Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 128 (2007) 827–831
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Asymmetric hydroboration and Matteson homologation for the preparation of fluorinated α-phenethanols

P. Veeraraghavan Ramachandran *, Michael P. Jennings

Herbert C. Brown Center for Borane Research, Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907-2084, United States

Received 15 February 2007; received in revised form 6 April 2007; accepted 9 April 2007
Available online 19 April 2007

Abstract

The asymmetric catalytic hydroboration–oxidation of ring-fluorinated styrenes (F-PhCH=CH_2) was achieved with catecholborane along with a combination of $[Rh(COD)_2]^+BF_4^-$ and (*R*)-BINAP providing 81–96% enantioselectivities for the product alcohols for *ortho*-unhindered styrenes. A deleterious effect of a 2,6-disubstitution on the enantioselectivity of the product alcohol was observed. 2-Trifluoromethylstyrene also provides only 53% ee, probably due to the steric bulk of the CF_3 group at the *ortho*-position of styrene. Asymmetric homologation of fluorophenylmetals (magnesium bromide or lithium) with pinanediol α-chloroethylboronate, followed by oxidation readily furnished the desired 1-(2,6-difluorophenyl)- and 1-(perfluorophenyl)ethanols in 94–95% ee.

Keywords: Fluorostyrenes; Asymmetric hydroboration; Asymmetric homologation; Fluoroalcohols

1. Introduction

The chemical and biological properties of organic molecules are usually altered by fluorine substitution [1]. Optically active fluorinated alcohols are important building blocks or end-products that have been applied in medicinal and materials chemistry [2]. Asymmetric syntheses of fluoroalcohols are challenging and organoborane chemistry provides a simple route to achieve them [3]. As part of our program on fluoroorganic syntheses via boranes, we had reported the preparation of fluoroalcohols via hydroboration–oxidation [4], reduction [5], allylboration [6], etc. In continuation of our research on the hydroboration of fluoroolefins [4], an investigation of asymmetric catalytic hydroboration of fluorinated styrenes was undertaken [7,8]. Following are the results of a systematic study and the enantioselectivities achieved for the hydroboration–oxidation of ring-fluorinated styrenes with catecholborane along with a combination of $[Rh(COD)_2]^+BF_4^-$ and (*R*)-BINAP.

2. Results and discussion

We began the study with the asymmetric hydroboration of 2,3,4,5,6-pentafluorostyrene (**1a**) with catecholborane (CBH) due to the potential importance of the corresponding chiral organoborane intermediate for the preparation of a variety of perfluorophenyl containing chiral organic molecules [9]. In addition, our earlier studies on the asymmetric reduction of 2′,3′,4′,5′,6′-pentafluoro- and 2′,6′-difluoroacetophenones with *B*-chlorodiisiopinocampheylborane (DIP-Chloride™) [10a] we encountered low ee for the product alcohols [10b]. Hayashi and co-workers have reported that catalytic asymmetric hydroboration at low temperatures provided high enantioselectivities for only a handful of substrates, i.e. styrene and *p*-substituted styrenes [11a].

2.1. Asymmetric catalytic hydroboration of fluorostyrenes

The initial chiral ligand screening for the asymmetric hydroboration of **1a** was performed at room temperature (rt) in tetrahydrofuran (THF), due to very high levels of regioselectivity for the 2°-ol [11a]. Chiral ligands with methylene backbones, such as (*R*,*R*)-DIOP, (*R*)-Prophos, and (*S*,*S*)-Chiraphos (Fig. 1), proceeded rapidly (0.5 h) and provided

* Corresponding author. Tel.: +1 765 494 5303; fax: +1 765 494 0239.
E-mail address: chandran@purdue.edu (P.V. Ramachandran).

