SUPPORTING INFORMATION

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**Title:** Copper-Catalyzed Borylation of Cyclic Sulfamidates: Access to Enantiomerically Pure (β- and γ-Aminoalkyl)boronic Esters

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| Section                                           | Page |
|--------------------------------------------------|------|
| General Experimental Details                     | 2    |
| Experimental Procedures                          |      |
| Synthesis of Cyclic Sulfamidates                 | 3    |
| Cu-Catalyzed Borylation of Cyclic Sulfamidates    | 13   |
| Stereochemical Proofs of Diastereomeric Boronic Ester 2u-w | 21   |
| Mechanistic Studies                              |      |
| TEMPO Trapping Experiment                        | 25   |
| Iodide vs Cyclic Sulfamidate; isolation of 9      | 25   |
| Copies of $^1$H and $^{13}$C NMR (for novel compounds) | 27   |
| Mass Spectra and IR data related to 9            | 53   |
| Yield optimization studies (solvent/ligand/Cu screen; temp; iodide loading) for conversion of 1a to 2a | 56   |
| Literature References                            | 58   |
General Experimental Details

All reagents requiring purification were purified using standard laboratory techniques. Anhydrous solvents were obtained by distillation using standard procedures or by passage through drying columns supplied by Anhydrous Engineering Ltd. All reactions were performed under an atmosphere of dry nitrogen, using standard Schlenk techniques unless otherwise stated. Flash column chromatography was performed using silica gel (Aldrich 40-63 µm, 230-400 mesh).

Analytical thin layer chromatography was performed using aluminium backed 60 F254 silica plates. Visualisation was achieved by UV fluorescence and/or a basic KMnO4 solution and heat. Proton nuclear magnetic resonance spectra (NMR) were recorded at 400 MHz or 500 MHz. 13C NMR spectra were recorded at 100 MHz or 125 MHz as stated. Coupling constants are quoted to the nearest 0.5 Hz.

All assignments of NMR spectra were based on 2D NMR data (COSY, HSQC and HMBC) and the numbering used is as the labelled chemical structure.

Mass spectra were recorded using a Fisons VG Analytical Autospec spectrometer (CI+ or EI+ mode), a Bruker Daltonics Apex IV (ESI+ mode) and a Bruker Daltonics MicroTof II (ESI+ mode). Infrared spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrometer as thin films or solids compressed on a diamond plate. Melting points were determined using Reichert melting point apparatus. Melting points are uncorrected.
Experimental Procedures

Synthesis of Cyclic Sulfamidate Substrates.

Sulfamidates 1a, 1b, 1c, 1d, 1e, 1f, 1g, 1i, 1j, 1k, 1m, 1q, 1r, 1s, and 1t were synthesised according to published literature procedures.

Cyclic Sulfamidate Substrate 1h

(±)-Benzyl 5-methyl-1,2,3-oxathiazolidine-3-carboxylate-2-oxide

\[
\begin{align*}
\text{CbzN} & \quad \text{O} \\
\text{O} & \quad \text{Me} \\
1 & \quad 2
\end{align*}
\]

Imidazole (1.55 g, 22.8 mmol) was dissolved in anhydrous CH2Cl2 (35 mL), followed by addition of Et3N (1.8 mL, 12.6 mmol) and cooling to -40 °C. SOCl2 (0.52 mL, 6.85 mmol) was then added, followed by dropwise addition of a solution of benzyl N-2-hydroxypropylcarbamate (1.19 g, 5.71 mmol) (Xu, J.; Xu, S.; Zhang, Q. Heteroat. Chemistry 2005, 16, 466-471) in anhydrous CH2Cl2 (25 mL) over a period of 20 min. The resulting pale yellow mixture was allowed to warm up to 0 °C and was stirred at this temperature for 3 h. Once the reaction was complete as indicated by TLC, the mixture was poured into water (40 mL). The organic layer was separated and washed with water (40 mL), brine (40 mL), dried over Na2SO4 and concentrated in vacuo to yield a crude mixture that was purified by flash column chromatography (EtOAc-hexane 3:7) to afford benzyl -5-methyl-1,2,3-oxathiazolidine-3-carboxylate-2-oxide (1.30 g, 89%, 1:1 d.r. A:B) as a pale yellow oil; \( \nu_{\text{max/cm}} \) 2979 (w), 1700 (s), 1526 (m), 1247 (s), 1141 (m); \( \delta_{\text{H}} \) (400 MHz, CDCl3) 1.55 (3H, d, \( J = 6.0 \) Hz, C\( \text{H}_3 \) of B), 1.69 (3H, d, \( J = 6.5 \) Hz, C\( \text{H}_3 \) of A), 3.20 (1H, apparent triplet, \( J = 10.0 \) Hz, 1-C\( \text{H} \)H of A and B), 3.67 (1H, dd, \( J = 10.0 \) and 6.5 Hz, 1-C\( \text{H} \)H of B), 3.95-4.01 (2H, m, 1-CH\( \text{H} \) of A and B), 4.99 (1H, m, 2-CH\( \text{H} \) of B), 5.22-5.34 (4H, m, CH\( \text{H}_2 \)Ph of A and B), 5.42 (1H, m, 2-CH of A), 7.35-7.41 (10H, m, ArCH of A and B); \( \delta_{\text{C}} \) (100 MHz, CDCl3) 17.4 (CH\( \text{H}_3 \) of B), 21.4 (CH\( \text{H}_3 \) of A), 48.9 (1-CH\( \text{H} \) of B), 50.5 (1-CH\( \text{H} \) of A), 68.5 and 68.6 (CH\( \text{H}_2 \)Ph of A and B), 79.9 (2-CH of A), 85.0 (2-CH of B), 128.1, 128.6 (ArCH \times 10 of A and B), 135.0 (ArC of A and B), 152.2 (C=O of A and B); \( m/z \) (%) ESI-MS 278.05 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 278.0457.

Benzyl 5-methyl-1,2,3-oxathiazolidine-3-carboxylate-2,2-dioxide Substrate 1h

\[
\begin{align*}
\text{CbzN} & \quad \text{O} \\
\text{O} & \quad \text{Me} \\
1 & \quad 2
\end{align*}
\]

To an ice-cooled (0 °C) solution of benzyl-5-methyl-1,2,3-oxathiazolidine-3-carboxylate-2,2-dioxide (400 mg, 1.57 mmol) in MeCN (12 mL) was added RuCl3 (0.9 mg, 0.20 mol%), NaIO4 (542 mg, 2.53 mmol) and then water (9 mL). The mixture was stirred at 0 °C for 2.5 h. The reaction mixture was then poured into water (15 mL) and extracted with EtOAc (3 × 30 mL). The organic extracts were combined, washed with brine (50 mL), dried over Na2SO4 and concentrated in vacuo to afford a pale brown solid. This
material was dissolved in EtOAc (15 mL) and DMSO (10 μL) was added. After stirring at r.t. for 3 h the mixture was pre-adsorbed onto SiO2 and purified by flash column chromatography (EtOAc-hexane 3:7) to afford cyclic sulfamidate 1h (422 mg, 99%) as a colorless crystalline solid; m.p. 89-91 °C (CH2Cl2-hexane); υmax/cm⁻¹ (neat) 2974 (w), 1737 (s), 1375 (s), 1316 (s), 1193 (s); δH (400 MHz, CDCl3) 1.60 (3H, d, J = 6.5 Hz, C(CH3)3), 3.72 (1H, apparent triplet, J = 10.0 Hz, 1-CH2H), 4.14 (1H, dd, J = 10.0 and 5.5 Hz, 1-CH3), 5.01 (1H, m, 2-CH2), 5.32 (2H, s, CH2Ph), 7.35-7.43 (5H, m, ArCH); δC (100 MHz, CDCl3) 18.0 (C(CH3)3), 51.9 (1-CH2), 69.4 (CH2Ph), 76.7 (2-CH), 128.0, 128.6 (ArCH × 5), 134.4 (ArC), 149.8 (C=O); m/z (%) ESI-MS 310.01 ([M+K]+) 294.04 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 294.0412, C11H13NO5SNa requires 294.0407.

Cyclic Sulfamidate 1l

(S)-tert-Butyl 4-benzyl-1,2,3-oxathiazinane-3-carboxylate-2-oxide

Imidazole (140 mg, 2.06 mmol) was dissolved in anhydrous CH2Cl2 (3 mL), followed by addition of Et3N (0.16 mL, 1.12 mmol) and cooling to -40 °C. SOCl2 (48 μL, 0.62 mmol) was then added, followed by dropwise addition of a solution of (S)-tert-butyl-4-hydroxy-1-phenylbutan-2-ylcarbamate[11] (138 mg, 0.52 mmol) in anhydrous CH2Cl2 (4 mL). The resulting pale yellow mixture was allowed to slowly warm up to r.t. and was stirred at this temperature for 3 h. The mixture was then poured into water (10 mL). The organic layer was separated and washed with water (10 mL), brine (10 mL), dried over Na2SO4 and concentrated in vacuo to yield a crude mixture that was purified by flash column chromatography (EtOAc-hexane 1:4) to furnish the title sulfamidite (124 mg, 77%, 13:1 d.r. A:B) as a pale yellow oil; υmax/cm⁻¹ (neat) 2977 (w), 1715 (s), 1695 (s), 1317 (s), 1166 (s), 1144 (m); δH (400 MHz, CDCl3) 1.52 (9H, s, C(CH3)3), 1.89 (1H, dddd, J = 14.5, 7.5, 3.5 and 1.5 Hz, 3-CH2H), 2.65 (1H, m, 3-CH2H), 2.88 (1H, dd, J = 13.5 and 10.5 Hz, 1-CH2H), 3.16 (1H, ddd, J = 13.5 and 5.0 Hz, 1-CH3), 4.26-4.33 (2H, m, 2-CH2 and 4-CH2), 4.51 (1H, ddd, J = 10.5, 8.0 and 1.5 Hz, 4-CH2H), 7.23-7.26 (3H, m, ArCH), 7.31-7.35 (2H, m, ArCH); δC (100 MHz, CDCl3) 22.4 (3-CH2), 28.2 (C(CH3)3), 38.6 (1-CH2), 51.7 (2-CH), 57.7 (4-CH2), 83.3 (CH2Ph), 126.7, 128.7, 129.0 (ArCH × 5), 137.8 (ArC), 154.0 (C=O); m/z (%) ESI-MS 334.11 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 334.1087, C15H21NO4SNa requires 334.1083. Only signals attributable to the major diastereomer were observed.

(S)-tert-Butyl-4-benzyl-1,2,3-oxathiazinane-3-carboxylate-2,2-oxide 1l

To an ice-cooled (0 °C) solution of (S)-tert-butyl-4-benzyl-1,2,3-oxathiazinane-3-carboxylate-2-oxide (109 mg, 0.35 mmol) in MeCN (4 mL) was added RuCl3 (0.5 mg, 0.20 mol%), NaIO4 (120 mg, 0.55 mmol) and then water (3 mL). The mixture was stirred at 0 °C for 6 h. The reaction mixture was then poured into water (5 mL) and extracted with EtOAc (3 × 5 mL). The organic extracts were combined, washed with brine (10 mL), dried over Na2SO4 and concentrated in vacuo to afford a pale brown solid.
that was purified by flash column chromatography (Et₂O-hexane 3:7) to afford cyclic sulfamidate 11 (92 mg, 80%) as a colorless crystalline solid; m.p. 79-81 °C (CH₂Cl₂-hexane); νmax/cm⁻¹ (neat) 2980 (w), 1728 (s), 1388 (s), 1301 (s), 1184 (s), 1147 (s); δH (400 MHz, CDCl₃) 1.48 (9H, s, C(CH₃)₃), 1.91 (1H, ddt, J = 14.5, 5.5 and 3.0 Hz, 3-CHH), 2.36 (1H, ddt, J = 14.5, 10.5 and 6.5 Hz, 3-CHH), 3.03 (1H, dd, J = 13.5 and 9.0 Hz, 1-CHH), 7.24-7.27 (2H, m, ArCH), 7.31-7.36 (3H, m, ArCH); δC (100 MHz, CDCl₃) 24.8 (3-C₄H₂), 27.9 (C(CH₃)₃), 38.9 (1-C₄H₂), 58.5 (2-C₄H), 69.4 (4-C₄H₂), 85.1 (C(CH₃)₃), 127.0, 128.8, 129.3 (ArCH × 5), 137.1 (ArC), 150.4 (C=O); m/z (%) ESI -MS 366.08 ([M+K]+), 350.10 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 350.1032, C₁₅H₂₁NO₅SNa requires 350.1033.

Cyclic Sulfamidate 1n

(S)-tert-Butyl 4-methyl-1,2,3-oxathiazinane-3-carboxylate-2-oxide

Imidazole (167 mg, 2.45 mmol) was dissolved in anhydrous CH₂Cl₂ (4 mL), followed by addition of Et₃N (0.19 mL, 1.36 mmol) and cooling to -40 °C. SOCl₂ (57 μL, 0.74 mmol) was then added, followed by dropwise addition of a solution of (S)-tert-butyl-4-hydroxy-butan-2-ylcarbamate (117 mg, 0.62 mmol) in anhydrous CH₂Cl₂ (3 mL). The resulting pale yellow mixture was allowed to slowly warm up to r.t. and was stirred at this temperature for 6 h. The mixture was then poured into water (10 mL). The organic layer was separated and washed with water (10 mL), brine (10 mL), dried over Na₂SO₄ and concentrated in vacuo to yield a crude mixture that was purified by flash column chromatography (EtOAc-hexane 1:4) to furnish the title sulfamidite (128 mg, 88%, 4:1 d.r. A:B) as a pale yellow oil; νmax/cm⁻¹ (neat) 2974 (w), 2937 (w), 1709 (s), 1369 (m), 1304 (m), 1256 (m), 1177 (s), 1148 (s); δH (400 MHz, CDCl₃) 1.38 (6H, d, J = 6.5 Hz, C(CH₃)₃ of A and B), 1.52 (18H, s, (C(CH₃)₃) of A and B), 1.73 (1H, dq, J = 14.0 and 2.5 Hz, 2-CHH of A), 2.36 (1H, m, 2-CHH of B), 2.86 (1H, m, 2-CHH of A), 3.92 (1H, dddd, J = 11.5, 4.5, 2.5 and 0.5 Hz, 3-CHH of B), 4.20-4.29 (2H, m, 1-C₄H and 3-C₄H of A), 4.34 (1H, m, 1-CH of B), 4.52 (1H, dddd, J = 10.5, 8.5, 1.5 and 0.5 Hz, 3-CHH of A), 4.91 (1H, dddd, J = 11.5, 10.0, 2.0 and 0.5 Hz, 3-CHH of B); δC (100 MHz, CDCl₃) 18.8 (C(CH₃)₃ of A and B), 21.1 (C(CH₃)₃ of B), 26.6 (2-CH₂ of A), 28.2 (C(CH₃)₃ of A), 28.2 (2-CH₂ of B), 46.2 (1-CH of A and B), 53.5 (3-CH₂ of A), 57.8 (3-CH₂ of B), 83.1 (C(CH₃)₃ of A), 83.2 (C(CH₃)₃ of B), 152.3 (C=O of A and B); m/z (%) ESI-MS 258.08 ([M+K]+), 258.10 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 258.0774, C₉H₁₇NO₄SNa requires 258.0770.

