Catalytic Asymmetric Deprotonation Using a Ligand Exchange Approach

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Supporting Information Available: Full experimental procedures and characterisation data.

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General

Water is distilled water. Et$_2$O and THF were freshly distilled from benzophenone ketyl or dried after degassing with N$_2$ by use of a Mbraun solvent purification system in which the solvents were passed through a column of 3 Å molecular sieves under a positive pressure of nitrogen. (–)-Sparteine, and diamines (+)-11 and 13 were distilled from CaH$_2$ before use. sec-BuLi was titrated against N-benzylbenzamide before use. Petrol refers to the fraction of petroleum ether with a boiling point range of 40-60 °C. All reactions were carried out under oxygen free nitrogen or argon using oven-dried and/or flame dried glassware. Flash column chromatography was carried out using Fluka Silica gel 60 (0.035-0.070 mm particle size). Thin layer chromatography was carried out using Merck F$_{254}$ alumina-backed silica plates. For Kugelrohr distillation, the temperatures quoted correspond to the oven temperatures.

Proton (400 MHz) and carbon (100.6 MHz) NMR spectra were recorded on a Jeol ECX-400 instrument using an internal deuterium lock. All samples were recorded in CDCl$_3$. Chemical shifts are quoted in parts per million and referenced to CHCl$_3$ (7.27). Carbon NMR spectra were recorded with broadband proton decoupling and were assigned using DEPT experiments. Infra-red spectra were recorded on an ATI Matteson Genesis FT-IR spectrometer. Chemical ionisation and high resolution mass spectra were recorded on a Fisons Analytical (VG) Autospec spectrometer.

Optical rotations were recorded at room temperature (20 °C) on a Jasco DIP-370 polarimenter and [α]$_D$, measurements are given in units of 10$^{-1}$ deg cm$^2$ g$^{-1}$. Chiral stationary phase HPLC was performed on a Gilson system with 712 controller software and a 118 UV/Vis diode array detector or on a Waters system with a Waters 255 pump and a Waters 2420 ELS light scattering detector or a Waters 2487 UV detector. GC was performed on an Agilent 6890 gas chromatograph fitted with an Agilent H-5 capillary column (30 m x 0.25 mm x 0.25 µm), injector temperature 250 °C, detector temperature 250 °C using helium as the carrier gas. N-Boc-pyrrolidine 1$^1$, O-alkyl carbamate 3$^{2,3}$ and diamine (+)-11$^4$ were prepared according to the literature procedures.
Experimental procedures and characterisation data

General Procedure A: Catalytic asymmetric lithiation-substitution of N-Boc pyrrolidine 1 using a chiral diamine and bispidine 13

A solution of (−)-sparteine or diamine (+)-11 (0.2 eq.) and bispidine 13 (1.2 eq.) in Et₂O (4.0 mL) was added dropwise to a stirred solution of s-BuLi (1.1 M solution in cyclohexane, 1.3 eq.) in Et₂O (4.0 mL) at −78 °C under Ar. After stirring for 10 min at −78 °C, a solution of N-Boc pyrrolidine 1 (488 mg, 2.85 mmol) in Et₂O (3.0 mL) was added dropwise over 10 min via a cannula and the resulting solution was stirred at −78 °C for 5 h. Then, Me₃SiCl (3.71 mmol) was added and the solution was allowed to warm to rt over 16 h. 5% H₃PO₄(aq) (10 mL) was added and the solution was stirred for 20 min. The layers were separated and the aqueous layer was extracted with Et₂O (3 × 10 mL). The combined Et₂O extracts were dried (MgSO₄) and evaporated under reduced pressure to give the crude product.

(S)-2-Trimethylsilyl-N-tert-butoxycarbonylpyrrolidine (S)-2
(0.2 eq. (−)-sparteine, Table 1, entry 1)

Using general procedure A, (−)-sparteine (133 mg, 0.568 mmol), bispidine 13 (720 mg, 3.43 mmol), s-BuLi (3.3 mL of a 1.14 M solution in cyclohexane, 3.71 mmol), N-Boc pyrrolidine 1 (488 mg, 2.85 mmol) and Me₃SiCl (0.47 mL, 3.71 mmol) in Et₂O (11 mL) gave the crude product. Purification by flash chromatography with 19:1 petrol-Et₂O as eluent gave adduct (S)-2 (529 mg, 76%, 90:10 er by chiral GC) as a colourless oil, [α]D +56.0 (c 1.0 in CHCl₃)(lit., [α]D +71.8 (c 2.6 in CHCl₃) for (S)-2 of 98:2 er); ¹H NMR (400 MHz, CDCl₃) δ: 3.62-3.38 (m, 1H, CHN), 3.28-3.13 (m, 2H, CH₂N), 2.05-1.96 (m, 1H), 1.83-1.74 (m, 3H), 1.47 (s, 9H, CMe₃), 0.05 (s, 9H, SiMe₃); GC: Betadex 120 30 m × 0.25 mm i.d. (β-cyclodextrin), T 95 °C isothermal, He carrier gas at 12 psi constant pressure, 100 min [(S)-2] 103 min [(R)-2]. Spectroscopic data consistent with that reported in the literature.
(R)-2-Trimethylsilyl-N-tert-butoxycarbonylpyrrolidine (R)-2

(0.2 eq. (+)-11, Table 1, entry 2)

Using general procedure A, diamine (+)-11 (81.4 mg, 0.419 mmol), bispidine 13 (529 mg, 2.52 mmol), s-BuLi (2.4 mL of a 1.14 M solution in cyclohexane, 2.73 mmol) and Me₃SiCl (0.37 mL, 2.94 mmol) in Et₂O (10 mL) gave the crude product. Purification by flash chromatography with 19:1 petrol-Et₂O as eluent gave adduct (R)-2 (336 mg, 66%, 94:6 er by chiral GC) as a colourless oil, [α]D −67.0 (c 2.0 in CHCl₃) (lit., [α]D +71.8 (c 2.6 in CHCl₃) for (S)-2 of 98:2 er); GC: Betadex 120 30 m × 0.25 mm i.d. (β-cyclodextrin), T 95 °C isothermal, He carrier gas at 12 psi constant pressure, 100 min [(S)-2] 103 min [(R)-2]. Spectroscopic data consistent with that reported in the literature.