0022-1139/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2007.04.014

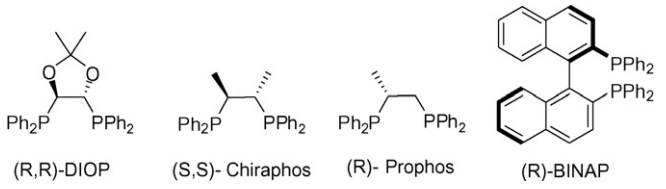
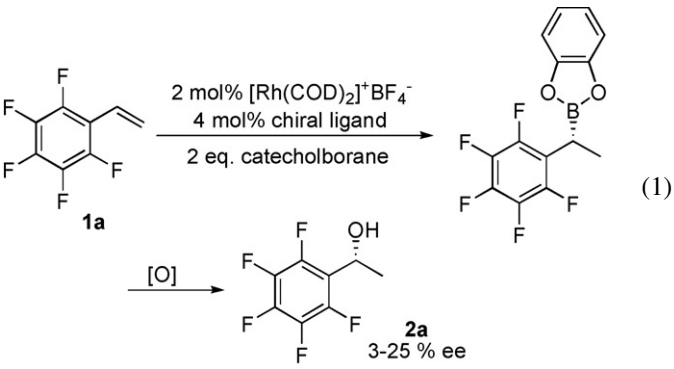


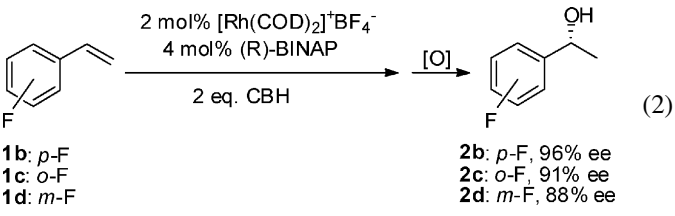
Fig. 1. Chiral ligands for asymmetric hydroboration.

high regioselectivites for the product 2°-alcohol. However, the enantiomeric excesses (ee) for the product 1-(perfluorophenyl)ethanol (**2a**) were very low (≤5%). On the basis of the reports by Hayashi and Dai [11a,b], (*R*)-BINAP (Fig. 1) was then examined. Although BINAP proved to be a better ligand, the ee observed was still low (20%) (Eq. (1)) [8] and interestingly, manipulation of solvent, temperature, and concentration had very little consequence on enantioselectivity. The maximum ee observed was only 25% in dimethoxyethane (DME). The results are summarized in Table 1.



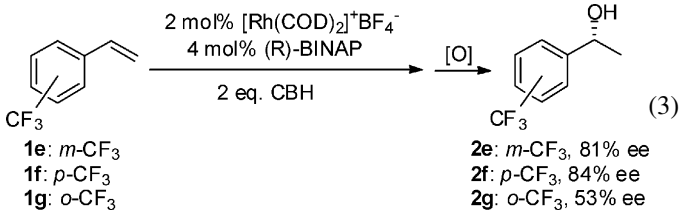
(1)

To understand the reasons for the poor ee in the case of 2,3,4,5,6-pentafluorostyrene, other ring-substituted fluorostyrenes were now examined. At −25 °C with (*R*)-BINAP, the catalyzed hydroboration of *p*-fluorostyrene **1b** in 0.5 M THF, followed by alkaline H_2O_2 oxidation furnished the 2°-ol, 1-(4-fluorophenyl)ethanol (**2b**) exclusively with moderate enantioselectivity (68%) in 86% yield. Changing the solvent from THF to DME provided an increase in ee (76%) and cooling the reaction to −40 °C in DME further increased the enantioselectivity to 87%. However, lowering the temperature to −78 °C and allowing the medium to slowly warm to rt, did not enhance the enantioselectivity. Finally, increasing the concentration (1 M in DME, −78 °C-rt) provided a very high enantioselectivity of 96% ee for **2b**. Under these optimized conditions, similar results were obtained for the asymmetric hydroboration of *o*-(**1c**) and *m*-fluorostyrenes (**1d**) as the products 1-(2-fluorophenyl)ethanol (**2c**) and 1-(3-fluorophenyl)ethanol (**2d**) revealed 91 and 88% ee, respectively (Eq. (2)).

