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Electronic Supplementary Information

Enantioselective Synthesis of α-Phenyl- and α-(Dimethylphenylsilyl)-alkylboronic Esters by Ligand Mediated Stereoinductive Reagent-Controlled Homologation Using Configurationally Labile Carbenoids

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1. Experimental Procedures

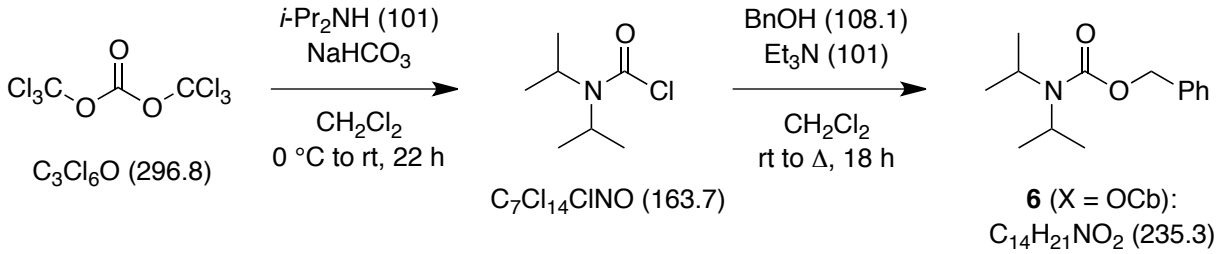
General Experimental and Analytical Techniques

All reactions requiring anhydrous/anaerobic conditions were conducted in flame-dried glassware under an atmosphere of Ar gas. Anhydrous THF and toluene were dispensed from a commercially available solvent purification system employing activated Al_2O_3 drying columns.[S1] Anhydrous cumene (*i*-PrPh) was obtained by distillation from CaH_2 under Ar. Preparative chromatographic separations were performed on silica gel 60 (35-75 μm) and reactions followed by TLC analysis using silica gel 60 plates (2-25 μm) with fluorescent indicator (254 nm) and visualized with UV or phosphomolybdic acid. All commercially available reagents were used as received unless otherwise noted. Melting points were determined from open capillary tubes on a melting point apparatus and are uncorrected. Infra-red (IR) spectra were recorded in Fourier transform mode using KBr disks for solids, while oils were supported between NaCl plates ("neat"). ^{1}H and ^{13}C NMR spectra were recorded in Fourier transform mode at the field strength specified and from the indicated deuterated solvents in standard 5 mm diameter tubes. Chemical shift in ppm is quoted relative to residual

S1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs and R. K. Rosen *Organometallics*, 1996, **15**, 1518.

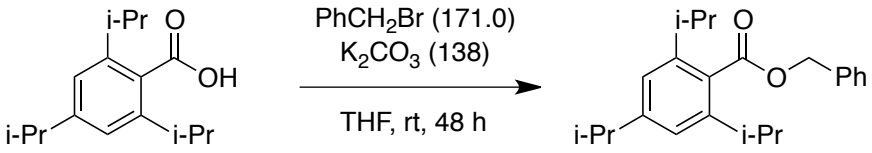
solvent signals calibrated as follows: $CDCl_3$ δ_H ($CHCl_3$) = 7.26 ppm, δ_C = 77.2 ppm; $(CD_3)_2SO$ δ_H (CD_3SOCHD_2) = 2.50 ppm, δ_C = 39.5 ppm. Multiplicities in the ^1H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Numbers in parentheses following carbon atom chemical shifts refer to the number of attached hydrogen atoms as revealed by the DEPT spectral editing technique. Low (MS) and high resolution (HRMS) mass spectra were obtained using either electron impact (EI) or electrospray (ES) ionization techniques. Ion mass/charge (*m/z*) ratios are reported as values in atomic mass units.

i-StReCH with Benzylic Carbenoids ***7*** *(Table 1 & Figure 2)*



***O*-Benzyl-*N,N*-diisopropylcarbamate (6, X = OCb).** Preparation of carbamoyl chloride: A cooled (0 °C) solution of diisopropylamine (2.92 mL, d = 0.717, 2.09 g, 20.7 mmol) in CH_2Cl_2 (44 mL) was added via cannula during 20 min to a stirred suspension of triphosgene (2.05 g, 6.91 mmol) and $NaHCO_3$ (1.92 g, 22.9 mmol) in CH_2Cl_2 (12 mL, in a 250 mL RB flask) at 0 °C under Ar. The resulting mixture was allowed to warm to rt and stirred for 22 h. After this time the mixture was filtered to remove inorganic solids and concentrated *in vacuo* to yield crude *N,N*-diisopropylcarbamoyl chloride (2.90 g, ≤17.7 mmol, ≤86%) as a colorless solid which was used immediately in the next step. Preparation of carbamate: A stirred solution of the crude carbamoyl chloride (2.90 g, ≤17.7 mmol) in CH_2Cl_2 (37 mL) at rt under Ar was treated with benzyl alcohol (1.93 mL, d = 1.045, 2.02 g, 18.7 mmol) followed by triethylamine (2.72 mL, d = 0.726, 1.97 g, 19.6 mmol). The resulting mixture was heated to reflux and stirred for 18 h. After this time, the mixture was cooled to rt and the solvent removed *in vacuo*. The residue was purified by column chromatography (SiO_2, eluting with 5-7% EtOAc in hexanes) to afford the title carbamate **6** (0.947 g, 4.02 mmol, 19%, 2 steps) as a colorless oil: IR (neat) 2970, 1693, 1440, 1369, 1306, 1290, 1059, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.38-7.30 (5H, s), 5.14 (2H, s), 4.12-3.76 (2H, br m), 1.21 (12H, d, *J* = 6.8 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.7 (0), 137.3 (0), 128.6 (2C, 1), 128.1 (2C, 1), 127.9 (1), 66.7 (2), 45.9 (1, br s), 21.2 (3, br s) ppm. ^1H and ^{13}C NMR spectral data are in agreement with those previously reported by Yus et al.[S2]

S2. E. Alonso, D. Guijarro, P. Martínez, D. J. Ramón and M. Yus *Tetrahedron*, 1999, **55**, 11027.

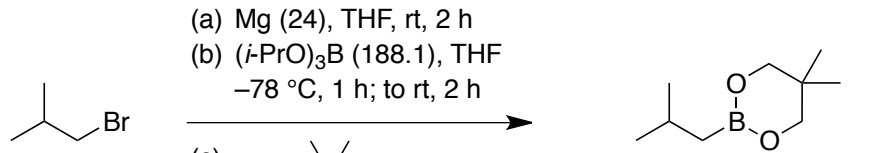


$C_{16}H_{24}O_2$ (248.4)

6 (X = OTIB): $C_{23}H_{30}O_2$ (338.5)

Benzyl 2,4,6-Triisopropylbenzoate (6, X = OTIB): To a stirred solution of 2,4,6-triisopropyl-benzoic acid (2.48 g, 10.0 mmol) in THF (20 mL) was added K_2CO_3 (2.07 g, 15.0 mmol) followed by benzyl bromide (1.78 mL, d = 1.438, 2.56 g, 15.0 mmol). The resulting suspension was stirred at rt for 48 hours and then it was partitioned between EtOAc (15 mL) and H_2O (10 mL). The layers were separated and the aqueous phase was extracted with EtOAc (2 x 15 mL). The combined organic phases were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, eluting with 2%-3% EtOAc in hexanes) to yield ester **6** (3.12 g, 9.22 mmol, 92%) as a colorless oil: IR (neat) 2962, 1728, 1607, 1461, 1250, 1067, 877, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.44 (2H, br d, *J* = 6.5 Hz), 7.40-7.32 (3H, m), 6.99 (2H, s), 5.35 (2H, s), 2.88 (1H, septet, *J* = 6.9 Hz), 2.81 (2H, septet, *J* = 6.8 Hz), 1.23 (6H, d, *J* = 6.9 Hz), 1.19 (12H, d, *J* = 6.8 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.8 (0), 150.4 (0), 145.1 (2C, 0), 135.8 (0), 130.4 (0), 129.0 (2C, 1), 128.7 (2C, 1), 128.5 (1), 121.0 (2C, 1), 67.0 (2), 34.6 (1), 31.6 (2C, 1), 24.3 (4C, 3), 24.1 (2C, 3) ppm. IR and ^1H spectral data are in agreement with those previously reported by Beak et al.[S3]

Experimental details and spectral data for neopentyl glycol boronic esters $RB[OCH_2(CMe_2)CH_2O]$ where R = $Ph(CH_2)_2$ (**9**), *n*-Bu, and *c*-C_6H_{11} (respective precursors for products **10**, **11**, and **13**) were previously disclosed in an earlier report.[S4] Details for preparation of the other six neopentyl glycol boronic ester substrates required to access the products shown in Figure 2 now follow.



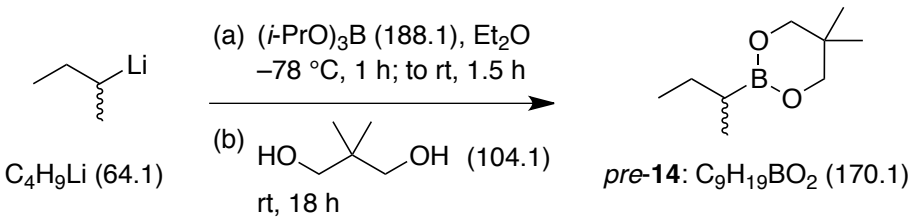
C_4H_9B (137.0)

pre-**12**: $C_9H_{19}BO_2$ (170.1)

2-Isobutyl-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-**12**)**:** Neat isobutyl bromide (1.08 mL, d = 1.27, 1.37 g, 10.0 mmol) was added dropwise during 5 min to a vigorously stirred suspension of mechanically activated magnesium turnings (250 mg, 10.4 mmol) in anhydrous THF (20 mL) at rt

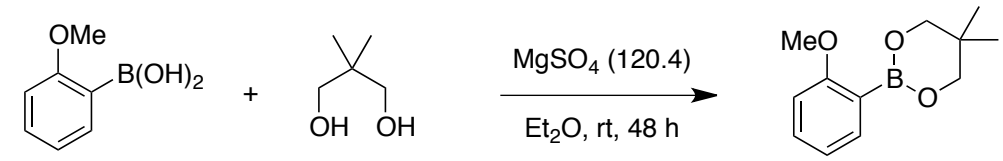
S3. P. Beak and L. G. Carter *J. Org. Chem.*, 1981, **46**, 2363.
S4. P. R. Blakemore, S. P. Marsden and H. W. Vater *Org. Lett.*, 2006, **8**, 773.

