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Planar chiral ferrocene salen-type ligands featuring additional central and axial chirality

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Abstract

We report on novel chiral tridentate $[NO_2]H_2$ and tetradentate $[N_2O_2]H_2$ Schiff base ligands containing a planar chiral ferrocene moiety linked to hydroxyl-imine or diimine donors with central or axial chirality. Structurally, these ligands resemble half-salen and salen systems designed for stereoselective applications of their transition metal complexes in homogeneous catalysis. The modular synthesis involves diastereoselective metalation of chiral ferrocene or pentamethylferrocene acetals, followed by stereoconservative hydroxyalkylation and condensation with chiral hydroxyamines or diamines, respectively. In comparison to salen-type systems, an important advantage of these ligands is their tunable steric protection of the alkoxide donor site. A total of 18 different ligands varying in electronic and steric properties have been prepared and fully characterized by NMR, IR, mass spectroscopy and by single crystal structure analysis of nine precursors and representatives.

Keywords: Ferrocene; Planar chirality; Central chirality; Axial chirality; N,O-ligands

1. Introduction

Since the pioneering work by Knowles [1] in 1968, homogeneous enantioselective catalysis by chiral transition metal complexes has been developed to an extremely valuable tool for the synthesis of a myriad of chiral compounds. The importance of this area of chemistry was recently acknowledged by the Nobel Prize in Chemistry 2001 awarded to William S. Knowles, Ryoji Noyori, and K. Barry Sharpless. In enantioselective homogeneous catalysis, the chirality at the active metal site of the catalyst is usually due to coordination of a suitable chelating chiral ligand which serves as stereodirecting group in the key step of the catalytic cycle. Among the many chiral ligands available, a few structural moieties – termed "privileged ligands [2] – have been proven as especially useful for a wide range of applications, inter alia chiral binaphthyl, metallocenyl, salen, bis(oxazoline), and bis(phosphine) ligand frameworks.

In this contribution, we report on a new family of tridentate $[NO_2]H_2$ Schiff base as well as tetradentate $[N_2O_2]H_2$ salen-type ligands which combine the planar chirality of 1,2-disubstituted ferrocenes with central and axial chirality in the residual ligand backbone. An important design criterion for these highly dissymetric ligand systems is a modular synthetic approach which allows simple improvements of the catalytic activity and selectivity by variation of the steric properties of the ligands. Possible applications of these ligands and their metal complexes include epoxide ring-opening, Diels–Alder, imine cyanation, conjugate addition, hydrogenation and other stereoselective reactions, in analogy to reactions of established Schiff base and salen metal catalysts [2,3]. Our specific interest lies in the stereoselective alternating copolymerization of carbon monoxide with propylene oxide [4–6] to yield enantiomerically enriched polyhydroxybutyrate.

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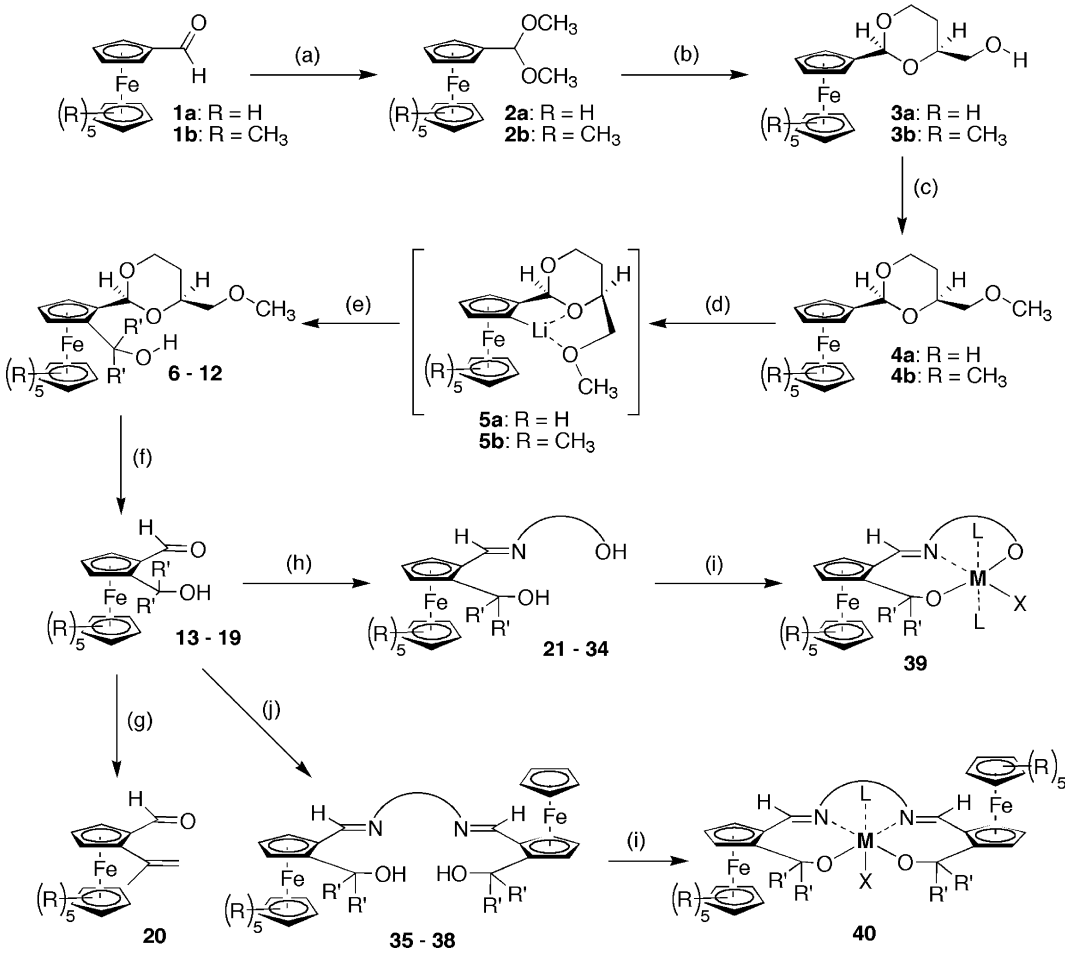
A forthcoming publication will deal with this application using the ligands reported in this paper.

2. Results and discussion

Our modular preparative approach to chiral Schiff base and salen-type ligands is shown in Scheme 1: In the first step, (pentamethyl)ferrocene aldehyde **1a** or **1b** is converted to dimethylacetals **2a** or **2b**, followed by transacetalization with chiral (*S*)-1,2,4-butanetriol to hydroxyacetals **3a** or **3b**, respectively. This chemistry has been developed by Kagan and coworkers [7] starting from ferrocenealdehyde **1a**, but not with pentamethylferrocenealdehyde [8] **1b**. The noteworthy feature of this acetalization is the selective formation of only one epimer in 80% yield on a preparative scale of up to 50 g of starting ferrocenealdehyde.

In the following step, chiral hydroxyacetals **3a** or **3b** are alkylated to the corresponding methyl ethers **4a** or **4b** in quantitative yield by reaction with sodium hydride and methyl iodide. Methoxyacetals **4a** or **4b** are the key precursors for the diastereoselective metalation of the ferrocenyl moiety. Under the experimental conditions developed by Kagan and coworkers [7] with *t*-butyl lithium as base at −80 °C in diethyl ether as solvent, exclusive *ortho*-deprotonation to only one diastereoisomer **5a** or **5b** is possible. Reaction with suitable electrophiles affords the corresponding planar chiral ferrocenes in a completely stereoconservative manner. Kagan and coworkers [7] has already shown that the following functional moieties can be stereoselectively attached to the ferrocene moiety: trialkylsilyl, carboxylate, phosphine, halogen, thioether, carbaldehyde, boronic acid, amine and hydroxyl. The latter derivative is a precursor to 2-hydroxy-1-formyl-ferrocene – a planar chiral analog of salicylaldehyde – and of special interest in view of the anticipated applications of such compounds as planar chiral nitrogen and oxygen-based ligands in stereoselective catalysis. However, hydroxyferrocenes [9–12] in general are only accessible in protected form by use of hazardous reagents and quite difficult to handle due to their facile oxidation by air, therefore this building block is of limited use for practical applications.

On the other hand, the air sensitivity of hydroxyferrocenes can be simply circumvented by introduction of a saturated one-carbon spacer between the redox active



Scheme 1. Synthetic route to planar chiral ferrocene salen-type ligands and metal complexes. Conditions: (a) H^+, trimethyl orthoformate; (b) H^+, (*S*)-1,2,4-butanetriol; (c) NaH, CH_3I; (d) *t*-butyl lithium; (e) $R'_2C{=}O$ (acetone, benzophenone, 9-fluorenone, paraformaldehyde, adamantanone, diisopropylketone); (f) H^+; (g) dehydration, $-H_2O$; (h) chiral aminoalcohol $H_2N\cdots OH$ (see main text); (i) *n*-butyl lithium, MX_3 (e.g., $CrCl_3$); (j) chiral diamine $H_2N\cdots NH_2$ (see main text).

ferrocene group and the hydroxyl functionality (Scheme 1). This new design principle has the following advantageous attributes: First, the hydroxyl functionality shows the common reactivity and has the same stability as in organic alcohols. Second, the synthesis of such spacered hydroxyferrocenes is easily achieved by simple hydroxyalkylation of **5a** or **5b** with various aldehydes or ketones, thereby allowing modular steric protection of the hydroxyl group by use of carbonyl components of different steric bulk. Third, if aldehydes R(C=O)H are used in this hydroxyalkylation, central chirality at the hydroxyl carbon will result, allowing in principle further dissymmetry in the target ligands and chiral metal catalysts **39** and **40**. However, to avoid the problem of separation of the anticipated diasteromeric product mixtures, we did not explore this additional opportunity, only hydroxyalkylations with ketones R_2C=O (acetone, benzophenone, 9-fluorenone, formaldehyde, adamantanone, diisopropylketone) are reported in this paper. Fourth, due to the one carbon spacer a 7-membered metal chelate is present in metal complexes **39** and **40**, in contrast to salen complexes which have a 6-membered metal chelate coordination geometry.

Chart 1 gives an overview of the synthesized hydroxyalkylated methoxyacetals **6**–**12** and of the corresponding planar chiral 2-hydroxyalkylated ferrocene-1-aldehydes **13**–**19**, respectively, showing the varying degree of steric protection at the hydroxyl moiety. Synthetically, the reaction of **5a** or **5b** with the ketones acetone, benzophenone, 9-fluorenone, formaldehyde, adamantanone, and diisopropylketone is very simple and affords the products **6**–**12** in 41–81% isolated yield, dependent on the ease of nucleophilic addition of **5a** or **5b** to the differently substituted carbonyl groups of the ketone reagents. Spectroscopically, ^{1}H and ^{13}C NMR spectra of **6**–**12** show one set of signals for the chiral methoxyacetal moiety in addition to the expected signals of the various diasterotopic alkylhydroxyl functionalities; a detailed spectral analysis is given in the experimental section. Furthermore, mass spectra display the expected molecular ions and in the IR spectra the anticipated hydroxyl bands >3000 cm^{-1} are detected. Fig. 1 shows the molecular structure of **8** obtained from a single crystal structure analysis. The molecule crystallizes in the chiral space group $P2_1$ and the chirality at the ferrocene moiety (R_P) and in the acetal group (S,S) is further corroborated by an absolute structure parameter of −0.007(13). All bond distances and angles are in the normal range and unexceptional but from inspection of Fig. 1 the steric protection of the hydroxyl group [O(1)] by the large 9-fluorenyl substituent is clearly evident.

The next step in the synthetic sequence (Scheme 1) consists in removal of the acetal group of compounds **6**–**12** by acidic hydrolysis. Planar chiral 2-hydroxyalkylated ferrocene-1-aldehydes **13**–**19** (Chart 1) are obtained in 36–84% yield by simply stirring acetals **6**–**12** with *p*-toluenesulfonic acid in dichloromethane solution for a few hours at ambient temperature. In the case of pentamethylated starting material **19** the yield is rather poor due to an unavoidable side reaction to dehydrated 2-propenyl-pentamethylferro-

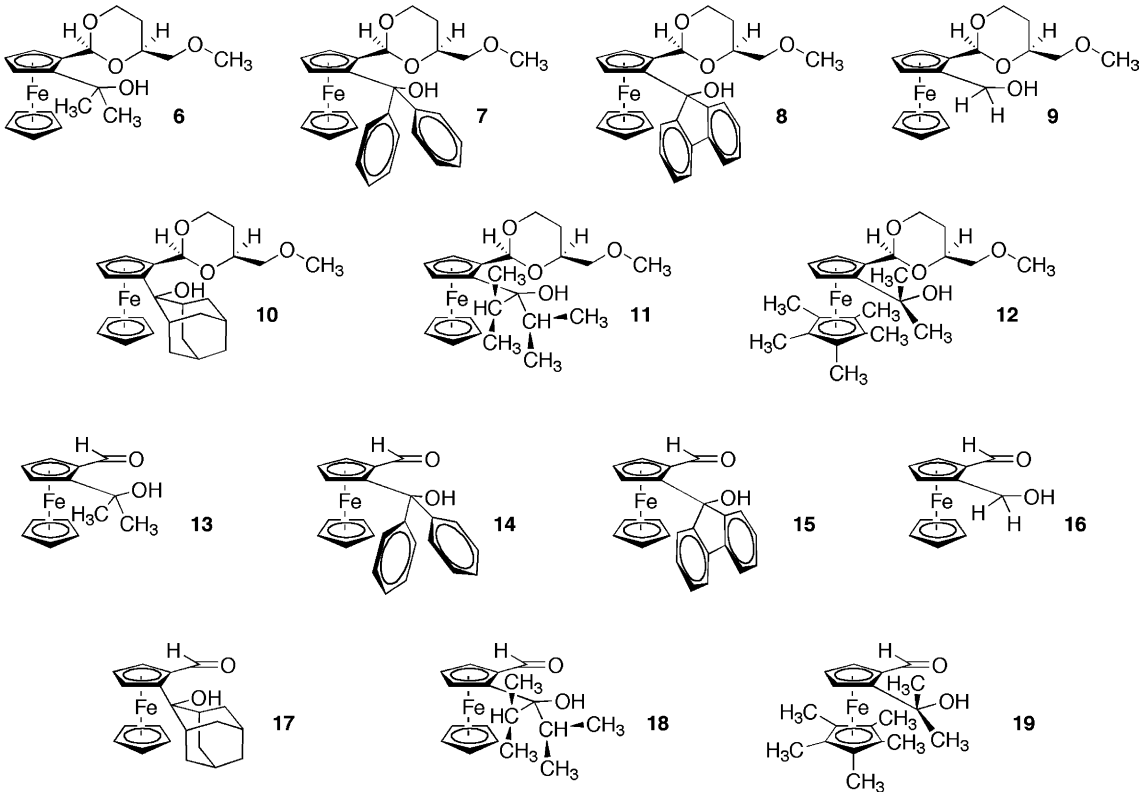


Chart 1. Hydroxyalkylferrocene acetals **6**–**12** and their corresponding planar chiral hydroxyalkylferrocenealdehydes **13**–**19**.

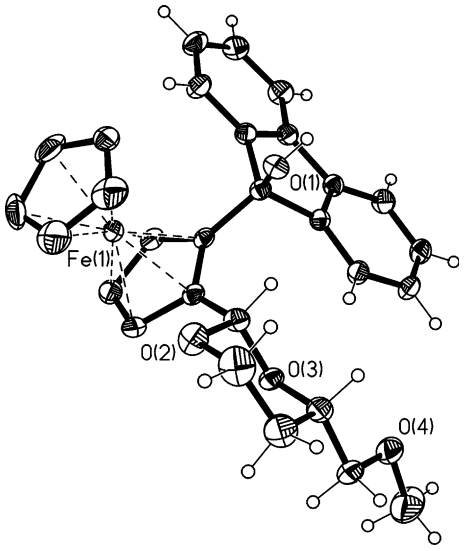


Fig. 1. Molecular structure of **8**. Hydrogen atoms at the ferrocene group are omitted for clarity.

cenealdehyde **20**. This undesired olefinic product is formed because the five electron-donating methyl groups facilitate the elimination of water due to the efficient electronic stabilization of the intermediate carbenium ion. Chart 1 shows the modular steric protection at the hydroxy functionality of these planar chiral ferrocene aldehydes. Spectroscopic characterization of **13**–**19** was performed by NMR, IR, and MS techniques, key properties include (i) NMR low field signals of the aldehyde group [$\delta(^1H) =$ 9.50–9.99 ppm, $\delta(^{13}C) = 195.0$–196.9 ppm], (ii) diastereotopic NMR signals for the substituents at the hydroxyl carbons, (iii) strong IR absorptions for the aldehyde functionalities ($\nu_{C=O} = 1634$–$1657\ cm^{-1}$), (iv) broad IR bands of the hydroxyl groups ($\nu_{C-OH} = 3288$–$3553\ cm^{-1}$), and (v) molecular ions in the FAB mass spectra. Further structural proof is given by two single crystal structures (Figs. 2 and 3). Both compounds crystallize in chiral space groups (**13**: $P2_12_12_1$; **15**: $P2_1$) and give excellent absolute structure parameters [**13**: 0.015(18); **15**: 0.011(10)] in line with their planar chirality R_P. As anticipated, all bond distances and angles are in the expected normal range and an intramolecular hydrogen bridge between the hydroxyl

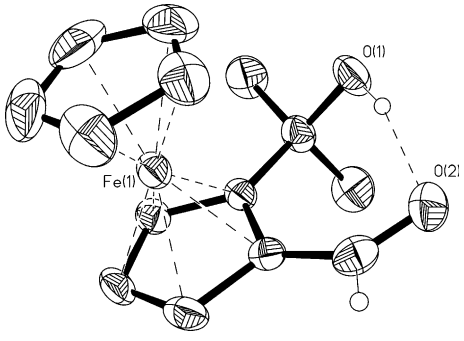


Fig. 2. Molecular structure of **13**. Hydrogen atoms are omitted for clarity, except for hydroxyl and aldehyde hydrogens.

