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Enantioselective alkylation of benzaldehyde with diethylzinc catalyzed by 1,1′- and 1,2-disubstituted ferrocenyl amino alcohols

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Abstract—Optically active 1,1′- and 1,2-disubstituted ferrocenyl amino alcohols have been synthesized from 1,1′- and 1,2-ferrocene dicarboxaldehyde. They have been used as chiral catalysts in the asymmetric addition of diethylzinc to benzaldehyde. 1-Phenylpropanol has been obtained in up to 83% enantiomeric excess. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

There has been rapid growth in research on catalytic asymmetric processes for carbon–carbon bond forming reactions, and a variety of strategies have proven to be successful in providing high levels of enantioselectivity.[1] In particular, increasing interest has been devoted to the study of enantioselective addition of dialkylzinc to aldehydes.[2] Thus, chiral amino alcohols,[3] diamines,[4] and diols[5] have been shown to be suitable catalysts for such transformations. Among them, C_2-symmetrical dimeric amino alcohols,[6] particularly bipyridine-based ligands,[7] have been much less developed. Interestingly, ferrocenyl amino alcohols have been reported allowing evaluation of not only the effects related to the stereogenic centers of the ligand but also those of the planar chirality of the ferrocenyl unit.[8–10]

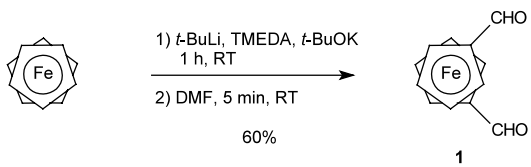
In a preliminary communication, we reported the synthesis of optically pure C_2-symmetrical 1,1′-disubstituted ferrocenyl amino alcohols and their application as catalysts for the addition of diethylzinc to benzaldehyde.[11] Herein, we describe the full details of our investigations including the synthesis of novel 1,2-disubstituted ferrocenyl amino alcohols and their application as catalysts in the enantioselective alkylation of benzaldehyde.

2. Results and discussion

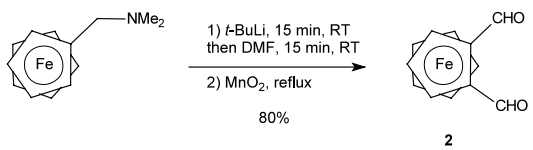
2.1. Synthesis of ferrocenyl amino alcohols

We first established a novel, easy and rapid methodology for the synthesis of ferrocene-1,1′-dicarboxaldehyde **1** based, in part, on conditions reported by Mueller–Westerhoff.[12] Thus, the lithiation of ferrocene was carried out in the presence of *tert*-BuLi, TMEDA and *tert*-BuOK at room temperature for 1 h in diethyl ether. After quenching by addition of DMF at room temperature and stirring for 5 min, complex **1** was isolated in 60% yield after work-up (Scheme 1).

Ferrocene-1,2-dicarboxaldehyde **2** was prepared from *N*,*N*-dimethylaminomethylferrocene by ortholithiation in the presence of *tert*-Buli, reaction of the anion with DMF,[13] followed by an oxidation with MnO_2 (Scheme 2).[14]



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



Scheme 2. Synthesis of ferrocene-1,2-dicarboxaldehyde **2**.

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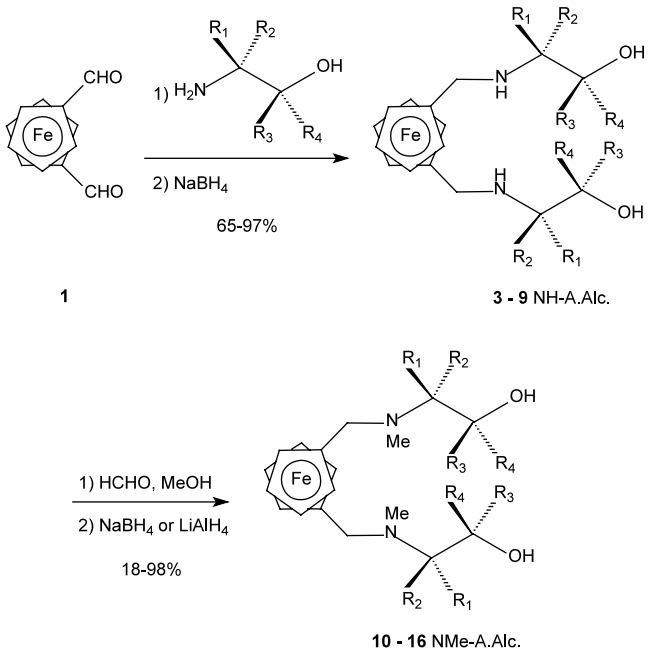
In separate experiments, ferrocene-1,1′-dicarboxaldehyde **1** was reacted in CH_2Cl_2 with commercially available (*S*)-valinol, (*R*)-phenylglycinol, (*S*)-leucinol, (*S*)-isoleucinol, (*S*)-*tert*-leucinol, (1*R*,2*S*)-norephedrine and (*S*)-2-amino-1,1-diphenyl-1-propanol in the presence of molecular sieves giving the corresponding imines (Scheme 3, substituents in Table 1). Reduction of the crude reaction mixtures with sodium borohydride in methanol provided the amino alcohols **3**–**9** in 65–97% overall yields after work-up. Enantiomerically pure ferrocenes **10**–**16** were obtained finally by *N*-methylation of the amino function of compounds **3**–**9** (Scheme 3, Table 1).

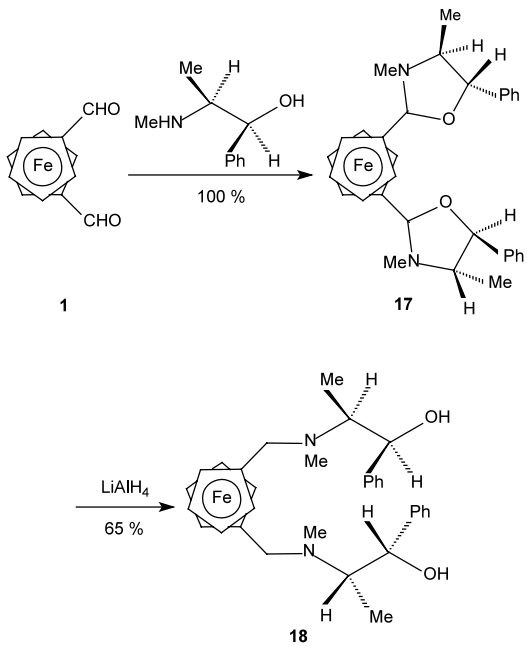
During the methylation reactions of **7** and **9**, stable intermediate oxazolidines were produced. The latter were reduced using $LiAlH_4$, purified by column chromatography and recrystallized to afford **14** and **16** in overall yields of 98 and 18%, respectively (Table 1).

Next, the reaction between commercial pseudoephedrine and ferrocene-1,1′-dicarboxaldehyde **1** led quantitatively to the oxazolidine **17** (Scheme 4). Reduction with excess $LiAlH_4$ in refluxing THF then afforded the amino alcohol **18** in 65% yield (Scheme 4).

Following the same procedure while starting from ferrocene-1,2-dicarboxaldehyde **2**, the 1,2-disubstituted ferrocenyl amino alcohols **19**–**24** were obtained by reaction of commercially available amino alcohols with **2**. In a similar manner, methylation of the isolated amino alcohols provided the desired 1,2-disubstituted *N*-methyl amino alcohols **25**–**30** (Table 1, Scheme 5). The



Scheme 3. Synthesis of 1,1′-disubstituted ferrocenyl amino alcohols **10**–**16**.

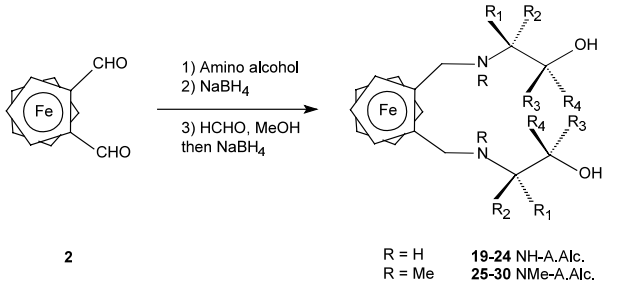


Scheme 4. Synthesis of amino alcohol **18**.