under Ar. The resulting mixture was stirred for 2 h at rt and then cooled to –78 °C and treated dropwise with neat triisopropylborate (1.91 mL, d = 0.818, 1.56 g, 8.31 mmol) during 10 min. The mixture was stirred for a further 1 h at –78 °C then allowed to warm to rt during 3 h. After this time, neopentyl glycol (864 mg, 8.30 mmol) was added in one portion and the reaction mixture allowed to stir for 16 h at rt. The mixture was then diluted with Et_2O (50 mL) and washed successively with sat. aq. NH_4Cl (30 mL) and H_2O (2x30 mL), dried (Na_2SO_4), and then concentrated *in vacuo*. The residue was distilled *in vacuo* using a kugelrohr apparatus to afford the title boronate *pre*-**12** (230 mg, 1.35 mmol, 16%) as a colorless oil: IR (neat) 2953, 1477, 1414, 1381, 1252, 1155, 912 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.59 (4H, s), 1.82 (1H, nonet, *J* = 6.7 Hz), 0.96 (6H, s), 0.91 (6H, d, *J* = 6.6 Hz), 0.66 (2H, d, *J* = 7.1 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 72.1 (2C, 2), 31.8 (0), 25.6 (3), 25.5 (1), 24.9 (3), 22.1 (2C, 3) ppm (*i*-Pr<u>C</u>H_2Bneo not clearly observed). ^1H and ^{13}C NMR spectral data in agreement with those previously reported.[S5]



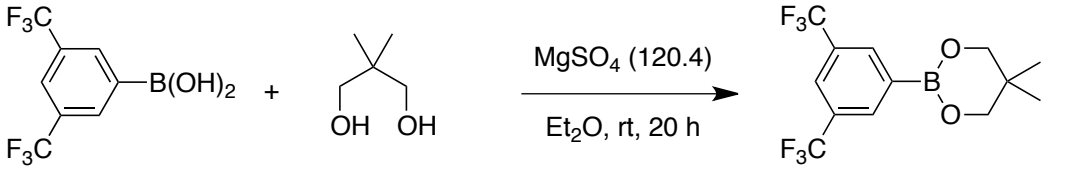
(±)-2-*sec*-Butyl-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-14): A freshly titrated commercial solution of *sec*-butyllithium (6.33 mL, 1.58 M in cyclohexane, 10.0 mmol) was added to anhydrous Et_2O (20 mL) at –78 °C under Ar. To the resulting cold ethereal solution of *s*-BuLi was added neat triisopropylborate (1.80 mL, d = 0.818, 1.47 g, 7.81 mmol) during 60 min. The mixture was allowed to warm to rt during 1.5 h, treated with neopentyl glycol (832 mg, 7.99 mmol) in one portion and then allowed to stir for 18 h at rt. The mixture was then diluted with Et_2O (50 mL) and washed successively with sat. aq. NH_4Cl (30 mL) and H_2O (2x30 mL), dried (Na_2SO_4), and then concentrated *in vacuo*. The residue was distilled *in vacuo* using a kugelrohr apparatus to afford the title boronate *pre*-**14** (620 mg, 3.64 mmol, 47%) as a colorless oil: IR (neat) 2960, 1477, 1414, 1350, 1253, 1195, 1151, 1015 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 3.59 (4H, s), 1.45 (1H, d of quintet, *J* = 13.3, 7.1 Hz), 1.27 (1H, d of quintet, *J* = 13.4, 6.2 Hz), 0.95 (6H, s), 0.93 (3H, d, *J* = 7.2 Hz), 0.89 (3H, t, *J* = 7.4 Hz), 0.85-0.78 (1H, m) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 72.1 (2C, 2), 31.8 (0), 26.4 (2), 22.0 (2C, 3), 15.6 (3), 13.7 (3) ppm (EtMe<u>C</u>HBneo not clearly observed).

S5. G. L. Heise and M. Myslinska US Patent Application US 2012/0289733 A1.



$C_7H_9BO_3$ (152.0) $C_5H_{12}O_2$ (104.1) *pre*-**15**: $C_{12}H_{17}BO_3$ (220.1)

2-(2-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-15): A 25 mL RB flask was charged with a stir bar and $MgSO_4$ (241 mg, 2.00 mmol) and flushed with Ar. The flask was briefly licked with a flame to thoroughly dry the $MgSO_4$ and then the anhydrous powder allowed to cool to rt under Ar. The flask was then further charged with 2-methoxyphenylboronic acid (304 mg, 2.00 mmol) and neopentyl glycol (208 mg, 2.00 mmol) and resealed. Anhydrous Et_2O (3 mL) was added and the resulting suspension stirred for 48 h at rt. After this time, the mixture was filtered through a celite pad and the residue washed with Et_2O (3x2 mL). The filtrate and combined washings were concentrated *in vacuo* to afford the title boronate *pre*-**15** (412 mg, 1.87 mmol) as a colorless solid: IR (neat) 2961, 1599, 1576, 1487, 1319, 1269, 1244, 1136 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.65 (1H, dd, *J* = 7.2, 1.1 Hz), 7.36 (1H, td, *J* = 6.8, 1.6 Hz), 6.94 (1H, t, *J* = 7.3 Hz), 6.87 (1H, d, *J* = 8.3 Hz), 3.84 (3H, s), 3.80 (4H, s), 1.04 (6H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.8 (0), 135.9 (1), 131.8 (1), 120.4 (1), 110.6 (1), 72.7 (2C, 2), 55.9 (3), 31.9 (0), 22.1 (2C, 3) ppm (CBneo not clearly observed). ^1H and ^{13}C NMR spectral data in agreement with those previously reported.[S6]

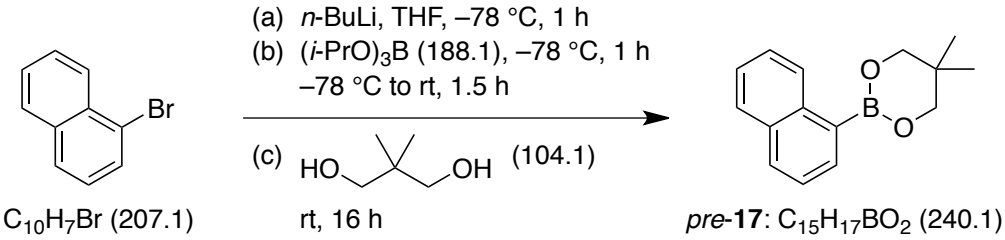


$C_8H_5BF_6O_2$ (257.9) $C_5H_{12}O_2$ (104.1) *pre*-**16**: $C_{13}H_{13}BF_6O_2$ (326.0)

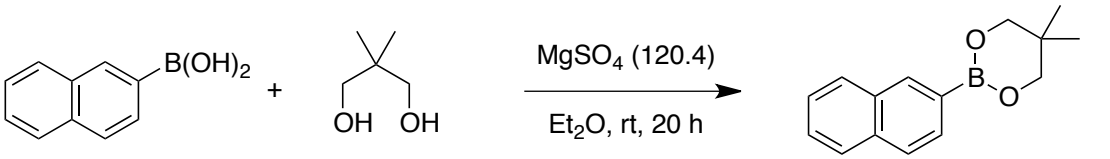
2-[3,5-Bis(trifluoromethyl)phenyl]-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-16): Prepared by analogy to *pre*-**15** above from 3,5-bis(trifluoromethyl)phenylboronic acid (258 mg, 1.00 mmol) to afford the title boronate *pre*-**16** (326 mg, 1.00 mmol, 100%) as a colorless solid: IR (neat) 2967, 1618, 1483, 1277, 1168, 1126, 987, 903 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.24 (2H, s), 7.91 (1H, s), 3.81 (4H, s), 1.04 (6H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 134.0 (2C, 1, q, J^3_{CF} = 2.3 Hz), 130.8 (2C, 0, q, J^2_{CF} = 33.0 Hz), 125.1 (1, septet, J^3_{CF} = 3.8 Hz), 124.7 (2C, 0, q, J^1_{CF} = 272.5 Hz), 72.7 (2C, 2), 32.2 (0), 22.0 (2C, 3) ppm (CBneo not clearly observed).

2-(1-Naphthyl)-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-17): A stirred solution of 1-bromo-naphthalene (414 mg, 2.00 mmol) in anhydrous THF (5 mL) at –78 °C under Ar was treated

S6. D. A. Wilson, C. J. Wilson, C. Moldoveanu, A. Resmerita, P. Corcoran, L. M. Hoang, B. M. Rosen and V. Percec *J. Am. Chem. Soc.*, 2010, **132**, 1800.

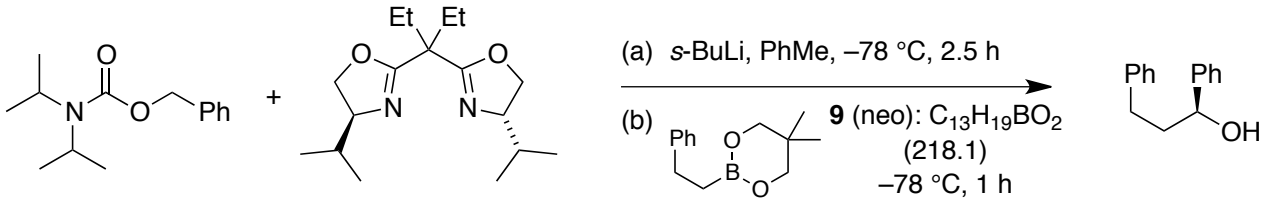


dropwise with *n*-BuLi (1.26 mL, 1.58 M in hexanes, 1.99 mmol) during 10 min. The resulting mixture was stirred at –78 °C for 1 h and then treated with dropwise with neat triisopropylborate (0.46 mL, d = 0.818, 376 mg, 2.00 mmol) during 10 min. The mixture was stirred for a further 1 h at –78 °C then allowed to warm to –15 °C during 3 h. After this time, a solution of neopentyl glycol (208 mg, 2.00 mmol) in anhydrous THF (1.0 mL) was added in one portion and the reaction mixture allowed to stir for 16 h at rt. The mixture was then concentrated *in vacuo* and the residue purified by column chromatography (SiO_2, eluting with 2-4% EtOAc in hexanes) to afford the title boronate *pre*-**17** (348 mg, 1.45 mmol, 72%) as a colorless solid: IR (neat) 2961, 1507, 1476, 1303, 1254, 1145, 804, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.76 (1H, d, *J* = 8.33 Hz), 8.04 (1H, d, *J* = 6.8 Hz), 7.90 (1H, d, *J* = 8.1 Hz), 7.83 (1H, d, *J* = 8.1 Hz), 7.54-7.43 (3H, m), 3.90 (4H, s), 1.10 (6H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 136.9 (0), 134.5 (1), 133.6 (0), 131.1 (1), 128.6 (1), 128.5 (1), 126.2 (1), 125.4 (1), 125.2 (1), 72.7 (2C, 2), 32.0 (0), 22.1 (2C, 3) ppm (CBneo not clearly observed). ^1H and ^{13}C NMR spectral data in agreement with those previously reported.[S7]



2-(2-Naphthyl)-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-18): Prepared by analogy to *pre*-**15** above from 2-naphthylboronic acid (345 mg, 2.01 mmol) to afford the title boronate *pre*-**18** (466 mg, 1.94 mmol, 97%) as a colorless solid: IR (neat) 2957, 1481, 1416, 1313, 1251, 1136, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (1H, s), 7.92-7.80 (4H, m), 7.54-7.43 (2H, m), 3.84 (4H, s), 1.07 (6H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.2 (1), 135.1 (0), 133.1 (0), 130.1 (1), 128.9 (1), 127.8 (1), 127.0 (1), 126.8 (1), 125.8 (1), 72.6 (2C, 2), 32.1 (0), 22.1 (2C, 3) ppm (CBneo not clearly observed). ^1H and ^{13}C NMR spectral data in agreement with those previously reported.[S8]

S7. B. M. Rosen, C. Huang and V. Percec *Org. Lett.*, 2008, **10**, 2597.
S8. M. Tobisu, H. Kinuta, Y. Kita, E. Rémond and N. Chatani *J. Am. Chem. Soc.*, 2012, **134**, 115.



