Supplementary Information

Zirconium catalysed enantioselective hydroamination/cyclisation

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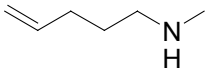
EXPERIMENTAL DETAILS

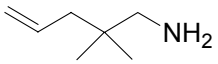
General comments. All manipulations of air-sensitive materials were carried out using standard Schlenk/glove box techniques under an atmosphere of dry argon. For inorganic and organometallic preparations, hydrocarbon and ether solvents were pre-dried over sodium wire. These were then dried under reflux 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 (δ = 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 $[Zr(CH_2Ph)_4]$[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]

SYNTHESES



1-(*N*-Methylamino)pent-4-ene (1)
Anal. calcd. for $C_6H_{13}N$: % C,72.66; H, 13.21; N, 14.12. Found: % C,72.11; H, 13.19; N, 13.46.
^{1}H-NMR ($CDCl_3$, 300 MHz): δ ppm 0.86 (bm, 1H, N*H*Me), 1.54 (m, 2H, CH_2), 2.03 (m, 2H, CH_2), 2.36 (d, 3H, NH*Me*, $^3J_{HH}$ = 6 Hz), 2.53 (m, 2H, CH_2), 4.90 (m, 2H, CH=CH_2), 5.78 (m, 1H, C*H*=CH_2).
^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz): δ ppm 29.5 (*C*H_2), 31.9 (*C*H_2), 36.9 (NH*Me*), 52.0 (*C*H_2), 114.9 (CH=*C*H_2), 138.9 (*C*H=CH_2).
IR (Golden Gate): cm^{-1} 3222, 2934, 2787, 1640, 1511, 1476, 1442, 1360, 1291, 1118, 994, 909, 801, 738.



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

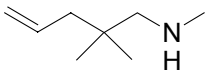
Anal. calcd. for $C_7H_{15}N$: % C, 74.27; H, 13.36; N, 12.37. Found: % C, 74.17; H, 13.34; N, 11.94.

^{1}H-NMR ($CDCl_3$, 300 MHz): δ ppm 0.78 (s, 6H, C*Me*$_2$), 0.90 (s, 2H, N*H*$_2$), 1.90 (d, 2H, C*H*$_2$CH=CH$_2$, $^3J_{HH}$ = 7 Hz), 2.38 (s, 2H, C*H*$_2$NH$_2$), 4.94 (m, 2H, CH=C*H*$_2$), 5.75 (m, 1H, C*H*=CH$_2$).

^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz): δ ppm 24.9 (C*Me*$_2$), 35.2 (*C*Me$_2$), 44.3 (*C*H$_2$CH=CH$_2$), 53.0 (C*H*$_2$NH$_2$), 117.2 (CH=*C*H$_2$), 135.7 (*C*H=CH$_2$).

IR (Golden Gate): cm^{-1} 2956, 1654, 1638, 1608, 1560, 1518, 1474, 1363,1318, 1290, 1063, 995, 911, 812, 744.

MS (EI): *m/z* 114 (M$^+$+1, 10%), 112 (M$^+$-1, 5%), 98 (35 %), 96 (18 %), 81 (22 %), 72 (31%), 71 (17 %), 67 (30 %), 57 (33 %), 56 (42 %), 55 (100%).



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).[6] 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. $LiAlH_4$ (2.00 g, 52.6 mmol) was added slowly and the reaction mixture was stirred at room temperature for 1 d.[7] 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 $MgSO_4$, filtered and the product isolated by fractional distillation. Yield = 1.53 g, 69 %.

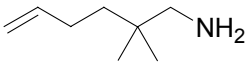
Anal. calcd. for $C_8H_{17}N$: % C, 75.52; H, 13.47; N, 11.01. Found: % C, 75.38; H, 13.52; N, 10.38.

^{1}H-NMR ($CDCl_3$, 300 MHz): δ ppm 0.74 (bs, 1H, N*H*Me), 0.82 (s, 6H, C*Me*$_2$), 1.93 (d, 2H, C*H*$_2$CH=CH$_2$, $^3J_{HH}$ = 7 Hz), 2.24 (s, 2H, C*H*$_2$NHMe), 2.36 (s, 3H, NH*Me*), 4.94 (m, 2H, CH=C*H*$_2$), 5.74 (m, 1H, C*H*=CH$_2$).

^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz): δ ppm 25.9 (C*Me*$_2$), 34.5 (*C*Me$_2$), 38.0 (NH*Me*), 45.2 (*C*H$_2$CH=CH$_2$), 63.5 (*C*H$_2$NHMe), 117.2 (CH=*C*H$_2$), 135.8 (*C*H=CH$_2$).

IR (Golden Gate): cm^{-1} 2956, 2787, 1638, 1560, 1470, 1364, 1318, 1153, 1107, 995, 911, 746.

MS (EI): *m/z* 126 (M$^+$, 15 %), 112 (100 %), 97 (23 %), 86 (33 %), 71(34 %).



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 $LiAlH_4$ in diethyl ether and isolated by fractional distillation. Yield = 6.67 g, 72 %.

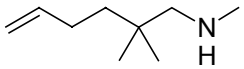
Anal. calcd. for $C_8H_{17}N$: % C, 75.52; H, 13.47; N, 11.01. Found: % C, 74.92; H, 13.48; N, 10.29.

^{1}H-NMR ($CDCl_3$, 300 MHz): δ ppm 0.79 (s, 6H, C*Me*$_2$), 0.89 (bs, 2H, N*H*$_2$), 1.22 (m, 2H, C*H*$_2$CH=CH$_2$), 1.96 (m, 2H, C*H*$_2$CMe$_2$), 2.39 (s, 2H, C*H*$_2$NH$_2$), 4.88 (m, 2H, CH=C*H*$_2$), 5.75 (m, 1H, C*H*=CH$_2$).

^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz): δ ppm 24.3 (C*Me*$_2$), 28.1 (*C*H$_2$CMe$_2$), 34.2 (*C*Me$_2$), 38.3 (C*H*$_2$CH=CH$_2$), 52.5 (*C*H$_2$NH$_2$), 113.6 (CH=*C*H$_2$), 139.2 (*C*H=CH$_2$).

IR (Golden Gate): cm^{-1} 2956, 2863, 1654, 1641, 1560, 1474, 1364, 1063, 994, 907, 807, 732.

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).

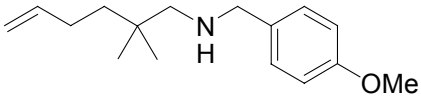
Anal. calcd. for $C_9H_{19}N$: % C, 76.53; H, 13.56; N, 9.92. Found: % C, 75.88; H, 13.60; N, 9.11.

^{1}H-NMR ($CDCl_3$, 300 MHz): δ ppm 0.66 (bs, 1H, N*H*Me), 0.84 (s, 6H, C*Me*$_2$), 1.24 (m, 2H, C*H*$_2$CH=CH$_2$), 1.95 (m, 2H, C*H*$_2$CMe$_2$), 2.27 (s, 2H, C*H*$_2$NHMe), 2.37 (s, 3H, NH*Me*), 4.86 (m, 2H, CH=C*H*$_2$), 5.72 (m, 1H, C*H*=CH$_2$).

^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz): δ ppm 25.3 (C*Me*$_2$), 28.2 (*C*H$_2$CMe$_2$), 33.5 (*C*Me$_2$), 37.4 (NH*Me*), 39.2 (*C*H$_2$CH=CH$_2$), 63.0 (*C*H$_2$NHMe), 113.6 (CH=*C*H$_2$), 139.3 (*C*H=CH$_2$).

IR (Golden Gate): cm^{-1} 2934, 2787, 1654, 1474, 1364, 1153, 1108, 994, 907, 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 $NaBH_4$ (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 $MgSO_4$, 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 %.

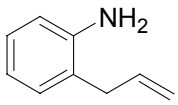
Anal. calcd. for $C_{16}H_{25}NO$: % C, 77.68; H, 10.19; N, 5.66. Found: % C, 77.61; H, 10.21; N, 5.70.

