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TETRAHEDRON: *ASYMMETRY*

New C_2-symmetrical ferrocenyl diamines as ligands for ruthenium catalyzed transfer hydrogenation

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Abstract

The new C_2-symmetrical ferrocenyl diamines **5–7** and **13** proved to be good ligands for the ruthenium catalyzed enantioselective transfer hydrogenation of unsymmetrical ketones. The stereocontrolled and highly flexible synthetic route to the new diamines made it possible to vary the ligand structure in an efficient manner. A short trial and error process led to a very active catalytic system with diamine **6a** as the ligand, which is capable of reducing ketones even at −30°C using 2-propanol as a hydrogen source. Enantioselectivities up to 90% were reached in the reduction of 1′-acetonaphthone.

1. Introduction

Development of asymmetric hydrogenation of double bonds using transition metal catalysis has gained much attention since the late sixties.[1] This interest is due to the fact that this reaction can be conducted with a cheap reducing agent (hydrogen) on a large scale without producing intrinsic by-products. Great success has been achieved as far as asymmetric induction and turnover numbers are concerned. Remaining problems are related to the high pressure equipment needed and the often difficult synthesis and handling of the chiral diphosphines used as ligands. Furthermore, not all types of substrates can be reduced enantioselectively by classical hydrogenation. In this respect, unfunctionalized olefins, simple ketones and imines posed a problem for a long time.[2] Catalytic transfer hydrogenation offers attractive solutions to the problems described above.[3] No autoclave is needed since the hydrogen sources (a secondary alcohol or formic acid) are easily handled liquids. Furthermore, ligands (e.g. **1–3**) developed by Lemaire, Noyori, Helmchen and others with nitrogen donor atoms, which are far more convenient to prepare than diphosphines, showed the best results, especially in the reduction of simple ketones and imines, while most carbon–carbon double bonds are not affected.[4] Thus catalytic transfer hydrogenation adds a valuable selective method to the arsenal of useful enantioselective reductions.

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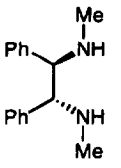

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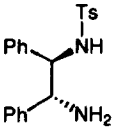

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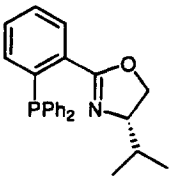

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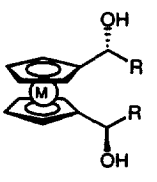
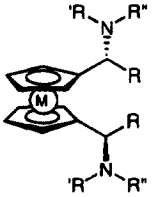
2. Results and discussion

2.1. Choice of the catalytic system

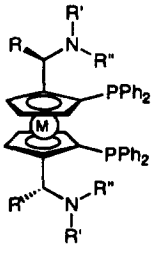
Recently, we described the enantioselective synthesis of a range of ferrocenyl diols, diamines and diphosphines (see Scheme 1).[5] As shown by the work of Noyori and Lemaire, modified diamines are suitable ligands for rhodium or ruthenium catalyzed transfer hydrogenations, so we decided to investigate the potential of the newly accessible ligands **4–9** for this reaction.



4: M = Fe, R = Ph



5: M = Fe, R = Me
6: M = Fe, R = Ph
7: M = Ru, R = Ph
8: M = Fe, R = *i*-Pr



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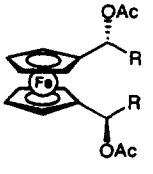
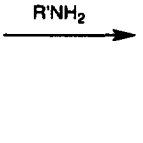
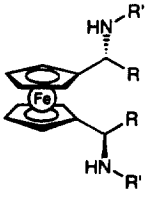


10a: R = Me
10b: R = Ph





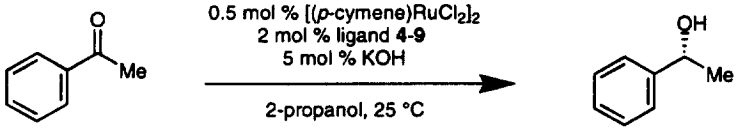
5b: R = Me, R' = (*R*)-PhEt, 63 %
5c: R = Me, R' = (*S*)-PhEt, 80 %
6b: R = Ph, R' = Pent, 78 %
6c: R = Ph, R' = $(CH_2)_2OMe$, 38 %
6d: R = Ph, R' = Bn, 86 % ← $Pd(OH)_2$ / C, H_2, 95 %
6e: R = Ph, R' = H

Scheme 1.

In order to screen the compounds **4–9** for their ability to form active transfer hydrogenation systems, a standard set of conditions consisting of 0.5 mol% $[Ru(p\text{-cymene})Cl_2]_2$ as the catalyst precursor and 2 mol% of the potential ligand using 2-propanol as the hydrogen source was established. As the base, KOH (5 mol%) was used and the reduction of acetophenone (0.05 M) was tried at room temperature. The diols **4**, the tertiary diamine **6b** and the amino phosphine **9** gave inactive or only very moderately active systems (Table 1, entries 1, 4 and 7).

In contrast, the secondary diamines **5a** and **6a** were able to form very active catalysts, which reduced acetophenone within a timescale of several minutes to a few hours at room temperature. The enantiomeric excess of the (*R*)-1-phenyl-1-ethanol formed was 63% for the methyl substituted diamine **5a** and 71% for the phenyl substituted ligand **6a**. No significant decrease of optical purity could be detected during the

Table 1
Catalytic activity of different C_2-symmetrical ferrocenyl ligands in ruthenium catalyzed transfer hydrogenation



Entry	Ligand	M	R	R'	R''	Conversion [%][a]	*ee* [%][a]
1	**4**	Fe	Ph	-	-	-	-
2	**5a**	Fe	Me	Me	H	23[b]	63
3	**6a**	Fe	Ph	Me	H	92	71
4	**6f**	Fe	Ph	Me	Me	2	0
5	**7**	Ru	Ph	Me	H	41[c]	64
6	**8**	Fe	*i*-Pr	Me	H	-	-
7	**9**	Fe	Ph	Me	Me	3	25

a) After 15 min reaction time; conversions and enantiomeric excesses were determined by GC on a chiral column. b)A conversion of 94 %was reached after 3 h. c)A conversion of 98 % was reached after 30 min.

reaction time as observed for other transfer hydrogenation systems.[6] This effect, which was traced back to the reversibility of the hydride transfer, also becomes important with our system if the reduction is carried out at reflux temperature (82°C) and in more concentrated solutions (1 M). As can be seen from Fig. 1, under these conditions using **6a** as the ligand (0.1 mol%) the enantiomeric excess of 1-phenyl-1-ethanol is 60% in the initial stage and drops to only 36% when 87% conversion is reached after 1 h.

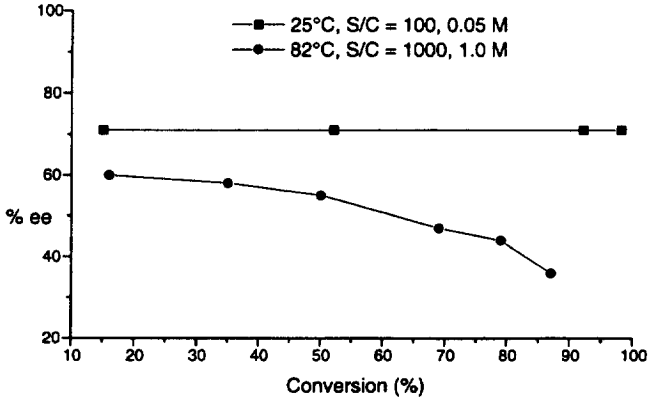


Fig. 1. Reduction of acetophenone using ligand **6a** (S/C=substrate/catalyst)

The metallocenyl backbone of the new diamines presented here allows the facile variation of the bite angle of the ligand by exchanging the central metal.[7] Thus, we tried the phenyl substituted ruthenocenyl diamine **7** which only gave results comparable to the ferrocenyl analog **6a** (Table 1, entry 5). In the last experiment of this first series, the effect of increased steric bulk of the substituent R (e.g. an isopropyl group in diamine **8**) was investigated and resulted again in an inactive system (entry 6). In order to improve these initial results we took diamine **6a** as a lead and tried variations of the ligand structure.

Table 2
Results of the variation of the *N*-alkyl substituent in the ferrocenyl diamine ligands **5** and **6**

Entry	Ligand	R	R'	Reaction time (h)	Conversion [%][a]	*ee* [%][a]
1	**6a**	Ph	Me	0.5	98	71
2	**6b**	Ph	Pent	16	93	69
3	**6c**	Ph	$(CH_2)_2OMe$	45	38	35
4	**6d**	Ph	Bn	-	-	-
5	**6e**	Ph	H	1	98	53
6	**5a**	Me	Me	3	94	63
7	**5b**	Me	(*R*)-Ph-Et	24	56	6
8	**5c**	Me	(*S*)-Ph-Et	24	45	31

a) Conversions and *ee* were determined by GC on a chiral column.

2.2. *Variations of the* N-*alkyl substituent*

Starting from the acetates **10**, the *N*-alkyl substituent R′ could be varied very easily by reaction with different primary amines ($R'NH_2$; Scheme 1).[5]

The diamines **5b,c** and **6b–e** were tested under the standard conditions described above. The exchange of the *N*-methyl group in **6a** for an *N*-pentyl group in **6b** resulted in a considerable loss of catalytic activity while the induction abilities were virtually unaltered (compare entries 1 and 2, Table 2).

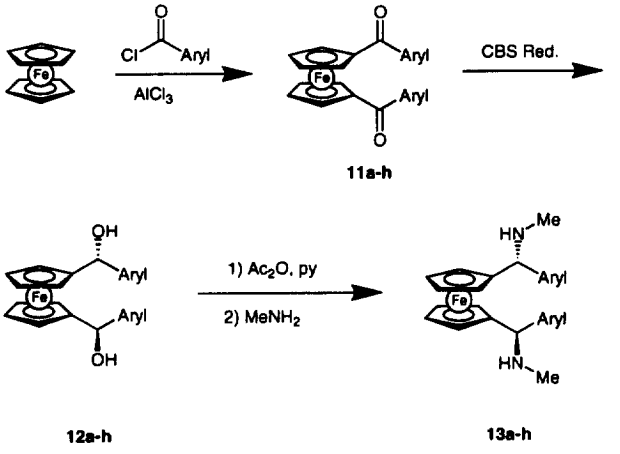
Introduction of a β-methoxy function, which may act as an additional ligation site for ruthenium, into the *N*-alkyl chain of the diamine **6c** caused a further drop of activity and in addition a decrease of the selectivity to only 35% *ee* (entry 3). The limit of tolerated steric demand of the *N*-alkyl substituent seems to be reached with an *N*-benzyl group in **6d** which gave an inactive system. Hydrogenolytic removal of the *N*-benzyl group provided the primary diamine **6e** and restored the catalytic activity without reaching the level of induction shown by *N*-methyl substituted **6a** (compare entries 1 and 5).

