Zirconium catalysed enantioselective hydroamination/cyclisation

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EXPERIMENTAL DETAILS

General comments. All manipulations of air-sensitive materials were carried out using standard Schlenk/glove box techniques under an atmosphere of dry argon. For inorganic and organometallic preparations, hydrocarbon and ether solvents were pre-dried over sodium wire. These were then dried under reflux conditions over sodium for toluene, potassium for THF and benzene, sodium-potassium alloy for diethyl ether, petroleum ether and pentane, then distilled and degassed before use. Other solvents were dried under reflux conditions over the appropriate agents (calcium hydride for dichloromethane, pyridine and acetonitrile), then distilled and degassed before use. Deuterated solvents were degassed by the freeze-thaw method and dried over the appropriate agent (potassium for toluene, benzene and THF; calcium hydride for bromobenzene, dichloromethane, acetonitrile and pyridine) before trap-to-trap distillation and storage in the glove box. All organic reagents were purchased from Aldrich Chemical Co. and used as received. NMR spectra were recorded on Bruker DPX-300, DPX-400, AC-400 and DPX-500 spectrometers and the spectra referenced internally using residual protio solvent resonances relative to tetramethylsilane ($\delta = 0.0$ ppm). ATR-Infra-red spectra were carried out using Golden Gate apparatus or Nujol mulls on a Perkin Elmer FT-IR spectrometer. EI and CI mass spectra were obtained on a VG Autospec mass spectrometer. Elemental analyses were performed by Warwick Analytical Services.

Reagents. The substrate 1-(N-methylamino)pent-4-ene (1)$_1$, substrate precursors; 1-amino-2,2-dimethylpent-4-ene$_2$ and o-allylaniline$_3$, and [Zr(CH$_2$Ph)$_4$]$_4$ were synthesized according to literature procedures. Substrates 1 – 3 were dried over sodium at 70 °C for 1 d and isolated by trap-to-trap vacuum distillation before storing in a glove box. Substrates 4 and 5 were dried in an ampoule connected to a vacuum line via a drying tube containing CaCl$_2$. The ampoule was then heated at 70 °C under constant vacuum for 3 h and stored in a glovebox. Synthesis of the proligands rac-H$_2$L$_1$, (S)-H$_2$L$_1$, rac-H$_2$L$_2$ and (S)-H$_2$L$_1$ have been reported previously.$^5$

SYNTHESSES

1-(N-Methylamino)pent-4-ene (1)

$^{1}$H-NMR (CDCl$_3$, 300 MHz): δ ppm 0.86 (bm, 1H, NMe), 1.54 (m, 2H, CH$_2$), 2.03 (m, 2H, CH$_2$), 2.36 (d, 3H, NHMe, $^3$J$_{HH} = 6$ Hz), 2.53 (m, 2H, CH$_2$), 4.90 (m, 2H, CH=CH$_2$), 5.78 (m, 1H, CH=CH$_2$).

$^{13}$C{$^1$H}-NMR (CDCl$_3$, 75 MHz): δ ppm 29.5 (CH$_2$), 31.9 (CH$_2$), 36.9 (NHMe), 52.0 (CH$_2$), 114.9 (CH=CH$_2$), 138.9 (CH=CH$_2$).

IR (Golden Gate): cm$^{-1}$ 3222, 2934, 2787, 1640, 1511, 1476, 1442, 1360, 1291, 1118, 994, 909, 801, 738.
in an ice bath and ice cautiously added followed by 2 M NaOH (aq). The reaction mixture was stirred at room temperature for 1 d. The formamide was dissolved in dry diethyl ether (50 ml) and bromobut-1-ene (9.78 g, 72.5 mmol) using the general method described in reference 2. This new amino olefin was synthesised in a two-step procedure from isobutyronitrile (5.00 g, 72.5 mmol) and ethylformate (20 ml). The nitrile was reduced with LiAlH4 (2.00 g, 52.6 mmol) was added slowly and the reaction mixture was stirred at room temperature for 1 d. The reaction mixture was cooled to 0 °C in an ice bath and ice cautiously added followed by 2 M NaOH (aq) (20 ml). The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 x 30 ml). The combined organic extracts were dried over anhydrous MgSO4, filtered and the product isolated by fractional distillation. Yield = 1.53 g, 69 %. Anal. calcd. for C8H17N: % C, 75.52; H, 13.47; N, 11.01. Found: % C, 75.38; H, 13.52; N, 10.38.

1-(N-Methylamino)-2,2-dimethylpent-4-ene (2)

A 50 ml round bottom flask was charged with 1-amino-2,2-dimethylpent-4-ene (2.00 g, 17.7 mmol) and ethylformate (20 ml). The reaction mixture was then heated to reflux temperature for 1 d and volatiles removed under reduced pressure. The formamide was dissolved in dry diethyl ether (50 ml) and cooled to 0 °C in an ice bath. LiAlH4 (2.00 g, 52.6 mmol) was added slowly and the reaction mixture was stirred at room temperature for 1 d. The reaction mixture was cooled to 0 °C in an ice bath and ice cautiously added followed by 2 M NaOH (aq) (20 ml). The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 x 30 ml). The combined organic extracts were dried over anhydrous MgSO4, filtered and the product isolated by fractional distillation. Yield = 1.53 g, 69 %.

