SYNTHESIS AND CATALYTIC ACTIVITY OF SPACED FERROCENE OXAZOLINES

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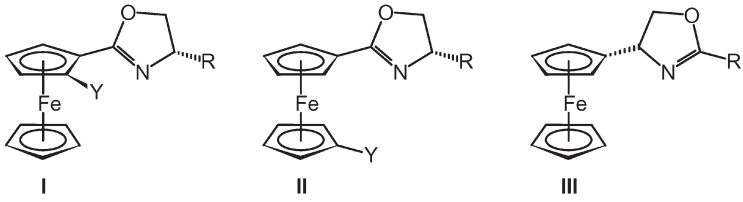
Received April 14, 2003
Accepted May 12, 2003

Chiral 2-[{*N*-aryl-*N*-(ferrocenylmethyl)amino}methyl]-4-(1-methylethyl)-4,5-dihydroxazoles with various substituents at the aryl ring were prepared by alkylation of *N*-(ferrocenylmethyl)anilines, $FcCH_2NHC_6H_4R$ (Fc = ferrocenyl), with (*S*)-2-(chloromethyl)-4-(1-methylethyl)-4,5-dihydrooxazole. The oxazoles, substituted anilines, and the precursors of the latter, the respective Schiff bases $FcCH{=}NC_6H_4R$, were characterized by standard methods and further studied by mass spectrometry. The oxazoles were further tested as chiral auxiliaries in the addition of diethylzinc to benzaldehyde but showed only negligible asymmetric induction (ee *ca* 10%), most likely due to steric hindrance of the nitrogen donor centres. This steric restriction seems to be lowered upon replacement of the substituted phenyl group with a benzyl substituent; compounds $FcCH_2NHCH_2Ph$ and (*R*)-$FcCH_2NHCH(Me)Ph$ are easily alkylated yielding $[FcCH_2NMe_2(CH_2Ph)]I$ (**9**) and 2-[{*N*-(1-phenylethyl)-*N*-(ferrocenylmethyl)amino}methyl]-4-(1-methylethyl)-4,5-dihydroxazole (**10**), respectively. Solid-state structures of $FcCH_2NHC_6H_4R$ (R = 2-Me and 4-Cl), **9**, and **10** have been determined by single-crystal X-ray diffraction.

Keywords: Oxazolines; Ferrocenes; Mass spectrometry; Organozinc reagents; Enantioselective catalysis; Crystal structure; Chiral ligands; Schiff bases; Imines; Amines; X-ray diffraction.

Chiral 2-ferrocenyl-4,5-dihydrooxazoles (henceforth referred to as corresponding oxazolines) having a functional group on the cyclopentadienyl ring in a position adjacent to the oxazolinyl moiety (type **I**) or on the other ring (type **II**) have been used with success as ligands in a number of catalyzed enantioselective reactions[1]. More recently, the class of ferrocenyloxazoline ligands has been further extended to 4-ferrocenyloxazolines[2]

(type **III**), which also proved to be efficient ligands for asymmetric catalysis, while some non-functionalized ferrocenyloxazolines were used as electrochemical sensors[3].



In addition, substituted 2-ferrocenyloxazolines **I** can be used as excellent starting materials for the preparation of planar-only chiral ferrocene compounds as they are readily accessible in stereomerically pure form *via* diastereoselective ortho-lithiation/functionalization of C-chiral oxazolines (**I**, Y = H), and the chiral auxiliary, the oxazoline ring, can be afterwards hydrolyzed and subsequently modified[4,5].

In this contribution, we describe the synthesis of variously substituted, chiral 2-[{*N*-aryl-*N*-(ferrocenylmethyl)amino}methyl]-4-(1-methylethyl)-4,5-dihydroxazoles and of 2-[{*N*-(1-phenylethyl)-*N*-(ferrocenylmethyl)amino}methyl]-4-(1-methylethyl)-4,5-dihydroxazole, in which the additional donor (nitrogen) atom and the oxazoline ring are separated by a methylene group. The ligands possess a chiral centre in position four of the the oxazoline nitrogen atom inherent in (*S*)-valinol, the ferrocene unit acting only as an electron-donating, sterically well-defined stereodiscriminating substituent. We also report catalytic activity of the former ligands in the addition of diethylzinc onto benzaldehyde and discuss the obtained catalytic results with regard to the solid-state structures of several intermediates and ligands, and also some model reactions.

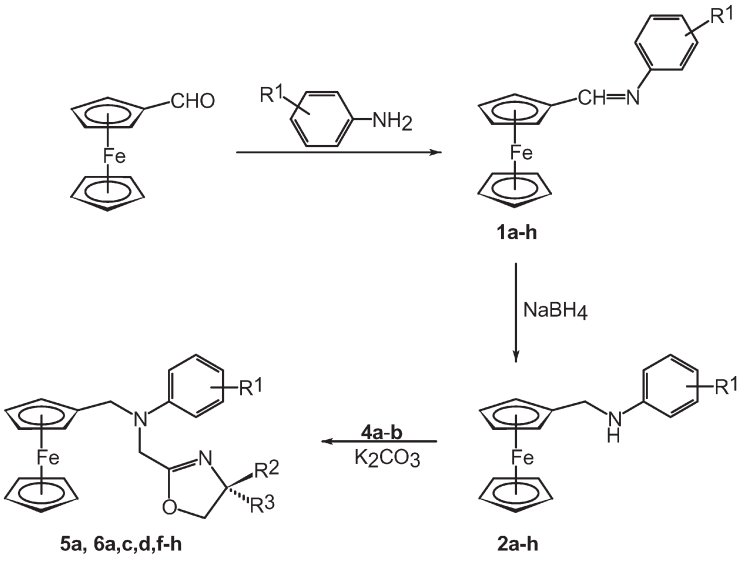
RESULTS AND DISCUSSION

2-[{N-Aryl-N-(ferrocenylmethyl)amino}methyl]-4-(1-methylethyl)-4,5-dihydroxazoles

Synthesis and Characterization

Synthesis of the title compounds bearing various substituent at the aryl and oxazoline rings, **5** and **6**, is outlined in Scheme 1. The starting amines **2** were prepared using an established procedure: by reacting ferrocene-

carboxaldehyde with ring-substituted anilines to give the respective Schiff bases **1** [6] and subsequent reduction of aldimines **1** with $NaBH_4$ in methanol. (Chloromethyl)oxazolines **4** were obtained by condensation of the respective β-aminoalcohols with glycolic acid under azeotropic water removal[7] and chloration of the resulting (hydroxymethyl)oxazolines **3** with

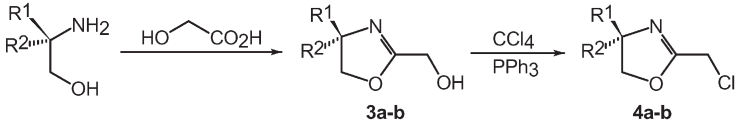


5 (R^2/R^3 = Me_2)
6 (R^2/R^3 = i-Pr/H)

R^1 = H (**a**), 2-Me (**b**), 3-Me (**c**), 4-Me (**d**), 4-MeO (**e**), 4-F (**f**), 4-Cl (**g**), 4-Br (**h**)

SCHEME 1

PPh_3/CCl_4 mixture[8] (Scheme 2). As the last step, oxazolines **5** and **6** were synthesized by alkylation of *N*-(ferrocenylmethyl)anilines **2** with (chloromethyl)oxazolines **4** (Scheme 1).



R^1/R^2 = Me_2 (**a**), H/i-Pr (**b**)

SCHEME 2

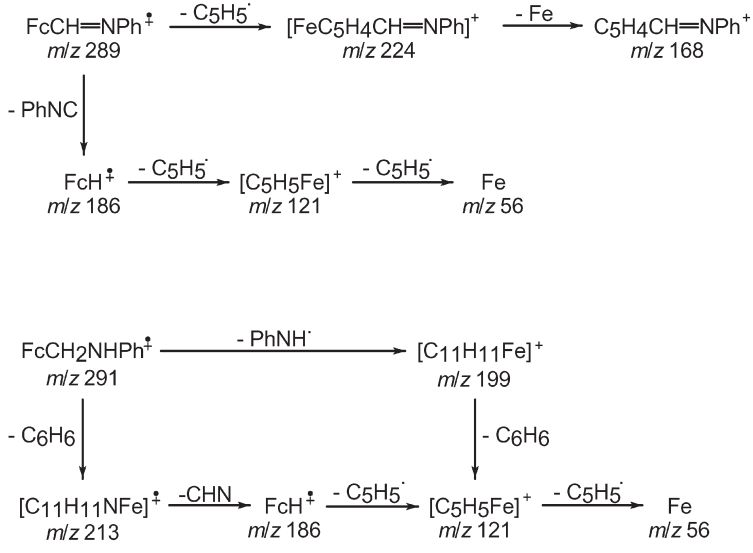
Unfortunately, the molecule-assembling alkylation step proved the most difficult in the reaction sequence. The alkylation of the simplest amine **2a** with non-chiral oxazoline **4a** to give **5a** was initially attempted by reacting the educts in acetonitrile, ethanol or *N*,*N*-dimethylformamide with or without added base (Na_2CO_3, K_2CO_3) at room temperature or by deprotonation of **2a** with LiBu followed by an addition of **4a**. In neither case, however, the alkylated product was detected by thin-layer chromatography, MS and NMR spectra. Finally, the alkylation reaction was effected by heating a **2a**–**4a** mixture (1:2 molar ratio) without a solvent in the presence of solid K_2CO_3 (excess) for 36 h to 100 or 150 °C (temperature in bath) under argon. Oxazolines **5** and **6** were then obtained using a similar procedure: a mixture of amine **2**, oxazoline **4** (2 equiv.) and K_2CO_3 (3 equiv.) was heated under argon to 80–90 °C for 48 h. The reaction produces complex mixtures from which the oxazolines were isolated by repeated column chromatography; only compounds **5**, and **6a**, **6c**, **6d**, **6f**–**6h** could be isolated in pure form. The reluctance of amines **2** to undergo the *N*-alkylation can be ascribed to steric factors, particularly to bulkiness of the substituents at the nitrogen atoms and possibly also to the presence of the conjugated electron-withdrawing aryl group (see below).

All compounds were characterized by spectral methods (NMR, IR and mass spectra) and elemental analysis (either standard or from high-resolution mass spectra). The Schiff bases, which were obtained as dark orange solids, exhibited typical strong band due to the $\nu_{C=N}$ stretching at *ca* 1620 cm^{-1} in their IR and signals due to the aldimine moiety at δ_H *ca* 8.3, δ_C *ca* 160 in the NMR spectra. Amines **2** are yellow solids, showing broad ν_{NH} bands in IR spectra and a broad resonance of the NH proton at δ_H 3.5–3.9 in ^1H NMR spectra. The incorporation of the oxazoline unit to form oxazolines **5** and **6** is best indicated by the ^{13}C NMR resonance of the pivotal carbon within the oxazoline ring at δ_C *ca* 164. Additionally, the presence of a chiral centre in **6** makes all ferrocene CH groups and the methylene protons, which are observed as degenerate (enantiotopic) signals in the case of the amines and Schiff bases, non-equivalent (diastereotopic).

Mass Spectrometry

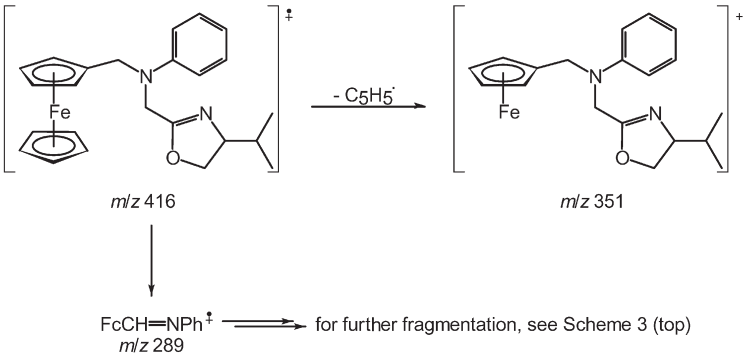
All the three series of compounds (Schiff bases, amines and oxazolines) were studied by mass spectrometry. As shown in Scheme 3 (top) for **1a**, molecular ions of Schiff bases ($\mathbf{1}^{\bullet+}$) decompose by either successive elimination of cyclopentadienyl radical ($\mathbf{1a}^{\bullet+} \rightarrow$ *m*/*z* 224) and the iron atom (*m*/*z* 224 $\rightarrow$ 168), or by an elimination of PhNC molecule to give ferrocene ion radical

(*m/z* 186), which fragments by a consecutive loss of its two cyclopentadienyl rings. The fragmentation of the amines, demonstrated for **2a** in Scheme 3 (bottom) is different: the molecular ion $\mathbf{2a}^{\bullet+}$ eliminates benzene molecule ($\mathbf{2a}^{\bullet+} \rightarrow$ *m/z* 213) or an aniline radical $PhNH^{\bullet}$ to give ferrocenylmethyl cation (or a product of its rearrangement; $\mathbf{2a}^{\bullet+} \rightarrow$ *m/z* 199). The former fragmentation route continues by a loss of HCN molecule to give ferrocene ion radical which fragments as given above. Thus, the two pathways virtually merge at the fragment ion $[FeC_5H_5]^+$ (*m/z* 121).



