Enantioselective Preparation of C_2-Symmetrical Ferrocenyl Ligands for Asymmetric Catalysis

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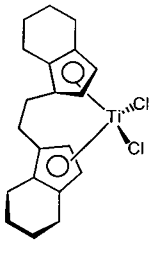
Abstract: Corey – Bakshi – Shibata (CBS) reduction of the 1,1′-diacylmetallocenes **5** and **7** provides the C_2-symmetrical diols **4** and **10**, which proved to be useful starting materials for stereocontrolled ligand synthesis. Diols **4** and **10** can be easily converted to a wide range of diamines, diphosphines, and dithioacetates by nucleophilic substitution of the hydroxyl function with full retention of configuration. Furthermore, the aminophosphines **30** and **31** become easily accessible. Compounds **30** and **31** have been used as ligands in enantioselective cross-coupling of racemic secondary Grignard reagents with vinyl bromides. A selectivity up to 93 % *ee* could be reached for the first time in the preparation of (*S*)-(*E*)-1,3-diphenyl-1-butene (**34b**), which was transformed into the enantiomerically pure chiral building block **37** with a pseudoasymmetric center in a straightforward, three-step synthesis.

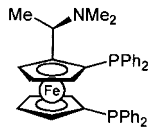
Keywords: asymmetric catalysis · chirality · enantioselective cross-coupling · sandwich complexes · reductions

Introduction

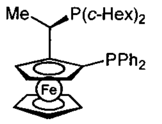
In the last two decades, stereoselective synthesis and, in particular, asymmetric catalysis have gained a great deal of attention.[1] A major role in this field has been taken over by transition metal complexes bearing chiral ligands. In particular, chiral cyclopentadienyl complexes of transition metals have found widespread applications as catalysts or ligands in enantioselective reactions.[2] The preparation of nearly all successful structures in this field, such as the *ansa*-metallocene **1** introduced by Brintzinger and the ferrocenyl diphosphine ligands **2** and **3** prepared by Hayashi and Togni, includes a resolution step.[3] In order to circumvent such cumbersome separations of enantiomers, which also limit the scope of the synthesis of these ligands, we envisioned the *stereocontrolled* preparation of chiral metallocenes that would open an easy access to new ligands for asymmetric catalysis.



1: (en)(thind)$_2$TiCl$_2$



2 : BPPFA



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Ferrocene derivatives have recently gained renewed interest for modern ligand design due to their promise for widespread applications both on a laboratory scale and in industry.[4] This interest is due to some exceptional features of ferrocene chemistry, which include the replacement of heteroatomic α-substituents with full retention of configuration and the possibility of diastereoselective directed metallations. The latter allows the introduction of additional functionality and an element of planar chirality into the ferrocenyl ligands.[4]

Herein we describe the synthesis of C_2-symmetrical[5] chiral ferrocenyl diols **4** and some of their derivatives, which lead to a broad range of new potential ligands. A first application in asymmetric catalysis is presented.

Results and Discussion

A retrosynthetic analysis applied to the diols **4** suggested the diketones **5** as precursors, which, in turn, are accessible by Friedel – Crafts acylation of ferrocene (disconnection A, Scheme 1) or by reaction of an appropriate organometallic reagent with ferrocenedicarbonyl dichloride (**6**; disconnection B).

Preparation of metallocenyl diketones: Acylation of ferrocene, one of the first reactions of a metallocene, has been

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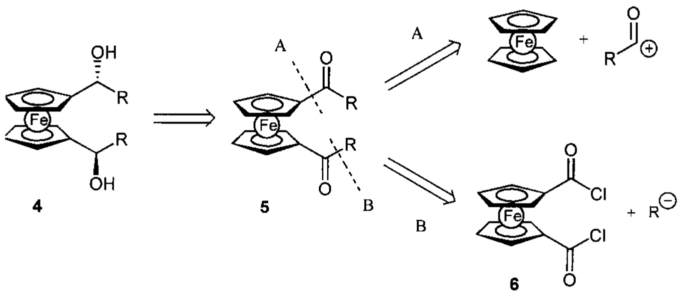
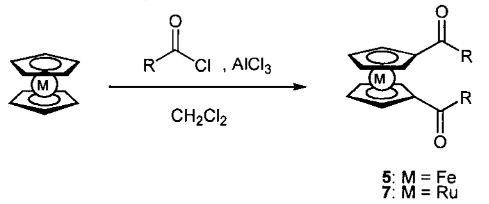


Scheme 1. Retrosynthetic analysis of the ferrocenyl diols **4**.

known since 1952.[6] The reaction can be controlled by a proper choice of the stoichiometry and the mode of addition to give either the mono- or diacylated products quite cleanly. Addition of ferrocene to a complex of $AlCl_3$ and an acid chloride (1:1 ratio, 2 equiv) in dichloromethane provides the 1,1′-diketones **5** in good yield. The reaction works equally well for alkyl and aryl substituents R. Several additional functionalities, like esters, ethers, and halogen atoms, are tolerated (Table 1, entries 1–14).

Table 1. Friedel-Crafts acylation of metallocenes.

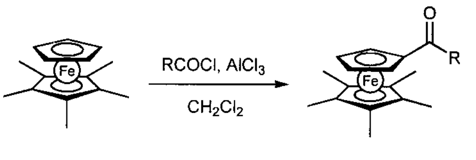


Entry	Diketone **5** or **7**	M	R	Yield [%]
1	**5a**	Fe	Me	85
2	**5b**	Fe	Me, Pent	85[a]
3	**5c**	Fe	Pent	92
4	**5d**	Fe	$(CH_2)_3Cl$	61
5	**5e**	Fe	$(CH_2)_2CO_2Me$	40
6	**5f**	Fe	*i*Pr	75
7	**5g**	Fe	*c*Hex	80
8	**5h**	Fe	*t*Bu	26
9	**5i**	Fe	Ph	82
10	**5j**	Fe	*o*-Tol	73
11	**5k**	Fe	p-$MeOC_6H_4$	64
12	**5l**	Fe	p-FC_6H_4	67
13	**5m**	Fe	1-naphthyl	72
14	**5n**	Fe	2-naphthyl	35
15	**7a**	Ru	Me	34
16	**7b**	Ru	Pent	47
17	**7c**	Ru	Ph	50

[a] Acetylferrocene was acylated with hexanoyl chloride.

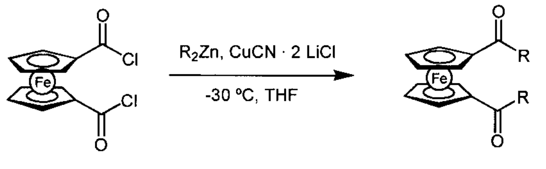
Non C_2-symmetrical diketones are obtained by sequential acylation with two different acid chlorides (entry 2). Ruthenocene is less reactive in Friedel–Crafts acylation[7] and only moderate yields of the diketones **7** could be obtained (entries 15–17). The reaction could also be extended to pentamethylferrocene for the first time, although the yield of the resulting ketones **8a,b** was again significantly lower than in the ferrocene case (Scheme 2).

An alternative to the Friedel–Crafts acylation was found in the reaction of (functionalized) zinc–copper reagents[8] with ferrocenedicarbonyl dichloride (**6**),[9] which also provides the diketones **5** in good yield (Scheme 3). This reaction should be useful if the required acid chlorides are unavailable or unstable.



8a: R = Me, 29 %
8b: R = Pent, 30 %

Scheme 2. Friedel–Crafts acylation of pentamethylferrocene.



5o: R = Et, 89 %
5p: R = $(CH_2)_3OPiv$, 80 %

Scheme 3. An alternative to Friedel–Crafts acylation: the reaction of zinc–copper reagents with **6** also provides diketones **5** in good yield.

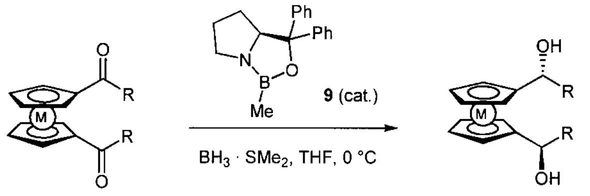
CBS reduction of metallocenyl ketones: For the asymmetric reduction of the metallocenyl ketones **5**, **7**, and **8**, the procedure developed by Corey and Itsuno was chosen because it had showed its broad utility during the last decade.[10] Previous attempts to reduce metallocenyl ketones enantioselectively were either restricted to monoacylated systems or led to diols with only poor optical purity.[11] Other methods for the enantioselective preparation of α-chiral ferrocenyl alcohols employed the addition of dialkylzincs to ferrocene aldehydes[12] or used a tedious enzymatic resolution.[13]

Our approach allows the easy preparation of nearly enantiomerically pure C_2-symmetrical ferrocenyl diols **4** contaminated with only small amounts of the *meso* diastereomers.[14] Thus, the reduction of 1,1′-diacetylferrocene (**5a**) can be performed with 60 mol% of the oxazaborolidine **9** and 2 equiv of $BH_3 \cdot SMe_2$ in THF at 0 °C (0.5 h) providing a nearly quantitative yield of the diol **4a** with a diastereomeric ratio *dl*:*meso* of 98.5:1.5. The optical purity found by chiral HPLC was >99% *ee* (Table 2, entry 1).

The situation changes only slightly for the reduction of the diketones **5** bearing higher alkyl chains. If R is ethyl or pentyl, a diastereoselectivity of ca. 88:12 is observed (entries 2 and 4). Ester- or chloro-functionalized alkyl chains do not disturb the reduction. The results with these substituents are even better than for the simple alkyl chains (entries 6–8).

A further increase in the steric bulk of R, for example, in an isopropyl or cyclohexyl group, leads to a decrease of the *dl*:*meso* ratio (85:15 and 80:20, respectively; entries 9 and 11). In such cases the result can be significantly improved by use of a stoichiometric amount (200 mol%) of the catalyst **9** (entries 5 and 10). Interestingly, even those diols that only show a diastereomeric excess of around 74% (*dl*:*meso* =

Table 2. CBS reduction of the diacetylmetallocenes **5** and **7** to yield the diols **4** and **10**.



5: M = Fe
7: M = Ru

4: M = Fe
10: M = Ru

Entry	R	**9** [mol %]	Diol **4** or **10**	Yield [%]	*dl*:*meso*	*ee* [%][a]
1	Me	60	**4a**	98	98.5 : 1.5	> 99
2	Et	60	**4b**	97	88 : 12	99.8
3	Me, Pent	60	**4c**	94	95 : 5	(> 99)
4	Pent	60	**4d**	98	87 : 13	99
5	Pent	200	**4d**	98	92 : 8	> 99
6	$(CH_2)_3Cl$	60	**4e**	91	94 : 6	(> 99)
7	$(CH_2)_3OPiv$	60	**4f**	82	89 : 11	> 99
8	$(CH_2)_2CO_2Me$	60	**4g**	84	95 : 5	(> 99)
9	*i*Pr	60	**4h**	91	85 : 15	98.9
10	*i*Pr	200	**4h**	91	94 : 6	> 99
11	*c*Hex	60	**4i**	98	80 : 20	97.6
12	*t*Bu	60	**4j**	99	51 : 49	–
13	Ph	60	**4k**	89	94 : 6[b]	(> 99)
14	*o*Tol	60	**4l**	94	95 : 5	(> 99)
15	*p*-MeO-C_6H_4	60	**4m**	58	92 : 8	(> 99)
16	*p*-F-C_6H_4	60	**4n**	94	90 : 10	(> 99)
17	1-naphthyl	60	**4o**	74	94 : 6	(> 99)
18	2-naphthyl	60	**4p**	80	86 : 14[c]	(99)
19	Me	60	**10a**	74	87 : 13	(99)
20	Pent	60	**10b**	87	85 : 15	(99)
21	Ph	60	**10c**	92	95 : 5	(> 99)

[a] Determined by chiral HPLC; values in parentheses are enantiomeric purities of derived products. [b] Repeated crystallization from MTBE gave *dl*:*meso* = > 98: < 2. [c] Single crystallization from THF gave *dl*:*meso* = 97:3.

87:13) were found to be nearly enantiomerically pure (> 99 % *ee*). This outcome is predicted by the Horeau principle, which is valid for the combination of two (or more) independent stereocenters in one molecule.[15] Thus, the assumption that the second reduction in the diketones **5** is not largely affected by the stereocenter already established seems to be justified.

If a quaternary center is attached to the carbonyl group (e.g., in diketone **5h**) the CBS reduction becomes very slow even at room temperature and is unselective (entry 12).

In summary, an increase in the steric demand of R leads to a lowering of the selectivity of the reduction (Figure 1).

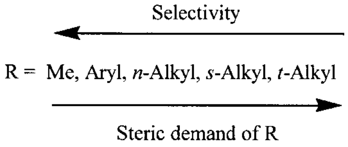


Figure 1. Selectivity vs. steric demand of substituent R in the reduction of metallocenyl diketones **5**.

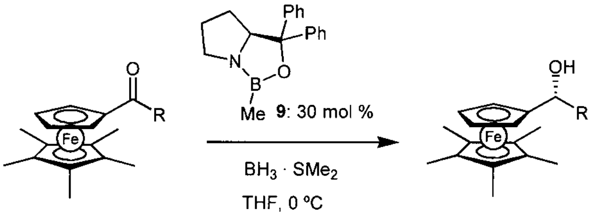
Beside the alkyl groups R discussed so far, various aryl moieties work equally well (entries 13–18). Even an *ortho* substituent in the aromatic ring is tolerated without loss of selectivity (entries 14 and 17).

The separation of the *meso* diastereomers from the desired C_2-symmetrical diols **4** is difficult and generally cannot be done by simple column chromatography. Recrystallization of alkyl-substituted diols **4** must be repeated quite often or is described to be ineffective.[16] We found that diols with aromatic substituents can be purified by recrystallization yielding nearly diastereomerically pure compounds (entries 13 and 18). In other cases, the *meso* diastereomer can be separated during later stages of ligand synthesis (see below and experimental procedure).

Thus, a wide variety of nearly enantiomerically pure diols **4** can be conveniently prepared from the corresponding diketones **5** by enantioselective reduction with good to excellent optical and chemical yields.

This statement also holds for the reduction of the analogous ruthenocenyl diketones **7** to the ruthenocenyl diols **9** (entries 18–20). Remarkably, the reduction of 1,1′-diacetylruthenocene (**7a**) is far less selective (*dl*:*meso* = 87:13) than that of 1,1′-diacetylferrocene (**5a**), which gives *dl*:*meso* = 98.5:1.5 (compare entries 1 and 18). On the other hand, for substituents like pentyl or phenyl no significant decrease is observed on changing the central metal from iron to ruthenium (compare entries 4 and 13 with 20 and 21).

Extension of the method to the heteroleptic ferrocenyl ketones **8a,b** was possible without problems and afforded the corresponding chiral alcohols **11a** and **11b** with > 95 % and 94 % *ee*, respectively (Scheme 4).



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11a: R = Me, 87 %, > 95 % *ee*
11b: R = Pent, 91 %, 94 % *ee*

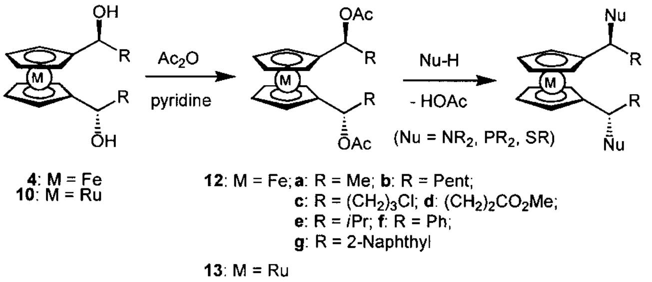
Scheme 4. Synthesis of chiral alcohols **11a** and **11b** from heteroleptic ferrocenyl ketones **8a,b.**

The newly accessible optically active α-chiral metallocenyl alcohols **4**, **10**, and **11** are the basis of the further transformations described below.

Formation of acetates and substitution by heteroatom nucleophiles: Since the pioneering work of Ugi in 1970 it is well documented that hydroxyl groups in α-position to a ferrocenyl moiety can be substituted with full retention of configuration by a broad range of heteroatom-centered nucleophiles.[17] We found that this reaction can be extended to 1,1′-disubstituted C_2-symmetrical systems.

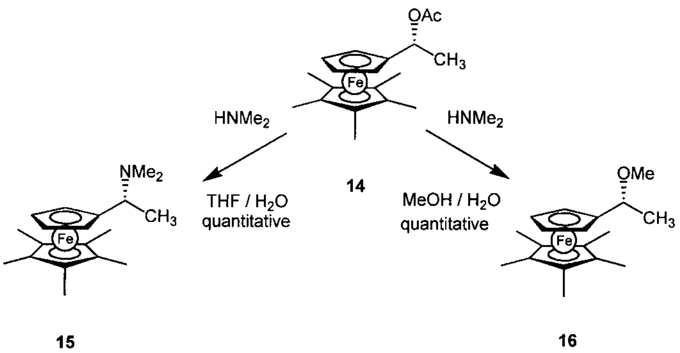
In a first step, the diols **4** and **10** are quantitatively converted to the corresponding diacetates **12** and **13** by treatment with acetic anhydride in pyridine. Removal of the volatiles in vacuum provides **12** and **13** as pure materials without the need for further purification. They can be used in the same reaction vessel for the reaction with the nucleophile. Only the sterically hindered, isopropyl-substituted diol **4h** needs more forcing conditions (Ac_2O, AcCl, DMAP, pyridine) for full conversion to the diacetate **12e**.

In the second step, substitution of the acetates is accomplished under mild solvolytic conditions using an excess of the nucleophile (Scheme 5).



Scheme 5. General reaction scheme for the two-step one-pot substitution of the hydroxyl funtions in C_2-symmetrical metallocenyl diols **4** and **10** with nucleophiles.

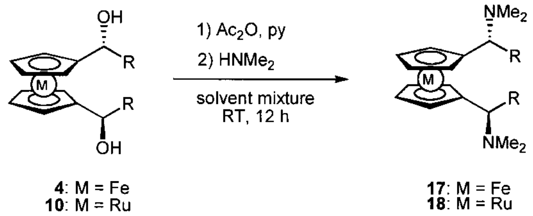
The solvent system THF/H_2O is appropriate for the more reactive aryl-substituted acetates, while alkyl-substituted acetates react only in a more polar mixture of methanol and water. The choice of the reaction medium is crucial, as can be seen from the reaction of acetate **14** with dimethylamine in THF/H_2O, which gives the desired amine **15** quantitatively.[18] When the reactive acetate **14** is treated with dimethylamine in $MeOH/H_2O$ only the undesired methoxy-substituted product **16** can be isolated (Scheme 6).



