Scandium-Catalyzed Allylboration of Aldehydes as a Practical Method for Highly Diastereo- and Enantioselective Construction of Homoallylic Alcohols

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General Information

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 Kugelrohr distillation prior to use. Thin layer chromatography (TLC) was performed on Merck Silica Gel 60 F254 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 (^1H) or the solvent carbons (^{13}C) were used as internal standards. Boron NMR spectra are referenced to external $\text{BF}_3\cdot\text{OEt}_2$; ^{19}F spectra are referenced to external CFCl_3 and were run by Glen Bigam of the University of Alberta Spectral Services. ^1H NMR data are presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; qt, quartet of triplets; dd, doublet of doublets; dt, doublet of triplets; AB, AB quartet; m, multiplet. 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 and optical rotations were recorded by University of Alberta Spectral Services and combustion analyses were performed by the University of Alberta Micro-Analytical Lab..

Determination of enantiomeric excess and absolute stereochemistry.

The enantiomeric excesses for compounds **9**, **13**, **15** were determined using integration of the ^{19}F NMR signals of the corresponding Mosher ester derivatives.¹ The enantiomeric excesses for compounds **5-8**, **10-12**, **14**, **16-18**, **20-22** were determined using an HP 1100 HPLC system. The enantiomeric excesses for compounds **19** and **23** were determined on the corresponding phenylisocyanate adduct using an HP 1100 HPLC system. Columns Chiralcel AD-RH, Chiralcel OD-RH, Chiralcel OD, and Chiralcel AD 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 **16**, **17**, **18**, **20**, and **22** 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 Dale, J.A.; Dull, D.L.; Mosher, H.S. *J. Org. Chem.* **1969**, *34*, 2543.

Preparation of boronates 1a-4a

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

To a solution of triethylborate (1.30 mL, 5.71 mmol) in Et₂O (12 mL) at –78°C was added a solution of allylmagnesium bromide (1.02 M in Et₂O, 5.00 ml, 5.14 mmol) dropwise and the resulting mixture was stirred at –78°C for 4 hours. The resulting suspension was poured onto an ice-cold mixture of 1 N HCl (50 mL), Et₂O (50 mL), and the diol **24**. The resulting mixture was stirred at ambient temperature for 30 minutes, then extracted with Et₂O (3 × 25 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. Flash chromatography (10% EtOAc/hexanes) yielded a colourless oil (1.104 g, 93%), which gave satisfactory analytical data.³ TLC (15% EtOAc/hexanes, PMA): 0.60;

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

To a solution of triethylborate (1.50 mL, 6.60 mmol) in Et₂O (12 ml) was added diol **24** (1.48 g, 6.00 mmol). The mixture was stirred at ambient temperature for 30 minutes, then concentrated on the rotary evaporator and co-evaporated with CH₂Cl₂ (3 ×). The remaining colourless oil was dissolved in Et₂O (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 hours, then poured on an ice-cold mixture of 1 N HCl (50 mL) and Et₂O (50 ml). The resulting mixture was stirred at ambient temperature for 30 minutes, then extracted with Et₂O (3 × 25 ml). The combined organic layers were combined, washed with brine, dried over MgSO₄, filtered, and concentrated under reduced pressure. Flash chromatography (10% EtOAc/hexanes, SiO₂ pre-treated with 5% Et₃N/hexanes) yielded a colourless oil (1.31 g, 70%).

TLC (15% EtOAc/hexanes, PMA): 0.60;

¹H NMR (300 MHz, CDCl₃): δ 7.44-7.41 (m, 2H), 7.37-7.25 (m, 3H), 4.73 (s, 1H), 4.62 (dd, *J* = 1.9 Hz, 1.4 Hz, 1H), 4.57 (d, *J* = 0.8 Hz, 1H), 1.88-1.76 (m, 1H), 1.75 (dd, *J* = 1.4 Hz, 0.8 Hz, 3H), 1.71 (s, 2H), 1.24 (s, 3H), 1.27-1.14 (m, 2H), 1.08-0.98 (m, 1H), 0.96 (s, 3H), 0.94 (s, 3H);

² This method was inspired by that of Roush and co-workers: Roush, W.R.; Ando, K.; Powers, D.B.; Palkowitz, A.D.; Halterman, R.L. *J. Am. Chem. Soc.* **1990**, *112*, 6339-6348.

³ Herold, T.; Schrott, U.; Hoffmann, R.W. *Chem. Ber.* **1981**, *114*, 359-374.