1-Amino-2,2-dimethylpent-4-ene

Anal. calcd. for C7H13N: % C, 74.27; H, 13.36; N, 12.37. Found: % C, 74.17; H, 13.34; N, 11.94.

\[ ^1H-NMR \ (CDCl_3, \ 300 \ MHz): \ \delta \ ppm \ 0.78 \ (s, \ 6H, \ CMe_2), \ 0.90 \ (s, \ 2H, \ NH_2), \ 1.90 \ (d, \ 2H, \ CH_2CH=CH_2), \ \delta J_{HH} = 7 \ Hz, \ 2.38 \ (s, \ 2H, \ CH_2NHMe), \ 4.94 \ (m, \ 2H, \ CH=CH_2), \ 5.75 \ (m, \ 1H, \ CH=CH_2). \]

\[ ^13C\{^1H\}-NMR \ (CDCl_3, \ 75 \ MHz): \ \delta \ ppm \ 29.5 \ (CH_2), \ 53.0 \ (CH_2NHMe), \ 117.2 \ (CH=CH_2), \ 135.7 \ (CH=CH_2). \]

MS (EI): m/z 126 (M+1, 15 %), 112 (M1, 5 %), 98 (35 %), 96 (18 %), 81 (22 %), 72 (31 %), 71 (17 %), 67 (30 %), 57 (33 %), 56 (42 %), 55 (100 %).

1-Amino-2,2-dimethylhex-5-ene

This new amino olefin was synthesised in a two-step procedure from isobutyronitrile (5.00 g, 72.5 mmol) and bromobut-1-ene (9.78 g, 72.5 mmol) using the general method described in reference 2. The nitrile was reduced with LiAlH4 in diethyl ether and isolated by fractional distillation. Yield = 6.67 g, 72 %.

Anal. calcd. for C8H17N: % C, 75.52; H, 13.47; N, 11.01. Found: % C, 74.92; H, 13.48; N, 10.29.

\[ ^1H-NMR \ (CDCl_3, \ 300 \ MHz): \ \delta \ ppm \ 0.79 \ (s, \ 6H, \ CMe_2), \ 0.89 \ (bs, \ 2H, \ NH_2), \ 1.22 \ (m, \ 2H, \ CH_2CH=CH_2), \ 1.96 \ (m, \ 2H, \ CH_2CMe_2), \ 2.39 \ (s, \ 2H, \ CH_2NHMe), \ 4.88 \ (m, \ 2H, \ CH=CH_2), \ 5.75 \ (m, \ 1H, \ CH=CH_2). \]

\[ ^13C\{^1H\}-NMR \ (CDCl_3, \ 75 \ MHz): \ \delta \ ppm \ 24.3 \ (CMe_2), \ 28.1 \ (CH_2CMe_2), \ 34.2 \ (CMe_2), \ 38.3 \ (CH_2CH=CH_2), \ 52.5 \ (CH_2NHMe), \ 113.6 \ (CH=CH_2), \ 139.2 \ (CH=CH_2). \]

MS (EI): m/z 128 (M+1, 84 %), 127 (M+, 9 %), 112 (27 %), 95 (12 %), 84 (10 %), 81 (29 %), 73 (24 %), 70 (43 %), 55 (100 %).
1-(N-Methylamino)-2,2-dimethylhex-5-ene (3)
This compound was obtained via N-formylation of 1-amino-2,2-dimethylhex-5-ene (2.00 g, 15.7 mmol) and reduction of the corresponding amide, using the method described for substrate 2. Yield = 1.21 g, 55 % (isolated by fractional distillation).

Anal. calcd. for C₉H₁₄N: % C, 76.53; H, 13.56; N, 9.92. Found: % C, 75.88; H, 13.60; N, 9.11.

1H-NMR (CDCl₃, 300 MHz): δ ppm 0.66 (bs, 1H, NHMe), 0.84 (s, 6H, CMe₂), 1.24 (m, 2H, CH₂CH=CH₂), 1.95 (m, 2H, CH₂CMe₂), 2.27 (s, 2H, CH₂NHMe), 2.37 (s, 3H, NHMe), 4.86 (m, 2H, CH=CH₂), 5.72 (m, 1H, CH=CH₂).

13C{¹H}-NMR (CDCl₃, 75 MHz): δ ppm 25.3 (CMe₂), 28.2 (CH₂CMe₂), 33.5 (CMe₂), 37.4 (NHMe), 39.2 (CH₂CH=CH₂), 63.0 (CH₂NHMe), 113.6 (CH=CH₂), 139.3 (CH=CH₂).

IR (Golden Gate): cm⁻¹ 2934, 2787, 1654, 1474, 1364, 1153, 1108, 994, 904, 738.

MS (EI): m/z 154 (100%), 140 (M⁻-1, 30%), 126 (24%), 112 (18 %), 98 (16 %), 91 (12 %), 70 (11%), 55 (19%).

1-(N-[p-Methoxybenzyl]amino)-hexe-5-ene (4)
A 50 ml round bottom flask was charged with 1-amino-2,2-dimethylhex-5-ene (0.95 g, 7.5 mmol) and p-anisaldehyde (0.97 g, 7.1 mmol). Methanol (30 ml) was added and the solution was heated at reflux temperature for 1 d, during which time the solution turned orange/yellow. The solution was allowed to cool to room temperature and NaBH₄ (0.54 g, 14.2 mmol) was added. The reaction mixture was stirred for 3 h at room temperature during which time the solution became colourless. Water (10 ml) was added and the solution was extracted with diethyl ether (3 x 30 ml). The combined organic extracts were dried over anhydrous MgSO₄, filtered and volatiles removed under reduced pressure. The residue was then distilled at 150 °C, 10⁻³ mm Hg, to yield a colourless oil. Yield = 1.48 g, 84 %.

Anal. calcd. for C₁₆H₂₃NO: % C, 77.68; H, 10.19; N, 5.66. Found: % C, 77.61; H, 10.21; N, 5.70.

1H-NMR (CDCl₃, 300 MHz): δ ppm 0.81 (s, 6H, CMe₂), 1.11 (bs, 1H, NH), 1.26 (m, 2H, CH₂CH=CH₂), 1.90 (m, 2H, CH₂CMe₂), 2.27 (s, 2H, CH₂NH), 3.65 (s, 2H, NCH₂Ar), 3.72 (s, 3H, NHMe), 4.85 (m, 2H, CH=CH₂), 5.73 (m, 1H, CH=CH₂), 6.79 (d, 2H, ArH, 3JHH = 8 Hz), 7.17 (d, 2H, ArH, 3JHH = 8 Hz).

