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. Deuteratedcholoroform 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 protio-solvent (^{1}H) or solvent (^{13}C) resonances; all coupling constants are quoted in Hertz. Where necessary, NMR assignments were confirmed by the use of two-dimensional ^{1}H-^{1}H or ^{1}H-^{13}C 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 onNaCl plates, or KBrpellets 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), phthalicanhydride (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). Theaqueous 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). ^{1}H NMR data ($CDCl_3$, 400.1 MHz, 293 K) δ_H = 7.87 (2 H, 2 × dd, J^3_{HH} = 5.4 Hz, J^3_{HH} = 5.4 Hz, Ar-*H*), 7.74 (2 H, 2 × dd, J^3_{HH} = 5.4 Hz, J^3_{HH} = 5.4 Hz, Ar-*H*), 4.63 (1 H, d, J^3_{HH} = 8.4 Hz, Ph^{t}NC*H*), 2.75 (1 H, m,

C*H*$(CH_3)_2$), 1.16 (3 H, d, J^3_{HH} = 6.7 Hz, (C*H*$_3)_2$CH), 0.91 (3 H, d, J^3_{HH} = 6.7 Hz, (C*H*$_3)_2$CH) ppm.

General procedure for the preparation of N-phthaloyl protected amino-amides: N-phthalylvaline(10 g, 40.4 mmol) was dissolved in dry thf (250 ml) to which $SOCl_2$ (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-phthalylvalinoylchoride was used without further purification. ^{1}H NMR data ($CDCl_3$, 400.1 MHz, 293 K) δ_H = 7.90 (2 H, 2 × dd, J^3_{HH} = 5.4 Hz, J^3_{HH} = 5.4 Hz, Ar-*H*), 7.80 (2 H, 2 × dd, J^3_{HH} = 5.4 Hz, J^3_{HH} = 5.4 Hz, Ar-*H*), 4.74 (1 H, d, J^3_{HH} = 8.4 Hz, Ph^{t}NC*H*), 2.74 (1 H, m, C*H*$(CH_3)_2$), 1.15 (3 H, d, J^3_{HH} = 6.7 Hz, (C*H*$_3)_2$CH), 0.91 (3 H, d, J^3_{HH} = 6.7 Hz, (C*H*$_3)_2$CH) 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-dimethylaminopyride (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 Na_2SO_4. After drying*in vacuo*, the protected amidewas obtained in a 50-90% yield.

Protected HNN^{tBu}: ^{1}H NMR data ($CDCl_3$, 400.1 MHz, 293 K): δ_H = 7.81 (2H, 2 × dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 5.4 Hz, Ph^{t}H), 7.69 (2H, 2 × dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 5.4 Hz, Ph^{t}H), 4.19 (1 H, d, $^3J_{HH}$ = 11.4 Hz, PhtNC*H*), 2.70 (1 H, m, CH$(CH_3)_2$), 1.27 (9 H, s, C$(CH_3)_3$), 1.03 (3 H, d, $^3J_{HH}$ = 6.6 Hz, CH(C*H*$_3)_2$), 0.76 (3 H, d, $^3J_{HH}$ = 6.6 Hz, CH(C*H*$_3)_2$) ppm.

Protected HNN^{iPr}: ^{1}H NMR data ($CDCl_3$, 400.1 MHz, 293 K): δ_H = 7.80 (2H, 2 × dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 5.5 Hz, Ph^{t}H), 7.69 (2H, 2 × dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 5.4 Hz, Ph^{t}H), 4.29 (1 H, d, $^3J_{HH}$ = 11.4 Hz, PhtNC*H*), 3.97 (1 H, sept, $^3J_{HH}$ = 6.7 Hz, C*H*$(CH_3)_2$), 2.73 (1 H, m, C*H*$(CH_3)_2$), 1.17 (3 H, d, $^3J_{HH}$ = 6.6 Hz, CH(*CH*$_3)_2$), 1.09 (3 H, d, $^3J_{HH}$ = 6.7 Hz, CH(*CH*$_3)_2$), 1.02 (3 H, d, $^3J_{HH}$ = 6.7 Hz, CH(*CH*$_3)_2$), 0.77 (3 H, d, $^3J_{HH}$ = 6.6 Hz, CH(*CH*$_3)_2$) ppm.