^{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 (128 MHz, CDCl_3): δ 33.6

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

HRMS (EI, m/z) Calcd for $\text{C}_{20}\text{H}_{27}\text{O}_2\text{B}$: 310.21042. Found: 310.21114;

Anal. Calcd for $\text{C}_{20}\text{H}_{27}\text{O}_2\text{B}$: C, 77.43; H, 8.77. Found: C, 77.40; H, 8.85;

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

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

A 200-mL three-neck round-bottom flask equipped with a magnetic stir bar and a thermometer was charged with 110 mL of THF and KOtBu (4.65 g, 41.5 mmol). This mixture was flushed with Ar and cooled to -78°C , and then *trans*-2-butene (2.46 g, 43.9 mmol), condensed into a rubber-stoppered 10-ml round-bottom flask kept at -78°C , was added via cannula. *n*-BuLi (1.43 M in hexane, 29 mL, 41.5 mmol) was then added dropwise over 1 hour with syringe pump, so that the internal temperature did not rise at all. After completion of the addition, the reaction mixture was allowed to warm until the internal temperature reached -52°C . The solution was maintained at -52°C for 15 minutes, then cooled back to -78°C . Triisopropylborate (10.53 mL, 45.6 mmol) was then added dropwise over 30 minutes through a syringe pump. The reaction mixture was maintained at -78°C for 2 hours, then sealed with Ar and stored in freezer for a few weeks without any noticeable change of its quality.

To make reaction boronate **3a**, 10 mL of the stored solution was reacted with 15 mL of 1 N HCl, and extracted by ether three times. The combined organic layers were mixed with 220 mg of diol **24** and was stirred at ambient temperature for 45 minutes, then concentrated under reduced pressure. Flash chromatography (5% EtOAc/hexanes, SiO_2 pre-treated with 5% Et_3N /hexanes) yielded a colourless oil 277 mg (99% yield).

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

^{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;

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

HRMS (EI, m/z) Calcd for $\text{C}_{20}\text{H}_{27}\text{O}_2\text{B}$: 310.21042. Found: 310.20994;

Anal. Calcd for C₂₀H₂₇O₂B: C, 77.43; H, 8.77. Found: C, 77.24; H, 8.86;

[α]_D²⁵ = +10.5° (*c* = 1.84, CHCl₃).

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

A 300-mL three-neck round-bottom flask equipped with a magnetic stir bar and a thermometer was charged with 110 mL of THF and KOtBu (2.86 g, 25.5 mmol). This mixture was flushed with Ar and cooled to -78°C, and then *cis*-2-butene (1.50 g, 26.8 mmol), condensed into a rubber-stoppered 10-ml round-bottom flask kept at -78°C, was added via cannula. *n*-BuLi (1.43 M in hexane, 17.9 mL, 25.5 mmol) was then added dropwise over 1 hour, 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 -25°C. The solution was maintained at -25°C for 30 minutes, then cooled back to -78°C. Triisopropylborate (6.48 mL, 28.1 mmol) was then added dropwise over 30 minutes. The reaction mixture was maintained at -78°C for 2 hours, then rapidly poured into a 500-mL separatory funnel containing 200 mL of 1 N HCl. The layers were separated, then the aqueous layer was extracted with Et₂O (2 × 100 mL). The combined organic layers were dried over MgSO₄ and filtered before being concentrated down on the rotary evaporator 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 diol **24** (246 mg, 1.00 mmol) and the resulting mixture was stirred at ambient temperature for 30 minutes, then concentrated under reduced pressure. Flash chromatography (10% EtOAc/hexanes, SiO₂ pre-treated with 5% Et₃N/hexanes) yielded a colourless oil (307 mg, 99%).

TLC (15% EtOAc/hexanes, PMA): 0.58;

¹H NMR (300 MHz, CDCl₃): δ 7.44-7.38 (m, 2H), 7.35-7.22 (m, 3H), 5.52-5.34 (m, 2H) 4.70 (s, 1H), 2.13 (d, *J* = 5.2 Hz, 1H), 1.87-1.74 (m, 1H), 1.66-1.61 (m, 2H), 1.54-1.50 (m, 3H), 1.21 (s, 3H), 1.21-1.10 (m, 2H), 1.07-0.96 (m, 1H), 0.94 (s, 3H), 0.91 (s, 3H);

¹³C NMR (125 MHz, CDCl₃): 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;

¹¹B NMR (128 MHz, CDCl₃): δ 34.1

IR (CH₂Cl₂ cast, cm⁻¹): 3020, 2957, 1446, 1340, 1035;

HRMS (EI, *m/z*) Calcd for C₂₀H₂₇O₂B: 310.21042. Found: 310.21036;

Anal. Calcd for C₂₀H₂₇O₂B: C, 77.43; H, 8.77. Found: C, 77.41; H, 8.77;

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

General procedure for the synthesis of homoallylic alcohols 5-15.

Scandium trifluoromethanesulfonate (16 mg, 0.03 mmol) was introduced in a 10-mL round-bottom flask, which was then flushed with Ar. CH_2Cl_2 (1.5 mL) was added and the mixture was cooled to -78°C . The aldehyde (0.33 mmol) was added, followed by a solution of boronate **4a** (0.36 mmol) in CH_2Cl_2 (0.5 mL) dropwise over 5 minutes. The resulting mixture was stirred at -78°C for 16 hours, 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 minutes, then 1 N HCl (5 mL) was added and the flask was allowed to warm up to ambient temperature. The resulting layers were separated, then the aqueous layer was extracted with Et_2O (3 $\times$ 5 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated. Flash chromatography afforded the pure homoallylic alcohol. The enantiomer of **2a** was used for **12**.