^{1}H-NMR ($CDCl_3$, 300 MHz): δ ppm 0.81 (s, 6H, C*Me*$_2$), 1.11 (bs, 1H, N*H*), 1.26 (m, 2H, C*H*$_2$CH=CH$_2$), 1.90 (m, 2H, C*H*$_2$CMe$_2$), 2.27 (s, 2H, C*H*$_2$NH), 3.65 (s, 2H, NC*H*$_2$Ar) 3.72 (s, 3H, ArO*Me*), 4.85 (m, 2H, CH=C*H*$_2$), 5.73 (m, 1H, C*H*=CH$_2$), 6.79 (d, 2H, Ar*H*, $^3J_{HH}$ = 8 Hz), 7.17 (d, 2H, Ar*H*, $^3J_{HH}$ = 8 Hz).

^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz): δ ppm 26.0 (C*Me*$_2$), 28.9 (C*H*$_2$CMe$_2$), 34.3 (*C*Me$_2$), 39.7 (*C*H$_2$CH=CH$_2$), 54.5 (N*C*H$_2$Ar), 55.7 (ArO*Me*), 60.0 (*C*H$_2$NH), 114.0 (Ar), 114.2 (CH=*C*H$_2$), 129.5 (Ar), 133.5 (Ar), 140.1 (*C*H=CH$_2$), 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 %)



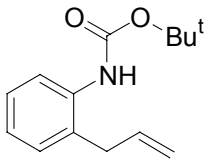
***o*-Allylaniline**

Anal. calcd. for $C_9H_{11}N$: % C, 81.16; H, 8.32; N, 10.52. Found: % C, 80.92; H, 8.40; N, 10.52.

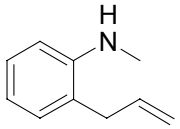
^{1}H-NMR ($CDCl_3$, 300 MHz): δ ppm 3.28 (d, 2H, C*H*$_2$CH=CH$_2$, $^3J_{HH}$ = 6 Hz), 3.59 (bs, 2H, N*H*$_2$), 5.09 (m, 2H, CH$_2$CH=C*H*$_2$), 5.93 (m, 1H, CH$_2$=C*H*CH$_2$), 6.65 (d, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz), 6.73 (dt, 1H, Ar*H*-, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.02 – 7.08 (m, 2H, Ar*H*).

^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz): δ ppm 36.2 (*C*H$_2$CH=CH$_2$), 115.6 (Ar), 115.9 (CH$_2$=CH*C*H$_2$), 118.6 (Ar), 123.8 (Ar), 127.3 (Ar), 129.9 (Ar), 135.7 (CH$_2$*C*H=CH$_2$), 144.6 (Ar).

IR (Golden Gate): cm^{-1} 3452, 3376, 3072, 3019, 1620, 1583, 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 %).



***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): δ ppm 1.51 (s, 9H, OC*Me*$_3$), 3.36 (d, 2H, C*H*$_2$CH=CH$_2$, $^3J_{HH}$ = 6 Hz), 5.10 (m, 2H, CH=C*H*$_2$), 5.95 (m, 1H, C*H*=CH$_2$), 6.46 (bs, 1H, N*H*), 7.03 (dt, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 1 Hz), 7.13 (dd, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.23 (dt, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 7.78 (bd, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz).
^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz): δ ppm 28.2 (OC*Me*$_3$), 36.3 (*C*H$_2$CH=CH$_2$), 80.1 (O*C*Me$_3$), 116.4 (CH=*C*H$_2$), 121.9 (Ar), 123.8 (Ar), 127.2 (Ar), 129.8 (Ar), 135.7 (*C*H=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^+, 46 %), 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): δ ppm 2.83 (s, 3H, NH*Me*), 3.26 (d, 2H, C*H*$_2$CH=CH$_2$, $^3J_{HH}$ = 6 Hz), 3.74 (bs, 1H, N*H*Me), 5.08 (m, 2H, CH=C*H*$_2$), 5.93 (m, 1H, C*H*=CH$_2$), 6.63 (d, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz), 6.70 (dt, 1H, Ar*H*, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.03 (dd, 1H, Ar*H*, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.18 (dt, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz).

$^{13}C\{^1H\}$-NMR ($CDCl_3$, 75 MHz): δ ppm 30.5 (NH*Me*), 36.2 (*C*H_2CH=CH_2), 109.7 (Ar), 116.0 (CH=*C*H_2), 116.9 (Ar), 123.4 (Ar), 127.6 (Ar), 129.5 (Ar), 135.9 (*C*H=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^1Cl_2]

An ampoule with stirrer bar was charged with H_2L^1 (420 mg, 0.62 mmol). To a Schlenk vessel was added [$Zr(NMe_2)_2Cl_2(THF)_2$] (245 mg, 0.62 mmol), which was dissolved in dichloromethane (30 ml) to give a pale green solution. The solution of [$Zr(NMe_2)_2Cl_2(THF)_2$] was added to the ampoule which was degassed and sealed before heating at 40 ºC for 5 d. During this time the solution became colourless. Filtration through a cannula and removal of volatiles under reduced pressure gave an off-white solid which was dissolved in toluene and the solution filtered. The solution was then concentrated and stored at –30 ºC for 48 h to yield a white crystalline solid. The solid was isolated by filtration and dried *in vacuo*. Yield = 366 mg, 70 %.

Anal. calcd. for $C_{46}H_{62}Cl_2N_2O_2Zr$: C, 66.00; H, 7.47; N, 3.35. Found: C, 67.73; H, 7.58; N, 2.97.
^1H-NMR (CD_2Cl_2, 300 MHz): δ ppm 1.35 (s, 18H, C*Me*$_3$), 1.53 (s, 18H, C*Me*$_3$), 1.90 (s, 6H, Ar*Me*), 2.63 (s, 6H, N*Me*), 3.92 (d, 2H, NC*H*$_2$, $^2J_{HH}$ = 12 Hz), 5.41 (d, 2H, NC*H*$_2$, $^2J_{HH}$ = 12 Hz), 7.15 (d, 2H, Ar*H*, $^4J_{HH}$ = 2 Hz), 7.32 (d, 2H, Ar*H*, $^3J_{HH}$ = 8 Hz), 7.41 (d, 2H, Ar*H*, $^4J_{HH}$ = 2 Hz), 7.49 (t, 2H, Ar*H*, $^3J_{HH}$ = 8 Hz), 7.61 (d, 2H, Ar*H*, $^3J_{HH}$ = 9 Hz).
$^{13}C\{^1H\}$-NMR (CD_2Cl_2, 75 MHz): δ ppm 21.2 (Ar*Me*), 30.3 (C*Me*$_3$), 31.5 (C*Me*$_3$), 34.4 (*C*Me$_3$), 35.3 (*C*Me$_3$), 45.7 (N*Me*), 62.8 (N*C*H$_2$), 119.6 (Ar), 125.0, 125.6, 126.7, 129.2, 129.4, 132.5, 136.2, 140.1, 143.3, 149.4, 157.6.
IR (Nujol mull): cm^{-1} 1594, 1573, 1413, 1359, 1305, 1257, 1239 (s, C-O), 1203, 1172, 1156, 1125, 1043, 1000, 973, 919, 898, 881, 856, 834, 816, 791, 787, 751, 742, 731, 696, 668, 648, 631, 621, 559.
MS (EI): *m/z* 836 $[M]^+$, 808 $[M\text{-}Cl]^+$.

[ZrL^2Cl_2]

The complex was synthesised in an analogous manner to [ZrL^1Cl_2] using H_2L^2 (500 mg, 0.77 mmol) and [$Zr(NMe_2)_2Cl_2(THF)_2$] (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 $C_{44}H_{58}Cl_2N_2O_2Zr$: C, 65.32; H, 7.23; N, 3.46. Found: C, 64.73; H, 7.21; N, 3.52.