To check the influence of additional chirality it was advisable to use the methyl substituted structures **5** in order to release some steric congestion from the α-position of the ferrocene. This allowed a secondary stereocenter to be placed at the nitrogen atoms of the ligand without completely losing catalytic activity. Thus, the acetate **10a** was treated with (*R*)- and (*S*)-1-phenylethylamine, respectively, to provide the diastereomeric diamines **5b** and **5c** with four controlled centers of chirality. Interestingly, a marked difference in stereoselection was found for the all-*R* combination of **5b** (6% *ee*) compared to the *R,R,S,S*-diamine **5c** (31% *ee*). So, there is a clear effect of cooperativity of the stereochemical information at the stereocenter α to the ferrocenyl core and the *N*-phenylethyl substituent, but neither combination showed an improvement with respect to the *N*-methyl substituent of the parent structure **5a** (compare entries 6–8).

In summary, the diamine **6a** bearing an *N*-methyl substituent in combination with a phenyl moiety (R=Ph) was found to be superior to all other derivatives tried so far. Thus, for the next series of variations we focused on the 'fine-tuning' of the aryl substructure.

2.3. Variations of the aryl moiety

The synthesis of the desired new aryl substituted diamines **13** followed the same route as developed for the diamines **5–8** (Scheme 2). All diamines **13** were found to give active catalysts in combination with $[Ru(p\text{-cymene})Cl_2]_2$.



Scheme 2.

Since the phenyl ring in **6a** seems to be crucial for both the activity and the selectivity of the final catalytic system, we decided to investigate if electronic properties of this moiety play an important role. However, neither a strongly electron withdrawing fluorine atom in the *para*-position (**13a**) nor an electron releasing *p*-methoxy group (**13b**) had a beneficial effect (compare entries 1–3, Table 3).

Increasing the steric bulk of the aryl moiety by introducing 1- or 2-naphthyl rings (**13c,d**) into the ligand had interesting effects. While the 2-naphthyl substituted diamine **13d** again showed no improvement compared to **6a**, the 1-naphthyl moiety in **13c** allowed the reduction of acetophenone to proceed to completion within 10 min at room temperature. This means a significant further enhancement of the reaction rate, which was already good with **6a** (entries 4–5). We reasoned that this positive effect may have its origin in the *ortho*-substitution of the basic phenyl ring, which is present in the 1-naphthyl but not in the 2-naphthyl group. Therefore, the effects of different substituents in the *ortho*-position were further investigated in some depth.[8]

The synthesis of the diamines **13e–h** again followed the general route depicted in Scheme 1. A chloro-, bromo-, or iodo atom was as easily introduced as a methyl group starting from commercially available *ortho*-substituted benzoyl chlorides. None of the diamines **13e–h** gave any further improvement of the reaction rate (entries 6–9), but the *o*-tolyl substituted ligand **13e** allowed the isolation of (*R*)-1-phenyl-1-ethanol with an optical purity of 80%, which is substantially higher than the value of 71% *ee* observed with the phenyl substituted diamine **6a** (compare entries 1 and 6).

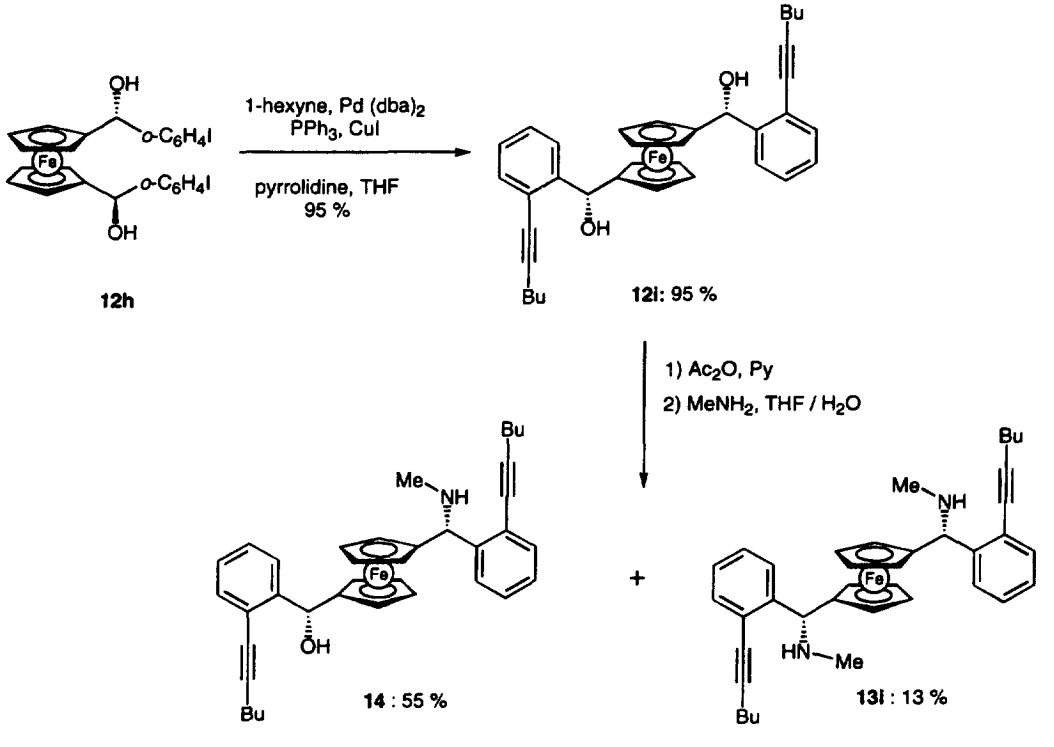
In the next optimization step the steric properties of the *ortho*-substituent were adjusted by exchanging the methyl group for other alkyl groups. As appropriate benzoyl chlorides were not easily available, the halogen atoms in the structures already prepared were used for further elaboration. A first synthetic approach to new *ortho*-substituted derivatives of **6a** utilized the double Sonogashira reaction of the diiododiol **12h** with 1-hexyne to provide the dialkynylated diol **12i** in an excellent yield of 95%[9] (Scheme 3).

Usual activation of the hydroxy function by acetylation and substitution with methylamine gave the desired diamine **13i** in low yield. With larger *ortho*-substituents, the substitution with methylamine in

Table 3
Results of the variation of the aryl moiety in the ferrocenyl diamine ligands **13**

Entry	Ligand	Aryl	Reaction time (h)	Conversion [%][a]	*ee* [%][a]
1	**6a**	Ph	0.5	98	71
2	**13a**	*p*-F-Ph	1	97	58
3	**13b**	*p*-MeO-Ph	1.5	98	30
4	**13c**	1-Naphthyl	**0.25**	98	60
5	**13d**	2-Naphthyl	2	97	54
6	**13e**	*o*-Tol	1.5	97	**80**
7	**13f**	*o*-Cl-Ph	3	93	70
8	**13g**	*o*-Br-Ph	3.5	96	64
9	**13h**	*o*-I-Ph	30	80	57
10	**13i**	*o*-C_6H_9-Ph	6	92	72
11	**14**	*o*-C_6H_9-Ph	7	75	75
12	**13j**	*o*-Pr-Ph	1	97	68
13	**13k**	*o*-Bn-Ph	3	94	65

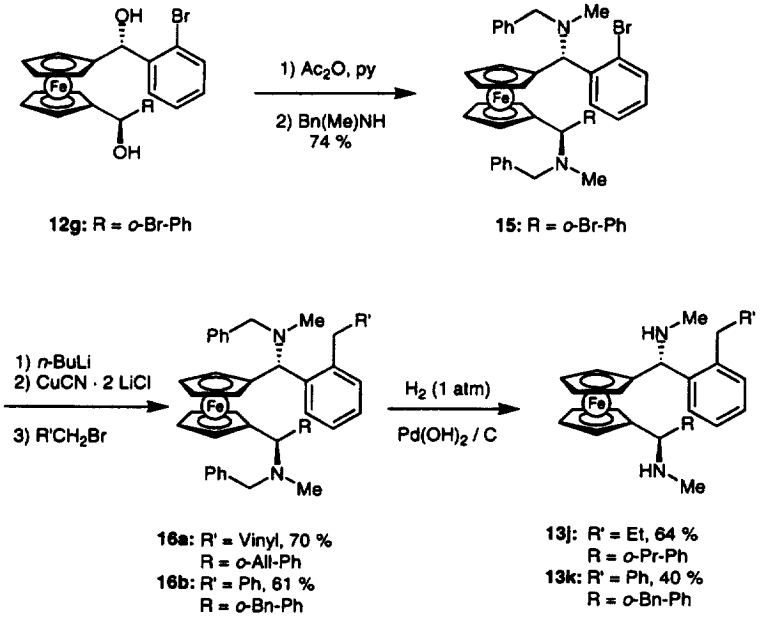
a) Conversions and *ee* were determined by GC on a chiral column.



Scheme 3.

the crowded α-position of the ferrocenyl moiety (Scheme 3) becomes a difficult process, because of the competitive attack of the nucleophile to the carbonyl carbon of the acetate function. Thus, products of aminolysis (hydrolysis) of the diacetate (e.g. the amino alcohol **14**) are the main products in such cases.

A second route started with the dibromodiol **12g** to which a benzyl protected *N*-methyl group was introduced by acetylation and subsequent reaction with *N*-benzyl-*N*-methylamine to yield the tertiary diamine **15**. A bromine–lithium exchange with *n*-BuLi and transmetallation to the corresponding copper derivative followed by addition of allyl and benzyl bromide gave access to the alkylated products **16a** and **16b**, respectively. These, in turn, could be deprotected by hydrogenolysis. This procedure also removed the unsaturation of the allyl groups in **16a** to give the *ortho*-propylphenyl substituted diamine **13j** directly (Scheme 4).