(S)-tert-Butyl-4-methyl-1,2,3-oxathiazinane-3-carboxylate-2,2-oxide 1n

To an ice-cooled (0 °C) solution of (S)-tert-butyl 4-methyl-1,2,3-oxathiazinane-3-carboxylate-2-oxide (120 mg, 0.51 mmol) in MeCN (5 mL) was added RuCl₃ (0.8 mg, 0.20 mol%), NaIO₄ (175 mg, 0.82
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure \( \beta \)- and \( \gamma \)-Aminoalkyl Boronic Esters

Supporting Information 6

mmol) and then water (4 mL). The mixture was stirred at 0 °C for 2 h. The reaction mixture was then poured into water (5 mL) and extracted with \( \text{EtOAc} \) (3 \( \times \) 5 mL). The organic extracts were combined, washed with brine (10 mL), dried over \( \text{Na}_2\text{SO}_4 \) and concentrated in vacuo to afford a pale brown solid that was purified by flash column chromatography (EtO-hexane 2:3) to afford cyclic sulfamidate \( \text{In} \) (100 mg, 78%) as a colorless crystalline solid; m.p. 107-110 °C (CH\(_2\)Cl\(_2\)-hexane); \( \nu_{\text{max}}/\text{cm}^{-1} \) (neat) 2982 (w), 1728 (s), 1384 (s), 1370 (s), 1297 (s), 1259 (m), 1183 (s), 1151 (s); \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 1.46 (3H, d, \( J = 7.0 \) Hz, C\( \text{H}_3 \)), 1.55 (9H, s, C(C\( \text{H}_3 \))\(_3\)), 1.86 (1H, ddt, \( J = 14.5, 5.0 \) and 2.5 Hz, 2-CH\(_2\)H), 2.53 (1H, m, 2-CH\(_2\)H), 4.70 (1H, dddd, \( J = 11.5, 6.5, 2.5 \) and 0.5 Hz, 3-CH\(_2\)H), 4.75 (1H, m, 1-CH\(_2\)H), 4.79 (1H, m, 3-CH\(_2\)H); \( \delta_{\text{C}} \) (100 MHz, CDCl\(_3\)) 18.6 (C\( \text{H}_3 \)), 27.9 (C(C\( \text{H}_3 \))\(_3\)), 28.1 (2-CH\(_2\)), 53.2 (1-CH\(_2\)), 69.3 (3-CH\(_2\)), 85.0 (C(CH\(_3\))\(_3\)), 150.5 (C=O); \( m/z \) (%) ESI-MS 290.05 ([M+K\(^+\)]\(^+\)), 274.07 ([M+Na\(^+\)]\(^+\)); HRMS (ESI): Found: ([M+Na\(^+\)]\(^+\)) 274.0725, C\(_9\)H\(_{17}\)NO\(_5\)SNa requires 274.0720.

Cyclic Sulfamidate \( \text{In} \)

(4S)-Dibenzyl 1,2,3-oxathiazinane-3,4-dicarboxylate-2-oxide

Imidazole (622 mg, 9.17 mmol) was dissolved in anhydrous CH\(_2\)Cl\(_2\) (15 mL), followed by addition of Et\(_3\)N (0.70 mL, 5.1 mmol) and cooling to -40 °C. SOCl\(_2\) (0.19 mL, 2.5 mmol) was then added, followed by dropwise addition of a solution of N-Cbz-L-homoserine benzyl ester (668 mg, 1.95 mmol) in anhydrous CH\(_2\)Cl\(_2\) (6 mL). The resulting pale yellow mixture was allowed to slowly warm up to 0 °C and was stirred at this temperature for 6 h. The mixture was then poured into water (15 mL). The organic layer was separated and washed with water (15 mL), brine (15 mL), dried over \( \text{Na}_2\text{SO}_4 \) and concentrated in vacuo to yield a crude mixture that was purified by flash column chromatography (EtOAc-hexane 3:7) to furnish the title sulfamidate (637 mg, 84%, 2:1 d.r. A:B) as a pale yellow oil; \( \nu_{\text{max}}/\text{cm}^{-1} \) 1724 (s), 1384 (m), 1288 (s), 1179 (s), 1150 (s), 1094 (m); \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 2.33 (1H, m, 2-CH\(_2\)H of B), 2.46 (1H, m, 2-CH\(_2\)H of B), 2.65 (1H, m, 2-CH\(_2\)H of A), 2.73 (1H, m, 2-CH\(_2\)H of A), 3.93 (1H, m, 3-CH\(_2\)H of A), 4.03 (1H, dt, \( J = 11.0 \) and 8.5 Hz, 3-CH\(_2\)H of A), 4.54 (1H, dddd, \( J = 11.0, 7.5 \) and 4.0 Hz, 3-CH\(_2\)H of A), 4.86-4.96 (3H, m, 1-CH of A and B and 3-CH\(_2\)H of B), 5.17-5.32 (8H, m, OC\(_2\)H\(_2\)Ph \( \times \) 2 of A and B), 7.32-7.39 (20H, m, ArCH of A and B); \( \delta_{\text{C}} \) (100 MHz, CDCl\(_3\)) 24.7 (2-CH\(_2\) of A and B), 51.3 (1-CH of A), 55.1 (3-CH\(_2\) of B), 56.9 (3-CH\(_2\) of A), 67.7, 68.7 (OCH\(_2\)Ph \( \times \) 4 of A and B), 128.0, 128.1, 128.5 (2 signals), 128.6 (ArCH \( \times \) 20 of A and B), 135.0, 135.1 (ArC \( \times \) 2 of A), 169.5 (2 signals, C=O of A and B), 179.5 (C=O of A); signals attributable to 1-CH of B, ArC of B and C=O (ester) of B were not observed; \( m/z \) (%) ESI-MS 412.08 ([M+Na\(^+\)]\(^+\)); HRMS (ESI): Found: ([M+Na\(^+\)]\(^+\)) 412.0837, C\(_{19}\)H\(_{19}\)NO\(_6\)SNa requires 412.0825.

(5S)-Dibenzyl-1,2,3-oxathiazinane-3,4-dicarboxylate-2,2-dioxide \( \text{I} \)

To an ice-cooled (0 °C) solution of sulfamidite \( c \) (see above) (615 mg, 1.58 mmol) in MeCN (13 mL) was added RuCl\(_3\) (1.4 mg, 0.40 mol%), NaIO\(_4\) (540 mg, 2.53 mmol) and then water (9 mL). The mixture

Supporting Information 6
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

was stirred at 0 °C for 6 h. The reaction mixture was then poured into water (15 mL) and extracted with EtOAc (3 × 20 mL). The organic extracts were combined, washed with brine (10 mL), dried over Na₂SO₄ and concentrated in vacuo to afford a pale brown solid that was dissolved in EtOAc (15 mL) and DMSO (0.15 mL) was added. After stirring at r.t. for 3 h the mixture was concentrated in vacuo and was purified by flash column chromatography (Et₂O-hexane 2:3) to afford cyclic sulfamidate 1p (540 mg, 84%) as a colorless oil that was triturated with hexane (in the freezer) to afford a colorless amorphous solid that was recrystallized from chloroform; m.p. 89-91 °C (CHCl₃); [α]D²² +10, (c = 0.4, CHCl₃); υ max/cm⁻¹ (neat) 1739 (s), 1396 (s), 1288 (s), 1180 (s); δH (400 MHz, CDCl₃) 2.48 (1H, dddd, J = 14.5, 11.0, 6.5 and 5.5 Hz, 2-CH₂H), 2.65 (1H, ddt, J = 14.5, 5.0 and 2.5 Hz, 2-CH₃H), 4.64 (1H, dddd, J = 11.0, 6.5, 2.5 and 1.0 Hz, 3-CH₃H), 4.75 (1H, td, J = 11.0 and 5.0 Hz, 3-CH₂H), 5.21 (2H, d, J = 9.5 Hz, OCH₂Ph), 5.26 (2H, d, J = 6.5 Hz, OCH₂Ph), 5.30 (1H, m, 1-CH), 7.34-7.37 (10H, m, ArCH); δC (100 MHz, CDCl₃) 24.4 (2-CH₂H), 57.7 (1-CH), 68.3, 69.8 (OCH₂Ph × 2), 70.9 (3-CH₂), 127.8, 128.2, 128.6 (2 signals) (ArCH × 10), 134.4, 134.7 (ArC × 2), 151.9 (C=O), 168.1 (C=O); m/z (%) ESI-MS 428.08 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 428.0780, C₁₉H₁₉NO₇SNa requires 428.0774.

Cyclic Sulfamidate 1u

(±)-Benzyl (3-hydroxybutan-2-yl)carbamate

To a rapidly stirred solution of 35% aqueous ammonia (160 mL) was added a solution of cis-2,3-epoxybutane (0.61 mL, 6.93 mmol) in ethanol (3 mL) and the reaction mixture was allowed to stir at r.t. overnight. The mixture was then concentrated to about 50 mL (care to be taken as the primary amine is fairly volatile) and NaHCO₃ (582 mg, 6.93 mmol) and CbzCl (0.99 mL, 6.93 mmol) were added. The resulting suspension was stirred for 2.5 h before being extracted with CH₂Cl₂ (3 × 50 mL) and the combined organic layers were dried over Na₂SO₄ and concentrated in vacuo to provide a pale yellow oil that was purified by flash column chromatography (EtOAc-hexane 2:3 to 3:2) to afford the title amino alcohol (1.40 g, 90%) as a colorless oil; υ max/cm⁻¹ (neat) 3408 (w), 3328 (w), 1690 (s), 1529 (m), 1454 (m), 1240 (s); δH (400 MHz, CDCl₃) 1.17 (3H, d, J = 6.5 Hz, CH₃), 1.18 (3H, d, J = 6.5 Hz, CH₃), 2.04 (1H, br s, OH), 3.67-3.74 (2H, m, 1-CH and 2-CH), 4.95 (1H, br s, NH), 5.12 (2H, s, OCH₂Ph), 7.35-7.39 (5H, m, ArCH), δC (100 MHz, CDCl₃) 18.1 (CH₃), 20.3 (CH₃), 52.3 (1-CH), 66.8 (OCH₂Ph), 70.8 (2-CH), 128.1, 128.5 (ArCH × 5), 136.5 (ArC), 156.6 (C=O); m/z (%) ESI-MS 246.11 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 246.0780, C₁₂H₁₇NO₃Na requires 246.0774.

(±)-Benzyl 4,5-dimethyl-1,2,3-oxathiazolidine-3-carboxylate-2-oxide

Imidazole (1.00 g, 14.7 mmol) was dissolved in anhydrous CH₂Cl₂ (25 mL), followed by addition of Et₃N (1.13 mL, 8.14 mmol) and cooling to -40 °C. SOCl₂ (0.30 mL, 4.07 mmol) was then added, followed by dropwise addition of a solution of the above amino alcohol (700 mg, 3.13 mmol) in anhydrous CH₂Cl₂ (8 mL) over a period of 5 minutes. The resulting pale yellow mixture was allowed to warm up to 0 °C and was stirred at this temperature for 1 h. Once the reaction was complete as indicated by TLC, the mixture was poured into water (30 mL). The organic layer was separated and
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 8

washed with water (30 mL), brine (30 mL), dried over Na₂SO₄ and concentrated in vacuo to yield a crude mixture that was purified by flash column chromatography (EtOAc-hexane 1:4) to furnish the title cyclic sulfamidite (789 mg, 94%, 7:1 d.r. A:B) as a pale yellow oil; \( \nu_{\text{max}} \text{/cm}^{-1} 1723 \text{ (s)}, 1386 \text{ (m)}, 1298 \text{ (s)}, 1189 \text{ (s)}, 1138 \text{ (s)}, 1037 \text{ (m)} \); \( \delta_{\text{H}} (400 \text{ MHz, CDCl₃}) 1.34 \text{ (3H, d, } J = 6.5 \text{ Hz, } \text{C-CH₃ of B}), 1.51 \text{ (3H, d, } J = 6.0 \text{ Hz, CH₃ of A}), 1.52 \text{ (3H, d, } J = 6.0 \text{ Hz, CH₃ of A}), 1.73 \text{ (3H, d, } J = 6.5 \text{ Hz, CH₃ of B}), 3.57 \text{ (1H, dq, } J = 9.5 \text{ and } 6.0 \text{ Hz, 1-CH of A}), 4.20 \text{ (1H, qd, } J = 6.5 \text{ and } 2.0 \text{ Hz, 1-CH of B}), 4.68 \text{ (1H, dq, } J = 6.5 \text{ and } 2.0 \text{ Hz, 2-CH of B}), 5.05 \text{ (1H, dq, } J = 9.5 \text{ and } 6.0 \text{ Hz, 2-CH of A}), 5.22 \text{ (1H, d, } J = 12.5 \text{ Hz, OCH2Ph of A}), 5.27-5.30 \text{ (2H, m, OCH2Ph of B)}, 5.32 \text{ (1H, d, } J = 12.5 \text{ Hz, OCH2Ph of A}), 7.30-7.41 \text{ (10H, m, ArCH of A and B); } \delta_{\text{C}} (100 \text{ MHz, CDCl₃}) 17.0 \text{ (CH₃ of A)}, 17.2 \text{ (CH₃ of A)}, 19.2 \text{ (CH₃ of B)}, 22.2 \text{ (CH₂ of B), 58.7 (1-CH of B), 59.4 (1-CH of A), 68.4 (OCH2Ph of A and B), 86.3 (2-CH of A), 91.1 (2-CH of B), 128.0, 128.1, 128.4, 128.5, 128.6 (ArCH × 10 of A and B), 135.1 (ArC of A and B), 152.4 (C=O of A and B); m/z (%) ESI-MS 292.06 ([M+Na]⁺), 270.08 ([M+H]⁺); HRMS (ESI): Found: ([M+Na]⁺) 292.0614, C12H15NO4SNa requires 292.0614.