6 (X = OCb): $C_{14}H_{21}NO_2$ (235.3)

8 (R^1/R^2 = *i*-Pr/Et): $C_{17}H_{30}N_2O_2$ (294.4)

10: $C_{15}H_{16}O$ (212.3)

Representative procedure for ligand mediated i-StReCH to α-phenylalkylboronates (Table 1, Entry 9): (–)-(*S*)-1,3-Diphenyl-propan-1-ol (10): A stirred solution of *O*-benzyl-*N*,*N*-diisopropyl-carbamate (**6**, X = OCb, 26 mg, 0.110 mmol) and (*S*,*S*)-bisoxazoline ligand **8** (R^1/R^2 = *i*-Pr/Et, 37 mg, 0.126 mmol)[S9] in anhydrous toluene (0.8 mL) at –78 °C under Ar was treated with *s*-BuLi (0.10 mL, 1.20 M in cyclohexane, 0.12 mmol). After stirring at –78 °C for 2.5 h, a solution of neopentyl glycol boronate **9** (22 mg, 0.101 mmol) in anhydrous toluene (0.2 mL) was added dropwise during 3 min. The resulting mixture was stirred at –78 °C for 1 h and then a freshly prepared ethereal solution of $MgBr_2$•OEt_2 (0.30 mmol in ≤ 1.0 mL Et_2O, see below*) was added dropwise during 3 min. The reaction mixture was allowed to stir for a further 30 min at –78 °C, allowed to warm to rt during 3 h, and then stirred for 16 h at rt. After this time, the reaction mixture was cooled to 0 °C and treated with 10 wt.% aq. NaOH (0.2 mL) followed by 30 wt.% aq. H_2O_2 (0.08 mL). The biphasic mixture was then allowed to warm to rt and stirred vigorously for 2 h. EtOAc (5 mL) and H_2O (3 mL) were added and the layers shaken and separated. The aqueous phase was extracted with EtOAc (3x5 mL) and the combind organic phases washed with brine (5 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, eluting with 6-12% EtOAc in hexanes) to afford the title carbinol **10** (13 mg, 0.061 mmol, 61%) as a colorless oil: $[\alpha]_D^{20}$ = –22.9 (c = 1.30, $CHCl_3$, at 83% ee); IR (neat) 3370, 3027, 2924, 1603, 1495, 1454, 1059, 1029, 914 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (4H, m), 7.31-7.26 (3H, m), 7.22-7.18 (3H, m), 4.70 (1H, t, *J* = 6.0 Hz), 2.77 (1H, ddd, *J* = 14.0, 9.8, 5.9 Hz), 2.68 (1H, ddd, *J* = 13.9, 9.3, 6.6 Hz), 2.20-1.99 (2H, m), 1.88 (1H, br s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.7 (0), 142.0 (0), 128.7 (2C, 1), 128.62 (2C, 1), 128.57 (2C, 1), 127.8 (1), 126.1 (2C, 1), 126.0 (1), 74.1 (1), 40.6 (2), 32.2 (2) ppm. ^1H and ^{13}C NMR spectral data in agreement with those previously reported.[S10]

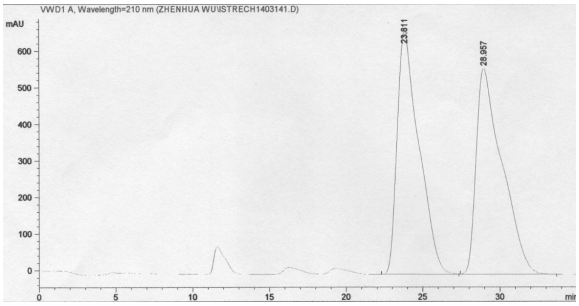
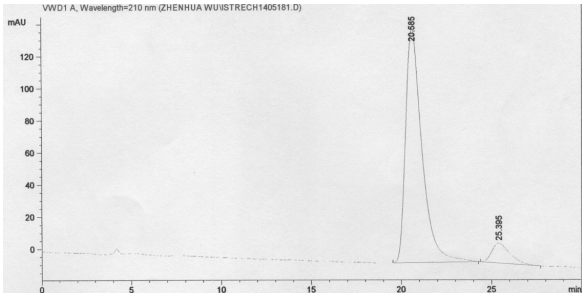
*Preparation of ethereal solution of $MgBr_2$•OEt_2: A stirred suspension of Mg ribbon (12 mg, 0.50 mmol) in anhydrous Et_2O (1 mL) in a 5 mL pear-shaped flask under Ar, was treated with 1,2-

S9. S. E. Denmark, N. Nakajima, O. J.-C. Nicaise, A.-M. Faucher and J. P. Edwards *J. Org. Chem.*, 1995, **60**, 4884.

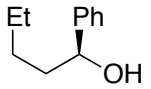
S10. Y. Liu, C.-S. Da, S.-L. Yu, X.-G. Yin. J.-R. Wang, X.-Y. Fan, W.-P. Li and R. Wang *J. Org. Chem.*, 2010, **75**, 6869.

dibromoethane (26 μL, d = 2.18, 56 mg, 0.30 mmol). The resulting mixture was stirred at 30 °C for 3 h, then cooled to rt before its addition to the i-StReCH reaction as described above.

Chiral stationary phase (CSP) HPLC analysis of (±)-**10**, obtained by $NaBH_4$ reduction of the corresponding ketone, performed with a Daicel Chiralcel® OD column (4.6 mm ID x 250 mm), eluting with 5% *i*-PrOH in hexanes at 1.0 mL min^{-1} and monitored by UV at 210 nm, showed resolved peaks: $t_{ret.}$ [(–)-(*S*)-**10**] = 23.8 min, $t_{ret.}$ [(+)-(*R*)-**10**] = 29.0 min. Analysis of the enantioenriched material prepared as described above via ligand mediated i-StReCH revealed an enantiomeric excess of 83% in favor of (–)-(*S*)-**10**. Absolute configuration established by correlation to literature data (optical rotation and CSP-HPLC) reported by Liu and coworkers.[S10]

(±)-**10**: left = 49.93%, right = 50.07%	(–)-(*S*)-**10** (83% ee): left = 91.4%, right = 8.6%
	

(–)-(*S*)-1-Phenylpentan-1-ol (11): Prepared from carbamate **6** (X = OCb, 26 mg, 0.110 mmol), (*S,S*)-bisoxazoline ligand **8** (R^1/R^2 = *i*-Pr/Et, 37 mg, 0.126 mmol),[S9] and 2-butyl-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-**11**, 17.0 mg, 0.100 mmol)[S4] according to the representative procedure shown above which yielded the title carbinol **11** (6.1 mg, 0.037 mmol, 37%) as a colorless oil: $[\alpha]_D^{20}$ = –8.8 (c = 0.16, $CHCl_3$, at 75% ee); IR (neat) 3415, 2925, 1661, 1456, 1378, 1278, 1136 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (4H, m), 7.30-7.26 (1H, m), 4.66 (1H, dd, *J* = 7.2, 6.0 Hz), 1.86-1.67 (3H, m), 1.45-1.22 (4H, m), 0.89 (3H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.1 (0), 128.6 (2C, 1), 127.7 (1), 126.1 (2C, 1), 74.9 (1), 39.0 (2), 28.2 (2), 22.8 (2), 14.2 (3) ppm. ^1H and ^{13}C NMR spectral data in agreement with those previously reported.[S11]

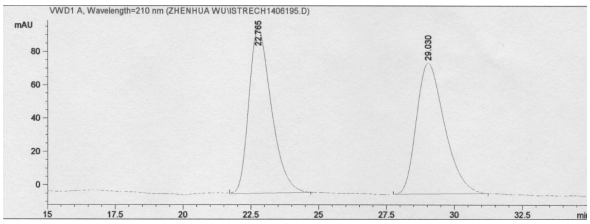
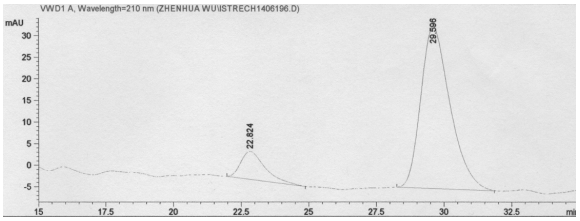


11: $C_{11}H_{16}O$ (164.24)

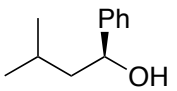
Chiral stationary phase (CSP) HPLC analysis of (±)-**11**, obtained by $NaBH_4$ reduction of the corresponding ketone, performed with a Daicel Chiralcel® OD column (4.6 mm ID x 250 mm), eluting with 0.5% *i*-PrOH in hexanes at 1.0 mL min^{-1} and monitored by UV at 210 nm, showed

S11. K.-H. Wu, S. Zhou, C.-A. Chen, M.-C. Yang, R.-T. Chiang, C.-R. Chen and H.-M. Gau *Chem. Commun.*, 2011, **47**, 11668.

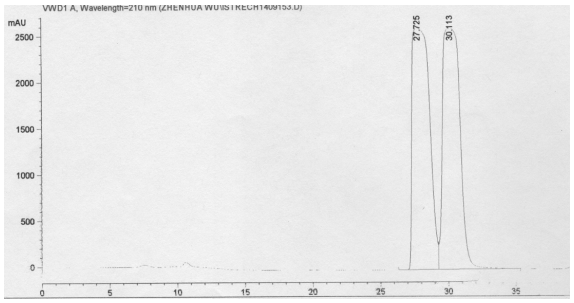
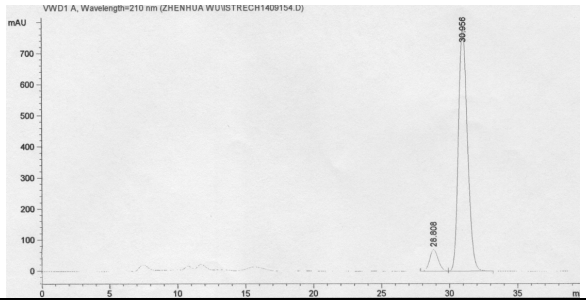
resolved peaks: $t_{ret.}$ [(+)-(*R*)-**11**] = 22.8 min, $t_{ret.}$ [(–)-(*S*)-**11**] = 29.0 min. Analysis of the enantioenriched material prepared as described above via ligand mediated i-StReCH revealed an enantiomeric excess of 75% in favor of (–)-(*S*)-**11**. Absolute configuration established by correlation to literature data (CSP-HPLC under same conditions) reported by Wu and coworkers.[S11]

(±)-**11**: left = 50.27%, right = 49.73%	(–)-(*S*)-**10** (75% ee): left = 12.55%, right = 87.45%
	

(–)-(*S*)-1-Phenyl-3-methylbutan-1-ol (12): Prepared from carbamate **6** (X = OCb, 26 mg, 0.110 mmol), (*S,S*)-bisoxazoline ligand **8** (R^1/R^2 = *i*-Pr/Et, 37 mg, 0.126 mmol),[S9] and 2-isobutyl-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-**12**, 17.0 mg, 0.100 mmol) according to the representative procedure shown above which yielded the title carbinol **12** (9.1 mg, 0.055 mmol, 55%) as a waxy colorless solid: $[\alpha]_D^{20}$ = –36.0 (c = 0.89, $CHCl_3$, at 84% ee); IR (neat) 3361, 2956, 1658, 1467, 1454, 1367, 1201, 1057, 912 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (4H, m), 7.30-7.25 (1H, m), 4.75 (1H, dd, *J* = 7.8, 5.2 Hz), 1.80-1.66 (3H, m), 1.56-1.49 (1H, m), 0.96 (3H, d, *J* = 6.4 Hz), 0.95 (3H, d, *J* = 6.4 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 145.4 (0), 128.7 (2C, 1), 127.7 (1), 126.0 (2C, 1), 73.0 (1), 48.6 (2), 25.0 (1), 23.3 (3), 22.4 (3) ppm. ^1H and ^{13}C NMR spectral data in agreement with those previously reported.[S12]



12: $C_{11}H_{16}O$ (164.24)

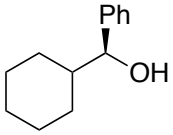
(±)-**12**: left = 49.85%, right = 50.15%	(–)-(*S*)-**10** (84% ee): left = 7.78%, right = 92.22%
	

Chiral stationary phase (CSP) HPLC analysis of (±)-**12**, obtained by $NaBH_4$ reduction of the corresponding ketone, performed with a Daicel Chiralcel® OD-H column (4.6 mm ID x 250 mm),

S12. E. Fernández-Mateos, B. Maciá, D. J. Ramón and M. Yus *Eur. J. Org. Chem.*, 2011, 6851.

