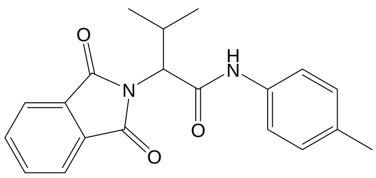
Experimental

General methods and instrumentation:

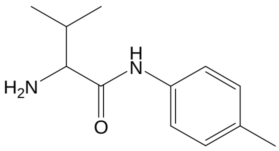
All manipulations of air and moisture sensitive species were performed under an atmosphere of argon or dinitrogen using standard Schlenk and glove box techniques. Solvents were dried by passing through an alumina drying column incorporated into a MBraun SPS800 solvent purification system, except in the 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 choloroform was passed through a column of basic alumina before being stored over 4Å molecular sieves prior to use. Benzene-d_6 and THF-d_8 were dried over potassium under an argon atmosphere before being vacuum transferred, freeze pump thaw degassed and stored in a 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 Bruker Avance 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, or externally to $CFCl_3$ (^{19}F); all coupling constants are quoted in Hertz. In all cases, 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 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}).

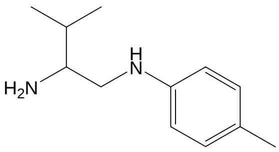
Preparation of Diamines (1a – c): Diamines **1b** and **1c** were prepared according to literature procedures.[1] Herein one new diamine analogue has been prepared from modified literature methods and in a similar fashion, data are reported for each synthetic step for $H_2NCH(^iPr)CH_2NHC_6H_4CH_3$ **(HNN^{ArMe}, 1a)**.



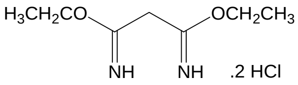
Protected HNN^{ArMe}: ^{1}H NMR data ($CDCl_3$, 400.1 MHz, 293 K): δ_H = 7.89 (2H, dd, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 5.4 Hz, PhtH), 7.77 (2H, dd, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 5.4 Hz, PhtH), 7.44 (2 H, d, $^3J_{HH}$ = 8.3 Hz, 4-$C_6H_4CH_3$), 7.10 (2 H, d, $^3J_{HH}$ = 8.3 Hz, 4-$C_6H_4CH_3$), 4.51 (1 H, d, $^3J_{HH}$ = 11.6 Hz, PhtNC*H*), 2.91 (1 H, m, C*H*(CH_3)$_2$), 2.29 (3 H, s, C_6H_4*CH_3*), 1.16 (3 H, d, $^3J_{HH}$ = 6.5 Hz, CH(*CH_3*)$_2$), 0.89 (3 H, d, $^3J_{HH}$ = 6.5 Hz, CH(*CH_3*)$_2$) ppm.



Deprotected HNN^{ArMe}: ^{1}HNMR data (D_2O, 400.1 MHz, 293 K): δ_H = 7.37 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 4-$C_6H_4CH_3$), 7.29 (2 H, d, $^3J_{HH}$ = 8.0 Hz, 4-$C_6H_4CH_3$), 3.97 (1 H, d, $^3J_{HH}$ = 6.2 Hz, H_2NC*H*), 2.35 (1 H, m, C*H*(CH_3)$_2$), 2.34 (3 H, s, C_6H_4*CH_3*), 1.12 (6 H, d, $^3J_{HH}$ = 6.9 Hz, CH(*CH_3*)$_2$) ppm.

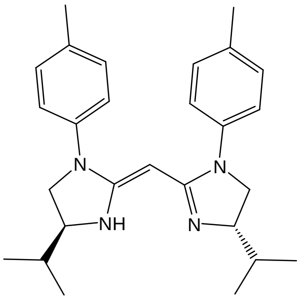


Diamine [HNN^{ArMe}] 1a; ^{1}H NMR data ($CDCl_3$, 500.1 MHz, 293 K): δ_H = 7.00 (2 H, d, $^3J_{HH}$ = 8.2 Hz, *o*-$C_6H_4CH_3$), 6.58 (2 H, d, $^3J_{HH}$ = 8.2 Hz, *m*-$C_6H_4CH_3$), 3.23 (1 H, dd, $^3J_{HH}$ = 3.4 Hz, $^2J_{HH}$ = 12.0 Hz, N*CH_2*), 2.84 (1 H, dd, $^3J_{HH}$ = 3.4 Hz, $^2J_{HH}$ = 12.0 Hz, NC*H_2*), 2.75 (1 H, m, H_2NC*H*), 2.25 (3H, s, C_6H_4*CH_3*), 1.69 (1 H, m, (CH_3)$_2$*CH*), 0.97 (6 H, dd, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 6.8 Hz, CH(*CH_3*)$_2$), ppm. ^{13}C{^{1}H} NMR data ($CDCl_3$, 100.6 MHz, 293 K): δ_C = 146.3 (*ipso*-$C_6H_4CH_3$), 129.6 (*o*-$C_6H_4CH_3$), 126.4 (*p*-$C_6H_4CH_3$), 113.1 (*m*-$C_6H_4CH_3$), 56.1 (H_2NC*H*), 48.2 (CH_2), 32.3 ((CH_3)$_2$*CH*), 20.3 (C_6H_4*CH_3*), 19.2 ($CH_{3\ isopropyl}$), 17.8 ($CH_{3\ isopropyl}$) ppm. IRdata:(NaCl disc, cm^{-1}) 3365 (m), 3029 (w), 2956 (s), 2905 (s), 2871 (s), 2831 (s), 2356 (w), 2065 (w), 1844 (w), 1733 (w), 1618 (m), 1588 (m), 1511 (s), 1464 (s), 1408 (m), 1386 (m), 1376 (m), 1926 (m), 1234 (s), 1179 (m), 1109 (w), 1076 (w), 1038 (s), 911 (w), 820 (s), 731 (w). HR-MS (ES) data:[M]$^+$, found (calc. for $C_{12}H_{21}N_2$) 193.1697 (193.1705).

