7.34–7.24 (m, 3 H), 5.43–5.30 (m, 2 H), 4.71 (s, 1 H), 2.13 (d, 1 H, *J* = 5.5 Hz), 1.84–1.78 (m, 1 H), 1.61–1.52 (m, 5 H), 1.20–1.13 (m, 5 H), 1.04–0.94 (m, 1 H), 0.93 (s, 3 H), 0.92 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.8, 127.4, 127.2, 126.7, 125.7, 125.2, 95.6, 88.5, 52.0, 50.2, 48.8, 29.6, 24.8, 23.6, 20.7, 18.0, 9.3.

^{11}B NMR (64 MHz, $CDCl_3$): δ = 34.2.

HRMS (EI): *m*/*z* calcd for $C_{20}H_{27}O_2B$: 310.21042; found: 310.20994.

Anal. Calcd for $C_{20}H_{27}O_2B$: C, 77.43; H, 8.77. Found: C, 77.24; H, 8.86.

(1*R*,2*S*,3*R*,4*S*)-2,3-*O*-[(*Z*)-2-Butenylboryl]-2-phenyl-1,7,7-trimethylbornanediol (8a)

A 300-mL three-neck round-bottom flask equipped with a magnetic stir bar and a thermometer was charged with THF (110 mL) and KO*t*-Bu (2.86 g, 25.5 mmol). This mixture was cooled to –78 °C, and *cis*-2-butene (1.50 g, 26.8 mmol) was added via cannula. *n*-BuLi (1.43 M in hexane, 17.9 mL, 25.5 mmol) was then added dropwise over 1 h, such that the internal temperature did not rise above –70 °C. After completion of the addition, the cooling bath was removed and the reaction mixture was allowed to warm up until the internal temperature reached –50 °C. The solution was maintained at that temperature for 30 min, then cooled back to –78 °C. Triisopropylborate (6.48 mL, 28.1 mmol) was added dropwise over 30 min. The reaction mixture was maintained at –78 °C for 2 h, then rapidly poured into a 500-mL separatory funnel containing 1 N HCl (200 mL). The layers were separated, then the aqueous layer was extracted with Et_2O (2 × 100 mL). The combined organic layers were dried over $MgSO_4$ and filtered before being concentrated in vacuo to a volume of 63 mL. The resulting solution was approximately 0.4 M in (*Z*)-2-butenylboronic acid, and could be kept at 4 °C for a few weeks without any noticeable change in its concentration or its reactivity with diols. To this solution (3.00 mL, 1.20 mmol) was added (1*R*,2*S*,3*R*,4*S*)-2-phenyl-1,7,7-trimethylbornanediol (**a**)[7] (246 mg, 1.00 mmol) and $MgSO_4$ (approx. 500 mg). The resulting mixture was stirred at ambient temperature for 30 min, filtered, and concentrated under reduced pressure. Flash chromatography (10% EtOAc–hexanes, SiO_2 pre-treated with 5% Et_3N–hexanes) yielded a colorless oil (307 mg, 99%).

TLC (15% EtOAc–hexanes, PMA): 0.58.

$[\alpha]^{25}_D$ +12.8 (*c* = 1.73, $CHCl_3$).

IR (CH_2Cl_2 cast): 3020, 2957, 1446, 1340, 1035 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.38 (m, 2 H), 7.35–7.22 (m, 3 H), 5.52–5.34 (m, 2 H), 4.70 (s, 1 H), 2.13 (d, 1 H, *J* = 5.2 Hz), 1.87–1.74 (m, 1 H), 1.66–1.61 (m, 2 H), 1.54–1.50 (m, 3 H), 1.21 (s, 3 H), 1.21–1.10 (m, 2 H), 1.07–0.96 (m, 1 H), 0.94 (s, 3 H), 0.91 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.8, 127.4, 127.2, 126.7. 124.9, 123.5, 95.7, 88.6, 52.0, 50.2, 48.9, 29.6, 24.7, 23.6, 20.7, 12.5, 9.3.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 34.1.

HRMS (EI): *m*/*z* calcd for $C_{20}H_{27}O_2B$: 310.21042; found: 310.21036.

Anal. Calcd for $C_{20}H_{27}O_2B$: C, 77.43; H, 8.77. Found: C, 77.41; H, 8.77.

Synthesis of Homoallylic Alcohols 9–23; General Procedure
Scandium trifluoromethanesulfonate (16 mg, 0.03 mmol) and CH_2Cl_2 (1.5 mL) were introduced in a 10-mL round-bottom flask, and the mixture was cooled to –78 °C. The aldehyde (0.33 mmol) was added, followed by a solution of boronate **5a** or **6a** (0.36 mmol) in CH_2Cl_2 (0.5 mL) dropwise over 5 min. The resulting mixture was stirred at –78 °C for 16 h, then DIBAL-H (1.0 M in toluene, 0.66 mL, 0.66 mmol) was added. The mixture was stirred at –78 °C for 30 min, then 1 N HCl (5 mL) was carefully added and the flask was allowed to warm up to ambient temperature. The resulting layers were separated, then the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash chromatography (5% EtOAc–hexanes) afforded the pure homoallylic alcohol.