13C{¹H}-NMR (CDCl₃, 75 MHz): δ ppm 26.0 (CMe₂), 28.9 (CH₂CMe₂), 34.3 (CMe₂), 39.7 (CH₂CH=CH₂), 54.5 (NCH₂Ar), 55.7 (ArOMe), 60.0 (CH₂NH), 114.0 (Ar), 114.2 (CH=CH₂), 129.5 (Ar), 133.5 (Ar), 140.1 (CH=CH₂), 158.9 (Ar).

IR (Golden Gate): cm⁻¹ 2954, 2822, 1639, 1612, 1512, 1466, 1358, 1301, 1244, 1172, 1106, 1037, 907, 819, 770, 701.

MS (EI): m/z 368 (97 %), 248 (M⁻+1, 29 %), 247 (24 %), 150 (32 %), 121 (100 %), 91 (5 %)

α-Allylaniline
Anal. calcd. for C₇H₁₁N: % C, 81.16; H, 8.32; N, 10.52. Found: % C, 80.92; H, 8.40; N, 10.52.

1H-NMR (CDCl₃, 300 MHz): δ ppm 3.28 (d, 2H, CH₂CH=CH₂, 3JHH = 6 Hz), 3.59 (bs, 2H, NH₂), 5.09 (m, 2H, CH₂CH=CH₂), 5.93 (m, 1H, CH=CHCH₂), 6.65 (d, 1H, ArH, 3JHH = 8 Hz), 6.73 (dt, 1H, ArH, 3JHH = 7 Hz, 4JHH = 1 Hz), 7.02 – 7.08 (m, 2H, ArH).

13C{¹H}-NMR (CDCl₃, 75 MHz): δ ppm 36.2 (CH₂CH=CH₂), 115.6 (Ar), 115.9 (CH₂=CHCH₂), 118.6 (Ar), 123.8 (Ar), 127.3 (Ar), 129.9 (Ar), 135.7 (CH₂CH=CH₂), 144.6 (Ar).
N-(tert-Butoxycarbonyl)-o-allylaniline.

This preparation is a modification of a literature procedure.\(^8\) A 100 ml round bottom flask was charged with o-allylaniline (6.03 g, 45.3 mmol) and tetrahydrofuran (40 ml). To this was added di-tert-butyl-dicarbonate (9.80 g, 44.9 mmol) and triethylamine (6.3 ml, 45.5 mmol). The solution was heated at reflux temperature for 1 d, during which time a white precipitate formed. The solvent was removed under reduced pressure and ethyl acetate (100 ml) was added to the residue. The solution was washed with 1 M citric acid\(_{aq}\) (3 x 70 ml) and saturated NaCl\(_{aq}\) (50 ml). The organic layer was dried over anhydrous MgSO\(_4\), filtered and volatiles removed under reduced pressure to give a mixture of a white solid and oil. This was extracted with hexane and the white solid removed by filtration. The hexane was removed under reduced pressure to yield a pale yellow oil, which was distilled at 140 °C, 10\(^{-3}\) mm Hg, to give a clear oil. Yield = 8.40 g, 80 %.

Anal. calcd. for C\(_{14}\)H\(_{19}\)NO\(_2\): % C, 72.07; H, 8.21; N, 6.00. Found: % C, 71.88; H, 8.20; N, 6.10.

\(^1\)H-NMR (CDCl\(_3\), 300 MHz): \(\delta\) ppm 1.51 (s, 9H, OC\(_{Me}\)_3), 3.36 (d, 2H, C\(_2\)H\(_2\)CH=CH\(_2\), \(^3\)J\(_{HH}\) = 6 Hz), 5.10 (m, 2H, CH=C\(_2\)H), 5.95 (m, 1H, CH=CH\(_2\)), 6.46 (bs, 1H, NH), 7.03 (dt, 1H, ArH, \(^3\)J\(_{HH}\) = 8 Hz, \(^4\)J\(_{HH}\) = 1 Hz), 7.13 (dd, 1H, ArH, \(^3\)J\(_{HH}\) = 8 Hz, \(^4\)J\(_{HH}\) = 2 Hz), 7.23 (dt, 1H, ArH, \(^3\)J\(_{HH}\) = 8 Hz, \(^4\)J\(_{HH}\) = 2 Hz), 7.78 (bd, 1H, ArH, \(^3\)J\(_{HH}\) = 8 Hz).

\(^{13}\)C\(_{\{1\}H}\)-NMR (CDCl\(_3\), 75 MHz): \(\delta\) ppm 28.2 (OC\(_{Me}\)_3), 36.3 (CH\(_2\)CH=CH\(_2\)), 80.1 (OCMe\(_3\)), 116.4 (CH=CH\(_2\)), 121.9 (Ar), 123.8 (Ar), 127.2 (Ar), 129.8 (Ar), 135.7 (CH=CH\(_2\)), 136.3 (Ar), 153.0 (Ar).

IR (Golden Gate): cm\(^{-1}\) 3426, 3334, 2979, 1724, 1697, 1589, 1514, 1451, 1392, 1366, 1297, 1230, 1153, 1046, 1024, 997, 913, 840, 751, 668, 642, 606.

MS (CI): \(m/z\) 234 (M\(^{+}\)+1, 29 %), 233 (M\(^{+}\)), 178 (75 %), 177 (49 %), 160 (33 %), 146 (42 %), 133 (100 %), 118 (43 %).

N-Methyl-2-allylaniline (5)

A 100 ml round bottom flask was charged with N-(tert-butoxycarbonyl)-o-allylaniline (4.00 g, 17.2 mmol) and tetrahydrofuran (50 ml). LiAlH\(_4\) (2.00 g, 52.6 mmol) was cautiously added and the reaction mixture was heated at reflux temperature for 1 d. The reaction mixture was cooled to 0 °C in an ice bath and water (10 ml) was added dropwise followed by 2 M NaOH\(_{aq}\) (10 ml). The mixture was then extracted with diethyl ether (2 x 50 ml) and the combined organic extracts were dried over anhydrous MgSO\(_4\) and filtered. Volatiles were removed under reduced pressure and the residue was purified by column chromatography (hexane:diethyl ether, 15:1). The similar fractions were collected and solvent removed under reduced pressure to yield a colourless oil. Yield = 1.50 g, 59 %.