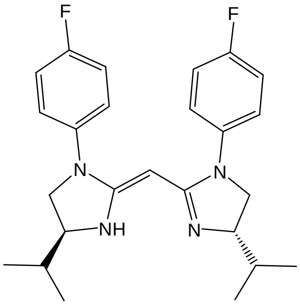


Diethyl malonimidate dihydrochloride; Prepared from a modified literature proceedure.[2] To a solution of malononitrile (10 g, 0.15 mol), in dry 1,4-dioxane (200 ml), ethanol (19.70 ml, 0.33 mol) was added. Dry $HCl_{(g)}$ was then passed through the solution for 6 hours where upon the system was sealed and allowed to stir under an HCl atmosphere for a further 18 hours. The solution was filtered away from the resulting diethyl malonimidate dihydrochloride precipitate. The precipitate was washed with dry 1,4 dioxane (2 × 20 mls) and dry diethyl ether (20 ml). The desired product was then dried *in vacuo* and stored in a glove box, giving near quantitative yields. Data were consistent with that previously reported.[2]

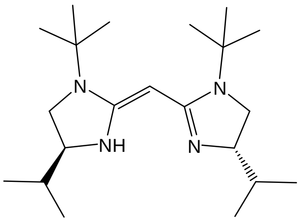
General procedure for bisimidazolines (2a–c); Prepared according to modified literature procedures.[3] Under an inert atmosphere, diethyl malonimidate dihydrochloride (26 mmol *ca.* 0.6 g) and HNN^R (1 g, 52 mmol) were dissolved in dry dichloromethane and heated at vigorous reflux for 4 days. Proceeding such time the solution was allowed to cool and washed with $NaHCO_3$ (10%, 2 × 25 ml). The organic solution was subsequently reduced in volume under reduced pressure. The relevant R-BIM was realized by column chromatography over silica gel (typical solvent systems were composed of ethyl acetate/methanol/Et_3N (9:1:1 v/v)) to yield the desired R-BIM as a white solid in approximately 35% yield.



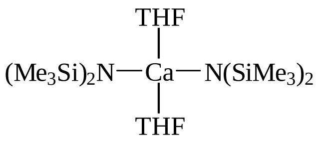
[Ar^{Me}-BIM] 2a; ^1H NMR data ($CDCl_3$, 500.1 MHz, 293 K): δ_H = 7.04 (8 H, app d, $^3J_{HH}$ = 1.5 Hz, m-$C_6H_4CH_3$ and *o*-$C_6H_4CH_3$), 3.79 (2 H, m, NCH_2), 3.63 (2 H, m, NCH_2CH), 3.44 (2 H, m, NCH_2), 2.28 (6 H, s, $C_6H_4CH_3$), 1.72 (2 H, m, $(CH_3)_2CH$), 1.09 (6 H, br d, $^3J_{HH}$ = 6.5Hz, $CH(CH_3)_2$), 0.93 (6 H, dd, $^3J_{HH}$ = 6.5Hz, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR data ($CDCl_3$, 100.6 MHz, 293 K): δ_C = 159.9 (C=N), 139.9 (*ipso*-$C_6H_4CH_3$), 132.5 (*p*-$C_6H_4CH_3$), 129.3 (*o*-$C_6H_4CH_3$), 122.2 (*m*-$C_6H_4CH_3$), 65.0 ($C{=}NCH_{\text{imidazoline}}$), 55.5 ($CH_{2\ \text{imidazoline}}$), ($CH_{2\ \text{bridge}}$ not observed), 33.8 ($(CH_3)_2CH$), 20.7 ($C_6H_4CH_3$) 19.6 ($CH_{3\ \text{isopropyl}}$), 19.1 ($CH_{3\ \text{isopropyl}}$) ppm. IR data: (KBr disc, cm^{-1}) 3031 (w), 2963 (s), 2917 (w), 2867 (w), 2823 (w), 1895 (w), 1623 (s), 1601 (s), 1571 (m), 1533 (s), 1509 (s), 1471 (m), 1385 (m), 1324 (m), 1260 (s), 1194 (m), 1171 (m), 1105 (s), 1023 (s), 862 (m), 801 (s), 722 (m), 711 (m), 631 (w), 550 (m), 502 (w). Accurate mass ES-MS for [Ar^{Me}-BIM+ H]$^+$: m/z = 417.3018 (calcd for $C_{27}H_{37}N_4$: 417.3006).



[Ar^F-BIM] 2b; ^{1}H NMR data (CDCl$_3$, 500.1 MHz, 293 K): δ_H = 7.06 (4 H, dd, $^3J_{HH}$ = 8.5Hz, *o*-C_6H_4F), 6.93 (4 H, app t, $^3J_{HH}$ = 8.5Hz, *m*-C_6H_4F), 3.75 (2 H, m, N*CH$_2$*), 3.64 (2 H, m, NCH$_2$C*H*), 3.39 (2 H, m, N*CH$_2$*), 1.72 (2 H, m, (CH$_3$)$_2$C*H*), 1.09 (6 H, br d, $^3J_{HH}$ = 6.3Hz, CH(*CH$_3$*)$_2$), 0.93 (6 H, dd, $^3J_{HH}$ = 6.3Hz, CH(*CH$_3$*)$_2$) ppm. ^{19}F NMR data (CDCl$_3$, 282.8 MHz, 293 K): δ_F = -118.45 (br s, *p*-C_6H_4*F*) ppm. ^{13}C{^{1}H} NMR data (CDCl$_3$, 100.6 MHz, 293 K): δ_C = 160.3 (C=N), 159.1 (d, $^1J_{CF}$ = 243.1Hz, *p*-C_6H_4F), 138.4 (*ipso*-C_6H_4F), 124.3 (d, $^3J_{CF}$ = 7.5Hz, *o*-C_6H_4F), 115.5 (d, $^2J_{CF}$ = 22.4Hz, *m*-C_6H_4F), 65.2 (C=NCH $_{imidazoline}$), 55.8 (CH$_2$ $_{imidazoline}$), (CH$_2$ $_{bridge}$ not observed), 33.8 ((CH$_3$)$_2$*CH*), 19.6 (CH$_3$ $_{isopropyl}$), 19.1 (CH$_3$ $_{isopropyl}$) ppm. IR data: (KBr disc, cm^{-1}) 3111 (w), 3078 (w), 3051 (w), 2959 (s), 2831 (s), 2608 (w), 1876 (m), 1616 (s), 1593 (s), 1536 (s), 1504 (s), 1469 (m), 1425 (m), 1390 (m), 1363 (m), 1306 (s), 1256 (s), 1232 (s), 1194 (s), 1168 (m), 1119 (s), 1090 (m), 1046 (m), 1010 (m), 904 (w), 832 (s), 799 (s), 723 (s), 638 (m), 593 (m), 564 (m), 551 (s), 503 (m), 435 (m). Accurate mass ES-MS for [Ar^F-BIM+ H]$^+$: m/z =425.2509 (calcd. for $C_{25}H_{31}N_2F_2$: 425.2517).