(1*R*)-1-Phenylbut-3-en-1-ol (9)[34]
Colorless oil (41 mg, 85%).

TLC (15% EtOAc–hexanes, PMA): 0.23.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.22 (m, 5 H), 5.78 (ddt, 1 H, *J* = 7.1, 10.0, 17.0 Hz), 5.13 (d, 1 H, *J* = 7.1 Hz), 5.11 (d, 1 H, *J* = 10.0 Hz), 4.72 (t, 1 H, *J* = 6.4 Hz), 2.51–2.45 (m, 2 H), 1.98 (br s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.8, 134.4, 128.3, 127.4, 125.8, 118.3, 73.2, 43.7.

HPLC: Chiralcel OD-RH, 40% *i*-PrOH–H_2O, 0.40 mL/min, UV detection at 210 nm, major peak at 22.3 min, minor peak at 25.7 min, 92% ee.

(3*S*)-1-Phenylhex-5-en-3-ol (10)[34]
Colorless oil (37 mg, 64%).

TLC (15% EtOAc–hexanes, PMA): 0.25.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.16 (m, 5 H), 5.89–5.74 (m, 1 H), 5.16 (d, 1 H, *J* = 1.7 Hz), 5.11 (d, 1 H, *J* = 1.3 Hz), 3.71–3.62 (m, 1 H), 2.93–2.62 (m, 2 H), 2.37–2.12 (m, 2 H), 1.82–1.25 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.0, 134.6, 138.4, 138.3, 125.8, 69.9, 42.0, 38.4, 32.0.

HPLC: Chiralcel OD-RH, 40% *i*-PrOH–H_2O, 0.40 mL/min, UV detection at 210 nm, major peak at 40.2 min, minor peak at 49.4 min, 97% ee.

(3*R*)-1-{[*t*-Butyl(diphenyl)silyl]oxy}hex-5-en-3-ol (11)[35]
Colorless oil (79 mg, 86%).

TLC (15% EtOAc–hexanes, PMA): 0.30.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, 4 H, *J* = 7.2 Hz), 7.47–7.37 (m, 6 H), 5.92–5.78 (m, 1 H), 5.13–5.08 (m, 2 H), 4.0–3.92 (m, 1 H), 3.92–3.79 (m, 2 H), 3.18 (br s, 1 H), 2.26 (t, 2 H, *J* = 6 Hz), 1.77–1.64 (m, 2 H), 1.05 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.6, 135.5, 134.9, 133.1, 133.0, 129.81, 129.80, 127.8, 117.4, 70.9, 63.3, 42.0, 37.8, 26.8, 19.0.

HPLC: Chiralcel AD-RH, 45% *i*-PrOH–H_2O, 0.40 mL/min, UV detection at 210 nm, major peak at 60.8 min, minor peak at 67.8 min, 93% ee.

(2*R*)-1-(Benzyloxy)pent-4-en-2-ol (12)[35]
Colorless oil (39 mg, 62%).

TLC (15% EtOAc–toluene, PMA): 0.15.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.32 (m, 5 H), 5.90–5.78 (m, 1 H), 5.16–5.08 (m, 2 H), 4.56 (s, 2 H), 3.94–3.85 (m, 1 H), 3.53 (dd, 1 H, *J* = 3.7, 10.0 Hz), 3.39 (dd, 1 H, *J* = 7.4, 9.3 Hz), 2.28 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.9, 134.2, 138.4, 127.8, 127.7, 127.6, 126.8, 117.7, 73.9, 73.4, 69.7, 37.9.

HPLC: Chiralcel OD, 2% *i*-PrOH–hexane, 0.40 mL/min, UV detection at 210 nm, major peak at 49.3 min, minor peak at 52.5 min, 77% ee.

(2*R*)-1-{[*t*-Butyl(dimethyl)silyl]oxy}pent-4-en-2-ol (13)[35]
Colorless oil (54 mg, 76%).

TLC (15% EtOAc–hexanes, PMA): 0.40.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90–5.78 (m, 1 H), 5.13–5.04 (m, 2 H), 3.82–3.63 (m, 1 H), 3.20 (dd, 1 H, *J* = 4.0, 10.8 Hz), 3.44 (dd, 1 H, *J* = 6.0, 10.8 Hz), 2.36, (br s, 1 H), 2.24 (t, 2 H, *J* = 7.2 Hz), 0.92 (s, 9 H), 0.07 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.4, 117.4, 71.2, 66.6, 37.7, 26.0, 18.3, –5.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –71.90 (major), –71.99 (minor); 90% ee on the Mosher ester derivative.[33]

(2*R*)-1-{[*t*-Butyl(diphenyl)silyl]oxy}pent-4-en-2-ol (14)[35]
Colorless oil (69 mg, 61%).