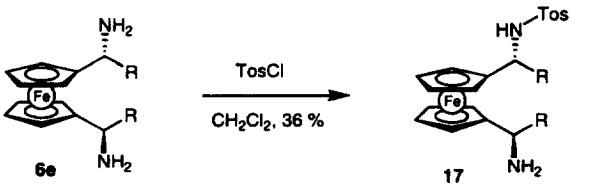


Scheme 4.

Unfortunately, neither the alkynylated ligand **13i** nor the propylated or benzylated diamines **13j** and **13k** provided any further improvement of the ruthenium catalyzed transfer hydrogenation of acetophenone (entries 10, 12 and 13, Table 3). The amino alcohol **14** was found to give similar results to its corresponding diamine **13i** (compare entries 10 and 11). Thus, only one primary or secondary amine function in the ligand seems to be required to give an active transfer hydrogenation catalyst.

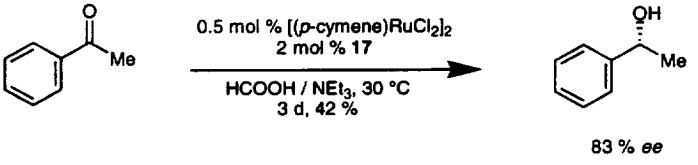
2.4. *Variation of the hydrogen source*

Brunner and Noyori showed that a mixture of formic acid and triethylamine (5:2) is a very convenient hydrogen source for asymmetric transfer hydrogenations.[10] With this solvent, hydride transfer becomes irreversible, so that reactions can go to completion even in concentrated solutions. Unfortunately, the ferrocenyl diamine based catalytic system lost activity on changing from 2-propanol to $HCOOH/NEt_3$ as reaction media. Nevertheless, monotosylation of the primary diamine **6e** (Scheme 5) was found to generate a suitable ligand (**17**) for use with the new hydrogen source.



Scheme 5.

After three days at room temperature, a conversion of only 42% was reached in the transfer hydrogenation of acetophenone but the selectivity improved to 83% *ee* which is higher than the best value obtained with the diamine/2-propanol system (Scheme 6).



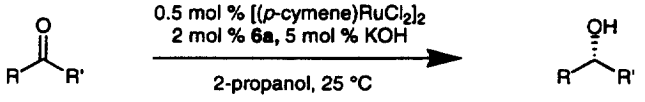
Scheme 6.

Due to the low catalytic activity found, we focused our attention back on the latter system and tried some variations of the substrate.

2.5. *Variations of the substrate*

In order to check the scope of the transfer hydrogenation system presented above, ketones other than acetophenone were subjected to the reduction using the standard conditions and ligand **6a**. First the effect of increasing α-substitution in phenyl alkyl ketones was studied. Exchanging the methyl group in acetophenone for a larger isopropyl group resulted in a drop in the selectivity to 20% (compare entries 1 and 2, Table 4). A *t*-butyl group caused a reversal in the configuration of the resulting chiral alcohol with selectivity also being low. Remarkably, the reduction was still quite a fast process (82% conversion after 2 h) while other transfer hydrogenations of this sterically hindered ketone are reported to be notoriously sluggish (entry 3).[11]

Table 4
Results of ruthenium catalyzed transfer hydrogenation of different substrates using diamine ligand **6a**

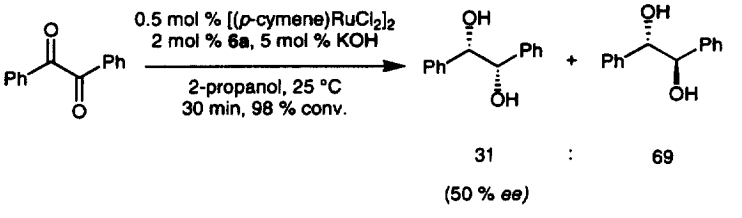


Entry	R	R'	Time [h]	Conversion [%][a]	*ee* [%][a]
1	Ph	Me	0.5	96	71
2	Ph	*i*-Pr	2	92	20
3	*t*-Bu	Ph	2	82	36
4	Me	*c*-Hex	1	79	15
5	Me	CH_2CO_2Et	3	92	20[b]

a) Conversions and *ee* were determined by GC on a chiral column. b) reaction temperature: 80 °C.

Reduction of dialkyl ketones is also fast, but selectivity is nearly completely lost (entry 4). This statement also holds for the reduction of β-ketoesters like ethyl acetoacetate, which requires heating to 80°C to be effective (entry 5).

In a last variation of the substrate, the reduction of dibenzoyl was tried, which displays an alternative to enantioselective dihydroxylation of stilbene following, for example, the Sharpless protocol.[12] Only moderate selectivity could be achieved. The product was a mixture of the *meso*- and *dl*-diastereomer (69:31). The *dl*-isomer showed an optical purity of 50% (Scheme 7).



Scheme 7.

2.6. *Variation of the reaction temperature*

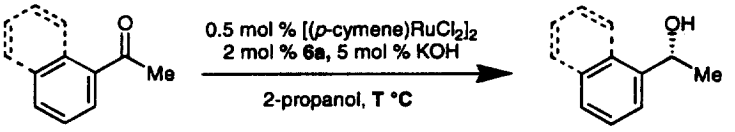
As described in the foregoing text, the combination of a ferrocenyl diamine (e.g. **6a**) with [Ru(*p*-cymene)Cl_2]$_2$ provides a very active transfer hydrogenation catalyst, which reduces ketones on a timescale of minutes to a few hours under the given standard conditions at room temperature. We therefore envisioned the possibility of lowering the reaction temperature with the aim of improving selectivity. This was first tried with acetophenone as the substrate. Conducting the reduction at 0°C had virtually no effect on the selectivity (entries 1 and 2, Table 5). However, lowering the temperature to −14°C showed a marked increase of the enantiomeric excess of 1-phenyl-1-ethanol to 79%. This result could be slightly improved to 80% *ee* at −30°C (entries 3 and 4).

The same beneficial temperature effect could also be verified for the reduction of 1′-acetonaphthone. The result was (*R*)-1-naphthyl-1-ethanol of 78% *ee* for the reaction at room temperature, whereas at −30°C the selectivity reaches a value of 90% (entries 5 and 6). On the other hand, reaction times were significantly longer (up to 5 days) at lower temperatures.

3. Conclusion

We have described the use of new C_2-symmetrical ferrocenyl diamines as ligands for the enantioselective ruthenium catalyzed transfer hydrogenation of unsymmetrical ketones with 2-propanol as the hydrogen source. The catalytic system is characterized by high reaction rates at room temperature and is even active at −30°C. No decrease of the optical purity of the product alcohols is observed during the course of the reaction. A wide range of substrates can be reduced. Depending on the ligand structure, substrate and reaction temperature, enantioselectivities of up to 90% could be reached. Furthermore, it was demonstrated that the ferrocenyl diamines used as ligands can be easily modified with respect to several substructural regions. We have demonstrated that our synthetic approach to a new diamine ligand system based on C_2-symmetric ferrocenyl diols obtained by enantioselective reduction of the corresponding ferrocenyl diketones is highly flexible and opens many possibilities for variations to allow an efficient modern ligand design (Scheme 8).

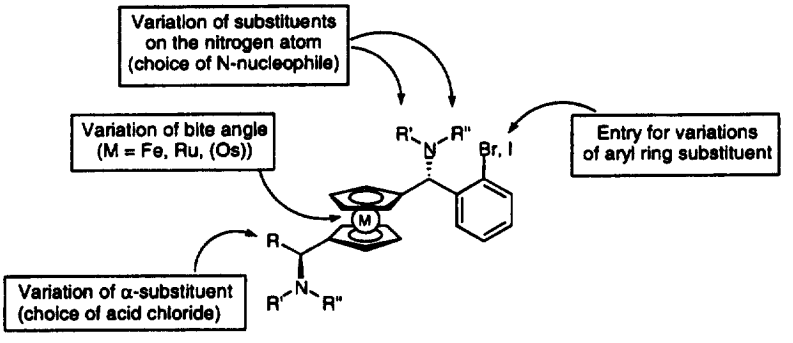
Table 5
Influence of the reaction temperature on the selectivity of the hydride transfer



A: acetophenone
B: 1'-acetonaphthone

Entry	Substrate	T [°C]	t [h]	Conversion [%][a]	*ee* [%][a]
1	A	22	0.5	98	71
2	A	0	2	96	72
3	A	-14	41	96	79
4	A	-30	120	95	**80**
5	B	22	0.5	99	78
6	B	-30	120	91	**90**

a) Conversions and *ee* were determined by GC on a chiral column.



Scheme 8. Options for variation of metallocenyl diamine ligands

Thus it was possible to improve the ligand properties within a short time by an efficient trial and error procedure.

4. Experimental section

4.1. General

Melting points are uncorrected. NMR spectra were recorded at room temperature in $CDCl_3$ on Bruker ARX 200, AC 300, AM 400 or AMX 500 instruments. Chemical shifts are given relative to the residual solvent peak (δ). Signals of the *meso*-diastereomer which appear separated from the *dl*-isomer are given for the sake of comparison even in such cases which allowed the isolation of the pure *dl*-isomer. Optical rotations were measured on a Perkin–Elmer 241 polarimeter. IR spectra were recorded on a Nicolet 510 FT-IR spectrometer. Electron impact (EI) mass spectra were recorded on a Varian CH 7A. Enantiomeric

excesses were determined by HPLC. A Chiralcel OD column (Daicel Chemical Industries) was used at room temperature with *n*-heptane/2-propanol as the mobile phase and detection by a diode array UV–VIS detector. Alternatively, determinations of enantiomeric excesses were performed by GC on a Chirasil-DEX CB column (Chrompak) using hydrogen as a carrier gas. Organic layers were dried over anhydrous $MgSO_4$. Column chromatography was carried out on silica gel 60 (70–230 mesh ASTM). Ether: MTBE (t-butylmethylether).