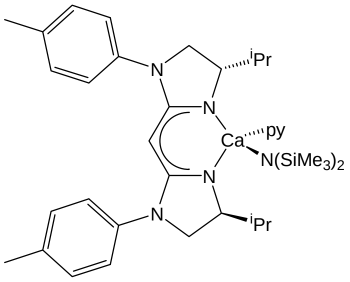
[^{t}Bu-BIM] 2c; ^{1}H NMR data (CDCl$_3$, 500.1 MHz, 293 K): δ_H = 3.42 (2 H, app t, $^3J_{HH}$ = 7.9 Hz, N*CH$_2$*), 3.25 (2 H, m, NCH$_2$C*H*) 2.85 (2 H, app t, $^3J_{HH}$ = 8.8 Hz, NC*H$_2$*), 1.54 (2 H, m, (CH$_3$)$_2$C*H*), 1.33 (9 H, s, C(*CH$_3$*)$_3$), 1.00 (6 H, d, $^3J_{HH}$ = 6.5 Hz, CH(*CH$_3$*)$_2$), 0.83 (6 H, d, $^3J_{HH}$ = 6.5 Hz, CH(*CH$_3$*)$_2$) ppm. ^{13}C{^{1}H} NMR data (CDCl$_3$, 100.6 MHz, 293 K): δ_C = 162.2 (C=N), 63.8 (C=NCH $_{imidazoline}$), 52.4 (CH$_2$ $_{imidazoline}$), 52.0 (*C*(CH$_3$)$_3$), (CH$_2$ $_{bridge}$ not observed), 33.7 ((CH$_3$)$_2$*CH*), 28.7 (C(*CH$_3$*)$_3$) 19.9 (CH$_3$ $_{isopropyl}$), 19.2 (CH$_3$ $_{isopropyl}$) ppm. IR data: (KBr disc, cm^{-1}) 3465 (m), 2964 (s), 2867 (m), 2810 (m), 1604 (s), 1529 (s), 1469 (m), 1391 (m), 1362 (m), 1294 (m), 1264 (s), 1227 (s), 1166 (w), 1122 (m), 1095 (m), 1065 (m), 1017 (m), 973 (w), 921 (w), 802 (s), 732 (s), 698 (w), 646 (w), 547 (w), 468 (w). Accurate mass ES-MS for $[^{t}\text{Bu-BIM+ H}]^{+}$: m/z =349.3344 (calcd. for $C_{21}H_{41}N_4$: 349.3331).



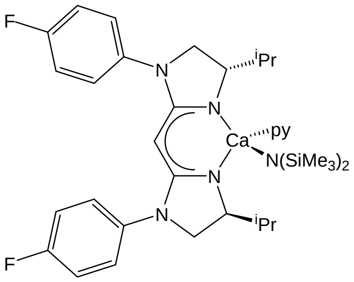
$$(Me_3Si)_2N-\underset{\text{THF}}{\overset{\text{THF}}{Ca}}-N(SiMe_3)_2$$

$[Ca\{N(SiMe_3)_2\}_2(THF)_2]$: CaI_2 (1.47g, 5 mmol) was added to $K(N(SiMe_3)$ (1.99g, 10 mmol) and dissolved in dry 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 white solid $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$. This was further dried *in vacuo* over night to approximately 2 × 10^{-2}mbar.[4, 5] Data were consistent with that previously reported.[6]

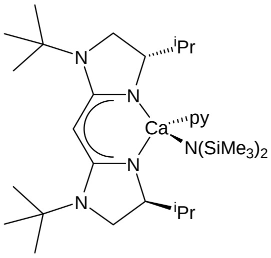
General procedure for the preparation of $[Ca(R\text{-}BIM)\{N(SiMe_3)_2\}(py)]$ (3a–c): $[Ca\{N(SiMe_3)_2\}_2(py)_2]$ was prepared from the corresponding analogue $[Ca\{N(SiMe_3)_2\}_2(THF)_2]$ (*vide supra*) *via* literature proceedures.[6] R-BIM (30mg, 0.07 mmol) in dry toluene (0.5ml) was added to 1 equivalent of $[Ca\{N(SiMe_3)_2\}_2(py)_2]$ (0.07 mmol *ca.* 0.037 g). The solution was agitated briefly and allowed to react for 18 hours at ambient temperature under an inert atmosphere. The resulting complex was typically realised as an orange powder when dried *in vacuo* to approximately 4 × 10^{-2} mbar.



$[Ca(Ar^{Me}\text{-}BIM)\{N(SiMe_3)_2\}(py)]$ 3a: ^{1}H NMR data (d_8-THF, 500.1 MHz, 293 K): δ_H = 8.56 (4 H, m, 2,6-NC_5H_5), 7.64 (2 H, m, 4-NC_5H_5), 7.24 (4 H, m, 3,5-NC_5H_5), 6.97-6.89 (8 H, m, *o*-$C_6H_4CH_3$ and *m*-$C_6H_4CH_3$), 3.89 (2 H, m, $NCH_2C\mathit{H}$), 3.69 (1 H, NCH_2), 3.67 (1 H, s, CH_{bridge}), 3.51 (1 H, NCH_2), 3.34 (1 H, NCH_2), 3.24 (1 H, NCH_2), 2.22 (3 H, br. s, $C_6H_5\mathit{CH_3}$), 2.20 (3 H, br. s, $C_6H_5\mathit{CH_3}$), 1.86 (2 H, m, $(CH_3)_2C\mathit{H}$), 0.87 (6 H, m, $CH(\mathit{CH_3})_2$), 0.77 (6 H, app t, $^{3}J_{HH}$ = 6.7 Hz, $CH(\mathit{CH_3})_2$), 0.11 (18 H, s, $N(Si(CH_3)_3)$ ppm. $^{13}C\{^{1}H\}$ NMR data (d_8-THF, 75.5 MHz, 293 K): δ_C = 164.8 (C=N), 164.1 (C=N), 150.8 (2,6-NC_5H_5), 142.7 (*ipso*-$C_6H_4CH_3$), 142.1 (*ipso*-$C_6H_4CH_3$), 136.3 (4-NC_5H_5), 132.0 (p-$C_6H_4CH_3$), 131.3 (p-$C_6H_4CH_3$), 129. 5 (o-$C_6H_4CH_3$), 129.4 (o-$C_6H_4CH_3$), 124.3 (3,5-NC_5H_5), 123.9 (m-$C_6H_4CH_3$), 123.2 (m-$C_6H_4CH_3$), 66.5 ($C{=}NCH_{\text{imidazoline}}$), 66.1 ($C{=}NCH_{\text{imidazoline}}$), 58.7 ($CH_{\text{bridge}}$), 51.8 ($CH_{2\ \text{imidazoline}}$), 51.2 ($CH_{2\ \text{imidazoline}}$), 34.9 ($(CH_3)_2\mathit{CH}$), 34.3 ($(CH_3)_2\mathit{CH}$), 20.8 ($C_6H_4\mathit{CH_3}$), 20.2 ($CH_{3\ \text{isopropyl}}$), 15.4 ($CH_{3\ \text{isopropyl}}$), 2.7 ($N(Si(CH_3)_3)_2$) ppm. IR data:(KBr disc, cm^{-1}) 3027 (w), 2936 (s), 2867 (w), 2241 (w), 2179 (w), 2129 (w), 1652 (m), 1515 (s), 1455 (w), 1417 (w), 1315 (m), 1261 (s), 1100 (s), 1020 (s), 934 (w), 800 (s), 703 (w), 667 (w), 618 (w), 552 (w), 479 (m).

