DERIVATIVES OF (*S*)-{[2-(METHOXYMETHYL)PYRROLIDIN-1-YL]-METHYL}FERROCENE – NEW PLANAR CHIRAL LIGANDS

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New planar chiral amino-alcohol ferrocene ligands based on (*S*)-2-(methoxymethyl)pyrrolidine were synthesized and employed in the enantioselective addition of diethylzinc to benzaldehyde with enantioselectivity up to 82%. The effect of planar chirality was evaluated.
Keywords: Amino alcohols; Ferrocenes; Metallocenes; Ferrocenyl ligands; Planar chirality; Asymmetric catalysis; Diethylzinc addition.

Chiral ferrocene derivatives are widely used as ligands in stereoselective transition metal catalysis[1]. Notably, 1,2-disubstituted ferrocenes possessing planar chirality attract considerable attention[2]. Since the pioneering work of Hayashi[3] with aminophosphine-BPPFA ligand, a number of planar chiral ferrocene ligands have been designed.

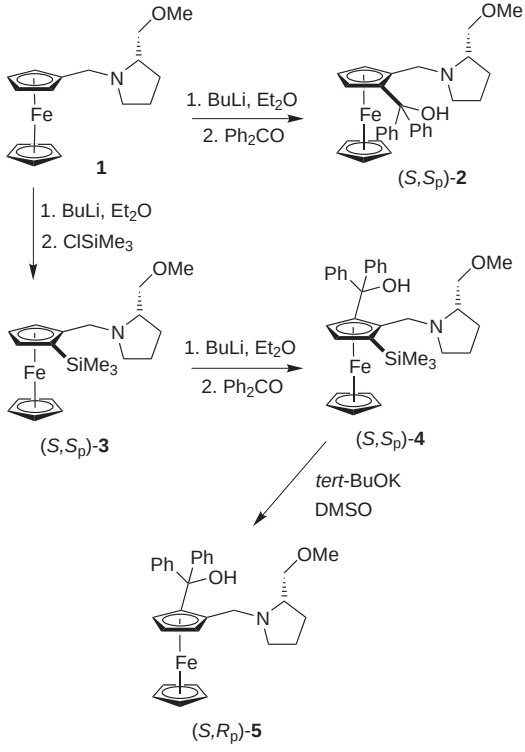
Although diethylzinc addition to aldehydes is a well known and widely studied reaction[4], it is still a useful test system in the ligand design process. Watanabe and coworkers introduced chiral ferrocene aminoalcohols as ligands for diethylzinc addition to aldehydes[5]. Planar chiral hydroxyferrocenyloxazoline derivatives can be mentioned as more recent examples[6].

Optically pure (or highly enriched) ferrocene 1,2-derivatives are mainly obtained by the diastereoselective ortho-lithiation of suitable homochiral ferrocenyl-substituted amines[7], oxazolines[8], dioxanes[9], hydrazones[10] or sulfoxides[11]. The (*S*)-2-(methoxymethyl)pyrrolidine unit attached to ferrocene was recently reported as a novel directing group[7b].

In this work, we wish to present the synthesis of new ligands based on (*S*)-{[2-(methoxymethyl)pyrrolidin-1-yl]methyl}ferrocene, their analogs with pyrrolidine possessing only planar chirality, and the application of the compounds to the enantioselective addition of diethylzinc to benzaldehyde.

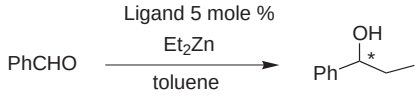
RESULTS AND DISCUSSION

(*S*)-{[2-(Methoxymethyl)pyrrolidin-1-yl]methyl}ferrocene **1** was prepared by the nucleophilic displacement of the trimethylammonium group with (*S*)-2-(methoxymethyl)pyrrolidine in an easily obtainable precursor – (ferrocenylmethyl)trimethylammonium iodide[7b].



SCHEME 1

Compound **1**[7b] was deprotonated by BuLi in diethyl ether and subsequent quenching of the anion with benzophenone gave compound **2**. The isomeric derivative **5** was also prepared by the procedure depicted in Scheme 1. Compounds **2** and **5** were employed as ligands in the addition of diethylzinc to benzaldehyde (Scheme 2), with selectivities 50 and 62% ee, respectively (Table I). Interestingly, the absolute configuration of the resulting alcohols depends on the configuration of the planar chiral unit of the ligand. We also evaluated compound **4** with the trimethylsilyl group, as it possesses a suitable amino alcohol arrangement as well. Surprisingly, the enantioselectivity rose to 76%, the configuration of the product being the same as in the case of **5**, because their planar chirality is identical.