SCHEME 3
The prominent fragmenation processes for Schiff bases **1** (top) and the respective amines **2** (bottom)

Oxazolines **5** and **6** (see Scheme 4 for fragmenation of **6a**) fragment upon electron impact by a loss of the unsubstituted cyclopentadienyl ring, a cleavage of the C–N bond to produce ions at *m/z* 199 due to $[FcCH_2]^+$ or an isomeric species, or give rise to ions isobaric with the respective Schiff base by a formal elimination of the corresponding 2-methyloxazoline from the molecular ions $\mathbf{6}^{\bullet+}$. The ions isobaric with $\mathbf{1}^{\bullet+}$, which dominate the spectra of oxazolines **5** and **6**, further fragment as mentioned above for Schiff bases **1** and, hence, are most likely structurally similar to those originating from ionization of the Schiff bases.

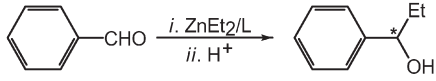


SCHEME 4
Fragmentation scheme of oxazolines **5** and **6** (shown for **6a**)

Catalysis

Since its discovery[9], enantioselective addition of diorganylzinc reagents to aldehydes has become an established tool for the synthesis of chiral secondary alcohols[10] and numerous ferrocene ligands[11], including functionalized ferrocenyloxazolines[11b–11e], were successfully used as chiral catalysts in this reaction.

Testing chiral oxazolines **6** as chiral auxiliaries (2.5 mole %) in addition of diethylzinc to benzaldehyde (Table I, Scheme 5) revealed that com-



SCHEME 5

TABLE I
Addition of diethylzinc to benzaldehyde[a]

Entry	Ligand	Yield, %	Enanatiomer ratio[b]
1	**6c**	36	55:45
2	**6d**	47	54:46
3	**6g**	62	55:45
4	**6h**	73	56:44

[a] For conditions, see Experimental. Alkylation in the presence of ligands **6a** and **6f** gave under the same conditions only dark intractable mixtures which contained no 1-phenylpropan-1-ol according to GC MS analysis. [b] Determined by GC MS analysis after converting to diastereomeric (–)-menthoxycarbonyl esters (see Experimental). Configuration was not assigned due to a very low asymmetric induction.

pounds **6c**, **6d**, **6g**, and **6h** exhibit only negligible asymmetric induction, whilst **6a** and **6f** gave under identical conditions intractable mixtures containing no 1-phenylpropan-1-ol according to GC-MS analysis. The observed poor catalytic activity of the oxazolines contrasts sharply with the previous reports about a very high efficiency of chiral, functionalized ferrocenyloxazolines in this reaction[6,11] and most likely reflects a hindered accessibility of the donor nitrogen atoms, in accordance with difficulties encountered in the alkylation of amines **2** (see above).

Structure Determination for **2b** and **2g**

Structures of amines **2b** and **2g** were determined by single-crystal X-ray diffraction. The molecular structures are shown in Figs 1 and 2 and the selected geometric data are reported in Tables II and III. The structures show no unexpected features, the individual bond and angles comparing well with those reported for the unsubstituted amine $FcCH_2NHPh$; *cf.* C(Fc)–C(11) 1.508(5), N–CH_2 1.438(4), and N–C(Ph) 1.387(4) Å [12].

Amine **2b** crystallizes with two crystallographically independent molecules within the triclinic unit cell. The molecules show nearly identical bond distances and angles but differ slightly in the mutual orientation of

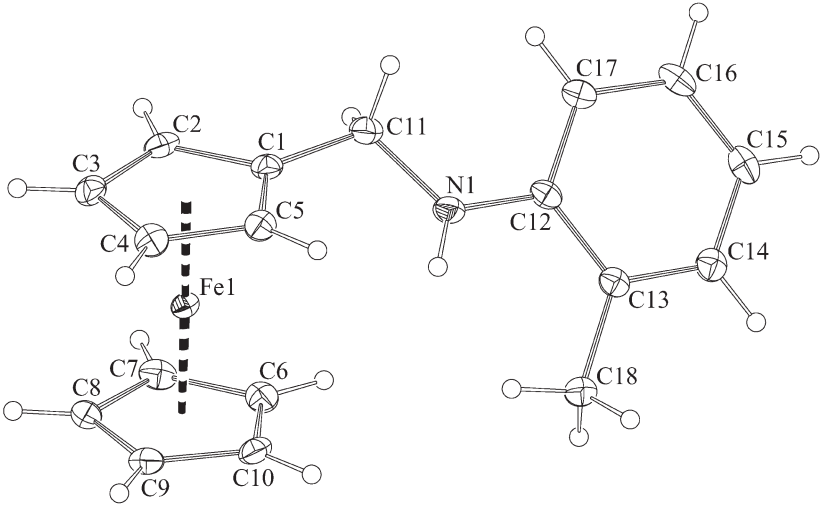


FIG. 1
A view of the molecular structure of **2b**, molecule 1 showing the thermal motion ellipsoids at the 30% probability level and the atom labelling scheme

the phenyl and substituted cyclopentadienyl planes. The dihedral angle of the respective least-squares planes are 52.9(2) (44.7(2)°) for molecules 1 (2). As indicated by the torsion angles τ(C(Ar)–N–CH_2–C(Fc)) of 176.9(2) (–173.6(3)°),

TABLE II
Selected bond lengths (Å), bond angles and dihedral angles (°) for **2b**

Molecule 1		Molecule 2	
N1–C11	1.457(3)	N2–C31	1.446(3)
N1–C12	1.389(3)	N2–C32	1.382(3)
C01–C11	1.500(4)	C21–C31	1.497(3)
C13–C18	1.505(4)	C33–C38	1.506(4)
C11–N1–C12	120.4(2)	C31–N2–C32	123.2(2)
N1–C11–C01	110.9(2)	N2–C31–C21	110.6(2)
N1–C12–C13	119.4(2)	N2–C32–C33	119.2(2)
N1–C12–C17	121.6(2)	N2–C32–C37	121.9(2)
Fe–C(Cp) av.	2.047(6)		2.045(5)
C–C(Cp) av.	1.421(5)		1.421(6)
C–C(Ph) av.	1.39(1)		1.39(1)
C–C–C(Cp) av.	108.0(3)		108.0(3)
C–C–C(Ph) av.	120(1)		120(1)

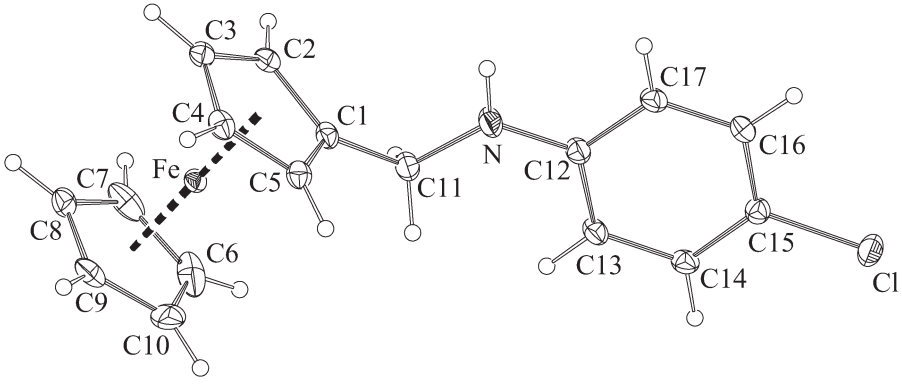


FIG. 2
The molecular structure of amine **2g** drawn with 30% thermal motion ellipsoids

the ferrocenyl and phenyl substituents adopt an antiperiplanar configuration, similar to the arrangement of amine $FcCH_2NHPh$ (*cf.* τ = 179.4(3)°, interplanar angle 35.9(2)°). The ferrocene cyclopentadienyls in **2b** exhibit only insignificant tilts (interplanar angles 3.2(2) (1.0(2)°)) and are bonded

TABLE III
Selected bond lengths (Å), bond angles and dihedral angles (°) for **2g**

C1–C11	1.498(2)	C2–C1–C11	126.9(2)
N–C11	1.455(2)	C5–C1–C11	125.7(2)
N–C12	1.375(2)	N–C11–C1	109.2(1)
Cl–C15	1.749(2)	C11–N–C12	123.8(2)
N–C12–C13	122.8(2)	Cl–C15–C14	119.8(1)
N–C12–C17	119.2(2)	Cl–C15–C16	119.1(1)
Fe–C(Cp) av.	2.040(7)	C–C–C(Cp) av.	108.0(6)
C–C(Cp) av.	1.42(1)	C–C–C(Ph) av.	120(1)
C–C(Ph) av.	1.39(1)		

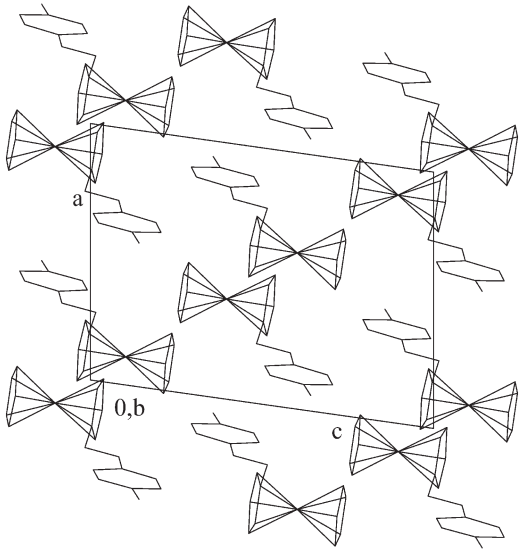


FIG. 3
Solid state packing of **2b** as viewed along the crystallographic *b* axis

at identical iron–ring distances Fe–Cg1 1.651(1) (1.651(1) Å), and Fe–Cg2 1.653(2) (1.649(2) Å) (Cg denotes the respective cyclopentadienyl-ring centroid).

As far as bond lengths and angles are concerned, the structure of amine **2g** does not differ much from $FcCH_2NHPh$ and **2b**. The cyclopentadienyl planes are tilted at an angle of 2.02(4)° and the iron-ring centroid distances are Fe–Cg(1) 1.6433(8) and Fe–Cg(2) 1.6477(9) Å. The molecule, however, differs slightly from the reference compounds in conformation. The arene and the substituted cyclopentadienyl planes are nearly perpendicular (dihedral angle 85.08(6)°) and the configuration at the $N–CH_2$ bond slightly departs from antiperiplanar towards anticlinal (τ = 164.1(2)°).

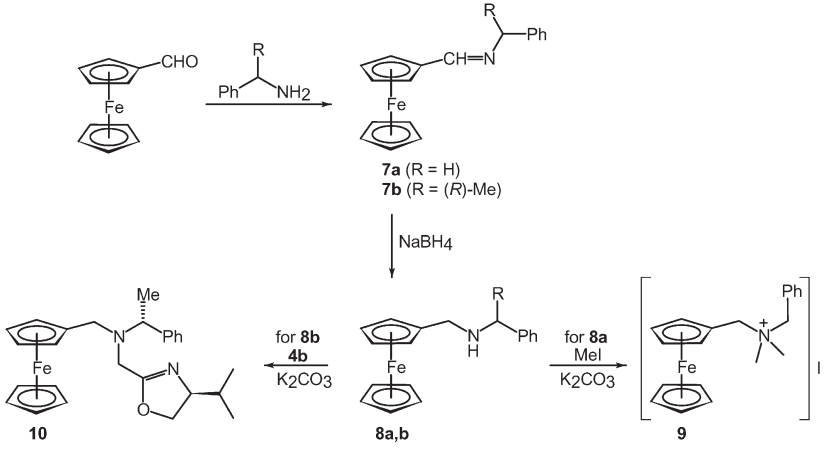
The solid-state packings of **2b** and **2g** are molecular without any apparent involvement of the NH groups in hydrogen bonding. In both cases, however, the molecular assembly is aided with offset π–π interactions of the phenyl rings and weak C–H···π-ring interactions. In the case of amine **2g**, the molecules are oriented so that the exactly parallel phenyl rings are stacked into tilted columns at ring centroid distances of 5.850(1) Å and interplanar separation of 3.71 Å (Fig. 3). A similar interaction is observed also for **2b** though with even closer contancts: ring centroid distance 5.541(2) Å, interplanar separation 3.03 Å.

2-[{N-Benzyl-N-(ferrocenylmethyl)amino}methyl]oxazolines

In order to prove our assumption that the steric inaccessibility of the nitrogen atom in amines **2** hampers the alkylation reaction and, more importantly, results in the very low catalytic efficiency of oxazolines **5** and **6**, we have synthesized benzyl(ferrocenylmethyl)amines **8a**, **8b** and further converted to ammonium salt **9** and oxazoline **10**, respectively (Scheme 6), which were characterized by X-ray crystallography (see below).

