

# Supporting Information for: **Highly Enantioselective Zirconium-Catalyzed Cyclization of Aminoalkenes**

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## Experiment details.

**General Procedures.** All reactions were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox unless otherwise indicated. Dry, oxygen-free solvents were used throughout. Benzene, toluene, pentane and tetrahydrofuran were degassed by sparging with nitrogen, filtered through activated alumina columns, and stored under  $\text{N}_2$ . Benzene- $d_6$ , toluene- $d_8$  and tetrahydrofuran- $d_8$  were vacuum transferred from Na/K alloy and stored under  $\text{N}_2$  in a glovebox. Sodium cyclopentadienide,<sup>1</sup> diphenylchloroborane,<sup>2</sup>  $\text{Zr}(\text{NMe}_2)_4$ ,<sup>3</sup>  $\text{Hf}(\text{NMe}_2)_4$ ,<sup>4</sup> 4*S*-isopropyl-5,5-dimethyl-2-oxazoline (2H-Ox<sup>*i*-PrMe2</sup>),<sup>5</sup> 2H-4*S*-*tert*-butyl-2-oxazoline (2H-Ox<sup>*t*-Bu</sup>),<sup>6</sup>  $\text{PhB}(\text{Ox}^{\text{Me2}})_2$ ,<sup>7</sup>  $\text{PhB}(\text{S-Ox}^{\text{Me2}})_2$ ,<sup>5</sup>  $\text{PhB}(\text{S-Ox}^{\text{Me2}})_2$ ,<sup>8</sup>  $\text{H}[\text{PhB}(\text{C}_5\text{H}_5)(\text{Ox}^{\text{Me2}})_2]$ ,<sup>9</sup>  $\text{H}[\text{PhB}(\text{C}_5\text{H}_5)(\text{S-Ox}^{\text{Me2}})_2]$ ,<sup>5</sup>  $\text{H}[\text{PhB}(\text{C}_5\text{H}_5)(\text{S-Ox}^{\text{Me2}})_2]$ ,<sup>8</sup>  $\text{PhB}(\text{C}_5\text{H}_4)(\text{Ox}^{\text{Me2}})_2\text{Zr}(\text{NMe}_2)_2$ ,<sup>9</sup>  $\text{PhB}(\text{C}_5\text{H}_4)(\text{S-Ox}^{\text{Me2}})_2\text{Zr}(\text{NMe}_2)_2$ ,<sup>5</sup>  $\text{PhB}(\text{C}_5\text{H}_4)(\text{S-Ox}^{\text{Me2}})_2\text{Zr}(\text{NMe}_2)_2$ ,<sup>8</sup> 2,2-diphenyl-4-penten-1-amine (**8a**),<sup>10</sup> C-(1-allyl-cyclopentyl)-methylamine (**9a**),<sup>11</sup> 2,2-dimethyl-4-penten-1-amine (**10a**),<sup>12</sup> 2,2-bis(2-propenyl)-4-pentenylamine (**11a**),<sup>13</sup> C-

(1-allyl-cyclohexyl)-methylamine (**12a**),<sup>11</sup> 4-penten-1-amine (**13a**),<sup>14</sup> 1-(3-butenyl-cyclohexyl)methylamine (**14a**),<sup>15</sup> 2,2-diphenyl-5-hexen-1-amine (**15a**),<sup>16</sup> 2,2-diphenyl-1-amino-6-heptene (**16a**),<sup>17</sup> *ortho*-allylaniline (**17a**),<sup>18</sup> 2-allyl-2-(4-bromophenyl)pent-4-enylamine (**19a**),<sup>8</sup> 2-allyl-2-methylpent-4-enylamine (**20a**),<sup>19</sup> 2,2-diphenyl-1-amino-4-hexene (**21a**),<sup>20</sup> 2-phenyl-4-penten-1-amine (**22a**),<sup>20</sup> and tetrakis(trimethylsilyl)silane<sup>21</sup> were prepared by published procedures. All aminoalkenes were distilled from CaH<sub>2</sub>, degassed and stored with freshly activated 4 Å molecular sieves in a glovebox prior to use. All other chemicals used here are commercially available. (+)-(*S*)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetyl chloride (*S*-Mosher's chloride) was obtained from Alfa-Aesar (>98%, (+)-137.3). Ti(NMe<sub>2</sub>)<sub>4</sub> and all other starting materials were purchased from Aldrich. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>11</sup>B, and <sup>19</sup>F{<sup>1</sup>H} NMR spectra were collected either on a Bruker DRX-400 spectrometer, Bruker Avance III 700 spectrometer or an Agilent MR 400 spectrometer. <sup>15</sup>N chemical shifts were determined by <sup>1</sup>H-<sup>15</sup>N HMBC experiments either on a Bruker Avance III 700 spectrometer or on a Bruker Avance III 600 spectrometer. <sup>15</sup>N chemical shifts were originally referenced to liquid NH<sub>3</sub> and recalculated to the CH<sub>3</sub>NO<sub>2</sub> chemical shift scale by adding -381.9 ppm. <sup>11</sup>B NMR spectra were referenced to an external sample of BF<sub>3</sub>·Et<sub>2</sub>O. Accurate mass ESI mass spectrometry was performed using an Agilent QTOF 6530 equipped with the Jet Stream ESI source. An Agilent ESI test mix was used for tuning and calibration. Accurate mass data was obtained in the positive ion mode using a reference standard with ions at 121.05087 and 922.00979. The mass resolution (FWHM) was maintained at 18,000. Elemental analysis was performed using a Perkin-Elmer 2400 Series II CHN/S by the Iowa State Chemical Instrumentation Facility. [ $\alpha$ ]<sub>D</sub> values were measured on a ATAGO AP-300 polarimeter at 23 °C.

#### **4*R*-isopropyl-5,5-dimethyl-2-oxazoline.**

**D-Valine methyl ester hydrochloride.**<sup>22</sup> Thionyl chloride (23.8 mL, 0.33 mol, 0.55 equiv) was added in a dropwise fashion over 2 h to methanol (150 mL) in a three-necked flask cooled in ice-salt bath and connected to an oil bubbler. D-Valine (35.0 g, 0.300 mol) was added in one portion to the solution, and the mixture was heated at 55 °C to dissolve all of the solids. The solution was then heated for 1 h. The solvent and excess reagents were removed by distillation. The resulting white solid was dried *in vacuo* for several hours and then dissolved in minimal amount of methanol (45 mL). The methanol solution was poured into Et<sub>2</sub>O (500 mL), and then

recrystallized at  $-30\text{ }^{\circ}\text{C}$ . The solid was collected, washed with cold  $\text{Et}_2\text{O}$ , and dried *in vacuo* to give the D-Valine methyl ester hydrochloride as white solid (45.4 g, 90.5 %).  $^1\text{H}$  NMR (300 MHz, chloroform-*d*):  $\delta$  8.91 (br, 3 H,  $\text{HCl}\cdot\text{NH}_2\text{CH}(\text{CHMe}_2)\text{CO}_2\text{Me}$ ), 3.93 (d,  $^3J_{\text{HH}} = 4.5\text{ Hz}$ , 1 H,  $\text{HCl}\cdot\text{NH}_2\text{CH}(\text{CHMe}_2)\text{CO}_2\text{Me}$ ), 3.84 (s, 3 H,  $\text{HCl}\cdot\text{NH}_2\text{CH}(\text{CHMe}_2)\text{CO}_2\text{Me}$ ), 2.47 (m, 1 H,  $\text{HCl}\cdot\text{NH}_2\text{CH}(\text{CHMe}_2)\text{CO}_2\text{Me}$ ), 1.16 (vt, 6 H,  $\text{HCl}\cdot\text{NH}_2\text{CH}(\text{CHMe}_2)\text{CO}_2\text{Me}$ ).

**2R-Amino-1,1,3-trimethylbutanol.** A solution of methylmagnesium bromide (180 mL, 3.0 M in  $\text{Et}_2\text{O}$ , 0.540 mol, 6.0 equiv) was diluted with  $\text{Et}_2\text{O}$  (500 mL). D-Valine methyl ester hydrochloride (15.0 g, 0.0896 mol) was added in portions over 1 h. The mixture was allowed to stir at room temperature overnight. Saturated aqueous  $[\text{NH}_4][\text{Cl}]$  was added in a dropwise fashion to quench the reaction. The white solid was separated from the diethyl ether solution, and the organic solution was dried over  $\text{Na}_2\text{SO}_4$ . The solid was dissolved in 300 mL saturated aqueous  $[\text{NH}_4][\text{Cl}]$  solution, and another 300 mL of distilled water was added. This aqueous solution was extracted with  $\text{Et}_2\text{O}$  ( $4 \times 200\text{ mL}$ ). The organic extracts were combined and dried over  $\text{Na}_2\text{SO}_4$ . The two organic solutions were filtered, combined, and evaporated under reduced pressure. The crude product was distilled ( $96\text{ }^{\circ}\text{C}$ , 40 mm Hg) to afford 2R-amino-1,1,3-trimethylbutanol as a clear, colorless oil (4.96 g, 42.3%).  $^1\text{H}$  NMR (300 MHz, chloroform-*d*):  $\delta$  2.41 (d,  $^3J_{\text{HH}} = 2.7\text{ Hz}$ , 1 H,  $\text{NH}_2\text{CH}(\text{CHMe}_2)\text{CMe}_2\text{OH}$ ), 1.93 (m, 1 H,  $\text{NH}_2\text{CH}(\text{CHMe}_2)\text{CMe}_2\text{OH}$ ), 1.20 (s, 3 H,  $\text{NH}_2\text{CH}(\text{CHMe}_2)\text{CMe}_2\text{OH}$ ), 1.12 (s, 3 H,  $\text{NH}_2\text{CH}(\text{CHMe}_2)\text{CMe}_2\text{OH}$ ), 0.97 (d,  $^3J_{\text{HH}} = 7.2\text{ Hz}$ , 3 H,  $\text{NH}_2\text{CH}(\text{CHMe}_2)\text{CMe}_2\text{OH}$ ), 0.88 (d,  $^3J_{\text{HH}} = 6.6\text{ Hz}$ , 3 H,  $\text{NH}_2\text{CH}(\text{CHMe}_2)\text{CMe}_2\text{OH}$ ).

**4R-isopropyl-5,5-dimethyl-2-oxazoline.**<sup>5,6</sup> DMF-DMA (13.7 mL, 103.3 mmol, 1.2 equiv) was added to degassed 2R-amino-1,1,3-trimethylbutanol (11.1 g, 84.7 mmol). This mixture was allowed to reflux at  $75\text{ }^{\circ}\text{C}$  for 7 h. The volatiles were removed under reduced pressure, and the mixture was triturated with hexane ( $4 \times 30\text{ mL}$ ). Then *p*-toluenesulfonic acid monohydrate (26.5 mg, 0.14 mmol, 0.0017 equiv) and hexane (40 mL) were added, an addition funnel with approximately 40 mL of molecular sieves inside was placed on top of the flask, and a condenser was placed on top of the funnel. The solution was heated at reflux ( $90\text{ }^{\circ}\text{C}$ ) for 24 h, and the condensed liquids washed over the sieves as the reaction proceeded. The reaction mixture was washed with saturated aqueous  $\text{NaHCO}_3$  solution (30 mL) and then with brine (50 mL). The

aqueous solutions were combined, back-extracted with Et<sub>2</sub>O (25 mL × 6), and then the organic extracts were combined with the organic solution and dried over Na<sub>2</sub>SO<sub>4</sub> overnight and filtered. Concentration of the filtrate gave a dark red oil which was distilled to provide 8.11 g (57.4 mmol, 68%) of 4*R*-isopropyl-5,5-dimethyl-2-oxazoline as a clear, colorless oil. 4*R*-isopropyl-5,5-dimethyl-2-oxazoline is spectroscopically identical to previously reported 4*S*-isopropyl-5,5-dimethyl-2-oxazoline, and the data are given here for convenience. Bp: 85 °C, 18 mm Hg. <sup>1</sup>H NMR (400 MHz, chloroform-*d*): δ 6.73 (s, 1 H, CHNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 3.23 (dd, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 1 H, CHNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 1.78 (m, 1 H, CHNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 1.43 (s, 3 H, CHNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 1.28 (s, 3 H, CHNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 1.06 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 3 H, CHNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 0.97 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 3 H, CHNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>, 176 MHz): δ 152.72 (CHNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 85.17 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 80.07 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 29.55 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 29.48 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 21.52, 21.47, 21.21 (overlapping CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O and CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O). <sup>15</sup>N NMR (benzene-*d*<sub>6</sub>, 71 MHz): δ -143.4. IR (KBr, cm<sup>-1</sup>): 3069 w, 2974 s, 2874 m, 1632 s (CN), 1471 m, 1462 m, 1386 m, 1372 s, 1336 w, 1303 w, 1272 w, 1243 w, 1202 w, 1172 m, 1134 m, 1114 s, 1082 s, 1015 m, 984 w, 936 m, 894 w, 856 w 813 w. [α]<sub>D</sub><sup>20</sup> = (+) 37.7 (C<sub>6</sub>H<sub>6</sub>).

**H[PhB(C<sub>5</sub>H<sub>4</sub>)(*R*-Ox<sup>*i*Pr,Me<sub>2</sub></sup>)<sub>2</sub>] (H<sub>2</sub>[*R*-2]).** A 100 mL Schlenk flask was charged with 4*R*-isopropyl-5,5-dimethyl-2-oxazoline (0.400 g, 2.83 mmol) and tetrahydrofuran (30 mL), and the flask was cooled to -78 °C. Using a syringe, 2.50 M *n*-BuLi (1.20 mL, 2.98 mmol) was added, and the solution was stirred for 1 h at -78 °C. Dichlorophenylborane (0.23 mL, 1.40 mmol) was slowly added to the flask, and the solution was stirred for 1 h at -78 °C and then allowed to gradually warm to room temperature. After stirring for 14 h at room temperature, the solvent was removed under reduced pressure to afford a light yellow solid. The solid was extracted with benzene and the solvent was evaporated to yield PhB(*R*-Ox<sup>*i*Pr,Me<sub>2</sub></sup>)<sub>2</sub> as a light yellow solid (0.50 g, 1.36 mmol). <sup>1</sup>H NMR (tetrahydrofuran-*d*<sub>8</sub>, 400 MHz): δ 7.45 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2 H, *ortho*-C<sub>6</sub>H<sub>5</sub>), 6.98 (m, 2 H, *meta*-C<sub>6</sub>H<sub>5</sub>), 6.87 (m, 1 H, *para*-C<sub>6</sub>H<sub>5</sub>), 3.19 (d, <sup>3</sup>J<sub>HH</sub> = 4.8 Hz, 2 H, CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 3.17 (d, <sup>3</sup>J<sub>HH</sub> = 4.8 Hz, 2 H, CNC<sup>*i*Pr</sup>HMe<sub>2</sub>O), 1.73 (m, 2 H, CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 1.22-0.95 (24 H, CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O). <sup>11</sup>B NMR (tetrahydrofuran-

$d_8$ , 128 MHz):  $\delta$  -7.2. IR (KBr,  $\text{cm}^{-1}$ ): 3071 w, 3046 w, 2961 s, 2932 s, 2872 m, 1588 s (CN), 1466 m, 1432 m, 1386 m, 1371 s, 1277 w, 1242 s, 1193 m, 1176 m, 1146 s, 1120 m, 1096 m, 1023 s, 995 m, 943 m, 879 m, 849 m, 802 m, 759 w.

A Schlenk flask was charged with  $\text{PhB}(R\text{-Ox}^{i\text{Pr,Me}_2})_2$  (0.500 g, 1.36 mmol) and  $\text{Na}[\text{C}_5\text{H}_5]$  (0.070 g, 0.799 mmol). Addition of THF (40 mL) provided a yellow solution that was stirred overnight. A precipitate formed after 12 h, and the solution was filtered. Solvent was removed under reduced pressure to afford a light yellow solid. This crude product was purified by silica gel column chromatography (hexane:EtOAc:Et<sub>3</sub>N = 9:1:1;  $R_f$  = 0.58) to afford an off-white solid of  $\text{H}[\text{PhB}(\text{C}_5\text{H}_5)(\text{Ox}^{i\text{Pr,Me}_2})_2]$  as a mixture of isomers. The product was dissolved in benzene and stirred over  $\text{P}_2\text{O}_5$  to remove residual water, affording 0.140 g of  $\text{H}[\text{PhB}(\text{C}_5\text{H}_5)(\text{Ox}^{i\text{Pr,Me}_2})_2]$  (0.321 mmol, 40.5%). <sup>1</sup>H NMR (acetonitrile- $d_3$ , 400 MHz):  $\delta$  7.71-7.00 (m, 5 H, C<sub>6</sub>H<sub>5</sub>), 6.67-6.19 (m, 3 H, C<sub>5</sub>H<sub>5</sub>), 3.39-3.25 (m, 2 H,  $\text{CNC}^i\text{PrH}\text{CMe}_2\text{O}$ ), 2.89-2.88 (m, 2 H, C<sub>5</sub>H<sub>5</sub>), 1.84 (m, 2 H,  $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ), 1.47-0.94 (24 H,  $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ). <sup>13</sup>C{<sup>1</sup>H} NMR (acetonitrile- $d_3$ , 176 MHz):  $\delta$  133.46 (*ortho*-C<sub>6</sub>H<sub>5</sub>), 129.10 (*meta*-C<sub>6</sub>H<sub>5</sub>), 128.24 (*para*-C<sub>6</sub>H<sub>5</sub>), 141.27 (C<sub>5</sub>H<sub>5</sub>; 10  $sp^2$  resonances for 3 isomers observed), 140.99 (C<sub>5</sub>H<sub>5</sub>), 135.25 (C<sub>5</sub>H<sub>5</sub>), 134.75 (C<sub>5</sub>H<sub>5</sub>), 134.20 (C<sub>5</sub>H<sub>5</sub>), 133.85 (C<sub>5</sub>H<sub>5</sub>), 133.83 (C<sub>5</sub>H<sub>5</sub>), 131.28 (C<sub>5</sub>H<sub>5</sub>), 128.90 (C<sub>5</sub>H<sub>5</sub>), 128.40 (C<sub>5</sub>H<sub>5</sub>), 94.11 ( $\text{CNC}^i\text{PrH}\text{CMe}_2\text{O}$ ), 66.67 ( $\text{CNC}^i\text{PrH}\text{CMe}_2\text{O}$ ), 47.49 (C<sub>5</sub>H<sub>5</sub>- $sp^3$ ), 43.18 (C<sub>5</sub>H<sub>5</sub>- $sp^3$ ), 30.25 ( $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ), 29.26 ( $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ), 29.91, 29.68, 22.09, 22.06, 21.80, 21.77, 21.38, 21.27 ( $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ). <sup>11</sup>B NMR (acetonitrile- $d_3$ , 128 MHz):  $\delta$  -15.6. IR (KBr,  $\text{cm}^{-1}$ ): 3069 m, 3047 m, 2972 s, 2932 s, 2875 s, 1582 s (CN), 1560 s (CN), 1470 m, 1433 m, 1394 s, 1375 s, 1353 m, 1335 w, 1313 w, 1276 m, 1262 m, 1246 m, 1198 m, 1177 m, 1148 m, 1104 m, 1047 m, 1030 s, 1005 m, 990 w, 958 m, 943 m, 863 m, 881 m, 802 s, 765 m, 741 s, 703 s, 680 m. Anal. Calcd for C<sub>27</sub>H<sub>39</sub>BN<sub>2</sub>O<sub>2</sub>: C, 74.65; H, 9.05; N, 6.45. Found: C, 74.77; H, 8.84; N 6.06.  $[\alpha]_D^{20}$  = (+) 63.2 (C<sub>6</sub>H<sub>6</sub>). Mp: 80-85 °C.

**K<sub>2</sub>[PhB(S-Ox<sup>iPr,Me<sub>2</sub></sup>)<sub>2</sub>C<sub>5</sub>H<sub>4</sub>] (K<sub>2</sub>[S-2]).** A round bottom Schlenk flask was charged with  $\text{H}[\text{PhB}(\text{S-Ox}^{i\text{Pr,Me}_2})_2\text{C}_5\text{H}_5]$  (0.122 g, 0.28 mmol) and  $\text{PhCH}_2\text{K}$  (0.072 g, 0.55 mmol). The solids were dissolved in THF (6 mL), and the resulting yellow solution was stirred for 3 h. The volatile materials were removed and dry *in vacuo* to give  $\text{K}_2[\text{PhB}(\text{S-Ox}^{i\text{Pr,Me}_2})_2\text{C}_5\text{H}_4]$  as a yellow solid (0.140 g, 0.274 mmol, 97.9%). <sup>1</sup>H NMR (tetrahydrofuran- $d_8$ , 400 MHz):  $\delta$  7.63 (d, <sup>3</sup> $J_{\text{HH}}$  = 7.2

Hz, 2 H, *ortho*-C<sub>6</sub>H<sub>5</sub>), 6.95 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2 H, *meta*-C<sub>6</sub>H<sub>5</sub>), 6.78 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 1 H, *para*-C<sub>6</sub>H<sub>5</sub>), 5.60 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 5.44 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 3.02 (m, 2 H, <sup>3</sup>J<sub>HH</sub> = 5.6 Hz, CNC<sup>*i*</sup>PrHMe<sub>2</sub>O), 1.73 (m, 2 H, CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 1.32 (s, 3 H, CNC<sup>*i*</sup>PrHMe<sub>2</sub>O), 1.22 (s, 3 H, CNC<sup>*i*</sup>PrHMe<sub>2</sub>O), 1.21 (s, 3 H, CNC<sup>*i*</sup>PrHMe<sub>2</sub>O), 1.15 (s, 3 H, CNC<sup>*i*</sup>PrHMe<sub>2</sub>O), 1.01 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 6 H, CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 0.93 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 6 H, CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O). <sup>13</sup>C{<sup>1</sup>H} NMR (tetrahydrofuran-*d*<sub>8</sub>, 100 MHz): δ 189.90 (CNC(CHMe<sub>2</sub>)HCH<sub>2</sub>O), 161.24 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 134.43 (*ortho*-C<sub>6</sub>H<sub>5</sub>), 126.85 (*meta*-C<sub>6</sub>H<sub>5</sub>), 122.81 (*para*-C<sub>6</sub>H<sub>5</sub>), 112.10 (C<sub>5</sub>H<sub>4</sub>), 104.48 (C<sub>5</sub>H<sub>4</sub>), 82.11 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 81.79 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 81.11 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 80.93 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 31.04 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O, overlapping), 30.61 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O, overlapping), 22.37 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O, overlapping), 21.96 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O, overlapping). <sup>11</sup>B NMR (tetrahydrofuran-*d*<sub>8</sub>, 128 MHz): δ -15.2. <sup>15</sup>N NMR (tetrahydrofuran-*d*<sub>8</sub>, 71 MHz): δ -153.4 (one <sup>15</sup>N cross peak was observed). IR (KBr, cm<sup>-1</sup>): 3044 w, 2967 s, 2931 s, 2872 m, 1583 s, 1467 m, 1430 w, 1384 m, 1367 m, 1331 w, 1245 m, 1199 m, 1176 m, 1134 s, 1094 s, 1042 m, 1019 m, 984 w, 941 m, 884 s, 856 m, 790 w, 737 m, 707 s. Anal. Calcd for C<sub>27</sub>H<sub>37</sub>BK<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 63.51; H, 7.30; N, 5.49. Found: C, 63.11; H, 7.61; N, 5.28. Mp: 138-143 °C, dec.

**H[Ph<sub>2</sub>B(C<sub>5</sub>H<sub>5</sub>)(*S*-Ox<sup>*i*</sup>Pr,Me<sub>2</sub>)] (H<sub>2</sub>[*S*-7]).** A 100 mL Schlenk flask was charged with 4-*isopropyl*-5,5-dimethyl-2-oxazoline (0.500 g, 3.54 mmol) and THF (40 mL), and the flask was cooled to -78 °C. Using a syringe, 2.50 M *n*-BuLi (1.20 mL, 2.98 mmol) was added, and the solution was stirred for 1 h at -78 °C. A THF (20 mL) solution of Ph<sub>2</sub>BCl (0.708 g, 3.54 mmol) in another Schlenk flask was slowly added to the flask containing lithium oxazolide, and the solution was stirred for 1 h at -78 °C and then allowed to slowly warm to room temperature. After stirring for 12 h at room temperature, the solvent was removed under reduced pressure to afford crude Ph<sub>2</sub>B(*S*-Ox<sup>*i*</sup>Pr,Me<sub>2</sub>) as a light yellow solid.

The Ph<sub>2</sub>B(*S*-Ox<sup>*i*</sup>Pr,Me<sub>2</sub>) and Na[C<sub>5</sub>H<sub>5</sub>] (0.312 g, 3.54 mmol) were dissolved in 40 mL THF and was stirred overnight at room temperature. The solution was filtered. Solvent was removed under reduced pressure to afford a yellow solid. This crude product was purified by silica gel column chromatography to afford an light yellow solid of H[Ph<sub>2</sub>B(C<sub>5</sub>H<sub>5</sub>)(*S*-Ox<sup>*i*</sup>Pr,Me<sub>2</sub>)] as a mixture of isomers. The product was dissolved in benzene and stirred over P<sub>2</sub>O<sub>5</sub> to remove residual water,

affording 0.120 g of  $\text{H}[\text{Ph}_2\text{B}(\text{C}_5\text{H}_5)(\text{S-Ox}^{i\text{Pr,Me}_2})]$  (0.323 mmol, 10.7%).  $^1\text{H}$  NMR (acetonitrile- $d_3$ , 400 MHz):  $\delta$  7.70-7.12 (m, 10 H,  $\text{C}_6\text{H}_5$ ), 6.48-6.32 (m, 3 H,  $\text{C}_5\text{H}_5$ ), 3.83 (d,  $^3J_{\text{HH}} = 6.4$  Hz, 1 H,  $\text{CNC}^i\text{PrH}\text{CMe}_2\text{O}$ ), 2.91 (m, 2 H,  $\text{C}_5\text{H}_5$ ), 1.84 (m, 1 H,  $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ), 1.47-0.98 (12 H,  $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (acetonitrile- $d_3$ , 150 MHz):  $\delta$  135.53 (*ortho*- $\text{C}_6\text{H}_5$ ), 129.69 (*meta*- $\text{C}_6\text{H}_5$ ), 128.03 (*para*- $\text{C}_6\text{H}_5$ ), 142.17 ( $\text{C}_5\text{H}_5$ ; 10  $sp^2$  resonances for 3 isomers observed), 141.95 ( $\text{C}_5\text{H}_5$ ), 136.26 ( $\text{C}_5\text{H}_5$ ), 134.92 ( $\text{C}_5\text{H}_5$ ), 134.25 ( $\text{C}_5\text{H}_5$ ), 133.85 ( $\text{C}_5\text{H}_5$ ), 133.23 ( $\text{C}_5\text{H}_5$ ), 131.87 ( $\text{C}_5\text{H}_5$ ), 128.23 ( $\text{C}_5\text{H}_5$ ), 128.57 ( $\text{C}_5\text{H}_5$ ), 95.09 ( $\text{CNC}^i\text{PrH}\text{CMe}_2\text{O}$ ), 67.07 ( $\text{CNC}^i\text{PrH}\text{CMe}_2\text{O}$ ), 48.34 ( $\text{C}_5\text{H}_5\text{-}sp^3$ ), 43.22 ( $\text{C}_5\text{H}_5\text{-}sp^3$ ), 31.25 ( $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ), 29.77, 22.19, 21.61, 21.29 ( $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ).  $^{11}\text{B}$  NMR (acetonitrile- $d_3$ , 128 MHz):  $\delta$  -10.0, -11.5, -12.4. IR (KBr,  $\text{cm}^{-1}$ ): 3087 w, 3069 w, 3035 w, 2982 s, 2870 m, 1594 s (CN), 1474 w, 1467 m, 1424 w, 1396 s, 1370 m, 1352 m, 1347 w, 1311 m, 1302 w, 1244w, 1227 w, 1215 m, 1167 w, 1145 m, 1096 w, 1027 m, 999 w, 956 m, 942 m, 853 w, 829 w. Anal. Calcd for  $\text{C}_{25}\text{H}_{30}\text{BNO}$ : C, 80.86; H, 8.14; N, 3.77. Found: C, 80.25; H, 7.73; N, 3.51. Mp: 67-72 °C.  $[\alpha]_{\text{D}}^{20} = -55.2^\circ$  ( $\text{C}_6\text{H}_6$ ).