Anal. calcd. for C\(_{10}\)H\(_{13}\)N: % C, 81.59; H, 8.90; N, 9.51. Found: % C, 81.16; H, 8.87; N, 9.53.

\(^1\)H-NMR (CDCl\(_3\), 300 MHz): \(\delta\) ppm 2.83 (s, 3H, NHMe), 3.26 (d, 2H, CH\(_2\)CH=CH\(_2\), \(^3\)J\(_{HH}\) = 6 Hz), 3.74 (bs, 1H, NHMe), 5.08 (m, 2H, CH=CH\(_2\)), 5.93 (m, 1H, CH=CH\(_2\)), 6.63 (d, 1H, ArH, \(^3\)J\(_{HH}\) = 8 Hz), 6.70 (dt, 1H, ArH, \(^3\)J\(_{HH}\) = 7 Hz, \(^4\)J\(_{HH}\) = 1 Hz), 7.03 (dd, 1H, ArH, \(^3\)J\(_{HH}\) = 7 Hz, \(^4\)J\(_{HH}\) = 2 Hz), 7.18 (dt, 1H, ArH, \(^3\)J\(_{HH}\) = 8 Hz, \(^4\)J\(_{HH}\) = 2 Hz).

IR (Golden Gate): 3452, 3376, 3072, 3019, 1620, 1494, 1458, 1432, 1316, 1276, 1157, 997, 915, 747, 692, 648, 610.

MS (EI): \(m/z\) 133 (M\(^{+}\), 100 %), 132 (M\(^{+}\)-1, 42 %), 118 (37 %), 115 (19 %), 106 (40 %), 77 (17 %).
Anal. calcd. for C_{46}H_{62}Cl_{2}N_{2}O_{2}Zr: C, 66.00; H, 7.47; N, 3.35. Found: C, 67.73; H, 7.58; N, 2.97.

1H-NMR (CD_{2}Cl_{2}, 300 MHz): δ ppm 1.65 (s, 18H, CMe), 1.89 (s, 18H, CMe), 2.00 (s, 6H, Me), 2.83 (d, 2H, CH), 3.72 (d, 2H, CH), 4.75 (d, 2H, ArH), 4.90 (d, 2H, ArH), 7.26 (d, 2H, ArH), 7.37 (d, 2H, ArH), 7.45 (d, 2H, ArH), 7.54 (d, 2H, ArH), 7.64 (d, 2H, ArH).

13C{1}H-NMR (CD_{2}Cl_{2}, 75 MHz): δ ppm 30.5 (NMMe), 36.2 (CH_{2}CH=CH_{2}), 109.7 (Ar), 116.0 (CH=CH_{2}), 116.9 (Ar), 123.4 (Ar), 127.6 (Ar), 129.5 (Ar), 135.9 (CH=CH_{2}), 147.2 (Ar).

IR (Golden Gate): cm\(^{-1}\) 3438, 2896, 2813, 1634, 1605, 1586, 1509, 1466, 1427, 1309, 1263, 1164, 1064, 1042, 997, 913, 745, 646, 614.

MS (EI): m/z 147 (M\(^{+}\), 100 %), 144 (54 %), 132 (87 %), 130 (33 %), 118 (83 %), 117 (48 %), 115 (43 %), 91 (32 %).

[ZrL\(^{2}\)Cl\(_{2}\)]

The complex was synthesised in an analogous manner to [ZrL\(^{1}\)Cl\(_{2}\)] using H\(_{2}\)L\(^{2}\) (500 mg, 0.77 mmol) and [Zr(NMe\(_{2}\))\(_{2}\)Cl\(_{2}\)(THF)]\(_{2}\) (304 mg, 0.77 mmol). A white crystalline solid was obtained after recrystallisation from toluene and thorough drying in vacuo. Yield = 349 mg, 56 %.

Anal. calcd. for C\(_{44}\)H\(_{58}\)Cl\(_{2}\)N\(_{2}\)O\(_{2}\)Zr: C, 64.73; H, 7.21; N, 3.52. Found: C, 64.73; H, 7.21; N, 3.52.

1H-NMR (CD_{2}Cl_{2}, 300 MHz): δ ppm 1.65 (s, 9H, CMe), 1.89 (s, 9H, CMe), 2.00 (s, 9H, CMe), 2.83 (d, 1H, ArH), 3.72 (d, 1H, ArH), 4.75 (d, 1H, ArH), 4.90 (d, 1H, ArH), 7.26 (d, 1H, ArH), 7.38 (d, 1H, ArH), 7.45 (d, 1H, ArH), 7.54 (d, 1H, ArH), 7.64 (d, 1H, ArH), 7.72 (d, 1H, ArH).

13C{1}H-NMR (CD_{2}Cl_{2}, 75 MHz): δ ppm 30.5 (NMMe), 36.2 (CH_{2}CH=CH_{2}), 109.7 (Ar), 116.0 (CH=CH_{2}), 116.9 (Ar), 123.4 (Ar), 127.6 (Ar), 129.5 (Ar), 135.9 (CH=CH_{2}), 147.2 (Ar).

IR (Golden Gate): cm\(^{-1}\) 3438, 2896, 2813, 1634, 1605, 1586, 1509, 1466, 1427, 1309, 1263, 1164, 1064, 1042, 997, 913, 745, 646, 614.