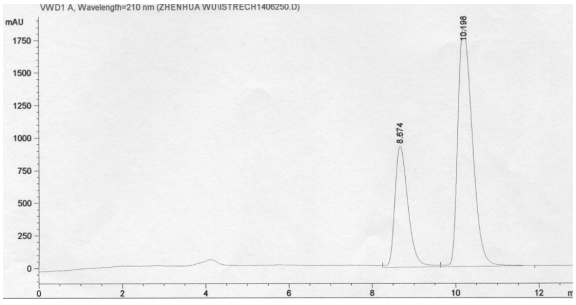
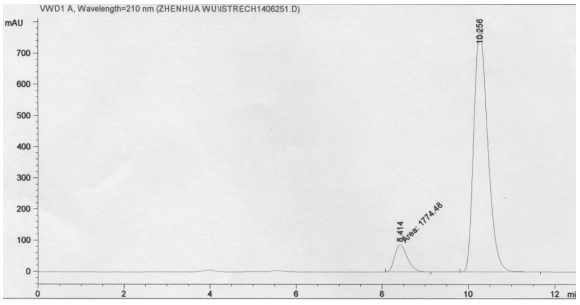
eluting with 1% *i*-PrOH in hexanes at 0.5 mL min^{-1} and monitored by UV at 210 nm, showed resolved peaks: $t_{ret.}$ [(+)-(*R*)-**12**] = 27.7 min, $t_{ret.}$ [(–)-(*S*)-**12**] = 30.1 min. Analysis of the enantioenriched material prepared as described above via ligand mediated i-StReCH revealed an enantiomeric excess of 84% in favor of (–)-(*S*)-**12**. Absolute configuration established by correlation to literature data (optical rotation) reported by Yus and coworkers.[S12]

(–)-(*S*)-Cyclohexyl(phenyl)methanol (13): Prepared from carbamate **6** (X = OCb, 26 mg, 0.110 mmol), (*S,S*)-bisoxazoline ligand **8** (R^1/R^2 = *i*-Pr/Et, 37 mg, 0.126 mmol),[S9] and 2-cyclohexyl-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-**13**, 20.0 mg, 0.102 mmol)[S4] according to the representative procedure shown above which yielded the title carbinol **13** (9.6 mg, 0.050 mmol, 50%) as a colorless solid: $[\alpha]_D^{20}$ = –26.9 (c = 0.95, $CHCl_3$, at 82% ee); IR (neat) 3416, 2917, 2851, 1493, 1450, 1324, 1011 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.20 (5H, m), 4.37 (1H, d, *J* = 7.2 Hz), 1.99 (1H, dm, *J* = 12.7 Hz), 1.81-1.73 (2H, m), 1.70-1.57 (2H, m), 1.37 (1H, dm, *J* = 12.8 Hz), 1.28-0.82 (6H, m) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.8 (0), 128.4 (2C, 1), 127.6 (1), 126.8 (2C, 1), 79.6 (1), 45.1 (1), 29.5 (2), 29.0 (2), 26.6 (2), 26.3 (2), 26.2 (2) ppm. ^1H and ^{13}C NMR spectral data in agreement with those previously reported.[S13]



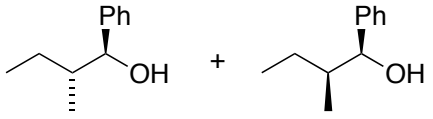
13: $C_{13}H_{18}O$ (190.3)

Chiral stationary phase (CSP) HPLC analysis of a scalemic sample of **13** of low ee, obtained by incomplete oxidation of (*S*)-**12** followed by $NaBH_4$ reduction of the product ketone/alcohol mixture, performed with a Daicel Chiralcel® AS-H column (4.6 mm ID x 250 mm), eluting with 1% *i*-PrOH in hexanes at 1.0 mL min^{-1} and monitored by UV at 210 nm, showed resolved peaks: $t_{ret.}$ [(+)-(*R*)-**13**] = 8.7 min, $t_{ret.}$ [(–)-(*S*)-**13**] = 10.2 min. Analysis of the enantioenriched material prepared as described above via ligand mediated i-StReCH revealed an enantiomeric excess of 82% in favor of (–)-(*S*)-**13**. Absolute configuration established by correlation to literature data (optical rotation and CSP-HPLC under same conditions) reported by Yus and coworkers.[S13]

Scalemic-**13**: left = 31.31%, right = 68.69%	(–)-(*S*)-**13** (82% ee): left = 9.14%, right = 90.86%
	

S13. E. Fernández-Mateos, B. Maciá and M. Yus *Eur. J. Org. Chem.*, 2012, 3732.

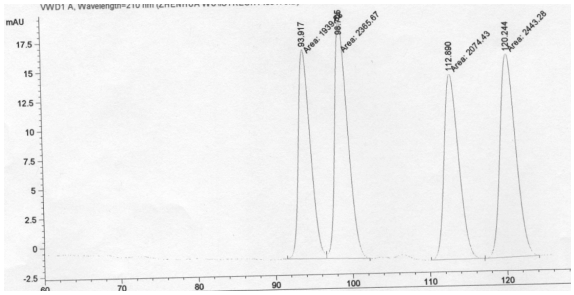
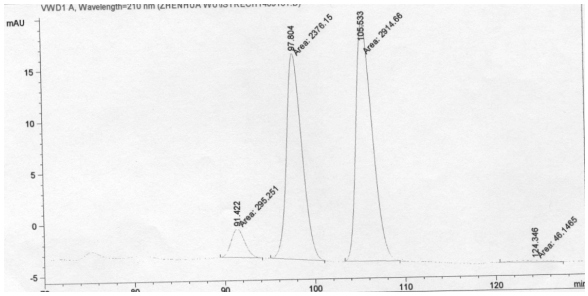
(1*S*,2*R*)-2-Methyl-1-phenylbutan-1-ol (*syn*-14) and (1*S*,2*S*)-2-methyl-1-phenylbutan-1-ol (*anti*-14): Prepared from carbamate **6** (X = OCb, 26 mg, 0.110 mmol), (*S*,*S*)-bisoxazoline ligand **8** (R^1/R^2 = *i*-Pr/Et, 37 mg, 0.126 mmol),[S9] and (±)-2-*sec*-butyl-5,5-dimethyl-1,3,2-dioxa-borinane (*pre*-**14**, 17.0 mg, 0.100 mmol) according to the representative procedure shown above which yielded a mixture of the title carbinols *syn*-**14** and *anti*-**14** (5.7 mg, 0.035 mmol, 35%; *syn*:*anti* = 51:49 as adjudged by ^{1}H NMR spectral analysis prior to chromatographic purification) as a colorless oil: IR (neat) 3401, 2961, 2927, 1493, 1454, 1379, 1276, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.20 (5H^{both}, m), 4.54 (1H^{syn}, d, *J* = 5.6 Hz), 4.45 (1H^{anti}, d, *J* = 6.9 Hz), 1.81-1.65 (2H^{both}, m), 1.45-1.05 (2H^{both}, m), 0.96-0.87 (6H^{both} + 3H^{syn}, m), 0.75 (3H^{anti}, d, *J* = 6.8 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.^{syn} (0), 143.8^{anti} (0), 128.4^{both} (2C, 1), 127.6^{anti} (1), 127.4^{syn} (1), 126.9^{anti} (2C, 1), 126.6^{syn} (2C, 1), 79.0^{anti} (1), 78.3^{syn} (1), 42.2^{syn} (1), 41.9^{anti} (1), 26.1^{syn} (2), 25.1^{anti} (2), 15.3^{anti} (3), 14.2^{syn} (3), 11.9^{syn} (3), 11.5^{anti} (3) ppm. ^{1}H and ^{13}C NMR spectral data in agreement with those previously reported for individual diastereoisomers.[S14]



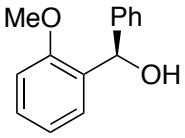
syn-**14**: $C_{11}H_{16}O$ (164.2) *anti*-**14**: $C_{11}H_{16}O$ (164.2)

note: absolute configuration not established for *syn*-**14** and *anti*-**14**, assignment indicated above made by analogy to i-StReCH reactions to **10**, **11**, **12**, and **13**

Chiral stationary phase (CSP) HPLC analysis of a sample of (±)-**14** with *syn*:*anti* = 56:44, obtained by addition of *s*-BuLi to benzaldehyde, performed with a Daicel Chiralcel® OD-H column (4.6 mm ID x 250 mm), eluting with 0.2% *i*-PrOH in hexanes at 1.0 mL min^{-1} and monitored by UV at 210 nm, showed resolved peaks (absolute configuration assignment tentative): $t_{ret.}$ [(1*R*,2*R*)-*anti*-**14**] = 93.9 min, $t_{ret.}$ [(1*S*,2*R*)-*syn*-**14**] = 98.7 min, [(1*S*,2*S*)-*anti*-**14**] = 112.9 min, $t_{ret.}$ [(1*R*,2*S*)-*syn*-**14**] = 120.2 min. Analysis of the enantioenriched material prepared as described above (and after column chromatography resulted in a change in sample dr to *syn*:*anti* = 43:57) via ligand mediated i-StReCH revealed an enantiomeric excess of 96% for *syn*-**14** and 82% for *anti*-**14**.