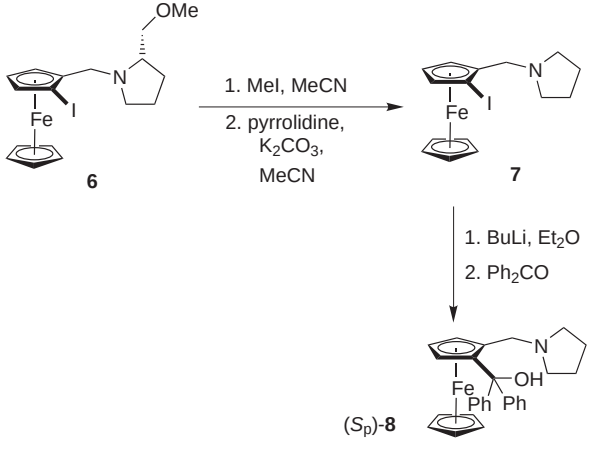
SCHEME 2

TABLE I
Addition of Et_2Zn to benzaldehyde

Ligand	Conversion[a], %	ee[b], %	Configuration[c]
2	92	50	*R*
4	99	76	*S*
5	99	62	*S*
8	96	74	*R*
10	99	82	*S*

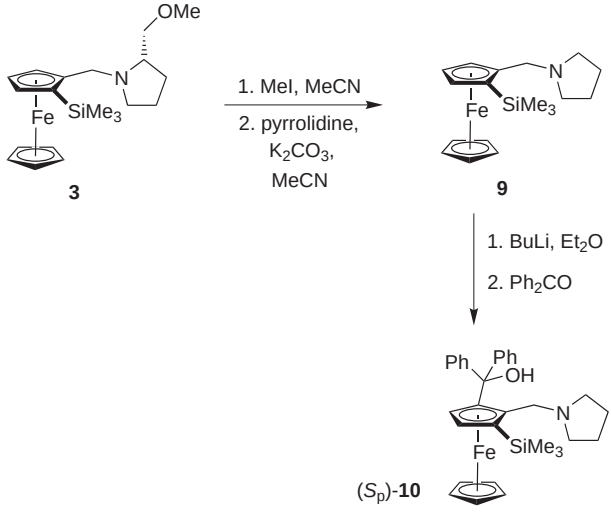
[a] Based on ^{1}H NMR analysis of the crude reaction mixture. [b] Enantioselectivity measured by GC on a Chirasil β-CD column. [c] Configuration determined by the comparison of the optical rotation with literature data[12].

To examine the effect of planar chirality in a more detailed way, we also synthesized aminoalcohol **8** having only planar chirality (Scheme 3). Iodo derivative **7** was prepared according to Xiao[13]. The enantioselectivity of the addition of Et_2Zn to benzaldehyde was 74%, with *R* configuration of the product.



SCHEME 3

Next we prepared compound **10** with the trimethylsilyl group in a similar manner from **3** (Scheme 4). The enantioselectivity was again higher (82%) than with derivative **8** without the trimethylsilyl group, and the configuration of the product was in agreement with planar chirality of the ligand.



SCHEME 4

The TMS group is often used in ferrocene chemistry for the synthesis of diastereoisomeric compounds with opposite planar chirality. Park and coworkers[14] have recently reported silylated bis(oxazolinyl) bis(diphenylphosphino)ferrocenes, in which the trialkylsilyl group dramatically improved the enantiomeric excess in a Pd-catalyzed allylic substitution compared to desilylated ligands. Our silylated ligands **4** and **10** showed enhanced enantioselectivity in the addition of Et_2Zn to benzaldehyde as well.

Bolm and coworkers[6a] reported hydroxy oxazolines as catalysts for Et_2Zn addition to aldehydes. Ligands with opposite planar chirality gave 93 *vs* 35% ee in the addition of Et_2Zn to benzaldehyde. The use of ligands with only planar chirality led to a lower enantiomeric excess (51%). Thus, they concluded that the appropriate combination of the two stereoelements and their interactions were of major importance for achieving high enantioselectivities[15]. Given the results of our work, we can conclude that compound **8** with mere planar chirality is even more effective than derivatives **2** and **5**, which possess a combination of two stereoelements. Consequently, planar chirality is crucial for the enantiomeric excess, and determines the absolute configuration of the resultant 1-phenylpropan-1-ol.