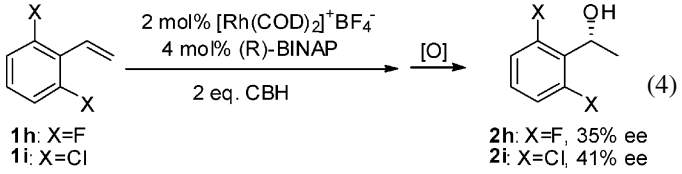


(2)

Having achieved high ee for monofluorostyrenes, ring-trifluoromethyl substituted stryenes were examined. Under conditions identical to that for the hydroboration of **1b**, *m*-(**1e**) and *p*-trifluoromethyl styrenes (**1f**) furnished slightly lower enantioselectivities for the alcohols 1-(3-(trifluoromethyl)phenyl)ethanol (**2e**) and 1-(4-(trifluoromethyl)phenyl)ethanol (**2f**) in 81 and 84%, respectively. Interestingly, *o*-trifluoromethyl styrene (**1g**) afforded only 53% ee for 1-(2-(trifluoromethyl)-phenyl)ethanol (**2g**) (Eq. (3)). This pointed to the effect of sterics at the *ortho*-position of styrene on the asymmetric hydroboration with BINAP and demanded the examination of 2,6-difluorinated styrenes. On the basis of the results from asymmetric reduction of 2′,6′-disubstituted acetophenones with DIP-Chloride™ [10b] and the asymmetric hydroboration of 2,3,4,5,6-pentafluorostyrene described above, a lower enantioselectivity was expected. Indeed, the hydroboration–oxidation of 2,6-difluorostyrene (**1h**), under the previously described conditions, afforded a very low enantioselectivity of 35% for 1-(2,6-difluorophenyl)ethanol (**2h**). The effect of diortho-substitution was further confirmed with the hydroboration–oxidation of 2,6-dichlorostyrene (**1i**), which also provided a similar low enantioselectivity of 41% for the product 1-(2,6-dichlorophenyl)ethanol (**2i**) obtained in 86% yield (Eq. (4)).

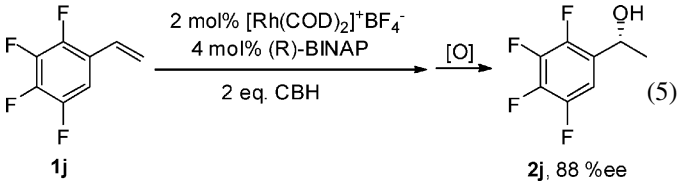


(3)



(4)

In the case of asymmetric reduction of ring-substituted fluoroketones with DIP-Chloride™, while poor ee was observed for 2′,3′,4′,5′,6′-pentafluoroacetophenone, 2′,3′,4′,5′-tetrafluoroacetophenone had provided high ee [10]. Analogous to this observation, the catalytic asymmetric hydroboration–oxidation of 2,3,4,5-tetrafluorostyrene (**1j**) readily furnished the Markovnikov alcohol (**2j**) with an enantioselectivity of 88% in 82% yield (Eq. (5)). This confirms that the substitution of a bulky group at the *ortho*-position or substitution of both *ortho*-positions of styrene is responsible for the decreased enantioselectivity achieved during the asymmetric catalytic hydroboration with CBH using BINAP as the auxiliary.



(5)

Table 1
Asymmetric hydroboration of 2,3,4,5,6-pentafluorostyrene (**1a**) with CBH in the presence of 2 mol% $[Rh(COD)_2]^+BF_4^-$ and 4 mol% chiral phosphine in THF[a]

Ligand	Temperature	Yield (%)	2°/1°-ol	% ee[b]	Configuration[c]
(*R*,*R*)-DIOP	rt	83	97/3	3	R
(*S*,*S*)-Chiraphos	rt	84	95/5	5	R
(*R*)-Prophos	rt	87	98/2	3	S
(*R*)-BINAP	rt	81	97/3	20	R
(*R*)-BINAP	rt	84	97/3	21[d]	R
(*R*)-BINAP	rt	83	98/2	22[e]	R
(*R*)-BINAP	0	84	98/2	21	R
(*R*)-BINAP	−25	86	98/2	22	R
(*R*)-BINAP	−40	84	98/2	22	R
(*R*)-BINAP	−25	82	98/2	25[f]	R

[a] Reactions ran at 0.5 M conc.
[b] The enantiomers were resolved using HPLC on a Chiralcel OD-H column.
[c] Configuration determined on the basis of rotation, Ref. [9].
[d] 1 M concentration.
[e] 0.3 M concentration.
[f] Reaction in DME.

