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1. General experimental information

Reaction mixtures were stirred magnetically. Air- and moisture-sensitive reactions were carried out in flame-dried glassware under argon atmosphere using standard Schlenk manifold technique. All required fine chemicals were purchased from Acros Organics, Alfa Aesar, Inochem-Frontier Scientific or Sigma-Aldrich and used as received unless otherwise mentioned. sec-Butyllithium (sBuLi) was received from Acros Organics as 1.3 M solution in cyclohexane/hexane 92:8 and the molarity was verified by titration with N-benzylbenzamidine.\(^1\) Petrol refers to the fraction of petroleum ether boiling at 40-60 °C. 1 M MgBr\(_2\) solutions in MeOH were prepared in advance by adding anhydrous MeOH to MgBr\(_2\) solid. TMEDA was distilled over CaH\(_2\) before use, (−)-sparteine and (+)-sparteine were isolated from the commercially available salt following a procedure by Beak.\(^2\) Anhydrous THF, CH\(_2\)Cl\(_2\), toluene, hexane, acetonitrile and Et\(_2\)O were dried by passing through a modified Grubbs system\(^3\) of alumina columns, manufactured by Anhydrus Engineering, and were transferred under argon via syringes. Microwave reactions were carried out in a Biotage Initiator EXP EU microwave synthesiser. \(^1\)H Nuclear Magnetic Resonance (NMR) spectra were recorded in CDCl\(_3\) or acetone-\(d_6\) at 301, 400 or 500 MHz on a Joel Lambda 300, Joel ECP 400, a Varian 400-MR or a VNMRS500a Fourier transform spectrometer. Chemical shifts (\(\delta_H\)) are quoted in parts per million (ppm) and referred to the residual protio solvent signals of CHCl\(_3\) (7.27 ppm) or acetone (2.05 ppm). \(^1\)H NMR coupling constants are reported in hertz and refer to apparent multiplicities. Data are reported as follows: chemical shift, multiplicity (s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, dd = doublet of doublet, etc.), coupling constant, integration, and assignment. \(^13\)C NMR spectra were recorded at 101 or 126 MHz. Chemical shifts (\(\delta_C\)) are quoted in ppm referenced to CHCl\(_3\) (77.0 ppm) or acetone (29.92 ppm). \(^11\)B NMR spectra were measured using Norell S-200-QTZ quartz NMR tubes at 96 or 128 MHz with complete proton decoupling. \(^19\)F NMR spectra were recorded at 283, 376 or 470 MHz. Mass spectra were recorded by the University of Bristol, School of Chemistry departmental mass spectrometry service using electron impact ionisation (EI), chemical ionisation (CI) or electrospray ionisation (ESI) techniques for low- and high-resolution mass spectra. HRMS EI and CI were performed on a VG Analytical Autospec mass spectrometer at 70 eV. HRMS ESI was performed on either a Bruker Daltonics Apex IV, 7-Tesla FT-ICR or micrOTOF II. Samples were submitted in EtOAc. For low resolution mass spectra (\(m/z\)) only molecular ions (M\(^+\) or MH\(^+\)) and major peaks are reported with intensities quoted as percentage of the base peak. All infrared spectra were recorded on the neat compounds using a PerkinElmer Spectrum One FT-IR spectrometer, irradiating between 4000 cm\(^{-1}\) and 600 cm\(^{-1}\). Only strong and selected absorbances (\(v_{\text{max}}\)) are reported. Analytical TLC was performed on aluminium backed silica plates (Merck, Silica Gel 60 F\(_{254}\), 0.25 mm). Compounds were visualised by fluorescence quenching or by staining the plates with 5% solution of phosphomolybdic acid.
(H₃PMo₁₂O₄₀) in EtOH followed by heating. Flash column chromatography was performed on silica gel (Aldrich, Silica Gel 60, 40–63 μm). All mixed solvent eluents are reported as v/v solutions. Optical rotations were obtained using a Bellingham + Stanley Ltd. ADP220 polarimeter at 589 nm (Na D-line) in a cell with a path length of 1 dm. Specific rotation values are given in (deg mL)/(g dm). Melting points were measured with a Reichert hot stage apparatus and are uncorrected. Chiral high performance liquid chromatography (HPLC) separations were performed on an Agilent 1100 Series HPLC unit equipped with UV-vis diode-array detector monitored at 210.8 nm, using Daicel Chiralpak ADH, IA, IB or IC columns (4.6 × 250 mm², 5 μm) fitted with respective guards (4 × 10 mm²). Supercritical fluid chromatography (SFC) was performed on a Thar SFC investigator using a Daicel Chiralpak IA column (4.6 × 250 mm², 5 μm).

2. Detailed procedures and analytical data

2.1 Preparation of secondary benzylic alcohols

(S)-1-(4-Methoxyphenyl)ethanol ((S)-31)

Methylmagnesium bromide solution (20.0 mL, 3.0 M in diethyl ether, 60.0 mmol, 1.2 equiv) was added slowly to a stirred solution of 4-methoxybenzaldehyde (6.81 g, 50.0 mmol, 1.0 equiv) in anhydrous diethyl ether (50 mL) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 20 h. The mixture was then cooled to 0 °C, aq. NH₄Cl solution (2%, 50 mL) was added slowly, and the mixture was stirred for 10 min. The solution was extracted with diethyl ether (4 × 100 mL). The combined organic fractions were dried over anhydrous MgSO₄, filtered, and the solvent was removed in vacuo to give racemic alcohol 31 (7.61 g, 50.0 mmol) as a colourless oil in quantitative yield, which was used without further purification. According to a procedure by Xu and co-workers,⁴ carrier-bound lipase from Candida antarctica (Novozym 435) (240 mg) was added to a solution of racemic alcohol 31 (6.01 g, 40.0 mmol, 1.0 equiv) and vinyl acetate (18.2 mL, 0.20 mol, 5.0 equiv) in diisopropyl ether (16.7 mL) and stirred for 12 h at 50 °C. The reaction was filtered, the solids were thoroughly washed with EtOAc, and the filtrate was concentrated in vacuo. The residue was subjected to column chromatography (SiO₂, pentane/EtOAc 9:1 → 4:1) to obtain alcohol (S)-31 (2.96 g, 19.4 mmol, 49%) as a colourless oil and (R)-1-(4-methoxyphenyl)ethyl acetate (3.97 g, 20.4 mmol, 51%) as a colourless oil.

Rt (pentane/EtOAc 9:1) 0.08.
$^1$H NMR (500 MHz, CDCl$_3$) $\delta$H ppm 7.31 (AA’BB’, $J = 8.5$ Hz, 2 H, CH$_{Ar}$), 6.89 (AA’BB’, $J = 8.5$ Hz, 2 H, CH$_{Ar}$), 4.86 (q, $J = 6.4$ Hz, 1 H, CHO), 3.81 (s, 3 H, OCH$_3$), 1.91 (br. s, 1 H, OH), 1.48 (d, $J = 6.4$ Hz, 3 H, CH$_3$).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$C ppm 158.9 (C), 137.9 (C), 126.6 (CH), 113.7 (CH), 69.9 (CHOH), 55.2 (OCH$_3$), 25.0 (CH$_3$).

$[\alpha]_{D}^{21} = -50.0$ ($c 1.00$, CHCl$_3$, for 99% ee). Lit. $[\alpha]_{D}^{22} = -40.3$ ($c 1.20$, CHCl$_3$, for 97% ee).

The spectral data match those reported in literature.

HPLC separation conditions: Chiralpak IB column with guard, 2.0% iPrOH in hexane, flow rate 0.7 mL/min, 20 °C; $t_R$ 26.5 min for (R)-enantiomer (minor) and $t_R$ 28.2 min for (S)-enantiomer (major).

e.r. = 99.6:0.4.

(S)-1-(4-Methoxyphenyl)propan-1-ol ((S)-43)

Following the procedure for the synthesis of (S)-1-(4-methoxyphenyl)ethanol ((S)-31) (vide supra), 4-methoxybenzaldehyde (6.81 g, 50.0 mmol, 1.0 equiv) and ethylmagnesium bromide solution (20.0 mL, 3.0 M in diethyl ether, 60.0 mmol, 1.2 equiv) in anhydrous diethyl ether (50 mL) afforded racemic alcohol 41 (8.30 g, 50.0 mmol) as colourless oil in quantitative yield. The crude alcohol 43 (7.65 g, 46.1 mmol, 1.0 equiv), vinyl acetate (23.0 mL, 0.25 mol, 5.4 equiv) and carrier-bound lipase from Candida antarctica (Novozym 435) (2.75 g) in diisopropyl ether (21.0 mL) gave after stirring for 26.5 h at 50 °C and column chromatography (SiO$_2$, pentane/ EtOAc 4:1) alcohol (S)-43 (3.60 g, 21.7 mmol, 47%) as a colourless oil and (R)-1-(4-methoxy-phenyl)propyl acetate (4.32 g, 20.7 mmol, 45%) as a colourless oil.

Rf (pentane/EtOAc 4:1) 0.16.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$H ppm 7.27 (AA’BB’, $J = 8.8$ Hz, 2 H, H$_{Ar}$), 6.89 (AA’BB’, $J = 8.8$ Hz, 2 H, H$_{Ar}$), 4.55 (t, $J = 6.7$ Hz, 1 H, CHO), 3.82 (s, 3 H, OCH$_3$), 1.89–1.68 (m, 3 H, CH$_2$+OH), 0.91 (t, $J = 7.5$ Hz, 3 H, CH$_3$).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 159.0 (C), 136.7 (C), 127.2 (CH), 113.7 (CH), 75.6 (CHOH), 55.2 (OCH$_3$), 31.7 (CH$_2$), 10.2 (CH$_3$).

$[\alpha]_D^{12} = -43.0$ (c 1.00, CHCl$_3$, for 99% ee). Lit. $[\alpha]_D^{12} = -23.4$ (c 0.30, CHCl$_3$, for 65% ee).

The analytical data correspond to the literature known compound.

HPLC separation conditions: Chiralpak IB column with guard, 3.0% iPrOH in hexane, flow rate 0.7 mL/min, 20 °C; $t_R$ 20.6 min for (R)-enantiomer (minor) and $t_R$ 22.0 min for (S)-enantiomer (major).

e.r. = 99.9:0.1.

**S-1-(4-Methoxyphenyl)propan-1-ol ((R)-43)**

The (R)-1-(4-methoxy-phenyl)propyl acetate isolated from the synthesis of (S)-43 was dissolved in MeOH (24 mL) and treated with 6 M aq. NaOH and stirred overnight. The solvent was removed, water (50 mL) was added to the residue which was extracted with EtOAc (4 × 50 mL).

The combined organics were washed with brine (20 mL), dried over MgSO$_4$, filtered and concentrated *in vacuo* to afford (R)-43 (3.43 g, 20.7 mmol, 45%)

$[\alpha]_D^{12} = +35.0$ (c 1.00, CHCl$_3$, for 99% ee). Lit. $[\alpha]_D^{12} = -23.4$ (c 0.30, CHCl$_3$, for 65% ee).

HPLC separation conditions: Chiralpak IB column with guard, 3.0% iPrOH in hexane, flow rate 0.7 mL/min, 20 °C; $t_R$ 20.6 min for (R)-enantiomer (major) and $t_R$ 22.0 min for (S)-enantiomer (minor).

e.r. = 99.9:0.1.
1-(3-Fluoro-4-methoxyphenyl)ethanol (44)

Sodium borohydride (284 mg, 7.5 mmol, 1.5 equiv) was added slowly to a solution of 1-(3-fluoro-4-methoxyphenyl)ethanone (841 mg, 5.0 mmol, 1.0 equiv) in anhydrous MeOH (10 mL) at 0 °C. After stirring for 2 h at room temperature H₂O (10 mL) was added slowly and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure to give alcohol 44 (851 mg, 5.0 mmol) as colourless oil in quantitative yield, which required no further purification.

¹H NMR (400 MHz, CDCl₃) δ_H ppm 7.13 (d, J = 12.3 Hz, 1 H, H_Ar), 7.07 (d, J = 8.4 Hz, 1 H, H_Ar), 6.93 (dd, J_HF = 8.4 Hz, J_HH = 8.4 Hz, 1 H, H_Ar), 4.85 (q, J = 6.4 Hz, 1 H, CHO), 3.89 (s, 3 H, OCH₃), 1.83 (br. s, 1 H, OH), 1.47 (d, J = 6.4 Hz, 3 H, CH₃).

¹³C NMR (101 MHz, CDCl₃) δ_C ppm 152.3 (d, ¹J_CF = 246.0 Hz, CF), 146.8 (d, ²J_COMe = 10.9 Hz, COMe), 139.0 (d, ³J_AR = 5.5 Hz, C), 121.0 (d, ⁴J_AR = 3.1 Hz, CH), 113.3 (d, ⁴J_AR = 18.7 Hz, CH), 113.2 (d, ⁴J_AR = 2.3 Hz, CH), 69.5 (CHOH), 56.3 (OCH₃), 25.1 (CH₃).

¹⁹F NMR (376 MHz, CDCl₃) δ_F ppm -137.1 (dd, J = 12.1, 8.2 Hz, CF).

ν_max (neat) = 3347, 2970, 1623, 1515, 1269, 1125, 1028, 875, 811, 760 cm⁻¹.

m/z (%) (CI⁺) 171 ([M+H]⁺, 64), 155 ([M–Me]⁺, 27), 153 ([M–OH]⁺, 100), 127 ([Ar+H]⁺, 28).

HRMS (CI⁺) calcd. for C₉H₁₂O₂F [M+H]⁺ 171.0821, found 171.0817.

2.2 Preparation of carbamates from alcohols

Propyl diisopropylcarbamate (28)

N,N-Diisopropylcarbamoyl chloride (1.64 g, 10.0 mmol, 1.0 equiv) was dissolved in 10.0 mL anhydrous n-propanol under an inert atmosphere in a microwave vial. The mixture was cooled to 0 °C and Et₃N (1.80 mL, 13.0 mmol, 1.3 equiv) was added slowly, the vial was sealed, and heated for 1 h at 150 °C in a microwave reactor. After cooling to ambient temperature, the salts were removed by filtration through a plug of silica and the solids were thoroughly washed with diethyl ether. The solvent was removed in vacuo to give primary carbamate 28 (1.73 g, 9.25 mmol, 92%) as a colourless oil, which showed no impurities in its NMR spectra.
**1H NMR** (400 MHz, CDCl₃) δH ppm 4.04 (t, J = 7.1 Hz, 2 H, CH₂OCb), 4.01 (br. m, 1 H, CH(CH₃)₂), 3.90 (br. m, 1 H, CH(CH₃)₂), 1.67 (sext, J = 7.1 Hz, 2 H, CH₂), 1.21 (d, J = 6.8 Hz, 12 H, 4×CH₃), 0.97 (t, J = 7.1 Hz, 3 H, CH₃).

**13C NMR** (101 MHz, CDCl₃) δC ppm 156.0 (NCO), 66.3 (CH₂OCb), 45.7 (br. m, CCH(CH₃)₂), 22.4 (CH₂), 21.0 (br., CH₃), 10.8 (CH₃).

The NMR data correspond to the literature known compound.⁸

**General procedure 1A (GP1A).** An alcohol (1.0 equiv) was added slowly to a suspension of sodium hydride (60% dispersion in mineral oil, 1.5 equiv) in anhydrous THF (0.2 M) and the mixture was stirred for 75 min at room temperature. A solution of N,N-diisopropylcarbamoyl chloride (1.2 equiv) in anhydrous THF (1.0 M) was added and the reaction mixture was heated under reflux for 24 h. The solvent was removed *in vacuo* and the residue was portioned between H₂O and diethyl ether. The phases were separated and the aqueous layer was re-extracted with diethyl ether (3 ×). The combined organic layers were dried over anhydrous MgSO₄ and concentrated under reduced pressure. The residue was subjected to flash chromatography (SiO₂, pentane/EtOAc) to give the pure carbamate.

**General procedure 1B (GP1B).** A secondary benzylic alcohol (1.0 equiv) and N,N-diisopropylcarbamoyl chloride (1.2 equiv) were dissolved in anhydrous toluene (1.0 M) under an inert atmosphere in a microwave vial. Et₃N (1.3 equiv) was added, the vial was sealed, and heated for 1 h at 150 °C in a microwave reactor. After cooling to ambient temperature, the salts were removed by filtration through a plug of silica and the solids were thoroughly washed with diethyl ether. The solvent was removed *in vacuo* and the residue was subjected to column chromatography (SiO₂, pentane/EtOAc) to afford the pure secondary benzylic carbamate.

**(S)-1-Phenylethyl diisopropylcarbamate ((S)-5)**

According to GP1A, (S)-1-phenylethanol (5.82 g, 47.6 mmol, 1.0 equiv), N,N-diisopropylcarbamoyl chloride (9.36 g, 57.2 mmol, 1.2 equiv) and sodium hydride (60% dispersion in mineral oil, 2.86 g, 71.5 mmol, 1.5 equiv) in anhydrous THF (150 mL) afforded after purification by column chromatography (SiO₂, pentane/EtOAc 6:1) carbamate (S)-5 (11.7 g, 46.9 mmol, 98%) as a colourless oil.

Rᵣ (pentane/EtOAc 6:1) 0.36.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$H ppm 7.39–7.33 (m, 4 H, H$_{Ar}$), 7.28 (m, 1 H, H$_{Ar}$), 5.86 (q, $J = 6.7$ Hz, 1 H, CHOC$_b$), 4.08 (br. m, 1 H, CH(CH$_3$)$_2$), 3.83 (br. m, 1 H, CH(H(CH$_3$)$_2$), 1.56 (d, $J = 6.7$ Hz, 3 H, CH$_3$), 1.28–1.17 (br. m, 12 H, 4 x CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$C ppm 155.0 (NCO), 142.8 (C), 128.3 (CH), 127.4 (CH), 126.0 (CH), 72.7 (CHOC$_b$), 46.1 (br, C$_H$(CH$_3$)$_2$), 45.3 (br, C$_H$(CH$_3$)$_2$), 22.8 (CH$_3$), 21.3 (br, CH$_3$), 20.8 (br, CH$_3$).

