Experimental

General methods and instrumentation:

All manipulations of air and moisture sensitive species were performed under an atmosphere of argon or dinitrogen using standard Schlenk and glove box techniques. Solvents were dried by passing through an alumina drying column incorporated into a MBraun SPS800 solvent purification system except in the case of tetrahydrofuran (thf), which was dried over potassium and distilled under argon. All solvents were degassed and stored under argon in Teflon valve ampoules. Deuterated chloroform was passed through a column of basic alumina before being stored over 4Å molecular sieves prior to use. Deuterated benzene and thf were dried over potassium under an argon atmosphere before being vacuum transferred, freeze pump thaw degassed and stored in the glove box. All other reagents were purchased from commercial suppliers and used as received unless otherwise stated.

Air sensitive samples for NMR spectroscopy were prepared in a glovebox under a dinitrogen atmosphere using 5 mm Nolan NMR tubes equipped with J. Young Teflon valves. All other samples were prepared in Wilmad 5 mm NMR tubes. NMR spectra were recorded on BrukerAvance DPX 250, 400, 500 or Jeol Eclipse 300 spectrometers. NMR spectra are quoted in ppm and were referenced internally relative to the residual proto-solvent (1H) or solvent (13C) resonances; all coupling constants are quoted in Hertz. Where necessary, NMR assignments were confirmed by the use of two-dimensional 1H-1H or 1H-13C correlation experiments (HSQC and HMBC). Mass spectra were recorded on a Waters LCT Premier XE or Waters GCT Premier mass spectrometer by the mass spectrometry service at the School of Chemistry, Cardiff University. Infrared spectra were prepared as liquid films on NaCl plates, or KBr pellets and were recorded on a Jasco 660-Plus FT/IR spectrometer. Infrared data are quoted in wavenumbers (cm⁻¹).

N-Phthaloylvaline: To a solution of L-valine (100 g 854 mmol) in toluene (1.5 l), phthalic anhydride (139.07 g, 939 mmol) and triethylamine (119.2 ml 854 mmol) were added. The system was refluxed for 18 hours before being allowed to cool. The product was washed using HCl (2M, 2 × 500 ml) and further washed with brine (500 ml). The aqueous fractions were combined and further washed using toluene (250 ml) before being reduced in volume under reduced pressure to realise a white crystalline solid (75% yield). 1H NMR data (CDCl₃, 400.1 MHz, 293 K) δH = 7.87 (2 H, 2 × dd, J3HH = 5.4 Hz, J3HH = 5.4 Hz, Ar-H), 7.74 (2 H, 2 × dd, J3HH = 5.4 Hz, J3HH = 5.4 Hz, Ar-H), 4.63 (1 H, d, J1HH = 8.4 Hz, Ph³NCH), 2.75 (1 H, m,
CH(CH₃)₂), 1.16 (3 H, d, J₃HH = 6.7 Hz, (CH₃)₂CH), 0.91 (3 H, d, J₃HH = 6.7 Hz, (CH₃)₂CH) ppm.

General procedure for the preparation of N-phthaloyl protected amino-amides: N-phthaloylvaline (10 g, 40.4 mmol) was dissolved in dry thf (250 ml) to which SOCl₂ (3.15 ml, 48.6 mmol) was added dropwise under a flow of argon. The solution was heated to reflux for 2.5 hours before removing the volatiles under reduced pressure and drying the solid in vacuo giving a cream solid. The N-phthaloylvalinoylchloride was used without further purification. ¹H NMR data (CDCl₃, 400.1 MHz, 293 K) δH = 7.90 (2 H, 2 × dd, J₁HH = 5.4 Hz, J₂HH = 5.4 Hz, Ar-H), 7.80 (2 H, 2 × dd, J₁HH = 5.4 Hz, J₂HH = 5.4 Hz, Ar-H), 4.74 (1 H, d, J₁HH = 8.4 Hz, PhtNCH), 2.74 (1 H, m, CH(CH₃)₂), 1.15 (3 H, d, J₁HH = 6.7 Hz, (CH₃)₂CH), 0.91 (3 H, d, J₁HH = 6.7 Hz, (CH₃)₂CH) ppm.

The protected valinoyl chloride was dissolved in dry thf (250 ml) and a solution of the desired amine (39.7 mmol) and triethylamine (6.8 ml, 48.6 mmol) in thf (50 ml) was added dropwise. N,N-dimethylaminopyridine (DMAP) can be added in catalytic amounts at this stage to give higher yields. The solution was allowed to stir at room temperature for 18 hours before being reduced in volume under reduced pressure. The product was dissolved in NaOH (10% solution, 75 ml) and extracted into dichloromethane (3 × 100 ml) before being dried over Na₂SO₄. After drying in vacuo, the protected amidewas obtained in a 50-90% yield.