(1R)-1-phenyl-3-buten-1-ol (**5**)

Flash chromatography (5% EtOAc/hexanes) yielded a colourless oil (41 mg, 85%), which gave satisfactory analytical data.⁹

TLC (15% EtOAc/Hexane, PMA): 0.23;

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.

(3S)-1-phenyl-5-hexen-3-ol (**6**)

Flash chromatography (5% EtOAc/hexanes) yielded a colourless oil (37 mg, 64%), which gave satisfactory analytical data.⁹

TLC (15% EtOAc/Hexane, PMA): 0.25;

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.

(3R)-1-(*t*-Butyldiphenylsilyloxy)-5-hexen-3-ol (**7**)

Flash chromatography (5% EtOAc/hexanes) yielded a colourless oil (79mg, 86%), which gave satisfactory analytical data.⁴

TLC (15% EtOAc/ hexanes, PMA): 0.30;

HPLC : Chiralcel AD-RH, 45% *i*PrOH/H₂O, 0.40 mL/min., UV detection at 210 nm, major peak at 60.8 min., minor peak at 67.8 min.. 93% ee.

(2R)-1-(Benzyloxy)-4-penten-2-ol (8)

Flash chromatography (5% EtOAc/Toluene) yielded a colourless oil (39 mg, 62%), which gave satisfactory analytical data.⁴

TLC (15% EtOAc/Toluene, PMA): 0.15;

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.

(2R)-1-(*t*-Butyldimethylsilyloxy)-4-penten-2-ol (9)

Flash chromatography (10% EtOAc/hexanes) yielded a colourless oil (54 mg, 75%), which gave satisfactory analytical data.⁴

TLC (15% EtOAc/hexanes, PMA): 0.40;

¹⁹F NMR (376 MHz, CDCl₃) δ -71.90 (Major), -71.99 (minor) 90% ee on Mosher ester derivative.

(3R)-1-(*t*-Butyldiphenylsilyloxy)-5-hexen-3-ol (10)

Flash chromatography (5% EtOAc/Hexanes) yielded a colourless oil (69 mg, 61%), which gave satisfactory analytical data.⁴

TLC (15% EtOAc/hexanes, PMA): 0.25;

HPLC : Chiralcel AD-RH, 45% *i*PrOH/H₂O, 0.33 mL/min., UV detection at 210 nm, major peak at 75.1 min., minor peak at 88.4 min.. 90% ee.

⁴ Roush, W.R.; Hoong, L.K.; Palmer, M.A.J.; Straub, J.A.; Palkowitz, A.D. *J. Org. Chem.* **1990**, 55, 4117-4126.

(1R)-3-Methyl-1-phenyl-3-buten-1-ol (11)

Flash chromatography (5% EtOAc/hexanes) yielded a colourless oil (30 mg, 64%), which gave satisfactory analytical data.⁹

TLC (15% EtOAc/hexanes, PMA): 0.25;

HPLC : Chiralcel AD-RH, 50% *i*PrOH/H₂O, 0.31 mL/min., UV detection at 210 nm, major peak at 18.0 min., minor peak at 20.2 min.. 98% ee.

(3R)-5-Methyl-1-phenyl-5-hexen-3-ol (12)

Flash chromatography (5% EtOAc/hexanes) yielded a colourless oil (44 mg, 76%), which gave satisfactory analytical data.⁹

TLC (15% EtOAc/hexanes, PMA): 0.25;

HPLC : Chiralcel OD-RH, 45% *i*PrOH/H₂O, 0.4 mL/min., UV detection at 210 nm, minor peak at 35.0 min., major peak at 39.9 min.. 97% ee.

(3S)-1-(*t*-Butyldiphenylsilyloxy)-5-methyl-5-hexen-3-ol (13)

Flash chromatography (5% EtOAc/hexanes) yielded a colourless oil (90 mg, 77%), which gave satisfactory analytical data.

TLC (15% EtOAc/hexanes, PMA): 0.30;

[α]_D²⁵ +0.89° (*c* = 1.23, CHCl₃)

¹H NMR (300 MHz, CDCl₃): δ 7.70-7.67 (m, 4H), 7.44-7.39 (m, 6H), 4.84 (dd, *J* = 3.7 Hz, 1.5 Hz, 1H), 4.57 (d, *J* = 0.8 Hz, 1H), 4.09-4.03 (m, 1H), 3.94-3.80 (m, 2H), 2.96 (d, *J* = 2.4 Hz, 1H), 2.29-2.14 (m, 2H), 1.77 (s, 3H), 1.76-1.68 (m, 2H), 1.06 (s, 9H);

¹³C NMR (125 MHz, CDCl₃): 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;

IR (CH₂Cl₂ cast, cm⁻¹): 3455, 3049, 29.31, 1472, 1427, 1111;

HRMS (EI, *m/z*) Calcd for C₂₃H₃₂O₂NaSi: 391.20638. Found: 391.20635;

¹⁹F NMR (376 MHz, CDCl₃) δ -71.69 (Major), -71.79 (minor) 97% ee on Mosher ester derivative.