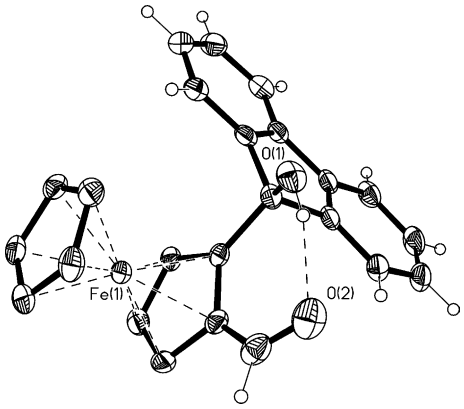


Fig. 3. Molecular structure of **15**. Hydrogen atoms of the ferrocene group are omitted for clarity.

group and the aldehyde functionality is observed. Note that a 7-membered ring system is formed by this hydrogen bridging, indicative of the analogous 7-membered coordination geometry in metal complexes **39** and **40** derived from these precursors. The main difference in these two structures is the different steric protection of the hydroxyl groups O(1): steric shielding in **13** by the two rather small methyl groups is much less compared to the situation in **15** containing the larger 9-fluorenyl substituent.

Besides these two hydroxyalkylferrocenealdehyde solid state structures of **13** and **15**, a crystal structure of the elimination side product **20** was obtained (Fig. 4). In this planar chiral molecule [space group $P2_12_12_1$, absolute structure parameter 0.013(15)] the steric bulk of the pentamethylcyclopentadienyl ring is the most prominent feature, in comparison to the former structures containing non-methylated ferrocenes.

Hydroxalkylated ferrocene aldehydes **13**–**19** are the key precursors for the target Schiff base ligands of this contribution. Condensation with suitable aminoalcohols in concentrated methanolic solution affords the tridentate $[N_2O]H_2$ ligands **21**–**34** in quantitative yield. Experimentally, the progress of this simple condensation can be conveniently monitored by IR spectroscopy (detection of the C=N imine stretching vibration versus the C=O band of

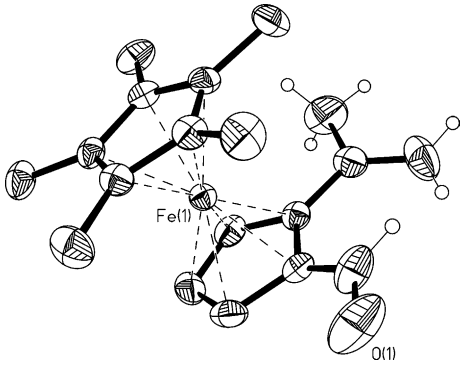


Fig. 4. Molecular structure of **20**. Hydrogen atoms of the ferrocene moiety are omitted for clarity.

the starting hydroxyalkylated aldehydes) but not by TLC analysis; due to facile hydrolysis on the stationary phase (silica or alumina) this common method is useless for this class of compounds. Physically, $[N_2O]H_2$ ligands **21**–**34** are air-stable red to orange solids with melting points mostly below 100 °C. Stereochemically, all these compounds are planar chiral (R_P) due to the 1,2-disubstituted ferrocene moiety and – with the exception of **21** – additionally central chiral (**22**–**32**) or axial chiral (**33**–**34**) due to the chirality of the corresponding aminoalcohol starting materials. Chart 2 shows stereochemical formulas with stereochemical descriptors for all ligands, indicating the high dissymmetry in this library of ligands, as well as the different steric bulk of the various substituents, indicating the modular steric protection possible. Note that the substituents point towards different spatial quadrants, thereby blocking different reaction pathways in the metal catalysts derived from these ligands. Both features – high chirality and modular steric protection – are essential for enantioselectivity in homogeneous catalysis. Spectroscopically, NMR measurements show in general quite complex spectra due to the high dissymmetry of these molecules. For a detailed assignment compare the data in the experimental section, only general features are discussed in this part: (i) The ferrocene moiety is clearly evident from one signal for the five isochronous hydrogens [**21**–**31**, **33**–**34**: $\delta(^1H) = 3.63$–4.48 ppm; $\delta(^{13}C) = 68.6$–71.2 ppm] or methyl groups [**32**: $\delta(^1H) = 1.9$ ppm; $\delta(^{13}C) = 11.3$ and 73.4 ppm] of the lower cyclopentadienyl ring, as well as three ^1H and five ^{13}C signals of the substituted upper cyclopentadienyl ring. (ii) The imine functionality is corroberated by low field ^1H and ^{13}C signals [**21**–**34**: $\delta(^1H) = 8.16$–9.12 ppm, $\delta(^{13}C) = 164.6$–167.6 ppm], slightly shifted to higher field in comparison to the C=O funtionality of hydroxyalkylferrocene aldehydes [**13**–**19**: $\delta(^1H) = 9.50$–9.99 ppm, $\delta(^{13}C) = 195.0$–196.9 ppm]. (iii) The diastereotopic substituents at the hydroxyalkyl moiety give rise to a set of separated signals. Quite interestingly, in case of two of the *R*-hydroxy-*S*-imineindanol ligands **29** and **31** two isomers ore observed in solution, most likely corresponding to different hydrogen-bridged species. In addition to these NMR spectral features, IR spectroscopic detection of the imine and hydroxyl functionalities [**21**–**34**: $\nu_{C=N} = 1587$–$1638\ cm^{-1}$, broad $\nu_{C-OH} = 3092$–$3477\ cm^{-1}$], mass spectroscopic measurements of the molecular ions, and elemental analysis are further proof of the identity of compounds **21**–**34**.

Figs. 5 and 6 show the single crystal X-ray structures of **21** and **33**, respectively. Both chiral molecules [**21**: space group $P2_12_12_1$, absolute structure parameter 0.00(2); **33**: space group $P2_1$, absolute structure parameter −0.008(17)] contain the same R_P chiral hydroxyisopropyl ferrocene subunit but differ in their hydroxyimine moiety. Whereas **21** has an achiral hydroxyimine unit derived from *o*-aminophenol, the additional axial chirality of **33** derived

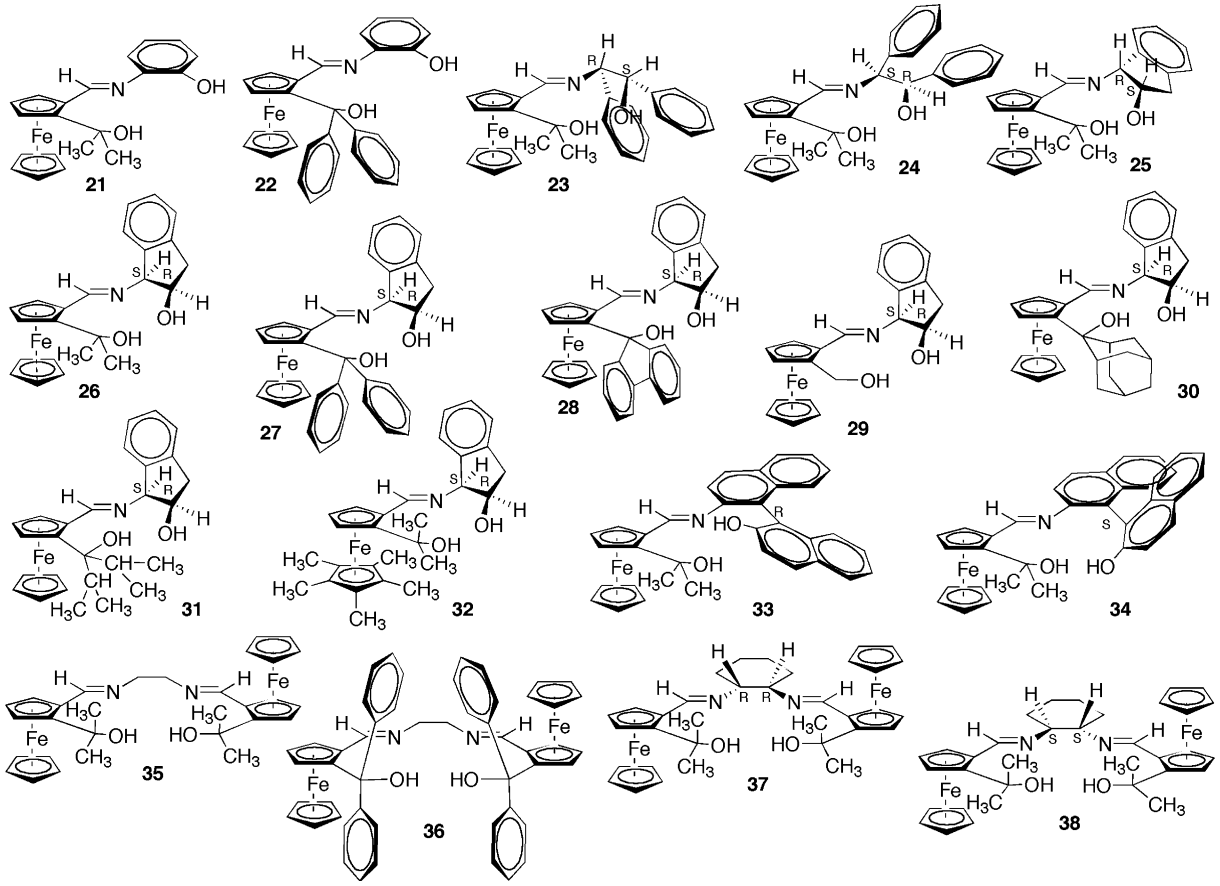


Chart 2. Overview of chiral $[NO_2]H_2$ **21**–**34** and $[N_2O_2]H_2$ ligands **35**–**38**.

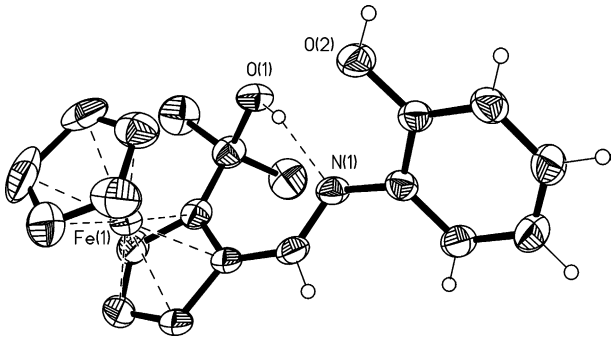


Fig. 5. Molecular structure of **21**. Hydrogen atoms of the ferrocene moiety and of the methyl groups are omitted for clarity.

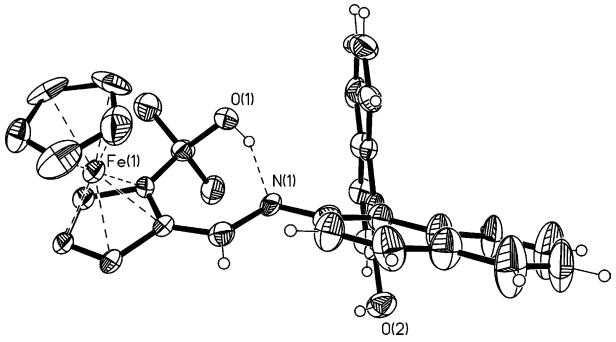


Fig. 6. Molecular structure of **33**. Hydrogen atoms of the ferrocene moiety and of the methyl groups are omitted for clarity.

from *S*-2-amino-2′-hydroxy-1,1′-binaphthyl is clearly visible. Similar as in other binaphthyl axial chiral systems, the angle between the two naphthyl planes is 82° (mean value of six independent molecules in the asymmetric unit). Analogously as in the precursor aldehyde **13** (Fig. 2) where intramolecular hydrogen bonding between the aldehyde oxygen and the hydroxyl group was observed, both these imine ligands contain a 7-membered ring formed by a hydrogen-bridge between the imine nitrogen and the isopropylhydroxyl group.

Hydroxalkylated ferrocene aldehydes **13** and **14** are also the key precursors for tetradentate salen-type $[N_2O_2]H_2$ ligands. Condensation under similar conditions as for the tridentate systems with achiral ethylenediamine or chiral cyclohexane-1,2-diamine affords ligands **35**–**38** in 67–99% isolated yield. Chart 2 shows stereochemical formulas of these compounds, indicating their structural diversity. Physically, **35**–**38** are air-stable orange solids with melting points ranging from 177 to 250 °C, significantly higher than for tridentate ligands **21**–**34**. Spectroscopically, similar features as discussed above are observed: (i) the imine functionality is evident from ^1H, ^{13}C and IR spectroscopy [$\delta(^1H) = 8.06$–9.00 ppm; $\delta(^{13}C) = 163.4$–165.7 ppm; $\nu_{C=N} = 1635$–$1641\ cm^{-1}$], (ii) the hydroxyl groups are detected by broad IR bands [$\nu_{C-OH} = 3019$–$3159\ cm^{-1}$], and (iii) the substituents at the hydroxylalkyl group show two sets of NMR signals due to their diastereotopicity. Unambiguous structural proof is given by single crystal structure analysis (Figs. 7–9) of ligands **35**, **37** and **38**. All three compounds crystallize in the chiral space group $P2_12_12_1$ and give excellent absolute structure parameters [**35**: 0.002(15); **37**: 0.009(13); **38**: −0.003(15)] in accordance with their chirality. Hydrogen bonding forming two 7-membered rings is observed in all three cases, indicative of the anticipated coordination geometry of metal complexes $[N_2O_2]ML_2$ **40** derived from these ligands. Compounds **37** and **38** are diastereoisomers containing the same planar chiral ferrocene subunit, but enantiomeric cyclohexanediamine building blocks (**37**: *R*,*R*; **38**: *S*,*S*), this is clearly seen by direct comparison of both molecular structures. Besides these general features, in all three structures normal bond distances and angles are observed, as anticipated.

With this new library of highly chiral tridentate (**21**–**34**) and tetradentate (**35**–**38**) ligand systems, a wide range of chiral metal complexes **39** and **40** is obviously accessible (Scheme 1). As mentioned in the introduction, applications of such catalysts might include stereoselective epoxide ring-opening, Diels–Alder, conjugate addition and other reactions. We anticipate that the ligand design developed in this work will lead to useful applications in stereoselective homogeneous catalysis.

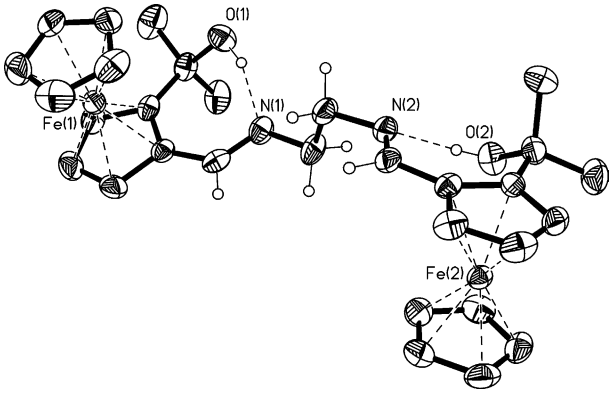


Fig. 7. Molecular structure of **35**. Hydrogen atoms of the ferrocene moiety and of the methyl groups are omitted for clarity.