General Procedure B: Catalytic asymmetric lithiation-substitution of O-alkyl carbamate 3 using a chiral diamine and bispidine 13

A solution of (−)-sparteine or diamine (+)-11 (0.2, 0.1 or 0.06 eq.) and bispidine 13 (1.2 eq.) in Et₂O (4.0 mL) was added dropwise to a stirred solution of s-BuLi (1.2 M solution in cyclohexane, 1.3 eq.) in Et₂O (4.0 mL) at −78 °C under Ar. After stirring for 10 min at −78 °C, a solution of O-alkyl carbamate 3 (666 mg, 2.53 mmol) in Et₂O (3.0 mL) was added dropwise over 10 min via a cannula and the resulting solution was stirred at −78 °C for 5 h. Then, Bu₃SnCl (3.29 mmol) was added dropwise and the solution was allowed to warm to rt over 16 h. 2 M HCl (aq) (10 mL) was added, the layers were separated and the aqueous layer was extracted with Et₂O (3 × 10 mL). The combined Et₂O extracts were washed with saturated KF (aq) (10 mL), dried (MgSO₄) and evaporated under reduced pressure to give the crude product.

Recovery of ligand mixture from a (−)-sparteine experiment: The above aqueous layer was basified by the addition of solid NaOH (2.0 g) and the resulting aqueous solution was extracted with Et₂O (3 × 10 mL). The combined Et₂O extracts were dried (MgSO₄) and evaporated under reduced pressure. Purification by Kugelrohr distillation gave a ~6:1 mixture (by ¹H NMR spectroscopy) of bispidine 13 and (−)-sparteine (580 mg) as a colourless oil, bp 150-170 °C/2 mmHg.
(S)-3-Phenyl-1-tributyltin-1-N,N-diisopropylcarbamoyloxypropane (S)-4

(0.2 eq. (–)-sparteine, Table 1, entry 3)

\[
\begin{align*}
\text{Ph} & \quad \text{SnBu}_3 \\
& \quad \text{OCb} \\
\text{(S)-4}
\end{align*}
\]

Using general procedure B, (–)-sparteine (117 mg, 0.507 mmol, 0.2 eq.), bispidine 13 (639 mg, 3.04 mmol), s-BuLi (3.0 mL of a 1.1 M solution in cyclohexane, 3.3 mmol), O-alkyl carbamate 3 (666 mg, 2.53 mmol) and Bu₃SnCl (0.89 mL, 3.3 mmol) in Et₂O (11 mL) gave the crude product. Purification by flash chromatography with 40:1 petrol-Et₂O as eluent gave adduct (S)-4 (1.09 g, 77%, 92:8 er by chiral HPLC) as a colourless oil, \([\alpha]_D +18.2 \ (c \ 1.2 \ \text{in CHCl}_3)\) (lit., \([\alpha]_D +21.9 \ (c \ 1.0 \ \text{in CHCl}_3)\) for (S)-4 of 98.5:1.5 er); ¹H NMR (400 MHz, CDCl₃) δ: 7.30 (t, \(J = 7 \ \text{Hz}, 2\text{H}, \text{m}-\text{Ph}\)), 7.21-7.18 (m, 3H, Ph), 4.70 (dd, \(J = 9.5, 5.0 \ \text{Hz}, 1\text{H}, \text{OCHSn}\)), 4.23-4.03 (m, 1H, \(\text{C}_\text{H}_\text{Me}_2\)), 3.84-3.64 (m, 1H, \(\text{C}_\text{H}_\text{Me}_2\)), 2.77 (ddd, \(J = 13.0, 11.0, 5.0 \ \text{Hz}, 1\text{H}, \text{PhC}_\text{H}_\text{A}_\text{H}_\text{B}\)), 2.65, (ddd, \(J = 13.0, 10.0, 6.0 \ \text{Hz}, 1\text{H}, \text{PhCH}_\text{A}_\text{H}_\text{B}\)), 2.29-2.18 (m, 1H, \(\text{C}_\text{H}_\text{A}_\text{H}_\text{B}\_\text{CHSnO}\)), 2.10-2.01 (m, 1H, \(\text{CH}_\text{A}_\text{H}_\text{B}\_\text{CHSnO}\)), 1.67-1.44 (m, 6H), 1.38-1.11 (m, 18H), 1.04-0.80 (m, 15H); HPLC: Daicel Chiralcel OD, 600:1 v/v hexane-iPrOH, 0.5 mL min⁻¹, 226 nm, 6.5 min [(S)-4], 7.1 min [(R)-4]. Spectroscopic data consistent with that reported in the literature.³

(R)-3-Phenyl-1-tributyltin-1-N,N-diisopropylcarbamoyloxypropane (R)-4

(0.2 eq. (+)-11, Table 1, entry 4)

\[
\begin{align*}
\text{Ph} & \quad \text{SnBu}_3 \\
& \quad \text{OCb} \\
\text{(R)-4}
\end{align*}
\]

Using general procedure B, diamine (+)-11 (100 mg, 0.515 mmol, 0.2 eq.), bispidine 11 (650 mg, 3.10 mmol), s-BuLi (3.0 mL of a 1.1 M solution in cyclohexane, 3.3 mmol), O-alkyl carbamate 3 (628 mg, 2.58 mmol) and Bu₃SnCl (0.91 mL, 3.35 mmol) in Et₂O (11 mL) gave the crude product. Purification by flash chromatography with 40:1 petrol-Et₂O as eluent gave adduct (R)-4 (1.02 g, 72%, 94:6 er by chiral HPLC) as a colourless oil, \([\alpha]_D –22.0 \ (c \ 1.4 \ \text{in CHCl}_3)\) (lit., \([\alpha]_D +21.9 \ (c \ 1.0 \ \text{in CHCl}_3)\) for (S)-4 of 98.5:1.5 er); HPLC: Daicel Chiralcel OD, 600:1 v/v hexane-iPrOH, 0.5 mL min⁻¹, 226 nm, 6.4 min [(S)-4], 6.9 min [(R)-4]. Spectroscopic data consistent with that reported in the literature.³
(S)-3-Phenyl-1-tributyltin-1-N,N-diisopropylcarbamoyloxypropane (S)-4

