# Novel $C_2$-Symmetric 1,1′-Disubstituted Ferrocenyl Aziridino Alcohol Ligands: Remarkable Improvement of Enantioselectivity in the Catalytic Asymmetric Addition of Diethylzinc to Aldehydes

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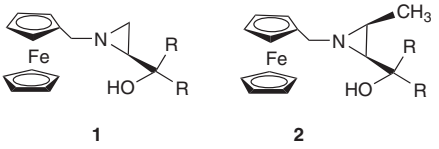
**Abstract:** A series of novel chiral $C_2$-symmetric 1,1′-disubstituted ferrocenyl aziridino alcohols have been readily synthesized and applied as catalysts to promote enantioselective addition of diethylzinc to aldehydes affording the corresponding 1-propanols in up to 99.5% enantiomeric excess with excellent yields. The effect of the ligand structure on the enantioselectivity was examined. The results showed that the $C_2$-symmetric ferrocenyl β-amino alcohol ligands could produce an excellent asymmetric environment for the asymmetric addition of diethylzinc to aldehydes. The absolute configuration of chiral $C_2$-symmetric ferrocenyl aziridino alcohol ligand **8j** was confirmed by X-ray diffraction analysis.

**Key words:** aziridino alcohols, ferrocenyl, asymmetric addition, diethylzinc, aldehydes

The design of economic and efficient chiral ligands for highly enantioselective transformations has been one of the major projects in asymmetric synthesis.[1] The asymmetric addition of organozincs to aldehydes remains the focus of much research activity in asymmetric C–C bond formation as evidenced by hundreds of research papers and several comprehensive review articles.[2] In addition, the reaction of diethylzinc with aldehydes has also become a classical test in the design of new ligands for catalytic enantioselective synthesis.

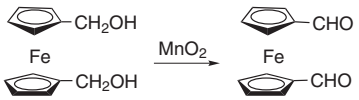
$C_2$-Symmetric chiral ligands were shown to be efficient for asymmetric induction and this has prompted chemists to synthesize a range of chiral ligands with $C_2$-symmetry.[3] Among them, $C_2$-symmetric ferrocenyl ligands have received much attention in recent years.[4] However, to the best of our knowledge, there has been only one example of a $C_2$-symmetric 1,1′-disubstituted chiral ferrocenyl with β-amino alcohol ligands.[5] Aziridino alcohols belong to the three-membered ring heterocycle class of ligands and they have attracted the interest of many chemists in the transition metal-catalyzed asymmetric synthesis[6] because of its rigid ring structure, that is considered to be the determining factor in its effectiveness in asymmetric catalysis. Recently, we reported the synthesis of chiral ferrocenyl aziridino alcohol ligands **1** and **2** and their application to the enantioselective addition of diethylzinc to aldehydes (Figure 1).[7] Good to excellent enantioselectivities were achieved in this asymmetric addition reaction. Now we set out to extend this study and to explore the chemistry of $C_2$-symmetric ferrocenyl aziridino alcohols. In this paper, we report the synthesis and use of a novel series of $C_2$-symmetric 1,1′-disubstituted chiral ferrocenyl aziridino alcohols as catalysts for the enantioselective addition of diethylzinc to aldehydes.




**1** **2**

**Figure 1**

We developed an improved procedure for the synthesis of ferrocene-1,1′-dicarboxaldehyde **4** from 1,1′-di(hydroxymethyl)ferrocene **3** based, in part, on conditions reported by Osgerby and Pauson.[8] Thus, the oxidation of diol **3** was carried out in the presence of 'active' manganese dioxide[9] in chloroform at reflux for four hours. The dialdehyde **4** was isolated in 69% yield after work-up (Scheme 1).




**3** **4**: 69%

**Scheme 1** Synthesis of ferrocene-1,1′-dicarboxaldehyde **4**

The ferrocenyl aziridino alcohols **8a–j** were then prepared in three steps as shown in Scheme 2. First, ferrocene-1,1′-dicarboxaldehyde **4** was reacted in methanol in the presence of triethylamine with methyl threonine ester hydrochloride giving the corresponding imines **5**. Then, reduction of **5**, carried out on the crude reaction mixture, with sodium borohydride in methanol provided compound **6** in 69% overall yield after work-up. Next, **6** was cyclized to aziridino ester **7** in 87% yield by reaction with triphenyl phosphine in the presence of tetrachloromethane in acetonitrile. Reduction with lithium aluminum hydride led to the aziridino alcohol **8a** in 66% chemical yield. Treatment of **7** with an excess of Grignard reagent afforded the ligands **8a–j** in 55–88% yield.

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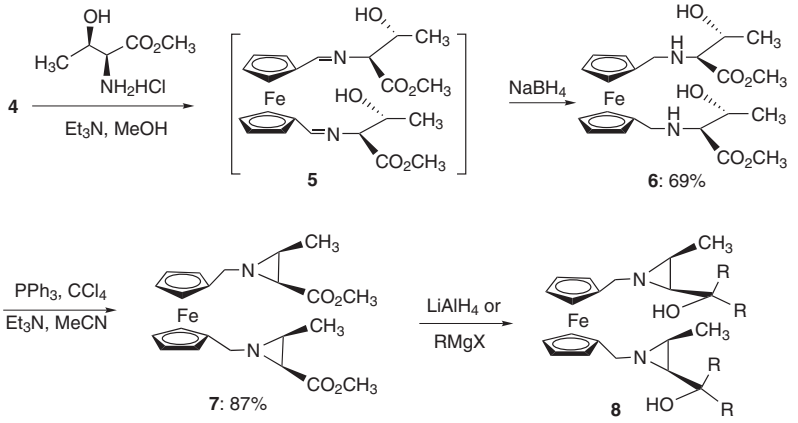



**8a**: R = H (66%); **8b**: R = Me (55%); **8c**: R = Et (62%); **8d**: R = *n*-Pr (64%); **8e**: R = *i*-Pr (62%); **8f**: R = *n*-Bu (58%); **8g**: R = *i*-Bu (53%); **8h**: R = *n*-$C_5H_{11}$ (73%); **8i**: R = *i*-$C_5H_{11}$ (64%); **8j**: R = Ph (88%)