Schiff bases **7** and amines **8** were obtained using the procedures described for the preparation of **1** and **2**. The IR and NMR spectra of **7** and **8** correspond well to the spectra of compounds **1** and **2**; however, the compounds differ in the mass spectra. The Schiff bases **7a** and **7b** fragment by a loss of a $[C_5H_6]$ fragment (possibly $[C_5H_5 + H]$) or the corresponding benzyl cations ($[C_7H_7]^+$ and $[C_7H_7Me]^+$ for **7a** and **7b**, respectively) from the molecular ions. Furthermore, the spectra show abundant signals due to "$[FcCH_2]^+$", Fc^+ (rather than $[FcH]^{\bullet+}$, see above), Fe^+, and the benzyl cations (*m/z* 91 and 105, respectively). Whereas the fragmentation pathways observed for Schiff bases **7a** and **7b** are similar, the initial fragmentation steps of amines **8a** and **8b** differ. The molecular ions fragment, respectively, by a loss of a

cyclopentadiene molecule (**8b**$^{\bullet+}$ → *m/z* 253) or $[C_5H_7]^{\bullet+}$ (likely $C_5H_6 + H^+$; **8a**$^{\bullet+}$ → *m/z* 238), and an elimination of benzyl cation (**8b**$^{\bullet+}$ → *m/z* 214) or benzyl cation together with two hydrogen atoms (**8a**$^{\bullet+}$ → *m/z* 212). The other important ionic species ($PhCH_2^+$ for **8a**; $PhCH(Me)^+$, $PhH^{\bullet+}$ and Ph^+ for **8b**) and the ferrocene fragments ("$[FcCH_2]^+$", $[FcH]^{\bullet+}$, $[FeC_5H_5]^+$, and Fe^+) are common to both spectra.



SCHEME 6

Subsequent akylation of **7a** with excess MeI in the presence of K_2CO_3 smoothly afforded the doubly methylated ammonium salt **9** in virtually quantitative yield. Oxazoline **10** was obtained by alkylation of **7b** with **4b** in the presence of a base as given above. In electron-impact mass spectra, the molecular ion **10**$^{\bullet+}$ eliminates a cyclopentadienyl radical (→ *m/z* 379), $PhCH(Me)^+$ cation (→ *m/z* 339) or the oxazoline substituent together with one hydrogen atom (→ *m/z* 317). The latter process generates ions isobaric with [**7b**]$^{\bullet+}$, which fragment similarly to the ions resulting by ionization of the Schiff base.

Crystal Structures of **9** and **10**

The structure of ammonium salt **9** is shown in Fig. 4 and the selected geometric parameters are listed in Table IV. Compared to the solid-state structure of an analogous amine, $FcCH_2NHCH_2(C_6H_4Me\text{-}4)$[13], compound **9** exhibits slightly longer N–C distances and, in accordance with a complete substitution of the nitrogen atom, the C–N–C angles less different from the values expected for an ideal tetrahedral environment. The solid-state packing of **9** is molecular.

TABLE IV
Selected interatomic distances (Å) and angles (°) for **9** [a]

Fe–Cg1	1.6442(9)	N–C11	1.537(2)
Fe–Cg2	1.654(1)	N–C12	1.498(2)
C1–C11	1.487(3)	N–C13	1.503(3)
C14–C15	1.503(3)	N–C14	1.535(3)
Cp1,Cp2	2.7(1)	N–C11–C1	113.9(2)
Ph,Cp1	56.9(1)	N–C14–C15	113.8(2)
C–N–C[b]	106.7(1)–110.5(2)		

[a] Cp1, Cp2 are the cyclopentadienyl rings C1–C5 and C6–C10, respectively. Cg1 and Cg2 denote the corresponding ring centroids. [b] The range of C–N–C angles.

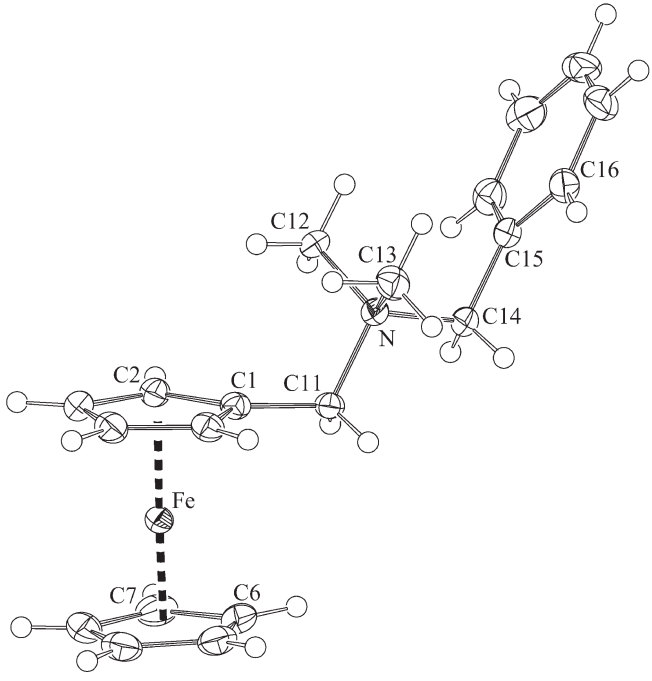


FIG. 4
A view of the cation in the structure of **9** with 30% thermal motion ellipsoids

The molecular structure of oxazoline **10** is shown in Fig. 5, while the selected distances and angles are given in Table V. The Flack parameter (Table VI) corroborates the unchanged configuration of the chiral centres originating from (*R*)-1-phenylethylamine and (*S*)-valinol. The side chain in **10** is nearly perpendicular to the ferrocene unit and so are both rings at its termini (*cf.* the dihedral angles: Ph *vs* Cp(1) 82.9(1)°, Ox *vs* Cp(1) 79.5(1)°, and Ox *vs* Ph 10.0(1)°). The nitrogen atoms are located at the more open side of the chain in a pocket defined by the ferrocenylmethyl, isopropyl and 1-phenylethyl groups. The oxazoline ring is very nearly planar with the deviations of the ring atoms from their least-squares plane lower than 0.05 Å. The distances and angles within the ring do not deviate in any significant way from the values reported for other ferrocenyloxazolines[14]. The solid-state arrangement of **10** is essentially molecular; there are no contacts shorter than the sum of van der Waals radii between the molecules within the crystal.

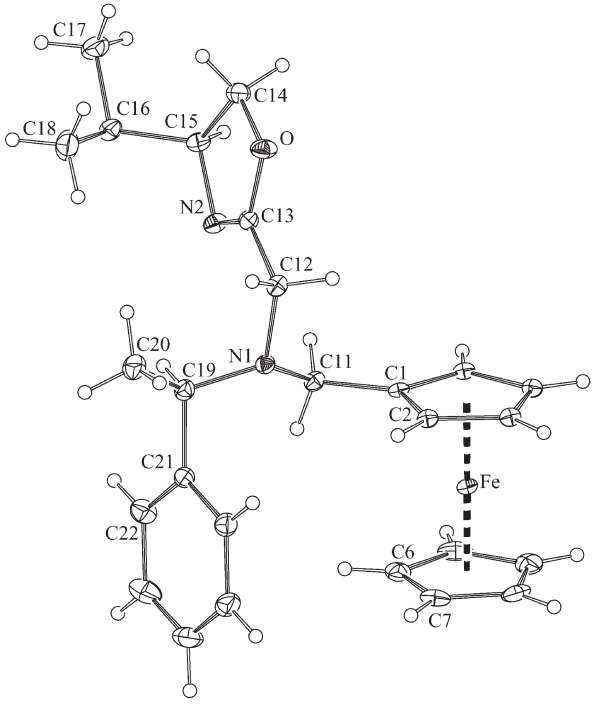


FIG. 5
The molecular structure of oxazoline **10**. The thermal motion ellipsoids correspond to the 30% probability level

Conclusions

We have demonstrated a novel approach to chiral oxazoline ligands bearing the ferrocenyl group as a substituent. Unfortunately, the preparation of chiral ferrocenyloxazolines **6** suffers from difficulties in the molecule-assembling step and the resulting oxazolines are nearly inactive as chiral auxiliaries in the addition of diethylzinc to benzaldehyde. This was tentatively ascribed to steric bulk of amines **2** and oxazolines **5** and **6**, which hinders the alkylation reaction and prevents effective encounters between the substrate, reagent, and oxazoline catalyst. As demonstrated by alkyl-

TABLE V
Selected bond lengths (Å) and angles (°) for **10** [a]

Fe–Cg1	1.6573(9)	Cp1,Cp2	0.6(1)
Fe–Cg2	1.649(1)		
C1–C11	1.518(3)	C1–C11–N1	111.2(2)
C11–N1	1.465(2)	C11–N1–C12	111.6(2)
N1–C19	1.474(2)	C11–N1–C19	112.9(2)
C19–C20	1.531(3)	C12–N1–C19	117.1(2)
C19–C21	1.520(2)	N1–C19–C20	111.1(2)
N1–C12	1.453(3)	N1–C19–C21	108.3(1)
C12–C13	1.502(3)	N1–C12–C13	117.6(2)
C13–O	1.369(2)	N2–C13–O	118.1(2)
O–C14	1.449(3)	C13–O–C14	105.6(2)
C14–C15	1.530(3)	O–C14–C15	104.4(2)
C15–N2	1.486(3)	C14–C15–N2	104.2(2)
N2–C13	1.268(3)	C15–N2–C13	106.9(2)
C15–C16	1.543(3)	C17–C16–C18	111.3(2)
C16–C17	1.529(3)	N2–C15–C16	110.3(2)
C16–C18	1.523(4)	C14–C15–C16	116.2(2)
C1–C11–N1–C12	–72.2(2)		
C1–C11–N1–C19	153.5(2)		
C11–N1–C19–C20	–176.9(2)		

[a] Cp1, Cp2 denote the cyclopentadienyl rings C1–C5 and C6–C10, respectively. Cg1 and Cg2 are the respective ring centroids.

TABLE VI
Crystallographic data, data collection and structure refinement for **2b**, **2g**, **9**, and **10**

Compound	**2b**	**2g**	**9**[d]	**10**[e]
Formula	$C_{18}H_{19}FeN$	$C_{17}H_{16}ClFeN$	$C_{20}H_{24}FeIN$	$C_{29}H_{31}FeN_2O$
M	305.19	325.61	461.15	886.76
Crystal size, mm^3	0.15 × 0.25 × 0.30	0.23 × 0.25 × 0.28	0.10 × 0.25 × 0.45	0.08 × 0.13 × 0.40
Crystal description	orange plate	orange brown prism	yellow block	orange prism
T, K	150	150	150	150
Crystal sysytem	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (No.2)	$P2_1/n$ (No.14)	$P2_1/n$ (No.14)	$P2_1$ (No.4)
a, Å; α, °	7.7849(2); 98.130(1)	9.6200(2); 90	13.3448(2); 90	12.8117(4); 90
b, Å; β, °	9.8259(2); 93.099(1)	11.4929(2); 98.047(1)	10.8758(1); 113.1278(8)	5.7114(1); 99.639(1)
c, Å; γ, °	20.6333(5); 111.935(1)	13.0030(3); 90	13.7043(2); 90	15.3260(5); 90
V, $Å^3$; *Z*	1439.50(6); 4	1423.48(5); 4	1829.13(4); 4	1105.61(5); 2
D_c, g ml^{-1}	1.408	1.519	1.675	1.332
F(000); μ(MoKα), mm^{-1}	640; 1.036	672; 1.234	920; 2.511	470; 0.702
θ_{max}, °; completeness, %	26.0; 98.9	27.5; 99.7	27.9; 99.6	27.5; 99.5
Collected diffractions	20 807	27 152	32 147	19 577
No. of unique diffractions	5630	3271	4360	5018
No. of observed diffractions[a]	4801	2972	4031	4747
No. of parameters	361	245	304	270
R, *wR* observed; diffractions, %[b]	3.84, 9.82	2.76, 6.87	2.48, 6.30	3.06, 6.87
R, *wR* all data, %[b]	4.82, 10.4	3.26, 7.22	2.77, 6.45	3.38, 7.01
S all data[c]	1.086	1.108	1.065	1.060
Residual electron density, e $Å^{-3}$	0.71, –0.64	0.32, –0.40	1.15, –1.06	0.62, –0.33

[a] Diffractions with $F_o > 4\sigma(F_o)$. [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{1/2}$. [c] $S = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$. [d] The data were corrected for absorption using a numerical routine (SORTAV) incorporated in the diffractometer software. Transmission coefficient range: 0.541–0.785. [e] Flack's enantiomorph parameter: 0.01(1).

ation reactions of amines **8**, the difficulties in the synthesis can be circumvented by an introduction of a methylene (or analogous) spacer between the nitrogen atom and the phenyl group. This indicates a direction for a further work.

EXPERIMENTAL

All syntheses were carried under argon blanket with exclusion of the direct daylight. Toluene and xylene were dried by standing with potassium metal and distilled under argon. Methanol was dried with sodium and freshly distilled. Halogenated solvents (CCl_4, $CHCl_3$, CH_2Cl_2) were dried over anhydrous potassium carbonate. Solvents for crystallizations and chromatography were used without purification. Other chemicals were used as obtained from commercial sources.

NMR spectra were recorded on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95; ^{13}C, 100.58 MHz) at 298 K. Chemical shifts (δ, ppm) are given relative to internal tetramethylsilane, coupling constants (*J*) are given in Hz. NMR signals were assigned with the aid of ^{1}H,^{1}H-COSY, ^{13}C APT, ^{13}C gHSQC and ^{13}C gHMBC experiments. For clarity, the symbol Ox indicates an oxazolinyl moiety (*e.g.*, in i-PrOx, Me_2Ox); CH_2Ox thus denotes the methylene group attached *to* the oxazoline ring while CH^{Ox} and CH_2^{Ox} stand for the methine and methylene groups, respectively, *within* the ring. IR spectra (ν, cm^{-1}) were recorded on an FT IR Nicolet Magna 650 instrument in the range of 400–4000 cm^{-1}. Melting points were determined on a Kofler apparatus and are uncorrected.