4.2. Materials

THF was distilled from potassium; Et_2O was distilled from sodium; CH_2Cl_2 was distilled from CaH_2; *i*-PrOH was distilled from sodium; HCO_2H and NEt_3 were distilled under argon and mixed in a 5:2 ratio; pyridine was dried over KOH. Commercial reagents were used without further purification. Experimental details for the preparation of compounds **4**, **5a**, **6a**, **6d–f**, **7–9**, **10**, **11a–e** and **12a–e** are reported elsewhere.[5] Lithium chloride was dried for 3 h at 140°C under vacuum (0.7 mmHg). $Pd(OH)_2$ (10% on C) was dried for 3 days at 80°C under vacuum. A solution of $BH_3 \cdot SMe_2$ in THF (1 M) was prepared from commercial $BH_3 \cdot SMe_2$ (10 M) directly before use. A solution of KOH (0.1 M) was prepared from KOH pellets and dry *i*-PrOH.

4.3. General procedure A for the ruthenium catalyzed transfer hydrogenation of ketones

Under argon, in a 100 mL Schlenk tube, $[Ru(p\text{-cymene})Cl_2]_2$ (3.6 mg, 5.8 μmol) was added to a solution of the diamine (23 μmol) in *i*-PrOH (5 mL). The mixture was stirred at 80°C for 30 min leading to a dark red homogeneous solution. After cooling to room temperature, *i*-PrOH (18 mL), the ketone (1.2 mmol) and KOH (0.1 M in *i*-PrOH, 0.58 mL) were added. The reaction was monitored by taking aliquots, and after a short filtration over silica gel, the samples were analyzed by chiral GC with respect to conversion and enantiomeric excesses of the product. Absolute configurations of the following alcohols were assigned by comparison with literature data for specific rotation. (*R*)-(+)-1-Phenyl-1-ethanol:[13] GC (CB, 100 kPa, 120°C): t_R/min=4.1 (*R*), 4.6 (*S*). (*R*)-(+)-2-Methyl-1-phenyl-1-propanol:[14] GC (CB, 100 kPa, 110°C): t_R/min=18.5 (*R*), 17.8 (*S*). (*S*)-(−)-2,2-Dimethyl-1-phenyl-1-propanol:[15] GC (CB, 100 kPa, 130°C): t_R/min=8.3 (*R*), 8.8 (*S*). (*S*)-(+)-1-Cyclohexyl-1-ethanol:[13] the crude alcohol was converted to its acetate (Ac_2O, DMAP cat.)[4j] and analyzed by GC (CB, 100 kPa, 90°C): t_R/min=16.1 (*R*), 11.7 (*S*). (*R*)-(+)-1-(1-Naphthyl)-1-ethanol:[13] GC (CB, 100 kPa, 160°C): t_R/min=10.9 (*R*), 10.2 (*S*). (*S,S*)-(−)-1,2-Diphenyl-1,2-ethanediol:[16] GC (CB, 100 kPa, 190°C): t_R/min=9.9 (*R,R*), 10.2 (*S,S*), 10.7 (*R,S*). (*S*)-(+)-Ethyl 3-hydroxybutanoate:[17] GC (CB, 100 kPa, 70°C): t_R/min=11.1 (*R*), 10.7 (*S*).

4.4. General procedure B for the diamines 5 and 6

The metallocenyl acetate **10a** (1.23 mmol) was dissolved in MeOH (10 mL; THF (10 mL) was used for reactions employing **10b**). An excess of the amine (2 g) together with water (2 mL) was added. More MeOH (THF) was added if the mixture was not a clear solution at this point. After stirring for 12 h at room temperature the reaction was poured into saturated aqueous NH_4Cl (50 mL) and extracted with MTBE (100 mL). After washing with water (2×50 mL) and brine (50 mL), the organic layer was dried and concentrated to give an oil which was purified by column chromatography.

4.4.1. (R,R)-1,1′-Bis[α-N-((R)-phenylethyl)aminoethyl]ferrocene **5b**

The diacetate **10a** (0.92 g, 3.3 mmol) was treated with (*R*)-phenylethylamine (5 mL) in MeOH/water. Chromatography (hexanes:MTBE=3:1) gave the diamine **5b** (1.00 g, 63%). Orange oil; $[\alpha]_D=-11.3$ (c=1.01, $CHCl_3$); IR (film): ν_{max}=3324 (w), 3083 (m), 3024 (m), 2965 (s), 2925 (m), 1450 (s), 1121 (s), 827 (m), 761 (s); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.41–7.23 (m, 10H), 4.17–4.02 (m, 8H), 3.87 (q, J=6.5 Hz, 2H), 3.39 (q, J=6.5 Hz, 2H), 1.50–1.46 (s, 2H), 1.48 (d, J=6.5 Hz, 6H), 1.27 (d, J=6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=146.11, 128.10, 126.11, 93.43, 68.30, 67.90, 67.45, 65.17, 55.02, 49.04, 25.20, 22.76; MS (EI, 70 eV): *m/z* (%): 480 (M^+, 97), 377 (33), 359 (83), 239 (80), 105 (100); HRMS for $C_{30}H_{36}FeN_2$: calcd 480.2228; found 480.2220.

4.4.2. (R,R)-1,1′-Bis[α-N-((S)-phenylethyl)aminoethyl]ferrocene **5c**

The diacetate **10a** (1.0 g, 3.65 mmol) was treated with (*S*)-phenylethylamine (5 mL) in MeOH/water. Chromatography (hexanes:MTBE=2:1) gave the diamine **5c** (1.40 g, 80%). Orange oil; $[\alpha]_D=-72.4$ (c=1.21, $CHCl_3$); IR (film): ν_{max}=3325 (w), 3083 (m), 3024 (m), 2966 (s), 2926 (m), 1452 (s), 1124 (m), 827 (m), 762 (s); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.36–7.21 (m, 10H), 4.03–3.84 (m, 10H), 3.24 (q, J=6.4 Hz, 2H), 1.36–1.32 (s, 2H), 1.34 (d, J=6.5 Hz, 6H), 1.25 (d, J=6.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=145.85, 128.41, 126.84, 126.57, 94.57, 67.79, 67.47, 66.27, 54.92, 48.52, 24.70, 20.87; MS (EI, 70 eV): *m/z* (%): 480 (M^+, 97), 391 (57), 359 (84), 239 (99), 105 (100); HRMS for $C_{30}H_{36}FeN_2$: calcd 480.2228; found 480.2233.

4.4.3. (R,R)-1,1′-Bis(α-N-pentylaminophenylmethyl)ferrocene **6b**

The diacetate **10b** (320 mg, 0.66 mmol) was treated with pentylamine (2 mL) in THF/water. Chromatography (hexanes:MTBE=3:1 with 1% NEt_3) gave the diamine **6b** (278 mg, 78%, *dl*:*meso*=92:8). Yellow oil; $[\alpha]_D=-18.8$ (c=0.78, $CHCl_3$); IR (KBr): ν_{max}=3320 (w), 3030 (w), 2910 (s), 2860 (s), 1445 (s), 820 (m); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.36–7.20 (m, 10H), 4.42–4.41 (s, *meso*), 4.34–4.33 (s, *dl*, 2H total), 4.29–4.28 (m, *dl*), 4.21–4.20 (m, *meso*, 2H total), 4.02–3.95 (m, 6H), 2.55–2.40 (m, 4H), 1.87 (s, 2H), 1.53–1.45 (m, 4H), 1.33–1.25 (m, 8H), 0.89 (t, J=6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=144.24, 128.15, 127.46, 126.91, 94.34, 68.12, 67.88, 67.83, 66.56, 62.67, 48.18, 29.94, 29.61, 22.60, 14.04 (*dl*); 94.45, 67.71, 66.64, 29.96 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 536 (M^+, 14), 449 (100), 392 (21), 211 (51), 182 (28); $C_{34}H_{44}FeN_2$ (536.58): calcd C 76.11, H 8.26, N 5.22; found C 75.81, H 8.30, N 5.24.

4.4.4. (R,R)-1,1′-Bis[α-N-(2-methoxyethylamino)phenylmethyl]ferrocene **6c**

The diacetate **10b** (280 mg, 0.58 mmol) was treated with 2-methoxyethylamine (2 mL) in THF/water. Chromatography (hexanes:MTBE=1:1 with 1% NEt_3) gave the diamine **6b** (112 mg, 38%). Yellow solid; m.p. 136°C; $[\alpha]_D=-28.7$ (c=0.68, $CHCl_3$); IR (KBr): ν_{max}=3332 (w), 3058 (w), 2930 (m), 2821 (m), 1445 (s), 1102 (s), 715 (m), 697 (s); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.35–7.32 (m, 4H), 7.26–7.21 (m, 4H), 7.17–7.13 (m, 2H), 4.35–4.32 (m, 4H), 4.05–4.03 (m, 6H), 3.59–3.40 (m, 4H), 3.36 (s, 6H), 2.74–2.56 (m, 4H), 2.43 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=144.14, 128.20, 127.45, 126.91, 94.50, 71.71, 68.15, 68.01, 67.93, 66.19, 62.51, 58.67, 47.73; MS (EI, 70 eV): *m/z* (%): 512 (M^+, 27), 437 (100), 392 (25), 348 (17), 211 (65), 182 (34); $C_{30}H_{36}FeN_2O_2$ (512.48): calcd C 70.31, H 7.08, N 5.47; found C 69.96, H 7.06, N 5.21.

4.5. General procedure C for the diketones 11f–h

To a suspension of aluminum(III) chloride (2.65 g, 20.0 mmol) in CH_2Cl_2 (10 mL) at 0°C was added the acid chloride (22.5 mmol). Ferrocene (8.10 mmol) in CH_2Cl_2 (10 mL) was added dropwise over 20 min. The reaction was warmed to room temperature and stirred for 2 h. Hydrolysis was performed at 0°C by dropwise addition of ice-cold water (50 mL; caution: gas evolution!). The reaction mixture was diluted with CH_2Cl_2 (100 mL) and washed twice with saturated aqueous K_2CO_3 (50 mL) and brine (50 mL). The organic layer was dried and concentrated to afford an oil which was purified by column chromatography.