Essentially exclusive Markovnikov regioselectivity was observed for the hydroboration–oxidation of **1b–h** and **1j**, which is attributable to a proposed η-3 complex with the metal center prior to the reductive elimination [11g]. On the contrary, a 3/2:2°/1° alcohols were furnished for the hydroboration–oxidation of **1i** under identical conditions to that of the hydroboration of **1b**. It was postulated that due to the dichloro substituents of **1i**, the stabilized η-3 complex could not be achieved entirely, presumably due to the disrupted co-planarity of the arene and alkene moiety [11g]. The results are summarized in Table 2.

2.2. Asymmetric homologation of fluoroaryl Grignard and fluoroaryllithium reagents

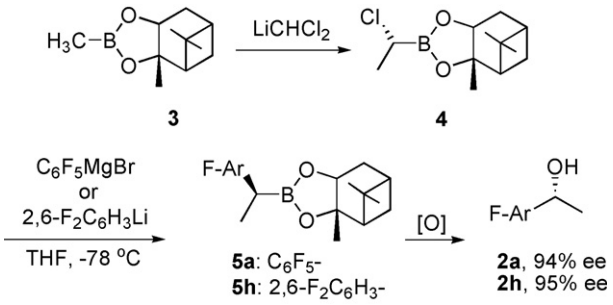
With the failed protocol of earlier reported DIP-Chloride™ reduction of 2′,6′-difluoroacetophenone and 2′,3′,4′,5′,6′-pentafluoroacetophenone and the current results of the catalytic asymmetric hydroboration–oxidation for the synthesis of **2a** and **2h**, the focus was now shifted to examining the Matteson asymmetric homologation [12] for achieving high enantioselectivity [13].

Table 2
Asymmetric hydroboration of fluorinated styrenes with CBH in the presence of 2 mol% $[Rh(COD)_2]^+BF_4^-$ and 4 mol% (*R*)-BINAP in DME

Styrene		Reaction temperature	Yield (%)	2°/1°-ol	% ee[a]	Configuration[b]
Subst.	#					
4-F	**1b**	−25	85	97/3	68[c]	R
4-F	**1b**	−25	86	97/3	76	R
4-F	**1b**	−40	87	98/2	87	R
4-F	**1b**	−78-rt	84	98/2	86	R
4-F	**1b**	−78-rt	82	98/2	96	R
2-F	**1c**	−78-rt	83	98/2	91	R
3-F	**1d**	−78-rt	86	98/2	88	R
3-CF_3	**1e**	−78-rt	84	98/2	81	R
4-CF_3	**1f**	−78-rt	85	98/2	84	R
2-CF_3	**1g**	−78-rt	88	95/5	53	R
2,6-F_2	**1h**	−78-rt	86	94/6	35	R
2,6-Cl_2	**1i**	−78-rt	86	60/40	41	R
2,3,4,5-F_4	**1j**	−78-rt	82	98/2	88	R

[a] The enantiomers were resolved by a Chiralcel OD-H HPLC column.
[b] Configuration on the basis of analogy with **2b**.
[c] Reaction in THF.

Under the procedure described earlier [12b] homologation of methyl-pinanediol boronate ester (**3**) with *in situ* generated $LiCHCl_2$ (formed from *sec*-butyllithium and CH_2Cl_2 in THF at −78 °C) readily provided the chiral 1-chloroethyl pinanediol boronate ester **4**. Subsequent addition of either (perfluorophenyl)magnesium bromide or (2,6-difluorophenyl)lithium at −78 °C in THF to **4** and allowing the reaction to warm to rt furnished the chiral pinanediol chloro(2,6-difluorophenyl)- and chloro(2,3,4,5,6-pentafluorophenyl)methylboronates **5a** and **5h**, respectively. Alkaline oxidation afforded the chiral alcohols **2a** and **2h**, respectively, in 84 and 88% yields and 94 and 95% ee, respectively (Eq. (6)).



(6)

3. Conclusion

In summary, we have observed that the low temperature catalytic hydroboration–oxidation of ring-fluorinated styrenes with catecholborane and a combination of $[Rh(COD)_2]^+BF_4^-$ and (*R*)-BINAP provided very high for the product 1-fluoro phenethanols, except in the cases of 2-trifluoromethyl-, 2,3,4,5,6-pentafluoro- and 2,6-dihalostyrenes. We achieved these classes of fluoro-α-phenethanols in 84–88% yields and 94–95% enantioselectivities via asymmetric homologation utilizing the corresponding fluoroaryl Grignard or lithium reagents and chiral α-chloroethyl pinanediol boronate.