CONCLUSION

In summary, we have prepared new amino alcohol ferrocenyl ligands with central and planar chirality based on (*S*)-2-methoxymethylpyrrolidine. By replacing (*S*)-2-(methoxymethyl)pyrrolidine unit with pyrrolidine, ligands possessing just planar chirality were synthesized. The latter were even more effective as catalysts in Et_2Zn addition to PhCHO than the former. Thus, planar chirality seems to be the key stereoelement for this type of compounds and catalytic reaction. We found that planar chirality of the ferrocene moiety determines the absolute configuration of the product in diethylzinc addition to benzaldehyde. An additional trimethylsilyl group has a positive influence on the enantioselectivity of the addition.

EXPERIMENTAL

All reactions were carried out under the atmosphere of Ar. The solvents were purified by standard methods and were freshly distilled prior to use. Reactions with BuLi were carried out using standard Schlenk techniques. For column chromatography, Al_2O_3 (Lachema) activity II-III and SiO_2 (Merck) 40–63 nm were used. NMR spectra were measured on a Varian Gemini 2000 spectrometer (300 and 75 MHz for ^1H and ^{13}C, respectively), in $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. Chemical shifts are given on the δ-scale (ppm), coupling constants (*J*) in Hz. IR spectra (wavenumbers in cm^{-1}) were recorded on a Perkin–Elmer 781 infrared spectrometer in chloroform or CCl_4. Melting points were determined on a Kofler apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer 241 polarimeter, and are given in deg cm^{-3} g^{-1} dm^{-1}.

(S,S_p)-1-[(Hydroxy)diphenylmethyl]-2-{[2-(methoxymethyl)pyrrolidin-1-yl]methyl}-ferrocene (**2**)

Compound **1** (137 mg, 0.438 mmol) was dissolved in anhydrous diethyl ether (3 ml) at –78 °C, and BuLi (0.19 ml, 0.482 mmol, 2.5 M solution in hexane) was added dropwise to the solution. The temperature was allowed to rise to –10 °C over 3 h, and benzophenone in diethyl ether was then added. The reaction mixture was allowed to warm to 20 °C over 18 h. Water (5 ml) was added to the solution, and the resultant mixture was extracted with diethyl ether (3 × 5 ml). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography on Al_2O_3 giving 70 mg of compound **1** (32%, orange oil). $[\alpha]_D^{20}$ –209.7 (*c* 0.31, $CHCl_3$), $[\alpha]_{578}^{20}$ –225.8 (*c* 0.31, $CHCl_3$), $[\alpha]_{546}^{20}$ –287.1 (*c* 0.31, $CHCl_3$). IR ($CHCl_3$): 2 890, 2 830, 1 500, 1 460, 1 120, 1 060. ^1H NMR (300 MHz, $CDCl_3$): 1.21–1.35 m, 3 H ($NCH_2C\mathbf{H}_2C\mathbf{H}H$); 1.70–1.86 m, 2 H ($NCH_2CH_2C\mathbf{H}H$, $NCH\mathbf{H}$); 2.17–2.36 m, 1 H ($NC\mathbf{H}H$); 2.50–2.53 m, 1 H (NCH); 2.83 d, 1 H, ^3J = 12.6 (Fc-C**H**H); 3.25–3.30 m, 1 H (MeOCH**H**); 3.43–3.48 m, 1 H (MeOC**H**H); 3.44 s, 3 H (OCH_3); 3.83–3.86 m, 1 H (Fc); 3.92 s, 5 H (Cp); 4.04–4.09 m, 1 H (Fc); 4.11–4.16 m, 1 H (Fc); 4.54 d, ^3J = 12.7 (Fc-CH**H**); 7.11–7.37 m, 8 H (C_5H_5); 7.47 br s, 1 H (OH); 7.63 m, 2 H (C_5H_5). ^{13}C NMR (75 MHz, $CDCl_3$): 22.2 (CH_2); 28.4 (CH_2); 53.4 (N-CH_2); 55.7 (Fc-CH_2); 59.3 (N-CH); 63.5 (OCH_3); 65.6 (Fc); 70.0 (Cp); 70.6 (Fc); 71.1 (Fc); 75.7 (CH_2-O); 78.1 (C_i); 81.9 (Ph_2C); 96.3 (C_i); 126.4, 126.5, 127.2,

127.4, 127.5, 147.7, 150.5 (2 × C_6H_5). For $C_{30}H_{33}FeNO_2$ (495.4) calculated: 72.73% C, 6.71% H, 2.83% N; found: 72.38% C, 6.57% H, 2.24% N.