Protected HNN^{Ph}: ^{1}H NMR data ($CDCl_3$, 400.1 MHz, 293 K): δ_H = 7.89 (2H, 2 × dd, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 5.4 Hz, Ph^{t}H), 7.73 (2H, 2 × dd, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 5.4 Hz, Ph^{t}H), 7.56 (2H, d, $^3J_{HH}$ = 8.5 Hz, ArH), 7.30 (2H, app.t, $^3J_{HH}$ = 7.5 Hz, ArH), 7.09 (1H, app.t, $^3J_{HH}$ = 7.5 Hz,

ArH), 4.52 (1H, d, $^3J_{HH}$ = 11.6 Hz, PhtNC*H*), 2.93 (1H, m, C*H*(CH_3)$_2$), 1.17 (3H, d, $^3J_{HH}$ = 6.5 Hz, CH(C*H*$_3$)$_2$), 0.90 (3H, d, $^3J_{HH}$ = 6.5 Hz, CH(C*H*$_3$)$_2$) ppm.

Protected HNN^{ArF}: ^{1}H NMR data ($CDCl_3$, 400.1 MHz, 293 K): δ_H = 7.90 (2H, 2 × dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 5.5 Hz, Ph^{t}H), 7.78 (2H, 2 × dd, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 5.5 Hz, Ph^{t}H), 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, Ph^{t}NC*H*), 2.90 (1H, m, C*H*(CH_3)$_2$), 1.16 (3H, d, $^3J_{HH}$ = 6.6 Hz, CH(C*H*$_3$)$_2$), 0.89 (3H, d, $^3J_{HH}$ = 6.6 Hz, CH(C*H*$_3$)$_2$) 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_2SO_4 and the solid dried *in vacuo*. Aqueous soluble deprotectedamides 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^{tBu}: NMR data ($CDCl_3$, 400.1 MHz, 293 K): δ_H = 3.03 (1 H, d, $^3J_{HH}$ = 3.9 Hz, C*H*(CH_3)$_2$), 2.20 (1H, m, C*H*(CH_3)$_2$), 1.28 (9 H, s, C(C*H*$_3$)$_3$) 0.90 (3H, d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 0.75 (3H, d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$) ppm.

Deprotected HNN^{iPr}: NMR data ($CDCl_3$, 400.1 MHz, 293 K): δ_H = 4.00 (1 H, sep, $^3J_{HH}$ = 6.6 Hz, C*H*(CH_3)$_2$), 3.12 (1 H, d, $^3J_{HH}$ = 4.8 Hz, H_2NC*H*), 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(C*H*$_3$)$_2$), 0.75 (3H, d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$) ppm.

Deprotected HNN^{Ph}: ^{1}H NMR data ($CDCl_3$, 400.1 MHz, 293 K): δ_H = 7.59 (2H, app. d, $^3J_{HH}$ = 8.6Hz, 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_2NC*H*), 2.40 (1H, m, C*H*(CH_3)$_2$), 1.02 (3H, d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$), 0.86 (3H, d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$) ppm.

Deprotected HNN^{ArF}: ^{1}H NMR data (D_2O, 400.1 MHz, 293 K): δ_H = 6.97 (2H, m, ArH), 6.87 (2H, m, ArH), 3.81 (1H, d, $^{3}J_{HH}$ = 2.2 Hz, H_2NCH), 2.09 (1H, m, $CH(CH_3)_2$), 1.09 (3H, d, $^{3}J_{HH}$ = 6.9Hz, $CH(CH_3)_2$) ppm.