(±)-Benzyl 4,5-dimethyl-1,2,3-oxathiazolidine-3-carboxylate-2,2-dioxide 1u

To an ice-cooled (0 °C) solution of the above cyclic sulfamidite (706 mg, 2.62 mmol) in MeCN (20 mL) was added RuCl₃ (1.1 mg, 0.20 mol%), NaIO₄ (894 mg, 4.19 mmol) and then water (15 mL). The mixture was stirred at 0 °C for 5.5 h. The reaction mixture was then poured into water (20 mL) and extracted with EtOAc (3 × 40 mL). The organic extracts were combined, washed with brine (50 mL), dried over Na₂SO₄ and concentrated in vacuo to afford a pale brown solid. This material was dissolved in EtOAc (15 mL) and DMSO (0.15 mL) was added. After stirring at r.t. for 3 h the mixture was pre-adsorbed onto SiO₂ and purified by flash column chromatography (EtOAc-hexane 1:3) to afford cyclic sulfamidate 1u (700 mg, 94%) as a colorless oil which upon trituration with hexane furnished a colorless amorphous solid; \( \nu_{\text{max}} \text{/cm}^{-1} 1734 \text{ (s)}, 1371 \text{ (s)}, 1296 \text{ (s)}, 1190 \text{ (s)}, 1167 \text{ (w)} \); \( \delta_{\text{H}} (400 \text{ MHz, CDCl₃}) 1.49 \text{ (3H, d, } J = 6.0 \text{ Hz, CH₃), 1.60 (3H, d, } J = 6.5 \text{ Hz, CH₃), 4.10 (1H, apparent quintet, } J = 6.0 \text{ Hz, 1-CH), 4.55 (1H, apparent quintet, } J = 6.5 \text{ Hz, 2-CH), 5.30 (1H, d, } J = 12.5 \text{ Hz, OCH2Ph), 5.35 (1H, d, } J = 12.5 \text{ Hz, OCH2Ph), 7.35-7.44 (5H, m, ArCH); } \delta_{\text{C}} (100 \text{ MHz, CDCl₃}) 17.0 \text{ (CH₃), 17.7 (CH₃), 60.3 (1-CH), 69.2 (OCH2Ph), 82.0 (2-CH), 127.9, 128.6 (ArCH × 5), 134.5 (ArC), 149.9 (C=O); m/z (%) ESI-MS 308.06 ([M+Na]⁺); HRMS (ESI): Found: ([M+Na]⁺) 308.0565, C12H15NO5SNa requires 308.0563.

Cyclic Sulfamidate 1v

\((2R, 3R)-3\text{-Hydroxy-2-methylbutanenitrile}\)

To a solution of (4R,5R)-4,5-dimethyl-1,3,2-dioxathiolane-2,2-dioxide\[13\] (1.69 g, 11.1 mmol) in anhydrous DMF (35 mL) was added NaCN (600 mg, 12.2 mmol) portionwise and the resulting mixture was heated to 70 °C for 3 h. The solvent was removed under high vacuum and the resulting residue was redissolved in THF (60 mL). To the stirred solution was added H₂O (0.18 mL) followed by conc. H₂SO₄ (0.47 mL) and the stirring was continued for 40 minutes. NaHCO₃ (2.1 g) was added and the mixture...
was stirred for a further 20 minutes before being filtered through Celite®, concentrated in vacuo, and purified by flash column chromatography (EtOAc-hexane 1:1) to afford the title nitrile (1.04 g, 95%) as a colourless oil; \( \nu_{\text{max}}/\text{cm}^{-1} \) (neat) 3415 (s), 2981 (m), 2245 (m), 1455 (s), 1383 (s), 1143 (s), 1113 (s), 1063 (m), 1022 (m); \( \delta_{\text{H}} \) (400 MHz, CDCl3) 1.29-1.36 (6H, m, 1-CH\textsubscript{3} and 4-CH\textsubscript{3}), 2.45 (1H, br s, OH), 2.75 (1H, qd, \( J = 7.0 \) and 5.5 Hz, 2-CH\textsubscript{2}), 3.88 (1H, apparent quintet, \( J = 6.0 \) Hz, 3-CH\textsubscript{2}); \( \delta_{\text{C}} \) (100 MHz, CDCl3) 13.7 (1-CH\textsubscript{3}), 19.8 (5-CH\textsubscript{3}), 33.8 (2-CH\textsubscript{2}), 68.4 (3-CH); \( m/z \) (%) ESI-MS 122.06 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 122.0579, C\textsubscript{5}H\textsubscript{9}NONa requires 122.0576.

**To an ice-cooled solution of above nitrile (600 mg, 6.06 mmol) in anhydrous THF (15 mL), was portionwise added LiAlH\textsubscript{4} (920 mg, 24.2 mmol). Once the gas evolution ceased, the reaction was allowed to warm up to r.t. and was stirred for 1 h. The reaction was then cooled to 0 °C and water (0.9 mL), aqueous 4M NaOH (0.9 mL) and then water again (2.7 mL) were added dropwise (caution: exotherm and vigorous gas evolution) to form a colourless precipitate. The mixture was then filtered through Celite® washing with copious amounts of Et\textsubscript{2}O and concentrated in vacuo (care: the free amine is volatile; pressure set to 300 mbar) to furnish the free amine which was used in the next step without purification.**

To an ice-cooled mixture of the free amine (625 mg, 6.06 mmol) and Et\textsubscript{3}N (0.93 mL, 6.66 mmol) in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (30 mL) was slowly added CbzCl (0.95 mL, 6.66 mmol). The reaction mixture was allowed to warm up to r.t. and was stirred for 3 h. The reaction was quenched by addition of aqueous 1M HCl (20 mL). The organic layer was separated, washed with brine (20 mL), dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuo. Flash column chromatography (EtOAc-hexane 2:3) afforded the title amino alcohol (1.10 g, 77%) as a colourless oil; \( \nu_{\text{max}}/\text{cm}^{-1} \) 3331 (m), 2970 (m), 1693 (s), 1521 (s), 1454 (m), 1247 (s), 1142 (s); \( \delta_{\text{H}} \) (400 MHz, CDCl3) 0.87 (3H, d, \( J = 7.0 \) Hz, 3-CH\textsubscript{3}), 1.16 (3H, d, \( J = 6.5 \) Hz, 5-CH\textsubscript{3}), 1.63 (1H, m, 2-CH\textsubscript{2}), 2.64 (1H, br s, OH), 3.04 (1H, dt, \( J = 14.0 \) and 5.5 Hz, 1-CH\textsubscript{2}H), 3.30 (1H, ddd, \( J = 14.0, 9.0 \) and 7.0 Hz, 1-CH\textsubscript{3}H), 3.88 (1H, m, 4-CH\textsubscript{2}), 5.11 (2H, s, OCH\textsubscript{2}Ph), 5.25 (1H, br s, NH), 7.31-7.37 (5H, m, ArCH\textsubscript{2}); \( \delta_{\text{C}} \) (100 MHz, CDCl3) 10.9 (3-CH\textsubscript{3}), 19.8 (5-CH\textsubscript{3}), 39.6 (2-CH), 44.1 (1-CH\textsubscript{2}), 66.8 (OCH\textsubscript{2}Ph), 67.3 (4-CH), 128.1 (2 signals), 128.5 (ArCH \times 5), 136.4 (ArC), 157.3 (C=O); \( m/z \) (%) ESI-MS 260.13 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 260.1262, C\textsubscript{13}H\textsubscript{19}NO\textsubscript{3}Na requires 260.1257.

**To an ice-cooled solution of above nitrile (600 mg, 6.06 mmol) in anhydrous THF (15 mL), was portionwise added LiAlH\textsubscript{4} (920 mg, 24.2 mmol). Once the gas evolution ceased, the reaction was allowed to warm up to r.t. and was stirred for 1 h. The reaction was then cooled to 0 °C and water (0.9 mL), aqueous 4M NaOH (0.9 mL) and then water again (2.7 mL) were added dropwise (caution: exotherm and vigorous gas evolution) to form a colourless precipitate. The mixture was then filtered through Celite® washing with copious amounts of Et\textsubscript{2}O and concentrated in vacuo (care: the free amine is volatile; pressure set to 300 mbar) to furnish the free amine which was used in the next step without purification. To an ice-cooled mixture of the free amine (625 mg, 6.06 mmol) and Et\textsubscript{3}N (0.93 mL, 6.66 mmol) in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (30 mL) was slowly added CbzCl (0.95 mL, 6.66 mmol). The reaction mixture was allowed to warm up to r.t. and was stirred for 3 h. The reaction was quenched by addition of aqueous 1M HCl (20 mL). The organic layer was separated, washed with brine (20 mL), dried over Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuo. Flash column chromatography (EtOAc-hexane 2:3) afforded the title amino alcohol (1.10 g, 77%) as a colourless oil; \( \nu_{\text{max}}/\text{cm}^{-1} \) 3331 (m), 2970 (m), 1693 (s), 1521 (s), 1454 (m), 1247 (s), 1142 (s); \( \delta_{\text{H}} \) (400 MHz, CDCl3) 0.87 (3H, d, \( J = 7.0 \) Hz, 3-CH\textsubscript{3}), 1.16 (3H, d, \( J = 6.5 \) Hz, 5-CH\textsubscript{3}), 1.63 (1H, m, 2-CH\textsubscript{2}), 2.64 (1H, br s, OH), 3.04 (1H, dt, \( J = 14.0 \) and 5.5 Hz, 1-CH\textsubscript{2}H), 3.30 (1H, ddd, \( J = 14.0, 9.0 \) and 7.0 Hz, 1-CH\textsubscript{3}H), 3.88 (1H, m, 4-CH\textsubscript{2}), 5.11 (2H, s, OCH\textsubscript{2}Ph), 5.25 (1H, br s, NH), 7.31-7.37 (5H, m, ArCH\textsubscript{2}); \( \delta_{\text{C}} \) (100 MHz, CDCl3) 10.9 (3-CH\textsubscript{3}), 19.8 (5-CH\textsubscript{3}), 39.6 (2-CH), 44.1 (1-CH\textsubscript{2}), 66.8 (OCH\textsubscript{2}Ph), 67.3 (4-CH), 128.1 (2 signals), 128.5 (ArCH \times 5), 136.4 (ArC), 157.3 (C=O); \( m/z \) (%) ESI-MS 260.13 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 260.1262, C\textsubscript{13}H\textsubscript{19}NO\textsubscript{3}Na requires 260.1257.

**Supporting Information 9**
pale yellow mixture was stirred at 0 °C for 2 h and then at r.t. for 1.5 h. After consumption of the amino alcohol, the mixture was poured into water (30 mL). The organic layer was separated and washed with water (20 mL), brine (20 mL), dried over Na2SO4 and concentrated in vacuo to yield a crude mixture that was purified by flash column chromatography (Et2O-hexane 2:3) to furnish the title cyclic sulfamidite (700 mg, 84%, 3:2 d.r. A:B) as a pale yellow oil; \( \nu_{\text{max}}/\text{cm}^{-1} 1719 (s), 1456 (m), 1384 (s), 1305 (s), 1236 (s), 1172 (s), 1119 (s); \delta_1 (400 MHz, CDCl3) 0.95 (3H, d, \text{J} = 7.0 \text{ Hz}, 3-\text{CH}_3 \text{ of } A), 1.26 (3H, \text{d, J = 6.5 Hz, 5-CH}_3 \text{ of } A), 1.58 \text{ (3H, d, J = 7.0 Hz, 5-CH}_3 \text{ of } B), 1.82 \text{ (1H, m, 2-CH}_2 \text{ of } A), 2.41 \text{ (1H, m, 2-CH}_2 \text{ of } B), 3.57 \text{ (1H, dd, } \text{J} = 14.0 \text{ and } 11.5 \text{ Hz, 1-CH}_2 \text{ of } A), 3.80 \text{ (1H, dd, } \text{J} = 13.5 \text{ and } 1.5 \text{ Hz, 1-CH}_2 \text{ of } B), 4.02 \text{ (1H, dd, } \text{J} = 7.0 \text{ and } 5.5 \text{ Hz, 4-CH}_2 \text{ of } B), 5.21 \text{ (1H, qd, } \text{J} = 6.5 \text{ and } 2.5 \text{ Hz, 4-CH}_2 \text{ of } A) \); \delta_2 (125 MHz, CDCl3) 9.6 (3-\text{CH}_3 \text{ of } A), 14.5 (3-\text{CH}_3 \text{ of } B), 17.0 (5-\text{CH}_3 \text{ of } A), 17.9 (5-\text{CH}_3 \text{ of } B), 32.3 (2-\text{CH of } A \text{ and } B), 37.5 (1-\text{CH}_2 \text{ of } B), 68.3, 68.4 (\text{OCH}_2 \text{Ph of } A \text{ and } B), 78.7 (4-\text{CH of } B), 128.0, 128.1, 128.4, 128.6 (\text{ArCH} \times 10 \text{ of } A \text{ and } B), 135.2 (\text{ArC of } A \text{ and } B), 153.2 (\text{C=O of } A \text{ and } B); m/z (%) ESI-MS 306.08 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 306.0770, C13H17NO4SNa requires 306.0770.