Protected HNNtBu: ¹H NMR data (CDCl₃, 400.1 MHz, 293 K): δH = 7.81 (2H, 2 × dd, J₁HH = 5.5 Hz, J₂HH = 5.4 Hz, PhtH), 7.69 (2H, 2 × dd, J₁HH = 5.5 Hz, J₂HH = 5.4 Hz, PhtH), 4.19 (1 H, d, J₁HH = 11.4 Hz, PhtNCH), 2.70 (1 H, m, CH(CH₃)₂), 1.27 (9 H, s, C(CH₃)₃), 1.03 (3 H, d, J₁HH = 6.6 Hz, CH(CH₃)₂), 0.76 (3 H, d, J₁HH = 6.6 Hz, CH(CH₃)₂) ppm.

Protected HNNiPr: ¹H NMR data (CDCl₃, 400.1 MHz, 293 K): δH = 7.80 (2H, 2 × dd, J₁HH = 5.5 Hz, J₂HH = 5.5 Hz, PhtH), 7.69 (2H, 2 × dd, J₁HH = 5.5 Hz, J₂HH = 5.4 Hz, PhtH), 4.29 (1 H, d, J₁HH = 11.4 Hz, PhtNCH), 3.97 (1 H, sept, J₁HH = 6.7 Hz, CH(CH₃)₂), 2.73 (1 H, m, CH(CH₃)₂), 1.17 (3 H, d, J₁HH = 6.6 Hz, CH(CH₃)₂), 1.09 (3 H, d, J₁HH = 6.7 Hz, CH(CH₃)₂), 1.02 (3 H, d, J₁HH = 6.7 Hz, CH(CH₃)₂), 0.77 (3 H, d, J₁HH = 6.6 Hz, CH(CH₃)₂) ppm.

Protected HNNPh: ¹H NMR data (CDCl₃, 400.1 MHz, 293 K): δH = 7.89 (2H, 2 × dd, J₁HH = 5.4 Hz, J₂HH = 5.4 Hz, PhtH), 7.73 (2H, 2 × dd, J₁HH = 5.4 Hz, J₂HH = 5.4 Hz, PhtH), 7.56 (2H, d, J₁HH = 8.5 Hz, ArH), 7.30 (2H, app.t, J₁HH = 7.5 Hz, ArH), 7.09 (1H, app.t, J₁HH = 7.5 Hz,
Protected HNN$^\text{ArF}$: $^1$H NMR data (CDCl$_3$, 400.1 MHz, 293 K): $\delta_H = 7.90$ (2H, 2 × dd, $^3J_{HH} = 5.5$ Hz, PhH), 7.78 (2H, 2 × dd, $^3J_{HH} = 5.5$ Hz, $^3J_{HH} = 5.5$ Hz, PhH), 7.53 (2H, dd, $^3J = 9.1$ Hz, ArH), 7.00 (2H, app.t, $^3J = 8.6$ Hz, ArH), 4.52 (1H, d, $^3J_{HH} = 11.6$ Hz, PhNCH), 2.90 (1H, m, CH$(CH_3)_2$), 1.16 (3H, d, $^3J_{HH} = 6.6$ Hz, CH$(CH_3)_2$), 0.89 (3H, d, $^3J_{HH} = 6.6$ Hz, CH$(CH_3)_2$) ppm.

General procedure for the deprotection of the phthaloylvaline: The protected N-phthaloyl amino amide (36.6 mmol) was dissolved in ethanol (250 ml) and hydrazine monohydrate (9.60 ml 51.2mmol) added. The reaction was allowed to stir at room temperature for 18 hours before conc. HCl (50 ml) was added and allowed to stir vigourously for 1 hour. After such time, the solution was reduced in volume under reduced pressure and dissolved in distilled water (50 ml). The solution was then made neutral using NaOH (10%) and washed with dichloromethane (3 × 50 ml). Deprotected amides soluble in dichloromethane were dried over Na$_2$SO$_4$ and the solid dried in vacuo. Aqueous soluble deprotected amides were reduced in volume and re-dissolved in THF, filtered to remove insoluble impurities and again dried under reduced pressure. The products were typically obtained as white or light orange solids in 60-94% yield.

Deprotected HNN$^\text{tBu}$: NMR data (CDCl$_3$, 400.1 MHz, 293 K): $\delta_H = 3.03$ (1 H, d, $^3J_{HH} = 3.9$ Hz, CH$(CH_3)_2$), 2.20 (1H, m, CH$(CH_3)_2$), 1.28 (9 H, s, C(C$(CH_3)_3)$), 0.90 (3H, d, $^3J_{HH} = 6.9$ Hz, CH$(CH_3)_2$), 0.75 (3H, d, $^3J_{HH} = 6.9$ Hz, CH$(CH_3)_2$) ppm.

Deprotected HNN$^\text{iPr}$: NMR data (CDCl$_3$, 400.1 MHz, 293 K): $\delta_H = 4.00$ (1 H, sep, $^3J_{HH} = 6.6$ Hz, CH$(CH_3)_2$), 3.12 (1 H, d, $^3J_{HH} = 4.8$ Hz, H$_2$NCH), 2.21 (1 H, m, CH$(CH_3)_2$), 1.09 (6 H, 2 × dd, $^3J_{HH} = 7.0$ Hz, CH$(CH_3)_2$), 0.91 (3H, d, $^3J_{HH} = 6.9$ Hz, CH$(CH_3)_2$), 0.75 (3H, d, $^3J_{HH} = 6.9$ Hz, CH$(CH_3)_2$) ppm.