$[\alpha]_D^{20}$ +6.5 (c 1.0, CHCl$_3$, for 99% ee). Lit. $[\alpha]_D^{20}$ +5.5 (c 1.2, CH$_2$Cl$_2$, for 99% ee).$^9$

The analytical data match those reported in literature.$^{10}$

HPLC separation conditions: Chiralpak IA column with guard, 5.0% tPrOH in hexane, flow rate 0.7 mL/min, 20 °C; $t_R$ 8.3 min for (R)-enantiomer (minor) and $t_R$ 9.5 min for (S)-enantiomer (major).

e.r. = 99.9:0.1.

N.B. For the synthesis of racemic 1-phenylethyl diisopropylcarbamate 5 racemic 1-phenylethanol was used as starting material.

(R)-1-Phenylethyl diisopropylcarbamate ((R)-5)

(R)-1-phenylethanol (12 g, 92 mmol, 1.0 equiv), N,N-diisopropylcarbamoyl chloride (18.0 g, 110 mmol, 1.2 equiv) and triethylamine (15.5mL, 110 mmol, 1.2 equiv) in anhydrous dichloromethane (200 mL) were heated at reflux for 48 h. The reaction mixture was cooled to room temperature and water (300 mL) was added. The organic phase was separated and the aqueous phase extracted with dichloromethane (3 x 300 mL) the organic phases were combined, dried (MgSO$_4$), filtered and concentrated in vacuo. Purification by column chromatography (SiO$_2$, pentane/EtOAc 6:1) afforded carbamate (R)-5 (21.6 g, 86 mmol, 94%) as a colourless oil.

$[\alpha]_D^{20}$ +7 (c 1.0, CHCl$_3$, for 99% ee). Lit. $[\alpha]_D^{20}$ +5.5 (c 1.2, CH$_2$Cl$_2$, for −99% ee).

Chiralpak IA column, eluent: 96% CO$_2$, 2% hexane, 2% iPrOH, flow rate 4.0 mL/min, 39.8 °C; $t_R$ 2.27 min for (S)-enantiomer (minor) and $t_R$ 2.74 min for (R)-enantiomer (major).
(S)-1-Phenylpropyl diisopropylcarbamate ((S)-6)

According to GP1B, (S)-1-phenylpropan-1-ol (1.01 g, 7.38 mmol, 1.0 equiv), N,N-diisopropylcarbamoyl chloride (1.45 g, 8.86 mmol, 1.2 equiv) and Et₃N (1.33 mL, 9.60 mmol, 1.3 equiv) in 8.0 mL anhydrous toluene afforded after purification by column chromatography (SiO₂, pentane/EtOAc 9:1) secondary benzylic carbamate (S)-6 (1.90 g, 7.21 mmol, 98%) as a colourless oil.

Rᵣ (pentane/EtOAc 9:1) 0.23.

¹H NMR (500 MHz, CDCl₃) δ ppm 7.38‒7.29 (m, 4 H, Hₐr), 7.26 (m, 1 H, Hₐr), 5.65 (t, J = 7.2 Hz, 1 H, CHOCb), 4.05 (br. m, 1 H, CH(CH₃)₂), 3.85 (br. m, 1 H, CH(CH₃)₂), 1.96 (dquin, J = 14.3, 7.2 Hz, 1 H, CHH), 1.84 (dquin, J = 14.3, 7.2 Hz, 1 H, CHH), 1.22 (br. m, 12 H, 4×CH₃), 0.91 (t, J = 7.2 Hz, 3 H, CH₃).

¹³C NMR (126 MHz, CDCl₃) δ ppm 155.1 (NCO), 141.5 (C), 128.2 (CH), 127.4 (CH), 126.5 (CH), 77.8 (CHOCb), 46.2 (br., CH(CH₃)₂), 45.3 (br., CH(CH₃)₂), 29.8 (CH₂), 21.5 (br., CH₃), 20.9 (br., CH₃), 10.0 (CH₃).

[α]²⁰D −8 (c 1.0, CHCl₃, for 99% ee). Lit. [α]²⁵D −8.0 (c 11, CH₂Cl₂, for 99% ee).¹¹

The spectral data are consistent with the literature known compound.¹¹

HPLC separation conditions: Chiralpak IA column with guard, 5.0% iPrOH in hexane, flow rate 0.7 mL/min, 20 °C; tᵣ 8.1 min for (R)-enantiomer (minor) and tᵣ 9.8 min for (S)-enantiomer (major).

e.r. = 99.1:0.9.

N.B. For the synthesis of racemic 1-phenylpropyl diisopropylcarbamate 6 racemic 1-phenylpropan-1-ol was used as starting material.
(R)-1-Phenylpropyl diisopropylcarbamate ((R)-6)

According to GP1B, (R)-1-phenylpropan-1-ol (1.01 g, 7.38 mmol, 1.0 equiv), N,N-diisopropycarbamoyl chloride (1.45 g, 8.86 mmol, 1.2 equiv) and Et₃N (1.33 mL, 9.60 mmol, 1.3 equiv) in 8.0 mL anhydrous toluene afforded after purification by column chromatography (SiO₂, pentane/EtOAc 9:1) secondary benzylic carbamate (S)-6 (1.80 g, 6.86 mmol, 93%) as a colourless oil.

[α]ᵢ₆⁺+7 (c 1.0, CHCl₃, for 99% ee). Lit. [α]ᵢ₆⁻−8.0 (c 11, CH₂Cl₂, for −99% ee).¹¹

HPLC separation conditions: Chiralpak IA column with guard, 5.0% iPrOH in hexane, flow rate 1 mL/min, 20 °C; tᵣ 4.2 min for (R)-enantiomer (major) and tᵣ 4.7 min for (S)-enantiomer (minor).
e.r. = 99.1:0.9.

(S)-1-(4-Methoxyphenyl)ethyl diisopropylcarbamate ((S)-32)

According to GP1A, (S)-1-(4-methoxyphenyl)ethanol ((S)-31) (7.61 g, 50.0 mmol, 1.0 equiv), N,N-diisopropycarbamoyl chloride (9.82 g, 60.0 mmol, 1.2 equiv) and sodium hydride (60% dispersion in mineral oil, 3.00 g, 75.0 mmol, 1.5 equiv) in anhydrous THF (150 mL) afforded after purification by flash chromatography (SiO₂, pentane/EtOAc 9:1 → 4:1) carbamate (S)-32 (13.9 g, 49.9 mmol, >99%) as a colourless oil.

Rᵣ (pentane/EtOAc 4:1) 0.49.

¹H NMR (400 MHz, CDCl₃) δH ppm 7.31 (AA’BB’, J = 8.5 Hz, 2 H, HAr), 6.88 (AA’BB’, J = 8.5 Hz, 2 H, HAr), 5.81 (q, J = 6.5 Hz, 2 H, CHOCb), 4.12 (br. m, 1 H, CH(CH₃)₂), 3.80 (s, 3 H, OCH₃), 3.73 (br. m, 1 H, CH(CH₃)₂), 1.54 (d, J = 6.5 Hz, 3 H, CH₃), 1.19 (d, J = 6.8 Hz, 12 H, 4×CH₃).

¹³C NMR (101 MHz, CDCl₃) δC ppm 158.9 (C), 155.1 (NCO), 134.9 (C), 127.4 (CH), 113.7 (CH), 72.3 (CHOCb), 55.2 (OCH₃), 46.3 (br., CH(CH₃)₂), 45.1 (br., CH(CH₃)₂), 22.6 (CH₃), 21.5 (br., CH₃), 20.8 (br., CH₃).
\([\alpha]_D^{22} +14.3 \ (c \ 1.12, \ \text{CH}_2\text{Cl}_2, \ for \ 99\% \ \text{ee}). \ \text{Lit.} \ [\alpha]_D^{24} +40.0 \ (c \ 1.0, \ \text{CH}_2\text{Cl}_2, \ for \ 96\% \ \text{ee})^1\]

The analytical data correspond to the literature known compound.\(^1\)

HPLC separation conditions: Chiralpak IC column with guard, 2.0\% \text{iPrOH} in hexane, flow rate 0.7 mL/min, 20 °C; \(t_R\) 19.1 min for (R)-enantiomer (minor) and \(t_R\) 27.0 min for (S)-enantiomer (major).

e.r. = 99.9:0.1.

\((R)-1-(4-\text{Methoxyphenyl})\text{propyl} \ \text{diisopropylcarbamate} \ ((R)-39)\)

According to GP1B, (S)-1-(4-methoxyphenyl)propan-1-ol ((R)-43) (1.80 g, 10.8 mmol, 1.0 equiv), \(N,N\)-diisopropylcarbamoyl chloride (2.13 g, 13.0 mmol, 1.2 equiv) and \(\text{Et}_3\text{N}\) (1.95 mL, 14.0 mmol, 1.3 equiv) in anhydrous toluene (10 mL) afforded after purification by column chromatography (SiO\(_2\), pentane/EtOAc 4:1) secondary benzylic carbamate (S)-37 (3.12 g, 10.6 mmol, 98\%, 99:1 e.r) as a colourless oil.

\(R_f\) (pentane/EtOAc 4:1) 0.48.

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) ppm 7.27 (AA’BB’, \(J = 8.8\) Hz, 2 H, H\(_{Ar}\)), 6.87 (AA’BB’, \(J = 8.8\) Hz, 2 H, H\(_{Ar}\)), 6.59 (t, \(J = 6.9\) Hz, 1 H, CHOcb), 4.07 (br. m, 1 H, CH(CH\(_3\))\(_2\)), 3.80 (s, 3 H, OCH\(_3\)), 3.79 (br. m, 1 H, CH(CH\(_3\))\(_2\)), 1.96 (m, 1 H, CHH), 1.80 (m, 1 H, CHH), 1.21 (br. m, 12 H, 4×CH\(_3\)), 0.88 (t, \(J = 7.3\) Hz, 3 H, CH\(_3\)).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) ppm 158.8 (NCO), 155.2 (C), 133.6 (C), 127.9 (CH), 113.6 (CH), 77.5 (CHOcb), 55.2 (OCH\(_3\)), 45.8 (br., CH(CH\(_3\))\(_2\)), 29.7 (CH\(_2\)), 21.2 (br., CH\(_3\)), 10.1 (CH\(_3\)).

\(\nu_{\text{max}}\) (neat) = 2968, 1682, 1514, 1285, 1047, 828 cm\(^{-1}\).

\(m/z\) (%) (CI\(^+\)) 294 ([M+H]\(^+\), 24), 149 ([M–Ocb]\(^+\), 95), 121 (12), 102 ([NH(iPr)\(_2\)+H]\(^+\), 40).

\(\text{HRMS}\) (CI\(^+\)) calcd. for C\(_{17}\)H\(_{28}\)NO\(_3\) [M+H]\(^+\) 294.2069, found 294.2065.

\([\alpha]_D^{23} +10 \ (c \ 1.0, \ \text{CHCl}_3, \ for \ 96\% \ \text{ee}).\)
SFC separation conditions: Chiralpak IA column, eluent: 80% CO$_2$, 18% hexane, 2% $i$PrOH, flow rate 4.0 mL/min, 39.8 °C; $t_R$ 4.95 min for (R)-enantiomer (major) and $t_R$ 5.62 min for (S)-enantiomer (minor).

1-(3-Fluoro-4-methoxyphenyl)ethyl diisopropylcarbamate (36)

According to GP1B, 1-(3-fluoro-4-methoxyphenyl)ethanol (44) (851 mg, 5.00 mmol, 1.0 equiv), $N,N$-diisopropylcarbamoyl chloride (982 mg, 6.00 mmol, 1.2 equiv) and Et$_3$N (901 µL, 6.50 mmol, 1.3 equiv) in 10 mL anhydrous toluene afforded after purification by column chromatography (SiO$_2$, pentane/EtOAc 9:1) secondary benzylic carbamate 36 (1.38 g, 4.64 mmol, 93%) as a colourless oil.

$R_f$ (pentane/EtOAc 9:1) 0.16.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ H ppm 7.13–7.05 (m, 2 H, $H_A$), 6.92 (dd, $J_{HF}$ = 8.4 Hz, $J_{HH}$ = 8.4 Hz, 1 H, $H_A$), 5.77 (q, $J$ = 6.6 Hz, 1 H, CHOcb), 4.08 (br. m, 1 H, CH(CH$_3$)$_2$), 3.88 (s, 3 H, OCH$_3$), 3.74 (br. m, 1 H, CH(CH$_3$)$_2$), 1.52 (d, $J$ = 6.6 Hz, 3 H, CH$_3$), 1.20 (d, $J$ = 6.6 Hz, 12 H, 4×CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ C ppm 154.9 (NCO), 152.2 (d, $^1$J = 245.5 Hz, CF), 146.8 (d, $^2$J = 10.9 Hz, COMe), 135.9 (d, $^3$J = 5.7 Hz, C), 121.9 (d, $^3$J = 3.5 Hz, CH), 113.8 (d, $^2$J = 18.9 Hz, CH), 113.1 (d, $^4$J = 2.0 Hz, CH), 71.8 (d, $^4$J = 1.3 Hz, CHOcb), 56.2 (OCH$_3$), 46.3 (br., CH(CH$_3$)$_2$), 45.2 (br., CH(CH$_3$)$_2$), 22.6 (CH$_3$), 21.4 (br., CH$_3$), 20.8 (br., CH$_3$).

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ F ppm −139.8 (dd, $J$ = 12.1, 8.7 Hz, CF).

$\nu_{max}$ (neat) = 2971, 1682, 1520, 1433, 1271, 1130, 1046, 900, 810, 761 cm$^{-1}$.

$m/z$ (%) (CI$^+$) 298 ([M+H]$^+$, 21), 153 ([M–OCH$_3$]$^+$, 100), 128 ([Cb]$^+$, 12).

HRMS (CI$^+$) calcd. for C$_{16}$H$_{25}$NO$_3$F [M+H]$^+$ 298.1818, found 298.1810.
2.3 Preparation of aryl pinacol boronic esters from boronic acids

2-(3-Fluoro-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29)

Based on a procedure by Roush and co-workers, 3-fluoro-4-methoxyphenylboronic acid (2.55 g, 15.0 mmol, 1.0 equiv) and pinacol (1.77 g, 15.0 mmol, 1.0 equiv) in 22.5 mL anhydrous diethyl ether were stirred at room temperature for 16 h. Flame-dried MgSO₄ (5.42 g, 45.0 mmol, 3.0 equiv) was added and the mixture was stirred for additional 2 h at room temperature. The solution was filtered through a plug of anhydrous MgSO₄ and the solids were thoroughly washed with diethyl ether. The combined filtrates were concentrated in vacuo and dried under high vacuum to give the boronic ester 29 (3.78 g, 15.0 mmol) as a white solid in quantitative yield, which required no further purification.

mp 88–89 °C (diethyl ether).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.54 (d, J = 8.2 Hz, 1 H, H₂Ar), 7.50 (d, J = 11.7 Hz, 1 H, H₃Ar), 6.96 (dd, J₇HF = 8.2 Hz, J₇HH = 8.2 Hz, 1 H, H₃Ar), 3.92 (s, 3 H, OCH₃), 1.34 (s, 12 H, 4×CH₃).

¹³C NMR (101 MHz, CDCl₃) δ ppm 152.0 (d, J₁ = 246.0 Hz, CF), 150.2 (d, J₂ = 10.7 Hz, COMe), 131.4 (d, J₃ = 3.7 Hz, CH), 121.7 (d, J₄ = 16.4 Hz, CH), 112.5 (d, J₅ = 1.2 Hz, CH), 83.8 (OC(CH₃)₂), 56.0 (OCH₃), 24.8 (CH₃).

¹¹B NMR (128 MHz, CDCl₃) δ ppm 30.3 (br. s).

¹⁹F NMR (376 MHz, CDCl₃) δ ppm –137.1 (dd, J = 11.3, 7.8 Hz, CF).

νmax (neat) = 2978, 1616, 1422, 1353, 1269, 1130, 1027, 967, 915, 853, 813, 758, 676 cm⁻¹.

m/z (%) (CI⁺) 253 ([M+H]⁺, 100), 252 ([M⁺, 38), 237 ([M–CH₃]⁺, 4), 233 ([M–F]⁺, 4) 127 ([Bpin]⁺, 5).

HRMS (CI⁺) calcd. for C₁₃H₁₉O₃¹¹BF [M+H]⁺ 253.1411, found 253.1408.

2-(3-fluoro-4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (38)

Based on a procedure by Roush and co-workers, 3-fluoro-4-methoxyphenylboronic acid (2.55 g, 15.0 mmol, 1.0 equiv) and neopentyl glycol (1.56 g, 15.0 mmol, 1.0 equiv) in 22.5 mL anhydrous diethyl ether were stirred at room temperature for 16 h. Flame-dried MgSO₄ (5.42 g, 45.0 mmol, 3.0 equiv) was added and the mixture was stirred for additional 2 h at room temperature. The solution was filtered through a plug of anhydrous
MgSO₄ and the solids were thoroughly washed with diethyl ether. The combined filtrates were concentrated \textit{in vacuo} and dried under high vacuum to give the boronic ester 38 (3.40 g, 14.3 mmol, 95\%) as a white solid, which required no further purification.

\textbf{mp} 65–66 °C (Et₂O).

\textbf{¹H NMR} (300 MHz, CDCl₃) δH ppm 7.59 – 7.42 (m, 2H), 6.95 (t, J=7.9, 1H), 3.91 (s, 3H), 3.76 (s, 4H), 1.02 (s, 6H).

\textbf{¹³C NMR} (101 MHz, CDCl₃) δC ppm 152.16 (d, J=245.4, CF), 149.81 (d, J=10.8, COMe), 130.41 (d, J=3.6, CH), 120.95 (d, J=16.0, CH), 112.48 (d, J=1.6, CH), 72.38 (CH₂), 56.09 (CH₃), 31.98 (C), 21.97 (CH₃).

\textbf{¹¹B NMR} (96 MHz, CDCl₃) δB ppm 25.4 (br. s).

\textbf{¹⁹F NMR} (283 MHz, CDCl₃) δF ppm −137.38 (dd, J=12.3, 8.3).

\(v_{\text{max}}\) (neat) = 2957, 2914, 2872, 1611, 1518, 1308, 1251, 1133, 1024, 814, 757, 669 cm\(^{-1}\).

\textbf{HRMS} (EI⁺) calcd. for C₁₂H₁₆O₃¹¹BF [M⁺] 238.1177, found 238.1178.