(0.1 eq. (−)-sparteine, Table 1, entry 5)

\[
\text{Ph} \quad \text{SnBu}_3 \\
\begin{array}{c}
\text{OCb} \\
\text{(S)-4}
\end{array}
\]

Using general procedure B, (−)-sparteine (56 mg, 0.22 mmol, 0.1 eq.), bispidine 13 (560 mg, 2.66 mmol), s-BuLi (2.25 mL of a 1.13 M solution in cyclohexane, 2.88 mmol), O-alkylcarbamate 3 (582 mg, 2.20 mmol) and Bu₃SnCl (0.78 mL, 2.88 mmol) in Et₂O (8 mL) gave the crude product. Purification by flash chromatography with 40:1 petrol-Et₂O as eluent gave adduct (S)-4 (681 mg, 54%, 81:19 er by chiral HPLC) as a colourless oil, \([\alpha]_D^\text{+}15.4 \ (c \ 1.0 \ \text{in CHCl}_3)\) (lit., \([\alpha]_D^\text{+}21.9 \ (c \ 1.0 \ \text{in CHCl}_3)\) for (S)-4 of 98.5:1.5 er); HPLC: Daicel Chiralcel OD 600:1 v/v hexane-iPrOH 0.5 mL min⁻¹, 226 nm, 6.5 min [(S)-4], 7.3 min [(R)-4]. Spectroscopic data consistent with that reported in the literature.³

(R)-3-Phenyl-1-tributyltin-1-N,N-diisopropylcarbamoyloxypropane (R)-4

(0.06 eq. (+)-11, Table 1, entry 6)

\[
\text{Ph} \quad \text{SnBu}_3 \\
\begin{array}{c}
\text{OCb} \\
\text{(R)-4}
\end{array}
\]

Using general procedure B, diamine (+)-11 (42 mg, 0.215 mmol, 0.06 eq.), bispidine 13 (902 mg, 4.29 mmol), s-BuLi (3.9 mL of a 1.2 M solution in cyclohexane, 4.65 mmol), O-alkyl carbamate 3 (950 mg, 3.58 mmol) and Bu₃SnCl (1.25 mL, 4.65 mmol) in Et₂O (11 mL) gave the crude product. Purification by flash chromatography with 40:1 petrol-Et₂O as eluent gave adduct (R)-4 (1.24 g, 63%, 85:15 er by chiral HPLC) as a colourless oil, \([\alpha]_D^\text{−}15.0 \ (c \ 0.9 \ \text{in CHCl}_3)\) (lit.,² \([\alpha]_D^\text{+}21.9 \ (c \ 1.0 \ \text{in CHCl}_3)\) for (S)-4 of 98.5:1.5 er); HPLC Daicel Chiralcel OD 600:1 v/v hexane-iPrOH, 0.5 mL min⁻¹, 226 nm, 6.5 min [(S)-4], 7.3 min [(R)-4]. Spectroscopic data was consistent with that reported in the literature.³

General Procedure C: Catalytic Asymmetric lithiation-substitution of phosphine-borane 14

using a chiral diamine and bispidine 13

A solution of (−)-sparteine or diamine (+)-11 (0.2 eq.) and bispidine 13 (1.2 eq.) in Et₂O (3 mL) was added dropwise to a stirred solution of s-BuLi (1.0 M solution in cyclohexane, 1.3 eq.) in Et₂O (3.0 mL) at
–78 °C under Ar. After stirring for 10 min at –78 °C, a solution of phosphine borane 14 (378 mg, 2.86 mmol) in Et₂O (6.0 mL) was added dropwise over 10 min via a cannula and the resulting solution was stirred at –78 °C for 3 h. Then, a solution of benzophenone (1.3 eq) in Et₂O (6.0 mL) was added dropwise and the solution was allowed to warm to rt over 16 h. 2 M HCl(aq) (10 mL) was added, the two layers were separated and the aqueous layer was extracted with EtOAc (3 × 10mL). The EtOAc extracts were dried (MgSO₄) and evaporated under reduced pressure to give the crude product.

(S)-P-(2,2-Diphenyl-2-hydroxyethyl)-P-methyl-tert-butyl-phosphine borane (S)-15

(0.2 eq. (−)-sparteine, Table 1, entry 7)

Using general procedure C, (−)-sparteine (176 mg, 0.752 mmol), bispidine 13 (950 mg, 4.52 mmol), s-BuLi (4.8 mL of a 1.0 M solution, 4.8 mmol), phosphine borane 14 (498 mg, 3.77 mmol) and benzophenone (889 mg, 4.78 mmol) in Et₂O (18 mL) gave the crude product. Purification by flash chromatography using 33:1 petrol-EtOAc as eluent gave adduct (S)-15 (780 mg, 67%, 83:17 er by chiral HPLC), mp 109-111 °C (lit.,⁷ 116.5-117.5 °C); [α]D +16.1 (c 1.5 in CHCl₃)(lit.,⁷ [α]D –14.9 (c 0.47 in CHCl₃ for (R)-15 of 96:4 er); ¹H NMR (400 MHz, CDCl₃) δ: 7.52 (d, J = 8.0 Hz, 2H, o-Ph), 7.48 (d, J = 8.0 Hz, 2H, o-Ph), 7.38-7.30 (m, 4H, Ph), 7.28-7.20 (m, 2H, Ph), 4.59 (s, 1H), 2.89 (app t, J = 14.0 Hz, 1H, PCH₂H₃), 2.68 (dd, J = 14.0, 6.5 Hz, PCH₂H₃), 1.18 (d, J = 14.0 Hz, 9H, CMe₃), 0.75 (d, J = 10.0 Hz, 3H, PMe), 0.89-0.23 (m, 3H, BH₃); ¹³C NMR (100MHz, CDCl₃) δ: 147.66 (d, J = 8.0 Hz, ipso-Ph), 145.19 (d, J = 2.5 Hz, ipso-Ph), 128.26 (CH, Ph), 128.15 (CH, Ph), 127.15 (CH, Ph), 125.25 (CH, Ph), 34.15 (d, J = 28.0 Hz, PCH₂), 27.99 (d, J = 36.0 Hz, CMe₃) 24.70 (d, J = 2.0 Hz, CMe₃), 6.42 (d, J = 35.0 Hz, PMe) (some aromatic signals not resolved). HPLC: Daicel Chiralcel OD, 1:19 v/v iPrOH-hexane, 0.5 mL min⁻¹, 254 nm, 11.5 min [(R)-15], 13.4 min [(S)-15]. Spectroscopic data consistent with that reported in the literature.⁷
(R)-P-(2,2-Diphenyl-2-hydroxyethyl)-P-methyl-tert-butyl-phosphine borane (R)-15