Deprotected HNN$^\text{Ph}$: $^1$H NMR data (CDCl$_3$, 400.1 MHz, 293 K): $\delta_H = 7.59$ (2H, app. d, $^3J_{HH} = 8.6$Hz, ArH), 7.30 (2H, app.t, $^3J_{HH} = 7.5$ Hz, ArH), 7.08 (1H, app.t, $^3J_{HH} = 7.5$ Hz, ArH), 5.27 (1H, app. s, H$_2$NCH), 2.40 (1H, m, CH$(CH_3)_2$), 1.02 (3H, d, $^3J_{HH} = 6.9$ Hz, CH$(CH_3)_2$), 0.86 (3H, d, $^3J_{HH} = 6.9$ Hz, CH$(CH_3)_2$) ppm.
Deprotected HNNArF: $^1$H NMR data (D$_2$O, 400.1 MHz, 293 K): $\delta$H = 6.97 (2H, m, ArH), 6.87 (2H, m, ArH), 3.81 (1H, d, $^3$J$_{HH} = 2.2$ Hz, H$_2$NCH), 2.09 (1H, m, CH(CH$_3$)$_2$), 1.09 (3H, d, $^3$J$_{HH} = 6.9$Hz, CH(CH$_3$)$_2$) ppm.

General procedure for the reduction of the amino amides: To a suspension of NaBH$_4$ (5.58g, 147.5mmol) in thf (250 ml), (CH$_3$)$_3$SiCl (23.57 ml, 184.3mmol) was added and refluxed under an inert atmosphere for 2 hours. The reaction was allowed to cool to room temperature and then further cooled to -78 °C before adding the amino amide (36.7mmol, ca. 7 g) which was dissolved in dry thf. The mixture was then heated to reflux under inert conditions for 4 days. After such time the solution was allowed to cool to room temperature and further cooled to 0°C. Methanol (10 ml) and water (10 ml) were sequentially added to destroy the excess borane. After the effervescence subsided, the solution was reduced in volume under reduced pressure, dissolved in NaOH (10%, 50 ml) and the product extracted with dichloromethane (3 × 50 ml). The organic layers were combined and dried over Na$_2$SO$_4$ before removing the solvent under reduced pressure. The crude diamine was then purified using column chromatography over silica gel typically using ethyl acetate and methanol (5-10% v/v). Once purified, the diamines were obtained as orange to dark orange/red oils with typical yields of 70%. NMR analysis after adding (R)-(−)-O-acetylmandelic acid indicated the presence of only a single enantiomer.

[HNN$^{iBu}$] 1a; $^1$H NMR data (CDCl$_3$, 500.1 MHz, 293 K) $\delta$H = 2.62 (1 H, dd, $^3$J$_{HH} = 3.4$ Hz, $^2$J$_{HH} = 10.9$ Hz, NCH$_2$), 2.47 (1 H, m, H$_2$NCH), 2.26 (1H, dd, $^3$J$_{HH} = 3.4$ Hz, $^2$J$_{HH} = 10.9$ Hz, NCH$_2$), 1.57 (1H, m, (CH$_3$)$_2$CH) 1.07 (9H, s, tBu), 0.89 (6H, app t, $^3$J$_{HH} = 6.9$Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C{1H} NMR data (CDCl$_3$, 100.6 MHz, 293 K) $\delta$C = 57.1 (H$_2$NCH), 50.2 (C(CH$_3$)$_3$), 46.3 (CH$_2$), 32.4 ((CH$_3$)$_2$CH), 28.9 ((CH$_3$)$_2$CH), 19.3 (CH$_{\text{isopropyl}}$), 17.7 (CH$_{\text{isopropyl}}$) ppm. IR data: (NaCl disc, cm$^{-1}$) 3366 (m), 3297 (m), 2961 (s), 2929 (s), 2871 (s), 2283 (w), 1658 (m), 1579 (m), 1519 (m), 1467 (m), 1388 (m), 1363 (m), 1317 (w), 1230 (m), 1169 (w), 1091 (w), 1024 (w), 878 (w), 805 (w), 716 (w). Accurate mass ES-MS for [H$_2$NCH(CH(CH$_3$)$_2$)CH$_2$NHC(CH$_3$)$_3$]$: m/z = 158.1782$ (caled for C$_9$H$_{22}$N$_2$: 158.1783).