2.4 \textit{Preparation of secondary boronic esters}

\((S)-4,4,5,5\)-\textit{Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane ((S)-8)

Following a procedure by Aggarwal and co-workers,\(^{14}\) a solution of \((S)-1\)-phenylethyl diisopropylcarbamate ((S)-5) (748 mg, 3.00 mmol, 1.0 equiv) in anhydrous diethyl ether (9.0 mL) was cooled to −78 °C. sBuLi (3.00 mL, 3.90 mmol, 1.3 equiv) was added dropwise and the reaction mixture was stirred at this temperature for 1 h. A solution of pinacolborane (871 µL, 6.00 mmol, 2.0 equiv) in anhydrous diethyl ether (4.5 mL) was added dropwise and the mixture was stirred for 2 h at −78 °C. The cooling bath was removed and the reaction mixture was stirred at ambient temperature for additional 2 h. The reaction mixture was then cooled to 0 °C and 1 M aqueous KH₂PO₄ was added slowly. After stirring for 10 min at room temperature, the phases were separated, and the aqueous phase was extracted with diethyl ether (4 × 20 mL). The combined organic layers were dried over anhydrous MgSO₄, filtered, and the solvent was removed \textit{in vacuo}. The crude product was purified by column chromatography (SiO₂, pentane/EtOAc 30:1) to give secondary benzylic boronic ester (S)-8 (641 mg, 2.76 mmol, 92\%) as a colourless oil. Enantiomeric excess of the chiral boronic ester was determined by HPLC analysis of an aliquot oxidised to 1-phenylethanol-1-ol according to GP3 (\textit{vide infra}).

R\text{f} (pentane/EtOAc 30:1) 0.11.
**1H NMR** (500 MHz, CDCl₃) δ H ppm 7.30‒7.22 (m, 4 H, H_{Ar}), 7.14 (m, 1 H, H_{Ar}), 2.45 (q, J = 7.6 Hz, 1 H, CHBpin), 1.34 (d, J = 7.6 Hz, 3 H, CH₃), 1.22 (s, 6 H, 2×CH₃), 1.21 (s, 6 H, 2×CH₃).

**13C NMR** (126 MHz, CDCl₃) δ C ppm 144.9 (C), 128.3 (CH), 127.8 (CH), 125.0 (CH), 83.3 (OC(CH₃)₂), 24.62 (CH₃), 24.57 (CH₃), 17.0 (CH₃).

**11B NMR** (96 MHz, CDCl₃) δ B ppm 32.6 (br. s).

[α]_{D}^{21} +10.0 (c 1.00, CHCl₃, for 98% ee). Lit. [α]_{D}^{20} –12.0 (c 1.50, CHCl₃, for 94% ee of the (R)-isomer).

The analytical data are consistent with the known product.

HPLC separation conditions for 1-phenylethan-1-ol: Chiralpak IB column with guard, 2.0% iPrOH in hexane, flow rate 0.7 mL/min, 20 °C; t_R 23.4 min for (R)-enantiomer (minor) and t_R 26.9 min for (S)-enantiomer (major).

e.r. = 98.9:1.1.

N.B. For the synthesis of racemic 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (8) racemic 1-phenylethyl diisopropylcarbamate (5) was used as starting material. Alternatively, a rhodium-catalysed hydroboration procedure by Shibata was followed.

4,4,5,5-Tetramethyl-2-(1-phenylpropyl)-1,3,2-dioxaborolane (9)

A solution of propyl 2,4,6-triisopropylbenzoate (307 mg, 1.06 mmol, 1.0 equiv) and TMEDA (205 µL, 1.37 mmol, 1.3 equiv) in anhydrous diethyl ether (3.0 mL) was cooled to –78 °C. sBuLi (1.06 mL, 1.37 mmol, 1.3 equiv) was added dropwise and the reaction mixture was stirred for 30 min. A solution of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (325 mg, 1.59 mmol, 1.5 equiv) in anhydrous diethyl ether (1.5 mL) was added dropwise and the mixture was stirred for 1 h at –78 °C. Afterwards, the cooling bath was removed and the reaction mixture was heated under reflux for 17 h. The reaction mixture was cooled to 0 °C and 1.0 M aq. KH₂PO₄ (2.0 mL) was added slowly. After stirring for 10 min at room temperature, the phases were separated, and the aqueous phase was extracted with diethyl ether (4 × 20 mL). The combined organic phases were dried over anhydrous MgSO₄, filtered, and the solvent was removed in vacuo. The crude product was purified by column
chromatography (SiO₂, pentane/EtOAc 30:1) to afford secondary boronic ester 9 (213 mg, 0.87 mmol, 82%) as a colourless oil.

Rᵣ (pentane/EtOAc 30:1) 0.23.

¹H NMR (400 MHz, CDCl₃) δH ppm 7.29–7.19 (m, 4 H, Hₐr), 7.14 (m, 1 H, Hₐr), 2.23 (t, J = 7.8 Hz, 1 H, CHBpin), 1.89 (m, 1 H, CH/H), 1.68 (m, 1 H, CH/H), 1.22 (s, 6 H, 2xCH₃), 1.21 (s, 6 H, 2xCH₃), 0.92 (t, J = 7.3 Hz, 3 H, CH₃).

¹³C NMR (126 MHz, CDCl₃) δC ppm 143.3 (C), 128.4 (CH), 128.2 (CH), 125.1 (CH), 83.2 (OC(CH₃)₂), 34.3 (br.s, CHBpin), 25.8 (CH₂), 24.64 (CH₃), 24.56 (CH₃), 13.9 (CH₃).

¹¹B NMR (96 MHz, CDCl₃) δB ppm 32.9 (br.s).

The spectral data match those reported in literature.¹⁸

(S)-5,5-dimethyl-2-(1-phenylpropyl)-1,3,2-dioxaborinane ((S)-11)

A solution of propyl 2,4,6-triisopropylbenzoate¹⁷ (3.89 g, 13.4 mmol, 1.5 equiv) and (+)-spartiene (2.93 mL, 12.5 mmol, 1.4 equiv) in anhydrous diethyl ether (40 mL) was cooled to -78 °C. sBuLi (9.60 mL, 12.5 mmol, 1.4 equiv) was added dropwise and the reaction mixture was stirred for 5 hours. A solution of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (1.70 g, 8.90 mmol, 1 equiv) in anhydrous diethyl ether (9 mL) was added dropwise and the mixture was stirred for 1 h at -78 °C. Afterwards, the cooling bath was removed and the reaction mixture was heated under reflux for 17 h. The reaction mixture was cooled to room temperature diluted with Et₂O (100 mL) and quenched through addition of 1M HCl (40 mL). The organic layer was separated, dried over MgSO₄, filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography (SiO₂, pentane/Et₂O 2.5% then 10% with 1% Et₃N) to afford secondary boronic ester (S)-11 (633 mg, 2.76 mmol, 31%, 97:3 er) as a colourless oil.

N.B. (S)-11 Decomposes on silica gel so it is important to perform column chromatography quickly using 2.5% Et₂O to remove excess propyl 2,4,6-triisopropylbenzoate and then 10% Et₂O to elute (S)-11.

Rᵣ (pentane/Et₂O 9:1) 0.51.

¹H NMR (300 MHz, CDCl₃) δH ppm 7.28-7.16 (m, J = 14.0, 4H, Hₐr), 7.11 (m, 1H, Hₐr), 3.57 (s, 4H, 2xOCH₃), 2.09 (s, 1H, CH), 1.86 (dq, J = 14.1, 7.1, 1H, CH/H), 1.63 (dq, J=14.1, 7.1, 1H, CH/H), 0.89 (s, 6H, C(CH₃)₂), 0.88 (t, J = 7.3, 3H, CH₂CH₃).
\[ ^{13}C \text{ NMR} \quad (101 \text{ MHz, CDCl}_3) \ \delta_c \text{ ppm} \ 144.6 \text{ (C)}, 128.4 \text{ (CH)}, 128.2 \text{ (CH)}, 125.0 \text{ (CH)}, 72.2 \text{ (CH}_2), 31.8 \text{ (C)}, 25.3 \text{ (CH}_2), 21.9 \text{ (CH}_3), 14.2 \text{ (CH}_3) \].

\[ ^{11}B \text{ NMR} \quad (96 \text{ MHz, CDCl}_3) \ \delta_b \text{ ppm} \ 28.7 \text{ ppm} \]

\[ \nu_{\text{max}} \text{ (neat)} = 2959, 2931, 2871, 1601, 1476, 1416, 1327, 1284, 1252, 1166, 699 \text{ cm}^{-1} \].

\[ \text{HRMS (EI\textsuperscript{+}) calcd. for C}_{14}H_{21}BO_2 [M]\textsuperscript{+} 232.1635, \text{ found 232.1625}. \]

\[ [\alpha]_{D}^{22} +21 \text{ (c 1, CHCl}_3) \].

HPLC separation conditions: Chiralcel OD column, 2.0\% iPrOH in hexane, flow rate 0.7 mL/min, 20 °C; \( t_R \) 14.8 min for (R)-enantiomer (minor) and \( t_R \) 16.9 min for (S)-enantiomer (major).

\((R)-2-(1-(3-fluoro-4-methoxyphenyl)propyl)-5,5-dimethyl-1,3,2-dioxaborinane \ ((R)-40)\)

A solution of propyl 2,4,6-triisopropylbenzoate\textsuperscript{17} (3.60 g, 12.4 mmol, 1.8 equiv) and (−)-sparteine (2.72 mL, 11.6 mmol, 1.7 equiv) in anhydrous diethyl ether (50 mL) was cooled to −78 °C. sBuLi (9.00 mL, 11.6 mmol, 1.7 equiv) was added dropwise and the reaction mixture was stirred for 5 hours. A solution of 2-(3-fluoro-4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane \textsuperscript{38} (1.77 g, 7.02 mmol, 1 equiv) in anhydrous diethyl ether (8 mL) was added dropwise and the mixture was stirred for 1 h at −78 °C. Afterwards, the cooling bath was removed and the reaction mixture was heated under reflux for 17 h. The reaction mixture was cooled to room temperature diluted with Et\textsubscript{2}O (100 mL) and quenched through addition of 1M HCl (100 mL). The organic layer was separated, dried over MgSO\textsubscript{4}, filtered, and the solvent was removed \textit{in vacuo}. The crude product was purified by column chromatography (SiO\textsubscript{2}, pentane/Et\textsubscript{2}O 7:3 with 1% Et\textsubscript{3}N) to afford secondary boronic ester (R)-40 (907 mg, 3.24 mmol, 46%) as a colourless oil.

\( R_t \) (pentane/Et\textsubscript{2}O 7:3) 0.55.

\[ [\alpha]_{D}^{12} +10 \text{ (c 0.4, CHCl}_3) \].

\[ ^1H \text{ NMR} \quad (400 \text{ MHz, CDCl}_3) \ \delta_h \text{ ppm} \ 6.99 – 6.81 \text{ (m, 3H)}, 3.86 \text{ (s, 3H)}, 3.59 \text{ (s, 4H)}, 2.02 \text{ (t, J=7.8, 1H)}, 1.83 \text{ (m, 1H)}, 1.58 \text{ (m, 1H)}, 0.90 \text{ (s, 6H)}, 0.87 \text{ (t, J=7.3, 1H)}. \]
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ C ppm 152.39 (d, J=244.2, CF), 144.99 (d, J=10.9, COMe), 137.89 (d, J=6.0, C), 123.72 (d, J=3.3, CH), 115.85 (d, J=17.8, CH), 113.37 (d, J=2.4, CH), 72.23 (CH$_2$), 73.1 (CH$_2$), 56.42 (OCH$_3$), 31.75 (C), 25.40 (CH$_2$), 21.85 (CH$_3$), 13.99 (CH$_3$).

$^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ B ppm 28.9 ppm

$^{19}$F NMR (283 MHz, CDCl$_3$) $\delta$ F ppm $-136.04$ (dd, $J=12.9$, 7.4)

$\nu$$_{\text{max}}$ (neat) = 2960, 2933, 2873, 1734, 1583, 1514, 1477, 1418, 1255, 1219, 1172, 1127 cm$^{-1}$.

HRMS (EI$^+$) calcd. for C$_{15}$H$_{22}$O$_3$BF [M$^+$] 280.1646, found 280.1652.

HPLC separation conditions: Chiralpak IB column with guard, 3.0% iPrOH in hexane, flow rate 1 mL/min, 20 $^\circ$C; $t_R$ 24.4 min for (R)-enantiomer (major) and $t_R$ 26.1 min for (S)-enantiomer (minor).

**General procedure 2A (GP2A).** A solution of a primary carbamate (1.0 equiv) and TMEDA, (+)-sparteine or (−)-sparteine (1.3 equiv respectively) in anhydrous diethyl ether (0.33 M) was cooled to $-78$ $^\circ$C. sBuLi (1.3 equiv) was added dropwise and the reaction mixture was stirred at this temperature for 5 h. A solution of the boronic ester (1.5 equiv) in anhydrous diethyl ether (0.75 M) was added dropwise and the mixture was stirred for 2 h at $-78$ $^\circ$C. Afterwards, the mixture was allowed to warm to room temperature and the solvent was removed under reduced pressure. Then anhydrous CHCl$_3$ (0.20 M) was added and the reaction mixture was heated under reflux until disappearance of the boron ate complex (5–8 ppm) monitored by $^{11}$B NMR. The reaction mixture was cooled to 0 $^\circ$C and 1.0 M aq. KH$_2$PO$_4$ was added slowly. After stirring for 10 min at room temperature, the phases were separated, and the aqueous phase was extracted with diethyl ether (4 ×). The combined organic phases were dried over anhydrous MgSO$_4$, filtered, and the solvent was removed in vacuo. The crude product was purified by flash chromatography (SiO$_2$, pentane/EtOAc 30:1) to afford the boronic ester.

**General procedure 2B (GP2B).** Following GP2A, after warming to ambient temperature the solvent was not removed in vacuo. The ethereal solution was heated under reflux until disappearance of the boron ate complex (5–8 ppm) monitored by $^{11}$B NMR.

(S)-2-(1-(3-Fluoro-4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((S)-30)

S18
According to GP2A, propyl diisopropylcarbamate (28) (936 mg, 5.00 mmol, 1.0 equiv), (+)-sparteine (1.49 mL, 1.30 mmol, 1.3 equiv), tBuLi (5.00 mL, 1.30 mmol, 1.3 equiv), and 2-(3-fluoro-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29) (1.89 g, 1.50 mmol, 1.5 equiv) in 25 mL anhydrous solvent were heated under reflux for 15 h. After purification by column chromatography (SiO₂, pentane/EtOAc 30:1) secondary boronic ester (S)-30 was obtained (1.12 g, 3.81 mmol, 76%) as a colourless oil. Enantiomeric excess of the chiral boronic ester was determined by HPLC analysis of an aliquot oxidised according to GP3 (vide infra).

Rf (pentane/EtOAc 30:1) 0.16.

1H NMR (400 MHz, CDCl₃) δH ppm 6.96 (dd, J = 12.8, 1.8 Hz, 1 H, H₅), 6.92–6.82 (m, 2 H, H₅), 3.86 (s, 3 H, OCH₃), 2.15 (t, J = 7.9 Hz, 1 H, CHBpin), 1.82 (m, 1 H, CHH), 1.63 (m, 1 H, CHH), 1.22 (s, 6 H, 2×CH₃), 1.21 (s, 6 H, 2×CH₃), 0.90 (t, J = 7.3 Hz, 3 H, CH₃).

13C NMR (101 MHz, CDCl₃) δC ppm 152.3 (d, 1J = 244.4 Hz, CF), 145.1 (d, 2J = 10.8 Hz, COMe), 136.6 (d, 3J = 6.0 Hz, C), 123.8 (d, 4J = 3.3 Hz, CH), 115.9 (d, 5J = 18.0 Hz, CH), 113.3 (d, 6J = 2.2 Hz, CH), 83.3 (OC(CH₃)₂), 56.3 (OCH₃), 33.2 (br. CHBpin), 25.8 (CH₂), 24.64 (CH₃), 24.58 (CH₃), 13.7 (CH₃).

11B NMR (128 MHz, CDCl₃) δB ppm 33.3 (br. s).

19F NMR (376 MHz, CDCl₃) δF ppm –136.0 (dd, J = 12.1, 8.7 Hz, CF).

νmax (neat) = 2976, 1514, 1368, 1268, 1141, 1031, 968, 867, 760 cm⁻¹.


HRMS (CI⁺) calcd. for C₁₆H₂₅O₃₁₁BF [M+H]⁺ 295.1881, found 295.1877.

[α]D²⁺ +18.5 (c 1.13, CHCl₃, for 96% ee).

(R)-2-(1-(3-Fluoro-4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((R)-30)

According to GP2B, propyl diisopropylcarbamate (28) (94 mg, 0.50 mmol, 1.0 equiv), (–)-sparteine (149 µL, 0.65 mmol, 1.3 equiv), tBuLi (500 µL, 0.65 mmol, 1.3 equiv), and 2-(3-fluoro-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29) (189 mg, 0.75 mmol, 1.5 equiv) in 2.5 mL anhydrous diethyl ether were heated
under reflux for 40 h. After purification by flash chromatography (SiO₂, pentane/EtOAc 30:1) secondary boronic ester (R)-30 was obtained (108 mg, 0.37 mmol, 73%) as a colourless oil. Enantiomeric excess of the chiral boronic ester was determined by HPLC analysis of an aliquot oxidised according to GP3 (vide infra).

\[ \alpha^1_D = -18.0 \ (c \ 1.00, \ CHCl_3, \ for \ 96\% \ ee) \]

**General procedure 3 (GP3).** A solution of the secondary benzylic boronic ester (0.1 mmol, 1.0 equiv) in THF (4.0 mL) was cooled to 0 °C and a mixture of 2 M aq. NaOH (2.0 mL) and 30% H₂O₂ (1.0 mL) was added under vigorous stirring. The cooling bath was removed and the reaction mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo and the residue was portioned between H₂O (15 mL) and diethyl ether (15 mL). The phases were separated and the aqueous layer was re-extracted with diethyl ether (2 × 15 mL). The combined organic layers were washed with brine (25 mL), dried over anhydrous MgSO₄, filtered, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (SiO₂, pentane/EtOAc 4:1) to give the pure alcohol.

(S)-1-(3-Fluoro-4-methoxyphenyl)propan-1-ol ((S)-45)

According to GP3, oxidation of boronic ester (S)-30 (108 mg, 0.37 mmol, 1.0 equiv) afforded after purification by column chromatography (SiO₂, pentane/EtOAc 4:1) secondary benzylic alcohol (S)-45 (61 mg, 0.33 mmol, 90%) as a colourless oil.