Scheme 6. Illustration of the strong influence of the reaction medium on the product of substitution reactions with ferrocenyl acetates.

Nevertheless, with a proper choice of solvent the reaction of all acetates with aqueous dimethylamine is clean and therefore suitable for determining the stereochemical course of the reaction by NMR analysis of the crude product (Table 3). Observation of only a slight change in the diastereomeric ratio on transformation of the diols **4** to the diamines **17** indicates that the substitutions proceed with >98% retention at one center (entries 1–4). This result is in accord with the reported value for a single substitution.[19] Also, no substantial loss of stereochemical information was detected during the conversion of the ruthenocenyl diol **10c** to the corresponding diamine **18** (entry 5).

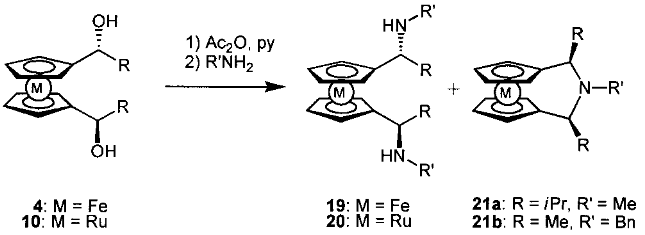
Table 3. Conversion of the metallocenyl diols **4** and **5** to the diamines **17** and **18** by double substitution.



Entry	Solvent	R	Amine **17**, **18**	Yield [%]	*dl*:*meso*	*dl*:*meso*	Retention [%][a]
1	$MeOH/H_2O$	Me	**17a**	91	98 : 2	98.5 : 1.5	>98
2	$MeOH/H_2O$	Pent	**17b**	90	89 : 11[b]	92 : 8	>98
3	THF/H_2O	Ph	**17c**	94	91 : 9	94 : 6	>98
4	THF/H_2O	2-naphthyl	**17d**	85	82 : 18[c]	86 : 14	>98
5	THF/H_2O	Ph	**18**	93	93 : 7	95 : 5	>97

[a] Calculated as retention at one stereogenic center. [b] Diastereomerically pure after chromatography. [c] The ratio *dl*:*meso* was 95:5 after recrystallization.

Table 4. Conversion of the metallocenyl diols **4** and **10** to the secondary diamines **19** and **20**.



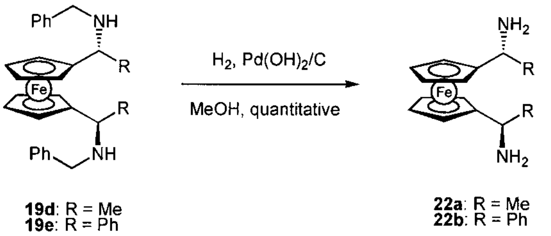
Entry	M	R	R′	Diamine **19** or **20**	Yield [%]	*dl* : *meso*[a]
1	Fe	Me	Me	**19a**	95[b]	>98 : 2
2	Fe	*i*Pr	Me	**19b**	20	>99 : 1
3	Fe	Ph	Me	**19c**	71	92 : 8
4	Ru	Ph	Me	**20**	64	95 : 5
5	Fe	Me	Bn	**19d**	78	>97 : 3
6	Fe	Ph	Bn	**19e**	86	>98 : 2
7	Fe	Me	Ph	**19f**	90	>98 : 2

[a] After chromatographic purification. [b] Yield of the crude diamine.

Primary amines react in the same manner with the diacetates **12** and **13** to yield the secondary diamines **19** and **20** (Table 4). The optically inactive cyclic amines **21** were identified in some cases as minor by-products. They may be formed by an internal S_N2-like attack of the amino function introduced in the first substitution on the remaining acetate. The stereochemical inversion in the intramolecular process causes symmetrization. Consequently, the *meso*-amines **21** are obtained. The reaction with methylamine (R′ = Me) is reliable for different substituents R (Table 4, entries 1, 3–4), although yields are moderate to low if steric hindrance becomes important (entry 2).

Other alkyl amines, like benzylamine (entries 5–6), are also suitable, as well as aniline (entry 7). In contrast to the tertiary diamines **17** and **18** the diastereomeric ratio of the crude secondary diamines **19** and **20** is often easily improved by simple column chromatography.

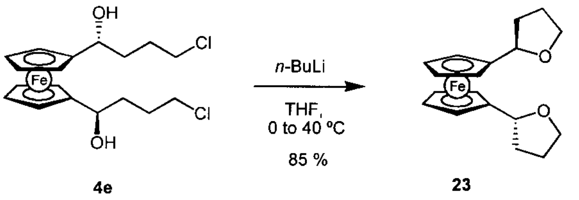
Debenzylation of the compounds **19d,e** affords the primary diamines **22a,b** in essentially quantitative yield (Scheme 7). Thus, chiral ferrocenyl diamines with all substitution patterns on nitrogen are now easily accessible.[20] Ligands with nitrogen donors attract considerable interest for transition metal



Scheme 7. Primary diamines **22a,b** are obtained in essentially quantitative yield from debenzylation of the compounds **19d,e**.

catalyzed reactions because they show several beneficial properties compared with those of the classical diphosphines, especially as far as synthesis is concerned.[21] For example, we found that the secondary diamines **19** and **20** are good ligands for the ruthenium-catalyzed transfer hydrogenation of ketones.[22]

As mentioned above, the CBS reduction of acylmetallocenes allows the facile preparation of metallocenyl diols with additional functionality. This can be used to synthesize new types of ferrocenyl ligands. Thus, the chloro-functionalized diol **4e** was cyclized to give the bis(tetrahydrofuranyl) derivative **23** by simple treatment with *n*BuLi in THF (Scheme 8). Ligand **23** may act as a chiral complexation agent for various kinds of metal centers.

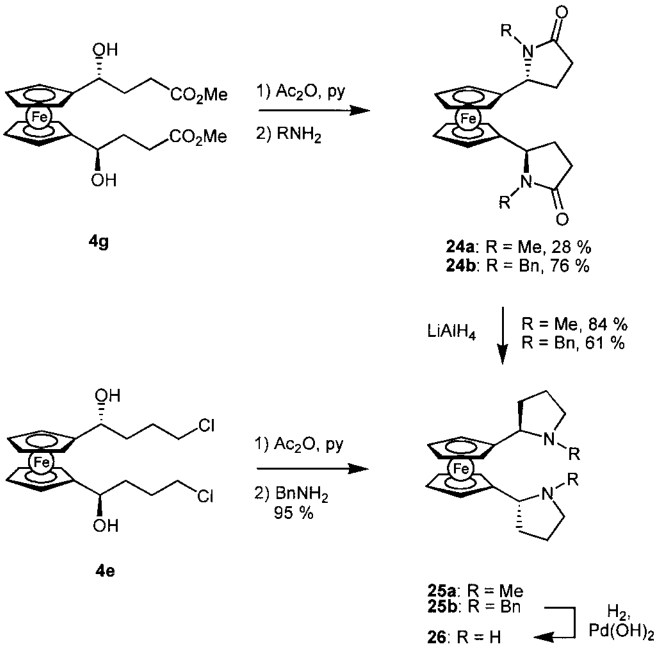


Scheme 8. Cyclization of diol **4e** to give the bis(tetrahydrofuranyl) derivative **23**.

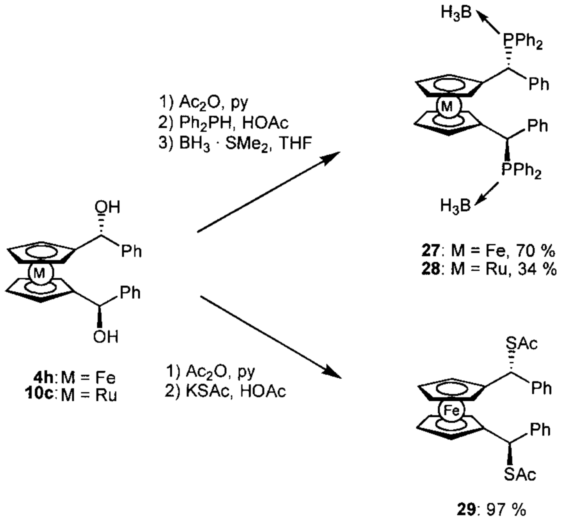
Aza-heterocycles are obtained directly when treating the acetates of the diols **4e** and **4g** with primary amines (Scheme 9). The ester-functionalized diol **4g** is transformed to the dipyrrolidinones **24** in variable yields, while the chloro-functionalized diol **4e** affords the dipyrrolidines **25**.

The dipyrrolidines **25** can also be obtained indirectly from the dipyrrolidinones **24** by $LiAlH_4$ reduction. Debenzylation of **25b** gives access to the N-unsubstituted dipyrrolidine **26** in nearly quantitative yield.

Phosphorous and sulfur nucleophiles: It has been shown by Hayashi and Togni that α-substitutions of ferrocenyl acetates by phosphorus and sulfur nucleophiles can be effected in acetic acid as reaction media.[23] We have investigated this reaction for the preparation of diphosphines and dithioacetates (Scheme 10). Thus, the diols **4h** and **10c** were acylated and allowed to react with an excess of diphenylphosphine in acetic acid at 50 °C for 3 h. The resulting diarylalkylphosphines are sensitive to oxygen and were therefore protected with borane after changing the solvent from acetic acid to THF. The borane-protected diphosphines **27** and **28** can be isolated very conveniently by standard workup and purification procedures.[24] After deprotection, **27** and **28** may be used as ligands for transition metal catalyzed hydrogenation.



Scheme 9. Synthesis of the ferocenyl pyrrolidinones **24** and pyrrolidines **25** and **26** from the diols **4g,e**.



Scheme 10. Substitution of metallocenyl diacetates by phosphorus and sulfur nucleophiles in acetic acid as reaction media leading to the diphosphines **27**–**28** and the dithioacetate **29**.

In the same way as the diphosphines, the dithioacetate **29** was obtained in nearly quantitative yield with KSAc as nucleophile. The dithioacetate **29** may serve as starting material for further ligand synthesis, for example, with respect to asymmetric copper-catalyzed reactions.

In conclusion, the diols **4** and **10** proved to be a rich source for one- or two-step synthesis of 1,1′-disubstituted α-chiral metallocenes bearing nitrogen, phosphorus, or sulfur donor atoms, which may serve as chiral ligands in a wide range of transition metal catalyzed reactions.

Conformational fixation of α-chiral metallocenes: Besides the facile substitution in the α-position there is a second very valuable reaction that is characteristic of ferrocenyl com-

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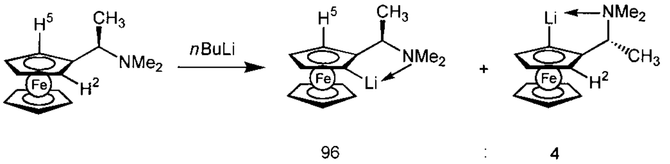
pounds: the directed diastereoselective *ortho*-metallation of α-(*N,N*-dimethylamino)alkylferrocenes. Ugi found that the protons H^2 and H^5 of (*R*)-α-(*N,N*-dimethylamino)ethylferrocene are abstracted by *n*BuLi with a selectivity of 96:4 (Scheme 11).[25]



Scheme 11. Ugi's abstraction of H^2 and H^5 of (*R*)-α-(*N,N*-dimethylamino)ethylferrocene.

In order to support the simple explanation that steric repulsion puts both the dimethylamino and the alkyl group above the ring plane and therefore adjusts the nitrogen as complexation site for *n*BuLi near to H^2, we performed an NOE experiment with the C_2-symmetrical diamine **17b** (Figure 2). Because the signals of the protons H^2 and H^5 were not sufficiently separated, they were distinguished by a ^{13}C edited NOE experiment.[26] The results confirm the picture drawn by Ugi with the modification that the alkyl chain seems to lie in or only slightly above the ring plane as indicated by the fact that the proton H^6 does not show an NOE with H^5 while strong interaction with H^2 is observed. This conclusion is in accord with a report by Butler, who performed similar measurements but had to use a somewhat perturbed model system to get the required signal separation.[27]

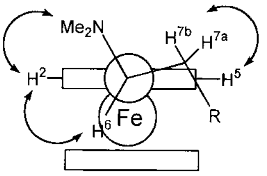
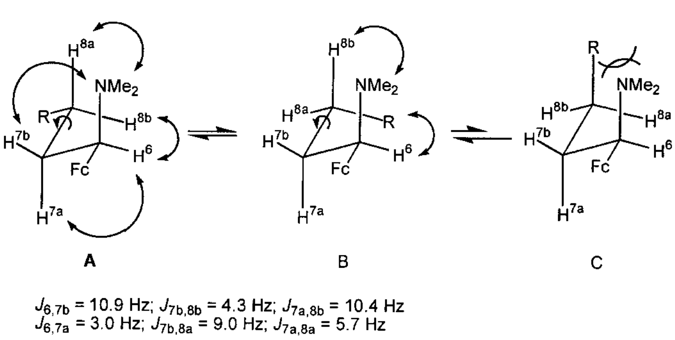


Figure 2. Preferred conformation of (*R*)-α-(*N,N*-dimethylamino)alkylferrocenes deduced from ^{13}C edited NOE measurements of diamine **17b** (R = Bu).

Conformational fixation of **17b** is not limited to the rotation about the C^1–C^6-bond but can also be seen for the C^6–C^7-bond. Only NOEs belonging to the set of rotamers shown in Scheme 12 were observed. The conformation depicted is supported by the values of the coupling constants of the methine proton H^6, which differ markedly and suggest a *trans*-relation between H^6 and H^{7b} ($^3J_{6,7b} = 10.9$ Hz). The preference for one rotamer is much smaller for the following C–C bond, which connects C^7 and C^8. NOEs must be assigned to two conformations (A and B) and more equilibrated ^3J coupling constants were observed. The third conformation C is avoided because of unfavorable *syn*-pentane interactions (Scheme 12).

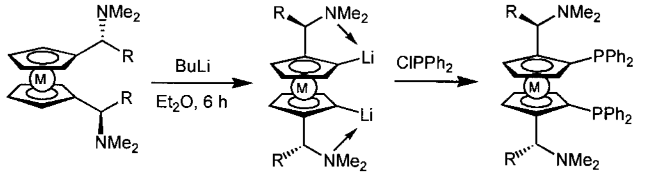


Scheme 12. Conformations of the C_6-C_7-C_8 region of the diamine **17b** (R = Bu).

In conclusion, the bulky ferrocenyl moiety together with a large α-substituent is a good anchor that is capable of fixing conformations in acyclic systems. Control over 2–3 bonds is reached and may be used to arrange functionalities along this region.

Double directed diastereoselective *ortho*-metallation: As mentioned above, the best known application of the stereochemical fixation of α-dimethylamino-substituted ferrocenes is the directed diastereoselective *ortho*-metallation. As a consequence, we tried to apply this reaction to the diamines **17** and **18**, which became easily available by the work described above. Thus, double deprotonation of the amines **17** could be effected by reaction with 3–5 equiv of *n*BuLi in diethyl ether for several hours at room temperature. In the case of the pentyl-substituted diamine **17b**, *t*BuLi was required to obtain efficient metallation. Reaction of the resulting dilithio-species with chlorodiphenylphosphine provides the C_2-symmetrical aminophosphine **30**, obtained in moderate yield as diastereomerically and nearly enantiomerically pure after chromatography (Table 5).[28]

Table 5. Conversion of the diamines **17** and **18** to the aminophosphines **30** and **31**.



17: M = Fe
18: M = Ru

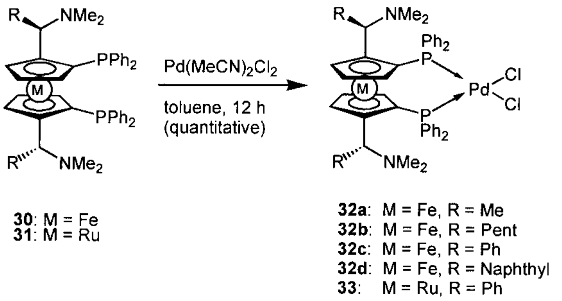
30: M = Fe
31: M = Ru

Entry	R	Base	Diphosphine **30** or **31**	Yield [%]	*ee* [%]
1	Me	*n*BuLi	**30a**	29	>98
2	Pent	*t*BuLi	**30b**	39	>98
3	Ph	*n*BuLi	**30c**	57	>98
4	2-naphthyl	*n*BuLi	**30d**	31	>98
5	Ph	*n*BuLi	**31**	43	>98

The major reason for the moderate yield is the formation of substantial amounts of the monophosphorylated diamines, although excess BuLi was always used for metallation.

The reaction sequence can also be applied to the ruthenocenyl diamine **18** to provide the diphosphines **31** with a larger bite angle compared with the structures **30**.[29]

Asymmetric cross-coupling: The aminophosphines **30** and **31** react quantitatively with a stoichiometric amount of $Pd(MeCN)_2Cl_2$ in toluene. However, only the phenyl-substituted ligand **30c** gave the expected C_2-symmetrical complex **32c** cleanly, as indicated by NMR analysis (Scheme 13). In all other cases, the reaction products turned out to be mixtures,

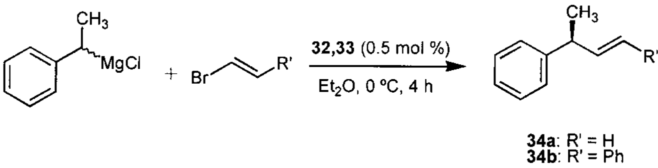


Scheme 13. Reaction of aminophosphines **30** and **31** with Pd(MeCN)$_2$Cl$_2$ in toluene; only **30c** gives the expected C_2-symmetrical complex **32c** cleanly.

which seem to be at least partially less symmetrical coordination isomers as previously observed in similar complexation reactions of other P,N-ligands.[30]

The palladium complexes **32** and **33** were found to catalyze the asymmetric cross-coupling of 1-phenylethylmagnesium chloride with vinyl bromide and β-bromostyrene under the standard conditions reported by Hayashi (Table 6).[31] In the reactions of vinyl bromide (R′ = H), the enantiomeric excess of the resulting 3-phenyl-1-butene (**34a**) was around 65 % and independent of the exact nature of the substituent R in the ligand (entries 1–4). This result was improved to 76 and 82 % *ee* by addition of two equivalents of zinc chloride and zinc iodide, respectively, to the Grignard reagent (entries 5 and 6).[32]

Table 6. Asymmetric cross-coupling of 1-phenylethylmagnesium chloride with vinyl bromide or β-bromostyrene catalyzed by the palladium complexes **32** and **33**.