TLC (15% EtOAc–hexanes, PMA): 0.25.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (d, 4 H, *J* = 7.2 Hz) 7.47–7.37 (m, 6 H), 5.92–5.78 (m, 1 H), 5.13–4.98 (m, 2 H), 3.82–3.72 (m, 1 H), 3.67 (dd, 1 H, *J* = 10.1, 3.9 Hz), 3.55 (dd, 1 H, *J* = 10.1, 6.9 Hz), 2.42 (br s, 1 H), 2.24 (t, 2 H, *J* = 6.8 Hz), 1.05 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.6, 135.5, 134.9, 133.1, 133.0, 129.9, 129.8, 127.8, 117.4, 70.9, 63.3, 42.0, 37.8, 26.8, 19.0.

HPLC: Chiralcel AD-RH, 45% *i*-PrOH–H_2O, 0.33 mL/min, UV detection at 210 nm, major peak at 75.1 min, minor peak at 88.4 min, 90% ee.

(4*R*)-Undec-1-en-5-yn-4-ol (15)[36]
Colorless oil (48 mg, 87%).

TLC (15% EtOAc–toluene, PMA): 0.20.

$[\alpha]^{25}_D$ +22.4 (*c* = 6.8, $CHCl_3$).

IR (CH_2Cl_2 cast): 3354, 3078, 2957, 2932, 2860, 1642, 1467, 1432, 1379, 1331, 1143 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.94–5.73, (m, 1 H), 5.24–5.15 (m, 2 H), 4.40 (m, 1 H), 2.42 (t, 2 H, *J* = 7.0 Hz), 2.20 (td, 2 H, *J* = 7.0, 2.0 Hz), 1.77 (br s, 1 H), 1.58–1.42 (m, 2 H), 1.42–1.25 (m, 4 H), 0.87 (m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 133.3, 118.7, 86.0, 80.5, 61.8, 42.6, 31.0, 28.3, 22.2, 18.6, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –71.95 (major), –72.18 (minor); 98% ee on the Mosher ester derivative.

HRMS (EI): *m*/*z* calcd for $C_{11}H_{18}ONa$: 189.12499; found: 189.12502.

(1*R*)-1-Cyclohexylbut-3-en-1-ol (16)[37]
Colorless oil (26 mg, 53%).

TLC (15% EtOAc–toluene, PMA): 0.30.

$[\alpha]^{25}_D$ –0.91 (*c* = 0.8, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90–5.79 (m, 1 H), 5.17–5.12 (m, 2 H), 3.40 (ddd, *J* = 9.0, 4.8, 3.5 Hz, 1 H), 2.37–2.30 (m, 1 H), 2.17–2.09 (m, 1 H), 1.89–1.65 (m, 5 H), 1.54 (br s, 1 H), 1.40–0.87 (m, 6 H).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –71.53 (minor), –71.59 (major); 90% ee on the Mosher ester derivative.

(1*R*)-3-Methyl-1-phenylbut-3-en-1-ol (17)[34]
Colorless oil (30 mg, 64%).

TLC (15% EtOAc–hexanes, PMA): 0.25.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.22 (m 5 H), 4.94 (s, 1 H), 4.86 (s, 1 H), 4.83 (t, 1 H, *J* = 6.8 Hz), 2.43 (d, 2 H, *J* = 6.8 Hz), 2.31 (s, 1 H), 1.82 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.0, 142.4, 128.4, 127.4, 135.7, 114.0, 71.4, 48.4, 22.3.

HPLC: Chiralcel AD-RH, 50% *i*-PrOH–H_2O, 0.31 mL/min, UV detection at 210 nm, major peak at 18.0 min, minor peak at 20.2 min, 98% ee.

(3*R*)-5-Methyl-1-phenylhex-5-en-3-ol (18)[34]
(Made from the enantiomer of **6a**)

Colorless oil (44 mg, 76%).

TLC (15% EtOAc–hexanes, PMA): 0.25.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.17 (m, 5 H), 4.91 (s, 1 H), 4.81 (s, 1 H), 3.83–3.74 (m, 1 H), 2.90–2.65 (m, 2 H), 2.30–2.10 (m, 2 H), 1.84–1.70 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.6, 142.1, 128.4, 128.3, 125.8, 113.6, 68.0, 46.2, 38.8, 32.1, 22.4.

HPLC: Chiralcel OD-RH, 45% *i*-PrOH–H_2O, 0.4 mL/min, UV detection at 210 nm, minor peak at 35.0 min, major peak at 39.9 min, 97% ee.

(3*R*)-1-{[*t*-Butyl(diphenyl)silyl]oxy}-5-methylhex-5-en-3-ol (19)
Colorless oil (90 mg, 77%).