**$\{\text{PhB}(\text{C}_5\text{H}_4)(\text{R-Ox}^{i\text{Pr,Me}_2})_2\}\text{Zr}(\text{NMe}_2)_2$  ( $\{\text{R-2}\}\text{Zr}(\text{NMe}_2)_2$ ).** A benzene solution of  $\text{H}[\text{PhB}(\text{C}_5\text{H}_5)(\text{R-Ox}^{i\text{Pr,Me}_2})_2]$  (0.120 g, 0.275 mmol) and  $\text{Zr}(\text{NMe}_2)_4$  (0.074 g, 0.275 mmol) was stirred for 7 h. The mixture was filtered, and the volatile materials were removed in vacuo to give a light yellow gel. The gel was triturated with pentane giving  $\{\text{PhB}(\text{C}_5\text{H}_4)(\text{R-Ox}^{i\text{Pr,Me}_2})_2\}\text{Zr}(\text{NMe}_2)_2$  as a off-white solid (0.154 g, 0.252 mmol, 91.4%).  $^1\text{H}$  NMR (benzene- $d_6$ , 400 MHz):  $\delta$  8.09 (d,  $^3J_{\text{HH}} = 7.2$  Hz, 2 H, *ortho*- $\text{C}_6\text{H}_5$ ), 7.49 (m, 2 H, *meta*- $\text{C}_6\text{H}_5$ ), 7.29 (m, 1 H, *para*- $\text{C}_6\text{H}_5$ ), 6.76 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 6.58 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 6.25 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 6.07 (m, 1 H,  $\text{C}_5\text{H}_4$ ), 3.24 (d, 1 H,  $^3J_{\text{HH}} = 5.6$  Hz,  $\text{CNC}^i\text{PrH}\text{CMe}_2\text{O}$ ), 3.20 (d, 1 H,  $^3J_{\text{HH}} = 5.6$  Hz,  $\text{CNC}^i\text{PrH}\text{CMe}_2\text{O}$ ), 2.80 (s, 6 H,  $\text{NMe}_2$ ), 2.68 (s, 6 H,  $\text{NMe}_2$ ), 1.73 (m, 2 H,  $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ), 1.33 (s, 3 H,  $\text{CNC}^i\text{PrH}\text{CMe}_2\text{O}$ ), 1.24 (s, 3 H,  $\text{CNC}^i\text{PrH}\text{CMe}_2\text{O}$ ), 1.18 (s, 3 H,  $\text{CNC}^i\text{PrH}\text{CMe}_2\text{O}$ ), 1.14 (s, 3 H,  $\text{CNC}^i\text{PrH}\text{CMe}_2\text{O}$ ), 1.12 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 3 H,  $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ), 1.09 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 3 H,  $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ), 0.97 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 3 H,  $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ), 0.89 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 3 H,  $\text{CNC}(\text{CHMe}_2)\text{H}\text{CMe}_2\text{O}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ , 176 MHz):  $\delta$  196.92 (br,  $\text{CNC}^i\text{PrHCH}_2\text{O}$ ), 194.35 (br,  $\text{CNC}^i\text{PrHCH}_2\text{O}$ ), 151.53 (br, *ipso*- $\text{C}_6\text{H}_5$ ), 135.13 (*ortho*- $\text{C}_6\text{H}_5$ ), 127.51 (*meta*- $\text{C}_6\text{H}_5$ ), 125.26

(*para*-C<sub>6</sub>H<sub>5</sub>), 123.49 (C<sub>5</sub>H<sub>4</sub>), 122.83 (C<sub>5</sub>H<sub>4</sub>), 113.93 (C<sub>5</sub>H<sub>4</sub>), 113.64 (C<sub>5</sub>H<sub>4</sub>), 85.08 (CNC<sup>*i*</sup>PrH<sub>2</sub>CM<sub>2</sub>O), 84.81 (CNC<sup>*i*</sup>PrH<sub>2</sub>CM<sub>2</sub>O), 79.11 (CNC<sup>*i*</sup>PrH<sub>2</sub>CM<sub>2</sub>O), 78.87 (CNC<sup>*i*</sup>PrH<sub>2</sub>CM<sub>2</sub>O), 44.51 (NMe<sub>2</sub>), 42.95 (NMe<sub>2</sub>), 30.44 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 30.27 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 30.24 (CNC<sup>*i*</sup>PrH<sub>2</sub>CM<sub>2</sub>O), 30.02 (CNC<sup>*i*</sup>PrH<sub>2</sub>CM<sub>2</sub>O), 21.96 (CNC<sup>*i*</sup>PrH<sub>2</sub>CM<sub>2</sub>O), 21.83 (CNC<sup>*i*</sup>PrH<sub>2</sub>CM<sub>2</sub>O), 20.69 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 20.46 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 20.37 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 20.17 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O). <sup>11</sup>B NMR (benzene-*d*<sub>6</sub>, 128 MHz): δ -14.5. <sup>15</sup>N NMR (benzene-*d*<sub>6</sub>, 71 MHz): δ -152.3, -155.1 (CNC<sup>*i*</sup>PrH<sub>2</sub>CM<sub>2</sub>O). IR (KBr, cm<sup>-1</sup>): 3071 w, 3045 w, 2966 s, 2931 s, 2869 s, 2768 s, 1559 s (CN), 1471 m, 1433 m, 1393 m, 1374 m, 1353 m, 1276 m, 1261 m, 1244 m, 1177 m, 1147 s, 1105 m, 1047 s, 1030 m, 1021 m, 990 w, 940 s, 881 m, 864 w, 804 s, 770 w, 741 s, 703 s, 680 w. Anal. Calcd for C<sub>31</sub>H<sub>49</sub>BN<sub>4</sub>O<sub>2</sub>Zr: C, 60.86; H, 8.07; N, 9.16. Found: C, 60.45; H, 7.97; N, 8.86. [α]<sub>D</sub><sup>20</sup> = 122.6 (C<sub>6</sub>H<sub>6</sub>). Mp: 66-71 °C.

**{PhB(C<sub>5</sub>H<sub>4</sub>)(S-Ox<sup>*i*</sup>Pr,Me<sub>2</sub>)<sub>2</sub>}Ti(NMe<sub>2</sub>)<sub>2</sub> ({S-2}Ti(NMe<sub>2</sub>)<sub>2</sub>).** H[PhB(C<sub>5</sub>H<sub>5</sub>)(S-Ox<sup>*i*</sup>Pr,Me<sub>2</sub>)<sub>2</sub>] (0.050 g, 0.115 mmol) and Ti(NMe<sub>2</sub>)<sub>4</sub> (0.026 g, 0.115 mmol) in benzene (5 mL) were stirred for 25 h. After filtration, the volatile materials were removed in vacuo to give a red gel which was triturated with pentane giving {PhB(C<sub>5</sub>H<sub>4</sub>)(S-Ox<sup>*i*</sup>Pr,Me<sub>2</sub>)<sub>2</sub>}Ti(NMe<sub>2</sub>)<sub>2</sub> as a off-white solid (0.056 g, 0.099 mmol, 86.1 %). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 400 MHz): δ 7.73 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2 H, *ortho*-C<sub>6</sub>H<sub>5</sub>), 7.39 (m, 2 H, *meta*-C<sub>6</sub>H<sub>5</sub>), 7.21 (m, 1 H, *para*-C<sub>6</sub>H<sub>5</sub>), 6.88 (m, 2 H, C<sub>5</sub>H<sub>4</sub>), 6.70 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 6.59 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 3.12 (s, 6 H, NMe<sub>2</sub>), 3.10 (s, 6 H, NMe<sub>2</sub>), 3.03 (d, 1 H, <sup>2</sup>J<sub>HH</sub> = 5.6 Hz, CNC<sup>*i*</sup>PrH<sub>2</sub>CM<sub>2</sub>O), 2.97 (d, 1 H, <sup>2</sup>J<sub>HH</sub> = 5.6 Hz, CNC<sup>*i*</sup>PrH<sub>2</sub>CM<sub>2</sub>O), 1.82 (m, 1 H, CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 1.70 (m, 1 H, CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 1.23-0.77 (24 H, CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>, 100 MHz): δ 195.50 (br, CNC<sup>*i*</sup>PrH<sub>2</sub>CM<sub>2</sub>O), 152.97 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 135.18 (*ortho*-C<sub>6</sub>H<sub>5</sub>), 134.91 (*meta*-C<sub>6</sub>H<sub>5</sub>), 133.46 (*para*-C<sub>6</sub>H<sub>5</sub>), 127.41 (C<sub>5</sub>H<sub>4</sub>), 125.38 (C<sub>5</sub>H<sub>4</sub>), 125.35 (C<sub>5</sub>H<sub>4</sub>), 84.79 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 84.49 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 79.28 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 78.92 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 44.38 (NMe<sub>2</sub>), 39.32 (NMe<sub>2</sub>), 31.51 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 31.41 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 30.63 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 30.11 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 22.23 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 22.19 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 21.72 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 20.53 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 20.49 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O), 20.29 (CNC(CHMe<sub>2</sub>)H<sub>2</sub>CM<sub>2</sub>O). <sup>11</sup>B NMR (benzene-*d*<sub>6</sub>, 128 MHz): δ -14.8. <sup>15</sup>N NMR

(benzene-*d*<sub>6</sub>, 71 MHz):  $\delta$  -153.8, -156.1. IR (KBr, cm<sup>-1</sup>): 3041 w, 2969 s, 2931 m, 2872 m, 2847 m, 2766 m, 1560 s (CN), 1468 m, 1433 w, 1409 w, 1389 w, 1368 m, 1245 m, 1226 m, 1193 m, 1147 s, 1050 m, 1020 m, 988 m, 941 s, 894 w, 811 w, 740 w, 703 m, 678 m. Anal. Calcd for C<sub>31</sub>H<sub>49</sub>BN<sub>4</sub>O<sub>2</sub>Ti: C, 65.50; H, 8.69; N, 9.86. Found: C, 59.91; H, 8.84; N, 9.51.  $[\alpha]_D = -94.71^\circ$  (C<sub>6</sub>H<sub>6</sub>). Mp: 89-93 °C.

**{PhB(C<sub>5</sub>H<sub>4</sub>)(S-Ox<sup>*i*Pr,Me<sub>2</sub></sup>)<sub>2</sub>}Hf(NMe<sub>2</sub>)<sub>2</sub> (**S-2**)Hf(NMe<sub>2</sub>)<sub>2</sub>}. A round bottom Schlenk flask was charged with H[PhB(C<sub>5</sub>H<sub>5</sub>)(S-Ox<sup>*i*Pr,Me<sub>2</sub></sup>)<sub>2</sub>] (0.125 g, 0.287 mmol) and Hf(NMe<sub>2</sub>)<sub>4</sub> (0.101 g, 0.287 mmol). The solids were dissolved in benzene (20 mL), and the resulting solution was stirred for 8 h. After filtration, the volatile materials were removed *in vacuo* to give a light yellow gel which was triturated with pentane giving {PhB(C<sub>5</sub>H<sub>4</sub>)(S-Ox<sup>*i*Pr,Me<sub>2</sub></sup>)<sub>2</sub>}Hf(NMe<sub>2</sub>)<sub>2</sub> as an off-white solid (0.185 g, 0.265 mmol, 92.0%). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 400 MHz):  $\delta$  8.06 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz, 2 H, *ortho*-C<sub>6</sub>H<sub>5</sub>), 7.46 (m, 2 H, *meta*-C<sub>6</sub>H<sub>5</sub>), 7.26 (m, 1 H, *para*-C<sub>6</sub>H<sub>5</sub>), 6.64 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 6.55 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 6.23 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 6.00 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 3.26 (d, 1 H, <sup>2</sup>*J*<sub>HH</sub> = 5.6 Hz, CNC<sup>*i*Pr</sup>HCM<sub>2</sub>O), 3.23 (d, 1 H, <sup>2</sup>*J*<sub>HH</sub> = 5.6 Hz, CNC<sup>*i*Pr</sup>HCM<sub>2</sub>O), 2.84 (s, 6 H, NMe<sub>2</sub>), 2.76 (s, 6 H, NMe<sub>2</sub>), 1.74 (m, 2 H, CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 1.35 (s, 3 H, CNC<sup>*i*Pr</sup>HCM<sub>2</sub>O), 1.24 (s, 3 H, CNC<sup>*i*Pr</sup>HCM<sub>2</sub>O), 1.19 (s, 3 H, CNC<sup>*i*Pr</sup>HCM<sub>2</sub>O), 1.15 (s, 3 H, CNC<sup>*i*Pr</sup>HCM<sub>2</sub>O), 1.11 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.8 Hz, 3 H, CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 1.07 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.8 Hz, 3 H, CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 0.99 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.8 Hz, 3 H, CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 0.89 (d, <sup>3</sup>*J*<sub>HH</sub> = 6.8 Hz, 3 H, CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>, 100 MHz):  $\delta$  151.36 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 135.07 (*ortho*-C<sub>6</sub>H<sub>5</sub>), 127.52 (*meta*-C<sub>6</sub>H<sub>5</sub>), 125.28 (*para*-C<sub>6</sub>H<sub>5</sub>), 122.43 (C<sub>5</sub>H<sub>4</sub>), 121.55 (C<sub>5</sub>H<sub>4</sub>), 113.38 (C<sub>5</sub>H<sub>4</sub>), 112.62 (C<sub>5</sub>H<sub>4</sub>), 85.31 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 79.02 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 44.20 (NMe<sub>2</sub>), 42.71 (NMe<sub>2</sub>), 30.51 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 30.38 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 30.32 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 30.08 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 22.02 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 21.84 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 20.42 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 20.32 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 20.00 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O). <sup>15</sup>N NMR (benzene-*d*<sub>6</sub>, 71 MHz):  $\delta$  -148.83, -150.66. <sup>11</sup>B NMR (benzene-*d*<sub>6</sub>, 128 MHz):  $\delta$  -14.6. IR (KBr, cm<sup>-1</sup>): 3071 m, 3044 m, 2967 s, 2932 s, 2870 s, 2822 s, 2770 s, 1559 s (CN), 1469 s, 1433 m, 1393 m, 1373 m, 1353 w, 1246 m, 1195 m, 1145 s, 1105 w, 1048 m, 1021 m, 946 s, 882 w, 856 w, 807 s, 769 w, 740 s, 703 s. Anal. Calcd for C<sub>31</sub>H<sub>49</sub>BN<sub>4</sub>O<sub>2</sub>Hf: C, 53.26; H, 7.07; N, 8.01. Found: C, 52.78; H, 7.32; N, 8.04.  $[\alpha]_D = -86.98^\circ$  (C<sub>6</sub>H<sub>6</sub>). Mp: 60-65 °C, dec.**

**PhB(C<sub>5</sub>H<sub>4</sub>)(S-Ox<sup>iPr,Me<sub>2</sub></sup>)<sub>2</sub>ZrCl<sub>2</sub> ({S-2}ZrCl<sub>2</sub>).** The compounds K<sub>2</sub>[PhB(C<sub>5</sub>H<sub>4</sub>)(S-Ox<sup>iPr,Me<sub>2</sub></sup>)<sub>2</sub>] (0.150 g, 0.294 mmol) and ZrCl<sub>4</sub> (0.070 g, 0.300 mmol) were dissolved in THF (10 mL), and the resulting solution was stirred for 1 h at room temperature to afford {S-2}ZrCl<sub>2</sub>. Unfortunately, the complex could not be isolated because it decomposes upon evaporation of the THF solvent. Instead, it was generated in situ and used below. <sup>1</sup>H NMR (tetrahydrofuran-*d*<sub>8</sub>, 400 MHz): δ 7.46 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, 2 H, *ortho*-C<sub>6</sub>H<sub>5</sub>), 7.03 (m, 2 H, *meta*-C<sub>6</sub>H<sub>5</sub>), 6.95 (m, 1 H, *para*-C<sub>6</sub>H<sub>5</sub>), 6.88 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 6.66 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 6.57 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 6.23 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 3.63 (m, 2 H, CNC<sup>iPr</sup>HCM<sub>2</sub>O), 1.63 (m, 2 H, CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 1.45 (s, 3 H, CNC<sup>iPr</sup>HCM<sub>2</sub>O), 1.39 (s, 3 H, CNC<sup>iPr</sup>HCM<sub>2</sub>O), 1.35 (s, 3 H, CNC<sup>iPr</sup>HCM<sub>2</sub>O), 1.08 (s, 3 H, CNC<sup>iPr</sup>HCM<sub>2</sub>O), 1.06 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 3 H, CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 0.98 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 3 H, CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 0.94 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 3 H, CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 0.85 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 3 H, CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O). <sup>11</sup>B NMR (tetrahydrofuran-*d*<sub>8</sub>, 128 MHz): δ -15.7.

**PhB(C<sub>5</sub>H<sub>4</sub>)(S-Ox<sup>iPr,Me<sub>2</sub></sup>)<sub>2</sub>Zr(NMe<sub>2</sub>)Cl ({S-2}Zr(NMe<sub>2</sub>)Cl).** A THF solution of {S-2}ZrCl<sub>2</sub> and LiNMe<sub>2</sub> (0.015 g, 0.294 mmol) allowed to stir for 1 h at room temperature. All the volatile materials were removed in vacuo, and the residue was extracted with benzene. Removal of solvent in vacuo provided {S-2}Zr(NMe<sub>2</sub>)Cl as a light yellow solid (0.141 g, 0.233 mmol, 79.3%). The spectroscopic data for the major isomer is given: <sup>1</sup>H NMR (tetrahydrofuran-*d*<sub>8</sub>, 400 MHz): δ 7.38 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2 H, *ortho*-C<sub>6</sub>H<sub>5</sub>), 7.06 (m, 2 H, *meta*-C<sub>6</sub>H<sub>5</sub>), 6.96 (t, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 1 H, *para*-C<sub>6</sub>H<sub>5</sub>), 6.19 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 6.15 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 6.07 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 5.84 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 3.86 (m, 2 H, CNC<sup>iPr</sup>HCM<sub>2</sub>O), 2.93 (s, NMe<sub>2</sub>), 1.72 (m, 2 H, CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 1.32 (s, 3 H, CNC<sup>iPr</sup>HCM<sub>2</sub>O), 1.59-1.19 (24 H, CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O). <sup>13</sup>C{<sup>1</sup>H} NMR (tetrahydrofuran-*d*<sub>8</sub>, 100 MHz): δ 189.59 (CNC(CHMe<sub>2</sub>)HCH<sub>2</sub>O), 161.55 (*ipso*-C<sub>6</sub>H<sub>5</sub>), 134.12 (*ortho*-C<sub>6</sub>H<sub>5</sub>), 130.42 (*meta*-C<sub>6</sub>H<sub>5</sub>), 128.13 (*para*-C<sub>6</sub>H<sub>5</sub>), 126.53 (C<sub>5</sub>H<sub>4</sub>), 122.49 (C<sub>5</sub>H<sub>4</sub>), 111.78 (C<sub>5</sub>H<sub>4</sub>), 104.16 (C<sub>5</sub>H<sub>4</sub>), 81.79 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 81.48 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 80.79 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 80.61 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 30.72 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O, overlapped), 30.31 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O, overlapped), 30.29 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 30.24 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 22.04 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O, overlapped), 21.64 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O), 21.58 (CNC(CHMe<sub>2</sub>)HCM<sub>2</sub>O). <sup>11</sup>B NMR (tetrahydrofuran-*d*<sub>8</sub>, 128

MHz):  $\delta$  -16.4.  $^{15}\text{N}$  NMR (tetrahydrofuran- $d_8$ , 71 MHz):  $\delta$  -153.4, -154.9 (oxazoline). IR (KBr,  $\text{cm}^{-1}$ ): 3059 w, 2958 s, 2924 m, 2878 m, 1578 s (CN), 1567 s (CN), 1484 w, 1459 m, 1428 w, 1380 w, 1361 m, 1342 w, 1290 m, 1250 m, 1190 m, 1120 s, 1056 w, 1037 m, 1017 w, 966 s, 936 w, 876m, 824 s, 792 w, 777 m, 747 s, 731 s, 704 m, 661 w. Anal. Calcd for  $\text{C}_{29}\text{H}_{43}\text{BClN}_3\text{O}_2\text{Zr}$ : C, 57.75; H, 7.19; N, 6.97. Found: C, 57.56; H, 6.49; N, 6.81. Mp: 123-127 °C, dec.  $[\alpha]_{\text{D}}^{20} = -111.4^\circ$ .

**{Ph<sub>2</sub>B(C<sub>5</sub>H<sub>4</sub>)(S-Ox<sup>*i*Pr,Me<sub>2</sub>)}</sup>**Zr(NMe<sub>2</sub>)<sub>2</sub> (**{S-7}Zr(NMe<sub>2</sub>)<sub>2</sub>**). The compounds H[Ph<sub>2</sub>B(C<sub>5</sub>H<sub>4</sub>)(S-Ox<sup>*i*Pr,Me<sub>2</sub>)] (0.040 g, 0.108 mmol) and Zr(NMe<sub>2</sub>)<sub>4</sub> (0.029 g, 0.108 mmol) were dissolved in benzene (4 mL), and the resulting solution was stirred for 20 min. The volatile materials were evaporated to afford {Ph<sub>2</sub>B(C<sub>5</sub>H<sub>4</sub>)(S-Ox<sup>*i*Pr,Me<sub>2</sub>)}Zr(NMe<sub>2</sub>)<sub>2</sub> as an off-white solid (0.054 g, 0.098 mmol, 91.5%).  $^1\text{H}$  NMR (benzene- $d_6$ , 400 MHz):  $\delta$  8.16 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 2 H, *ortho*-C<sub>6</sub>H<sub>5</sub>), 8.06 (d,  $^3J_{\text{HH}} = 7.2$  Hz, 2 H, *ortho*-C<sub>6</sub>H<sub>5</sub>), 7.46 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2 H, *meta*-C<sub>6</sub>H<sub>5</sub>), 7.34 (t,  $^3J_{\text{HH}} = 7.6$  Hz, 2 H, *meta*-C<sub>6</sub>H<sub>5</sub>), 7.27 (m, 1 H, *para*-C<sub>6</sub>H<sub>5</sub>), 7.17 (m, 1 H, *para*-C<sub>6</sub>H<sub>5</sub>), 6.64 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 6.55 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 6.23 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 6.01 (m, 1 H, C<sub>5</sub>H<sub>4</sub>), 3.24 (d, 1 H,  $^3J_{\text{HH}} = 5.6$  Hz, CNC<sup>*i*</sup>PrHMe<sub>2</sub>O), 2.84 (s, 6 H, NMe<sub>2</sub>), 2.76 (s, 6 H, NMe<sub>2</sub>), 1.74 (m, 1 H, CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 1.35 (s, 3 H, CNC<sup>*i*</sup>PrHMe<sub>2</sub>O), 1.24 (s, 3 H, CNC<sup>*i*</sup>PrHMe<sub>2</sub>O), 1.16 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 3 H, CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 0.99 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 3 H, CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O).  $^{13}\text{C}\{^1\text{H}\}$  NMR (benzene- $d_6$ , 150 MHz):  $\delta$  194.29 (br, CNC<sup>*i*</sup>PrHCH<sub>2</sub>O), 152.26 (br, *ipso*-C<sub>6</sub>H<sub>5</sub>), 151.51 (br, *ipso*-C<sub>6</sub>H<sub>5</sub>), 135.14 (*ortho*-C<sub>6</sub>H<sub>5</sub>), 133.11 (*ortho*-C<sub>6</sub>H<sub>5</sub>), 127.51 (*meta*-C<sub>6</sub>H<sub>5</sub>), 126.42 (*meta*-C<sub>6</sub>H<sub>5</sub>), 125.93 (*para*-C<sub>6</sub>H<sub>5</sub>), 125.01 (*para*-C<sub>6</sub>H<sub>5</sub>), 123.51 (C<sub>5</sub>H<sub>4</sub>), 123.33 (C<sub>5</sub>H<sub>4</sub>), 114.41 (C<sub>5</sub>H<sub>4</sub>), 113.64 (C<sub>5</sub>H<sub>4</sub>), 84.61 (CNC<sup>*i*</sup>PrHMe<sub>2</sub>O), 78.03 (CNC<sup>*i*</sup>PrHMe<sub>2</sub>O), 44.51 (NMe<sub>2</sub>), 41.99 (NMe<sub>2</sub>), 30.44 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 30.02 (CNC<sup>*i*</sup>PrHMe<sub>2</sub>O), 21.96 (CNC<sup>*i*</sup>PrHMe<sub>2</sub>O), 20.68 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O), 20.21 (CNC(CHMe<sub>2</sub>)HMe<sub>2</sub>O).  $^{11}\text{B}$  NMR (benzene- $d_6$ , 128 MHz):  $\delta$  -11.7.  $^{15}\text{N}\{^1\text{H}\}$  NMR (benzene- $d_6$ , 71 MHz):  $\delta$  -155.2 (CNC<sup>*i*</sup>PrHMe<sub>2</sub>O). IR (KBr,  $\text{cm}^{-1}$ ): 3045 w, 3008 w, 2967 s, 2931 s, 2772 w, 1562 m (CN), 1489 w, 1467 s, 1431 w, 1388 m, 1260 s, 1194 s, 1093 s, 1054 s, 947 s, 884 w, 855 w, 804 s, 734 s. Anal. Calcd for  $\text{C}_{29}\text{H}_{40}\text{BN}_3\text{OZr}$ : C, 63.48; H, 7.35; N, 7.66. Found: C, 63.31; H, 7.01; N, 7.19. Mp: 121-124 °C, dec.  $[\alpha]_{\text{D}}^{20} = -82.02^\circ$  (C<sub>6</sub>H<sub>6</sub>).</sup></sup>

**2,2-Diethoxypent-4-enenylamine (18a).** 2,2-Diethoxypent-4-enenitrile was synthesized according to the published procedure.<sup>23</sup> An oven-dried 2-neck Schlenk flask fitted with reflux condenser was charged with LiAlH<sub>4</sub> (0.350 g, 9.22 mmol). The flask was cooled to 0 °C and diethyl ether (60 mL) was added. 2,2-Diethoxypent-4-enenitrile (0.630 g, 3.72 mmol) was added in a dropwise to the suspension cooled to 0 °C. The resulting solution was stirred overnight at room temperature. Then, the solution was cooled to 0 °C and 3 mL water was added slowly. The solution stirred 1 h at room temperature. The ether layer was decanted, and the white precipitation was extracted with diethyl ether (3×). All the organic solutions were combined, dried with Na<sub>2</sub>SO<sub>4</sub> and filtered. The solvent was removed in vacuo to give crude 2,2-diethoxypent-4-enenylamine. Vacuum distillation (80 °C, 5 mm Hg) of the crude product afforded the pure 2,2-diethoxypent-4-enenylamine as a colorless oil, which was stored in glovebox with activated molecular sieves (0.52 g, 3.00 mmol, 80% yield). <sup>1</sup>H NMR (benzene-*d*<sub>6</sub>, 400 MHz): δ 5.90-5.79 (m, 1 H, CH=CH<sub>2</sub>), 5.08-5.01 (m, 2 H, CH=CH<sub>2</sub>), 3.40-3.31 (m, 4 H, OCH<sub>2</sub>CH<sub>3</sub>), 2.79 (s, 2 H, NH<sub>2</sub>CH<sub>2</sub>), 2.55 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2 H, =CHCH<sub>2</sub>), 3.40-3.31 (t, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, OCH<sub>2</sub>CH<sub>3</sub>), 0.63 (br s, 2 H, NH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-*d*<sub>6</sub>, 100.6 MHz): δ 134.74 (CH=CH<sub>2</sub>), 117.70 (CH=CH<sub>2</sub>), 103.20 (C(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 55.98 (C(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 44.81 (CH<sub>2</sub>NH<sub>2</sub>), 37.97 (=CHCH<sub>2</sub>), 15.99 (C(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>). <sup>15</sup>N NMR (benzene-*d*<sub>6</sub>, 61 MHz): δ 364.6. IR (KBr, cm<sup>-1</sup>): 3396 w, 3077 m, 2976 s, 2930 s, 2883 s, 1641 m, 1621 w, 1481 w, 1456 m, 1443 s, 1417 w, 1389 m, 1365 w, 1316 w, 1266 w, 1218 s, 1157 s, 1116 s, 1080 s, 1053 s, 1001 s, 915 s, 879 w, 825 s, 770 w, 677 w. MS (ESI) exact mass Calcd for C<sub>9</sub>H<sub>19</sub>NNaO<sub>2</sub>: m/z 196.1308 ([M<sup>+</sup>+Na<sup>+</sup>]), Found: 196.1303 (Δ 2.89 ppm).