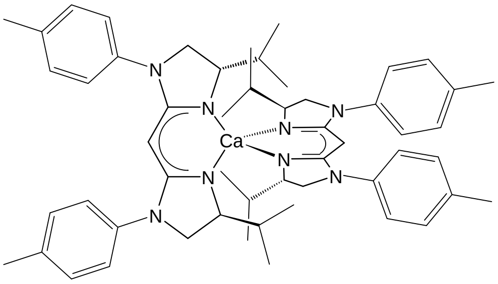


[Ca(Ar^F-BIM){N(SiMe$_3$)$_2$}(py)] 3b: ^1H NMR data (d_8-THF, 500.1 MHz, 293 K): $\delta_H = 8.54$ (2 H, m, 2,6-NC_5H_5), 7.64 (1 H, m, 4-NC_5H_5), 7.24 (2 H, m, 3,5-NC_5H_5), 7.10-7.02 (4 H, m, *o*-C_6H_4F), 6.87 (4 H, app t, $^3J = 8.7$ Hz, *m*-C_6H_4F), 3.90 (2 H, m, $NCH_2C\mathit{H}$), 3.52 (2 H, NCH_2), 3.48 (1 H, s, CH_{bridge}), 3.40 (2 H, NCH_2), 2.04 (2 H, m, $(CH_3)_2C\mathit{H}$), 0.89 (6 H, d, $^3J_{HH} = 6.8$ Hz, $CH(\mathit{CH_3})_2$), 0.78 (6 H, d, $^3J_{HH} = 6.8$ Hz, $CH(\mathit{CH_3})_2$), 0.10 (18 H, s, $N(Si(CH_3)_3)$ ppm. $^{13}C\{^1H\}$ NMR data (d_8-THF, 75.5 MHz, 293 K): $\delta_C = 164.4$ (C=N), 159.2 (d, $^1J_{CF} = 239.9$ Hz, *p*-C_6H_4F), 150.8 (2,6-NC_5H_5), 141.9 (d, $^4J_{CF} = 2.3$ Hz, *ipso*-C_6H_4F), 136.3 (4-NC_5H_5), 125.8 (d, $^3J_{CF} = 7.5$ Hz, *o*-C_6H_4F), 124.3 (3,5-NC_5H_5), 115.4 (d, $^2J_{CF} = 22.5$ Hz, *m*-C_6H_4F), 66.5 ($C{=}NCH_{\text{imidazoline}}$), 57.8 ($CH_{\text{bridge}}$), 52.1 ($CH_{2\ \text{imidazoline}}$), 34.2 ($(CH_3)_2\mathit{CH}$), 20.7 ($CH_{3\ \text{isopropyl}}$), 15.7 ($CH_{3\ \text{isopropyl}}$), 2.7 ($N(Si(CH_3)_3)_2$) ppm. ^{19}F NMR data (d_8-THF, 282.8 MHz, 293 K): $\delta_F = -121.80$ (s, *p*-$C_6H_4\mathit{F}$) ppm. IR data: (KBr disc, cm^{-1}) 3419 (br. w) 2960 (m), 2873 (w), 2240 (w), 1621 (m) 1593 (w), 1544 (s), 1479 (w), 1428 (w), 1387 (w), 1316 (w), 1260 (m), 1222 (m), 1097 (m), 1018 (m), 837 (m), 798 (m), 720 (w), 668 (w), 594 (w), 551 (m), 422 (w), 417 (w).



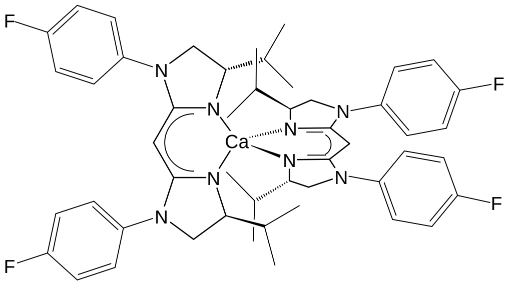
[Ca(^{t}Bu-BIM){N(SiMe$_3$)$_2$}(py)] 2c: ^1H NMR data (d_8-THF, 500.1 MHz, 293 K): $\delta_H = 8.55$ (2 H, m, 2,6-NC_5H_5), 7.64 (1 H, m, 4-NC_5H_5), 7.23 (2 H, m, 3,5-NC_5H_5), 3.83 (1 H, s, CH_{bridge}), 3.63-3.56 (2 H, m, partially obscured by solvent peak, $\mathrm{NCH_2C}\mathit{H}$), 3.20-3.12 (2 H, m, $\mathrm{N}\mathit{CH_2}$), 3.10-3.02 (2 H, m, $\mathrm{N}\mathit{CH_2}$), 1.84-1.70 (2 H, m, partially obscured by solvent peak $\mathrm{(CH_3)_2C}\mathit{H}$), 1.37 (18 H, s, $\mathrm{C(}\mathit{CH_3}\mathrm{)_3}$), 0.85 (3 H, d, $^3J_{HH}$ = 6.9 Hz, $\mathrm{CH(}\mathit{CH_3}\mathrm{)_2}$), 0.81 (3 H, app t, $^3J_{HH}$ = 6.9 Hz, $\mathrm{CH(}\mathit{CH_3}\mathrm{)_2}$), 0.78 (3 H, d, $^3J_{HH}$ = 6.9 Hz, $\mathrm{CH(}\mathit{CH_3}\mathrm{)_2}$), 0.74 (3 H, app t, $^3J_{HH}$ = 6.9 Hz, $\mathrm{CH(}\mathit{CH_3}\mathrm{)_2}$), 0.10 (18 H, $\mathrm{N(Si(CH_3)_2)}$ ppm. ^{13}C{^{1}H} NMR data (d_8-THF, 75.5 MHz, 293 K): δ_C = 167.0 (C=N), 150.8 (2,6-$\mathrm{NC_5H_5}$), 136.3 (4-$\mathrm{NC_5H_5}$), 124.3 (3,5-$\mathrm{NC_5H_5}$), 64.5 ($\mathrm{C{=}NCH_{imidazoline}}$), 62.5 ($\mathrm{CH_{bridge}}$), 53.0 ($\mathit{C}\mathrm{(CH_3)_3}$), 47.7 ($\mathrm{CH_{2\ imidazoline}}$), 35.9 ($\mathrm{((CH_3)_2}\mathit{CH}\mathrm{)}$), 29.87 ($\mathrm{(C(}\mathit{CH_3}\mathrm{)_2)}$, 20.2 ($\mathrm{CH_{3\ isopropyl}}$), 15.8 ($\mathrm{CH_{3\ isopropyl}}$), 2.7($\mathrm{N(Si(CH_3)_3)_2}$) ppm. IR data: (KBr disc, cm^{-1}) 2960 (s), 2871 (m), 1597 (s), 1528 (m), 1503 (w), 1464 (m), 1444 (w), 1396 (m), 1361 (m), 1312 (w), 1258 (s), 1229 (s), 1175 (w), 1101 (s), 1047 (s), 1018 (s), 929 (w), 861 (w), 802 (s), 748 (w), 699 (w), 670 (m), 640 (w), 615 (w), 527 (w), 473 (w).