**Rr** (pentane/EtOAc 4:1) 0.18.

**1H NMR** (400 MHz, CDCl₃) δH ppm 7.10 (dd, J = 12.2, 2.1 Hz, 1 H, HAr), 7.04 (m, 1 H, HAr), 6.93 (dd, J_HF = 8.4 Hz, J_HH = 8.4 Hz, 1 H, HAr), 4.55 (t, J = 6.6 Hz, 1 H, CHO), 3.89 (s, 3 H, OCH₃), 1.86–1.66 (m, 3 H, CH₂+OH), 0.91 (t, J = 7.4 Hz, 3 H, CH₃).

**13C NMR** (126 MHz, CDCl₃) δC ppm 152.3 (d, J = 245.1 Hz, CF), 146.8 (d, J = 11.4 Hz, COMe), 137.7 (d, J = 5.7 Hz, C), 121.6 (d, J = 3.8 Hz, CH), 113.7 (d, J = 18.1 Hz, CH), 113.1 (d, J = 1.9 Hz, CH), 75.1 (CHOH), 56.3 (OCH₃), 31.8 (CH₂), 10.0 (CH₃).

**19F NMR** (470 MHz, CDCl₃) δF ppm −135.0 (dd, J = 12.7, 8.5 Hz, CF).

ν_max (neat) = 3361, 2964, 1514, 1442, 1271, 1125, 1025, 871, 810, 760 cm⁻¹.

m/z (%) (Cl⁺) 185 ([M+H⁺], 34), 169 ([M−Me⁺], 17), 167 ([M−OH]⁺, 57), 155 ([M−Et⁺], 7), 152 (10), 139 (10).
HRMS (CI⁺) calcd. for C₁₀H₁₄O₂F [M+H]⁺ 185.0978, found 185.0981.

[α]₀⁺₂¹D ‒31.0 (c 1.47, CHCl₃, for 96% ee).

HPLC separation conditions: Chiralpak IB column with guard, 3.0% iPrOH in hexane, flow rate 0.7 mL/min, 20 °C; tᵣ 21.7 min for (R)-enantiomer (minor) and tᵣ 23.1 min for (S)-enantiomer (major).
e.r. = 97.9:2.1.

(R)-1-(3-Fluoro-4-methoxyphenyl)propan-1-ol ((R)-45)

According to GP3, oxidation of boronic ester (R)-30 (29 mg, 0.1 mmol, 1.0 equiv) afforded after purification by column chromatography (SiO₂, pentane/EtOAc 4:1) secondary benzylic alcohol (R)-45 (16 mg, 87 µmol, 87%) as a colourless oil.

[α]₀⁺₂³D +31.0 (c 1.00, CHCl₃, for 96% ee).

HPLC separation conditions: Chiralpak IB column with guard, 3.0% iPrOH in hexane, flow rate 0.7 mL/min, 20 °C; tᵣ 24.4 min for (R)-enantiomer (major) and tᵣ 26.1 min for (S)-enantiomer (minor).
e.r. = 98.2:1.8.

4,4,5,5-Tetramethyl-2-(pentan-3-yl)-1,3,2-dioxaborolane (10)

According to GP2B, propyl diisopropylcarbamate (22) (214 mg, 1.14 mmol, 1.0 equiv), TMEDA (221 µL, 1.49 mmol, 1.3 equiv), sBuLi (1.14 mL, 1.49 mmol, 1.3 equiv), and 2-ethyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane¹⁹ (267 mg, 1.71 mmol, 1.5 equiv) in anhydrous diethyl ether (6.0 mL) afforded
after purification by flash chromatography (SiO₂, pentane/EtOAc 30:1) boronic ester 10 (120 mg, 0.61 mmol, 53%) as a colourless oil.

**Rt** (pentane/EtOAc 30:1) 0.28.

**¹H NMR** (400 MHz, CDCl₃) δH ppm 1.47–1.37 (m, 4 H, 2×CH₂), 1.26 (s, 12 H, 4×CH₃), 0.91 (t, J = 7.4 Hz, 6 H, 2×CH₃), 0.85 (m, 1 H, CHBpin).

**¹³C NMR** (101 MHz, CDCl₃) δC ppm 82.8 (OCC(CH₃)₂), 27.8 (br., CHBpin), 24.8 (CH₃), 24.0 (CH₂), 17.3 (CH₃).

**¹¹B NMR** (96 MHz, CDCl₃) δB ppm 33.5 (br. s).

ν_max (neat) = 2959, 1463, 1370, 1142, 967, 856 cm⁻¹.

m/z (%) (EI⁺) 198 ([M]⁺, 21), 183 ([M‒Me]⁺, 68), 112 (25).

**HRMS** (EI⁺) calcd. for C₁₁H₂₃O₂B [M]⁺ 198.1791, found 198.1789.

**5,5-dimethyl-2-(pentan-3-yl)-1,3,2-dioxaborinane (12)**

3-Bromopentane (2.00 g, 13.2 mmol, 1 equiv) was added to a mixture of CuI (250 mg, 1.32 mmol, 0.1 equiv), PPh₃ (449 mg, 1.72 mmol, 0.13 equiv), LiOMe (1.50 g, 39.6 mmol, 2 equiv) and B₂neo₂ (4.49 g, 19.8 mmol, 1.5 equiv) in DMF (13 mL) and stirred at 40 °C for 48 h. The reaction mixture was cooled to room temperature, diluted with pentane (200 mL) and filtered through a short plug of celite. The filtrate was washed with brine (4 × 50 mL), dried over MgSO₄ and concentrated under mild vacuum ~20 mbar. The crude residue was purified by Kugelrohr distillation (1 mbar, 110 °C) to afford 12 as a colourless oil (1.00 g, 5.40 mmol, 41%).

**¹H NMR** (400 MHz, CDCl₃) δH ppm 3.62 (s, 4H, 2×OCH₂), 1.46-1.28 (m, 4H, 2×CH₂CH₃), 0.91 (t, J = 7.4, 6H, 2×CH₂CH₃), 0.68 (p, J=6.8, 1H, CH).

**¹³C NMR** (101 MHz, CDCl₃) δC ppm 71.8 (CH₂), 31.6 (C), 23.9 (CH₂), 21.9 (CH₃), 13.8 (CH₃).

**¹¹B NMR** (96 MHz, CDCl₃) δB ppm 30.0 (br. s).

ν_max (neat) = 2959, 2930, 2874, 1598, 1476, 1270, 1245, 1140, 699 cm⁻¹.

**HRMS** (EI⁺) calcd. for C₁₀H₂₀BO₂ [M–H]⁺ 183.1556, found 183.1559.
2.5 Preparation of tertiary boronic esters

**General procedure 4A (GP4A).** A solution of secondary benzylic carbamate (5 or 6) (1.00 mmol, 1.0 equiv) in anhydrous diethyl ether (3.0 mL) was cooled to -78 °C. sBuLi (1.00 mL, 1.30 mmol, 1.3 equiv) was added dropwise and the reaction mixture was stirred at this temperature for 1 h. A solution of the boronic ester (7, 8, 9, 10, 11 or 12) (1.50 mmol, 1.5 equiv) in anhydrous diethyl ether (1.5 mL) was added dropwise and the mixture was stirred for 2 h at -78 °C [ate complex formation]. Afterwards, the cooling bath was removed and the reaction mixture was stirred at ambient temperature until disappearance of the boronate complex (5‒8 ppm) monitored by $^{11}$B NMR. The reaction mixture was then cooled to 0 °C and 1.0 M aq. KH$_2$PO$_4$ (2.0 mL) was added slowly. After stirring for 10 min, the phases were separated, and the aqueous phase was re-extracted with diethyl ether (4 x 20 mL). The combined organic phases were dried over anhydrous MgSO$_4$, filtered, and the solvent was removed *in vacuo*. The crude product was purified by column chromatography (SiO$_2$, pentane/EtOAc 30:1) to afford the tertiary boronic ester. If the starting pinacol boronic ester was still present, the mixture was dissolved in diethyl ether, the organic phase was washed several times with 0.5 M aq. NaOH solution, and the solvent was removed *in vacuo* to give the pure tertiary pinacol boronic ester.

**General procedure 4B (GP4B).** Following GP4A, 2 h after addition of the boronic ester a 1.0 M solution of MgBr$_2$ in anhydrous MeOH (1.30 mL, 1.30 mmol, 1.3 equiv) was added slowly at -78 °C. After 5 min, the cooling bath was removed and stirring was continued at room temperature.

4,4,5,5-Tetramethyl-2-(3-methyl-2-phenylbutan-2-yl)-1,3,2-dioxaborolane (13)

According to GP4A, 1-phenylethyl diisopropylcarbamate (5) (249 mg, 1.00 mmol, 1.0 equiv), sBuLi (1.00 mL, 1.30 mmol, 1.3 equiv), and 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7) (255 mg, 1.50 mmol, 1.5 equiv) in anhydrous diethyl ether (4.5 mL) afforded after purification by flash chromatography (SiO$_2$, pentane/EtOAc 30:1) tertiary boronic ester 13 (222 mg, 0.81 mmol, 81%) as a colourless oil.

$R_t$ (pentane/EtOAc 30:1) 0.14.

$^1$H NMR (400 MHz, CDCl$_3$) δ$_H$ ppm 7.40–7.34 (m, 2 H, H$_{Ar}$), 7.30–7.24 (m, 2 H, H$_{Ar}$), 7.13 (m, 1 H, H$_{Ar}$), 2.37 (sept, $J$ = 6.8 Hz, 1 H, CH(CH$_3$)$_2$), 1.26 (s, 3 H, CH$_3$), 1.20 (s, 6 H, 2$x$CH$_3$), 1.17 (s, 6 H, 2$x$CH$_3$), 1.00 (d, $J$ = 6.8 Hz, 3 H, CH$_3$), 0.59 (d, $J$ = 6.8 Hz, 3 H, CH$_3$).
$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$C ppm 146.2 (C), 127.7 (CH), 127.3 (CH), 124.8 (CH), 83.1 (OC(CH$_3$)$_2$), 34.2 (CH), 24.6 (CH$_3$), 24.5 (CH$_3$), 20.3 (CH$_3$), 16.5 (CH$_3$), 13.9 (CH$_3$).

$^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$B ppm 33.0 (br. s).

The analytical data match those reported in literature.$^{11}$

4,4,5,5-Tetramethyl-2-(2-methyl-3-phenylpentan-3-yl)-1,3,2-dioxaborolane (14)

According to GP4B, 1-phenylpropyl diisopropylcarbamate (6) (263 mg, 1.00 mmol, 1.0 equiv), sBuLi (1.00 mL, 1.30 mmol, 1.3 equiv), 2-isopropyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7)$^{20}$ (255 mg, 1.50 mmol, 1.5 equiv), and MgBr$_2$ (1.30 mL, 1.0 M solution in anhydrous MeOH, 1.30 mmol, 1.3 equiv) in anhydrous diethyl ether (4.5 mL) furnished after purification by flash chromatography (SiO$_2$, pentane/EtOAc 30:1) tertiary boronic ester 14 (173 mg, 0.60 mmol, 60%) as a colourless oil.

$R_t$ (pentane/EtOAc 30:1) 0.29.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$H ppm 7.32–7.23 (m, 4 H, H$_{Ar}$), 7.15 (m, 1 H, H$_{Ar}$), 2.14 (sept, $J = 6.8$ Hz, 1 H, CH$_3$), 1.98–1.80 (m, 2 H, CH$_2$), 1.33 (s, 6 H, 2×CH$_3$), 1.32 (s, 6 H, 2×CH$_3$), 0.92 (d, $J = 6.8$ Hz, 3 H, CH$_3$), 0.77 (t, $J = 7.3$ Hz, 3 H, CH$_3$), 0.77 (d, $J = 6.8$ Hz, 3 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$C ppm 143.5 (C), 129.5 (CH), 127.3 (CH), 125.1 (CH), 83.2 (OC(CH$_3$)$_2$), 34.0 (CH), 28.1 (CH$_2$), 25.1 (CH$_3$), 24.9 (CH$_3$), 20.3 (CH$_3$), 18.5 (CH$_3$), 10.6 (CH$_3$).

$^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$B ppm 34.0 (br. s).

The spectral data correspond to the literature known compound.$^{11}$

2-(2,3-Diphenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15)

According to GP4B, carbamate 5 (249 mg, 1.00 mmol, 1.0 equiv), sBuLi (929 µL, 1.30 mmol, 1.3 equiv), 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (8) (348 mg, 1.50 mmol, 1.5 equiv), and MgBr$_2$ (1.30 mL, 1.0 M solution in anhydrous MeOH, 1.30 mmol, 1.3 equiv) in anhydrous diethyl ether (4.5 mL) gave after purification by flash chromatography (SiO$_2$, pentane/EtOAc 30:1) tertiary boronic ester 15 (312 mg, 0.93 mmol, 93%) as a colourless oil. The product was obtained as a mixture of diastereomers ($anti$:syn 86:14) [ratio of diastereomers for reaction without MgBr$_2$/MeOH ($anti$:syn 70:30)].
Analytical data of the major *anti* diastereomer.

**1H NMR** (500 MHz, CDCl$_3$) $\delta$ ppm 7.26–7.15 (m, 5 H, H$_{Ar}$), 7.08–7.00 (m, 3 H, H$_{Ar}$), 6.84–6.75 (m, 2 H, H$_{Ar}$), 3.47 (q, $J = 7.2$ Hz, 1 H, CH), 1.45 (d, $J = 7.2$ Hz, 3 H, CH$_3$), 1.29 (s, 6 H, 2×CH$_3$), 1.28 (s, 3 H, CH$_3$), 1.25 (s, 6 H, 2×CH$_3$).

**13C NMR** (126 MHz, CDCl$_3$) $\delta$ ppm 145.4 (C), 143.2 (C), 129.0 (CH), 127.6 (CH), 127.5 (CH), 126.8 (CH), 125.5 (CH), 125.2 (CH), 83.4 (OC(CH$_3$)$_2$), 47.0 (CH), 24.8 (CH$_3$), 24.6 (CH$_3$), 17.9 (CH$_3$), 15.1 (CH$_3$).

**11B NMR** (96 MHz, CDCl$_3$) $\delta$ ppm 33.0 (br. s).

$\nu_{\text{max}}$ (neat) = 2975, 1600, 1451, 1306, 1144, 964, 852, 770, 699 cm$^{-1}$.


**HRMS (CI$^+$)** calcd. for C$_{22}$H$_{30}$O$_2$B [M+H]$^+$ 337.2339, found 337.2338.

Analytical data of the minor *syn* diastereomer.

**1H NMR** (500 MHz, CDCl$_3$) $\delta$ ppm 7.40–7.28 (m, 4 H, H$_{Ar}$), 7.26–7.18 (m, 4 H, H$_{Ar}$), 7.13–7.08 (m, 2 H, H$_{Ar}$), 3.53 (q, $J = 7.3$ Hz, 1 H, CH), 1.29 (s, 3 H, CH$_3$), 1.18 (s, 6 H, 2×CH$_3$), 1.10 (s, 6 H, 2×CH$_3$), 1.06 (d, $J = 7.0$ Hz, 3 H, CH$_3$).

**13C NMR** (126 MHz, CDCl$_3$) $\delta$ ppm 144.6 (C), 144.4 (C), 129.6 (CH), 128.4 (CH), 127.5 (CH), 127.2 (CH), 125.9 (CH), 125.3 (CH), 83.3 (OC(CH$_3$)$_2$), 45.9 (CH), 24.8 (CH$_3$), 24.3 (CH$_3$), 16.5 (CH$_3$), 15.0 (CH$_3$).

2-(2,3-Diphenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16)

According to GP4B, carbamate 6 (263 mg, 1.00 mmol, 1.0 equiv), $\text{sBuLi}$ (1.00 mL, 1.30 mmol, 1.3 equiv), 4,4,5,5-tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane (8) (348 mg, 1.50 mmol, 1.5 equiv), and MgBr$_2$ (1.30 mL, 1.0 M solution in anhydrous MeOH, 1.30 mmol, 1.3 equiv) in anhydrous diethyl ether (4.5 mL) afforded after purification by column chromatography (SiO$_2$, pentane/EtOAc 30:1) tertiary boronic ester 16 (200 mg, 0.57 mmol, 57%) as a colourless oil. The product was obtained as a mixture of diastereomers (*anti*:syn 95:5) [ratio of diastereomers for reaction without MgBr$_2$/MeOH (*anti*:syn 44:56)].

$R_f$ (pentane/EtOAc 30:1) 0.31.
Analytical data for the major anti diastereomer.

**\(^1\)H NMR** (300 MHz, CDCl₃) δ H ppm 7.25–7.11 (m, 8 H, Hₐr), 7.00–6.93 (m, 2 H, Hₐr), 3.28 (q, J = 7.2 Hz, 1 H, CH), 1.96 (m, 1 H, CHH), 1.82 (m, 1 H, CHH), 1.30 (s, 6 H, 2xCH₃), 1.27 (s, 6 H, 2xCH₃), 1.21 (d, J = 7.2 Hz, 3 H, CH₃), 0.80 (t, J = 7.3 Hz, 3 H, CH₃).

**\(^13\)C NMR** (126 MHz, CDCl₃) δ C ppm 145.1 (C), 142.4 (C), 130.0 (CH), 129.5 (CH), 127.1 (CH), 127.0 (CH), 125.8 (CH), 125.3 (CH), 83.3 (OC(CH₃)₂), 47.2 (CH), 27.6 (CH₂), 25.5 (CH₃), 24.9 (CH₃), 16.8 (CH₃), 10.9 (CH₃).

**\(^{11}\)B NMR** (96 MHz, CDCl₃) δ B ppm 33.2 (br. s).

\(\nu\) max (neat) = 2976, 1451, 1371, 1303, 1255, 1143, 968, 909, 855, 731, 700 cm⁻¹.


HRMS (CI⁺) calcd. for C₂₃H₃₂O₂^{11}B [M+H]⁺ 351.2495, found 351.2502.

Analytical data for the minor syn diastereomer.