^1H-NMR (CD_2Cl_2, 300 MHz): δ ppm 1.16 (s, 9H, C*Me*$_3$), 1.20 (s, 9H, C*Me*$_3$), 1.29 (s, 9H, C*Me*$_3$), 1.52 (s, 9H, C*Me*$_3$), 1.54 (s, 3H, Ar*Me*), 2.16 (s, 3H, Ar*Me*), 2.95 (s, 3H, N*Me*), 3.54 (s, 3H, N*Me*), 6.32 (d, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz), 6.51 (d, 1H, Ar*H*, $^3J_{HH}$ = 7 Hz), 6.53 (d, 1H, Ar*H*, $^4J_{HH}$ = 2 Hz), 6.80 (t, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz), 6.91 (d, 1H, Ar*H*, $^4J_{HH}$ = 2 Hz), 6.96 (d, 1H, Ar*H*, $^4J_{HH}$ = 2 Hz), 7.34 (d, 1H, Ar*H*, $^4J_{HH}$ = 2 Hz), 7.39 (dd, 1H, Ar*H*, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 2 Hz), 7.58 (d, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz), 7.62 (t, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz).

$^{13}C\{^1H\}$-NMR (CD_2Cl_2, 75 MHz): δ ppm 21.0 (Ar*Me*), 21.6 (Ar*Me*), 29.3 (C*Me*$_3$), 29.9 (C*Me*$_3$), 31.3 (C*Me*$_3$), 31.5 (C*Me*$_3$), 34.6 (*C*Me$_3$), 34.8 (*C*Me$_3$), 35.0 (*C*Me$_3$), 35.2 (*C*Me$_3$), 47.8 (N*Me*), 51.1 (N*Me*), 116.7 (Ar), 118.7, 119.8, 121.2, 122.9, 123.5, 126.6, 127.9, 128.7, 129.0, 129.2, 133.4, 136.7, 137.6, 139.7, 139.7, 142.9, 144.1, 144.2, 144.4, 146.3, 147.2, 152.3, 154.9.

IR (Nujol mull): cm^{-1} 1594, 1574, 1417, 1410, 1360, 1297, 1259 (s, C-O), 1214, 1201, 1164, 1132, 1108, 1045, 1016, 942, 917, 895, 875, 855, 845, 804, 794, 776, 771, 754, 740, 690, 667, 650, 557.

MS (EI): *m/z* 809 $[M]^+$, 773 $[M\text{-}Cl]^+$.

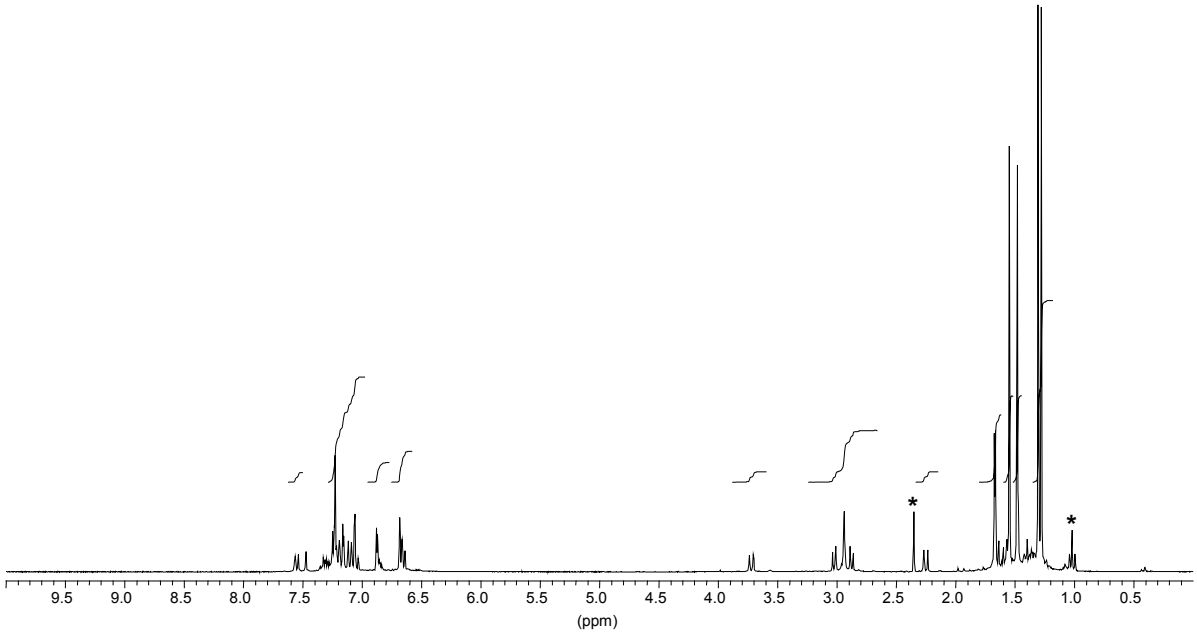
[Zr(*rac*-$L^{2'}$)CH_2Ph)]

An ampoule was charged with *rac*-$H_2\mathbf{L^2}$ (212 mg, 0. 33 mmol) and [$Zr(CH_2Ph)_4$] (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.

^{1}H-NMR (C_6D_5Br, 300 MHz): δ ppm 1.28 (s, 9H, C*Me*$_3$), 1.30 (s, 9H, C*Me*$_3$), 1.48 (s, 9H, C*Me*$_3$), 1.54 (s, 9H, C*Me*$_3$), 1.66 (s, 3H, Ar*Me*), 1.67 (s, 3H, Ar*Me*), 2.25 (d, 1H, ZrC*H*$_2$Ph, $^2J_{HH}$ = 10 Hz), 2.87 (d, 1H, ZrC*H*$_2$N, $^2J_{HH}$ = 7 Hz), 2.94 (bs, 3H, N*Me*), 3.02 (d, 1H, ZrC*H*$_2$N, $^2J_{HH}$ = 7 Hz), 3.72 (d, 1H, Zr*C*H$_2$Ph, $^2J_{HH}$ = 10 Hz), 6.64 – 6.68 (m, 3H, Ar*H*), 6.87 (d, 1H, Ar*H*, $^4J_{HH}$ = 2 Hz), 7.03 – 7.25 (m, 10H, Ar*H*), 7.55 (d, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz).

^{13}C{^{1}H}-NMR (C_6D_5Br, 75 MHz): δ ppm 21.4 (Ar*Me*), 21.9 (Ar*Me*), 30.5 (C*Me*$_3$), 30.6 (C*Me*$_3$), 32.0 (C*Me*$_3$), 32.1 (C*Me*$_3$), 34.5 (*C*Me$_3$), 34.6 (*C*Me$_3$), 35.2 (*C*Me$_3$), 35.3 (*C*Me$_3$), 46.3 (N*Me*), 53.9 (Zr*C*H$_2$N), 76.1 (Zr*C*H$_2$Ph), 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^+-CH_2Ph, 39 %), 721 (100 %).



^{1}H NMR spectrum of [Zr(*rac*-$L^{2'}$)CH_2Ph] in C_6D_5Br at 298 K. *Traces of toluene and pentane.

[Zr({*S*}-$L^{2'}$)CH_2Ph]

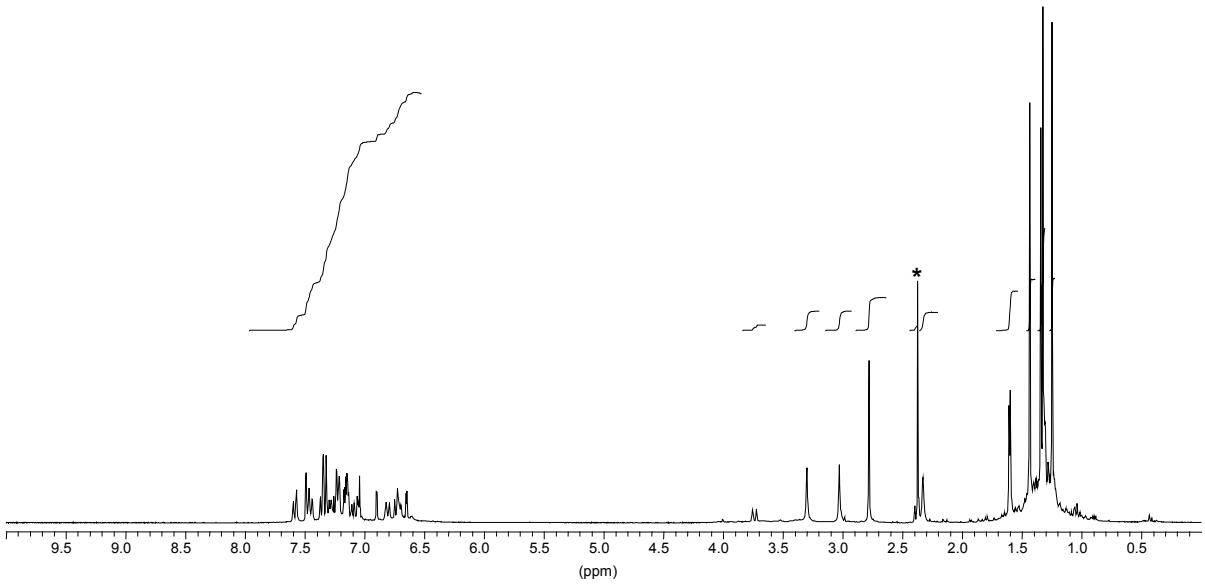
The complex was synthesised in a similar manner to [Zr(*rac*-$\mathbf{L^{2'}}$)CH_2Ph] using (*S*)-$H_2\mathbf{L^2}$. Spectroscopic data was identical to that observed for [Zr(*rac*-$\mathbf{L^{2'}}$)CH_2Ph].