Table 1. Synthesis of 1,1′- and 1,2-disubstituted ferrocenyl amino alcohols

Starting amino alcohols	R_1	R_2	R_3	R_4	1,1′-Disubstituted ferrocene				1,2-Disubstituted ferrocene			
					NH-A.Alc.[a]	Yield (%)	NMe-A.Alc.[b]	Yield (%)	NH-A.Alc.[a]	Yield (%)	NMe-A.Alc.[b]	Yield (%)
(*S*)-Valinol	*i*Pro	H	H	H	3	65	10	66	19	60	25	66
(*R*)-Phenylglycinol	H	Ph	H	H	4	97	11	78	20	77	26	31
(*S*)-Leucinol	*i*Bu	H	H	H	5	96	12	87	21	82	27	47
(*S*)-Isoleucinol	*s*Bu	H	H	H	6	75	13	96	22	75	28	43
(*S*)-Terleucinol	*t*Bu	H	H	H	7	86	14	98	23	84	29	56
(1*R*,2*S*)-Norephedrine	Me	H	H	Ph	8	75	15	82	24	33	30	58
(*S*)-2-Amino-1,1-diphenyl-1-propanol	Me	H	Ph	Ph	9	79	16	18				
(1*S*,2*S*)-Pseudoephedrine	Me	H	Ph	H			18				32	

[a] NH-A.Alc.: amino alcohols with a NH moiety.
[b] NMe-A.Alc.: *N*-methyl amino alcohols.



Scheme 5. Synthesis of 1,2-disubstituted ferrocenyl amino alcohols.

yields of the isolated derivatives are reported in Table 1. Following the trend mentioned above, an intermediate oxazolidine was obtained during the methylation step of **23**. The reduction of this intermediate with $LiAlH_4$ led to amino alcohol **29** in 56% global yield.

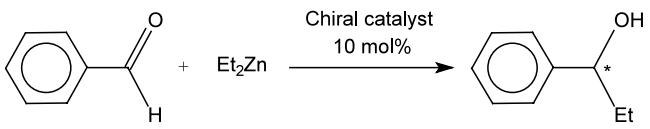
Using a route analogous to that developed for the preparation of **18** (Scheme 4), the condensation of pseudoephedrine with ferrocene-1,2-dicarboxaldehyde **2** produced an intermediate oxazolidine **31** which was reduced with $LiAlH_4$, providing the 1,2-disubstituted ferrocenyl amino alcohol **32** in 24% overall yield. Steric hindrance effects in the 1,2-derivatives led to lower yields than those obtained with the previously described 1,1′-disubstituted analogue.

All of the amino alcohols prepared have been fully characterized, as reported in Section 4.

2.2. Catalytic addition of Et_2Zn to benzaldehyde

The reaction of diethylzinc with benzaldehyde was then investigated in the presence of the synthesized 1,1′- and 1,2-disubstituted ferrocenyl amino alcohols at room temperature (Scheme 6). The results are summarized in Table 2.

As can be seen from Table 2, the addition of diethylzinc to benzaldehyde led to 1-phenylpropanol in 44–100% yields with e.e.s of 7–83%. All catalytic reactions were carried out using 10 mol% of the catalyst. As a matter of fact, when using only 5 mol% of chiral auxiliary, even if the overall yield was only slightly affected, a significant decrease in product e.e. was observed (entry 3 versus 2). In addition, the presence of an NH moiety was also detrimental to the enantioselectivity and slightly to the catalytic activity. For example, catalyst **3** provided the addition product in 15% e.e. (entry 1), whereas the *N*-Methylated catalyst **10** gave 47% e.e. (entry 3). Catalysts **19** and **25** can be compared similarly (46% e.e. versus 66% e.e., entry 11 versus 12).



Scheme 6. Addition of diethylzinc to benzaldehyde.

As expected, the sense of the asymmetric induction and the levels of enantioselectivity seen are highly dependant upon the stereochemical properties of the catalyst. Specific features can be deduced when considering the properties of the catalyst skeleton at the position either adjacent to the nitrogen atom or next to the hydroxy group. First, when taking into consideration all catalysts bearing only one stereogenic center, which is near to the nitrogen atom (ligands **10**–**14** and **25**–**29**), it appears that an *iso*-propyl residue induces the highest enantiodifferentiation (47% e.e. for **10**, entry 3 and 66% e.e. for **25**, entry 12) when compared to *sec*-butyl (entry 15), *tert*-butyl (entries 7 and 16), *iso*-butyl (entries 5 and 14) and phenyl (entries 4 and 13). The above tendency was also expected for **13** (ca. 40% e.e. estimated). However, in experiments carried out with **13**, the presence of a precipitate, attributed to the low solubility of **13** in the reaction conditions, lowered the effective catalyst availability leading to the detrimental effect mentioned above.

We also note that, in these two series of catalysts, the 1,2-disubstituted ferrocenyl ligands are more enantioselective overall than their 1,1′-disubstituted congeners (66–34% versus 47–13% e.e.). In addition, the configuration of the prevailing enantiomer is not always the same when considering products obtained with 1,1′- and 1,2-disubstituted catalysts bearing the same lateral chains. As such, catalysts **12** and **27**, both formed from leucinol, induced opposite enantioselectivities during

Table 2. Enantioselective addition of diethylzinc to benzaldehyde in the presence of ferrocenyl 1,1′- and 1,2-disubstituted amino alcohols[a]

Entry	Catalyst	Yield[b] (%)	E.e.[c] (%)	Config.[d]
1	**3**	74	15	*R*
2	**10**[e]	97	35	*R*
3	**10**	94	47	*R*
4	**11**	76	37	*S*
5	**12**	96	24	*S*
6	**13**	44	13	*S*
7	**14**	99	36	*R*
8	**15**	98	70	*R*
9	**16**	100	83	*R*
10	**18**	94	64	*S*
11	**19**	87	46	*R*
12	**25**	95	66	*R*
13	**26**	92	50	*S*
14	**27**	97	34	*R*
15	**28**	95	63	*R*
16	**29**[f]	63	53	*R*
17	**30**[f]	90	7	*R*
18	**32**	89	46	*S*

[a] The reactions were performed in dry toluene over 43 h under nitrogen with 10 mol% catalyst using benzaldehyde and diethylzinc in a 1:2 ratio at room temperature.
[b] Determined by ^1H NMR, the by-products or the other products being benzyl alcohol and unreacted benzaldehyde.
[c] Determined by GC analysis on FS-Cyclodex β-I/P (30 m×0.24).
[d] Determined from the comparison of the sign of the specific rotation with the literature data.
[e] Using 5 mol% catalyst.
[f] The reaction was performed over 1 week.

catalysis (entries 5 and 14). The same behavior is observed with catalysts **13** (entry 6) and **28** (entry 15). Moreover, when considering the 1,1′-catalysts possessing identical configurations (**10**, **12**, **13**, and **14)**, a reversal of the configuration of the produced 1-phenylpropanol is also observed in two cases (**12** versus **10** and **14**, and **13** versus **10** and **14**). Thus, even if it is quite difficult to draw a rationale from these results, these two features (sense and degrees of enantioselectivities) strongly suggest that both lateral chains can interact with a single zinc species in the 1,2- and the 1,1′-auxiliaries. It is possible that several catalytic species featuring different coordination modes, from a single chain per zinc up to two chains per zinc, participate with their own kinetics and enantioselectivity, accounting for the global results obtained.

Quite important differences are also observed within the two series when a second stereogenic center is introduced α to the hydroxy group. The most surprising one resulted from the catalysts 1,1′-(*R*,*S*)-**15** and 1,2-(*R*,*S*)-**30** featuring norephedrine based lateral chains. As a matter of fact, 70% e.e. (*R*) was obtained with the 1,1′-disubstituted catalyst **15** (entry 8), whereas a marked decrease in the e.e. to 7% (*R*) was obtained with the 1,2-disubstituted auxiliary **30** (entry 17). If the diastereomers 1,1′-(*R*,*R*)-**18** and 1,2-(*R*,*R*)-**32** are compared, a reversal of configuration was seen and the predominant 1-phenylpropanol produced had (*S*)-configuration (64% e.e. for **18** and 46% e.e. for **32**).

In general, the enantiodifferentiation induced by the 1,1′-auxiliaries bearing two stereogenic centers are superior to those induced by the 1,2-analogue. Interestingly, the variation in the level of enantioselectivity is opposite to that given above. Indeed, an increase is observed within the 1,2-disubstituted series (7 versus 46% e.e., entry 17 versus 18), whereas a slight decrease is obtained in the 1,1′-disubstituted series (70% versus 64% e.e., entry 8 versus 10). Thus, the diastereomers providing the highest enantioselectivities within each series present stereogenic centers with different configurations. The overall steric hindrance and conformational constraints within each series can account for the observed catalytic properties of the reported amino alcohols. A rationale based on these results would be hazardous. An interesting comparison can be made with the results reported by Butsugan while using the monosubstituted analogue of **15** (93% e.e., (*S*)-isomer, 2 h, 100%).[8a]

Finally, the highest enantiodifferentiation was reached with the α to OH-diphenyl substituted 1,1′-ferrocenyl catalyst **16** (83% e.e., entry 9). In addition using **16**, quantitative (unoptimized) conversion of benzaldehyde was also obtained. It is possible that because of the steric hindrance from the diphenyl substituted residue, the behaviour of 1,1′-(*R*)-**16** is moving towards that of a monosubstituted ferrocenyl auxiliary. Both the enantioselectivity and activity support this hypotheses. The analogue of **16** in the 1,2-disubstituted series has not been synthesized because of the very low activity and enantioselectivity obtained, with catalyst **30** possessing only one phenyl group (entry 17, 1 week, 7% e.e.).