**Scheme 2** Synthesis of chiral ligands **8a–j**

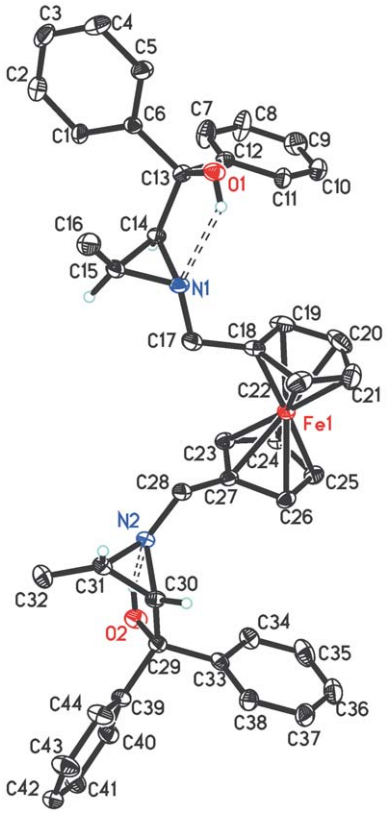


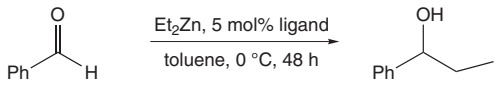

**Figure 2** Perspective view of compound **8j**. Selected bond distances (Å) and angles (°) are: O(1)–C(13), 1.420 (5); O(2)–C(29), 1.421 (5); O(1)–H(1), 0.78 (4); O(2)–H(2), 0.79(5); N(1)–H(1), 2.12 (4); N(2)–H(2), 1.995; N(1)–C(14), 1.462 (5); N(1)–C(15), 1.462 (5); N(1)–C(17), 1.487 (5); N(2)–C(30), 1.468 (5); N(2)–C(31), 1.476 (5); N(2)–C(28), 1.481 (5); (13)–C(14), 1.531 (5); C(14)–C(15), 1.484 (6); C(15)–C(16), 1.510 (6); C(29)–C(30), 1.534 (6); C(30)–C(31), 1.492 (6); C(31)–C(32), 1.503 (6); O(1)–H(1)–N(1), 130 (4); O(2)–H(2)–N(2), 138 (5)

All new ferrocenyl ligands were air-stable and gave satisfactory analytical and spectroscopic data. The absolute configuration of chiral $C_2$-symmetric ferrocenyl ligand **8j** was confirmed by X-ray diffraction analysis[10] (Figure 2). The crystal structure of compound **8j** reveals that the nitrogen atom on the aziridine ring is also a stereocenter, possibly due to the strong interaction between the bulky ferrocenyl group on the nitrogen atom of the aziridine ring and the bulky diphenylhydroxymethyl group on the three-membered ring, which leads to a tetrahedral structure with a stable conformation. The stereocenter could also result from the formation of an intramolecular hydrogen bond, which further barricades nitrogen pyramidal inversion. From the X-ray studies it was deduced that hydrogen bonds are present in compound **8j**. The N1–H1 and N2–H2 distances in **8j** are determined from the X-ray diffraction data and are shown to be 2.12 and 1.99 Å, respectively. These distances between the aziridine nitrogen and the hydroxyl hydrogen atom are indicative of the presence of intramolecular hydrogen bonds in aziridine alcohol **8j**, which are close to the expected average value for a hydrogen bond present in a five-membered ring structure.

With these new ligands in hand, the addition reaction of diethylzinc to benzaldehydes was carried to determine the asymmetric induction achieved (Table 1).

As can be seen from Table 1, the addition of diethylzinc to benzaldehyde led to 1-phenylpropanol in 65–90% yields with 2.1–92.6% ee (Table 1, entries 1–10). The enantioselectivity of the reaction is highly dependent on the structure of the chiral catalyst. The ee increased as the bulkiness of the R group increased (Table 1, entries 1–4). The best asymmetric induction (92.6% ee) was observed with ligand **8e**, where R was a secondary alkyl substituent, an isopropyl group. When the carbon chain length was increased further the enantioselectivity was found to decrease (Table 1, compare entry 5 versus 6, 7, 8, and 9). The presence of two phenyl groups in **8j** resulted in the lowest ee (2.1% ee). These results might reflect the different steric effects on the enantioselectivity resulting from the differently sized R groups. More interestingly, the configuration of 1-phenylpropanol, with ligand **8c**, was

**Table 1** Addition of Diethylzinc to Benzaldehyde Catalyzed by Ligands **8**[a]



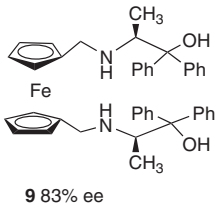

| Entry | Ligand | Yield (%)[b] | ee (%)[c] | Configuration[d] |
|---|---|---|---|---|
| 1 | **8a** | 72 | 13.8 | S |
| 2 | **8b** | 84 | 20.4 | *S* |
| 3 | **8c** | 65 | 30.1 | R |
| 4 | **8d** | 88 | 68.5 | *S* |
| 5 | **8e** | 68 | **92.6** | *S* |
| 6 | **8f** | 80 | 64.8 | *S* |
| 7 | **8g** | 89 | 63.4 | *S* |
| 8 | **8h** | 90 | 68.7 | *S* |
| 9 | **8i** | 65 | 47.2 | *S* |
| 10 | **8j** | 71 | 2.1 | *S* |

[a] Reagents: $Et_2Zn$ (2 equiv), aldehyde (1 equiv).
[b] Isolated yields.
[c] Determined by HPLC using a chiral OD column.
[d] Absolute configuration assigned by comparison with the sign of optical rotation of known compound and known elution order from a Chiralcel OD column.

found to be the opposite to that observed with all other ligands, although the chirality of the ligand itself was the same. A similar phenomenon was observed by Sibi[11] and Wang[12] using β-amino alcohols as chiral ligands in the addition of diethylzinc to benzaldehyde.