4. Experimental

Unless otherwise noted, all manipulations were carried out under an inert atmosphere using flame-dried glassware. Techniques for handling air-sensitive compounds have been previously described [14]. THF was freshly distilled before use from over sodium-benzophenone ketyl and anhydrous ethyl ether (Mallinckrodt) was used as received. All other chemicals were obtained from Aldrich Chemical Co.

The ^1H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were plotted on a Varian Gemini-300 spectrometer (300, 75 and 282 MHz, respectively) with a Nalorac-quad probe. ^1H NMR spectra were obtained using $CDCl_3$ as the solvent with either tetramethylsilane (TMS: 0 ppm) or chloroform ($CHCl_3$: 7.2 ppm) as the internal standard. ^{19}F

NMR spectra were recorded in $CDCl_3$ using $CFCl_3$ or trifluoroacetic acid (TFA) as the internal standard. ^1H NMR data are reported as chemical shifts (δ ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), and integration. Chromatography was performed on 40–60 μm silica gel (230–400 mesh). Enantiomeric excesses (% ee) were measured using a Dynamax HPLC fitted with an HPXL Solvent Delivery System and a Dynamax UV (λ 254 nm) detector, and a Chiralcel OD-H chiral HPLC column. Mass spectra were recorded using a Hewlett Packard 5989B mass spectrometer/5890 series II gas chromatograph or a Finnigan mass spectrometer model 4000. The chemical ionization gas used was isobutene.

5. Experimental procedure

5.1. Asymmetric hydroboration–oxidation of fluorostyrenes

A typical experimental procedure for the asymmetric catalyzed hydroboration of fluorostyrenes with CBH in the presence of $[Rh(COD)_2]^+BF_4^-$ and (*R*)-BINAP is as follows. In an Ar filled glove bag, 2 mol% of $[Rh(COD)_2]^+BF_4^-$ and 4 mol% of (*R*)-BINAP were placed into a dry, 50 mL round-bottomed flask and subsequently filled with 9 mL of dry THF. The mixture was allowed to stir for 20–40 min at rt, and then cooled to −78 °C to which the olefin (3 mmol) was added. After 30 min, catecholborane (6 mmol) was added slowly and the solution stirred during the slow warming period to rt (generally overnight). The corresponding solution was cooled to 0 °C, and the chiral boronate ester was then oxidized by adding 4 mL of 3 M NaOH and 4 mL of 30% H_2O_2, slowly. The solution was then allowed to warm to rt and left to oxidize completely for an additional 2 h. Diethyl ether (Et_2O) and H_2O were now added to the solution. The product was extracted with Et_2O (3× 10 mL), followed by 3 M NaOH (2× 10 mL) to remove the catechol side product. The organic extracts were then washed with deionized H_2O, followed by saturated ammonium chloride (NH_4Cl) solution. The organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was then analyzed by GC using a Carbowax 20 column, ^1H, and ^{19}F NMR to determine regioselectivity. Column chromatography on silica gel using hexanes:ethyl acetate (95:5) as eluent furnished the pure alcohols in good yields. The spectral characteristics of the product alcohols matched with those reported in the literature [10b].

5.2. Asymmetric homologation

A typical experimental procedure for the asymmetric homologation of pentafluorophenylmagnesium bromide is as follows. A solution of (*S*)-pinanediol methylboronate (**3**) (10 mmol) and dichloromethane (11 mmol) in THF (20 mL) was cooled to −78 °C. *sec*-BuLi (11 mmol) was added dropwise to the solution slowly marinating the temperature of the solution as −78 °C. The reaction mixture was stirred at −78 °C for 15 min and to this was added freshly fused anhydrous $ZnCl_2$ (5.5 mmol). The resulting solution was then stirred for 16–18 h at rt. The reaction was monitored by ^{11}B NMR spectroscopy of the crude reaction mixture for the appearance of the product boronate at δ 32 ppm. THF was removed under reduced pressure and the crude product was dissolved in *n*-pentane (50 mL) and the resulting solution was filtered under N_2. The filtrate was concentrated under vacuum and the crude product was distilled to give (*S*)-pinanediol (*R*)-1-chloroethylboronate **4** in 80% yield.