(2R)-1-(Benzyloxy)-4-methyl-4-penten-2-ol (14)

Flash chromatography (5% EtOAc/toluene) yielded a colourless oil (46 mg, 70%).

TLC (15% EtOAc/hexanes, PMA): 0.15;

$[\alpha]_D^{25} -1.86^\circ$ ($c = 1.30$, CHCl_3)

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

^{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;

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

MS (ES, m/z) 229.1 (M+Na);

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.

(2R)-1-(*t*-Butyldimethylsilyloxy)-4-methyl-4-penten-2-ol (15)

Flash chromatography (10% EtOAc/hexanes) yielded a colourless oil (38 mg, 58%).

TLC (15% EtOAc/Toluene, PMA): 0.40;

$[\alpha]_D^{25} -1.86^\circ$ ($c = 1.30$, CHCl_3)

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

^{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;

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

^{19}F NMR (376 MHz, CDCl_3) δ -71.91 (Major), -71.99 (minor) 95% ee on Mosher ester derivative.

General procedure for the synthesis of homoallylic alcohols 16-19.

Scandium trifluoromethanesulfonate (16 mg, 0.03 mmol) was introduced in a 10-mL round-bottom flask, which was then flushed with Ar. CH_2Cl_2 (0.3 mL) was added and the mixture was cooled to -78°C . The aldehyde (0.45 mmol) was added, followed by a solution of boronate **3a** (0.3 mmol) in CH_2Cl_2 (0.3 mL) dropwise over 5 minutes. The resulting mixture was stirred at -78°C for 24 hours, then

DIBAL-H (1.0 M in toluene, 0.67 mL, 0.67 mmol) was added. The mixture was stirred at -78°C for 60 minutes, then 1 N HCl (5 mL) was added and the flask was allowed to warm up to ambient temperature. The resulting layers were separated, then the aqueous layer was extracted with Et₂O (3 × 5 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated. Flash chromatography afforded the pure homoallylic alcohol.

(1R, 2R)-2-Methyl-1-phenyl-3-buten-1-ol (16)

Flash chromatography (2.5% EtOAc/Hexane) gave the pure product as a colourless oil (60% yield), which gave satisfactory analytical data.⁵

$[\alpha]_D^{25} = +92.0^\circ$ ($c = 1.62$, CHCl₃, lit.:² -73.4° (66%ee) for the enantiomer)

HPLC : Chiralcel OD-RH, 30% *i*PrOH/H₂O, 0.45 mL/min., UV detection at 210 nm, major peak at 106.8 min., minor peak at 118 min., 97% ee.

(3S, 4R)-4-Methyl-1-phenyl-5-hexen-3-ol (17)

Flash chromatography (5% EtOAc/Hexane) gave the pure product as a colourless oil (71% yield), which gave satisfactory analytical data.²

$[\alpha]_D^{25} = -14.7^\circ$ ($c = 1.42$, CHCl₃, lit.:² +13.8° (86%ee) for the enantiomer)

HPLC : Chiralcel AD-RH, 40% *i*PrOH/H₂O, 0.33 mL/min., UV detection at 210 nm, major peak at 64.8 min., minor peak at 73.3min., 96% ee.

(3S, 4R)-1-(*t*-Butyldiphenylsilyloxy)-4-methyl-5-hexen-3-ol (18)

Flash chromatography (2.5% EtOAc/Hexane) gave the pure product as a colourless oil (63% yield), which gave satisfactory analytical data.⁶

$[\alpha]_D^{25} = +4.4^\circ$ ($c = 1.46$, CHCl₃, lit.:⁶ +3.0 (mixture of diastereomers))

⁵ Tokuda, M.; Satoh, S.; Suginome, H. *J.Org.Chem.* **1989**, 54, 5608-5613.

⁶ Chemler, S.R.; Roush, W.R. *J. Org. Chem.* **1998**, 63, 3800-3801.

HPLC : Chiralcel AD-RH, 55% *i*PrOH/H₂O, 0.31 mL/min., UV detection at 210 nm, minor peak at 27.7 min., major peak at 31.9min., 94% ee.

(2*R*, 3*R*)-1-(*t*-Butyldimethylsilyloxy)-3-methyl-4-penten-2-ol (19)

Flash chromatography (5% EtOAc/hexanes) gave the pure product as a colourless oil (63% yield), which gave satisfactory analytical data.⁷

¹H NMR (300 MHz, CDCl₃): δ 5.84 (m, 1H), 5.06-5.02 (m, 2H), 3.63-3.60 (m, 1H) 3.50-3.47 (m, 2H), 2.35 (d, *J* = 2 Hz, 1H), 2.30 (apparent sextet, *J* = 7.0 Hz, 1H), 1.02 (d, *J* = 6.8 Hz, 3H), 0.88 (s, 9H), 0.05 (s, 6H);

¹³C NMR (125 MHz, CDCl₃): 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 (C₁₂H₂₆O₂Si - *t*-Bu): 173.09978. Found: 173.09970.