TLC (15% EtOAc–hexanes, PMA): 0.30.

$[\alpha]^{25}_D$ +0.89 (*c* = 1.23, $CHCl_3$).

IR (CH_2Cl_2 cast): 3455, 3049, 2931, 1472, 1427, 1111 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.67 (m, 4 H), 7.44–7.39 (m, 6 H), 4.84 (dd, 1 H, *J* = 3.7, 1.5 Hz), 4.57 (d, 1 H, *J* = 0.8 Hz), 4.09–4.03 (m, 1 H), 3.94–3.80 (m, 2 H), 2.96 (d, 1 H, *J* = 2.4 Hz), 2.29–2.14 (m, 2 H), 1.77 (s, 3 H), 1.76–1.68 (m, 2 H), 1.06 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.7, 135.5, 135.5, 133.2, 133.1, 129.7, 127.7, 112.9, 68.6, 62.9, 46.0, 38.3, 26.8, 22.5, 19.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –71.69 (major), –71.79 (minor); 97% ee on the Mosher ester derivative.

HRMS (EI): *m*/*z* calcd for $C_{23}H_{32}O_2NaSi$: 391.20638; found: 391.20635.

(2*R*)-1-(Benzyloxy)-4-methylpent-4-en-2-ol (20)
Colorless oil (46 mg, 70%).

TLC (15% EtOAc–hexanes, PMA): 0.15.

$[\alpha]^{25}_D$ –1.86 (*c* = 1.30, $CHCl_3$).

IR (CH_2Cl_2 cast): 3445, 3070, 3030, 2913, 1646, 1453, 1099 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.26 (m, 5 H), 4.83 (dd, 1 H, *J* = 1.7, 1.7 Hz), 4.76 (dd, 1 H, *J* = 1.0, 1.0 Hz), 4.55 (s, 2 H), 3.99–3.95 (m, 1 H), 3.50 (dd, 1 H, *J* = 9.5, 3.5 Hz), 3.37 (dd, 1 H, *J* = 9.5, 7.1 Hz), 2.27 (d, 1 H, *J* = 2.9 Hz), 2.22–2.16 (m, 2 H), 1.75 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.0, 138.0, 128.4, 127.7, 127.7, 127.7, 113.2, 74.2, 73.4, 68.2, 41.9, 22.5.

HPLC: Chiralcel OD-RH, 65% *i*-PrOH–H_2O, 0.45 mL/min, UV detection at 210 nm, minor peak at 52.7 min, major peak at 55.9 min, 97% ee.

(2*R*)-1-{[*t*-Butyl(dimethyl)silyl]oxy}-4-methylpent-4-en-2-ol (21)
Colorless oil (67 mg, 88%).

TLC (15% EtOAc–toluene, PMA): 0.40.

$[\alpha]^{25}_D$ –1.86 (*c* = 1.30, $CHCl_3$).

IR (CH_2Cl_2 cast): 3467, 3076, 2955, 2929, 1648, 1472, 1361, 1120 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.81 (dd, 1 H, *J* = 1.4, 1.4 Hz), 4.76 (dd, 1 H, *J* = 2.0, 1.0 Hz), 3.81–3.77 (m, 1 H), 3.60 (dddd, 1 H, *J* = 10.0, 4.8, 3.9, 0.9 Hz), 3.45 (dd, 1 H, *J* = 10.0, 7.0 Hz), 2.33 (d, 1 H, *J* = 2.9 Hz), 2.15 (d, 2 H, *J* = 6.8 Hz), 1.75 (s, 3 H), 0.89 (s, 9 H), 0.06 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.3, 112.9, 69.7, 66.9, 41.7, 26.0, 22.7, 18.4, –5.1, –5.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –71.91 (major), –71.99 (minor); 95% ee on the Mosher ester derivative.

(4*R*)-2-Methylundec-1-en-5-yn-4-ol (22)
(Performed on a 5.87 mmol scale)

Colorless oil (1.06 g, 95%).

TLC (15% EtOAc–toluene, PMA): 0.20.

$[\alpha]^{25}_D$ +35.2 (*c* = 8.0, $CHCl_3$).

IR (CH_2Cl_2 cast): 3362, 3076, 2957, 2932, 1648, 1456, 1377, 1330, 1137 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.90 (dd, 1 H, *J* = 1.9, 1.9 Hz), 4.84 (dd, 1 H, *J* = 1.0, 1.0 Hz), 4.54–4.41 (m, 1 H), 2.44 (d, 2 H, *J* = 7.0 Hz), 2.20 (td, 2 H, *J* = 7.0, 1.0 Hz), 1.80 (s, 3 H), 1.60–1.25 (m, 7 H), 0.87 (t, 3 H, *J* = 7.1 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.3, 114.7, 85.7, 80.7, 60.6, 46.5, 31.0, 28.3, 22.6, 22.2, 18.6, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –71.92 (major), –72.07 (minor); 97% ee on the Mosher ester derivative.