**\(^1\)H NMR** (500 MHz, CDCl₃) δ H ppm 7.25–7.06 (m, 6 H, Hₐr), 7.04–6.95 (m, 2 H, Hₐr), 6.57 (d, J = 7.6 Hz, 2 H, Hₐr), 3.26 (q, J = 7.3 Hz, 1 H, CH), 1.77 (q, J = 7.3 Hz, 2 H, CH₂), 1.37 (s, 6 H, 2xCH₃), 1.35 (s, 6 H, 2xCH₃), 1.26 (d, J = 7.0 Hz, 3 H, CH₃), 0.86 (t, J = 7.3 Hz, 3 H, CH₃).

**\(^13\)C NMR** (126 MHz, CDCl₃) δ C ppm 143.2 (C), 139.9 (C), 131.0 (CH), 129.7 (CH), 126.8 (CH), 126.7 (CH), 125.8 (CH), 125.5 (CH), 83.5 (OC(CH₃)₂), 46.5 (CH), 27.9 (CH₂), 25.1 (CH₃), 24.9 (CH₃), 20.0 (CH₃), 10.7 (CH₃).

(2S,3R)-2,3-Diphenylpentan-3-ol (2S,3R)-46

According to GP3, oxidation of 2-((2R,3S)-2,3-diphenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((2R,3S)-16) (110 mg, 0.31 mmol, 1.0 equiv) afforded after purification by column chromatography (SiO₂, pentane/EtOAc 19:1) tertiary benzylic alcohol (2S,3R)-46 (56 mg, 0.23 mmol, 74%) as a white solid.

**mp** 64–65 °C (diethyl ether).

Rt (pentane/EtOAc 19:1) 0.27.
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$H ppm 7.45–7.22 (m, 10 H, H$_{Ar}$), 3.13 (q, $J = 7.1$ Hz, 1 H, CH), 1.87 (dq, $J = 14.5$, 7.3 Hz, 1 H, CH/H), 1.54 (br. s, 1 H, OH), 1.41 (dq, $J = 14.5$, 7.3 Hz, 1 H, CH/H), 1.06 (d, $J = 7.1$ Hz, 3 H, CH$_3$), 0.56 (t, $J = 7.3$ Hz, 3 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$C ppm 144.5 (C), 143.0 (C), 129.3 (CH), 128.1 (CH), 127.9 (CH), 126.6 (CH), 126.2 (CH), 125.8 (CH), 78.9 (COH), 50.4 (CH), 34.3 (CH$_2$), 16.0 (CH$_3$), 7.8 (CH$_3$).

$\nu_{\text{max}}$ (neat) = 3582, 2970, 2917, 1493, 1451, 1148, 963, 903, 700 cm$^{-1}$.

$\text{m/z}$ (%) (ESI$^+$) 263 ([M+Na]$^+$, 100), 223 ([M‒OH]$^+$, 13), 167 (14), 105 ([PhC$_2$H$_4$]$^+$, 15).

HRMS (ESI$^+$) calcd. for C$_{17}$H$_{20}$ONa [M+Na]$^+$ 263.1406, found 263.1404.

$[\alpha]_{D}^{20}$ –21.0 ($c 1.00$, CHCl$_3$, for 99% ee).

SFC separation conditions: Chiralpak IA column, eluent: 90% CO$_2$, 5% hexane, 5% iPrOH, flow rate 4.0 mL/min, 39.8 °C, 123 bar; $t_R$ 3.96 min for (S,R)-enantiomer (major) and $t_R$ 5.67 min for (R,S)-enantiomer (minor).

e.r. = 99.8:0.2.

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### (2R,3R)-2,3-Diphenylpentan-3-ol ((2R,3R)-46)

According to GP3, oxidation of 2-((2S,3S)-2,3-diphenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((2S,3S)-16) (69 mg, 0.20 mmol, 1.0 equiv) afforded after purification by column chromatography (SiO$_2$, pentane/EtOAc 19:1) tertiary benzylic alcohol.
(2R,3R)-46 (44 mg, 0.18 mmol, 93%) as a colourless oil.

Rt (pentane/EtOAc 19:1) 0.20.

$^1$H NMR (400 MHz, CDCl$_3$) δH ppm 7.29–7.23 (m, 2 H, H$_{Ar}$), 7.22–7.12 (m, 6 H, H$_{Ar}$), 6.98–6.92 (m, 2 H, H$_{Ar}$), 3.18 (q, J = 7.1 Hz, 1 H, CH), 2.04 (dq, J = 14.4, 7.3 Hz, 1 H, CH$_2$), 1.92 (dq, J = 14.4, 7.3 Hz, 1 H, CH$_2$), 1.76 (br. s, 1 H, OH), 1.35 (d, J = 7.1 Hz, 3 H, CH$_3$), 0.73 (t, J = 7.3 Hz, 3 H, CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) δC ppm 144.1 (C), 142.4 (C), 129.3 (CH), 127.6 (CH), 127.5 (CH), 126.4 (CH), 126.3 (CH), 126.2 (CH), 79.1 (COH), 50.7 (CH), 30.8 (CH$_2$), 15.2 (CH$_3$), 7.9 (CH$_3$).

$\nu_{\text{max}}$ (neat) = 3570, 2971, 1493, 1451, 1137, 963, 910, 771, 754, 699 cm$^{-1}$.

$m/z$ (%) (ESI$^+$) 263 ([M+Na]$^+$, 100), 223 ([M–OH]$^+$, 17), 146 (19), 105 ([PhC$_2$H$_4$]$^+$, 15).

HRMS (ESI$^+$) calcd. for C$_{17}$H$_{20}$ONa [M+Na]$^+$ 263.1406, found 263.1407.

$[\alpha]_{D}^{21} +92.0$ (c 1.29, CHCl$_3$, for 99% ee).

SFC separation conditions: Chiralpak IA column, eluent: 95% CO$_2$, 4.5% hexane, 0.5% iPrOH, flow rate 4.0 mL/min, 41.5 °C, 124 bar; $t_R$ 10.51 min for (R,R)-enantiomer (major) and $t_R$ 11.84 min for (S,S)-enantiomer (minor).

e.r. = 99.9:0.1.

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According to GP4B, carbamate 5 (54 mg, 0.22 mmol, 1.0 equiv), sBuLi (217 µL, 0.28 mmol, 1.3 equiv), 4,4,5,5-tetramethyl-2-(1-phenylpropyl)-1,3,2-dioxaborolane (9) (80 mg, 0.33 mmol, 1.5 equiv), and MgBr₂ (282 µL, 1.0 M solution in anhydrous MeOH, 0.28 mmol, 1.3 equiv) in anhydrous diethyl ether (1.5 mL) afforded after purification by column chromatography (SiO₂, pentane/EtOAc 30:1) tertiary boronic ester 17 (51 mg, 0.15 mmol, 67%) as a colourless oil. The product was obtained as a mixture of diastereomers (anti:syn 70:30) [ratio of diastereomers for reaction without MgBr₂/MeOH (anti:syn 69:31)].

Rᵣ (pentane/EtOAc 30:1) 0.20.

Analytical data for the major anti diastereomer.

¹H NMR (400 MHz, CDCl₃) δ_H ppm 7.25–7.12 (m, 5 H, Hₐ), 7.05–7.01 (m, 3 H, Hₐ), 6.85–6.79 (m, 2 H, Hₐ), 3.11 (dd, J = 11.7, 2.7 Hz, 1 H, CH), 1.97 (m, 1 H, CH), 1.76 (m, 1 H, CH₃H), 1.29 (s, 3 H, CH₃), 1.28 (s, 6 H, 2×CH₃), 1.24 (s, 6 H, 2×CH₃), 0.76 (t, J = 7.2 Hz, 3 H, CH₃).

¹³C NMR (126 MHz, CDCl₃) δ_C ppm 145.4 (C), 140.9 (C), 129.6 (CH), 127.49 (CH), 127.48 (CH), 126.9 (CH), 125.5 (CH), 125.0 (CH), 83.4 (OC(CH₃)₂), 55.7 (CH), 25.4 (CH₃), 24.73 (CH₃), 24.67 (CH₃), 16.0 (CH₃), 13.2 (CH₃).

¹¹B NMR (96 MHz, CDCl₃) δ_B ppm 33.0 (br. s).

ν_max (neat) = 2975, 1600, 1451, 1306, 1144, 966, 849, 775, 699 cm⁻¹.

m/z (%) (ESI⁺) 373 ([M+Na]⁺, 100).

HRMS (ESI⁺) calcd. for C₂₃H₃₁O₂₁₁Na[M+Na]⁺ 373.2309, found 373.2297.

Analytical data for the minor syn diastereomer.

¹H NMR (400 MHz, CDCl₃) δ_H ppm 7.41–7.37 (m, 2 H, Hₐ), 7.32–7.28 (m, 2 H, Hₐ), 7.25–7.12 (m, 4 H, Hₐ), 7.09–7.05 (m, 2 H, Hₐ), 3.18 (dd, J = 12.0, 2.9 Hz, 1 H, CH), 1.60 (m, 1 H, CHH), 1.44 (m, 1 H, CHH), 1.32 (s, 3 H, CH₃), 1.14 (s, 6 H, 2×CH₃), 1.03 (s, 6 H, 2×CH₃), 0.58 (t, J = 7.3 Hz, 3 H, CH₃).

¹³C NMR (126 MHz, CDCl₃) δ_C ppm 144.7 (C), 142.1 (C), 130.5 (CH), 128.3 (CH), 127.5 (CH), 127.2 (CH), 125.9 (CH), 125.2 (CH), 83.2 (OC(CH₃)₂), 54.6 (CH), 24.7 (CH₃), 24.2 (CH₃), 22.7 (CH₂), 16.9 (CH₃), 12.8 (CH₃).
2-(2,3-diphenylpentan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (21)

According to GP4A, 1-phenylethyl diisopropylcarbamate 5 (125 mg, 0.5 mmol, 1 equiv), sBuLi (0.5 mL, 0.65 mmol, 1.3 equiv) and 5,5-dimethyl-2-(1-phenylpropyl)-1,3,2-dioxaborinane 11 (174 mg, 0.75 mmol, 1.5 equiv) in anhydrous diethyl ether (3.25 mL) afforded after purification by flash chromatography (SiO$_2$, pentane/Et$_2$O 9:1) tertiary boronic ester 21 (119 mg, 0.36 mmol, 71%) as a colourless oil. The product was obtained as a mixture of diastereomers (anti:syn 91:9).

R$_t$ (pentane/Et$_2$O 9:1) 0.50.

Analytical data of the major anti diastereomer.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$H ppm 7.24-7.09 (m, 4 H, H$_{Ar}$), 7.06-6.97 (m, 4 H, H$_{Ar}$), 6.84-6.75 (m, 2 H, H$_{Ar}$), 3.66 (d, J = 11.2, 2H, 2xOCHH), 3.62 (d, J = 11.2, 2H, 2xOCHH), 3.16 (dd, J = 11.7, 2.8, 1H, CH), 1.93 (ddq, J=14.2, 11.7, 7.3, 1H, CHH), 1.75 (ddq, J=14.2, 7.3, 2.8, 1H, CHH), 1.23 (s, 3H, CH$_3$), 0.92 (s, 6H, C(CH$_3$)$_2$), 0.74 (t, J = 7.3, 3H, CH$_2$CH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$C ppm 146.4 (C), 141.3 (C), 129.7 (CH), 127.5 (CH), 127.3 (CH), 126.8 (CH), 125.3 (CH), 124.8 (CH), 72.1 (CH$_2$), 55.2 (CH), 31.5 (C), 25.6 (CH$_2$), 22.1f (CH$_3$), 15.7 (CH$_3$), 13.3 (CH$_3$).

$^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$B ppm 28.7 (br. s).

Analytical data of the minor syn diastereomer.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$H ppm 7.42-7.09 (m, 10 H, H$_{Ar}$), 3.49 (d, J=11.0, 2H), 3.44 (d, J=11.0, 2H), 3.25 (dd, J=12.0, 2.9, 1H), 1.58 (ddq, J=14.7, 12.0, 7.2, 1H), 1.39 (ddq, J=14.7, 7.2, 2.9, 1H), 1.27 (s, 3H), 0.73 (s, 6H), 0.57 (t, J=7.2, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$C ppm 146.0 (C), 142.8 (C), 130.4 (CH), 128.1 (CH), 127.5 (CH), 127.3 (CH), 125.7 (CH), 124.9 (CH), 71.9 (CH$_2$), 53.9 (CH), 31.4 (C), 22.6 (CH$_2$), 21.8 (CH$_3$), 16.7 (CH$_3$), 13.0 (CH$_3$).

2-((2S,3R)-2,3-diphenylpentan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane ((2S,3R)-21)

According to GP4A, (S)-1-phenylethyl diisopropylcarbamate (S)-5 (107 mg, 0.43 mmol, 1 equiv), sBuLi (0.43 mL, 0.56 mmol, 1.3 equiv) and (S)-5,5-dimethyl-2-(1-phenylpropyl)-1,3,2-dioxaborinane (150 mg, 0.75 mmol, 1.5 equiv) in anhydrous diethyl ether (2.80 mL) afforded after purification by flash chromatography (SiO$_2$, pentane/Et$_2$O 9:1) tertiary boronic ester (2S,3R)-21 (100
mg, 0.30 mmol, 69%, >99:1 dr, >99:1 er) as a white solid.

\( R_f \) (pentane/Et_{2}O 9:1) 0.50.

\( mp \) 139–140 °C (pentane/Et_{2}O).

\( [\alpha]_{D}^{22} = -115 \) (c 1, CHCl_{3}).

\(^1\)H NMR (400 MHz, CDCl_{3}) \( \delta_{H} \) ppm 7.24-7.09 (m, 4 H, H_{Ar}), 7.06-6.97 (m, 4 H, H_{Ar}), 6.84-6.75 (m, 2 H, H_{Ar}), 3.66 (d, \( J = 11.2 \), 2H, 2xOCHH), 3.62 (d, \( J = 11.2 \), 2H, 2xOCHH), 3.16 (dd, \( J = 11.7 \), 2.8, 1H, CH), 1.93 (ddq, \( J = 14.2, 11.7 \), 7.3, 1H, CHH), 1.75 (dqd, \( J = 14.2, 7.3 \), 2.8, 1H, CHH), 1.23 (s, 3H, CH3), 0.92 (s, 6H, C(CH3)_{2}), 0.74 (t, \( J = 7.3 \), 3H, CH2CH3).

\(^{13}\)C NMR (101 MHz, CDCl_{3}) \( \delta_{C} \) ppm 146.4 (C), 141.3 (C), 129.7 (CH), 127.5 (CH), 127.3 (CH), 126.8 (CH), 125.3 (CH), 124.8 (CH), 72.1 (CH2), 55.2 (CH), 31.5 (C), 25.6 (CH2), 22.1 (CH3), 15.7 (CH3), 13.3 (CH3).

\( \nu_{\text{max}} \) (neat) = 3027, 2962, 2932, 2873, 1600, 1476, 1413, 1375, 1266, 1246, 1126, 700 cm\(^{-1}\).

HRMS (ESI) calcd. for C_{22}H_{29}BO_{2}Na[M+Na]^+ 359.2157, found 359.2153.

HPLC separation conditions: Chiralpak IA column with guard, 5.0% iPrOH in hexane, flow rate 1 mL/min, 20 °C; Major diastereoisomer: \( t_R \) 6.5 min for (S,R)-enantiomer (major) 7.2 min for (R,S)-enantiomer (minor). Minor diastereoisomer: \( t_R \) 6.8 min for (S,S)-enantiomer, 7.8 min for (R,R)-enantiomer.

2-((2R,3R)-2,3-diphenylpentan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane ((2R,3R)-21)

According to GP4A, (R)-1-phenylethyl diisopropylcarbamate (R)-5 (107 mg, 0.43 mmol, 1 equiv), sBuLi (0.43 mL, 0.56 mmol, 1.3 equiv) and (S)-5,5-dimethyl-2-(1-phenylpropyl)-1,3,2-dioxaborinane (150 mg, 0.75 mmol, 1.5 equiv) in anhydrous diethyl ether (2.80 mL) afforded after purification by flash chromatography (SiO\(_2\), pentane/Et_{2}O 9:1) tertiary boronic ester xx (90 mg, 0.27 mmol, 63%, 93:7 dr, >99:1 er) as a viscous oil.

\( R_f \) (pentane/Et_{2}O 9:1) 0.50.

\( [\alpha]_{D}^{22} = -24 \) (c 1, CHCl_{3}).
$^1$H NMR (400 MHz, CDCl$_3$) $\delta$H ppm 7.42-7.09 (m, 10 H, HAr), 3.49 (d, J=11.0, 2H), 3.44 (d, J=11.0, 2H), 3.25 (dd, J=12.0, 2.9, 1H), 1.58 (ddq, J=14.7, 12.0, 7.2, 1H), 1.39 (ddq, J=14.7, 7.2, 2.9, 1H), 1.27 (s, 3H), 0.73 (s, 6H), 0.57 (t, J=7.2, 1H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$C ppm 146.0 (C), 142.8 (C), 130.4 (CH), 128.1 (CH), 127.5 (CH), 127.3 (CH), 125.7 (CH), 124.9 (CH), 71.9 (CH$_2$), 53.9 (CH), 31.4 (C), 22.6 (CH$_2$), 21.8 (CH$_3$), 16.7 (CH$_3$), 13.0 (CH$_3$).

$\nu_{\text{max}}$ (neat) = 3028, 2960, 2932, 2872, 1599, 1476, 1414, 1266, 1248, 1136, 701 cm$^{-1}$.

HRMS (ESI) calcd. for C$_{22}$H$_{29}$BO$_2$Na[M+Na]$^+$ 359.2157, found 359.2153.

HPLC separation conditions: Chiralpak IA column with guard, 5.0% iPrOH in hexane, flow rate 1 mL/min, 20 °C; Major diasteroisomer: $t_R$ 6.8 min for (S,S)-enantiomer (minor) 7.8 min for (R,R)-enantiomer (major). Minor diasteroisomer: $t_R$ 6.5 min for (S,R)-enantiomer 7.2 min for (R,S)-enantiomer.