Previously, we reported the synthesis of monosubstituted ferrocenyl aziridino alcohol ligands **2** and their application in the enantioselective addition of diethylzinc to aldehydes.[7c] The best asymmetric induction (only 69% ee) was obtained for the catalytic asymmetric addition of diethylzinc to benzaldehyde in the presence of ligand **2** (R = *n*-$C_4H_9$, 5 mol%). Comparison of the disubstituted ligand **8e** with $C_2$-axial symmetry and the corresponding monosubstituted ligands **2** (R = *i*-$C_3H_7$) with $C_1$-axial symmetry is noteworthy: the stereodifferentiating ability of the 1,1′-disubstituted ligand **8e** (92.6% ee) is greater than the corresponding monosubstituted ligands **2** (R = *i*-$C_3H_7$, 52% ee), under the same conditions. This result indicates that the introduction of $C_2$-axial symmetry leads to a dramatic improvement in the enantioselectivity in the addition of diethylzinc to benzaldehyde. It is possibly due to the homotopic nature of the remaining coordination sites of the complexes formed by the ligand results in reducing the number of competing diastereomeric pathways. These results suggest that the symmetry of ligands **8e** with $C_2$-axial symmetry are comparable with the corresponding monosubstituted ligands **2** (R = *i*-$C_3H_7$) with $C_1$-axial symmetry.

Recently, the $C_2$-symmetric ferrocene-based bis(amino alcohol)s such as **9** (Figure 3) with various substituents at the nitrogen and oxygen carbons were reported by Pélinski et al. for the catalytic asymmetric addition of diethylzinc to benzaldehyde with 83% ee.[5b] They concluded that the disubstituted ferrocenyl derivatives generally appear to be unsuited as ligands in the addition of diethylzinc to benzaldehyde. Comparison of our results with those of Pélinski et al. demonstrates that the rigid structure (three-membered heterocycle, see crystal structure) and fine-tuning of the disubstituted ferrocenyl derivatives could lead to substantial improvement in the enantioselectivity. These results also show that the $C_2$-symmetric ferrocenyl β-amino alcohol ligands can produce an excellent asymmetric environment for asymmetric alkylation of benzaldehyde.




**9** 83% ee

**Figure 3**

The ferrocenyl aziridino alcohol **8e** was chosen as the best chiral ligand for further investigation into the effects of the catalytic amount and temperature on the asymmetric induction, and the results are shown in Table 2. The best result was obtained with 5 mol% of **8e** at 0 °C (Table 2, entry 3). When the reaction was carried out at room temperature (20–25 °C) the selectivity decreased from 92.6% to 87.2%.

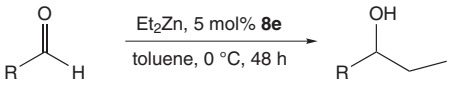
**Table 2** Asymmetric Addition of Diethylzinc to Benzaldehyde Using Ligand **8e**[a]

| Entry | Temperature (°C) | **8e** mol% | Yield (%)[b] | ee (%)[c] | Configuration[d] |
|---|---|---|---|---|---|
| 1 | 0 | 0.5 | 60 | 21.3 | S |
| 2 | 0 | 2 | 69 | 70.0 | *S* |
| 3 | 0 | 5 | 91 | **92.6** | *S* |
| 4 | 0 | 8 | 85 | 92.3 | *S* |
| 5 | 0 | 10 | 83 | 91.9 | *S* |
| 6 | r.t. | 5 | 88 | 87.2 | *S* |

[a] Reagents: $Et_2Zn$ (2 equiv), aldehyde (1 equiv).
[b] Isolated yields.
[c] Determined by HPLC using a chiral OD column.
[d] Absolute configuration assigned by comparison with the sign of optical rotation of a known compound and known elution order from a Chiralcel OD column.

The chiral ligand **8e** was applied to the asymmetric addition of diethylzinc to a series of aldehydes under the optimized conditions (Table 3). As can be seen from Table 3, the reaction proceeded very well with various arylaldehydes containing *ortho*-, *meta*-, and *para*-substituents on the benzene ring to provide the corresponding chiral 1-aryl propanols in 78–97% yields with high to outstanding enantioselectivities (82.4–99.5% ee). The best asymmetric induction of 99.5% ee was found using *meta*-chlorobenzaldehyde as substrate (Table 3, entry 5). The chiral ligand **8e** was also very effective in the enantioselective addition of diethylzinc to α,β-unsaturated aliphatic aldehyde (Table 3, entry 9)

**Table 3** Asymmetric Addition of Diethylzinc to Aldehydes Using Ligand **8e**[a]




| Entry | RCHO | Yield (%)[b] | ee (%)[c] | Configuration[d] |
|---|---|---|---|---|
| 1 | $C_6H_5CHO$ | 91 | 92.6 | S |
| 2 | *p*-$MeC_6H_4CHO$ | 78 | 87.0 | *S* |
| 3 | *m*-$MeOC_6H_4CHO$ | 86 | 92.3 | *S* |
| 4 | *o*-$MeOC_6H_4CHO$ | 96 | 82.4 | *S* |
| 5 | *m*-$ClC_6H_4CHO$ | 84 | 99.5 | *S* |
| 6 | *m*-$BrC_6H_4CHO$ | 88 | 91.7 | *S* |
| 7 | Heliotripine | 98 | 90.9 | *S* |
| 8 | Ferrocenecarboxaldehyde | 97 | 90.1 | *S* |
| 9 | $C_6H_5CH{=}CHCHO$ | 68 | 87.0 | *S* |

[a] Reagents: $Et_2Zn$ (2 equiv), aldehyde (1 equiv).
[b] Isolated yields.
[c] Determined by HPLC using a chiral OD column.
[d] Absolute was configuration assigned by comparison with the sign of optical rotation of a known compound and known elution order from a Chiralcel OD column.