(0.2 eq (+)-11, Table 1, entry 8)

Using general procedure C, diamine (+)-11 (111 mg, 0.572 mmol), bispidine 13 (721 mg, 3.43 mmol), s-BuLi (3.71 mL, 1.0 M in cyclohexane, 3.71 mmol), phosphine borane 14 (375 mg, 2.86 mmol) and benzophenone (660 mg, 3.7 mmol) in Et₂O (18 mL) gave the crude product. Purification by flash chromatography using 33:1 petrol-EtOAc as eluent gave (R)-15 (614 mg, 68%, 89:11 er by chiral HPLC), mp 110-112 °C (lit., 7116.5-117.5 °C); [α]D −14.4 (c 1.0 in CHCl₃) (lit., 7[α]D −14.9 (c 0.47 in CHCl₃) for (R)-15 of 96:4 er); HPLC: Daicel Chiralcel OD, 1:19 v/v iPrOH-hexane, 0.5 mL min⁻¹, 254 nm 11.5 min [(R)-15] 13.4 min [(S)-15]. Spectroscopic data consistent with that reported in the literature. ⁷

General Procedure D: Catalytic asymmetric lithiation-dimerisation of phosphine-borane 14 using a chiral diamine and bispidine 13

A solution of (–)-sparteine or diamine (+)-11 (0.2 eq.) and bispidine 13 (1.2 eq.) in Et₂O (3.0 mL) was added dropwise to a stirred solution of s-BuLi (1.2 M solution in cyclohexane, 1.3 eq) in Et₂O (3.0 mL) at −78 °C under Ar. After stirring for 10 min at −78 °C, a solution of phosphine borane 14 (284 mg, 2.15 mmol) in Et₂O (6 mL) was added dropwise over 10 min via a cannula and the resulting solution was stirred at −78 °C for 3 h. Then, solid anhydrous CuCl₂ (1.6 eq.) was added in one portion and the resulting solution was stirred at −78 °C for 1 h and then allowed to warm to rt over 2 h. After stirring the brown suspension for 1 h, 25% NH₃(aq) (3.0 mL) was added. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 10 mL) and the combined EtOAc extracts were washed with 5 % NH₃(aq) (10 mL) and 1 M HCl(aq) (10 mL), dried (MgSO₄) and evaporated under reduced pressure to give the crude product.

(S,S)-1,2-Bis(boranato)(tert-butyl)methylphosphino)ethane (S,S)-16
Using general procedure D, (−)-sparteine (100 mg, 0.431 mmol), bispidine 13 (543 mg, 2.59 mmol), s-BuLi (2.8 mL of a 1.0 M solution in cyclohexane, 2.8 mmol), phosphine borane 14 (284 mg, 2.15 mmol) and anhydrous CuCl₂ (463 mg, 3.44 mmol) in Et₂O (9 mL) gave the crude product. Purification by flash chromatography using 9:1 petrol-EtOAc as eluent gave adduct *meso*-16 (35 mg, 12%) as a white solid, mp 181-183 °C (lit.,8 176-179 °C); *R*₁(4:1 petrol-EtOAc) 0.42; ¹H NMR (400 MHz, CDCl₃) δ: 1.96-1.89 (m, 2H, PCH₃H₃), 1.60-1.56 (m, 2H, PCH₃H₃), 1.22 (d, J = 9.5 Hz, 6H, PMe), 1.17 (d, J = 14.0 Hz, 18H, PMe₀), 0.37 (q, J = 97.0 Hz, 6H, BH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 27.50 (d, J = 34.5 Hz, CMe₀), 24.97 (s, CMe₀), 14.76 (d, J = 30.5 Hz, PCH₂), 4.60 (d, J = 33.5 Hz, PMe) and adduct (S,S)-16 (130 mg, 46%, >99:1 er by chiral HPLC) as a white solid, mp 168-170 °C (lit.,8 169-171 °C); *R*₁(4:1 petrol-EtOAc) 0.25; [α]d⁻⁹.1 (c 0.37 in CHCl₃)(lit.,8 [α]d⁻⁹.1 (c 1.21 in CHCl₃) for (S,S)-16 of >99:1 er); ¹H NMR (400 MHz, CDCl₃) δ: 2.04-1.97 (m, 2H, PCH₃H₃), 1.66-1.58 (m, 2H, PCH₃H₃), 1.22 (d, J = 9.0 Hz, 6H, PMe), 1.18 (d, J = 14.0 Hz, 18H, CMe₀), 0.39 (q, J = 96.0 Hz, 6H, BH₃); ¹³C NMR (100 MHz, CDCl₃) δ: 27.69 (d, J = 34.0 Hz, CMe₀), 25.14 (d, J = 2.5 Hz, CMe₀), 15.92 (d, J = 32.0 Hz, PCH₂), 5.63 (d, J = 34.0 Hz, PCH₂); HPLC: Daicel Chiralcel OD, 1:9 v/v iPrOH-hexane, 0.5 mL min⁻¹, light scattering detector, 14.3 min [(S,S)-16]. Spectroscopic data consistent with that reported in the literature.8