MS (EI): m/z 809 [M\(^{+}\)], 773 [M-Cl\(^{+}\)].
[Zr(rac-L²)CH₂Ph]

An ampoule was charged with rac-H₂L² (212 mg, 0.33 mmol) and [Zr(CH₂Ph)₄] (155 mg, 0.34 mmol). To this was added toluene (20 ml) and the solution stirred in the absence of light for 5 d. The yellow solution was then transferred to a Schlenk vessel and volatiles were removed under reduced pressure. The sticky solid was then dissolved in pentane (10 ml) and filtered through a cannula. The solvent was removed under reduced pressure to give a yellow solid. Yield = 246 mg, 91 %. Attempts to crystallize failed.

1H-NMR (C₆D₅Br, 300 MHz): δ ppm 1.28 (s, 9H, CMe₃), 1.30 (s, 9H, CMe₃), 1.48 (s, 9H, CMe₃), 1.54 (s, 9H, CMe₃), 1.66 (s, 3H, ArMe), 1.67 (s, 3H, ArMe), 2.25 (d, 1H, ZrCH₂Ph, ²JHH = 10 Hz), 2.87 (d, 1H, ZrCH₂N, ²JHH = 7 Hz), 2.94 (bs, 3H, NMe), 3.02 (d, 1H, ZrCH₂N, ²JHH = 7 Hz), 3.72 (d, 1H, ZrCH₂Ph, ²JHH = 10 Hz), 6.64 – 6.68 (m, 3H, ArH), 6.87 (d, 1H, ArH, ³JHH = 2 Hz), 7.03 – 7.25 (m, 10H, ArH), 7.55 (d, 1H, ArH, ³JHH = 8 Hz).

13C{¹H}-NMR (C₆D₅Br, 75 MHz): δ ppm 21.4 (ArMe), 21.9 (ArMe), 30.5 (CMe₃), 30.6 (CMe₃), 32.0 (CMe₃), 32.1 (CMe₃), 34.5 (CMe₃), 34.6 (CMe₃), 35.2 (CMe₃), 35.3 (CMe₃), 46.3 (NMe), 53.9 (ZrCH₂N), 76.1 (ZrCH₂Ph), 117.1 (Ar), 117.3, 117.3, 119.5, 121.5, 122.4, 123.0, 126.7, 126.9, 127.2, 128.3, 128.9, 130.4, 132.6, 133.4, 135.8, 136.8, 138.5, 138.7, 139.7, 140.2, 142.9, 143.8, 144.1, 145.6, 147.0, 155.0, 157.2.

MS (CI): 753 (39 %), 738 (M⁺-CH₂Ph, 39 %), 721 (100 %).

[Zr({S}-L²)CH₂Ph]

The complex was synthesised in a similar manner to [Zr(rac-L²)CH₂Ph] using (S)-H₂L². Spectroscopic data was identical to that observed for [Zr(rac-L²)CH₂Ph].

In situ characterisation of [Zr(rac-L²)CH₂Ph]+.

An NMR tube sealed with a Young’s concentric stopcock was charged with [Zr(rac-L²)CH₂Ph] (20 mg, 0.024 mmol) and [PhNMe₂H][B(C₆F₅)₄] (19.4 mg, 0.024 mmol). Addition of d₅-bromobenzene gave rise to a yellow/orange solution.

1H-NMR (C₆D₅Br, 300 MHz): δ ppm 1.25 (s, 9H, CMe₃), 1.32 (s, 9H, CMe₃), 1.34 (s, 9H, CMe₃), 1.43 (CMe₃), 1.60 (s, 3H, ArMe), 1.61 (s, 3H, ArMe), 2.33 ([PhNMe₂H⁺]), 2.38 (d, 1H, ZrCH₂Ph, ²JHH = 10 Hz), 2.78 (s, 6H, PhNMe₂), 3.03 (bs, 3H, NMe), 3.30 (bs, 3H, NMe), 3.74 (d, 1H, ZrCH₂Ph, ²JHH = 10 Hz), 6.64 – 7.60 (ArH).
$^{13}$C-$\text{H}$-NMR ($C_6D_5Br$, 75 MHz): $\delta$ ppm 21.0 (ArMe), 21.5 (ArMe), 30.1 (CMe$_3$), 30.4 (CMe$_3$), 31.6 (CMe$_3$), 31.8 (CMe$_3$), 34.7 (CMe$_3$), 34.8 (CMe$_3$), 34.9 (CMe$_3$), 35.0 (CMe$_3$), 43.4 ([$\text{PhNMe}_2$H] + ), 43.7 (PhNMe$_2$), 44.7 (NMe), 47.6 (NMe), 76.4 ($\text{ZrCH}_2\text{Ph}$), 115.5 (Ar), 116.8, 116.9, 117.3, 118.3, 120.5, 123.3, 123.4, 124.2, 125.9, 128.5, 129.0, 129.2, 129.6, 129.8, 130.4, 132.5, 134.4, 135.2, 135.4 (br, Ar), 136.7, 137.0, 137.9, 138.7 (br, Ar), 139.8, 140.3, 140.5, 140.7, 142.0, 142.1, 143.8, 144.0, 144.5, 145.7, 147.5 (br, Ar), 150.6 (br, Ar), 152.1, 153.7.

$^1$H NMR spectrum of [Zr(rac-$\text{L}$-$^2$)$\text{CH}_2\text{Ph}$]$^+$[B($C_6F_5$)$_4$] – in $C_6D_5Br$ at 298 K. *Toluene.

**In situ characterisation of [Zr($\text{S}$-$\text{L}$-$^2$)$\text{CH}_2\text{Ph}$]$^+$.**

This species was generated in a similar manner to [Zr(rac-$\text{L}$-$^2$)$\text{CH}_2\text{Ph}$]$^+$ using [Zr($\text{S}$-$\text{L}$-$^2$)$\text{CH}_2\text{Ph}$]. Spectroscopic data was identical [Zr(rac-$\text{L}$-$^2$)$\text{CH}_2\text{Ph}$]$^+$

**Typical catalytic reaction.**

In the glove box, the precatalyst [Zr(rac-$\text{L}$-$^2$)$\text{CH}_2\text{Ph}$] or [Zr($\text{S}$-$\text{L}$-$^2$)$\text{CH}_2\text{Ph}$] (10 mg, 0.12 mmol) was loaded into a sample vial. This was dissolved in $d_5$-bromobenzene (0.7 ml) and [PhNMe$_2$H]$^+$[B($C_6F_5$)$_4$] (9.5 mg, 0.012 mmol) was added. This was mixed for 10 min before addition of addition of the secondary amine substrate (0.12 mmol, 10 molar equivalents). The solution was then transferred to an NMR tube sealed with a Young’s concentric stopcock and the reaction monitored by $^1$H NMR spectroscopy.