General procedure for the reduction of the amino amides:[1,2] To a suspension of $NaBH_4$ (5.58g, 147.5mmol) in thf (250 ml), $(CH_3)_3SiCl$ (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 andfurther cooled to 0°C. Methanol (10 ml) and water (10 ml)were sequentiallyadded 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_2SO_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^{tBu}] 1a; ^{1}H NMR data ($CDCl_3$, 500.1 MHz, 293 K) δ_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_2NCH), 2.26 (1H, dd, $^{3}J_{HH}$ = 3.4 Hz, $^{2}J_{HH}$ = 10.9 Hz, NCH_2), 1.57 (1H, m, $(CH_3)_2CH$)) 1.07 (9H, s, ^{t}Bu), 0.89 (6H, app t, $^{3}J_{HH}$ 6.9Hz, $CH(CH_3)_2$) ppm. $^{13}C\{^{1}H\}$ NMR data ($CDCl_3$, 100.6 MHz, 293 K) δ_C= 57.1 (H_2NCH), 50.2 ($C(CH_3)_3$), 46.3 (CH_2), 32.4 ($(CH_3)_2CH$), 28.9 ($(CH_3)_3CH$), 19.3 ($CH_{3isopropyl}$), 17.7 ($CH_{3isopropyl}$) 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 $[H_3NCH(CH(CH_3)_2)CH_2NHC(CH_3)_3]^+$: *m/z* = 158.1782 (calcd for $C_9H_{22}N_2$: 158.1783).

[HNN^{iPr}] 1b; ^{1}H NMR data ($CDCl_3$, 500.1 MHz, 293 K): δ_H = 2.67 (1H, 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_2NCH), 2.21 (1 H, app t, $^{2}J_{HH}$ = 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. $^{13}C\{^{1}H\}$ NMR data ($CDCl_3$, 100.6 MHz, 293 K): δ_C=

56.1 (H_2NCH), 50.5 (CH_2), 49.0 ($NHCH(CH_3)_2$), 32.3 ($CH(CH_3)_2$), 22.3 ($NHCH(CH_3)_2$), 22.1 ($NHCH(CH_3)_2$), 19.1 ($CH_{3isopropyl}$), 17.7 ($CH_{3isopropyl}$) ppm. IR data: (NaCl disc, cm^{-1}) 3668 (w), 3350 (m), 2962 (s), 2873 (m), 2361 (w), 2342 (w), 2251 (w), 1587 (m), 1497 (w), 1468 (m), 1414 (w), 1383 (m), 1368 (m), 1338 (w), 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 $[H_3NCH(CH(CH_3)_2)CH_2NHCH(CH_3)_2]^+$: m/z = 145.1700 (calcd for $C_8H_{21}N_2$: 145.1705).

[HNN^{Ph}] 1c; ^1H NMR data ($CDCl_3$, 500.1 MHz, 293 K):δ_H = 7.18 (2 H, app t, $^3J_{HH}$= 7.4 Hz, m-C_6H_5), 6.70 (1 H, app t, $^3J_{HH}$ = 7.4 Hz, *p*-C_6H_5), 6.65 (2 H, d, $^3J_{HH}$ = 7.7 Hz, *o*-C_6H_5), 3.25 (1 H, dd, $^3J_{HH}$ = 3.2 Hz, $^2J_{HH}$ = 11.9 Hz, NCH_2), 2.85 (1 H, app t, $^2J_{HH}$ = 11.9 Hz, NCH_2), 2.76 (1 H, m, H_2NCH), 1.69 (1 H, m, $(CH_3)_2CH$), 0.98 (3 H, d, $^3J_{HH}$ = 9.6Hz, $CH(CH_3)_2$), 0.96 (6 H, d, $^3J_{HH}$ = 9.6 Hz, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR data ($CDCl_3$, 100.6 MHz, 293 K):δ_C= 148.6 (*ipso*-C_6H_5), 129.1 (*m*-C_6H_5), 117.2 (*p*-C_6H_5), 112.9 (*o*-C_6H_5), 56.0 (H_2NCH), 47.9 (CH_2), 32.4 ($(CH_3)_2CH$), 19.2 ($CH_{3isopropyl}$), 17.8 ($CH_{3isopropyl}$) 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 (m), 868 (m), 749 (s), 692 (s). Accurate mass ES-MS for $[H_3NCH(CH(CH_3)_2)CH_2NH(C_6H_5)]^+$: m/z = 178.1465 (calcd for $C_{11}H_{18}N_2$: 178.1470).[3, 4]