In situ characterisation of [Zr(*rac*-L^2)CH_2Ph)]$^+$.

An NMR tube sealed with a Young's concentric stopcock was charged with [Zr(*rac*-$\mathbf{L^{2'}}$)CH_2Ph] (20 mg, 0.024 mmol) and [$PhNMe_2H$]$^+$[$B(C_6F_5)_4$]$^-$ (19.4 mg, 0.024 mmol). Addition of d_5-bromobenzene gave rise to a yellow/orange solution.

^{1}H-NMR (C_6D_5Br, 300 MHz): δ ppm 1.25 (s, 9H, C*Me*$_3$), 1.32 (s, 9H, C*Me*$_3$), 1.34 (s, 9H, C*Me*$_3$), 1.43 (C*Me*$_3$), 1.60 (s, 3H, Ar*Me*), 1.61 (s, 3H, Ar*Me*), 2.33 ([PhN*Me*$_2$H]$^+$), 2.38 (d, 1H, ZrC*H*$_2$Ph, $^2J_{HH}$ = 10 Hz), 2.78 (s, 6H, PhN*Me*$_2$), 3.03 (bs, 3H, N*Me*), 3.30 (bs, 3H, N*Me*), 3.74 (d, 1H, ZrC*H*$_2$Ph, $^2J_{HH}$ = 10 Hz), 6.64 – 7.60 (Ar*H*).

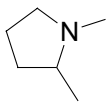
$^{13}C\{^{1}H\}$-NMR (C_6D_5Br, 75 MHz): δ ppm 21.0 (Ar*Me*), 21.5 (Ar*Me*), 30.1 (C*Me*$_3$), 30.4 (C*Me*$_3$), 31.6 (C*Me*$_3$), 31.8 (C*Me*$_3$), 34.7 (*C*Me$_3$), 34.8 (*C*Me$_3$), 34.9 (*C*Me$_3$), 35.0 (*C*Me$_3$), 43.4 ([PhN*Me*$_2$H]$^+$), 43.7 (PhN*Me*$_2$), 44.7 (N*Me*), 47.6 (N*Me*), 76.4 (Zr*C*H$_2$Ph), 115.5 (Ar), 116.8, 116.9, 117.3, 118.3, 120.5, 123.3, 123.4, 124.2, 125.9, 128.5, 128.7, 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.



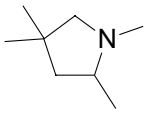
^{1}H NMR spectrum of [Zr(*rac*-L^2)CH$_2$Ph]$^+$[B(C$_6$F$_5$)$_4$]$^-$ in C_6D_5Br at 298 K. *Toluene .

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

Typical catalytic reaction.
In the glove box, the precatalyst [Zr(*rac*-**L$^{2'}$**)CH$_2$Ph] or [Zr({*S*}-**L$^{2'}$**)CH$_2$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$_6$F$_5$)$_4$ (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 eqivalents). 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.

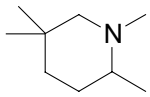


1,2-Dimethylpyrrolidine (6)
This cyclised amine was synthesised as described in the typical NMR-scale reactions.
^{1}H-NMR (C_6D_5Br, 300 MHz): δ ppm 1.16 (d, 3H, CH*Me*, $^3J_{HH}$ = 6 Hz), 1.46 (m, 1H, C*H*$_2$), 1.66 (m, 1H, C*H*$_2$), 1.78 (m, 1H, C*H*$_2$), 1.92 (m, 1H, C*H*$_2$), 2.06 – 2.21 (m, 2H, C*H*Me and NC*H*$_2$), 2.32 (s, 3H, N*Me*), 3.07 (m, 1H, NC*H*$_2$).
$^{13}C\{^{1}H\}$-NMR (C_6D_5Br, 75 MHz): δ ppm 19.2 (CH*Me*), 22.2 (*C*H$_2$), 33.6 (*C*H$_2$), 40.5 (N*Me*), 57.6 (NCH$_2$), 61.9 (*C*HMe).

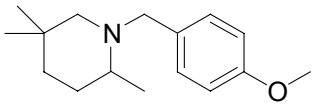


1,2,4,4-Tetramethylpyrrolidine (7)

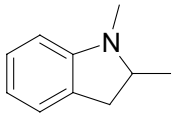
This cyclised amine was synthesised as described in the typical NMR-scale reactions.
^{1}H-NMR (C_6D_5Br, 300 MHz): δ ppm 1.10 (s, 3H, C*Me*$_2$), 1.17 (d, 3H, CH*Me*, $^3J_{HH}$ = 6 Hz), 1.24 (s, 3H, C*Me*$_2$), 1.34 (dd, 1H, C*H*$_2$, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 9 Hz), 1.75 (dd, 1H, C*H*$_2$, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 7 Hz), 2.07 (d, 1H, NC*H*$_2$, $^2J_{HH}$ = 9 Hz), 2.29 (s, 3H, N*Me*), 2.29 (m, 1H, C*H*Me), 2.82 (d, 1H, NC*H*$_2$, $^2J_{HH}$ = 9 Hz).
^{13}C{^{1}H}-NMR (C_6D_5Br, 75 MHz): δ ppm 19.6 (CH*Me*), 29.5 (C*Me*$_2$), 31.4 (C*Me*$_2$), 35.8 (*C*Me$_2$), 40.7 (N*Me*), 49.9 (*C*H$_2$), 62.4 (*C*HMe), 72.1 (N*C*H$_2$).



1,2,5,5-Tetramethylpiperidine (8)
This cyclised amine was synthesised as described in the typical NMR-scale reactions.
^{1}H-NMR (C_6D_5Br, 300 MHz): δ ppm 0.97 (s, 3H, C*Me*$_2$), 1.15 (d, 3H, CH*Me*, $^3J_{HH}$ = 6 Hz), 1.18 (s, 3H, C*Me*$_2$), 1.24 (m, 1H, C*H*$_2$), 1.39 – 1.55 (m, 3H, C*H*$_2$), 1.81 (m, 1H, C*H*Me), 1.85 (d, 1H, NC*H*$_2$, $^2J_{HH}$ = 11 Hz), 2.25 (s, 3H, N*Me*), 2.42 (dd, 1H, NC*H*$_2$, $^2J_{HH}$ = 11 Hz, $^4J_{HH}$ = 2 Hz).
^{13}C{^{1}H}-NMR (C_6D_5Br, 75 MHz): δ ppm 20.4 (CH*Me*), 25.4 (C*Me*$_2$), 30.2 (C*Me*$_2$), 31.3 (*C*Me$_2$), 31.9 (*C*H$_2$), 38.1 (*C*H$_2$), 44.0 (N*Me*), 60.0 (*C*HMe), 69.3 (N*C*H$_2$).