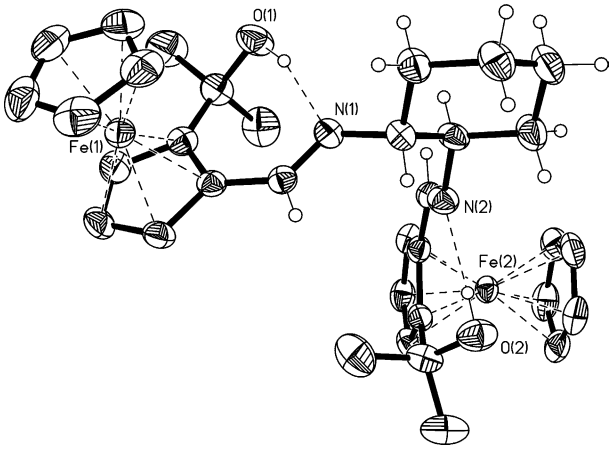


Fig. 8. Molecular structure of **37**. Hydrogen atoms of the ferrocene moiety and of the methyl groups are omitted for clarity.

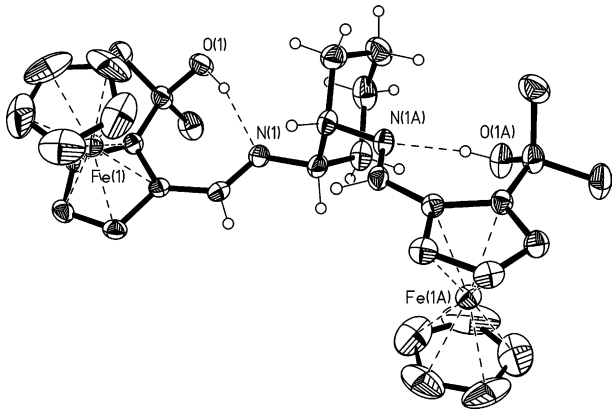


Fig. 9. Molecular structure of **38**. Hydrogen atoms of the ferrocene moiety and of the methyl groups are omitted for clarity.

3. Conclusions

Two new families of chiral tridentate $[NO_2]H_2$ and tetradentate $[N_2O_2]H_2$ ligands have been synthesized by a versatile and modular synthetic sequence. Structurally, these ligands were designed according to half-salen and salen systems. The novel structural features of this ligand library are (i) combination of planar chirality based on 1,2-disubstituted ferrocenes with central and axial chirality in the residual ligand backbone, (ii) tunable steric protection at the alkoxide donor site, and (iii) formation of a 7-membered chelate ring in the metal catalysts derived from these ligands. Key steps of the synthesis include (i) diasteroselective metalation of ferrocene and pentamethylferrocene acetals, (ii) stereoconservative hydroxalkylation with various ketones, (iii) deprotection of the stereodirecting acetal group by acidic hydrolysis, and (iv) condensation with various chiral aminoalcohols and diamines, respectively. Eighteen different ligands with varying stereoelectronic properties have been synthesized and fully characterized by spectroscopic methods (NMR, IR, MS) as well as by single crystal structure analysis of selected precursors and representatives.

4. Experimental

Reactions were performed in Schlenk glassware under an Ar atmosphere by techniques common in organometallic chemistry. Commercially available starting materials were used as received. Solvents were dried, deoxygenated, and saturated with Ar. Starting materials **2a**, **3a**, **4a** [7] as well as pentamethylferrocene carbaldehyde **1b** [8] were prepared according to literature procedures. NMR Spectroscopy: ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer with signals referenced to (residual) solvent peaks as internal standards. Mass spectroscopy: positive mode FAB spectra (20 kV, 2 μA; matrix, *m*-nitrobenzyl alcohol) or EI mass spectra (70 eV) were obtained on a Finnigan MAT95 spectrometer. IR Spectroscopy: IR spectra of the solid samples were measured on a Nicolet 5700 FT-IR spectrometer equipped with a Smart Orbit diamond ATR unit.

4.1. 1′,2′,3′4′,5′-Pentamethylferrocene-1-aldehyde-dimethylacetal *2b*

A Schlenk tube was charged with **1b** (500 mg, 1.76 mmol), trimethyl orthoformate (373 mg, 3.5 mmol), *p*-toluene sulfonic acid (20 mg, 0.1 mmol), and dry methanol (20 mL). The mixture was refluxed over night. Workup: after the mixture was allowed to cool to room temperature, approximately 0.5 g potassium carbonate was added to neutralize acids. Solvents and volatile materials were removed on a rotary evaporator, the residue was dissolved in diethyl ether, the organic solution was washed with water, followed by saturated aqueous sodium bicarbonate solution and brine solution. The organic layer was dried over magnesium sulfate, filtered, and reduced to dryness, yielding **2b** as a brown oil (566 mg, 1.71 mmol, 97%). The purity of this material is sufficient for the next step as evidenced by its NMR spectra: ^1H NMR ($CDCl_3$): 5.31 (1H, s, H[8]); 3.76 (2H, t, H[7] and H[4]); 3.66 (2H, t, H[6] and H[5]); 3.21 (6H, s, H[9] and H[10]); 1.87 (15H, s, H[1]) ppm. ^{13}C NMR ($CDCl_3$): 101.0 (C[8]); 83.9 (C[2]); 80.4 (C[3]); 71.9 (C[7], C[4]); 69.4 (C[6], C[5]); 51.3 (C[9], C[10]); 11.0 (C[1]) ppm (see Fig. 10).

4.2. (2S,4S)-4-(Hydroxymethyl)-2-(1′,2′,3′,4′,5′-pentamethylferrocene)-1,3-dioxane *3b*

A dry 250 mL round bottom flask was charged with dry dichloromethane (50 mL), activated 3 Å molecular sieve (1 g), **2b** (1.123 g, 3.4 mmol), (*S*)-1,2,4-butanetriol (0.361 g, 3.4 mmol), and *p*-toluene sulfonic acid (35 mg, 0.17 mmol). The dark red mixture was stirred over night and worked up: the molecular sieve was removed by filtration, the organic solution was washed with aqueous sodium bicarbonate solution followed by water, the organic solution was dried over magnesium sulfate, and reduced to dryness on a rotary evaporator. The crude product was chromatographed on a short alumina column using *n*-hexane/diethyl ether as eluent, affording **3b** as a yellow oil (0.588 mg, 1.58 mmol) in 46% yield. ^1H NMR ($CDCl_3$): 5.31 (1H, s, H[8]); 4.25–4.20 (1H, q, H[11]); 3.95–3.91 (2H, m, H[4] and H[7]); 3.84 (2H, m, H[9]); 3.69–3.59 (4H, m, H[12], H[6], H[5]); 2.20 (1H, t, H[12′]); 1.89–1.76 (1H, d, H[2]); 1.85 (15H, s, H[1]); 1.38 (1H, d, H[2]) ppm. ^{13}C NMR ($CDCl_3$): 99.9 (C[8]); 84.9 (C[11]); 80.5 (C[12]); 77.0

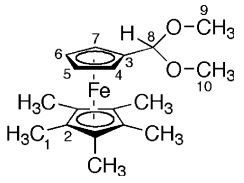


Fig. 10. Numbering of **2b** for NMR assignment.

(C[9]); 72.4 (C[3]); 72.4 (C[4]); 68.9 (C[2]); 68.6 (C[7]); 66.2 (C[5]); 65.6 (C[6]); 26.7 (C[10]); 11.0 (C[1]) ppm (see Fig. 11). MS (FAB): 273 ($M^+ + H$), 272 (M^+), 271 ($M^+ - H$) *m/e*.

4.3. (2S,4S)-4-(Methoxymethyl)-2-(1′,2′,3′,4′,5′-pentamethylferrocenyl)-1,3-dioxane **4b**

A Schlenk tube was charged with dry tetrahydrofuran (20 mL) and **3b** (588 mg, 1.58 mmol). The mixture was cooled to −40 °C and sodium hydride (57 mg, 2.37 mmol) was added in one portion under protection from the atmosphere. The resulting suspension was magnetically stirred and allowed to warm to room temperature over a period of 2.5 h. Methyl iodide (448 mg, 3.16 mmol) was added and stirring was continued over night at ambient temperature. Workup: methanol was added in small portions until a clear solution was obtained, all volatile materials were removed on a rotary evaporator, the residue was dissolved in diethyl ether, the organic solution was washed with three portions of water followed by one portion of brine solution, the organic phase was dried over sodium sulfate, filtered, and reduced to dryness, affording **4b** (611 mg, 1.575 mmol) as a yellow-brown oil in 99% yield. ^{1}H NMR ($CDCl_3$): 5.29 (1H, s, H[8]); 4.24–4.11 (1H, q, H[11]); 4.05–3.84 (2H, m, H[12]); 3.84 (1H, s, H[4]); 3.80 (1H, s, H[5]); 3.66 (2H, s, H[6], H[7]); 3.58–3.36 (2H, m, H[9]); 3.41 (3H, s, H[13]); 1.91 (1H, m, H[10]); 1.49 (1H, d, H[10]); 1.89 (15H, s, H[1]) ppm. ^{13}C NMR ($CDCl_3$): 99.9 (C[8]), 84.9 (C[11]), 80.4 (C[3]), 75.8 (C[9]), 75.6 (C[12]), 72.1 (C[7], C[4]), 68.6 (C[5], C[6]), 66.4 (C[2]), 59.2 (C[13]), 27.9 (C[10]), 11.0 (C[1]) ppm (see Fig. 12). MS (FAB): 387 ($M^+ + H$), 386 (M^+), 385 ($M^+ - H$) *m/e*.

4.4. Representative procedure for diastereoselective hydroxyalkylation; synthesis of hydroxyalkylacetals **6–12**

A Schlenk tube was charged under an atmosphere of Ar with a stirring bar, dry tetrahydrofuran (50 mL), and (2*S*,4*S*)-4-methoxymethyl-2-ferrocenyl-1,3-dioxane **4a** (1.566 g, 4.95 mmol). After cooling of the yellow solution to −80 °C, *t*-butyl lithium (5.00 mmol, 3.3 mL of a 1.5 M solution in pentane) was added via syringe and the stirred mixture was allowed to warm to ambient temperature. Stirring was continued for 1 h, and dry acetone (10.9 mmol, 0.8 mL) was added in one portion. The mixture was stirred overnight at room temperature, completeness of the reaction was checked by TLC (no spot of starting material (2*S*,4*S*)-4-methoxymethyl-2-ferrocenyl-1,3-dioxane **4a** with $R_f = 0.71$ on neutral silica with *n*-hexane/diethyl ether v/v = 1/1 as eluent). Workup: solvents and volatile materials were removed on a rotary evaporator, the residue was dissolved in diethyl ether, the solution was washed with water until the aqueous layer was neutral, the organic layer was washed with a saturated aqueous sodium chloride solution, the organic solution was dried over magnesium sulfate and evaporated to dryness. The crude material was chromatographed on a short column of basic silica, affording **6** (1.197 g, 3.2 mmol) as an orange oil in 65% yield. All compounds **6–12** were synthesized according to this general procedure, details (starting materials, scale, properties) are given below.

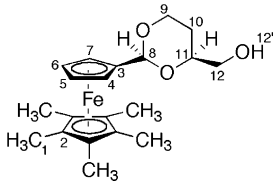


Fig. 11. Numbering of **3b** for NMR assignment.

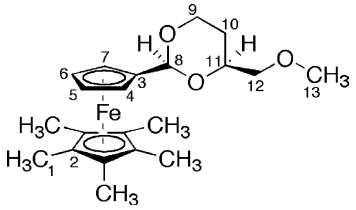


Fig. 12. Numbering of **4b** for NMR assignment.

4.4.1. R_P-(2S,4S)-4-(Methoxymethyl)-2-((2-methyl-2-hydroxy)ethyl)ferrocenyl-1,3-dioxane **6**

Starting materials and reagents: **4a** (1.566 g, 4.95 mmol); *t*-butyl lithium (5 mmol); acetone (0.8 mL, 10.9 mmol). Yield: **6** as an orange oil (1.197 g, 3.2 mmol, 65%). ^{1}H NMR ($CDCl_3$): 5.55 (1H, s, H[7]); 4.32 (1H, t, H[5]); 4.22–4.18 (5 + 1 H, m, H[1] and H[4]); 4.13–4.12 (1H, m, H[6]); 4.05–4.01 (3H, m, H[14] and H[8′]); 3.92–3.83 (1H, t × d, H[13]); 3.49–3.34 (5H, m, H[11] and H[15]); 1.82–1.67 (1H, d × q, H[12]); 1.55 (3H, s, H[9]); 1.46–1.39 (5H, m, H[10] and H[12]) ppm. ^{13}C NMR ($CDCl_3$): 100.5 (C[7]), 96.4 (C[8]), 81.2 (C[13]), 76.0 (C[14]), 75.1 (C[11]), 69.2 (C[1]), 68.9 (C[2]), 68.28 (C[3]), 68.25 (C[6]), 66.5 (C[4]), 65.7 (C[5]), 59.0 (C[15]), 32.3 (C[9]), 30.2 (C[10]), 27.4 (C[12]) ppm (see Fig. 13).

4.4.2. R_P-(2S,4S)-4-(Methoxymethyl)-2-(2-hydroxy-2-phenylbenzyl)ferrocenyl-1,3-dioxane **7**

Starting materials and reagents: **4a** (4.124 g, 13 mmol); *t*-butyl lithium (17 mmol); benzophenone (1.21 g, 20.8 mmol). Yield: **7**, yellow oil (4.428 g, 8.9 mmol, 68%). ^{1}H NMR (CD_2Cl_2): 7.49 (d, 1H, H[18]); 7.47 (d, 1H, H[13]); 7.32–7.16 (m, 8H, H[11, 12, 14, 15, 16, 17, 19, 20]); 5.82 (s, 1H, H[7]); 4.74 (s, 1H, H[8′]); 4.38 (t, 1H, H[5]); 4.32 (s, 5H, H[1]); 4.03 (t, 1H, H[6]); 3.98 (d, 1H, H[4]); 3.75–3.67 (m, 1H, H[23]); 3.48–3.28 (m, 7H, H[21, 24, 25]);

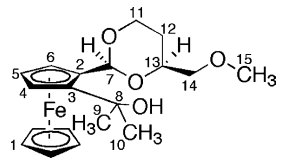


Fig. 13. Numbering of **6** for NMR assignment.

1.61 (m, 1H, H[22]); 1.29 (d × m, 1H, H[22]) ppm. ^{13}C NMR (CD_2Cl_2): 148.2 (C[9]), 146.0 (C[10]), 127.6 (C[20]), 127.4 (C[15]), 127.2 (C[19, 17, 14, 12]), 127.2 (C[18, 13]), 126.6 (C[16]), 126.4 (C[11]), 99.3 (C[7]), 97.3 (C[8]), 82.4 (C[23]), 77.2 (C[2]), 76.0 (C[21]), 75.3 (C[24]), 73.2 (C[3]), 69.7 (C[1]), 68.9 (C[6]), 66.1 (C[4]), 65.4 (C[5]), 59.4 (C[25]), 27.4 (C[22]) ppm (see Fig. 14).

4.4.3. R_P-(2S,4S)-2-[1-(4-Methoxymethyl-[1,3]dioxane-2-yl)-ferrocenyl]-9H- fluorene-9-ol **8**

Starting materials and reagents: **4a** (2.700 g, 8.5 mmol); *t*-butyl lithium (10.2 mmol); 9-fluorenone (3.060 g, 17 mmol). Yield: **8**, orange solid, (1.716 g, 3.46 mmol, 41%). ^{1}H NMR (CD_2Cl_2): 7.87 (1H, s, H[17]); 7.85 (1H, s, H[14]); 7.65–7.55 (2H, m, H[18, 13]); 7.44–7.35 (2H, m, H[20, 11]); 7.30–7.17 (2H, m, H[19, 12]); 5.55 (1H, s, H[7]); 5.11 (1H, s, H[8′]); 4.38 (8H, m, H[1, 4, 5, 6]); 3.98 (3H, m, H[23, 21]); 3.34 (5H, m, H[25, 24]); 1.49 (1H, d, H[22]); 1.92–1.78 (1H, m, H[22]) ppm. ^{13}C NMR (CD_2Cl_2): 151.8 (C[9]), 149.9 (C[10]), 139.9 (C[16]), 138.7 (C[15]), 129.0 (C[19, 12]), 128.5 (C[20]), 127.9 (C[11]), 127.5 (C[18, 13]), 125.6 (C[17]), 125.0 (C[14]), 100.5 (C[7]), 93.9 (C[8]), 81.5 (C[23]), 81.4 (C[2]), 76.6 (C[21]), 75.5 (C[24]), 70.3 (C[1]), 69.4 (C[3]), 69.3 (C[6]), 67.1 (C[4]), 66.9 (C[5]), 59.3 (C[25]), 27.8 (C[22]) ppm (see Fig. 15). X-ray single crystal structure: Fig. 1 and Table 1.