In conclusion, chiral $C_2$-symmetric 1,1′-disubstituted ferrocenyl aziridino alcohols have been synthesized and applied as catalysts to promote enantioselective addition of diethylzinc to aldehydes with good to excellent enantioselectivity. The effect of the ligand structures on the enantioselectivity was then examined. Our results have demonstrated that the introduction of $C_2$-axial symmetry led to a dramatic improvement in the enantioselectivity in the addition of diethylzinc to benzaldehyde. Our results also show that the $C_2$-symmetric ferrocenyl β-amino alcohol ligands can produce an excellent asymmetric environment for asymmetric alkylation of aldehydes. Our efforts to develop novel ferrocenyl aziridino alcohols as chiral ligands for asymmetric synthesis are continuing, results will be reported elsewhere.

Methyl threonine ester hydrochloride was prepared according to the published procedure.[13] All other reagents were commercially available and used as received. THF and $Et_2O$ were distilled from sodium benzophenone ketyl. Petroleum ether with a bp range 60–90 °C was used. Melting points were determined using YRT-3 melting point apparatus, and were uncorrected. Optical rotations were measured with Perkin Elmer, model 341 Polarimeter at 20 °C in $CHCl_3$.

The ee was determined by HPLC using a chiral column with hexane–*i*-PrOH as the eluent. HPLC was conducted on a JASCO model PU-1580 intelligent HPLC pump and a JASCO model UV-1575 intelligent UV/Vis detector (254 nm). The injection loop had a 20 μL capacity. The column used was a Chiralcel OD (250 × 4.6mm) from Daicel Chemical Ind., Ltd (Japan). The column was operated at ambient temperature.

NMR Spectra ($^1H$ and $^{13}C$) were performed on a Bruker DPX 400 (400 MHz) spectrometer in $CDCl_3$ (TMS as internal reference); *J* values are given in Hz. IR Spectra were determined on a Therme Nicolet IR 200 spectrophotometer. TLC was performed on dry silica gel plates with hexane–EtOAc as eluent. Mass spectra were obtained using a Bruker esquire-3000 instrument with an electrospray ionization source (ESIMS). All the ESIMS spectra were performed with MeOH as the solvent.

**Ferrocene-1,1′-dicarboxaldehyde (4)**

To a soln of 1,1′-di(hydroxymethyl)ferrocene (1 g) in $CHCl_3$ (10 mL) was added 'active' $MnO_2$ (9.4 g).The reaction mixture was heated under reflux for 4 h. The reaction was monitored by TLC (petroleum ether–EtOAc, 1:1). The product mixture was filtered and washed carefully with $CHCl_3$ until the washings were colorless. The solvent was removed under reduced pressure. The resulting residue was recrystallized from $Et_2O$–hexane to afford red crystal needles in 69% yield (0.69 g); mp 183 °C (lit.[8] 183–184 ºC).

IR (KBr): 3112, 1684, 1455, 1399, 1369, 1244, 1038, 834 $cm^{-1}$.

**Bis[(1*S*,2*R*)-2-hydroxy-1-methoxycarbonylpropyl]-1,1′-ferrocenylmethyldiamine (6)**

Methyl L-threonine ester hydrochloride (2.9 g, 17.1 mmol) was dissolved in anhyd MeOH (30 mL) and cooled to 0 °C. $Et_3N$ (2.5 mL, 17.2 mmol) was added, and the reaction was stirred for 10 min. Ferrocene-1,1′-dicarboxaldehyde **4** (1.8 g, 7.52 mmol) was added, the reaction mixture was stirred for 1 h, and was monitored by TLC. $NaBH_4$ (1.14 g) was added portionwise to the reaction mixture over a period of 0.5 h and the resulting mixture was stirred for 5 h. MeOH was removed under reduced pressure at 40 °C. The resulting residue was carefully neutralized with 3% HCl to pH 7–8 and then extracted with EtOAc (3 × 20 mL). The combined ethereal extracts were washed with brine (20 mL) and dried over $Na_2SO_4$. The solvent was removed under reduced pressure. The resulting residue was purified by preparative TLC (petroleum–EtOAc, 1:3) to afford **6** in 69% yield (2.47 g); $[\alpha]_D^{20}$ –55.0 (*c* 1.00, $CHCl_3$).

IR (KBr): 3447, 3325, 3143, 2979, 2949, 2843, 1734, 1449, 1401, 1270, 1241, 1201, 1168, 1104, 1029, 992, 811 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.19 (d, *J* = 6 Hz, 6 H, 2 × $CHCH_3$), 3.02 (d, *J* = 7.6 Hz, 2 H, 2 × COCH), 3.43 (d, *J* = 12.8 Hz, 2 H, 2 × NHCH*H*), 3.48 (d, *J* = 12.8 Hz, 2 H, 2 × NHC*H*H), 3.63 (m, 2 H, 2 × $CH_3CH$), 3.72 (s, 6 H, 2 × $OCH_3$), 4.08–4.11 (m, 6 H, Fc), 4.17 (s, 2 H, Fc).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 18.37, 46.72, 50.97, 66.65, 66.91, 67.28, 67.36, 67.49, 67.83, 85.30, 173.13.

MS (ESI): *m*/*z* = 499 $[M + Na]^+$, 515 $[M + K]^+$.

HRMS (MALDI): *m*/*z* calcd for $C_{22}H_{32}FeN_2O_6$ $[M + Na]^+$, 499.1502; found, 499.1542.

**1,1′-Bis[(2*S*,3*S*)-2-methoxycarbonyl-3-methylaziridin-1-methylenyl]ferrocene (7)**

To a stirred soln of $PPh_3$ (3.14 g, 12 mmol) in MeCN (63 mL) was added $CCl_4$ (18 mL). The soln turned yellow over a period of 0.5 h, at which time **6** (952 mg, 2 mmol) was added dropwise in a soln of $Et_3N$ (1.8 mL, 13 mmol) and MeCN (15 mL). The reaction mixture was stirred for 2 h at 0 °C and then at r.t. for 14 h. The solvent was removed under reduced pressure. The resulting residue was purified by preparative TLC (petroleum ether–$Et_2O$–$Et_3N$, 3:6:1) to afford **7** in 77% yield (680 mg); $[\alpha]_D^{20}$ –88.1 (*c* 1.01, $CHCl_3$).