HRMS (ES): *m*/*z* calcd for $C_{12}H_{20}ONa$: 203.14064; found: 203.14084.

(1*R*)-1-Cyclohexyl-3-methylbut-3-en-1-ol (23)[38]
Colorless oil (35 mg, 63%).

TLC (15% EtOAc–toluene, PMA): 0.30.

$[\alpha]^{25}_D$ –0.82 (*c* = 2.7, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.91 (s, 1 H), 4.82 (s, 1 H), 3.52–3.43 (m, 1 H), 2.32–2.05 (m, 2 H), 1.95–1.63 (m, 6 H), 1.78 (s, 1 H), 1.0–1.44 (m, 8 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.3, 113.4, 72.5, 43.5, 43.0, 29.1, 28.2, 26.6, 26.3, 26.2, 22.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –71.53 (minor), –71.69 (major); 92% ee on the Mosher ester derivative.

Synthesis of Homoallylic Alcohols 24–28; General Procedure

Scandium trifluoromethanesulfonate (16 mg, 0.03 mmol) and CH_2Cl_2 (0.3 mL) were introduced in a 10-mL round-bottom flask, and the mixture was cooled to –78 °C. The aldehyde (0.45 mmol) was added, followed by a solution of boronate **7a** (93 mg, 0.30 mmol) in CH_2Cl_2 (0.3 mL) dropwise over 5 min. The resulting mixture was stirred at –78 °C for 24 h, then DIBAL-H (1.0 M in toluene, 0.67 mL, 0.67 mmol) was added. The mixture was stirred at –78 °C for 30 min, then 1 N HCl (5 mL) was carefully added and the flask was allowed to warm up to ambient temperature. The resulting layers were separated, then the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash chromatography (5% EtOAc–hexanes) afforded the pure homoallylic alcohol.

(1*R*,2*R*)-2-Methyl-1-phenylbut-3-en-1-ol (24)[39]
Colorless oil (29 mg, 60%).

$[\alpha]^{25}_D$ +92.0 [*c* = 1.62, $CHCl_3$, lit.[13] –73.4 (66% ee) for the opposite enantiomer].

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.35–7.24 (m, 5 H), 5.80 (ddd, 1 H, *J* = 17.2, 10.5, 8.2 Hz), 5.20–5.15 (m, 2 H), 4.35 (d, 1 H, *J* = 7.8 Hz), 2.49–2.45 (m, 1 H), 2.15 (br s, 1 H), 0.86 (d, 3 H, *J* = 6.8 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.4, 140.6, 128.2, 127.6, 126.8, 116.8, 77.9, 46.3, 16.5.

HPLC: Chiralcel OD-RH, 30% *i*-PrOH–H_2O, 0.45 mL/min, UV detection at 210 nm, major peak at 106.8 min, minor peak at 118 min, 97% ee.

(3*S*,4*R*)-4-Methyl-1-phenylhex-5-en-3-ol (25)[13]
Colorless oil (41 mg, 71%).

$[\alpha]^{25}_D$ –14.7 [*c* = 1.42, $CHCl_3$, lit.[13] +13.8 (86% ee) for the opposite enantiomer].

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28–7.15 (m, 5 H), 5.73 (ddd, 1 H, *J* = 16.7, 10.8, 8.2 Hz), 5.12–5.08 (m, 2 H), 3.40 (ddd, 1 H, *J* = 9.1, 6.0, 3.1 Hz), 2.85–2.63 (m, 2 H), 2.23–2.19 (m, 1 H), 1.86–1.65 (m, 2 H), 1.56 (br s, 1 H), 1.02 (d, 3 H, *J* = 6.9 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.2, 140.1, 128.4, 128.3, 125.7, 116.4, 74.0, 44.4, 36.2, 32.2, 16.3.

HPLC: Chiralcel AD-RH, 40% *i*-PrOH–H_2O, 0.33 mL/min, UV detection at 210 nm, major peak at 64.8 min, minor peak at 73.3 min, 96% ee.

(3*S*,4*R*)-1-{[*t*-Butyl(diphenyl)silyl]oxy}-4-methylhex-5-en-3-ol (26)[40]
Colorless oil (70 mg, 63%).

$[\alpha]^{25}_D$ +4.4 [*c* = 1.46, $CHCl_3$, lit.[40] +3.0 (mixture of diastereomers)].

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72–7.67 (m, 4 H), 7.44–7.35 (m, 6 H), 5.90 (ddd, 1 H, *J* = 16.7, 11.1, 8.0 Hz), 5.08–5.04 (m, 2 H), 3.90–3.82, (m, 2 H), 3,77–3.74 (m, 1 H), 2.97 (br s, 1 H), 2.27–2.23 (m, 1 H), 1.71–1.63 (m, 2 H), 1.06 (d, 3 H, *J* = 6.9 Hz), 1.05 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.6, 135.6, 133.2, 129.8, 127.7, 115.2, 74.5, 63.3, 43.9, 35.6, 26.8, 19.0, 15.8.