(R,R)-1,2-Bis(boranato(tert-butyl)methylphosphino)ethane (R,R)-16

![Chemical structure of (R,R)-1,2-Bis(boranato(tert-butyl)methylphosphino)ethane (R,R)-16](image)

Using general procedure D, diamine (+)-11 (94 mg, 0.484 mmol), bispidine 13 (611 mg, 2.90 mmol), s-BuLi (2.63 mL of a 1.2 M solution in cyclohexane, 3.16 mmol), phosphine borane 14 (319 mg, 2.42 mmol) and anhydrous CuCl₂ (520 mg, 3.87 mmol) in Et₂O (12 mL) gave the crude product. Purification by flash chromatography gave *meso*-16 (56 mg, 15%) as a white solid, mp 182-184 °C (lit.,8 176-179 °C) and adduct (R,R)-16 (169 mg, 53%, >99:1 er by chiral HPLC) as a white solid, mp 166-168 °C (lit.,8 169-171 °C); [α]d₊10.5 (c 0.24 in CHCl₃)(lit.,8 [α]d₋9.1 (c 1.21 in CHCl₃) for (S,S)-16 of >99:1 er); HPLC: Daicel Chiralcel OD, 1:9 v/v iPrOH-hexane, 0.5 mL min⁻¹, light scattering detector, 10.20 min [(R,R)-16]. Spectroscopic data were consistent with that reported in the literature.8
Lithiation-substitution of O-alkyl carbamate 3 using (−)-sparteine and bispidine 13

\begin{align*}
\text{(S)-3-Phenyl-1-trimethylsilyl-1-N,N-diisopropylcarbamoyloxypropane}\\
\text{Ph} & \quad \text{SiMe}_3 \\
\end{align*}

A solution of (−)-sparteine (140 mg, 0.60 mmol, 0.2 eq.) and bispidine 13 (740 mg, 3.5 mmol) in Et₂O (4.0 mL) was added dropwise to a stirred solution of s-BuLi (3.6 mL, of a 1.1 M solution in cyclohexane, 3.8 mmol) in Et₂O (4.0 mL) at −78 °C under Ar. After stirring for 10 min at −78 °C, a solution of O-alkyl carbamate 3 (780 mg, 3.0 mmol) in Et₂O (3.0 mL) was added dropwise and the resulting solution was stirred at −78 °C for 5 h. Then, Me₃SiCl (0.49 mL, 3.83 mmol) was added dropwise and the solution was allowed to warm to rt over 16 h. Saturated NH₄Cl (aq) (10 mL) was added, the layers were separated and the aqueous layer was extracted with Et₂O (3 × 10 mL). The combined Et₂O extracts were dried (1.5 g of a 1:2 mixture by weight of NaHCO₃/MgSO₄) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography using 94:5:9:0.1 petrol-Et₂O-NH₃(aq) gave the (S)-trimethylsilyl adduct (687 mg, 69%, 89:11 er by chiral HPLC) as a colourless oil, [α]₃₆₅ −3.5 (c 1.0 in CH₂Cl₂)(lit.,² [α]₃₆₅ −4.5 (c 1.0 in CH₂Cl₂) for the (S) adduct of >95:5 er); ¹H NMR (400 MHz, CDCl₃) δ: 7.31-7.17 (m, 5H, Ph), 4.80 (dd, J = 11.0, 3.5 Hz, CHSi), 4.27-4.07 (m, 1H, CHMe₂), 3.86-3.66 (m, 1H, CHMe₂), 2.75 (ddd, 1H, J = 14.0, 12.0, 5.0 Hz, PhCH₂H₃), 2.62 (ddd, 1H, J = 14.0, 11.0, 6.0 Hz, PhCH₂H₃), 2.01-1.80 (m, 2H, CH₂CHSi), 1.29-1.17 (m, 12H), 0.07 (s, 9H, SiMe₃); HPLC: Daicel Chiralcel OD, 99:1 v./v hexane-iPrOH, 0.5 mLmin⁻¹, 206 nm, 7.8 min [(S)], 8.6 min [(R)]. Spectroscopic data consistent with that reported in the literature.²

Lithiation-substitution of O-alkyl carbamate 3 using stoichiometric (−)-sparteine

\begin{align*}
\text{(S)-3-Phenyl-1-trimethylsilyl-1-N,N-diisopropylcarbamoyloxypropane}\\
\text{Ph} & \quad \text{SiMe}_3 \\
\end{align*}

A solution of (−)-sparteine (920 mg, 3.93 mmol, 1.4 eq.) in Et₂O (4.0 mL) was added dropwise to a stirred solution of s-BuLi (3.6 mL of a 1.1 M solution in cyclohexanes, 3.93 mmol) in Et₂O (4.0 mL) at −78 °C under Ar. After stirring for 10 min at −78 °C, a solution of O-alkyl carbamate 3 (740 mg, 2.80 mmol) in Et₂O (3.0 mL) was added dropwise and the resulting solution was stirred at −78 °C for 5 h.
Then, Me$_3$SiCl (0.50 mL, 3.9 mmol) was added dropwise and the solution was allowed to warm to rt over 16 h. Saturated NH$_4$Cl (aq) (10 mL) was added, the layers were separated and the aqueous layer was extracted with Et$_2$O (3 × 10 mL). The combined Et$_2$O extracts were dried (1.5 g of a 1:2 mixture by weight of NaHCO$_3$/MgSO$_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography using 94:5:9:0.1 petrol-Et$_2$O-NH$_3$(aq) gave the (S)-trimethylsilyl adduct (600 mg, 64%, 98:2 er by chiral HPLC) as a colourless oil, [α]$_{365}^D$ −4.3 (c 1.0 in CH$_2$Cl$_2$)(lit.,$^2$ [α]$_{365}^D$ −4.5 (c 1.0, CH$_2$Cl$_2$) for the (S) adduct of 95:5 er); HPLC: Daicel Chiralcel OD, 99:1 v/v hexane-iPrOH, 0.5 mL min$^{-1}$, 206 nm, 7.7 min [(S)], 8.7 min [(R)]. Spectroscopic data consistent with that reported in the literature.$^2$