3. Conclusion

We have described the synthesis of a novel series of optically active 1,1′- and 1,2-disubstituted ferrocenyl amino alcohols from 1,1′- and 1,2-ferrocene dicarboxaldehydes. The enantioselective ethylation of benzaldehyde with diethylzinc was investigated in the presence of a catalytic amount of the new diamino alcohols and the effects of the ligand structures on the enantioselectivity was then examined. Even though the corresponding 1-phenylpropanol was obtained with up to 83% e.e., the disubstituted ferrocenyl derivatives generally appear unsuited as ligands in the addition of diethylzinc to benzaldehyde. Nevertheless, such ligands, with the ability to provide either polydentate coordination properties or additional secondary interaction, might be of interest for application in other catalytic reactions.

4. Experimental

4.1. General

Reactions were performed in oven-dried glassware under an atmosphere of nitrogen. Air- and moisture-sensitive compounds were introduced via syringe through a rubber septum. Tetrahydrofuran and toluene were distilled from sodium/benzophenone ketyl just before use. All other reagents were obtained from Aldrich and used without purification. Column chromatographies were performed on SiO_2 (Merck, 70–230 mesh, Kieselgel 60). ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard, mass spectra were obtained with a RIBER 10-10 or Concept II H-H (Kustros Analytical, FAB) mass spectrometer, optical rotations were measured with a Perkin Elmer 241 polarimeter at wavelength 589 nm (sodium D line). HRMS were performed on a JEOL JMS-700m Station mass spectrometer. Enantiomeric excesses were determined using a gas chromatograph equipped with a chiral column (FS-Cyclodex β-I/P, 30 m×0.24). Melting points were obtained on a Kofler apparatus and are uncorrected.

4.2. Synthesis of ferrocene-1,1′-dicarboxaldehyde 1

Under nitrogen, ferrocene (250 mg, 1.34 mmol) and *tert*-BuOK (150 mg, 1.34 mmol) were dissolved in dry diethyl ether (20 mL) in the presence of TMEDA (500 μL, 3.35 mmol). *tert*-BuLi (1.5 M in pentane, 2.24 mL, 3.35 mmol) was added dropwise with a syringe. After stirring at room temperature for 1 h, DMF (360 μL, 4.69 mmol) was added to the reaction mixture. After 5 min stirring, the solution was quenched with water (10 mL) and extracted with Et_2O (3×20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified through column chromatography (eluent: petroleum ether/diethyl ether: 5/5) giving the ferrocene-1,1′-dicarboxaldehyde **1** (195 mg, 60%).[15]

4.3. Synthesis of ferrocene-1,2-dicarboxaldehyde 2

N,*N*-Dimethylferrocenylmethylamine (486 mg, 2 mmol) was dissolved in dry diethyl ether (20 mL). After 5 min, *tert*-BuLi (2 mL, 3 mmol, 1.5 M in pentane) was added slowly and the solution was stirred for another 15 min. Then, DMF (320 μL, 4 mmol) was added. The solution was stirred for 15 min, quenched with water and extracted with diethyl ether (2×20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (eluent: petroleum ether/diethyl ether/triethylamine: 2/7/1) producing 2-(*N*,*N*-dimethylaminomethyl)ferrocene carboxaldehyde in 94% yield (510 mg).[13] The 2-(*N*,*N*-dimethylaminomethyl)ferrocene carboxaldehyde (534 mg, 1.95 mmol) was dissolved in toluene (50 mL) in the presence of MnO_2 (3.056 g, 35 mmol). The mixture was heated at 90°C for 45 min, then at 100°C for 2 h. MnO_2 was removed by filtration over Celite 545 and the solvent was evaporated from the filtrate under reduced pressure. The crude product was purified through silica gel column chromatography (eluent: petroleum ether/diethyl ether: 1/1) giving the ferrocene-1,2-dicarboxaldehyde **2** (401 mg, 85%).[14]

4.4. General procedure for the synthesis of ferrocenyl amino alcohols

A mixture of ferrocenedicarboxaldehyde (200 mg, 0.83 mmol) and the appropriate amino alcohol (2.5 mmol) in anhydrous CH_2Cl_2 (50 mL) containing molecular sieves (4 Å, 5 g) was stirred under reflux for 10 h. The mixture was filtered through Celite 545. The solvent was evaporated from the filtrate under reduced pressure. The residue was dissolved in MeOH (30 mL) and $NaBH_4$ (0.15 g, 4.2 mmol) was added in small portions. The mixture was stirred at room temperature for 1 h, hydrolysed by addition of a saturated solution of NH_4Cl (50 mL) and extracted with CH_2Cl_2 (3×30 mL). The solvent was removed from the combined organic layers and the residue purified by column chromatography (eluent: petroleum ether/diethyl ether/triethylamine).

4.4.1. (*S*)-Bis[*N*-(2-hydroxy-1-isopropyl)ethyl]-1,1′-ferrocenylmethyldiamine 3. Following the general procedure starting from (*S*)-valinol (258 mg, 2.5 mmol), (*S*)-bis[*N*-(2-hydroxy-1-isopropyl)ethyl]-1,1′-ferrocenylmethyldiamine **3** was obtained as yellow crystals (223 mg, 65%). Mp 73°C. $[\alpha]_D^{20}=+15.6$ (*c* 0.26, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 0.91 (d, $J=6.8$ Hz, 6H, CH_3), 0.97 (d, $J=6.8$ Hz, 6H, CH_3), 1.77–1.89 (m, 2H, CH(CH_3)$_2$), 2.45–2.50 (m, 2H, NC*Hi*Pro), 3.37 (dd, $J=7.3$ and 10.7 Hz, 2H, C*H*HOH), 3.42 (d, $J=12.7$ Hz, 2H, FcC*H*HN), 3.52 (d, $J=12.7$ Hz, 2H, FcC*H*HN), 3.65 (dd, $J=4.1$ and 10.7 Hz, 2H, C*H*HOH), 4.09 (m, 4H, Cp), 4.15 (m, 2H, Cp), 4.18 (m, 2H, Cp). ^{13}C NMR ($CDCl_3$), δ 18.33, 19.66, 28.81, 46.17, 60.44, 64.13, 68.08, 68.28, 68.40, 68.45, 87.73. MS: $m/z=439$ (M^++Na), 416 (M^+), 386, 320, 314. Anal. calcd for $C_{22}H_{36}FeN_2O_2$: C, 63.46, H, 8.71, N, 6.73. Found: C, 63.55, H, 8.41, N, 6.78%.

4.4.2. (*R*)-Bis[*N*-(2-hydroxy-1-phenyl)ethyl]-1,1′-ferrocenylmethyldiamine 4. Following the general procedure starting from (*R*)-phenylglycinol (343 mg, 2.5 mmol), (*R*)-bis[*N*-(2-hydroxy-1-phenyl)ethyl]-1,1′-ferrocenylmethyldiamine **4** was obtained as yellow–brown crystals (389 mg, 97%). Mp 129°C. $[\alpha]_D^{20}=-30.7$ (*c* 0.23, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 3.08 (d, $J=12.7$ Hz, 2H, FcC*H*HN), 3.37 (d, $J=12.7$ Hz, 2H, FcC*H*HN), 3.66 (dd, $J=9.5$ and 11.4 Hz, 2H, C*H*HOH), 3.78 (dd, $J=4.1$ and 11.4 Hz, 2H, CH*H*OH), 3.95 (dd, $J=4.1$ and 9.5 Hz, 2H, C*H*Ph), 4.12 (m, 6H, Cp), 4.35 (m, 2H, Cp), 7.26–7.38 (m, 10H, Ph). HRMS calcd for $C_{28}H_{33}FeN_2O_2$ (M^++H) 485.4292, found 485.4250.