Electron ionization mass spectra were recorded on a VG 7070E spectrometer (conditions: electron energy 80 eV, ion source temperature 200 °C). The samples were introduced *via* a direct insertion probe. Accurate mass (HR MS) measurements were performed by the peak matching technique using perfluorokerosene as the internal mass scale standard. GC MS were performed on a Finnigan MAT INCOS 50 mass spectrometer interfaced to a Varian 3400 gas chromatograph (SPB-5 capillary column, He carried gas). The mass spectra were acquired at ionizing electron energy 70 eV.

Synthesis of Schiff Bases **1a**–**1h**. General Procedure

Ferrrocenecarboxaldehyde and the appropriate aniline (molar ratio 1:1) were dissolved in dry toluene (50 ml). Catalytic amount of K_2CO_3 (5–10 mg) was added, the reaction vessel was flushed with argon, and the mixture was refluxed under Dean–Stark trap for 24 h. Then, the reaction mixture was treated with 4 Å molecular sieves (*ca* 25 ml, beads 8–12 mesh) while hot and stirring was continued at room temperature for 48 h. Filtration and evaporation under reduced pressure afforded the corresponding Schiff base in pure form.

FcCH=NPh (**1a**). Starting from FcCHO (4.92 g, 23 mmol) and aniline (2.10 ml, 23 mmol), the general procedure gave **1a** as an orange solid (4.07 g, 91%). EI MS, *m/z* (relative abundance): 290 (21), 289 (100, $M^{\bullet+}$), 288 (8), 287 (9), 224 (27, $[M - C_5H_5]^+$), 223 (12), 222 (8), 214 (11), 198 (9), 196 (5), 186 (21, $[FcH]^{\bullet+}$), 184 (6), 168 (16, $[M - C_5H_5Fe]^+$), 167 (10), 141 (9), 129 (8), 121 (31, $[C_5H_5Fe]^+$), 115 (7), 97 (5), 95 (7), 85 (5), 83 (5), 81 (7), 77 (15, Ph^+), 73 (9), 71 (7), 70 (30), 69 (8), 65 (4), 60 (9), 57 (12), 56 (34, Fe^+). IR (Nujol): 1620 (s), 1585 (s), 1466 (vs), 1252 (m), 1169 (m), 1103 (m), 1005 (m), 820 (m), 766 (s), 695 (s), 513 (m), 496 (s), 485 (m). For NMR data see ref.[12]

FcCH=NC$_6$H$_4$Me-2 (**1b**). Starting from FcCHO (5.79 g, 27 mmol) and *o*-toluidine (2.89 ml, 27 mmol), the general procedure afforded **1b** as an orange solid (5.59 g, 68%). M.p. 106–108 °C (ref.[6c] 122–126 °C). ^{1}H NMR ($CDCl_3$): 2.33 (s, 3 H, Me), 4.23 (s, 5 H, C_5H_5), 4.47, 4.80 (2 × apparent t, 2 H, C_5H_4); 6.82–7.22 (m, 4 H, C_6H_4), 8.21 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$): 17.84 (Me), 68.96 (CH, C_5H_4), 69.27 (C_5H_5), 71.07 (CH, C_5H_4), 80.75 (C_{ipso}, C_5H_4), 117.96, 124.87, 126.71, 130.14 (CH, C_6H_4); 130.89, 152.18 (C_{ipso}, C_6H_4); 160.44 (CH=N). EI MS, *m/z* (relative abundance): 304 (22), 303 (100, $M^{\bullet+}$), 302 (12), 301 (22), 238 (24, $[M - C_5H_5]^+$), 237 (17), 236 (7), 235 (8), 212 (5), 208 (7), 186 (31, $[FcH]^{\bullet+}$), 184 (5), 182 (9, $[M - C_5H_5Fe]^+$), 181 (9), 180 (11), 165 (6), 121 (25, $[C_5H_5Fe]^+$), 92 (13), 91 (64, $[C_7H_7]^+$), 65 (15), 56 (32, Fe^+). IR (Nujol): 1626 (vs), 1591 (s), 1248 (m), 1218 (m), 1180 (m), 1111 (m), 1105 (s), 1040 (s), 967 (m), 824 (s), 806 (m), 754 (vs), 731 (s), 498 (s), 485 (s). For $C_{18}H_{17}FeN$ (302.4) calculated: 71.30% C, 5.66% H, 4.62% N; found: 71.50% C, 5.83% H, 4.42% N.

FcCH=NC$_6$H$_4$Me-3 (**1c**). Starting from FcCHO (1.99 g, 9.3 mmol) and *m*-toluidine (1.00 ml, 9.3 mmol), the procedure as above gave **1c** as an orange solid (2.26 g, 80%). M.p. 54–56 °C. ^{1}H NMR ($CDCl_3$): 2.38 (s, 3 H, Me), 4.23 (s, 5 H, C_5H_5), 4.46, 4.78 (2 × apparent t, 2 H, C_5H_4); 6.92–7.27 (m, 4 H, C_6H_4), 8.31 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$): 21.43 (Me), 69.00 (CH, C_5H_4), 69.24 (C_5H_5), 71.19 (CH, C_5H_4), 80.50 (C_{ipso}, C_5H_4), 117.55, 121.39, 125.94, 128.91 (CH, C_6H_4); 138.86, 152.85 (C_{ipso}, C_6H_4); 161.02 (CH=N). EI MS, *m/z* (relative abundance): 304 (19), 303 (100, $M^{\bullet+}$), 302 (12), 301 (10), 238 (26, $[M - C_5H_5]^+$), 237 (14), 236 (5), 214 (8), 212 (15), 186 (10, $[FcH]^{\bullet+}$), 184 (8), 182 (11), 180 (7), 152 (5), 152 (5), 129 (9), 121 (41, $[C_5H_5Fe]^+$), 92 (7), 91 (22, $[C_7H_7]^+$), 65 (13), 57 (7), 56 (31, Fe^+). IR (Nujol): 1620 (vs), 1582 (vs), 1462 (vs), 1238 (m), 1152 (m), 1107 (m), 1043 (m), 1003 (m), 930 (m), 820 (s), 783 (s), 695 (s), 514 (m), 502 (s), 484 (s). For $C_{18}H_{17}FeN$ (302.4) calculated: 71.30% C, 5.66% H, 4.62% N; found: 70.91% C, 5.57% H, 4.48% N.

FcCH=NC$_6$H$_4$Me-4 (**1d**). Starting from FcCHO (5.56 g, 26 mmol) and *p*-toluidine (2.81 g, 26.2 mmol), compound **1d** was obtained as an orange solid (7.16 g, 91%). M.p. 87–89 °C (ref.[6c] 130–132 °C). ^{1}H NMR ($CDCl_3$): 2.35 (s, 3 H, Me), 4.23 (s, 5 H, C_5H_5), 4.46, 4.78 (2 × apparent t, 2 H, C_5H_4); 7.06, 7.16 (2 × d, 2 H, C_6H_4); 8.32 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$): 20.96 (Me), 68.97 (CH, C_5H_4), 69.23 (C_5H_5), 71.16 (CH, C_5H_4), 80.58 (C_{ipso}, C_5H_4), 120.49, 129.70 (CH, C_6H_4); 134.88, 150.30 (C_{ipso}, C_6H_4); 160.57 (CH=N). EI MS, *m/z* (relative abundance): 304 (26), 303 (100, $M^{\bullet+}$), 302 (14), 301 (10), 239 (6), 238 (31, $[M - C_5H_5]^+$), 237 (17), 236 (5), 212 (9), 211 (5), 210 (10), 186 (11, $[FcH]^{\bullet+}$), 182 (10, $[M - C_5H_5Fe]^+$), 181 (9), 155 (5), 154 (5), 153 (6), 152 (5), 129 (7), 121 (15, $[C_5H_5Fe]^+$), 92 (6), 91 (17, $[C_7H_7]^+$), 83 (5), 73 (13), 71 (9), 69 (8), 65 (11), 60 (10), 57 (14), 56 (28, Fe^+). IR (Nujol): 1618 (vs), 1591 (vs), 1509 (s), 1326 (m), 1250 (m), 1188 (m), 1106 (s), 1044 (s), 1024 (s), 1003 (s), 818 (vs), 635 (m), 527 (m), 519 (m), 513 (m), 487 (vs), 478 (vs). For $C_{18}H_{17}FeN$ (302.4) calculated: 71.30% C, 5.66% H, 4.62% N; found: 71.42% C, 5.69% H, 4.57% N.

FcCH=NC$_6$H$_4$OMe-4 (**1e**). Using the general procedure, FcCHO (5.24 g, 24.5 mmol) and *p*-anisidine (3.02 g, 24.5 mmol) gave **1e** as an orange solid (7.40 g, 95%). M.p. 105–107 °C. ^{1}H NMR ($CDCl_3$): 3.81 (s, 3 H, OMe), 4.23 (s, 5 H, C_5H_5), 4.45, 4.78 (2 × apparent t, 2 H, C_5H_4); 6.87–7.17 (m, 4 H, C_6H_4), 8.32 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$): 55.48 (OMe), 68.85 (CH, C_5H_4), 69.20 (C_5H_5), 71.06 (CH, C_5H_4), 80.76 (C_{ipso}, C_5H_4), 114.34, 121.68 (CH, C_6H_4); 145.94, 157.61 (C_{ipso}, C_6H_4); 159.58 (CH=N). EI MS, *m/z* (relative abundance): 320 (23), 319 (100, $M^{\bullet+}$), 318 (6), 317 (8), 304 (12, $[M - Me]^+$), 254 (12, $[M - C_5H_5]^+$), 253 (8), 239 (7, $[M - Me - C_5H_5]^{\bullet+}$), 238 (6), 198 (5, $[M - C_5H_5Fe]^+$), 186 (12, $[FcH]^{\bullet+}$), 184 (5), 160 (7), 155 (6), 154 (7), 149 (6), 129 (9), 128 (5), 121 (30, $[C_5H_5Fe]^+$), 97 (5), 85 (5), 83 (7), 81 (7), 77 (5), 73 (13), 71 (8), 70 (4), 69 (14), 60 (9), 57 (18), 56 (24, Fe^+). IR (Nujol): 1618 (vs), 1593 (m),

1577 (m), 1505 (vs), 1464 (vs), 1441 (m), 1291 (m), 1244 (vs), 1187 (m), 1104 (m), 1030 (s), 833 (vs), 822 (s), 784 (m), 523 (m), 504 (m), 481 (m). For $C_{18}H_{17}FeNO$ (302.4) calculated: 67.72% C, 5.38% H, 4.39% N; found: 67.77% C, 5.43% H, 4.36% N.

FcCH=NC$_6$H$_4$F-4 (**1f**). Starting from FcCHO (2.00 g, 9.3 mmol) and *p*-fluoroaniline (0.86 ml, 9.1 mmol), the procedure as above afforded **1f** as an orange solid (2.02 g, 71%). M.p. 96–98 °C. ^{1}H NMR ($CDCl_3$): 4.24 (s, 5 H, C_5H_5), 4.48, 4.78 (2 × apparent t, 2 H, C_5H_4); 7.02–7.13 (m, 4 H, C_6H_5), 8.30 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$): 69.03 (CH, C_5H_4), 69.27 (C_5H_5), 71.33 (CH, C_5H_4), 80.33 (C_{ipso}, C_5H_4), 115.8 (d, $^2J_{FC}$ = 22, CH, C_6H_4), 121.9 (d, $^3J_{FC}$ = 8, CH, C_6H_4); 149.00 (d, $^4J_{FC}$ = 3, CN, C_6H_4), 160.80 (d, $^1J_{CF}$ = 243, CF, C_6H_4); 161.3 (CH=N). EI MS, *m/z* (relative abundance): 308 (22), 307 (100, $M^{\bullet+}$), 306 (9), 305 (7), 242 (12, $[M - C_5H_5]^+$), 241 (17), 240 (5), 216 (7), 214 (9), 187 (6), 186 (57, $[M - C_5H_5Fe]^+$ and $[FcH]^{\bullet+}$), 185 (9), 184 (16), 166 (6), 149 (8), 141 (7), 140 (11), 139 (17), 129 (13), 128 (6), 122 (5), 121 (47, $[C_5H_5Fe]^+$), 119 (5), 115 (7), 111 (6), 109 (5), 97 (12), 95 (13), 85 (8), 83 (11), 82 (5), 81 (11), 81 (5), 77 (5), 75 (5), 73 (15), 71 (16), 70 (7), 69 (18), 67 (7), 65 (12), 60 (13), 57 (22), 56 (49, Fe^+). IR (Nujol): 1622 (vs), 1502 (s), 1209 (s), 1186 (s), 1104 (m), 1090 (m), 1047 (m), 833 (s), 820 (m), 808 (m), 791 (s), 536 (m), 500 (s), 479 (s). For $C_{17}H_{14}FFeN$ (306.4) calculated: 66.47% C, 4.60% H, 4.56% N; found: 66.32% C, 4.59% H, 4.40% N.