IR (KBr): 3106, 2999, 2953, 2933, 2823, 1746, 1439, 1395, 1361, 1327, 1291, 1261, 1235, 1196, 1176, 1147, 1122, 1056, 1025, 924, 825, 804 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.20 (d, *J* = 5.6 Hz, 6 H, 2 × CHC*H*$_3$), 1.89–1.95 (m, 2 H, 2 × CH$_3$C*H*), 2.18 (d, *J* = 6.8 Hz, 2 H, 2 × COCH), 3.32 (d, *J* = 13.2 Hz, 2 H, 2 × NC*H*H), 3.36 (d, *J* = 13.2 Hz, 2 H, 2 × NCH*H*), 3.70 (s, 6 H, 2 × OCH$_3$), 4.05 (d, *J* = 0.8 Hz, 4 H, Fc), 4.11 (s, 4 H, Fc).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 13.17, 40.87, 41.79, 51.91, 58.65, 68.73, 68.82, 69.48, 69.64, 83.32,170.29.

MS (ESI): *m*/*z* = 463 $[M + Na]^+$, 479 $[M + K]^+$.

HRMS (MALDI): *m*/*z* calcd for $C_{22}H_{28}FeN_2O_4$ $[M + Na]^+$: 463.1291; found: 463.1291.

**1,1′-Bis[(2*S*,3*S*)-2-hydroxymethyl-3-methylaziridin-1-methylenyl]ferrocene (8a)**

To a stirred suspension of $LiAlH_4$ (83 mg, 2.1 mmol) in anhyd THF (4 mL), under $N_2$, cooled to 0 °C, a soln of **7** (100 mg, 0.23 mmol) in anhyd THF (2 mL) was added dropwise over 15 min. The resulting mixture was stirred for 8 h, then wet $Et_2O$ (10 mL) and a sat. aq soln of $NH_4Cl$ (10 mL) were added carefully at 0 °C. The resultant gel was filtered through glass wool and washed carefully with $Et_2O$. The filtrate was dried over $Na_2SO_4$ and the solvents were removed under reduced pressure giving a orange red oil, which was further purified by preparative TLC (hexane–EtOAc–MeOH, 2:2:1) to afford **8a** as a orange red oil in 66% yield (60 mg); $[\alpha]_D^{20}$ +20.3 (*c* 1.08, $CHCl_3$).

IR (KBr): 3481–3130, 3039, 3011, 2986, 2962, 1399, 1323, 1158, 1123, 1086, 1029, 955, 816 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.14 (d, *J* = 6 Hz, 6 H, 2 × CH$_3$), 1.66–1.76 [m, 4 H, 2 × (CH)$_2$N], 3.20 (d, *J* = 12.8 Hz, 2 H, 2 × C*H*HN), 3.34 (d, *J* = 12.8 Hz, 2 H, 2 × CH*H*N), 3.45 (dd, *J* = 7.2 Hz, *J* = 4.4 Hz, 2 H, 2 × C*H*HOH), 3.68 (dd, *J* = 7.2, 4.4 Hz, 2 H, 2 × CH*H*OH), 4.08 (s, 4 H, Fc), 4.11 (d, *J* = 1.6 Hz, 2 H, Fc), 4.21 (s, 2 H, Fc).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 13.29, 38.91, 44.18, 59.49, 60.10, 68,63, 68.66, 68.98, 69.21, 85.00.

MS (ESI): *m*/*z* = 427 $[M + Na]^+$, 443 $[M + K]^+$.

Anal. Calcd for $C_{20}H_{28}FeN_2O_2$: C, 62.51; H, 7.34; N, 7.29. Found: C, 62.55; H, 7.29; N, 7.26.

**1,1′-Bis[(2*S*,3*S*)-2-dimethylhydroxymethyl-3-methylaziridin-1-methylenyl]ferrocene (8b)**

A Grignard reagent was prepared in the usual way from Mg (87 mg, 3.6 mmol) and MeI (0.224 mL, 3.6 mmol) in $Et_2O$ (5 mL). The soln was cooled to 0 °C and a soln of **7** (100 mg, 0.227 mmol) in $Et_2O$ (2 mL) was added. The reaction mixture was stirred for 3 h at 0 °C and then heated at reflux for 5 h. The reaction was quenched by the addition of a sat. aq soln of $NH_4Cl$ (10 mL) at 0 °C. The aqueous phase was separated and extracted with $Et_2O$ (3 × 10 mL). The combined organic phases were washed with brine (10 mL), dried over $Na_2SO_4$, filtered, and the solvent was removed under reduced pressure. The resulting residue was purified by preparative TLC (hexane–EtOAc, 1:1) to give **8b** in 55% yield (55 mg); $[\alpha]_D^{20}$ –1.3 (*c* 0.638, $CHCl_3$).

IR (KBr): 3500–2999, 2985, 2962, 2927, 2872, 2847, 1640, 1450, 1397, 1328, 1265, 1235, 1152, 1083, 1040, 926, 826 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.08 (s, 6 H, 2 × CH$_3$), 1.16 (s, 6 H, 2 × CH$_3$), 1.30 (d, *J* = 6 Hz, 6 H, 2 × CHC*H*$_3$), 1.35 (d, *J* = 6.4 Hz, 2 H, 2 × NCH), 1.60–1.64 (m, 2 H, 2 × C*H*CH$_3$), 2.89 (br s, 2 H, 2 × OH), 3.15(d, *J* = 12.8 Hz, 2 H, FcCH$_2$), 3.52 (d, *J* = 12.8 Hz, 2 H, FcCH$_2$), 4.04–4.08 (m, 6 H, Fc), 4.16 (d, *J* = 1.2 Hz, 2 H, Fc).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 13.68, 25.62, 31.89, 40.01, 50.00, 59.54, 67.21, 68.45, 68.95, 69.32, 69.66, 84.77.