**1,2-Dimethylpyrrolidine (6)**

This cyclised amine was synthesised as described in the typical NMR-scale reactions.

$^1$H-NMR ($C_6D_5Br$, 300 MHz): $\delta$ ppm 1.16 (d, 3H, CHMe, $^3J_{HH} = 6$ Hz), 1.46 (m, 1H, CH$_2$), 1.66 (m, 1H, CH$_2$), 1.78 (m, 1H, CH$_2$), 1.92 (m, 1H, CH$_2$), 2.06–2.21 (m, 2H, CHMe and NCH$_2$), 2.32 (s, 3H, NMe), 3.07 (m, 1H, NCH$_2$).

$^{13}$C-$^1$H-NMR ($C_6D_5Br$, 75 MHz): $\delta$ ppm 19.2 (CHMe), 22.2 (CH$_2$), 33.6 (CH$_2$), 40.5 (NMe), 57.6 (NCH$_2$), 61.9 (CHMe).

**1,2,4,4-Tetramethylpyrrolidine (7)**
This cyclised amine was synthesised as described in the typical NMR-scale reactions.

1H-NMR (CD3Br, 300 MHz): δ ppm 1.10 (s, 3H, CMe2), 1.17 (d, 3H, CHMe, JHH = 6 Hz), 1.24 (s, 3H, CMe2), 1.34 (dd, 1H, CH2, JHH = 12 Hz, JHH = 9 Hz), 1.75 (dd, 1H, CH2, JHH = 12 Hz, JHH = 7 Hz), 2.07 (d, 1H, NCH2, JHH = 9 Hz), 2.29 (s, 3H, NMe), 2.29 (m, 1H, CHMe), 2.82 (d, 1H, NCH2, JHH = 9 Hz).

13C{1H}-NMR (CD3Br, 75 MHz): δ ppm 19.6 (CHMe), 29.5 (CMe2), 31.4 (CMe2), 35.8 (CMe2), 40.7 (NMe), 49.9 (CH2), 62.4 (CHMe), 72.1 (NCH2).

1,2,5,5-Tetramethylpiperidine (8)
This cyclised amine was synthesised as described in the typical NMR-scale reactions.

1H-NMR (CD3Br, 300 MHz): δ ppm 0.97 (s, 3H, CMe2), 1.15 (d, 3H, CHMe, JHH = 6 Hz), 1.18 (s, 3H, CMe2), 1.24 (m, 1H, CH2), 1.39 – 1.55 (m, 3H, CH2), 1.81 (m, 1H, CHMe), 1.85 (d, 1H, NCH2, JHH = 11 Hz), 2.25 (s, 3H, NMe), 2.42 (dd, 1H, NCH2, JHH = 11 Hz, JHH = 2 Hz).

13C{1H}-NMR (CD3Br, 75 MHz): δ ppm 20.4 (CHMe), 25.4 (CMe2), 30.2 (CMe2), 31.3 (CMe2), 31.9 (CH2), 38.1 (CH2), 44.0 (NMe), 60.0 (CHMe), 69.3 (NCH2).

1-(p-methoxybenzyl)-2,5,5-trimethylpiperidine (9)
This cyclised amine was synthesised as described in the typical NMR-scale reactions.

1H-NMR (CD3Br, 300 MHz): δ ppm 0.91 (s, 3H, CMe2), 1.08 (s, 3H, CMe2), 1.23 (d, 3H, CHMe, JHH = 6 Hz), 1.24 (m, 1H, CH2), 1.43 (m, 1H, CH2), 1.57 – 1.65 (m, 2H, CH2), 1.84 (d, 1H, NCH2, JHH = 11 Hz), 2.36 (m, 1H, CHMe), 2.50 (dd, 1H, NCH2, JHH = 11 Hz, JHH = 2 Hz), 3.16 (d, 1H, NCH2Ar, JHH = 14 Hz), 3.68 (s, 3H, ArOMe), 4.05 (d, 1H, NCH2Ar, JHH = 14 Hz), 6.96 (d, 2H, ArH, JHH = 9 Hz), 7.38 (d, 2H, ArH, JHH = 9 Hz).

13C{1H}-NMR (CD3Br, 75 MHz): δ ppm 19.1 (CHMe), 25.6 (CMe2), 29.2 (CMe2), 31.1 (CMe2), 31.9 (CH2), 37.3 (CH2), 55.2 (ArOMe), 57.3 (CHMe), 58.1 (NCH2Ar), 63.7 (NCH2), 114.2 (Ar), 122.7, 130.2, 159.2.

1,2-Dimethylindoline (10)
This cyclised amine was synthesised as described in the typical NMR-scale reactions.

1H-NMR (CD3Br, 400 MHz): δ ppm 1.26 (d, 3H, CHMe, JHH = 6 Hz), 2.53 (dd, 1H, CH2, JHH = 15 Hz, JHH = 10 Hz), 2.63 (s, 3H, NMe), 3.01 (dd, 1H, CH2, JHH = 15 Hz, JHH = 8 Hz), 3.29 (m, 1H, CHMe), 6.49 (d, 1H, ArH, JHH = 8 Hz), 6.86 (t, 1H, ArH, JHH = 7 Hz), 7.13 (d, 1H, ArH, JHH = 7 Hz), 7.21 (t, 1H, ArH, JHH = 8 Hz).