HPLC: Chiralcel AD-RH, 55% *i*-PrOH–H_2O, 0.31 mL/min, UV detection at 210 nm, minor peak at 27.7 min, major peak at 31.9 min, 94% ee.

(2*R*,3*R*)-1-{[*t*-Butyl(dimethyl)silyl]oxy}-3-methylpent-4-en-2-ol (27)[41]
Colorless oil (44 mg, 63%).

$[\alpha]^{25}_D$ +2.8 (*c* = 0.73, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.84 (m, 1 H), 5.06–5.02 (m, 2 H), 3.63–3.60 (m, 1 H), 3.50–3.47 (m, 2 H), 2.35 (d, 1 H, *J* = 2 Hz), 2.30 (apparent sextet, 1 H, *J* = 7.0 Hz), 1.02 (d, 3 H, *J* = 6.8 Hz), 0.88 (s, 9 H), 0.05 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.3, 115.0, 74.8, 65.2, 41.4, 25.8, 18.2, 16.1, –5.4.

HRMS (EI): *m*/*z* calcd for $C_8H_{17}O_2Si$ (M – *t*-Bu): 173.09978; found: 173.09970.

HPLC (performed on the carbamate derivative from reaction with phenylisocyanate): Chiralcel OD, 2% *i*-PrOH–hexane, 0.30 mL/min, UV detection at 210 nm, major peak at 26.2 min, minor peak at 24.8 min, 96% ee.

(3*R*,4*R*)-3-Methylundec-1-en-5-yn-4-ol (28)
Colorless oil (48 mg, 78%).

$[\alpha]^{25}_D$ +16.55 (*c* = 2.00, $CHCl_3$).

IR (CH_2Cl_2 cast): 3363, 2959, 2932, 1457, 1378, 1019 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.82 (ddd, 1 H, *J* = 17.7, 10.4, 7.6 Hz), 5.17–5.12 (m, 2 H), 4.19 (ddd, 1 H, *J* = 6.2, 3.8, 1.9 Hz), 2.44–2.40 (m, 1 H), 2.21 (ddd, 2 H, *J* = 9.0, 7.1, 1.9 Hz), 1.82 (br s, 1 H), 1.54–1.48 (m, 2 H), 1.40–1.29 (m, 4 H), 1.12 (d, 3 H, *J* = 7.1 Hz), 0.90 (t, 3 H, *J* = 7.1 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.6, 116.4, 86.6, 79.5, 66.4, 44.7, 31.0, 28.3, 22.1, 18.6, 15.2, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –71.88 (major), –72.14 (minor); 97% ee on the Mosher ester derivative.

HRMS (ES): *m*/*z* calcd for $C_{12}H_{20}ONa$: 203.14064; found: 203.14084.

Synthesis of *syn*-Homoallylic Alcohols 29–33; General Procedure
Scandium trifluoromethanesulfonate (16 mg, 0.03 mmol) and CH_2Cl_2 (0.3 mL) were introduced in a 10-mL round-bottom flask, and the mixture was cooled to –78 °C. The aldehyde (0.50 mmol) was added, followed by a solution of boronate **8a** (102 mg, 0.33 mmol) in CH_2Cl_2 (0.3 mL) dropwise over 5 min. The resulting mixture was stirred at –78 °C for 24 h, then DIBAL-H (1.0 M in toluene, 1.00 mL, 1.00 mmol) was added. The mixture was stirred at –78 °C for 30 min, then 1 N HCl (5 mL) was carefully added and the flask was allowed to warm up to ambient temperature. The resulting layers were separated, then the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash chromatography (5% EtOAc–hexanes) afforded the pure homoallylic alcohol.

(1*R*,2*S*)-2-Methyl-1-phenylbut-3-en-1-ol (29)[42]
Colorless oil (28.5 mg, 53%).

TLC (10% EtOAc–toluene, PMA): 0.23.

$[\alpha]^{25}_D$ +12.0 (*c* = 1.47, $CHCl_3$, lit.[13,42] –15.0 for the opposite enantiomer, +15.2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.24 (m, 5 H), 5.83–5.70 (m, 1 H), 5.10–5.07 (m, 1 H), 5.05–5.02 (m, 1 H), 4.63 (d, 1 H, *J* = 5.5 Hz), 2.66–2.53 (m, 1 H), 1.91 (br s, 1 H), 1.02 (d, 3 H, *J* = 6.8 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.5, 140.3, 128.0, 127.3, 126.5, 115.5, 77.3, 44.6, 14.0.