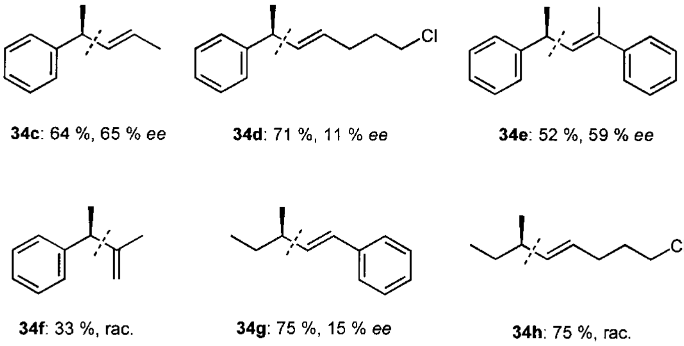


Entry	R′	Pd-complex 32 or 33	R	Yield [%]	*ee* [%]	Additive
1	H	**32b**	Pent	82	64	–
2	H	**32c**	Ph	81	63	–
3	H	**32d**	2-naphthyl	84	63	–
4	H	**33**	Ph	82	68	–
5	H	**32c**	Ph	88	76	$ZnCl_2$
6	H	**32c**	Ph	86	82	ZnI_2
7	Ph	**32a**	Me	73	68	–
8	Ph	**32b**	Pent	78	80	–
9	Ph	**32c**	Ph	89	93	–
10	Ph	**32c**	Ph	82	29	$ZnCl_2$

A different situation was found when cross-coupling was tried with β-bromostyrene. The optical purity of product **34b** increased significantly from 68 % to 80 % and 93 % *ee* on changing the substituent R in the ligand from methyl to pentyl and phenyl (entries 7–9). The last result compares well with the highest value of 73 % *ee* reported so far for this specific reaction.[33] Contrary to the coupling of vinyl bromide the addition of zinc chloride to the reaction mixture had a negative effect on the optical purity of **34b** (entry 10).

Hayashi has already reported the preparation and use of the aminophosphine **30a** and its palladium complex **32a** for asymmetric cross-coupling eight years ago.[34] However, since very tedious resolution and separation procedures were necessary to obtain the pure ligand, further development was strongly hampered. Our approach allows the facile construction of the aminophosphines **30** and **31**, avoiding the need to search for good resolution procedures for every new substituent R. Variations can now be done easily in a flexible and predictable manner. Optimization of the ligand structure in a short time becomes possible by a simple trial and error approach.

Attempted extension of the asymmetric cross-coupling to other vinyl bromides and the use of *s*BuMgCl as coupling reagent with the palladium complex **32c** were generally unsuccessful. Only the reaction of 1-phenylethylmagnesium chloride with 1-bromo-1-propene gave a satisfactory selectivity of 65 % *ee* (Scheme 14, compound **34c**).



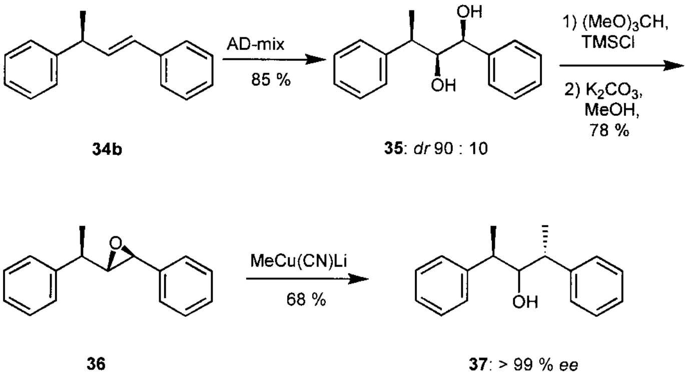
Scheme 14. Cross-coupling products **34c–h** obtained from the reaction of 1-phenylethylmagnesium chloride or *sec*-butylmagnesium chloride with different vinyl bromides and palladium complex **32c** as catalyst.

The use of a larger alkenyl bromide like (*E*)-1-bromo-5-chloro-1-pentene gave a product of low optical purity (**34d**). Introduction of a methyl group into the α-position of β-bromostyrene caused a drop in the selectivity from 93 to 59 % *ee* (**34e**), which was also accompanied by a reduced yield due to the formation of the homocoupling product of the vinyl bromide. A methyl group in a geminal position to the vinylic bromide, as found in 2-bromo-1-propene, causes a total loss of selectivity. Furthermore, the proton *trans* to the bromide makes this starting material sensitive to elimination of hydrobromic acid by the basic Grignard reagent, which explains the poor yield of 33 % (**34f**).

The exchange of 1-phenylethylmagnesium chloride for *sec*-butylmagnesium chloride resulted in the formation of virtually racemic products in all cases, although the yields were quite reasonable (compounds **34g,h**).

In conclusion, asymmetric cross-coupling of racemic Grignard reagents is still limited to very few good examples. Nevertheless our work now allows the preparation of (*S*)-(*E*)-1,3-diphenyl-1-butene (**34b**) with 93 % *ee* by this method.

With optically active **34b** in hand we sought an application in asymmetric synthesis that uses the double bond for further elaboration. Thus, **34b** can be stereoselectively dihydroxylated according to the Sharpless procedure in 85 % yield to provide the diol **35** as a 90:10 mixture of diastereomers.[35] A two-step, one-pot dehydration allows the isolation of the epoxide **36** in 78% yield.[36] This epoxide can be opened by MeCu(CN)Li in a regioselective and stereospecific manner to give the pseudo-C_2-symmetrical alcohol **37**.[37] This new chiral building block is obtained diastereomerically pure in 68% yield and >99% *ee* after chromatography (Scheme 15).



Scheme 15. Conversion of the cross-coupling product **34b** to the enantiomerically pure chiral building block **37**.

A combination of the newly introduced ligand **32c** for palladium catalyzed asymmetric cross-coupling and the now well established asymmetric dihydroxylation chemistry made it therefore possible to synthesize the chiral building block **37** as a single enantiomer that may find applications in the preparation of a new class of chiral ligands with pseudoasymmetric centers.

Conclusion

A highly flexible, efficient and enantioselective synthetic route to (nearly) enantiomerically pure C_2-symmetrical α-chiral metallocenyl diols **4** and **10** relying on the CBS reduction protocol was developed. The diols can be easily substituted with retention of configuration under very mild solvolytic conditions by various heteroatom-centered nucleophiles. A broad range of diamines (**17**–**20**, **22**) with all kinds of substitution patterns is accessible, along with some diphosphines (**27**, **28**) and the dithioacetate **29**.

These structures open the way to multiple uses as chiral ligands for transition metal catalyzed reactions. For an initial example, the diamines **17** and **18** were converted to the aminophosphines **30** and **31** by diastereoselective directed *ortho*-metallation and subsequent reaction with chlorodiphenylphosphine. The palladium complex of **30c** catalyzed the asymmetric cross-coupling of 1-phenylethylmagnesium chloride and β-bromostyrene providing (*S*)-1,3-diphenyl-1-butene (**34b**) with 93% *ee*. This cross-coupling product was converted to the enantiomerically pure (>99% *ee*) chiral building block **37** with a pseudoasymmetric center in a straightforward 3-step synthesis. Further applications of the new C_2-symmetrical ferrocenyl ligands are under investigation.

Experimental Section

General: Melting points are uncorrected. NMR spectra were recorded at room temperature in $CDCl_3$ on Bruker ARX200, AC300, AM400, or AMX500 instruments. Chemical shifts are given relative to the residual solvent peak (δ). Signals of the *meso* diastereomer that appear separated from the *dl* isomer are given for sake of comparison even in such cases in which the isolation of the pure *dl* isomer was possible. 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 Varian CH7A. Enantiomeric excesses were determined by HPLC. A Chiralcel OD column (Daicel Chemical Industries) was used at room temperature with *n*-heptane/2-propanol as mobile phase and detection by a diode array UV/Vis detector. Alternatively, determination of optical purity was carried out by GC on a Chirasil-DEX CB column (Chrompak) with hydrogen as carrier gas. Racemic compounds were used to choose the operating conditions for the resolution of the enantiomer and diastereomer peaks. Ether in workup procedures refers to *tert*-butyl methyl ether (MTBE). Organic layers were dried over anhydrous $MgSO_4$. Column chromatography was carried out on silica gel 60 (70–230 mesh ASTM).

Materials: THF was distilled from potassium, Et_2O was distilled from sodium, CH_2Cl_2 was distilled from CaH_2. Pyridine was dried over KOH. Commercial reagents were used without further purification. The following starting materials were prepared according to literature procedures: pentamethylferrocene,[38] ruthenocene,[39] acetylferrocene,[40] 1,1′-ferrocenedicarbonyl dichloride (**6**),[9] (*E*)-1-bromo-2-phenyl-1-propene,[41] and 1-phenylethylmagnesium chloride.[42] Lithium chloride was dried for 3 h at 140 °C in vacuum (0.7 mmHg). $Pd(OH)_2$ (10% on C) was dried for 3 d at 80 °C in vacuum. A 1M solution of $BH_3 \cdot SMe_2$ in THF was prepared from commercial $BH_3 \cdot SMe_2$ (10M) directly before use.

General procedure A for diacylmetallocenes 5 and 7 by Friedel–Crafts acylation: The acid chloride (22.5 mmol) was added to a suspension of aluminum(III) chloride (2.65 g, 20.0 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The metallocene (8.10 mmol) in CH_2Cl_2 (10 mL) was added dropwise within 20 min. The reaction was warmed to room temperature and stirred for 2 h. Hydrolysis was done 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.

1,1′-Diacetylferrocene (5a): From ferrocene (1.50 g, 8.10 mmol), acetyl chloride (1.6 mL, 22.5 mmol), and aluminum(III) chloride (2.65 g, 20.0 mmol) a yield of 85% (1.87 g) was obtained after chromatography (hexanes/MTBE 1:1). Brown-red solid; m.p. 122–124 °C; IR (KBr): $\tilde{\nu}_{max} = 3104$ (w), 3089 (w), 3074 (w), 1660 (vs), 1456 (s), 1375 (s), 1279 (s), 1116 (m), 844 (w); ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 4.73-4.72$ (m, 4H), 4.47–4.46 (m, 4H), 2.31 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 201.01$, 80.55, 73.49, 70.85, 27.54; MS (EI, 70 eV): *m*/*z* (%): 270 (M^+, 100), 255 (8), 227 (12), 199 (24), 163 (13), 121 (11); $C_{14}H_{14}FeO_2$ (270.11): calcd C 62.25, H 5.22; found C 62.42, H 5.29.

1-Acetyl-1′-hexanoylferrocene (5b): From acetylferrocene (0.75 g, 3.30 mmol), hexanoyl chloride (603 mg, 4.30 mmol) and aluminum(III) chloride (1.1 g, 8.3 mmol) a yield of 85% (924 mg) was obtained after chromatography (hexanes/MTBE 3:1). Deep red solid; m.p. 56–57 °C; IR (KBr): $\tilde{\nu}_{max} = 3091$ (w), 2952 (m), 2929 (m), 2869 (m), 1656 (vs), 1456 (s), 1373 (m), 1281 (m), 841 (m); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 4.63$ (t, $J = 1.8$ Hz, 2H), 4.61 (t, $J = 1.8$ Hz, 2H), 4.35–4.34 (m, 4H), 2.50 (t, $J = 7.5$ Hz, 2H), 2.21 (s, 3H), 1.57–1.51 (m, 2H), 1.24–1.19 (m, 4H), 0.79 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 203.07$, 200.58, 80.34, 80.30, 73.16, 73.05, 70.37, 39.55, 31.28, 27.27, 23.60, 22.23, 13.68; MS (EI, 70 eV): *m*/*z* (%): 326 (M^+, 100), 270 (15), 255 (14), 199 (21), 163 (6), 148 (3), 121 (19); $C_{18}H_{22}FeO_2$ (326.22): calcd C 66.27, H 6.80; found C 66.30, H 6.78.

1,1′-Dihexanoylferrocene (5c): From ferrocene (1.11 g, 6.00 mmol), hexanoyl chloride (2.7 g, 20.0 mmol) and aluminum(III) chloride (2.4 g, 18.0 mmol) a yield of 92% (2.12 g) was obtained after chromatography (hexanes/MTBE 8:1). Red solid; m.p. 44–45 °C; IR (KBr): $\tilde{\nu}_{max} = 3095$ (w), 2956 (m), 2928 (s), 2860 (w), 1679 (vs), 1463 (m), 1372 (w), 1258 (m), 1219 (m), 824 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 4.61-4.59$ (m, 4H), 4.32–4.30 (m, 4H), 2.49 (t, $J = 7.3$ Hz, 4H), 1.55–1.51 (m, 4H), 1.23–1.20 (m, 8H), 0.77 (t, $J = 6.0$ Hz, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): $\delta = 203.30$, 80.10, 73.00, 70.25, 39.50, 31.26, 23.62, 22.21, 13.64; MS (EI, 70 eV): *m*/*z* (%): 382 (M^+, 100), 326 (7), 311 (7), 186 (15), 121 (19); $C_{22}H_{30}FeO_2$ (382.33): calcd C 69.11, H 7.91; found C 69.11, H 8.06.

1,1′-Bis(δ-chlorobutanoyl)ferrocene (**5d**): From ferrocene (1.11 g, 6.00 mmol), 4-chlorobutanoyl chloride (2.8 g, 20.0 mmol), and aluminum(III) chloride (2.4 g, 18.0 mmol) a yield of 61 % (1.45 g) was obtained after chromatography (hexanes/MTBE 3:1). Red solid; m.p. 81 °C; IR (KBr): $\tilde{\nu}_{max} = 3099$ (w), 3083 (w), 2924 (m), 1663 (vs), 1459 (m), 1252 (m), 818 (m); ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 4.78$ (s, 4H), 4.49 (s, 4H), 3.66 (t, $J = 6.1$ Hz, 4H), 2.84 (t, $J = 6.8$ Hz, 4H), 2.14 (quin, $J = 6.2$ Hz, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz): $\delta = 202.12$, 79.97, 73.48, 70.51, 44.65, 36.14, 26.35; MS (EI, 70 eV): *m*/*z* (%): 396 (M^+, 94), 394 (M^+, 100), 358 (16), 183 (38), 92 (41); $C_{18}H_{20}Cl_2FeO_2$ (395.11): calcd C 54.72, H 5.10; found C 54.55, H 5.18.

1,1′-Bis(γ-carbomethoxypropanoyl)ferrocene (**5e**): From ferrocene (0.80 g, 4.30 mmol), 3-carbomethoxypropanoyl chloride (2.26 g, 15.0 mmol), and aluminum(III) chloride (6.0 g, 45.0 mmol) a yield of 40 % (0.71 g) was obtained after chromatography (hexanes/MTBE 1:1). Red solid; m.p. 100–101 °C; IR (film): $\tilde{\nu}_{max} = 3100$ (w), 3000 (w), 2960 (m), 2930 (w), 2860 (w), 1740 (vs), 1670 (vs), 1455 (m), 1370 (m), 1230 (s), 1085 (m), 845 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 4.74$ (t, $J = 1.8$ Hz, 4H), 4.45 (t, $J = 1.8$ Hz, 4H), 3.58 (s, 6H), 2.89 (t, $J = 6.4$ Hz, 4H), 2.56 (t, $J = 6.3$ Hz, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz): $\delta = 200.98$, 173.04, 79.46, 73.39, 70.35, 51.40, 34.05, 27.09; MS (EI, 70 eV): *m*/*z* (%): 414 (M^+, 100), 383 (5), 235 (22), 175 (24), 115 (20); $C_{20}H_{22}FeO_6$ (414.24): calcd C 57.99, H 5.35; found C 57.71, H 5.50.

1,1′-Bis(β-methylpropanoyl)ferrocene (**5f**): From ferrocene (1.10 g, 6.00 mmol), 2-methylpropanoyl chloride (1.70 g, 16.0 mmol), and aluminum(III) chloride (2.4 g, 18.0 mmol) a yield of 75 % (1.47 g) was obtained after chromatography (hexanes/MTBE 5:1). Red solid; m.p. 124 °C; IR (film): $\tilde{\nu}_{max} = 3100$ (w), 2965 (s), 2935 (m), 2875 (w), 1660 (vs), 1450 (s), 1380 (m), 1245 (s), 1050 (m), 835 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 4.70$–4.66 (m, 4H), 4.43–4.38 (m, 4H), 3.00–2.92 (m, 2H), 1.14–1.08 (m, 12H); ^{13}C NMR (CDCl$_3$, 75 MHz): $\delta = 207.54$, 79.07, 73.30, 70.48, 37.24, 19.14; MS (EI, 70 eV): *m*/*z* (%): 326 (M^+, 100), 283 (62), 213 (15), 185 (16), 121 (20); $C_{18}H_{22}FeO_2$ (326.22): calcd C 66.27, H 6.80; found C 65.96, H 6.88.

1,1′-Bis(cyclohexylcarbonyl)ferrocene (**5g**): From ferrocene (1.10 g, 6.00 mmol), cyclohexylcarbonyl chloride (2.40 g, 18.0 mmol), and aluminum(III) chloride (2.4 g, 18.0 mmol) a yield of 80 % (1.96 g) was obtained after chromatography (hexanes/MTBE 5:1). Red solid; m.p. 134–135 °C; IR (KBr): $\tilde{\nu}_{max} = 3134$ (w), 2930 (s), 2853 (m), 1663 (vs), 1449 (s), 1382 (w), 1265 (m), 1225 (m), 840 (w); ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 4.74$ (t, $J = 1.8$ Hz, 4H), 4.45 (t, $J = 1.8$ Hz, 4H), 2.76–2.65 (m, 2H), 1.85–1.25 (m, 20H); ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta = 207.00$, 79.38, 73.35, 70.51, 47.77, 29.53, 25.81; MS (EI, 70 eV): *m*/*z* (%): 406 (M^+, 100), 323 (5), 213 (4), 185 (7), 121 (12), 81 (5); $C_{24}H_{30}FeO_2$ (406.35): calcd C 70.94, H 7.44; found C 70.86, H 7.37.

1,1′-Dipivaloylferrocene (**5h**): From ferrocene (1.11 g, 6.00 mmol), pivaloyl chloride (2.10 g, 18.0 mmol), and aluminum(III) chloride (1.76 g, 18.0 mmol) a yield of 26 % (0.55 g) was obtained after chromatography (hexanes/MTBE 10:1). (A suspension of aluminum(III) chloride in CH$_2$Cl$_2$ was added dropwise to a solution of ferrocene and pivaloyl chloride). Red solid; m.p. 125–126 °C; IR (KBr): $\tilde{\nu}_{max} = 3112$ (w), 2954 (m), 2927 (m), 2869 (w), 1654 (vs), 1476 (m), 1438 (m), 1368 (m), 1287 (m), 1213 (m), 1070 (m), 874 (m); ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 4.84$ (t, $J = 1.8$ Hz, 4H), 4.41 (t, $J = 1.8$ Hz, 4H), 1.29 (s, 18H); ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta = 209.54$, 77.78, 73.46, 72.08, 44.36, 27.94; MS (EI, 70 eV): *m*/*z* (%): 354 (M^+, 100), 297 (45), 205 (27); $C_{20}H_{26}FeO_2$ (354.27): calcd C 67.81, H 7.40; found C 67.90, H 7.36.