A solution of (*S*)-pinanediol (*R*)-1-chloroethylboronate **4** (10 mmol) in 20 mL THF was cooled to −78 °C. To the reaction mixture pentafluorophenylmagnesium bromide (10 mmol, 1 M solution in Et_2O) was added dropwise slowly at −78 °C. The reaction mixture was gradually allowed to warm rt and stirred till completion of the reaction. The reaction, monitored by ^{11}B NMR spectroscopy showed the product (*S*)-pinanediol (*R*)-1-fluoroarylethylboronate **5** peak at δ 34 ppm. The reaction mixture was then oxidized by the addition of 3 M NaOH (12 mmol) and 30% H_2O_2 (12 mmol) for 2 h. The crude reaction mixture was extracted with ethyl acetate (2× 50 mL), washed with sat. NH_4Cl (30 mL) and dried over $MgSO_4$. Removal of solvents under *vacuo* provided crude alcohol, which was purified by column chromatography (silica gel, hexanes:ethyl acetate:: 95:5) to give corresponding pure alcohol **2** in 85% yield.

5.3. Determination of enantiomeric excesses

The pure 2°-ol (50 mg) was dissolved in 3 mL of CH_2Cl_2 and cooled to 0 °C. To this solution was added *p*-nitrobenzoyl chloride (PNB-Cl, 1.1 equiv.) followed by Et_3N. The solution was warmed to rt and allowed to stir for 2 h. Dilute HCl (0.5 M) was added to the mixture and the product was extracted with Et_2O (2× 5 mL), washed with H_2O, brine, and dried over $MgSO_4$. Removal of the solvent *in vacuo* and column chromatography (5% ethyl acetate in hexane) provided the pure chiral ester. The enantioselectivity was determined on a Chiralcel OD-H HPLC column using a solution of hexane and isopropanol.

Acknowledgement

We gratefully acknowledge Herbert C. Brown Center for Borane Research for support of this research.

References

[1] (a) R.D. Chambers, Fluorine in Organic Chemistry, Blackwell, Oxford, 2004;
(b) P. Kirsch, Modern Fluoroorganic Chemistry, Wiley–VCH, Weinheim, 2004;
(c) V.A. Soloshonok (Ed.), EPC-synthesis of Fluoroorganic Compounds: Stereochemical Challenges and Biomedical Targets, John Wiley, Chichester, West Sussex, UK, 1999.

[2] (a) P.V. Ramachandran (Ed.), Asymmetric Fluoroorganic Chemistry, ACS Symposium Series 746, American Chemical Society, Washington, DC, 2000;
(b) S. Sun, A. Adejare, Curr. Top. Med. Chem. 6 (2006) 1457;
(c) C. Presenti, F. Viani, ChemBioChem (2004) 590;
(d) X.L. Qiu, W.D. Meng, F.L. Qing, Tetrahedron 60 (2004) 6711;

(e) F.M.D. Ismail, J. Fluorine Chem. 118 (2002) 27;
(f) J.A. Sikorski, J. Med. Chem. 49 (2006) 1;
(g) K. Iseki, Tetrahedron: Asymmetry 9 (1998) 13887;
(h) T. Kitazume, T. Yamazaki, Experimental Methods in Organic Fluorine Chemistry, Gordon and Breach Science, Amsterdam, 1998.

[3] P.V. Ramachandran, H.C. Brown, in: P.V. Ramachandran (Ed.), Asymmetric Fluoroorganic Chemistry: Synthesis, Applications, and Future Directions, ACS Symposium Series 746, American Chemical Society, Washington, DC, 2000 , pp. 22–37 (Chapter 2).

[4] (a) P.V. Ramachandran, M.P. Jennings, H.C. Brown, Org. Lett. 1 (1999) 1399;
(b) H.C. Brown, G.-M. Chen, M.P. Jennings, P.V. Ramachandran, Angew. Chem. Int. Ed. Engl. 38 (1999) 2052;
(c) P.V. Ramachandran, M.P. Jennings, Chem. Commun. (2002) 386;
(d) P.V. Ramachandran, M.P. Jennings, Org. Lett. 3 (2001) 3789;
(e) P.V. Ramachandran, S. Madhi, M.J. O'Donnell, J. Fluorine Chem. 127 (2006) 1252.