4.5.1. 1,1′-Bis(o-chlorobenzoyl)ferrocene 11f

From ferrocene (4.0 g, 21.5 mmol), 2-chlorobenzoyl chloride (8.3 g, 47.3 mmol) and aluminum(III) chloride (6.3 g, 47.3 mmol), a combined yield of 60% (5.9 g) was obtained after crystallization of the crude product (CH_2Cl_2) and chromatography of the concentrated mother liquor (hexanes:MTBE=3:1). Red solid; m.p. 162°C; IR (KBr): ν_{max}=3108 (m), 3094 (m), 1646 (vs), 1445 (s), 1376 (s), 1295 (s), 1035 (s), 838 (m), 755 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=7.64–7.44 (m, 8H), 4.79 (s, 4H), 4.67 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=197.48, 138.71, 131.19, 131.09, 130.46, 128.83, 126.47, 79.86, 74.79, 72.51; MS (EI, 70 eV): *m/z* (%): 462 (M^+, 100), 195 (13), 139 (54), 115 (13), 92 (15); $C_{24}H_{16}Cl_2FeO_2$ (462.85): calcd C 62.22, H 3.45; found C 61.84, H 3.51.

4.5.2. 1,1′-Bis(o-bromobenzoyl)ferrocene 11g

From ferrocene (2.78 g, 15.0 mmol), 2-bromobenzoyl chloride (7.28 g, 33.3 mmol) and aluminum(III) chloride (4.34 g, 33 mmol), a combined yield of 74% (6.15 g) was obtained after crystallization of the crude product (CH_2Cl_2) and chromatography of the concentrated mother liquor (hexanes:MTBE=4:1). Red solid; m.p. 193°C; IR (KBr): ν_{max}=3105 (m), 3092 (m), 2923 (m), 1647 (vs), 1443 (s), 1291 (s), 1035 (m), 838 (m), 743 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.56–7.26 (m, 8H), 4.77 (s, 4H), 4.66 (s, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=198.16, 140.51, 133.53, 131.22, 128.84, 126.95, 119.46, 79.58, 74.66, 72.50; MS (EI, 70 eV): *m/z* (%): 552 (M^+, 100), 185 (23), 168 (41), 139 (99), 115 (29), 83 (19); $C_{24}H_{16}Br_2FeO_2$ (551.68): calcd C 52.20, H 2.90; found C 51.98, H 2.92.

4.5.3. 1,1′-Bis(o-iodobenzoyl)ferrocene 11h

From ferrocene (1.5 g, 8.0 mmol), 2-iodobenzoyl chloride (4.7 g, 17.7 mmol) and aluminum(III) chloride (2.4 g, 17.7 mmol) a yield of 46% (2.4 g) was obtained after crystallization of the crude product (CH_2Cl_2). Red solid; m.p. 199–201°C; IR (KBr): ν_{max}=3103 (w), 3090 (w), 1648 (vs), 1441 (s), 1377 (s), 1288 (s), 1034 (s), 837 (m), 738 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=7.85 (d, *J*=7.3 Hz, 2H), 7.48–7.00 (m, 6H), 4.78–4.76 (m, 4H), 4.69–4.67 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=199.75, 143.70, 140.21, 131.37, 128.54, 127.66, 92.46, 79.04, 74.70, 72.72; MS (EI, 70 eV): *m/z* (%): 646 (M^+, 100), 323 (19), 230 (20), 139 (29); $C_{24}H_{16}Fe\,I_2O_2$ (645.67): calcd C 44.60, H 2.48; found C 44.45, H 2.57.

4.6. General procedure D for the ferrocenyl diols 12f–h

Under argon, the oxazaborolidine (330 mg, 1.20 mmol; prepared from (*S*)-α,α-diphenylprolinol and methaneboronic acid) was dissolved in THF (12 mL) and cooled to 0°C. From a syringe charged with $BH_3 \cdot SMe_2$ (1 M in THF, 4 mL), 20% of the final amount (0.8 mL) was added to the catalyst solution. After 5 min of stirring, the remaining $BH_3 \cdot SMe_2$ and a solution of the diketone (2.00 mmol) in THF (5 mL) were added simultaneously over 20 min. The red color of the ketone turns to yellow upon reduction.

After 15 min at 0°C the excess $BH_3 \cdot SMe_2$ was quenched by dropwise addition of methanol (2 mL; gas evolution!). After the hydrolysis reaction had ceased, the mixture was poured into saturated aqueous NH_4Cl (150 mL) and extracted with MTBE (200 mL). The organic layer was washed with water (2×100 mL) and brine (100 mL), dried and then concentrated to give an oil which was purified by column chromatography.

For comparison (NMR, HPLC), racemic samples of the diols **12f–h** were prepared by $LiAlH_4$ or $NaBH_4$ reduction of the diketones **11f–h**. They contained comparable amounts of the *dl*- and *meso*-diastereomers.

4.6.1. (R,R)-1,1′-Bis(α-hydroxy-o-chlorophenylmethyl)ferrocene ***12f***

Diketone **11f** (1.5 g, 3.2 mmol) was reduced (addition time: 18 h, reaction time: 3 h) giving after chromatography (hexanes:MTBE=3:1) **12f** in 85% yield (1.27 g, *dl*:*meso*=90:10). Orange solid; m.p. 164–166°C; $[\alpha]_D$=−43 (*c*=1.00, $CHCl_3$); IR (KBr): ν_{max}=3279 (w), 2972 (m), 2928 (m), 1470 (m), 1439 (m), 1058 (s), 1042 (s), 747 (vs); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.47–7.06 (m, 8H), 5.97 (s, *dl*), 5.87 (s, *meso*, 2H total), 5.30 (s, *meso*), 5.19 (s, *dl*, 2H total), 4.41 (s, 2H), 4.37 (s, 2H), 4.25 (s, 2H), 4.12 (s, *dl*), 3.76 (s, *meso*, 2H total); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=141.41, 131.87, 129.17, 128.61, 128.00, 126.98, 92.71, 68.55, 68.15, 67.90, 66.86, 66.78 (*dl*); 126.87, 67.37 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 466 (M^+, 10), 236 (10), 188 (11), 153 (18), 70 (100); $C_{24}H_{20}Cl_2FeO_2$ (466.85): calcd C 61.69, H 4.28; found C 61.84, H 4.41.

4.6.2. (R,R)-1,1′-Bis(α-hydroxy-o-bromophenylmethyl)ferrocene ***12g***

Diketone **11g** (1.0 g, 1.8 mmol) was reduced (addition time: 1 h, reaction time: 2.5 h) giving after chromatography (hexanes:MTBE=4:1 to 1:1) **12g** in quantitative yield (1.0 g, *dl*:*meso*=93:7). Orange solid; m.p. 165°C; $[\alpha]_D$=−14.7 (*c*=1.03, $CHCl_3$); IR (KBr): ν_{max}=3267 (w), 3100 (m), 3067 (m), 2917 (m), 1466 (s), 1434 (m), 1048 (s), 1013 (s), 744 (vs); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.62–6.99 (m, 8H), 5.97 (s, *dl*), 5.88 (s, *meso*, 2H total), 5.31 (s, *meso*), 5.19 (s, *dl*, 2H total), 4.45 (s, 4H), 4.27 (s, *dl*), 4.23 (s, *meso*, 2H total), 4.15 (s, *dl*), 4.07 (s, *meso*, 2H total); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=142.89, 132.47, 128.86, 128.00, 127.67, 122.18, 92.85, 70.96, 68.26, 67.95, 66.97 (*dl*); 127.67, 70.30, 67.54 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 555 (M^+, 13), 537 (13), 153 (100); $C_{24}H_{20}Br_2FeO_2$ (555.68): calcd C 51.83, H 3.60; found C 51.99, H 3.74.

4.6.3. (R,R)-1,1′-Bis(α-hydroxy-o-iodophenylmethyl)ferrocene ***12h***

Diketone **11h** (1.5 g, 2.3 mmol) was reduced in THF (130 mL), (addition time: 5 h at room temperature, reaction time: 3 h at room temperature) giving after chromatography (hexanes:MTBE=15:1 to 5:1) **12h** in 86% yield (1.3 g, *dl*:*meso*=94:6). Orange solid; m.p. 94–96°C; $[\alpha]_D$=+16.9 (*c*=1.00, $CHCl_3$); IR (KBr): ν_{max}=3395 (w), 2964 (m), 2907 (m), 1460 (m), 1433 (m), 1045 (s), 1020 (s), 806 (m), 741 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.60 (d, *J*=7.7 Hz, 2H), 7.34 (d, *J*=7.7 Hz, 2H), 7.20 (t, *J*=7.3 Hz, 2H), 6.77 (t, *J*=7.3 Hz, 2H), 5.74 (s, *dl*), 5.67 (s, *meso*, 2H total), 5.30 (s, *meso*), 5.19 (s, *dl*, 2H total), 4.45 (s, 2H), 4.36 (s, 2H), 4.25 (s, *dl*), 4.15 (s, *meso*, 2H total), 4.08 (s, *dl*), 4.02 (s, *meso*, 2H total); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=145.95, 138.84, 128.95, 128.32, 127.47, 97.77, 93.01, 75.35, 68.16, 67.80, 66.94, 66.84 (*dl*); 145.36, 97.96, 74.81, 67.20 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 650 (M^+, 2), 418 (4), 236 (3), 153 (71), 70 (100); $C_{24}H_{20}FeI_2O_2$ (649.67): calcd C 44.33, H 3.07; found C 44.41, H 3.16.