4.4.4. R_P-(2S,4S)-4-(Methoxymethyl)-2-(hydroxymethyl)-ferrocenyl-1,3-dioxane **9**

Starting materials and reagents: **4a** (2.833 g, 8.96 mmol); *t*-butyl lithium (9.35 mmol); paraformaldehyde (0.545 g, 18 mmol). Yield: **9**, yellow oil, (1.623 g, 4.7 mmol, 52%). ^{1}H NMR ($CDCl_3$): 5.56 (1H, s, H[7]); 4.57–4.52 (1H, d × d, H[5]); 4.32 (1H, t, H[4]); 4.22–4.13 (3H, m, H[6, 8]); 4.10 (5H, s, H[1]); 4.03 (2H, t, H[9]); 3.91–3.82 (1H, t × d, H[11]); 3.46–3.33 (3H, m, H[12, 8′]); 3.32 (3H, s, H[13]); 1.76–1.62 (1H, q × d, H[10]); 1.42–1.37 (1H, d, H[10]) ppm. ^{13}C NMR ($CDCl_3$): 100.1 (C[7]), 85.5 (C[11]), 84.3 (C[2]), 75.3 (C[9]),75.0 (C[12]), 67.0 (C[3]), 68.9 (C[1]), 67.4 (C[6]), 66.4 (C[4]), 66.1 (C[5]), 59.4 (C[13]), 58.8 (C[8]), 27.0 (C[10]) ppm (see Fig. 16).

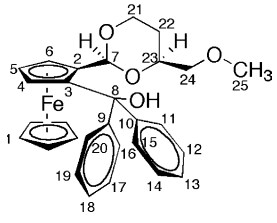


Fig. 14. Numbering of **7** for NMR assignment.

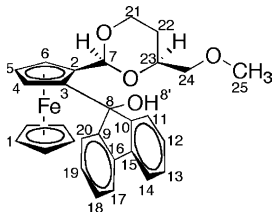


Fig. 15. Numbering of **8** for NMR assignment.

4.4.5. R_P-(2S,4S)-4-(Methoxymethyl)-2-(2-hydroxyadamantyl)ferrocenyl-1,3-dioxane **10**

Starting materials and reagents: **4a** (1.022 g, 3.23 mmol); *t*-butyl lithium (3.87 mmol); adamantanone (0.720 g, 4.84 mmol). Yield: **10**, orange oil, (1.067 g, 2.3 mmol, 71%). ^{13}C NMR ($CDCl_3$): 100.0 (C[7]), 98.2 (C[8]), 82.7 (C[20]), 75.9 (C[18]), 75.3 (C[21]), 73.0 (C[2]), 70.5 (C[3]), 69.3 (C[1]), 68.3 (C[6]), 66.6 (C[4]), 65.4 (C[5]), 59.2 (C[22]), 38.1 (C[14]), 37.6 (C[11]), 37.0 (C[13]), 36.4 (C[16]), 34.2 (C[17]), 33.7 (C[12]), 33.5 (C[15]), 27.8 (C[19]), 27.2 (C[9]), 27.0 (C[10]) ppm (see Fig. 17).

4.4.6. R_P-(2S,4S)-4-(Methoxymethyl)-2-(1-hydroxy-1-isopropyl-2-methyl-propyl)ferrocenyl-1,3-dioxane **11**

Starting materials and reagents: **4a** (1.091 g, 3.45 mmol); *t*-butyl lithium (4.14 mmol); 2,4-dimethylpentan-3-one (0.594 g, 5.20 mmol). Yield: **11**, orange oil, (2.102 g, 2.79 mmol, 81%). ^{1}H NMR ($CDCl_3$): 5.53 (1H, s, H[7]); 4.30 (1H, d × d, H[5]); 4.23 (2H, m, H[4, 6]); 4.16 (5H, s, H[1]); 4.15–3.88 (3H, m, H[17, 18]); 3.83 (1H, s, H[8′]); 3.48–3.35 (5H, m, H[15, 19]); 2.33 (1H, sept, H[9]); 1.97 (1H, sept, H[10]); 1.77 (1H, d × d, H[16]); 1.47 (1H, d × d, H[16]); 1.24 (6H, 2d, H[11, 12]); 0.74 (3H, d, H[13]); 0.69 (3H, d, H[14]) ppm. ^{13}C NMR ($CDCl_3$): 100.7 (C[7]), 95.9 (C[8]), 82.6 (C[17]), 78.1 (C[18]), 76.3 (C[15]), 75.6 (C[2]), 70.4 (C[1]), 70.3 (C[3]), 67.0 (C[6]), 66.8 (C[4]), 66.5 (C[5]), 59.5 (C[19]), 38.5 (C[9]), 35.9 (C[10]), 28.0 (C[16]), 19.3 (C[11]), 19.0 (C[12]), 18.5 (C[13]), 18.2 (C[14]) ppm (see Fig. 18).

4.4.7. R_P-(2S,4S)-4-(Methoxymethyl)-2-((2-methyl-2-hydroxy)ethyl)-1′,2′,3′,4′,5′-pentamethylferrocenyl-1,3-dioxane **12**

Starting materials and reagents: **4b** (611 mg, 1.58 mmol); *t*-butyl lithium (1.74 mmol); acetone (186 mg, 3.2 mmol). Yield: **12**, yellow oil, (358 mg, 0.8 mmol, 51%). ^{1}H NMR ($CDCl_3$): 5.47 (1H, s, H[8]); 4.24–4.20 (1H, m, H[14]); 4.08–4.00 (1H, m, H[15]); 3.95–3.87 (1H, m, H[15]); 3.92 (1H, s, H[9′]); 3.83 (1H, s, H[5]); 3.65 (1H, s, H[6]); 3.56 (1H, t, H[7]); 3.53–3.38 (2H, m, H[12]); 3.36 (3H, s, H[16]); 1.87 (15H, s, H[1]); 1.93–1.72 (1H, m, H[13]); 1.54 (3H, s, H[10]); 1.47 (1H, d, H[13]); 1.41 (3H, s, H[11]) ppm. ^{13}C NMR ($CDCl_3$): 100.3 (C[8]), 95.8 (C[9]), 80.5 (C[14]), 79.8 (C[3]), 75.9 (C[12]), 75.2 (C[15]), 71.8 (C[7]), 71.1 (C[5]), 69.4 (C[6]), 66.4 (C[2]), 59.0 (C[16]), 32.5 (C[10]), 29.7 (C[11]), 27.7 (C[13]), 11.1 (C[1]) ppm (see Fig. 19).

4.5. General procedure for removal of acetal-stereodirecting group; synthesis of hydroxyalkylaldehydes **13–19**

A 100 ml round bottom flask was charged with a stirring bar, 0.5–1.0 mmol of hydroxyalkylferroceneacetal **6–12**,

Table 1
Crystallographic data for **8**, **13**, **15**, **20**, **21**, **33**, **35**, **37**, **38**

	8	**13**	**15**	**20**	**21**
Molecular formula	$C_{29}H_{28}FeO_4$	$C_{14}H_{16}FeO_2$	$C_{24}H_{18}FeO_2$	$C_{19}H_{24}FeO$	$C_{20}H_{21}FeNO_2$
Molecular weight	496.36	272.12	394.23	324.23	363.23
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	829.37(3)	749.27(2)	744.21(2)	751.06(2)	884.61(4)
b (Å)	1278.84(3)	1178.90(4)	1248.00(4)	1378.09(4)	1166.31(3)
c (Å)	1155.87(4)	1420.71(5)	956.68(3)	1599.57(5)	1711.03(7)
α (deg)	90	90	90	90	90
β (deg)	105.312(2)	90	95.934(2)	90	90
γ (deg)	90	90	90	90	90
V (Å^3)	1.18243(7)	1.25493(7)	0.88378(5)	1.65560(8)	1.76532(12)
Z	2	4	2	4	4
Temperature (K)	233(2)	233(2)	233(2)	233(2)	233(2)
D_c (Mg m^{-3})	1.394	1.440	1.481	1.301	1.367
μ (mm^{-1})	0.672	1.188	0.870	0.907	0.865
F(000)	520	568	408	688	760
Color, habit	Orange prism	Red prism	Red prism	Red prism	Red plate
Crystal size (mm)	$0.4 \times 0.2 \times 0.12$	$0.3 \times 0.2 \times 0.15$	$0.35 \times 0.2 \times 0.15$	$0.45 \times 0.2 \times 0.15$	$0.35 \times 0.15 \times 0.05$
θ Limit (deg)	1.83–25.00	2.24–25.99	2.14–25.99	1.95–26.00	2.11–24.00
Index ranges hkl	$-9 \leqslant h \leqslant 9$; $-14 \leqslant k \leqslant 15$; $-13 \leqslant l \leqslant 13$	$-8 \leqslant h \leqslant 9$; $-14 \leqslant k \leqslant 14$; $-17 \leqslant l \leqslant 15$	$-9 \leqslant h \leqslant 8$; $-14 \leqslant k \leqslant 15$; $-11 \leqslant l \leqslant 11$	$-9 \leqslant h \leqslant 7$; $-16 \leqslant k \leqslant 16$; $-19 \leqslant l \leqslant 19$	$-9 \leqslant h \leqslant 10$; $-13 \leqslant k \leqslant 13$; $-19 \leqslant l \leqslant 17$
No. of refections collected	6097	7518	5885	10430	8740
No. of independent reflections	3898	2459	3291	3239	2767
No. of reflections with $I \geqslant 2\sigma(I)$	3769	2359	3239	3101	2413
No. of data/restraints/ parameters	3898/2/312	2459/0/159	3291/2/249	3239/0/197	2767/2/226
Goodness-of-fit on F^2	1.048	1.070	1.036	1.046	1.048
Final R indices ($I \geqslant 2\sigma(I)$)	$R_1 = 0.027$ $wR_2 = 0.066$	$R_1 = 0.022$ $wR_2 = 0.055$	$R_1 = 0.020$ $wR_2 = 0.048$	$R_1 = 0.023$ $wR_2 = 0.057$	$R_1 = 0.038$ $wR_2 = 0.091$
R indices (all data)	$R_1 = 0.029$ $wR_2 = 0.068$	$R_1 = 0.024$ $wR_2 = 0.056$	$R_1 = 0.020$ $wR_2 = 0.049$	$R_1 = 0.025$ $wR_2 = 0.058$	$R_1 = 0.048$ $wR_2 = 0.095$
Absolute structure parameters	−0.007(13)	0.015(18)	0.011(10)	0.013(15)	0.00(2)
Largest difference peak and hole (e nm^{-3})	411 and −277	190 and −205	221 and −153	174 and −197	469 and −328

	33	**35**	**37**	**38**
Molecular formula	$C_{34}H_{29}FeNO_2 \times 0.667\ Et_2O$	$C_{30}H_{36}Fe_2N_2O_2$	$C_{34}H_{42}Fe_2N_2O_2 \times C_7H_8$	$C_{34}H_{42}Fe_2N_2O_2$
Molecular weight	588.85	568.31	714.53	622.40
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	2205.85(6)	802.32(2)	1024.77(2)	2595.64(6)
b (Å)	1982.21(8)	1215.60(3)	1393.56(2)	741.64(2)
c (Å)	2241.61(9)	2776.26(7)	2606.91(6)	800.35(2)
α (deg)	90	90	90	90
β (deg)	109.495(2)	90	90	90
γ (deg)	90	90	90	90
V (Å^3)	9.2394(6)	2.70769(12)	3.72287(12)	1.54070(7)
Z	12	4	4	2
Temperature (K)	233(2)	233(2)	233(2)	233(2)
D_c (Mg m^{-3})	1.270	1.394	1.275	1.342
μ (mm^{-1})	0.525	1.101	0.815	0.974
F(000)	3720	1192	1512	656
Color, habit	Red prism	Red prism	Red plate	Red prism
Crystal size (mm)	$0.3 \times 0.1 \times 0.05$	$0.3 \times 0.15 \times 0.15$	$0.45 \times 0.4 \times 0.15$	$0.4 \times 0.4 \times 0.15$
θ Limit (deg)	1.59–21.50	1.83–24.99	2.14–24.99	2.66–25.99
Index ranges hkl	$-22 \leqslant h \leqslant 22$; $-20 \leqslant k \leqslant 20$; $-23 \leqslant l \leqslant 23$	$-9 \leqslant h \leqslant 9$; $-14 \leqslant k \leqslant 14$; $-33 \leqslant l \leqslant 32$	$-9 \leqslant h \leqslant 12$; $-14 \leqslant k \leqslant 16$; $-27 \leqslant l \leqslant 31$	$-31 \leqslant h \leqslant 32$; $-9 \leqslant k \leqslant 7$; $-9 \leqslant l \leqslant 9$
No. of reflections collected	40514	14138	16885	6364
No. of independent reflections	21203	4751	6469	2813
No. of reflections with $I \geqslant 2\sigma(I)$	14039	4363	6035	2753
No. of data/restraints/parameters	21203/1/2245	4751/2/334	6469/2/428	2813/1/186
Goodness-of-fit on F^2	1.014	1.033	1.052	1.055

Table 1 (*continued*)

	33	**35**	**37**	**38**
Final R indices ($I \geqslant 2\sigma(I)$)	$R_1 = 0.068$	$R_1 = 0.028$	$R_1 = 0.031$	$R_1 = 0.024$
	$wR_2 = 0.143$	$wR_2 = 0.061$	$wR_2 = 0.074$	$wR_2 = 0.056$
R indices (all data)	$R_1 = 0.115$	$R_1 = 0.033$	$R_1 = 0.036$	$R_1 = 0.0243$
	$wR_2 = 0.161$	$wR_2 = 0.063$	$wR_2 = 0.077$	$wR_2 = 0.0566$
Absolute structure parameters	−0.008(17)	0.002(15)	0.009(13)	−0.003(15)
Largest difference peak and hole (e nm^{-3})	309 and −249	190 and −190	248 and −229	227 and −160

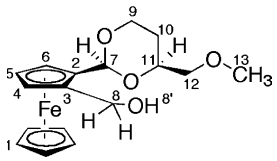


Fig. 16. Numbering of **9** for NMR assignment.

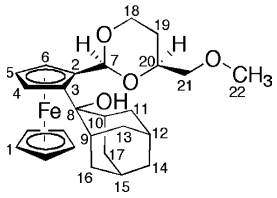


Fig. 17. Numbering of **10** for NMR assignment.

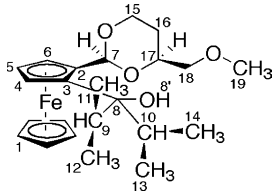


Fig. 18. Numbering of **11** for NMR assignment.

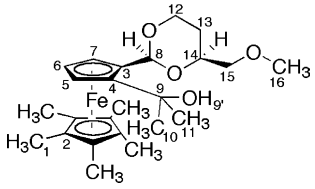


Fig. 19. Numbering of **12** for NMR assignment.

dichloromethane (7 mL), water (3 mL), and *p*-toluenesulfonic acid (200 mg). The mixture was stirred at ambient temperature for 1–5 h, until complete deprotection was evidenced by TLC analysis. Workup: 50 mL dichloromethane were added, the organic solution was washed with four portions of an aqueous saturated sodium bicarbonate solution followed by one portion of water as well as one portion of brine solution. The organic solution was dried with magnesium sulfate, filtered, and reduced to dryness on a rotary evaporator, affording the crude product. Chromatography on silica yielded the pure products **13**–**19** with properties detailed below.

4.5.1. R_P-2-(2-Methyl-2-hydroxyethyl)ferrocenealdehyde *13*

Starting materials and reagents: **6** (1.197 g, 3.2 mmol); *p*-toluenesulfonic acid (0.269 g, 2 mmol). Yield: **13**, red waxy solid, m.p. 67.6–70.2 °C (0.711 g, 2.6 mmol, 82%). ^{1}H NMR ($CDCl_3$): 9.82 (1H, s, H[7]); 5.45 (1H, s, H[8′]); 4.66–4.64 (1H, m, H[5]); 4.63–4.62 (1H, m, H[4]); 4.53 (1H, t, H[6]); 4.35 (5H, s, H[1]); 1.60 (3H, s, H[9]); 1.35 (3H, s, H[10]) ppm. ^{13}C NMR ($CDCl_3$): 196.9 (C[7]), 102.2 (C[8]), 74.4 (C[2]), 74.1 (C[3]), 73.4 (C[6]), 71.5 (C[4]), 70.5 (C[1]), 67.9 (C[5]), 33.2 (C[9]), 28.6 (C[10]) ppm (see Fig. 20). IR (ATR): 3373 br (ν_{OH}), 3089 w, 2975 m, 1709 w, 1634 s ($\nu_{C=O}$), 1444 w, 1410 w, 1372 w, 1355 m, 1344 m, 1268 w, 1249 m, 1208 w, 1181 m, 1137 w, 1106 w, 1087 w, 1045 w, 1001 m, 955 m, 820 s, 757 m, 691 w, 617 m, 538 w, 498 m, 475 m, 459 m, 445 m cm^{-1}. MS (EI): 273 ($M^+ + H$), 272 (M^+) *m/e*. X-ray single crystal structure: Fig. 2 and Table 1.