**Lithiation-substitution of N-Boc pyrrolidine 1 using sub-stoichiometric (−)-sparteine only**

![N-Boc pyrrolidine structure](image)

A solution of s-BuLi (4.8 mL of a 1.12 M solution in cyclohexane, 5.3 mmol) was added dropwise to a stirred solution of (−)-sparteine (192 mg, 0.121 mmol) in Et$_2$O (12 mL) at −78 °C under Ar. After stirring for 10 min at −78 °C, a solution of N-Boc pyrrolidine 1 (702 mg, 4.1 mmol) in Et$_2$O (4.0 mL) was added dropwise and the resulting solution was stirred at −78 °C for 5 h. Then, Me$_3$SiCl (0.73 mL, 5.3 mmol) was added and the solution was allowed to warm to rt over 16 h. 5% H$_3$PO$_4$(aq) (10 mL) was added, the layers were separated and the aqueous layer was extracted with Et$_2$O (3 × 10 mL). The combined Et$_2$O layers were dried (MgSO$_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography gave adduct (S)-2 (340 mg, 34%, 75:5 er by chiral GC) as a colourless oil, [α]$_D$ +35.5 (c 0.89 in CHCl$_3$)(lit.,$^5$ [α]$_D$ +71.8 (c 2.6 in CHCl$_3$) for (S)-2 of >95:5 er); GC: Betadex 120 30 m × 0.25 mm i.d.(β-cyclodextrin), T 95 °C isothermal, He carrier gas at 14 psi constant pressure, 91 min [(S)-2] 93 min [(R)-2]. Spectroscopic data consistent with that reported in the literature.$^5$
Lithiation-substitution of O-alkyl carbamate 3 using sub-stoichiometric (-)-sparteine only

\[
\begin{array}{c}
\text{Ph} \text{OCb} \\
\text{SnBu}_3
\end{array}
\]

A solution of (-)-sparteine (184 mg, 0.786 mmol, 0.2 eq.) in Et\textsubscript{2}O (3.0 mL) was added dropwise to a stirred solution of s-BuLi (5.0 mL of a 1.0 M solution in cyclohexane, 5.0 mmol) in Et\textsubscript{2}O (4.0 mL) at −78 °C under Ar. After stirring for 10 min at −78 °C, a solution of O-alkyl carbamate 3 (1.03 g, 3.9 mmol) in Et\textsubscript{2}O (4.0 mL) was added dropwise and the resulting solution was stirred at −78 °C for 5 h. Then, Bu\textsubscript{3}SnCl (1.2 mL, 5.1 mmol) was added and the solution was allowed to warm to rt over 16 h. 2 M HCl\textsubscript{(aq)} (10 mL) was added, the layers were separated and the aqueous layer was extracted with Et\textsubscript{2}O (3 × 10 mL). The combined Et\textsubscript{2}O layers were washed with saturated KF\textsubscript{(aq)} (10 mL), dried (MgSO\textsubscript{4}) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography using 40:1 petrol-Et\textsubscript{2}O as eluent gave adduct (S)-4 (365 mg, 17%, 85:15 er by chiral HPLC) as a colourless oil, [\(\alpha\)]\text{D}\textsubscript{+}10.0 (c 1.0 in CHCl\textsubscript{3})(lit., [\(\alpha\)]\text{D}\textsubscript{+}21.9 (c 1.0 in CHCl\textsubscript{3}) for (S)-4 of 98.5:1.5 er); HPLC: Daicel Chiralcel OD, 600:1 v/v hexane-iPrOH, 0.5 mL min\textsuperscript{−1}, 226 nm, 6.5 min [(S)-4] 7.1 min [(R)-4]. Spectroscopic data consistent with that reported in the literature.

Lithiation-substitution of O-alkyl carbamate 3 using stoichiometric (-)-sparteine

\[
\begin{array}{c}
\text{Ph} \text{OCb} \\
\text{SnBu}_3
\end{array}
\]

A solution of (-)-sparteine (576 mg, 2.46 mmol, 1.4 eq) in Et\textsubscript{2}O (3.0 mL) was added dropwise to a stirred solution of s-BuLi (2.5 mL of a 1.0 M solution in cyclohexane, 2.5 mmol) in Et\textsubscript{2}O (3.0 mL) at −78 °C under Ar. After stirring for 10 min at −78 °C, a solution of O-alkyl carbamate 3 (462 mg, 1.75 mmol) in Et\textsubscript{2}O (3.0 mL) was added dropwise and the resulting solution was stirred at −78 °C for 5 h. Then, Bu\textsubscript{3}SnCl (0.68 mL, 2.5 mmol, 1.4 eq) was added dropwise and the solution was allowed to warm to rt over 16 h. 2 M HCl\textsubscript{(aq)} (10 mL) was added, the layers were separated and the aqueous layer was extracted with Et\textsubscript{2}O (3 × 10 mL). The combined Et\textsubscript{2}O layers were washed with saturated KF\textsubscript{(aq)} (10 mL), dried (MgSO\textsubscript{4}) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography using 40:1 petrol-Et\textsubscript{2}O as eluent gave adduct (S)-4 (710 mg, 73%, 99:1 er by chiral HPLC) as a colourless oil,
[(α)D +22 (c 1.0 in CHCl₃)(lit.,³ [(α)D +21.9 (c 1.0 in CHCl₃) for (S)-4 of 98.5:1.5 er); HPLC: Daicel
Chiralcel OD, 600:1 v/v hexane-iPrOH, 0.5 mL min⁻¹, 226 nm, 6.5 min [(S)-4] 7.1 min [(R)-4].
Spectroscopic data consistent with that reported in the literature.³

**Lithiation-substitution of N-Boc pyrrolidine 1 using bispidine 13**

![Image of N-Boc pyrrolidine](image)