[HNN^{ArF}] 1d; ^1H NMR data ($CDCl_3$, 500.1 MHz, 293 K): δ_H = 6.82 (2 H, app t, $^3J_{HH}$= 8.8 Hz, *m*-C_6H_4F), 6.57 (2 H, dd, $^3J_{HH}$ = 8.8 Hz, $^3J_{HF}$ = 4.3 Hz, *o*-C_6H_4F), 3.38 (1 H, dd, $^3J_{HH}$ = 3.4 Hz, $^2J_{HH}$ = 14.0 Hz, NCH_2), 3.27 (1 H, dd, $^3J_{HH}$ = 3.4 Hz, $^2J_{HH}$ = 14.0 Hz, NCH_2), 3.03 (1 H, m, H_2NCH), 2.04 (1 H, m, $(CH_3)_2CH$), 1.05 (6 H, app t, $^3J_{HH}$ = 6.5 Hz, $CH(CH_3)_2$), ppm. ^{19}F NMR data ($CDCl_3$, 282.8 MHz, 293 K): δ_F = -128.11 (s, *p*-C_6H_4F) ppm. $^{13}C\{^1H\}$ NMR data ($CDCl_3$, 100.6 MHz, 293 K): δ_C= 156.1 (d, J_{CF} = 235.9 Hz, *p*- C_6H_4F), 143.5 (d, J_{CF} = 1.7 Hz, *ipso*-C_6H_4F), 115.8 (d, J_{CF} = 22.3 Hz, *m*-C_6H_4F), 113.9 (d, J_{CF} = 7.3 Hz, *o*-C_6H_4F), 57.6 (H_2NCH), 44.2 (CH_2), 29.2 ($(CH_3)_2CH$), 18.8 ($CH_{3isopropyl}$), 18.8 ($CH_{3isopropyl}$) 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), 1216 (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 $[H_3NCH(CH(CH_3)_2)CH_2NH(C_6H_4F)]^+$: m/z = 196.1372 (calcd for $C_{11}H_{17}N_2F$: 196.1376).

[Ca{N(SiMe$_3$)$_2$}$_2$(thf)$_2$]: CaI_2 (1.47g, 5 mmol) was added to K(N(SiMe$_3$) (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(SiMe$_3$)$_2$}$_2$(thf)$_2$]. This was further dried *in vacuo* over night to approximately 2×10^{-2}mbar.[5, 6]Data were consistent with that previously reported.[7]