**To an ice-cooled (0 °C) solution of the above cyclic sulfamidite (635 mg, 2.24 mmol) in MeCN (17 mL) was added RuCl3 (1.8 mg, 0.40 mol%), NaIO4 (766 mg, 3.59 mmol) and then water (13 mL). The mixture was stirred at 0 °C for 6 h. Then the reaction mixture was poured into water (30 mL) and extracted with EtOAc (3 × 30 mL). The organic extracts were combined, washed with brine (50 mL), dried over Na2SO4 and concentrated in vacuo to afford a pale brown oil. This material was dissolved in EtOAc (10 mL) and DMSO (10 μL) was added. After stirring at r.t. for 3 h the mixture was pre-adsorbed onto SiO2 and purified by flash column chromatography (Et2O-hexane 1:1) to afford cyclic sulfamidate 1v (550 mg, 82%) as a colorless oil.**

**To an ice-cooled (0 °C) solution of the above cyclic sulfamidite (635 mg, 2.24 mmol) in MeCN (17 mL) was added RuCl3 (1.8 mg, 0.40 mol%), NaIO4 (766 mg, 3.59 mmol) and then water (13 mL). The mixture was stirred at 0 °C for 6 h. Then the reaction mixture was poured into water (30 mL) and extracted with EtOAc (3 × 30 mL). The organic extracts were combined, washed with brine (50 mL), dried over Na2SO4 and concentrated in vacuo to afford a pale brown oil. This material was dissolved in EtOAc (10 mL) and DMSO (10 μL) was added. After stirring at r.t. for 3 h the mixture was pre-adsorbed onto SiO2 and purified by flash column chromatography (Et2O-hexane 1:1) to afford cyclic sulfamidate 1v (550 mg, 82%) as a colorless oil which upon trituration with hexane (in the freezer) furnished a colorless crystalline solid; m.p. 32-34 °C (hexane); \([\alpha]_D^{21} +10, (c = 1.0, \text{CHCl}_3); \nu_{\text{max}}/\text{cm}^{-1} \text{(neat)} 1732 (s), 1393 (s), 1295 (s), 1245 (s), 1178 (s), 1122; \delta_3 (400 MHz, CDCl3) 1.10 (3H, d, \text{J} = 7.0 \text{ Hz, 3-CH}_3 \text{ of } A), 1.41 \text{ (3H, d, J = 6.5 Hz, 5-CH}_3 \text{ of } A), 2.05 \text{ (1H, q, J = 7.0 and 3.5 Hz, 2-CH}_2 \text{ of } A), 3.85 \text{ (1H, dd, J = 7.0 and 3.0 Hz, 4-CH}_2 \text{ of } A), 4.19 \text{ (1H, dd, J = 13.5 and 3.5 Hz, 1-CH}_2 \text{ of } A), 5.21 \text{ (1H, qd, J = 6.5 and 3.0 Hz, 2-CH}_2 \text{ of } A). \delta_4 (100 MHz, CDCl3) 9.8 (3-CH), 17.3 (5-CH), 152.2 (C=O); m/z (%) ESI-MS 338.05 ([M+K]+), 322.07 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 322.0770, C13H17NO5SNa requires 322.0770.**
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 11

Cyclic Sulfamidate 1w

\((4R,6R)-4,6\text{-dimethyl}-1,3,2\text{-dioxathiane}-2,2\text{-dioxide}\)

SOCl\(_2\) (0.27 mL, 3.8 mmol) was added dropwise to a solution of \((2R, 4R)-2,4\text{-pentanediol}\) (300 mg, 2.9 mmol) in anhydrous CH\(_2\)Cl\(_2\) (6 mL) and after effervescence ceased (ca. 5 minutes.) the reaction was heated to 60 °C in a sealed tube for 2 h. The reaction mixture was then cooled to r.t. and concentrated in vacuo. MeCN (3 mL), NaIO\(_4\) (870 mg, 4.1 mmol) and RuCl\(_3\)H\(_2\)O (0.3 mg, 0.06 mol%) were then added to the solution, followed by cooling to 0 °C and addition of water (4.5 mL). After 5 minutes, the reaction was complete as indicated by TLC and was diluted with Et\(_2\)O (10 mL). The aqueous layer was separated and the organic layer was washed sequentially with water (10 mL), aqueous NaHCO\(_3\) (10 mL) and brine (10 mL) before being dried over Na\(_2\)SO\(_4\), concentrated in vacuo and filtered through a plug of silica (eluting with EtOAc) to afford a colorless oil that was triturated with hexane to yield the title cyclic sulfate (420 mg, 88%) a colorless solid; m.p. 32-33 °C (Et\(_2\)O-hexane) [Lit. 34-35 °C (Et\(_2\)O-hexane)]; \(\delta^H\) (400 MHz, CDCl\(_3\)) 1.58 (6H, d, \(J = 6.5\) Hz, \(1\text{-CH}_3\)), 2.03 (2H, t, \(J = 5.5\) Hz, 2-\(\text{CH}_2\)), 5.06-5.10 (2H, m, \(1\text{-CH}_2\)); \(\delta^C\) (100 MHz, CDCl\(_3\)) 19.9 (2-\(\text{CH}_2\)), 35.2 (2-\(\text{CH}_2\)), 80.1 (1-\(\text{CH}\)). The spectroscopic properties of this compound were consistent with the data available in literature.[14]

\((2S,4R)\)-Benzyl-(4-hydroxypentan-2-yl)carbamate

To a solution of \((2R,4S)-4\text{-azidopentan-2-ol}[15]\) (685 mg, 5.30 mmol) in MeOH (30 mL), was slowly added Pd/C (10 wt % of Pd, 553 mg, 10 mol%) and the reaction mixture was put under a H\(_2\) atmosphere. After the reaction was complete as indicated by TLC (18 h) the reaction mixture was filtered through Celite\textsuperscript® washing with copious amounts of Et\(_2\)O. Concentration in vacuo (care: the free amine is volatile; pressure set to 300 mbar) furnished the free amine which was used in the next step without purification. To an ice-cooled mixture of the free amine (545 mg, 5.30 mmol) and Et\(_3\)N (0.89 mL, 6.36 mmol) in anhydrous CH\(_2\)Cl\(_2\) (60 mL) was slowly added CbzCl (0.88 mL, 6.36 mmol). The reaction mixture was allowed to warm up to r.t. and was stirred overnight at this temperature. The reaction was quenched by addition of aqueous 1M HCl (50 mL). The organic layer was separated, washed with brine (50 mL), dried over Na\(_2\)SO\(_4\) and concentrated in vacuo. Flash column chromatography (EtOAc-hexane 1:1) afforded the title compound (906 mg, 72%) as a colorless oil; \(\nu_{\text{max}}/\text{cm}^{-1}\) 3316 (w), 1690 (s), 1532 (m), 1455 (m), 1336 (m), 1253 (m), 1455 (m), 1336 (m), 1253 (s), 1086 (s), 1076 (s); \(\delta^H\) (400 MHz, CDCl\(_3\)) 1.19 (6H, apparent triplet, \(J = 6.5\) Hz, 1-\(\text{CH}_3\) and 5-\(\text{CH}_3\)), 1.51 (1H, dt, \(J = 14.0\) and 5.0 Hz, 3-\(\text{CHH}\)), 1.63 (1H, m, 3-\(\text{CHH}\)), 2.09 (1H, br s, OH), 3.81-3.91 (2H, m, 2-\(\text{CH}\) and 4-\(\text{CH}\)), 4.93 (1H, br s, NH), 5.04-5.11 (2H, m, OCH\(_2\)Ph), 7.29-7.37 (5H, m, Ar\(\text{CH}\)), \(\delta^C\) (100 MHz, CDCl\(_3\)) 21.7, 24.1 (1-\(\text{CH}_3\) and 5-\(\text{CH}_3\)), 45.7 (2-\(\text{CH}\)), 46.3 (3-\(\text{CH}\)), 66.2 (4-\(\text{CH}\)), 66.6 (OCH\(_2\)Ph), 128.0, 128.5 (Ar\(\text{CH} \times 5\)), 136.5 (ArC), 156.0 (C=O); \(m/z\) (% ESI-MS 260.13 ([M+Na\(^+\)], 238.14 ([M+H\(^+\)])); HRMS (ESI): Found: ([M+Na\(^+\)] 260.1265, C\(_{11}\)H\(_9\)NO\(_3\)Na requires 260.1257.

Supporting Information 11
Imidazole (336 mg, 4.95 mmol) was dissolved in anhydrous CH2Cl2 (8 mL), followed by addition of Et3N (0.38 mL, 2.74 mmol) and cooling to -40 °C. SOCl2 (0.10 mL, 1.37 mmol) was then added, followed by dropwise addition of a solution of the above amino alcohol (250 mg, 1.05 mmol) in anhydrous CH2Cl2 (5 mL) over a period of 3 minutes. The resulting pale yellow mixture was allowed to warm up to 0 °C and was stirred at this temperature for 4 h. Once the reaction was complete as indicated by TLC, the mixture was poured into water (20 mL). The organic layer was separated and washed with water (20 mL), brine (20 mL), dried over Na2SO4 and concentrated in vacuo to yield a crude mixture that was purified by flash column chromatography (Et2O-hexane 2:3) to furnish the title cyclic sulfamidite (263 mg, 89%, 5:1 d.r. A:B) as a pale yellow oil; υ max/cm−1 1720 (s), 1382 (s), 1294 (s), 1262 (s), 1178 (s), 1098 (m); δH (400 MHz, CDCl3) 1.43-1.47 (12H, m, 1-C3H3 and 5-C3H3 of A and B), 1.78 (1H, dt, J = 14.0 and 6.0 Hz, 3-CHH of A), 2.13 (1H, ddd, J = 14.5, 7.0 and 2.5 Hz, 3-CHH of B), 2.44 (1H, ddd, J = 14.0, 6.5 and 5.0 Hz, 3-CHH of A), 2.73 (1H, dt, J = 14.5 and 12.0 Hz, 3-CHH of B), 4.21 (1H, m, 2-CH of B), 4.33-4.41 (2H, m, 2-CH of A and 4-CH of B), 4.93 (1H, sextet, J = 6.5 Hz, 4-CH of A), 5.22-5.29 (4H, m, OC3H2Ph of A and B), 7.31-7.41 (10H, m, ArCH of A and B); δC (100 MHz, CDCl3) 21.3, 22.3 (1-C3H3 and 5-C3H3 of A and B), 22.7, 22.9 (1-C3H and 5-C3H of A), 35.0 (3-CH2 of B), 35.4 (3-CH2 of A), 46.2 (2-CH of A), 49.9 (2-CH of B), 65.0 (4-CH of A), 68.0 (OCH2Ph of A), 68.2 (OCH2Ph of B), 76.0 (4-CH of B), 127.9, 128.0, 128.3, 128.4, 128.6 (ArCH × 10 of A and B), 135.3 (ArC of A and B), 153.7 (C=O of A and B); m/z (%) ESI-MS 306.08 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 306.0769, C13H17NO4SNa requires 306.0770.

To an ice-cooled (0 °C) solution of the above cyclic sulfamidite (244 mg, 0.86 mmol) in MeCN (7 mL) was added RuCl3 (0.4 mg, 0.20 mol%), NaIO4 (294 mg, 1.37 mmol) and then water (5 mL). The mixture was stirred at 0 °C for 2.5 h. The reaction mixture was then poured into water (20 mL) and extracted with EtOAc (3 × 25 mL). The organic extracts were combined, washed with brine (25 mL), dried over Na2SO4 and concentrated in vacuo to afford a pale brown oil. This material was dissolved in EtOAc (10 mL) and DMSO (0.1 mL) was added. After stirring at r.t. for 3 h the mixture was pre-adsorbed onto SiO2 and purified by flash column chromatography (EtO-hexane 2:3) to afford cyclic sulfamidate 1w (208 mg, 81%) as a colorless oil; [α]D21 -17, (c = 1.0, CHCl3); υ max/cm−1 (neat) 1732 (s), 1377 (s), 1289 (s), 1178 (s), 1122 (w); δH (400 MHz, CDCl3) 1.49 (3H, d, J = 7.0 Hz, 1-CH3), 1.57 (3H, d, J = 6.5 Hz, 5-CH3), 1.75 (1H, ddd, J = 14.0, 7.0 and 3.0 Hz, 3-CHH), 2.55 (1H, dt, J = 14.0 and 7.0 Hz, 3-CHH), 4.79 (1H, quintet of d, J = 7.0 and 3.0 Hz, 2-CH), 4.99 (1H, sextet, J = 6.5 Hz, 4-CH), 5.30-5.37 (2H, m, OCH2Ph), 7.32-7.44 (5H, m, ArCH); δC (100 MHz, CDCl3) 21.9, 22.1 (1-CH3 and 5-CH3), 35.3 (3-CH2), 53.5 (2-CH), 69.3 (OCH2Ph), 80.2 (4-CH), 127.7, 128.4, 128.6 (ArCH × 5), 134.8 (ArC), 151.9 (C=O); m/z (%) ESI-MS 322.07 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 322.0723, C13H17NO5SNa requires 322.0720.
Cu-Catalyzed Borylation of Cyclic Sulfamidates

**General procedure A.**

Copper(I) iodide (2.4 mg, 10 mol%), triphenylphosphine (4.4 mg, 13 mol%), cyclic sulfamidate (0.13 mmol, 1.0 eq), Bu₄NI (70.9 mg, 0.19 mmol), B₂pin₂ (48.8 mg, 0.19 mmol) and LiOtBu (20.5 mg, 0.26 mmol) were added to an oven-dried Schlenk tube followed by addition of anhydrous DMF (1.0 mL). The reaction mixture was stirred at r.t. for 2 h. Aqueous 3 M H₂SO₄ (0.15 mL) was then added and after stirring for 2 h at r.t. the solution was basified with saturated aqueous NaHCO₃. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 5 mL). The combined organic extracts were dried over Na₂SO₄, and concentrated *in vacuo*. Where possible, *in situ* yield prior to flash column chromatography was determined by ¹H NMR spectroscopy using 1,4-dinitrobenzene as an internal standard. Flash column chromatography was used to isolate the boronic ester product.

The product boronic esters were found to decompose partially on prolonged contact with silica. To prevent this, oven-dried silica (for flash chromatography) was used and the contact with silica was kept to a minimum.