General procedure for the preparation of the [Ca(R-BIM)$_2$] (4a-c): R-BIM (50mg, 0.31 mmol) in dry toluene (0.5ml) was added to $\mathrm{[Ca\{N(SiMe_3)_2\}_2(py)_2]}$ (82.0mg, 0.16 mmol). The solution was agitated briefly and allowed to react for 18 hours at ambient temperature under an inert atmosphere. The resulting complex was typically realised as a dark orange/magenta powder when dried *in vacuo* to approximately 4×10^{-2} mbar. Despite obtaining spectroscopically pure complexes, and repeated recrystallization attempts, satisfactory elemental analyses could not be obtained. Given the highly air and moisture sensitive nature of these compounds, and literature precedence, this is unsurprising.[7,12]

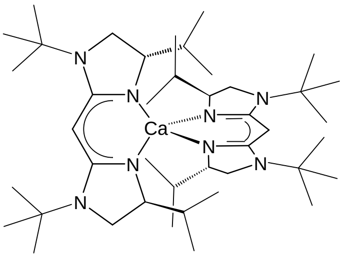


[Ar-^{Me}Ca(BIM)$_2$] 4a: ^{1}H NMR data (d_8-THF, 500.1 MHz, 293 K): δ_H = 7.04-6.97 (8 H, m, *o*-$\mathrm{C_6H_4CH_3}$), 6.96-6.89 (8 H, m, *m*-$\mathrm{C_6H_4CH_3}$), 3.96-3.82 (4 H, m, $\mathrm{NCH_2C}\mathit{H}$), 3.72 (1 H, s, $\mathrm{CH_{bridge}}$), 3.70 (1 H, s, $\mathrm{CH_{bridge}}$), 3.68 (2 H, app t, ^3J = 4.6 Hz,$\mathrm{NCH_2}$), 3.52 (2 H, app t, ^3J = 8.4 Hz,$\mathrm{NCH_2}$), 3.35 (2 H, m, $\mathrm{NCH_2}$), 3.26-3.91 (2 H, m, $\mathrm{NCH_2}$), 2.21 (6 H, s, $\mathrm{C_4H_5}\mathit{CH_3}$), 2.20 (6 H, s, $\mathrm{C_4H_5}\mathit{CH_3}$), 2.10-1.96 (2 H, m, $\mathrm{(CH_3)_2C}\mathit{H}$), 1.94-1.79 (2 H, m, $\mathrm{(CH_3)_2C}\mathit{H}$), 0.89-0.82 (12 H, m, $\mathrm{CH(}\mathit{CH_3}\mathrm{)_2}$), 0.81-0.72 (12 H, m, $\mathrm{CH(}\mathit{CH_3}\mathrm{)_2}$) ppm. ^{13}C{^{1}H} NMR data (d_8-THF, 75.5 MHz, 293 K): δ_C = 164.4 (C=N), 164.2 (C=N), 163.5 (C=N), 163.4 (C=N), 143.25 (*ipso*-$\mathrm{C_6H_4CH_3}$), 143.18 (*ipso*-$\mathrm{C_6H_4CH_3}$), 142.5 (*ipso*-$\mathrm{C_6H_4CH_3}$), 142.3 (*ipso*-$\mathrm{C_6H_4CH_3}$), 132.7 (p-

$C_6H_4CH_3$), 131.3 (p-$C_6H_4CH_3$), 130.4 (*p*-$C_6H_4CH_3$), 130.0 (*p*-$C_6H_4CH_3$), 129. 43 (*o*-$C_6H_4CH_3$), 129.40 (*o*-$C_6H_4CH_3$), 129. 38 (*o*-$C_6H_4CH_3$), 129.37 (*o*-$C_6H_4CH_3$), 124.0 (*m*-$C_6H_4CH_3$), 123.9 (*m*-$C_6H_4CH_3$), 122.60 (*m*-$C_6H_4CH_3$), 122.59 (*m*-$C_6H_4CH_3$), 66.42 ($C{=}NCH_{\text{imidazoline}}$), 66.40 ($C{=}NCH_{\text{imidazoline}}$), 66.25 ($C{=}NCH_{\text{imidazoline}}$), 66.24 ($C{=}NCH_{\text{imidazoline}}$), 55.7 ($CH_{\text{bridge}}$), 52.0 ($CH_{\text{bridge}}$), 51.9 ($CH_{2\ \text{imidazoline}}$), 51.6 ($CH_{2\ \text{imidazoline}}$), 50.9 ($CH_{2\ \text{imidazoline}}$), 50.6 ($CH_{2\ \text{imidazoline}}$), 34.47 ($(CH_3)_2\mathit{CH}$), 34.42 ($(CH_3)_2\mathit{CH}$), 34.3 ($(CH_3)_2\mathit{CH}$), 34.2 ($(CH_3)_2\mathit{CH}$),20.88 ($C_6H_4\mathit{CH_3}$),20.80 ($C_6H_4\mathit{CH_3}$), 20.6 ($CH_{3\ \text{isopropyl}}$), 20.4 ($CH_{3\ \text{isopropyl}}$), 15.7 ($CH_{3\ \text{isopropyl}}$), 15.4 ($CH_{3\ \text{isopropyl}}$) ppm. IR data: (KBr disc, cm^{-1}) 3031 (w), 2962 (m), 2868 (w), 1603 (m), 1573 (w), 1515 (m), 1478 (w), 1386 (w), 1361 (w), 1314 (w), 1260 (s), 1094 (s), 1018 (s), 798 (s), 705 (w), 614 (w), 551 (m), 499 (w).