[5] (b) P.V. Ramachandran, H.C. Brown, in: V.A. Soloshonok (Ed.), Enantiocontrolled-Synthesis of Fluoroorganic Compounds: Stereochemical Challenges and Biomedical Targets, John Wiley, Chichester, West Sussex, UK, 1999 , pp. 179–228 (Chapter 6);
(b) P.V. Ramachandran, A.V. Teodorovic, H.C. Brown, Tetrahedron 49 (1993) 1725;
(c) P.V. Ramachandran, B. Gong, A.V. Teodorovic, H.C. Brown, Tetrahedron: Asymmetry 5 (1994) 1061;
(d) P.V. Ramachandran, B. Gong, A.V. Teodorovic, H.C. Brown, Tetrahedron: Asymmetry 5 (1994) 1075;
(e) P.V. Ramachandran, B. Gong, H.C. Brown, J. Org. Chem. 60 (1995) 61.

[6] (a) D. Kumar, S. Madhavan, P.V. Ramachandran, H.C. Brown, Tetrahedron: Asymmetry 11 (2000) 4629;
(b) P.V. Ramachandran, K.J. Padiya, V. Rauniyar, M.V.R. Reddy, H.C. Brown, Tetrahedron Lett. 45 (2004) 1015;
(c) P.V. Ramachandran, K.J. Padiya, M.V.R. Reddy, H.C. Brown, J. Fluorine Chem. 125 (2004) 579;
(d) P.V. Ramachandran, K.J. Padiya, V. Rauniyar, M.V.R. Reddy, H.C. Brown, J. Fluorine Chem. 125 (2004) 615.

[7] (a) P.V. Ramachandran, M.P. Jennings, H.C. Brown, Asymmetric hydroboration of fluoroolefins, in: Paper # FLUO 1 Presented at the 219th National Meeting of the American Chemical Society, San Francisco, CA, March 26, 2000;
(b) M.P. Jennings, PhD thesis, Purdue University, 2001.

[8] A.M. Segarra, C. Claver, E. Fernandez, Chem. Commun. 8 (2004) 464.

[9] C.O. Meese, Ann. Chem. (1986) 2004.

[10] (a) H.C. Brown, J. Chandrasekharan, P.V. Ramachandran, J. Am. Chem. Soc. 110 (1988) 1539;
(b) P.V. Ramachandran, B.Q. Gong, H.C. Brown, J. Francisco, Tetrahedron Lett. 45 (2004) 2603.

[11] (a) T. Hayashi, Y. Matsumoto, Y. Ito, Tetrahedron: Asymmetry 2 (1991) 601;
(b) J. Zhang, B. Lou, G. Guo, L. Dai, J. Org. Chem. 56 (1991) 1670;
(c) H. Doucet, E. Fernandez, T.P. Layzell, J.M. Brown, Chem. Eur. J. 5 (1999) 1320;
(d) D.A. Evans, G.C. Fu, B.A. Anderson, J. Am. Chem. Soc. 114 (1992) 6679;
(e) For reviews on catalyzed hydroboration, see
(f) K. Burgess, M.J. Ohlmeyer, Chem. Rev. 91 (1991) 1179;
(g) I. Beletskaya, A. Pelter, Tetrahedron 53 (1997) 4957–5026;
(h) A.M. Carroll, T.P. O'Sullivan, P.J. Guiry, Adv. Synth. Catal. 347 (2005) 609–631;
(i) C.M. Crudden, D. Edwards, Eur. J. Org. Chem. (2003) 4695–4712.

[12] (a) D.S. Matteson, Chem. Rev. 89 (1989) 1535;
(b) M.V. Rangaishenvi, B. Singaram, H.C. Brown, J. Org. Chem. 56 (1991) 3286.

[13] For asymmetric homologation with chiral 1,2-cyclohexanediol based boronate esters for the synthesis of fluorinated aryl ethanols, see: R.P. Singh, B. Twamley, L. Fabry-Asztalos, D.S. Matteson, J.M. Shreeve, J. Org. Chem. 65 (2000) 81.

[14] H.C. Brown, G.W. Kramer, A.B. Levy, M.M. Midland, Organic Synthesis via Boranes, Wiley–Interscience, New York, 1975 (Chapter 9).