4.5.2. R_P-2-(2-Phenyl-2-hydroxybenzyl)-ferrocenealdehyde *14*

Starting materials and reagents: **7** (4.428 g, 8.9 mmol); *p*-toluenesulfonic acid (1.859 g, 9.7 mmol). Yield: **14**, red-orange solid, m.p. 194.9–195.5 °C (1.270 g, 3.2 mmol, 36%). ^{1}H NMR (CD_2Cl_2): 9.68 (1H, s, H[7]); 7.46 (2H, d, H[18, 13]); 7.35–7.25 (3H, m, H[20, 19, 17]); 7.16 (3H, m, H[11, 12, 14]); 7.10 (2H, m, H[16, 15]); 6.61 (1H, s, H[8′]); 4.77 (1H, t, H[5]); 4.59 (1H, t, H[4]); 4.34 (5H, s, H[1]); 4.08 (1H, t, H[6]) ppm. ^{13}C NMR (CD_2Cl_2): 196.9 (C[7]), 149.4 (C[9]), 145.8 (C[10]), 127.9 (C[13, 18]), 127.7 (C[12, 17]), 127.5 (C[14, 19]), 127.4 (C[11, 20]), 127.1 (C[15, 16]), 101.6 (C[8]), 78.8 (C[2]), 77.0 (C[3]), 75.2 (C[6]), 74.2 (C[4]), 72.0 (C[5]), 71.1 (C[1]) ppm (see Fig. 21). IR (KBr): 3288 s (ν_{OH}), 3052 w, 2827 w, 1643 s ($\nu_{C=O}$), 1489 m, 1448 s, 1376 m, 1344 m, 1235 m, 1177 m, 1154 w, 1108 w, 1041 s, 999 w, 903 w, 828 s, 756 s, 703 s, 665 w, 631 w, 525 m, 482 m, 456 m cm^{-1}. MS (EI): 398.2 ($M^+ + 2H$), 397.2 ($M^+ + H$), 396.2 (M^+) *m/e*.

4.5.3. R_P-2-(9H-9-Hydroxyfluorenyl)ferrocenealdehyde *15*

Starting materials and reagents: **8** (1.716 g, 3.46 mmol); *p*-toluenesulfonic acid (0.80 g, 4.20 mmol). Yield: **15**, red

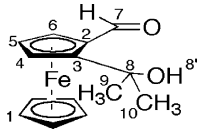


Fig. 20. Numbering of **13** for NMR assignment.

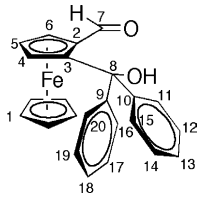


Fig. 21. Numbering of **14** for NMR assignment.

crystals, m.p. 176.5–181.0 °C (0.641 g, 2.51 mmol, 73%). ^{1}H NMR (CD_2Cl_2): 9.96 (1H, s, H[7]); 7.87–7.86 (1H, d × d, H[17]); 7.84–7.71 (1H, d × d, H[14]); 7.58–7.56 (1H, d × d, H[18]); 7.46 (2H, q × q, H[19, 12]); 7.34–7.31 (1H, d × d, H[13]); 7.27 (1H, d × t, H[20]); 7.11 (1H, d × t, H[11]); 6.76 (1H, s, H[8′]), 4.76 (1H, t, H[5]); 4.54 (5H, s, H[1]); 4.44 (1H, t, H[4]); 3.85 (1H, t, H[6]) ppm. ^{13}C NMR (CD_2Cl_2): 196.9 (C[7]), 152.1 (C[9]), 148.0 (C[10]), 140.3 (C[16]), 138.2 (C[15]), 129.4 (C[19]), 128.7 (C[20]), 128.2 (C[12]),127.8 (C[11]), 125.5 (C[18]), 123.5 (C[13]), 120.3 (C[17]), 120.2 (C[14]), 99.5 (C[8]), 80.2 (C[2]), 75.8 (C[3]), 75.0 (C[6]), 73.5 (C[4]), 72.4 (C[5]), 71.4 (C[1]) ppm (see Fig. 22). IR (KBr): 3289 s (ν_{OH}), 3092 w, 2855 w, 1637 s ($\nu_{C=O}$), 1440 m, 1416 m, 1376 w, 1343 w, 1281 w, 1233 m, 1196 m, 1105 w, 1052 m, 828 m, 748 s, 731 s, 673 m, 645 m, 550 w, 484 w cm^{-1}. MS (FAB): 395 ($M^+ + H$), 394 (M^+) *m/e*. X-ray single crystal structure: Fig. 3 and Table 1.

4.5.4. R_P-2-Hydroxymethylferrocenealdehyde **16**

Starting materials and reagents: **9** (1.600 g, 4.6 mmol); *p*-toluenesulfonic acid (1.00 g, 5.26 mmol). Yield: **16**, red solid, m.p. 87.6–90.3 °C (0.709 g, 3.85 mmol, 84%). ^{1}H NMR ($CDCl_3$): 9.93 (1H, s, H[7]); 4.70 (1H, s, H[5]); 4.67 (1H, s, H[4]); 4.51 (3H, m, H[6, 8]); 4.30 (5H, s, H[1]); 3.94 (1H, d, H[8′]) ppm. ^{13}C NMR ($CDCl_3$): 196.1 (C[7]), 90.4 (C[8]), 74.9 (C[2]), 73.2 (C[3]), 71.6 (C[6]), 70.2 (C[1]), 59.4 (C[5, 4]) ppm (see Fig. 23). IR (KBr): 3441 s (ν_{OH}), 3087 w, 2955 s, 2988 s, 2860 s, 2823 w, 1657 s ($\nu_{C=O}$), 1466 m, 1437 m, 1408 m, 1381 m, 1359 w, 1268 s, 1213 w, 1140 w, 1105 w, 1053 w, 1003 m, 901 w, 857 w, 836 m, 766 w, 730 w, 650 w, 639 m, 497 s, 461 w cm^{-1}. MS (FAB): 245 ($M^+ + 1$); 244 (M^+) *m/e*.

4.5.5. R_P-2-(2-Hydroxyadamantyl)ferrocenealdehyde **17**

Starting materials and reagents: **10** (1.076 g, 2.3 mmol); *p*-toluenesulfonic acid (0.60 g, 3.16 mmol). Yield: **17**, red solid, m.p. 143.7–144.8 °C (0.615 g, 1.7 mmol, 74%). ^{1}H NMR ($CDCl_3$): 9.99 (1H, s, H[7]); 5.03 (1H, s, H[8′]); 4.64 (1H, t, H[5]); 4.58–4.57 (2H, m, H[4, 6]); 4.32 (5H, s, H[1]); 2.52 (2H, t, H[14]); 2.22 (2H, m, H[12, 15]); 1.81–1.51 (12H, m, H[9–17]) ppm. ^{13}C NMR ($CDCl_3$): 195.3 (C[7]), 103.3 (C[8]); 75.9 (C[2]), 74.4 (C[7]), 72.5 (C[6, 4]), 70.8 (C[1]), 70.6 (C[5]), 40.2 (C[14]), 38.1 (C[13]), 36.4 (C[11]), 34.0 (C[16, 17]), 33.7 (C[12]), 33.6 (C[15]), 27.2 (C[9]), 27.1 (C[10]) ppm (see Fig. 24). IR (ATR): 3396 br (ν_{OH}), 2896 m, 2848 m, 1665 m, 1638 s ($\nu_{C=O}$), 1519 w, 1491 w, 1468 m, 1448 m, 1438 m, 1427 w, 1410 w, 1383 w, 1352 w, 1333 w, 1280 w, 1263 w, 1234 w, 1218 w, 1188 m, 1137 w, 1101 m, 1085 w, 1058 w, 1043 w, 1012 m, 960 w, 935 w, 902 w, 882 w, 856 w, 832 w, 819 w, 792 w, 755 s, 694 m, 677 w, 573 m, 529 m, 509 m, 480 w, 455 m, 436 m, 417 w cm^{-1}. MS (FAB): 365 ($M^+ + H$), 364 (M^+) *m/e*.

4.5.6. R_P-2-(1-Hydroxy-1-isopropyl-2-methyl-propyl)-ferrocenealdehyde **18**

Starting materials and reagents: **11** (1.201 g, 2.79 mmol); *p*-toluenesulfonic acid (0.60 g, 3.16 mmol). Yield: **18**, red solid, m.p. 109.2–111.5 °C (0.535 g, 1.67 mmol, 63%). ^{1}H NMR ($CDCl_3$): 9.81 (1H, s, H[7]); 5.19 (1H, s, H[8′]); 4.69 (1H, t, H[5]); 4.63 (1H, d × d, H[4]); 4.55 (1H, bs, H[6]); 4.28 (5H, bs, H[1]); 2.22 (1H, sept, H[9]); 2.02 (1H, sept., H[10]); 1.49 (3H, d, H[11]); 1.09 (3H, d, H[12]); 0.62 (3H, d, H[13]); 0.57 (3H, d, H[14]) ppm. ^{13}C NMR ($CDCl_3$): 195.0 (C[7]), 97.7 (C[8]), 77.2 (C[2]), 74.5 (C[3]), 72.1 (C[6]), 71.8 (C[4]), 71.7 (C[1, 5]), 38.4 (C[9]), 33.1 (C[10]), 19.9 (C[11]), 18.5 (C[12]), 18.3 (C[13]), 17.8 (C[14]) ppm (see Fig. 25). IR (ATR): 3553 m (ν_{OH}), 3112

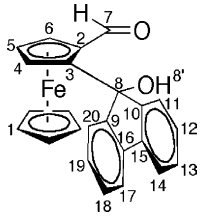


Fig. 22. Numbering of **15** for NMR assignment.

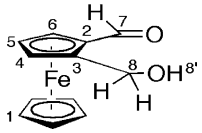


Fig. 23. Numbering of **16** for NMR assignment.

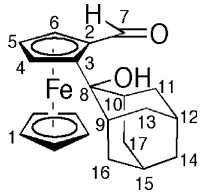


Fig. 24. Numbering of **17** for NMR assignment.

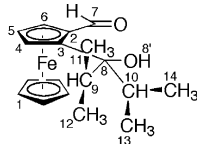


Fig. 25. Numbering of **18** for NMR assignment.

w, 2970 m, 2863 w, 1648 s ($\nu_{C=O}$), 1521 w, 1475 m, 1419 w, 1411 w, 1384 m, 1353 w, 1314 m, 1297 w, 1282 w, 1256 m, 1206 m, 1176 w, 1157 w, 1138 w, 1118 w, 1107 m, 1076 m, 1043 m, 1020 w, 996 s, 957 m, 915 w, 857 s, 843 w, 826 m, 760 s, 684 m, 638 w, 617 w, 587 m, 589 w, 507 s, 482 s, 461 w, 433 w cm^{-1}. MS (FAB): 329 ($M^+ + H$), 328 (M^+) *m/e*.

4.5.7. R_P-2-((2-Methyl-2-hydroxy)ethyl)-1′,2′,3′,4′,5′-pentamethylferrocenyl-1-aldehyde **19** and R_P-2-((2-propenyl)-1′,2′,3′,4′,5′-pentamethylferrocenyl)-1-aldehyde **20**

Starting materials and reagents: **12** (134 mg, 0.3 mmol); *p*-toluenesulfonic acid (125 mg, 0.66 mmol).

Yield target product: **19**, red oil, (60 mg, 0.17 mmol, 57%). ^{1}H NMR ($CDCl_3$): 9.50 (1H, s, H[8]); 5.47 (1H, s, H[9′]); 4.19 (1H, m, H[6]); 4.14 (1H, s, H[5]), 4.13 (1H, s, H[7]); 1.81 (15H, s, H[1]); 1.54 (3H, s, H[10]); 1.25 (3H, s, H[11]) ppm. ^{13}C NMR ($CDCl_3$): 195.8 (C[8]), 100.4 (C[9]), 83.0 (C[7]), 77.9 (C[5]), 73.7 (C[2]), 68.3 (C[6]), 34.4 (C[10]), 27.5 (C[11]), 11.1 (C[1]) ppm (see Fig. 26). IR (ATR): 3364 br (ν_{OH}), 2969 m, 2904 m, 1638 s ($\nu_{C=O}$), 1475 m, 1444 m, 1427 m, 1374 m, 1354 m, 1249 w, 1210 w, 1180 w, 1136 w, 1071 w, 1030 m, 992 w, 956 m, 823 m, 759 m, 686 w, 655 w, 648 w, 641 w, 634 w, 626 w, 618 w, 604 w, 596 w, 588 w, 581 w, 573 w, 530 m cm^{-1}. MS (FAB): 343 ($M^+ + H$), 342 (M^+) *m/e*.

Yield side product: **20**, orange oil, (39 mg, 0.12 mmol, 40%). ^{1}H NMR ($CDCl_3$): 9.90 (s, 1H, H[8]); 5.14 (t, 1H, H[10b]); 5.11 (s, 1H, H[10a]); 4.34 (d × d, 1H, H[7]); 4.28 (d × d, 1H, H[5]); 4.17 (t, 1H, H[6]); 2.08 (s, 3H, H[11]); 1.75 (s, 15H, H[1])ppm. ^{13}C NMR ($CDCl_3$): 191.2 (C[8]); 136.6 (C[9]); 112.7 (C[10]); 89.9 (C[3, 4]); 80.7 (C[6]); 75.5 (C[7]); 75.0 (C[5]); 70.8 (C[2]); 21.2 (C[10]); 8.8 (C[1]) ppm (see Fig. 27). IR (ATR): 3091 w, 2952 s, 2916 s, 2853 s, 1728 m ($\nu_{C=C}$), 1656 s ($\nu_{C=O}$), 1456 w, 1426 w, 1380 m, 1337 w, 1288 w, 1261 m, 1232 m, 1207 w, 1120 w, 1070 w, 1030 m, 879 m, 823 w, 800 w, 777 w, 737 w, 703 w, 669 w, 636 w, 578 w, 528 w, 491 w, 460 m cm^{-1}. MS (FAB): 325 ($M^+ + H$), 324 (M^+) *m/e*. X-ray single crystal structure: Fig. 4 and Table 1.

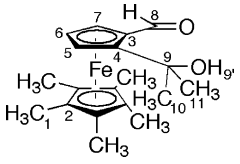


Fig. 26. Numbering of **19** for NMR assignment.

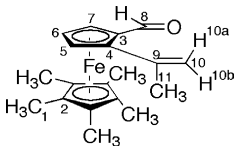


Fig. 27. Numbering of **20** for NMR assignment.

4.6. General procedure for the synthesis of tridentate [ONO] ligands **21–34**

A small Schlenk tube was charged under an atmosphere of Ar with a stirring bar, hydroxyalkylferrocenealdehyde **13–19** and the respective aminoalcohol (see below) in equimolar amounts. Dry methanol was added to obtain a concentrated solution. This mixture was stirred at ambient temperature or at reflux temperature for 1–2 days, until complete condensation was evidenced by IR spectroscopy (note: TLC analysis of the reaction mixture is useless, because these Schiff bases hydrolyze at least in part to the starting materials on silica or alumina, therefore progress of the reaction cannot be monitored by this common method). Workup: solvents and volatile materials were removed on a rotary evaporator, the residue was dissolved in dichloromethane or diethyl ether, the solution was filtered through a short pad of celite®, and all volatiles were removed in vacuo, affording the product in quantitative yield as solid powders. Details and properties for **21–34** are given below.

4.6.1. R_P-2-{[1-[2-(1-Hydroxy-1-methylethyl)ferrocenyl]-meth-(*E*)-ylidene]amino}phenol **21**

Starting materials: **13** (500 mg, 1.84 mmol); *o*-aminophenol (201 mg, 1.84 mmol); methanol (6 mL). Yield: **21** (662 mg, 1.82 mmol, 99%) as purple crystals, m.p. 167.5–169.3 °C. ^{1}H NMR ($CDCl_3$): 8.66 (1H, s, H[7]); 7.20–7.12 (2H, m, H[13, 14]); 7.00 (1H, d, H[12]); 6.90 (1H, t, H[15]); 6.62 (1H, bs, H[8′]); 4.68 (1H, m, H[5]); 4.53 (1H, m, H[4]); 4.47 (1H, t, H[6]); 4.31 (5H, s, H[1]); 1.71 (3H, s, H[9]); 1.49 (3H, s, H[10]) ppm. ^{13}C NMR ($CDCl_3$): 163.1 (C[7]), 150.7 (C[16]), 136.5 (C[11]), 127.8 (C[14]), 120.4 (C[13]), 116.6 (C[12]), 115.5 (C[15]), 100.4 (C[8]), 74.7 (C[2]), 73.0 (C[3]), 72.3 (C[6]), 70.1 (C[4]), 69.8 (C[1]), 68.7 (C[5]), 32.7 (C[9]), 29.5 (C[10]) ppm (see Fig. 28). IR (ATR): 3374 m, 3302 m, 3095 bm (ν_{OH}), 2970 m, 1620 s ($\nu_{C=N}$), 1590 s, 1509 m, 1488 w, 1455 m, 1411 w, 1373 w, 1346 m, 1292 w, 1274 w, 1254 s, 1241 m, 1212 w, 1195 w, 1178 w, 1158 w, 1140 w, 1104 m, 1089 m, 1002 bs, 974 w, 954 m, 924 m, 897 w, 875 w, 843 w, 815 s, 798 s, 749 s, 740 s, 697 w, 624 w, 598 w, 573 w, 563 w, 540 w, 527 w, 503 w, 470 s, 449 s, 418 w cm^{-1}. MS (EI): 364.0 ($M^+ + H$); 363.0 (M^+) *m/e*. Anal. Calc. for $C_{20}H_{21}FeNO_2$ (363.07 g mol^{-1}): C, 66.13; H, 5.83; N, 3.86. Found: C, 64.3; H, 6.0; N, 4.1. X-ray single crystal structure: Fig. 5 and Table 1.