General procedure for the preparation of the [Ca(NN^R){N(SiMe$_3$)$_2$}(py)$_n$] (2a – d): [Ca{N(SiMe$_3$)$_2$}$_2$(py)$_2$] was prepared from the corresponding analogue [Ca{N(SiMe$_3$)$_2$}$_2$(thf)$_2$] (*vide supra*)*via* literature proceedures.[7]HNN^R (300 mg, 1.5mmol) in toluene (20 ml) was added to 1 equivalent of [Ca{N(SiMe$_3$)$_2$}$_2$(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 a 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(NN^{tBu}){N(SiMe$_3$)$_2$}(py)] 2a: ^{1}H NMR data (d$_8$-thf, 300.5 MHz, 293 K): δ_H = 8.54 (2 H, m, *o*-C_5H_5N), 7.66 (1 H, app. tt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.9 Hz, *p*-C_5H_5N), 7.25 (2 H, m, *m*-C_5H_5N), 2.80 (1 H, br. m, N*C*H$_2$), 2.60 (1 H, br. m, H$_2$NC*H*), 2.45 (1 H, br. m, N*C*H$_2$), 1.57 (1 H, m, (CH$_3$)$_2$C*H*), 1.07 (9 H, br. s, C(CH$_3$)$_3$), 0.88 (6 H, br. t, $^3J_{HH}$ = 6.6 Hz, CH(*C*H$_3$)$_2$), 0.10 (18 H, s, N(SiMe$_3$)$_2$) ppm. ^{1}H NMR data (d$_8$-thf, 300.5 MHz, 263 K): δ_H = 8.55 (2 H, m, *o*-C_5H_5N), 7.68 (1 H, app. tt, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.9 Hz, *p*-C_5H_5N), 7.28 (2 H, m, *m*-C_5H_5N), 2.79 (1 H, br. m, N*C*H$_2$), 2.59 (1 H, br. m, H$_2$NC*H*), 2.45 (1 H, br. m, N*C*H$_2$), 1.57 (1 H, m, (CH$_3$)$_2$C*H*), 1.08 (9 H, br. s, C(CH$_3$)$_3$), 0.88 (6 H, br. t, $^3J_{HH}$ = 6.6 Hz, CH(*C*H$_3$)$_2$), 0.10 (18 H, s, N(SiMe$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR data (d$_8$-thf, 75.5 MHz, 263 K): δ_C= 150.6 (*o*-C_5H_5N), 136.2 (*p*-C_5H_5N), 124.2 (*m*-C_5H_5N), 58.1 (H$_2$N*C*H), 50.6 (N*C*(CH$_3$)$_3$), 47.2 (CH$_2$), 33.2 ((CH$_3$)$_2$*C*H), 29.3 ((CH$_3$)$_3$CN), 19.7 (CH$_{3isopropyl}$), 17.9 (CH$_{3isopropyl}$), 1.2 (N(SiMe$_3$)$_2$) 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(NN^{iPr}){N(SiMe$_3$)$_2$}(py)] 2b: ^{1}H NMR data (d$_8$-thf, 300.5 MHz, 293 K): δ_H = 8.58 (2 H, m, *o*-C_5H_5N), 7.66 (1 H, m, *p*-C_5H_5N), 7.26 (2 H, m, *m*-C_5H_5N), 2.90 (1 H, br. m, N*C*H$_2$), 2.66 (1 H, br. m, H$_2$NC*H*), 2.52 (1 H, br. m, N*C*H$_2$), 1.67-1.47(2 H, br. m, (CH$_3$)$_2$C*H*), 1.24-1.03 (6 H, br. m, CH(*C*H$_3$)$_2$), 0.94-0.76 (6 H, br. m, CH(*C*H$_3$)$_2$) 0.03 (18 H, s, N(SiMe$_3$)$_2$) ppm. ^{1}H NMR data (d$_8$-thf, 300.5 MHz, 263 K): δ_H = 8.55 (2 H, m, *o*-C_5H_5N), 7.69 (1 H, app. tt, $^3J_{HH}$ = 7.6 Hz,

$^{4}J_{HH}$ = 1.8 Hz, *p*-C_5H_5N), 7.28 (2 H, m, *m*-C_5H_5N), 3.10-2.80 (2 H, br. m, H_2NCH and NCH_2), 2.65 (1 H, br. m, NCH_2), 1.67 (1 H, br. m, $(CH_3)_2CH$), 1.37 (1 H, br. m, $(CH_3)_2CH$), 1.19-1.06 (6 H, br. m, $CH(CH_3)_2$), 0.93-0.80 (6 H, br. m, $CH(CH_3)_2$) 0.03 (18 H, s, $N(SiMe_3)_2$) ppm. $^{13}C\{^1H\}$ NMR data (d_8-thf, 75.5 MHz, 293 K): δ_C= 150.6 (*o*-C_5H_5N), 136.2 (*p*-C_5H_5N), 124.1 (*m*-C_5H_5N), 58.3 (H_2NCH), 55.8 ($NCH(CH_3)_2$), 49.0 (CH_2), 36.7 ($(CH_3)_2CH$), 23.0 ($CH_{3isopropyl}$), 22.1 ($CH_{3isopropyl}$), 19.9 ($CH_{3isopropyl}$), 18.7 ($CH_{3isopropyl}$), 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), 702 (w).