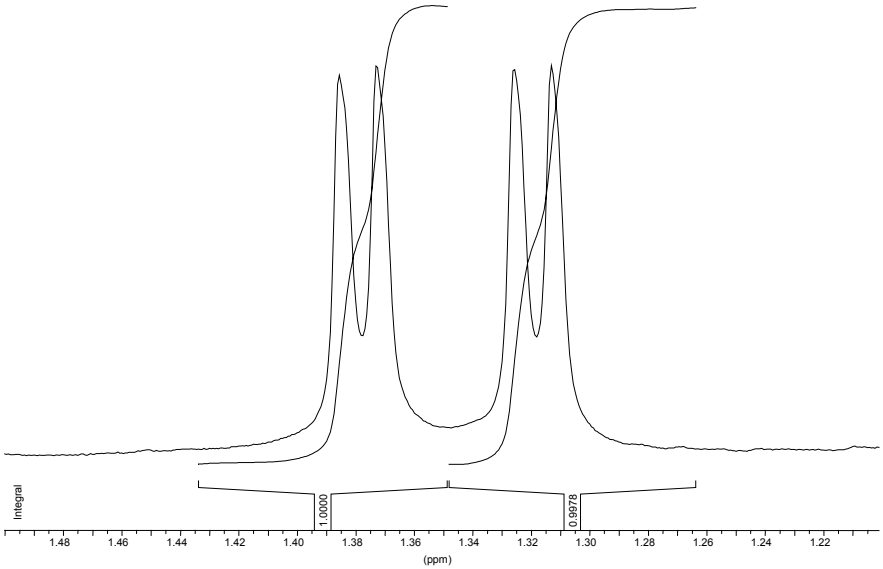
1-(*p*-methoxybenzyl)-2,5,5-trimethylpiperidine (9)
This cyclised amine was synthesised as described in the typical NMR-scale reactions.
^{1}H-NMR (C_6D_5Br, 300 MHz): δ ppm 0.91 (s, 3H, C*Me*$_2$), 1.08 (s, 3H, C*Me*$_2$), 1.23 (d, 3H, CH*Me*, $^3J_{HH}$ = 6 Hz), 1.24 (m, 1H, C*H*$_2$), 1.43 (m, 1H, C*H*$_2$), 1.57 – 1.65 (m, 2H, C*H*$_2$), 1.84 (d, 1H, NC*H*$_2$, $^2J_{HH}$ = 11 Hz), 2.36 (m, 1H, C*H*Me), 2.50 (dd, 1H, NC*H*$_2$, $^2J_{HH}$ = 11 Hz, $^4J_{HH}$ = 2 Hz), 3.16 (d, 1H, NC*H*$_2$Ar, $^2J_{HH}$ = 14 Hz), 3.68 (s, 3H, ArO*Me*), 4.05 (d, 1H, NC*H*$_2$Ar, $^2J_{HH}$ = 14 Hz), 6.96 (d, 2H, Ar*H*, $^3J_{HH}$ = 9 Hz), 7.38 (d, 2H, Ar*H*, $^3J_{HH}$ = 9 Hz).
^{13}C{^{1}H}-NMR (C_6D_5Br, 75 MHz): δ ppm 19.1 (CH*Me*), 25.6 (C*Me*$_2$), 29.2 (C*Me*$_2$), 31.1 (*C*Me$_2$), 31.9 (*C*H$_2$), 37.3 (*C*H$_2$), 55.2 (ArO*Me*), 57.3 (*C*HMe), 58.1 (N*C*H$_2$Ar), 63.7 (N*C*H$_2$), 114.2 (Ar), 122.7, 130.2, 159.2.



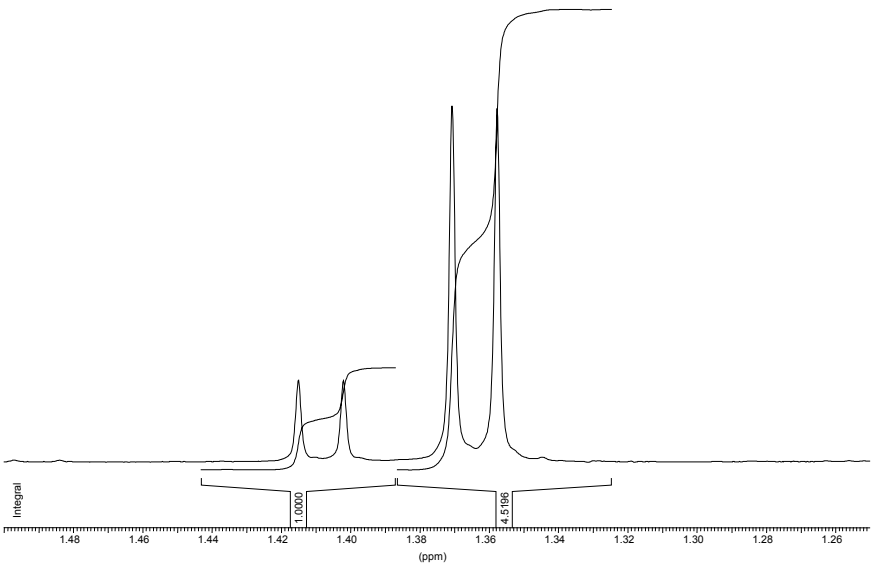
1,2-Dimethylindoline (10)
This cyclised amine was synthesised as described in the typical NMR-scale reactions.
^{1}H-NMR (C_6D_5Br, 400 MHz): δ ppm 1.26 (d, 3H, CH*Me*, $^3J_{HH}$ = 6 Hz), 2.53 (dd, 1H, C*H*$_2$, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 10 Hz), 2.63 (s, 3H, N*Me*), 3.01 (dd, 1H, C*H*$_2$, $^2J_{HH}$ = 15 Hz, $^3J_{HH}$ = 8 Hz), 3.29 (m, 1H, C*H*Me), 6.49 (d, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz), 6.86 (t, 1H, Ar*H*, $^3J_{HH}$ = 7 Hz), 7.13 (d, 1H, Ar*H*, $^3J_{HH}$ = 7 Hz), 7.21 (t, 1H, Ar*H*, $^3J_{HH}$ = 8 Hz).
^{13}C{^{1}H}-NMR (C_6D_5Br, 100 MHz): δ ppm 19.0 (CH*Me*), 34.2 (N*Me*), 37.7 (*C*H$_2$), 63.3 (*C*HMe), 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-(triflouromethyl)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 $CDCl_3$ (stored over 4 Å molecular sieves) and the enantiomeric excesses determined by ^{1}H NMR spectroscopy at various temperatures (in order to obtain the best resolution). Comparisons were

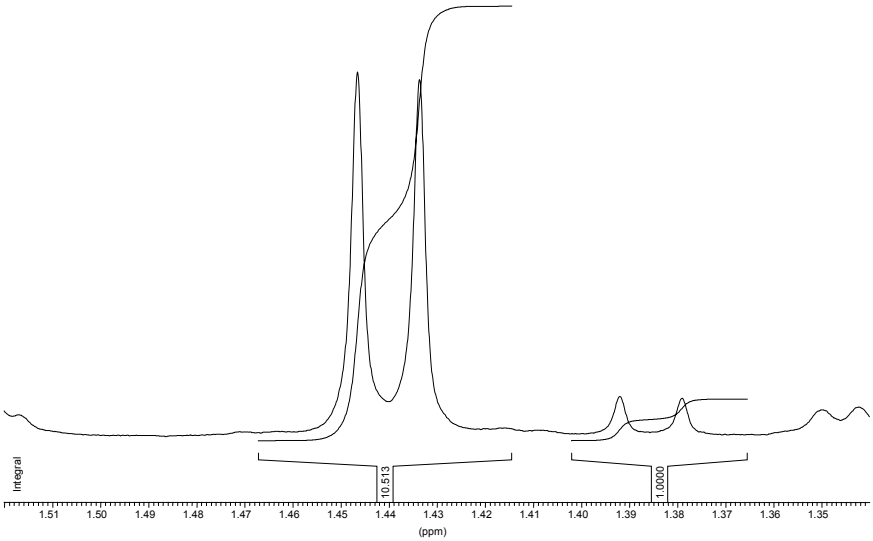
made with racemic products in all cases. The spectrum of *rac*-**6**/Mosher's acid and that obtained from the enantioselective reaction (ee = 64%) is shown below. The N-CH*Me* doublet resonances proved the most useful, but ee values were confirmed with reference to other less well resolved peaks also. The spectrum of **8**(ee = 82%)/Mosher's acid is also given.