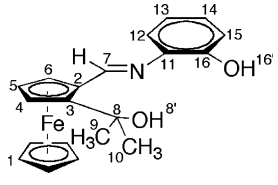


Fig. 28. Numbering of **21** for NMR assignment.

4.6.2. R_P-2-{[1-[2-(Hydroxydiphenylmethyl)ferrocenyl]-meth-(E)-ylidene]amino}phenol ***22***

Starting materials: **14** (202 mg, 0.50 mmol); *o*-aminophenol (60 mg, 0.56 mmol); methanol (10 mL). Yield: **22** (242 mg, 0.50 mmol, >99%) as burgundy solid, m.p. 82.1–86.7 °C. ^{1}H NMR (CD_2Cl_2): 8.40 (1H, s, H[7]); 7.49 (3H, m, H[18, 13, 25]); 7.37–7.18 (8H, m, H[11, 12, 14, 15, 16, 17, 19, 20]); 7.11–7.06 (2H, t, H[8′, 23]); 6.86 (1H, t, H[24]); 6.75 (1H, d, H[22]); 4.83 (1H, bs, H[26′]); 4.83 (1H, s, H[5]); 4.51 (1H, s, H[4]); 4.35 (5H, s, H[1]); 3.95 (1H, s, H[6]) ppm. ^{13}C NMR (CD_2Cl_2): 164.6 (C[7]), 150.4 (C[26]), 149.9 (C[9]), 146.2 (C[10]), 136.8 (C[21]), 128.3 (C[24]), 128.0 (C[18]), 127.9 (C[13]),127.5 (C[12, 17]), 127.3 (C[14, 19]), 127.2 (C[11, 20]), 127.0 (C[15, 16]), 120.6 (C[23]), 117.0 (C[22]), 115.2 (C[25]), 99.8 (C[8]), 77.6 (C[2]), 77.4 (C[3]), 74.9 (C[6]), 70.7 (C[1]), 70.2 (C[4]), 65.9 (C[5]) ppm (see Fig. 29). IR (KBr): 3477 s (ν_{OH}), 3055 w, 1617 s ($\nu_{C=N}$), 1596 s, 1489 s, 1446 s, 1357 m, 1288 m, 1256 m, 1216 m, 1175 m, 1149 w, 1106 m, 1031 s, 817 s, 749 s, 698 s, 676 s, 533 m, 466 s cm^{-1}. MS (FAB): 488 ($M^+ + H$); 487 (M^+) *m/e*. Anal. Calc. for $C_{30}H_{35}FeNO_2$ (487.41 g mol^{-1}): C, 72.43; H, 7.09; N, 2.82. Found: C, 73.6; H, 5.8; N, 3.0.

4.6.3. R_P-2-(2-{[(E)-2-Hydroxy-(1R,2S)-1,2-diphenylethylimino]methyl}ferrocenyl)propan-2-ol ***23***

Starting materials: **13** (136 mg, 0.50 mmol); (1*R*,2*S*)-2-amino-1,2-diphenylethanol (117 mg, 0.55 mmol); methanol (5 mL). Yield: **23** (226 mg, 0.48 mmol, 96%) as brown-red solid, m.p. 65.8–68.2 °C. ^{1}H NMR (CD_2Cl_2): 7.92 (1H, s, H[7]); 7.48–7.19 (11H, m, H[8′, 13–18, 20–24]); 5.05 (1H, d, H[12]); 4.47 (1H, d, H[11]); 4.26 (1H, d, H[6]); 4.20 (1H, s, H[4]); 4.17 (1H, t, H[5]); 3.88 (5H, s, H[1]); 2.19 (1H, bs, H[12′]); 1.53 (3H, s, H[9]); 1.25 (3H, s, H[10]) ppm. ^{13}C NMR (CD_2Cl_2): 166.2 (C[7]), 142.0 (C[19]), 141.6 (C[13]), 128.8 (C[17, 15, 23, 21]), 128.4 (C[22]), 128.3 (C[24, 20]), 128.0 (C[18, 14]), 127.9 (C[16]), 100.4 (C[8]), 81.9 (C[12]), 78.2 (C[11]), 73.8 (C[2]), 73.6 (C[3]), 72.0 (C[6]), 67.0 (C[1]), 68.7 (C[4]), 68.0 (C[5]), 32.8 (C[9]), 29.3 (C[10]) ppm (see Fig. 30). IR (KBr): 3400 bs (ν_{OH}), 3086 w, 2975 m, 2864 m, 1638 s ($\nu_{C=N}$), 1452 m, 1025 s, 817 m, 754 m, 701 s cm^{-1}. MS (EI): 469.2 ($M^+ + 2H$); 468.2 ($M^+ + H$); 467.2 (M^+) *m/e*. Anal. Calc. for $C_{28}H_{29}FeNO_2$ (467.41 g mol^{-1}): C, 71.95; H, 6.25; N, 3.00. Found: C, 72.1; H, 6.6; N, 3.8.

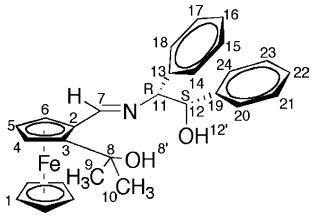


Fig. 30. Numbering of **23** for NMR assignment.

4.6.4. R_P-2-(2-{[(E)-2-Hydroxy-(1S,2R)-1,2-diphenylethylimino]methyl}ferrocenyl)propan-2-ol ***24***

Starting materials: **13** (163 mg, 0.60 mmol); (1*S*,2*R*)-2-amino-1,2-diphenylethanol (140 mg, 0.66 mmol); methanol (5 mL). Yield: **24** (278 mg, 0.60 mmol, >99%) as an orange solid, m.p. 53.0–56.5 °C. ^{1}H NMR (CD_2Cl_2): 7.85 (1H, s, H[7]), 7.63 (1H, s, H[8′]); 7.46–7.19 (10H, m, H[14–18, 20–24]); 5.09 (1H, d, H[12]); 4.41 (1H, d, H[11]); 4.30 (1H, s, H[5]); 4.29 (2H, d, H[4, 6]); 3.96 (5H, s, H[1]); 2.24 (1H, bs, H[12′]); 1.54 (3H, s, H[9]); 1.25 (3H, s, H[10]) ppm. ^{13}C NMR (CD_2Cl_2): 166.2 (C[7]), 141.9 (C[19]), 141.5 (C[13]), 129.0 (C[17, 15, 23, 21]), 128.3 (C[22]), 128.0 (C[24, 20]), 127.9 (C[18, 14]), 127.7 (C[16]), 101.0 (C[8]), 81.4 (C[12]), 77.9 (C[11]), 73.8 (C[2]), 73.6 (C[3]), 71.8 (C[6]), 69.9 (C[1]), 68.9 (C[4]), 68.1 (C[5]), 33.4 (C[9]), 29.3 (C[10]) ppm (see Fig. 31). IR (ATR): 3088 bm (ν_{OH}), 3028 m, 2976 m, 2858 m, 1635 s ($\nu_{C=N}$), 1519 m, 1492 m, 1452 m, 1427 w, 1373 w, 1354 w, 1266 w, 1248 w, 1188 s, 1163 m, 1141 w, 1107 w, 1080 w, 1047 w, 1021 w, 1000 m, 957 s, 914 w, 844 m, 813 m, 753 s, 697 s, 648 w, 615 w, 585 m, 537 w, 511 m, 486 m, 478 m, 449 s cm^{-1}. MS (FAB): 469 ($M^+ + 2H$); 468 ($M^+ + H$); 467 (M^+) *m/e*. Anal. Calc. for $C_{28}H_{29}FeNO_2$ (467.41 g mol^{-1}): C, 71.95; H, 6.25; N, 3.00. Found: C, 71.9; H, 6.4; N, 3.0.

4.6.5. R_P-2-{[1-[2(R)-(1-Hydroxy-1-methylethyl)ferrocenyl]meth-(E)-ylidene]amino}indan-1(S)-ol ***25***

Starting materials: **13** (136 mg, 0.50 mmol); (1*R*,2*S*)-(+)-*cis*-1-aminoindan-2-ol (75 mg, 0.5 mmol); methanol (5 mL). Yield: **25** (200 mg, 0.50 mmol, >99%) as orange-brown solid, m.p. 39.8–42.3 °C. ^{1}H NMR (CD_2Cl_2): 8.45 (1H, s, H[7]); 7.29–7.21 (4H, m, H[15–18]); 6.76 (1H, bs, H[8′]); 4.66 (1H, d, H[11]); 4.57 (1H, q, H[12]); 4.52 (1H, s, H[5]); 4.41 (1H, s, H[4]); 4.36 (1H, t, H[6]); 4.24 (5H, s, H[1]); 3.10 (2H, d × d × d, H[13]); 2.37 (1H, bs, H[12′]); 1.53 (3H, s, H[9]); 1.33 (3H, s, H[10]) ppm. ^{13}C NMR

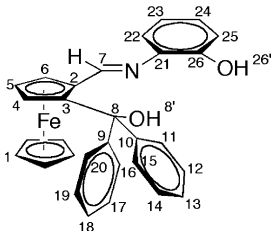


Fig. 29. Numbering of **22** for NMR assignment.

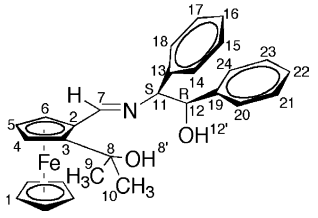


Fig. 31. Numbering of **24** for NMR assignment.

(CD_2Cl_2): 167.6 (C[7]), 141.7 (C[14]), 141.5 (C[19]), 128.5 (C[16]), 127.3 (C[18]), 125.7 (C[15]), 124.5 (C[17]), 100.8 (C[8]), 76.5 (C[12]), 75.6 (C[2]), 74.4 (C[3]), 73.8 (C[6]), 72.1 (C[4]), 70.3 (C[1]), 69.4 (C[11]), 68.1 (C[5]), 40.1 (C[13]), 32.9 (C[9]), 29.3 (C[10]) ppm (see Fig. 32). IR (KBr): 3286 bs (ν_{OH}), 3092 w, 2976 m, 2890 m, 2846 m, 1638 s ($\nu_{C=N}$), 1560 w, 1429 w, 1356 m, 1318 w, 1188 m, 1104 m, 1056 w, 954 w, 817 s, 744 s, 638 w, 508 w cm^{-1}. MS (EI): 403.2 (M^+), 404.2 ($M^+ + H$), 405.2 ($M^+ + 2H$) *m/e*. Anal. Calc. for $C_{23}H_{25}FeNO_2$ (403.32 g mol^{-1}): C, 68.50; H, 6.25; N, 3.47. Found: C, 67.5; H, 6.5; N, 3.4.

4.6.6. R_P-2-{[1-[2(S)-(1-Hydroxy-1-methylethyl)ferrocenyl]meth-(E)-ylidene]amino}indan-1(R)-ol **26**

Starting materials: **13** (500 mg, 1.80 mmol); (1*S*,2*R*)-(−)-*cis*-1-aminoindan-2-ol (283 mg, 1.9 mmol); methanol (5 mL). Yield: **26** (724 mg, 1.79 mmol, >99%) as orange solid, m.p. 47.7–50.5 °C. ^1H NMR: complex, non-assignable spectrum. ^{13}C NMR (CD_2Cl_2): main isomer: 166.6 (C[7]), 141.8 (C[19]), 141.3 (C[14]), 128.4 (C[15]), 127.0 (C[17]), 125.6 (C[16]), 124.9 (C[18]), 100.9 (C[8]), 76.4 (C[12]), 75.8 (C[11]), 73.4 (C[2]), 71.7 (C[3]), 70.4 (C[5]), 69.5 (C[6]), 69.1 (C[4]), 68.4 (C[5]), 40.2 (C[13]), 32.8 (C[9]), 29.4 (C[10]); minor isomer (<10%): 142.9, 141.5, 128.6, 127.4, 125.8, 125.1, 89.0, 80.2, 74.6, 70.8, 70.2, 69.3, 68.5, 68.4, 65.8, 39.8, 32.9, 30.4 ppm (see Fig. 33). IR (ATR): 3286 bw (ν_{OH}), 3094 w, 2976 w, 2847 w, 1636 s ($\nu_{C=N}$), 1560 w, 1519 m, 1491 w, 1478 w, 1459 w, 1426 m, 1372 w, 1355 w, 1312 w, 1248 w, 1210 w, 1186 m, 1166 m, 1137 w, 1105 m, 1096 m, 1044 w, 1018 w, 1000 m, 952 s, 895 w, 843 m, 809 s, 743 s, 692 w, 669 m, 636 w, 593 m, 539 m, 519 w, 482 w, 472 w, 448 m, 416 s cm^{-1}. MS (FAB): 403 (M^+), 404 ($M^+ + H$), 405 $M^+ + 2H$) *m/e*. Anal. Calc. for $C_{23}H_{25}FeNO_2$ (403.32 g mol^{-1}): C, 68.50; H, 6.25; N, 3.47. Found: C, 68.2; H, 6.8; N, 3.1.

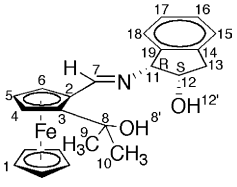


Fig. 32. Numbering of **25** for NMR assignment.

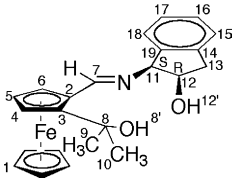


Fig. 33. Numbering of **26** for NMR assignment.

4.6.7. R_P-2(S)-{[1-[2-(Hydroxydiphenylmethyl)ferrocenyl]meth-(E)-ylidene]amino}indan-1(R)-ol **27**

Starting materials: **14** (340 mg, 1.00 mmol); (1*S*,2*R*)-(−)-*cis*-1-aminoindan-2-ol (150 mg, 1.00 mmol); methanol (5 mL). Yield: **27** (453 mg, 0.94 mmol, 94%) as orange solid, m.p. 71.1–75.1 °C. ^1H NMR: complex, non-assignable spectrum. ^{13}C NMR (CD_2Cl_2): 166.6 (C[7]), 149.8 (C[24]), 146.8 (C[29]), 141.1 (C[9]), 140.4 (C[10]), 128.2–125.4 (C[11–20, 25–28]), 100.9 (C[8]), 76.1 (C[22]), 75.5 (C[21]), 74.5 (C[2]), 73.7 (C[3]), 70.7 (C[1]), 69.8 (C[6]), 69. 6 (C[4]), 68.8 (C[5]), 39.6 (C[23]) ppm (see Fig. 34). IR (ATR): 3544 w, 3024 bw (ν_{OH}), 2843 bw, 2319 w, 1635 s ($\nu_{C=N}$), 1520 w, 1489 m, 1446 m, 1412 w, 1312 w, 1263 w, 1237 w, 1174 m, 1106 m, 1045 m, 1028 m, 1001 w, 972 w, 950 w, 932 w, 902 w, 850 w, 815 s, 751 s, 699 s, 678 m, 631 w, 567 w, 536 m, 489 m cm^{-1}. MS (FAB): 527 (M^+), 528 ($M^+ + H$), 529 ($M^+ + 2H$) *m/e*. Anal. Calc. for $C_{33}H_{29}NO_2$ (471.59 g mol^{-1}): C, 84.05; H, 6.20; N, 2.97. Found: C, 84.8; H, 5.8; N, 2.9.