(R)-*tert*-Butyl (1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)carbamate 2a

Flash column chromatography (hexane 100% to Et₂O-hexane 1:4) afforded 2a (26.0 mg, 56%) as a colorless crystalline solid; m.p. 105-107°C (CH₂Cl₂-hexane); *ν* max /cm⁻¹ (neat) 3424 (w), 2977 (m), 1701 (s), 1496 (s), 1365 (s), 1323 (s), 1166 (s), 1141 (s); *δ*₁H (400 MHz, CDCl₃) 0.94-1.06 (2H, m, 3-C₆H₂), 1.26 (6H, s, C₆H₃ of Bpin), 1.27 (6H, s, C₆H₃ of Bpin), 1.40 (9H, s, C(C₆H₃)₃), 2.73 (1H, dd, *J* = 13.0 and 7.0 Hz, 1-CH₂), 2.83 (1H, m, CH₂H), 4.04 (1H, m, 2-C₆H), 4.74 (1H, d, *J* = 6.0 Hz, N-H), 7.17-7.20 (3H, m, ArC₆H), 7.26-7.30 (2H, m, ArCH₂); *δ*₁C (125 MHz, CDCl₃), 28.4 (C(CH₃)₃), 43.2 (1-CH₂), 48.7 (2-CH), 78.7 (C(CH₃)₃), 83.3 (C(CH₃)₂ of Bpin), 126.1, 128.2, 129.6 (ArCH₉CH), 138.6 (ArC), 155.1 (C=O); *δ*₁B (96.4 MHz, CDCl₃) 32.3; *m/z* (%) ESI-MS 400.2 ([M+K]⁺), 384.2 ([M+Na]⁺); HRMS (ESI): Found: ([M+Na]⁺) 384.2319, C₂₀H₃₂NO₄BNa requires 384.2310; Anal. Found: C, 66.68; H, 9.10; N, 4.23. Calc’d for C₂₀H₃₂NO₄B: C, 66.49; H, 8.93; N, 3.88.

Boronic ester 2a was obtained as a single enantiomer, which was determined by chiral HPLC (Chiralcel OJ-H, isocratic hexanes-iPrOH 99:1, 0.25 ml/min, 25 °C, detection wavelength = 225 nm); *t*ᵣ = 19.67 min.

Racemic boronic ester 2a was synthesised (starting with racemic 1a) and was used to determine HPLC conditions in order to validate an ability to separate the enantiomers. Racemic 2a was also prepared as a control to exclude a reaction pathway (for conversion of 1a to 2a) involving elimination (to give an enamine) followed by hydroboration, which would lead to a racemic product. This potential issue was previously recognised by Ito (see ref [5e] in main paper). Using enantiomerically pure 1a to provide 2a, we were able to confirm (by chiral HPLC) that no loss of enantiomeric purity had occurred in this conversion which excluded this alternative pathway. Based on this outcome, there is an
assumption that other related 1,2- and 1,3-cyclic sulfamidates reported retain their stereochemical purity, except where noted in Table 1 and Schemes 4 and 5 (in the main paper).

CCDC 1433121 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre. We thank Dr Mairi Haddow (University of Bristol) for carrying out the crystallographic analysis of 2a.

(R)-Benzyl (1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)carbamate 2b

Flash column chromatography (Et₂O-hexane 1:4) afforded 2b (31 mg, 61 %) as a colorless oil; $\nu_{\text{max}}$/cm⁻¹ (neat) 3335 (w), 2977 (w), 1705 (m), 1497 (m), 1371 (s), 1327 (s), 1249 (m), 1214 (m), 1142 (s), 1026 (m); $\delta$H (400 MHz, CDCl₃) δH (400 MHz, CDCl₃) 0.91-1.09 (2H, m, 3-CH₂), 1.24 (6H, s, CH₃ of Bpin), 1.25 (6H, s, CH₃ of Bpin), 2.77 (1H, dd, $J = 13.0$ and 7.0 Hz, 1-CHH), 2.85 (1H, dd, $J = 13.0$ and 5.5 Hz, CHH), 4.14 (1H, m, 2-CH), 5.05 (1H, br s, NH), 5.07 (2H, s, CH₂Ph), 7.16-7.35 (10H, m, ArCH); $\delta$C (125 MHz, CDCl₃) 16.9 (br s, 3-CH₂), 24.7 (CH₃ of Bpin), 24.9 (CH₃ of Bpin), 43.0 (1-CH₂), 49.3 (2-CH), 66.3 (CH₂Ph), 83.4 (C(CH₃)₂ of Bpin), 126.3, 127.9, 128.3, 130.0 (ArCH× 10), 136.9, 138.3 (ArC × 2), 155.5 (C=O); $\delta$B (96.4 MHz, CDCl₃) 32.5; m/z (%) ESI-MS 434.2 ([M+K]+), 418.2 ([M+Na]+); HRMS (ESI): Found: [M+Na]+ 418.2167, C₂₀H₃₂NO₄BNa requires 418.2160.

(S)-tert-Butyl (1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)carbamate 2f

Flash column chromatography (Et₂O-hexane 1:4) afforded 2f (23 mg, 63 %) as a colorless oil (67 % in situ); $\nu_{\text{max}}$/cm⁻¹ (neat) 3362 (w), 2977 (m), 1703 (s), 1505 (m), 1365 (s), 1327 (s), 1247 (m), 1168 (s),
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 15

1142 (s), 1055 (m); δH (400 MHz, CDCl3) 1.02-1.10 (2H, m, 2-CH2), 1.15 (3H, d, J = 6.5 Hz, CH3), 1.25 (12H, s, CH3 of Bpin), 1.44 (9H, s, C(CH3)3), 3.90 (1H, br signal, 1-CH), 4.71 (1H, br s, NH); δC (125 MHz, CDCl3) 20.0 (br s, 2-C2H2), 23.3 (CH3), 24.7 (CH3 of Bpin), 28.5 (C(CH3)3), 43.6 (1-CH), 78.7 (C(CH3)3), 83.2 (C(CH3)2 of Bpin), 155.1 (C=O); δB (96.4 MHz, CDCl3) 32.4; m/z (%) ESI-MS 324.2 ([M+K] +), 308.2 ([M+Na] +); HRMS (ESI): Found: [M+Na] + 308.2011, C14H28NO4BNa requires 308.2004.

(R)-Benzyl (3,3-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)carbamate 2g

Flash column chromatography (Et2O-hexane 1:9 to 3:7) afforded 2g (16 mg, 35%) as a colorless solid (36% in situ); m.p. °C (CH2Cl2-hexane) 84-86 °C; νmax/cm-1 (neat) 3343(w), 2966 (s), 1716 (s), 1517 (m), 1370 (s), 1335 (m), 1243 (m), 1145 (s); δH (500 MHz, CDCl3) 0.86 (1H, m, 2-C2H2H), 0.89 (9H, s, (C2H3)3), 1.08 (1H, dd, J = 15.5 and 4.5 Hz, 2-C2H2H), 1.19 (6H, s, C2H3 of Bpin), 1.20 (6H, s, C2H3 of Bpin), 3.74 (1H, td, J = 10.0 and 4.5 Hz, 1-CH), 4.86 (1H, d, J = 10.0 Hz, NH), 5.08 (2H, s, CH2Ph), 7.29-7.37 (5H, m, ArCH); δC (125 MHz, CDCl3) 13.0 (br s, 2-C2H2), 24.6 ((C2H3)2 of Bpin), 24.9 ((C2H3)2 of Bpin), 26.2 ((CH3)3), 35.6 ((C(CH3)3), 56.4 (1-CH), 66.4 (CH2Ph), 83.3 (C(CH3)2 of Bpin), 127.9, 128.1, 128.4 (ArCH × 5), 136.9 (ArC), 156.0 (C=O); δB (96.4 MHz, CDCl3) 31.9; m/z (%) ESI-MS 384.23 ([M+Na] +), 362.25 ([M+H] +); HRMS (ESI): Found: ([M+Na] +) 384.2332, C20H32NO4BNa requires 384.2320.

Benzyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate 2h

Flash column chromatography (Et2O-hexane 1:4 to 2:3) afforded 2h (23 mg, 56%) as a colorless oil; νmax/cm-1 (neat) 3345 (w), 2927 (m), 1716 (s), 1521 (m), 1458 (m), 1372 (m), 1321 (m), 1252 (m), 1143 (s); δH (500 MHz, CDCl3) 0.99 (3H, d, J = 7.5 Hz, C2H3), 1.23 (12H, s, CH3 of Bpin), 1.24 (1H, m, 2-CH2), 3.16-3.28 (2H, m, 1-CH2), 5.08-5.15 (3H, m, CH2Ph and NH), 7.29-7.37 (5H, m, ArCH); δC (125 MHz, CDCl3) 13.0 (C2H3), 18.2 (br s, 2-CH2), 24.7 (CH3 of Bpin), 43.9 (1-CH2), 66.4 (CH2Ph), 83.3 (C(CH3)2 of Bpin), 128.0, 128.1, 128.4 (ArCH × 5), 136.9 (ArC), 156.4 (C=O); δB (96.4 MHz, CDCl3) 31.9; m/z (%) ESI-MS 342.19 ([M+Na] +), 320.20 ([M+H] +); HRMS (ESI): Found: ([M+Na] +) 342.1855, C17H26NO4BNa requires 342.1850.

Racemic sulfamidate 1h was synthesised from the corresponding racemic amino alcohol and subject to the same borylation reaction conditions to give racemic 2h. Chiral HPLC revealed that 2h (prepared using enantiomerically pure 1h) was also racemic.

Chiral HPLC conditions: Column: Chiralpak IB; Solvent: isocratic hexane-i-PrOH (98.5:1.5, 0.5 mL/min, 12 °C); detection wavelength: 250 nm; tR = 27.9 min and tR = 34.2 min.

Pd-catalyzed borylation of R-1h.

To an oven-dried Schlenk tube were added K3PO4.H2O (58.8 mg, 0.255 mmol), B2pin2 (36.1 mg, 0.153 mmol), Pd2dba3 (0.5 mol%, 0.6 mg), [tBu2MePH][BF4] (3 mol%, 0.9 mg) and cyclic sulfamidate 1h

Supporting Information 15
(34.7 mg, 0.128 mmol). The Schlenk tube was then put under nitrogen followed by addition of degassed tBuOH (1 mL) and degassed water (30 μL) and the reaction mixture was heated to 60 °C overnight. After cooling to r.t., aqueous 3 M H2SO4 (0.15 mL) was added and after stirring for 2 h at r.t. the solution was basified with saturated aqueous NaHCO3. The organic layer was separated, and the aqueous layer extracted with EtOAc (3 × 5 mL). The combined organic extracts were dried over Na2SO4, concentrated in vacuo and purified by flash column chromatography (Et2O-hexane 1:9 to 3:7) to afford tert-Butyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)carbamate 2i (19 mg, 52%) as a colorless oil (71% in situ); $\nu_{\text{max}}$/cm$^{-1}$ (neat) 3391 (w), 2978 (m), 1715 (s), 1382 (s), 1346 (s), 1248 (m), 1178 (m), 1145 (s); δH (500 MHz, CDCl3) 1.03 (2H, t, $J = 7.5$ Hz, 2-CH$_2$), 1.25 (12H, s, CH$_3$ of Bpin), 1.44 (9H, s, C(CH$_3$)$_3$), 3.23 (2H, t, $J = 7.0$ Hz, 1-CH$_2$), 4.70 (1H, br s, NH); δC (125 MHz, CDCl3) 12.7 (br s, 2-CH$_2$), 24.1 (2-CH$_2$), 24.8 (CH$_3$ of Bpin), 28.4 (C(CH$_3$)$_3$), 36.3 (1-CH$_2$), 78.8 (C(CH$_3$)$_3$), 83.3 (C(CH$_3$)$_2$ of Bpin), 155.8 (C=O); δB (96.4 MHz, CDCl3) 33.1; m/z (%) ESI-MS 294.18 ([M+Na]$^+$); HRMS (ESI): Found: ([M+Na]$^+$) 294.1839, C$_{13}$H$_{26}$NO$_4$BNa requires 294.1850.

**tert-Butyl (3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate 2k**

Flash column chromatography (Et2O-hexane 1:4) afforded 2k (28 mg, 77%) as a colorless oil (80% in situ); $\nu_{\text{max}}$/cm$^{-1}$ (neat) 3371 (w), 2978 (m), 2932 (m), 1705 (s), 1519 (m), 1367 (s), 1248 (m), 1169 (s), 1145 (s); δH (500 MHz, CDCl3) 0.79 (2H, t, $J = 7.5$ Hz, 3-CH$_2$), 1.24 (12H, s, CH$_3$ of Bpin), 1.43 (9H, s, C(CH$_3$)$_3$), 1.59 (2H, apparent quintet, $J = 7.0$ Hz, 2-CH$_2$), 3.09 (2H, t, $J = 7.0$ Hz, 1-CH$_2$), 4.73 (1H, br s, NH); δC (125 MHz, CDCl3) 8.5 (br s, 3-CH$_3$), 24.1 (2-CH$_2$), 24.8 (CH$_3$ of Bpin), 28.4 (C(CH$_3$)$_3$), 42.6 (1-CH$_2$), 78.8 (C(CH$_3$)$_3$), 83.1 (C(CH$_3$)$_2$ of Bpin), 155.9 (C=O); δB (96.4 MHz, CDCl3) 33.0; m/z
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 17

(% ESI-MS 308.20 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 308.12, C14H28NO4BNa requires 308.2004.