**4,4-Diethoxy-2-methyl-pyrrolidine (18b).** <sup>1</sup>H NMR (chloroform-*d*, 400 MHz): δ 3.41-3.36 (m, 4 H, OCH<sub>2</sub>CH<sub>3</sub>), 3.22-3.17 (m, 1 H, CHMeNH), 3.01 (d, <sup>2</sup>J<sub>HH</sub> = 11.6 Hz, 1 H, CH<sub>2</sub>NH), 2.81 (d, <sup>2</sup>J<sub>HH</sub> = 11.6 Hz, 1 H, CH<sub>2</sub>NH), 2.06-2.01 (m, 1 H, CH<sub>2</sub>CHMe), 1.47 (br, 2 H, NH<sub>2</sub>), 1.43-1.37 (m, CH<sub>2</sub>CHMe), 1.12 (t, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 6 H, OCH<sub>2</sub>CH<sub>3</sub>), 1.09 (d, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz, CHMeNH). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, chloroform-*d*): δ 111.99 C(OCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, 57.54 (OCH<sub>2</sub>CH<sub>3</sub>), 55.39 (CH<sub>2</sub>NH), 53.58 (CHMeNH), 44.17 (CH<sub>2</sub>CHMe), 21.37 (CHCH<sub>3</sub>), 15.61 (OCH<sub>2</sub>CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 2975 s, 2930 s, 2883 s, 1641 w, 1542 w, 1481 w, 1444 m, 1391 s, 1350 m, 1336 m, 1321 m, 1265 m, 1234 m, 1158 s, 1126 s, 1077 s, 1054 s, 1012 m, 949 m, 888

w, 810 m. MS (ESI) exact mass Calcd. for C<sub>9</sub>H<sub>19</sub>NO<sub>2</sub>: m/z 174.1489 ([M<sup>+</sup>+H<sup>+</sup>]), Found: 174.1488 (Δ 0.32 ppm).

### General procedure for catalytic hydroamination/cyclization

a) **NMR scale catalysis at r.t.:** In a typical small-scale hydroamination experiment, a J. Young style NMR tube with a resealable Teflon valve was charged with 50 μmol of aminoalkene substrate, 5.0 μmol of catalyst, and 0.5 mL of solvent (benzene-*d*<sub>6</sub>, methylene chloride-*d*<sub>2</sub>, toluene-*d*<sub>8</sub> or tetrahydrofuran-*d*<sub>8</sub>). The vessel was sealed, and the reaction was monitored by <sup>1</sup>H NMR spectroscopy at regular intervals.

b) **Micromolar scale catalysis at 0 °C:** The appropriate aminoalkene (50 μmol) was dissolved in 0.3 mL of toluene-*d*<sub>8</sub> and transferred to a NMR tube. The NMR tube was sealed with a rubber septum and cooled to 0 °C for 0.5 h. The appropriate catalyst (5.0 μmol) was placed in a small test tube and dissolved in 0.2 mL of toluene-*d*<sub>8</sub>. The test tube was capped with a rubber septum and cooled to 0 °C for 0.5 h. Then, the catalyst solution was quickly transferred to the NMR tube at 0 °C by syringe. The NMR tube containing the reaction mixture was allowed to stand at 0 °C for 10 to 12 h continuously and was then checked by <sup>1</sup>H NMR spectroscopy.

c) **Micromolar scale catalysis at –30 °C:** The appropriate aminoalkene (50 μmol) and catalyst (5.0 μmol) were placed in two separate vials. Toluene-*d*<sub>8</sub> (0.4 mL) was added to both vials, which were then cooled to –30 °C in the glovebox freezer for 30 min. Then, the cold solution of aminoalkene was added to the catalyst, and the reaction mixture was placed in the freezer. The cold solution was taken out from the glove box and quenched immediately, and was checked by NMR spectroscopy.

d) **Procedure for isolation of optically active pyrrolidines.** A flask was charged with the catalyst {PhB(C<sub>5</sub>H<sub>4</sub>)(*S*-Ox<sup>*i*Pr,Me<sub>2</sub></sup>)<sub>2</sub>}Zr(NMe<sub>2</sub>)<sub>2</sub> (0.060 g, 0.103 mmol), benzene (20–30 mL) and the appropriate aminoalkene (2.58 mmol). The solution was stirred at room temperature for 3 h. Then, the products were purified by fractional distillation in vacuo to afford the cyclic amines as colorless oils.

2-Methyl-4,4-diphenylpyrrolidine (**8b**) was purified by Kugelrohr distillation. Yield: 93%, bp: 125 °C, 10<sup>–5</sup> mBar (dynamic vacuum on a high vacuum line).

3-Methyl-2-aza-spiro[4,4]nonane (**9b**). Yield: 81%, bp: 46–51 °C, 2 mm Hg.

2,4,4-Trimethylpyrrolidine (**10b**). Yield: 82%, bp: 123–128 °C.

2-Methyl-4,4-bis(2-propenyl)pyrrolidine (**11b**). Yield: 94%, bp: 86–90 °C, 5 mm Hg.

3-Methyl-2-aza-spiro[4,5]decane (**12b**); Yield: 88%, bp: 100-105 °C, 0.1 mm Hg (dynamic vacuum).

2-Methyl-6,6-diphenylazepane (**16b**); Yield: 64%, purified by silica gel column chromatography (hexane:EtOAc = 8:1).

2-Methylindoline (**17b**). Yield: 85%, bp: 75-79 °C, 8 mm Hg.

2-Methyl-4,4-diethoxypyrrolidine (**18b**); Yield: 83%, bp: 80 °C, 5 mm Hg.

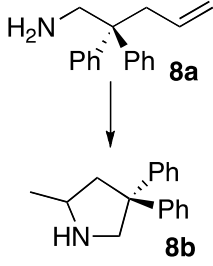
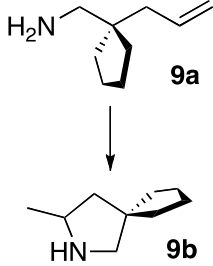
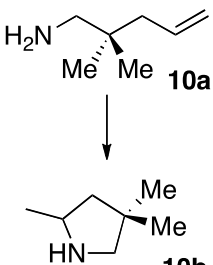
4-Allyl-2-methyl-4-(4-bromophenyl)pyrrolidine (**19b**): Yield: 95%, bp: 120-125 °C, 0.1 mm Hg (dynamic vacuum).

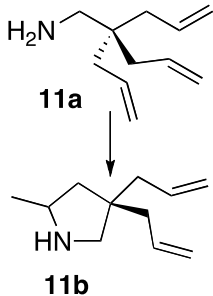
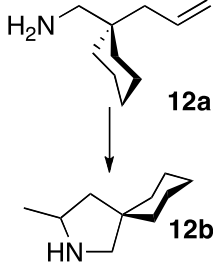
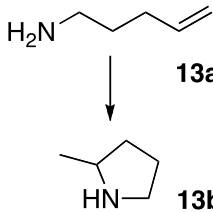
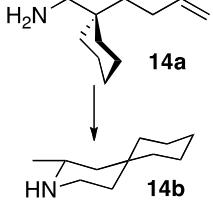
4-Allyl-2,4-dimethyl-pyrrolidine (**20b**). Yield: 90%, bp: 47-52 °C, 5 mm Hg.

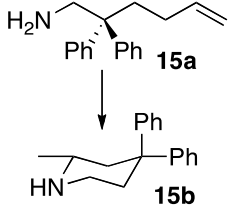
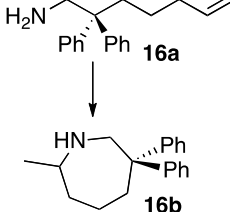
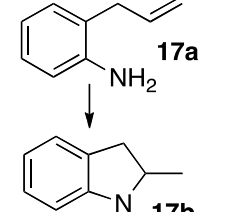
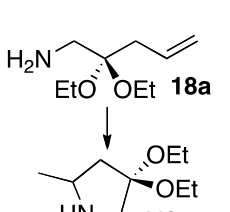
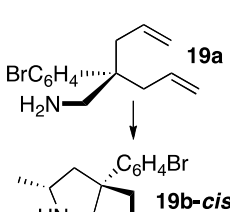
2-Ethyl-4,4-diphenylpyrrolidine (**21b**). Yield: 77%, purified by silica gel column chromatography (hexane:EtOAc = 7:1).

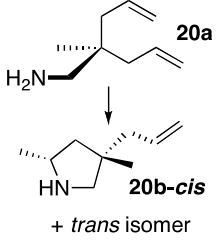
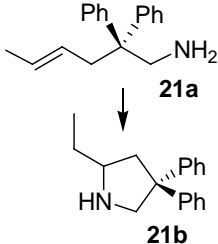
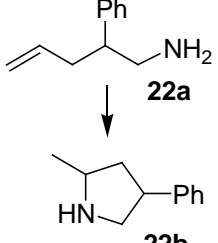
2-Methyl-4-phenylpyrrolidine (**22b**), Yield: 89%, bp: 47-52 °C, 5 mm Hg.

**Table S1. Catalytic cyclization of aminoalkenes with achiral and optically active group 4 compounds coordinated by mixed cyclopentadienyl bis(oxazolinyl)borato ligands.<sup>a</sup>**

Reactant to Product	Entry	Precatalyst	Solvent	Time (h)	Yield (%) <sup>b</sup>	ee (%) <sup>c</sup>
 <p><b>8a</b></p> <p><b>8b</b></p>	1 <sup>d</sup>	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	11	90 (84)	racemic
	2 <sup>d</sup>	{ <b>1</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	24	29	racemic
	3 <sup>e</sup>	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	1.25	95 (93)	93 ( <i>R</i> )
	4 <sup>e</sup>	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	6	95 <sup>f</sup>	93 ( <i>R</i> )
	5 <sup>e</sup>	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	THF- <i>d</i> <sub>8</sub>	5	95	95 ( <i>R</i> )
	6 <sup>e</sup>	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	CD <sub>2</sub> Cl <sub>2</sub>	5	95	94 ( <i>R</i> )
	7	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>7</sub> D <sub>8</sub>	5 d	98 <sup>g</sup>	98 ( <i>R</i> ) <sup>h</sup>
	8	{ <i>R</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	1.25	95	93 ( <i>S</i> )
	9	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	5	97 (93)	91 ( <i>R</i> )
	10	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>7</sub> D <sub>8</sub>	15	98 <sup>i</sup>	97 ( <i>R</i> ) <sup>h</sup>
	11	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	CD <sub>2</sub> Cl <sub>2</sub>	15	96 <sup>i</sup>	94 ( <i>R</i> )
	12	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	THF- <i>d</i> <sub>8</sub>	20	98 <sup>i</sup>	96 ( <i>R</i> ) <sup>h</sup>
	13	{ <i>S</i> - <b>2</b> }Ti(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	5 d	93	76 ( <i>R</i> )
	14 <sup>j</sup>	{ <i>S</i> - <b>3</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	18	95 (89)	93 ( <i>R</i> )
 <p><b>9a</b></p> <p><b>9b</b></p>	15	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	11	88	racemic
	16 <sup>e</sup>	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	4	88 (81)	92 ( <i>R</i> )
	17	{ <i>R</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	4	88	92 ( <i>S</i> )
	18	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	20	90	94 ( <i>R</i> )
	19	[ <i>S</i> - <b>2</b> ]Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>7</sub> D <sub>8</sub>	8	85 <sup>i</sup>	95 ( <i>R</i> ) <sup>h</sup>
	20	{ <i>S</i> - <b>2</b> }Ti(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	48	0	-
21 <sup>j</sup>	{ <i>S</i> - <b>3</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	11	77	88 ( <i>R</i> )	
 <p><b>10a</b></p> <p><b>10b</b></p>	22 <sup>d</sup>	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	11	85	racemic
	23 <sup>e</sup>	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	7	89 (82)	89
	24	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>7</sub> D <sub>8</sub>	8 d	95 <sup>g</sup>	93
	25	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	20	90	87
	26	{ <i>S</i> - <b>2</b> }Ti(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	72	0	-
	27	{ <i>S</i> - <b>3</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	48	20	-

	28	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	11	98	racemic
	29	{ <i>S</i> -2}Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	0.75	98 (94)	92 ( <i>R</i> )
	30	{ <i>S</i> -2}Zr(NMe <sub>2</sub> ) <sub>2</sub>	CD <sub>2</sub> Cl <sub>2</sub>	1	98	94 ( <i>R</i> )
	31	{ <i>S</i> -2}Zr(NMe <sub>2</sub> ) <sub>2</sub>	THF- <i>d</i> <sub>8</sub>	1.25	96	94 ( <i>R</i> )
	32	{ <i>S</i> -2}Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	5	98 (92)	90 ( <i>R</i> )
	33	{ <i>S</i> -2}Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>7</sub> H <sub>8</sub>	20	90 (85) <sup><i>i</i></sup>	96 ( <i>R</i> ) <sup><i>h</i></sup>
34	{ <i>S</i> -2}Ti(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	5 d	90	82 ( <i>R</i> )	
35 <sup><i>j</i></sup>	{ <i>S</i> -3}Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	30	97	88 ( <i>R</i> )	
	36 <sup><i>d</i></sup>	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	11	92 (87)	racemic
	37 <sup><i>e</i></sup>	{ <i>S</i> -2}Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	1.25	96 (88)	90 ( <i>R</i> )
	38 <sup><i>e</i></sup>	{ <i>S</i> -2}Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	6.5	92 <sup><i>f</i></sup>	90 ( <i>R</i> )
	39	{ <i>S</i> -2}Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>7</sub> D <sub>8</sub>	10	94 <sup><i>i</i></sup>	91 ( <i>R</i> )
	40 <sup><i>e</i></sup>	{ <i>S</i> -2}Zr(NMe <sub>2</sub> ) <sub>2</sub>	THF- <i>d</i> <sub>8</sub>	11	92 <sup><i>i</i></sup>	94 ( <i>R</i> )
	41	{ <i>S</i> -2}Zr(NMe <sub>2</sub> ) <sub>2</sub>	CD <sub>2</sub> Cl <sub>2</sub>	10	95 <sup><i>i</i></sup>	93 ( <i>R</i> )
	42	{ <i>R</i> -2}Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	1.25	96	90 ( <i>S</i> )
	43	{ <i>S</i> -2}Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	5	95 (91)	93 ( <i>R</i> )
	44	{ <i>S</i> -2}Ti(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	5 d	75	83 ( <i>R</i> )
45 <sup><i>j</i></sup>	{ <i>S</i> -3}Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	30	92	87 ( <i>R</i> )	
	46	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	15	90	racemic
	47 <sup><i>e</i></sup>	{ <i>S</i> -2}Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	15	24 <sup><i>k</i></sup>	-
	48	{ <i>S</i> -2}Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	48	0	-
	49	{ <i>S</i> -2}Ti(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	48	0	-
	50	{ <i>S</i> -3}Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	48	0	-
	51 <sup><i>d</i></sup>	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	11	87 (80)	racemic
	52 <sup><i>e</i></sup>	{ <i>S</i> -2}Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	40	48	31 <sup><i>h</i></sup>
	53	{ <i>S</i> -2}Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	30	85 <sup><i>l</i></sup>	26 <sup><i>h</i></sup>
	54	{ <i>S</i> -2}Ti(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	0	0	-
	55	{ <i>S</i> -3}Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	48	80	29

	56	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	4 d	95	racemic
	57 <sup>e</sup>	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	4 d	65	46
	58	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	20	89 <sup>l</sup>	18
	59	{ <i>S</i> - <b>2</b> }Ti(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	0	0	-
	60	{ <i>S</i> - <b>3</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	48	0	-
	61	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	5 d	56	racemic
	62	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	5 d	73 (64)	91
	63	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	5 d	0	-
	64	{ <i>S</i> - <b>2</b> }Ti(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	5 d	0	-
	65	{ <i>S</i> - <b>3</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	5 d	0	-
	66	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	72	90	racemic
	67	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	3 d	92 (85)	95
	68	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	5 d	80	94
	69	{ <i>S</i> - <b>2</b> }Ti(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	72	0	-
	70	{ <i>S</i> - <b>3</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	72	0	0
	71	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	30	90	racemic
	72	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	30	90 (83)	97
	73	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	5 d	90	96
	74	{ <i>S</i> - <b>2</b> }Ti(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	72	0	-
	75	{ <i>S</i> - <b>3</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	5 d	15	-
	76	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	20	100, d.r. = 4:1	racemic
	77	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	0.33	100, d.r. = 1.2:1 (95)	97, 95
	78	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>7</sub> D <sub>8</sub>	2 d	100 <sup>g</sup> , d.r. = 1.3:1	99, 99 <sup>h</sup>
	79	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	3	90, d.r. = 2:1 (84)	93, 95.6
	80 <sup>j</sup>	{ <i>S</i> - <b>3</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	48	100, d.r. = 1.2:1	96, 98

 <p>20a H<sub>2</sub>N 20b-cis + trans isomer</p>	81	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	30	85, d.r. = 1.5:1	racemic
	82 <sup>e</sup>	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	0.5	98, d.r. = 1.1:1	93, 92
	83	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	20	90, d.r. = 1.4:1	87, 63
	84 <sup>j</sup>	{ <i>S</i> - <b>3</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	30	85, d.r. = 1.2:1	92, 91
 <p>Ph Ph 21a NH<sub>2</sub> 21b HN</p>	85	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	4 d	20	racemic
	86	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	4 d	85 (77)	89
	87	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	4 d	15	-
	88	{ <i>S</i> - <b>2</b> }Ti(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	4 d	0	-
	89	{ <i>S</i> - <b>3</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	4 d	0	-
 <p>Ph 22a NH<sub>2</sub> 22b HN</p>	90	{ <b>1</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	20	95, d.r. = 1.4:1	racemic
	91	{ <i>S</i> - <b>2</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	15	95, d.r. = 3:1	66, 57 <sup>h</sup>
	92	{ <i>S</i> - <b>2</b> }Hf(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	24	90, d.r. = 2.5:1	65, 58 <sup>h</sup>
	93	{ <i>S</i> - <b>3</b> }Zr(NMe <sub>2</sub> ) <sub>2</sub>	C <sub>6</sub> D <sub>6</sub>	48	20, d.r. = 3:1	-

<sup>a</sup> Reaction conditions: 10 mol % catalyst, r.t. unless noted. <sup>b</sup> Yield of isolated product is given in parentheses. <sup>c</sup> % ee ( $\pm 0.5\%$ ) was determined by <sup>1</sup>H and/or <sup>19</sup>F NMR spectroscopy by integration of the spectra of Mosher amide derivatives. <sup>d</sup> The reaction reported previously in ref. 9. <sup>e</sup> The reaction reported previously in ref. 5. <sup>f</sup> 2 mol % catalyst. <sup>g</sup> Reaction performed at -30 °C. <sup>h</sup> % ee verified by HPLC. <sup>i</sup> Reaction performed at 0 °C. <sup>j</sup> The reaction reported previously in ref. 8. <sup>k</sup> Reaction performed at 110 °C. <sup>l</sup> Reaction performed at 85 °C.

**Procedures for NMR kinetic measurements.** Reaction progress was monitored by single scan acquisition of a series of <sup>1</sup>H NMR spectra at regular intervals on a Bruker DRX400 spectrometer. The concentrations of C-(1-allyl-cyclohexyl)-methylamine and 3-methyl-2-aza-spiro[4,5]decane were determined by integration of resonances corresponding to species of interest and integration of a tetrakis(trimethylsilyl)silane standard of accurately known and constant concentration (4.36 mM in toluene-*d*<sub>8</sub>). The temperature in the NMR probe was preset for each experiment, and it was kept constant and monitored during each experiment. For reactions heated above 296 K, the probe temperature was calibrated using an 80% ethylene glycol sample in 20% DMSO-*d*<sub>6</sub> using the equation:  $T = [(4.218 - \Delta)/0.009132] \text{ K}$  ( $\Delta$  equals the chemical shift difference of the two

ethylene glycol resonances). For reactions at performed at 296 K or below, the probe was calibrated using CH<sub>3</sub>OH using the equation  $T = [-23.832 \cdot \Delta^2 - 29.46 \cdot \Delta + 403]$  K ( $\Delta$  = chemical shift difference of two peaks of CH<sub>3</sub>OH).

**Representative example:** Catalytic conversion of *C*-(1-allyl-cyclohexyl)-methylamine into 3-methyl-2-aza-spiro[4,5]decane using 10 mol % [ $\{\text{PhB}(\text{C}_5\text{H}_4)(\text{S-Ox}^{i\text{Pr,Me}_2})_2\}\text{Zr}(\text{NMe}_2)_2$ ] as a catalyst is described. A 5 mL stock solution in toluene-*d*<sub>8</sub> containing a known concentration of the internal standard tetrakis(trimethylsilyl)silane (0.0070 g, 0.0218 mmol, 4.36 mM) was prepared using a 5 mL volumetric flask. The stock solution (0.50 mL) was added by a 1 mL glass syringe to a known amount of [ $\{\text{PhB}(\text{C}_5\text{H}_4)(\text{S-Ox}^{i\text{Pr,Me}_2})_2\}\text{Zr}(\text{NMe}_2)_2$ ] (0.0040 g, 6.52 μmol) in a glass vial. The resulting solution was transferred to a NMR tube, capped with a rubber septum, and a <sup>1</sup>H NMR spectrum was acquired. The concentration of [ $\{\text{PhB}(\text{C}_5\text{H}_4)(\text{S-Ox}^{i\text{Pr,Me}_2})_2\}\text{Zr}(\text{NMe}_2)_2$ ] was determined from this <sup>1</sup>H NMR spectrum by comparison of integration of resonances assigned to [ $\{\text{PhB}(\text{C}_5\text{H}_4)(\text{S-Ox}^{i\text{Pr,Me}_2})_2\}\text{Zr}(\text{NMe}_2)_2$ ] with that from the internal standard. Neat substrate *C*-(1-allyl-cyclohexyl)-methylamine (0.010 g, 65.2 μmol) was added to the NMR tube by injecting through the rubber septum. Then, the NMR tube was quickly placed in the NMR probe. Single scan spectra were acquired automatically at preset time intervals at 23 °C. The concentration of substrate and product at any given time was determined by integration of substrate and product resonances relative to the integration of the internal standard. A linear least squares analysis of substrate concentrations (M) vs. time correlated to the equation  $\text{Ln}[\text{substrate}]_t = \text{Ln}[\text{substrate}]_0 - k_{\text{obs}}t$ .

**Measurement of initial rates of cyclization (saturation kinetics).** A 5 mL stock solution in toluene-*d*<sub>8</sub> containing a known concentration of internal standard tetrakis(trimethylsilyl)silane (0.0070 g, 0.0218 mmol, 4.36 mM) and catalyst (5.39 mM) was prepared using a 5 mL volumetric flask. The stock solution (0.50 mL) was added by a 1 mL glass syringe to a NMR tube, capped with rubber septum and was taken a <sup>1</sup>H NMR spectra.

The initial rates for the hydroamination of *C*-(1-allyl-cyclohexyl)-methylamine (**12a**) were measured for several substrate concentrations at constant catalyst concentration (5.39 mM). Linear regression fits for versus time for the first 504 s of the reaction provided the initial rate ( $d[\mathbf{12a}]/dt$ ) for a particular initial substrate concentration (calculated as average substrate

concentration over 504 s). A non-linear least squares regression analysis of  $d[\mathbf{12a}]/dt$  vs.  $[\mathbf{12a}]_{\text{ini}}$  showed good correlation to the equation:

$$\frac{-d[\mathbf{12a}]}{dt} = \frac{k_2\{\mathbf{S-2}\}\text{Zr}(\text{NMe}_2)_2 \{[\mathbf{12a}] - \{\mathbf{S-2}\}\text{Zr}(\text{NMe}_2)_2\}}{K' + \{[\mathbf{12a}] - \{\mathbf{S-2}\}\text{Zr}(\text{NMe}_2)_2\} + K_{\text{SI}}\{[\mathbf{12a}] - \{\mathbf{S-2}\}\text{Zr}(\text{NMe}_2)_2\}^2} \quad (\text{S1})$$

which is a modified version of the general equation:

$$\frac{-d[\text{substrate}]}{dt} = \frac{k_2[\text{substrate}][\text{catalyst}]}{K' + [\text{substrate}] + \frac{[\text{substrate}]^2}{K_{\text{SI}}}} \quad (\text{S2})$$

Particular modifications:

(a) One equiv of substrate is consumed in a pre-catalyst activation step. Thus, the observed substrate concentration must be modified to include this factor, which does not otherwise appear in the rate law or the reaction mechanism. Thus  $[\text{substrate}] = [\mathbf{12a}] - [\text{catalyst}]$ .