4.6.8. R_P-9-(2-{[(E)-1(R)-Hydroxyindan-2(S)-ylimino]-methyl}ferrocenyl)-9H-fluoren-9-ol **28**

Starting materials: **15** (335 mg, 0.86 mmol); (1*S*,2*R*)-(−)-*cis*-1-aminoindan-2-ol (128 mg, 0.86 mmol); methanol (10 mL). Yield: **28** (446 mg, 0.85 mmol, 99%) as brown solid, m.p. 102.7–107.3 °C. ^1H NMR (CD_2Cl_2): 9.12 (1H, s, H[7]); 8.50 (1H, s, H[8′]); 7.94 (1H, m, H[17]); 7.62 (1H, m, H[14]); 7.49–7.42 (3H, m, H[27, 28, fluorenyl]); 7.32–7.24 (5H, m, H[fluorenyl]); 7.10 (1H, t, H[fluorenyl]); 7.02 (1H, d, H[25]); 6.74 (1H, t, H[26]); 4.78 (1H, d, H[21]); 4.69 (1H, d, H[22]); 4.60 (1H, d, H[6]); 4.48 (5H, s, H[1]); 4.20 (1H, t, H[5]); 3.50 (1H, s, H[4]); 3.25–3.03 (2H, d × d × d, H[23]); 2.69 (1H, bs, H[22′]) ppm (see Fig. 35). ^{13}C NMR (CD_2Cl_2): 165.9 (C[7]), 153.1 (C[9]), 148.9 (C[10]), 141.3 (C[29]), 140.3 (C[24]), 137.8 (C[15, 16]); 129.1, 128.7, 128.1, 127.7, 127.6, 127.1, 125.7, 125.0,

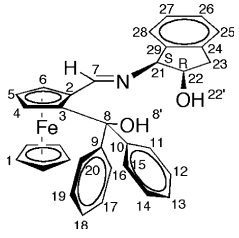


Fig. 34. Numbering of **27** for NMR assignment.

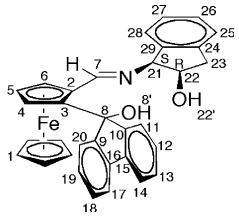


Fig. 35. Numbering of **28** for NMR assignment.

123.9 (C[9–13, 18–20, 25–28]); 112.0 (C[17]), 119.8 (C[14]), 98.4 (C[8]), 80.7 (C[22]), 76.3 (C[21]), 75.5 (C[2]), 73.9 (C[3]), 73.8 (C[6]), 72.8 (C[4]), 71.0 (C[1]), 69.4 (C[5]), 34.0 (C[23]) ppm. IR (ATR): 3352 bm, 3063 bm (ν_{OH}), 2850 bs, 1713 w, 1634 s ($\nu_{C=N}$), 1585 m, 1519 w, 1490 w, 1476 w, 1459 w, 1445 m, 1412 w, 1383 w, 1367 w, 1347 w, 1310 w, 1282 w, 1264 w, 1233 w, 1199 m, 1168 w, 1152 w, 1106 s, 1049 m, 1018 w, 1001 w, 951 m, 911 w, 883 w, 850 w, 812 s, 770 s, 748 s, 729 s, 692 w, 673 m, 643 w, 629 w, 619 w, 605 w, 591 w, 580 w, 558 w, 523 s cm^{-1}. MS (FAB): 525 (M^+), 526 ($M^+ + H$), 527 ($M^+ + 2H$) *m/e*. Anal. Calc. for $C_{33}H_{25}FeNO_2$ (523.4 g mol^{-1}): C, 75.73; H, 4.81; N, 2.68. Found: C, 74.4; H, 5.7; N, 2.7.

4.6.9. R_P-2-{[1-(2(S)-Hydroxymethylferrocenyl)meth-(E)-ylidene]amino}indan-1(R)-ol **29**

Starting materials: **16** (150 mg, 0.61 mmol); (1*S*,2*R*)-(−)-*cis*-1-aminoindan-2-ol (92 mg, 0.61 mmol); methanol (5 mL). Yield: **29** (225 mg, 0.60 mmol, >99%) as red-brown solid, m.p. 48.4–52.2 °C. ^{1}H NMR (CD_2Cl_2): 8.49 (1H, s, H[7]); 7.41–7.15 (5H, m, H[13, 14, 15, 16, 8′]); 5.08–4.07 (12H, m, H[1, 4, 5, 6, 8, 10, 9]); 3.34–3.01 (3H, m, H[11, 10′]) ppm. ^{13}C NMR (CD_2Cl_2): 2 isomers in a 1:1 ratio: 165.5 (C[7]); 142.9, 141.8 (C[17]); 141.4, 141.2 (C[12]); 128.7, 128.4 (C[13]); 127.5, 127.0 (C[15]); 125.9, 125.6 (C[14]); 125.1, 124.8 (C[16]); 88.8, 88.7 (C[9]); 86.5, 84.9 (C[10]); 80.3, 78.9 (C[2]); 76.5, 75.4 (C[3]); 72.9, 72.5 (C[6]); 70.1, 69.4 (C[1]); 69.3, 68.6 (C[4]); 67.1, 66.3 (C[5]); 59.9, 59.7 (C[8]) ppm (see Fig. 36). IR (ATR): 3293 bs (ν_{OH}), 3078 w, 2921 s, 1630 s ($\nu_{C=N}$), 1478 w, 1459 w, 1424 w, 1379 w, 1334 w, 1258 w, 1187 w, 1105 m, 1037 m, 998 m, 947 w, 899 w, 811 s, 743 s, 685 w, 638 w, 580 w, 558 w, 533 w, 484 m cm^{-1}. MS (FAB): 375 (M^+), 376 ($M^+ + H$), 377 ($M^+ + 2H$) *m/e*. Anal. Calc. for $C_{21}H_{21}FeNO_2$ (375.24 g mol^{-1}): C, 67.22; H, 5.64; N, 3.73. Found: C, 68.7; H, 6.5; N, 3.9.

4.6.10. R_P-2-(2-{[(E)-1(R)-Hydroxyindan-2(S)-ylimino]- methyl}ferrocenyl)adamantan-2-ol **30**

Starting materials: **17** (245 mg, 0.67 mmol); (1*S*,2*R*)-(−)-*cis*-1-aminoindan-2-ol (100 mg, 0.67 mmol); methanol (5 mL). Yield: **30** (282 mg, 0.57 mmol, 85%) as orange-brown solid, m.p. 78.1–81.2 °C. ^{1}H NMR: complex, non-assignable spectrum. ^{13}C NMR (CD_2Cl_2): 165.5 (C[7]), 142.0 (C[26]), 141.7 (C[21]), 128.2 (C[22]), 126.8 (C[23]), 125.7 (C[24]), 124.6 (C[25]), 102.1 (C[8]), 75.8 (C[19]), 75.0 (C[18]), 73.2 (C[2]), 73.1 (C[3]), 71.1 (C[6]), 70.2 (C[5]), 70.0 (C[4]), 68.6 (C[1]), 40.1 (C[20]), 39.9 (C[9]), 38.4 (C[10]), 37.9 (C[12]), 36.7 (C[15]), 34.4 (C[11]), 33.9 (C[13]), 27.7 (C[16]), 27.6 (C[17]) ppm (see Fig. 37). IR (ATR): 3531 w, 3092 w (ν_{OH}), 2899 s, 2847 m, 1634 s ($\nu_{C=N}$), 1571 w, 1520 m, 1477 s, 1447 s, 1352 w, 1329 m, 1264 m, 1221 w, 1189 s, 1167 s, 1101 s, 1056 w, 999 m, 963 w, 934 w, 894 w, 844 m, 815 m, 803 m, 733 s, 696 w, 650 w, 632 w, 580 m, 527 m, 479 m, 460 m, 454 m, 445 m, 438 s cm^{-1}. MS (FAB): 495 (M^+), 496 ($M^+ + H$), 497 ($M^+ + 2H$) *m/e*. Anal. Calc. for $C_{30}H_{33}FeNO_2$ (495.43 g mol^{-1}): C, 72.73; H, 6.71; N, 2.83. Found: C, 72.9; H, 7.2; N, 2.7.

4.6.11. R_P-1-{[1-[2-(1(S)-Hydroxy-1-isopropyl-2-methylpropyl)ferrocenyl]meth-(Z)-ylidene]amino}indan-2(R)-ol **31**

Starting materials: **18** (243 mg, 0.8 mmol); (1*S*,2*R*)-(−)-*cis*-1-aminoindan-2-ol (120 mg, 0.8 mmol); methanol (5 mL). Yield: **31** (340 mg, 0.78 mmol, 98%) as orange solid, m.p. 44.3–47.9 °C. ^{1}H NMR (CD_2Cl_2): 8.45 (1H, s, H[7]); 7.28–7.1 (4H, m, H[19–22]); 6.59 (1H, s, H[8′]); 4.66 (1H, s, H[16]), 4.56 (1H, s, H[15]); 4.49 (1H, s, H[6]); 4.33 (1H, s, H[4]), 4.23 (5H, s, H[1]), 4.17 (1H, s, H[5]); 3.23–3.00 (3H, m, H[17, 16′); 2.20 (1H, sept, H[9]), 1.90, (1H, sept, H[10]); 1,43 (3H, d, H[11]); 1.03 (3H, d, H[14]); 0.51 (6H, d, H[12, 13]) ppm (see Fig. 38). ^{13}C NMR (CD_2Cl_2): major isomer: 166.5 (C[7]), 141.8 (C[23]), 141.5 (C[18]), 128.3 (C[19]), 126.9 (C[21]), 125.5 (C[20]), 125.0 (C[22]), 97.2 (C[8]), 77.4 (C[16]), 76.4 (C[15]), 75.5 (C[2]), 74.1 (C[3]), 71.5 (C[6]), 71.2 (C[1]), 70.2 (C[4]), 68.9 (C[5]), 40.0 (C[17]), 38.7 (C[9]), 33.3 (C[10]), 20.0 (C[11]), 18.5 (C[12]), 18.4 (C[13]), 17.9 (C[14]); minor isomer: 142.9, 141.4, 128.5, 127.4, 126.0, 97.3, 89.4, 88.7, 83.0, 80.7, 80.1, 77.7, 74.7, 69.9, 66.9, 66.3, 65.8, 39.9, 38.4, 36.8, 36.3, 19.1, 18.9, 18.2, 17.8 ppm. IR (ATR): 3352 bs (ν_{OH}), 3085 w, 2961 m, 2873 m, 1635 s ($\nu_{C=N}$), 1518 w, 1476 m, 1436 w, 1382 w,

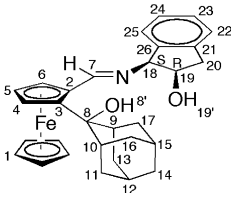


Fig. 37. Numbering of **30** for NMR assignment.

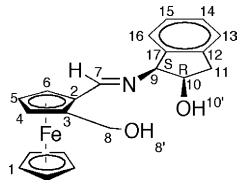


Fig. 36. Numbering of **29** for NMR assignment.

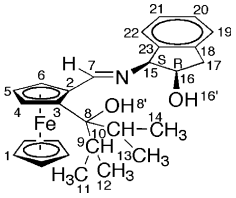


Fig. 38. Numbering of **31** for NMR assignment.

1297 m, 1231 w, 1175 w, 1106 m, 1049 w, 1002 s, 951 w, 894 w, 814 s, 739 s, 691 w, 675 w, 635 w, 580 w, 549 w, 527 m cm^{-1}. MS (FAB): 459 (M^+), 460 ($M^+ + H$), 461 ($M^+ + 2H$) *m/e*. Anal. Calc. for $C_{25}H_{33}FeNO_2$ (435.38 g mol^{-1}): C, 68.97; H, 7.64; N, 3.22. Found: C, 69.9; H, 7.4; N, 3.1.

4.6.12. R_P-2-{[1-[2(S)-(1-Hydroxy-1-methylethyl)-1′,2′,3′,4′,5′-pentamethylferrocenyl]meth-(E)-ylidene]amino}-indan-1(R)-ol **32**

Starting materials: **19** (60 mg, 0.17 mmol); (1*S*,2*R*)-(−)-*cis*-1-aminoindan-2-ol (26 mg, 0.17 mmol); methanol (3 mL). Yield: **32** (80 mg, 0.17 mmol, >99%) as orange-brown solid, m.p. 111.4–116.7 °C. ^{1}H NMR (CD_2Cl_2): 8.16 (1H, s, H[8]); 7.29–7.19 (4H, m, H[16–19]); 7.09 (1H, d, H[9′]); 4.73 (1H, d, H[13]); 4.65 (1H, d, H[12]); 3.95 (3H, m, H[5, 6, 7]); 3.10 (2H, d × d × d, H[14]); 1.85 (15H, s, H[1]); 1.72 (1H, s, H[13′]); 1.52 (3H, s, H[10]); 1.17 (3H, s, H[11]) ppm (see Fig. 39). ^{13}C NMR (CD_2Cl_2): 167.2 (C[8]), 141.8 (C[20]), 141.3 (C[15]), 128.2 (C[19]), 126.8 (C[17]), 125.6 (C[18]), 124.7 (C[16]), 99.5 (C[9]), 81.9 (C[13]), 77.9 (C[12]), 76.6 (C[3]), 76.0 (C[4]), 75.0 (C[7]), 74.2 (C[5]), 73.4 (C[2]), 68.7 (C[6]), 40.1 (C[14]), 33.9 (C[10]), 28.2 (C[11]), 11.3 (C[1]) ppm. IR (ATR): 3309 bs (ν_{OH}), 2900 bs, 2853 bs, 1628 s ($\nu_{C=N}$), 1521 w, 1476 w, 1457 w, 1426 w, 1374 w, 1351 w, 1307 w, 1262 w, 1248 w, 1185 m, 1100 m, 1058 w, 1031 m, 992 w, 954 m, 861 w, 843 w, 811 m, 737 s, 687 w, 669 w, 579 m, 535 m, 497 w, 463 s cm^{-1}. MS (FAB): 473 (M^+), 474 ($M^+ + H$), 475 ($M^+ + 2H$) *m/e*. Anal. Calc. for $C_{28}H_{35}FeNO_2$ (473.43 g mol^{-1}): C, 71.03; H, 7.45; N, 2.96. Found: C, 71.3; H, 8.1; N, 3.1.

4.6.13. R_P-2′-{[1-[2-(1-Hydroxy-1-methylethyl)ferrocenyl]-meth-(E)-ylidene]amino}-[1,1′]binaphthalenyl-2-ol **33**

Starting materials: **13** (190 mg, 0.7 mmol); *R*-(−)-2-amino-2′-hydroxy-1,1′-binaphthyl (200 mg, 0.7 mmol); methanol (5 mL). Yield: **33** (231 mg, 0.43 mmol, 61%) as red solid (crystallized from diethylether), m.p. 121.6–123.8 °C. ^{1}H NMR (CD_2Cl_2): 8.37 (1H, bs, H[22′]); 8.24 (1H, s, H[7]); 8.02–7.90 (3H, m, H[13–29]); 7.83–7.80 (1H, m, H[13–29]); 7.67 (1H, bs, H[8′]); 7.52 (1H, d, H[13–29]); 7.45–7.40 (1H, d × t, H[13–29]); 7.30–7.21 (5H, m, H[13–29]); 6.98–6.95 (1H, m, H[13–29]); 4.34–4.25 (3H, 3s, H[4, 5, 6]); 3.63 (5H, s, H[1]); 1.40 (3H, s, H[9]); 1.05 (3H, s, H[10]) ppm. ^{13}C NMR (CD_2Cl_2): 166.3 (C[7]), 152.5 (C[11]), 148.9 (C[22]), 134.9 (C[25]), 133.8 (C[19]), 132.2 (C[14]), 129.7 (C[17]), 129.5 (C[12]), 129.3 (C[18]), 128.4 (C[13]), 128.3 (C[30]), 126.9 (C[24]), 126.7 (C[26]), 125.9 (C[15]), 125.3 (C[28]), 124.6 (C[16]), 124.4 (C[27]), 123.0 (C[29]), 120.6 (C[20]), 119.9 (C[21]), 116.9 (C[23]), 100.3 (C[8]), 74.1 (C[2]), 74.0 (C[3]), 72.1 (C[6]), 70.2 (C[1]), 69.4 (C[4]), 68.6 (C[5]), 32.0 (C[9]), 28.5 (C[10]) ppm (see Fig. 40). IR (ATR): 3047, 2972 bs (ν_{OH}), 1607, 1587 s ($\nu_{C=N}$),1504 s, 1427 m, 1373 w, 1344 w, 1302 w, 1280 w, 1247 w, 1205 w, 1182 w, 1161 w, 1140 w, 1108 w, 1072 w, 1048 w, 1000 w, 981 w, 956 w, 927 w, 860 w, 846 w, 814 m, 798 w, 774 w, 742 m, 693 w, 667 w, 622 w, 609 w, 594 w, 582 w, 553 w, 526 w, 505 w, 489 w, 473 w, 451 m cm^{-1}. MS (FAB): 539 (M^+), 540 ($M^+ + H$), 541 ($M^+ + 2H$) *m/e*. Anal. Calc. for $C_{34}H_{29}FeNO_2$ (539.44 g mol^{-1}): C, 75.70; H, 5.42; N, 2.60. Found: C, 75.3; H, 6.3; N, 2.5.