(S,S_p)-1-[(Hydroxy)diphenylmethyl]-2-{[2-(methoxymethyl)pyrrolidin-1-yl]methyl}-3-(trimethylsilyl)ferrocene (**4**)

Compound **3** [7b] (385 mg, 1.00 mmol) was dissolved in anhydrous diethyl ether (10 ml), and the solution was cooled to –40 °C. BuLi (0.52 ml, 1.30 mmol, 2.5 M solution in hexane) was subsequently added dropwise. The temperature was allowed to rise to 0 °C over 3 h, then benzophenone (237 mg, 1.30 mmol) in diethyl ether (2 ml) was added and the mixture was warmed to 20 °C and stirred for 18 h. Water (10 ml) was added to the reaction mixture and the phases were separated. The water phase was further extracted with diethyl ether (2 × 5 ml). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and evaporated *in vacuo*. The crude product was purified by chromatography on Al_2O_3 (hexane–diethyl ether 4 : 1) giving 350 mg of compound **4** (62%, orange solid). M.p. 126–128 °C. $[\alpha]_D^{25}$ +66.4 (*c* 0.25, $CHCl_3$). IR (CCl_4): 2 810, 2 790, 1 545, 1 250, 1 120, 1 110, 840. ^{1}H NMR (300 MHz, $CDCl_3$): 0.30 s, 9 H ($SiMe_3$); 1.23–1.39 m, 3 H (NCH_2CH_2CHH); 1.88–1.96 m, 1 H (NCH_2CH_2CHH); 2.10–2.14 m, 1 H (NC**H**H); 2.25–2.30 m, 2 H (NCH**H**); 2.47–2.50 m, 1 H (NCH); 2.55–2.61 m, 1 H (MeOC**H**H); 2.96 s, 3 H (OCH_3); 3.10 d, 1 H, ^3J = 14.1 (Fc-C**H**H); 3.30 d, 1 H, ^3J = 14.3 (Fc-CH**H**); 3.67 d, 1 H, ^3J = 2.4 (Fc); 3.80 m, 1 H (MeOCH**H**); 4.00 d, 1 H, ^3J = 2.4 (Fc); 4.10 s, 5 H (Cp); 7.04–7.43 m, 10 H (C_6H_5); 9.33 br s, 1 H (OH). ^{13}C NMR (75 MHz, $CDCl_3$): 0.7 ($SiMe_3$); 23.0 (CH_2); 29.0 (CH_2); 53.7 (CH_2); 54.5 (CH_2); 58.8 (OMe); 64.7 (NCH); 70.1 (Cp); 71.6 (Fc); 72.0, 74.3 (Fc-CH_2); 74.4 ($MeOCH_2$); 88.1 (Fc); 98.4 (Ph_2C); 126.0, 126.4, 126.7, 126.9, 127.6, 127.9, 128.1, 147.7, 149.6 (C_6H_5). For $C_{33}H_{41}FeNO_2Si$ (567.6) calculated: 69.82% C, 7.28% H, 2.47% N; found: 69.38% C, 7.09% H, 2.22% N.

(S,R_p)-1-[(Hydroxy)diphenylmethyl]-2-{[2-(methoxymethyl)pyrrolidin-1-yl]methyl}-ferrocene (**5**)