4.6.4. (R,R)-1,1′-Bis(α-hydroxy-o-hexynylphenylmethyl)ferrocene ***12i***

In a three-necked flask equipped with a condenser, were placed under argon, $Pd(dba)_2$ (79.6 mg, 0.138 mmol), triphenylphosphine (72.5 mg, 0.276 mmol), **12h** (0.90 g, 1.38 mmol), THF (15 mL), pyrrolidine

(8 mL), CuI (53 mg, 0.14 mmol) and 1-hexyne (0.9 mL, 7.8 mmol, 5.7 equiv.). The solution was heated at 50°C for 8 h and stirred at room temperature for 12 h. The mixture was then poured into saturated aqueous NH_4Cl (100 mL) and extracted with MTBE (200 mL). The organic layer was washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$ and concentrated. The crude oil obtained was then purified by chromatography (hexanes:MTBE=20:1 to 10:1) giving **12i** in 95% yield (0.73 g, *dl*:*meso*=93:7). Yellow–brown oil; $[\alpha]_D$=+142.2 (*c*=0.72, $CHCl_3$); IR (KBr): ν_{max}=3348 (w), 3094 (m), 3065 (m), 2929 (w), 2228 (s), 1044 (s), 1016 (s), 753 (m); ^1H NMR ($CDCl_3$, 200 MHz): δ=7.55–7.09 (m, 8H), 6.15 (s, *dl*), 6.02 (s, *meso*, 2H total), 4.92 (s, *meso*), 4.82 (s, *dl*, 2H total), 4.44 (s, 2H), 4.39 (s, 2H), 4.21 (s, 2H), 4.09 (d, *J*=1.0 Hz, 2H), 2.53 (t, *J*=6.8 Hz, 4H), 1.65 (m, 8H), 1.04 (t, *J*=7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=145.86, 131.83, 127.86, 126.77, 125.3, 121.22, 94.97, 93.55, 78.92, 69.98, 67.87, 67.42, 66.51, 66.25, 30.78, 22.03, 19.25, 13.68 (*dl*); 145.44, 69.23 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 558 (M^+, 72), 540 (100), 234 (25), 165 (28), 28 (56); HRMS for $C_{36}H_{38}FeO_2$: calcd 558.2221; found 558.2217.

4.7. *General procedure E for the diamines 13 and 15*

The metallocenyl diol (2.92 mmol) was treated under argon with acetic anhydride (2 mL) and pyridine (5 mL) and the solution was stirred for 12 h at room temperature. Volatile matter was removed under vacuum (0.7 mmHg, 5 h). The crude product was already >95% pure as indicated by NMR analysis. The yield was quantitative. The crude product was dissolved in THF (10 mL) in the same flask and treated with methylamine (40% in water, 2 mL). More THF was added if the mixture was not a clear solution at this point. After stirring for 12 h at room temperature the reaction was poured into saturated aqueous NH_4Cl (50 mL) and extracted with MTBE (100 mL). After washing with water (2×50 mL) and brine (50 mL) the organic layer was dried and concentrated to give an oil which was purified by column chromatography.

4.7.1. (R,R)-*1,1′-Bis*(α-N-*methylamino*-p-*fluorophenylmethyl*)*ferrocene* **13a**

The diol **12a** (252 mg, 0.58 mmol) was treated with acetic anhydride (1 mL) and pyridine (2 mL). The resulting crude diacetate was treated with methylamine (40% in water, 2 mL) in THF/water. Chromatography (ethyl acetate with 1% NEt_3) gave the diamine **13a** (233 mg, 87%, *dl*:*meso*=91:9). Yellow solid; m.p. 110°C; $[\alpha]_D$=+56.4 (*c*=1.55, $CHCl_3$); IR (KBr): ν_{max}=3269 (s), 3078 (w), 2927 (w), 2777 (m), 1600 (m), 1504 (s), 1225 (s), 847 (s); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.26–7.19 (m, 4H), 6.96–6.90 (m, 4H), 4.23–4.21 (m), 4.16–4.15 (m, *meso*), 4.01–3.92 (m), 3.88–3.87 (m, *dl*, 10H total), 2.27 (s, *meso*), 2.26 (s, *dl*, 6H total), 2.24 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=161.87 (d, *J*=245 Hz), 139.29 (d, *J*=3.0 Hz), 128.91 (d, *J*=7.9 Hz), 115.05 (d, *J*=21.2 Hz), 93.62, 68.27, 67.89, 67.49, 66.72, 63.93, 34.69 (*dl*); 139.12 (d, *J*=3.0 Hz), 93.83, 68.29, 68.02, 66.47, 63.90, 34.82 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 460 (M^+, 17), 429 (100), 401 (13), 322 (15), 229 (30), 214 (23), 136 (24); $C_{26}H_{26}F_2FeN_2$ (460.35): calcd C 67.84, H 5.69, N 6.09; found C 67.50, H 5.89, N 5.95.

4.7.2. (R,R)-*1,1′-Bis*(α-N-*methylamino*-p-*methoxyphenylmethyl*)*ferrocene* **13b**

The diol **12b** (275 mg, 0.60 mmol) was treated with acetic anhydride (1 mL) and pyridine (2 mL). The resulting crude diacetate was treated with methylamine (40% in water, 2 mL) in THF/water. Chromatography (hexanes:MTBE=1:1 with 1% NEt_3) gave the diamine **13b** (180 mg, 62%, *dl*:*meso*=80:20). Yellow solid; m.p. 131°C; $[\alpha]_D$=+39.4 (*c*=0.68, $CHCl_3$); IR (KBr): ν_{max}=3335 (w), 3053 (w), 2934 (m), 2788 (w), 1511 (s), 1431 (m), 1251 (s), 1029 (s), 838 (m); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.21–7.15 (m, 4H), 6.80–6.77 (m, 4H), 4.21–4.20 (m, 2H), 4.16 (s, 2H), 3.99–3.88 (m, 4H), 3.99–3.88 (m, 4H),

3.72 (s, 6H), 2.28 (s), 2.27 (s, 6H total), 2.46 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=158.61, 135.84, 128.46, 113.60, 94,05, 68.07, 67.66, 67.55, 66.72, 63.95, 55.14, 34.71 (*dl*); 135.64, 94.20, 68.12, 67.81, 66.56, 34.81 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 484 (M^+, 7), 453 (100), 361 (60), 241 (20), 226 (23), 149 (65); HRMS for $C_{28}H_{32}FeN_2O_2$: calcd 484.1813; found 484.1816.

4.7.3. (R,R)-1,1′-Bis[α-N-methylamino-(1-naphthyl)methyl]ferrocene ***13c***

The diol **12c** (409 mg, 0.82 mmol) was treated with acetic anhydride (1 mL) and pyridine (2 mL). The resulting crude diacetate was treated with methylamine (40% in water, 2 mL) in THF/water. Crystallization from MTBE gave the diamine **13c** (80 mg, 19%, *dl*:*meso*=96:4). Yellow solid; m.p. 141°C; $[\alpha]_D$=−5.2 (*c*=2.32, $CHCl_3$); IR (KBr): ν_{max}=3343 (w), 3051 (w), 2936 (w), 2840 (w), 2782 (w), 1431 (m), 783 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=8.38–8.35 (m, 2H), 7.94–7.91 (m, 2H), 7.83–7.75 (m), 7.57–7.52 (m, 10H total), 5.28 (s, *meso*), 5.26 (s, *dl*, 2H total), 4.35–4.34 (m, *dl*), 4.24–4.16 (m, 8H total), 2.46 (s, *meso*), 2.45 (s, *dl*, 6H total), 2.38 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=139.22, 133.94, 131.77, 128.82, 127.43, 125.52, 125.22, 124.65, 123.50, 93.92, 68.01, 67.79, 67.67, 67.55, 59.87, 34.96 (*dl*); 139.13, 131.81, 124.58, 94.06, 68.04, 67.50, 35.07 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 524 (M^+, 7), 493 (100), 464 (6), 289 (35), 274 (28), 202 (45); $C_{34}H_{32}FeN_2$ (524.85): calcd C 77.86, H 6.15, N 5.34; found C 77.60, H 6.13, N 5.01.

4.7.4. (R,R)-1,1′-Bis[α-N-methylamino-(2-naphthyl)methyl]ferrocene ***13d***

The diol **12d** (309 mg, 0.62 mmol) was treated with acetic anhydride (1 mL) and pyridine (2 mL). The resulting crude diacetate was treated with methylamine (40% in water, 2 mL) in THF/water. Chromatography (hexanes:MTBE=1:1 with 1% NEt_3) gave the diamine **13d** (260 mg, 80%, *dl*:*meso*=>96:<4). Yellow solid; m.p. 177–178°C; $[\alpha]_D$=+189.5 (*c*=0.78, $CHCl_3$); IR (KBr): ν_{max}=3335 (m), 3054 (w), 2950 (m), 2838 (m), 2777 (s), 1430 (s), 1115 (s), 823 (s), 783 (m); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.85–7.79 (m, 6H), 7.68 (s, 2H), 7.50–7.46 (m, 6H), 4.40–4.39 (m, 2H), 4.35 (s, 2H), 4.13–4.12 (m, 2H), 4.10–4.08 (m, 2H), 4.04–4.03 (m, 2H), 2.36 (s, 6H), 2.24 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=141.05, 133.30, 132.87, 128.04, 127.73, 127.61, 126.26, 125.86, 125.50, 125.47, 93.61, 68.17, 67.87, 67.71, 66.80, 64.74, 34.80; MS (EI, 70 eV): *m/z* (%): 524 (M^+, 14), 493 (100), 464 (10), 366 (2), 354 (12), 261 (28), 246 (18), 234 (5), 203 (27), 168 (19); $C_{34}H_{32}FeN_2$ (524.49): calcd C 77.86, H 6.15, N 5.34; found C 77.54, H 5.84, N 5.13.

4.7.5. (R,R)-1,1′-Bis(α-N-methylamino-o-tolylmethyl)ferrocene ***13e***

The diol **12e** (388 mg, 0.91 mmol) was treated with acetic anhydride (1 mL) and pyridine (2 mL). The resulting crude diacetate was treated with methylamine (40% in water, 2 mL) in THF/water. Chromatography (hexanes:MTBE=1:1 with 1% NEt_3) gave the diamine **13e** (174 mg, 42%, *dl*:*meso*=>98:<2). Yellow oil; $[\alpha]_D$=−33.5 (*c*=2.00, $CHCl_3$); IR (film): ν_{max}=3260 (w), 3020 (w), 2920 (s), 2850 (s), 2780 (m), 1430 (s), 1090 (m), 730 (m); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.40–7.34 (m, 2H), 7.14–7.04 (m, 6H), 4.61 (s), 4.60 (s, 2H total), 4.17–4.16 (m, *dl*), 4.12–4.11 (m, *meso*), 4.05–4.04 (m, *meso*), 3.99–3.98 (m, 8H total), 2.34 (s, 6H), 2.29 (s, 6H), 2.12 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=141.65, 135.39, 130.06, 126.68, 126.38, 126.06, 93.89, 67.86, 67.32, 67.23, 67.17, 59.24, 34.58, 19.56 (*dl*); 34.16, 19.48 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 452 (M^+, 25), 421 (100), 393 (15), 318 (37), 225 (36), 165 (22), 132 (31); $C_{28}H_{32}FeN_2$ (452.42): calcd C 74.34, H 7.13, N 6.19; found C 74.14, H 7.43, N 6.52.