4.4.3. (*S*)-Bis[*N*-(2-hydroxy-1-isobutyl)ethyl]-1,1′-ferrocenylmethyldiamine 5. Following the general procedure starting from (*S*)-leucinol (293 mg, 2.5 mmol), (*S*)-bis[*N*-(2-hydroxy-1-isobutyl)ethyl]-1,1′-ferrocenylmethyldiamine **5** was obtained as yellow crystals (354 mg, 96%). Mp 92°C. ^{1}H NMR ($CDCl_3$), δ 0.90 (d, $J=5.8$ Hz, 6H, CH(CH_3)$_2$), 0.92 (d, $J=5.8$ Hz, 6H, CH(CH_3)$_2$), 1.17–1.25 (m, 2H, CH_2CH(CH_3)$_2$), 1.32–1.43 (m, 2H, CH_2CH(CH_3)$_2$), 1.57–1.66 (m, 2H, CH_2C*H*(CH_3)$_2$), 2.77 (m, 2H, NC*H*CH_2OH), 3.32 (m, 2H, CH*H*OH), 3.33 (d, $J=12.7$ Hz, 2H, FcCH*H*N), 3.51 (d, $J=12.7$ Hz, 2H, FcC*H*HN), 3.69 (dd, $J=3.6$ and 10.9 Hz, 2H, CH*H*OH), 4.10 (m, 4H, Cp), 4.15 (m, 2H, Cp), 4.23 (m, 2H, Cp). HRMS calcd for $C_{24}H_{41}FeN_2O_2$ (M^++H) 445.4488, found 445.4463.

4.4.4. (*S*)-Bis[*N*-(1-*sec*-butyl-2-hydroxy)ethyl]-1,1′-ferrocenylmethyldiamine 6. Following the general procedure starting from (*S*)-isoleucinol (293 mg, 2.5 mmol), (*S*)-bis[*N*-(1-*sec*-butyl-2-hydroxy)ethyl]-1,1′-ferrocenylmethyldiamine **6** was obtained as a yellow oil (276 mg, 75%). ^{1}H NMR ($CDCl_3$), δ 0.87 (d, $J=6.9$ Hz, 6H, CH(CH_3)CH_2CH_3), 0.93 (t, $J=7.3$ Hz, 6H, CH(CH_3)-CH_2CH_3), 1.15–1.25 (m, 2H, CH(CH_3)C$H_2$$CH_3$), 1.40–1.49 (m, 2H, CH($CH_3$)C$H_2$$CH_3$), 1.58–1.64 (m, 2H, C*H*(CH_3)CH_2CH_3), 2.62 (ddd, $J=4.0$, 5.5 and 7.9 Hz, 2H, NC*H*CH_2OH), 3.35 (d, $J=12.7$ Hz, 2H, FcCH*H*N), 3.37 (dd, $J=7.9$ and 10.7 Hz, 2H, CH*H*OH), 3.53 (d, $J=12.7$ Hz, 2H, FcCH*H*N), 3.62 (dd, $J=4.0$ and 10.7 Hz, 2H, CH*H*OH), 4.10 (m, 4H, Cp), 4.16 (m, 2H, Cp), 4.21 (m, 2H, Cp). HRMS calcd for $C_{24}H_{41}FeN_2O_2$ (M^++H) 445.4488, found 445.4492.

4.4.5. (*S*)-Bis[*N*-(1-*tert*-butyl-2-hydroxy)ethyl]-1,1′-ferrocenylmethyldiamine 7. Following the general procedure starting from (*S*)-*tert*-leucinol (293 mg, 2.5 mmol), (*S*)-bis[*N*-(1-*tert*-butyl-2-hydroxy)ethyl]-1,1′-ferrocenylmethyldiamine **7** was obtained as yellow crystals (317 mg, 86%). Mp 135°C. ^{1}H NMR ($CDCl_3$), δ 0.94 (s, 18H, C(CH_3)$_3$), 2.35 (dd, $J=4.7$ and 6.6 Hz, 2H, C*H*C(CH_3)$_3$), 3.37 (dd, $J=6.6$ and 10.5 Hz, 2H, CH*H*OH), 3.54 (d, $J=12.8$ Hz, 2H, FcCH*H*N), 3.61 (d, $J=12.8$ Hz, 2H, FcCH*H*N), 3.62 (dd, $J=4.7$ and 10.5 Hz, 2H, CH*H*OH), 4.09 (m, 4H, Cp), 4.16 (m,

4H, Cp). ^{13}C NMR ($CDCl_3$), δ 27.26, 34.30, 49.08, 59.95, 66.96, 68.25, 68.33, 68.44, 68.73, 87.41. MS: m/z = 444 (M^+), 327, 296, 270, 192, 134. Anal. calcd for $C_{24}H_{40}FeN_2O_2$: C, 64.86; H, 9.07; N, 6.30. Found: C, 64.99; H, 8.63; N, 6.08%.

4.4.6. (1*S*,2*R*)-Bis[*N*-(2-hydroxy-1-methyl-2-phenyl)-ethyl]-1,1′-ferrocenylmethyldiamine 8. Following the general procedure starting from (1*R*,2*S*)-norephedrine (378 mg, 2.5 mmol), (1*S*,2*R*)-bis[*N*-(2-hydroxy-1-methyl-2-phenyl)ethyl]-1,1′-ferrocenylmethyldiamine **8** was obtained as yellow crystals (319 mg, 75%). Mp 122°C. ^{1}H NMR ($CDCl_3$), δ 0.85 (d, J = 6.4 Hz, 6H, CHCH_3), 2.97 (qd, J = 4.0 and 6.4 Hz, 2H, NCH(CH_3)), 3.55 (s, 4H, FcCH_2N), 4.04 (m, 4H, Cp), 4.10 (m, 2H, Cp), 4.12 (m, 2H, Cp), 4.74 (d, J = 4.0 Hz, 2H, CHPh), 7.24–7.34 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$), δ 14.80, 45.96, 57.86, 68.36, 68.41, 68.48, 68.61, 73.20, 87.19, 126.14, 127.14, 128.14, 141.37. MS: m/z = 477, 372, 349, 199. Anal. calcd for $C_{30}H_{36}FeN_2O_2$: C, 70.31; H, 7.08; N, 5.46. Found: C, 70.21; H, 6.94; N, 5.44%.

4.4.7. (*S*)-Bis[*N*-(2-hydroxy-1-methyl-2,2-diphenyl)-ethyl]-1,1′-ferrocenylmethyldiamine 9. Following the general procedure starting from (*S*)-2-amino-1,1-diphenyl-1-propanol (568 mg, 2.5 mmol), (*S*)-bis[*N*-(2-hydroxy-1-methyl-2,2-diphenyl)ethyl]-1,1′-ferrocenylmethyldiamine **9** was obtained as a yellow oil (435 mg, 79%). ^{1}H NMR ($CDCl_3$), δ 0.98 (d, J = 6.2 Hz, 6H, CHCH_3), 3.18 (d, J = 13.0 Hz, 2H, FcCHHN), 3.40 (d, J = 13.0 Hz, 2H, FcCHHN), 3.77–3.81 (m, 10H, Cp+CHCH$_3$), 7.13–7.63 (m, 20H, Ph). HRMS calcd for $C_{42}H_{45}FeN_2O_2$ (M^++H) 665.6785, found 665.6737.

4.4.8. (*S*)-Bis[*N*-(2-hydroxy-1-isopropyl)ethyl]-1,2-ferrocenylmethyldiamine 19. Following the general procedure starting from (*S*)-valinol (258 mg, 2.5 mmol), (*S*)-bis-[*N*-(2-hydroxy-1-isopropyl)ethyl]-1,2-ferrocenylmethyldiamine **19** was obtained as a yellow oil (207 mg, 60%). $[\alpha]_D^{20}$ = +64.8 (*c* 0.22, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 0.87–0.97 (m, 12H, CH(CH_3)$_2$), 1.77 (m, 2H, CH(CH_3)$_2$), 2.32 (m, 1H, NCHCH$_2$OH), 2.41 (m, 1H, NCHCH$_2$OH), 3.24–3.99 (m, 8H, FcCH_2N+CH_2OH), 4.04 (s+m, 6H, Cp+Cp′), 4.11 (m, 1H, Cp), 4.15 (m, 1H, Cp). MS: m/z = 455 (M^++K), 439 (M^++Na), 417 (MH^+), 314. Anal. calcd for $C_{22}H_{36}FeN_2O_2$: C, 63.46; H, 8.71; N, 6.73. Found: C, 63.53; H, 8.52; N, 6.85%.

4.4.9. (*R*)-Bis[*N*-(2-hydroxy-1-phenyl)ethyl]-1,2-ferrocenylmethyldiamine 20. Following the general procedure starting from (*R*)-phenylglycinol (343 mg, 2.5 mmol), (*R*)-bis[*N*-(2-hydroxy-1-phenyl)ethyl]-1,2-ferrocenylmethydiamine **20** was obtained as a yellow oil (309 mg, 77%). $[\alpha]_D^{20}$ = −71.9 (*c* 0.76, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 3.20 (d, J = 13.2 Hz, 1H, FcCHHN), 3.34 (d, J = 11.9 Hz, 1H, FcCHHN), 3.59–3.88 (m, 8H, FcCHHN+CH_2OH+CHPh), 3.92 (s, 5H, Cp′), 3.99 (m, 2H, Cp), 4.04 (m, 1H, Cp), 7.16–7.41 (m, 10H, Ph). MS: m/z = 523 (M^++K), 507 (M^++Na), 379, 348. HRMS calcd for $C_{28}H_{32}FeN_2O_2$ (M^+) 484.4213, found 484.4219.