(b)  $K_{\text{SI}}$  (equilibrium constant for substrate inhibition) is normally defined as:  $K_{\text{SI}} = [\text{substrate}][\text{catalyst-substrate}]/[\text{catalyst-substrate}^2]$  (*i.e.*, a *dissociation* constant). For more straightforward chemical interpretation,  $K_{\text{SI}}$  is defined here as the substrate binding constant:  $K_{\text{SI}} = [\text{catalyst-substrate}^2]/[\text{substrate}][\text{catalyst-substrate}]$ .

### Kinetics Data

From the non-linear regression analysis for initial rates plots of  $(-d[\mathbf{12a}]/dt)/[\{\mathbf{S-2}\}\text{Zr}(\text{NMe}_2)_2]$  vs.  $[\mathbf{12a}]_{\text{ave}}$  at 273 K:

$$y = (m1*(x-0.00539))/(m2+(x-.00539)+(m3*(x-0.00539)^2))$$

	<b>Value</b>	<b>Error</b>
$m1 = k_2^{\text{H}}$	0.01232	0.004853
$m2 = K^{\text{H}}$	0.1014	0.04828
$m3 = K_{\text{SI}}^{\text{H}}$	23.25	12.36
Chisq	$1.473 \times 10^{-7}$	NA
R	0.9904	NA

From the non-linear regression analysis for initial rates plots of  $(-d[\mathbf{12a}]/dt)/[\{S-2\}Zr(NMe_2)_2]$  vs.  $[\mathbf{12a}]_{ave}$  at 294 K:

$$y = (m1*(x-0.00539))/(m2+(x-.00539)+(m3*(x-0.00539)^2))$$

	<u>Value</u>	<u>Error</u>
$m1 = k_2^H$	0.01674	0.002586
$m2 = K^H$	0.02767	0.007189
$m3 = K_{SI}^H$	5.219	2.071
Chisq	$4.479 \times 10^{-6}$	NA
R	0.983	NA

From the non-linear regression analysis for initial rates plots of  $(-d[\mathbf{12a}]/dt)/[\{S-2\}Zr(NMe_2)_2]$  vs.  $[\mathbf{12a}]_{ave}$  at 314 K:

$$y = (m1*(x-0.00539))/(m2+(x-.00539)+(m3*(x-0.00539)^2))$$

	<u>Value</u>	<u>Error</u>
$m1 = k_2^H$	0.0619	0.007105
$m2 = K^H$	0.03972	0.006689
$m3 = K_{SI}^H$	3.626	1.569
Chisq	$6.904 \times 10^{-6}$	NA
R	0.9977	NA

From the non-linear regression analysis for initial rates plots of  $(-d[\mathbf{12a}]/dt)/[\{S-2\}Zr(NMe_2)_2]$  vs.  $[\mathbf{12a}]_{ave}$  at 322 K:

$$y = (m1*(x-0.00413))/(m2+(x-.00413)+(m3*(x-0.00413)^2))$$

	<u>Value</u>	<u>Error</u>
$m1 = k_2^H$	0.08442	0.01171
$m2 = K^H$	0.03949	0.008158
$m3 = K_{SI}^H$	7.679	2.425
Chisq	$1.529 \times 10^{-5}$	NA
R	0.9946	NA

### Measurement of the activation parameters.

**1. Eyring plot from second-order rate constants:** Rate constants  $k$  were measured at the constant catalyst and initial substrate concentrations, over five temperatures ranging from 266 K to 314 K using the method described above. The plot  $\ln(k'/T)$  vs.  $1/T$  provides the values of  $11.0(6)$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = -24(2)$  cal·mol<sup>-1</sup>K<sup>-1</sup> using standard Eyring analysis.

**2. Eyring plot from initial rates:** Using the initial rate method described above, the rate constants  $k_2$  were measured at temperatures ranging from 273 K to 322 K, keeping the catalyst

and initial substrate concentration constant in each experiment. The plot  $\ln(k_2/T)$  vs.  $1/T$  provides the values of  $\Delta H^\ddagger = 6.7(2)$  kcal·mol<sup>-1</sup> and  $\Delta S^\ddagger = -43(7)$  cal·mol<sup>-1</sup>K<sup>-1</sup> are calculated, using standard Eyring analysis.

**Error analysis for isotope effects.** Errors were obtained from linear least squares fits of  $k'_{\text{obs}}$  vs.  $[\{S-2\}Zr(NMe_2)_2]$  plots. Errors obtained from linear regression analysis were propagated in the standard fashion:

$$\begin{aligned}k'_{\text{obs}}^{(H)} &= 0.1275 \pm 0.007 \text{ M}^{-1}\text{s}^{-1} \\k'_{\text{obs}}^{(D)} &= 0.0386 \pm 0.002 \text{ M}^{-1}\text{s}^{-1} \\k'_{\text{obs}}^{(H)}/k'_{\text{obs}}^{(D)} &= (0.1275/0.03862) = 3.3014\end{aligned}$$

$$\begin{aligned}\delta(k'_{\text{obs}}^{(H)}/k'_{\text{obs}}^{(D)}) &= [\{\delta(k'_{\text{obs}}^{(H)})/k'_{\text{obs}}^{(H)}\}^2 + \{\delta(k'_{\text{obs}}^{(D)})/k'_{\text{obs}}^{(D)}\}^2]^{1/2} \times \{k'_{\text{obs}}^{(H)}/k'_{\text{obs}}^{(D)}\} \\&= [\{(0.007)/(0.12750)\}^2 + \{(0.002)/(0.0386)\}^2]^{1/2} \times 3.3 \\&= (0.0030 + 0.0027)^{1/2} \times 3.3 = 0.2491 \\k'_{\text{obs}}^{(H)}/k'_{\text{obs}}^{(D)} &= 3.3 \pm 0.2\end{aligned}$$

**Error analysis for isotope effect from saturation kinetics.** Errors were obtained from non-linear least squares fits of raw data to Equation S1 where [catalyst] =  $[\{S-2\}Zr(NMe_2)_2]$ . Errors obtained from non-linear regression analysis were propagated in the standard fashion:

$$\begin{aligned}k_2^{(H)} &= 1.670 \times 10^{-2} \pm 2.603 \times 10^{-3} \text{ s}^{-1} \\k_2^{(D)} &= 7.223 \times 10^{-3} \pm 5.181 \times 10^{-4} \text{ s}^{-1} \\k_2^{(H)}/k_2^{(D)} &= (1.670 \times 10^{-2}/7.223 \times 10^{-3}) = 2.311\end{aligned}$$

$$\begin{aligned}\delta\{k_2^{(H)}/k_2^{(D)}\} &\approx [\{\delta(k_2^{(H)})/k_2^{(H)}\}^2 + \{\delta(k_2^{(D)})/k_2^{(D)}\}^2]^{1/2} \times \{k_2^{(H)}/k_2^{(D)}\} \\&= [\{(2.603 \times 10^{-3})/(1.670 \times 10^{-2})\}^2 + \{(5.181 \times 10^{-4})/(7.223 \times 10^{-3})\}^2]^{1/2} \times 2.3 \\&= (0.024 + 0.005)^{1/2} \times 2.3 = 0.3917\end{aligned}$$

$$k_H/k_D = 2.311 \pm 0.3917 = 2.3 \pm 0.4$$

**Determination of  $k_H^R/k_D^R$  and  $k_H^S/k_D^S$  and error analysis (from  $k_2$ ).**

$$k_H = k_H^R + k_H^S = 1.670 \times 10^{-2} \pm 2.603 \times 10^{-3} \text{ s}^{-1}$$

From the ratio of enantiomers  $S:R = 95:5$

$$k_H^S \times 19 = k_H^R$$

$$k_H = k_H^S + 19 \times k_H^S = 1.670 \times 10^{-2} \pm 2.603 \times 10^{-3} \text{ s}^{-1}$$

$$k_H^S = (1.670 \times 10^{-2} \pm 2.603 \times 10^{-3} \text{ s}^{-1})/20$$

$$k_H^S = 8.348794 \times 10^{-4} \pm 6.50742 \times 10^{-6} \text{ s}^{-1}$$

$$k_H^R = k_H^S \times 19 = (8.348794 \times 10^{-4} \pm 6.50742 \times 10^{-6}) \times 19$$

$$k_H^R = \mathbf{1.58627 \times 10^{-2} \pm 2.34918 \times 10^{-3} \text{ s}^{-1}}$$

$$k_D = k_D^S + k_D^R = 7.223 \times 10^{-3} \pm 5.181 \times 10^{-4} \text{ s}^{-1}$$

From the ratio of enantiomers  $S:R = 98.5:1.5$

$$k_D^S \times 65.667 = k_H^R$$

$$k_D = k_D^S + 65.667 \times k_D^S = 7.223 \times 10^{-3} \pm 5.181 \times 10^{-4} \text{ s}^{-1}$$

$$k_D^S = (7.223 \times 10^{-3} \pm 5.181 \times 10^{-4} \text{ s}^{-1}) / 66.667$$

$$k_D^S = \mathbf{1.08357 \times 10^{-4} \pm 1.16574 \times 10^{-7} \text{ s}^{-1}}$$

$$k_D^R = k_D^R \times 65.667 = (1.08357 \times 10^{-4} \pm 1.16574 \times 10^{-7}) \times 65.667$$

$$k_D^R = \mathbf{7.115413 \times 10^{-3} \pm 5.02679 \times 10^{-4} \text{ s}^{-1}}$$

$$k_H^S / k_D^S = \mathbf{7.705 \pm 0.06876 = 7.7 \pm 0.1}$$

$$k_H^R / k_D^R = \mathbf{2.229 \pm 0.4876 = 2.2 \pm 0.5}$$

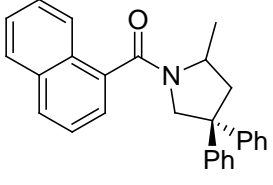
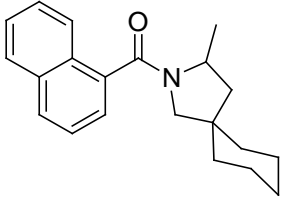
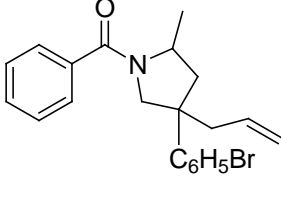
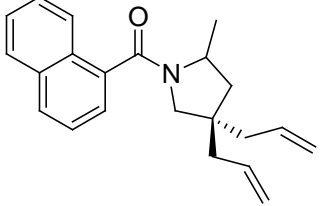
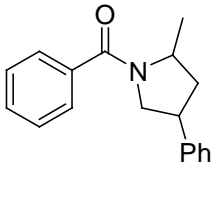
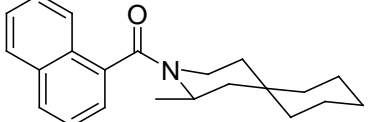
**Procedure for determination of enantiomeric excess of pyrrolidine products.**

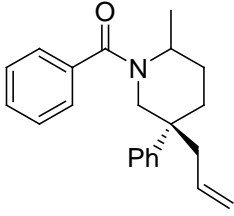
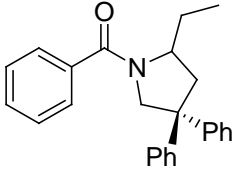
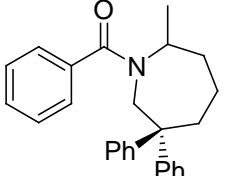
**NMR spectroscopy.** The  $^1\text{H}$  and  $^{19}\text{F}$  NMR methods were used to evaluate the % ee of the pyrrolidines products of enantioselective hydroamination/cyclization. Benzene (2 mL) and triethylamine (5.0 equivalent based on the amount of aminoalkene used during catalysis) were added to the purified pyrrolidine. To this solution, (+)-(*S*)- $\alpha$ -methoxy- $\alpha$ -(trifluoromethyl)phenylacetyl chloride (1.2 equivalent based on the amount of aminoalkene used during catalysis) was added. The solution was mixed and immediately a white suspension appeared ( $[\text{HNEt}_3][\text{Cl}]$ ). The mixture was stirred for 1 h, and all the solvents were removed under vacuum. The white residue was extracted with pentane. Pentane was removed under vacuum to give the corresponding Mosher-amide as a clear colorless oil. No further purification was performed, since crystallization, chromatography, or sublimation could result in biased results by separation of the diastereomers. The enantioselectivities were determined by either integration of  $^1\text{H}$  NMR (23 °C,  $\text{CDCl}_3$ ) or  $^{19}\text{F}$  NMR (60 °C,  $\text{CDCl}_3$ ) signals; these were referenced to literature values and compared against authentic diastereomers of racemic samples reproduced in our laboratory.

**HPLC analysis.** The enantiomeric excess of chiral pyrrolidines were also determined by HPLC analysis of the naphthoyl derivatized product (flow rate = 1.0 mL/min,  $\lambda$  = 254 nm) using Regis (*S,S*)-Whelk O1 column (Spherical Kromasil® Silica, column dimensions = 25 cm  $\times$  4.6 mm i.d., particle size = 5  $\mu\text{m}$ , 100 Å) following literature procedures.

Typical procedure of derivatization: In a glove box, 1-naphthoyl chloride (1.05 equiv) or benzoyl chloride was added to a  $\text{CH}_2\text{Cl}_2$  solution of pyrrolidine (1.0 equiv) and triethylamine (3.0 equiv) at room temperature. The resultant mixture was stirred for 2 h, and then the volatile materials were removed by rotary evaporation giving a white solid. The product was extracted with pentane and pentane was removed in vacuo. The crude product was purified by preparative silica gel TLC with appropriate eluent.

**Table S2. Chiral Stationary Phase HPLC Conditions for Determination of Enantiomeric Excess**

Compounds	Eluent of preparative TLC to purify product derivative	Eluent ratio of HPLC	Back pressure during HPLC	Retention time in HPLC
	cyclohexane/EtOAc; 3/1	hexane:EtOH; 75:25	55 bar	22.1 min 66.4 min
	hexane/EtOAc; 2/1	hexane:EtOH; 75:25	55 bar	13.9 min 82.8 min
	hexane/EtOAc; 2/1	hexane:EtOH; 96:4	40 bar	42.7 min 57.8 min 107.7 min 115.2 min
	hexane/EtOAc; 3/2	hexane:EtOH; 75:25	56 bar	11.8 min 74.1 min
	hexane/Et <sub>2</sub> O; 1/7	hexane:EtOH; 95:5	41 bar	38.5 min 58.6 min 62.4 min 67.3 min
	hexane/EtOAc; 3/2	hexane:EtOH; 75:25	52 bar	11.4 min 59.6 min

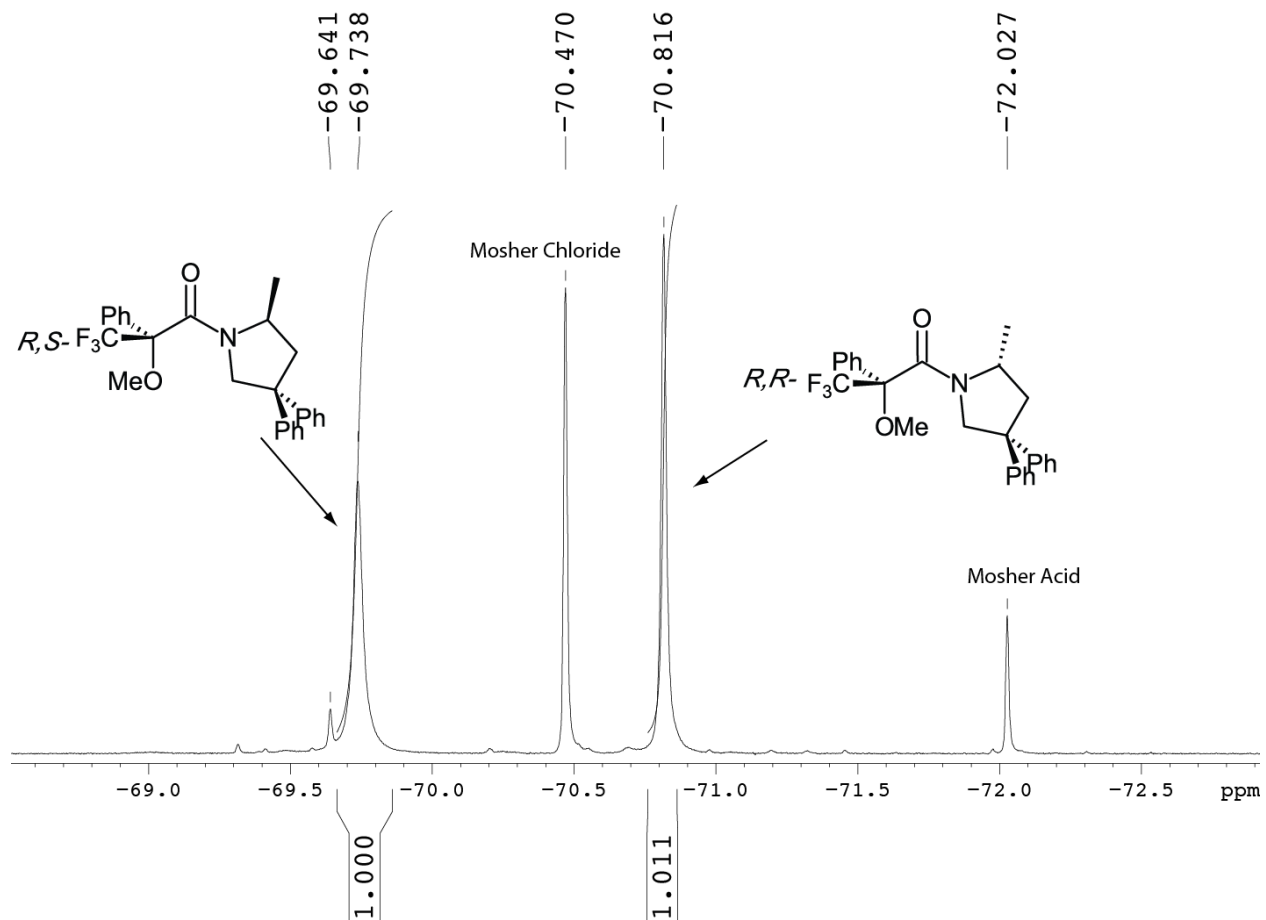
	hexane/EtOAc; 2/1	hexane:EtOH; 70:30	56 bar	7.8 min 10.4 min 12.8 min 13.5 min
	hexane/EtOAc; 3/1	hexane:EtOH; 75:25	55 bar	29.6 min 93.2 min
	hexane/EtOAc; 2/1	hexane:EtOH; 75:25	55 bar	33.3 min 105.5 min

**Assignment of absolute configuration of the stereocenter of 4-allyl-4-(4-bromophenyl)-2-methylpyrrolidine (19b) and 4-allyl-2,4-dimethylpyrrolidine (20b).** Although the absolute configuration of the stereocenters in **19b** and **20b** are not established by X-ray crystallography, inspection of HPLC traces of benzoyl derivatives and  $^{19}\text{F}$  NMR spectra of *R*-Mosher amide derivatives suggest that the stereocenter obtained from C-N bond formation with  $\{S\text{-}2\}\text{Zr}(\text{NMe}_2)_2$  is *R* for both diastereomers for both methyl (**19b**) and *para*-bromophenyl (**20b**) products. In particular, the *R* enantiomer of **8b** and **10b** give compounds for which the assigned configuration is established by X-ray crystallography and correlated with  $[\alpha]_D^{25}$ .<sup>10,14</sup> In these cases, the *R* enantiomer elutes before the *S* product from a Regis (*S,S*)-Whelk O1 column on the HPLC column; additionally the peak from the *R* enantiomer is sharp and early whereas a broad, slower moving band is assigned to the *S* isomer. In the mixtures of diastereomers obtained from cyclization of substrates **19a** and **20a** by  $\{S\text{-}2\}\text{Zr}(\text{NMe}_2)_2$ , four peaks were observed in the HPLC trace that appeared in pairs. The two peaks associated with the major *R* enantiomers elute together and earlier than the *S* disfavored enantiomers, following the same elution trend established with **8b** and **10b**.<sup>10,14</sup> The early bands in the HPLC are narrow, whereas the disfavored enantiomers of the diastereomeric pairs are broad. Likewise, in the  $^{19}\text{F}$  NMR spectra of the Mosher amides of **19b** and **20b**, the *R,R*-pyrrolidine Mosher amide resonances are upfield

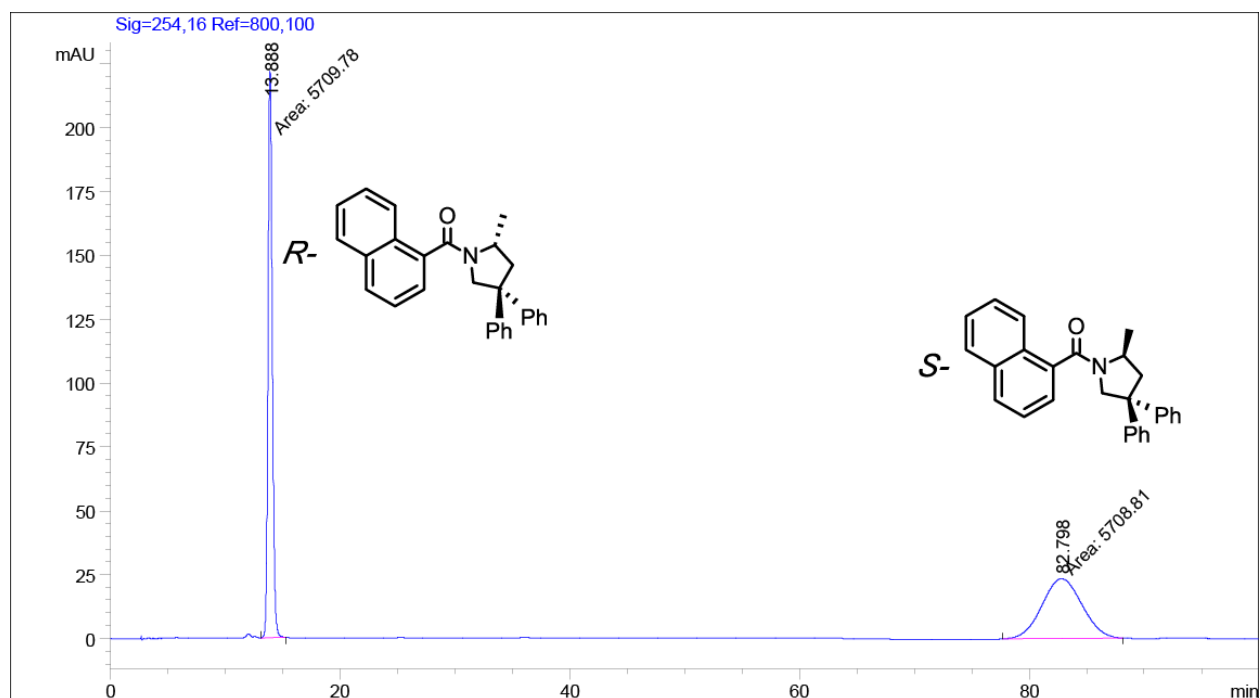
and sharp whereas the *S,R*-pyrrolidine Mosher amides resonances are broad and downfield. In particular, in the  $^{19}\text{F}$  NMR spectra of **19b** and **20b** acquired at 60 °C, two sharp, upfield singlets were observed as the major species present (**19b**: -73.73 and -70.83 ppm; **20b**: -70.83 and -71.07 ppm); the minor species were detected as a pair of broad downfield signals (**19b**: -69.98 and -69.89 ppm; **20b**: -70.15 and -70.04 ppm) in chloroform- $d_1$ . In summary, the consistent relative peak positions and signal shape for the *R* vs. *S* enantiomers and the tendency of {*S*-**2**}Zr(NMe<sub>2</sub>)<sub>2</sub> to provide the *R* enantiomer in **8b** and **10b**, we assign the configurations of the major enantiomers of the two diastereomers of **19b** and **20b** as 2*R*.

**Error analysis for enantioselectivity.** % ee values are given based on average % ee determined from multiple (> 3) catalytic experiments run under identical conditions; the standard deviation for the % ee's for a particular set of conditions, calculated from  $^{19}\text{F}$  NMR integration, was determined to be  $\pm 0.5$  (e.g., the % ee for **8b**, cyclized in benzene- $d_6$  at 23 °C is  $93 \pm 0.5\%$ ).  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra of Mosher amides, obtained by reaction of the pyrrolidine products with Mosher chloride are shown below for both the racemic and representative enantioenriched samples.