[HNN$^{iPr}$] 1b; $^1$H NMR data (CDCl$_3$, 500.1 MHz, 293 K): $\delta$H = 2.67 (1 H, m, HN(CH(CH$_3$)$_2$), 2.60 (1 H, dd, $^3$J$_{HH} = 3.2$ Hz, $^2$J$_{HH} = 11.3$ Hz, NCH$_2$), 2.46 (1H, m, H$_2$NCH), 2.21 (1 H, app t, $^3$J$_{HH} = 11.3$ Hz, NCH$_2$), 1.49 (1 H, m, CH(CH$_3$)$_2$), 0.97 (6 H, d, $^3$J$_{HH} = 6.2$ Hz, CH(CH$_3$)$_2$), 0.81 (6 H, d, $^3$J$_{HH} = 9.0$ Hz, CH(CH$_3$)$_2$) ppm. $^{13}$C{1H} NMR data (CDCl$_3$, 100.6 MHz, 293 K): $\delta$C =
56.1 (H₂NCH), 50.5 (CH₃), 49.0 (NHCH(CH₃)₂), 32.3 (CH(CH₃)₂), 22.3 (NHCH(CH₃)₂), 22.1 (NHCH(CH₃)₂), 19.1 (CH₃isopropyl), 17.7 (CH₃isopropyl) ppm. IR data: (NaCl disc, cm⁻¹) 3668 (w), 3350 (s), 2962 (s), 2873 (m), 2361 (w), 2342 (w), 2251 (w), 1587 (m), 1497 (w), 1468 (m), 1414 (w), 1383 (m), 1338 (m), 1321 (w), 1261 (m), 1168 (w), 1071 (m), 1013 (m), 909 (s), 868 (w), 811 (m), 731 (s), 646 (m). Accurate mass ES-MS for [H₃NCH(CH(CH₃)₂)CH₂NH(CH(CH₃)₂)⁺]: m/z = 145.1700 (calcd for C₈H₂₁N₂: 145.1705).

[HNN⁺] 1c; ¹H NMR data (CDCl₃, 500.1 MHz, 293 K): δ_H = 7.18 (2 H, app t, 3J_HH = 7.4 Hz, m-C₆H₅), 6.70 (1 H, app t, 3J_HH = 7.4 Hz, p-C₆H₅), 6.65 (2 H, d, 3J_HH = 7.7 Hz, o-C₆H₅), 3.25 (1 H, dd, 3J_HH = 3.2 Hz, J_HH = 11.9 Hz, NCH₂), 2.85 (1 H, app t, 3J_HH = 11.9 Hz, NCH₂), 2.76 (1 H, m, H₂NCH), 1.69 (1 H, m, (CH₃)₂CH), 0.98 (3 H, d, 3J_HH = 9.6 Hz, CH(CH₃)₂), 0.96 (6 H, d, 3J_HH = 9.6 Hz, CH(CH₃)₂) ppm. ¹³C{¹H} NMR data (CDCl₃, 100.6 MHz, 293 K): δ_C = 148.6 (ipso-C₆H₅), 129.1 (m-C₆H₅), 117.2 (p-C₆H₅), 112.9 (o-C₆H₅), 56.0 (H₂NCH), 47.9 (CH₃), 32.4 ((CH₃)₂CH), 19.2 (CH₃isopropyl), 17.8 (CH₃isopropyl) ppm. IR data: (NaCl disc, cm⁻¹) 3370 (m), 3050 (m), 3021 (m), 2958 (s), 2871 (s), 2602 (w), 1918 (w), 1734 (m), 1675 (m), 1603 (s), 1506 (s), 1466 (m), 1442 (m), 1431 (m), 1387 (m), 1368 (m), 1321 (m), 1251 (m), 1179 (m), 1153 (m), 1068 (m), 1046 (m), 1028 (m), 991 (s), 868 (m), 749 (m), 692 (m). Accurate mass ES-MS for [H₃NCH(CH(CH₃)₂)CH₂NH(C₆H₅)]⁺: m/z = 178.1465 (calcd for C₁₁H₁₈N₂: 178.1470).