(±)-*syn*-**14** + (±)-*anti*-**14** (*syn*:*anti* = 56:44): (1-4 l-r) 1 = 21.99%, 2 = 26.81%, 3 = 23.51%, 4 = 27.69%	(1*S*,2*R*)-*syn*-**14** (96% ee) + (1*S*,2*S*)-*anti*-**14** (82% ee): 1 = 5.24%, 2 = 42.19%, 3 = 51.75, 4 = 0.82%
	

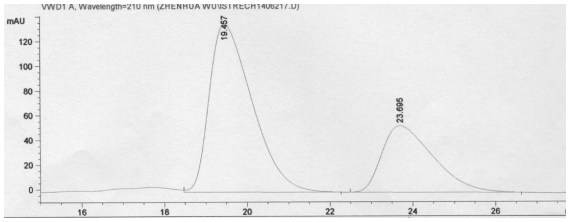
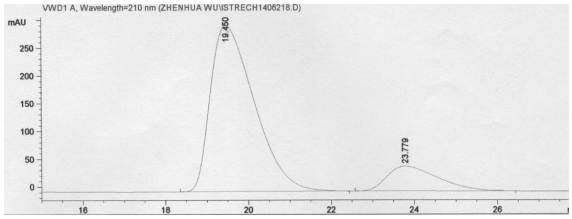
S14. M. A. Nichols, A. T. McPhail and E. M. Arnett *J. Am. Chem. Soc.*, 1991, **113**, 6222.

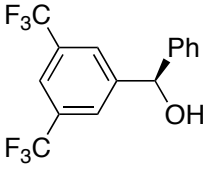


15: $C_{14}H_{14}O_2$ (214.3)

(+)-(*R*)-(2-Methoxyphenyl)phenylmethanol (15): Prepared from carbamate **6** (X = OCb, 26 mg, 0.110 mmol), (*S,S*)-bisoxazoline ligand **8** (R^1/R^2 = *i*-Pr/Et, 37 mg, 0.126 mmol),[S9] and 2-(2-meth-oxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-**15**, 22.0 mg, 0.100 mmol) according to the representative procedure shown above which yielded the title carbinol **15** (14.3 mg, 0.067 mmol, 67%) as a pale yellow solid: $[\alpha]_D^{20}$ = +22.8 (c = 1.27, $CHCl_3$, at 70% ee); IR (neat) 3401, 2924, 1601, 1490, 1463, 1243, 1027, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (2H, dm, *J* = 7.4 Hz), 7.33 (2H, tm, *J* = 7.8 Hz), 7.29-7.23 (3H, m), 6.95 (1H, tm, *J* = 7.4 Hz), 6.90 (1H, d, *J* = 8.3 Hz), 6.07 (1H, s), 3.82 (3H, s), 3.04 (1H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.9 (0), 143.4 (0), 132.1 (0), 128.9 (1), 128.3 (2C, 1), 128.0 (1), 127.3 (1), 126.7 (2C, 1), 121.0 (1), 110.9 (1), 72.5 (1), 55.6 (3) ppm. ^1H and ^{13}C NMR spectral data in agreement with those previously reported.[S11]

Chiral stationary phase (CSP) HPLC analysis of a scalemic sample of **15** of low ee, obtained by incomplete oxidation of (*R*)-**15** followed by $NaBH_4$ reduction of the product ketone/alcohol mixture, performed with a Daicel Chiralcel® OJ column (4.6 mm ID x 250 mm), eluting with 10% *i*-PrOH in hexanes at 1.0 mL min^{-1} and monitored by UV at 210 nm, showed resolved peaks: $t_{ret.}$ [(+)-(*R*)-**15**] = 19.5 min, $t_{ret.}$ [(–)-(*S*)-**15**] = 23.7 min. Analysis of the enantioenriched material prepared as described above via ligand mediated i-StReCH revealed an enantiomeric excess of 70% in favor of (+)-(*R*)-**15**. Absolute configuration established by correlation to literature data (CSP-HPLC under same conditions) reported by Gau and coworkers.[S11] In addition, (*S*)-**15** reported to be levorotatory [(–)-(*S*)-**15**, $[\alpha]_D^{20}$ = –33.6 (c = 1.00, $CHCl_3$, at 84%ee)] by Sato and coworkers.[S15]

Scalemic-**15**: left = 68.01%, right = 31.99%	(+)-(*R*)-**15** (70% ee): left = 85.23%, right = 14.77%
	



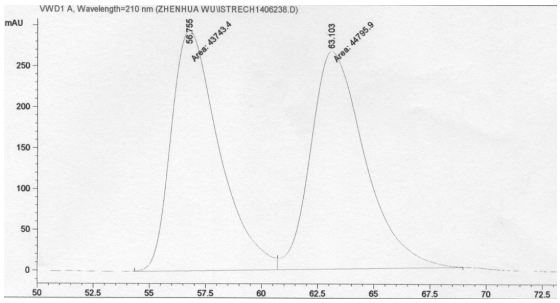
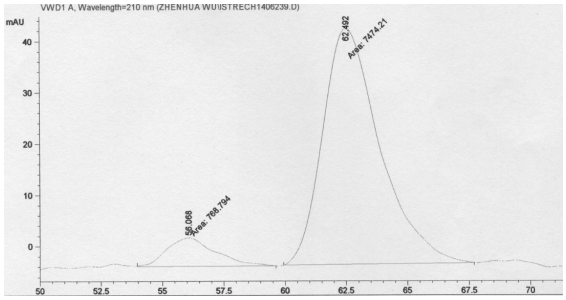
16: $C_{15}H_{10}F_6O$ (320.2)

(–)-(*R*)-(2-Methoxyphenyl)phenylmethanol (16): Prepared from carbamate **6** (X = OCb, 26 mg, 0.110 mmol), (*S,S*)-bisoxazoline ligand **8** (R^1/R^2 = *i*-Pr/Et, 37 mg, 0.126 mmol),[S9] and 2-[3,5-bis-(trifluoromethylphenyl]-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-**16**, 24.0 mg, 0.074 mmol) according to the representative procedure shown above which yielded the title carbinol **16** (8.0 mg, 0.025 mmol, 34%) as a colorless solid: $[\alpha]_D^{20}$ = –38.6 (c = 0.80, $CHCl_3$, at 81% ee); $[\alpha]_D^{20}$ = –

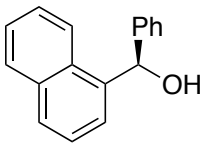
S15. I. Sato, Y. Toyota and N. Asakura *Chem. Commun.*, 2007, 2608.

27.8 (c = 0.45, MeOH, at 81% ee); IR (neat) 3325, 1625, 1379, 1172, 1127, 901 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (2H, s), 7.78 (1H, s), 7.42-7.33 (5H, m), 5.94 (1H, s), 2.44 (1H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.3 (0), 142.6 (0), 131.9 (2C, 0, q, J^2_{CF} = 33.3 Hz), 129.3 (2C, 1), 128.9 (1), 127.0 (2C, 1), 126.7 (2C, 1, q, J^3_{CF} = 3.8 Hz), 123.6 (2C, 0, q, J^1_{CF} = 272.7 Hz), 121.6 (1, septet, J^3_{CF} = 3.7 Hz), 75.5 (1) ppm. ^1H and ^{13}C NMR spectral data in agreement with those previously reported.[S16]

Chiral stationary phase (CSP) HPLC analysis of (±)-**16**, obtained by $NaBH_4$ reduction of the corresponding ketone, performed with a Daicel Chiralcel® OD column (4.6 mm ID x 250 mm), eluting with 0.5% *i*-PrOH in hexanes at 1.0 mL min^{-1} and monitored by UV at 210 nm, showed resolved peaks: $t_{ret.}$ [(+)-(*S*)-**16**] = 56.8 min, $t_{ret.}$ [(–)-(*R*)-**16**] = 63.1 min. Analysis of the enantioenriched material prepared as described above via ligand mediated i-StReCH revealed an enantiomeric excess of 81% in favor of (–)-(*R*)-**16**. Absolute configuration established by correlation to literature data (optical rotation) reported by Shea and coworkers.[S16]

(±)-**16**: left = 49.41%, right = 50.59%	(–)-(*R*)-**16** (81% ee): left = 9.33%, right = 90.67%
	

(+)-(*R*)-(1-Naphthyl)phenylmethanol (17): Prepared from carbamate **6** (X = OCb, 26 mg, 0.110 mmol), (*S,S*)-bisoxazoline ligand **8** (R^1/R^2 = *i*-Pr/Et, 37 mg, 0.126 mmol),[S9] and 2-(1-naphthyl)-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-**17**, 24.0 mg, 0.100 mmol) according to the representative procedure shown above which yielded the title carbinol **17** (17.0 mg, 0.073 mmol, 73%) as a pale yellow solid: $[\alpha]_D^{20}$ = +33.3 (c = 1.70, $CHCl_3$, at 74% ee); IR (neat) 3351, 3059, 2923, 1598, 1494, 1452, 1395, 1164 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (1H, dm, *J* = 8.8 Hz), 7.88 (1H, dm, *J* = 7.1 Hz), 7.83 (1H, d, *J* = 8.2 Hz), 7.65 (1H, d, *J* = 7.1 Hz), 7.52-7.40 (5H, m), 7.34 (2H, tm, *J* = 7.6 Hz), 7.29 (1H, dm, *J* = 7.1 Hz), 6.54 (1H, s), 2.30 (1H, br s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.3 (0), 139.0 (0), 134.1 (0), 130.9 (0), 128.9 (1), 128.71 (2C, 1), 128.67 (1),

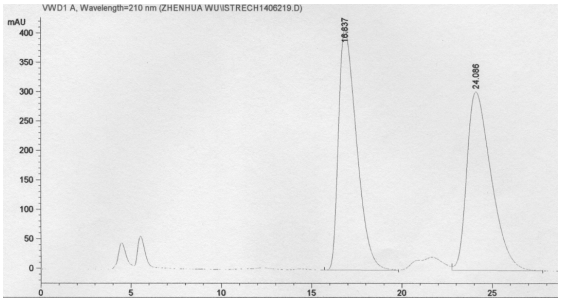
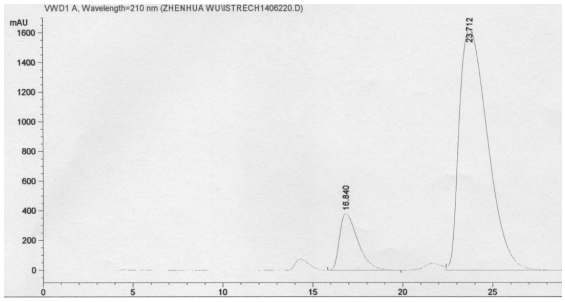


17: $C_{17}H_{14}O$ (234.3)

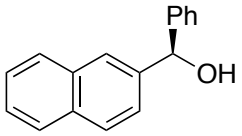
S16. Y. Bolshan, C.-y. Chen, J. R. Chilenski, F. Gosselin, D. J. Mathre, P. D. O'Shea, A. Roy, R. D. Tillyer *Org. Lett.*, 2004, **6**, 111.