(R)-tert-Butyl-(1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)carbamate 2l

Flash column chromatography (Et2O-toluene 1:9) afforded 2l (31 mg, 65%) as a colorless oil; $\nu_{\text{max}}$/cm$^{-1}$ (neat) 3369 (w), 2978 (m), 2933 (m), 1708 (s), 1503 (m), 1373 (s), 1169 (s), 1145 (s); $\delta_H$ (500 MHz, CDCl3) 0.82 (2H, apparent triplet, $J$ = 7.5 Hz, 4-CH$_2$), 1.24 (6H, s, CH$_3$ of Bpin), 1.25 (6H, s, CH$_3$ of Bpin), 1.40 (9H, s, C(CH$_3$)$_3$), 1.42 (1H, m, 3-CH$_2$H), 2.69 (1H, dd, $J$ = 13.0 and 7.0 Hz, 1-CH$_2$H), 2.85 (1H, dd, $J$ = 13.0 and 5.5 Hz, 1-CHH), 3.72 (1H, br signal, 2-CH), 4.61 (1H, d, $J$ = 8.0 Hz, NH), 7.18-7.21 (3H, m, ArCH), 7.26-7.29 (2H, m, ArCH); $\delta_C$ (125 MHz, CDCl3) 7.8 (br s, 4-CH$_2$), 24.7 (CH$_3$ of Bpin), 24.9 (CH$_3$ of Bpin), 27.7 (3-CH$_2$), 28.4 (C(CH$_3$)$_3$), 41.6 (1-CH$_2$), 53.8 (2-CH), 78.8 (C(CH$_3$)$_2$ of Bpin), 126.1, 128.2, 129.5 (ArCH × 5), 138.6 (ArC), 155.5 (C=O); $\delta_B$ (96.4 MHz, CDCl$_3$) 32.9; m/z (%) ESI-MS 398.28 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 398.2475, C21H34NO4BNa requires 398.2477.

(S)-tert-Butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)benzenesulfonamide 2m

Flash column chromatography (Et$_2$O-toluene 1:4) afforded 2m (13 mg, 24%) as a colorless oil; $\nu_{\text{max}}$/cm$^{-1}$ (neat) 3286 (w), 2997 (w), 1724 (s), 1379 (s), 1323 (s), 1265 (s), 1157 (s), 1150 (s), 1096 (s); $\delta_H$ (400 MHz, CDCl$_3$) 0.66-0.73 (2H, apparent triplet, $J$ = 7.5 Hz, 4-CH$_2$), 1.23 (6H, s, CH$_3$ of Bpin), 1.43 (1H, m, 3-CHH), 1.59 (1H, m, 3-CHH), 2.41 (3H, s, ArCH$_3$), 2.67 (1H, dd, $J$ = 13.5 and 7.5 Hz, 1-CHH), 2.77 (1H, dd, $J$ = 13.5 and 5.5 Hz, 1-CHH), 3.39 (1H, m, 2-CH$_2$), 4.68 (1H, d, $J$ = 7.5 Hz, NH), 7.03-7.06 (2H, m, ArCH), 7.17-7.24 (5H, m, ArCH), 7.66-7.68 (2H, m, ArCH); $\delta_C$ (125 MHz, CDCl$_3$) 6.8 (br s, 4-CH$_2$), 21.5 (ArCH$_3$), 24.8 (CH$_3$ of Bpin), 24.9 (CH$_3$ of Bpin), 27.9 (3-CH$_2$), 41.4 (1-CH$_2$), 56.7 (2-CH), 83.3 (C(CH$_3$)$_2$ of Bpin), 126.4, 127.0, 128.4, 129.5 (ArCH× 9), 137.5, 137.9, 142.9 (ArC × 3); $\delta_B$ (96.4 MHz, CDCl$_3$) 32.8; m/z (%) ESI-MS 452.2 ([M+Na]+), 430.2 ([M+H]+); HRMS (ESI): Found: [M+Na]+ 452.2475, C23H32NO4BSNa requires 452.2477.

(R)-4-Methyl-N-(1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)carbamate 2n

(R)-4-Methyl-N-(1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)carbamate 2n

(S)-tert-Butyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)carbamate 2n

Supporting Information 17
Flash column chromatography (Et\(_2\)O-hexane 1:3) afforded \(\text{2n} (28\ \text{mg}, 73\%)\) as a colorless oil; \(v_{\text{max}}/\text{cm}^{-1}\) (neat) 3360 (w), 2977 (m), 2932 (m), 1704 (s), 1515 (m), 1369 (s), 1321 (m), 1245 (m), 1170 (s), 1146 (s); \(\delta_H (500\ \text{MHz, CDCl}_3) 0.80 (2H, \text{apparent triplet, } J = 8.0\ \text{Hz, } 3-\text{CH}\_2), 1.10 (3H, d, J = 6.5\ \text{Hz, } \text{CH}_3),\)
\[1.24 (6H, s, \text{CH}_3 \text{of Bpin}), 1.25 (6H, s, \text{CH}_3 \text{of Bpin}), 1.43 (9H, s, C(C(H\_3))_3), 1.44-1.58 (2H, m, 2-\text{CH}_2), 3.57 (1H, m, 1-\text{CH}), 4.54 (1H, br s, NH); \delta_C (100\ \text{MHz, CDCl}_3) 7.5 (br s, 3-\text{CH}_2), 21.1(\text{CH}_3), 24.7 (\text{CH}_3 \text{of Bpin}), 24.9 (\text{CH}_3 \text{of Bpin}), 28.4 (\text{C(CH}_3)_3), 30.9 (2-\text{CH}_2), 48.3 (1-\text{CH}), 78.8 (\text{C(CH}_3)_2 \text{of Bpin}), 83.2 (\text{C(CH}_3)_2 \text{of Bpin}), 155.4 (\text{C}=\text{O}); \delta_B (96.4\ \text{MHz, CDCl}_3) 33.0; m/z (%) ESI-MS 338.19 ([M+K]+), 322.22 ([M+Na]+); HRMS (ESI): Found: ([M+Na]+) 322.2159, \text{C}_{15}\text{H}_{30}\text{NO}_4\text{BNa} \text{requires} 322.2163.

(S)-tert-Butyl (1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)carbamate 2o

Flash column chromatography (Et\(_2\)O-hexane 1:4) afforded \(\text{2o} (36\ \text{mg}, 78\%)\) as a colorless solid; m.p. 71-73°C (CH\(_2\)Cl\(_2\)-hexane); \([\alpha]_{D}^{20} -26, (c = 0.7, \text{CHCl}_3); v_{\text{max}}/\text{cm}^{-1}\) (neat) 3362 (w), 1699 (s), 1495 (m), 1366 (s), 1240 (m), 1215 (m), 1166 (s), 1143 (s); \(\delta_H (500\ \text{MHz, CDCl}_3) 0.75-0.86 (2H, m, 3-\text{CH}_2), 1.24 (6H, s, \text{CH}_3 \text{of Bpin}), 1.25 (6H, s, \text{CH}_3 \text{of Bpin}), 1.40 (9H, br s, C(C(H\_3))_3), 1.79-1.84 (2H, m, 2-\text{CH}_2), 4.53 (1H, br m, 1-\text{CH}), 4.54 (1H, br s, NH), 7.21-7.35 (5H, m, Ar\text{CH}); \delta_C (125\ \text{MHz, CDCl}_3) 8.2 (br s, 3-\text{CH}_2), 24.8 (\text{CH}_3 \text{of Bpin}), 24.9 (\text{CH}_3 \text{of Bpin}), 28.4 (\text{C(CH}_3)_3), 31.2 (2-\text{CH}_2), 56.8 (1-\text{CH}), 79.1 (\text{C(CH}_3)_2 \text{of Bpin}), 126.2, 126.8, 128.3 (\text{ArCH} \times 5), 143.4 (\text{ArC}), 155.4 (\text{C}=\text{O}); \delta_B (96.4\ \text{MHz, CDCl}_3) 32.8; m/z (%) ESI-MS 384.23 ([M+Na]+), 362.25 ([M+H]+); HRMS (ESI): Found: ([M+Na]+) 384.2328, \text{C}_{20}\text{H}_{32}\text{BNO}_4\text{Na} \text{requires} 384.2320.

(S)-Benzyl-2-(((benzyloxy)carbonyl)amino)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate 2p

Flash column chromatography (Et\(_2\)O-CH\(_2\)Cl\(_2\) 1:49) afforded \(\text{2p} (35\ \text{mg}, 60\%)\) as a colorless oil; \([\alpha]_{D}^{20} -4, (c = 1.6, \text{CHCl}_3); v_{\text{max}}/\text{cm}^{-1}\) (neat) 3345 (w), 1724 (s), 1524 (m), 1381 (s), 1322 (m), 1214 (m), 1168 (m), 1143 (s); \(\delta_H (500\ \text{MHz, CDCl}_3) 0.78-0.86 (2H, m, 3-\text{CH}_2), 1.21 (6H, s, \text{CH}_3 \text{of Bpin}), 1.22 (6H, s, \text{CH}_3 \text{of Bpin}), 1.83 (1H, m, 2-\text{CH}_2), 1.98 (1H, m, 2-\text{CH}_2), 4.38 (1H, td, J = 8.0 and 4.5 Hz, 1-\text{CH}), 5.11-5.17 (4H, m, OC\text{H}_2\text{Ph} \times 2), 5.57 (1H, d, J = 8.0 \text{Hz, NH}), 7.28-7.36 (10H, m, Ar\text{CH}); \delta_C (125\ \text{MHz, CDCl}_3) 66.9 (O\text{C}\text{H}_2\text{Ph} \times 2), 83.4 (\text{C(CH}_3)_2 \text{of Bpin}), 126.1, 126.8, 128.3 (\text{ArCH} \times 5), 143.4 (\text{ArC}), 155.4 (\text{C}=\text{O}); \delta_B (96.4\ \text{MHz, CDCl}_3) 32.8; m/z (%) ESI-MS 476.22 ([M+Na]+), 454.24 ([M+H]+); HRMS (ESI): Found: ([M+Na]+) 476.2204, \text{C}_{25}\text{H}_{32}\text{BNO}_6\text{Na} \text{requires} 476.2219.

(±)-Benzyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)carbamate 2u

Done according to procedure A, but with an increased amount of B\text{pin}_2 (2 eq., 65.1 mg, 0.25 mmol). Flash column chromatography (Et\(_2\)O-hexane 1:4) afforded racemic \(\text{1u} (19\ \text{mg}, 45\%)\) as a colorless oil.
and as a single diastereomer (based on $^1$H and $^{13}$C NMR); $\nu_{\text{max}}$/cm$^{-1}$ (neat) 3416 (w), 3336 (w), 1700 (s), 1511 (s), 1454 (m), 1380 (s), 1372 (s), 1319 (s), 1273 (s), 1212 (s), 1143 (s), 1058 (s), 1011 (s); $\delta_1$ (500 MHz, CDCl3) 0.99 (2H, d, $J = 7.5$ Hz, 4-CH$_3$), 1.12 (3H, d, $J = 6.5$ Hz, 1-CH$_3$), 1.24 (12H, s, CH$_3$ of Bpin), 1.26 (1H, m, 3-CH), 3.79 (1H, m, 2-CH$_3$), 5.10 (2H, s, OCH$_2$Ph), 5.19 (1H, d, $J = 9.0$ Hz, NH), 7.33 (1H, m, ArCH), 7.36-7.39 (4H, m, ArCH$_3$); $\delta_2$ (125 MHz, CDCl3) 12.8 (4-CH$_3$), 19.5 (1-CH$_3$), 24.1 (br s, 3-CH$_3$), 24.7 (CH$_3$ of Bpin), 24.8 (CH$_3$ of Bpin), 49.7 (2-CH$_3$), 66.3 (OCH$_2$Ph), 83.3 (C(CH$_3$)$_2$ of Bpin), 127.9, 128.1, 128.4 (ArCH × 5), 136.9 (ArC), 155.7 (C=O); $\delta_3$ (96.4 MHz, CDCl3) 33.0; m/z (%) ESI-MS 356.20 ([M+Na]$^+$), 334.22 ([M+H]$^+$); HRMS (ESI): Found: ([M+Na]$^+$) 356.2005, C$_{18}$H$_{28}$BNO$_4$Na requires 356.2007.

((2$S$,3$R$)-Benzyl 2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)carbamate 2v

Flash column chromatography (Et$_2$O-hexane 1:4 to 2:3) afforded 2v (7 mg, 16%) as a colorless oil; $\nu_{\text{max}}$/cm$^{-1}$ (neat) 3355 (w), 2974 (m), 1711 (s), 1531 (m), 1456 (m), 1372 (m), 1316 (m), 1256 (m), 1143 (s); $\delta_1$ (500 MHz, CDCl3) 0.92 (3H, d, $J = 7.5$ Hz, 3-CH$_3$), 0.97 (3H, d, $J = 6.5$ Hz, 5-CH$_3$), 1.04 (1H, m, 4-CH$_3$), 1.23 (12H, s, CH$_3$ of Bpin), 1.79 (1H, m, 2-CH$_3$), 3.15-3.19 (2H, m, 1-CH$_2$), 5.10 (2H, s, OCH$_2$Ph), 5.13 (1H, br s, NH), 7.29-7.39 (5H, m, ArCH); $\delta_2$ (125 MHz, CDCl3) 16.6 (3-CH$_3$), 20.5 (br s, 4-CH$_3$), 24.8 (CH$_3$ of Bpin), 36.0 (2-CH$_3$), 45.9 (1-CH$_3$), 66.5 (OCH$_2$Ph), 83.1 (C(CH$_3$)$_2$ of Bpin), 128.0, 128.1, 128.4 (ArCH × 5), 136.8 (ArC), 156.5 (C=O); m/z (%) ESI-MS 370.22 ([M+Na]$^+$), 348.05 ([M+H]$^+$); HRMS (ESI): Found: ([M+Na]$^+$) 370.2165, C$_{19}$H$_{30}$BNO$_4$Na requires 370.2164.

The major by-product was the reduction product 5[$^{16}$] isolated in 45% yield.