FcCH=NC$_6$H$_4$Cl-4 (**1g**). Starting from FcCHO (6.49 g, 30.3 mmol) and *p*-chloroaniline (3.82 g, 30 mmol), the general procedure gave **1g** as an orange solid (7.98 g, 81%). M.p. 98–100 °C. ^{1}H NMR ($CDCl_3$): 4.24 (s, 5 H, C_5H_5), 4.50, 4.78 (2 × apparent t, 2 H, C_5H_4); 7.04–7.34 (m, 4 H, C_6H_4), 8.30 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$): 69.11 (CH, C_5H_4), 69.31 (CH, C_5H_5), 71.48 (CH, C_5H_4), 80.11 (C_{ipso}, C_5H_4), 121.91, 129.16 (CH, C_6H_4); 130.60, 151.36 (C_{ipso}, C_6H_4); 161.85 (CH=N). EI MS, *m/z* (relative abundance): 325 (19), 324 (13), 323 (57, $M^{\bullet+}$), 258 (11, $[M - C_5H_5]^+$), 257 (7), 232 (6), 214 (19), 202 (4, $[M - C_5H_5Fe]^+$), 187 (7), 186 (55, $[FcH]^{\bullet+}$), 184 (9), 167 (13), 166 (11), 140 (6), 139 (11), 129 (6), 121 (38, $[C_5H_5Fe]^+$), 115 (5), 94 (5), 93 (6), 92 (49), 91 (100), 81 (6), 69 (8), 65 (14), 63 (8), 60 (5), 57 (10), 56 (32, Fe^+). IR (Nujol): 1617 (vs), 1579 (m), 1491 (m), 1464 (vs), 1252 (m), 1213 (m), 1172 (m), 1107 (m), 1008 (m), 841 (m), 830 (s), 822 (s), 522 (m), 515 (m), 501 (s), 480 (m), 437 (m). For $C_{17}H_{14}ClFeN$ (322.8) calculated: 63.09% C, 4.37% H, 4.33% N; found: 63.37% C, 4.62% H, 4.19% N.

FcCH=NC$_6$H$_4$Br-4 (**1h**). Starting from FcCHO (2.00 g, 9.3 mmol) and *p*-bromoaniline (1.31 g, 7.6 mmol), the general procedure gave **1h** as an orange solid (1.95 g, 57%). M.p. 113–115 °C. ^{1}H NMR ($CDCl_3$): 4.24 (s, 5 H, C_5H_5), 4.50, 4.78 (2 × apparent t, 2 H, C_5H_4); 6.98–7.49 (m, 4 H, C_6H_4), 8.30 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$): 69.13 (CH, C_5H_4), 69.32 (C_5H_5), 71.50 (CH, C_5H_4), 80.11 (C_{ipso}, C_5H_4), 118.39 (CBr, C_6H_4), 122.33, 132.11 (CH, C_6H_4); 151.86 (C_{ipso}, C_6H_4), 161.88 (CH=N). EI MS, *m/z* (relative abundance): 367 (4, $M^{\bullet+}$), 214 (27), 186 (19, $[FcH]^{\bullet+}$), 184 (5), 149 (5), 129 (9), 121 (28, $[C_5H_5Fe]^+$), 115 (5), 97 (8), 95 (6), 92 (22), 91 (47), 85 (10), 83 (12), 82 (5), 81 (14), 77 (5), 73 (17), 71 (14), 70 (7), 69 (21), 67 (6), 65 (10), 61 (5), 60 (18), 57 (31), 56 (37, Fe^+). IR (Nujol): 1691 (m), 1616 (vs), 1577 (s), 1490 (s), 1464 (vs), 1412 (m), 1251 (m), 1212 (s), 1172 (s), 1107 (s), 1072 (s), 1044 (m), 1024 (m), 1005 (s),846 (m), 821 (vs), 634 (m), 514 (s), 498 (s), 480 (s). For $C_{17}H_{14}BrFeN$ (367.3) calculated: 55.47% C, 3.84% H, 3.81% N; found: 56.07% C, 3.93% H, 3.36% N.

Synthesis of Amines **2a**–**2h**. General Procedure

Solid $NaBH_4$ (4 molar equiv.) was slowly added into an ice-cooled solution of Schiff bases **1a**–**1h** in dry MeOH (25 ml) with stirring (in air). After stirring for 1 h, aqueous 1 M NaOH solution (30 ml) was added and the product was extracted into chloroform (3 × 50 ml). Drying of the combined organic phase ($MgSO_4$) followed by evaporation under vacuum afforded pure amines **2a**–**2h**.

FcCH$_2$NHPh (**2a**). Starting from **1a** (1.74 g, 6 mmol) and $NaBH_4$ (0.91 g, 24 mmol), the general procedure gave **2a** as a yellow solid (1.28 g, 73%). EI MS, *m/z* (relative abundance): 292 (9), 291 (45, $M^{\bullet+}$), 213 (7, $[M - PhH]^{\bullet+}$), 200 (18), 199 (100, $[C_{11}H_{11}Fe]^+$), 198 (4), 197 (8), 186 (11, $[FcH]^{\bullet+}$), 122 (5), 121 (52, $[C_5H_5Fe]^+$), 93 (24, $[PhNH_2]^{\bullet+}$), 92 (14), 91 (17), 85 (20), 83 (26), 77 (7), 69 (9), 66 (7), 65 (7), 57 (5), 56 (27, Fe^+). HR MS: for $C_{17}H_{17}FeN$ calculated 291.0710, found 291.0690. IR (Nujol): 3401 (s), 1604 (s), 1505 (s), 1428 (s), 1331 (m), 1317 (s), 1255 (m), 1180 (m), 1105 (s), 999 (m), 866 (m), 826 (m), 808 (m), 748 (s), 693 (s), 491 (s). For other characterization data see ref.[12]

FcCH$_2$NHC$_6$H$_4$Me-2 (**2b**). Starting from **1b** (0.91 g, 3 mmol) and $NaBH_4$ (0.46 g, 12.2 mmol), the general procedure gave **2b** as a yellow solid (0.83 g, 92%). ^{1}H NMR ($CDCl_3$): 2.20 (s, 3 H, Me), 3.81 (s, 1 H, NH), 3.97 (s, 2 H, CH_2), 4.17 (apparent t, 2 H, C_5H_4), 4.20 (s, 5 H, C_5H_5), 4.28 (apparent t, 2 H, C_5H_4), 6.65–7.19 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$): 17.57 (Me), 42.99 (CH_2), 67.87, 67.93 (CH, C_5H_4); 68.48 (C_5H_5), 86.70 (C_{ipso}, C_5H_4), 109.71, 117.02 (CH, C_6H_4); 121.68 (C_{ipso}, C_6H_4), 127.23, 130.09 (CH, C_6H_4); 146.19 (C_{ipso}, C_6H_4). EI MS, *m/z* (relative abundance): 306 (6), 305 (30, $M^{\bullet+}$), 200 (12), 199 (100, $[C_{11}H_{11}Fe]^+$), 197 (6), 161 (4), 121 (37, $[C_5H_5Fe]^+$), 106 (5), 91 (4), 69 (4), 56 (17, Fe^+). HR MS: for $C_{18}H_{19}FeN$ calculated 305.0867, found 305.0874. IR (Nujol): 3416 (s), 1605 (s), 1582 (m), 1514 (s), 1503 (s), 1444 (m), 1314 (m), 1260 (m), 1133 (m), 1104 (s), 1025 (m), 1002 (m), 924 (m), 830 (m), 815 (m), 749 (s), 495 (m), 487 (m), 444 (m).

FcCH$_2$NHC$_6$H$_4$Me-3 (**2c**). Starting from **1c** (1.57 g, 5.2 mmol) and $NaBH_4$ (1.12 g, 30 mmol), the general procedure gave **2c** as a yellow solid (1.43 g, 90%). ^{1}H NMR ($CDCl_3$): 2.30 (s, 3 H, Me), 3.82 (s, 1 H, NH), 3.94 (s, 2 H, CH_2), 4.14 (apparent t, 2 H, C_5H_4), 4.18 (s, 5 H, C_5H_5), 4.24 (apparent t, 2 H, C_5H_4), 6.45–7.12 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$): 21.64 (Me), 43.36 (CH_2), 67.85, 68.07 (CH, C_5H_4); 68.47 (C_5H_5), 86.59 (C_{ipso}, C_5H_4), 109.98, 113.57, 118.46, 129.15 (CH, C_6H_4); 139.06, 148.35 (C_{ipso}, C_6H_4). EI MS, *m/z* (relative abundance): 306 (8), 305 (37, $M^{\bullet+}$), 227 (6), 200 (15), 197 (6), 121 (39, $[C_5H_5Fe]^+$), 107 (3), 106 (4), 91 (5), 83 (4), 69 (5), 57 (4), 56 (15, Fe^+). HR MS: for $C_{18}H_{19}FeN$ calculated 305.0867, found 305.0885. IR (Nujol): 3410 (vs), 1603 (s), 1588 (m), 1509 (s), 1306 (s), 1256 (m), 1166 (m), 1104 (m), 992 (m), 926 (m), 817 (s), 775 (s), 693 (m), 505 (m), 487 (m).

FcCH$_2$NHC$_6$H$_4$Me-4 (**2d**). Starting from **1d** (1.82 g, 6 mmol) and $NaBH_4$ (0.91 g, 24 mmol), the general procedure gave **2d** as a yellow solid (1.70 g, 93%). ^{1}H NMR ($CDCl_3$): 2.25 (s, 3 H, Me), 3.73 (s, 1 H, NH), 3.93 (s, 2 H, CH_2), 4.12 (apparent t, 2 H, C_5H_4), 4.16 (s, 5 H, C_5H_5), 4.23 (apparent t, 2 H, C_5H_4), 6.56–7.03 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$): 20.41 (Me), 43.75 (CH_2), 67.82, 68.07 (CH, C_5H_4); 68.45 (C_5H_5), 86.69 (C_{ipso}, C_5H_4), 113.03 (CH, C_6H_4), 126.72 (C_{ipso}, C_6H_4), 129.75 (CH, C_6H_4), 146.10 (C_{ipso}, C_6H_4). EI MS, *m/z* (relative abundance): 306 (6), 305 (29, $M^{\bullet+}$), 227 (3), 200 (13), 197 (5), 186 (9, $[FcH]^{\bullet+}$), 121 (42, $[C_5H_5Fe]^+$), 106 (5), 91 (5), 69 (3), 56 (14, Fe^+). HR MS: for $C_{18}H_{19}FeN$ calculated 305.0867, found 305.0854. IR (Nujol): 3395 (s), 1611 (s), 1521 (vs), 1404 (m), 1317 (s), 1304 (m), 1252 (s), 1185 (m), 1125 (m), 1104 (s), 1034 (m), 820 (m), 811 (m), 522 (m), 511 (s), 499 (m), 483 (s).

$FcCH_2NHC_6H_4OMe$-4 (**2e**). Starting from **1e** (1.92 g, 6 mmol) and $NaBH_4$ (0.91 g, 24 mmol), the general procedure gave **2e** as a yellow solid (1.60 g, 83%). ^{1}H NMR ($CDCl_3$): 3.52 (s, 1 H, NH), 3.74 (s, 3 H, OMe), 3.91 (s, 2 H, CH_2), 4.12 (apparent t, 2 H, C_5H_4), 4.16 (s, 5 H, C_5H_5), 4.22 (apparent t, 2 H, C_5H_4), 6.59–6.82 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$): 44.41 (CH_2), 55.80 (OMe), 67.81, 68.07 (CH, C_5H_4); 68.44 (CH, C_5H_5), 86.66 (C_{ipso}, C_5H_4), 114.19, 114.91 (CH, C_6H_4); 142.61, 152.22 (C_{ipso}, C_6H_4). EI MS, *m/z* (relative abundance): 322 (4), 321 (21, $M^{\bullet+}$), 319 (5), 228 (4), 214 (5), 200 (14), 199 (100, $[C_{11}H_{11}Fe]^+$), 197 (6), 123 (34, $[MeOC_6H_4NH_2]^{\bullet+}$), 121 (48, $[C_5H_5Fe]^+$), 108 (47), 80 (22), 65 (5), 57 (5), 56 (17, Fe^+). HR MS: for $C_{18}H_{19}FeNO$ calculated 321.0816, found 321.0747. IR (Nujol): 3367 (s), 1512 (s), 1408 (m), 1298 (m), 1248 (m), 1233 (s), 1180 (m), 1105 (m), 1037 (m), 1002 (m), 814 (s), 773 (m), 504 (m), 486 (m), 447 (m).

$FcCH_2NHC_6H_4F$-4 (**2f**). Starting from **1f** (1.73 g, 5.63 mmol) and $NaBH_4$ (0.89 g, 24 mmol), the general procedure gave **2f** as a yellow solid (1.63 g, 94%). ^{1}H NMR ($CDCl_3$): 3.75 (s, 1 H, NH), 3.92 (s, 2 H, CH_2), 4.14 (apparent t, 2 H, C_5H_4), 4.18 (s, 5 H, C_5H_5), 4.23 (apparent t, 2 H, C_5H_4), 6.55–6.94 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$): 44.13 (CH_2), 67.94, 68.11 (CH, C_5H_4), 68.50 (CH, C_5H_5), 86.29 (C_{ipso}, C_5H_4), 113.65 (d, $^3J_{FC}$ = 8, CH, C_6H_4), 115.68 (d, $^2J_{FC}$ = 22, CH, C_6H_4), 144.69 (d, $^4J_{FC}$ = 2, CN, C_6H_4), 155.90 (d, $^1J_{FC}$ = 235, CF, C_6H_4). EI MS, *m/z* (relative abundance): 310 (6), 309 (31, $M^{\bullet+}$), 200 (13), 199 (100, $[C_{11}H_{11}Fe]^+$), 197 (6), 186 (3, $[FcH]^{\bullet+}$), 122 (4), 121 (41, $[C_5H_5Fe]^+$), 69 (6), 57 (4), 56 (19, Fe^+). HR MS: for $C_{17}H_{16}FFeN$ calculated 309.0616, found 309.0575. IR (Nujol): 3409 (s), 1604 (m), 1507 (s), 1402 (m), 1314 (m), 1250 (m), 1210 (s), 1154 (m), 1102 (s), 1036 (m), 824 (s), 788 (m), 514 (s), 499 (m), 482 (s).