4.4.10. (*S*)-Bis[*N*-(2-hydroxy-1-isobutyl)ethyl]-1,2-ferrocenylmethyldiamine 21. Following the general procedure starting from (*S*)-leucinol (293 mg, 2.5 mmol), (*S*)-bis[*N*-(2-hydroxy-1-isobutyl)ethyl]-1,2-ferrocenylmethyldiamine **21** was obtained as a yellow oil (302 mg, 82%). ^{1}H NMR ($CDCl_3$), δ 0.91 (m, 12H, (CH_3)$_2$), 1.18–1.35 (m, 3H, CH(CH_3)$_2$+CH_2CH(CH_3)$_2$), 1.62 (m, 1H, CH(CH_3)$_2$), 1.85 (m, 2H, CH_2CH(CH_3)$_2$), 2.60 (m, 1H, NCHCH$_2$OH), 2.75 (m, 1H, NCHCH$_2$OH), 3.16–4.01 (m, 8H, FcCH_2N+CH_2OH), 4.05 (m+s, 6H, Cp+Cp′), 4.12 (m, 1H, Cp), 4.14 (m, 1H, Cp). HRMS calcd for $C_{24}H_{40}FeN_2O_2$ (M^+) 444.4409, found 444.4419.

4.4.11. (*S*)-Bis[*N*-(1-*sec*-butyl-2-hydroxy)ethyl]-1,2-ferrocenylmethyldiamine 22. Following the general procedure starting from (*S*)-isoleucinol (293 mg, 2.5 mmol), (*S*)-bis[*N*-(1-*sec*-butyl-2-hydroxy)ethyl]-1,2-ferrocenylmethyldiamine **22** was obtained as a yellow oil (276 mg, 75%). ^{1}H NMR ($CDCl_3$), δ 0.88 (m, 12H, CH(CH_3)CH$_2$CH$_3$+CH(CH_3)CH$_2$CH_3), 1.19 (m, 2H, CH(CH_3)CH$_2$CH$_3$), 1.37–1.60 (m, 4H, CH(CH_3)CH_2CH$_3$), 2.45 (m, 1H, NCHCH$_2$OH), 2.54 (m, 1H, NCHCH$_2$OH), 3.23–3.98 (m, 8H, CH_2OH+FcCH_2N), 4.05 (s+m, 6H, Cp+Cp′), 4.10 (m, 1H, Cp), 4.15 (m, 1H, Cp). MS: m/z = 483 (M^++K), 467 (M^++Na), 445 (MH^+), 328. HRMS calcd for $C_{24}H_{41}FeN_2O_2$ (M^++H) 445.4488, found 445.4490.

4.4.12. (*S*)-Bis[*N*-(1-*tert*-butyl-2-hydroxy)ethyl]-1,2-ferrocenylmethyldiamine 23. Following the general procedure starting from (*S*)-*tert*-leucinol (293 mg, 2.5 mmol), (*S*)-bis[*N*-(1-*tert*-butyl-2-hydroxy)ethyl]-1,2-ferrocenylmethyldiamine **23** was obtained as yellow crystals (309 mg, 84%). Mp 90°C. ^{1}H NMR ($CDCl_3$), δ 0.94 (s, 18H, C(CH_3)$_3$), 2.22 (dd, J = 3.4 and 7.2 Hz, 1H, CHC(CH_3)$_3$), 2.38 (dd, J = 3.7 and 8.6 Hz, 1H, CHC(CH_3)$_3$), 3.22 (dd, J = 7.2 and 11.3 Hz, 1H, CHHOH), 3.33 (dd, J = 3.4 and 11.3 Hz, 1H, CHHOH), 3.48 (m, 3H, FcCHHN+CHHOH), 3.63 (d, J = 11.9 Hz, 1H, FcCHHN), 3.68 (dd, J = 3.7 and 11.1 Hz, 1H, CHHOH), 3.74 (d, J = 11.9 Hz, 1H, FcCHHN), 4.03 (s, 5H, Cp′), 4.06–4.13 (m, 3H, Cp). MS: m/z = 445 (MH^+), 328. HRMS calcd for $C_{24}H_{41}FeN_2O_2$ (M^++H) 445.4488, found 445.4495.

4.4.13. (1*S*,2*R*)-Bis[*N*-(2-hydroxy-1-methyl-2-phenyl)-ethyl]-1,2-ferrocenylmethyldiamine 24. Following the general procedure starting from (1*R*,2*S*)-norephedrine (378 mg, 2.5 mmol), (1*S*,2*R*)-bis[*N*-(2-hydroxy-1-methyl-2-phenyl)ethyl]-1,2-ferrocenylmethyldiamine **24** was obtained as a yellow oil (140 mg, 33%). ^{1}H NMR ($CDCl_3$), δ 0.83 (d, J = 6.5 Hz, 3H, CH_3), 0.93 (d, J = 6.5 Hz, 3H, CH_3), 2.95–3.03 (m, 2H, CH(CH_3), 3.60 (d, J = 12.8 Hz, 1H, FcCHHN), 3.63 (d, J = 12.2 Hz, 1H, FcCHHN), 3.75 (d, J = 12.8 Hz, 1H, FcCHHN), 3.88 (d, J = 12.2 Hz, 1H, FcCHHN), 4.08 (s+m, 6H, Cp+Cp′), 4.22 (m, 2H, Cp), 4.7 (d, J = 3 Hz, 1H, CHPh), 5.07 (d, J = 2.6 Hz, 1H, CHPh), 7.25–7.36 (m, 10H, Ph). MS: m/z = 551 (M^++K), 535 (M^++Na), 513 (MH^+), 362, 323, 254, 213. HRMS calcd for $C_{30}H_{36}FeN_2O_2$ (M^+) 512.4751, found 512.4742.

4.5. General procedure for *N*-methylation of amino alcohols

A mixture of amino alcohol (0.1 g) and 37% aqueous solution of formaldehyde (10 equiv.) in 10 mL of MeOH was stirred under reflux for 30 min. The mixture was cooled to room temperature and $NaBH_4$ (5 equiv.) was slowly added. The mixture was stirred at room temperature for 1 h, treated with 20 mL of H_2O, extracted with CH_2Cl_2 (3×20 mL) and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography (eluent: petroleum ether/diethyl ether/triethylamine).

4.5.1. (*S*)-Bis[*N*-(2-hydroxy-1-isopropyl)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine 10. Following the general procedure starting from amino alcohol **3** (100 mg, 0.24 mmol), (*S*)-bis[*N*-(2-hydroxy-1-isopropyl)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine **10** was obtained as a yellow oil (70 mg, 66%). $[\alpha]_D^{20}=-18.9$ (*c* 0.32, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 0.84 (d, $J=6.7$ Hz, 6H, $CHCH_3$), 1.03 (d, $J=6.7$ Hz, 6H, $CHCH_3$), 1.81–1.88 (m, 2H, $CH(CH_3)_2$), 2.25 (s, 6H, NCH_3), 2.39–2.47 (m, 2H, $NCHCH_2OH$), 3.16 (dd, $J=10.3$ and 10.3 Hz, 2H, $CHHOH$), 3.50 (d, $J=13.0$ Hz, 2H, $FcCHHN$), 3.53 (dd, $J=10.3$ and 5.1 Hz, 2H, $CHHOH$), 3.64 (d, $J=13.0$ Hz, 2H, $FcCHHN$), 4.05–4.10 (m, 8H, Cp). ^{13}C NMR ($CDCl_3$), δ 19.82, 22.45, 28.13, 35.58, 54.87, 59.21, 68.71, 69.98, 70.03, 85.67. MS: $m/z=467$ (M^++Na), 444 (M^+), 370, 328. Anal. calcd for $C_{24}H_{40}FeN_2O_2$: C, 64.86; H, 9.07; N, 6.30. Found: C, 64.61; H, 9.20; N, 6.35.