2-(3,4-Diphenylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18)

According to GP4B, 1-phenylpropyl diisopropylcarbamate (6) (51 mg, 0.20 mmol, 1.0 equiv), sBuLi (195 µL, 0.25 mmol, 1.3 equiv), 4,4,5,5-tetramethyl-2-(1-phenylpropyl)-1,3,2-dioxaborolane (9) (72 mg, 0.29 mmol, 1.5 equiv), and MgBr$_2$ (253 µL, 1.0 M solution in anhydrous MeOH, 0.25 mmol, 1.3 equiv) in anhydrous diethyl ether (1.5 mL) afforded after purification by column chromatography (SiO$_2$, pentane/EtOAc 30:1) tertiary boronic ester 18 (22 mg, 62 µmol, 32%) as a colourless oil as an inseparable mixture with starting material 9. The product was obtained as a mixture of diastereomers (anti:syn 65:35) [ratio of diastereomers for reaction without MgBr$_2$/MeOH (anti:syn 43:57)].

R$_f$ (pentane/EtOAc 30:1) 0.18.

2-(3,4-diphenylhexan-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane 22

According to GP4A, 1-phenylpropyl diisopropylcarbamate 6 (132 mg, 0.5 mmol, 1 equiv), sBuLi (0.5 mL, 0.65 mmol, 1.3 equiv) and 5,5-dimethyl-2-(1-phenylpropyl)-1,3,2-dioxaborinane (174 mg, 0.75 mmol, 1.5 equiv) in anhydrous diethyl ether (3.25 mL) afforded after purification by flash
chromatography (SiO₂, pentane/Et₂O 9:1) tertiary boronic ester 22 (126 mg, 0.36 mmol, 72%) as a colourless oil. The product was obtained as a mixture of diastereomers (anti:syn 83:17).

Rᵣ (pentane/Et₂O 9:1) 0.50.

Analytical data of the major anti diastereomer.

¹H NMR (400 MHz, CDCl₃) δH ppm 7.30 – 6.97 (m, 10H, Hₐₐ), 3.62 (s, 4H, 2×OCH₂), 2.94 (dd, J = 10.9, 4.0, 1H, CH), 1.78 – 1.58 (m, 4H, 2×CH₂), 1.00 (s, 6H, C(CH₃)₂), 0.60 (t, J = 7.4, 1H, CH₂CH₃), 0.59 (t, J = 7.4, 1H, CH₂CH₃).

¹³C NMR (101 MHz, CDCl₃) δC ppm 144.7 (C), 143.3 (C), 129.8 (CH), 129.5 (CH), 127.4 (CH), 127.3 (CH), 125.8 (CH), 125.0 (CH), 71.8 (CH₂), 56.5 (CH), 31.2 (C), 30.0 (CH₂), 23.9 (CH₂), 22.3 (CH₃), 10.9 (CH₃).

¹¹B NMR (96 MHz, CDCl₃) δB ppm 30.0 (br. s).

Analytical data of the minor syn diastereomer.

¹H NMR (400 MHz, CDCl₃) δH ppm 7.25 – 6.96 (m, 8H), 6.47 (d, J = 7.1, 2H), 3.68 (s, 4H), 2.96 (dd, J = 12.1, 2.8, 0H), 1.82 (ddq, J = 14.7, 7.2, 2.8, 1H), 1.64 (t, J = 7.3, 2H), 1.52 (ddq, J = 14.7, 12.1, 7.2, 1H), 1.05 (s, 6H), 0.83 (t, J = 7.4, 3H), 0.59 (t, J = 7.2, 3H).

¹³C NMR (101 MHz, CDCl₃) δC ppm 141.5 (C), 141.3 (C), 131.0 (CH), 130.3 (CH), 126.7 (CH), 126.58 (CH), 125.62 (CH), 125.3 (CH), 72.1 (CH₂), 54.6 (CH), 31.5 (C), 28.0 (CH₂), 27.8 (CH₂), 22.3 (CH₃), 13.1 (CH₃), 10.9 (CH₃).

2-((3S,4R)-3,4-diphenylhexan-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane ((3S,4R)-22)

According to GP4A, (S)-1-phenylpropyl diisopropylcarbamate (S)-6 (113 mg, 0.43 mmol, 1 eq.), sBuLi (0.43 mL, 0.56 mmol, 1.3 eq.) and (S)-5,5-dimethyl-2-(1-phenylpropyl)-1,3,2-dioxaborinane (150 mg, 0.65 mmol, 1.5 eq.) in anhydrous diethyl ether (2.80 mL) afforded after purification by flash chromatography (SiO₂, pentane/Et₂O 9:1) tertiary boronic ester (S,R)-22 (103 mg, 0.30 mmol, 69%, 98:2 dr, >99:1 er) as a colourless oil.

Rᵣ (pentane/Et₂O 9:1) 0.50.

[α]²⁺₂ +2 (c 1, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δH ppm 7.30 – 6.97 (m, 10H, Hₐₐ), 3.62 (s, 4H, 2×OCH₂), 2.94 (dd, J = 10.9, 4.0, 1H, CH), 1.78 – 1.58 (m, 4H, 2×CH₂), 1.00 (s, 6H, C(CH₃)₂), 0.60 (t, J = 7.4, 1H, CH₂CH₃), 0.59 (t, J = 7.4, 1H, CH₂CH₃).

S33
$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 144.7 (C), 143.3 (C), 129.8 (CH), 129.5 (CH), 127.4 (CH), 127.3 (CH), 125.8 (CH), 125.0 (CH), 71.8 (CH$_2$), 56.5 (CH), 31.2 (C), 30.0 (CH$_3$), 23.9 (CH$_2$), 22.3 (CH$_3$), 13.1 (CH$_3$), 10.9 (CH$_3$).

ν$_{\text{max}}$ (neat) = 3025, 2962, 2874, 1600, 1475, 1412, 1245, 756, 701 cm$^{-1}$.

HRMS (ESI) calcd. for C$_{23}$H$_{31}$BO$_2$Na$[M+Na]^+$ 373.2313, found 373.2325.

HPLC separation conditions: Chiralpak IA column with guard, 2.0% iPrOH in hexane, flow rate 1 mL/min, 20 °C; Major diasteroisomer: $t_R$ 6.4 min for (S,R)-enantiomer (major) 9.5 min for (R,S)-enantiomer (minor). Minor diasteroisomer: $t_R$ 7.9 min for (S,S)-enantiomer and 8.8 min for (R,R)-enantiomer.

2-((3R,4R)-3,4-diphenylhexan-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane ((3R,4R)-22)

According to GP4A, (R)-1-phenylpropyl diisopropylcarbamate (R)-5 (113 mg, 0.43 mmol, 1 eq.), sBuLi (0.43 mL, 0.56 mmol, 1.3 eq.) and (S)-5,5-dimethyl-2-(1-phenylpropyl)-1,3,2-dioxaborinane (150 mg, 0.65 mmol, 1.5 eq.) in anhydrous diethyl ether (2.80 mL) afforded after purification by flash chromatography (SiO$_2$, pentane/Et$_2$O 9:1) tertiary boronic ester (R,R)-22 (95 mg, 0.27 mmol, 63%, 90:10 dr, >99:1 er) as a colourless oil.

R$_R$ (pentane/Et$_2$O 9:1) 0.50.

$^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.25 – 6.96 (m, 8H), 6.47 (d, $J = 7.1$, 2H), 3.68 (s, 4H), 2.96 (dd, $J = 12.1$, 2.8, 0H), 1.82 (dq, $J = 14.7$, 7.2, 2.8, 1H), 1.64 (t, $J = 7.5$, 2H), 1.52 (ddq, $J = 14.7$, 12.1, 7.2, 1H), 1.05 (s, 6H), 0.83 (t, $J = 7.4$, 3H), 0.59 (t, $J = 7.2$, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 141.5 (C), 141.3 (C), 131.0 (CH), 130.3 (CH), 126.7 (CH), 126.58 (CH), 125.62 (CH), 125.3 (CH), 72.1 (CH$_2$), 54.6 (CH), 31.5 (C), 28.0 (CH$_2$), 27.8 (CH$_2$), 22.3 (CH$_3$), 13.1 (CH$_3$), 10.8 (CH$_3$).

ν$_{\text{max}}$ (neat) = 3025, 2961, 2932, 2873, 1600, 1476, 1412, 1243, 1137, 701 cm$^{-1}$.

HRMS (ESI) calcd. for C$_{23}$H$_{31}$BO$_2$Na$[M+Na]^+$ 373.2313, found 373.2325.

[α]$_b$$^2$+55 (c 1, CHCl$_3$).
HPLC separation conditions: Chiralpak IA column with guard, 2.0% iPrOH in hexane, flow rate 1 mL/min, 20 °C; Major diastereoisomer: $t_R$ 7.9 min for (S,S)-enantiomer (minor) and 8.8 min for (R,R)-enantiomer (major). Minor diastereoisomer: $t_R$ 6.4 min for (S,R)-enantiomer, 9.5 min for (R,S)-enantiomer.

According to GP4B, 1-phenylethyl diisopropylcarbamate (5) (50 mg, 0.20 mmol, 1.0 equiv), sBuLi (200 µL, 0.26 mmol, 1.3 equiv), and 4,4,5,5-tetramethyl-2-(pentan-3-yl)-1,3,2-dioxaborolane (10) (59 mg, 0.30 mmol, 1.5 equiv), in anhydrous diethyl ether (1.5 mL) afforded after purification by column chromatography (SiO$_2$, pentane/EtOAc 30:1) tertiary boronic ester 19 (20 mg, 66 µmol, 33%) as a colourless oil. Before purification the yield of 19 in the crude reaction mixture was determined by $^1$H NMR spectroscopy with 1,3,5-trimethoxybenzene as internal standard and was measured to be 41%.

$R_t$ (pentane/EtOAc 30:1) 0.27.

$^1$H NMR (500 MHz, CDCl$_3$) δ$_H$ ppm 7.43–7.38 (m, 2 H, H$_{Ar}$), 7.29–7.24 (m, 2 H, H$_{Ar}$), 7.12 (tt, $J = 7.3$, 1.2 Hz, 1 H, H$_{Ar}$), 1.89 (tt, $J = 7.7$, 3.7 Hz, 1 H, CH(CHO)$_2$), 1.43–1.32 (m, 2 H, CH$_2$), 1.26 (s, 3 H, CH$_3$), 1.16 (s, 6 H, 2xCH$_3$), 1.13 (s, 6 H, 2xCH$_3$), 1.10 (m, 1 H, CH$_2$H), 1.05 (t, $J = 7.4$ Hz, 3 H, CH$_3$), 0.98 (m, 1 H, CH$_2$H), 0.69 (t, $J = 7.4$ Hz, 3 H, CH$_3$).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ$_C$ ppm 146.2 (C), 127.7 (CH), 127.5 (CH), 124.7 (CH), 83.1 (OC(CHO)$_2$), 48.1 (CH), 28.1 (CH$_2$), 24.5 (CH$_3$), 24.4 (CH$_3$), 23.3 (CH$_2$), 14.7 (CH$_3$), 14.5 (CH$_3$), 14.3 (CH$_3$).

$^{11}$B NMR (96 MHz, CDCl$_3$) δ$_B$ ppm 33.1 (br. s).

$\nu_{\text{max}}$ (neat) = 2962, 1464, 1334, 1305, 1135, 965, 849, 699 cm$^{-1}$.

$m/z$ (%) (ESI$^+$): 325 ([M+Na]$^+$, 100), 320 ([M+NH$_4$]$^+$, 12), 303 ([M+H]$^+$, 13).

HRMS (ESI$^+$) calcd. for C$_{19}$H$_{31}$O$_2$BNa [M+Na]$^+$ 325.2309, found 325.2319.

2-(3-ethyl-2-phenylpentan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (23)
According to GP4A, 1-phenylethyl diisopropylcarbamate 5 (125 mg, 0.5 mmol, 1 equiv), sBuLi (0.5 mL, 0.65 mmol, 1.3 equiv) and 5,5-dimethyl-2-(pentan-3-yl)-1,3,2-dioxaborinane (138 mg, 0.75 mmol, 1.5 equiv) in anhydrous diethyl ether (3.25 mL) afforded after purification by flash chromatography (SiO₂, pentane/Et₂O 9:1) tertiary boronic ester 23 (118 mg, 0.41 mmol, 82%) as a colourless oil.

Rᵣ (pentane/Et₂O 9:1) 0.50.

¹H NMR (400 MHz, CDCl₃) δH ppm 7.39 (d, J = 7.3, 2H, H₆), 7.24 (t, J = 7.7, 2H, H₆), 7.09 (t, J = 7.3, 1H, H₆), 3.55 (d, J = 11.4, 2H, 2xOCH₂), 3.52 (d, J = 11.4, 2H, 2xOCH₂), 1.93 (tt, J = 7.7, 3.7, 1H, CH), 1.45 – 1.30 (m, 2H, 2xCH₂H₃), 1.18 (s, 3H), 0.74 (t, J = 7.5, 3H, CH₂CH₃), 0.79 (s, 6H, C(CH₃)₂), 0.70 (t, J = 7.5, 3H, CH₂CH₃).

¹³C NMR (101 MHz, CDCl₃) δC ppm 147.5 (C), 127.7 (CH), 127.3 (CH), 124.5 (CH), 72.0 (CH₂), 47.5 (CH), 31.5 (C), 28.1 (CH₂), 23.4 (CH₂), 21.8 (CH₃), 14.5 (CH₃), 14.4 (CH₃), 14.2 (CH₃).

¹¹B NMR (96 MHz, CDCl₃) δB ppm 29.9 (br. s).

νₘₐₓ (neat) = 2959, 2930, 2874, 1598, 1476, 1270, 1245, 1140, 699 cm⁻¹.

HRMS (ESI) calcd. for C₁₈H₂₉BO₂Na [M+Na]⁺ 311.2156, found 311.2154.

2-(4-ethyl-3-phenylhexan-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane 24

According to GP4A, 1-phenylpropyl diisopropylcarbamate 6 (125 mg, 0.5 mmol, 1 equiv), sBuLi (0.5 mL, 0.65 mmol, 1.3 equiv) and 5,5-dimethyl-2-(pentan-3-yl)-1,3,2-dioxaborinane (138 mg, 0.75 mmol, 1.5 equiv) in anhydrous diethyl ether (3.25 mL) afforded after purification by flash chromatography (SiO₂, pentane/Et₂O 9:1) tertiary boronic ester 24 (125 mg, 0.42 mmol, 83%) as a colourless oil.

Rᵣ (pentane/Et₂O 9:1) 0.50.

¹H NMR (400 MHz, CDCl₃) δH ppm 7.31 – 7.20 (m, 4H, H₆), 7.15 – 7.06 (m, 1H, H₆), 3.61 (s, 4H, 2xOCH₂), 1.89 (dq, J = 14.9, 7.6, 1H, CH₂H₃), 1.81 (dq, J = 14.9, 7.6, 1H, CH₂H₃), 1.65 (app. td, J = 7.9, 3.9, 1H, CH), 1.55 (m, 1H, CH₂H₃), 1.44 (dt, J = 14.9, 7.5, 2.9, 1H, CH₂H₃), 1.13 (dq, J = 14.6, 7.4, 1H, CH₂H₃), 0.96 (s, 6H, C(CH₃)₂), 0.91 (t, J = 7.5, 3H, CH₂CH₃), 0.86 (t, J = 7.5, 3H, CH₂CH₃), 0.74 (t, J = 7.4, 3H, CH₂CH₃).
$^{13}$C NMR (101 MHz, CDCl$_3$) δ$_C$ ppm 145.4 (C), 129.2 (CH), 127.3 (CH), 124.7 (CH), 71.9 (CH$_2$), 48.3 (CH), 31.3 (C), 27.6 (CH$_2$), 26.6 (CH$_2$), 25.7 (CH$_2$), 22.2 (CH$_3$), 14.8 (CH$_3$), 14.5 (CH$_3$), 10.8 (CH$_3$).

$^{11}$B NMR (96 MHz, CDCl$_3$) δ$_B$ ppm 29.9 (br. s).

ν$_{\text{max}}$ (neat) = 2959, 2931, 2874, 1599, 1475, 1410, 1242, 1147, 699 cm$^{-1}$.

HRMS (ESI) calcd. for C$_{19}$H$_{31}$BO$_2$Na[M+Na]$^+$ 325.2313, found 325.2309.

(S)-2-(3-ethyl-2-phenylpentan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (S)-24

According to GP4A, (S)-1-phenylpropyl diisopropylcarbamate (S)-6 (125 mg, 0.5 mmol, 1 eq.), sBuLi (0.5 mL, 0.65 mmol, 1.3 eq.) and 5,5-dimethyl-2-(pentan-3-yl)-1,3,2-dioxaborinane (138 mg, 0.75 mmol, 1.5 eq.) in anhydrous diethyl ether (3.25 mL) afforded after purification by flash chromatography (SiO$_2$, pentane/Et$_2$O 9:1) tertiary boronic ester (S)-24 (121 mg, 0.40 mmol, 80%) as a colourless oil.

[α]$^D_{12}$+2 (c 1, CHCl$_3$).

HPLC separation conditions: Chiralpak IA column with guard, 2.0% iPrOH in hexane, flow rate 1 mL/min, 20 °C; $t_R$ 6.6 min for (S)-enantiomer (major) and 7.3 min for (R)-enantiomer (minor).

(R)-2-(3-ethyl-2-phenylpentan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (R)-24

According to GP4A, (R)-1-phenylpropyl diisopropylcarbamate (R)-6 (125 mg, 0.5 mmol, 1 eq.), sBuLi (0.5 mL, 0.65 mmol, 1.3 eq.) and 5,5-dimethyl-2-(pentan-3-yl)-1,3,2-dioxaborinane (138 mg, 0.75 mmol, 1.5 eq.) in anhydrous diethyl ether (3.25 mL) afforded after purification by flash chromatography (SiO$_2$, pentane/Et$_2$O 9:1) tertiary boronic ester (R)-24 (120 mg, 0.40 mmol, 79%) as a colourless oil.

[α]$^D_{12}$−2 (c 1, CHCl$_3$).
HPLC separation conditions: Chiralpak IA column with guard, 2.0% iPrOH in hexane, flow rate 1 mL/min, 20 °C; \( t_R \) 6.6 min for (S)-enantiomer (major) and 7.3 min for (R)-enantiomer (minor).