[HNN⁺] 1d; ¹H NMR data (CDCl₃, 500.1 MHz, 293 K): δ_H = 6.82 (2 H, app t, 3J_HH = 8.8 Hz, m-C₆H₄F), 6.57 (2 H, dd, 3J_HH = 8.8 Hz, J_HF = 4.3 Hz, o-C₆H₄F), 3.38 (1 H, dd, 3J_HH = 3.4 Hz, J_HH = 14.0 Hz, NCH₂), 3.27 (1 H, dd, 3J_HH = 3.4 Hz, J_HH = 14.0 Hz, NCH₂), 3.03 (1 H, m, H₂NCH), 2.04 (1 H, m, (CH₃)₂CH), 1.05 (6 H, dd, 3J_HH = 6.5 Hz, CH(CH₃)₂), ppm. ¹⁹F NMR data (CDCl₃, 282.8 MHz, 293 K): δ_F = -128.11 (s, p-C₆H₄F) ppm. ¹³C{¹H} NMR data (CDCl₃, 100.6 MHz, 293 K): δ_C = 156.1 (d, J_CF = 235.9 Hz, p-C₆H₄F), 143.5 (d, J_CF = 1.7 Hz, ipso-C₆H₄F), 115.8 (d, J_CF = 22.3 Hz, m-C₆H₄F), 113.9 (d, J_CF = 7.3 Hz, o-C₆H₄F), 57.6 (H₂NCH), 44.2 (CH₃), 29.2 ((CH₃)₂CH), 18.8 (CH₃isopropyl), 18.8 (CH₃isopropyl) ppm. IR data: (NaCl disc, cm⁻¹) 3345 (m), 3252 (w), 2965 (s), 2556 (w), 2458 (w), 1652 (w), 1609 (w), 1575 (m), 1529 (s), 1507 (s), 1470 (s), 1381 (w), 1321 (m), 1261 (m), 1156 (w), 1135 (w), 1104 (m), 1086 (w), 1014 (w), 916 (w), 872 (w), 821 (s), 799 (s), 754 (w), 706 (w), 692 (w). Accurate mass ES-MS for [H₃NCH(CH(CH₃)₂)CH₂NH(C₆H₄F)]⁺: m/z = 196.1372 (calcd for C₁₁H₁₉F₂N₂: 196.1376).
[Ca{N(SiMe3)2}2(thf)2]: CaI2 (1.47g, 5 mmol) was added to K(N(SiMe3)2) (1.99g, 10 mmol) and dissolved in thf and allowed to stir for 18 hours under an inert atmosphere. The solution was filtered away from the resulting salt precipitate and the solvent removed under reduced pressure to yield the solid [Ca{N(SiMe3)2}2(thf)2]. This was further dried in vacuo overnight to approximately 2 × 10⁻² mbar. Data were consistent with that previously reported.

General procedure for the preparation of the [Ca(NNR){N(SiMe3)2}(py)n] (2a – d): [Ca{N(SiMe3)2}2(py)2] was prepared from the corresponding analogue [Ca{N(SiMe3)2}(thf)2] (vide supra) via literature procedures. HNNR (300 mg, 1.5mmol) in toluene (20 ml) was added to 1 equivalent of [Ca{N(SiMe3)2}(py)2] (793 mg, 1.5mmol). The solution was agitated briefly and allowed to react for 18 hours at ambient temperature. The resulting complex was typically realised as an orange/red powder when dried in vacuo to approximately 4 × 10⁻² mbar. The absolute configuration at the calcium of the diastereomeric complexes could not be determined owing to the highly fluxional nature of the spectroscopic data.

[Ca(NNiPr){N(SiMe3)2}(py)] 2a: ¹H NMR data (d₈-thf, 300.5 MHz, 293 K): δ_H = 8.54 (2 H, m, o-C₅H₅N), 7.66 (1 H, app. tt, 3JHH = 7.6 Hz, 4JHH = 1.9 Hz, p-C₅H₅N), 7.25 (2 H, m, m-C₅H₅N), 7.28 (1 H, br. m, NCH₂), 2.60 (1 H, br. m, H₂NCH), 2.45 (1 H, br. m, NCH₂), 1.57 (1 H, m, (CH₃)₂CH), 1.07 (9 H, br. s, C(CH₃)₃), 0.88 (6 H, br. t, 3JHH = 6.6 Hz, CH(CH₂)₂), 0.10 (18 H, s, N(SiMe₃)₂) ppm. ¹H NMR data (d₈-thf, 300.5 MHz, 263 K): δ_H = 8.55 (2 H, m, o-C₅H₅N), 7.68 (1 H, app. tt, 3JHH = 7.6 Hz, 4JHH = 1.9 Hz, p-C₅H₅N), 7.28 (2 H, m, m-C₅H₅N), 2.59 (1 H, br. m, H₂NCH), 2.45 (1 H, br. m, NCH₂), 1.57 (1 H, m, (CH₂)₂CH), 1.08 (9 H, br. s, C(CH₃)₃), 0.88 (6 H, br. t, 3JHH = 6.6 Hz, CH(CH₂)₂), 0.10 (18 H, s, N(SiMe₃)₂) ppm.

¹³C{¹H} NMR data (d₈-thf, 75.5 MHz, 263 K): δ_C = 150.6 (o-C₅H₅N), 136.2 (p-C₅H₅N), 124.2 (m-C₅H₅N), 58.1 (H₂NCH), 50.6 (NC(CH₃)₂), 47.2 (CH₂), 33.2 ((CH₂)₂CH), 29.3 ((CH₃)₃CN), 19.7 (CH₃isopropyl), 17.9 (CH₃isopropyl), 1.2 (N(SiMe₃)₂) ppm. IR data: (KBr pellet, cm⁻¹) 3247 (w), 2962 (s), 2871 (w), 1597 (m), 1466 (m), 1442 (w), 1393 (w), 1367 (m), 1261 (s), 1234 (w), 1218 (w), 1098 (s), 1021 (s), 894 (w), 859 (w), 803 (s), 749 (s), 749 (w).