4.5.2. (*R*)-Bis[*N*-(2-hydroxy-1-phenyl)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine 11. Following the general procedure starting from amino alcohol **4** (100 mg, 0.21 mmol), (*R*)-bis[*N*-(2-hydroxy-1-phenyl)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine **11** was obtained as a yellow oil (83 mg, 78%). $[\alpha]_D^{20}=-72.6$ (*c* 0.25, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ 2.07 (s, 6H, NCH_3), 3.15 (d, $J=12.9$ Hz, 2H, $FcCHHN$), 3.39 (d, $J=12.9$ Hz, 2H, $FcCHHNMe$), 3.62 (dd, $J=5.0$ and 10.3 Hz, 2H, $CHHOH$), 3.73 (dd, $J=5.0$ and 9.2 Hz, 2H, $CHHOH$), 3.91 (dd, $J=9.2$ and 10.3 Hz, 2H, $NCHPh$), 4.01–4.09 (m, 8H, Cp), 7.18–7.23 (m, 4H, Ph), 7.31–7.40 (m, 6H, Ph). MS: $m/z=512$ (M^+), 379, 362, 348, 284, 213. Anal. calcd for $C_{30}H_{36}FeN_2O_2$: C, 70.31; H, 7.08; N, 5.47. Found: C, 70.20; H, 6.97; N, 5.41%.

4.5.3. (*S*)-Bis[*N*-(2-hydroxy-1-isobutyl)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine 12. Following the general procedure starting from amino alcohol **5** (100 mg, 0.22 mmol), (*S*)-bis[*N*-(2-hydroxy-1-isobutyl)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine **12** was obtained as a yellow oil (90 mg, 87%). $[\alpha]_D^{20}=+28.4$ (*c* 0.98, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 0.90 (d, $J=7.0$ Hz, 6H, $(CH_3)_2CH$), 0.92 (d, $J=7.0$ Hz, 6H, $(CH_3)_2CH$), 0.98–1.50 (m, 6H, $(CH_3)_2CHCH_2$), 2.12 (s, 6H, NCH_3), 2.80 (m, 2H, $NCHCH_2OH$), 3.17–3.27 (m, 4H, $FcCH_2N$+CH_2OH), 3.46–3.50 (m, 4H, $FcCH_2N$+CH_2OH), 4.08 (m, 8H, Cp). MS: $m/z=511$ (M^++K), 495 (M^++Na), 472 (M^+), 391, 342, 264, 213. Anal. calcd for $C_{26}H_{44}FeN_2O_2$: C, 66.09; H, 9.38; N, 5.93. Found: C, 65.71; H, 9.17; N, 5.86%.

4.5.4. (*S*)-Bis[*N*-(1-*sec*-butyl-2-hydroxy)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine 13. Following the general procedure starting from amino alcohol **6** (100 mg, 0.22 mmol), (*S*)-bis[*N*-(1-*sec*-butyl-2-hydroxy)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine **13** was obtained as a yellow oil (99 mg, 96%). $[\alpha]_D^{20}=-6.4$ (*c* 0.11, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 0.81 (d, $J=6.7$ Hz, 6H, $(CH_3)CHCH_2CH_3$), 0.93 (t, $J=7.3$ Hz, 6H, $(CH_3)CHCH_2CH_3$), 1.13–1.27 (m, 2H, $(CH_3)CHCH_2CH_3$), 1.47–1.60 (m, 2H, $(CH_3)CHCH_2CH_3$), 1.62–1.71 (m, 2H, $(CH_3)CHCH_2CH_3$), 2.23 (s, 6H, NCH_3), 2.56 (ddd, $J=5.0$, 7.4 and 10.3 Hz, 2H, $CHCH_2OH$), 3.23 (dd, $J=10.3$ and 10.3 Hz, 2H, $CHHOH$), 3.44 (d, $J=13.0$ Hz, 2H, $FcCHHN$), 3.51 (dd, $J=5.0$ and 10.3 Hz, 2H, $CHHOH$), 3.62 (d, $J=13.0$ Hz, 2H, $FcCHHN$), 4.05–4.15 (m, 8H, Cp). MS: $m/z=473$ (MH^+), 353, 342, 264, 213. Anal. calcd for $C_{26}H_{44}FeN_2O_2$: C, 66.09; H, 9.38; N, 5.93. Found: C, 65.97; H, 9.16; N, 6.09%.

4.5.5. (*S*)-Bis[*N*-(1-*tert*-butyl-2-hydroxy)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine 14. A mixture of amino alcohol **7** (0.1g) and 37% aqueous solution of formaldehyde (170 μL) in 10 mL of MeOH was stirred under reflux for 30 min. The mixture was treated with 20 mL of H_2O, extracted with CH_2Cl_2 (3×20 mL) and dried over Na_2SO_4. After evaporation of the solvent, the residue was dissolved in anhydrous THF (10 mL) and added dropwise to a suspension of $LiAlH_4$ (0.034 g, 0.9 mmol) in THF (20 mL). The mixture was refluxed under nitrogen for 5 h. The solution was cooled to room temperature, quenched by the addition of a saturated aqueous ammonium chloride solution and extracted with Et_2O (3×30 mL). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give (*S*)-bis[*N*-(1-*tert*-butyl-2-hydroxy)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine **14** as yellow crystals (102 mg, 98%). Mp 67°C. $[\alpha]_D^{20}=+12.3$ (*c* 0.24, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 0.99 (s, 18H, $C(CH_3)_3$), 2.37 (s, 6H, NCH_3), 2.56 (dd, $J=4.6$ and 10.5 Hz, 2H, $CH(CH_3)_3$), 3.45 (dd, $J=10.5$ and 10.5 Hz, 2H, $CHHOH$), 3.55 (dd, $J=4.6$ and 10.5 Hz, 2H, $CHHOH$), 3.59 (d, $J=13.2$ Hz, 2H, $FcCHHN$), 3.76 (d, $J=13.2$ Hz, 2H, $FcCHHN$), 4.05–4.10 (m, 8H, Cp). ^{13}C NMR ($CDCl_3$), δ 28.96, 36.57, 36.77, 56.18, 57.83, 68.66, 68.73, 69.74, 70.02, 73.28, 86.05. MS: $m/z=472$ (M^+), 342, 264, 213, 100. Anal. calcd for $C_{26}H_{44}FeN_2O_2$: C, 66.09; H, 9.38; N, 5.93. Found: C, 66.15; H, 9.01; N, 6.12%.

4.5.6. (1*S*,2*R*)-Bis[*N*-(2-hydroxy-1-methyl-2-phenyl)-ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine 15. Following the general procedure starting from amino alcohol **8** (100 mg, 0.19 mmol), (1*R*,2*S*)-bis[*N*-(2-hydroxy-1-methyl-2-phenyl)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine **15** was obtained as a yellow oil (84 mg, 82%). $[\alpha]_D^{20}=+85.5$ (*c* 0.18, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 0.82 (d, $J=6.8$ Hz, 6H, $CHCH_3$), 2.15 (s, 6H, NCH_3), 2.82 (qd, $J=4.3$ and 6.8 Hz, 2H, $CHCH_3$), 3.42 (d, $J=13.5$ Hz, 2H, $FcCHHN$), 3.48 (d, $J=13.5$

Hz, 2H, FcCH*H*N), 4.06 (m, 6H, Cp), 4.11 (m, 2H, Cp), 4.84 (d, $J=4.3$ Hz, 2H, C*H*Ph), 7.2–7.38 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$), δ 10.31, 38.69, 54.08, 61.86, 68.71, 68.76, 70.48, 70.59, 72.55, 83.70, 126.09, 126.83, 127.95, 142.21. MS: $m/z=563$ (M^++Na), 537, 376. Anal. calcd for $C_{32}H_{40}FeN_2O_2$: C, 71.11; H, 7.46; N, 5.18. Found: C, 70.97; H, 6.22; N, 4.95%.

4.5.7. (*S*)-Bis[*N*-(2-hydroxy-1-methyl-2,2-diphenyl)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine 16. A mixture of amino alcohol **9** (0.1 g) and 37% aqueous solution of formaldehyde (113 μL) in 10 mL of MeOH was stirred under reflux for 30 min. The mixture was treated with 20 mL of H_2O, extracted with CH_2Cl_2 (3×20 mL) and dried over Na_2SO_4. After evaporation of the solvent, the residue was dissolved in anhydrous THF (10 mL) and added dropwise to a suspension of $LiAlH_4$ (0.034 g, 0.9 mmol) in THF (20 mL). The mixture was refluxed under nitrogen for 5 h. The solution was cooled to room temperature, quenched by the addition of a saturated aqueous ammonium chloride solution and extracted with Et_2O (3×30 mL). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give (*S*)-bis[*N*-(2-hydroxy-1-methyl-2,2-diphenyl)ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine **16** as a yellow oil (18 mg, 18%). $[\alpha]_D=+12.2$ (*c* 1.23, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 1.08 (d, $J=7.1$ Hz, 6H, CHC*H*$_3$), 1.91 (s, 6H, NCH$_3$), 2.98 (d, $J=12.8$ Hz, 2H, FcCH*H*N), 3.13 (d, $J=12.8$ Hz, 2H, FcCH*H*N), 3.64 (q, $J=7.1$ Hz, 2H, NC*H*CH$_3$), 3.91–4.1 (m, 8H, Cp), 7.17–7.49 (m, 20H, Ph). MS: $m/z=731$ (M^++K), 715 (M^++Na), 692 (M^+), 482, 452, 243, 213. Anal. calcd for $C_{44}H_{48}FeN_2O_2$: C, 76.29; H, 6.98; N, 4.04. Found: C, 76.01; H, 6.91; N, 4.03%.