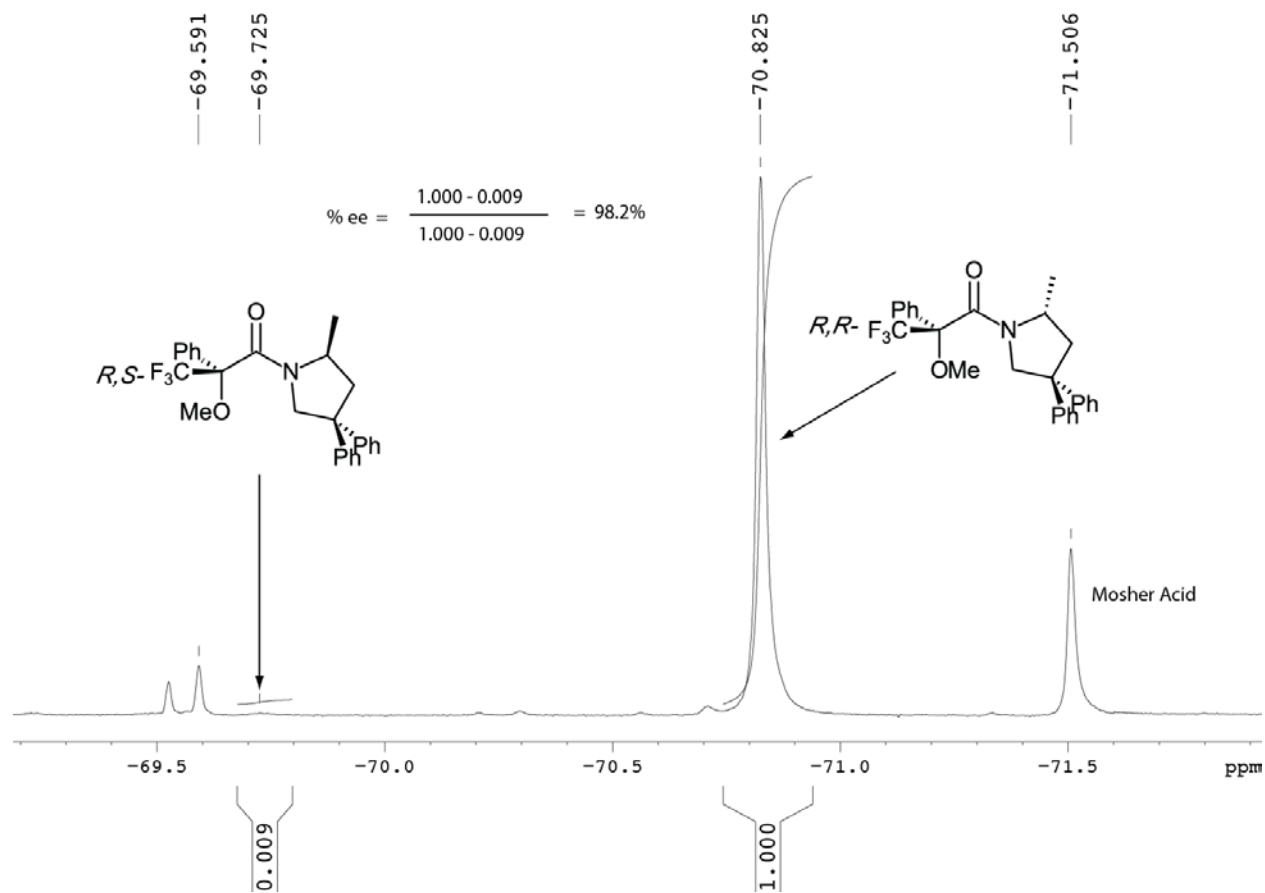
**Figure S1.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 60  $^\circ\text{C}$ ) spectrum of diastereomers of the (*R*)-Mosher amide of racemic ( $\pm$ )-2-methyl-4,4-diphenylpyrrolidine ( $\pm$ -**8b**) obtained by its treatment with (*S*)-Mosher chloride. This  $^{19}\text{F}$  NMR spectrum was previously reported in the Supporting Information of Ref 5 and is given here for the reader's convenience.



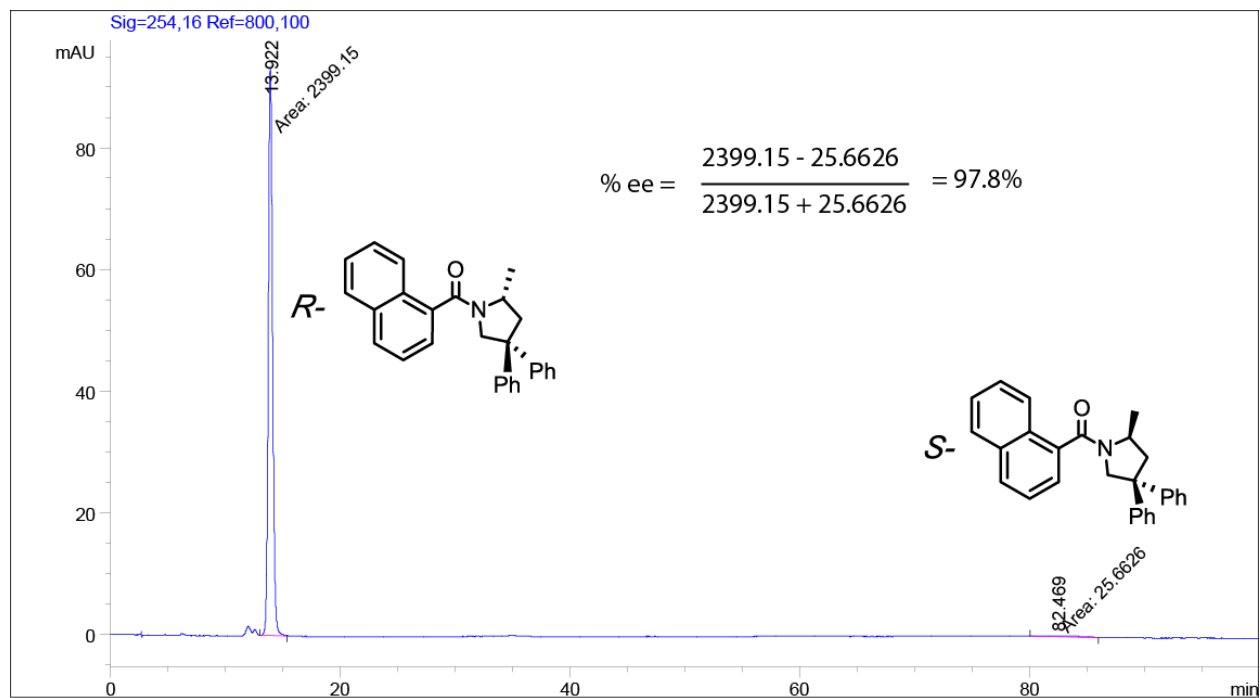
**Figure S2.** HPLC trace and integration data from racemic ( $\pm$ )-2-methyl-4,4-diphenylpyrrolidine ( $\pm$ -**8b**) as its naphthylamide. This data was also previously reported in the Supporting Information of Ref 5 and is given here for the reader's convenience.



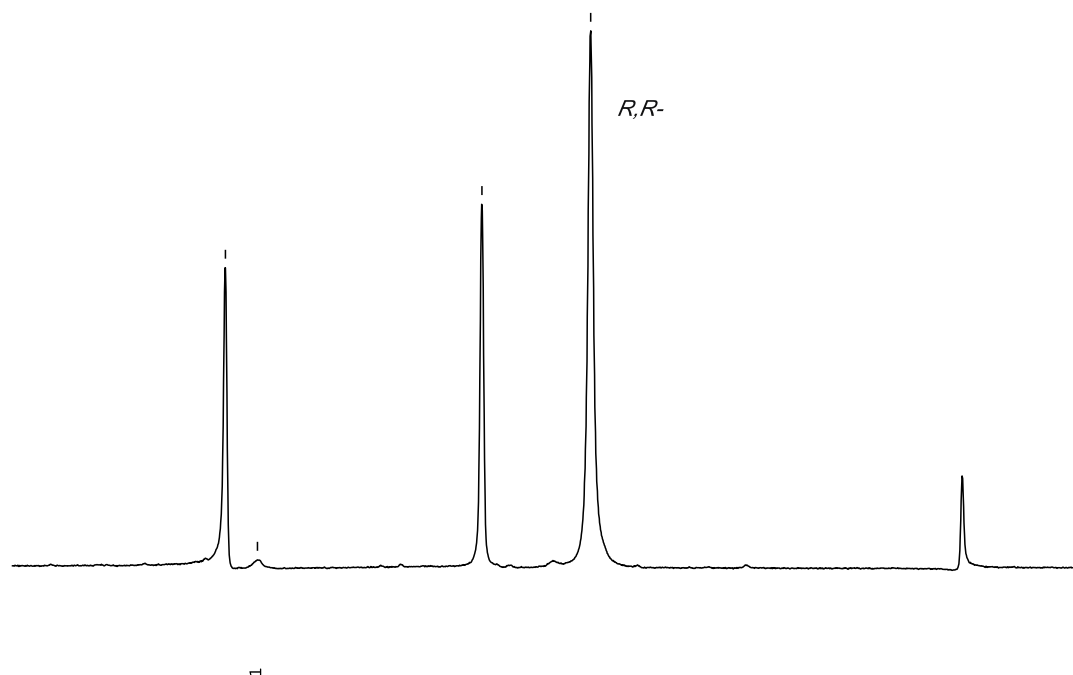
**Figure S3.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 60 °C) spectrum of (*R*)-Mosher amide of 2-methyl-4,4-diphenylpyrrolidine product (**8b**) obtained from catalytic asymmetric hydroamination. The (*S*)-Mosher chloride was used to form the amide derivative. Conditions for catalysis: 10 mol % {*S*-2}Zr(NMe<sub>2</sub>)<sub>2</sub>, toluene at -30 °C (Table S1, entry 7).



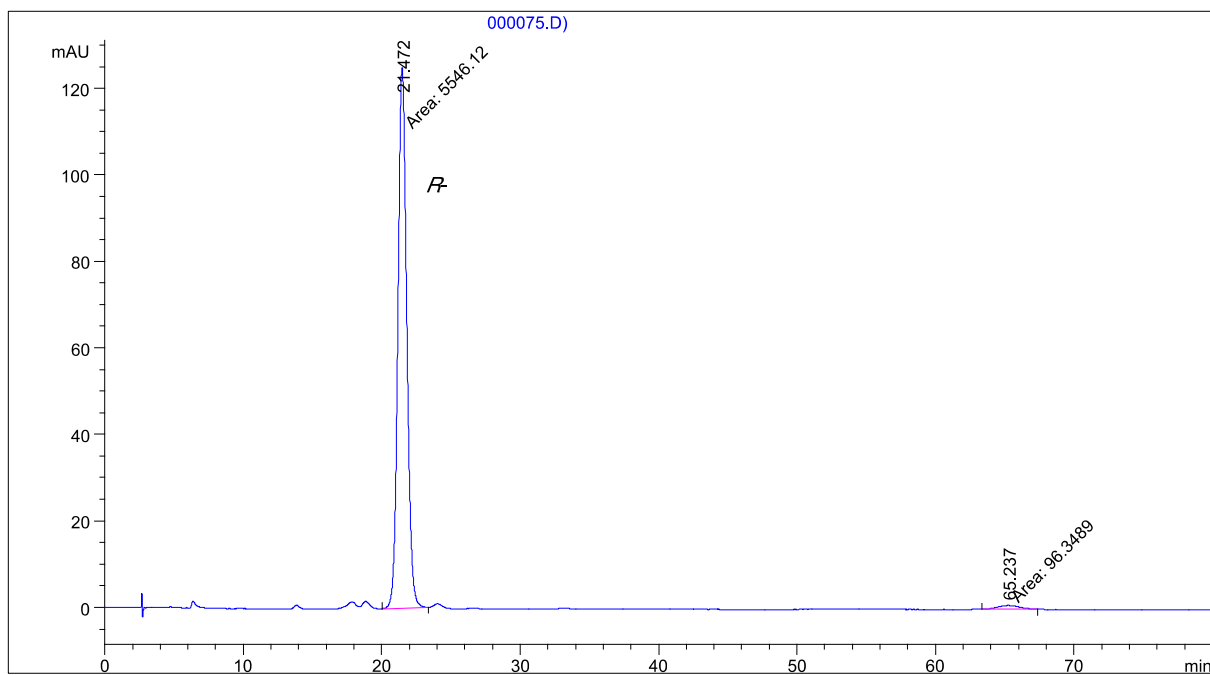
**Figure S4.** HPLC trace and integration data from naphthylamide of 2-methyl-4,4-diphenylpyrrolidine product (**8b**) obtained from catalytic asymmetric hydroamination. Conditions for catalysis: 10 mol % {*S*-2}Zr(NMe<sub>2</sub>)<sub>2</sub>, toluene at -30 °C (Table S1, entry 7).



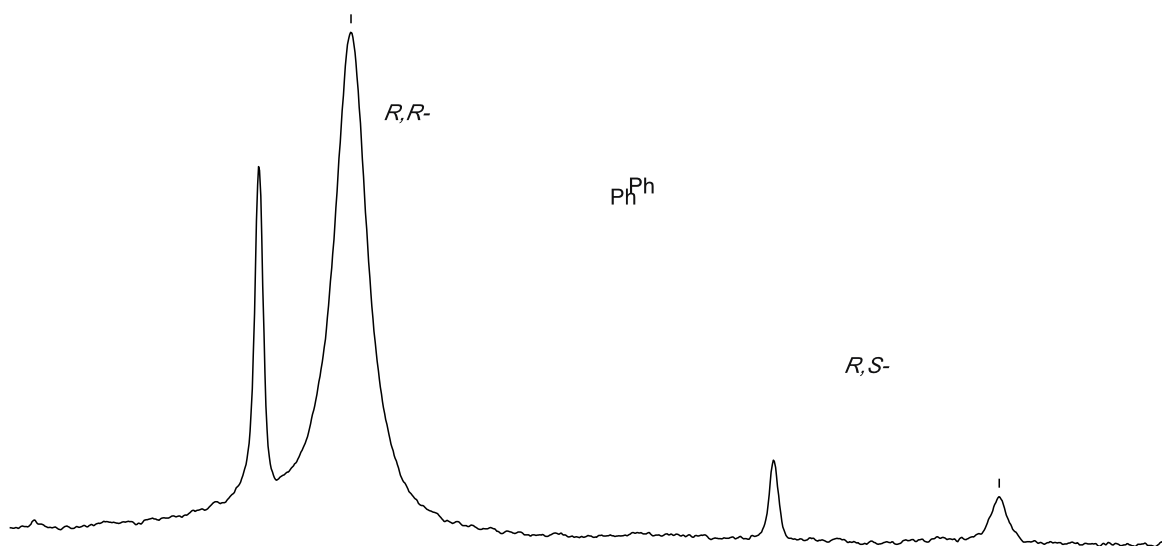
**Figure S5.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60 °C) of (*R*)-Mosher amide of 2-methyl-4,4-diphenylpyrrolidine product (**8b**) obtained from catalytic asymmetric hydroamination of 2,2-diphenyl-4-penten-1-amine (**8a**) and after treatment with (*S*)-Mosher chloride. Conditions for catalysis: 10 mol %  $\{\text{S-2}\}\text{Hf}(\text{NMe}_2)_2$ , toluene- $d_8$  at 0 °C (Table S1, entry 10).



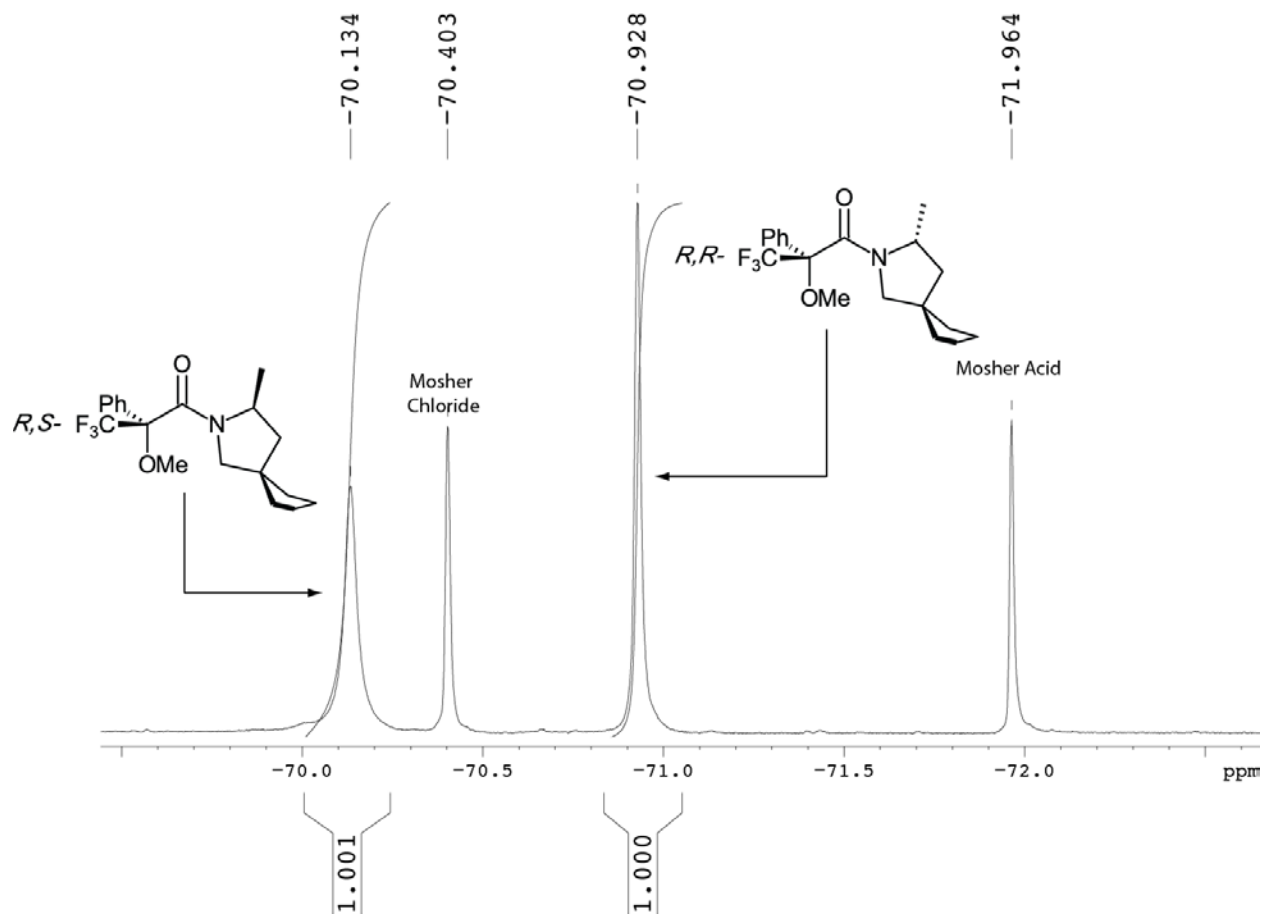
**Figure S6.** HPLC trace and integration data from naphthylamide of 2-methyl-4,4-diphenylpyrrolidine product (**8b**) obtained from catalytic asymmetric hydroamination. Conditions for catalysis: 10 mol % {*S*-2}Hf(NMe<sub>2</sub>)<sub>2</sub>, toluene-*d*<sub>8</sub> at 0 °C (Table S1, entry 10).



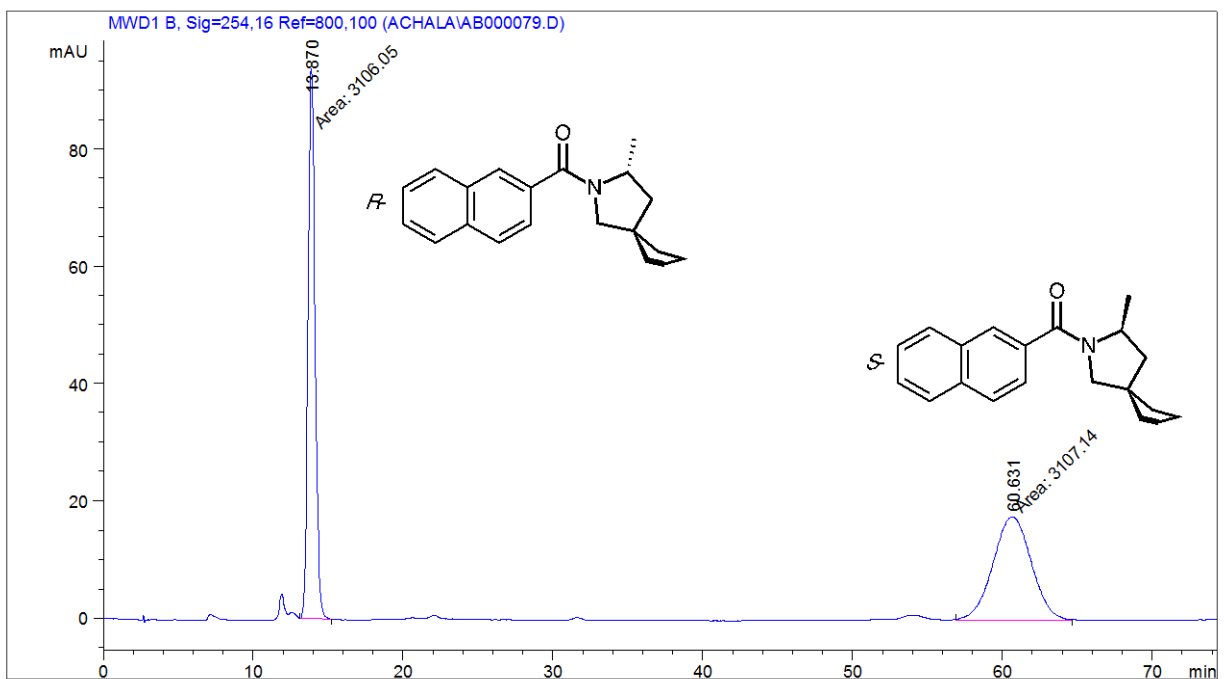
**Figure S7.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60 °C) of (*R*)-Mosher amide of 2-methyl-4,4-diphenylpyrrolidine product (**8b**) obtained from catalytic asymmetric hydroamination of 2,2-diphenyl-4-penten-1-amine (**8a**) and after treatment with (*S*)-Mosher chloride. Conditions for catalysis: 10 mol %  $\{R-2\}\text{Zr}(\text{NMe}_2)_2$ , benzene- $d_6$  at 23 °C (Table S1, entry 8).



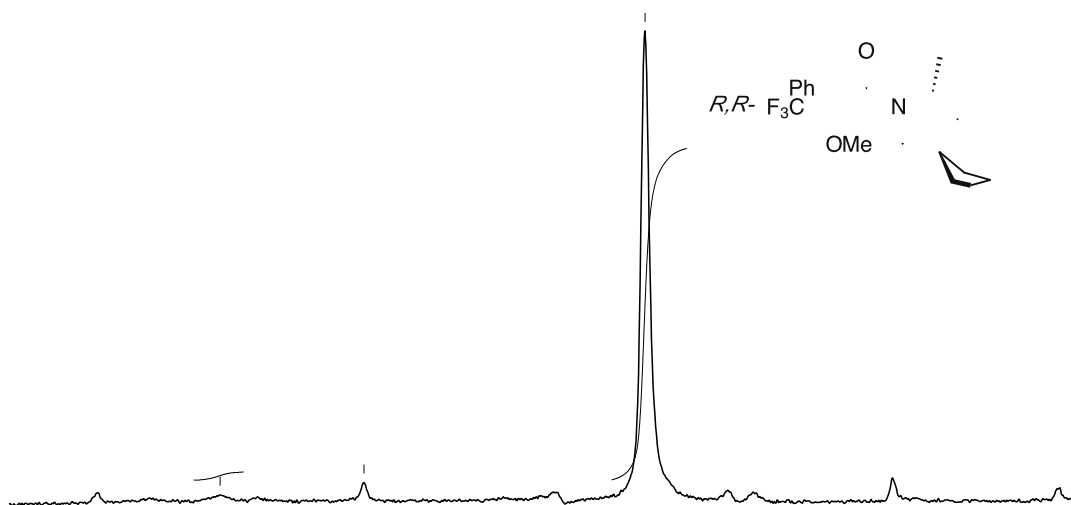
**Figure S8.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60  $^\circ\text{C}$ ) of (*R*)-Mosher amide of ( $\pm$ )-3-methyl-2-azo-spiro[4.4]nonane ( $\pm$ -**9b**) obtained after treatment with (*S*)-Mosher chloride. This  $^{19}\text{F}$  NMR spectrum was also previously reported in the Supporting Information of Ref. 5 and is given here for the reader's convenience.



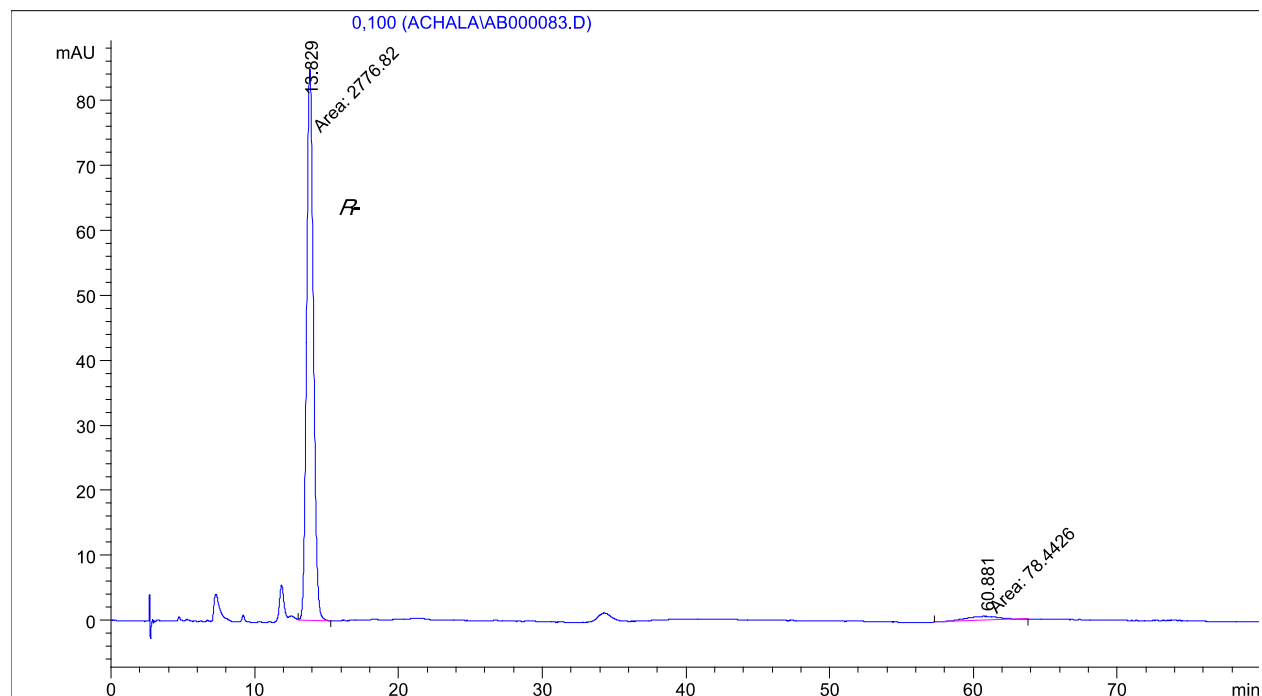
**Figure S9.** HPLC trace and integration data from racemic ( $\pm$ )-3-methyl-2-azo-spiro[4.4]nonane ( $\pm$ -**9b**) as its naphthylamide.