127.9 (1), 127.2 (2C, 1), 126.3 (1), 125.8 (1), 125.5 (1), 124.8 (1), 124.2 (1), 73.8 (1) ppm. ^{1}H and ^{13}C NMR spectral data in agreement with those previously reported.[S11]

Chiral stationary phase (CSP) HPLC analysis of (±)-**17**, obtained by $NaBH_4$ reduction of the corresponding ketone, performed with a Daicel Chiralcel® OJ column (4.6 mm ID x 250 mm), eluting with 20% *i*-PrOH in hexanes at 1.0 mL min^{-1} and monitored by UV at 210 nm, showed resolved peaks: $t_{ret.}$ [(–)-(*S*)-**17**] = 16.8 min, $t_{ret.}$ [(+)-(*R*)-**17**] = 24.1 min. Analysis of the enantioenriched material prepared as described above via ligand mediated i-StReCH revealed an enantiomeric excess of 74% in favor of (+)-(*R*)-**17**. Absolute configuration established by correlation to literature data (CSP-HPLC under same conditions) reported by Gau and coworkers.[S11]

(±)-**17**: left = 49.91%, right = 50.09%	(+)-(*R*)-**17** (74% ee): left = 13.24%, right = 86.76%
	

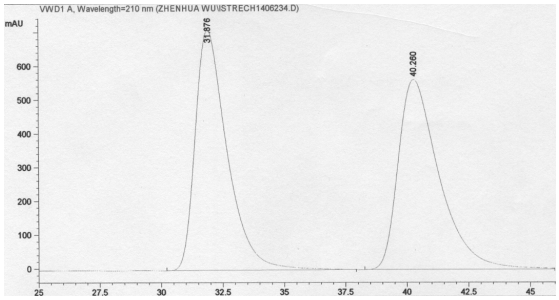
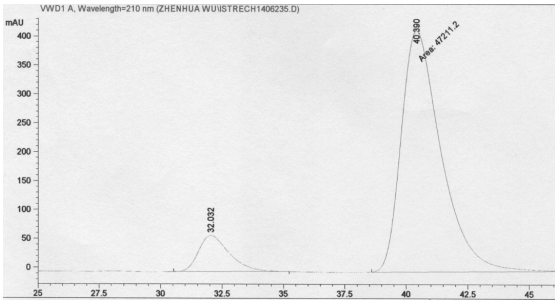
(–)-(*R*)-(2-Naphthyl)phenylmethanol (18): Prepared from carbamate **6** (X = OCb, 26 mg, 0.110 mmol), (*S,S*)-bisoxazoline ligand **8** (R^1/R^2 = *i*-Pr/Et, 37 mg, 0.126 mmol),[S9] and 2-(2-naphthyl)-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-**18**, 24.0 mg, 0.100 mmol) according to the representative procedure shown above which yielded the title carbinol **18** (14.5 mg, 0.062 mmol, 62%) as a colorless solid: $[\alpha]_D^{20}$ = –9.3 (c = 0.43, $CHCl_3$, at 79% ee); IR (neat) 3370, 2924, 1601, 1453, 1364, 1164, 1022, 813 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (1H, s), 7.86-7.78 (3H, m), 7.50-7.46 (3H, m), 7.45-7.41 (2H, m), 7.35 (2H, tm, *J* = 7.7 Hz), 7.28 (1H, dm, *J* = 7.2 Hz), 6.02 (1H, s), 1.70 (1H, br s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.8 (0), 141.3 (0), 133.4 (0), 133.1 (0), 128.8 (2C, 1), 128.5 (1), 128.3 (1), 127.88 (1), 127.86 (1), 126.9 (2C, 1), 126.4 (1), 126.2 (1), 125.2 (1), 124.9 (1), 76.6 (1) ppm. ^{1}H and ^{13}C NMR spectral data in agreement with those previously reported.[S11]



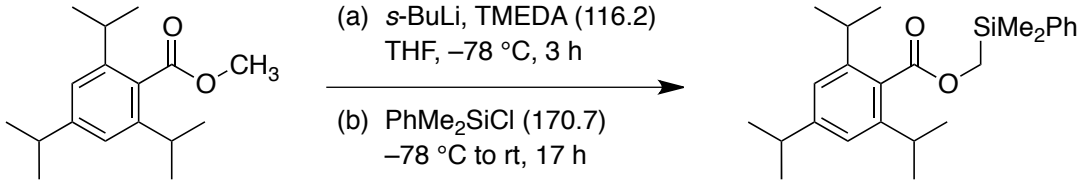
18: $C_{17}H_{14}O$ (234.3)

Chiral stationary phase (CSP) HPLC analysis of (±)-**18**, obtained by $NaBH_4$ reduction of the corresponding ketone, performed with a Daicel Chiralcel® OD column (4.6 mm ID x 250 mm), eluting with 5% *i*-PrOH in hexanes at 1.0 mL min^{-1} and monitored by UV at 210 nm, showed resolved peaks: $t_{ret.}$ [(+)-(*S*)-**18**] = 31.9 min, $t_{ret.}$ [(–)-(*R*)-**18**] = 40.3 min. Analysis of the

enantioenriched material prepared as described above via ligand mediated i-StReCH revealed an enantiomeric excess of 79% in favor of (–)-(*R*)-**18**. Absolute configuration established by correlation to literature data (CSP-HPLC under same conditions) reported by Gau and coworkers.[S11]

(±)-**18**: left = 49.77%, right = 51.23%	(–)-(*R*)-**18** (79% ee): left = 10.40%, right = 89.60%
	

*i-StReCH with Silylated Carbenoid **20** (Table 2 & Figure 3)*



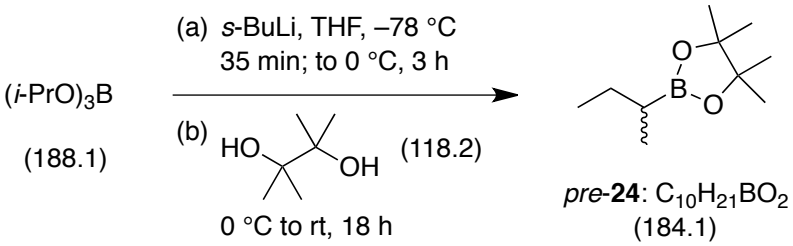
pre-**19**: $C_{17}H_{26}O_2$ (262.4) **19**: $C_{25}H_{36}O_2Si$ (396.6)

(Dimethylphenylsilyl)methyl 2,4,6-triisopropylbenzoate (19): A stirred solution of methyl 2,4,6-triisopropylbenzoate (*pre*-**19**, 2.50 g, 9.53 mmol)[S17] and tetramethylethylene diamine (TMEDA, 2.13 mL, d = 0.775, 1.65 g, 14.2 mmol) in anhydrous THF (38 mL) at –78 °C under Ar was treated dropwise with *s*-BuLi (10.8 mL, 1.11 M in cyclohexane, 12.0 mmol) during 13 min. The resulting solution was stirred for 2.75 h at –78 °C and then treated dropwise with neat chlorodimethylphenylsilane (1.99 mL, d = 1.03, 2.05 g, 12.0 mmol) during 6 min. The reaction mixture was allowed to warm to rt and stirred for 17 h before being poured into sat. aq. NH_4Cl (150 mL) at 0-5 °C. The mixture was partitioned between EtOAc (100 mL) and H_2O (100 mL) and the layers separated. The aqueous phase was extracted with EtOAc (2x100 mL) and the combined organic phases washed with brine (20 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, eluting with 5% EtOAc in hexanes) to yield 3.34 g of a mixture of **19**, *pre*-**19**, and bis(dimethylphenylsilyl)methyl 2,4,6-triisopropylbenzoate. The methyl ester impurity *pre*-**19** was removed by Kugelrohr distillation (oven temp. 135 °C, ca. 0.5 mmHg) to leave as a residue

S17. (a) P. Beak and B. G. McKinnie *J. Am. Chem. Soc.*, 1977, **99**, 5213; (b) P. Beak and L. G. Carter *J. Org. Chem.*, 1981, **46**, 2363.

the desired product **19** and a little of the disilylated material (2.53 g, 91 wt.% **19**, effectively 2.30 g, 5.80 mmol, 61%) as a colorless oil. This material is of sufficient purity for i-StReCH experiments but pure **19** can be obtained if desired by further Kugelrohr distillation (oven temp. 145 °C, ca. 0.5 mmHg). Data for pure **19**: IR (neat) 2962, 1726, 1606, 1462, 1428, 1293, 1249, 1235, 1104, 1075, 840 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57-7.54 (2H, m), 7.39-7.33 (3H, m), 6.98 (2H, s), 4.19 (2H, s), 2.87 (1H, septet, *J* = 6.9 Hz), 2.73 (2H, septet, *J* = 6.8 Hz), 1.24 (6H, d, *J* = 6.9 Hz), 1.17 (12H, d, *J* = 6.8 Hz), 0.39 (6H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.1 (0), 150.1 (0), 145.0 (2C, 0), 136.3 (0), 134.0 (2C, 1), 131.0 (0), 129.8 (1), 128.1 (3C, 1), 121.0 (1), 57.1 (2), 34.6 (1), 31.7 (2C, 1), 24.3 (4C, 3), 24.1 (2C, 3), –4.1 (2C, 3) ppm; MS (EI+) *m/z* 396 (2%, $M^{+\bullet}$), 381 (18), 353 (4), 319 (16), 231 (100), 213 (5); HRMS (EI+) *m/z* 396.2496 (calcd. for $C_{25}H_{36}O_2Si$: 396.2485).

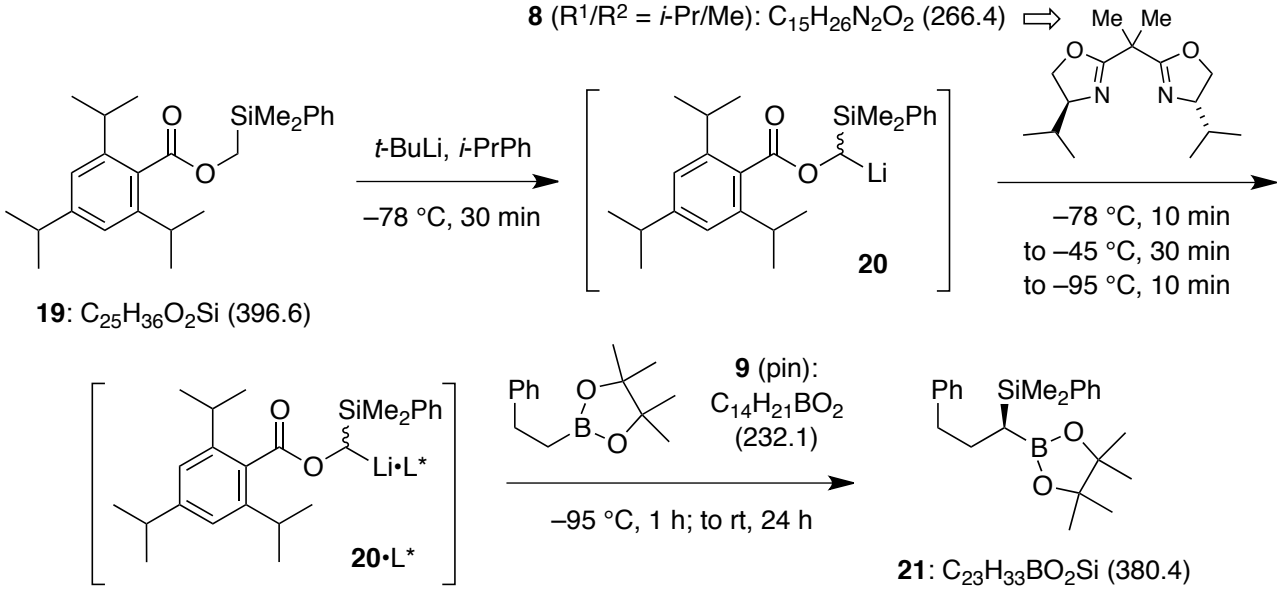
Experimental details and spectral data for pinacol boronic esters $RB[O(CMe_2)_2O]$ where R = $Ph(CH_2)_2$ (**9**) and *c*-C_6H_{11} (respective precursors for products **21** and **23**) were previously disclosed in an earlier report.[S18] Details for preparation of the remaing pinacol boronic ester precursor (*pre*-**24**) required to access the other product (**24**) successfully documented in Figure 3 now follows.