4.5.8. (*S*)-Bis[*N*-(2-hydroxy-1-isopropyl)ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine 25. Following the general procedure starting from amino alcohol **19** (100 mg, 0.24 mmol), (*S*)-bis[*N*-(2-hydroxy-1-isopropyl)ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine **25** was obtained as a yellow oil (70 mg, 66%). $[\alpha]_D^{20}=-11.3$ (*c* 0.09, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 0.78 (d, $J=6.6$ Hz, 3H, CH(C*H*$_3$)$_2$), 0.80 (d, $J=6.6$ Hz, 3H, CH(C*H*$_3$)$_2$), 0.96 (d, $J=6.6$ Hz, 3H, CH(C*H*$_3$)$_2$), 0.99 (d, $J=6.6$ Hz, 3H, CH(C*H*$_3$)$_2$), 1.85 (m, 2H, C*H*(CH$_3$)$_2$), 2.09 (s, 3H, NC*H*$_3$), 2.24 (s, 3H, NC*H*$_3$), 2.42 (m, 2H, C*H*CH$_2$OH), 3.19–3.70 (m, 8H, FcC*H*$_2$N+C*H*$_2$OH), 3.98 (s, 5H, Cp′), 3.99–4.11 (m, 3H, Cp). MS: $m/z=483$ (M^++K), 467 (M^++Na), 445 (MH^+), 328. Anal. calcd for $C_{24}H_{40}FeN_2O_2$: C, 64.86; H, 9.07; N, 6.30. Found: C, 64.98; H, 8.85; N, 6.24%.

4.5.9. (*R*)-Bis[*N*-(2-hydroxy-1-phenyl)ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine 26. Following the general procedure starting from amino alcohol **20** (100 mg, 0.21 mmol), (*R*)-bis[*N*-(2-hydroxy-1-phenyl)ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine **26** was obtained as a yellow oil (33 mg, 31%). $[\alpha]_D^{20}=-114.4$ ($c=0.31$, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 2.05 (s, 3H, NC*H*$_3$), 2.20 (s, 3H, NC*H*$_3$), 3.06 (d, $J=12.5$ Hz, 1H, FcC*H*$_2$N), 3.17 (d, $J=12.9$ Hz, 1H, FcC*H*$_2$N), 3.49 (dd, $J=3.6$ and 10.9 Hz, 1H, C*H*$_2$OH), 3.66 (dd, $J=3.60$ and 11.7 Hz, 1H, C*H*$_2$OH), 3.79–3.88 (m, 4H, C*H*$_2$OH+FcC*H*$_2$N), 4.01 (s, 5H, Cp′), 4.01–4.25 (m, 5H, Cp+C*H*Ph), 7.16–7.40 (m, 10H, Ph). MS: $m/z=551$ (M^++K), 535 (M^++Na), 513 (MH^+), 379, 362. Anal. calcd for $C_{30}H_{36}FeN_2O_2$: C, 70.31; H, 7.08; N, 5.47. Found: C, 70.45; H, 7.12; N, 5.53%.

4.5.10. (*S*)-Bis[*N*-(2-hydroxy-1-isobutyl)ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine 27. Following the general procedure starting from amino alcohol **21** (100 mg, 0.22 mmol), (*S*)-bis[*N*-(2-hydroxy-1-isobutyl)ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine **27** was obtained as a yellow oil (49 mg, 47%). $[\alpha]_D^{20}=+33.3$ (*c* 0.33, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 0.91 (m, 12H, CH$_2$CH(C*H*$_3$)$_2$), 1.02 (m, 2H, C*H*$_2$CH(CH$_3$)$_2$), 1.30 (m, 2H, C*H*$_2$CH(CH$_3$)$_2$), 1.51 (m, 2H, C*H*(CH$_3$)$_2$), 2.09 (s, 3H, NC*H*$_3$), 2.20 (s, 3H, NC*H*$_3$), 2.75 (m, 2H, C*H*CH$_2$OH), 3.07–3.72 (m, 8H, FcC*H*$_2$N+C*H*$_2$OH), 4.04 (s+m, 6H, Cp+Cp′), 4.15 (m, 2H, Cp). MS: $m/z=511$ (M^++K), 495 (M^++Na), 473 (MH^+), 379, 342, 213. Anal. calcd for $C_{26}H_{44}FeN_2O_2$: C, 66.09; H, 9.38; N, 5.93. Found: C, 66.02; H, 9.25; N, 6.03.

4.5.11. (*S*)-Bis[*N*-(1-*sec*-butyl-2-hydroxy)ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine 28. Following the general procedure starting from amino alcohol **22** (100 mg, 0.22 mmol), (*S*)-bis[*N*-(1-*sec*-butyl-2-hydroxy)-ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine **28** was obtained as a yellow oil (45 mg, 43%). $[\alpha]_D^{20}=+19.3$ (*c* 0.77, $CHCl_3$). ^{1}H NMR ($CDCl_3$), δ 0.82 (d, $J=7.9$ Hz, 3H, C*H*$_3$CHCH$_2$CH$_3$), 0.84 (d, $J=7.9$ Hz, 3H, C*H*$_3$CHCH$_2$CH$_3$), 0.94 (t, $J=7.3$ Hz, 3H, CH$_3$CHCH$_2$C*H*$_3$), 0.97 (t, $J=7.3$ Hz, 3H, CH$_3$CHCH$_2$C*H*$_3$), 1.10–1.32 (m, 3H, CH$_3$C*H*CH$_2$CH$_3$), 1.41–1.81 (m, 3H, CH$_3$C*H*CH$_2$CH$_3$), 2.14 (s, 3H, NC*H*$_3$), 2.31 (s, 3H, NC*H*$_3$), 2.52–2.68 (m, 2H, C*H*CH$_2$OH), 3.36–3.59 (m, 7H, FcC*H*$_2$N+C*H*$_2$OH), 3.74 (d, $J=13.0$ Hz, 1H, FcCH*H*N), 4.04 (s, 5H, Cp′), 4.07 (m, 1H, Cp), 4.15 (m, 1H, Cp), 4.18 (m, 1H, Cp). MS: $m/z=512$ (MH^++K), 496 (MH^++Na), 470, 342, 213. Anal. calcd for $C_{26}H_{44}FeN_2O_2$: C, 66.09; H, 9.38; N, 5.93. Found: C, 66.28; H, 9.45; N, 6.07%.

4.5.12. (*S*)-Bis[*N*-(1-*tert*-butyl-2-hydroxy)ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine 29. A mixture of amino alcohol **23** (0.1 g) and 37% aqueous solution of formaldehyde (170 μL) in MeOH (10 mL) was stirred under reflux for 30 min. The mixture was treated with H_2O (20 mL), extracted with CH_2Cl_2 (3×20 mL) and dried over Na_2SO_4. After evaporation of the solvent, the residue was dissolved in anhydrous THF (10 mL) and added dropwise to a suspension of $LiAlH_4$ (0.034 g, 0.9 mmol) in THF (20 mL). The mixture was refluxed under nitrogen for 5 h. The solution was cooled to room temperature, quenched by the addition of a saturated aqueous ammonium chloride solution and extracted with Et_2O (3×30 mL). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography to give (*S*)-bis[*N*-(1-*tert*-butyl-2-hydroxy)ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine **29** as a yellow oil (59 mg, 56%).

$[\alpha]_D^{20}=-5.6$ (*c* 1.25, $CHCl_3$). ^1H NMR ($CDCl_3$), δ 1.01 (s, 9H, $C(CH_3)_3$), 1.02 (s, 9H, $C(CH_3)_3$), 2.38 (s, 3H, NCH_3), 2.47 (s, 3H, NCH_3), 2.54–2.61 (m, 2H, $CHCH_2OH$), 3.52–3.60 (m, 4H, CH_2OH), 3.72 (d, $J=$ 13.3 Hz, 1H, $FcCH_2N$), 3.83 (s, 2H, $FcCH_2N$), 3.92 (d, $J=13.3$ Hz, 1H, $FcCH_2N$), 4.04 (s, 5H, Cp′), 4.07 (m, 1H, Cp), 4.22 (m, 2H, Cp). MS: $m/z=511$ (M^++K), 495 (M^++Na), 469, 342. Anal. calcd for $C_{26}H_{44}FeN_2O_2$: C, 66.09; H, 9.32; N, 5.93. Found: C, 66.13; H, 9.47; N, 5.85%.