1,1′-Dibenzoylferrocene (**5i**): From ferrocene (1.11 g, 6.00 mmol), benzoyl chloride (2.50 g, 17.8 mmol), and aluminum(III) chloride (2.4 g, 18 mmol) a yield of 82 % (1.95 g) was obtained after chromatography (hexanes/MTBE 3:1). Red solid; m.p. 97–100 °C; IR (KBr): $\tilde{\nu}_{max} = 3267$ (w), 3113 (w), 3064 (w), 1637 (vs), 1448 (s), 1288 (s), 1048 (m), 846 (m), 726 (s), 698 (s); ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 7.77$–7.72 (m, 4H), 7.50–7.38 (m, 6H), 4.88 (t, $J = 1.8$ Hz, 4H), 4.53 (t, $J = 1.8$ Hz, 4H); ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta = 197.71$, 138.94, 131.76, 128.18, 127.95, 79.36, 74.46, 72.95; MS (EI, 70 eV): *m*/*z* (%): 394 (M^+, 100), 289 (2), 225 (3), 77 (7); $C_{24}H_{18}FeO_2$ (394.25): calcd C 73.12, H 4.60; found C 72.86, H 4.83.

1,1′-Di(*o*-toluoyl)ferrocene (**5j**): From ferrocene (1.43 g, 7.70 mmol), *o*-toluoyl chloride (2.50 g, 16.2 mmol), and aluminum(III) chloride (2.25 g, 16.9 mmol) a yield of 73 % (2.36 g) was obtained after chromatography (hexanes/MTBE 3:1). Red solid; m.p. 124–125 °C; IR (KBr): $\tilde{\nu}_{max} = 3085$ (w), 2923 (w), 1647 (vs), 1443 (m), 1273 (s), 840 (m), 737 (s); ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 7.50$–7.24 (m, 8H), 4.84 (t, $J = 1.9$ Hz, 4H), 4.67 (t, $J = 1.9$ Hz, 4H), 2.34 (s, 6H); ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta = 200.78$, 138.92, 136.13, 131.14, 130.13, 127.71, 124.97, 80.49, 74.09, 72.44, 19.70; MS (EI, 70 eV): *m*/*z* (%): 422 (M^+, 100), 303 (16), 212 (9), 119 (18), 91 (63); $C_{26}H_{22}FeO_2$ (422.31): calcd C 73.95, H 5.25; found C 74.01, H 5.34.

1,1′-Bis(*p*-methoxybenzoyl)ferrocene (**5k**): From ferrocene (5.60 g, 30.0 mmol), *p*-methoxybenzoyl chloride (10.2 g, 60.0 mmol), and aluminum(III) chloride (8.4 g, 63.0 mmol) a yield of 64 % (8.75 g) was obtained after chromatography (hexanes/MTBE 4:1). Red solid; m.p. 130 °C; IR (KBr): $\tilde{\nu}_{max} = 3114$ (w), 2954 (w), 2840 (w), 1633 (s), 1615 (s), 1598 (vs), 1441 (s), 1292 (s), 1164 (s), 1029 (m), 844 (m), 770 (m); ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 7.83$–7.77 (m, 4H), 6.89–6.83 (m, 4H), 4.66 (t, $J = 1.9$ Hz, 4H), 4.52 (t, $J = 1.9$ Hz, 4H), 3.84 (s, 6H); ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta = 196.10$, 162.62, 131.63, 130.43, 113.41, 80.01, 74.13, 73.03, 55.34; MS (EI, 70 eV): *m*/*z* (%): 454 (M^+, 100), 319 (4), 255 (7), 135 (12); $C_{26}H_{22}FeO_4$ (454.31): calcd C 68.74, H 4.85; found C 68.74, H 4.88.

1,1′-Bis(*p*-fluorobenzoyl)ferrocene (**5l**): From ferrocene (1.86 g, 10.0 mmol), *p*-fluorobenzoyl chloride (3.57 g, 22.5 mmol), and aluminum(III) chloride (3.32 g, 25.0 mmol, 14 h reaction time) a yield of 67 % (2.90 g) was obtained after chromatography (hexanes/MTBE 3:1). Red solid; m.p. 127 °C; IR (KBr): $\tilde{\nu}_{max} = 3105$ (w), 3092 (w), 1639 (vs), 1630 (s), 1506 (s), 1290 (s), 855 (m), 770 (s); ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 7.82$–7.75 (m, 4H), 7.12–7.04 (m, 4H), 4.86 (t, $J = 1.9$ Hz, 4H), 4.57 (t, $J = 1.9$ Hz, 4H); ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta = 196.14$, 164.99 (d, $J = 253$ Hz), 135.13, 130.57 (d, $J = 9.1$ Hz), 115.38 (d, $J = 21.6$ Hz), 79.52, 74.37, 73.19; MS (EI, 70 eV): *m*/*z* (%): 430 (M^+, 100), 243 (12), 151 (19); $C_{24}H_{16}F_2FeO_2$ (430.23): calcd C 67.00, H 3.75; found C 66.85, H 4.04.

1,1′-Di(α-naphthoyl)ferrocene (**5m**): From ferrocene (1.86 g, 10.0 mmol), 1-naphthoyl chloride (4.36 g, 22.5 mmol), and aluminum(III) chloride (3.32 g, 25.0 mmol) a yield of 72 % (3.56 g) was obtained after chromatography (hexanes/MTBE 4:1). Red solid; m.p. 132 °C; IR (KBr): $\tilde{\nu}_{max} = 3086$ (w), 3046 (w), 1642 (vs), 1445 (m), 1285 (s), 786 (s); ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 8.01$–7.96 (m, 2H), 7.68–7.64 (m, 4H), 7.46–7.08 (m, 8H), 4.69 (m, 4H), 4.42–4.41 (m, 4H); ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta = 199.32$, 136.31, 133.36, 130.92, 129.84, 128.19, 126.86, 126.04, 125.93, 123.83, 80.71, 74.07, 72.46; MS (EI, 70 eV): *m*/*z* (%): 494 (M^+, 100), 339 (18), 273 (29), 183 (32), 127 (23); $C_{32}H_{22}FeO_2$ (494.37): calcd C 77.74, H 4.49; found C 77.65, H 4.64.

1,1′-Di(β-naphthoyl)ferrocene (**5n**): From ferrocene (1.86 g, 10.0 mmol), 2-naphthoyl chloride (4.20 g, 22.0 mmol), and aluminum(III) chloride (3.50 g, 26.0 mmol) a yield of 35 % (1.72 g) was obtained after chromatography (hexanes/MTBE/CH$_2$Cl$_2$ 4:1:1). Red solid; m.p. 183–184 °C; IR (KBr): $\tilde{\nu}_{max} = 3100$ (w), 3055 (w), 1642 (vs), 1447 (m), 1294 (s), 810 (m), 778 (s), 757 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta = 8.30$–8.29 (m, 2H), 7.84–7.73 (m, 8H), 7.58–7.51 (m, 4H), 4.99 (t, $J = 1.9$ Hz, 4H), 4.63 (t, $J = 1.9$ Hz, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz): $\delta = 197.54$, 136.23, 134.91, 132.25, 129.16, 128.97, 128.11, 127.84, 127.73, 126.65, 124.48, 79.86, 74.49, 73.29; MS (EI, 70 eV): *m*/*z* (%): 494 (M^+, 100), 183 (22), 155 (48), 127 (21), 84 (46), 73 (85), 49 (86); $C_{32}H_{22}FeO_2$ (494.37): calcd C 77.74, H 4.49; found C 77.48, H 4.48.

1,1′-Diacetylruthenocene (**7a**): From ruthenocene (0.75 g, 3.25 mmol), acetyl chloride (785 mg, 10.0 mmol), and aluminum(III) chloride (1.60 g, 12.0 mmol) a yield of 34 % (0.35 g) was obtained after chromatography (hexanes/ethyl acetate 1:2). Yellow solid; m.p. 136–142 °C; IR (KBr): $\tilde{\nu}_{max} = 3100$ (w), 2920 (m), 2851 (w), 1666 (vs), 1459 (m), 1447 (m), 1378 (m), 1279 (s), 1114 (s), 1040 (w), 828 (m); ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 5.07$ (t, $J = 1.5$ Hz, 4H), 4.77 (t, $J = 1.6$ Hz, 4H), 2.16 (s, 6H); ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta = 198.56$, 85.68, 74.97, 72.56, 26.68; MS (EI, 70 eV): *m*/*z* (%): 316 (M^+, 100), 301 (52), 245 (40), 167 (26), 43 (37); $C_{14}H_{14}O_2Ru$ (315.33): calcd C 53.36, H 4.47; found C 53.43, H 4.63.

1,1′-Dihexanoylruthenocene (**7b**): From ruthenocene (0.46 g, 2.00 mmol), hexanoyl chloride (538 mg, 4.00 mmol), and aluminum(III) chloride (1.06 g, 8.0 mmol) a yield of 34 % (0.35 g) was obtained after chromatography (hexanes/ethyl acetate 5:1). Yellow solid; m.p. 70 °C; IR (KBr): $\tilde{\nu}_{max} = 3103$ (w), 2953 (m), 2930 (s), 2860 (m), 1677 (vs), 1465 (m), 1260 (m), 1218 (m), 820 (s); ^{1}H NMR (CDCl$_3$, 200 MHz): $\delta = 5.06$ (t, $J = 1.8$ Hz, 4H), 4.73 (t, $J = 1.8$ Hz, 4H), 2.45 (t, $J = 7.4$ Hz, 4H), 1.70–1.45 (m, 4H), 1.35–1.15 (m, 8H), 0.87 (t, $J = 6.6$ Hz, 6H); ^{13}C NMR (CDCl$_3$, 50 MHz): $\delta = 201.45$, 85.30, 74.75, 72.18, 39.01, 31.49, 24.14, 22.44, 13.89; MS (EI, 70 eV): *m*/*z*

(%): 428 (M^+, 100), 372 (29), 357 (45), 329 (29), 231 (47), 97 (53), 69 (62), 55 (51), 43 (74); $C_{22}H_{30}O_2Ru$ (427.55): calcd C 61.80, H 5.19; found C 61.62, H 5.26.

1,1′-Dibenzoylruthenocene(7c): From ruthenocene (924 mg, 4.00 mmol), benzoyl chloride (1.30 g, 9.00 mmol), and aluminum(III) chloride (1.60 g, 12.0 mmol, 2 h at reflux) a yield of 50% (899 mg) was obtained after chromatography (hexanes/ethyl acetate 3:1). Yellow solid; m.p. 124–125 °C; IR (KBr): $\tilde{\nu}_{max} = 3092$ (w), 3063 (w), 1637 (vs), 1449 (m), 1372 (s), 1286 (s), 725 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.83 - 7.78$ (m, 4H), 7.49–7.35 (m, 6H), 5.20 (t, $J = 1.9$ Hz, 4H), 4.86 (t, $J = 1.8$ Hz, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 195.90$, 138.71, 128.35, 128.20, 84.08, 75.87, 74.90; MS (EI, 70 eV): m/z (%): 440 (M^+, 100), 363 (6), 335 (2), 306 (20), 105 (24), 77 (26); $C_{24}H_{18}O_2Ru$ (439.48): calcd C 65.59, H 4.13; found C 65.21, H 4.19.

1-Acetyl-1′-pentamethylferrocene (8a): From pentamethylferrocene (415 mg, 1.42 mmol), acetyl chloride (170 mg, 2.30 mmol), and aluminum(III) chloride (276 mg, 2.00 mmol) a yield of 29% (124 mg) was obtained after chromatography (hexanes/MTBE 3:1). A mixture of the acid chloride and aluminum(III) chloride was added to a solution of the metallocene within 1 h. Red solid; m.p. 99–100 °C; IR (KBr): $\tilde{\nu}_{max} = 3093$ (w), 3078 (w), 2953 (m), 2912 (s), 2855 (m), 1656 (vs), 1453 (s), 1378 (m), 1276 (s), 1111 (w), 1031 (m), 819 (m); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 4.22$ (t, $J = 1.9$ Hz, 2H), 4.01 (t, $J = 1.9$ Hz, 2H), 2.22 (s, 3H), 1.79 (s, 15H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 201.02$, 81.31, 80.85, 76.50, 72.00, 27.58, 10.45; MS (EI, 70 eV): m/z (%): 298 (M^+, 100), 255 (23), 133 (10), 121 (11); $C_{17}H_{22}FeO$ (298.21): calcd C 68.47, H 7.44; found C 68.66, H 7.68.

1-Hexanoyl-1′-pentamethylferrocene (8b): From pentamethylferrocene (350 mg, 1.10 mmol), hexanoyl chloride (206 mg, 1.53 mmol), and aluminum(III) chloride (256 mg, 1.92 mmol) a yield of 30% (119 mg) was obtained after chromatography (hexanes/MTBE 10:1). A mixture of the acid chloride and aluminum(III) chloride was added to a solution of the metallocene within 1 h. Red oil; IR (film): $\tilde{\nu}_{max} = 3080$ (w), 2920 (vs), 2870 (s), 1655 (vs), 1445 (s), 1375 (s), 1250 (m), 1065 (m), 1025 (m), 820 (m); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 4.23$ (t, $J = 1.9$ Hz, 2H), 3.99 (t, $J = 1.9$ Hz, 2H), 2.53 (t, $J = 7.8$ Hz, 2H), 1.79 (s, 15H), 1.73–1.54 (m, 2H), 1.36–1.30 (m, 4H), 0.91–0.87 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 203.55$, 81.33, 80.63, 76.17, 71.67, 40.08, 31.70, 24.20, 22.50, 13.90, 10.54; MS (EI, 70 eV): m/z (%): 354 (M^+, 100), 255 (14), 133 (9), 121 (8); $C_{21}H_{30}FeO$ (354.32): calcd C 71.19, H 8.53; found C 70.91, H 8.54.

General procedure B for diacyl ferrocenes 5 by zinc–copper reagent substitution of 1,1′-ferrocenedicarbonyl dichloride (6): Under argon copper(I) cyanide (262 mg, 2.92 mmol) and lithium chloride (248 mg, 5.85 mmol) were dissolved in THF (2.5 mL). At −78 °C the dialkylzinc reagent (3.00 mmol) was added dropwise. After the addition was finished the solution was warmed to 0 °C for 5 min and then cooled again to −78 °C. 1,1′-Ferrocenedicarbonyl dichloride (**6**, 303 mg, 0.98 mmol) in THF (3 mL) was added within 15 min. The reaction was warmed to −25 °C, stirred for 5 h, and then poured into saturated aqueous NH_4Cl (20 mL). After extraction with ether (4 × 50 mL) the combined organic layers were dried and concentrated to give an oil, which was purified by column chromatography.

1,1′-Dipropionylferrocene (5o): From 1,1′-ferrocenedicarbonyl dichloride (**6**, 303 mg, 0.98 mmol) and diethylzinc (370 mg, 3.00 mmol) a yield of 87% (259 mg) was obtained after chromatography (hexanes/MTBE 3:1). Red solid; m.p. 50–51 °C; IR (KBr): $\tilde{\nu}_{max} = 3096$ (w), 2934 (w), 1674 (vs), 1458 (s), 1242 (s), 1102 (m), 1048 (m), 807 (m); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 4.88 - 4.85$ (m, 4H), 4.59–4.56 (m, 4H), 2.84–2.71 (m, 4H), 1.34–1.23 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 203.68$, 79.90, 72.92, 70.17, 32.68, 7.82; MS (EI, 70 eV): m/z (%): 298 (M^+, 100), 269 (24), 213 (27), 186 (6), 121 (27); $C_{16}H_{18}FeO_2$ (298.16): calcd C 64.45, H 6.08; found C 64.25, H 6.05.

1,1′-Bis(δ-pivaloxybutanoyl)ferrocene (5p): From 1,1′-ferrocene dicarbonyldichloride (**6**, 435 mg, 1.40 mmol) and di(3-pivaloxypropyl)zinc (from 3-iodopropyl pivalate (1.62 g, 6.0 mmol) and diethylzinc (1 mL)) a yield of 80% (590 mg) was obtained after chromatography (hexanes/MTBE 2:1). Red oil; IR (KBr): $\tilde{\nu}_{max} = 3100$ (w), 2960 (s), 1720 (vs), 1670 (vs), 1455 (m), 1380 (w), 1280 (s); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 4.66$ (t, $J = 1.8$ Hz, 4H), 4.38 (t, $J = 1.9$ Hz, 4H), 4.07 (t, $J = 6.4$ Hz, 4H), 2.62 (t, $J = 7.2$ Hz, 4H), 1.92 (quin, $J = 6.8$ Hz, 4H), 1.10 (s, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 202.02$, 177.24, 79.99, 73.25, 70.38, 63.47, 38.59, 35.82, 27.08, 22.96; MS (EI, 70 eV): m/z (%): 526 (M^+, 93), 412 (78), 249 (91), 57 (100); $C_{28}H_{38}FeO_6$ (526.45): calcd C 63.88, H 7.28; found C 63.61, H 7.47.

General procedure C for the metallocenyl diols 4 and 10: Preparation of the oxazaborolidine 9: (*S*)-α,α-Diphenylprolinol (1.50 g, 6.00 mmol), methaneboronic acid (360 mg, 6.00 mmol), and toluene (25 mL) were heated to reflux for 5 h. Water was removed with the help of a Dean–Stark trap. The solvent was evaporated under vacuum to leave a solid, which was directly used in the next step.

CBS reduction of metallocenyl diketones 5 and 7: The oxazaborolidine **9** (330 mg, 1.20 mmol) was dissolved in THF (12 mL) and cooled to 0 °C under argon. From a syringe charged with $BH_3 \cdot SMe_2$ (1M in THF, 4 mL) 20% of the final amount (0.8 mL) was added to the catalyst solution. After 5 min stirring the remaining $BH_3 \cdot SMe_2$ and a solution of the diketone (2.00 mmol) in THF (5 mL) were added simultaneously within 20 min. The red color of the ketone turned to yellow on reduction. After 15 min at 0 °C the excess $BH_3 \cdot SMe_2$ was quenched by dropwise addition of methanol (2 mL; **caution**: gas evolution!). After the hydrolysis had ceased the mixture was poured into saturated aqueous NH_4Cl (150 mL) and extracted with ether (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 **4** and **10** were prepared by $LiAlH_4$ or $NaBH_4$ reduction of the diketones **5** and **7**. They contained comparable amounts of the *dl* and *meso* diastereomers.