(±)-2-*sec*-Butyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*pre*-24): A stirred solution of triisopropyl borate (1.40 mL, d = 0.815, 1.14 g, 6.07 mmol) in anhydrous THF (24 mL) at –78 °C under Ar was treated dropwise with *s*-BuLi (7.31 mL, 0.829 M in cyclohexane, 6.06 mmol) during 35 min. The resulting mixture was allowed to warm to 0 °C during 3 h. After this time, neat powdered pinacol (716 mg, 6.06 mmol) was added in one portion and the mixture allowed to warm to rt and stirred for 18 h. Sat. aq. NH_4Cl (25 mL) was then added and the mixture was partitioned between Et_2O (50 mL) and H_2O (25 mL). The layers were separated and the aqueous phase extracted with Et_2O (2x50 mL). The combined organic phases were then washed with brine (10 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue (0.798 g) was purified by distillation (110-120 °C, 760 mmHg) in a Hinkman still to afford the title racemic boronate (±)-*pre*-**24** (436 mg, 2.37 mmol, 39%) as a colorless oil: IR (neat) 2979, 1462, 1387, 1314, 1210, 1145, 1010, 967, 852 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.51-1.40 (1H, m), 1.37-1.26 (1H, m), 1.24 (12H, s), 0.98-

S18. P. R. Blakemore and M. S. Burge *J. Am. Chem. Soc.*, 2007, **129**, 3068.

0.93 (4H, m), 0.90 (3H, t, J = 7.4 Hz) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ = 83.0 (2C, 0), 26.3 (2), 24.95 (4C, 3), 19.0 (1, br), 15.4 (3), 13.6 (3) ppm. ^{1}H spectral data in agreement with those previously reported.[S19]

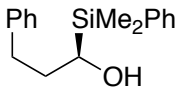


Representative procedure for ligand mediated i-StReCH to α-(dimethylphenylsilyl)alkylboronates (Table 2, Entry 6): (–)-(*S*)-2-[1-(Dimethylphenylsilyl)-3-phenylpropyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (21): A stirred solution of (dimethylphenylsilyl)methyl 2,4,6-triisopropylbenzoate (**19**, 179 mg, 0.451 mmol) in anhydrous cumene (1.3 mL) at –78 °C under Ar was treated dropwise with *t*-BuLi (0.190 mL, 1.57 M in pentane, 0.298 mmol) and allowed to stir for 30 min. The reaction mixture was then treated with (*S,S*)-bisoxazoline ligand **8** (R^1/R^2 = *i*-Pr/Me, 80 mg, 0.300 mmol)[S20] in anhydrous cumene (0.40 mL) and the mixture incubated for 10 min at –78 °C. After this time, the reaction vessel was transferred to another cold bath held at –45 °C, stirred for 30 min, then transferred to a third cold bath held at –95 °C and stirred for an additional 10 min. A solution of *B*-phenethyl pinacol boronate **9** (58.0 mg, 0.250 mmol) in anhydrous cumene (0.40 mL) was then added dropwise during 3 min and the mixture allowed to stir for a further 1 h at –95 °C before the cold bath was removed and the vessel allowed to warm to rt during 24 h. Sat. aq. NH_4Cl (4.0 mL) was added and the mixture partitioned between EtOAc (15 mL) and H_2O (6 mL). The layers were separated and the aqueous phase extracted with EtOAc (2x7 mL). The combined organic phases were washed with brine (2 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue (396 mg) was purfied by column chromatography (SiO_2, eluting with 0-5% Et_2O in hexanes) to afford the title compound (*S*)-**21** (65.8 mg, 0.173 mmol, 69%) as a colorless oil: $[\alpha]_D^{20}$ =

S19. A. B. Shenvi US Patent 1985, 4,537,773.

S20. D. A. Evans, K. A. Woerpel, B. Nosse, A. Schall, Y. Shinde, E. Jezek, M. M. Haque, R. B. Chhor and O. Reiser *Org. Synth.*, 2006, **83**, 97.

–11.8 (c = 1.00, $CHCl_3$, at 57% ee) [lit.[S21] for (*R*)-**21** $[\alpha]_D^{20}$ = +24 (c = 1.0, $CHCl_3$ at %ee ≥ 94%]; IR (neat) 2977, 1353, 1308, 1249, 1145, 1112, 995, 847, 815 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (2H, m), 7.35-7.32 (3H, m), 7.28-7.25 (1H, m), 7.24 (1H, dm, *J* = 7.5 Hz), 7.16 (1H, tt, *J* = 7.4, 2.2 Hz), 7.12 (2H, dm, *J* = 6.9 Hz), 2.71 (1H, ddd, *J* = 13.8, 9.8, 4.9 Hz), 2.47 (1H, ddd, *J* = 13.4, 9.7, 6.8 Hz), 1.90 (1H, dddd, *J* = 13.6, 11.5, 9.8, 5.0), 1.65 (1H, dddd, *J* = 13.0, 9.9, 6.9, 3.1 Hz), 1.24 (6H, s), 1.21 (6H, s), 0.72 (1H, dd, *J* = 12.0, 3.0 Hz), 0.33 (3H, s), 0.31 (3H, s) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 142.8 (0), 139.0 (0), 134.0 (2C, 1), 129.0 (1), 128.7 (2C, 1), 128.4 (2C, 1), 127.8 (2C, 1), 125.8 (1), 83.0 (2C, 0), 39.6 (2), 28.2 (2), 25.4 (2C, 3), 24.9 (2C, 3), 13.8 (1, br R<u>C</u>HBpin), –2.1 (3), –3.2 (3) ppm. ^1H and ^{13}C NMR spectral data in agreement with those previously reported by Aggarwal and coworkers [absolute configuration assigned by comparison to the previously reported optical rotation value for the dextrorotatory compound (*R*)-**21**].[S21]



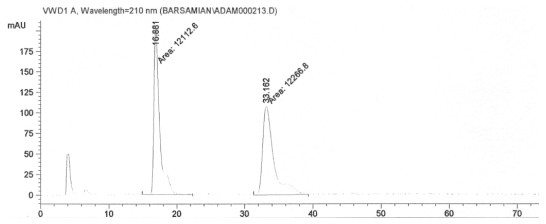
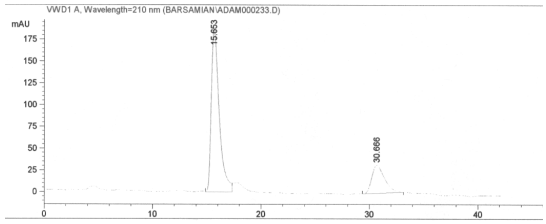
ox-**21**: $C_{17}H_{22}OSi$ (270.4)

Enantiomeric excess for **21** determined indirectly by conversion to its more polar oxidation product *ox*-**21** followed by CSP HPLC analysis. <u>Preparation of *ox*-**21**</u>: A stirred solution of boronate **21** (16.0 mg, 0.042 mmol) in THF (1.5 mL) at 0 °C was treated with aq. NaOH (0.050 mL) followed by 30 wt.% aq. H_2O_2 (0.015 mL). The resulting biphasic mixture was allowed to warm to rt stirred vigorously for 13 h. EtOAc (8 mL) and H_2O (2 mL) was added and the layers shaken and separated. The aqueous phase was extracted with EtOAc (2x5 mL) and the combined organic phases washed with brine (1 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, eluting with 0-5% EtOAc in hexanes) to afford carbinol *ox*-**21** (6.1 mg, 0.023 mmol, 54%) as a colorless oil: IR (neat) 3437, 2924, 1603, 1496, 1454, 1427, 1249, 1113, 1027, 830, 813, 781, 736, 700 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.56-7.54 (2H, m), 7.40-7.35 (3H, m), 7.27 (2H, tm, *J* = 7.6 Hz), 7.18 (1H, tm, *J* = 7.4 Hz), 7.15 (2H, dm, *J* = 6.9 Hz), 3.56-3.51 (1H, non-first order AMM´ pattern), 2.90 (1H, dt, *J* = 14.2, 7.4 Hz), 2.62 (1H, dt, *J* = 13.8, 7.9 Hz), 1.88-1.81 (2H, m), 0.34 (3H, s), 0.33 (3H, s) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ = 142.3 (0), 136.7 (0), 134.3 (2C, 1), 129.6 (1), 128.7 (2C, 1), 128.6 (2C, 1), 128.2 (2C, 1), 126.0 (1), 65.1 (1), 35.4 (2), 33.5 (2), –5.2 (3), –5.5 (3) ppm.

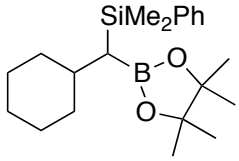
Chiral stationary phase (CSP) HPLC analysis of (±)-*ox*-**21**, obtained by aq. NaOOH oxidation of (±)-**21** prepared as above using TMEDA in place of the chiral bisoxazoline ligand, performed with a Daicel Chiralcel® OD column (4.6 mm ID x 250 mm), eluting with 10% *i*-PrOH in hexanes at 1.0 mL min^{-1} and monitored by UV at 210 nm, showed resolved peaks: $t_{ret.}$ [(*R*)-*ox*-**21**] = 16.9 min, $t_{ret.}$ [(*S*)-*ox*-**21**] = 33.2 min. Analysis of the enantioenriched material prepared as described above via

S21. V. K. Aggarwal, M. Binanzer, M. C. de Ceglie, M. Gallanti, B. W. Glasspoole, S. J. K. Kendrick, R. P. Sonawane, A. Váquez-Romero and M. P. Webster *Org. Lett.*, 2011, **13**, 1490.

ligand mediated i-StReCH revealed an enantiomeric excess of 57% in favor of (*R*)-*ox*-**21** (note: same absolute configuration as (*S*)-**21**).