2.6 Synthesis of bifluranol

2-((2S,3R)-3-(3-Fluoro-4-methoxyphenyl)-2-(4-methoxyphenyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (33)

![HPLC chromatogram](image1)

A solution of (S)-1-(4-methoxyphenyl)ethyl diisopropylcarbamate ((S)-32) (92 mg, 0.33 mmol, 1.0 equiv) and TMEDA (64 µL, 0.43 mmol, 1.3 equiv) in anhydrous diethyl ether (2.0 mL) was cooled to −78 °C. \( \text{sBuLi} \) (330 µL, 0.43 mmol, 1.3 equiv) was added dropwise and the reaction mixture was stirred at this temperature for 1 h. A solution of (S)-2-(1-(3-fluoro-4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((S)-30) (145 mg, 0.49 mmol, 1.5 equiv) in anhydrous diethyl ether (1.0 mL) was added dropwise and the mixture was stirred for 2 h at −78 °C. The cooling bath was removed and stirring was continued at room temperature for 14 h. The reaction mixture was cooled to 0 °C and 1.0 M aqueous KH\(_2\)PO\(_4\) (2.0 mL) was added slowly. After stirring for 10 min at room temperature, the phases were separated, and the aqueous phase was extracted with diethyl ether (4 × 10 mL). The combined organic phases were dried over anhydrous MgSO\(_4\), filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography (SiO\(_2\), pentane/EtOAc 30:1) to afford tertiary boronic ester 33 (134 mg, 0.31 mmol, 95%) as a white solid. The ratio of diastereomers was measured by \(^1\)H NMR and accounted to >20:1 (anti:syn).

\textbf{mp} 108–109 °C (CHCl\(_3\)).

\textbf{R}t (pentane/EtOAc 30:1) 0.07.

\(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) ppm 7.10 (AA’BB’, \( J = 8.9 \) Hz, 2 H, H\(_{A'}\)), 6.73 (AA’BB’, \( J = 8.9 \) Hz 2 H, H\(_{A'}\)), 6.67–6.60 (m, 2 H, H\(_{A'}\)), 6.45 (d, \( J = 8.2 \) Hz, 1 H, H\(_D\)), 3.80 (s, 3 H, OCH\(_3\)), 3.76 (s, 3 H, OCH\(_3\)), 2.98 (dd, \( J = 11.7, 2.6 \) Hz, 1 H, CH), 1.82 (m, 1 H, CHH), 1.71
(m, 1 H, CHH), 1.27 (s, 6 H, 2×CH3), 1.24 (s, 3 H, CH3), 1.22 (s, 6 H, 2×CH3), 0.74 (t, 
J = 7.2 Hz, 3 H, CH3).

13C NMR (126 MHz, CDCl3) δC ppm 157.2 (COMe), 151.5 (d, 1J = 244.4 Hz, CF), 145.2 (d, 
2J = 10.8 Hz, COMe), 137.1 (C), 134.5 (d, 3J = 5.7 Hz, C), 128.4 (CH), 125.5 (d, 3J = 3.8 Hz, 
CH), 116.7 (d, 2J = 17.2 Hz, CH), 113.0 (CH), 111.8 (CH), 83.4 (OC(CH3)2), 56.1 (OCH3), 
55.1 (OCH3), 55.0 (CH), 25.3 (CH2), 24.72 (CH3), 24.67 (CH3), 16.3 (CH3), 13.1 (CH3).

11B NMR (96 MHz, CDCl3) δB ppm 33.0 (br s).

19F NMR (470 MHz, CDCl3) δF ppm –137.4 (dd, 
J = 12.7, 8.5 Hz, CF).

νmax (neat) = 2963, 1512, 1458, 1308, 1266, 1130, 1086, 1029, 854, 740 cm−1.

m/z (%) (ESI+) 451 ([M+Na]+, 100), 321 ([M–ArOMe]+, 16), 303 ([M–ArFOMe]+, 13).


[α]D21 =–132 (c 0.29, CHCl3).

2-Fluoro-1-methoxy-4-((2S,3R)-2-(4-methoxyphenyl)pentan-3-yl)benzene (34)

A solution of tertiary boronic ester 33 (120 mg, 0.28 mmol, 
1.0 equiv) and TBAF·3H2O (265 mg, 0.84 mmol, 3.0 equiv) 
in anhydrous toluene (3.0 mL) was heated under reflux for 
3 h. After cooling to ambient temperature, H2O (15 mL) and 
diethyl ether (15 mL) were added and the organic phase was washed with H2O (3 × 15 mL), 
dried over anhydrous MgSO4, filtered, and the solvent was removed under reduced pressure. 
The residue was purified by column chromatography (SiO2, pentane/EtOAc 30:1) to give 
protodeboronated product 34 (84 mg, 0.28 mmol, 99%) as a white solid. The product was 
obtained as a mixture of diastereomers (anti:syn >20:1).

mp 80–81 °C (pentane/EtOAc).

Rr (pentane/EtOAc 30:1) 0.20.

1H NMR (400 MHz, CDCl3) δH ppm 7.11 (AA’BB’, J = 8.6 Hz, 2 H, HAr), 6.94–6.83 (m, 
5 H, HAr), 3.90 (s, 3 H, OCH3), 3.82 (s, 3 H, OCH3), 2.74 (dq, J = 10.1, 7.1 Hz, 1 H, CH), 
2.42 (td, J = 10.1, 3.4 Hz, 1 H, CH), 1.46 (m, 1 H, CHH), 1.30 (m, 1 H, CHH), 0.97 (d, 
J = 7.1 Hz, 3 H, CH3), 0.58 (t, J = 7.3 Hz, 3 H, CH3).

13C NMR (126 MHz, CDCl3) δC ppm 157.9 (COMe), 152.4 (d, 1J = 245.1 Hz, CF), 145.7 (d, 
2J = 10.5 Hz, COMe), 138.6 (C), 137.5 (d, 3J = 5.7 Hz, C), 128.3 (CH), 124.1 (d, 3J = 2.9 Hz,
CH), 115.4 (d, $^2J = 18.1$ Hz, CH), 113.7 (CH), 113.0 (CH), 56.3 (OCH$_3$), 55.2 (OCH$_3$), 54.5 (CH), 45.4 (CH), 27.2 (CH$_2$), 20.9 (CH$_3$), 12.2 (CH$_3$).

$^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ ppm $-135.9$ (dd, $J = 12.7$, 8.5 Hz, CF).

$\nu_{\text{max}}$ (neat) $= 2961$, 1614, 1511, 1457, 1308, 1252, 1029, 854, 832 cm$^{-1}$.

$m/z$ (%) (EI$^+$) 302 ([M$^+$], 39), 273 ([M$-$Et$^+$], 5), 243 (14), 167 ([ArFOMeC$_3$H$_6$$^+$], 18), 139 (15), 135 ([ArOMeC$_2$H$_4$$^+$], 100).

HRMS (EI$^+$) calcd. for C$_{19}$H$_{23}$O$_2$F [M$^+$] 302.1682, found 302.1674.

[$[\alpha]_{D}^{22}$] $-14.2$ (c 0.32, CHCl$_3$).

2-Bromo-4-((2S,3R)-3-(3-fluoro-4-methoxyphenyl)pentan-2-yl)-1-methoxybenzene (35)

A mixture of 2-fluoro-1-methoxy-4-((2S,3R)-2-(4-methoxyphenyl)pentan-3-yl)benzene (34) (82 mg, 0.27 mmol, 1.0 equiv) and NBS (53 mg, 0.30 mmol, 1.1 equiv) in anhydrous MeCN (2.0 mL) was stirred at room temperature for 21 h. The mixture was concentrated under reduced pressure, H$_2$O (5.0 mL) was added and the mixture was extracted with EtOAc (4 × 10 mL). The combined organic phases were washed with brine, dried over anhydrous MgSO$_4$, filtered, and the solvent was removed in vacuo. After purification by column chromatography (SiO$_2$, pentane/EtOAc 30:1) 2-bromo-4-((2S,3R)-3-(3-fluoro-4-methoxyphenyl)pentan-2-yl)-1-methoxybenzene (35) (97 mg, 0.25 mmol, 94%) was obtained as a white solid as a mixture of diastereomers (anti:syn >20:1).

mp 85.5–86.5 °C (CHCl$_3$).

R$_f$ (pentane/EtOAc 30:1) 0.10.

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ ppm 7.37 (d, $J = 2.1$ Hz, 1 H, H$_{Ar}$), 7.07 (dd, $J = 8.2$, 2.1 Hz, 1 H, H$_{Ar}$), 6.93–6.81 (m, 4 H, H$_{Ar}$), 3.90 (s, 6 H, 2×OCH$_3$), 2.71 (dq, $J = 10.2$, 7.0 Hz, 1 H, CH), 2.40 (dt, $J = 10.2$, 3.5 Hz, 1 H, CH), 1.45 (m, 1 H, CHH), 1.30 (m, 1 H, CHH), 0.96 (d, $J = 7.0$ Hz, 3 H, CH$_3$), 0.59 (t, $J = 7.3$ Hz, 3 H, CH$_3$).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ ppm 154.1 (COMe), 152.4 (d, $^1J = 244.2$ Hz, CF), 145.8 (d, $^2J = 10.5$ Hz, COMe), 140.2 (C), 136.9 (d, $^3J = 4.8$ Hz, C), 132.1 (CH), 127.5 (CH), 124.2 (d, $^3J = 3.8$ Hz, CH), 115.3 (d, $^2J = 18.1$ Hz, CH), 113.1 (CH), 111.8 (CH), 111.5 (CBr), 56.3 (OCH$_3$), 56.2 (OCH$_3$), 54.4 (CH), 45.2 (CH), 27.1 (CH$_2$), 20.8 (CH$_3$), 12.2 (CH$_3$).
\[^{19}\text{F} \text{NMR} \text{ (470 MHz, CDCl}_3\text{)} \delta \text{F ppm} -135.7 \text{ (dd, } J = 12.7, 8.5 \text{ Hz, CF).}

\[\nu_{\text{max}} \text{ (neat)} = 2959, 1519, 1491, 1452, 1277, 1256, 1131, 1053, 872, 806, 760 \text{ cm}^{-1}.\]

\[m/z \text{ (%) (ESI}^+\text{)} 403 ([M+Na]^+, 100), 255 ([M–ArFOMe]^+, 6), 195 ([M–ArBrOMe]^+, 12).\]

\[\text{HRMS (ESI}^+\text{) calcd. for } \text{C}_{19}\text{H}_{22}\text{O}_2\text{79BrFNa [M+Na]}^+ 403.0679, \text{ found 403.0680.}\]

[\[\alpha\rceil_{22}^\text{D}] -14.0 (c 0.72, CHCl}_3\text{).}\]

\text{4,4’-((2S,3R)-Pentane-2,3-diyl)bis(2-fluorophenol), Bifluranol (1)}

A solution of 2-bromo-4-((2S,3R)-3-(3-fluoro-4-methoxyphenyl)pentan-2-yl)-1-methoxybenzene (35) (42 mg, 0.11 mmol, 1.0 equiv) in anhydrous THF (2.0 mL) was cooled to -78 °C. \text{n-Butyllithium (89 µL, 1.60 M solution in hexanes, 0.14 mmol, 1.3 equiv) was added dropwise and the mixture was stirred at this temperature for 30 min. A solution of NFSI (42 mg, 0.13 mmol, 1.2 equiv) in anhydrous THF (0.5 mL) was added dropwise and the mixture was stirred for 2 h at -78 °C. The cooling bath was removed and the mixture was allowed to warm to room temperature. H}_2\text{O (5.0 mL) was added slowly and the solution was extracted with EtOAc (4 × 10 mL). The combined organic layers were washed with H}_2\text{O, dried over anhydrous Na}_2\text{SO}_4\text{, filtered, and the solvent was removed in vacuo.} The crude product was dissolves in anhydrous CH}_2\text{Cl}_2\text{ (1.5 mL) and cooled to -20 °C. According to a procedure of Katzenellenbogen and co-workers,}^{21} \text{a solution of BBr}_3\text{ (330 µL, 1.0 M in CH}_2\text{Cl}_2\text{, 0.33 mmol, 3.0 equiv) was added dropwise. The reaction mixture was stirred for 30 min at -20 °C and then allowed to warm to 4 °C and stirred for 16 h. Afterwards, the mixture was cooled to -78 °C and anhydrous MeOH (0.5 mL) was added dropwise followed by conc. aq. NH}_3\text{ solution (0.5 mL). The mixture was allowed to warm to room temperature, the solvent was removed in vacuo, and the residue was portioned between H}_2\text{O (10 mL) and EtOAc (10 mL). The aqueous layer was extracted with EtOAc (3 × 10 mL) and the combined organic phases were washed with brine (20 mL), dried over anhydrous MgSO}_4\text{, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO}_2\text{, pentane/EtOAc 9:1 → 4:1) to afford bifluranol (1) (14 mg, 48 µmol, 43%) as a white solid as single diastereomer.}\]

\text{mp 155–157 °C (acetone).}\]

\text{R}_f \text{ (pentane/EtOAc 4:1) 0.25.
**1H NMR** (500 MHz, acetone-d6) δ ppm 8.38 (s, 2 H, OH), 7.03–6.86 (m, 6 H, H_Ar), 2.49 (dt, J = 10.3, 3.7 Hz, 1 H, CH), 1.42 (m, 1 H, C_HH), 1.34 (m, 1 H, CHH), 0.94 (d, J = 7.0 Hz, 3 H, CH3), 0.56 (t, J = 7.3 Hz, 3 H, CH3).

**13C NMR** (126 MHz, acetone-d6) δ ppm 152.4 (d, J = 239.4 Hz, CF), 152.3 (d, J = 239.4 Hz, CF), 143.9 (d, J = 10.5 Hz, COH), 143.8 (d, J = 10.5 Hz, COH), 140.0 (d, J = 4.8 Hz, C), 137.2 (d, J = 5.7 Hz, C), 125.4 (d, J = 3.8 Hz, CH), 124.5 (d, J = 2.9 Hz, CH), 118.5 (d, J = 2.9 Hz, CH), 118.4 (d, J = 2.9 Hz, CH), 116.2 (d, J = 18.1 Hz, CH), 115.5 (d, J = 17.2 Hz, CH), 55.0 (CH), 46.1 (CH), 28.0 (CH2), 21.5 (CH3), 12.6 (CH3).

**19F NMR** (283 MHz, acetone-d6) δ ppm –138.6 (dd, J = 13.0, 8.1 Hz, CF), –138.8 (dd, J = 12.2, 8.9 Hz, CF).

ν <sub>max</sub> (neat) = 3307, 2961, 1603, 1515, 1439, 1273, 1231, 1107, 866, 817, 780 cm<sup>-1</sup>.

m/z (%) (EI<sup>+</sup>) 292 ([M]<sup>+</sup>, 36), 201 (18), 199 (24), 153 ([ArC<sub>3</sub>H<sub>6</sub>]<sup>+</sup>, 100), 139 ([ArC<sub>2</sub>H<sub>4</sub>]<sup>+</sup>, 92), 125 ([ArCH<sub>2</sub>]<sup>+</sup>, 67).

HRMS (EI<sup>+</sup>) calcd. for C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>F<sub>2</sub>[M]<sup>+</sup> 292.1275, found 292.1270.

[α]<sub>22D</sub> = −4.6 (c 0.44, acetone).

### 2.7 Synthesis of fluorohexestrol

2-((3R,4S)-4-(3-fluoro-4-methoxyphenyl)-3-(4-methoxyphenyl)hexan-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane (3R,4S)-41

A solution of (S)-1-(4-methoxyphenyl)propyl diisopropylcarbamate ((R)-39) (293 mg, 1.00 mmol, 1.0 equiv) and TMEDA (0.204 mL, 1.30 mmol, 1.3 equiv) in anhydrous diethyl ether (5.0 mL) was cooled to −78 °C. sBuLi (1.00 mL, 1.30 mmol, 1.3 equiv) was added dropwise and the reaction mixture was stirred at this temperature for 1 h. A solution of (R)-2-(1-(3-fluoro-4-methoxyphenyl)propyl)-5,5-dimethyl-1,3,2-dioxaborinane ((R)-40) (420 mg, 1.50 mmol, 1.5 equiv) in anhydrous diethyl ether (1.5 mL) was added dropwise and the mixture was stirred for 3 h at −78 °C. The cooling bath was removed and stirring was continued at room temperature for 14 h. The reaction mixture was quenched through the addition of water (20 mL), the phases were separated, and the aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic phases were dried over anhydrous MgSO<sub>4</sub>, filtered, and the solvent was removed <i>in vacuo</i>. The crude product was purified by column chromatography (SiO<sub>2</sub>, pentane/Et<sub>2</sub>O 85:15) to afford tertiary boronic ester 41 (301 mg,
0.70 mmol, 70%) as a colourless oil. The ratio of diastereomers was measured by $^1$H NMR and accounted to 20:1 (anti:syn).

$R_f$ (pentane/EtOAc 9:1) 0.27.

$^1$H NMR (400 MHz, CDCl$_3$) 7.13 – 7.07 (m, 2H), 6.84 – 6.63 (m, 5H), 3.88 (s, 3H, OCH$_3$), 3.81 (s, 3H, OCH$_3$), 3.64 (s, 4H, OCH$_2$), 2.84 (dd, J=12.1, 2.8, 1H, CH), 1.79 – 1.64 (m, 3H, CH$_2$CH$_3$), 1.47 (m, 1H, CH$_2$CH$_3$), 0.99 (s, 6H), 0.67 (t, J=7.3, 3H, CH$_2$), 0.59 (t, J=7.3, 3H, CH$_2$CH$_3$).

$^{13}$C NMR (126 MHz, CDCl$_3$) 157.1 (COMe), 151.7 (d, J=243.0, CF), 145.4 (d, J=10.8, COMe), 136.8 (d, J=5.4, C), 130.6 (CH), 125.7 (d, J=3.3, CH), 117.0 (d, J=17.9, CH), 112.7 (CH), 112.0 (d, J=2.0, CH), 71.8 (CH$_2$), 56.2 (OCH$_3$), 55.4 (OCH$_3$), 55.1 (CH), 31.2 (C), 29.6 (CH$_2$), 23.4 (CH$_2$), 12.9 (CH$_3$), 11.0 (CH$_3$).

$^{11}$B NMR (96 MHz, CDCl$_3$) $\delta$ ppm 29.6 (br. s).

$^{19}$F NMR (283 MHz, CDCl$_3$) $\delta$ ppm -136.94 (dd, $J$=13.5, 9.2)

$\nu$$_{max}$ (neat) = 2961, 2933, 2874, 2837, 1757, 1608, 1579, 1511, 1247, 1182, 1129, 1034 cm$^{-1}$.