(*R*,*R*)-1,1′-Bis(α-hydroxyethyl)ferrocene (4a): Diketone **5a** (540 mg, 2.00 mmol) was reduced with 60 mol% **9** and the crude product purified by chromatography (hexanes/MTBE 1:1). Yield: 535 mg (98%; *dl*:*meso* = 98.5:1.5, *ee* > 99%). Yellow solid; m.p. 70–72 °C; HPLC (OD, 5% *i*PrOH, 0.9 mL/min, 215 nm): t_R/min = 11.11 (*SS* and *RS*), 15.72 (*RR*). $[\alpha]_D = -97.7$ ($c = 2.34$, $CHCl_3$), −78.1 ($c = 2.84$, benzene (*dl*:*meso* 84:16)); IR (KBr): $\tilde{\nu}_{max} = 3301$ (s), 3103 (w), 3080 (w), 2970 (m), 1366 (m), 1094 (s), 1004 (s), 804 (m); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 5.15$ (s)/5.12 (s, 2H total), 4.64 (q, $J = 6.2$ Hz, *dl*)/4.60 (q, $J = 6.2$ Hz, *meso*, 2H total), 4.25–4.24 (m, *meso*)/4.16–4.15 (m)/4.14–4.13 (m)/4.12–4.11 (m, 8H total), 1.39 (d, $J = 6.6$ Hz, *meso*)/1.36 (d, $J = 6.6$ Hz, *dl*, 6H total); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 95.20$, 67.57, 67.48, 66.13, 65.92, 65.40, 25.56 (*dl*); 67.74, 67.32, 66.52, 65.50, 65.06, 25.16 (*meso*, separated signals); MS (EI, 70 eV): m/z (%): 274 (M^+, 12), 256 (100), 241 (8), 213 (13), 164 (53), 147 (16), 121 (15), 92 (23); $C_{14}H_{18}FeO_2$ (274.14): calcd C 61.34, H 6.62; found C 61.44, H 6.52.

(*R*,*R*)-1,1′-Bis(α-hydroxypropyl)ferrocene (4b): Diketone **5o** (75 mg, 0.25 mmol) was reduced with 60 mol% **9** and the crude product purified by chromatography (hexanes/MTBE 2:1). Yield: 73 mg (97%; *dl*:*meso* = 90:10, *ee* = 99.8%). Yellow oil; HPLC (OD, 5% *i*PrOH, 0.9 mL/min, 215 nm): t_R/min = 6.52 (*SS*), 7.28 (*RS*), 9.58 (*RR*); $[\alpha]_D = -92.4$ ($c = 1.31$, benzene). IR (film): $\tilde{\nu}_{max} = 3320$ (s), 3080 (w), 2930 (m), 2860 (m), 1460 (m), 1380 (m), 1030 (s), 810 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 5.04$ (s)/4.94 (s, 2H total), 4.43 (t, $J = 6.2$ Hz, *dl*)/4.32 (t, $J = 6.2$ Hz, *meso*, 2H total), 4.27–4.26 (m, *meso*)/4.22–4.21 (m, *dl*, 2H total), 4.15–4.10 (m, 6H), 1.74–1.48 (m, 4H), 0.93 (t, $J = 7.4$ Hz, *meso*)/0.87 (t, $J = 7.4$ Hz, *dl*, 6H total); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 93.45$, 71.29, 67.34, 67.31, 66.32, 66.30, 32.69, 9.79 (*dl*); 93.90, 70.49, 67.44, 67.24, 66.93, 65.41, 31.88, 10.02 (*meso*); MS (EI, 70 eV): m/z (%): 302 (M^+, 22), 284 (44), 266 (100), 255 (12), 226 (15), 178 (24), 160 (68), 91 (75); $C_{16}H_{22}FeO_2$ (302.20): calcd C 63.59, H 7.34; found C 63.43, H 7.41.

(*R*,*R*)-1-(α-Hydroxyethyl)-1′-(α-hydroxyhexyl)ferrocene (4c): Diketone **5b** (163 mg, 0.50 mmol) was reduced with 60 mol% of **9** and the crude product purified by chromatography (hexanes/MTBE 2:1). Yield: 155 mg (94%; (*RR*):(*RS*) = 90:10). Yellow oil; $[\alpha]_D = -47.1$ ($c = 2.07$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3330$ (vs), 3095 (w), 2935 (s), 2860 (s), 1400 (m), 1370 (m), 1100 (m), 1040 (m), 810 (m), 760 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 4.94$ (s, 2H), 4.67 (q, $J = 6.3$ Hz, *RR*)/4.60 (q, $J = 6.3$ Hz, *SR*, 1H total), 4.46 (t, $J = 6.5$ Hz, *RR*)/4.41 (t, $J = 6.4$ Hz, *SR*, 1H total), 4.26–4.12 (m, 8H), 1.64–1.17 (m, 8H), 1.42 (d, $J = 6.4$ Hz, *SR*)/1.37 (d, $J = 6.4$ Hz, *RR*, 3H total), 0.87–0.83 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 95.07$, 94.14, 69.78, 67.50, 67.41, 67.37, 67.30, 66.39, 66.12, 65.76, 65.69, 39.79, 31.75, 25.89, 25.27, 13.94 (*RR*); 95.22, 94.19, 69.48, 67.68, 67.22, 66.77, 66.05, 65.59, 65.34, 64.74, 39.50, 31.73, 24.77 (*SR*, separated signals); MS (EI, 70 eV): m/z (%): 330 (M^+, 91), 312 (35), 294 (5), 241 (10), 200 (91), 164 (51), 92 (100); $C_{18}H_{26}FeO_2$ (330.25): calcd C 65.47, H 7.94; found C 65.49, H 7.63.

(*R,R*)-1,1′-Bis(*α*-hydroxyhexyl)ferrocene (**4d**): Diketone **5c** (191 mg, 0.50 mmol) was reduced with 200 mol% **9** and the crude product purified by chromatography (hexanes/MTBE 4:1). Yield: 190 mg (98%; *dl*:*meso* = 91:9, *ee* >99%). Yellow oil; HPLC (OD, 2% *i*PrOH, 1.0 mL min^{-1}, 254 nm): t_R/min = 6.10 (*SS*), 7.40 (*RS*), 8.69 (*RR*); $[\alpha]_D = -29.6$ ($c = 2.30$, CHCl$_3$); IR (film): $\tilde{\nu}_{max}$ = 3320 (s), 3090 (w), 2920 (vs), 2860 (s), 1460 (m), 1400 (w), 1380 (w), 1115 (m), 1040 (s), 810 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.85–4.65 (s, 2H), 4.47 (t, J = 6.3 Hz, *dl*)/4.38 (dd, J = 7.3, 5.1 Hz, *meso*, 2H total), 4.27–4.26 (m, *meso*)/4.21–4.20 (m, *dl*, 2H total), 4.15–4.10 (m, 6H), 1.65–1.20 (m, 16H), 0.86 (t, J = 6.6 Hz, *meso*)/0.84 (t, J = 6.9 Hz, *dl*, 6H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 93.75, 69.87, 67.27, 67.18, 66.13, 65.97, 39.86, 31.04, 25.04, 22.38, 13.79 (*dl*); 94.12, 69.07, 67.12, 67.09, 66.71, 65.16, 39.04, 31.62, 25.25 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 386 (M^+, 42), 368 (77), 350 (55), 200 (100), 121 (21), 92 (68), 78 (31); $C_{22}H_{34}FeO_2$ (386.36): calcd C 68.39, H 8.87; found C 68.40, H 8.93.

(*R,R*)-1,1′-Bis(*α*-hydroxy-*δ*-chlorobutyl)ferrocene (**4e**): Diketone **5d** (934 mg, 2.36 mmol) was reduced with 60 mol% **9** and the crude product purified by chromatography (hexanes/MTBE 1:1). Yield: 861 mg (91%; *dl*:*meso* = 94:6). Yellow oil; $[\alpha]_D = -14.9$ ($c = 1.62$, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3414 (s), 3100 (w), 2953 (m), 1026 (s), 810 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.65 (s, 2H), 4.53 (t, J = 5.6 Hz, 2H), 4.19–4.15 (m, 8H), 3.50 (t, J = 6.0 Hz, 4H), 1.86–1.69 (m, 8H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 93.20, 69.38, 67.77, 66.43, 66.18, 45.01, 36.91, 28.56 (*dl*); 93.54, 68.83, 68.72, 66.92, 65.49, 36.22, 28.78 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 382 ([$M^+ - H_2O$], 72), 380 ([$M^+ - H_2O$], 100), 362 (31), 172 (19), 117 (30); $C_{18}H_{24}Cl_2FeO_2$ (399.14): calcd C 54.17, H 6.06; found C 54.30, H 6.17.

(*R,R*)-1,1′-Bis(*α*-hydroxy-*δ*-pivaloxybutyl)ferrocene (**4f**): Diketone **5p** (220 mg, 0.41 mmol) was reduced with 60 mol% **9** and the crude product purified by chromatography (hexanes/MTBE 3:1). Yield: 178 mg (82%; *dl*:*meso* = 89:11, *ee* > 99%). Yellow oil; HPLC (OD, 10% *i*PrOH, 0.9 mL min^{-1}, 215 nm): t_R/min = 7.70 (*SS*), 8.80 (*RR*), 9.86 (*RS*); $[\alpha]_D = -28.5$ ($c = 0.53$, benzene); IR (film): $\tilde{\nu}_{max}$ = 3360 (s), 3090 (w), 2960 (vs), 2880 (s), 1725 (vs), 1480 (m), 1400 (m), 1370 (w), 1290 (s), 1160 (vs), 1040 (m), 810 (w); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.67 (s, 2H), 4.47–4.46 (m, *dl*)/4.38–4.36 (m, *meso*, 2H total), 4.19–4.18 (m, *meso*)/4.14–4.13 (m)/4.10–4.09 (m)/4.06–4.04 (m, 8H total), 3.97–3.94 (m, 4H), 1.75–1.52 (m, 8H), 1.11 (s, *meso*)/1.10 (s, *dl*, 18H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 178.55, 93.54, 69.52, 67.70, 66.45, 66.14, 64.19, 38.69, 36.01, 27.04, 24.77 (*dl*); 93.90, 68.86, 67.83, 67.60, 66.90, 65.43, 35.35, 24.95 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 530 (M^+, 58), 512 (48), 494 (8), 428 (41), 190 (31), 57 (100); $C_{28}H_{42}FeO_6$ (530.48): calcd C 63.40, H 7.98; found C 63.62, H 7.93.

(*R,R*)-1,1′-Bis(*α*-hydroxy-*γ*-carbomethoxypropyl)ferrocene (**4g**): Diketone **5e** (207 mg, 0.50 mmol) was reduced with 60 mol% **9** and the crude product purified by chromatography (hexanes/MTBE 1:1). Yield: 176 mg (84%; *dl*:*meso* = 96:4). Yellow oil; $[\alpha]_D = -23.7$ ($c = 1.77$, CHCl$_3$); IR (film): $\tilde{\nu}_{max}$ = 3380 (s), 3100 (w), 2950 (s), 1730 (vs), 1440 (m), 1260 (s), 1165 (s), 1070 (s), 1020 (m), 810 (w); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.61 (s, 2H), 4.51 (t, J = 5.9 Hz, *dl*)/4.42 (dd, J = 7.0, 5.0 Hz, 2H total), 4.28 (s, *meso*)/4.15–4.14 (m)/4.12–4.10 (m)/4.09–4.07 (m, 8H total), 2.43–2.30 (m, 4H), 1.96–1.81 (m, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 174.35, 92.83, 69.00, 67.71, 67.61, 66.35, 66.18, 51.48, 34.19, 29.91 (*dl*); 93.19, 68.34, 67.78, 67.52, 66.69, 65.50, 33.67, 30.10 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 418 (M^+, 100), 400 (17), 386 (33), 369 (19), 354 (62), 235 (34), 164 (52), 105 (62); $C_{20}H_{26}FeO_6$ (418.27): calcd C 57.43, H 6.27; found C 57.53, H 6.30.

(*R,R*)-1,1′-Bis(*α*-hydroxy-*β*-methylpropyl)ferrocene (**4h**): Diketone **5f** (169 mg, 0.50 mmol) was reduced with 200 mol% **9** and the crude product purified by chromatography (hexanes/MTBE 3:1). Yield: 150 mg (91%; *dl*:*meso* = 94:6, *ee* > 99%). Yellow solid; m.p. 60–62 °C; HPLC (OD, 1% *i*PrOH, 1.0 mL min^{-1}, 254 nm): t_R/min = 7.49 (*SS*), 11.46 (*RS*), 12.55 (*RR*). $[\alpha]_D = -46.7$ ($c = 1.62$, CHCl$_3$), -85.0 ($c = 1.08$, benzene); IR (KBr): $\tilde{\nu}_{max}$ = 3240 (vs), 3090 (w), 2955 (vs), 2875 (s), 1460 (m), 1385 (m), 1365 (m), 1255 (m), 1040 (s), 810 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.28–4.07 (m, 12H), 1.78–1.65 (m, 2H), 0.88–0.76 (m, 12H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 91.52, 75.40, 67.26, 67.24, 67.13, 67.08, 35.67, 18.06, 18.03 (*dl*); 92.55, 74.60, 67.78, 67.29, 67.26, 65.63, 35.34, 18.36, 18.17 (*meso*); MS (EI, 70 eV): *m*/*z* (%): 330 (M^+, 100), 212 (7), 294 (5), 269 (24), 240 (14), 192 (28), 174 (57), 121 (15), 105 (62); $C_{18}H_{26}FeO_2$ (330.25): calcd C 65.47, H 7.94; found C 65.73, H 8.20.

(*R,R*)-1,1′-Bis(*α*-hydroxycyclohexylmethyl)ferrocene (**4i**): Diketone **5g** (203 mg, 0.50 mmol) was reduced with 60 mol% **9** and the crude product purified by chromatography (hexanes/MTBE 4:1). Yield: 205 mg (99%; *dl*:*meso* = 80:20, *ee* = 97.6%). Yellow solid; m.p. 100–104 °C; HPLC (OD, 1% *i*PrOH, 1.0 mL min^{-1}, 254 nm): t_R/min = 7.80 (*SS*), 8.82 (*RS*), 14.51 (*RR*); $[\alpha]_D = -18.2$ ($c = 2.30$, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3350 (s), 3090 (w), 2920 (s), 2855 (s), 1445 (m), 1400 (m), 1215 (s), 1040 (s), 1015 (s), 810 (m), 755 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.45 (s, 2H), 4.30–4.06 (m, 10H), 1.77–0.78 (m, 22H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 91.61, 74.66, 67.18, 67.12, 67.02, 66.97, 45.52, 28.83, 28.30, 26.35, 26.09, 26.04 (*dl*); 92.89, 73.82, 67.69, 67.33, 65.63, 45.22, 28.76 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 410 (M^+, 48), 392 (100), 374 (40), 326 (1), 309 (8), 280 (8), 227 (11), 212 (40), 121 (18), 83 (43); $C_{24}H_{34}FeO_2$ (410.38): calcd C 70.24, H 8.35; found C 70.11, H 8.60.

(*R,R*)-1,1′-Bis(*α*-hydroxy-*β*,*β*-dimethylpropyl)ferrocene (**4j**): Diketone **5g** (177 mg, 0.50 mmol) was reduced with 60 mol% **9** (18 h at room temperature) and purified by chromatography (hexanes/MTBE 4:1). Yield: 178 mg (99%; *dl*:*meso* = 51:49). Yellow solid; m.p. 110–114 °C; IR (KBr): $\tilde{\nu}_{max}$ = 3499 (s), 3094 (w), 2961 (s), 2865 (m), 1461 (m), 1363 (s), 1062 (s), 998 (m), 820 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.26 (s, *meso*)/4.19 (s, *dl*, 2H total), 4.15–4.00 (m, 8H), 3.20 (s)/2.65 (s, 2H total), 0.82 (s, 18H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 90.43, 78.56, 68.60, 67.58, 67.22, 67.02, 35.54, 25.75 (*dl*); 91.77, 77.87, 69.41, 67.51, 67.29, 65.99, 35.30, 25.89 (*meso*); MS (EI, 70 eV): *m*/*z* (%): 358 (M^+, 100), 283 (87), 214 (37), 119 (39); $C_{20}H_{30}FeO_2$ (358.30): calcd C 67.04, H 8.44; found C 67.02, H 8.78.

(*R,R*)-1,1′-Bis(*α*-hydroxyphenylmethyl)ferrocene (**4k**): Diketone **5i** (197 mg, 0.50 mmol) was reduced with 60 mol% **9** and the crude product purified by chromatography (hexanes/MTBE 3:1). Yield: 177 mg (89%; *dl*:*meso* = 94:6). Repeated crystallization from MTBE gave *dl*:*meso* = 98:2. Yellow solid; m.p. 130–132 °C; HPLC (OD, 5% *i*PrOH, 1.0 mL/min, 254 nm): t_R/min = 23.23 (*SS* and *RS*), 25.55 (*RR*). $[\alpha]_D = -75.1$ ($c = 0.05$, CHCl$_3$), -74.3 ($c = 0.97$, benzene); IR (KBr): $\tilde{\nu}_{max}$ = 3526 (vs), 3081 (w), 3026 (w), 1491 (m), 1452 (m), 1049 (m), 1017 (m), 828 (m), 721 (s), 699 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.35–7.20 (m, 10H), 5.42 (s, 4H), 4.43 (s)/4.27 (s, *meso*)/4.22 (s)/4.16 (s)/4.11 (s)/4.04 (s, *meso*, 8H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 144.19, 128.13, 127.19, 126.13, 93.45, 72.49, 67.98, 67.79, 66.67, 66.60 (*dl*); 143.73, 128.03, 93.94, 71.60, 68.13, 67.54, 67.10, 66.36 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 398 (M^+, 35), 380 (50), 226 (14), 154 (100); $C_{24}H_{22}FeO_2$ (398.28): calcd C 72.38, H 5.57; found C 72.32, H 5.68.