MS (ESI): *m*/*z* = 441 $[M + H]^+$, 463 $[M + Na]^+$.

Anal. Calcd for $C_{24}H_{36}FeN_2O_2$: C, 65.45; H, 8.24; N, 6.36. Found: C, 65.58; H, 8.10; N, 6.27.

**Aziridino Alcohols 8c–j; General Procedure**

A Grignard reagent was prepared in the usual way from Mg (87 mg, 3.6 mmol) and alkyl bromide (3.6 mmol) in THF (5 mL). The soln was cooled to –20 °C and then a soln of **7** (100 mg, 0.227 mmol) in THF (1 mL) was added. The temperature of the reaction mixture was allowed to reach r.t. and was stirred for 24 h. A sat. aq soln of $NH_4Cl$ (10 mL) was added at 0 °C. The aqueous phase was extracted with $Et_2O$ (3 × 10 mL). The combined organic phases were washed with brine (15 mL), dried over $Na_2SO_4$, filtered, and the solvent was removed under reduced pressure. The resulting residue was purified by preparative TLC to afford **8c–j**.

**1,1′-Bis[(2*S*,3*S*)-2-diethylhydroxymethyl-3-methylaziridin-1-methylenyl]ferrocene (8c)**

Preparative TLC (hexane–EtOAc, 1:1) afforded **8c** in 62% yield (70 mg); $[\alpha]_D^{20}$ –28.3 (*c* 0.61, $CHCl_3$).

IR (KBr): 3425, 3129, 2966, 2929, 1455, 1401, 1319, 1152, 1082, 1034, 972, 819 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 0.91–0.94 (m, 12 H, 4 × CH$_3$), 1.30 (d, *J* = 6 Hz, 6 H, 2 × CHC*H*$_3$), 1.25–1.55 (m, 10 H, 4 × CH$_2$, 2 × NCH), 1.57–1.63 (m, 2 H, 2 × C*H*CH$_3$), 2.93 (br s, 2 H, 2 × OH), 3.20 (d, *J* = 12.8 Hz, 2 H, 2 × FcCH$_2$), 3.49 (d, *J* = 12.8 Hz, 2 H, 2 × FcCH$_2$), 4.07 (d, *J* = 1.6 Hz, 6 H, Fc), 4.13 (d, *J* = 1.6 Hz, 2 H, Fc).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 7.74, 8.02, 14.15, 28.92, 32.81, 39.21, 47.63, 59.07, 68.47, 68.78, 69.13, 69.47, 68.84, 71.22, 84.71.

MS (ESI): *m*/*z* = 497 $[M + H]^+$, 519 $[M + Na]^+$.

Anal. Calcd for $C_{28}H_{44}FeN_2O_2$: C, 67.73; H, 8.93; N, 5.64. Found: C, 67.68; H, 8.81; N, 5.72.

**1,1′-Bis[(2*S*,3*S*)-2-dipropylhydroxymethyl-3-methylaziridin-1-methylenyl]ferrocene (8d)**

Preparative TLC (hexane–EtOAc, 1:1) afforded **8d** in 64% yield (80 mg); $[\alpha]_D^{20}$ –16.1 (*c* 1.128, $CHCl_3$).

IR (KBr): 3429, 3093, 2957, 2930, 2871, 1456, 1403, 1378, 1326, 1265, 1235, 1149, 1123, 1086, 1037, 1025, 1000, 925, 907, 825, 812 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 0.86–0.92 (m, 12 H, 4 × CH$_2$C*H*$_3$), 1.31 (d, *J* = 6 Hz, 6 H, 2 × CHC*H*$_3$), 1.32–1.46 (m, 18 H, 4 × C*H*$_2$C*H*$_2$CH$_3$, 2 × NCH), 1.57–1.60 (m, 2 H, 2 × CH$_3$C*H*), 2.94 (s, 2 H, 2 × OH), 3.23 (d, *J* = 12.8 Hz, 2 H, 2 × CH*H*N), 3.44 (d, *J* = 12.8 Hz, 2 H, 2 × C*H*HN), 4.06–4.08 (m, 6 H, Fc), 4.13 (s, 2 H, Fc).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 14.25, 14.71, 14.92, 16.74, 16.98, 39.48, 43.78, 48.26, 59.21, 68.52, 68.86, 69.18, 69.55, 71.01, 84.83.

MS (ESI): *m*/*z* = 553 $[M + H]^+$.

Anal. Calcd for $C_{32}H_{52}FeN_2O_2$: C, 69.55; H, 9.48; N, 5.07. Found: C, 69.44; H, 9.69; N, 4.85.

**1,1′-Bis[(2*S*,3*S*)-2-diisopropylhydroxymethyl-3-methylaziridin-1-methylenyl]ferrocene (8e)**

Preparative TLC (hexane–EtOAc, 2:1) afforded **8e** in 62% yield (78 mg); $[\alpha]_D^{20}$ –48 (*c* 0.68, $CHCl_3$).

IR (KBr): 3422, 3118, 2962, 2935, 2879, 1643, 1399, 1326, 1274, 1155, 1126, 1087, 1026, 924, 823 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 0.97–1.01 (m, 24 H, 8 × $CH_3$), 1.29 (d, *J* = 6 Hz, 6 H, 2 × CHC*H*$_3$), 1.47 (d, *J* = 6.4 Hz, 2 H, 2 × NCH), 1.51–1.54 (m, 2 H, 2 × $CH_3$C*H*), 1.90–2.02 [m, 4 H, 4 × C*H*$(CH_3)_2$], 2.79 (d, *J* = 13.9 Hz, 2 H, CH*H*N), 3.97 (d, *J* = 13.9 Hz, 2 H, C*H*HN), 2.86 (s, 2 H, 2 × OH), 4.09–4.10 (m, 6 H, Fc), 4.15 (s, 2 H, Fc).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 15.27 15.32, 17.86, 18.05, 18.17, 18.38, 34.43, 35.59, 38.37, 45.24, 58.38, 68.76, 69.17, 69.42, 74.75, 84.67.