A solution *t*-BuOK (65 mg, 0.778 mmol) in DMSO (2 ml) was added dropwise to the solution of compound **4** (150 mg, 0.353 mmol) in the same solvent (2 ml) at 20 °C, and the reaction mixture was stirred for 18 h. Diethyl ether (10 ml) was added, the mixture was cooled in cold water and saturated NaCl solution (10 ml) was added. The phases were separated, and the water phase was extracted with diethyl ether (2 × 5 ml). The combined organic layers were dried, filtered and the solvent evaporated *in vacuo*. The crude product was purified by chromatography on Al_2O_3 (hexane–diethyl ether 2 : 1) giving 124 mg of compound **5** (95%, orange oil). $[\alpha]_D^{25}$ +143 (*c* 0.33, $CHCl_3$), $[\alpha]_{578}^{25}$ +161 (*c* 0.33, $CHCl_3$), $[\alpha]_{546}^{25}$ +235 (*c* 0.33, $CHCl_3$). IR (CCl_4): 2 740, 1 655, 1 580, 1 535, 1 475, 1 430, 1 090, 1 035. ^{1}H NMR (300 MHz, $CDCl_3$): 1.25–1.34 m, 2 H (NCH_2CH_2); 1.79–1.93 m, 2 H ($NCH_2CH_2CH_2$); 2.19–2.30 m, 2 H (NCH_2); 2.43–2.52 m, 1 H (NCH); 2.57–2.63 m, 1 H (MeOC**H**H); 2.95 s, 3 H (OMe); 3.04 d, 1 H, ^3J = 14.3 (Fc-C**H**H); 4.43 d, 1 H, ^3J = 14.4 (Fc-CH**H**); 3.53 m, 1 H (Fc); 3.82 m, 1 H (MeOC**H**H); 4.06–4.09 m, 2 H (Fc); 4.11 s, 5 H (Cp); 7.06–7.45 m, 10 H (C_6H_5); 8.83 br s, 1 H (OH). ^{13}C NMR (75 MHz, $CDCl_3$): 23.0 (CH_2); 28.8 (CH_2); 54.2 (N-CH_2); 55.1 (Fc-CH_2); 58.7 (N-CH); 64.4 (O-CH_3); 65.2 (Fc); 69.3 (Fc); 70.0 (Cp); 71.6 (Fc); 74.5 (O-CH_2); 84.1 (Fc(C_i)); 95.2 (Fc(C_i)); 125.9, 126.2, 126.5, 126.6, 127.4, 127.7, 127.9 (Ph, C-OH); 147.3, 149.5 (Ph(C)). For $C_{30}H_{33}FeNO_2$ (495.4) calculated: 72.73% C, 6.71% H, 2.83% N; found: 72.31% C, 6.29% H, 2.40% N.

(S_p)-1-Iodo-2-(pyrrolidin-1-ylmethyl)ferrocene (**7**)

Methyl iodide (184 mg, 81 μl, 1.30 mmol) was added dropwise to the solution of compound **6** [13] (190 mg, 0.432 mmol) in anhydrous CH_3CN (2 ml) and the mixture was stirred at room temperature for 1 h. The solvent was then evaporated, and the residue redissolved in acetonitrile (5 ml). Anhydrous K_2CO_3 (119 mg, 0.860 mmol) and pyrrolidine (92 mg, 1.29 mmol) were added to the solution and the reaction mixture was heated under reflux for 18 h. The solution was filtered and the white solid was further washed with CH_2Cl_2, and the filtrate evaporated *in vacuo*. The residue was purified by chromatography on Al_2O_3 (hexane–diethyl ether 2 : 1) giving 154 mg of compound **7** (90%, orange oil). $[\alpha]_D^{25}$ +6.8 (*c* 0.43, $CHCl_3$), $[\alpha]_{578}^{25}$ +8.9 (*c* 0.43, $CHCl_3$), $[\alpha]_{546}^{25}$ +17.2 (*c* 0.43, $CHCl_3$). IR (CCl_4): 2 780, 1 560, 1 110, 830. ^{1}H NMR (300 MHz, $CDCl_3$): 1.71–1.78 m, 4 H (CH_2CH_2); 2.44–2.63 m, 4 H ($N(CH_2)_2$); 3.47 d, 1 H, ^2J = 13.0 (Fc-C**H**H); 3.76 d, 1 H, ^2J = 13.0 (Fc-CH**H**); 4.11 s, 5 H (Cp); 4.18–4.21 m, 1 H (Fc); 4.32 m, 1 H (Fc); 4.41 m, 1 H (Fc). ^{13}C NMR (75 MHz, $CDCl_3$): 23.6 (CH_2CH_2); 53.9 (CH_2NCH_2); 54.8 (Fc-CH_2); 68.7 (Fc); 69.1 (Fc); 71.7 (Cp); 74.7 (Fc); 75.9 (Fc); 85.8 (Fc). For $C_{15}H_{18}FeIN$ (395.1) calculated: 45.60% C, 4.59% H, 3.55% N; found: 45.12% C, 4.32% H, 3.29% N.