(*R,R*)-1,1′-Bis(*α*-hydroxy-*o*-tolylmethyl)ferrocene (**4l**): Diketone **5j** (580 mg, 1.37 mmol) was reduced with 60 mol% **9** and the crude product purified by chromatography (hexanes/MTBE 5:2). Yield: 551 mg (94%; *dl*:*meso* = 95:5). Yellow solid; m.p. 138 °C; $[\alpha]_D = -46.3$ ($c = 0.67$, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3270 (vs), 3077 (w), 2926 (w), 1043 (s), 820 (m), 738 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.49–7.46 (m, *meso*)/7.35–7.31 (m, *dl*, 2H total), 7.14–7.00 (m, 6H), 5.70 (s, *dl*)/5.60 (s, *meso*, 2H total), 5.27 (s, *meso*)/5.24 (s, 2H total), 4.32–4.31 (m, *dl*)/4.23–4.22 (m)/4.17–4.16 (m, *meso*)/4.10–4.09 (m, *dl*)/4.02–4.01 (m, *meso*, 8H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 142.04, 134.82, 130.08, 127.10, 126.23, 125.81, 93.42, 68.76, 67.91, 67.63, 67.55, 66.69, 19.06 (*dl*); 141.81, 134.69, 129.97, 127.04, 126.07, 93.54, 68.07, 67.99, 67.30, 18.95 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 426 (M^+, 51), 407 (6), 168 (100), 153 (29); $C_{26}H_{26}FeO_2$ (426.34): calcd C 73.25, H 6.15; found C 73.21, H 5.99.

(*R,R*)-1,1′-Bis(*α*-hydroxy-*p*-methoxyphenylmethyl)ferrocene (**4m**): Diketone **5k** (454 mg, 1.00 mmol) was reduced with 60 mol% **9** and the crude product purified by chromatography (hexanes/MTBE 3:1). Yield: 265 mg (58%; *dl*:*meso* = 92:8). Yellow solid; m.p. 108 °C; $[\alpha]_D = +22.4$ ($c = 0.41$, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3270 (vs), 3086 (w), 3000 (w), 2869 (w), 1610 (m), 1511 (s), 1251 (s), 1039 (s), 831 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.25–7.19 (m, 4H), 6.82–6.75 (m, 4H), 5.48–5.42 (m, 2H), 4.91 (s, 2H), 4.44–4.43 (m, *dl*)/4.30–4.29 (m, *meso*)/4.25–4.24 (m, *dl*)/4.18–4.17 (m, *meso*)/4.15–4.13 (m), 4.09–4.08 (m, *meso*, 8H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 158.86, 136.72, 127.42, 113.62, 93.69, 72.22, 68.06, 67.78, 66.70, 66.55, 55.18 (*dl*); 113.53, 71.40, 68.20, 67.06, 66.32 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 440 ([$M^+ - H_2O$], 100), 317 (24), 256 (47), 182 (15), 105 (19), 70 (25); $C_{26}H_{26}FeO_4$ (458.32): calcd C 68.14, H 5.72; found C 68.02, H 6.11.

(*R,R*)-1,1′-Bis(*α*-hydroxy-*p*-fluorophenylmethyl)ferrocene (**4n**): Diketone **5l** (500 mg, 1.16 mmol) was reduced with 60 mol% **9** and the crude product purified by chromatography (hexanes/MTBE 3:1). Yield: 475 mg (94%; *dl*:*meso* = 90:10). Yellow solid; m.p. 134 °C; $[\alpha]_D = -4.3$ ($c = 1.11$, CHCl$_3$);

IR (KBr): $\tilde{\nu}_{max}$ = 3285 (vs), 3081 (w), 2867 (w), 1602 (m), 1508 (s), 1219 (s), 1045 (m), 842 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.27–7.14 (m, 4H), 6.96–6.84 (m, 4H), 5.49–5.30 (m, 4H), 4.42–4.41 (m, *dl*)/4.26–4.25 (m)/4.22–4.19 (m, *meso*)/4.16–4.15 (m)/4.08–4.07 (m, *meso*, 8H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 162.02 (d, *J* = 246 Hz), 140.00 (d, *J* = 3.0 Hz), 127.73 (d, *J* = 8.1 Hz), 114.98 (d, *J* = 21.4 Hz), 93.30, 72.00, 68.27, 67.98, 66.58, 66.53 (*dl*); 139.48 (d, *J* = 3.0 Hz), 114.91 (d, *J* = 21.4 Hz), 93.84, 71.14, 68.40, 67.70, 67.09, 66.24 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 434 (M^+, 13), 416 (78), 401 (4), 244 (23), 172 (100), 152 (21); $C_{24}H_{20}F_2FeO_2$ (434.27): calcd C 66.38, H 4.64; found C 66.50, H 4.53.

(*R*,*R*)-1,1′-Bis(*α*-hydroxy-(1-naphthyl)methyl)ferrocene (**4o**): Diketone **5m** (499 mg, 1.01 mmol) was reduced with 60 mol % of **9** and the crude product purified by chromatography (hexanes/MTBE 3:1). Yield: 374 mg (74 %; *dl*:*meso* = 94:6). Yellow solid; m.p. 142 °C; $[\alpha]_D$ = +78.9 (*c* = 0.55, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3344 (vs), 3047 (w), 2923 (w), 1510 (m), 1393 (w), 1043 (m), 783 (vs); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.17–8.12 (m, 2H), 7.85–7.76 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.44–7.37 (m, 6H), 7.31 (t, *J* = 7.5 Hz, 2H), 6.20 (s, *dl*)/6.14 (s, *meso*, 2H total), 5.23 (s, 2H), 4.36–4.35 (m, *dl*)/4.27–4.26 (m, *dl*)/4.22–4.21 (m, *dl*)/4.15–4.14 (m, *meso*)/4.09–4.07 (m, *dl*), 3.98–3.97 (m, *meso*, 8H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 139.59, 133.65, 130.74, 128.56, 128.07, 125.88, 125.38, 125.24, 124.08, 123.73, 93.15, 69.17, 68.20, 67.76, 67.18 (*dl*); 139.31, 133.54, 127.93, 125.82, 125.35, 123.87, 93.42, 68.33, 67.90, 67.70, 67.53 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 498 (M^+, 4), 480 (46), 337 (20), 203 (100); $C_{32}H_{26}FeO_2$ (498.40): calcd C 77.12, H 5.26; found C 76.83, H 5.26.

(*R*,*R*)-1,1′-Bis(*α*-hydroxy-(2-naphthyl)methyl)ferrocene (**4p**): Diketone **5n** (996 mg, 2.00 mmol) was reduced with 60 mol % **9** and the crude product purified by chromatography (hexanes/THF 1:1) and crystallization from THF. Yield: 793 mg (80 %; *dl*:*meso* = 97:3). Yellow solid; m.p. 187–188 °C; $[\alpha]_D$ = +61.5 (*c* = 0.63, THF); IR (KBr): $\tilde{\nu}_{max}$ = 3380 (s), 3053 (w), 2863 (w), 1054 (m), 1017 (m), 786 (m), 751 (m); ^{1}H NMR ([D$_8$]THF, 300 MHz): δ = 7.76–7.64 (m, 8H), 7.49–7.43 (m, 2H), 7.32–7.28 (m, 4H), 5.65–5.64 (m, 2H), 5.61 (d, *J* = 2.5 Hz, *dl*)/5.56 (d, *J* = 3.1 Hz, *meso*, 2H total), 4.39 (m, *dl*)/4.26–4.25 (m, *meso*, 2H total), 4.16–4.11 (m)/4.03–3.96 (m, 6H total), 2.50 (s, 2H); ^{13}C NMR ([D$_8$]THF, 75 MHz): δ = 142.90, 133.03, 132.92, 127.30, 126.82, 125.09, 124.76, 124.35, 123.85, 94.06, 71.92, 67.26, 67.10, 66.40, 66.22 (*dl*); 142.61, 124.45, 123.97, 94.38, 71.21, 67.35, 66.91, 66.22 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 498 (M^+, 11), 494 (16), 480 (100), 276 (23), 204 (45); $C_{32}H_{26}FeO_2$ (498.40): calcd C 77.12, H 5.26; found C 76.90, H 5.44.

(*R*,*R*)-1,1′-Bis(*α*-hydroxyethyl)ruthenocene (**10a**): Diketone **7a** (126 mg, 0.40 mmol) was reduced with 60 mol % of **9** and the crude product purified by chromatography (hexanes/MTBE 1:1). Yield: 95 mg (74 %; *dl*:*meso* = 87:13). Pale yellow solid; m.p. 86–88 °C; $[\alpha]_D$ = −45.5 (*c* = 2.36, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3265 (vs), 3099 (w), 2970 (m), 1393 (w), 1364 (m), 1096 (s), 1021 (m), 807 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.66–4.65 (m, 2H), 4.60–4.58 (m, 2H), 4.50–4.49 (m, 4H), 4.42–4.34 (m, 2H), 3.45 (s, 2H), 1.34 (d, *J* = 6.3 Hz, *meso*)/1.33 (d, *J* = 6.3 Hz, *dl*, 6H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 99.91, 70.06, 70.00, 69.48, 68.73, 63.97, 24.45 (*dl*); 99.78, 70.15, 69.95, 69.55, 68.52, 64.35, 24.69 (*meso*); MS (EI, 70 eV): *m/z* (%): 320 (M^+, 83), 302 (33), 287 (31), 259 (100), 232 (30), 167 (29), 43 (93); $C_{14}H_{18}O_2Ru$ (319.37): calcd C 52.65, H 5.68; found C 52.65, H 5.80.

(*R*,*R*)-1,1′-Bis(*α*-hydroxyhexyl)ruthenocene (**10b**): Diketone **7b** (171 mg, 0.40 mmol) was reduced with 60 mol % **9** and the crude product purified by chromatography (hexanes/MTBE 3:1). Yield: 150 mg (87 %; *dl*:*meso* = 86:14, *ee* = 99 %). Pale yellow solid; m.p. 40–42 °C; HPLC (OD, 2.5 % *i*PrOH, 0.5 mL min^{-1}, 254 nm): t_R/min = 11.04 (*SS*), 11.46 (*RS*), 11.84 (*RR*). $[\alpha]_D$ = −53.0 (*c* = 2.37, CHCl$_3$); IR (film): $\tilde{\nu}_{max}$ = 3320 (s), 3095 (w), 2930 (vs), 2865 (s), 1710 (w), 1655 (w), 1465 (m), 1045 (s), 810 (m); ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 4.73–4.72 (m, *meso*)/4.71–4.70 (m, *meso*/4.69–4.68 (m, *dl*)/4.66–4.65 (m, *dl*, 4H total), 4.57–4.55 (m, 4H), 4.16–4.11 (m, 2H), 2.49 (s, 2H), 1.70–1.25 (m, 16H), 0.90 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (CDCl$_3$, 200 MHz): δ = 99.44, 70.38, 70.13, 69.89, 68.56, 68.32, 38.48, 31.72, 25.68, 22.56, 13.98 (*dl*); 70.41, 70.17, 69.91, 68.44, 68.21 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 432 (M^+, 32), 414 (24), 343 (33), 99 (100), 71 (48); $C_{22}H_{34}O_2Ru$ (431.58): calcd C 61.23, H 7.94; found C 61.22, H 8.20.

(*R*,*R*)-1,1′-Bis(*α*-hydroxyphenylmethyl)ruthenocene (**10c**): Diketone **7c** (1.47 g, 3.43 mmol) was reduced with 60 mol % of **9** and the crude product purified by chromatography (hexanes/MTBE 3:1). Yield: 1.36 g (92 %; *dl*:*meso* = 95:5). Pale yellow solid; m.p. 139–140 °C; $[\alpha]_D$ = −158.5 (*c* = 0.74, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3365 (vs), 3078 (w), 3022 (w), 2870 (w), 1489 (m), 1450 (m), 1409 (m), 1386 (m), 1038 (m), 819 (s), 716 (s), 699 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.37–7.25 (m, 10H), 5.30 (s, *dl*)/5.27 (s, *meso*, 2H, total), 4.75–4.72 (m) / 4.62–4.61 (m)/4.57–4.53 (m)/4.50–4.48 (m, *meso*, 8H total), 3.86 (s, *meso*)/3.76 (s, *dl*, 2H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 143.65, 128.47, 127.71, 126.43, 99.17, 71.32, 70.85, 70.77, 70.70, 70.08 (*dl*); 143.59, 128.44, 99.21, 71.11, 70.92 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 444 (M^+, 17), 426 (13), 409 (2), 321 (29), 105 (100); $C_{24}H_{22}O_2Ru$ (443.51): calcd C 65.00, H 5.00; found C 64.84, H 4.99.

(*R*)-1-(*α*-Hydroxyethyl)-1′-pentamethylferrocene (**11a**): Ketone **8a** (70 mg, 0.23 mmol) was reduced according to general procedure C with 30 mol % of **9** and the crude product was purified by chromatography (hexanes/MTBE 5:1). Yield: 60 mg (87 %; *ee* > 95 %). The enantiomeric excess was determined by addition of 4 mol % Eu(hfc)$_3$ to a ^{1}H NMR sample (CDCl$_3$, 500 MHz) and integration of separated diastereomeric signals at δ = 4.42 (s) and 4.38 (s). Yellow solid; m.p. 78–79 °C; $[\alpha]_D$ = −52.2 (*c* = 1.09, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3437 (vs), 3086 (w), 2969 (s), 2946 (s), 1455 (m), 1067 (s), 866 (m), 812 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.58–4.53 (m, 1H), 3.78 (s, 1H), 3.67 (s, 2H), 3.64 (s, 1H), 1.89 (s, 15H), 1.76–1.75 (m, 1H), 1.38 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 93.74, 80.14, 72.35, 72.12, 68.23, 67.67, 65.39, 34.07, 11.23; MS (EI, 70 eV): *m/z* (%): 300 (M^+, 100), 282 (14), 208 (49), 190 (98), 133 (21); $C_{17}H_{24}FeO$ (300.22): calcd C 68.01, H 8.06; found C 68.34, H 8.21.

(*R*)-1-(*α*-Hydroxyhexyl)-1′-pentamethylferrocene (**11b**): Ketone **8b** (90 mg, 0.25 mmol) was reduced according to general procedure C with 30 mol % **9** and the crude product purified by chromatography (hexanes/MTBE 10:1). Yield: 83 mg (91 %; *ee* = 95 %). The enantiomeric excess was determined by addition of 3 mol % Eu(hfc)$_3$ to a ^{1}H NMR sample and integration of separated diastereomeric signals at δ = 4.27 (s) and 4.14 (s). Yellow oil; $[\alpha]_D$ = −38.9 (*c* = 3.74, CHCl$_3$); IR (film): $\tilde{\nu}_{max}$ = 3440 (m), 3070 (w), 2920 (s), 2860 (s), 1460 (m), 1380 (m), 1035 (m), 815 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.31 (t, *J* = 5.6 Hz, 1H), 3.80–3.63 (m, 4H), 1.88 (s, 15H), 1.65–1.25 (m, 9H), 0.89 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 93.66, 80.18, 72.18, 72.06, 69.30, 66.87, 38.71, 31.83, 25.63, 22.59, 13.99, 11.20; MS (EI, 70 eV): *m/z* (%): 356 (M^+, 83), 338 (93), 208 (67), 190 (100), 174 (19), 133 (29); $C_{21}H_{32}FeO$ (356.33): calcd C 70.79, H 9.05; found C 70.83, H 9.10.

General procedure D for the acetates 12, 13, and 14: 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 in vacuum (0.7 mmHg, 5 h). The crude product was already > 95 % pure, as indicated by NMR analysis. The yield was quantitative. If desired the acetates can be further purified by rapid column chromatography on silica gel deactivated by addition of NEt$_3$ to the eluent. **Care** should be taken as the acetates **12**, **13**, and **14** are strong alkylating agents and therefore potentially carcinogenic.

(*R*,*R*)-1,1′-Bis(*α*-acetoxyethyl)ferrocene (**12a**): The diol **4a** (805 mg, 2.92 mmol) was treated with acetic anhydride (2 mL) and pyridine (5 mL) to give a quantitative yield of the diacetate **12a** (*dl*:*meso* = 98:2). Yellow solid; m.p. 57–58 °C; $[\alpha]_D$ = −58.5 (*c* = 1.41, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3104 (w), 3082 (w), 2997 (m), 2947 (w), 1729 (vs), 1369 (m), 1238 (vs), 1040 (s), 838 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 5.72 (q, *J* = 6.6 Hz, 2H), 4.17–4.14 (m, 2H), 4.10–4.08 (m, 2H), 4.06–4.04 (m, 4H), 1.95 (s, 6H), 1.46 (d, *J* = 6.6 Hz)/1.45 (d, *J* = 6.6 Hz, 6H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 169.86, 169.84, 88.50, 88.43, 68.80, 68.56, 68.46, 68.14, 68.11, 66.34, 66.32, 20.97, 20.04, 19.84 (signal set of the diastereomeric mixture); MS (EI, 70 eV): *m/z* (%): 358 (M^+, 12), 206 (8), 147 (7), 92 (100); $C_{18}H_{22}FeO_4$ (358.22): calcd C 60.35, H 6.19; found C 60.62, H 6.30.

(*R*,*R*)-1,1′-Bis(*α*-acetoxyhexyl)ferrocene (**12b**): The diol **4d** (270 mg, 0.69 mmol) was treated with acetic anhydride (1.5 mL) and pyridine (4 mL) to give a quantitative yield of the diacetate **12b**. Yellow oil; $[\alpha]_D$ = −20.6 (*c* = 1.90, CHCl$_3$); IR (film): $\tilde{\nu}_{max}$ = 3095 (w), 2956 (s), 2933 (vs), 2861 (s), 1737 (vs), 1468 (m), 1372 (s), 1243 (vs), 1014 (s), 829 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 5.70 (t, *J* = 6.5 Hz, 2H), 4.18–4.16 (m, 2H), 4.09–4.08 (m, 2H), 4.07–4.05 (m, 4H), 2.07 (s, 6H), 1.80–1.70 (m, 4H), 1.23 (s, 12H), 0.86 (t, *J* = 6.7 Hz, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 170.30, 88.72, 88.69, 71.75, 68.72, 68.42, 67.92, 67.85, 67.09, 67.02, 35.22, 35.17, 31.41, 25.22, 22.40, 21.07, 13.84 (signal set of the diastereomeric mixture); MS (EI, 70 eV): *m/z* (%): 470 (M^+, 15), 410 (3), 350 (17), 262 (42), 200

(8), 92 (100), 148 (18); $C_{26}H_{38}FeO_4$ (470.43): calcd C 66.38, H 8.14; found C 66.33, H 7.98.