4.7.6. (R,R)-1,1′-Bis(α-N-methylamino-o-chlorophenylmethyl)ferrocene ***13f***

The diol **12f** (1.0 g, 2.1 mmol) was treated with acetic anhydride (3 mL) and pyridine (6 mL). The resulting crude diacetate was treated with methylamine (40% in water, 12 mL) in acetonitrile (20 mL). Chromatography (hexanes:MTBE=1:1 to MTBE with 1% NEt_3) gave the diamine **13f** (0.37 g, 37%, *dl*:*meso*=90:10). Recrystallization from diethyl ether/pentane gave the pure *dl*-diastereoisomer. Yellow solid; m.p. 98°C; $[\alpha]_D$=+7 (*c*=1.01, $CHCl_3$); IR (KBr): ν_{max}=3438 (w), 3067 (m), 2965 (m), 2840 (m), 2786 (m), 1466 (m), 1029 (m), 827 (s), 750 (vs); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.55–6.97 (m, 8H), 5.04 (s, 2H), 4.34–4.33 (m, 2H), 4.24–4.23 (m, 2H), 4.12–4.09 (m, 4H), 2.40 (s, 6H), 2.18 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=141.19, 133.53, 129.28, 128.49, 127.87, 127.07, 93.27, 68.13, 67.67, 67.50, 66.70, 59.38, 34.61; MS (EI, 70 eV): *m/z* (%): 492 (M^+, 31), 461 (59), 209 (17), 182 (70), 153 (54), 113 (100), 70 (73); $C_{26}H_{26}Cl_2FeN_2$ (492.85): calcd C 63.30, H 5.27, N 5.68; found C 63.58, H 5.50, N 5.64.

4.7.7. (R,R)-1,1′-Bis(α-N-methylamino-o-bromophenylmethyl)ferrocene ***13g***

The diol **12g** (0.7 g, 1.2 mmol) was treated with acetic anhydride (2 mL) and pyridine (4 mL). The resulting crude diacetate was treated with methylamine (40% in water, 6 mL) in acetonitrile (10 mL). Chromatography (hexanes:MTBE=1:1 to MTBE with 1% NEt_3) gave the diamine **13g** (0.17 g, 23%, *dl*:*meso*=92:8). Yellow–orange solid; m.p. 58–68°C (decomp.); $[\alpha]_D$=+39.5 (*c*=0.95, $CHCl_3$); IR (KBr): ν_{max}=3472 (w), 3074 (m), 2970 (m), 2848 (m), 2791 (m), 1438 (m), 1021 (m), 747 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.55–7.52 (m, 4H), 7.31–7.26 (m, 2H), 7.07–7.05 (m, 2H), 5.03 (s, *dl*), 5.02 (s, *meso*, 2H total), 4.32–4.28 (m, 4H), 4.14–4.11 (m, 4H), 2.43 (s, *dl*), 2.42 (s, *meso*, 6H total), 2.28 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=142.82, 132.52, 128.77, 128.27, 127.72, 124.12, 93.41, 68.17, 67.65, 67.48, 66.59, 61.96, 34.61 (*dl*); 142.63, 93.53, 66.27, 61.77 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 582 (M^+, 14), 551 (28), 182 (100), 153 (63), 70 (24); $C_{26}H_{26}Br_2FeN_2$ (581.65): calcd C 53.64, H 4.47, N 4.81; found C 53.89, H 4.69, N 4.51.

4.7.8. (R,R)-1,1′-Bis(α-N-methylamino-o-iodophenylmethyl)ferrocene ***13h***

The diol **12h** (0.7 g, 1.07 mmol) was treated with acetic anhydride (3 mL) and pyridine (6 mL). The resulting crude diacetate was treated with methylamine (40% in water, 5 mL) in acetonitrile (10 mL). Chromatography (hexanes:MTBE=2:1 to MTBE with 10% NEt_3) gave the diamine **13h** (0.1 g, 14%, *dl*:*meso*=93:7). Yellow–orange oil; $[\alpha]_D$=+65 (*c*=1.30, $CHCl_3$); IR (film): ν_{max}=3400 (w), 3072 (m), 2970 (m), 2850 (m), 2795 (m), 1435 (m), 1008 (s), 746 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): δ=7.77–7.75 (m, 2H), 7.41–7.22 (m, 4H), 6.86–6.85 (m, 2H), 4.89 (s, *dl*), 4.83 (s, *meso*, 2H total), 4.33 (s, 4H), 4.08 (s, 4H), 2.38 (s, 6H), 2.32 (s, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz): δ=145.60, 139.26, 128.93, 128.66, 128.45, 100.75, 93.63, 68.37, 67.72, 67.39, 67.07, 66.49, 34.60; MS (EI, 70 eV): *m/z* (%): 676 (M^+, 46), 645 (22), 238 (18), 182 (100), 153 (61); HRMS for $C_{26}H_{26}FeI_2N_2$: calcd 675.9535; found 675.9536.

4.7.9. (R,R)-1,1′-Bis(α-N-methylamino-o-hexynylphenylmethyl)ferrocene ***13i***

The diol **12i** (0.23 g, 0.41 mmol) was treated with acetic anhydride (1.5 mL) and pyridine (3 mL). The resulting crude diacetate was treated with methylamine (40% in water, 8 mL) in THF/water. Chromatography (hexanes:MTBE=1:1 to MTBE with 1% NEt_3) gave the aminoalcohol **14** (0.182 g, 55%, *dl*:*meso*=>99:<1) and the diamine **13i** (0.03 g, 13%, *dl*:*meso*=92:8). Yellow–orange oil; $[\alpha]_D$=+72 (*c*=0.95, $CHCl_3$); IR (film): ν_{max}=3337 (w), 3065 (m), 2956 (s), 2929 (s), 2789 (m), 2227 (m), 1105 (m), 757 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.43–7.37 (m, 4H), 7.27–7.20 (m, 2H), 7.12–7.10 (m, 2H), 5.10 (s, *dl*), 5.05 (s, *meso*, 2H total), 4.33 (s, 2H), 4.19 (s, 2H), 4.08 (s, 2H), 4.02 (s, 2H), 2.56 (t, *J*=6.8 Hz, 4H), 2.39 (s, 6H), 1.73–1.52 (m, 6H), 1.02 (t, *J*=10.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=145.56, 132.12, 127.85, 126.54, 126.33, 123.13, 94.65, 93.73, 79.41, 68.06, 67.60, 67.13, 67.03, 60.98,

34.63, 30.88, 22.03, 19.27, 13.61 (*dl*); 145.24, 60.78 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 584 (M^+, 37), 552 (36), 319 (100), 262 (25), 200 (62); HRMS for $C_{38}H_{44}FeN_2$: calcd 584.2854; found 584.2866.

4.7.10. (R,R)-[1-(α-N-Methylamino-o-hexynylphenylmethyl)-1′-(α-hydroxy-o-hexynylphenylmethyl)]-ferrocene ***14***

Orange–brown oil; $[\alpha]_D$=+231 (*c*=0.85, $CHCl_3$); IR (film): ν_{max}=3256 (w), 3091 (w), 2929 (w), 2802 (m), 2227 (m), 1480 (m), 1103 (s), 1060 (s), 756 (s); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.46–7.00 (m, 8H), 6.23 (s, 1H), 5.21 (s, 1H), 4.35 (s, 1H), 4.28 (s, 2H), 4.15 (s, 2H), 4.08 (s, 1H), 4.02–4.00 (m, 2H), 2.54–2.44 (m, 5H), 2.34 (s, 3H), 1.73–1.49 (m, 9H), 1.02–0.97 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=146.95, 145.41, 132.56, 131.91, 128.21, 128.06, 126.76, 126.20, 126.56, 125.73, 122.86, 121.41, 95.70, 95.18, 94.40, 92.32, 79.55, 79.14, 69.57, 68.08, 67.97, 67.83, 67.63, 67.57, 67.07, 66.68, 65.70, 61.38, 33.63, 31.05, 30.95, 22.20, 19.44, 13.80; MS (EI, 70 eV): *m/z* (%): 571 (M^+, 100), 540 (72), 510 (17), 319 (30), 200 (56), 165 (22), 28 (58); HRMS for $C_{37}H_{41}FeON$: calcd 571.2538; found 571.2545.

4.7.11. (R,R)-1,1′-Bis(α-N-benzyl-N-methylamino-o-bromophenylmethyl)ferrocene ***15***

The diol **12g** (2.3 g, 4.17 mmol) was treated with acetic anhydride (5 mL) and pyridine (10 mL). The resulting crude diacetate was treated with *N*-benzyl-*N*-methylamine (3 mL, 25.2 mmol) in THF/water. Chromatography (hexanes:MTBE=30:1) gave the diamine **15** (2.35 g, 74%, *dl*:*meso*=92:8). Orange solid; m.p. 146°C; $[\alpha]_D$=+31.6 (*c*=0.98, $CHCl_3$); IR (KBr): ν_{max}=3112 (m), 3083 (m), 2957 (m), 2836 (m), 2791 (m), 1639 (m), 1618 (m), 755 (s); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.63–7.61 (m, 4H), 7.33–7.31 (m, 2H), 7.21–6.96 (m, 12H), 4.86 (s, *dl*), 4.71 (s, *meso*, 2H total), 4.27 (m, 2H), 3.76 (d, *J*=1.0 Hz, 2H), 3.64 (m, 4H), 3.33 (d, *J*=13.1 Hz, 2H), 3.21 (d, *J*=13.1 Hz, 2H), 1.83 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=142.43, 140.19, 132.68, 130.10, 128.50, 128.27, 128.01, 127.32, 126.57, 125.29, 89.91, 71.73, 69.83, 6.79, 68.15, 67.59, 67.32, 58.98, 39.46; MS (EI, 70 eV): *m/z* (%): 762 (M^+, 100), 523 (78), 408 (26), 289 (21), 153 (84), 91 (90); $C_{40}H_{38}Br_2FeN_2$ (761.68): calcd C 63.02, H 4.99, N 3.67; found C 62.57, H 4.25, N 3.56.