4.6.14. R_P-2′-{[1-[2-(1-Hydroxy-1-methylethyl)ferrocenyl]-meth-(E)-ylidene]amino}-[1,1′]binaphthalenyl-2-ol **34**

Starting materials: **13** (165 mg, 0.61 mmol); *S*-(+)-2-amino-2′-hydroxy-1,1′-binaphthyl (174 mg, 0.61 mmol); methanol (5 mL). Yield: **34** (297 mg, 0.55 mmol, 90%) as red solid (crystallized from toluene), m.p. 111–114 °C. ^{1}H NMR (CD_2Cl_2): 8.41 (1H, s, H[7]); 8.02 (1H, d, H[13–29]); 7.92 (2H, t, H[13–29]); 7.82 (1H, d, H[13–29]); 7.52 (1H, d, H[13–29]); 7.44–7.10 (10H, m, H[13–29, 22′]); 6.90 (1H, d, H[8′]); 4.41 (1H, t, H[5]), 4.28 (2H, d, H[4, 6]); 4.10 (5H, s, H[1]); 1.41 (3H, s, H[9]); 0.44 (3H, s; H[10]) ppm. ^{13}C NMR (CD_2Cl_2): 164.6 (C[7]), 152.3 (C[22]), 147.1 (C[11]); 134.6, 134.0, 132.5, 130.0, 129.5, 129.5, 129.2, 128.3, 128.25, 127.0, 126.4, 126.2, 125.6, 124.6, 122.9, 119.2, 118.7, 117.0 (C[12–30]); 100.6 (C[8]), 74.4 (C[2]), 74.1 (C[3]), 75.3 (C[6]), 70.3 (C[1]), 69.6 (C[4]), 68.3 (C[5]), 31.7 (C[9]), 28.8 (C[10]) ppm (see Fig. 41). IR (ATR): 3503 w, 3053 bm (ν_{OH}), 2975 m, 2922 m, 1621 s ($\nu_{C=N}$), 1606 s, 1586 s, 1513 m, 1503 m, 1433 m, 1344 m, 1305 w, 1274 w, 1248 w, 1203 w, 1178 w, 1141 w, 1127 w, 1106 w, 1090 w, 1072 w, 1047 w, 1025 w, 1001 w, 977 w, 956 s, 861 w, 812 s, 774 w, 744 s,

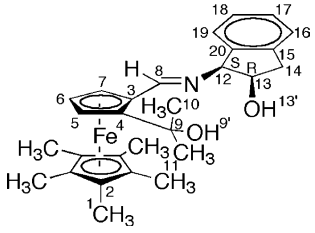


Fig. 39. Numbering of **32** for NMR assignment.

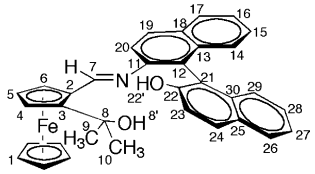


Fig. 40. Numbering of **33** for NMR assignment.

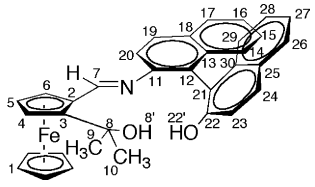


Fig. 41. Numbering of **34** for NMR assignment.

692 w, 666 w, 629 w, 578 w, 528 m, 503 w, 489 m, 472 m, 450 m cm^{-1}. MS (FAB): 539 (M^+), 540 ($M^+ + H$), 541 ($M^+ + 2H$) *m/e*. Anal. Calc. for $C_{34}H_{29}FeNO_2$ (539.44 g mol^{-1}): C, 75.70; H, 5.42; N, 2.60. Found: C, 78.3; H, 6.2; N, 2.5. X-ray single crystal structure: Fig. 6 and Table 1.

4.7. General procedure for the synthesis of tetradentate $[O_2N_2]$ ligands 35–38

A small Schlenk tube was charged under an atmosphere of Ar with a stirring bar and hydroxyalkylferrocenealdehyde **13** or **14**. Dry methanol was added to obtain a concentrated solution. To this solution, 0.5 mole equivalents of diamine dissolved in dry methanol was added dropwise under efficient stirring. After the addition was completed, the mixture was stirred for 24 h at ambient temperature. IR spectroscopy showed quantitative reaction after this reaction period (*Note*. TLC analysis of the reaction mixture is useless, because these Schiff bases hydrolyze at least in part to the starting materials on silica or alumina, therefore progress of the reaction cannot be monitored by this common method.). Workup: solvents and volatile materials were removed on a rotary evaporator, the residue was triturated with a small amount of diethyl ether, and all volatiles were removed in vacuo, affording the product in quantitative yield as solid powder. Details and properties for **35**–**38** are given below.

4.7.1. R_P-2-{5-[((E)-2-{[1-[2-(1-Hydroxy-1-methylethyl)-ferrocenyl]meth-(E)-ylidene]amino}ethylimino)methyl]-ferrocenyl}propan-2-ol 35

Starting materials: **13** (751 mg, 2.76 mmol); ethylenediamine (166 mg, 2.76 mmol); methanol (12 mL). Yield: **35** (648 mg, 1.14 mmol, 83%) as orange solid (crystallized from toluene), m.p. 177.7–179.4 °C. ^{1}H NMR ($CDCl_3$): 8.09 (1H, s, H[7]); 7.72 (1H, s, H[8′]); 4.31 (2H, d, H[11]); 4.24 (6H, bs, H[5, 1]); 3.86 (1H, d, H[4]); 3.66 (1H, d, H[6]); 1.58 (3H, s, H[9]); 1.24 (3H, s, H[10]) ppm. ^{13}C NMR ($CDCl_3$): 165.7 (C[7]), 100.5 (C[8]), 74.1 (C[2]), 73.0 (C[3]), 71.0 (C[6]), 69.9 (C[1]), 68.2 (C[4]), 67.7 (C[5]), 60.4 (C[11]), 32.7 (C[9]), 29.3 (C[10]) ppm (see Fig. 42). IR (ATR): 3159 bs (ν_{OH}), 2971 m, 2927 w, 2837 w, 2362 m, 2342 w, 1772 w, 1641 s ($\nu_{C=N}$), 1488 w, 1463 w, 1448 w, 1427 w, 1410 w, 1368 w, 1349 w, 1287 w, 1248 m, 1213 w, 1187 m, 1163 w, 1140 w, 1123 w, 1105 m, 1046 w, 1014 m, 1001 m, 974 w, 958 m, 892 w, 849 w, 841 w, 821 s (Fec), 781 w, 732 s, 693 w, 619 w, 573 w, 550 w, 528 m, 521 s, 493 m, 481 s, 450 s, 436 w, 424 w cm^{-1}. MS (EI): 568.0 (M^+), 569.1 ($M^+ + 1H$) *m/e*. Anal. Calc. for $C_{30}H_{36}Fe_2N_2O_2$ (568.31 g mol^{-1}): C, 63.40; H, 6.38; N, 4.93. Found: C, 62.8; H, 7.0; N, 4.6. X-ray single crystal structure: Fig. 7 and Table 1.

4.7.2. R_P-{5-[((E)-2-{[1-[2-(Hydroxy diphenylmethyl)-ferrocenyl]meth-(E)-ylidene]amino}ethylimino)methyl]-ferrocenyl} diphenylmethanol 36

Starting materials: **14** (214 mg, 0.54 mmol); ethylenediamine (32 mg, 0.54 mmol); methanol (10 mL). Yield: **36** (294 mg, 0.36 mmol, 67%) as orange solid, m.p. 250 °C (dec.). ^{1}H NMR (CD_2Cl_2): 9.00 (1H, s, H[7]); 7.48 (2H, d, H[11–20]); 7.32–7.07 (8H, m, H[11–20]); 6.90 (H[8′]); 4.35 (1H, s, H[5]); 4.25 (1H, t, H[4]); 4.18 (5H, s, H[1]); 3.72 (1H, s, H[6]); 3.57 (1H, d, H[21]); 2.68 (1H, d, 21) ppm. ^{13}C NMR (CD_2Cl_2): 165.4 (C[7]), 150.3 (C[9]), 147.0 (C[10]), 128.1 (C[13, 18]), 127.7 (C[12, 17]), 127.5 (C[14, 19]), 127.3 (C[11, 20]), 126.7 (C[15]), 126.5 (C[16]), 100.5 (C[8]), 76.9 (C[2]), 75.4 (C[3]), 74.8 (C[6]), 73.7 (C[4]), 70.4 (C[1]), 68.3 (C[5]), 59.4 (C[21]) ppm (see Fig. 43). IR (ATR): 3019 bs (ν_{OH}), 2798 bs, 1639 s ($\nu_{C=N}$), 1595 m, 1519 m, 1487 m, 1444 m, 1334 m, 1271 w, 1239 w, 1220 w, 1197 w, 1166 m, 1124 w, 1106 m, 1058 w, 1047 w, 1027 w, 998 m, 972 w, 950 w, 901 w, 848 m, 816 s, 809 s, 753 s, 689 s, 674 w, 637 w, 609 w, 567 w, 557 w, 534 m, 515 m, 488 m, 460 m cm^{-1}. MS (FAB): 816 (M^+), 817 ($M^+ + 1H$), 818 ($M^+ + 2H$) *m/e*. Anal. Calc. for $C_{50}H_{44}Fe_2N_2O_2$ (816.66 g mol^{-1}): C, 73.54; H, 5.43; N, 3.43. Found: C, 72.7; H, 5.2; N, 3.6.

4.7.3. R_P-2-{5-[((E)-2R-{[1R-[2-(1-Hydroxy-1-methylethyl)ferrocenyl]-meth-(E)-ylidene]amino}cyclohexylimino)methyl]ferrocenyl}propan-2-ol 37

Starting materials: **13** (220 mg, 0.8 mmol); (1*R*,2*R*)-cylohexane-1,2-diamine (46 mg, 0.4 mmol); methanol (5 mL). Yield: **37** (233 mg, 0.37 mmol, 92.5%) as orange solid, m.p. 194–196 °C. ^{1}H NMR ($CDCl_3$): 8.06 (1H, bs, H[8′]); 7.99 (1H, s, H[7]); 4.23 (1H, s, H[5]); 4.22 (1H, s, H[4]); 4.18 (5H, s, H[1]); 4.16 (1H, t, H[6]); 3.24 (1H, t, H[11]); 1.83 (2H, m, H[12]); 1.54 (3H, s, H[9]); 1.47–1.20 (2H, m, H[13]); 1.15 (3H, s, H[10]) ppm. ^{13}C NMR ($CDCl_3$): 163.5 (C[7]), 100.5 (C[8]), 73.9 (C[2]), 73.3 (C[3]), 72.8 (C[6]), 70.9 (C[4]), 70.0 (C[1]), 68.1 (C[5]), 67.6 (C[11]), 33.2 (C[12]), 32.8 (C[9]), 29.1 (C[10]), 24.2 (C[13]) ppm (see Fig. 44). IR (KBr): 3092 bw (ν_{OH}), 2970 w, 2921 w,

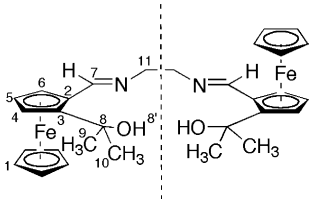


Fig. 42. Numbering of **35** for NMR assignment.

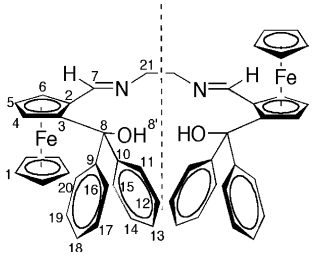


Fig. 43. Numbering of **36** for NMR assignment.

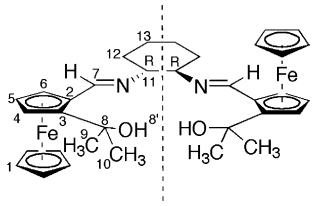


Fig. 44. Numbering of **37** for NMR assignment.

2852 w, 1640 s ($\nu_{C=N}$), 1518 w, 1483 w, 1446 w, 1424 w, 1370 w, 1351 m, 1291 w, 1248 m, 1189 m, 1162 w, 1135 w, 1106 w, 1092 w, 1079 w, 1042 w, 1000 m, 959 m, 935 w, 877 w, 861 w, 815 s, 775 w, 750 w, 724 w, 694 w, 626 w, 612 w, 586 w, 573 w, 549 w, 540 m, 524 w, 509 w, 498 w, 480 s cm^{-1}. MS (FAB): 621.1 ($M^+ - 1H$), 622.1 (M^+), 623.1 ($M^+ + 1H$), 624.1 ($M^+ + 2H$) *m/e*. Anal. Calc. for $C_{34}H_{42}Fe_2N_2O_2$ (622.43 g mol^{-1}): C, 65.61; H, 6.80; N, 4.50. Found: C, 65.3; H, 7.1: N, 4.5. X-ray single crystal structure: Fig. 8 and Table 1.

4.7.4. R_P-2-{5-[((Z)-2S-{[1S-[2-(1-Hydroxy-1-methylethyl)ferrocenyl]meth-(E)-ylidene]amino}cyclohexylimino)methyl]ferrocenyl}propan-2-ol ***38***

Starting materials: **13** (220 mg, 0.8 mmol); (1*S*,2*S*)-cylohexane-1,2-diamine (46 mg, 0.4 mmol); methanol (5 mL). Yield: **38** (250 mg, 0.4 mmol, >99%) as orange solid, m.p. 235 °C (dec.). ^{1}H NMR ($CDCl_3$): 8.28 (1H, s, H[7]); 7.42 (1H, bs, H[8′]); 4.44 (1H, s, H[5]); 4.25 (7H, bs, H[4, 6, 1]); 3.36 (1H, s, H[11]); 1.86–1.41 (10H, m, H[12, 13, 9, 10]) ppm. ^{13}C NMR ($CDCl_3$): 163.4 (C[7]), 100.3 (C[8]), 75.0 (C[2]), 72.2 (C[3]), 72.1 (C[6]), 70.7 (C[4]), 69.9 (C[1]), 68.2 (C[5]), 68.19 (C[11]), 32.6 (C[9]), 32.0 (C[12]), 29.7 (C[10]), 22.9 (C[13]) ppm (see Fig. 45). IR (ATR): 3106 bm (ν_{OH}), 2980 w, 2962 m, 2930 m, 2853 m, 1635 s ($\nu_{C=N}$), 1519 w, 1494 w, 1457 w, 1430 w, 1386 w, 1369 w, 1350 w, 1291 w, 1267 w, 1247 w, 1192 m, 1159 w, 1140 w, 1117 w, 1105 m, 1015 m, 1000 w, 960 m, 902 w, 866 w, 850 w, 820 s, 754 s, 697 w, 682 w, 606 w, 589 w, 552 m, 525 m, 504 m, 481 s, 468 s cm^{-1}. MS (FAB): 621 ($M^+ - 1H$), 622 (M^+), 623 ($M^+ + 1H$), 624 ($M^+ + 2H$) *m/e*. Anal. Calc. for $C_{34}H_{42}Fe_2N_2O_2$ (622.43 g mol^{-1}): C, 65.61; H, 6.80; N, 4.50. Found: C, 65.3; H, 7.2; N, 4.3. X-ray single crystal structure: Fig. 9 and Table 1.

4.8. X-ray crystallography

Single crystals suitable for X-ray crystal analysis were obtained from concentrated solutions of dichloromethane or diethyl ether. The data collection was performed on a Nonius Kappa-CCD equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and a nominal crystal-to-area-detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK [13]. Several scans in φ and ω direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces an empirical absorption correction. The structures were solved by direct methods (SHELXS-86) and refined against F^2 (SHELXL-97) [14]. Hydrogen atoms at carbon atoms were added geometrically and refined using a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data for **8**, **13**, **15**, **20**, **21**, **33**, **35**, **37**, **38** are given in Table 1. CIF files for compounds **8**, **13**, **15**, **20**, **21**, **33**, **35**, **37**, **38** are available in the supplementary material.

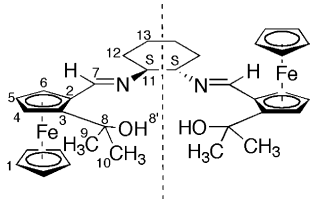


Fig. 45. Numbering of **38** for NMR assignment.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 292619, 292620, 292621, 292622, 292623, 292624, 292625, 292626, 292627 for compounds **8**, **13**, **15**, **20**, **21**, **33**, **35**, **37**, **38**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. Fax. (int code) +44 1223 336 003 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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