A solution of bispidine 13 (410 mg, 1.75 mmol) in Et₂O (3.0 mL) was added dropwise to a stirred
solution of s-BuLi (2.1 mL of a 1.0 M solution in cyclohexane, 2.1 mmol) at −78 °C under Ar. After
stirring for 10 min at −78 °C, a solution of N-Boc pyrrolidine 1 (278 mg, 1.63 mmol) in Et₂O (2.0 mL) was
added dropwise and the resulting solution was stirred at −78 °C for 5 h. Then, Me₃SiCl (0.27 mL, 2.1
mmol) was added dropwise and the solution was allowed to warm to rt over 16 h. 5% H₃PO₄ (aq) (5 mL)
was added and the solution was stirred for 20 min. The layers were separated and the aqueous layer was
extracted with Et₂O (3 × 10 mL). The combined Et₂O extracts were dried (MgSO₄) and evaporated under
reduced pressure to give the crude product. Purification by flash chromatography using 19:1 petrol-EtOAc
as eluent gave adduct rac-2 (19 mg, 5%) as a colourless oil. Spectroscopic data consistent with that
reported in the literature.⁵

**Lithiation-substitution of O-alkyl carbamate 3 using bispidine 13**

![Image of O-alkyl carbamate](image)

A solution of bispidine 13 (266 mg, 1.32 mmol) in Et₂O (2.0 mL) was added dropwise to a stirred
solution of s-BuLi (1.32 mL of a 1.0 M solution in cyclohexane, 1.32 mmol) in Et₂O (2.0 mL) at −78 °C
under Ar. After stirring for 10 min at −78 °C, a solution of O-alkyl carbamate 3 in Et₂O (2.0 mL) was
added dropwise and the resulting solution was stirred at −78 °C for 5 h. Then, Bu₃SnCl (0.36 mL, 1.32
mmol) was added dropwise and the solution was allowed to warm to rt over 16 h. 2 M HCl (aq) (10 mL) was
added, the layers were separated and the aqueous layer was extracted with Et₂O (3 × 10 mL). The
combined Et₂O layers were washed with saturated KF (aq) (10 mL), dried (MgSO₄) and evaporated under
reduced pressure to give the crude product. Purification by flash chromatography gave adduct $\textit{rac-4}$ (80 mg, 15%) as a colourless oil. Spectroscopic data consistent with that reported in the literature.\(^3\)

**Lithiation-substitution of $N$-Boc pyrrolidine 1 in the absence of diamine**

![N-Boc pyrrolidine rac-2](image)

A solution of $N$-Boc pyrrolidine 1 (360 mg, 2.05 mmol) in $\text{Et}_2\text{O}$ (3.0 mL) was added dropwise to a stirred solution of $s$-BuLi (2.5 mL of a 1.0 M solution in cyclohexane, 2.5 mmol) in $\text{Et}_2\text{O}$ (2.5 mL) at $-78$ °C under Ar. After stirring for 5 h at $-78$ °C, $\text{Me}_3\text{SiCl}$ (0.37 mL, 2.90 mmol) was added and the solution was allowed to warm to rt over 16 h. 5% $\text{H}_3\text{PO}_4$ (5 mL) was added and the solution was stirred for 20 min. The layers were separated and the aqueous layer was extracted with $\text{Et}_2\text{O}$ (3 × 10 mL). The combined $\text{Et}_2\text{O}$ extracts were dried ($\text{MgSO}_4$) and evaporated under reduced pressure to give the crude product. Purification by flash chromatography using 19:1 petrol-$\text{EtOAc}$ as eluent gave adduct $\textit{rac-2}$ (68 mg, 13%) as a colourless oil. Spectroscopic data consistent with that reported in the literature.\(^5\)

**Lithiation-substitution of $O$-alkyl carbamate 3 in the absence of diamine**

![O-alkyl carbamate rac-4](image)

A solution of $O$-alkyl carbamate 3 (400 mg, 1.52 mmol) in $\text{Et}_2\text{O}$ (2.0 mL) was added dropwise to a stirred solution of $s$-BuLi (1.8 mL of a 1.1 M solution in cyclohexane, 2.0 mmol) in $\text{Et}_2\text{O}$ (4.0 mL) at $-78$ °C under Ar. After stirring for 5 h at $-78$ °C, $\text{Bu}_3\text{SnCl}$ (0.54 mL, 2.0 mmol) was added and the solution was allowed to warm to rt over 16 h. Then, 2 M $\text{HCl}_{(\text{aq})}$ (10 mL) was added, the layers were separated and the aqueous layer was extracted with $\text{Et}_2\text{O}$ (3 × 10 mL). The combined $\text{Et}_2\text{O}$ extracts were washed with saturated $\text{KF}_{(\text{aq})}$ (10 mL), dried ($\text{Na}_2\text{SO}_4$) and evaporated under reduced pressure. Purification by flash chromatography using 40:1 petrol-$\text{Et}_2\text{O}$ gave adduct $\textit{rac-4}$ (148 mg, 17%) as a colourless oil and starting $O$-alkyl carbamate 3 (230 mg, 58%) as a colourless oil. Spectroscopic data consistent with that reported in the literature.\(^3\)
3,7-Diisopropyl-3,7-diazabicyclo[3.3.1]nonane-9-one

Isopropylamine (1.8 mL, 21 mmol) was added dropwise to a stirred solution of N-isopropylpiperidine (3.0 g, 21 mmol), acetic acid (1.3 mL, 22 mmol) and paraformaldehyde (1.8 g, 63 mmol) in MeOH (30 mL) at rt under N\textsubscript{2}. The resulting mixture was heated at reflux for 16 h. After cooling to rt, the solvent was evaporated under reduced pressure. Then, 50% KOH\textsubscript{(aq)} (100 mL) was added to the residue and the mixture was extracted with Et\textsubscript{2}O (3 × 100 mL). The combined Et\textsubscript{2}O extracts were dried (MgSO\textsubscript{4}) and evaporated under reduced pressure to give the crude product. Purification by Kugelrohr distillation gave the bispidinone (3.2 g, 69%) as a colourless oil, bp 220-240 °C/2 mm Hg (lit.,\textsuperscript{6} 110-120 °C/10-5 mm Hg); IR (film) 2963, 1734 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ: 3.03 (dd, J = 10.0, 2.0 Hz, 4H, CHN), 2.88 (dd, J= 10.0, 6.0 Hz, 4H, CHN), 2.85-2.77 (m, 2H, CHMe\textsubscript{2}), 2.67-2.73 (m, 2H, CH bridgehead), 1.00 (d, J = 7.0 Hz, 12H, Me); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ: 215.82 (C=O), 53.46 (CH\textsubscript{2}N), 53.39 (CHN), 47.02 (CH), 18.23 (Me). Spectroscopic data consistent with that reported in the literature.\textsuperscript{6}