N-CH*Me* region of ^{1}H NMR spectrum of rac-1,2-dimethylpyrrolidine (6) + [(+)-Mosher's acid] in $CDCl_3$ at 253 K.



N-CH*Me* region of ^{1}H NMR spectrum of non-racemic 1,2-dimethylpyrrolidine + [(+)-Mosher's acid] in $CDCl_3$ at 253 K.



N-CH*Me* region of ^{1}H NMR spectrum of non-racemic 1,2,5,5-tetramethylpiperidine + [(+)-Mosher's acid] in $CDCl_3$ at 298 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 $MgSO_4$ 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.

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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

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COSIER, J. & GLAZER, A. M. (1986), J. Appl. Cryst. 19, 105-107.
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SHELDRICK,G.M.(1996), SHELX-96 (beta-test) (including SHELXS and SHELXL)
SIEMENS (1994), SMART User's manual, Siemens Industrial Automation Inc, Madison, Wis. USA.

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

Identification code	daz
Empirical formula	C51 H66 Cl2 N2 O2 Zr
Formula weight	901.18
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 22.7186(9) A alpha = 90 deg. b = 10.2902(4) A beta = 99.4450(10) deg. c = 20.7759(9) A gamma = 90 deg.
Volume, Z	4791.1(3) A^3, 4
Density (calculated)	1.249 Mg/m^3
Absorption coefficient	0.381 mm^-1
F(000)	1904
Crystal size	0.35 x 0.26 x 0.13 mm
Theta range for data collection	1.82 to 29.43 deg.
Limiting indices	-30<=h<=28, -13<=k<=13, -28<=l<=26
Reflections collected	30886
Independent reflections	11948 [R(int) = 0.1341]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9522 and 0.8783
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11948 / 0 / 540
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0842, wR2 = 0.1449
R indices (all data)	R1 = 0.1978, wR2 = 0.1919
Largest diff. peak and hole	0.715 and -1.326 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for daz. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Zr(1)	2625(1)	18331(1)	6116(1)	21(1)
Cl(1)	2225(1)	19741(2)	6871(1)	37(1)
Cl(2)	2369(1)	19844(1)	5208(1)	31(1)
O(1)	3445(2)	18725(3)	6506(2)	27(1)
O(2)	2520(2)	16725(3)	6609(2)	24(1)
N(1)	3322(2)	17395(4)	5397(2)	20(1)
N(2)	1807(2)	17013(4)	5496(2)	20(1)
C(1)	2152(2)	13256(5)	4778(3)	32(1)
C(2)	2652(2)	14008(5)	5185(3)	23(1)
C(3)	3047(2)	13346(5)	5652(3)	28(1)
C(4)	3518(2)	13991(5)	6028(3)	29(1)
C(5)	3603(2)	15303(5)	5934(3)	25(1)
C(6)	3217(2)	15986(5)	5463(2)	20(1)
C(7)	2727(2)	15364(5)	5096(3)	20(1)
C(8)	2258(2)	16005(5)	4604(3)	19(1)
C(9)	1795(2)	16744(5)	4797(2)	18(1)
C(10)	1339(2)	17221(5)	4329(3)	25(1)
C(11)	1334(2)	16972(6)	3678(3)	33(1)
C(12)	1788(2)	16263(6)	3482(3)	31(1)
C(13)	2255(2)	15783(5)	3936(3)	22(1)
C(14)	2758(2)	15084(6)	3688(3)	33(1)
C(15)	3250(2)	17860(5)	4703(3)	25(1)
C(16)	3930(2)	17795(5)	5710(3)	24(1)
C(17)	4433(2)	17532(5)	5438(3)	26(1)
C(18)	4986(2)	17972(5)	5742(3)	26(1)
C(19)	5014(2)	18660(5)	6327(3)	27(1)
C(20)	4518(2)	18940(5)	6616(3)	22(1)
C(21)	3968(2)	18493(5)	6284(3)	22(1)
C(22)	5541(3)	17710(6)	5425(3)	34(1)
C(23)	5456(4)	18239(9)	4743(4)	82(3)
C(24)	5651(3)	16249(7)	5399(4)	66(2)
C(25)	6108(3)	18313(10)	5811(5)	103(4)
C(26)	4557(2)	19717(5)	7251(3)	29(1)
C(27)	4192(3)	20981(6)	7127(3)	41(2)
C(28)	5206(3)	20094(7)	7528(3)	46(2)
C(29)	4314(3)	18910(7)	7776(3)	45(2)
C(30)	1307(2)	17888(5)	5622(3)	27(1)
C(31)	1741(2)	15816(5)	5871(2)	18(1)
C(32)	1302(2)	14909(5)	5673(3)	22(1)
C(33)	1243(2)	13851(5)	6082(3)	25(1)
C(34)	1629(2)	13782(5)	6672(3)	25(1)
C(35)	2071(2)	14694(5)	6891(3)	22(1)
C(36)	2119(2)	15737(5)	6465(3)	22(1)
C(37)	752(2)	12819(5)	5896(3)	28(1)
C(38)	365(3)	12744(8)	6420(4)	63(2)
C(39)	349(3)	13127(7)	5245(4)	66(2)
C(40)	1030(3)	11496(6)	5828(4)	60(2)
C(41)	2449(3)	14624(5)	7567(3)	28(1)
C(42)	3119(3)	14632(7)	7527(3)	47(2)
C(43)	2326(3)	13380(6)	7936(3)	46(2)
C(44)	2293(3)	15794(7)	7969(3)	47(2)
C(100)	802(4)	14330(9)	8827(4)	85(3)
C(101)	427(3)	13268(8)	8494(3)	54(2)
C(102)	674(4)	12050(7)	8398(4)	55(2)
C(103)	322(4)	11074(8)	8116(4)	70(2)

C(104)	-288(5)	11234(9)	7925(4)	75(3)
C(105)	-535(4)	12400(10)	8010(4)	69(2)
C(106)	-173(3)	13439(8)	8296(3)	56(2)

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

Zr(1)-O(1)	1.948(3)
Zr(1)-O(2)	1.978(4)
Zr(1)-Cl(1)	2.4200(15)
Zr(1)-Cl(2)	2.4421(15)
Zr(1)-N(2)	2.484(4)
Zr(1)-N(1)	2.539(4)
O(1)-C(21)	1.365(6)
O(2)-C(36)	1.366(6)
O(1)-Zr(1)-O(2)	98.46(15)
O(1)-Zr(1)-Cl(1)	92.34(11)
O(2)-Zr(1)-Cl(1)	94.36(11)
O(1)-Zr(1)-Cl(2)	106.18(12)
O(2)-Zr(1)-Cl(2)	153.97(10)
Cl(1)-Zr(1)-Cl(2)	92.92(5)
O(1)-Zr(1)-N(2)	155.86(14)
O(2)-Zr(1)-N(2)	70.70(13)
Cl(1)-Zr(1)-N(2)	109.59(10)
Cl(2)-Zr(1)-N(2)	83.32(10)
O(1)-Zr(1)-N(1)	71.18(14)
O(2)-Zr(1)-N(1)	97.32(14)
Cl(1)-Zr(1)-N(1)	161.00(10)
Cl(2)-Zr(1)-N(1)	83.07(10)
N(2)-Zr(1)-N(1)	88.47(13)

Symmetry transformations used to generate equivalent atoms:

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

Zr(1)-O(1)	1.948(3)
Zr(1)-O(2)	1.978(4)
Zr(1)-Cl(1)	2.4200(15)
Zr(1)-Cl(2)	2.4421(15)
Zr(1)-N(2)	2.484(4)
Zr(1)-N(1)	2.539(4)
O(1)-C(21)	1.365(6)
O(2)-C(36)	1.366(6)
N(1)-C(6)	1.479(6)
N(1)-C(16)	1.486(6)
N(1)-C(15)	1.502(6)
N(2)-C(9)	1.474(6)
N(2)-C(31)	1.479(6)
N(2)-C(30)	1.505(6)
C(1)-C(2)	1.513(7)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.388(7)
C(2)-C(7)	1.421(7)
C(3)-C(4)	1.386(8)
C(3)-H(3A)	0.9500