(*R*,*R*)-1,1′-Bis(*α*-acetoxy-*δ*-chlorobutyl)ferrocene (12c): The diol **4d** (399 mg, 1.00 mmol) was treated with acetic anhydride (2 mL) and pyridine (4 mL) to give a quantitative yield of the diacetate **12c**. Yellow oil; $[\alpha]_D = -19.0$ ($c = 1.02$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3093$ (w), 2962 (w), 1737 (vs), 1372 (s), 1242 (s), 1025 (s) 832 (m); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 5.74$ (dd, $J = 8.7$, 3.9 Hz, 2 H), 4.20–4.19 (m, 2 H), 4.12–4.08 (m, 6 H), 3.59–3.49 (m, 4 H), 2.12–1.99 (m, 2 H), 2.06 (s, 6 H), 1.91–1.74 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 170.34$, 88.12, 70.86, 68.97, 68.72, 68.11, 67.07, 44.43, 32.27, 28.51, 21.07 (*dl*); 67.00 (*meso*, separated signal); MS (EI, 70 eV): *m*/*z* (%): 484 (M^+, 10), 482 (M^+, 15), 380 (33), 268 (31), 154 (100), 119 (35); $C_{22}H_{28}Cl_2FeO_4$ (483.22): calcd C 54.68, H 5.84; found C 54.60, H 5.77.

(*R*,*R*)-1,1′-Bis(*α*-acetoxy-*γ*-carbomethoxypropyl)ferrocene (12d): The diol **4g** (536 mg, 1.28 mmol) was treated with acetic anhydride (2 mL) and pyridine (4 mL) to give after chromatography (hexanes/MTBE 1:1, 1% NEt_3) the diacetate **12d**. Yield: 545 mg (85%). Yellow oil; $[\alpha]_D = -35.3$ ($c = 1.12$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3090$ (w), 2950 (m), 1730 (vs), 1440 (m), 1370 (s), 1240 (vs), 1020 (s), 835 (m); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 5.71$ (dd, $J = 9.0$, 3.5 Hz, 2 H), 4.19–4.18 (m, 2 H), 4.11–4.10 (m, 2 H), 4.09–4.08 (m, 4 H), 3.62 (s, 6 H), 2.31 (t, $J = 6.6$ Hz, 4 H), 2.26–2.11 (m, 2 H), 2.07–1.95 (m, 2 H), 2.02 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 173.08$, 170.22, 87.63, 70.76, 69.03, 68.76, 68.24, 66.92, 51.48, 29.99, 20.95; MS (EI, 70 eV): *m*/*z* (%): 502 (M^+, 33), 442 (19), 382 (76), 278 (60), 219 (43), 189 (43), 189 (18), 164 (100), 135 (22), 105 (63); $C_{24}H_{30}FeO_8$ (502.35): calcd C 57.38, H 6.02; found C 57.41, H 6.06.

(*R*,*R*)-1,1′-Bis(*α*-acetoxy-*β*-methylpropyl)ferrocene (12e): The diol **4h** was dissolved in pyridine (2 mL) and acetic anhydride (1 mL), acetyl chloride (0.3 mL), and DMAP (30 mg) were added at 0 °C. After stirring for 2 h at room temperature the reaction was poured into saturated aqueous $NaHCO_3$ (20 mL) and extracted into ether (40 mL). After washing with water (20 mL) and brine (20 mL) the organic layer was dried and evaporated to give an oil, which was purified by rapid column chromatography (hexanes/MTBE 3:1, 1% NEt_3). Yield: 202 mg (88%, *dl*:*meso* = 90:10). Yellow oil; $[\alpha]_D = +3.5$ ($c = 1.24$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3080$ (w), 2930 (s), 1720 (vs), 1440 (m), 1370 (s), 1240 (vs), 1020 (m), 820 (m); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 5.60$ (d, $J = 5.3$ Hz, *dl*)/5.58 (d, $J = 5.7$ Hz, *meso*, 2 H total), 4.06–4.00 (m, 8 H), 2.19 (s, *meso*)/2.16 (s, *dl*, 6 H total), 1.84–1.73 (m, 2 H), 0.77 (d, $J = 6.7$ Hz, 6 H), 0.76 (d, $J = 6.7$ Hz, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 170.07$, 87.67, 76.26, 68.73, 68.42, 68.21, 66.31, 34.19, 21.09, 18.24, 17.77 (*dl*); 170.25, 68.28, 68.07, 67.88, 66.74, 34.25, 18.13, 17.68 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 414 (M^+, 20), 354 (4), 294 (14), 234 (74), 120 (47), 105 (100); $C_{22}H_{30}FeO_4$ (414.32): calcd C 63.78, H 7.30; found C 63.48, H 7.20.

(*R*,*R*)-1,1′-Bis(*α*-acetoxyphenylmethyl)ferrocene (12f): The diol **4k** (143 mg, 0.36 mmol) was treated with acetic anhydride (1 mL) and pyridine (3 mL) to give a quantitative yield of the diacetate **12 f** (*dl*:*meso* = 93:7). Yellow oil; $[\alpha]_D = -30.0$ ($c = 1.81$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3089$ (w), 3066 (w), 3035 (m), 2937 (w), 1733 (vs), 1372 (s), 1241 (vs), 1019 (s), 830 (m), 731 (s), 700 (s); ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 7.30$–7.26 (m, 10 H), 6.59 (s, 2 H), 4.26–4.25 (m, *dl*)/4.18–4.17 (m, *meso*)/4.04–4.02 (m)/3.99–3.98 (m)/3.94–3.93 (m, *meso*)/3.86–3.85 (m, *dl*, 8 H total), 2.04 (s, *dl*)/2.03 (s, *meso*, 6 H total); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 169.75$, 139.82, 128.15, 127.93, 127.04, 88.32, 73.89, 69.21, 69.10, 68.43, 68.22, 21.12; MS (EI, 70 eV): *m*/*z* (%): 482 (M^+, 16), 364 (18), 269 (8), 208 (7), 154 (100); $C_{28}H_{26}FeO_4$ (482.36): calcd C 69.72, H 5.43; found C 69.67, H 5.72.

(*R*,*R*)-1,1′-Bis(*α*-acetoxy-(2-naphthyl)methyl)ferrocene (12g): The diol **4o** (867 mg, 1.74 mmol) was treated with acetic anhydride (3 mL) and pyridine (7 mL) to give a quantitative yield of the diacetate **12g** (*dl*:*meso* = 86:14). Yellow oil; $[\alpha]_D = -3.5$ ($c = 0.51$, $CHCl_3$); IR (KBr): $\tilde{\nu}_{max} = 3054$ (w), 2957 (w), 1732 (vs), 1373 (m), 1233 (vs), 1043 (m), 1021 (m), 788 (m), 761 (m); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.89$–7.87 (m, 8 H), 7.55–7.49 (m, 6 H), 6.96 (s, *meso*)/6.90 (s, *dl*, 2 H total), 4.48–4.47 (m, *dl*)/4.40–4.39 (m, *meso*, 2 H total), 4.21–4.13 (m)/4.02–4.01 (m, *dl*, 6 H), 2.18 (s)/2.16 (s, 6 H total); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 169.70$, 137.21, 132.88, 127.94, 127.52, 126.08, 124.85, 88.44, 74.07, 69.23, 69.16, 68.50, 68.41, 68.35, 21.08 (*dl*); 137.30, 132.91, 124.90, 88.54, 74.02, 21.05 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 582 (M^+, 1), 464 (18), 203 (81), 60 (62), 45 (100); $C_{36}H_{30}FeO_4$ (582.48): calcd C 74.23, H 5.22; found C 74.34, H 5.19.

(*R*,*R*)-1,1′-Bis(*α*-acetoxy-phenylmethyl)ruthenocene (13): The diol **10c** (1.45 g, 3.26 mmol) was treated with acetic anhydride (5 mL) and pyridine (12 mL) to give a quantitative yield of the diacetate **13** (*dl*:*meso* >96:4). Pale yellow solid; m.p. 113–114 °C; $[\alpha]_D = +77.6$ ($c = 0.88$, $CHCl_3$); IR (KBr): $\tilde{\nu}_{max} = 3067$ (w), 3030 (w), 2931 (w), 1737 (vs), 1368 (m), 1229 (vs), 1017 (m), 816 (m), 729 (m), 699 (m); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.36$–7.28 (m, 10 H), 6.47 (s, *dl*)/6.45 (s, *meso*, 2 H total), 4.70–4.69 (m, *dl*)/4.62–4.61 (m, *meso*)/4.43–4.42 (m)/4.38–4.37 (m)/4.30–4.29 (m, 8 H total), 2.09 (s, *dl*)/2.08 (s, *meso*, 6 H total); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 169.61$, 139.82, 127.97, 127.81, 126.93, 92.16, 73.44, 71.74, 71.63, 70.99 (*dl*); 139.73, 127.85, 126.99, 73.49, 71.83, 71.69, 71.53, 71.10 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 528 (M^+, 56), 469 (20), 425 (22), 374 (83), 315 (100), 255 (51), 105 (41), 43 (23); $C_{28}H_{26}O_4Ru$ (527.58): calcd C 63.75, H 4.97; found C 63.59, H 4.80.

(*R*)-1-(*α*-Acetoxyethyl)-1′-pentamethylferrocene (14): The alcohol **11a** (90 mg, 0.30 mmol) was treated with acetic anhydride (2 mL) and pyridine (2 mL) to give a quantitative yield of the acetate **14**. Yellow oil; $[\alpha]_D = -93.7$ ($c = 1.46$, $CHCl_3$); IR (KBr): $\tilde{\nu}_{max} = 3087$ (w), 2906 (s), 1733 (vs), 1372 (s), 1245 (s), 1023 (s), 814 (m); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 5.78$ (q, $J = 6.4$ Hz, 1 H), 3.76–3.75 (m, 1 H), 3.67–3.65 (m, 3 H), 1.87 (s, 15 H), 2.03 (s, 3 H), 1.49 (d, $J = 6.5$ Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 170.53$, 87.66, 80.37, 72.89, 71.99, 70.35, 68.71, 67.60, 21.48, 19.95, 11.12; MS (EI, 70 eV): *m*/*z* (%): 342 (M^+, 24), 300 (4), 282 (100), 250 (94), 190 (32), 133 (18); $C_{19}H_{26}FeO_2$ (342.26): calcd C 66.68, H 7.66; found C 67.04, H 7.53.

General procedure E for the reaction of metallocenyl acetates with amines in THF/H_2O or MeOH/H_2O: The metallocenyl acetate (1.23 mmol) was dissolved in MeOH (10 mL; THF (10 mL) was used for the more reactive aryl-substituted acetates and the derivatives of pentamethylferrocene). 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 mixture was poured into saturated aqueous NH_4Cl (50 mL) and extracted with ether (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.

(*R*)-1-(*α*-*N*,*N*-Dimethylaminoethyl)-1′-pentamethylferrocene (15): The acetate **14** (200 mg, 0.58 mmol) was treated with dimethylamine (40% in water, 1.5 mL) in THF/water. Chromatography (THF with 1% NEt_3) gave the amine **15** (180 mg, 95%). The enantiomeric excess could be estimated by comparison with a literature value of optical rotation[18] to be >96%. Yellow oil; $[\alpha]_D = -10.1$ ($c = 0.76$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3080$ (w), 2900 (vs), 2780 (w), 1450 (m), 1375 (m), 1030 (m), 810 (m); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 3.65$–3.57 (m, 5 H), 2.05 (s, 6 H), 1.86 (s, 15 H), 1.32 (d, $J = 6.8$ Hz, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 87.24$, 79.74, 72.42, 71.63, 71.21, 68.62, 57.22, 40.30, 13.76, 11.13; MS (EI, 70 eV): *m*/*z* (%): 327 (M^+, 69), 312 (51), 282 (100), 156 (21). The analytical data are in accord with those in the literature.[18]

(*R*)-1-(*α*-Methoxyethyl)-1′-pentamethylferrocene (16): The above reaction leading to **15** carried out in MeOH/water instead of THF/water gave the undesired methoxy derivative **16** in quantitative yield. Yellow oil; $[\alpha]_D = -17.25$ ($c = 1.31$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3087$ (w), 2970 (m), 2903 (s), 2817 (w), 1453 (m), 1380 (s), 1113 (s), 814 (m); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 4.15$ (q, $J = 5.9$ Hz, 1 H), 3.78 (s, 1 H), 3.72 (s, 3 H), 3.27 (s, 3 H), 1.80 (s, 15 H), 1.45 (d, $J = 6.2$ Hz, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 88.85$, 79.95, 73.97, 72.42, 71.75, 70.49, 67.55, 54.93, 19.15, 11.12; MS (EI, 70 eV): *m*/*z* (%): 314 (M^+, 85), 282 (33), 222 (20), 190 (100); $C_{18}H_{26}FeO$ (314.25): calcd C 68.80, H 8.34; found C 68.87, H 8.33.

(*R*,*R*)-1,1′-Bis(*α*-*N*,*N*-dimethylaminoethyl)ferrocene (17a): The diacetate **12a** (390 mg, 1.09 mmol) was treated with dimethylamine (40% in water, 2 mL) in MeOH/water. Chromatography (MTBE with 5% NEt_3) gave the diamine **17a** (325 mg, 91%, *dl*:*meso* = 98:2). Yellow oil; $[\alpha]_D = +28.7$ ($c = 0.63$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3080$ (w), 2940 (s), 2780 (m), 1450 (m), 1370 (m), 1040 (m), 825 (m); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 3.96$–3.94 (m, 8 H), 3.48 (q, $J = 6.9$ Hz, 2 H), 1.97 (s, 12 H), 1.34 (d, $J = 6.9$ Hz)/1.33 (d, $J = 6.8$ Hz, 6 H total); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 87.28$, 70.13, 68.28, 68.02, 66.90, 58.46, 40.55, 15.94 (*dl*); 87.41, 69.83, 68.08, 67.80, 67.17, 58.37, 40.50, 15.78 (*meso*); MS (EI, 70 eV): *m*/*z* (%): 328 (M^+, 39), 283 (79), 239 (100), 225 (36), 178 (32), 149 (39), 72 (56); $C_{18}H_{28}FeN_2$ (328.28): calcd C 65.86, H 8.60, N 8.53; found C 65.63, H 8.90, N 8.46.

(*R*,*R*)-1,1′-Bis(*α*-*N*,*N*-dimethylaminohexyl)ferrocene (**17b**): The diacetate **12b** (140 mg, 0.30 mmol) was treated with dimethylamine (40% in water, 2 mL) in MeOH/water. The crude product showed *dl*:*meso* = 89:11 by NMR analysis. Chromatography (hexanes/MTBE 3:1 with 5% NEt$_3$) gave the diastereomerically pure diamine **17b** (118 mg, 90%). Yellow oil; $[\alpha]_D$ = +24.2 (c = 3.15, CHCl$_3$); IR (film): $\tilde{\nu}_{max}$ = 3091 (w), 2956 (s), 2930 (vs), 2856 (s), 2821 (m), 2779 (m), 1457 (m), 1027 (m), 826 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 3.99–3.98 (m, 2H), 3.97–3.96 (m, 2H), 3.94–3.93 (m, 4H), 3.29 (dd, J = 10.8, 3.1 Hz, 2H), 1.95 (s, 12H), 1.94–1.82 (m, 2H), 1.77–1.51 (m, 4H), 1.47–1.27 (m, 10H), 0.91 (t, J = 6.7 Hz, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 85.67, 70.00, 68.03, 67.77, 67.59, 63.04, 40.48, 32.21, 31.43, 27.19, 22.75, 14.15 (*dl*); 85.82, 69.87, 67.82, 67.65, 67.51, 31.47 (*meso*, separated signals); MS (EI, 70 eV): m/z (%): 440 (M^+, 21), 395 (25), 369 (22), 352 (27), 324 (22), 281 (56), 178 (38), 149 (100), 135 (24); $C_{26}H_{44}FeN_2$ (440.49): calcd C 70.89, H 10.07, N 6.36; found C 70.68, H 10.09, N 6.40.

(*R*,*R*)-1,1′-Bis(*α*-*N*,*N*-dimethylaminophenylmethyl)ferrocene (**17c**): The diacetate **12e** (265 mg, 0.55 mmol) was treated with dimethylamine (40% in water, 2 mL) in THF/water. Chromatography (hexanes/MTBE 3:1 with 1% NEt$_3$) gave the diamine **17c** (234 mg, 94%, *dl*:*meso* = 91:9). Yellow solid; m.p. 49–50 °C; $[\alpha]_D$ = +103.5 (c = 2.40, CHCl$_3$); IR (film): $\tilde{\nu}_{max}$ = 3060 (w), 3030 (w), 2950 (m), 2860 (w), 2810 (w), 2770 (s), 1455 (s), 1300 (m), 1005 (s), 830 (m), 740 (s), 700 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.41–7.26 (m, 10H), 3.89–3.88 (m, *meso*)/3.87–3.86 (m, *dl*, 2H total), 3.58 (s, *dl*)/3.57–3.54 (m)/3.50–3.46 (m)/3.43 (s, *meso*, 8H total), 1.97 (s, *dl*)/1.94 (s, *meso*, 12H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 143.24, 128.23, 127.83, 126.85, 90.26, 72.23, 71.22, 69.95, 67.58, 67.52, 44.38 (*dl*); 143.43, 128.35, 127.87, 126.89, 71.97, 71.67, 69.14, 67.70, 67.08, 44.27 (*meso*, separated signals); MS (EI, 70 eV): m/z (%): 452 (M^+, 33), 407 (13), 365 (100), 211 (55); $C_{28}H_{32}FeN_2$ (452.42): calcd C 74.33, H 7.13, N 6.19; found C 74.23, H 7.10, N 6.05.

(*R*,*R*)-1,1′-Bis(*α*-*N*,*N*-dimethylamino(2-naphthyl)methyl)ferrocene (**17d**): The diacetate **12g** (3.07 g, 5.28 mmol) was treated with dimethylamine (40% in water, 10 mL) in THF/water. Chromatography (hexanes/MTBE 3:1 with 1% NEt$_3$) gave the diamine **17d** (2.48 g, 85%, *dl*:*meso* = 82:18). One recrystallization from hexanes/ether gave *dl*:*meso* = 95:5. Yellow solid; m.p. 141–142 °C; $[\alpha]_D$ = −47.1 (c = 0.47, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3058 (w), 2979 (w), 2944 (w), 2810 (m), 2762 (s), 1296 (m), 1011 (s), 828 (s), 762 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.95–7.41 (m, 14H), 3.96–3.95 (m, 2H), 3.75 (s, *dl*)/3.59 (s)/3.56 (s, *meso*)/3.52 (s, *meso*)/3.50 (s, *meso*)/3.42 (s, *dl*, 8H total), 2.00 (s, *dl*)/1.92 (s, *meso*, 12H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 140.74, 133.16, 132.70, 127.90, 127.67, 127.50, 126.78, 126.65, 125.90, 125.52, 90.37, 72.23, 70.98, 70.06, 68.10, 67.67, 44.52 (*dl*); 140.92, 133.26, 132.81, 127.05, 126.97, 126.00, 90.18, 71.89, 69.03, 67.17, 44.32 (*meso*, separated signals); MS (EI, 70 eV): m/z (%): 552 (M^+, 31), 507 (21), 465 (100), 261 (78), 232 (41), 203 (32), 184 (28); $C_{36}H_{36}FeN_2$ (552.54): calcd C 78.26, H 6.57, N 5.07; found C 77.98, H 6.86, N 4.87.