$FcCH_2NHC_6H_4Cl$-4 (**2g**). Starting from **1g** (1.94 g, 6 mmol) and $NaBH_4$ (0.91 g, 24 mmol), the above procedure afforded **2g** as a yellow solid (1.84 g, 99%). ^{1}H NMR ($CDCl_3$): 3.88 (s, 1 H, NH), 3.92 (s, 2 H, CH_2), 4.15 (apparent t, 2 H, C_5H_4), 4.17 (s, 5 H, C_5H_5), 4.22 (apparent t, 2 H, C_5H_4), 6.54–7.16 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$): 43.51 (CH_2), 67.99, 68.11 (CH, C_5H_4); 68.51 (CH, C_5H_5), 86.00 (C_{ipso}, C_5H_4), 113.85 (CH, C_6H_4), 122.00 (C_{ipso}, C_6H_4), 129.08 (CH, C_6H_4), 146.79 (C_{ipso}, C_6H_4). EI MS, *m/z* (relative abundance): 327 (7), 326 (5), 325 (24, $M^{\bullet+}$), 216 (5), 200 (17), 199 (100, $[C_{11}H_{11}Fe]^+$), 197 (7), 187 (5), 186 (40, $[FcH]^{\bullet+}$), 138 (10), 129 (18), 128 (5), 127 (54), 122 (5), 121 (64, $[C_5H_5Fe]^+$), 100 (6), 99 (5), 95 (5), 92 (14), 91 (7), 85 (23), 83 (5), 83 (45), 81 (8), 71 (6), 69 (16), 65 (25), 64 (5), 63 (7), 57 (12), 56 (40, Fe^+). HR MS: for $C_{17}H_{16}{}^{35}ClFeN$ calculated 325.0321, found 325.0292. IR (Nujol): 3421 (s), 1595 (s), 1499 (s), 1400 (s), 1320 (s), 1248 (m), 1185 (m), 1174 (m), 1119 (m), 1103 (s), 1035 (m), 998 (m), 821 (s), 636 (m), 507 (s), 487 (s), 435 (m).

$FcCH_2NHC_6H_4Br$-4 (**2h**). Following the general procedure, **1h** (1.84 ml, 5 mmol) and $NaBH_4$ (1.37 g, 36 mmol) yielded **2h** as a yellow solid (1.86 g, 99%). ^{1}H NMR ($CDCl_3$): 3.90 (s, 1 H, NH), 3.92 (s, 1 H, CH_2), 4.15 (apparent t, 2 H, C_5H_4), 4.17 (s, 5 H, C_5H_5), 4.22 (apparent t, 2 H, C_5H_4), 6.50–7.29 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$): 43.41 (CH_2), 68.01, 68.11 (CH, C_5H_4); 68.52 (C_5H_5), 85.95 (C_{ipso}, C_5H_4), 109.01 (C_{ipso}, C_6H_4), 114.34, 131.96 (CH, C_6H_4); 147.19 (C_{ipso}, C_6H_4). EI MS, *m/z* (relative abundance): 371 (16, $M^{\bullet+}$), 370 (4), 369 (17), 200 (16), 199 (100, $[C_{11}H_{11}Fe]^+$), 197 (7), 173 (19), 171 (21), 168 (4), 167 (4), 121 (36, $[C_5H_5Fe]^+$), 92 (13), 91 (4), 65 (17), 63 (6), 56 (13, Fe^+). HR MS: for $C_{17}H_{16}{}^{71}BrFeN$ calculated 370.9795, found 370.9814. IR (Nujol): 3407 (s), 1592 (s), 1498 (s), 1312 (s), 1176 (m), 1104 (s), 1070 (m), 998 (s), 832 (m), 808 (s), 508 (m), 495 (s), 485 (s).

Synthesis of (Hydroxymethyl)oxazolines **3**

A solution of glycolic acid and the respective β-aminoalcohol (1 equiv.) in dry xylene was refluxed under Dean–Stark trap for 15 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue distilled under vacuum. The oxazolines were characterized by NMR spectroscopy and directly used in the next step.

Compound **3a**: Yield 12.82 g (50%) at 198 mmol scale; colourless crystalline solid. ^{1}H NMR ($CDCl_3$): 1.30 (s, 6 H, Me), 4.01 and 4.22 (2 × s, 2 H, CH_2), 4.63 (br s, 1 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$): 28.24 (Me), 56.98 (CH_2), 66.69 (CMe_2), 79.82 (CH_2), 166.84 (C=N).

Compound **3b**: Yield 6.28 g (48%) at 92 mmol scale; colourless crystalline solid. $[\alpha]_D^{22}$ –98 (*c* 0.51, EtOH), $[\alpha]_D^{22}$ –60.5 (*c* 0.99, $CHCl_3$). Characterization data were consistent with the literature data[15] ($[\alpha]_D$ –48.5 (*c* 2.0, CH_2Cl_2)).

Conversion of (Hydroxymethyl)oxazolines **3** to (Chloromethyl)oxazolines **4**

Triphenylphosphine (25.2 g, 96 mmol) was added to a solution of oxazoline **3a** (93 mmol) in CCl_4 (90 ml), and the mixture was refluxed under argon for 19 h. After cooling to room temperature, the volatiles were removed under reduced pressure and the semisolid residue was extracted with hexane (5 × 100 ml). The extracts were combined, hexane was evaporated and the residue distilled under vacuum (at *ca* 65 Pa) to give oxazoline **4a**. Oxazoline **4b** was obtained similarly from **3a** (20.0 g, 140 mmol), PPh_3 (37.9 g, 145 mmol) and CCl_4 (150 ml).

Compound **4a**: Yield 9.31 g (54%), colourless liquid. ^{1}H NMR ($CDCl_3$): 1.31 (s, 6 H, Me), 4.05 and 4.09 (2 × s, 2 H, CH_2). Analytical data correspond to those published in ref.[16]

Compound **4b**: Yield 14.6 g (65%), colourless liquid. ^{1}H NMR ($CDCl_3$): 0.90 (d, $^3J_{HH}$ = 6.8, 3 H, CHMe), 0.98 (d, $^3J_{HH}$ = 6.8, 3 H, CHMe), 1.70–1.85 (m, 1 H, $CHMe_2$), 3.93–4.02 (m, 1 H, CH^{Ox}), 4.04–4.39 (m, 2 H, $CH_2{}^{ox}$), 4.12 (s, 2 H, CH_2Cl). $[\alpha]_D^{22}$ –79.6 (*c* 1.1, $CHCl_3$).

Alkylation of Ferroceneamines **2** with Chlorooxazolines **4**. General Procedure

Oxazolines **5** and **6** were synthesized by heating a stirred mixture of amine **1** (1 mmol), oxazoline **4** (2 mmol), and K_2CO_3 (3 mmo) to 80–90 °C (temperature in bath) under an argon atmosphere for 48 h. Then, the dark mixture was cooled to room temperature and extracted into chloroform (3 × 5 ml). The combined extracts were evaporated and the residue was purified by chromatography on silica gel using chloroform as the eluent. The second orange band was collected, evaporated and the residue chromatographed once again on silica gel column with ethyl acetate–hexane (1:1, v/v). Evaporation and drying in vacuum (65 Pa, 60 °C, 1 h) afforded oxazolines **5**, and **6a**, **6c**, **6d**, **6f**–**6h**, respectively, as dark orange oils in the yields not exceeding 30%. In other cases (**6b**, **6e**), intractable dark mixtures were obtained from which no defined product could be isolated.

FcCH$_2$N(CH$_2$Me$_2$Ox)Ph (**5**). ^{1}H NMR ($CDCl_3$): 1.26 (s, 6 H, Me), 3.91 (s, 2 H, CH_2), 4.04 (s, 2 H, CH_2), 4.10 (apparent t, 2 H, C_5H_4), 4.16 (s, 5 H, C_5H_5), 4.22 (apparent t, 2 H, C_5H_4), 4.37 (s, 2 H, CH_2), 6.70–7.24 (m, 5 H, C_6H_5). ^{13}C NMR ($CDCl_3$): 28.31 (Me), 46.85, 50.47 (CH_2); 67.14 (CMe_2^{Ox}), 67.96 (CH, C_5H_4), 68.61 (C_5H_5), 69.21 (CH, C_5H_4), 79.25 (CH_2^{Ox}), 83.94 (C_{ipso}, C_5H_4), 113.42, 117.46, 129.01 (CH, C_6H_5); 148.57 (C_{ipso}, C_6H_5), 163.45 (C_{ipso}^{Ox}). EI MS, *m/z* (relative abundance): 402 (12, $M^{\bullet+}$), 337 (6, $[M - C_5H_5]^+$), 291 (6), 290 (37), 289 (100, [**1a**]$^{\bullet+}$), 287 (7), 224 (5), 204 (18), 200 (8), 199 (52, $[C_{11}H_{11}Fe]^+$), 187 (9), 132 (9), 121

(31, $[C_5H_5Fe]^+$), 106 (20), 105 (11), 104 (10), 77 (12), 56 (11, Fe^+). HR MS: for $C_{23}H_{26}FeN_2O$ calculated 402.1395, found 402.1385.

(S)-FcCH$_2$N(CH$_2$i-PrOx)Ph (**6a**). ^{1}H NMR ($CDCl_3$): 0.86, 0.93 (2 × d, $^3J_{HH}$ = 6.8, 3 H, CH**Me**$_2$); 1.70–1.82 (m, 1 H, C**H**Me$_2$), 3.89–3.98 (m, 2 H, CH_2^{Ox} and CH^{Ox}), 4.08 (bs, 2 H, CH_2Ox), 4.10 (apparent t, 2 H, C_5H_4), 4.16 (s, 5 H, C_5H_5), 4.16–4.24 (m, 3 H, C_5H_4 and CH_2^{Ox}), 4.35, 4.39 (2 × d, $^2J_{HH}$ = 15.4, 1 H, AB system of $FcCH_2$); 6.69–7.24 (m, 5 H, C_6H_5). ^{13}C NMR ($CDCl_3$): 17.98, 18.76 (CH**Me**$_2$); 32.34 (**C**HMe$_2$), 46.53 (CH_2Ox), 50.39 ($FcCH_2$), 67.94 (CH, C_5H_4), 68.62 (C_5H_5), 69.13 (CH, C_5H_4), 70.03 (CH_2^{Ox}), 71.96 (CH^{Ox}), 84.00 (C_{ipso}, C_5H_4), 113.41, 117.44, 129.02 (CH, C_6H_5); 148.54 (C_{ipso}, C_6H_5), 164.81 (C_{ipso}^{Ox}). EI MS, *m/z* (relative abundance): 416 (10, $M^{\bullet+}$), 351 (5, $[M - C_5H_5]^+$), 291 (9), 290 (37), 289 (100, [**1a**]$^{\bullet+}$), 287 (6), 200 (7), 199 (46, $[C_{11}H_{11}Fe]^+$), 187 (10), 121 (29, $[C_5H_5Fe]^+$), 104 (5), 77 (6), 56 (10, Fe^+). HR MS: for $C_{24}H_{28}FeN_2O$ calculated 416.1551, found 416.1552.

(S)-FcCH$_2$N(CH$_2$i-PrOx)(C$_6$H$_4$Me-3) (**6c**). ^{1}H NMR ($CDCl_3$): 0.86 (d, $^3J_{HH}$ = 6.8, 3 H, CH**Me**$_2$), 0.93 (d, $^3J_{HH}$ = 6.7, 3 H, CH**Me**$_2$), 1.70–1.82 (m, 1 H, C**H**Me$_2$), 2.29 (s, 3 H, C_6H_4**Me**), 3.89–3.97 (m, 2 H, CH_2^{Ox} and CH^{Ox}), 4.05, 4.08 (2 × br d, $^2J_{HH}$ = 16.8, 1 H, AB system of CH_2Ox); 4.10 (apparent t, 2 H, C_5H_4), 4.16 (s, 5 H, C_5H_5), 4.17–4.26 (m, 3 H, C_5H_4 and CH_2^{Ox}), 4.34, 4.37 (2 × d, $^2J_{HH}$ = 15.4, 1 H, AB system of $FcCH_2$); 6.50–7.13 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$): 17.98, 18.74 (CH**Me**$_2$); 21.90 (C_6H_4**Me**), 32.32 (**C**HMe$_2$), 46.54 (CH_2Ox), 50.40 ($FcCH_2$), 67.90 (CH, C_5H_4), 68.61 (C_5H_5), 69.13 (CH, C_5H_4), 70.00 (CH_2^{Ox}), 71.93 (CH^{Ox}), 84.17 (C_{ipso}, C_5H_4), 110.60, 114.12, 118.38, 128.87 (CH, C_6H_4); 138.66 (**C**Me, C_6H_4), 148.61 (CN, C_6H_4), 164.94 (C_{ipso}^{Ox}). EI MS, *m/z* (relative abundance): 430 (9, $M^{\bullet+}$), 365 (5, $[M - C_5H_5]^+$), 306 (4), 305 (21), 304 (39), 303 (100, [**1c**]$^{\bullet+}$), 301 (7), 238 (6), 232 (5), 201 (10), 200 (14), 199 (80, $[C_{11}H_{11}Fe]^+$), 196 (5), 121 (38, $[C_5H_5Fe]^+$), 120 (9), 119 (6), 118 (7), 107 (4), 91 (12), 84 (4), 81 (6), 69 (14), 65 (4), 57 (6), 56 (14, Fe^+). HR MS: for $C_{25}H_{30}FeN_2O$ calculated 431.1712, found 431.1707.