[Ca(NNiPr){N(SiMe3)2}(py)] 2b: ¹H NMR data (d₈-thf, 300.5 MHz, 293 K): δ_H = 8.58 (2 H, m, o-C₅H₅N), 7.66 (1 H, m, p-C₅H₅N), 7.26 (2 H, m, m-C₅H₅N), 2.90 (1 H, br. m, NCH₂), 2.66 (1 H, br. m, H₂NCH), 2.52 (1 H, br. m, NCH₂), 1.67-1.47(2 H, br. m, (CH₂)₂CH), 1.24-1.03 (6 H, br. m, CH(CH₂)₂), 0.94-0.76 (6 H, br. m, CH(CH₂)₂) 0.03 (18 H, s, N(SiMe₃)₂) ppm. ¹H NMR data (d₈-thf, 300.5 MHz, 263 K): δ_H = 8.55 (2 H, m, o-C₅H₅N), 7.69 (1 H, app. tt, 3JHH = 7.6 Hz,
$^4$J$_{HH}$ = 1.8 Hz, $p$-C$_5$H$_4$N), 7.28 (2 H, m, C$_5$H$_4$N), 3.10-2.80 (2 H, br. m, H$_2$NCH and NCH$_2$), 2.65 (1 H, br. m, NCH$_2$), 1.67 (1 H, br. m, (CH$_3$)$_2$CH), 1.37 (1 H, br. m, (CH$_3$)$_2$CH), 1.19-1.06 (6 H, br. m, CH(CH$_3$)$_2$), 0.93-0.80 (6 H, br. m, CH(CH$_3$)$_2$) ppm.

$^1$H NMR data (d$_8$-thf, 500.1 MHz, 263 K): $\delta_H = 8.57$ (2 H, m, o-C$_5$H$_4$N), 7.67 (1 H, app. tt, $^3$J$_{HH}$ = 7.7 Hz, $^4$J$_{HH}$ = 1.5 Hz, p-C$_5$H$_4$N), 7.26 (2 H, m, m-C$_5$H$_4$N), 6.53 (2 H, app. t, $^3$J$_{HH}$ = 8.2 Hz, m-C$_5$H$_4$F), 6.06 (2 H, br. m, o-C$_5$H$_4$F), 2.86 (1 H, app. d, $^3$J$_{HH}$ = 9.5 Hz, NCH$_2$), 2.59 (2 H, br. m, H$_2$NCH and NCH$_2$), 1.65 (1 H, br. m, (CH$_3$)$_2$CH), 0.93 (6 H, app. d, $^3$J$_{HH}$ = 6.1 Hz, CH(CH$_3$)$_2$) ppm. $^1$H NMR data (d$_8$-thf, 300.5 MHz, 293 K): $\delta_H = 8.59$ (2 H, m, o-C$_5$H$_4$N), 7.69 (1 H, app. tt, $^3$J$_{HH}$ = 7.5 Hz, $^4$J$_{HH}$ = 1.8 Hz, p-C$_5$H$_4$N), 7.28 (2 H, m, C$_5$H$_4$N), 3.10-2.80 (2 H, br. m, H$_2$NCH and NCH$_2$), 2.65 (1 H, br. m, NCH$_2$), 1.67 (1 H, br. m, (CH$_3$)$_2$CH), 1.37 (1 H, br. m, (CH$_3$)$_2$CH), 1.19-1.06 (6 H, br. m, CH(CH$_3$)$_2$), 0.93-0.80 (6 H, br. m, CH(CH$_3$)$_2$) ppm. $^13$C{$_1$H} NMR data (d$_8$-thf, 75.5 MHz, 293 K): $\delta_C$ = 150.6 (o-C$_5$H$_4$N), 136.2 (p-C$_5$H$_4$N), 124.1 (m-C$_5$H$_4$N), 58.3 (H$_2$NCH), 55.8 (NCH(CH$_3$)$_2$), 49.0 (CH$_2$), 36.7 ((CH$_3$)$_2$CH), 23.0 (CH$_3$isopropyl), 22.1 (CH$_3$isopropyl), 19.9 (CH$_3$isopropyl), 18.7 (CH$_3$isopropyl), 2.4 (N(SiMe$_3$)$_2$) ppm. IR data: (KBr pellet, cm$^{-1}$) 3248 (w), 2959 (s), 2870 (m), 1597 (m), 1553 (m), 1465 (m), 1442 (m), 1386 (m), 1368 (m), 1324 (w), 1259 (s), 1165 (w), 1057 (s), 950 (w), 931 (w), 881 (m), 822 (s), 750 (w).
C₅H₅N), 7.29 (2 H, m, m-C₅H₅N), 6.53 (2 H, app. t, JHH = 7.7 Hz, m-C₅H₅F), 6.04 (2 H, br. m, o-C₅H₅F), 2.83 (1 H, br. m, NCH₂), 2.58 (2 H, br. m, H₂NCH and NCH₂), 1.66 (1 H, br. m, (CH₃)₂CH), 0.94 (6 H, app. d, JHH = 5.0 Hz, p-C₅H₅N), 6.53 (2 H, app. t, 3JHH = 7.7 Hz, m-C₅H₅N), 6.04 (2 H, br. m, o-C₅H₅F), 2.83 (1 H, br. m, NCH₂), 2.58 (2 H, br. m, H₂NCH and NCH₂), 1.66 (1 H, br. m, (CH₃)₂CH), 0.94 (6 H, app. d, JHH = 5.0 Hz, p-C₅H₅N), 127.6 (d, J CF = 274.0 Hz, p-C₆H₄F), 124.1 (m-C₅H₅N), 115.3 (d, J CF = 19.7 Hz, m-C₆H₄F), 110.7 (o-C₆H₄F), 60.4 (H₂NCH), 54.7 (CH₂), 34.1 ((CH₃)₂CH), 19.5 (CHisopropyl), 18.6 (CHisopropyl), 2.4 (N(SiMe₃)₂) ppm. 13C{1H} NMR data (d₈-thf, 75.5 MHz, 263 K): δC = 157.8 (ipso-C₆H₄F), 150.6 (o-C₅H₅N), 136.2 (p-C₅H₅N), 127.6 (d, JCF = 274.0 Hz, p-C₆H₄F), 124.1 (m-C₅H₅N), 115.3 (d, JCF = 19.7 Hz, m-C₆H₄F), 110.7 (o-C₆H₄F), 60.4 (H₂NCH), 54.7 (CH₂), 34.1 ((CH₃)₂CH), 19.5 (CHisopropyl), 18.6 (CHisopropyl), 2.4 (N(SiMe₃)₂) ppm. 19F NMR data (d₈-THF, 282.8 MHz, 293 K): δF = -141.57 (br s, p-C₆H₄F) ppm. 19F NMR data (d₈-thf, 282.8 MHz, 263 K): δF = -141.62 (s, p-C₆H₄F) ppm. IR data: (KBr pellet, cm⁻¹) 3341 (w), 3254 (w), 3061 (w), 3038 (w), 2960 (m), 2874 (m), 1596 (m), 1510 (s), 1466 (w), 1441 (m), 1389 (w), 1370 (w), 1304 (w), 1261 (m), 1219 (s), 1156 (w), 1101 (m), 1016 (m), 820 (s), 736 (w).