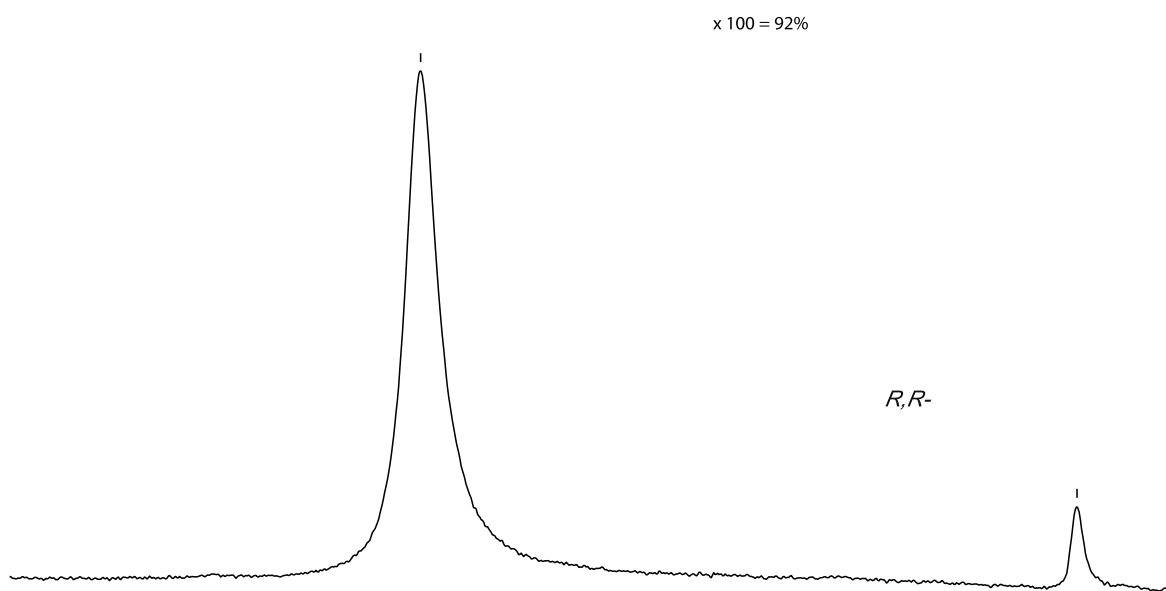
**Figure S10.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60  $^\circ\text{C}$ ) of (*R*)-Mosher amide derivative of 3-methyl-2-azo-spiro[4.4]nonane (**9b**) from stereoselective hydroamination obtained after treatment with (*S*)-Mosher chloride. Catalysis conditions: 10 mol % {*S*-**2**}Hf(NMe<sub>2</sub>)<sub>2</sub>, toluene-*d*<sub>8</sub> at 0  $^\circ\text{C}$  (Table S1, entry 19).



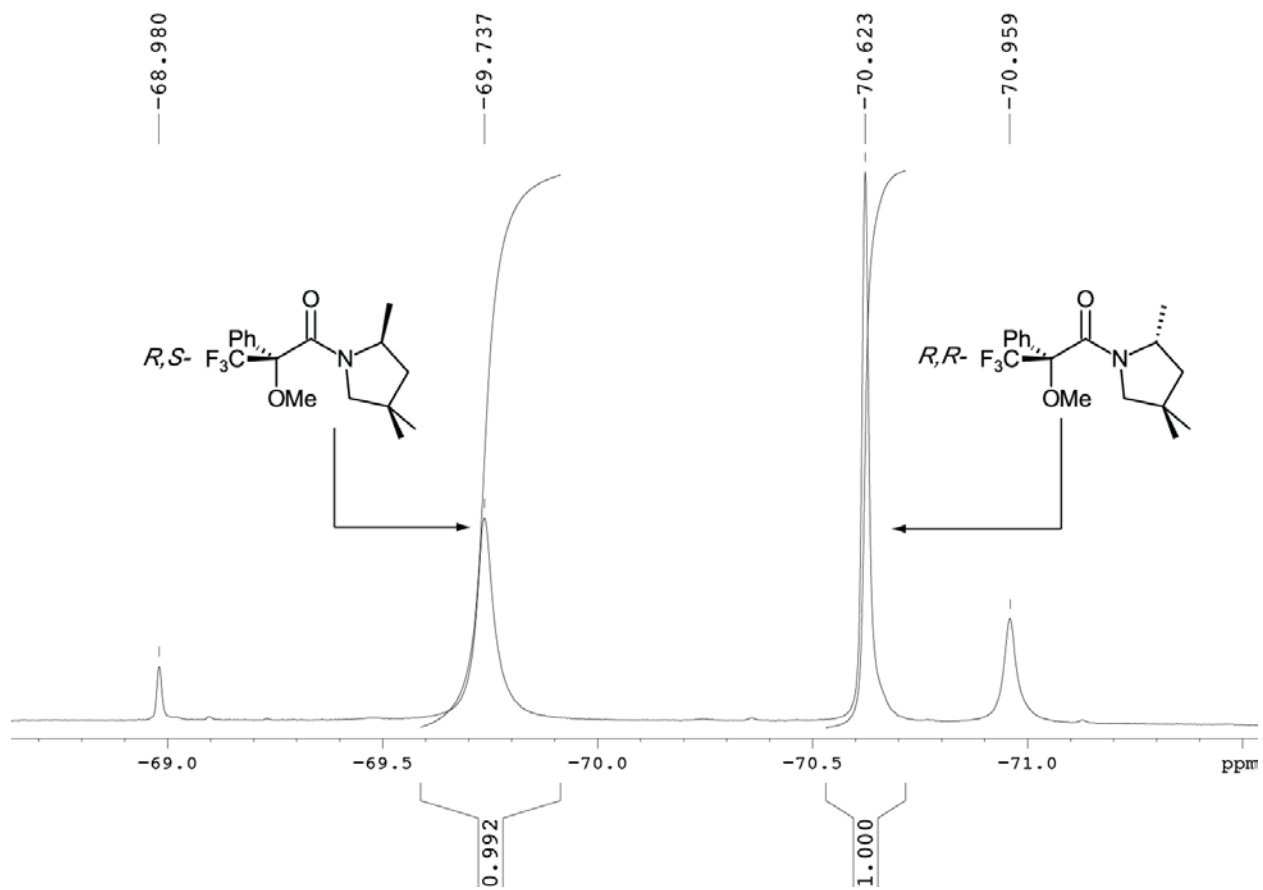
**Figure S11.** HPLC trace and integration data from 3-methyl-2-azo-spiro[4.4]nonane (**9b**) obtained from catalytic asymmetric hydroamination, as its naphthylamide. Conditions for catalysis: 10 mol % {*S*-2}Hf(NMe<sub>2</sub>)<sub>2</sub>, toluene-*d*<sub>8</sub> at 0 °C (Table S1, entry 19).



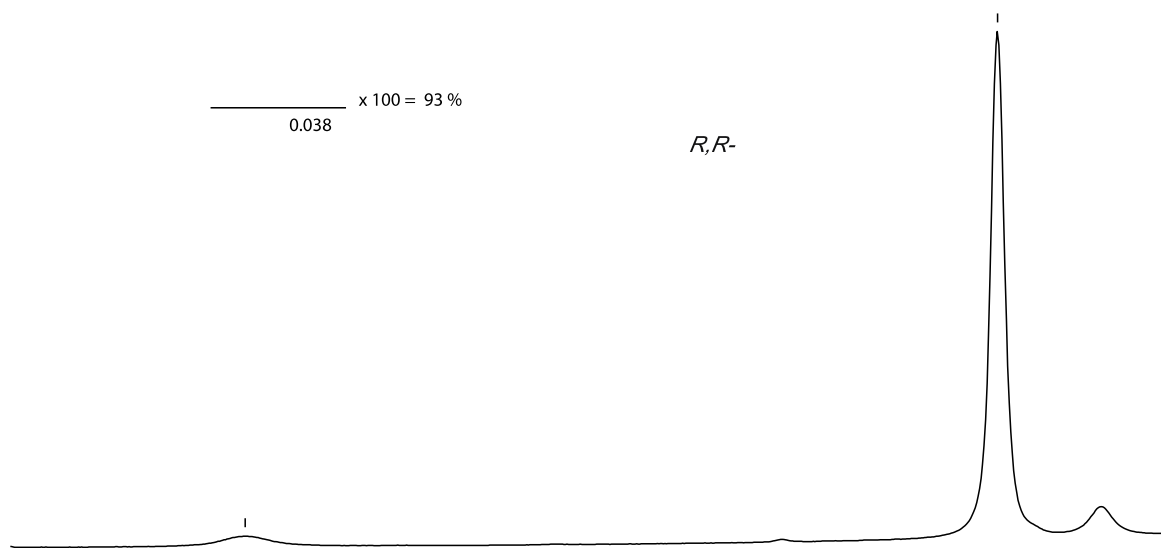
**Figure S12.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60 °C) of (*R*)-Mosher amide derivative of 3-methyl-2-azo-spiro[4.4]nonane (**9b**) from stereoselective hydroamination obtained after treatment with (*S*)-Mosher chloride. Catalysis conditions: 10 mol %  $\{R\text{-}2\}\text{Zr}(\text{NMe}_2)_2$ , benzene at 23 °C (Table S1, entry 17).



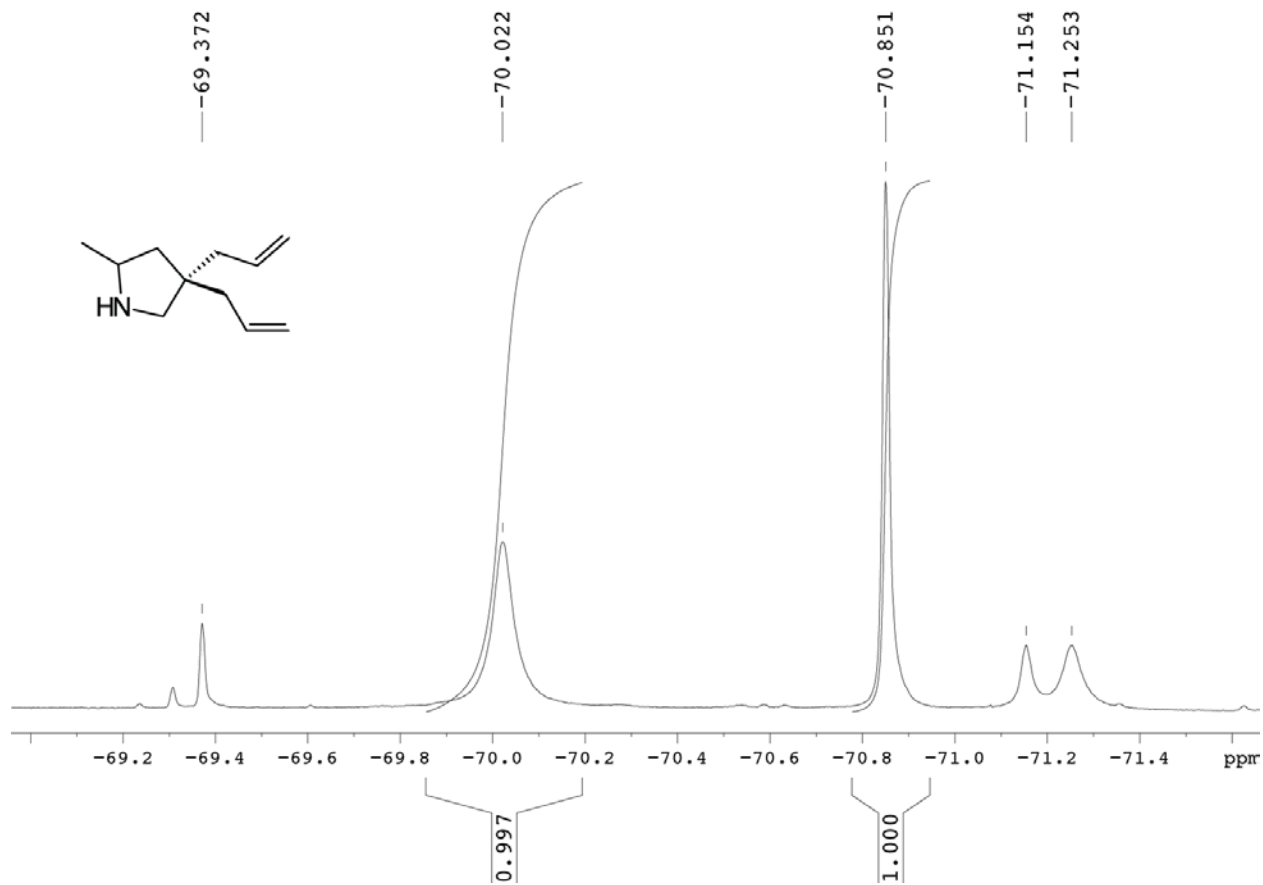
**Figure S13.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 60  $^\circ\text{C}$ ) spectrum of the (*R*)-Mosher amide derivative of ( $\pm$ )-2,4,4-trimethylpyrrolidine (**10b**).



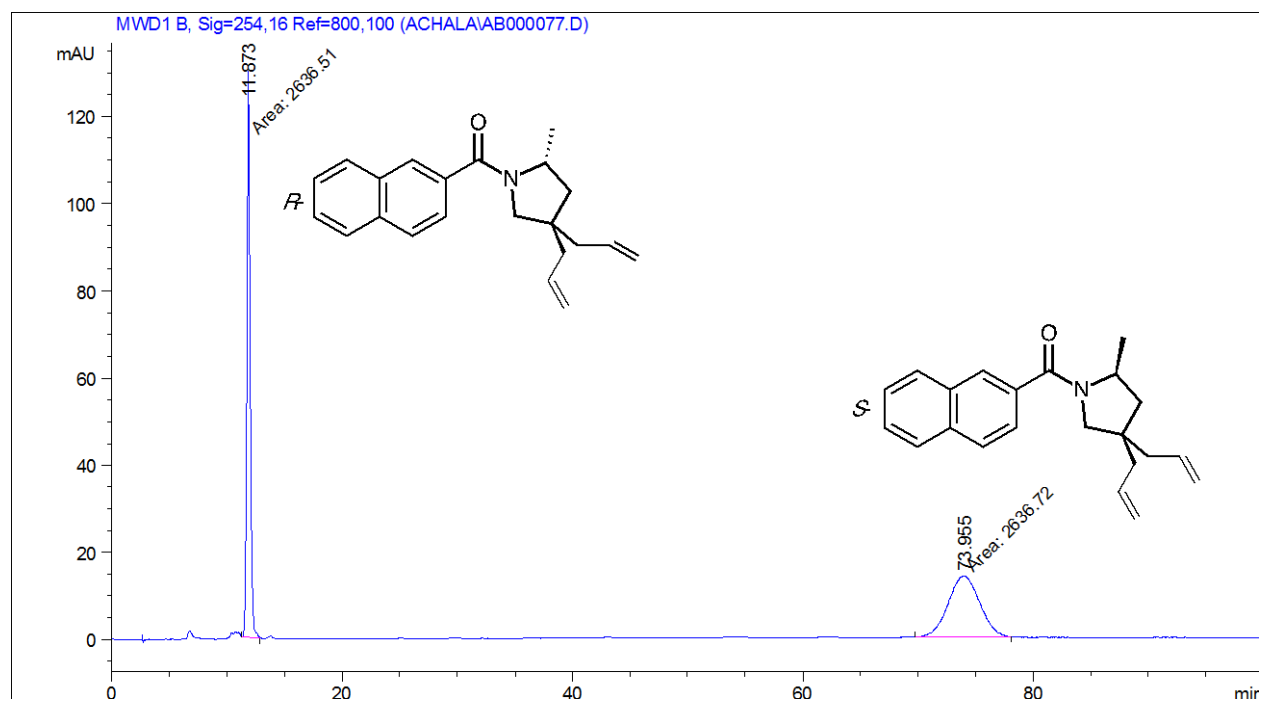
**Figure S14.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60 °C) of (*R*)-Mosher amide derivative of 2,4,4-trimethylpyrrolidine (**10b**) from stereoselective hydroamination obtained after treatment with (*S*)-Mosher chloride. Catalysis conditions: 10 mol % {*S*-2}Zr(NMe<sub>2</sub>)<sub>2</sub>, toluene-*d*<sub>8</sub> at -30 °C (Table S1, entry 24).



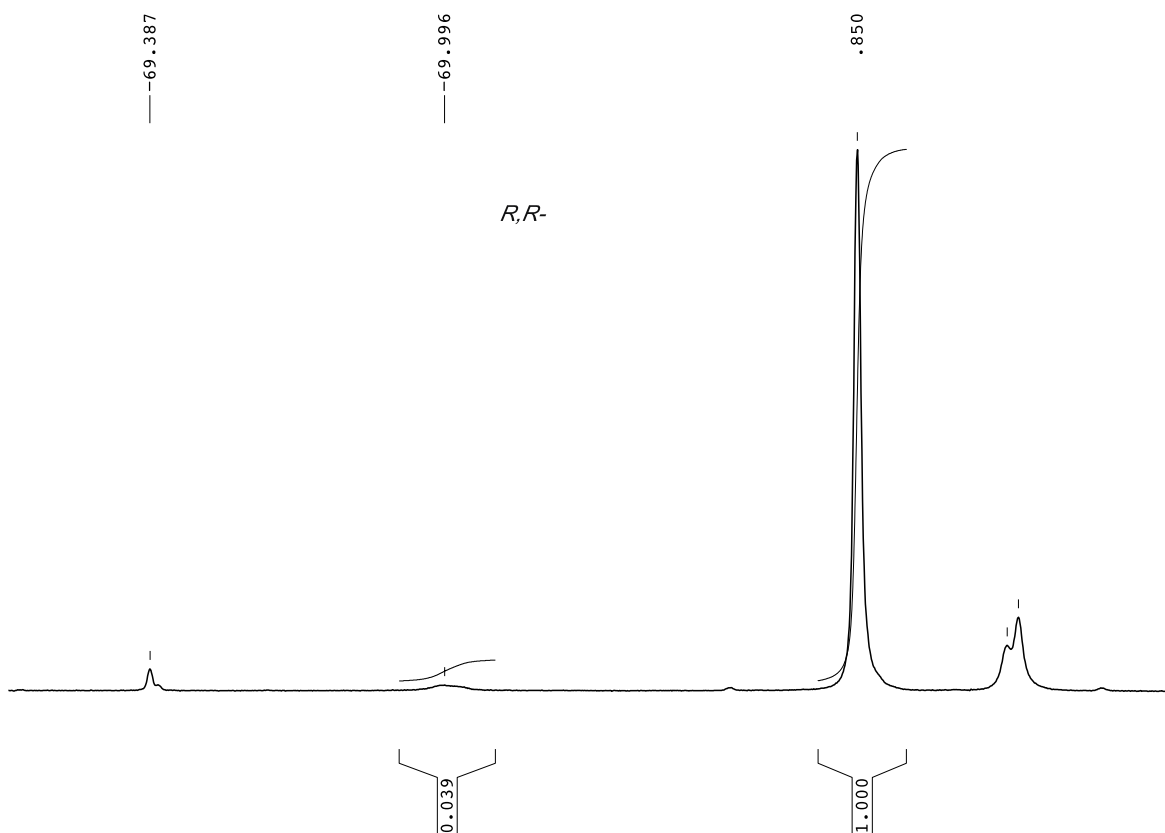
**Figure S15.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60 °C) of (*R*)-Mosher amide of racemic ( $\pm$ )-2-methyl-4,4-bis(2-propenyl)pyrrolidine ( $\pm$ -**11b**) obtained after treatment with (*S*)-Mosher chloride.



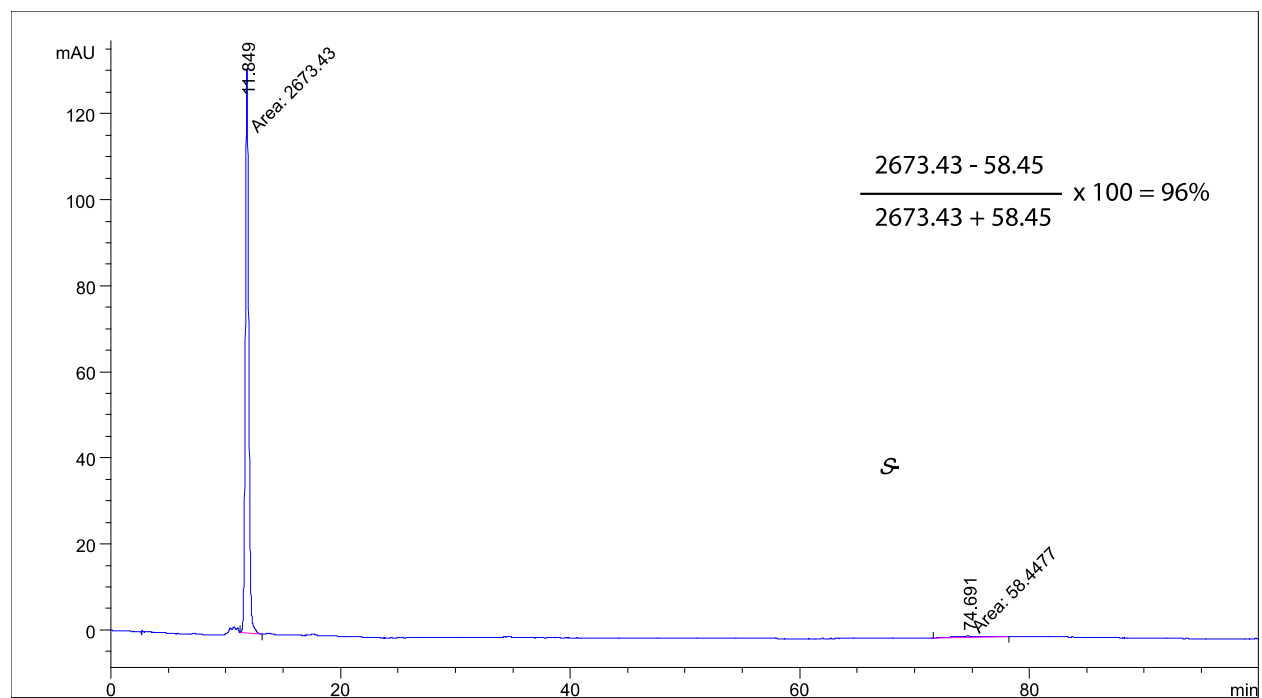
**Figure S16.** HPLC trace and integration data from racemic ( $\pm$ )-2-methyl-4,4-bis(2-propenyl)pyrrolidine ( $\pm$ -**11b**) as its naphthylamide.



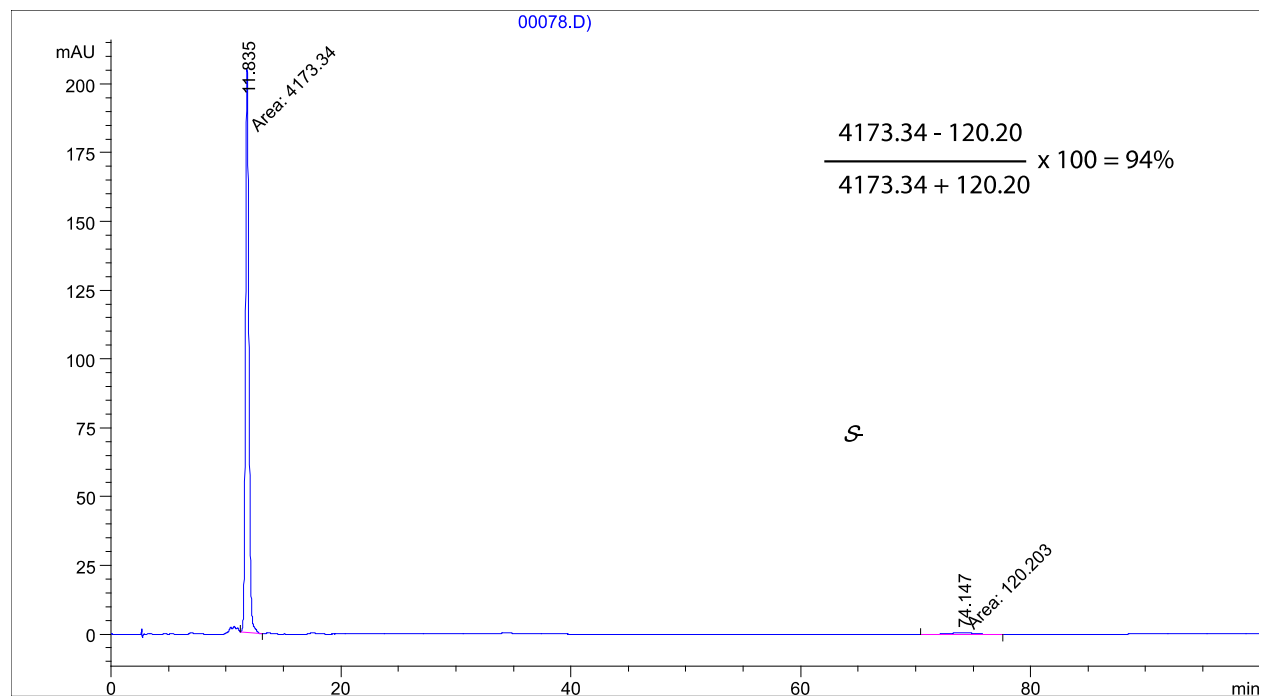
**Figure S17.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 60  $^\circ\text{C}$ ) spectrum of (*R*)-Mosher amide derivative of 2-methyl-4,4-bis(2-propenyl)pyrrolidine (**11b**) from enantioselective hydroamination obtained after treatment with (*S*)-Mosher chloride. Catalysis conditions: 10 mol %  $\{\text{S-2}\}\text{Zr}(\text{NMe}_2)_2$ , benzene at 23  $^\circ\text{C}$  (Table S1, entry 29).