(S_p)-1-[(Hydroxy)diphenylmethyl]-2-(pyrrolidin-1-ylmethyl)ferrocene (**8**)

Compound **7** (110 mg, 0.278 mmol) was dissolved in anhydrous diethyl ether (4 ml) and the solution was cooled to –40 °C. BuLi (0.14 ml, 0.361 mmol, 2.5 M solution in hexane) was added dropwise to the solution. The temperature was raised to 0 °C over 3 h, benzophenone (66 mg, 0.361 mmol) in diethyl ether (1 ml) was then added and the mixture was warmed to 20 °C and stirred for 18 h. Water (5 ml) was added to the reaction mixture and the phases were separated. The water phase was further extracted with diethyl ether (2 × 5 ml). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and evaporated *in vacuo*. The crude product was purified by chromatography on SiO_2 (hexane–diethyl ether 2 : 1) giving 75 mg of compound **8** (60%, orange oil). $[\alpha]_D^{25}$ –216.9 (*c* 0.325, $CHCl_3$), $[\alpha]_{578}^{25}$ –235.4 (*c* 0.325, $CHCl_3$), $[\alpha]_{546}^{25}$ –309.2 (*c* 0.325, $CHCl_3$). IR (CCl_4): 2 810, 1 560, 1 495, 1 455, 1 115, 1 055. ^{1}H NMR (300 MHz, $CDCl_3$): 1.37–1.46 m, 2 H (C**H**$_2$CH$_2$); 1.52–1.64 m, 2 H (CH$_2$C**H**$_2$); 2.10–2.19 m, 2 H (NCH_2); 2.47–2.55 m, 2 H (NCH_2); 2.89 d, 1 H, ^2J = 13.7 (Fc-C**H**H); 3.70 m, 1 H (Fc); 3.76 d, 1 H, ^2J = 13.5 (Fc-CH**H**); 4.03 s, 5 H (Cp); 3.99–4.04 m, 1 H (Fc); 4.07 m, 1 H (Fc); 7.12–7.56 m, 8 H (C_6H_5); 8.83 br s, 1 H (OH). ^{13}C NMR (75 MHz, $CDCl_3$): 23.4 (CH_2CH_2); 53.9 ($N(CH_2)_2$); 55.4 (Fc-CH_2); 65.3 (Fc); 69.90 (Cp); 69.93 (Fc); 71.1 (Fc); 77.7 (C_i); 83.1 (C_i); 96.6 (Ph_2C-OH); 126.4, 126.5, 127.2, 127.45, 127.55, 127.58 (CH_{arom}); 147.4, 150.1 (C_{arom}). For $C_{28}H_{29}FeNO$ (451.4) calculated: 74.50% C, 6.48% H, 3.10% N; found: 74.87% C, 6.55% H, 3.29% N.

(S_p)-1-(Pyrrolidin-1-ylmethyl)-2-(trimethylsilyl)ferrocene (**9**)

Methyl iodide (238 mg, 104 μl, 1.675 mmol) was added to a solution of trimethylsilyl derivative **3** [7b] (215 mg, 0.558 mmol) in anhydrous acetonitrile (2 ml) and the mixture was stirred at room temperature for 1 h. The solvent was then evaporated and the residue redissolved in acetonitrile (5 ml). Anhydrous K_2CO_3 (154 mg, 1.12 mmol) and pyrrolidine (119 mg, 1.68 mmol) were added to the solution and the reaction mixture was heated at reflux for 18 h. The solution was filtered, the white solid washed with CH_2Cl_2 and the filtrate evaporated *in vacuo*. The residue was purified by chromatography on Al_2O_3 (hexane–diethyl