General procedure for the preparation of the [Ca(NN'R)₂] (3a and 3b): HNNR (50mg, 0.31 mmol) in toluene (0.5ml) was added to [Ca{N(SiMe₃)₂}(thf)₂] (82.0mg, 0.16 mmol). The solution was agitated briefly and allowed to react for 18 hours at ambient temperature. The resulting complex was typically realised as a dark orange/magenta powder when dried in vacuo to approximately 4 × 10⁻² mbar.

[Ca(NN'tBu)₂] 3a: 1H NMR data (d₈-thf, 300.5 MHz, 293 K): δH = 2.60 (2 H, br. m, NCH₂), 2.43 (2 H, br. m, H₂NCH), 2.30 (m, 2 H, NCH₂), 1.57 (2 H, m, (CH₃)₂CH), 1.07 (18 H, br. s, NC(CH₃)₃), 0.88 (12 H, app. t, JHH = 6.3 Hz, CH(CH₃)₂), 2.99 (2 H, br. m, NCH₂), 2.44 (2 H, br. m, H₂NCH), 2.29 (m, 2 H, NCH₂), 1.57 (2 H, m, (CH₃)₂CH), 1.07 (18 H, br. s, NC(CH₃)₃), 0.88 (12 H, app. t, JHH = 6.3 Hz, CH(CH₃)₂), 2.59 (2 H, m, NCH₂), 2.44 (2 H, br. m, H₂NCH), 2.29 (m, 2 H, NCH₂), 1.57 (2 H, m, (CH₃)₂CH), 1.07 (18 H, br. s, NC(CH₃)₃), 0.88 (12 H, app. t, JHH = 6.3 Hz, CH(CH₃)₂) ppm. 13C{1H} NMR data (d₈-thf, 62.9 MHz, 293 K): δC = 58.3 (H₂NCH), 50.5 (NC(CH₃)₃), 47.4 (CH₂), 33.1 ((CH₃)₂CH), 29.4 ((CH₃)₂CN), 19.7 (CHisopropyl), 17.9 (CHisopropyl) ppm. IR data: (KBr pellet, cm⁻¹) 3295 (w), 3241 (w), 3061 (w), 2962 (m), 2866 (w), 1586 (m), 1470 (m), 1388 (m), 1365 (m), 1257 (m), 1232 (m), 1078 (m), 1023 (w), 898 (w), 824 (w), 746 (w).