C(4)-C(5)	1.383(7)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.393(7)
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
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
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
C(18)-C(19)	1.399(8)
C(18)-C(22)	1.540(8)
C(19)-C(20)	1.391(7)
C(19)-H(19A)	0.9500
C(20)-C(21)	1.401(7)
C(20)-C(26)	1.534(7)
C(22)-C(23)	1.500(9)
C(22)-C(24)	1.527(9)
C(22)-C(25)	1.533(9)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-C(28)	1.541(8)
C(26)-C(27)	1.541(8)
C(26)-C(29)	1.543(8)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-C(32)	1.378(7)
C(31)-C(36)	1.385(7)
C(32)-C(33)	1.401(7)
C(32)-H(32A)	0.9500
C(33)-C(34)	1.387(7)

C(33)-C(37)	1.542(7)
C(34)-C(35)	1.395(7)
C(34)-H(34A)	0.9500
C(35)-C(36)	1.407(7)
C(35)-C(41)	1.522(7)
C(37)-C(38)	1.507(8)
C(37)-C(40)	1.517(8)
C(37)-C(39)	1.537(9)
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(40)-H(40A)	0.9800
C(40)-H(40B)	0.9800
C(40)-H(40C)	0.9800
C(41)-C(42)	1.538(8)
C(41)-C(44)	1.540(8)
C(41)-C(43)	1.540(8)
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800
C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800
C(44)-H(44C)	0.9800
C(100)-C(101)	1.485(10)
C(100)-H(10B)	0.9800
C(100)-H(10C)	0.9800
C(100)-H(10D)	0.9800
C(101)-C(106)	1.369(10)
C(101)-C(102)	1.400(10)
C(102)-C(103)	1.356(11)
C(102)-H(10E)	0.9500
C(103)-C(104)	1.386(11)
C(103)-H(10F)	0.9500
C(104)-C(105)	1.349(12)
C(104)-H(10G)	0.9500
C(105)-C(106)	1.418(11)
C(105)-H(10H)	0.9500
C(106)-H(10I)	0.9500

O(1)-Zr(1)-O(2)	98.46(15)
O(1)-Zr(1)-Cl(1)	92.34(11)
O(2)-Zr(1)-Cl(1)	94.36(11)
O(1)-Zr(1)-Cl(2)	106.18(12)
O(2)-Zr(1)-Cl(2)	153.97(10)
Cl(1)-Zr(1)-Cl(2)	92.92(5)
O(1)-Zr(1)-N(2)	155.86(14)
O(2)-Zr(1)-N(2)	70.70(13)
Cl(1)-Zr(1)-N(2)	109.59(10)
Cl(2)-Zr(1)-N(2)	83.32(10)
O(1)-Zr(1)-N(1)	71.18(14)
O(2)-Zr(1)-N(1)	97.32(14)
Cl(1)-Zr(1)-N(1)	161.00(10)
Cl(2)-Zr(1)-N(1)	83.07(10)
N(2)-Zr(1)-N(1)	88.47(13)
C(21)-O(1)-Zr(1)	130.6(3)
C(36)-O(2)-Zr(1)	129.9(3)
C(6)-N(1)-C(16)	112.6(4)
C(6)-N(1)-C(15)	114.1(4)

C(16)-N(1)-C(15)	106.1(4)
C(6)-N(1)-Zr(1)	101.0(3)
C(16)-N(1)-Zr(1)	105.2(3)
C(15)-N(1)-Zr(1)	117.7(3)
C(9)-N(2)-C(31)	112.1(4)
C(9)-N(2)-C(30)	113.1(4)
C(31)-N(2)-C(30)	105.2(4)
C(9)-N(2)-Zr(1)	120.3(3)
C(31)-N(2)-Zr(1)	108.2(3)
C(30)-N(2)-Zr(1)	96.0(3)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-C(7)	119.7(5)
C(3)-C(2)-C(1)	118.7(5)
C(7)-C(2)-C(1)	121.6(5)
C(4)-C(3)-C(2)	120.7(5)
C(4)-C(3)-H(3A)	119.7
C(2)-C(3)-H(3A)	119.7
C(5)-C(4)-C(3)	120.0(5)
C(5)-C(4)-H(4A)	120.0
C(3)-C(4)-H(4A)	120.0
C(4)-C(5)-C(6)	120.4(5)
C(4)-C(5)-H(5A)	119.8
C(6)-C(5)-H(5A)	119.8
C(5)-C(6)-C(7)	120.4(5)
C(5)-C(6)-N(1)	117.8(5)
C(7)-C(6)-N(1)	121.7(5)
C(6)-C(7)-C(2)	118.7(5)
C(6)-C(7)-C(8)	125.6(5)
C(2)-C(7)-C(8)	115.7(4)
C(13)-C(8)-C(9)	119.1(5)
C(13)-C(8)-C(7)	119.3(4)
C(9)-C(8)-C(7)	121.4(5)
C(10)-C(9)-C(8)	119.9(5)
C(10)-C(9)-N(2)	120.8(4)
C(8)-C(9)-N(2)	119.3(4)
C(11)-C(10)-C(9)	120.4(5)
C(11)-C(10)-H(10A)	119.8
C(9)-C(10)-H(10A)	119.8
C(10)-C(11)-C(12)	120.2(5)
C(10)-C(11)-H(11A)	119.9
C(12)-C(11)-H(11A)	119.9
C(11)-C(12)-C(13)	120.9(5)
C(11)-C(12)-H(12A)	119.6
C(13)-C(12)-H(12A)	119.6
C(12)-C(13)-C(8)	119.5(5)
C(12)-C(13)-C(14)	118.3(5)
C(8)-C(13)-C(14)	122.2(5)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
N(1)-C(15)-H(15A)	109.5
N(1)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
N(1)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5

C(17)-C(16)-C(21)	121.0(5)
C(17)-C(16)-N(1)	122.6(5)
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)	118.0(5)
C(17)-C(18)-C(22)	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(18)-C(19)-H(19A)	118.1
C(19)-C(20)-C(21)	116.0(5)
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
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(22)-C(25)-H(25A)	109.5
C(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(20)-C(26)-C(28)	111.6(5)
C(20)-C(26)-C(27)	110.1(5)
C(28)-C(26)-C(27)	107.8(5)
C(20)-C(26)-C(29)	110.5(5)
C(28)-C(26)-C(29)	107.7(5)
C(27)-C(26)-C(29)	109.1(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
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(26)-C(29)-H(29A)	109.5
C(26)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(26)-C(29)-H(29C)	109.5

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(34)-C(33)-C(37)	120.8(5)
C(32)-C(33)-C(37)	121.4(5)
C(33)-C(34)-C(35)	124.8(5)
C(33)-C(34)-H(34A)	117.6
C(35)-C(34)-H(34A)	117.6
C(34)-C(35)-C(36)	115.7(5)
C(34)-C(35)-C(41)	122.4(5)
C(36)-C(35)-C(41)	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(38)-C(37)-C(40)	108.8(6)
C(38)-C(37)-C(39)	108.2(6)
C(40)-C(37)-C(39)	107.4(6)
C(38)-C(37)-C(33)	109.7(5)
C(40)-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
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
C(37)-C(39)-H(39A)	109.5
C(37)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
C(37)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(37)-C(40)-H(40A)	109.5
C(37)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(37)-C(40)-H(40C)	109.5
H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
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)
C(41)-C(42)-H(42A)	109.5
C(41)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
C(41)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
C(41)-C(43)-H(43A)	109.5
C(41)-C(43)-H(43B)	109.5