Replacing DMF with benzonitrile, flash column chromatography (Et$_2$O-hexane 1:4 to 2:3) afforded benzyl 3-iodo-2-methylbutyl)carbamate A (18 mg, 40%; as a single isomer but stereochemistry undefined) as a colorless oil; $\nu_{\text{max}}$/cm$^{-1}$ (neat) 3326 (w), 2965 (s), 1698 (s), 1529 (m), 1455 (w), 1260 (s), 1140 (m); $\delta_1$ (400 MHz, CDCl3) 1.03 (3H, d, $J = 6.5$ Hz, 3-CH$_3$), 1.69 (1H, m, 2-CH$_3$), 1.92 (3H, d, $J = 7.0$ Hz, 5-CH$_3$), 3.02 (1H, dt, $J_1 = 13.5$ and 6.5 Hz, 1-CH$_2$), 3.41 (1H, dt, $J_2 = 13.5$ and 6.5 Hz, 1-CH$_2$), 4.28 (1H, m, 4-CH$_3$), 4.86 (1H, br s, NH), 5.11 (2H, s, OCH$_2$Ph), 7.29-7.39 (5H, m, ArCH); $\delta_2$ (125 MHz, CDCl3) 16.6 (3-CH$_3$), 25.2 (5-CH$_3$), 34.2 (4-CH$_3$), 42.2 (2-CH$_3$), 45.5 (1-CH$_3$), 66.8 (OCH$_2$Ph), 128.2, 128.6 (ArCH × 5), 136.5 (ArC), 156.5 (C=O); m/z (%) ESI-MS 370.03 ([M+Na]$^+$), 348.05 ([M+H]$^+$); HRMS (ESI): Found: ([M+H]$^+$) 348.0452, C$_{13}$H$_{19}$INO$_2$ requires 348.0455.

((2$S$,4$S$)-Benzyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-yl)carbamate 2w

Flash column chromatography (Et$_2$O-hexane 1:4 to 2:3) afforded 2w (12 mg, 27%) as a colorless oil; $\nu_{\text{max}}$/cm$^{-1}$ (neat) 3333 (w), 2974 (m), 1707 (s), 1524 (m), 1456 (m), 1372 (s), 1316 (s), 1227 (s), 1143 (s); $\delta_1$ (500 MHz, CDCl3) 0.99 (3H, d, $J = 7.5$ Hz, 5-CH$_3$), 1.11 (1H, m, 4-CH$_3$), 1.14 (3H, d, $J = 6.5$ Hz, 1-CH$_3$), 1.21 (6H, s, CH$_3$ of Bpin), 1.23 (6H, s, CH$_3$ of Bpin), 1.55 (1H, m, 3-CH$_2$H), 1.61 (1H, m, 5-CH$_3$).
The major by-product was the reduction product 6\textsuperscript{[17]} isolated in 30% yield.

**Suppressing formation of reduction products 5 and 6:**

Preliminary efforts to suppress the formation of reduction products 5 and 6 centered on the choice of solvent, but despite screening a wide range of alternatives, DMF proved to be the most effective. The formation of reduction products issue is not linked to the initial ring opening of the cyclic sulfamidate (secondary iodides were isolable under these conditions – see above) but associated with the borylation step. Earlier studies relating to Cu-catalyzed borylation of secondary iodides do not mention reduction as a significant side reaction. Although many of the reduced products would inevitably be volatile and difficult to detect there are others where this would not present such an issue and good isolated yields of adducts have also been reported. As a result, further studies are needed to define more precisely the mechanism of the reduction step in the cases where we do observe this and these are underway.
Stereochemical Proofs of Diasteromeric Boronic Esters 2u-w.

Stereochemical proof of (±)-2u.

Oxidation of 2u; (±)-Benzyl-(3-hydroxybutan-2-yl)carbamate 4

To a stirred solution of boronic ester 2u (26 mg, 0.078 mmol) in THF (1 mL) was added aqueous 2M NaOH (0.66 mL) followed by 30% H2O2 (0.33 mL). After 3 h the reaction mixture was diluted with water (2 mL) and extracted with Et2O (3 × 5 mL). The organic layers were combined, dried over Na2SO4 and concentrated in vacuo to yield a crude reaction mixture that was purified by flash column chromatography (EtOAc-hexane 1:1) to afford amino alcohol 4 (13.5 mg, 78%) as a colorless crystalline solid; m.p. 69-71 °C (CH2Cl2-hexane); δH (400 MHz, CDCl3) 1.12 (3H, d, J = 7.0 Hz, CH3), 1.16 (3H, d, J = 6.5 Hz, CH3), 2.18 (1H, br s, OH), 3.77 (1H, m, 1-CH), 3.89 (1H, m, 2-CH), 4.95 (1H, br s, NH), 5.11 (2H, s, OCH2Ph), 7.32-7.39 (5H, m, ArCH); δC (100 MHz, CDCl3) 14.6 (CH3), 18.8 (CH3), 52.0 (1-CH), 66.9 (OCH2Ph), 70.3 (2-CH), 128.1, 128.5 (ArCH × 5), 136.4 (ArC), 156.4 (C=O).

Oxidation of the boronic ester 2u gave an N-Cbz aminoalcohol, that was either the same or different to the diasteromer used to prepare the precursor cyclic sulfamidate 1u. Stereochemical determinations involved (i) starting with a diasteromeric mixture of epoxides and making the other amino alcohol diastereomer (in order to establish that the two amino alcohols isomers could be differentiated) and (ii) spectroscopic comparison of this isomer mixture with the oxidation product from 2u.

Oxidation of 2u gave the other amino alcohol, in other words NOT the diastereomer used to make cyclic sulfamidate 1u. From this we conclude that the borylation resulted in inversion of stereochemistry at the reacting center of the cyclic sulfamidate 1u.

Stereochemical proof of 2v. We employed the same procedure for oxidation of 2v as was used above for 2u.

Stereochemical determinations involved starting with a diasteromeric mixture of epoxides and making the other amino alcohol diastereomer (to establish that the two amino alcohol isomers could be differentiated). Oxidation of 2v gave the same amino alcohol diastereomer as was used to make cyclic sulfamidate 1v. Note, and for convenience, we used RACEMIC material in this aspect of the work, given that it was the diastereomer identity that was to be determined.

From this we conclude that the borylation resulted in retention of stereochemistry at the reacting center of the cyclic sulfamidate 1v.
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 22

1. LiAlH4, THF, r.t.
2. CbzCl, Et3N, CH2Cl2, r.t.

\[ \text{syn} + \text{anti} \]

\[ \text{mixture} \]

Used to make cyclic sulfamidate 1v AND oxidation product derived from boronic ester 2v

\[ \text{89% (over 2 steps)} \]

\[(4S^*,5R^*)\) -4,5-Dimethyl-1,3,2-dioxathiolane-2,2-dioxide

SOCl\(_2\) (1.04 mL, 14.4 mmol) was added dropwise to a solution of meso-2,3-butanediol (1.01 mL, 11.1 mmol) in anhydrous CH\(_2\)Cl\(_2\) (19 mL) and after effervescence ceased (ca. 5 minutes) the reaction was heated to 60 °C in a sealed tube for 2 h. The reaction mixture was then cooled to r.t. and concentrated in vacuo. MeCN (12 mL), NaIO\(_4\) (3.35 g, 15.7 mmol) and RuCl\(_3\)·H\(_2\)O (3.5 mg, 0.06 mol%) were then added to the solution, followed by cooling to 0 °C and addition of water (17 mL). After 10 minutes, the reaction was complete as indicated by TLC and was diluted with Et\(_2\)O (30 mL). The aqueous layer was separated and the organic layer was washed sequentially with water (20 mL), aqueous NaHCO\(_3\) (20 mL) and brine (20 mL) before being dried over Na\(_2\)SO\(_4\), concentrated in vacuo, and filtered through a plug of silica (eluting with EtOAc) to afford the title compound (1.57 g, 93%) as a colorless crystalline solid; m.p. 35-36 °C (EtOAc-hexane); \(\delta^H\) (400 MHz, CDCl\(_3\)) 1.49-1.52 (6H, m, CH\(_3\)), 5.07-5.13 (2H, m, CH); \(\delta^C\) (100 MHz, CDCl\(_3\)) 14.2 (1-CH\(_3\)), 82.3 (CH).

\[(2R^*,3S^*)\) 3-Hydroxy-2-methylbutanenitrile

To a solution of the above cyclic sulfate (1.69 g, 11.1 mmol) in anhydrous DMF (35 mL) was added NaCN (600 mg, 12.2 mmol) portionwise and the resulting mixture was heated to 70 °C for 3 h. The solvent was removed under high vacuum and the resulting residue was redissolved in THF (60 mL). To the stirred solution was added H\(_2\)O (0.18 mL) followed by conc. H\(_2\)SO\(_4\) (0.47 mL) and the stirring was continued for 40 minutes. NaHCO\(_3\) (2.1 g) was added and the mixture was stirred for a further 20 minutes before being filtered through Celite®, concentrated in vacuo, and purified by flash column chromatography (EtOAc-hexane 1:1) to afford the title nitrile (909 mg, 83%) as a pale yellow oil; \(\delta^H\) (400 MHz, CDCl\(_3\)) 1.49-1.52 (6H, m, CH\(_3\)), 5.07-5.13 (2H, m, CH); \(\delta^C\) (100 MHz, CDCl\(_3\)) 14.2 (1-CH\(_3\)), 82.3 (CH).
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

(2R*,3S*)-Benzyl-3-hydroxy-2-methylbutyl)carbamate

To an ice-cooled solution of the above nitrile (600 mg, 6.06 mmol) in anhydrous THF (15 mL), was portionwise added LiAlH₄ (920 mg, 24.2 mmol). Once the gas evolution ceased, the reaction was allowed to warm up to r.t. and was stirred for 1 h. The reaction was then cooled to 0 °C and water (0.9 mL), aqueous 4M NaOH (0.9 mL) and then water again (2.7 mL) were added dropwise (caution: exotherm and vigorous gas evolution) to form a colourless precipitate. The mixture was then filtered through Celite® washing with copious amounts of Et₂O and concentrated in vacuo (care: the free amine is volatile; pressure set to 300 mbar) to furnish the free amine which was used in the next step without purification. To an ice-cooled mixture of the free amine (625 mg, 6.06 mmol) and Et₃N (0.93 mL, 6.66 mmol) in anhydrous CH₂Cl₂ (30 mL) was slowly added CbzCl (0.95 mL, 6.66 mmol). The reaction mixture was allowed to warm up to r.t. and was stirred for 3 h. The reaction was quenched by addition of aqueous 1M HCl (20 mL). The organic layer was separated, washed with brine (20 mL), dried over Na₂SO₄ and concentrated in vacuo. Flash column chromatography (EtOAc-hexane 2:3) afforded the title compound (1.27 g, 89%) as a pale yellow oil; δH (400 MHz, CDCl₃) 0.90 (3H, d, J = 7.0 Hz, 3-C₃H₃), 1.21 (3H, d, J = 6.5 Hz, 5-C₃H₃), 1.58 (1H, m, 2-C₃H), 3.02-3.09 (2H, m, 1-C₃H₂H and O₃H), 3.42-3.65 (2H, m, 1-CH₃H and 4-C₃H), 5.11 (2H, s, OC₃H₂Ph), 5.22 (1H, br s, NH), 7.31-7.37 (5H, m, ArC₆H), δC (100 MHz, CDCl₃) 14.7 (3-C₃H₃), 21.0 (5-C₃H₃), 41.2 (2-C₃H), 52.2 (1H, s, OCH₂Ph), 66.9 (OCH₂Ph), 69.9 (4-C₃H), 128.1 (2 signals), 128.5 (ArCH × 5), 136.4 (ArC), 157.4 (C=O).

Stereochemical proof of 2w. We employed the same procedure for oxidation of 2w as was used above for 2u. Stereochemical determinations involved starting with a diasteromeric mixture of 1,3-diols (in order to establish that the two amino alcohol diasteromers could be differentiated). Oxidation of 2w gave the other amino alcohol to that used to make cyclic sulfamidate 1w. From this we conclude that the borylation resulted in inversion of stereochemistry at the reacting center of the cyclic sulfamidate 1w. Note, and for convenience, we used racemic starting material in this aspect of the work, given that it was the diastereomer identify that was to be determined.
4,6-Dimethyl-1,3,2-dioxathiane 2,2-dioxide

![4,6-Dimethyl-1,3,2-dioxathiane 2,2-dioxide](image)

The title cyclic sulfate was synthesised from 2,4-pentanediol using the same procedure as described above (see page 11) affording the cyclic sulfate (0.430 g, 90%) as a colorless oil and as a 1:1 mixture of diastereomers. For data on the anti diastereomer, see page 11; syn diastereomer δH (400 MHz, CDCl3) 1.44 (6H, d, J = 6.5 Hz, CH3), 1.79 (1H, dt, J = 14.5 and 11.5 Hz, 2-CH2H), 1.94 (1H, dt, J = 14.5 and 2.5 Hz, 2-CH2H); δC (100 MHz, CDCl3) 20.4 (CH3), 38.1 (2-CH2), 81.4 (1-CH). The spectroscopic properties of this compound were consistent with the data available in literature.[18]

4-Azidopentan-2-ol

![4-Azidopentan-2-ol](image)

The title azide[15] was synthesised from the above mixture of cyclic sulfates affording the azide (0.831 g, 89%) as a pale yellow oil and a 1:1 mixture of diastereomers. For data on the syn diastereomer (see Vidari[15]); anti diastereomer δH (400 MHz, CDCl3) 1.22 (3H, d, J = 6.0 Hz, 1-CH3), 1.30 (3H, d, J = 6.5 Hz, 5-CH3), 1.49-1.56 (2H, m, 3-CH2), 1.82 (1H, br s, OH), 3.93 (1H, m, 2-CH2), 4.01 (1H, m, 4-CH2); δC (100 MHz, CDCl3) 19.8 (1-CH3), 24.1 (5-CH3), 45.1 (3-CH2), 54.9 (2-CH), 64.7 (4-CH). The spectroscopic properties of this compound were consistent with the data available in literature.[19]

Benzyl (4-hydroxypentan-2-yl)carbamate

![Benzyl (4-hydroxypentan-2-yl)carbamate](image)

The mixture of amino alcohol diastereomers was synthesised from the above azide as described on page 11 affording the amino alcohol (1.01 g, 80%) as a colorless oil and a 1:1 mixture of diastereomers. For data on the syn diastereomer, see above (page 11); anti diastereomer δH (400 MHz, CDCl3) 1.19 (6H, apparent triplet, J = 6.0 Hz, 1-CH3 and 5-CH3), 1.36 (1H, ddd, J = 14.0, 11.0 and 2.5 Hz, 3-CH2H), 1.56 (1H, ddd, J = 14.0, 10.5 and 3.0 Hz, 3-CH2H), 3.65 (1H, br s, OH), 3.83 (1H, m, 4-CH2), 3.99 (1H, m, 2-CH2), 4.79 (1H, br d, J = 8.5 Hz, NH), 5.11 (2H, s, OCH2Ph), 7.29-7.39 (5H, m, ArCH); δC (100 MHz, CDCl3) 21.4, 22.8 (1-CH3 and 5-CH3), 44.2 (2-CH2), 47.5 (3-CH2), 63.8 (4-CH), 67.0 (OCH2Ph), 128.1, 128.2, 128.5 (ArCH × 5), 136.3 (ArC), 157.1 (C=O).
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Mechanistic Studies