[Ca(Ar^F-BIM)$_2$] 4b: ^{1}H NMR data (d_8-THF, 500.1 MHz, 293 K): δ_H = 7.07 (6 H, m, *m*-C_6H_4F), 6.97 (4 H, m, *o*-C_6H_4F), 6.88 (6 H, m, *m*-C_6H_4F and *o*-C_6H_4F), 4.10 (1 H, s, CH_{bridge}), 3.90 (2 H, m, $NCH_2C\mathit{H}$), 3.63 (2 H, m, $NCH_2C\mathit{H}$), 3.52 (4 H, NCH_2), 3.48 (1 H, s, CH_{bridge}), 3.39 (4 H, m, NCH_2), 2.05 (2 H, m, $(CH_3)_2C\mathit{H}$), 1.66 (2 H, m, $(CH_3)_2C\mathit{H}$), 1.04 (6 H, d, $^3J_{HH}$ = 6.7 Hz, $CH(\mathit{CH_3})_2$), 0.93 (6 H, d, $^3J_{HH}$ = 6.7 Hz, $CH(\mathit{CH_3})_2$), 0.89 (6 H, d, $^3J_{HH}$ = 6.7 Hz, $CH(\mathit{CH_3})_2$), 0.79 (6 H, d, $^3J_{HH}$ = 6.7 Hz, $CH(\mathit{CH_3})_2$) ppm. $^{13}C\{^1H\}$ NMR data (d_8-THF, 75.5 MHz, 293 K): δ_C = 164.4 (C=N), 160.6 (C=N), 159.7 (d, $^1J_{CF}$ = 241.7 Hz, *p*-C_6H_4F), 159.2 (d, $^1J_{CF}$ = 239.4 Hz, *p*-C_6H_4F), 141.9 (d, $^4J_{CF}$ = 2.3 Hz, *ipso*-C_6H_4F), 140.0 (d, $^4J_{CF}$ = 2.3 Hz, *ipso*-C_6H_4F), 125.8 (d, $^3J_{CF}$ = 8.0 Hz, *o*-C_6H_4F), 124.7 (d, $^3J_{CF}$ = 8.0 Hz, *o*-C_6H_4F), 116.1 (d, $^2J_{CF}$ = 22.5 Hz, *m*-C_6H_4F), 115.4 (d, $^2J_{CF}$ = 22.5 Hz, *m*-C_6H_4F), 66.7 ($C{=}NCH_{\text{imidazoline}}$), 66.5 ($C{=}NCH_{\text{imidazoline}}$), 57.8 ($CH_{\text{bridge}}$), 57.7 ($CH_{\text{bridge}}$), 55.9 ($CH_{2\ \text{imidazoline}}$), 52.1 ($CH_{2\ \text{imidazoline}}$), 34.7 ($(CH_3)_2\mathit{CH}$), 34.2 ($(CH_3)_2\mathit{CH}$), 20.7 ($CH_{3\ \text{isopropyl}}$), 19.5 ($CH_{3\ \text{isopropyl}}$), 15.7 ($CH_{3\ \text{isopropyl}}$), 15.2 ($CH_{3\ \text{isopropyl}}$) ppm. ^{19}F NMR data (d_8-THF, 282.8 MHz, 293 K): δ_F = -122.29 and -120.80 (s, *p*-$C_6H_4\mathit{F}$) ppm. IR data: (KBr disc, cm^{-1}) 3104 (w), 3051 (w), 2959 (s), 2870 (m), 2238 (m), 2119 (w), 2098 (w), 1886 (w), 1619 (s), 1591 (m), 1542 (m), 1509 (s), 1427 (m), 1384 (m), 1362 (m), 1309 (m), 1260 (s), 1229 (s), 1171 (w), 1138 (m), 1122 (m), 1091 (m), 1041 (m), 1011 (m), 836 (s), 797 (s), 719 (m), 664 (w), 632 (w), 596 (w), 549 (s), 524 (w), 505 (w), 482 (w), 434 (w).



[Ca(^{t}Bu-BIM)$_2$] 4c: ^{1}H NMR data (d$_8$-THF, 500.1 MHz, 293 K): δ_H = 3.70 (2 H, s, CH $_{\text{bridge}}$), 3.50 (4 H, d t, $^3J_{HH}$ = 9.1 Hz, $^4J_{HH}$ = 2.7 Hz, NCH$_2$C*H*), 3.14 (4 H, dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.7 Hz, N*CH$_2$*), 3.05 (4 H, app t, $^3J_{HH}$ = 9.1 Hz,N*CH$_2$*), 1.83-1.75 (4 H, m, (CH$_3$)$_2$C*H*), 1.37 (36 H, br s, C(CH$_3$)$_3$), 0.82 (12 H, d, $^3J_{HH}$ = 6.9 Hz, CH(*CH$_3$*)$_2$), 0.73 (12 H, d, $^3J_{HH}$ = 6.9 Hz, CH(*CH$_3$*)$_2$), ppm. ^{13}C{^{1}H} NMR data (d$_8$-THF, 75.5 MHz, 293 K): δ_C = 166.6 (C=N), 166.4 (C=N), 65.3 (C=NCH $_{\text{imidazoline}}$), 64.3 (C=NCH $_{\text{imidazoline}}$), 62.0 (CH $_{\text{bridge}}$), 61.8 (CH $_{\text{bridge}}$), 52.9 (*C*(CH$_3$)$_3$), 52.7 (*C*(CH$_3$)$_3$), 47.9 (CH$_2$ $_{\text{imidazoline}}$), 47.8 (CH$_2$ $_{\text{imidazoline}}$), 35.5 ((CH$_3$)$_2$*CH*), 35.2 ((CH$_3$)$_2$*CH*), 30.0 (C(*CH$_3$*)$_2$), 29.82 (C(*CH$_3$*)$_2$), 20.9 (CH$_3$ $_{\text{isopropyl}}$), 20.2 (CH$_3$ $_{\text{isopropyl}}$), 16.2 (CH$_3$ $_{\text{isopropyl}}$), 15.7 (CH$_3$ $_{\text{isopropyl}}$) ppm. IR data: (KBr disc, cm^{-1}) 2955 (s), 2866 (s), 1601 (s), 1526 (s), 1467 (m), 1442 (w), 1393 (m), 1363 (m), 1313 (w), 1259 (s), 1229 (s), 1174 (w), 1100 (s), 1016 (s), 927 (w), 863 (m), 793 (s), 734 (w), 699 (w), 659 (w), 545 (w), 520 (w), 466 (w).

Equilibrium coefficients were determined by integration of the ^{1}H NMR spectra; ΔG values were obtained using the equation $\Delta G=-RT\ln K$.

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 R-BIM (0.04 mmol) was predissolved in C_6D_6 (0.7 ml) and successively added to [Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$] (0.04 mmol). The resulting mixture was agitated by hand and left for two minutes. To this solution was added the corresponding amino olefin (0.4 mmol). The solution was transferred to a J. Young Teflon valve equipped NMR tube and sealed. All catalyst reactions were monitored *via* ^{1}HNMR periodically to monitor conversion (conversion was determined from notable resonances in the spectra corresponding to the pyrrolidine product).[10] Upon conversion ceasing, a solution of (R)-(-)-*O*-acetylmandelic acid (0.41 mmol) predissolved in a minimal amount of CDCl$_3$ was added to the reaction mixture producing the diastereomeric salts. The resulting enantioexcess (e.e) was then determined from ^{1}H NMR spectroscopy.[11]

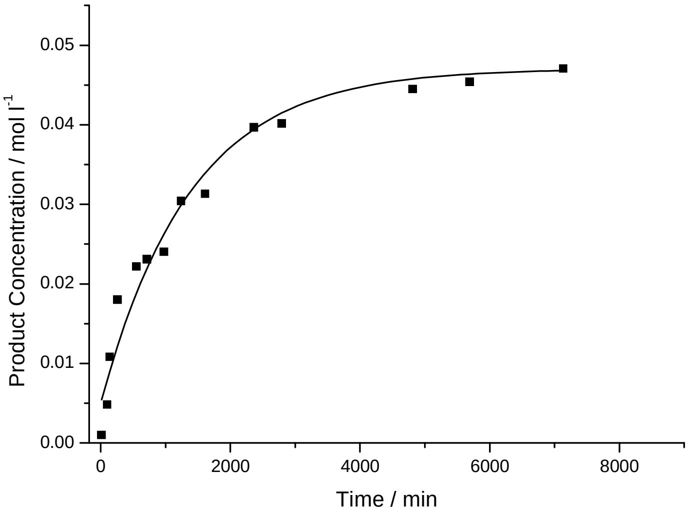
Determination of Rate Constants from Conversion Curves:

The conversion curves were curve fitted to an exponential decay function $y=Ae^{-bx}$. The initial rate, given by the slope at the origin (x=0), were determined by differentiation of the equation: $dy/dx = -A/b$.