[Ca(NN^{Ph}){$N(SiMe_3)_2$}(py)] 2c: ^1H NMR data (d_8-thf, 300.5 MHz, 293 K): δ_H = 8.54 (2 H, m, *o*-C_5H_5N), 7.66 (1 H, m, *p*-C_5H_5N), 7.25 (2 H, m, *m*-C_5H_5N), 6.76 (2 H, br. m, *o*-C_6H_5), 6.13 (2 H, br. m, *m*-C_6H_5), 5.89 (1 H, br. m, *p*-C_6H_5), 2.92 (1 H, br. m, NCH_2), 2.63 (2 H, br. m, H_2NCH and NCH_2), 1.58 (1 H, br. m, $(CH_3)_2CH$), 0.91 (6 H, br. m, $CH(CH_3)_2$), 0.04 (18 H, s, $N(SiMe_3)_2$) ppm. ^1H NMR data (d_8-thf, 300.5 MHz, 243 K): δ_H = 8.56 (2 H, m, *o*-C_5H_5N), 7.73 (1 H, m, *p*-C_5H_5N), 7.31 (2 H, m, *m*-C_5H_5N), 6.78 (2 H, br. m, *o*-C_6H_5), 6.78-5.97 (2 H, br. m, *m*-C_6H_5), 5.87 (1 H, br. m, *p*-C_6H_5), 2.87 (1 H, br. m, NCH_2), 2.75 (1H, br. m, H_2NCH), 2.63 (1 H, br. m, and NCH_2), 1.50 (1 H, br. m, $(CH_3)_2CH$), 0.97 (6 H, br. m, $CH(CH_3)_2$), 0.04 (18 H, s, $N(SiMe_3)_2$) ppm. $^{13}C\{^1H\}$ NMR data (d_8-thf, 75.5 MHz, 293 K): δ_C= 160.1 (*ipso*-C_6H_5), 150.7 (*o*-C_5H_5N), 136.2 (*p*-C_5H_5N), 129.2 (*o*-C_6H_5), 124.1 (*m*-C_5H_5N), 111.6 (*m*-C_6H_5), 107.7 (*p*-C_6H_5), 60.4 (H_2NCH), 54.1 (CH_2), 34.2 ($(CH_3)_2CH$), 20.1 ($CH_{3isopropyl}$), 19.5 ($CH_{3isopropyl}$), 1.8 ($N(SiMe_3)_2$ ppm. $^{13}C\{^1H\}$ NMR data (d_8-thf, 75.5 MHz, 243 K): δ_C= 160.6 (*ipso*-C_6H_5), 150.6 (*o*-C_5H_5N), 136.5 (*p*-C_5H_5N), 129.9 (*o*-C_6H_5), 124.4 (*m*-C_5H_5N), 116.8 (*m*-C_6H_5), 106.9 (*p*-C_6H_5), 60.7 (H_2NCH), 54.3 (CH_2), 34.1 ($(CH_3)_2CH$), 20.2 ($CH_{3isopropyl}$), 19.5 ($CH_{3isopropyl}$), 2.1 ($N(SiMe_3)_2$ ppm. IR data: (KBr pellet, cm^{-1}) 3339 (m), 3257 (m), 3051 (m), 3022 (w), 2957 (s), 2931 (s), 2869 (s), 2498 (w), 1927 (w), 1596 (s), 1552 (m), 1484 (s), 1441 (s), 1369 (m), 1303 (m), 1261 (s), 1182 (m), 1150 (m), 1100 (s), 1035 (s), 1010 (s), 879 (w), 804 (m), 750 (s).

[Ca(NN^{ArF}){$N(SiMe_3)_2$}(py)] 2d: ^1H NMR data (d_8-thf, 300.5 MHz, 293 K): δ_H = 8.57 (2 H, m, *o*-C_5H_5N), 7.67 (1 H, app. tt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.5 Hz, *p*-C_5H_5N), 7.26 (2 H, m, *m*-C_5H_5N), 6.53 (2 H, app. t, $^3J_{HH}$ = 8.2 Hz, *m*-C_6H_4F), 6.06 (2 H, br. m, *o*-C_6H_4F), 2.86 (1 H, app. d, $^3J_{HH}$ = 9.5 Hz, NCH_2), 2.59 (2 H, br. m, H_2NCH and NCH_2), 1.65 (1 H, br. m, $(CH_3)_2CH$), 0.93 (6 H, app. d, $^3J_{HH}$ = 6.1 Hz, $CH(CH_3)_2$), 0.04 (18 H, ($N(SiMe_3)_2$) ppm. ^1H NMR data (d_8-thf, 500.1 MHz, 263 K): δ_H = 8.59 (2 H, m, *o*-C_5H_5N), 7.69 (1 H, app. tt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.8 Hz, *p*-