(S)-FcCH$_2$N(CH$_2$i-PrOx)(C$_6$H$_4$Me-4) (**6d**). ^{1}H NMR ($CDCl_3$): 0.85 (d, $^3J_{HH}$ = 6.8, 3 H, CH**Me**$_2$), 0.93 (d, $^3J_{HH}$ = 6.7, 3 H, CH**Me**$_2$), 1.71–7.81 (m, 1 H, C**H**Me$_2$), 2.23 (s, 3 H, C_6H_4**Me**), 3.87–3.96 (m, 2 H, CH_2^{Ox} and CH^{Ox}), 4.04 (bs with weak AB satellites, 2 H, CH_2Ox), 4.08 (apparent t, 2 H, C_5H_4), 4.15 (s, 5 H, C_5H_5), 4.13–4.22 (m, 3 H, C_5H_4 and CH_2^{Ox}), 4.31, 4.35 (2 × d, $^2J_{HH}$ = 15.3, 1 H, AB system of $FcCH_2$); 6.72–7.04 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$): 18.02, 18.78 (CH**Me**$_2$); 20.28 (C_6H_4**Me**), 32.37 (**C**HMe$_2$), 46.78 (CH_2Ox), 50.75 ($FcCH_2$), 67.89 (CH, C_5H_4), 68.58 (C_5H_5), 69.18 (CH, C_5H_4), 70.01 (CH_2^{Ox}), 71.95 (CH^{Ox}), 84.05 (C_{ipso}, C_5H_4), 113.89 (CH, C_6H_4), 126.77 (**C**Me, C_6H_4), 129.53 (CH, C_6H_4), 146.47 (CN, C_6H_4), 165.00 (C_{ipso}^{Ox}). EI MS, *m/z* (relative abundance): 430 (9, $M^{\bullet+}$), 365 (4, $[M - C_5H_5]^+$), 305 (12), 304 (38), 303 (100, [**1d**]$^{\bullet+}$), 301 (7), 300 (5), 299 (24), 268 (8), 238 (4), 233 (5), 232 (33), 231 (4), 201 (9), 200 (15), 199 (87, $[C_{11}H_{11}Fe]^+$), 197 (6), 186 (9), 159 (8), 146 (4), 139 (4), 127 (5), 122 (4), 121 (49, $[C_5H_5Fe]^+$), 120 (36), 119 (30), 118 (14), 114 (11), 107 (4), 106 (7), 91 (18), 84 (6), 77 (6), 72 (13), 70 (7), 69 (11), 66 (4), 65 (8), 60 (10), 57 (7), 56 (23, Fe^+). HR MS: for $C_{25}H_{30}FeN_2O$ calculated 431.1712, found 431.1728.

(S)-FcCH$_2$N(CH$_2$i-PrOx)(C$_6$H$_4$F-4) (**6f**). ^{1}H NMR ($CDCl_3$): 0.85 (d, $^3J_{HH}$ = 6.8, 3 H, CH**Me**$_2$), 0.92 (d, $^3J_{HH}$ = 6.8, 3 H, CH**Me**$_2$), 1.70–1.80 (m, 1 H, C**H**Me$_2$), 3.88–3.97 (m, 2 H, CH_2^{Ox} and CH^{Ox}), 3.99, 4.02 (2 × b d, $^2J_{HH}$ = 16.8, 1 H, AB system of CH_2Ox); 4.10 (apparent t, 2 H, C_5H_4), 4.14 (s, 5 H, C_5H_5), 4.15–4.23 (m, 3 H, CH_2^{Ox} and C_5H_4), 4.29, 4.33 (2 × d, $^2J_{HH}$ = 15.1, 1 H, AB system of $FcCH_2$); 6.75–6.94 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$): 17.97, 18.71 (CH**Me**$_2$); 32.33 (**C**HMe$_2$), 47.10 (CH_2Ox), 51.41 ($FcCH_2$), 68.01 (CH, C_5H_4), 68.61 (CH, C_5H_5), 69.20 (CH, C_5H_4), 70.01 (CH_2^{Ox}), 71.95 (CH^{Ox}), 83.51 (C_{ipso}, C_5H_4), 115.25 (d, $^2J_{FC}$ = 11.0, CH, C_6H_4), 115.40 (d, $^3J_{FC}$ = 4.0, CH, C_6H_4), 145.19 (d, $^4J_{FC}$ = 1.8, CN, C_6H_4), 156.02

(d, $^1J_{FC}$ = 237, CF, C_6H_4), 163.61 (C_{ipso}^{Ox}). EI MS, *m/z* (relative abundance): 434 (10, $M^{\bullet+}$), 369 (5, $[M - C_5H_5]^+$), 309 (6), 308 (34), 307 (100), 305 (6), 242 (3), 205 (7), 200 (8), 199 (52, $[C_{11}H_{11}Fe]^+$), 197 (3), 186 (3), 127 (5), 122 (4), 121 (31, $[C_5H_5Fe]^+$), 114 (3), 95 (3), 84 (5), 56 (9, Fe^+). HR MS: for $C_{24}H_{27}FFeN_2O$ calculated 434.1457, found 434.1454.

(S)-FcCH$_2$N(CH$_2$i-PrOx)(C$_6$H$_4$Cl-4) (**6g**). ^{1}H NMR ($CDCl_3$): 0.86 (d, $^3J_{HH}$ = 6.7, 3 H, CH**Me**$_2$), 0.93 (d, $^3J_{HH}$ = 6.8, 3 H, CH**Me**$_2$), 1.70–1.80 (m, 1 H, C**H**Me$_2$), 3.90–3.98 (m, 2 H, CH_2^{Ox} and CH^{Ox}), 4.05 (bs, 2 H, CH_2Ox), 4.11 (apparent t, 2 H, C_5H_4), 4.16 (s, 5 H, C_5H_5), 4.15–4.23 (m, 3 H, CH_2^{Ox} and C_5H_4), 4.32, 4.35 (2 × d, $^2J_{HH}$ = 15.2, 1 H, AB system of $FcCH_2$); 6.72–7.17 (m, 4 H, C_6H_5). ^{13}C NMR ($CDCl_3$): 17.98, 18.74 (CH**Me**$_2$); 32.33 (**C**HMe$_2$), 46.67 (CH_2Ox), 50.68 (CH_2Fc), 68.06 (CH, C_5H_4), 68.66 (C_5H_5), 69.05 (CH, C_5H_4), 70.10 (CH_2^{Ox}), 71.97 (CH_2^{Ox}), 83.56 (C_{ipso}, C_5H_4), 114.59 (CH, C_6H_4), 122.25 (C_{ipso}, C_6H_4), 128.90 (CH, C_6H_4), 147.10 (C_{ipso}, C_6H_4), 164.36 (C_{ipso}^{Ox}). EI MS, *m/z* (relative abundance): 450 (6, $M^{\bullet+}$), 326 (8), 325 (28), 324 (21), 323 (59, [**1g**]$^{\bullet+}$), 321 (4), 300 (4), 299 (20), 283 (6), 268 (7), 254 (19), 253 (10), 252 (53), 251 (6), 214 (7), 209 (7), 200 (17), 199 (100, $[C_{11}H_{11}Fe]^+$), 197 (13), 197 (7), 186 (12), 185 (5), 181 (8), 179 (20), 166 (8), 142 (21), 141 (18), 140 (68), 139 (36), 138 (15), 129 (4), 127 (17), 127 (12), 122 (5), 121 (51, $[C_5H_5Fe]^+$), 114 (29), 113 (5), 111 (12), 105 (5), 84 (14), 78 (5), 77 (11), 75 (8), 72 (15), 70 (15), 69 (20), 66 (6), 65 (6), 60 (9), 57 (6), 56 (28, Fe^+). HR MS: for $C_{24}H_{27}ClFeN_2O$ calculated 450.1161, found 450.1149.

(S)-FcCH$_2$N(CH$_2$i-PrOx)(C$_6$H$_4$Br-4) (**6h**). ^{1}H NMR ($CDCl_3$): 0.85 (d, $^3J_{HH}$ = 6.8, 3 H, CH**Me**$_2$), 0.92 (d, $^3J_{HH}$ = 6.8, 3 H, CH**Me**$_2$), 1.70–1.80 (m, 1 H, C**H**Me$_2$), 3.90–9.97 (m, 2 H, CH^{Ox} and CH_2^{Ox}), 4.04 (bs, 2 H, CH_2Ox), 4.10 (apparent t, 2 H, C_5H_4), 4.15 (s, 5 H, C_5H_5), 4.15–4.23 (m, 3 H, CH_2Ox and C_5H_4), 4.31, 4.34 (2 × d, $^2J_{HH}$ = 15.4, 1 H, AB system of $FcCH_2$); 4.32 (m, 2 H, $FcCH_2$), 6.67–7.30 (m, 4 H, C_6H_4). ^{13}C NMR ($CDCl_3$): 17.99, 18.75 (CH**Me**$_2$); 32.35 (**C**HMe$_2$), 46.61 (CH_2Ox), 50.60 ($FcCH_2$), 68.07 (CH, C_5H_4), 68.67 (C_5H_5), 69.02 (CH, C_5H_4), 70.11 (CH_2^{Ox}), 72.00 (CH^{Ox}), 83.55 (C_{ipso}, C_5H_4), 109.38 (C_{ipso}, C_6H_4), 115.00 (CH, C_6H_4), 131.69 (CH, C_6H_4), 147.50 (C_{ipso}, C_6H_4), 164.30 (C_{ipso}^{Ox}). EI MS, *m/z* (relative abundance): 496 (6, $M^{\bullet+}$), 494 (6), 371 (7), 370 (22), 369 (69, [**1h**]$^{\bullet+}$), 368 (23), 367 (67), 365 (4), 300 (9), 299 (46), 298 (4), 297 (4), 290 (7), 289 (21), 269 (4), 268 (16), 256 (5), 226 (4), 213 (7), 200 (16), 199 (100, $[C_{11}H_{11}Fe]^+$), 197 (6), 197 (7), 187 (6), 186 (18), 185 (5), 184 (6), 148 (4), 129 (4), 127 (11), 122 (6), 121 (68, $[C_5H_5Fe]^+$), 119 (4), 114 (12), 84 (9), 78 (4), 77 (7), 69 (8), 56 (28, Fe^+). HR MS: for $C_{24}H_{27}{}^{79}BrFeN_2O$ calculated 495.0690, found 495.0677.

Addition of Diethylzinc to Benzaldehyde

A solution of $ZnEt_2$ (1.1 ml 1.1 M in toluene, 1.2 mmol) was added to a solution of ligand (0.025 mmol, 2.5 mole %) and PhCHO (1 mmol) in dry toluene (2 ml). The mixture was stirred at room temperature for 72 h and then it was quenched by adding EtOH (5 ml) and 1 M HCl. The mixture was extracted with $CHCl_3$ (3 × 5 ml), the solvent evaporated under reduced pressure and the brown residue purified by chromatography on silicagel column using ethyl acetate–hexane (1:1, v/v) as the eluent. The purified 1-phenylethan-1-ol was immediately mixed with pyridine and (1*R*)-(–)-menthyl chloroformate (molar ratios 1:1.2:1.3) and the mixture was stirred overnight. Enatiomeric purity was then determined by GC analysis of the resulting mixture containing diastereomeric menthoxycarbonyl esters[17]. The results are summarized in Table I.

Synthesis of Schiff Bases **7**. General Procedure

Schiff bases **7** were obtained as given above for **1**. Thus, compound **7a** was obtained as a dark orange solid (5.55 g, 92%) from benzylamine (2.16 ml, 19.8 mmol) and ferrocenecarboxaldehyde (4.24 g, 19.8 mmol) while compound **7b** was isolated as a viscous deep orange oil, which crystallized upon standing (0.83 g, 52%) from FcCHO (1.070 g, 5.0 mmol) and (*R*)-1-phenylethylamine (0.636 ml, 5.0 mmol).

FcCH=NCH$_2$Ph (**7a**)[18]. ^{1}H NMR ($CDCl_3$): 4.17 (s, 5 H, C_5H_5), 4.37 (apparent t, 2 H, C_5H_4), 4.66 (br s, 2 H, CH_2), 4.68 (apparent t, 2 H, C_5H_4), 7.22–7.37 (m, 5 H, Ph), 8.24 (unresolved t, 1 H, CH=N). ^{13}C NMR ($CDCl_3$): 65.13 (CH_2), 68.58 (CH, C_5H_4), 69.06 (C_5H_5), 70.48 (CH, C_5H_4), 80.52 (C_{ipso}, C_5H_4), 126.87, 127.87, 128.48 (CH, Ph); 139.64 (C_{ipso}, Ph), 162.20 (CH=N). EI MS, *m/z* (relative abundance): 304 (22), 303 (100, $M^{\bullet+}$), 301 (7), 237 (14, $[M - C_5H_6]^+$), 212 (10, $[M - PhCH_2]^+$), 211 (8), 208 (6), 199 (16, $[C_{11}H_{11}Fe]^+$), 186 (7, $[FcH]^{\bullet+}$), 185 (9), 159 (4), 146 (7), 133 (4), 129 (14), 121 (37, $[FeC_5H_5]^+$), 91 (18, $[C_7H_7]^+$), 81 (4), 77(5), 65 (7), 56 (36, Fe^+). HR MS: for $C_{18}H_{17}FeN$ calculated 303.0710, found 303.0703. For $C_{18}H_{17}FeN$ (302.4) calculated: 71.31% C, 5.65% H, 4.62% N; found: 71.30% C, 5.79% H, 4.57% N.