Product Conversion Curves

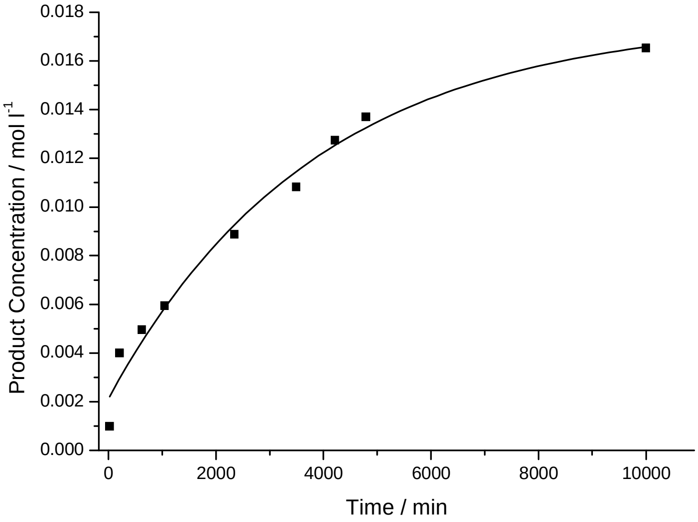
[Ca(Ar^{Me}-BIM){N(SiMe$_3$)$_2$}(THF)]

10 mol%, catalytic substrate A, Initial Rate = $5.1(5) \times 10^{-7}$ mol $L^{-1}s^{-1}$.



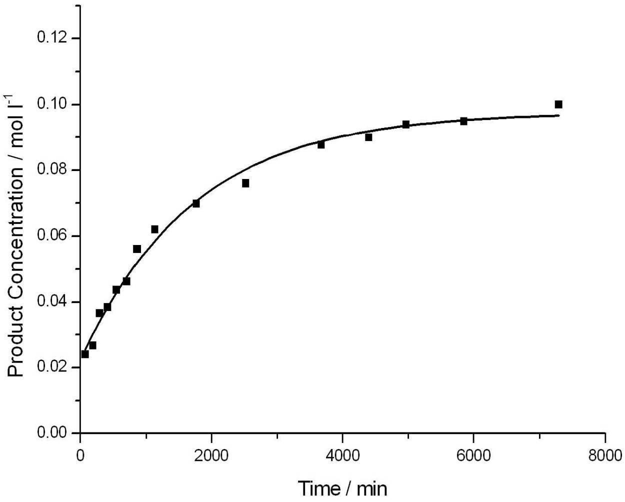
[Ca(Ar^{F}-BIM){N(SiMe$_3$)$_2$}(THF)]

10 mol%, catalytic substrate A, Initial Rate = $6.8(3) \times 10^{-8}$ mol $L^{-1}s^{-1}$.



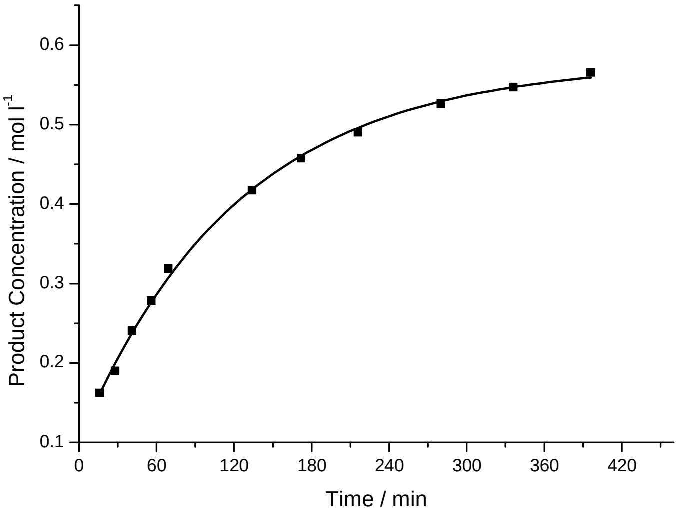
[Ca(^{t}Bu-BIM){N(SiMe$_3$)$_2$}(THF)]

10 mol%, catalytic substrate A, Initial Rate = 7.3(4)×10^{-7} mol L^{-1}s^{-1}.



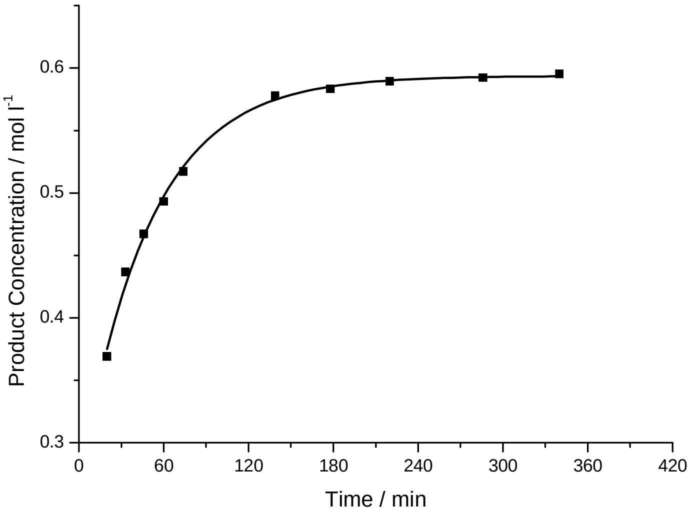
[Ca(^{t}Bu-BIM){N(SiMe$_3$)$_2$}(THF)]

10 mol%, catalytic substrate B, Initial Rate = 6.4(3) ×10^{-5} mol L^{-1}s^{-1}.