(a) TEMPO Trapping experiment

\((S)-\text{tert-Butyl-}(1-((2,2,6,6\text{-tetramethylpiperidin-1-yl})\text{oxy})\text{propan-2-yl})\text{carbamate} \text{ 10}\)

![Chemical Structure of 10]

Using general procedure A and replacing B\(_2\text{pin}_2\) with TEMPO (1 eq., 0.13 mmol), flash column chromatography (Et\(_2\)O-hexane 1:9 to 1:1) afforded 10 (15 mg, 37%) as a colorless crystalline solid; m.p. 66-67 °C (CH\(_2\)Cl\(_2\)-hexane); \(\nu_{\text{max}}/\text{cm}^{-1}\) (neat) 3345 (w), 2975 (s), 2932 (s), 1706 (s), 1366 (m), 1248 (m), 1173 (s); \(\delta_\text{H}\) (400 MHz, CDCl\(_3\)) 1.12-1.15 (12H, m, 3-C\(_\text{H}_3\) and 4-C\(_\text{H}_3\)), 1.21 (3H, d, \(J = 6.5 \text{ Hz, CH}_3\)), 1.32 (1H, m, 7-CH\(_3\)), 1.45 (14H, br s, 6-CH\(_2\), 7-CH\(_2\) and C(CH\(_3\))\(_3\)), 3.70 (1H, dd, \(J = 8.5 \text{ and } 4.0 \text{ Hz, } 2-\text{CH}_2\)), 3.76-3.81 (2H, m, 1-CH\(_2\) and 2-CH\(_2\)), 4.66 (1H, dd, \(J = 6.5 \text{ Hz, NH}\)); \(\delta_\text{C}\) (125 MHz, CDCl\(_3\)) 17.0 (7-C\(_\text{H}_2\)), 18.4 (CH\(_3\)), 20.2 (3-C\(_\text{H}_2\)), 28.4 (C(CH\(_3\))\(_3\)), 33.0 (4-CH\(_2\)), 39.7 (6-CH\(_2\)), 46.1 (1-CH\(_2\)), 60.0 (5-C), 79.0 (C(CH\(_3\))\(_3\)), 155.3 (C=O); \(m/z\) (%) ESI-MS 337.25 ([M+Na\(^+\)], 315.26 ([M+H\(^+\)]); HRMS (ESI): Found: ([M+H\(^+\)]) 315.2640, C\(_{17}\)H\(_{35}\)N\(_2\)O\(_3\) requires 315.2642.

(b) Iodide vs Cyclic Sulfamidates and Isolation and Conversion of N-Sulfate Intermediate

\((S)-\text{N-tert-Butyl (1-iodo-3-phenylpropan-2-yl)carbamate} \text{ 7}\)

Iodide 7 was synthesised according to literature procedure.\(^{[20]}\) Using general procedure A but omitting Bu\(_4\)NI and replacing cyclic sulfamidate 1\(a\) with iodide 7, boronic ester 2\(a\) was isolated in 55% yield after 18 h at 75 °C. This compares to essentially the same isolated yield of 2\(a\) (56%) after 2 h at r.t. when cyclic sulfamidate 1\(a\) was used.

![Chemical Structure Diagram]

Supporting Information 25
**N-tert-Butyl (3-iodopropyl)carbamate 8**

Iodide 8 was synthesised according to a literature procedure.[21] Using general procedure A but omitting Bu₄NI and replacing cyclic sulfamidate 1k with iodide 8, boronic ester 2k was afforded in 40% yield after 2 h at r.t. This compares to an isolated yield of 2k of 77% after 2 h at r.t. when cyclic sulfamidate 1k was used.

![Chemical structure of 8 and 2k](image)

Addition of Bu₄NI was found to have no effect on the yield; when this reaction was carried out in the presence of 1.5 eq. of Bu₄NI, a 40% yield of 2k was obtained.

On the basis of these two observations relating to yield /rates (and the mass spectroscopy data – see below) we conclude that alkyl iodides, such as 7 and 8, are not intermediates in the borylation reaction of cyclic sulfamidates, rather that the sulfated variants such as 9 (see below) are involved, with loss of the sulfate occurring on workup/chromatography.

**Sodium tert-butoxycarbonyl(3-iodopropyl)sulfamate 9**

To a solution of cyclic sulfamidate 1k (100 mg, 0.42 mmol) in anhydrous acetone (6 mL) was added Et₃N (60 μL, 0.42 mmol) and NaI (63.2 mg, 0.42 mmol). The reaction mixture was stirred at r.t. for 0.5 h. The solvent was then removed in vacuo to afford N-sulfate iodide 9 (163 mg, quantitative) as a colorless solid; δH (400 MHz, DMSO-d$_6$ – 9 was insoluble in CDCl$_3$) 1.40 (9H, s, C(C$_3$H$_3$)$_3$), 2.03 (2H, quint, J = 7.0 Hz, 2-CH$_2$), 3.18 (2H, t, J = 7.0 Hz, 3-CH$_2$), 3.48 (2H, t, J = 7.0 Hz, 1-CH$_2$); m/z (%) ESI-MS 363.97 ([M-Na]); HRMS (ESI): Found: [M-Na] 363.9727, C$_8$H$_{15}$INO$_5$S requires 363.9721.

We were unable to determine the melting point or $^{13}$C NMR of 9 as this intermediate was found to quickly hydrolyse to the corresponding iodide (i.e. 8 based on $^1$H NMR and TLC) under heating (in air) or in solution.

For comparison purposes, the $^1$H NMR data (in DMSO-d$_6$) for iodide 8 are presented here.

Iodide 8: δH (400 MHz, DMSO-d$_6$; $\Delta$δH the downfield shift in ppm associated with the corresponding signals for 9 (see above) are shown in red) 1.36 (+0.04) (9H, s, C(CH$_3$)$_3$), 1.88 (+0.15) (2H, quint, J = 7.0 Hz, 2-CH$_2$), 2.98 (+0.20) (2H, t, J = 7.0 Hz, 3-CH$_2$), 3.22 (+0.26) (2H, t, J = 7.0 Hz, 1-CH$_2$).
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Chemical Shift (ppm)

Supporting Information 28
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 32
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 33
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 34
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 35
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure $\beta$- and $\gamma$-Aminoalkyl Boronic Esters

Supporting Information 36
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure $\beta$- and $\gamma$-Aminoalkyl Boronic Esters

Supporting Information 37
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure $\beta$- and $\gamma$-Aminoalkyl Boronic Esters

Supporting Information 38
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure \( \beta \)- and \( \gamma \)-Aminoalkyl Boronic Esters

Supporting Information 39
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 40
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure $\beta$- and $\gamma$-Aminoalkyl Boronic Esters

Supporting Information 41
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 43
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 44
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 47
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Supporting Information 49
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure $\beta$- and $\gamma$-Aminoalkyl Boronic Esters

Supporting Information 51
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure $\beta$- and $\gamma$-Aminoalkyl Boronic Esters

Supporting Information 52
Mass Spectra of Intermediate 9

Low Resolution Mass Spectrum of Intermediate 9

![Low Resolution Mass Spectrum of Intermediate 9](image1)

High Resolution Mass Spectrum of Intermediate 9

![High Resolution Mass Spectrum of Intermediate 9](image2)

**HRMS:** Found: ([M]+) 363.9727, C₈H₁₅INO₅S requires 363.9721
IR Spectra
A change in the C=O stretching frequency of the Boc group was observed; the borylation reaction mixture using sulfamidate 1k (1674 cm\(^{-1}\)), iodide 8 (1683 cm\(^{-1}\)) and sulfamidate 1k (1719 cm\(^{-1}\)). See IR spectra below.

**IR Spectrum of Cyclic Sulfamidate 1k**

| cm\(^{-1}\) | %T  |
|-------------|-----|
| 796.07      | 796.07 |
| 733.16      | 733.16 |
| 1151.29     | 1151.29 |
| 995.08      | 995.08 |
| 674.23      | 674.23 |
| 763.92      | 763.92 |
| 669.04      | 669.04 |
| 1342.69     | 1342.69 |
| 1323.04     | 1323.04 |
| 1719.21     | 1719.21 |

**IR Spectrum of Borylation Reaction Mixture** (using cyclic sulfamidate 1k, CuI, PPh\(_3\), LiO\(_t\)Bu, Bu\(_4\)NI and B\(_2\)pin\(_2\)). DMF has been removed \textit{via} a toluene azeotrope.

| cm\(^{-1}\) | %T  |
|-------------|-----|
| 1045.16     | 1045.16 |
| 1146.74     | 1146.74 |
| 1234.61     | 1234.61 |
| 1368.53     | 1368.53 |
| 1460.67     | 1460.67 |
| 1510.02     | 1510.02 |
| 1543.48     | 1543.48 |
| 1580.91     | 1580.91 |
| 1631.50     | 1631.50 |
| 1673.60     | 1673.60 |
| 1701.76     | 1701.76 |
| 2874.47     | 2874.47 |
| 968.06      | 968.06 |
| 847.51      | 847.51 |
| 580.91      | 580.91 |
| 3420.90     | 3420.90 |

Supporting Information 54
IR Spectrum of Iodide 8

$^{13}$C NMR shift of the Boc C=O changed across this series, but not significantly: sulfamidate 1k (155.9 ppm); the borylation reaction mixture using sulfamidate 1k (155.1 ppm); iodide 8 (155.9 ppm).
Yield Optimization Studies (as tables) for Conversion of 1a to 2a

The optimized conditions for the conversion of 1a to 2a are shown below in the Scheme. These conditions were based on a series of optimization studies which are summarized here in Tables 1-6. Conditions below essentially used these optimized conditions, but with one component varied.

In addition to Bu₄NI, other iodide sources (LiI, NaI, KI and CsI) were assessed and all gave about 40% of boronic ester 2a. The choice of the copper catalyst was not critical, with CuCl and CuBr providing comparable yields to CuI. CuI was chosen for further studies due to its ease of use relative to CuBr and CuCl; there was no requirement for purification of CuI prior to use.

**Table 1. Solvent Screen (1 eq. of Bu₄NI was used)**

| Entry | Solvent | Yield/ %\(^a\) |
|-------|---------|----------------|
| 1     | DMF     | 45             |
| 2     | MeCN    | 26             |
| 3     | THF     | 29             |
| 4     | dioxane | 21             |
| 5     | toluene | 11             |
| 6     | DMSO    | 0              |
| 7     | DMA     | <5             |
| 8     | DMF     | 46\(^b\)       |

\(^a\)Isolated yield. \(^b\)Reaction carried out in air with wet DMF.

**Table 2. Loading of Bu₄NI (using DMF, r.t)**

| Entry | Equivalents of Bu₄NI | Yield/\(^a\)% |
|-------|----------------------|---------------|
| 1     | 0                    | 13            |
| 2     | 0.5                  | 48            |
| 3     | 1                    | 45            |
| 4     | 1.25                 | 46            |
| 5     | 1.5                  | 56            |
| 6     | 1.75                 | 43            |
| 7     | 2                    | 44            |
| 8     | 3                    | 38            |

\(^a\)Isolated yield.
Borylation of Cyclic Sulfamidates. Access to Enantiomerically Pure β- and γ-Aminoalkyl Boronic Esters

Table 3. Temperature Screen (Bu₄NI in DMF)

| Entry | Temperature | Yield/%a |
|-------|-------------|----------|
| 1     | r.t.        | 56       |
| 2     | 0           | 45       |
| 3     | 60          | 43       |
| 4     | 90          | 21       |

aIsolated yield.

Table 4. Ligand Screen (Bu₄NI in DMF, r.t.)

| Entry | Ligand | Yield/ %a |
|-------|--------|-----------|
| 1     | PPh₃   | 56        |
| 2     | [tBu₃PH][BF₄] | trace |
| 3     | PCy₃   | 33        |
| 4     | [tBu₂MePH][BF₄] | 55 |
| 5     | CuCl·SiPr | 55  |
| 6     | P(4-(Me)Ph)₃ | 55 |
| 7     | P(2-(CF₃)Ph)₃ | 41 |
| 8     | P(4-(Me)Ph)₃ | 35 |
| 9     | P(4-(OMe)Ph)₃ | 46 |
| 10    | P(2-(OMe)Ph)₃ | 50 |
| 11    | Dppe    | 0         |
| 12    | 4-methylpyridine | 40 |
| 13    | Phenanthroline | 35 |
| 14    | Bipyridine | 40 |
| 15    | P(OPh)₃ | 28        |

aIsolated yield.

Table 5. Base Screen (Bu₄NI, PPh₃ in DMF, r.t)

| Entry | Base       | Yield/%a |
|-------|------------|----------|
| 1     | LiOttBu    | 45       |
| 2     | NaOttBu    | 33       |
| 3     | KOttBu     | 20       |
| 4     | NaOMe      | 38       |
| 5     | LiOMe      | 7        |
| 6     | Li₂CO₃     | 0        |
| 7     | K₂CO₃      | 0        |

aIsolated yield.
No difference in yield was observed when the catalyst loading was increased to 20 and 50 mol% (catalyst:ligand ratio maintained the same). Increase and decrease in concentration (0.26 and 0.07M) resulted in a decrease in yield in both cases.

Table 6. Copper Source Screen (Bu₄NI, PPh₃ in DMF, r.t)

| Entry | Copper source | Yield/%a | Entry | Copper source | Yield/%a |
|-------|---------------|----------|-------|---------------|----------|
| 1     | CuI           | 45       | 4     | Cu(OTf)(MeCN)₄ | 42       |
| 2     | CuBr          | 40       | 5     | Cu(BF₄)(MeCN)₄ | 30       |
| 3     | CuCl          | 43       | 6     | Cu(OTf)₂      | 42       |

*aIsolated yield.

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