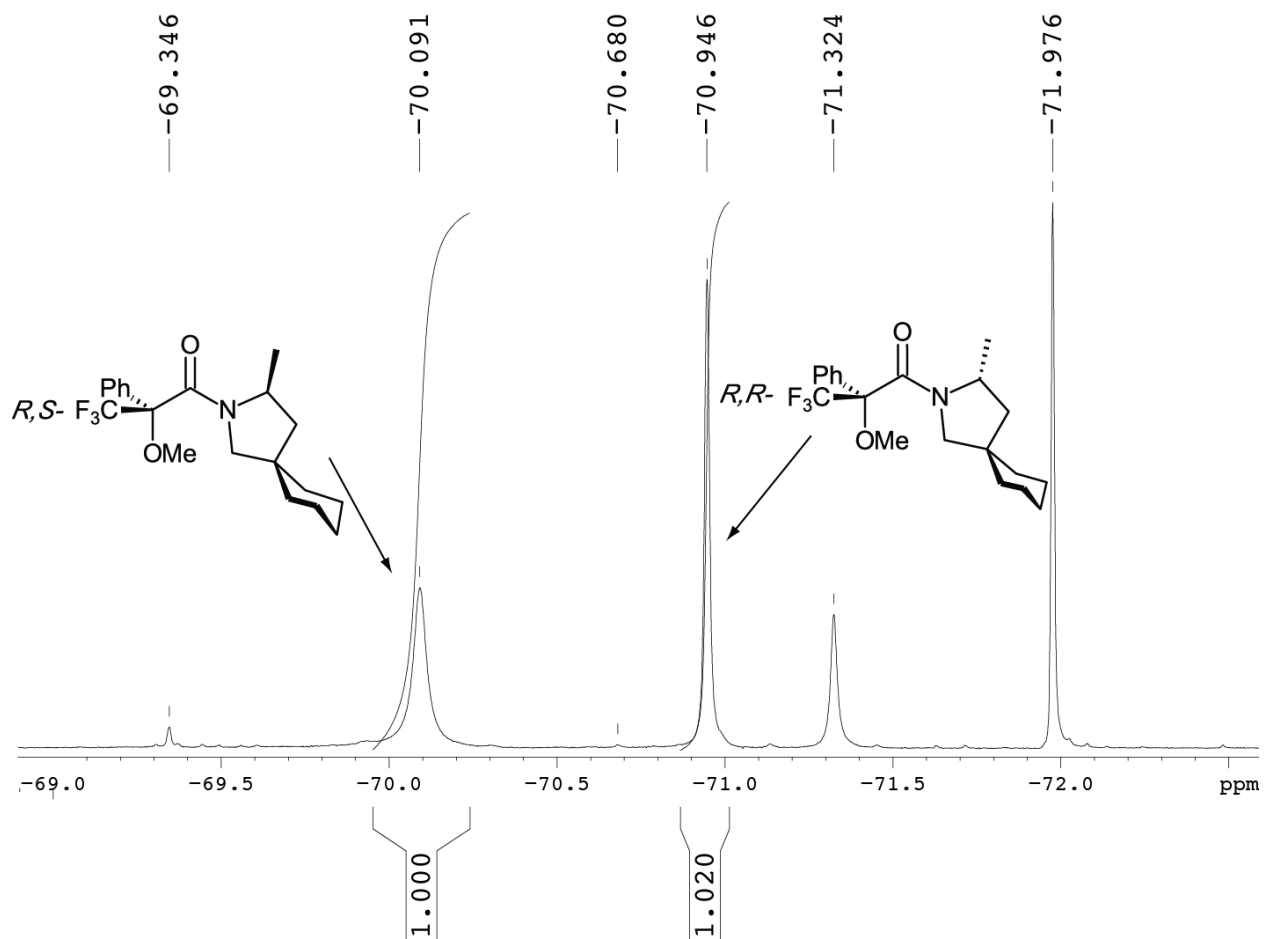
**Figure S18.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 60 °C) spectrum of (*R*)-Mosher amide derivative of 2-methyl-4,4-bis(2-propenyl)pyrrolidine (**11b**) from stereoselective hydroamination obtained after treatment with (*S*)-Mosher chloride. Catalysis conditions: 10 mol % {*S*-2}Hf(NMe<sub>2</sub>)<sub>2</sub>, toluene-*d*<sub>8</sub> at 0 °C (Table S1, entry 33).



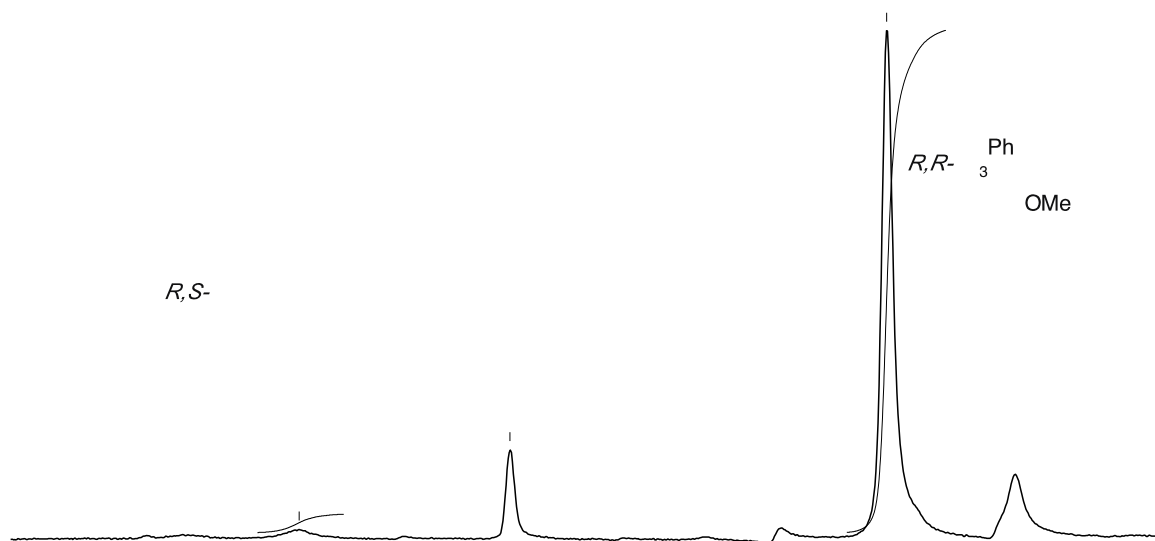
**Figure S19.** HPLC trace and integration data from naphthylamide of 2-methyl-4,4-bis(2-propenyl)pyrrolidine (**11b**) obtained from catalytic asymmetric hydroamination. Conditions for catalysis: Catalysis conditions: 10 mol % {*S*-2}Zr(NMe<sub>2</sub>)<sub>2</sub>, toluene at 0 °C (Table S1, entry 31).



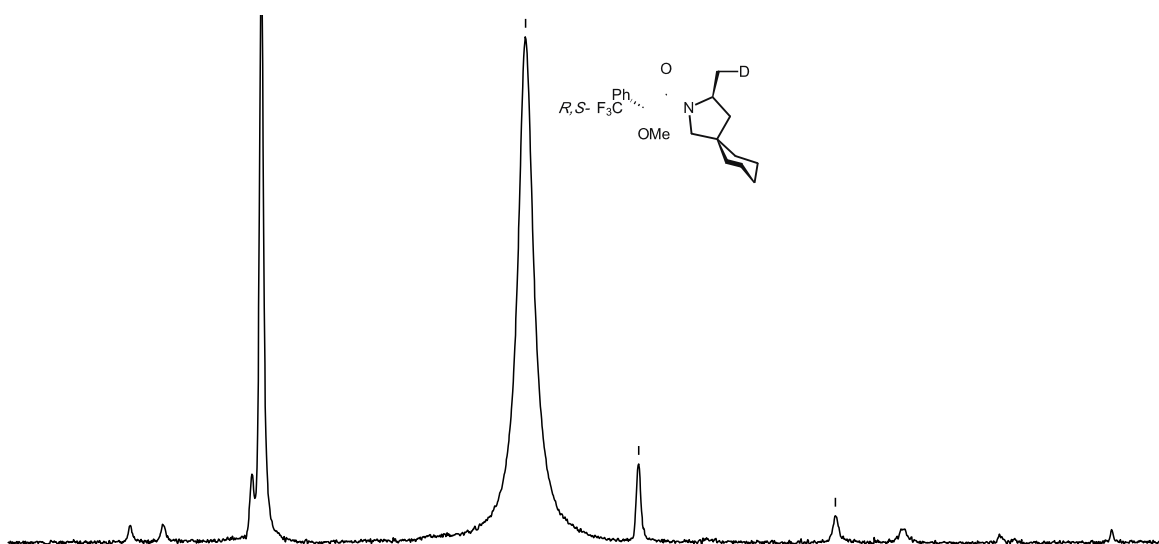
**Figure S20.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ ,  $60^\circ\text{C}$ ) of (*R*)-Mosher amide of racemic ( $\pm$ )-3-methyl-2-azo-spiro[4.5]decane ( $\pm$ -**12b**) obtained after treatment with (*S*)-Mosher chloride. This  $^{19}\text{F}$  NMR spectrum was previously reported in the Supporting Information of Ref. 5 and is given here again for the reader's convenience.



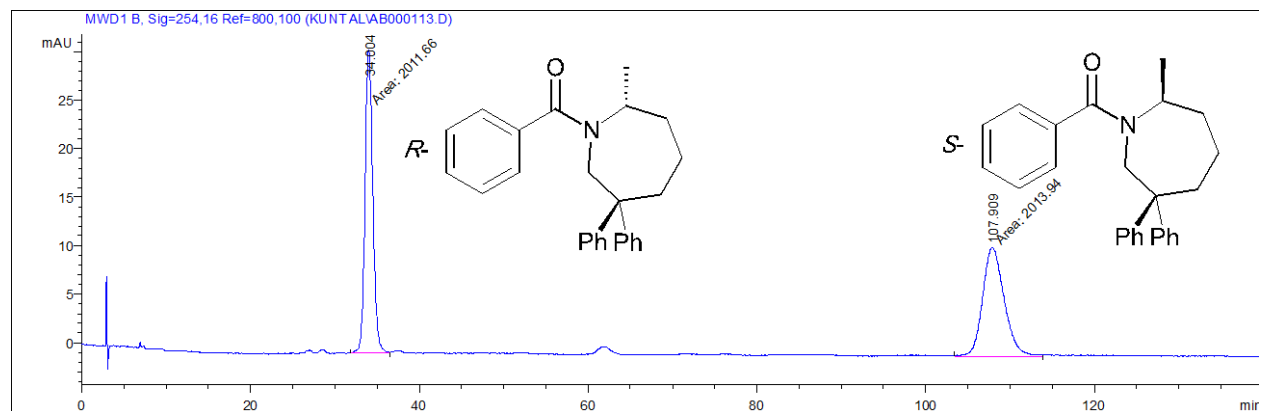
**Figure S21.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60 °C) of (*R*)-Mosher amide derivative of 3-methyl-2-azo-spiro[4.5]decane (**12b**) from stereoselective hydroamination obtained after treatment with (*S*)-Mosher chloride. Catalysis conditions: 10 mol % {*S*-**2**}Hf(NMe<sub>2</sub>)<sub>2</sub>, benzene at 23 °C (Table S1, entry 43).



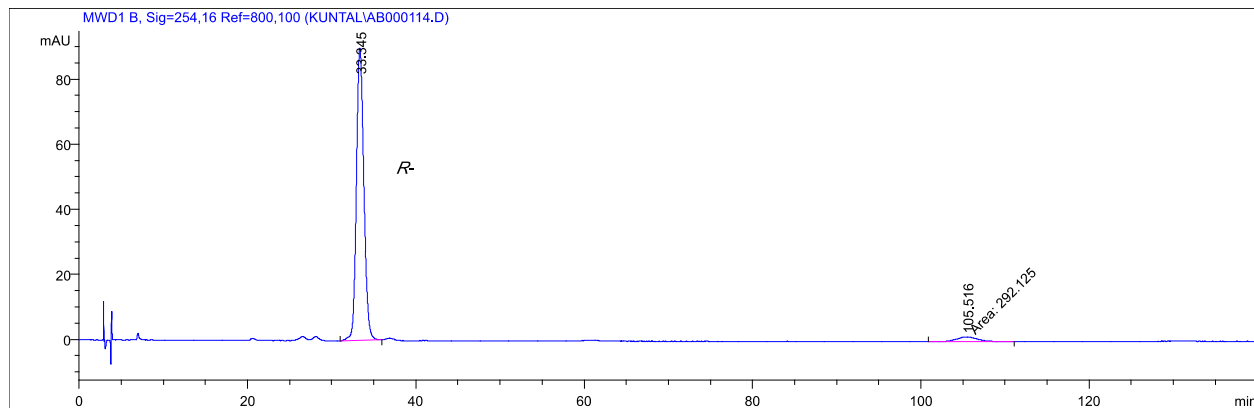
**Figure S22.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60  $^\circ\text{C}$ ) of (*R*)-Mosher amide derivative of 3-methyl-2-azo-spiro[4.5]decane (**12b-d<sub>2</sub>**) from stereoselective hydroamination obtained after treatment with (*S*)-Mosher chloride. Catalysis conditions: 10 mol % {*R*-2}Zr(NMe<sub>2</sub>)<sub>2</sub>, benzene at 23  $^\circ\text{C}$ .



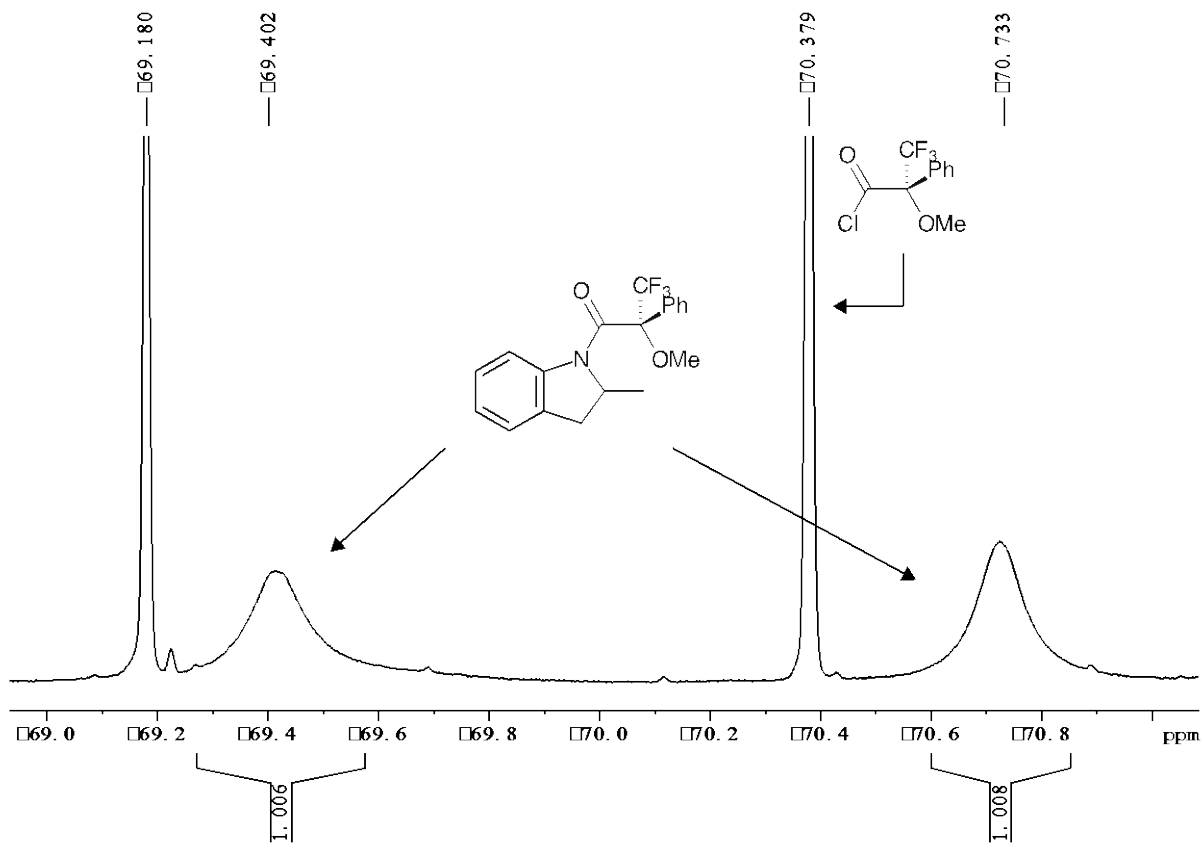
**Figure S23.** HPLC trace and integration data from benzylamide of racemic 2-methyl-6,6-diphenylazepane (**16b**).



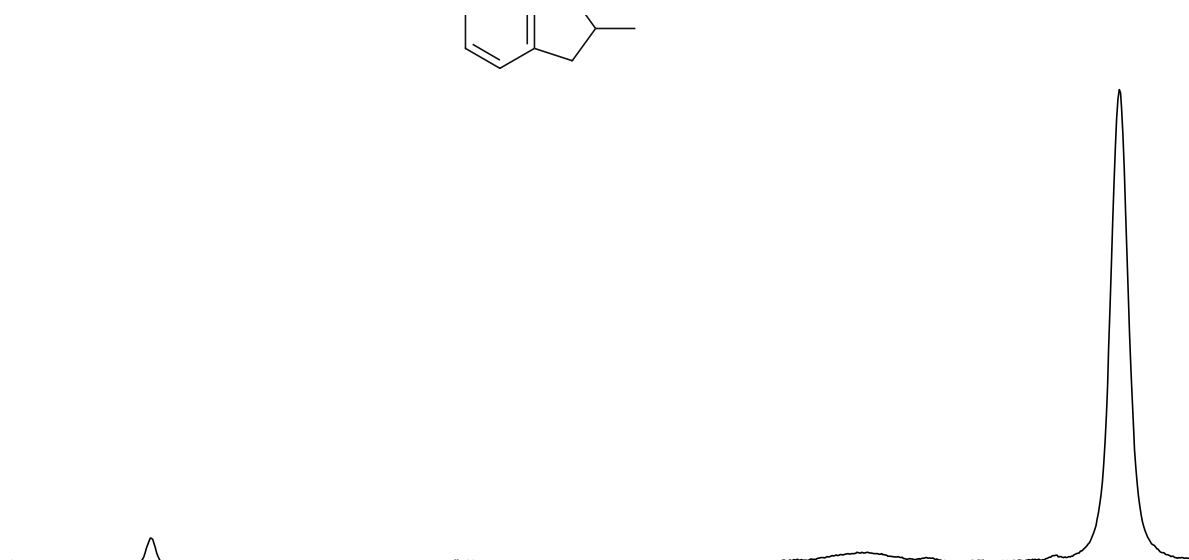
**Figure S24.** HPLC trace and integration data from benzylamide of 2-methyl-6,6-diphenylazepane (**16b**) from stereoselective hydroamination. Catalysis conditions: 10 mol % **{S-2}**Zr(NMe<sub>2</sub>)<sub>2</sub>, benzene at 23 °C.



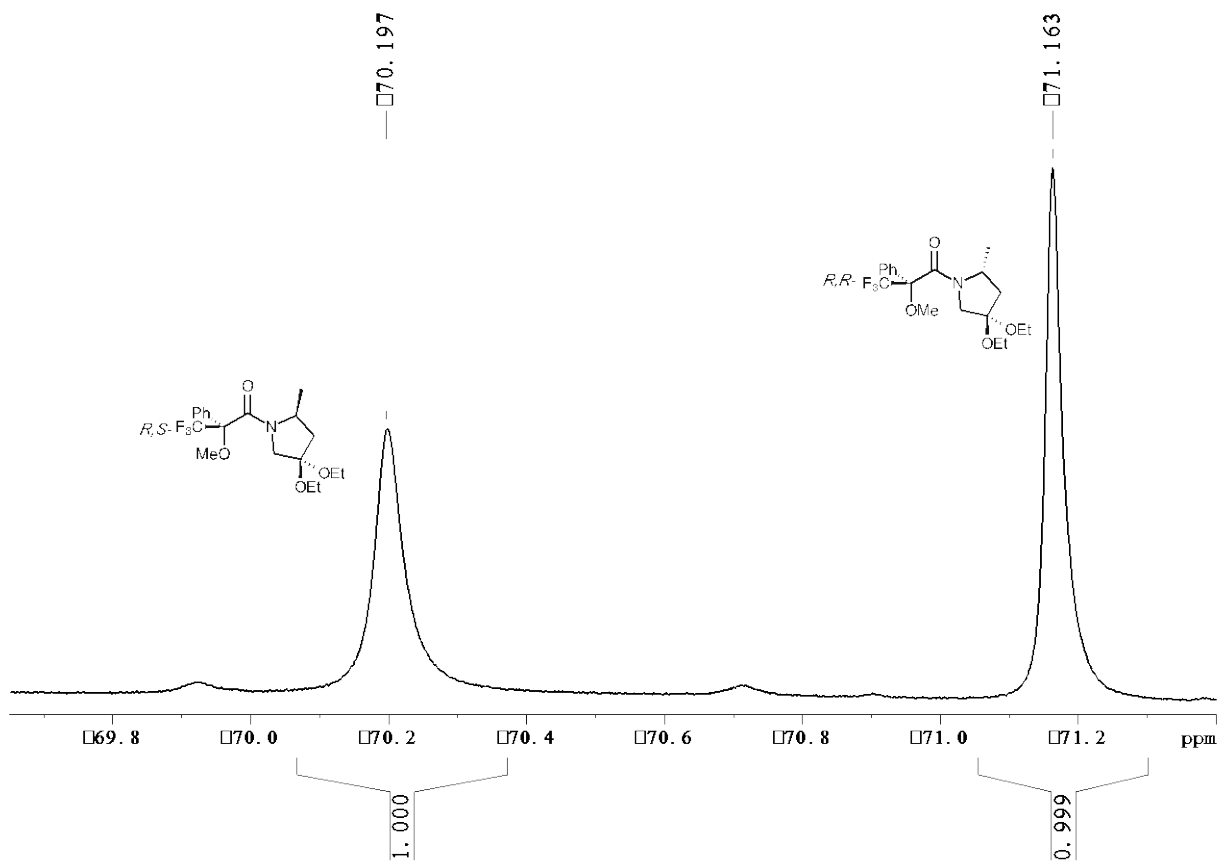
**Figure S25.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60  $^\circ\text{C}$ ) of (*R*)-Mosher amide of racemic ( $\pm$ )-2-methyl indoline (**18b**) obtained after treatment with (*S*)-Mosher chloride.



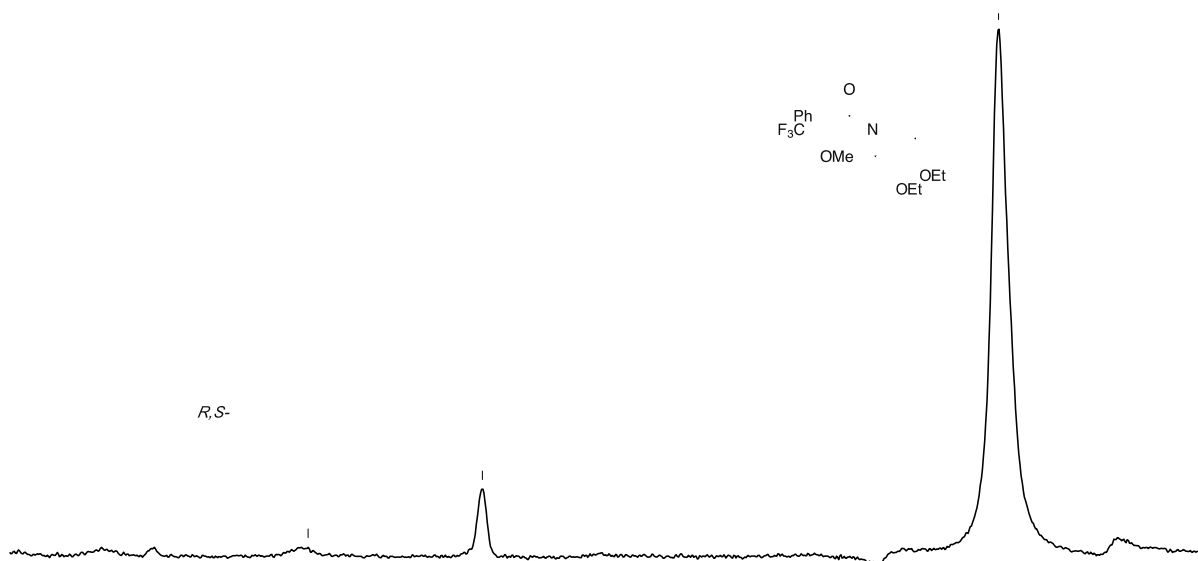
**Figure S26.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60 °C) of (*R*)-Mosher amide derivative of 2-Methyl indoline (**18b**) from stereoselective hydroamination obtained after treatment with (*S*)-Mosher chloride. Catalysis conditions: 10 mol %  $\{S\text{-}2\}\text{Zr}(\text{NMe}_2)_2$ , benzene at 23 °C (Table S1, entry 67).



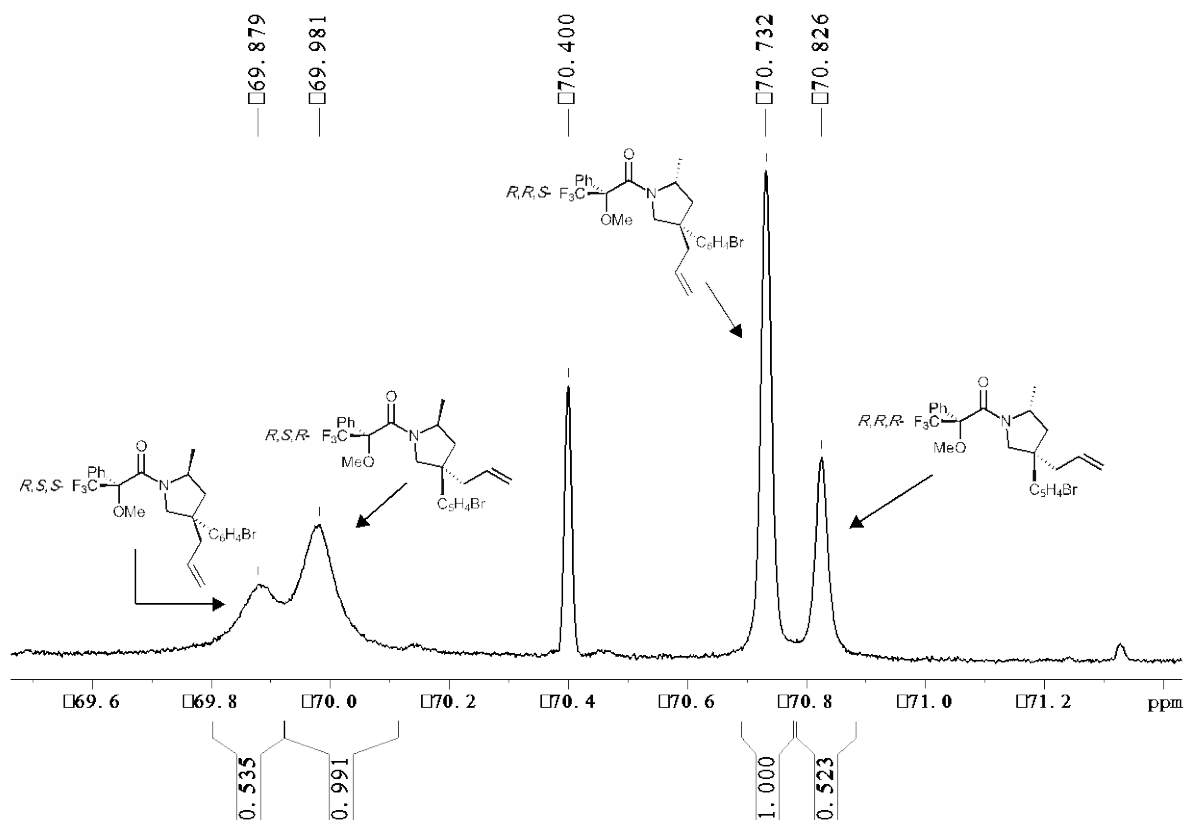
**Figure S27.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60  $^\circ\text{C}$ ) of (*R*)-Mosher amide of racemic ( $\pm$ )-4,4-diethoxy-2-methyl-pyrrolidine (**18b**) obtained after treatment with (*S*)-Mosher chloride.