$[\alpha]_D^{25} = +2.8^\circ$ (*c* = 0.73 g/mL, CHCl₃).

HPLC (performed on the carbamate product from the 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.

General procedure for the synthesis of *syn*-homoallylic alcohols 20-23.

Scandium trifluoromethanesulfonate (16 mg, 0.03 mmol) and 4 Å molecular sieves (33 mg) were introduced in a 10-mL round-bottom flask, which was then flushed with Ar. CH₂Cl₂ (0.3 mL) was added and the mixture was cooled to -78°C. The aldehyde (0.50 mmol) was added, followed by a solution of boronate **4a** (0.33 mmol) in CH₂Cl₂ (0.3 mL) dropwise over 5 minutes. The resulting mixture was stirred at -78°C for 24 hours, 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 minutes, then 1 N HCl (5 mL) was 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 $\times$ 5 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated. Flash chromatography afforded the pure homoallylic alcohol.

(1*R*, 2*S*)-2-Methyl-1-phenyl-3-buten-1-ol (20)

⁷ Wipf, P.; Reeves, J.T. *Chem. Commun.*; **2002**, 2066-2067.

Flash chromatography (5% EtOAc/Toluene) yielded a colourless oil (28.5 mg, 53%), which gave satisfactory analytical data.⁸

TLC (10% EtOAc/toluene, PMA): 0.23;

$[\alpha]_D^{25} +12.0^\circ$ ($c = 1.47$, CHCl_3 , lit.:^{2,8} -15.0° for the enantiomer, $+15.2^\circ$)

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.

(3S, 4S)-4-Methyl-1-phenyl-5-hexen-3-ol (21)

Flash chromatography (5% EtOAc/Toluene) yielded a colourless oil (32 mg, 51%), which gave satisfactory analytical data.⁹

TLC (10% EtOAc/toluene, PMA): 0.35;

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

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.

(3S, 4S)-1-(*t*-Butyldiphenylsilyloxy)-4-methyl-5-hexen-3-ol (22)

Flash chromatography (5% EtOAc/Toluene) yielded a colourless oil (69.5 mg, 57%), which gave satisfactory analytical data.^{10,11}

TLC (5% EtOAc/toluene, PMA): 0.29;

$[\alpha]_D^{25} -4.4^\circ$ ($c = 1.89$, CHCl_3 , lit.:^{10,11} $+3.3^\circ$, $+5.5^\circ$ for the enantiomer)

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.

⁸ Iseki, K.; Kuroki, Y.; Takahashi, M.; Kishimoto, S.; Kobayashi, Y. *Tetrahedron* **1997**, *53*, 3513-3526.

⁹ Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620-6628.

¹⁰ Boeckman, R.K.; Charette, A.B.; Asberom, T.; Johnston, B.H. *J. Am. Chem. Soc.* **1991**, *113*, 5337-5353.

(2R, 3S)-1-(*t*-Butyldimethylsilyloxy)-3-methyl-4-penten-2-ol (23)

Flash chromatography (5% EtOAc/hexanes) gave the pure product as a colourless oil (43 mg, 57%).

TLC (5% EtOAc/toluene, PMA): 0.20;

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

^{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;

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

HRMS (EI, m/z) Calcd for $\text{C}_{12}\text{H}_{26}\text{O}_2\text{NaSi}$: 253.15943. Found: 253.15936.

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

HPLC (performed on the carbamate product from the reaction with phenylisocyanate) : Chiralcel OD, 2% *i*PrOH/hexane, 0.30 mL/min., UV detection at 210 nm, major peak at 23.3 min., minor peak at 24.3 min., 96% ee.

(1R, 2S, 3R, 4S)-2-phenyl-1,7,7-trimethylbornanediol (24).

This compound was prepared according to published procedures.³

¹¹ Scarlato, G.R.; DeMattei, J.A.; Chong, L.S.; Ogawa, A.K.; Lin, M.R.; Armstrong, R.W. *J. Org. Chem.* **1996**, *61*, 6139-6152.

Copies of ^1H and ^{13}C NMR spectra

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

^1H and APT ^{13}C NMR

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

^1H and APT ^{13}C NMR

Solvent: cdc13
Temp.: 27.5 C / 300.6 K
INDVA-300 "1300"
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.999 sec
Width 3001.2 Hz
16 repetitions
OBSERVE H1, 299.9696605 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec

Hugo Lechance, HLH-3-27-1, APT
100.58 MHz ^{13}C [1H] in cdc13

exp2 apt

SAMPLE DEC. & VT
date Apr 15 2003 dfrq 400.127
solvent CDCl3 dn H1
file /mnt/d600/nmr~ dpwr 40
labdata/HLH/MUD/-/ dof 0
ap15s4_HLH-3-27-1~ dm yny
APT.fid dm w
ACQUISITION dmf 10582
sfrq 100.624 dseq
tn C13 dres 1.0
at 1.202 homo n
np 84462
sw 35133.9 dfrq2 0
fb not used dn2 1
bs 4 dpwr2 0
tpwr 55 dof2 0
pw 9.2 dm2 n
pl 17.6 dmm2 c
d1 0.500 dm2 10582
d2 0.007 dseq2
d3 0.001 dres2 1.0
toif 3055.6 homo2 n
nt 50000 PROCESSING
ct 256 lb 1.00
atock n wfile
gain not used proc ft
FLAS n math not used f
il n
in n verr
dp y wepp
hs nn wbs
DISPLAY nn wnt
sp -195.7
wp 17333.2
vs 68
sc 0
wc 180
hzm 96.30
ls 500.00
rf1 12765.6
rfp 7753.1
th 100.000
ins no ph

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

03050101
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.24 ppm), temp 27.2 C -> actual temp = 27.0 C, sv500 probe
date:Mar 11 2003 seqfil:s2pu1 hz/mm:20.06 sweep width[Mz]:5006 spectrometer:1300 file:/mnt/d600/hallnmrdata/Xiaosong/allylboration/03031101.fid
acq.time[s]:2.0 relax.time[s]:3.0 dig.res.[Hz/pt]:0.08 # of scans: 16

Pulse Sequence: s2pu1

0303011702 160 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 77.24 ppm), temp 27.2 C -> actual temp = 27.0 C, sv500 probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date:Jun 17 2003 seqfil:apt hz/mm:130.41 sweep width[Mz]:31239 spectrometer:1300 file:/mnt/d600/hallnmrdata/Xiaosong/allylboration/03061702-APT.fid
acq.time[s]:2.0 relax.time[s]:0.1 dig.res.[Hz/pt]:0.48 # of scans:3111

(1*R*, 2*S*, 3*R*, 4*S*)-2,3-O-[(*Z*)-2-butenylboryl]-2-phenyl-1,7,7-trimethylbornanediol (**4a**) ¹H and APT ¹³C NMR

(1R)-1-phenyl-3-buten-1-ol (5)

^1H and APT ^{13}C NMR

NLN-2-189-1a, Feb 12, 2003.
500 MHz ^1H in CDCl_3 (ref. to CDCl_3 @ 7.24 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe

Pulse Sequence: zgpg30

Solvent: cdcl_3
Temp: 27.2 C / 300.4 K
INNOVA-500 "1hds"
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 2.000 sec
Width 5000.0 Hz
12 repetitions
OBSERVE H1, 499.1194456 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec

25 MHz APT in CDCl_3 (ref. to CDCl_3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe *HLM-3-089-1a*
A CH2 same, CH & CH3 opposite side of solvent signal
etc:Jun 6 2003 seq:ll:apt hz/mm:130.41 sweep width[Hz]:31259 spectrometer:ld5 file:exp
cq.time[s]:2.0 relax. time[s]:0.1 dig.res.[Hz/pt]:0.48 # of scans:168

Pulse Sequence: apt

(3S)1-phenyl-5-hexen-3-ol (6)

^1H and APT ^{13}C NMR

sw nmz 10 in CDCl3 (ref. to CDCl3 @ 7.24 ppm), temp 27.0 C -> actual temp = 27.0 C, 1d probe

HLH-2-198-1a

Solvent: cdcl3
Temp: 27.0 C / 300.6 K
INNOVA-300 ^1H NMR

Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.999 sec
Width 3001.2 Hz
16 repetitions
OBSERVE H1, 299.9896605 MHz
DATA PROCESSING
F1 size 131072
Total time 1 min, 30 sec

HLH-2-198-1
125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: May 28 2003 seq: fl: apt hz/mm: 130.41 sweep width [Hz]: 31299 spectrometer: lbt5 file: exp
acq. time [s]: 2.0 relax. time [s]: 0.1 dig. res. [Hz/pt]: 0.48 # of scans: 217
Pulse Sequence: ap.

(3*R*)-1-(*t*-Butyldiphenylsilyloxy)-5-hexen-3-ol (**7**)

^1H and APT ^{13}C NMR

(2*R*)-1-(Benzyloxy)-4-penten-2-ol (**8**)

¹H and APT ¹³C NMR

(2R)-1-(*t*-Butyldimethylsilyloxy)-4-penten-2-ol (**9**)

^1H NMR and APT ^{13}C NMR

HLH-3-109-1a, June 10, 2003.
500 MHz ^{13}C NMR in CDCl_3 (ref. to CDCl_3 @ 7.24 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe

Pulse Sequence: ...pu1

Solvent: cdcl_3
Temp: 27.2 C / 300.4 K
INOVIA-500 "1bds"
Relax: delay 3.000 sec
Pulse 45.0 degrees
Acq: time 1.958 sec
Width 5000.0 Hz
16 repetitions
OBSERVE ^{13}C 400.119456 MHz
DATA PROCESSING
FT 6128 131072
Total time 1 min, 30 sec

(3R)-1-(*t*-Butyldiphenylsilyloxy)-5-hexen-3-ol (**10**)

^1H and APT ^{13}C NMR

(1R)-3-Methyl-1-phenyl-3-buten-1-ol (**11**)