HPLC: Chiralcel OD-RH, 35% *i*-PrOH–H_2O, 0.40 mL/min, UV detection at 210 nm, major peak at 61.5 min, minor peak at 68.7 min, 59% ee.

(3*S*,4*S*)-4-Methyl-1-phenylhex-5-en-3-ol (30)[34]
Colorless oil (32 mg, 52%).

TLC (10% EtOAc–toluene, PMA): 0.35.

$[\alpha]^{25}_D$ –32.5 (*c* = 0.80, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.28–7.24 (m, 2 H), 7.20–7.14 (m, 3 H), 5.79–5.72 (m, 1 H), 5.10–5.07 (m, 1 H), 5.06–5.05 (m, 1 H), 3.50 (ddd, 1 H, *J* = 8.8, 5.0, 3.1 Hz), 2.84 (ddd, 1 H, *J* = 13.9, 10.2, 5.3 Hz), 2.63 (ddd, 1 H, *J* = 13.7, 9.8, 6.7 Hz), 2.32–2.24 (m, 1 H), 1.84–1.77 (m, 1 H), 1.72–1.63 (m, 1 H), 1.41 (br s, 1 H), 1.01 (d, 3 H, *J* = 6.9 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.2, 140.7, 128.4, 128.4, 125.8, 115.5, 74.1, 43.6, 35.8, 32.4, 14.2.

HPLC: Chiralcel AD-RH, 40% *i*-PrOH–H_2O, 0.33 mL/min, UV detection at 210 nm, major peak at 53.9 min, minor peak at 60.0 min, 96% ee.

(3*S*,4*S*)-1-{[*t*-Butyl(diphenyl)silyl]oxy}-4-methylhex-5-en-3-ol (31)[43,44]

Colorless oil (69.5 mg, 57%).

TLC (5% EtOAc–toluene, PMA): 0.29.

$[\alpha]^{25}_D$ –4.4 (*c* = 1.89, $CHCl_3$, lit.[43,44] +3.3, +5.5 for the opposite enantiomer).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68–7.65 (m, 4 H), 7.44–7.36 (m, 6 H), 5.77 (ddd, 1 H, *J* = 17.4, 10.4, 7.6 Hz), 5.60–5.00 (m, 2 H), 3.90–3.80 (m, 2 H), 3.74 (ddd, 1 H, *J* = 8.8, 6.0, 2.6 Hz), 3.12 (br s, 1 H), 2.32–2.24 (m, 1 H), 1.74–1.60 (m, 2 H), 1.11 (d, 3 H, *J* = 6.9 Hz), 1.05 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.1, 135.6, 135.5, 135.5, 133.1, 133.0, 129.8, 129.8, 127.7, 114.8, 74.8, 63.6, 43.9, 35.5, 26.8, 19.0, 15.1.

HPLC: Chiralcel AD-RH, 55% *i*-PrOH–H_2O, 0.30 mL/min, UV detection at 210 nm, minor peak at 24.6 min, major peak at 28.2 min, 96% ee.

(2*R*,3*S*)-1-{[*t*-Butyl(dimethyl)silyl]oxy}-3-methylpent-4-en-2-ol (32)

Colorless oil (43 mg, 57%).

TLC (5% EtOAc–toluene, PMA): 0.20.

$[\alpha]^{25}_D$ –15.9 (*c* = 0.83, $CHCl_3$).

IR (CH_2Cl_2 cast): 3574, 3482, 3078, 2956, 2929, 2857, 1640, 1463, 1257, 1100, 837 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.70 (ddd, 1 H, *J* = 18.3, 10.3, 8.0 Hz), 5.06–4.97 (m, 2 H), 3.66–3.60 (m, 1 H), 3.48–3.39 (m, 2 H), 2.44 (d, 1 H, *J* = 3.7 Hz), 2.26 (apparent sextet, 1 H, *J* = 7.0 Hz), 1.07 (d, 3 H, *J* = 6.8 Hz), 0.88 (s, 9 H), 0.05 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.5, 114.9, 74.7, 65.2, 41.0, 25.8, 18.2, 16.0, –5.4.

HRMS (EI): *m*/*z* calcd for $C_{12}H_{26}O_2NaSi$: 253.15943; found: 253.15936.

HPLC (performed on the carbamate derivative from reaction with phenylisocyanate): Chiralcel OD, 2% *i*-PrOH–hexane, 0.30 mL/min, UV detection at 210 nm, major peak at 20.8 min, minor peak at 23.3 min, 98% ee.

(3*S*,4*R*)-3-Methylundec-1-en-5-yn-4-ol (33)

Colorless oil (36 mg, 61%).

TLC (15% EtOAc–hexanes, PMA): 0.34.

$[\alpha]^{25}_D$ +22.7 (*c* = 1.27, $CHCl_3$).