13C{1H}-NMR (CD3Br, 100 MHz): δ ppm 19.0 (CHMe), 34.2 (NMe), 37.7 (CH2), 63.3 (CHMe), 108.0 (Ar), 119.0, 124.6, 128.0, 129.6, 153.3.

Determination of enantioselectivity
The heterocycles 6 - 8 were distilled from the NMR tube reaction vessel into an ampoules at 10\(^{-3}\) mm Hg. Pentane (5 ml) and (R)-(+)α-methoxy-α-(trifluoromethyl)phenylacetic acid [(+) - Mosher’s acid] (ca. 1 molar equivalent) was added and the solution was stirred for 1 h. Volatiles were removed under reduced pressure and the residue was dried in vacuo. The residue was then dissolved in CDCl3 (stored over 4 Å molecular sieves) and the enantiomeric excesses determined by 1H NMR spectroscopy at various temperatures (in order to obtain the best resolution). Comparisons were
made with racemic products in all cases. The spectrum of rac-6/Mosher’s acid and that obtained from the enantioselective reaction (ee = 64%) is shown below. The N-CHMe doublet resonances proved the most useful, but ee values were confirmed with reference to other less well resolved peaks also. The spectrum of 8 (ee = 82%)/Mosher’s acid is also given.

N-CHMe region of $^1$H NMR spectrum of rac-1,2-dimethylpyrrolidine (6) + [(+)-Mosher’s acid] in CDCl$_3$ at 253 K.

N-CHMe region of $^1$H NMR spectrum of non-racemic 1,2-dimethylpyrrolidine + [(+)-Mosher’s acid] in CDCl$_3$ at 253 K.
The heterocycles 9 and 10 were isolated by addition of the reaction mixture to 2 M HCl (aq) (15 ml), followed by washing with pentane (2 x 10 ml) to remove deuterated bromobenzene and ligand. The aqueous phase was then adjusted to pH 10 with sodium hydroxide and was extracted with diethyl ether (3 x 10 ml). The combined organic extracts were dried over anhydrous MgSO₄ and filtered. Removal of volatiles under reduced pressure yielded a clear oil. The ee for 10 was determined from NMR studies of the (+)-Mosher’s acid salt as above. For 9 this method proved unsuccessful, as did chiral HPLC under various conditions and using a number of column types. We further attempted to cleave the p-methoxybenzyl group from the piperidine using ammonium cerium(IV) nitrate (4 molar equivalents) in acetonitrile, followed by isolation and reaction with (R)(-)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride [(-)-Mosher’s acid chloride] to generate the corresponding amides. TLC analysis indicated that a reaction had occurred with ammonium cerium(IV) nitrate, but we have been unsuccessful in obtaining the amides.

References
CRYSTALLOGRAPHY

Siemens SMART (Siemens, 1994) three-circle system with CCD area detector. The crystal was held at 180(2) K with the Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986). Maximum theta was 29.43 deg. The hkl ranges were -30/ 28, -13/ 13, -28/ 26. 30886 reflections measured, 11948 unique [R(int) = 0.1341].

Absorption correction by Semi-empirical from equivalents; minimum and maximum transmission factors: 0.8783; 0.9522.

No crystal decay

Structure Analysis and Refinement.

Systematic absences indicated space group P2(1)/c and shown to be correct by successful refinement.

The structure was solved by direct methods using SHELXS (Sheldrick, 1990) (TREF) with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model with freely rotating methyl groups. Anisotropic displacement parameters were used for all non-H atoms; H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached. The absolute structure of the individual crystal chosen was checked by refinement of a delta-f" multiplier. Floating origin constraints were generated automatically. The weighting scheme was calc. Goodness-of-fit on F^2 was 1.044, R1[for 6021 reflections with I>2sigma(I)] = 0.0842, wR2 = 0.1919.

Data / restraints / parameters 11948/ 0/ 540. Largest difference Fourier peak and hole 0.715 and -1.326 e.A^-3.

Refinement used SHELXL 96 (Sheldrick, 1996).

We thank EPSRC and Siemens Analytical Instruments for grants in support of the diffractometer.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and the remaining bond lengths and angles.

References
Table 1. Crystal data and structure refinement for [ZrL(2)Cl2].

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Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å$^2 	imes 10^3$) for daz. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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Table 3.  Selected bond lengths [Å] and angles [deg] for daz.

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Symmetry transformations used to generate equivalent atoms:

Table 4.  Bond lengths [Å] and angles [deg] for daz.