MS (ESI): *m*/*z* = 553 $[M + H]^+$.

Anal. Calcd for $C_{32}H_{52}FeN_2O_2$: C, 69.55; H, 9.48; N, 5.07. Found: C, 69.53; H, 9.74; N, 4.79.

**1,1′-Bis[(2*S*,3*S*)-2-dibutylhydroxymethyl-3-methyl-aziridin-1-methylenyl]ferrocene (8f)**

Preparative TLC (hexane–EtOAc, 4:1) afforded **8f** in 58% yield (80 mg); $[\alpha]_D^{20}$ –14.9 (*c* 1.43, $CHCl_3$).

IR (KBr): 3434, 3100, 2955, 2932, 2862, 1458, 1403, 1379, 1326, 1263, 1234, 1154, 1123, 1058, 1073, 1005, 822 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 0.87–0.92 (m, 12 H, 4 × $CH_2$C*H*$_3$), 1.36 (d, *J* = 5.6 Hz, 6 H, 2 × $CH_3$), 1.24–1.35 [m, 24 H, 4 × $(CH_2)_3$], 1.52 (d, *J* = 6.8 Hz, 2 H, 2 × NCH), 1.71–1.74 (m, 2 H, 2 × $CH_3$C*H*), 3.14 (d, *J* = 12.8 Hz, 2 H, C*H*HN), 3.59 (d, *J* = 12.8 Hz, 2 H, CH*H*N), 4.08–4.11 (m, 6 H, Fc), 4.16 (d, *J* = 0.8 Hz, 2 H, Fc).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 13.66, 14.06, 14.14, 23.23, 23.43, 25.58, 25.82, 36.27, 40.78, 40.22, 48.78, 58.43, 67.25, 68.78, 69.21, 69.49, 69.78, 71.10, 83.79.

MS (ESI): *m*/*z* = 609 $[M + H]^+$, 631 $[M + Na]^+$.

Anal. Calcd for $C_{36}H_{60}FeN_2O_2$: C, 71.03; H, 9.94; N, 4.60. Found: C, 71.32; H, 9.78; N, 4.42.

**1,1′-Bis[(2*S*,3*S*)-2-di-*iso*-butylhydroxymethyl-3-methylaziridin-1-methylenyl]ferrocene (8g)**

Preparative TLC (hexane–EtOAc, 4:1) afforded **8g** in 53% yield (73 mg); $[\alpha]_D^{20}$ –19.9 (*c* 0.52, $CHCl_3$).

IR (KBr): 3421, 3133, 2953, 2936, 2868, 1460, 1401, 1324, 1157, 1124, 1086, 1037, 825 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 0.94 (m, 24 H, 8 × $CH_3$), 1.32 (d, *J* = 5.6 Hz, 6 H, 2 × CHC*H*$_3$), 1.26–1.51 (m, 10 H, 4 × $CH_2$, 2 × NCH), 1.58–1.61 (m, 2 H, 2 × $CH_3$C*H*), 1.73–1.83 (m, 4 H, 4 × CH), 2.98 (s, 2 H, 2 × OH), 3.16 (d, *J* = 12.8 Hz, 2 H, 2 × C*H*HN), 3.55 (d, *J* = 12.8 Hz, 2 H, 2 × CH*H*N), 4.09 (d, *J* = 4.4 Hz, 6 H, Fc), 4.13 (s, 2 H, Fc).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 14.19, 23.89, 24.12, 24.83, 24.87, 25.08, 39.83, 46.41, 49.51, 50.21, 59.15, 68.55, 68.86, 69.11, 69.50, 72.24, 84.96.

MS (ESI): *m*/*z* (%) = 609 $[M + H]^+$, 631 $[M + Na]^+$.

Anal. Calcd for $C_{36}H_{60}FeN_2O_2$: C, 71.03; H, 9.94; N, 4.60. Found: C, 71.21; H, 9.68; N, 4.35.

**1,1′-Bis[(2*S*,3*S*)-2-dipentylhydroxymethyl-3-methylaziridin-1-methylenyl]ferrocene (8h)**

Preparative TLC (hexane–EtOAc, 4:1) afforded **8h** in 73% yield (110 mg); $[\alpha]_D^{20}$ –15.8 (*c* 1.12, $CHCl_3$).

IR (KBr): 3434, 3095, 2953, 2930, 2863, 1460, 1403, 1380, 1327, 1265, 1155, 1125, 1086, 1038, 822 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 0.88–0.94 (m, 12 H, 4 × $CH_2$C*H*$_3$), 1.21–1.50 [m, 40 H, 4 × $(CH_2)_4$, 2 × CHC*H*$_3$, 2 × NCH], 1.58–1.62 (m, 2 H, 2 × $CH_3$C*H*), 2.93 (br s, 2 H, 2 × OH), 3.27 (d, *J* = 12.8 Hz, 2 H, 2 × CH*H*N), 3.41 (d, *J* = 12.8 Hz, 2 H, 2 × CH*H*N), 4.07 (d, *J* = 1.2 Hz, 6 H, Fc), 4.13 (s, 2 H, Fc).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 14.09, 14.15, 22.62, 22.71, 23.10, 23.38, 32.43, 32.64, 36.95, 41.24, 39.60, 48.31, 59.18, 68.54, 68.92, 69.25, 71.03, 84.77.

MS (ESI): *m*/*z* = 665 $[M + H]^+$, 687 $[M + Na]^+$.

Anal. Calcd for $C_{40}H_{68}FeN_2O_2$: C, 72.26; H, 10.31; N, 4.21. Found: C, 72.38; H, 10.23; N, 4.06.

**1,1′-Bis[(2*S*,3*S*)-2-di-*iso*-pentylhydroxymethyl-3-methylaziridin-1-methylenyl]ferrocene (8i)**

Preparative TLC (hexane–EtOAc, 3.5:1) afforded **8i** in 64% yield (96 mg); $[\alpha]_D^{20}$ –12.7 (*c* 0.96, $CHCl_3$).