H(43A)-C(43)-H(43B)	109.5
C(41)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5
C(41)-C(44)-H(44A)	109.5
C(41)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
C(41)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5
C(101)-C(100)-H(10B)	109.5
C(101)-C(100)-H(10C)	109.5
H(10B)-C(100)-H(10C)	109.5
C(101)-C(100)-H(10D)	109.5
H(10B)-C(100)-H(10D)	109.5
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 (A^2 x 10^3) for daz.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Zr(1)	22(1)	19(1)	21(1)	0(1)	4(1)	1(1)
Cl(1)	44(1)	39(1)	30(1)	-7(1)	8(1)	10(1)
Cl(2)	38(1)	22(1)	34(1)	6(1)	6(1)	4(1)
O(1)	23(2)	31(2)	26(2)	-9(2)	5(2)	-5(2)
O(2)	24(2)	25(2)	22(2)	1(2)	-3(2)	-3(2)
N(1)	19(2)	22(2)	20(2)	0(2)	0(2)	-3(2)
N(2)	22(2)	19(2)	19(2)	4(2)	6(2)	3(2)
C(1)	32(3)	22(3)	41(4)	-4(3)	2(3)	-1(3)
C(2)	25(3)	18(3)	26(3)	2(2)	7(2)	-2(2)
C(3)	29(3)	18(3)	36(3)	1(3)	5(3)	6(3)
C(4)	32(3)	27(3)	26(3)	3(3)	3(3)	10(3)
C(5)	26(3)	27(3)	21(3)	-4(2)	2(2)	3(2)
C(6)	22(3)	18(3)	19(3)	-3(2)	4(2)	2(2)
C(7)	19(3)	21(3)	21(3)	-3(2)	5(2)	-1(2)
C(8)	17(3)	17(3)	23(3)	1(2)	2(2)	-1(2)

C(9)	21(3)	15(2)	19(3)	1(2)	4(2)	-2(2)
C(10)	20(3)	34(3)	21(3)	6(2)	1(2)	4(2)
C(11)	26(3)	41(4)	29(3)	8(3)	-2(3)	4(3)
C(12)	31(3)	41(4)	21(3)	1(3)	0(3)	-4(3)
C(13)	22(3)	24(3)	22(3)	-3(2)	5(2)	-6(2)
C(14)	27(3)	46(4)	27(3)	-7(3)	6(3)	4(3)
C(15)	31(3)	23(3)	21(3)	6(2)	7(2)	-6(2)
C(16)	19(3)	22(3)	30(3)	-8(2)	1(2)	-1(2)
C(17)	22(3)	34(3)	23(3)	-10(3)	4(2)	-1(2)
C(18)	24(3)	24(3)	32(3)	-1(2)	8(3)	-2(2)
C(19)	25(3)	25(3)	31(3)	1(2)	2(2)	-3(2)
C(20)	26(3)	16(3)	22(3)	0(2)	-1(2)	-1(2)
C(21)	27(3)	17(3)	24(3)	1(2)	7(2)	1(2)
C(22)	28(3)	42(4)	32(4)	-6(3)	8(3)	-6(3)
C(23)	68(5)	125(8)	64(6)	36(6)	43(5)	53(6)
C(24)	54(5)	64(5)	89(7)	9(5)	37(5)	20(4)
C(25)	49(5)	146(9)	122(8)	-90(8)	41(5)	-41(6)
C(26)	26(3)	27(3)	30(3)	-9(3)	-4(3)	0(2)
C(27)	37(4)	36(4)	49(4)	-13(3)	0(3)	3(3)
C(28)	37(4)	54(4)	41(4)	-24(3)	-12(3)	5(3)
C(29)	60(5)	53(4)	23(3)	-5(3)	7(3)	-1(4)
C(30)	26(3)	30(3)	25(3)	-2(2)	4(2)	4(2)
C(31)	21(3)	19(3)	15(3)	4(2)	4(2)	2(2)
C(32)	18(3)	25(3)	22(3)	1(2)	0(2)	3(2)
C(33)	27(3)	17(3)	30(3)	2(2)	7(3)	1(2)
C(34)	28(3)	24(3)	24(3)	8(2)	8(3)	5(2)
C(35)	25(3)	25(3)	18(3)	4(2)	7(2)	3(2)
C(36)	23(3)	18(3)	25(3)	3(2)	5(2)	4(2)
C(37)	23(3)	23(3)	38(4)	3(3)	9(3)	-2(2)
C(38)	54(5)	72(5)	72(6)	-27(4)	35(4)	-37(4)
C(39)	54(5)	61(5)	70(5)	24(4)	-27(4)	-34(4)
C(40)	35(4)	28(4)	116(7)	-19(4)	5(4)	-2(3)
C(41)	36(3)	27(3)	22(3)	9(2)	7(3)	3(3)
C(42)	38(4)	62(5)	37(4)	17(3)	-5(3)	4(3)
C(43)	53(4)	46(4)	35(4)	19(3)	-4(3)	-3(3)
C(44)	64(5)	49(4)	26(4)	5(3)	1(3)	3(4)
C(100)	109(8)	69(6)	76(7)	1(5)	14(6)	-26(6)
C(101)	64(5)	58(5)	41(4)	4(4)	16(4)	-6(4)
C(102)	70(5)	50(5)	47(5)	11(4)	13(4)	12(4)
C(103)	76(6)	54(5)	78(6)	16(5)	6(5)	18(5)
C(104)	98(8)	72(6)	58(6)	5(5)	17(5)	-12(6)
C(105)	64(6)	114(8)	30(4)	9(5)	14(4)	10(6)
C(106)	68(5)	61(5)	45(4)	2(4)	25(4)	19(4)

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

	x	y	z	U(eq)
H(1A)	2048	12506	5026	48
H(1B)	2283	12956	4376	48
H(1C)	1803	13821	4667	48
H(3A)	2994	12442	5715	33
H(4A)	3783	13531	6351	34
H(5A)	3927	15741	6191	30
H(10A)	1028	17723	4461	30
H(11A)	1017	17290	3362	39
H(12A)	1782	16101	3031	37
H(14A)	3025	14698	4056	50

H(14B)	2981	15703	3463	50
H(14C)	2593	14398	3384	50
H(15A)	3466	17275	4450	37
H(15B)	3413	18740	4692	37
H(15C)	2826	17867	4512	37
H(17A)	4399	17050	5044	31
H(19A)	5393	18952	6539	33
H(23A)	5377	19174	4752	123
H(23B)	5117	17801	4477	123
H(23C)	5817	18086	4554	123
H(24A)	5701	15889	5841	99
H(24B)	6013	16089	5211	99
H(24C)	5310	15832	5127	99
H(25A)	6448	18126	5589	154
H(25B)	6183	17942	6251	154
H(25C)	6057	19255	5839	154
H(27A)	3773	20767	6967	62
H(27B)	4349	21506	6801	62
H(27C)	4221	21472	7535	62
H(28A)	5446	19305	7620	69
H(28B)	5214	20591	7931	69
H(28C)	5369	20625	7208	69
H(29A)	3901	18650	7612	68
H(29B)	4325	19434	8171	68
H(29C)	4561	18132	7877	68
H(30A)	923	17455	5478	41
H(30B)	1320	18702	5380	41
H(30C)	1351	18076	6090	41
H(32A)	1044	15001	5267	27
H(34A)	1589	13061	6947	30
H(38A)	614	12540	6839	95
H(38B)	64	12063	6309	95
H(38C)	166	13581	6451	95
H(39A)	53	12433	5140	98
H(39B)	593	13188	4898	98
H(39C)	144	13955	5281	98
H(40A)	1297	11279	6234	91
H(40B)	1258	11517	5467	91
H(40C)	715	10839	5739	91
H(42A)	3213	15399	7284	71
H(42B)	3221	13844	7304	71
H(42C)	3350	14657	7969	71
H(43A)	1904	13356	7985	69
H(43B)	2575	13378	8368	69
H(43C)	2419	12617	7689	69
H(44A)	1861	15825	7960	71
H(44B)	2424	16598	7782	71
H(44C)	2496	15705	8421	71
H(10B)	614	14681	9182	127
H(10C)	842	15022	8512	127
H(10D)	1198	13989	9005	127
H(10E)	1089	11907	8532	67
H(10F)	498	10259	8048	84
H(10G)	-528	10531	7738	90
H(10H)	-951	12527	7877	82
H(10I)	-348	14260	8351	67