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C(5)–H(5A)  0.9500
C(6)–C(7)   1.397(7)
C(7)–C(8)   1.502(7)
C(8)–C(13)  1.404(7)
C(8)–C(9)   1.409(7)
C(9)–C(10)  1.389(7)
C(10)–C(11) 1.376(8)
C(10)–H(10A) 0.9500
C(11)–C(12) 1.379(8)
C(11)–H(11A) 0.9500
C(12)–C(13) 1.389(7)
C(12)–H(12A) 0.9500
C(13)–C(14) 1.510(7)
C(14)–H(14A) 0.9800
C(14)–H(14B) 0.9800
C(14)–H(14C) 0.9800
C(15)–H(15A) 0.9800
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C(16)–C(17) 1.381(7)
C(16)–C(21) 1.383(7)
C(17)–C(18) 1.387(7)
C(17)–H(17A) 0.9500
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C(19)–C(20) 1.391(7)
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C(20)–C(26) 1.534(7)
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C(22)–C(24) 1.527(9)
C(22)–C(25) 1.533(9)
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O(1) - Zr(1) - Cl(1)  92.34(11)
O(1) - Zr(1) - Cl(2)  106.18(12)
O(2) - Zr(1) - Cl(2)  153.97(10)
Cl(1) - Zr(1) - Cl(1)  92.92(5)
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N(1) - Zr(1) - Zr(1)  130.6(3)
N(1) - Zr(1) - Zr(1)  129.9(3)
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C(21)-C(16)-N(1)          116.4(4)
C(16)-C(17)-C(18)         119.9(5)
C(16)-C(17)-H(17A)        120.1
C(18)-C(17)-H(17A)         120.1
C(17)-C(18)-C(19)          119.5(5)
C(19)-C(18)-C(22)          122.4(5)
C(20)-C(19)-C(18)         123.7(5)
C(20)-C(19)-H(19A)        118.1
C(19)-C(20)-C(21)          118.1
C(19)-C(20)-C(26)         122.9(5)
C(21)-C(20)-C(26)         121.0(5)
O(1)-C(21)-C(16)           116.5(5)
O(1)-C(21)-C(20)          122.1(5)
C(16)-C(21)-C(20)         121.3(5)
C(23)-C(22)-C(24)         108.7(6)
C(23)-C(22)-C(25)         108.4(7)
C(24)-C(22)-C(25)         106.7(6)
C(23)-C(22)-C(18)         110.7(5)
C(24)-C(22)-C(18)         109.7(5)
C(25)-C(22)-C(18)         112.5(5)
C(22)-C(23)-H(23A)        109.5
C(22)-C(23)-H(23B)        109.5
H(23A)-C(23)-H(23B)      109.5
C(22)-C(23)-H(23C)        109.5
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C(22)-C(24)-H(24B)        109.5
H(24A)-C(24)-H(24B)     109.5
C(22)-C(24)-H(24C)        109.5
C(24)-C(25)-H(25A)        109.5
C(22)-C(25)-H(25A)        109.5
H(25A)-C(25)-H(25B)    109.5
C(22)-C(25)-H(25B)        109.5
H(25A)-C(25)-H(25C)    109.5
C(26)-C(27)-H(27A)        109.5
C(26)-C(27)-H(27B)        109.5
H(27A)-C(27)-H(27B)     109.5
C(26)-C(27)-H(27C)        109.5
C(27)-C(28)-H(28A)        109.5
C(27)-C(28)-H(28B)        109.5
H(28A)-C(28)-H(28B)     109.5
C(26)-C(28)-H(28C)        109.5
C(26)-C(28)-H(28D)        109.5
H(28D)-C(28)-H(28C)     109.5
C(26)-C(29)-H(29A)        109.5
C(26)-C(29)-H(29B)        109.5
C(29A)-C(29)-H(29B)      109.5
C(26)-C(29)-H(29C)        109.5

18
H(29A)-C(29)-H(29C)       109.5
H(29B)-C(29)-H(29C)       109.5
N(2) - C(30) - H(30A)     109.5
N(2) - C(30) - H(30B)     109.5
H(30A) - C(30) - H(30B)   109.5
N(2) - C(30) - H(30C)     109.5
H(30A) - C(30) - H(30C)   109.5
H(30B) - C(30) - H(30C)   109.5
C(32) - C(31) - C(36)     122.5 (5)
C(32) - C(31) - N(2)      122.5 (4)
C(36) - C(31) - N(2)      114.7 (4)
C(31) - C(32) - C(33)     118.9 (5)
C(31) - C(32) - H(32A)    120.6
C(33) - C(32) - H(32A)    120.6
C(34) - C(33) - C(32)     117.7 (5)
C(32) - C(33) - C(37)     120.8 (5)
C(33) - C(34) - C(35)     121.4 (5)
C(33) - C(34) - C(35)     124.8 (5)
C(33) - C(34) - H(34A)    117.6
C(34) - C(35) - C(36)     117.6
C(34) - C(35) - C(41)     115.7 (5)
C(36) - C(35) - C(41)     122.4 (5)
C(35) - C(36) - C(31)     121.8 (5)
O(2) - C(36) - C(31)      116.4 (4)
O(2) - C(36) - C(35)      123.3 (5)
C(31) - C(36) - C(35)     120.3 (5)
C(31) - C(36) - C(35)     108.8 (6)
C(38) - C(37) - C(39)     108.2 (6)
C(38) - C(37) - C(39)     107.4 (6)
C(38) - C(37) - C(33)     109.7 (5)
C(38) - C(37) - C(33)     110.2 (5)
C(39) - C(37) - C(33)     112.3 (5)
C(37) - C(38) - H(38A)    109.5
C(37) - C(38) - H(38B)    109.5
H(38A) - C(38) - H(38B)   109.5
C(37) - C(38) - H(38C)    109.5
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H(38B) - C(38) - H(38C)   109.5
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C(35) - C(41) - C(42)     111.3 (5)
C(35) - C(41) - C(44)     108.6 (5)
C(42) - C(41) - C(44)     110.0 (5)
C(35) - C(41) - C(43)     112.2 (5)
C(42) - C(41) - C(43)     107.0 (5)
C(44) - C(41) - C(43)     107.7 (5)
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H(10C)–C(100)–H(10D)  109.5
C(106)–C(101)–C(102)  118.3(7)
C(106)–C(101)–C(100)  120.8(8)
C(102)–C(101)–C(100)  120.8(8)
C(103)–C(102)–C(101)  120.2(8)
C(103)–C(102)–H(10E)  119.9
C(101)–C(102)–H(10E)  119.9
C(102)–C(103)–C(104)  121.8(8)
C(102)–C(103)–H(10F)  119.1
C(104)–C(103)–H(10F)  119.1
C(105)–C(104)–C(103)  119.1(9)
C(105)–C(104)–H(10G)  120.5
C(103)–C(104)–H(10G)  120.5
C(104)–C(105)–C(106)  120.0(8)
C(104)–C(105)–H(10H)  120.0
C(106)–C(105)–H(10H)  120.0
C(101)–C(106)–C(105)  120.6(7)
C(101)–C(106)–H(10I)  119.7
C(105)–C(106)–H(10I)  119.7

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters (Å² x 10³) for daz.
The anisotropic displacement factor exponent takes the form:
-2 pi² \[ h^2 a^*^2 U11 + \ldots + 2 h k a^* b^* U12 \]

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Table 6. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters (Å$^2$ x $10^3$) for daz.

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