IR (KBr): 3423, 3117, 2954, 2929, 2925, 2869, 1466, 1401, 1367, 1325, 1265, 1234, 1156, 1124, 1085, 1037, 1025, 923, 824, 812 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 0.85–0.91 (m, 24 H, 8 × $CH_3$), 1.33 (d, *J* = 6.8 Hz, 6 H, 2 × CHC*H*$_3$), 1.16–1.50 (m, 22 H, 4 × $CH_2CH_2CH$, 2 × NCH), 1.58–1.61 (m, 1 H, $CH_3$C*H*), 2.93 (s, 2 H, 2 × OH), 3.31 (d, *J* = 12.8 Hz, 2 H, 2 × C*H*HN), 3.36 (d, *J* = 12.8 Hz, 2 H, 2 × CH*H*N), 4.06–4.08 (m, 6 H, Fc), 4.14 (s, 2 H, Fc).

$^{13}C$ NMR (100 MHz, $CDCl_3$):δ = 14.23, 22.49, 22.54, 22.66, 22.79, 28.56 28.64, 32.25, 32.69, 34.50, 38.84, 39.59, 48.30, 59.29, 68.49, 68.92, 69.23, 70.98, 84.81.

MS (ESI): *m*/*z* = 665 $[M + H]^+$, 687 $[M + Na]^+$.

Anal. Calcd for $C_{40}H_{68}FeN_2O_2$: C, 72.26; H, 10.31; N, 4.21. Found: C, 72.11; H, 10.52; N, 4.15.

**1,1′-Bis[(2*S*,3*S*)-2-diphenylhydroxymethyl-3-methylaziridin-1-methylenyl]ferrocene (8j)**

Preparative TLC (hexane–EtOAc, 4:1) afforded **8j** in 88% yield (137 mg); mp 188 °C; $[\alpha]_D$ +54.8 (*c* 0.99, $CHCl_3$).

IR (KBr): 3375–3088, 3058, 3027, 2990, 2953, 2925, 2852, 1599, 1490, 1449, 1405, 1330, 1266, 12378, 1170, 1080, 1015, 813, 728, 700 $cm^{-1}$.

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.01 (d, *J* = 5.4 Hz, 6 H, 2 × $CH_3$), 1.83–1.87 (m, 2 H, 2 × $CH_3$C*H*), 2.32 (d, *J* = 6.4 Hz, 2 H, 2 × $CH_3$CHC*H*), 3.30 (d, *J* = 12.8 Hz, 2 H, 2 × CH*H*N), 3.39 (d, *J* = 12.8 Hz, 2 H, 2 × C*H*HN), 3.80 (s, 2 H, Fc), 3.92 (d, *J* = 0.8 Hz, 2 H, Fc), 4.00 (s, 4 H, Fc), 4.56 (s, 2 H, 2 × OH), 7.15–7.48 (m, 20 H, Ph).

$^{13}C$ NMR (100 MHz, $CDCl_3$): δ = 13.51, 39.77, 50.74, 58.57, 68.71, 69.01, 69.37, 84.26, 73.59, 125.90, 126.37, 126.41, 126.79,127.88, 128.04.

MS (ESI): *m*/*z* = 689 $[M + H]^+$, 711 $[M + Na]^+$.

Anal. Calcd for $C_{44}H_{44}FeN_2O_2$ requires: C, 76.74; H, 6.44; N, 4.07. Found: C, 76.71; H, 6.57; N, 4.05.

**Enantioselective Addition of $Et_2Zn$ to Arylaldehydes; General Procedure**

A soln of $Et_2Zn$ (1 M, hexane; 1.1 mL) was added to a soln of a chiral catalyst (0.025 mmol, 5 mol%) in anhyd toluene under a nitrogen atmosphere. The mixture was cooled to 0 °C and stirred for 30 min. Freshly distilled benzaldehyde (0.05 mL, 0.5 mmol) was added to the mixture. The resulting mixture was stirred at 0–5 °C for 10 h, then allowed to warm to r.t. and stirring was continued for an additional 38 h. The reaction was quenched by the addition of a sat.

aq soln of $NH_4Cl$ (4 mL) and extracted with $Et_2O$ (3 × 8 mL). The combined organic layers were washed with brine (8 mL), dried over anhyd $Na_2SO_4$, and the solvent was removed under reduced pressure. Purification of the residue by preparative TLC (hexane–EtOAc, 4:1) afforded the (*S*)-1-phenyl-1-propanol. The ee was determined by HPLC analysis using a chiral column.

**X-Ray Crystallographic Study**

An orange-red crystal of approximate dimensions 0.20 × 0.18 × 0.16 mm was mounted on a glass fiber. Crystallographic data for **8j** were measured on a Rigaku RAXIS-IV imaging plate area detector. The data were collected at 291(2) K using graphite monochromated Mo Kα(λ = 0.71073 Å), 2.03°<θ<27.51°. The structures were solved by a direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package. Crystal data for **8j**: Monoclinic $P2_1$: $a$ = 10.171 (2), $b$ = 17.682 (4), $c$ = 10.374 (2) Å, δ = 105.13 (3)°; V = 1801.1(6) Å$^3$; formula unit $C_{44}H_{44}FeN_2O_2$ with Z = 2; $D_{calcd}$ = 1.270 gcm$^{-3}$; F(000) = 728; μ(MoKα) = 0.458 mm$^{-1}$. Full-matrix least-squares refinement on $F^2$ based on 6067 independent reflections ($R_{int}$ = 0.0249) converged with 452 parameters. Final $R$ indices [I>2σ(I)]: $R1$ = 0.0460, w$R2$ = 0.0982; $R$ indices (all data): $R1$ = 0.0730, w$R2$ = 0.1050; GoF = 0.985.

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(10) Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-272339. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, CAMBRIDGE, CB2 1EZ, UK [fax: +44(1223)336033, e-mail: deposit@ccdc.cam.ac.uk].

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