ether 2 : 1) giving 141 mg of compound **9** (74%, orange oil). $[\alpha]_D^{25}$ +8.9 (*c* 0.70, $CHCl_3$), $[\alpha]_{578}^{25}$ +13.0 (*c* 0.70, $CHCl_3$), $[\alpha]_{546}^{25}$ +33.4 (*c* 0.70, $CHCl_3$). IR (CCl_4): 2 790, 1 690, 1 160, 1 115, 1 050, 870, 850. ^{1}H NMR (300 MHz, $CDCl_3$): 0.27 s, 9 H ($SiMe_3$); 1.69 m, 4 H (CH_2CH_2); 2.38 m, 4 H ($N(CH_2)_2$); 3.14 d, 1 H, ^2J = 12.7 (Fc-C**H**H); 3.68 d, 1 H, ^2J = 12.6 (Fc-CH**H**); 4.01 m, 1 H (Fc); 4.08 s, 5 H (Cp); 4.22 m, 1 H (Fc); 4.32 m, 1 H (Fc). ^{13}C NMR (75 MHz, $CDCl_3$): 0.28 ($SiMe_3$); 23.5 (CH_2CH_2); 53.6 ($N(CH_2)_2$); 55.6 (Fc-CH_2); 68.7 (Cp); 69.3 (Fc); 71.7 (C_i-Si); 73.1, 74.1 (Fc); 90.7 (C_i-CH_2). For $C_{18}H_{27}FeNSi$ (341.3) calculated: 63.33% C, 7.97% H, 4.10% N; found: 63.75% C, 7.56% H, 4.26% N.

(S_p)-1-[(Hydroxy)diphenylmethyl]-2-(pyrrolidin-1-ylmethyl)-3-(trimethyl)ferrocene (**10**)

BuLi (0.15 ml, 0.363 mmol, 2.5 M solution in hexane) was added dropwise to a solution of compound **9** (95 mg, 0.279 mmol) in anhydrous diethyl ether (4 ml) at 25 °C and the reaction mixture was stirred at this temperature for 4 h. Benzophenone (66 mg, 0.363 mmol) in diethyl ether (1 ml) was then added to the reaction mixture and the solution was stirred for 18 h. Water (5 ml) was added to the reaction mixture and the phases were separated. The water phase was further extracted with diethyl ether (2 × 5 ml). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and evaporated *in vacuo*. The crude mixture was purified by chromatography on SiO_2 (hexane–diethyl ether 9 : 1) giving 121 mg of compound **10** (83%, orange solid). M.p. 119–121 °C. $[\alpha]_D^{25}$ +158.8 (*c* 0.33, $CHCl_3$), $[\alpha]_{578}^{25}$ +173.0 (*c* 0.33, $CHCl_3$), $[\alpha]_{546}^{25}$ +231.5 (*c* 0.33, $CHCl_3$). IR (CCl_4): 2 810, 1 570, 1 560, 1 260, 1 020, 850. ^{1}H NMR (300 MHz, $CDCl_3$): 0.29 s, 9 H ($SiMe_3$); 1.43–1.62 m, 4 H (CH_2CH_2); 2.08–2.13 m, 2 H (N-CH); 2.57 m, 2 H (N-CH); 2.92 d, 1 H, ^2J = 14.0 (Fc-CH); 3.64 d, ^2J = 14.1; 3.83 m, 1 H (Fc); 3.97 m, 1 H (Fc); 4.03 s, 5 H (Cp); 7.13–7.54 m, 10 H (C_6H_5); 9.34 br s, 1 H (OH). ^{13}C NMR (75 MHz, $CDCl_3$): 0.79 ($SiMe_3$); 23.2 (CH_2CH_2); 53.7 ($N(CH_2)_2$); 54.5 ($FcCH_2$); 69.9 (Cp); 71.3 (Fc); 71.8 (Fc); 73.6 (Fc); 76.5 (Fc); 87.3 (Fc); 99.6 (Ph_2COH); 126.0, 126.2, 126.3, 127.0, 127.4, 128.1, 147.3, 149.8 (C_6H_5). For $C_{31}H_{37}FeNOSi$ (523.6) calculated: 71.11% C, 7.12% H, 2.68% N; found: 70.92% C, 7.03% H, 2.49% N.

General Procedure for Diethylzinc Addition

Oven-dried flask with a ligand (0.025 mmol) was purged with argon, and freshly distilled toluene (1.3 ml) was added. Diethylzinc (1 ml, 1 mmol, 1 M solution in hexane) was subsequently added *via* syringe. The solution was stirred at 20 °C for 20 min and benzaldehyde (0.5 mmol) was added and the reaction mixture was stirred at 20 °C for 24 h. Saturated NH_4Cl solution (3 ml) was added, and the resultant mixture was extracted with diethyl ether (3 × 2 ml). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude mixture was purified by chromatography on SiO_2 (hexane–diethyl ether 4 : 1). The results are summarized in Table I.

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