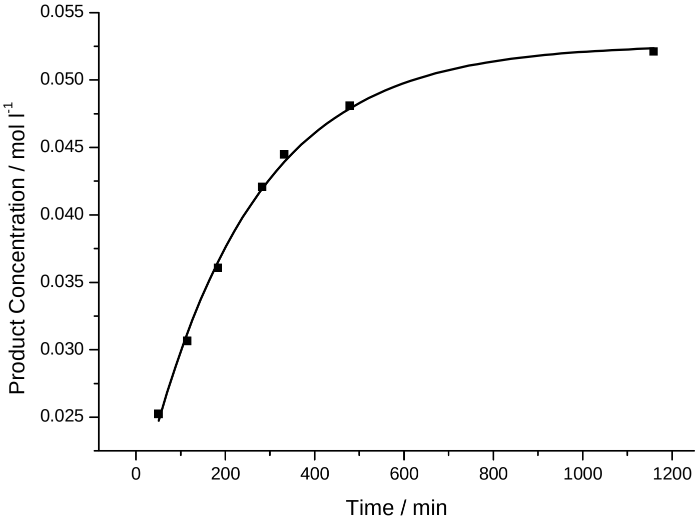
[Ca(^{t}Bu-BIM){N(SiMe$_3$)$_2$}(THF)]

20 mol%, catalytic substrate B, Initial Rate = 1.1(1) ×10^{-4} mol L^{-1}s^{-1}.



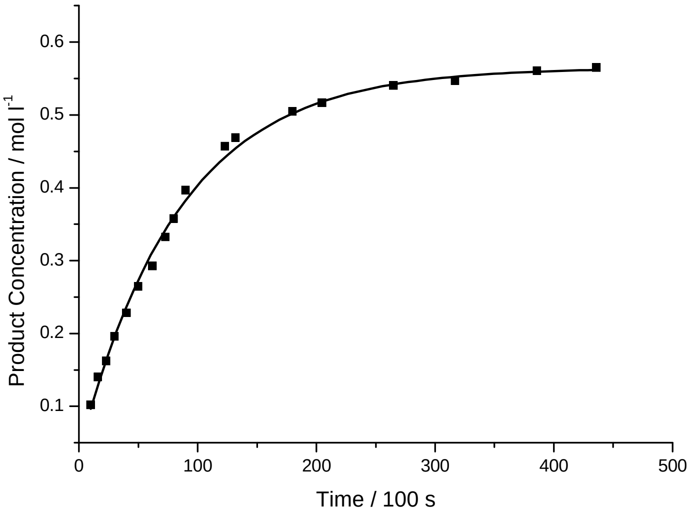
[Ca(Ar^{Me}-BIM){N(SiMe$_3$)$_2$}(THF)]

5 mol%, catalytic substrate B, Initial Rate = 2.5(1) ×10^{-6} mol L^{-1}s^{-1}.



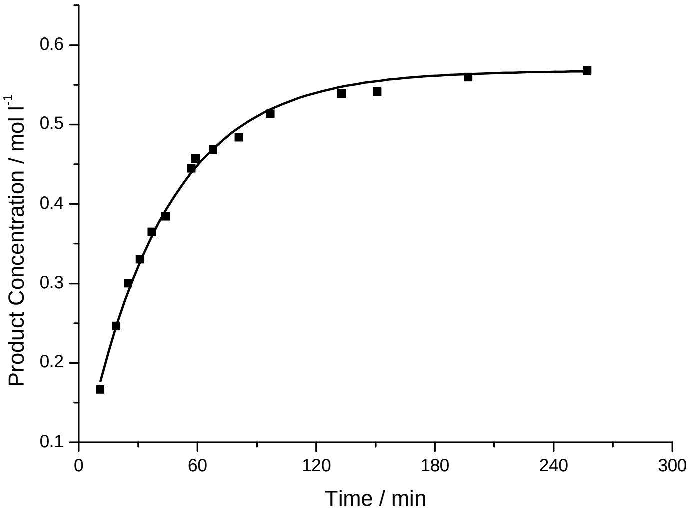
[Ca(Ar^{Me}-BIM){N(SiMe$_3$)$_2$}(THF)]

10 mol%, catalytic substrate B, Initial Rate = 1.0(1) ×10^{-4} mol L^{-1}s^{-1}.



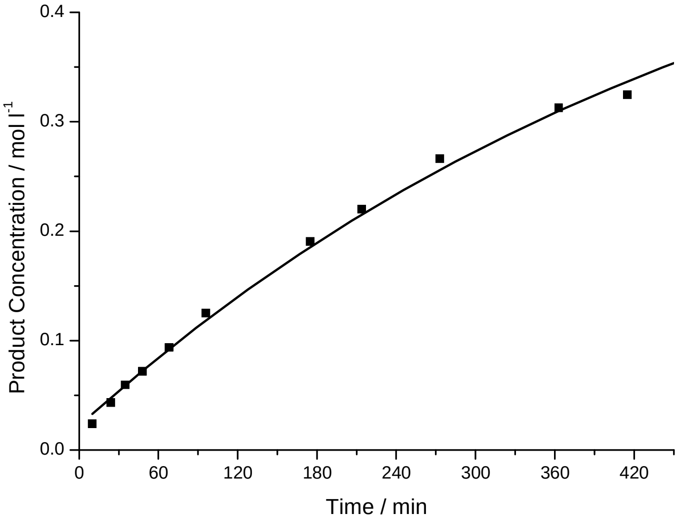
[Ca(Ar^{Me}-BIM){N(SiMe$_3$)$_2$}(THF)]

20 mol%, catalytic substrate B, Initial Rate = 2.1(2) ×10^{-4} mol L^{-1}s^{-1}.



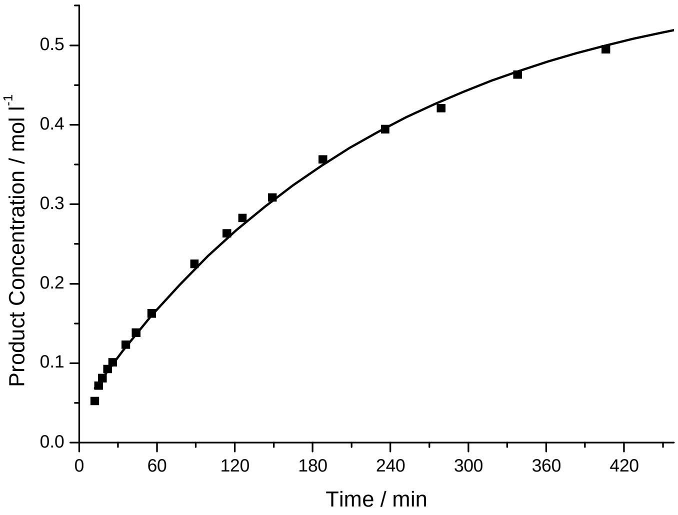
[Ca(Ar^F-BIM){N(SiMe$_3$)$_2$}(THF)]

10 mol%, catalytic substrate B, Initial Rate = 1.8(1) ×10^{-5} mol L^{-1}s^{-1}.



[Ca(Ar^F-BIM){N(SiMe$_3$)$_2$}(THF)]

20 mol%, catalytic substrate B, Initial Rate = 4.0(3) ×10^{-5} mol L^{-1}s^{-1}



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