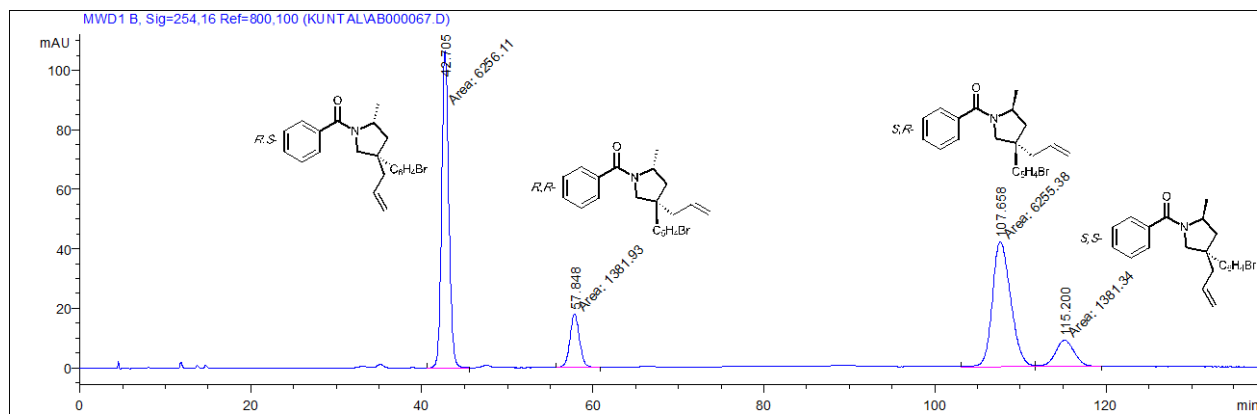
**Figure S28.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60 °C) of (*R*)-Mosher amide derivative of 2-4,4-diethoxy-pyrrolidine (**18b**) from stereoselective hydroamination obtained after treatment with (*S*)-Mosher chloride. Catalysis conditions: 10 mol %  $\{S\text{-}2\}\text{Zr}(\text{NMe}_2)_2$ , benzene at 23 °C (Table S1, entry 72).



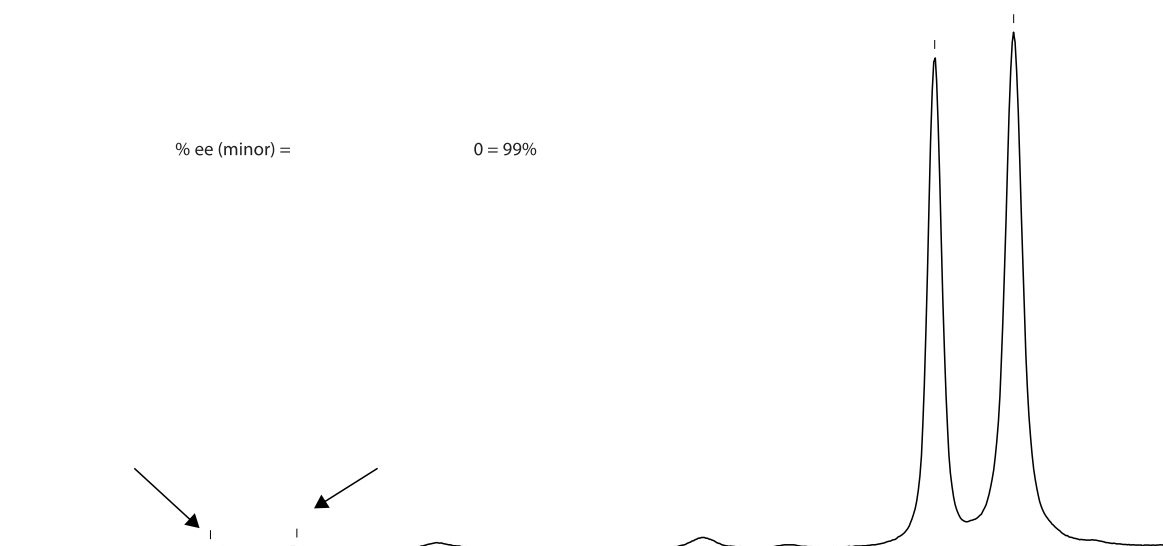
**Figure S29.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60  $^\circ\text{C}$ ) of (*R*)-Mosher amide of racemic ( $\pm$ )-4-allyl-2-methyl-4-(4-bromophenyl)pyrrolidine ( $\pm$ -**19b**) obtained after treatment with (*S*)-Mosher chloride.



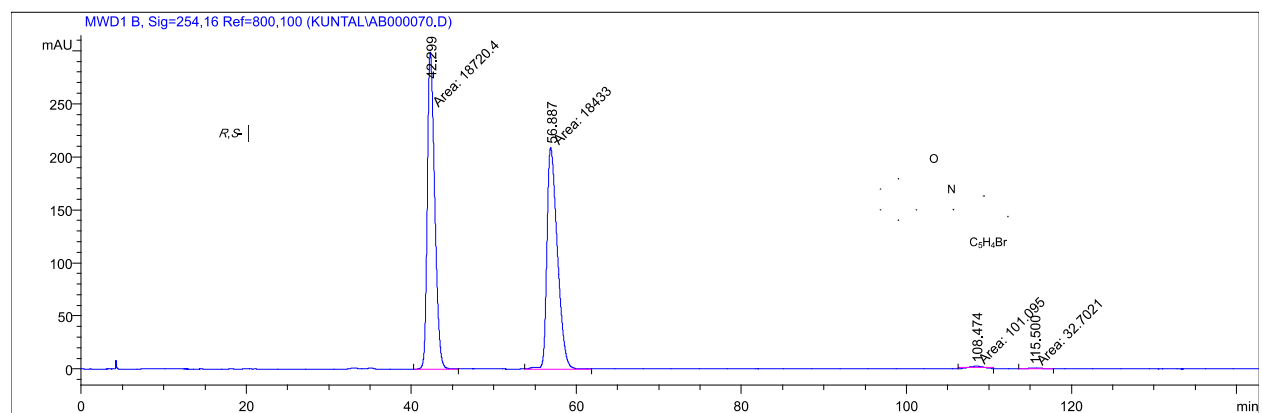
**Figure S30.** HPLC trace and integration data from racemic ( $\pm$ )-4-allyl-2-methyl-4-(4-bromophenyl)pyrrolidine ( $\pm$ -**19b**) as its benzoylamide.



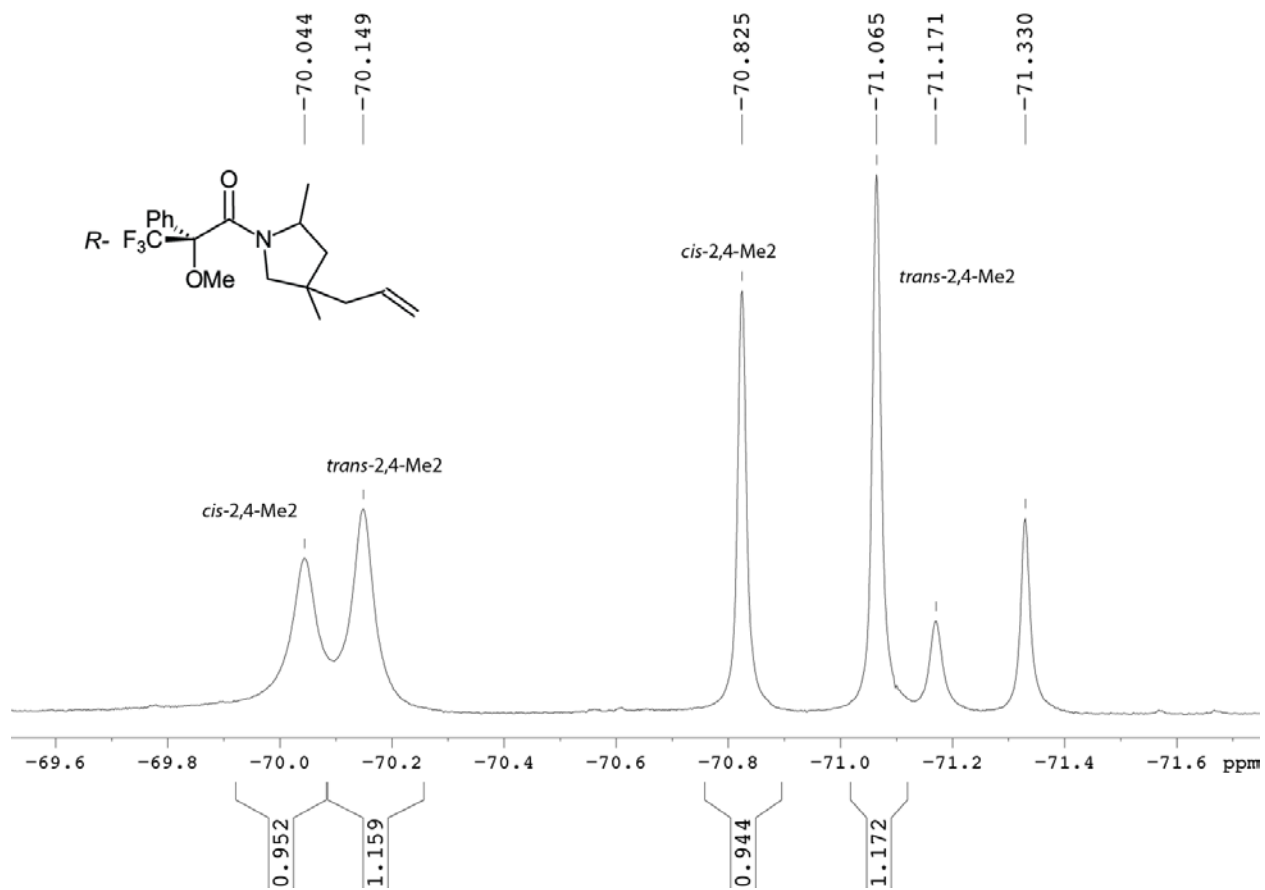
**Figure S31.**  $^{19}\text{F}$  NMR spectrum (376 MHz,  $\text{CDCl}_3$ , 60 °C) of (*R*)-Mosher amide derivative of 4-allyl-2-methyl-4-(4-bromophenyl)pyrrolidine (**19b**) from stereoselective hydroamination obtained after treatment with (*S*)-Mosher chloride. Catalysis conditions: 10 mol % {*S*-**2**}Zr(NMe<sub>2</sub>)<sub>2</sub>, toluene-*d*<sub>8</sub> at -30 °C (Table S1, entry 78).



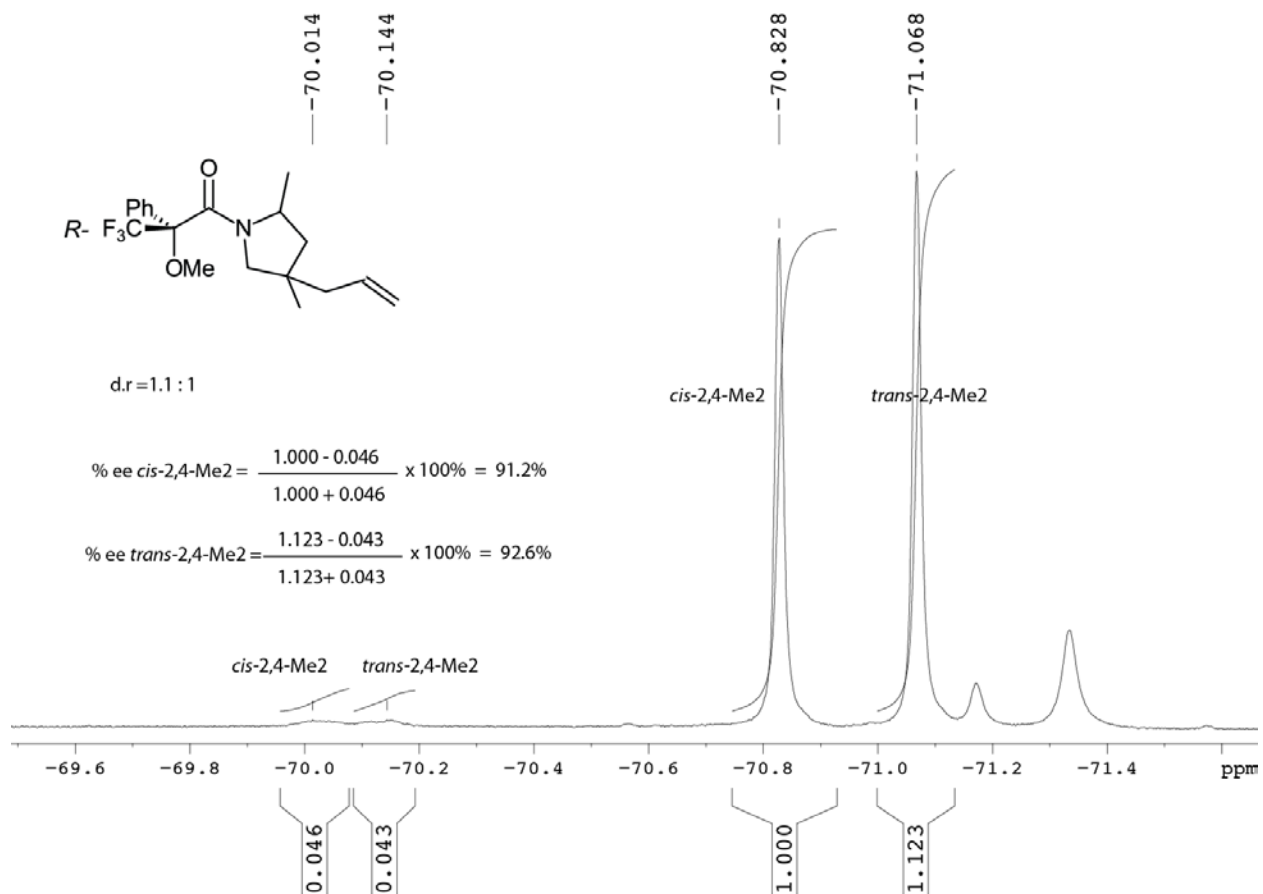
**Figure S32.** HPLC trace and integration data from benzoylamide of 4-allyl-2-methyl-4-(4-bromophenyl)pyrrolidine (**19b**) obtained from catalytic asymmetric hydroamination. Conditions for catalysis: Catalysis conditions: 10 mol % {*S*-**2**}Zr(NMe<sub>2</sub>)<sub>2</sub>, toluene-*d*<sub>8</sub> at -30 °C (Table S1, entry 78).



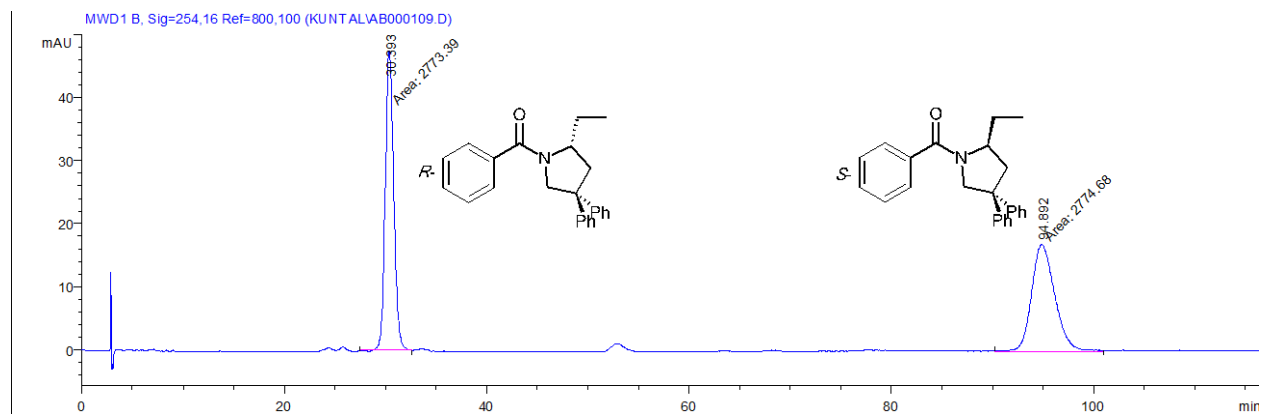
**Figure S33.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 60  $^\circ\text{C}$ ) spectrum of the (*R*)-Mosher amide derivative of racemic ( $\pm$ )-2,4-dimethyl-4-allylpyrrolidine ( $\pm$ -**20b**). This spectrum was previously given in reference 5.



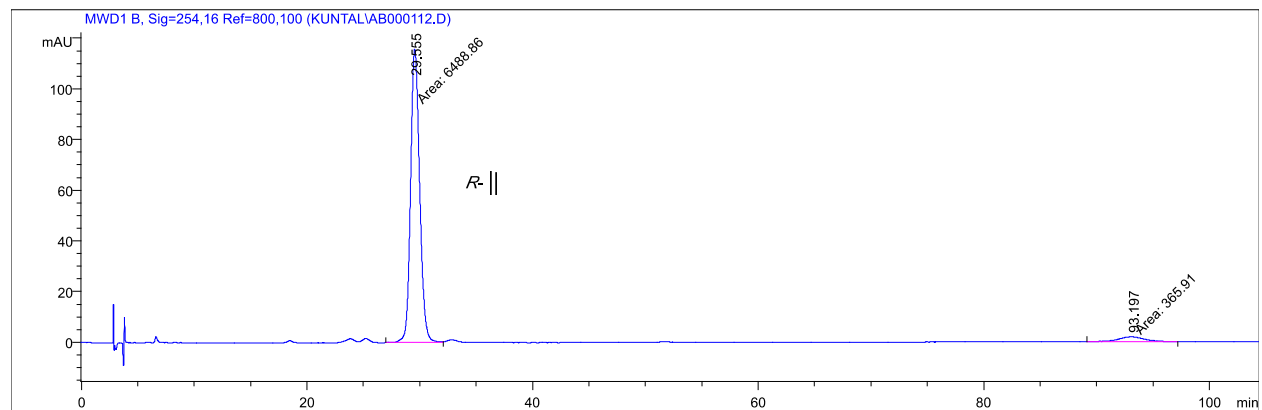
**Figure S34.**  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ , 60  $^\circ\text{C}$ ) spectrum of (*R*)-Mosher amide of 2,4-dimethyl-4-allylpyrrolidine product (**21b**) obtained from catalytic asymmetric hydroamination and (*S*)-Mosher chloride. Conditions for catalysis: 10 mol % {*S*-**2**}Zr(NMe<sub>2</sub>)<sub>2</sub>, benzene-*d*<sub>6</sub> at 23  $^\circ\text{C}$ . This spectrum was previously reported in reference 5.



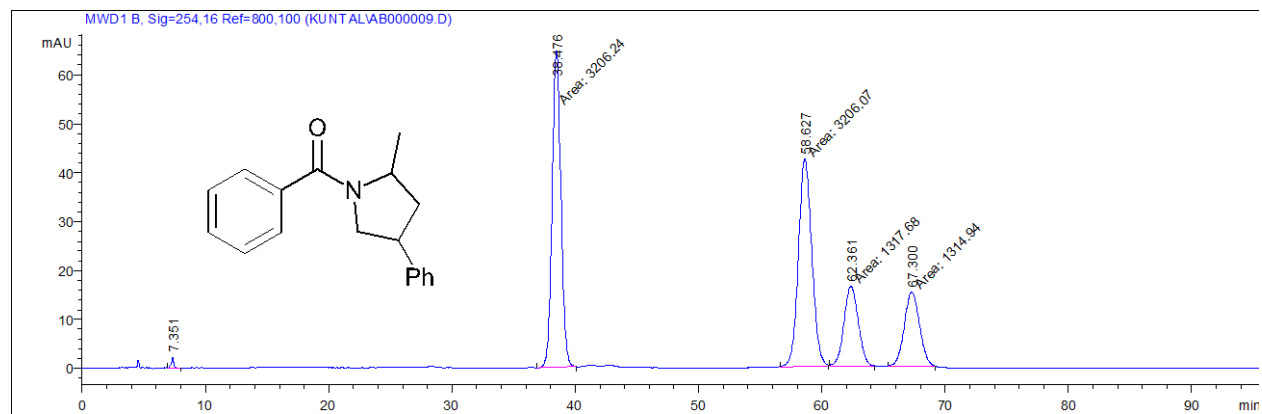
**Figure S35.** HPLC trace of the benzamide derivative of racemic ( $\pm$ )-2-ethyl-4,4-diphenylpyrrolidine pyrrolidine ( $\pm$ -**21b**).



**Figure S36.** HPLC trace of the benzamide of 2-ethyl-4,4-diphenylpyrrolidine product (**21b**) obtained from catalytic asymmetric hydroamination and (*S*)-Mosher chloride. Conditions for catalysis: 10 mol % {*S*-2}Zr(NMe<sub>2</sub>)<sub>2</sub>, benzene-*d*<sub>6</sub> at 23 °C (Table S1, entry 86).



**Figure S37.** HPLC trace and integration data from racemic ( $\pm$ )-2-methyl-4-phenylpyrrolidine ( $\pm$ -**22b**) as its benzoylamide.



**Figure S38.** HPLC trace and integration data from benzoylamide of 2-methyl-4-phenylpyrrolidine (**22b**) obtained from catalytic asymmetric hydroamination. Conditions for catalysis: Conditions for catalysis: 10 mol % {*S*-**2**}Zr(NMe<sub>2</sub>)<sub>2</sub>, benzene-*d*<sub>6</sub> at 23 °C (Table S1, entry 91).

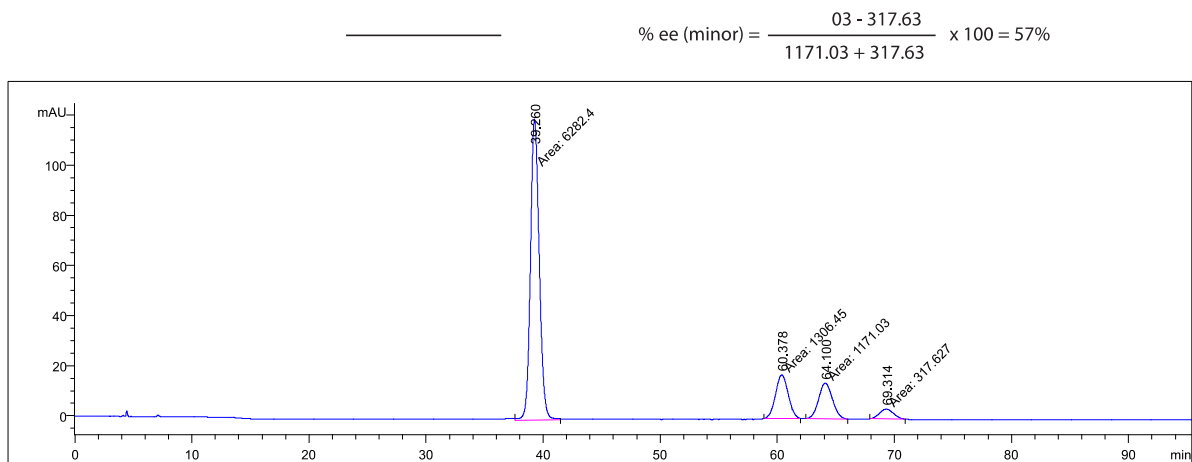
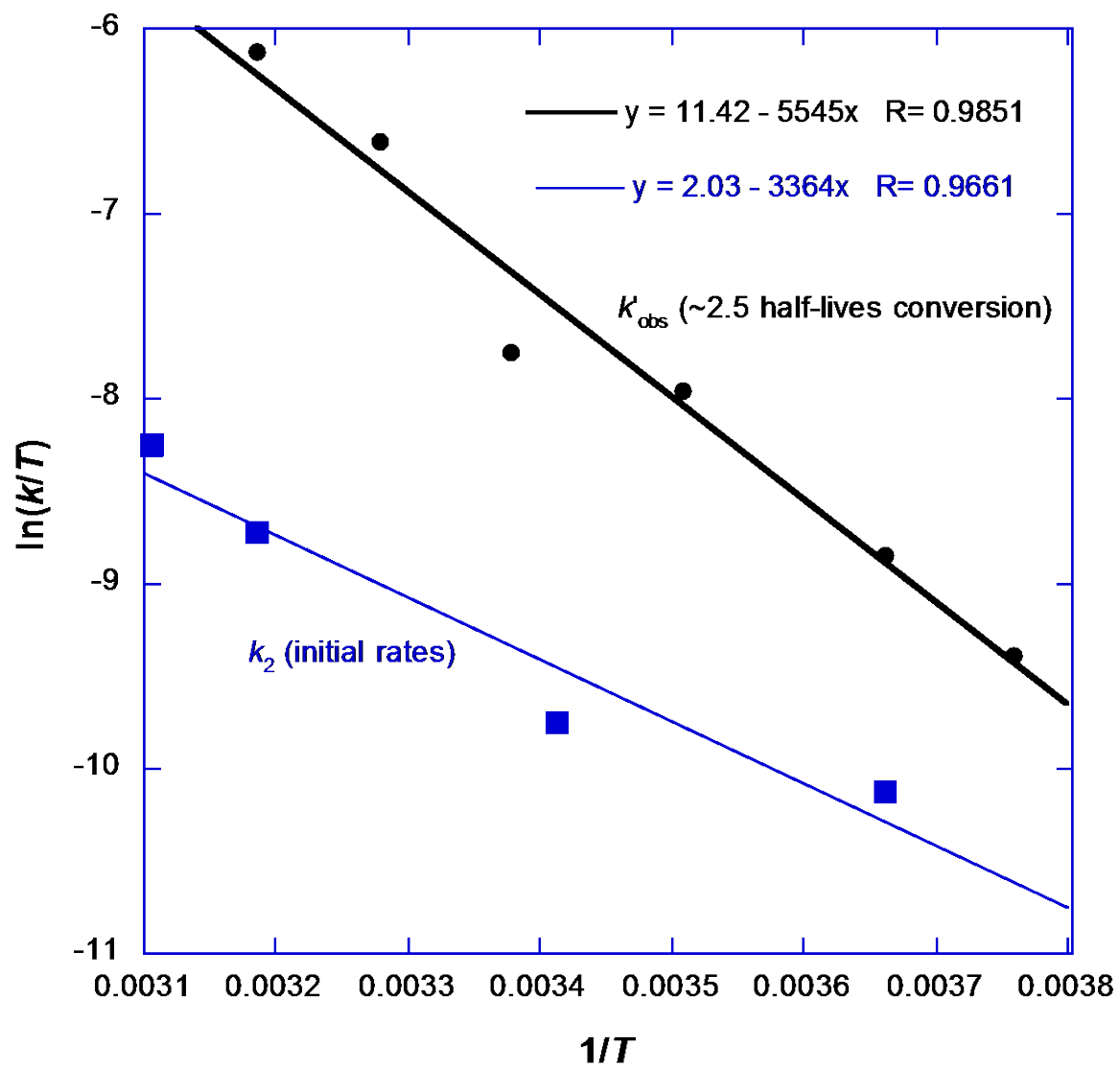


Figure S39. Eyring plots for conversion ( $k'_{\text{obs}}$ ) and initial rates ( $k_2$ ).



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