C_5H_5N), 7.29 (2 H, m, *m*-C_5H_5N), 6.53 (2 H, app. t, $^3J_{HH}$ = 7.7 Hz, *m*-C_6H_4F), 6.04 (2 H, br. m, *o*-C_6H_4F), 2.83 (1 H, br. m, NCH_2), 2.58 (2 H, br. m, H_2NCH and NCH_2), 1.66 (1 H, br. m, $(CH_3)_2CH$), 0.94 (6 H, app. d, $^3J_{HH}$ = 5.0 Hz, $CH(CH_3)_2$), 0.04 (18 H, $(N(SiMe_3)_2)$ ppm. $^{13}C\{^1H\}$ NMR data (d_8-thf, 75.5 MHz, 263 K): δ_C= 157.8 (*ipso*-C_6H_4F), 150.6 (*o*-C_5H_5N), 136.2 (*p*-C_5H_5N), 127.6 (d, J_{CF} = 274.0 Hz, *p*-C_6H_4F), 124.1 (*m*-C_5H_5N), 115.3 (d, J_{CF} = 19.7 Hz, *m*-C_6H_4F), 110.7 (*o*-C_6H_4F), 60.4 (H_2NCH), 54.7 (CH_2), 34.1 ($(CH_3)_2CH$), 19.5 ($CH_{3isopropyl}$), 18.6 ($CH_{3isopropyl}$), 2.4 ($N(SiMe_3)_2$) ppm. ^{19}F NMR data (d_8-THF, 282.8 MHz, 293 K): δ_F = -141.57 (br s, *p*-C_6H_4F) ppm. ^{19}F NMR data (d_8-thf, 282.8 MHz, 263 K): δ_F = -141.62 (s, *p*-C_6H_4F) 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): HNN^R (50mg, 0.31 mmol) in toluene (0.5ml) was added to $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$ (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 (d_8-thf, 300.5 MHz, 293 K): δ_H = 2.60 (2 H, br. m, NCH_2), 2.43 (2 H, br. m, H_2NCH), 2.30 (m, 2 H, NCH_2), 1.57 (2 H, m, $(CH_3)_2CH$), 1.07 (18 H, br. s, $NC(CH_3)_3$), 0.88 (12 H, app. t, J^3_{HH} = 6.3 Hz, $CH(CH_3)_2$) ppm.^1H NMR data (d_8-THF, 300.5 MHz, 263 K): δ_H = 2.59 (2 H, m, NCH_2), 2.44 (2 H, br. m, H_2NCH), 2.29 (m, 2 H, NCH_2), 1.57 (2 H, m, $(CH_3)_2CH$), 1.07 (18 H, br. s, $NC(CH_3)_3$), 0.88 (12 H, app. t, J^3_{HH} = 6.5 Hz, $CH(CH_3)_2$) ppm.$^{13}C\{^1H\}$ NMR data (d_8-thf, 62.9 MHz, 293 K): δ_C= 58.3 (H_2NCH), 50.5 ($NC(CH_3)_3$), (47.4 (CH_2), 33.1 ($(CH_3)_2CH$), 29.4 ($(CH_3)_3CN$), 19.7 ($CH_{3isopropyl}$), 17.9 ($CH_{3isopropyl}$) ppm. IR data: (KBr pellet, cm^{-1}) 3295 (w), 3241 (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 (d_8-thf, 300.5 MHz, 293 K): δ_H = 6.70 (4 H, br. m, *m*-C_6H_5F), 6.42 (4 H, br. m, *o*-C_6H_5F), 2.99 (2H, br. m NCH_2), 2.67 (4 H, br. m, NCH_2 and H_2NCH), 1.63 (2 H, br. m, $(CH_3)_2CH$), 0.92 (12 H, br. m, $CH(CH_3)_2$) ppm. ^1H NMR data (d_8-thf, 300.5 MHz, 183 K): δ_H = 6.89 (3 H, br. m, NC_6H_5F), 6.69 (2 H, br. m, NC_6H_5F), 6.57 (2 H, br. m, NC_6H_5F), 6.38 (1 H, br. m, NC_6H_5F), 3.02 (2H, br. m NCH_2 2.73 (2H, br. m, NCH_2), 2.55 (2 H, br. m, H_2NCH), 1.67 (2 H, br. m, $(CH_3)_2CH$ partially obscured by solvent peak), 0.91 (12 H, br. m,

$CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR data (d_8-THF, 75.5 MHz, 293 K): δ_C= 129.4 (*ipso*-C_6H_5F), 127.2 (d, J_{CF} = 216.9 Hz, *p*-C_6H_5F), 115.4 (d, J_{CF} = 21.6, *m*-C_6H_5F), 113.3 (*o*-C_6H_5F), 59.6* (br. s, H_2NCH), 50.5* (br. s, CH_2), 33.6 ($(CH_3)_2CH$), 19.6 ($CH_{3\ isopropyl}$), 18.0 ($CH_{3\ isopropyl}$) ppm. * Resonances are very broad but comparable to low temperature $^{13}C\{^1H\}$ NMR of homoleptic species. $^{13}C\{^1H\}$ NMR data (d_8-thf, 75.5 MHz, 183 K):): δ_C= 129.5 (*ipso*-C_6H_5F), 127.4 (d, J_{CF} = 217.4 Hz, *p*-C_6H_5F), 115.7 (d, J_{CF} = 21.8, *m*-C_6H_5F), 115.0 (*o*-C_6H_5F partially obscured *m*-C_6H_5F), 56.5 (H_2NCH), 49.2 (CH_2), 33.3 ($(CH_3)_2CH$), 19.4 ($CH_{3isopropyl}$), 17.8 ($CH_{3isopropyl}$) ppm. ^{19}F NMR data (d_8-thf, 282.8 MHz, 293 K): δ_F = -141.57 (br s, *p*-C_6H_4F), -130.64 (br s, *p*-C_6H_4F) ppm. ^{19}F NMR data (d_8-thf, 282.8 MHz, 183 K): δ_F = -141.09 (s, *p*-C_6H_4F), -130.37 (br s, *p*-C_6H_4F) 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 HNN^R (15 mg 0.08 mmol) was predissolved in C_6D_6 (0.5 ml) and successively added to $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$ (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* ^1H 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 0.8mmol) predissolved in a minimal amount of $CDCl_3$ was added to the reaction mixture producing the diasteromeric salts. The resulting enantioexcess (e.e) was then determined by ^1H 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

1 S. W. Coghlan, R. L. Giles, J. A. K. Howard, L. G. F. Patrick, M. R. Probert, G. E. Smith, and A. Whiting, *J. Organomet. Chem.*, 2005, **690**, 4784.
2 H. C. Brown and P. Heim, *J. Org. Chem.*, 1973, **38**, 912.
3 A. J. Davenport, D. L. Davies, J. Fawcett, and D. R. Russell, *J. Organomet. Chem.*, 2006, **691**, 3445.
4 D. Rix, S. Labat, L. Toupet, C. Crévisy, and M. Mauduit, *Eur. J. Inorg. Chem.*, 2009, 1989.
5 J. S. Alexander and K. Ruhlandt-Senge, *Eur. J. Inorg. Chem*, 2002, 2761.
6 W. D. Buchanan, D. G. Allis, and K. Ruhlandt-Senge, *Chem. Commun.*, 2010, **46**, 4449.
7 D. C. Bradley, M. B. Hursthouse, A. A. Ibrahim, K. M. Abdul Malik, M. Motevalli, R. Moseler, H. Powell, J. D. Runnacles, and A. C. Sullivan, *Polyhedron*, 1990, **9**, 2959.
8 J. Y. Kim and L. Tom, *Org. Lett.*, 2005, **7**, 1737.
9 S. Hong, S. Tian, M. V. Metz, and T. J. Marks, *J. Am. Chem. Soc.*, 2003, **125**, 14768.
10 M. R. Crimmin, I. J. Casely, and M. S. Hill, *J. Am. Chem. Soc.*, 2005, **127**, 2042.
11 G. Zi, F. Zhang, L. Xiang, Y. Chen, W. Fang, and H. Song, *Dalton Trans.*, 2010, **39**, 4048.
12 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, Y. Piskorz, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, in *Gaussian 03, Revision E.03*, 2003.