IR (neat): 3389, 3080, 2933, 1459, 1020 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.94–5.80 (m, 1 H), 5.20–5.17 (m, 1 H), 5.15–5.12 (m, 1 H), 4.26 (ddd, 1 H, *J* = 4.8, 2.0, 2.0 Hz), 2.50–2.38 (m, 1 H), 2.22 (ddd, 2 H, *J* = 6.9, 6.9, 2.0 Hz), 1.72 (br s, 1 H), 1.57–1.46 (m, 2 H), 1.44–1.26 (m, 4 H), 1.11 (d, 3 H, *J* = 6.9 Hz), 0.91 (t, 3 H, *J* = 6.9 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.2, 116.8, 86.7, 79.2, 66.3, 44.5, 31.0, 28.4, 22.1, 18.6, 15.6, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –71.90 (major), –72.19 (minor); 95% ee on the Mosher ester derivative.

HRMS (EI): *m*/*z* calcd for $C_{12}H_{20}O$: 180.15141; found: 180.15092.

Gram-Scale Synthesis of Homoallylic Alcohols (Table 3): (3*S*,4*R*)-3-Methylundec-1-en-5-yn-4-ol (33); Typical Procedure

Scandium trifluoromethanesulfonate (238 mg, 0.48 mmol) and CH_2Cl_2 (5 mL) were introduced in a 50-mL round-bottom flask, and the mixture was cooled to –78 °C. 2-Octynal (1.03 mL, 7.25 mmol) was added, followed by a solution of boronate **8a** (1.50 g, 4.83 mmol) in CH_2Cl_2 (7 mL) dropwise over 30 min. The resulting mixture was stirred at –78 °C for 24 h, then DIBAL-H (1.0 M in toluene, 14.5 mL, 14.5 mmol) was added. The mixture was stirred at –78 °C for 1 h, then carefully poured into a 250-mL separatory funnel containing 1 N NaOH (50 mL). The resulting layers were separated, then the aqueous layer was extracted with EtOAc (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash chromatography (5% EtOAc–hexanes) afforded homoallylic alcohol **33** as a colorless oil (570 mg, 72%). The fractions containing the diol auxiliary and the ones containing diolboronate derivatives were concentrated, then treated with a solution of THF (2 mL), 1 N NaOH (1 mL), and H_2O_2 (1 mL of a 30% aq solution) for 16 h. The resulting mixture was diluted with H_2O (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Flash chromatography (5% EtOAc–hexanes) afforded (1*R*,2*S*,3*R*,4*S*)-2-phenyl-1,7,7-trimethylbornanediol (**a**) (891 mg, 75%).

(4*S*)-2-Methyloct-1-en-4-ol (35)[45]

Same procedure used as for homoallylic alcohols **9**–**23**, on a 2.0 mmol scale and using 3.0 equiv of pentanal (**34**).

Volatile colorless oil (257 mg, 89%).

TLC (15% EtOAc–toluene, PMA): 0.30.

$[\alpha]^{25}_D$ –9.2 (*c* = 0.65, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.88 (s, 1 H), 4.80 (s, 1 H), 3.77–3.67 (m, 1 H), 2.30–2.06 (m, 2 H), 1.78 (s, 3 H), 1.65 (br s, 1 H), 1.55–1.25 (m, 6 H), 0.92 (t, 3 H, *J* = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.9, 113.3, 68.6, 46.2, 36.8, 27.9, 22.7, 22.4, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –71.60 (minor), –71.69 (major); 98% ee on the Mosher ester derivative.

(4*S*)-2-Methyloctan-4-ol (36)[29]

In a flame-dried round bottom flask, alcohol **35** (144 mg, 1.0 mmol) was dissolved in MeOH (1.0 mL). Palladium on charcoal (10 mol%, 10 mg) was added, and the resulting suspension was stirred for 16 h at r.t. under an atmosphere of H_2. The suspension was then filtered on celite and diluted with pentane (5 mL). The solution was washed with H_2O (3 × 5 mL), dried over $MgSO_4$, filtered and concentrated. Flash chromatography (5% EtOAc–hexanes) yielded a volatile colorless oil (135 mg, 92%).

TLC (15% EtOAc–toluene, PMA): 0.35.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.70–3.65 (m, 1 H), 1.83–1.75 (m, 1 H), 1.50–1.20 (m, 9 H), 0.95–0.85 (m, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 70.0, 46.9, 34.1,27.2, 24.6, 23.4, 22.7, 22.3, 14.0.

Acknowledgment

This work was funded by the Natural Sciences and Engineering Research Council (NSERC) of Canada, the University of Alberta, and by an AstraZeneca Award in Chemistry (D.G.H.). M.G. thanks NSERC and the Alberta Heritage Foundation for Medical Research (AHFMR), and H.L. thanks the Alberta Ingenuity Fund for graduate scholarships. The authors thank Dr. Jason Kennedy and Vivek Rauniyar for helpful advice and discussions.

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