^1H and APT ^{13}C NMR

HLH-2-092a, June 4, 2003.
500 MHz ^1H in CDCl_3 (ref. to CDCl_3 @ 7.24 ppm), temp 27.2 C -> actual temp = 27.0 C, sv500 probe

Pulse Sequence: zgpg30

Solvent: cdcl_3
Temp: 27.2 C / 300.4 K
INOVA-500 "1bd5"

Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.358 sec
Width 3008.3 Hz
15 repetitions
OBSERVE ^1H , 499.1194456 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec

HLH-2-092a

125 MHz APT in CDCl_3 (ref. to CDCl_3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sv probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Jun 4 2003 seq: 1: apt hz/mm: 125.41 sweep width [Hz]: 31293 spectrometer: 1bd5 file: exp
acq. time [s]: 2.0 relax. time [s]: 0.1 dig. res. [Hz/pt]: 0.48 # of scans: 96

Pulse Sequence: apzgpg30

(3R)-5-Methyl-1-phenyl-5-hexen-3-ol (12)

^1H and APT ^{13}C NMR

300 MHz ^1H in CDCl_3 (ref. to CDCl_3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, 1d probe

ACH-2-198-1a

Solvent: cdCl_3
Temp: 27.5 C / 300.6 K
INOVA-300 "1300"

Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.995 sec
Width 3001.2 Hz
16 repetitions
OBSERVE H1 299.9696605 MHz
DATA PROCESSING
F1 size 131072
Total time 1 min, 30 sec

ACH-2-198-1

125 MHz APT in CDCl_3 (ref. to CDCl_3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: May 28 2003 seq: f1apt hz/mm: 130.41 sweep width [Hz]: 31299 spectrometer: 1bd5 file: exp
acq. time [s]: 12.0 relax. time [s]: 0.1 dig. res. [Hz/pt]: 0.48 # of scans: 217

Pulse Sequence: ap.

(3S)-1-(*t*-Butyldiphenylsilyloxy)-5-methyl-5-hexen-3-ol (**13**)

^1H and APT ^{13}C NMR

(2R)-1-(Benzyloxy)-4-methyl-4-penten-2-ol (**14**)

^1H and APT ^{13}C NMR

HLH-3-039-2b, June 17, 2003,
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.24 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe

Pulse Sequence: s2pul

Solvent: cdc13
Temp: 27.2 C / 300.4 K
INNOVA-500 "1bd5"
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.398 sec
Width 5000.2 Hz
16 repetitions
OBSERVE H1, 498.1194456 MHz
DATA PROCESSING
FT size 321072
Total time 1 min, 30 sec

125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe HLH-3-039-2b, June 17, 2003 Pulse Sequence: apt
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Jun 17 2003 seqfil: apt hz/mm: 130.41 sweep width [Hz]: 31299 spectrometer: 1bd5 file: exp
acq.time[s]: 2.0 relax. time[s]: 0.1 dig.res. [Hz/pt]: 0.48 # of scans: 216

(2*R*)-1-(*t*-Butyldimethylsilyloxy)-4-methyl-4-penten-2-ol (**15**)

^1H and APT ^{13}C NMR

HLH-3-111-1a, June 10, 2003,
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.24 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe

ruise sequence: szpu l

```
Solvent: cdc13
Temp. 27.2 C / 300.4 K
INOVA-500 "ibds"

Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 5006.3 Hz
12 repetitions
OBSERVE H1, 498.119456 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec
```

[illegible]

(1*R*, 2*R*)-2-Methyl-1-phenyl-3-buten-1-ol (**16**)

03061504
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.24 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe
date: Jun 15 2003 seqfil:s2pu1 hz/mm:20.86 sweep width(Hz):5006 spectrometer:ibds file:/mnt/d600/hallmrdata/Xiaosong/allylboration/03061504.fid
acq.time[s]:2.0 relax.time[s]:3.0 dig.res.[Hz/pt]:0.08 # of scans: 16

03061504-APT 125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Jun 15 2003 seqfil:apt hz/mm:130.41 sweep width(Hz):31293 spectrometer:ibds file:/mnt/d600/hallmrdata/Xiaosong/allylboration/03061504-APT.fid
acq.time[s]:2.0 relax.time[s]:0.1 dig.res.[Hz/pt]:0.48 # of scans: 671

(3*S*, 4*R*)-4-Methyl-1-phenyl-5-hexen-3-ol (**17**)

(3*S*, 4*R*)-1-(*t*-Butyldiphenylsilyloxy)-4-methyl-5-hexen-3-ol (**18**)

(2*R*, 3*R*)-1-(*t*-Butyldimethylsilyloxy)-3-methyl-4-penten-2-ol (**19**)

(1*R*, 2*S*)-2-Methyl-1-phenyl-3-buten-1-ol (**20**)

^1H and APT ^{13}C NMR

Solvent: cdCl_3
Temp: 27.5 °C / 300.6 K
INOVA-300 "1300"

Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.919 sec
Width 3001.2 Hz
12 repetitions
OBSERVE H1, 299.9686605 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec

mgh-14-26B

125 MHz APT in CDCl_3 (ref. to CDCl_3 @ 77.0 ppm), temp 27.2 °C -> actual temp = 27.0 °C, sw probe
C & CH2 same, CH & CH3 opposite side of solvent signal
Pulse Sequence: apt
date: Jun 7 2003 seqfill: apt hz/mm: 69.24 sweep width [Hz]: 31299 spectrometer: i300 file: /mnt/d600/hallnmrdata/Michel/mgh-14-26b-cl3-1500.fid
acq.time[s]: 2.0 relax.time[s]: 0.1 dig.res. [Hz/pt]: 0.48 # of scans: 5473

(3*S*, 4*S*)-4-Methyl-1-phenyl-5-hexen-3-ol (**21**)

^1H and APT ^{13}C NMR

(3*S*, 4*S*)-1-(*t*-Butyldiphenylsilyloxy)-4-methyl-5-hexen-3-ol (**22**)

^1H and APT ^{13}C NMR

(2R, 3S)-1-(*t*-Butyldimethylsilyloxy)-3-methyl-4-penten-2-ol (**23**)

^1H and APT ^{13}C NMR

Solvent: cdc13
Temp. 26.0 C / 299.9 K
INOVA-400 "1400"

Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.999 sec
Width 4001.6 Hz
16 repetitions
OBSERVE H1, 399.7923405 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec

MCH-14-52B

125 MHz APT in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH2 same, CH & CH3 opposite side of solvent signal
date: Jun 8 2003 seqfil: apt hz/mm: 130.41 sweep width [Hz]: 31299 spectrometer: lbd5 file: exp
acq. time [s]: 2.0 relax. time [s]: 0.1 dig. res. [Hz/pt]: 0.48 # of scans: 928

Pulse Sequence: apt

Representative HPLC chromatograms

Typical Chiral HPLC for reactions with boronate **1a**.
Compound **6**

Racemic sample

Chiralcel AD-RHCD-CC012 column (0.46cm x 15cm). 45% iPrOH and 55% water over 80 minutes at 0.33mL/min. Det. 210 nm. Temp 25 C. Injection: 2 ul / 97bar(090503)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	75.054	BB	4.2986	2.57531e4	91.75156	40.0720
2	88.404	PB	4.4704	3.85140e4	122.68706	59.9280

Enantioselective reaction

Chiralcel AD-RHCD-CC012 column (0.46cm x 15cm). 45% iPrOH and 55% water over 80 minutes at 0.33mL/min. Det. 210 nm. Temp 25 C. Injection: 2 ul / 97bar(090503)

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	73.717	BB	4.4792	9.29263e4	324.27936	94.6217
2	88.834	PB	3.7618	5281.93311	19.10329	5.3783

Typical Chiral HPLC for reactions with boronate **2a**.
Compound **12**

Racemic sample

Chiralcel OD-RHCD-CC012 column (0.46cm x 15cm). 45% iPrOH and 55% water over 60 minutes at 0.4mL/min. Det. 210 nm. Temp 25 C

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.650	BV	1.3006	7.99201e4	950.80774	49.6540
2	40.508	VBA	1.6510	8.10337e4	760.57489	50.3460

Enantioselective reaction

Chiralcel OD-RHCD-CC012 column (0.46cm x 15cm). 45% iPrOH and 55% water over 60 minutes at 0.4mL/min. Det. 210 nm. Temp 25 C

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.956	VV	1.5530	2825.30176	26.22364	1.2220
2	39.868	VB	2.1203	2.28374e5	1716.44421	98.7780

Typical Chiral HPLC for reactions with boronate **3a**.
Compound **17**

Racemic sample

chiral AD-RH HPLC with 40% isopropanol/H₂O for 80 minutes; DAD detector; flow rate of 0.30 ml/min

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	65.877	BB	2.0392	2.11752e4	153.89787	50.0759
2	73.575	BB	2.3274	2.11110e4	133.02913	49.9241

Enantioselective reaction

chiral AD-RH HPLC with 40% isopropanol/H₂O for 80 minutes; DAD detector; flow rate of 0.300 ml/min

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	64.840	BB	2.7141	2.46126e5	1256.07239	98.2725
2	73.316	MM	2.2231	4326.52490	32.43549	1.7275

Typical Chiral HPLC for reactions with boronate **4a**.
Compound **21**

Racemic sample

Chiralcel AD-RHCD-CC012 column (0.46cm x 15cm). 40% iPrOH and 60% water over 80 minutes
33mL/min. Det. 210 nm. Temp 25 C. Injection: 0.3 ul

Enantioselective reaction

Chiralcel AD-RHCD-CC012 column (0.46cm x 15cm). 40% iPrOH and 60% water over 80 minutes
33mL/min. Det. 210 nm. Temp 25 C. Injection: 0.3 ul

Representative ^{19}F NMR spectra

Typical ^{19}F NMR for reactions with boronate **1a**
Compound **9**

Racemic sample

Enantioselective reaction