[Ca(NN'ArF)₂] 3b: 1H NMR data (d₈-thf, 300.5 MHz, 293 K): δH = 6.70 (2 H, br. m, NCH₂), 6.42 (4 H, br. m, o-C₆H₅F), 2.99 (2H, br. m NCH₂), 2.67 (4 H, br. m, NCH₂ and H₂NCH), 1.63 (2 H, br. m, (CH₃)₂CH), 0.92 (12 H, br. m, CH(CH₃)₂) ppm. 11C{1H} NMR data (d₈-thf, 72.1 MHz, 293 K): δC = 157.8 (ipso-C₆H₄F), 150.6 (o-C₅H₅N), 136.2 (p-C₅H₅N), 124.1 (m-C₅H₅N), 115.3 (d, JCF = 19.7 Hz, m-C₆H₄F), 110.7 (o-C₆H₄F), 60.4 (H₂NCH), 54.7 (CH₂), 34.1 ((CH₃)₂CH), 19.5 (CHisopropyl), 18.6 (CHisopropyl), 2.4 (N(SiMe₃)₂) ppm. 19F NMR data (d₈-THF, 282.8 MHz, 293 K): δF = -141.57 (br s, p-C₆H₄F) ppm. 19F NMR data (d₈-thf, 282.8 MHz, 263 K): δF = -141.62 (s, p-C₆H₄F) ppm. IR data: (KBr pellet, cm⁻¹) 3295 (w), 3241 (w), 3061 (w), 2962 (m), 2866 (w), 1586 (m), 1470 (m), 1388 (m), 1365 (m), 1257 (m), 1232 (m), 1078 (m), 1023 (w), 898 (w), 824 (w), 746 (w).
CH(CH₂)₃ ppm. $^{13}$C{¹H} NMR data (d₅-THF, 75.5 MHz, 293 K): δ_C = 129.4 (ipso-C₆H₅F), 127.2 (d, J_CF = 216.9 Hz, p-C₆H₅F), 115.4 (d, J_CF = 21.6, m-C₆H₅F), 113.3 (o-C₆H₅F), 59.6* (br. s, H₂NCH), 50.5* (br. s, CH₂), 33.6 ((CH₃)₂CH), 19.6 (CH₃ isopropyl), 18.0 (CH₃ isopropyl) ppm. * Resonances are very broad but comparable to low temperature $^{13}$C{¹H} NMR of homoleptic species. $^{13}$C{¹H} NMR data (d₈-thf, 75.5 MHz, 183 K): δ_C = 129.5 (ipso-C₆H₅F), 127.4 (d, J_CF = 217.4 Hz, p-C₆H₅F), 115.7 (d, J_CF = 21.8, m-C₆H₅F), 115.0 (o-C₆H₅F partially obscured m-C₆H₅F), 56.5 (H₂NCH), 49.2 (CH₂), 33.3 ((CH₃)₂CH), 19.4 (CH₃ isopropyl), 17.8 (CH₃ isopropyl) ppm. $^{19}$F NMR data (d₈-thf, 282.8 MHz, 293 K): δ_F = -141.57 (br s, p-C₆H₄F), -130.64 (br s, p-C₆H₄F) ppm. $^{19}$F NMR data (d₈-thf, 282.8 MHz, 183 K): δ_F = -141.09 (s, p-C₆H₄F), -130.37 (br s, p-C₆H₄F) ppm. IR data: (KBr disc, cm⁻¹) 3343 (w), 3234 (w), 3058 (w), 2960 (s), 2931 (m), 2871 (m), 2045 (w), 1851 (w), 1735 (w), 1609 (m), 1584 (m), 1510 (s), 1389 (m), 1369 (m), 1307 (w), 1260 (m), 1218 (s), 1157 (m), 1101 (m), 1017 (m), 884 (w), 820 (s), 736 (m).

**General procedure for hydroamination catalysis:** Both the 1-amino 2,2-dimethylpent-4-ene and 1-amino 2,2-diphenylpent-4-ene were prepared according to literature methods.⁸,⁹ In a dinitrogen filled glovebox HNNR (15 mg 0.08 mmol) was predissolved in C₆D₆ (0.5 ml) and successively added to [Ca{N(SiMe₃)₂}₂(thf)] (53 mg, 0.08 mmol). The resulting mixture was agitated by hand and left for two minutes. To this solution was added the corresponding amino olefin (0.19g, 0.8 mmol). The solution was transferred to a J. Young Teflon valve equipped NMR tube and sealed. All catalyst reactions were monitored via $^1$H NMR periodically to monitor conversion (Conversion was checked against notable resonances in the spectra corresponding to the cyclic amide product).¹⁰ Upon conversion ceasing, a solution of (S)-(+) O-acetylmandelic acid (0.18g 0.8 mmol) predissolved in a minimal amount of CDCl₃ was added to the reaction mixture producing the diastereomeric salts. The resulting enantioexcess (e.e) was then determined by $^1$H NMR spectroscopy.¹¹

**Calculations**

Calculations were performed using the Gaussian 03 program.¹² Calculations were carried out using the B3PW91 hybrid functional, and the 6-31G(d,p) basis set for the calcium and all coordinating atoms, with the 6-31G basis set for the remaining centres. All geometry optimisations were carried out without geometry restraints, and were followed by frequency calculations in order to ascertain the nature of the stationary point (minimum or saddle point).

**References**