$[\alpha]_{D}^{20}$ $-7$ (c 1, CHCl$_3$).

2-Fluoro-1-methoxy-4-((3S,4R)-4-(4-methoxyphenyl)hexan-3-yl)benzene (42)

A solution of tertiary boronic ester 41 (150 mg, 0.35 mmol, 1.0 equiv) and TBAF-3H$_2$O (332 mg, 1.05 mmol, 3.0 equiv) in anhydrous toluene (4.0 mL) was heated under reflux for 3 h. After cooling to ambient temperature, H$_2$O (20 mL) and diethyl ether (20 mL) were added and the organic phase was washed with H$_2$O (3 × 15 mL), dried over anhydrous MgSO$_4$, filtered, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO$_2$, pentane/EtOAc 20:1) to give protodeboronated product 42 (90 mg, 0.28 mmol, 81%) as a white solid. The product was obtained as a mixture of diastereomers (anti:syn 93:7).

mp 126–127 °C (pentane/EtOAc).

$R_f$ (pentane/EtOAc 30:1) 0.21.

Analytical data of the major anti diastereomer.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.07 (AA’BB’, J = 8.6 Hz, 2 H, H$_{Ar}$), 6.94–6.85 (m, 5 H, H$_{Ar}$), 3.90 (s, 3 H, OCH$_3$), 3.82 (s, 3 H, OCH$_3$), 2.52–2.41 (m, 2 H, CH), 1.46–1.35 (m,
2 H, 2×CHH), 1.33–1.18 (m, 2 H, 2×CHH), 0.552 (t, J = 7.3 Hz, 3 H, CH₃), 0.546 (t, J = 7.3 Hz, 3 H, CH₃).

¹³C NMR (126 MHz, CDCl₃) δ ppm 157.9 (COMe), 152.4 (d, J = 245.1 Hz, CF), 145.6 (d, J = 10.5 Hz, COMe), 137.9 (d, J = 4.8 Hz, C), 136.1 (C), 129.1 (CH), 124.1 (d, J = 3.8 Hz, CH), 115.3 (d, J = 18.1 Hz, CH), 113.6 (CH), 113.1 (CH), 56.3 (OCH₃), 55.2 (OCH₃), 53.6 (CH), 53.4 (CH), 27.3 (CH₂), 27.26 (CH₂), 12.2 (CH₃), 12.1 (CH₃).

¹⁹F NMR (470 MHz, CDCl₃) δ ppm –135.8 (dd, J = 12.1, 8.9 Hz, CF).

ν max (neat) = 2957, 1610, 1511, 1440, 1250, 1130, 1025, 831, 759 cm⁻¹.

m/z (%) (ESI⁺) 339 ([M+Na]⁺, 100).


[α]₂² D ±0.0 (c 0.51, CHCl₃).

The analytical data match those reported in literature for the racemic compound.²¹,²²

2-Fluoro-4-((2S,3R)-3-(4-hydroxyphenyl)pentan-2-yl)phenol, Fluorohexestrol (2)

According to a procedure of Katzenellenbogen and co-workers,²¹ a solution of BBr₃ (1.28 mL, 1.0 M in CH₂Cl₂, 1.28 mmol, 3.0 equiv) was added dropwise to a solution of diaryl ⁴² (135 mg, 0.43 mmol, 1.0 equiv) in anhydrous CH₂Cl₂ (4.3 mL) at -20 °C. The reaction mixture was stirred for 30 min at -20 °C and then allowed to warm to 4 °C and stirred for 15 h. Afterwards, the mixture was cooled to -78 °C and anhydrous MeOH (0.5 mL) was added dropwise followed by conc. aq. NH₃ solution (0.5 mL). The mixture was allowed to warm to room temperature, the solvent was removed in vacuo, and the residue was portioned between H₂O (10 mL) and EtOAc (10 mL). The aqueous layer was extracted with EtOAc (3 × 10 mL) and the combined organic phases were washed with brine (20 mL), dried over anhydrous MgSO₄, filtered, and the solvent was removed under reduced pressure to give 2-fluoro-4-(4-(4-hydroxyphenyl)hexan-3-yl)phenol (121 mg, 0.42 mmol, 99%) as off-white solid as a mixture of diastereomers. To separate the isomers, the residue was purified by flash chromatography (SiO₂, pentane/EtOAc 9:1 → 1:1) to afford 2-fluoro-4-((2S,3R)-3-(4-hydroxyphenyl)pentan-2-yl)phenol (2) (89 mg, 0.31 mmol, 72%) as white crystalline solid and 2-fluoro-4-((3S,4S)-4-(4-hydroxyphenyl)hexan-3-yl)phenol (47) (20 mg, 69 µmol, 16%) as a colourless oil, which crystallised upon standing (vide infra).

Analytical data for 2-fluoro-4-((2S,3R)-3-(4-hydroxyphenyl)pentan-2-yl)phenol (2)
mp 197‒201 °C (pentane/EtOAc). Lit. 200.5‒201.5 °C (THF/cyclohexane).²¹

Rt (pentane/EtOAc 4:1) 0.22.

¹H NMR (500 MHz, acetone-d₆) δ ppm 8.35 (s, 1 H, OH), 8.07 (s, 1 H, OH), 7.05 (AA’BB’, J = 8.6 Hz, 2 H, Hₐ), 6.98 (dd, J = 12.5, 1.8 Hz, 1 H, Hₐ), 6.95 (dd, J = 8.9, 8.2 Hz, 1 H, Hₐ), 6.88 (dd, J = 8.2, 1.8 Hz, 1 H, Hₐ), 6.80 (AA’BB’, J = 8.6 Hz, 2 H, Hₐ), 2.56–2.47 (m, 2 H, 2×CH), 1.43–1.35 (m, 2 H, 2×CH₂), 1.33–1.24 (m, 2 H, 2×CH₂), 0.52 (t, J = 7.4 Hz, 6 H, 2×CH₃).

¹³C NMR (101 MHz, acetone-d₆) δ ppm 156.6 (COH), 152.4 (d, ¹J = 239.4 Hz, CF), 143.7 (d, ²J = 13.0 Hz, COH), 137.9 (d, ³J = 4.8 Hz, C), 135.9 (C), 130.0 (CH), 125.3 (d, ³J = 2.7 Hz, CH), 118.3 (d, ⁴J = 2.3 Hz, CH), 116.1 (d, ²J = 17.7 Hz, CH), 116.0 (CH), 54.3 (CH), 54.2 (CH), 28.2 (CH₂), 28.1 (CH₂), 12.59 (CH₃), 12.55 (CH₂).

¹⁹F NMR (470 MHz, acetone-d₆) δ ppm −138.8 (br. m).

νmax (neat) = 3298, 2958, 1600, 1512, 1437, 1222, 1106, 830, 804, 775 cm⁻¹.

m/z (%) (CI⁺) 288 ([M⁺], 8), 287 ([M‒H]⁺, 26), 269 ([M‒F]⁺, 35), 259 ([M‒Et]⁺, 30), 223 (16), 195 ([M‒Ar]⁺, 99), 177 ([M‒ArF]⁺, 48), 153 ([ArFC₃H₇]⁺, 46), 135 ([ArC₃H₇]⁺, 100), 125 ([ArFCH₂]⁺, 62), 107 ([ArCH₂]⁺, 35), 93 ([PhOH]⁺, 7).

HRMS (EI⁺) calcd. for C₁₈H₂₁O₂F [M⁺] 288.1526, found 288.1535.

[α]21D +1.0 (c 1.0, CHCl₃).

The analytical data are consistent with those reported in literature for the racemic compound.²¹

HPLC separation conditions: Chiralpak ADH column with guard, 10.0% iPrOH in hexane, flow rate 0.7 mL/min, 20 °C; tᵣ 23.1 min for anti-diastereomer (major) and tᵣ 25.7 and 34.3 min for syn-diastereomers (minor).

d.r. = 100:0.0.

In order to measure the enantiomeric excess, fluorohexestrol (2) was converted into the mono protected benzyl ether (48).²³
HPLC separation conditions: Chiralpak IA column with guard, 5.0% iPrOH in hexane, flow rate 0.7 mL/min, 20 °C; \( t_R \) 39.0 min for (R,S)-enantiomer (major) and \( t_R \) 43.6 min for (S,R)-enantiomer (minor).

e.r. = 99.8:1.2.

2-Fluoro-4-((3S,4S)-4-(4-hydroxyphenyl)hexan-3-yl)phenol (47)

mp 106–107 °C (pentane/EtOAc).

Rr (pentane/EtOAc 4:1) 0.16.

\(^1\text{H NMR}\) (400 MHz, acetone-d6) \( \delta \) ppm 8.20 (br. s, 1 H, OH), 7.96 (br. s, 1 H, OH), 6.76 (AA’BB’, \( J = 8.8 \) Hz, 2 H, \( H_{A} \)), 6.71 (m, 1 H, \( H_{A} \)), 6.62 (AA’BB’, \( J = 8.8 \) Hz, 2 H, \( H_{A} \)), 6.61–6.56 (m, 2 H, \( H_{A} \)), 2.70–2.56 (m, 2×CH), 1.94–1.82 (m, 2×CHH), 1.57–1.46 (m, 2 H, \( 2×CH_{2} \)), 0.71 (t, \( J = 7.3 \) Hz, 3 H, \( CH_{3} \)), 0.707 (t, \( J = 7.3 \) Hz, 3 H, \( CH_{3} \)).

\(^{13}\text{C NMR}\) (126 MHz, acetone-d6) \( \delta \) ppm 156.2 (COH), 151.8 (d, \( ^3J = 239.4 \) Hz, CF), 143.3 (d, \( ^2J = 13.4 \) Hz, COH), 136.7 (d, \( ^3J = 4.8 \) Hz, C), 134.6 (C), 130.7 (CH), 125.9 (d, \( ^3J = 2.9 \) Hz, CH), 117.6 (d, \( ^4J = 2.9 \) Hz, CH), 116.9 (d, \( ^3J = 18.1 \) Hz, CH), 115.3 (CH), 53.3 (CH), 53.2 (CH), 26.99 (CH2), 26.98 (CH2), 12.71 (CH3), 12.68 (CH2).

\(^{19}\text{F NMR}\) (470 MHz, acetone-d6) \( \delta \) ppm –139.7 (dd, \( J = 12.7, 10.6 \) Hz, CF).

\( \nu_{\text{max}} \) (neat) = 3317, 2961, 1598, 1511, 1439, 1365, 1226, 1111, 827, 777 cm\(^{-1}\).

HRMS (EI+) calcd. for C$_{18}$H$_{21}$O$_2$F [M]$^+$ 288.1526, found 288.1534.

$\alpha_\text{D}^\text{1} = -12.0$ ($c$ 0.67, CHCl$_3$, for 64% ee).

HPLC separation conditions: Chiralpak ADH column with guard, 10.0% $i$PrOH in hexane, flow rate 0.7 mL/min, 20 °C; $t_R$ 25.7 min for (R,R)-enantiomer (minor) and 34.3 min for (S,S)-enantiomer (major).

e.r. = 81.9:18.1.
3. X-ray structure of Fluorohexestrol (2)

Bond precision: C-C = 0.0106 Å
Wavelength = 1.54178 Å

Cell: 
- a = 5.8233(7) Å
- b = 16.811(3) Å
- c = 21.303(3) Å
- alpha = 90°
- beta = 97.041(7)°
- gamma = 90°

Temperature: 100 K

Volume: 2069.7(5) Å³

Space group: P 21
Hall group: P 2yb

Moiety formula: C18 H21 F O2, C4 H10 O
Sum formula: C22 H31 F O3

Mr: 362.47
DX, g cm⁻³: 1.163
Z: 4
μ (mm⁻¹): 0.659
F₀₀₀: 784.0

h, k, l max: 6, 19, 25
Nref: 7153 [3710]
Tmin, Tmax: 0.965, 0.974
Tmin’: 0.865

Correction method: MULTI-SCAN

Data completeness: 0.97/0.50
Theta (max): 65.820°

R(reflections) = 0.0780 (2972)
WR2(reflections) = 0.2150 (3609)
S = 1.021

Npar = 590
4. \(^1\text{H}\) NMR and \(^{13}\text{C}\) NMR spectra

\((S)-1-(4-\text{Methoxyphenyl})\text{ethanol} \quad ((S)-31)\)

\(^1\text{H}\) NMR (500 MHz, CDCl\(_3\))
(S)-1-(4-Methoxyphenyl)propan-1-ol ((S)-43)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
1-(3-Fluoro-4-methoxyphenyl)ethanol (44)

\( ^1H \) NMR (400 MHz, CDCl\(_3\))

\[ \text{Chemical Shift (ppm)} \]

\[ \begin{align*}
\text{Normalized Intensity} & \quad 3.89 \\
& \quad 4.82 \\
& \quad 4.84 \\
& \quad 4.85 \\
& \quad 4.87 \\
& \quad 6.91 \\
& \quad 6.93 \\
& \quad 6.95 \\
& \quad 7.08 \\
& \quad 7.11 \\
& \quad 7.12 \\
& \quad 7.14 \\
& \quad 7.27 \\
\end{align*} \]

\( ^13C \) NMR (101 MHz, CDCl\(_3\))

\[ \text{Chemical Shift (ppm)} \]

\[ \begin{align*}
\text{Normalized Intensity} & \quad 56.30 \\
& \quad 69.47 \\
& \quad 76.68 \\
& \quad 77.00 \\
& \quad 77.32 \\
& \quad 113.19 \\
& \quad 113.38 \\
& \quad 120.99 \\
& \quad 121.02 \\
& \quad 138.95 \\
& \quad 146.71 \\
& \quad 146.82 \\
& \quad 151.10 \\
& \quad 153.55 \\
\end{align*} \]

S51
Propyl diisopropylcarbamate (28)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
(S)-1-Phenylethyl diisopropylcarbamate ((S)-5)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
(S)-1-Phenylpropyl diisopropylcarbamate ((S)-6)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
(S)-1-(4-Methoxyphenyl)ethyl diisopropylcarbamate ((S)-32)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)

S55
$(R)$-1-(4-Methoxyphenyl)propyl diisopropylcarbamate ($R$)-39

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
1-(3-Fluoro-4-methoxyphenyl)ethyl diisopropylcarbamate (36)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
2-(3-Fluoro-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (29)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
2-(3-fluoro-4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (38)
(S)-4,4,5,5-Tetramethyl-2-(1-phenylethyl)-1,3,2-dioxaborolane ((S)-8)

\(^1\)H NMR (500 MHz, CDCl\(_3\))

\[^{13}\text{C}\] NMR (126 MHz, CDCl\(_3\))

S60
4,4,5,5-Tetramethyl-2-(1-phenylpropyl)-1,3,2-dioxaborolane (9)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
(S)-5,5-dimethyl-2-(1-phenylpropyl)-1,3,2-dioxaborinane ((S)-11)
(R)-2-(1-(3-fluoro-4-methoxyphenyl)propyl)-5,5-dimethyl-1,3,2-dioxaborinane ((R)-40)
(S)-2-(1-(3-Fluoro-4-methoxyphenyl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((S)-30)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
(S)-1-(3-Fluoro-4-methoxyphenyl)propan-1-ol ((S)-45)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
4,4,5,5-Tetramethyl-2-(pentan-3-yl)-1,3,2-dioxaborolane (10)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
5,5-dimethyl-2-(pentan-3-yl)-1,3,2-dioxaborinane (12)
4,4,5,5-Tetramethyl-2-(3-methyl-2-phenylbutan-2-yl)-1,3,2-dioxaborolane (11)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
4,4,5,5-Tetramethyl-2-(2-methyl-3-phenylpentan-3-yl)-1,3,2-dioxaborolane (15)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
2-(2,3-Diphenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
2-(2,3-Diphenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16)

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
2-(2,3-Diphenylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
2-(2,3-diphenylpentan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (21)
2-((2S,3R)-2,3-diphenylpentan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane ((2S,3R)-21)
2-((2R,3R)-2,3-diphenylpentan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane ((2R,3R)-21)
2-(3,4-diphenylhexan-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane 22
2-((3S,4R)-3,4-diphenylhexan-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane ((3S,4R)-22)
2-((3R,4R)-3,4-diphenylhexan-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane ((3R,4R)-22)
2-(3-Ethyl-2-phenylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
2-(3-ethyl-2-phenylpentan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (23)
(S)-2-(3-ethyl-2-phenylpentan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (S)-24
(2S,3R)-2,3-Diphenylpentan-3-ol ((2S,3R)-39)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
(2R,3R)-2,3-Diphenylpentan-3-ol ((2R,3R)-39)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (101 MHz, CDCl$_3$)
2-((2S,3R)-3-(3-Fluoro-4-methoxyphenyl)-2-(4-methoxyphenyl)pent-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (33)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)

S84
2-Fluoro-1-methoxy-4-((2S,3R)-2-(4-methoxyphenyl)pentan-3-yl)benzene (34)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
2-Bromo-4-((2S,3R)-3-(3-fluoro-4-methoxyphenyl)pentan-2-yl)-1-methoxybenzene (35)

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
4,4’-((2S,3R)-Pentane-2,3-diyi)bis(2-fluorophenol), Bifuranol (1)

$^1$H NMR (500 MHz, acetone-d6)

$^{13}$C NMR (126 MHz, acetone-d6)
2-((3R,4S)-4-(3-fluoro-4-methoxyphenyl)-3-(4-methoxyphenyl)hexan-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane (3R,4S)-41
2-Fluoro-1-methoxy-4-((3S,4R)-4-(4-methoxyphenyl)hexan-3-yl)benzene (42)

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
2-Fluoro-4-((2S,3R)-3-(4-hydroxyphenyl)pentan-2-yl)phenol, Fluorohexestrol (2)

$^1$H NMR (500 MHz, acetone-d6)

$^{13}$C NMR (101 MHz, acetone-d6)
2-Fluoro-4-((3S,4S)-4-(4-hydroxyphenyl)hexan-3-yl)phenol (47)

$^1$H NMR (400 MHz, acetone-d6)

$^{13}$C NMR (126 MHz, acetone-d6)

5. Determination of diastereomeric ratio of tertiary boronic esters via $^1$H NMR
2-(2,3-Diphenylbutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15)

2-(2,3-Diphenylpentan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16)
2-(2,3-Diphenylpentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17)

2-(3,4-Diphenylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18)

6. References