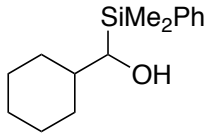
(±)-*ox*-**21**: left = 49.68%, right = 50.32%	(*R*)-**18** (57% ee): left = 78.41%, right = 21.59%
	

2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23): Prepared from TIB ester **19** (179 mg, 0.451 mmol), *t*-BuLi (0.173 mL, 1.73 M in pentane, 0.299 mmol), (*S,S*)-bisoxazoline ligand **8** (R^1/R^2 = *i*-Pr/Me, 80 mg, 0.300 mmol),[S20] and 2-cyclohexyl-5,5-dimethyl-1,3,2-dioxaborinane (53 mg, 0.252 mmol)[S18] according to the representative procedure shown above which, following a single chromatography (SiO_2, eluting with 1-5% Et_2O in pentane), yielded a five component mixture (146 mg) of co-polar compounds containing the title boronate **23** (21.6 wt%. as adjuged by ^1H NMR spectral analysis, effectively 31.5 mg, 0.088 mmol, 35%), **19**, *pre*-**19**, bis(dimethylphenylsilyl)methyl 2,4,6-triisopropylbenzoate, and unreacted substrate 2-cyclohexyl-5,5-dimethyl-1,3,2-dioxaborinane. A pure sample of silylboronate **23** was obtained by Kugelrohr distillation (oven temp. 130-145 °C at ca. 0.4 mmHg) followed by additional column chromatography (SiO_2, 0-1% Et_2O in pentane). Data for **21**: colorless oil; IR (neat) 2924, 1447, 1427, 1371, 1339, 1302, 1248, 1145, 1111, 848, 819, 731, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57-7.52 (2H, m), 7.34-7.29 (3H, m), 1.72 (1H, br d, *J* = 9.8 Hz), 1.68-1.50 (7H, m), 1.25-1.05 (2H, m), 1.17 (6H, s), 1.12 (6H, s), 0.96-0.85 (1H, m), 0.67 (1H, d, *J* = 7.8 Hz), 0.34 (3H, s), 0.33 (3H, s) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ = 140.5 (0), 134.0 (2C, 1), 128.7 (1), 127.7 (2C, 1), 82.8 (2C, 0), 36.9 (2), 35.7 (2), 27.0 (2), 26.4 (2), 25.4 (2C, 3), 25.2 (2C, 3), –1.06 (3), –1.10 (3) ppm (RCBSi not clearly observed and other methine signal obscured). ^1H and ^{13}C NMR spectral data in agreement with those previously reported.[S22]



23: $C_{21}H_{35}BO_2Si$ (358.4)

Enantiomeric excess for **23** determined indirectly by conversion to its more polar oxidation product *ox*-**23** followed by CSP HPLC analysis. *Ox*-**23** was prepared by analogy to *ox*-**21** as described above. Data for *ox*-**23**: colorless oil; IR (neat) 3446, 2924, 2852, 1449, 1427, 1248, 1112, 977, 833, 817, 700 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.58-7.56 (2H, m), 7.38-7.35 (3H, m), 3.34 (1H,

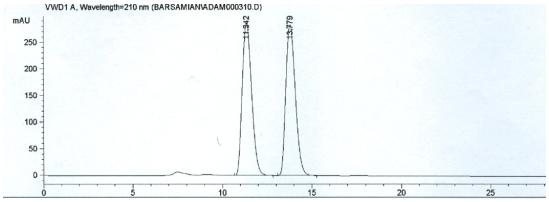
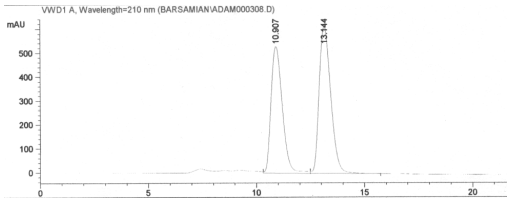


ox-**23**: $C_{15}H_{24}OSi$ (248.4)

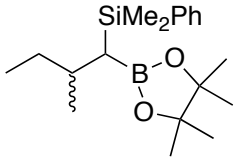
S22. H. Li, X. Shangguan, Z. Zhang, S. Huang, Y. Zhang, J. Wang *Org. Lett.*, 2013, **16**, 448.

d, *J* = 6.0 Hz), 1.83 (1H, dm, *J* = 12.9 Hz), 1.74-1.68 (2H, m), 1.62 (1H, dm, *J* = 12.7 Hz), 1.56-1.50 (2H, m), 1.24-1.01 (6H, m), 0.37 (3H, s), 0.36 (3H, s) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ = 138.0 (0), 134.2 (2C, 1), 129.3 (1), 128.1 (2C, 1), 71.2 (1), 42.2 (1), 31.0 (2), 29.7 (2), 26.6 (2), 26.5 (2), 26.4 (2), –3.6 (3), –4.1 (3) ppm. HRMS (ES+) *m/z* 249.1679 (calcd. for $C_{15}H_{25}OSi$: 249.1675).

Chiral stationary phase (CSP) HPLC analysis of (±)-*ox*-**23**, obtained by aq. NaOOH oxidation of (±)-**23** prepared as above using TMEDA in place of the chiral bisoxazoline ligand, performed with a Daicel Chiralcel® AS-H column (4.6 mm ID x 250 mm), eluting with 10% *i*-PrOH in hexanes at 1.0 mL min^{-1} and monitored by UV at 210 nm, showed resolved peaks: $t_{ret.}$ [*ox*-**23**] = 11.3 min, $t_{ret.}$ [*ent-ox*-**23**] = 13.8 min. Analysis of the enantioenriched material prepared as described above via ligand mediated i-StReCH revealed an enantiomeric excess of 9%.

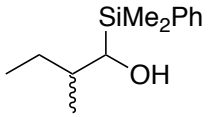
(±)-*ox*-**23**: left = 50.01%, right = 49.99%	**23** (9% ee): left = 45.60%, right = 54.40%
	

2-[1-(Dimethylphenylsilyl)-2-methylbutyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24): Prepared from TIB ester **19** (179 mg, 0.451 mmol), *t*-BuLi (0.173 mL, 1.73 M in pentane, 0.299 mmol), (*S,S*)-bisoxazoline ligand **8** (R^1/R^2 = *i*-Pr/Me, 80 mg, 0.300 mmol),[S20] and (±)-2-*sec*-butyl-5,5-dimethyl-1,3,2-dioxaborinane (*pre*-**24**, 50.0 mg, 0.272 mmol) according to the representative procedure shown above which yielded the title boronate **24** (39.1 mg, 0.118 mmol, 43%, dr = 58:42) as a colorless oil [note: Kugelrohr distillation (oven temp. 95 °C, ca. 0.4 mmHg) was employed following column chromatography to obtain a pure mixture of product diastereomers; dr assessed by ^{1}H NMR spectral analysis before purification operations were applied]: IR (neat) 2961, 1341, 1307, 1145, 1112, 969, 850, 731, 700 cm^{-1}; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.57-7.54 (2H^{both}, m), 7.33-7.30 (3H^{both}, m), 1.73-1.67 (1H^{maj}, m), 1.60 (1H^{min}, septet, *J* = 7.0 Hz), 1.45 (1H^{maj}, dqd, *J* = 13.5, 7.5, 3.2 Hz), 1.34 (1H^{min}, dqd, *J* = 13.3, 7.4, 5.7 Hz), 1.28-1.12 (13H^{min}+ 16H^{maj}, m), 0.96 (1H^{maj}, d, *J* = 6.8 Hz), 0.85 (3H^{min}, d, *J* = 6.7 Hz), 0.79 (3H^{maj}, t, *J* = 7.4 Hz), 0.77 (3H^{min}, t, *J* = 7.4 Hz), 0.36 (3H^{min}, s), 0.35 (3H^{maj}, s), 0.34 (3H^{maj}, s), 0.32 (3H^{min}, s) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ = 140.5^{maj} (0), 140.1^{min} (0), 134.1^{both} (2C, 1), 128.8^{both} (1), 127.7^{both} (2C, 1), 82.8^{maj} (2C, 0), 82.7^{min} (2C, 0), 33.5^{both} (1), 32.9^{min} (2), 31.6^{maj} (2), 25.4^{maj} (2C, 3), 25.3^{maj} (2C, 3), 25.1^{min} (2C, 3), 25.0^{min} (2C, 3), 22.1^{maj} (3), 20.7^{min} (3), 11.9^{min} (3), 11.7^{maj} (3), –1.05^{maj} (3),



24: $C_{19}H_{33}BO_2Si$ (332.4)

–1.07^{maj} (3), –1.10^{min} (3), –1.43^{min} (3) ppm (RCHSiB not clearly observed); MS (ES+) *m/z* 355 $(M+Na)^+$; HRMS (ES+) *m/z* = 355.2253 (calcd. for $C_{19}H_{33}BNaO_2Si$: 355.2241).



ox-**24**: $C_{13}H_{22}OSi$ (222.4)

Enantiomeric excess for **24** diastereomers determined indirectly by conversion to the more polar oxidation products *ox*-**24** followed by CSP HPLC analysis. *Ox*-**24** isomers prepared by analogy to *ox*-**21** as described above. Selected data for *ox*-**24** (from a ca. 2:1 mixture of diastereomers): colorless oil; IR (neat) 3468, 2959, 2929, 1462, 1427, 1248, 1111, 834, 701 cm^{-1}; ^1H NMR (700 MHz, $CDCl_3$) δ 7.59-7.56 (2H^{both}, m), 7.38-7.35 (3H^{both}, m), 3.54 (1H^{maj}, d, *J* = 4.2 Hz), 3.37 (1H^{min}, d, *J* = 7.0 Hz), 1.66-1.61 (1H^{min}, m), 1.43 (1H^{maj}, dqd, *J* = 13.8, 7.5, 6.0 Hz), 1.30-1.13 (3H^{both}, m), 0.89 (3H^{maj}, d, *J* = 6.8 Hz), 0.87-0.84 (6H^{min} + 3H^{maj}, m), 0.383 (3H^{min}, s), 0.379 (3H^{maj}, s), 0.375 (3H^{min}, s), 0.36 (3H^{maj}, s) ppm; ^{13}C NMR (175 MHz, $CDCl_3$) δ = 138.0^{both} (0), 134.3^{both} (2C, 1), 129.4^{both} (1), 128.1^{both} (2C, 1), 70.7^{min} (1), 69.4^{maj} (1), 39.0^{min} (1), 38.6^{maj} (1), 27.4^{maj} (2), 25.9^{min} (2), 16.7^{min} (3), 15.8^{maj} (3), 12.1^{maj} (3), 11.4^{min} (3), –3.5^{min} (3), –3.8^{maj} (3), –4.05^{maj} (3), –4.08^{min} (3) ppm.

Chiral stationary phase (CSP) HPLC analysis of a diastereomeric mixture of (±)-*ox*-**24** [with dr = 66 (*ox*-**24**):34 (*ox*-**24´**)], obtained by aq. NaOOH oxidation of racemic diastereomers of **24** prepared as above using TMEDA in place of the chiral bisoxazoline ligand, performed with a Daicel Chiralcel® OJ column (4.6 mm ID x 250 mm), eluting with 3% *i*-PrOH in hexanes at 1.0 mL min^{-1} and monitored by UV at 210 nm, showed significantly, but not fully base-line resolved peaks: $t_{ret.}$ [*ox*-**24**] = 37.1 min, $t_{ret.}$ [*ox*-**24´**] = 41.0 min, $t_{ret.}$ [*ent-ox*-**24´**] = 46.4 min, [*ent-ox*-**24**] = 54.1 min. Analysis of enantioenriched material *ox*-**24** [with dr = 35 (*ox*-**24**):65 (*ox*-**24´**)] prepared as described above via ligand mediated i-StReCH, revealed an enantiomeric excess of ca. 26% ee for diastereomer *ox*-**24´** and ca. 14% ee for diastereomer *ox*-**24**.

(±)-*ox*-**24** + (±)-*ox*-**24´** (dr = 66:34): (1-4 l-r) 1 = 29.0%, 2 = 16.9%, 3 = 20.1%, 4 = 34.0%	*ox*-**24** + *ox*-**24´** (dr = 35:65): (1-4 l-r) 1 = 15.0%, 2 = 24.1%, 3 = 40.6%, 20.3%