4.8. General procedure F for the aryl alkylated diamines ***16***

To a solution of diamine **15** in dry THF was added at −78°C under an argon atmosphere, *n*-BuLi (2.2 equiv., 1.46 M in hexane). The mixture was stirred at −78°C for 1 h. Then CuCN·2LiCl (2.2 equiv., 1 M in THF) was added and the mixture was stirred for 1 h. Finally an excess of the alkyl bromide (8 equiv.) was added and the reaction was allowed to warm to room temperature overnight. The mixture was then carefully hydrolyzed and extracted with MTBE (2×50 mL). The organic layer was washed with brine (2×50 mL), dried over $MgSO_4$ and concentrated. The oil obtained was purified by chromatography.

4.8.1. (R,R)-1,1′-Bis(α-N-benzyl-N-methylamino-o-allylphenylmethyl)ferrocene ***16a***

The diamine **15** (1.0 g, 1.3 mmol) in dry THF (10 mL) was treated with *n*-BuLi (2 mL, 2.9 mmol), CuCN·2LiCl (1 M in THF, 2.9 mmol) and allyl bromide (0.9 mL, 10.4 mmol). After chromatography (hexanes:MTBE=40:1 to 20:1) the diamine **16a** was obtained in 70% yield (0.63 g, *dl*:*meso*=93:7). Orange oil; $[\alpha]_D$=+160.7 (*c*=1.07, $CHCl_3$); IR (film): ν_{max}=3062 (s), 3026 (s), 2838 (s), 2780 (s), 1637 (s), 1493 (s), 1452 (s), 1129 (s), 752 (s); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.94 (d, *J*=7.6 Hz, *meso*), 7.81 (d, *J*=7.6 Hz, *dl*, 2H total), 7.40–7.26 (m, 16H), 6.18 (m, 2H), 5.30 (s, 4H), 5.26–5.24 (m, 2H), 4.09–4.08 (m, 2H), 3.98–3.68 (m, 10H), 3.46–3.23 (m, 4H), 1.95 (s, *dl*), 1.90 (s, *meso*, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=142.42, 140.39, 137.36, 129.45, 128.58, 127.98, 126.76, 126.50, 126.23, 116.17, 91.30, 71.14,

69.89, 67.80, 67.52, 64.42, 59.85, 40.20, 37.67; MS (EI, 70 eV): *m/z* (%): 684 (M^+, 74), 644 (12), 316 (36), 249 (35), 129 (26), 91 (100); HRMS for $C_{46}H_{48}FeN_2$: calcd 684.3167; found 684.3174.

4.8.2. (R,R)-1,1′-Bis(α-N-benzyl-N-methylamino-o-benzylphenylmethyl)ferrocene ***16b***

The diamine **15** (0.73 g, 0.96 mmol) in THF (8 mL) was treated with *n*-BuLi (2.2 mmol), CuCN·2LiCl (2.2 mmol) and benzyl bromide (0.9 mL, 7.9 mmol). After chromatography (hexanes:MTBE=10:1) the diamine **16b** was obtained in 61% yield (0.46 g, *dl*:*meso*=92:8). Yellow–orange oil; $[\alpha]_D$=+213.7 (*c*=1.02, $CHCl_3$); IR (film): ν_{max}=3060 (m), 3024 (m), 2838 (m), 1639 (s), 1618 (s), 1452 (s), 1127 (m), 732 (m); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.83 (d, *J*=7.6 Hz, 2H), 7.44–7.27 (m, 26H), 4.61–4.37 (m, 6H), 4.11–4.10 (m, 2H), 3.93 (s, 2H), 3.63 (s, 2H), 3.39 (s, 2H), 3.30 (d, *J*=13.4 Hz, 2H), 3.00 (d, *J*=13.4 Hz, 2H), 2.06 (s, *meso*), 1.83 (s, *dl*, 6H total); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=143.00, 140.76, 140.46, 138.05, 130.64, 129.17, 128.88, 128.42, 128.31, 127.95, 126.68, 126.48, 126.11, 91.11, 71.10, 70.06, 67.68, 67.43, 64.07, 59.43, 39.83 (*dl*); 91.13, 69.57, 59.11, 39.56 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 784 (M^+, 38), 694 (18), 545 (12), 420 (17), 300 (76), 91 (100); HRMS for $C_{54}H_{52}FeN_2$: calcd 784.3480; found 784.3483.

4.9. General procedure G for the diamines ***13j–k*** *by debenzylation/hydrogenation*

In a three-necked flask, the diamine **16** was dissolved under argon in a mixture of methanol and ethyl acetate (1:1). One drop of HCO_2H and $Pd(OH)_2/C$ (about 10 mol%) were then added giving a black heterogeneous solution. The flask was connected to a vacuum and purged with hydrogen from a balloon. The mixture was then vigorously stirred at room temperature for 24 h. Filtration over Celite and evaporation of the solvents left an oil which was purified by chromatography.

4.9.1. (R,R)-1,1′-Bis(α-N-methylamino-o-propylphenylmethyl)ferrocene ***13j***

Hydrogenation of the diamine **16a** (426 mg, 0.62 mmol) gave after chromatography (hexanes:MTBE=1:1 to MTBE with 5% NEt_3) the diamine **13j** in 64% yield (200 mg, *dl*:*meso*=93:7). Orange oil; $[\alpha]_D$=−4 (*c*=0.87, $CHCl_3$); IR (film): ν_{max}=3337 (w), 3068 (s), 3016 (s), 2957 (s), 2784 (s), 1485 (s), 1467 (s), 1126 (s), 1039 (m), 816 (s), 750 (s); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.42 (dd, *J*=6.7 Hz, 1.5 Hz, 2H), 7.17–7.09 (m, 6H), 4.70 (s, *dl*), 4.68 (s, *meso*, 2H total), 4.19–4.16 (m, 2H), 4.08–4.00 (m, 6H), 2.79–2.64 (m, *dl*), 2.62–2.49 (m, *meso*, 4H total), 2.35 (s, 6H), 2.10 (s, 2H), 1.70–1.58 (m, 4H), 1.02 (t, *J*=7.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=141.46, 140.24, 129.31, 127.02, 126.55, 126.22, 94.57, 68.12, 67.55, 67.49, 67.40, 58.62, 34.75, 24.86, 14.30 (*dl*); 94.70, 67.16 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 508 (M^+, 51), 477 (100), 449 (22), 346 (51), 162 (31); HRMS for $C_{32}H_{40}FeN_2$: calcd 508.2541; found 508.2541.

4.9.2. (R,R)-1,1′-Bis(α-N-methylamino-o-benzylphenylmethyl)ferrocene ***13k***

Debenzylation of the diamine **16b** (270 mg, 0.34 mmol) gave after chromatography (hexanes:MTBE=1:1 to MTBE with 5% NEt_3) the diamine **13k** in 40% yield (80 mg, *dl*:*meso*=93:7). Orange oil; $[\alpha]_D$=+51.8 (*c*=0.81, $CHCl_3$); IR (film): ν_{max}=3338 (w), 3083 (s), 3024 (s), 2851 (s), 2786 (s), 1494 (s), 1472 (s), 1125 (s), 1039 (m), 817 (m), 743 (s); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.28 (dd, *J*=7.6 Hz, 1.3 Hz, 2H), 7.23–7.10 (m, 16H), 4.67 (s, *dl*), 4.63 (s, *meso*, 2H), 4.16–4.18 (m, 6H), 3.93–3.86 (m, 4H), 3.58 (s, 2H), 2.21 (s, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=142.50, 141.35, 138.17, 130.67, 128.94, 128.47, 127.68, 127.08, 126.75, 126.11, 94.12, 68.11, 67.50, 67.38, 67.10, 58.76, 39.12, 34.46 (*dl*); 128.30, 67.90 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 604 (M^+, 33), 573 (65), 314 (65), 300 (100), 165 (38); HRMS for $C_{40}H_{40}FeN_2$: calcd 604.2541; found 604.2539.

4.10. (R,R)-(N-Tosyl)-1,1′-bis(α-aminophenylmethyl)ferrocene 17

The diamine **6e** (297 mg, 0.75 mmol) was dissolved in CH_2Cl_2 (5 mL) and the solution cooled to 0°C. Tosyl chloride (143 mg, 0.75 mmol) was added and stirring was continued for 10 min at 0°C. After stirring for 1 h at room temperature the reaction mixture was poured into saturated aqueous K_2CO_3 (20 mL). The product was extracted into MTBE (3×20 mL) and the combined organic layers dried over $MgSO_4$. Concentration and rapid chromatography (CH_2Cl_2:ethyl acetate=2:1 with 1% NEt_3) gave the monotosylated diamine **17** (150 mg, 36%). Yellow solid; m.p. 155°C; $[\alpha]_D=-31.7$ (c=2.52, $CHCl_3$); IR (KBr): ν_{max}=3304 (w), 3083 (w), 3060 (w), 2919 (w), 1454 (m), 1301 (m), 1151 (s), 698 (s); ^1H NMR ($CDCl_3$, 300 MHz): δ=7.45–7.41 (m, 2H), 7.28–7.03 (m, 12H), 5.26–5.25 (m, 1H), 4.79 (s, 1H), 4.33–4.32 (m, 1H), 4.18–4.17 (m, 1H), 4.15–4.14 (m, 1H), 4.08–3.90 (m, 6H), 2.32 (s, 3H), (NH_2 not observed); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=146.56, 142.32, 141.38, 138.54, 128.94, 128.52, 127.88, 127.11, 127.02, 126.92, 126.86, 126.12, 93.89, 91.75, 68.26, 68.21, 67.93, 67.90, 67.80, 67.59, 67.33, 57.42, 55.27, 21.33; MS (EI, 70 eV): *m/z* (%): 550 (M^+, 19), 378 (100), 275 (17), 224 (27), 153 (70), 91 (84); $C_{31}H_{30}FeN_2O_2S$ (550.50): calcd C 67.64, H 5.49, N 5.09; found C 67.59, H 5.32, N 5.01.

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