3,7-Diisopropyl-3,7-diazabicyclo[3.3.1]nonane 13

Anhydrous hydrazine (4.9 mL, 150 mmol) was added dropwise to a vigorously stirred suspension of 3,7-diisopropyl-3,7-diazabicyclo[3.3.1]nonane-9-one (6.3 g, 28 mmol) and KOH (20 g, 320 mmol) in diethylene glycol (60 mL) at rt. The resulting mixture was heated to 180 °C for 4 h. After cooling to rt, water (100 mL) was added and the mixture was extracted with Et\textsubscript{2}O (4 × 50 mL). The combined Et\textsubscript{2}O extracts were washed with 20% NaOH\textsubscript{(aq)} (6 × 80 mL), dried (MgSO\textsubscript{4}) and evaporated under reduced pressure to give the crude product as a yellow oil. Purification by careful Kugelrohr distillation gave bispidine 13 (2.2 g, 38%) as a colourless oil, bp 130-160 °C/2mm Hg; IR (film) 2983, 2962, 1460, 1358, 1150 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ: 2.70-2.58 (m, 2H, CHMe\textsubscript{2}), 2.55 (dd, J= 10.0, 5.5 Hz, 4H,
CHN) 2.49 (br d, $J = 10.0$ Hz, 4H, CHN), 1.95-2.00 (m, 2H, bridgehead CH), 1.47-1.46 (m, 2H, bridge CH$_2$) 0.99 (d, $J = 6.5$ Hz, 12H, Me). $^{13}$C NMR (100 MHz, CDCl$_3$) 53.96 (CHN), 52.36 (CH$_2$N), 28.10 (bridge CH$_2$), 27.72 (bridgehead CH), 18.17 (Me); HRMS (Cl, NH$_3$) $m/z$ [M + H]$^+$ calcd for C$_{13}$H$_{26}$N$_2$ 211.2174 found 211.2172.

**tert-Butyldimethyl phosphine borane 14**

![14]

Methylmagnesium chloride (100 mL of a 3 M solution in Et$_2$O, 300 mmol) was added dropwise to a stirred solution of tert-butyldichlorophosphine (10 g, 63 mmol) in THF (50 mL) at 0 °C under N$_2$. The resulting solution was stirred at rt for 1 h. After cooling to 0 °C, BH$_3$•SMe$_2$ (80 mL of a 2 M solution in THF, 160 mmol) was added dropwise. Then, the solution was stirred at rt for 1 h and poured onto a mixture of ice (300 g) and concentrated HCl$_{aq}$ (30 mL). The mixture was extracted with EtOAC (3 × 100 mL). The combined EtOAc extracts were dried (MgSO$_4$) and evaporated under reduced pressure to give the crude product. Purification by sublimation in a Kugelrohr apparatus (180-200 °C/1 mm Hg) gave phosphine borane 14 (5.6 g, 67%) as white needles, mp 162-164 °C (lit.,$^8$ 160-163 °C); $R_p$(4:1 petrol-Et$_2$O) 0.4; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.21 (d, $J = 10.0$ Hz, 6H, PMe), 1.14 (d, $J = 14.0$ Hz, CMe$_3$), 0.41 (qd, $J = 95.0$, 13.0 Hz, BH$_3$). Spectroscopic data consistent with that reported in the literature.$^8$
$^1$H/$^13$C NMR spectra of 3,7-diisopropyl-3,7-diazabicyclo[3.3.1]nonane-9-one
$^1$H/$^{13}$C NMR spectra of 3,7-diisopropyl-3,7-diazabicyclo[3.3.1]nonane 13

![NMR Spectra Diagram]
$^1$H NMR spectrum of (S)-3-phenyl-1-tributyltin-1-$N,N$-diisopropylcarbamoylpropane (S)-4

$^1$H NMR spectrum of (S)-3-phenyl-1-trimethylsilyl-1-$N,N$-diisopropylcarbamoylpropane
$^1$H/$^13$C NMR spectra of (R)-P-(2,2-diphenyl-2-hydroxyethyl)-P-methyl-tert-butyl-phosphine borane (R)-15
$^1$H/$^{13}$C NMR spectra of (S,S)-1,2-bis(boranato(tert-butyl)methylphosphino)ethane (S,S)-16
\(^1\text{H}/\text{C}^\text{13}\) NMR spectra of (R,S)-1,2-bis(boranato(tert-butyl)methylphosphino)ethane meso-16

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Chiral GC of (R)- and (S)-2-Trimethylsilyl-\textit{N}-\textit{tert}-butoxycarbonylpyrrolidine 2

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\]

(S)-2

\[
\text{Boc-SiMe}_3
\]

(R)-2
Chiral HPLC of (S)- and (R)-3-phenyl-1-tributyltin-1-N,N-diisopropylcarbamoylpropane 4

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Chiral HPLC of (S)- and (R)-P-(2,2-diphenyl-2-hydroxyethyl)-P-methyl-tert-butyl-phosphine borane 15
Chiral HPLC of (S,S)- and (R,R)-1,2-bis(boranato(tert-butyl)methylphosphino)ethane 16
References for supporting information:


(8) Imamoto, T.; Watanabe, J.; Wada, Y.; Masuda, H.; Yamada, H.; Tsuruta, H.; Matsukawa, S.;