(R)-FcCH=NCH(Me)Ph (**7b**). ^{1}H NMR ($CDCl_3$): 1.57 (d, $^3J_{HH}$ = 6.8, 3 H, CH**Me**), 4.10 (s, 5 H, C_5H_5), 4.31–4.35 (m, 2 H, C_5H_4), 4.41 (q, $^3J_{HH}$ = 6.7, 1 H, C**H**Me), 4.63, 4.70 (2 × dt, J_{HH} = 2.5, 1.3, 1 H, C_5H_4); 7.12–7.40 (m, 5 H, Ph), 8.19 (s, 1 H, CH=N). ^{13}C NMR ($CDCl_3$): 24.27 (CH**Me**), 68.28, 68.87 (CH, C_5H_4 and CHMe); 68.95 (C_5H_5), 69.40, 70.31, 70.37 (CH, C_5H_4 and CHMe); 80.71 (C_{ipso}, C_5H_4), 126.53, 126.66, 128.34 (CH, Ph); 145.33 (C_{ipso}, Ph), 159.53 (CH=N). EI MS, *m/z* (relative abundance): 318 (23), 317 (100, $M^{\bullet+}$), 315 (7), 302 (19, $[M - Me]^+$), 251 (9, $[M - C_5H_6]^+$), 212 (11, $[M - PhCH(Me)]^+$), 211 (9), 199 (11, $[C_{11}H_{11}Fe]^+$), 186 (8), 185 (14, Fc^+), 129 (12), 121 (34, $[FeC_5H_5]^+$), 105 (23, $[C_8H_9]^+$), 77 (13), 56 (29, Fe^+). HR MS: for $C_{19}H_{19}FeN$ calculated 317.0867, found 317.0866.

Synthesis of Amines **8**. General Procedure

Amines **8** were synthesized as given in detail for **2**. Compound **7a** (2.00 g, 6.6 mmol) in methanol (40 ml) was reduced with $NaBH_4$ (1.06 g, 28 mmol) to give, after isolation as given above, amine **8a** (1.937 g, 96%) as an orange viscous oil. Compound **8b** was obtained similarly from **7b** (0.665 g, 2.10 mmol) and $NaBH_4$ (0.328 g, 8.7 mmol) in methanol (20 ml) and isolated as a viscous orange oil (0.607 g, 91%).

FcCH$_2$NCH$_2$Ph (**8a**). ^{1}H NMR ($CDCl_3$): 3.50, 3.79 (2 × s, 2 H, CH_2); 4.07 (s, 5 H, C_5H_5), 4.08, 4.17 (2 × apparent t, 2 H, C_5H_4); 7.20–7.34 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$): 48.11, 53.26 (CH_2); 67.65, 68.25 (CH, C_5H_4); 68.32 (C_5H_5), 86.86 (C_{ipso}, C_5H_4), 126.82, 128.01, 128.32 (CH, Ph); 140.31 (C_{ipso}, Ph). IR (Nujol): 3317 (br m), 3061 (w), 3086 (s), 3026 (m), 1495 (s), 1357 (m), 1328 (m), 1230 (m), 1105 (vs), 1038 (m), 1022 (m), 1001 (s), 819 (vs), 737 (vs), 699 (vs), 582 (m), 483 (vs). EI MS, *m/z* (relative abundance): 306 (24), 305 (100, $M^{\bullet+}$), 303 (7), 238 (19, $[M - C_5H_5 - 2\ H]^+$), 226 (6), 225 (6), 214 (9), 213 (23), 212 (47, $[M - PhCH_2 - 2\ H]^+$), 200 (37), 199 (25, $[C_{11}H_{11}Fe]^+$), 186 (12, $[FcH]^{\bullet+}$), 161 (6), 148 (18), 134 (6), 131 (34, $[FeC_5H_5]^+$), 106(5), 91 (10, $[C_7H_7]^+$), 78 (5), 65 (6), 56 (31, Fe^+). HR MS: for $C_{18}H_{19}FeN$ calculated 305.0867, found 305.0873.

(R)-FcCH$_2$NHCH(Me)Ph (**8b**). ^{1}H NMR ($CDCl_3$): 1.33 (d, $^3J_{HH}$ = 6.6, 3 H, CH**Me**), 1.57 (br s, 1 H, NH), 3.34, 3.37 (2 × d, $^2J_{HH}$ = 13.0, 1 H, AB system of CH_2); 3.81 (q, $^3J_{HH}$ = 6.6, 1 H, C**H**Me), 4.06 (s, 5 H, C_5H_5), 4.08 (apparent t, 2 H, C_5H_4), 4.13, 4.15 (2 × apparent q, 1 H, C_5H_4); 7.22–7.37 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$): 24.59 (CH**Me**), 46.62 (**C**HMe), 57.55 (CH_2), 67.60, 67.70, 68.09 (CH, C_5H_4); 68.35 (C_5H_5), 68.41 (CH, C_5H_4), 87.18 (C_{ipso}, C_5H_4),

126.67, 126.87, 128.44 (CH, Ph); 145.65 (C_{ipso}, Ph). IR (Nujol): 3324 (br m), 1352 (m), 1306 (m), 1123 (m), 1105 (vs), 1037 (m), 1023 (m), 1001 (s), 819 (s), 763 (s), 702 (vs), 588 (m), 548 (m), 521 (m), 483 (vs). EI MS, *m/z* (relative abundance): 320 (5), 319 (100, $M^{\bullet+}$), 317 (15), 253 (18, $[M - C_5H_6]^{\bullet+}$), 226 (13), 214 (18, $[M - PhCH(Me)]^+$), 213 (12), 200 (34), 199 (41, $[C_{11}H_{11}Fe]^+$), 186 (14, $[FcH]^{\bullet+}$), 152 (17), 149 (28), 122 (15), 121 (45, $[FeC_5H_5]^+$), 105 (12, $[C_8H_9]^+$), 77 (10, Ph^+), 56 (22, Fe^+). HR MS: for $C_{19}H_{21}FeN$ calculated 319.1023, found 319.1039. $[\alpha]_D^{20}$ +50.5 (*c* 1.0, $CHCl_3$).

Alkylation of **8a** with MeI

Amine **8a** (0.100 g, 0.33 mmol) was dissolved in dry dichloromethane (10 ml), K_2CO_3 (0.114 g, 0.87 mmol) was added, and the reaction flask was flushed with argon. Then, iodomethane (0.103 ml, 1.6 mmol) was introduced and the mixture was stirred at room temperature for 2 days in the dark. Methanol (3 ml) and water (3 ml) were added, the yellow organic layer was separated, washed with water, and dried over $MgSO_4$. A subsequent evaporation followed by drying under vacuum (65 Pa, 60 °C, 1 h) afforded **9** as a yellow microcrystalline solid in quantitative yield. ^{1}H NMR ($CDCl_3$): 3.05 (s, 6 H, NMe_2), 4.30 (s, 5 H, C_5H_5), 4.35, 4.62 (2 × apparent t, 2 H, C_5H_4); 4.98, 5.10 (2 × s, 2 H, CH_2); 7.71–7.69 (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$): 48.25 (NMe_2), 65.83, 66.64 (CH_2); 69.67 (C_5H_5); 70.71 (CH, C_5H_4), 72.14 (C_{ipso}, C_5H_4), 72.47 (CH, C_5H_4). For $C_{20}H_{24}FeIN$ (460.4) calculated: 52.09% C, 5.25% H, 3.04% N; found: 51.78% C, 5.40% H, 2.74% N.

Synthesis of Oxazoline **10**

Oxazoline **10** was obtained as given above for compounds **5** and **6** by stirring a mixture of **7b** (1 mmol), **4b** (2 mmol) and K_2CO_3 at 90 °C (bath temperature) under argon in the dark for 2.5 days. The crude material was purified by chromatography (silica gel, $CHCl_3$), and then recrystallized from hot ethyl acetate to give **10** as an orange crystalline solid (yield not determined). ^{1}H NMR ($CDCl_3$): 0.94, 1.02 (2 × d, $^3J_{HH}$ = 6.7, 3 H, CH**Me**$_2$); 1.38 (d, $^3J_{HH}$ = 6.5, 3 H, CH**Me**), 1.81 (octet, $^3J_{HH}$ = 6.7, 1 H, C**H**Me_2), 3.32 (s, 2 H, CH_2Ox), 3.51, 3.65 (2 × d, $^2J_{HH}$ = 14.0, 1 H, AB system of $FcCH_2$); 3.80 (q, $^3J_{HH}$ = 6.5, 1 H, C**H**Me), 3.87–3.95 (m, 1 H, CH^{Ox}), 3.98 (dd, $J_{HH,1} \approx J_{HH,2} \approx 8.0$, 1 H, $CH_2{}^{Ox}$), 4.01 (s, 5 H, C_5H_5), 4.09 (br apparent t, 2 H, C_5H_4), 4.17 (br d of apparent t, 1 H, C_5H_4), 4.21 (dd, J_{HH} = 8.2, $J_{HH,2}$ = 9.7, 1 H, $CH_2{}^{Ox}$), 4.30 (br d of apparent t, 1 H, C_5H_4), 7.21–7.42 (m, 5 H). ^{13}C NMR ($CDCl_3$): 18.25, 18.89 (CH**Me**$_2$); 19.68 (CH**Me**), 32.55 (**C**HMe_2), 46.40 (CH_2Ox), 49.36 (CH_2Fc), 59.70 (**C**HMe), 67.78, 67.84 (CH, C_5H_4); 68.34 (C_5H_5), 69.72 ($CH_2{}^{Ox}$), 69.78, 70.55 (CH, C_5H_4); 71.86 (CH^{Ox}), 83.25 (C_{ipso}, C_5H_4), 126.85, 127.59, 128.25 (CH, Ph); 144.83 (C_{ipso}, Ph), 165.59 (C_{ipso}, Ox). EI MS, *m/z* (relative abundance): 444 (7, $M^{\bullet+}$), 379 (3, $[M - C_5H_5]^+$), 339 (10, $[M - PhCH(Me)]^+$), 318 (36), 317 (100, $[M - CH_2Ox - H]^{\bullet+}$, isobaric with $[\mathbf{7b}]^{\bullet+}$), 214 (12, [*m/z* 317 – $PhCH(Me)]^+$), 199 (31, $[C_{11}H_{11}Fe]^+$), 186 (9, $[FcH]^{\bullet+}$), 160 (5), 121 (39, $[FeC_5H_5]^+$), 120 (18), 105 (33, $[C_8H_9]^+$), 91 (8, $[C_7H_7]^+$), 77 (19, Ph^+), 56 (19, Fe^+). HR MS: for $C_{26}H_{32}FeN_2O$ calculated 444.1864, found 444.1910. $[\alpha]_D^{20}$ –17.4 (*c* 1.0, $CHCl_3$).

X-Ray Crystallography

Compound **2b**. Crystals suitable for X-ray analysis were obtained by evaporation of a diethyl ether solution. Diffraction data were collected on an Nonius KappaCCD diffractometer equipped with Oxford Cryostream cooler at 150 K using graphite monochromatized MoKα

radiation (λ = 0.71073 Å) and analyzed by HKL program package[19]. The cell parameters were determined by least-squares fitting from 16 230 partial diffractions with $1.0 \le \theta \le 26.0°$. The phase problem was solved by direct methods (SIR92 [20]). Non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 (SHELXL97 [21]). Hydrogen atoms were included in calculated positions with fixed C–H bond lengths (aromatic 0.93, CH_2 0.97, CH_3 0.96, and NH 0.86 Å) and assigned $U_{iso}(H) = 1.2\ U_{eq}(X)$, where X is the adjacent C or N.

Compound **2g**. Crystals were grown by slow evaporation of a methanol solution. Diffraction data were collected and analyzed as above. The cell parameters were determined by least-squares fitting from 20 676 partial diffractions with $1.0 \le \theta \le 27.5°$. The structure was solved by direct methods (SIR92). Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were identified on a difference electron density map and freely isotropically refined. The refinement was carried out by full-matrix least-squares on F^2 (SHELXL97).

Compound **9**. Single crystals were obtained by recrystallization from hot methanol. Diffraction data were collected as given above for **2b**. Cell parameters were determined by least-squares fitting from 16 230 partial diffractions with $1.0 \le \theta \le 27.9°$. The phase problem was solved by direct methods (SIR92). Non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 (SHELXL97). All hydrogen atoms were identified on the difference electron density maps and freely refined with isotropic thermal motion parameters.

Compound **10**. Crystals were grown by recrystallization from ethyl acetate. The dffraction data were collected as given for **2b**. The cell parameters were determined by least-squares analysis from 15 821 partial diffractions with $1.0 \le \theta \le 27.5°$. The structure was solved by direct methods (SIR92). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions with fixed C–H bond lengths (aromatic CH 0.93, methine 0.98, CH_2 0.97, and CH_3 0.96 Å) and assigned $U_{iso}(H) = 1.2\ U_{eq}(C)$. The refinement was carried out by full-matrix least-squares on F^2 (SHELXL97).

CCDC-207928 (**2b**), -207929 (**2g**), -207930 (**9**), and -207931 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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