4.5.13. (1*S*,2*R*)-Bis[*N*-(2-hydroxy-1-methyl-2-phenyl)-ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine 30. Following the general procedure starting from amino alcohol **24** (100 mg, 0.19 mmol), (1*R*,2*S*)-bis[*N*-(2-hydroxy-1-methyl-2-phenyl)ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine **30** was obtained as a yellow oil (59 mg, 58%). $[\alpha]_D^{20}=+7.6$ (*c* 0.53, $CHCl_3$). ^1H NMR ($CDCl_3$), δ 0.91 (d, $J=7.02$ Hz, 3H, $CHCH_3$), 0.94 (d, $J=6.9$ Hz, 3H, $CHCH_3$), 2.15 (s, 3H, NCH_3), 2.16 (s, 3H, NCH_3), 2.69 (m, 1H, $CHCH_3$), 2.89 (m, 1H, $CHCH_3$), 3.00 (d, $J=12.5$ Hz, 1H, $FcCH_2N$), 3.19 (d, $J=12.7$ Hz, 1H, $FcCH_2N$), 3.97 (d, $J=12.7$ Hz, 1H, $FcCH_2N$), 4.09 (m+s, 6H, $FcCH_2N$+Cp′), 4.23 (m, 3H, Cp), 4.71 (m, 1H, CHPh), 5.27 (m, 1H, CHPh), 7.18–7.43 (m, 10H, Ph). MS: $m/z=579$ (M^++K), 563 (M^++Na), 542 (MH_2^+), 376, 362, 213. Anal. calcd for $C_{32}H_{40}FeN_2O_2$: C, 71.11; H, 7.46; N, 5.18. Found: C, 71.25; H, 7.23; N, 5.25%.

4.6. General procedure for the synthesis of oxazolidine

A mixture of ferrocenedicarboxaldehyde (0.2 g, 0.83 mmol) and (1*S*,2*S*)-pseudoephedrine (0.272 g, 1.65 mmol) in anhydrous CH_2Cl_2 (15 mL) containing molecular sieves (1.5 g, 4 Å) was stirred at room temperature for 10 h. The molecular sieves was separated by filtration and the solvent was evaporated under reduced pressure. The oxazolidine was used in the next step without further purification.

4.6.1. Oxazolidine 17. Following the general procedure starting from ferrocene-1,1′-dicarboxaldehyde **1**, the oxazoline **29** was obtained as an oil. ^1H NMR ($CDCl_3$), δ 1.17 (d, $J=6.0$ Hz, 6H, $CH(CH_3)$), 2.26 (s, 6H, NCH_3), 2.44 (qd, $J=6.0$ and 8.7 Hz, 2H, $CH(CH_3)$), 4.25 (m, 4H, Cp), 4.37 (m, 2H, Cp), 4.46 (m, 2H, Cp), 4.65 (d, $J=8.7$ Hz, 2H, CHPh), 4.98 (s, 2H, FcCHNO), 7.29–7.48 (m, 10H, Ph).

4.6.2. Oxazolidine 31. Following the general procedure starting from the ferrocene-1,2-dicarboxaldehyde **2**, the oxazoline **31** was obtained as an oil. ^1H NMR ($CDCl_3$), δ 1.13 (d, $J=6.0$ Hz, 3H, $CHCH_3$), 1.17 (d, $J=6.0$ Hz, 3H, $CHCH_3$), 2.22 (s, 3H, NCH_3), 2.38 (m+s, 5H, $CHCH_3$+NCH_3), 4.21 (m, 1H, Cp); 4.25 (m, 1H, Cp), 4.30 (s, 5H, Cp′), 4.50 (m, 1H, Cp), 4.61 (d, $J=8.5$ Hz, 1H, CHPh), 4.64 (d, $J=8.5$ Hz, 1H, CHPh), 4.92 (s, 1H, NCHO), 5.34 (s, 1H, FcCHNO), 7.26–7.47 (m, 10H, Ph).

4.7. Reduction of oxazolidine

A solution of oxazolidine in anhydrous THF (30 mL) was added dropwise to a suspension of $LiAlH_4$ (0.125 g, 3.3 mmol) in THF (20 mL). The mixture was refluxed under nitrogen for 5 h. The solution was cooled to room temperature, quenched by the addition of a saturated aqueous ammonium chloride solution and extracted with Et_2O (3×30 mL). The solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography.

4.7.1. (1*S*,2*S*)-Bis[*N*-(2-hydroxy-1-methyl-2-phenyl)-ethyl-*N*-methyl]-1,1′-ferrocenylmethyldiamine 18. Following the general procedure starting from the oxazolidine **17**, (1*S*,2*S*) - bis - [*N* - (2 - hydroxy - 1 - methyl - 2-phenyl)ethyl-*N*-methyl-]-1,1′-ferrocenylmethyldiamine **18** was obtained as yellow crystals (290 mg, 65%). Mp 117°C. $[\alpha]_D^{20}=+86.2$ (*c* 0.28, $CHCl_3$). ^1H NMR ($CDCl_3$), δ 0.73 (d, $J=6.6$ Hz, 6H, $CH(CH_3)$), 2.19 (s, 6H, NCH_3), 2.70 (qd, $J=6.6$ and 9.6 Hz, 2H, $CH(CH_3)$), 3.33 (d, $J=12.8$ Hz, 2H, FcCHHN), 3.56 (d, $J=12.8$ Hz, 2H, FcCHHN), 4.11–4.19 (m, 8H, Cp), 4.21 (d, $J=9.6$ Hz, 2H, CHPh), 7.24–7.32 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$): $\delta=7.61$, 35.38, 53.73, 64.45, 68.76, 69.01, 70.28, 70.45, 74.66, 84.65, 127.38, 127.65, 128.20, 142.10. MS: $m/z=579$ (M^++K), 563 (M^++Na), 376, 298. Anal. calcd for $C_{32}H_{40}FeN_2O_2$: C, 71.11; H, 7.46; N, 5.18. Found: C, 71.07; H, 7.10; N, 4.95%.

4.7.2. (1*S*,2S)-Bis[*N*-(2-hydroxy-1-methyl-2-phenyl)-ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine 32. Following the general procedure starting from oxazolidine **31**, (1*S*,2*S*)-bis[*N*-(2-hydroxy-1-methyl-2-phenyl)ethyl-*N*-methyl]-1,2-ferrocenylmethyldiamine **32** was obtained as a yellow oil (107 mg, 24%). $[\alpha]_D^{20}=+50.0$ (*c* 0.24, $CHCl_3$). ^1H NMR ($CDCl_3$), δ 0.73 (d, $J=6.8$ Hz, 3H, $CHCH_3$), 0.75 (d, $J=6.8$ Hz, 3H, $CHCH_3$), 2.16 (s, 3H, NCH_3), 2.31 (s, 3H, NCH_3), 2.89–2.92 (m, 2H, $CHCH_3$), 3.41 (d, $J=13.0$ Hz, 1H, FcCHHN), 3.49 (d, $J=12.7$ Hz, 1H, FcCHHN), 3.92 (d, $J=12.7$ Hz, 1H, FcCHHN), 4.05 (d, $J=13.0$ Hz, 1H, FcCHHN), 4.16 (m+s, 6H, Cp+Cp′), 4.21 (m, 1H, Cp), 4.29 (m, 1H, Cp), 4.38 (d, $J=6.1$ Hz, 1H, CHPh), 4.41 (d, $J=6.1$ Hz, 1H, CHPh), 7.22–7.35 (m, 10H, Ph). MS: $m/z=$ 579 (M^++K), 563 (M^++Na), 541 (MH^+), 376, 213. Anal. calcd for $C_{32}H_{40}FeN_2O_2$: C, 71.11; H, 7.46; N, 5.18. Found: C, 70.92; H, 7.5; N, 5.37%.

4.8. General procedure for the condensation of diethylzinc on benzaldehyde

Aldehyde (1.1 mmol), chiral amino alcohol complex (0.11 mmol) and toluene (5 mL) were placed in a schlenk tube with a valve and gas inlet. Diethylzinc (2.2 mL, 2.2 mmol, 1 M in hexane) was injected to the reaction mixture via syringe. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by GC. Aqueous HCl (1N, 10 mL) was added to quench the reaction. The mixture was extracted with Et_2O (3×20 mL). The organic layer was washed with brine, dried over Na_2SO_4 and evaporated under vacuum. The residue was purified by column chromatography.

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