(*R*,*R*)-1,1′-Bis(*α*-*N*,*N*-dimethylaminophenylmethyl)ruthenocene (**18**): The diacetate **13** (0.60 g, 1.14 mmol) was treated with dimethylamine (40% in water, 5 mL) in THF/water. Chromatography (hexanes/MTBE 3:1 with 1% NEt$_3$) gave the diamine **18** (526 mg, 93%, *dl*:*meso* = 93:7). Pale yellow solid; m.p. 141–142 °C; $[\alpha]_D$ = +10.0 (c = 0.24, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3080 (w), 2939 (w), 2771 (m), 1450 (m), 1007 (m), 814 (m), 724 (s), 701 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.25–7.12 (m, 10H), 4.25–4.24 (m)/3.90–3.89 (m, *meso*)/3.87–3.86 (m, *dl*)/3.81–3.79 (m, 8H total), 3.32 (s, *dl*)/3.19 (s, *meso*, 2H total), 2.00 (s, *dl*)/1.99 (s, *meso*, 12H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 145.05, 127.86, 127.71, 126.71, 95.35, 74.18, 72.48, 72.27, 70.54, 70.18, 45.06 (*dl*); 145.17, 127.99, 126.73, 95.31, 74.55, 72.05, 71.72, 70.81, 69.73, 44.97 (*meso*, separated signals); MS (EI, 70 eV): m/z (%): 453 ([$M^+ - NMe_2$], 20), 410 (100), 319 (7), 257 (9), 205 (11), 166 (21), 134 (32); $C_{28}H_{32}N_2Ru$ (497.64): calcd C 67.58, H 6.48, N 5.63; found C 67.23, H 6.70, N 5.33.

(*R*,*R*)-1,1′-Bis(*α*-*N*-methylaminoethyl)ferrocene (**19a**): The diacetate **12a** (440 mg, 1.23 mmol) was treated with methylamine (40% in water, 3 mL) in MeOH/water. The crude diamine **19a** (390 mg, 90% pure (95%), *dl*:*meso* = 97:3) could not be purified further. Yellow oil; $[\alpha]_D$ = −5.7 (c = 1.73, CHCl$_3$); IR (film): $\tilde{\nu}_{max}$ = 3260 (m), 3080 (w), 2930 (s), 2790 (m), 1440 (m), 1370 (w), 1310 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 3.95 (t, J = 1.8 Hz, 4H), 3.90 (t, J = 1.8 Hz, 4H), 3.25 (q, J = 6.5 Hz, 2H), 2.25 (s, 6H), 1.34 (s, 2H), 1.20 (d, J = 6.5 Hz, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 93.25, 67.80, 67.71, 67.48, 65.70, 53.58, 33.77, 20.79 (*dl*); 93.50 (*meso*, separated signal); MS (EI, 70 eV): m/z (%): 300 (M^+, 19), 269 (100), 254 (51), 242 (22), 162 (20), 147 (24), 56 (26); $C_{16}H_{24}FeN_2$ (300.23): calcd C 64.01, H 8.06, N 9.33; found C 63.91, H 8.13, N 9.16.

(*R*,*R*)-1,1′-Bis(*α*-*N*-methylamino-*β*-methylpropyl)ferrocene (**19b**): The diacetate **12e** (230 mg, 0.55 mmol) was treated with methylamine (40% in water, 2 mL) in MeOH/water. Chromatography (ether with 1% NEt$_3$) gave the diastereomerically pure diamine **19b** (40 mg, 20%). Yellow solid; m.p. 79–80 °C; $[\alpha]_D$ = −91.3 (c = 0.78, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3346 (w), 3091 (w), 2952 (s), 1431 (s), 1363 (m), 1101 (s), 820 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.14 (s, 2H), 4.01–3.97 (m, 6H), 3.00 (d, J = 3.6 Hz, 2H), 2.52 (s, 6H), 2.00–1.84 (m, 4H), 0.73 (d, J = 6.8 Hz, 12H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 90.84, 69.04, 67.32, 66.99, 66.75, 65.22, 35.70, 29.66, 19.76, 16.18; MS (EI, 70 eV): m/z (%): 356 (M^+, 11), 325 (9), 282 (100), 135 (27); $C_{20}H_{32}FeN_2$ (356.33): calcd C 67.41, H 9.05, N 7.86; found C 67.67, H 9.05, N 7.73. The *meso*-isomer (***meso*-19b**) was also obtained (11 mg, 6%). Yellow oil; IR (KBr): $\tilde{\nu}_{max}$ = 3353 (w), 3091 (w), 2955 (s), 2786 (m), 1467 (m), 1380 (m), 818 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.15–4.14 (m, 2H), 4.04–4.01 (m, 6H), 3.01 (d, J = 3.5 Hz, 2H), 2.55 (s, 6H), 2.01–1.90 (m, 4H), 0.76 (d, J = 6.9 Hz, 6H), 0.64 (d, J = 6.7 Hz, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 91.01, 69.07, 67.42, 67.03, 66.75, 65.24, 35.71, 29.79, 19.80, 16.36; MS (EI, 70 eV): m/z (%): 356 (M^+, 7), 325 (15), 282 (100), 162 (18), 135 (35); $C_{20}H_{32}FeN_2$ (356.33): calcd C 67.41, H 9.05, N 7.86; found C 67.56, H 9.03, N 7.83. As a second by-product (6*R*,8*S*)-6,8-diisopropyl-7-methyl-7-aza[3]ferrocenophane (**21a**) was found (99 mg, 55%, *cis*:*trans* = 88:12). Yellow oil; IR (film): $\tilde{\nu}_{max}$ = 3080 (w), 2900 (s), 1450 (m), 1365 (m), 1015 (m), 800 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.13–3.91 (m, 10H), 2.46 (s, *trans*)/2.43 (s, *cis*, 3H total), 1.94–1.76 (m, 2H), 1.02 (d, J = 6.4 Hz, 6H), 0.75 (d, J = 6.5 Hz)/0.71 (d, J = 6.9 Hz, 6H total); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 92.82, 72.17, 69.45, 69.11, 67.84, 66.47, 30.61, 28.52, 21.61, 21.26 (*cis*); 91.98, 38.41 (*trans*, separated signals); MS (EI, 70 eV): m/z (%): 325 (M^+, 34), 282 (100), 135 (12); $C_{19}H_{27}FeN$ (325.28): calcd C 70.16, H 8.37, N 4.31; found C 70.30, H 8.53, N 4.44.

(*R*,*R*)-1,1′-Bis(*α*-*N*-methylaminophenylmethyl)ferrocene (**19c**): The diacetate **12e** (0.40 g, 0.83 mmol) was treated with methylamine (40% in water, 2 mL) in THF/water. Chromatography (hexanes/MTBE 3:1 with 1% NEt$_3$) gave the diamine **19c** (250 mg, 71%, *dl*:*meso* = 92:8). Yellow solid; m.p. 129–130 °C; $[\alpha]_D$ = +56.2 (c = 0.63, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3083 (w), 2944 (w), 2871 (w), 1492 (m), 1124 (m), 1022 (m), 823 (m), 730 (m), 698 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.38–7.25 (m, 10H), 4.33–4.24 (m, 4H), 4.08–3.99 (m, 6H), 2.38 (s, *meso*)/2.37 (s, *dl*, 6H total), 2.07 (s, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 143.58, 128.25, 127.52, 127.08, 93.70, 68.15, 67.78, 67.65, 66.87, 64.63, 34.80 (*dl*); 142.42, 93.86, 68.22, 67.91, 66.72, 34.92 (*meso*, separated signals); MS (EI, 70 eV): m/z (%): 424 (M^+, 15), 393 (100), 364 (16), 211 (33), 196 (19), 153 (21); $C_{26}H_{28}FeN_2$ (424.37): calcd C 73.59, H 6.65, N 6.60; found C 73.80, H 6.76, N 6.34.

(*R*,*R*)-1,1′-Bis(*α*-*N*-methylaminophenylmethyl)ruthenocene (**20**): The diacetate **13** (330 mg, 0.63 mmol) was treated with methylamine (40% in water, 2 mL) in THF/water. Chromatography (MTBE with 1% NEt$_3$) gave the diamine **20** (187 mg, 64%, *dl*:*meso* = 95:5). Pale yellow solid; m.p. 151–151 °C; $[\alpha]_D$ = −74.2 (c = 0.55, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3311 (w), 3082 (w), 2942 (m), 2780 (m), 1432 (m), 730 (s), 698 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.30–7.15 (m, 10H), 4.57–4.56 (m, 2H), 4.47–4.46 (m, 2H), 4.37–4.34 (m, 4H), 4.00 (s, 2H), 2.24 (s, 6H), 1.70 (s, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 143.15, 127.93, 127.16, 126.80, 98.26, 70.49, 70.18, 70.00, 69.57, 63.67, 34.58; MS (EI, 70 eV): m/z (%): 469 (M^+, 1), 438 (100), 410 (28), 348 (15), 319 (15), 219 (25), 118 (79); $C_{26}H_{28}N_2Ru$ (469.59): calcd C 66.50, H 6.01, N 5.97; found C 66.60, H 5.95, N 6.13.

(*R*,*R*)-1,1′-Bis(*α*-*N*-benzylaminoethyl)ferrocene (**19d**): The diacetate **12a** (2.08 g, 5.80 mmol) was treated with benzylamine (3 mL) in THF/water. Chromatography (MTBE with 1% NEt$_3$) gave the diamine **19d** (2.04 g, 78%, *dl*:*meso* > 97:3). Yellow oil; $[\alpha]_D$ = −97.6 (c = 0.71, CHCl$_3$); IR (film): $\tilde{\nu}_{max}$ = 3070 (w), 3030 (w), 2970 (m), 2840 (w), 1455 (s), 1370 (m), 830 (m), 740 (s), 698 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.40–7.28 (m, 10H), 4.18–4.16 (m, 4H), 4.12–4.10 (m, 4H), 3.93 (d, J = 13.2 Hz, 2H), 3.83 (d, J = 13.1 Hz, 2H), 3.60 (q, J = 6.5 Hz, 2H), 1.61 (s, 2H), 1.46 (d, J = 6.5 Hz, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 140.62, 128.26, 127.97, 126.71, 93.80, 67.74, 67.41, 66.19, 51.24, 51.14, 21.52 (*dl*); 67.85, 67.35, 66.25 (*meso*, separated signals); MS (EI, 70 eV): m/z (%): 452 (M^+, 17), 345 (100), 330 (25), 254 (28), 239 (33), 162 (19), 91 (52); $C_{28}H_{32}FeN_2$ (452.42): calcd C 74.34, H 7.13, N 6.19; found C 74.45, H 6.92, N 6.28. As a minor by-product (6*R*,8*S*)-7-benzyl-6,8-dimethyl-7-aza[3]ferrocenophane (**21b**) was found. Yellow solid; m.p. 88–89 °C; IR (KBr): $\tilde{\nu}_{max}$ = 3077 (w), 2960 (m), 2880 (m), 1453 (m), 1372 (m), 1135 (m), 1020 (m), 733 (s), 703 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.48–7.46 (m, 2H), 7.36–7.31 (m, 2H), 7.25–7.20 (m, 1H), 4.19–4.17 (m, 2H), 4.13–4.06 (m, 8H), 3.49 (q, *J* = 7.1 Hz, 2H), 1.30 (d, *J* = 7.2 Hz, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 142.66, 128.16, 127.74, 126.49, 91.37, 69.84, 68.64, 68.57, 67.72, 53.73, 51.82, 18.35; MS (EI, 70 eV): *m*/*z* (%): 345 (*M*$^+$, 100), 330 (40), 238 (37), 212 (19); C$_{21}$H$_{23}$FeN (345.27): calcd C 73.05, H 6.71, N 4.06; found C 73.22, H 6.75, N 4.24.

***(R,R)*-1,1′-Bis(*α-N*-benzylaminophenylmethyl)ferrocene (19e)**: The diacetate **12e** (1.27 g, 2.63 mmol) was treated with benzylamine (5 mL) in THF/water. Chromatography (hexanes/ether 2:1 with 1% NEt$_3$) gave the diastereomerically pure diamine **19e** (1.31 g, 86%). Yellow solid; m.p. 118–120°C; $[\alpha]_D$ = −39.5 (*c* = 0.59, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3070 (w), 3030 (w), 2970 (s), 2820 (m), 1450 (s), 1205 (m), 1085 (m), 830 (m), 700 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.41–7.26 (m, 20H), 4.46 (s, *meso*)/4.39 (s, *dl*, 2H total), 4.28–4.27 (m, *dl*)/4.20–4.19 (m, 2H total), 4.00–3.92 (m, 6H), 3.78 (d, *J* = 13.3 Hz, 2H), 3.58 (d, *J* = 13.3 Hz)/3.56 (d, *J* = 13.3 Hz, 2H total), 2.14 (s, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 143.80, 140.59, 128.40, 128.27, 127.53, 127.05, 126.91, 94.04, 68.11, 67.84, 67.69, 66.31, 61.03, 51.53 (*dl*); 94.15, 66.44, 61.13, 51.59 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 576 (*M*$^+$, 64), 469 (100), 378 (51), 289 (17), 211 (69), 91 (100); C$_{38}$H$_{36}$FeN$_2$ (576.56): calcd C 79.16, H 6.29, N 4.86; found C 78.75, H 6.48, N 4.51.

***(R,R)*-1,1′-Bis(*α-N*-phenylaminoethyl)ferrocene (19f)**: The diacetate **12a** (344 mg, 0.97 mmol) was treated with aniline (2 mL) in MeOH/water. Chromatography (hexanes/ether 10:1) gave the diastereomerically pure diamine **19f** (369 mg, 90%). Yellow oil; $[\alpha]_D$ = +9.6 (*c* = 0.95, CHCl$_3$); IR (film): $\tilde{\nu}_{max}$ = 3380 (m), 2970 (m), 1595, 1490 (s), 1425 (m), 1310 (s), 825 (m), 745 (s), 690 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.34–7.29 (m, 4H), 6.86–6.75 (m, 6H), 4.50–4.23 (m, 10H), 4.02 (s, 2H), 1.62 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 147.37, 129.33, 117.30, 113.36, 93.88, 68.26, 68.00, 67.44, 66.59, 47.24, 21.09 (*dl*); 113.27, 67.20, 66.81, 21.21 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 424 (*M*$^+$, 15), 331 (31), 239 (100), 147 (27), 93 (20); C$_{26}$H$_{28}$FeN$_2$ (424.37): calcd C 73.59, H 6.65, N 6.60; found C 73.61, H 6.86, N 6.39.

General procedure F for debenzylation of amines 19d,e: The dibenzylated diamine (0.85 mmol) was dissolved in MeOH (5 mL). Pd(OH)$_2$ (20 mg, 10% on C) and one drop of formic acid were added. The flask was connected to vacuum and purged twice with argon. After evacuating a third time the flask was purged with hydrogen from a balloon and stirred rapidly for 12 h. The catalyst was removed by filtration (Celite, 5 cm). The filtrate was concentrated and taken into ether (30 mL) and 10% aqueous NaOH (20 mL). The organic layer was washed with brine (20 mL), dried, and evaporated to provide a quantitative yield of the deprotected amine **22**.

***(R,R)*-1,1′-Bis(*α*-aminoethyl)ferrocene (22a)**: The dibenzylated diamine **19d** (1.10 g, 2.43 mmol) afforded on debenzylation the diamine **22a** (664 mg, ca. 90% pure by NMR analysis). Attempts to further purify the amine by chromatography were not successful. Yellow oil; ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.13–4.07 (m, 8H), 3.82–3.78 (m, 2H), 1.72 (s, 4H), 1.31 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 96.55, 67.79, 67.72, 66.00, 65.91, 45.90, 25.01.

***(R,R)*-1,1′-Bis(*α*-aminophenylmethyl)ferrocene (22b)**: The dibenzylated diamine **19e** (1.17 g, 2.03 mmol) afforded on debenzylation the diamine **22b** (802 mg, 99%, *dl*:*meso* = 96:4). Yellow solid; m.p. 88–90°C; $[\alpha]_D$ = +29.6 (*c* = 2.39, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3391 (w), 3078 (w), 3062 (w), 2853 (m), 1598 (m), 1490 (m), 1450 (m), 1026 (w), 831 (m), 710 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.35–7.21 (m, 10H), 4.86 (s, 2H), 4.35–4.32 (m, 2H), 4.17–4.05 (m, 6H), 1.95 (s, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 145.72, 128.18, 126.56, 94.58, 68.21, 67.71, 67.51, 66.37, 55.22; MS (EI, 70 eV): *m*/*z* (%): 396 (*M*$^+$, 17), 379 (100), 364 (9), 290 (20), 224 (23), 153 (33); C$_{24}$H$_{24}$FeN$_2$ (396.31): calcd C 72.74, H 6.10, N 7.07; found C 72.70, H 6.10, N 6.93.

***(R,R)*-1,1′-Bis(2-tetrahydrofuranyl)ferrocene (23)**: The diol **4e** (113 mg, 0.28 mmol) was dissolved in THF (5 mL) at 0°C and *n*BuLi (1.4 M in hexanes, 0.5 mL) was added dropwise. After 30 min at 0°C the solution was gradually warmed to 40°C and stirred for 2 h. The reaction was poured into saturated aqueous NH$_4$Cl (20 mL) and extracted with ether (30 mL). The organic layer was washed with water (2 × 20 mL) and brine (15 mL), then dried and concentrated to give an oil which was purified by column chromatography (hexanes/MTBE 3:1) to afford the bis(tetrahydrofuran) **23** (77 mg, 85%, *dl*:*meso* = 91:9, 99.5% *ee*). Yellow oil; HPLC (OD, 10% *i*PrOH, 1.0 mL min^{-1}, 254 nm): t_R/min = 8.56 (*SS*), 9.38 (*RS*), 9.96 (*RR*); $[\alpha]_D$ = +28.6 (*c* = 1.63, CHCl$_3$); IR (film): $\tilde{\nu}_{max}$ = 3080 (w), 2950 (vs), 2860 (s), 1050 (vs), 825 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.72–4.68 (m, 2H), 4.16 (s, 2H), 4.10 (s, 6H), 3.91–3.85 (m, 2H), 3.81–3.74 (m, 2H), 2.22–2.15 (m, 2H), 1.95–1.84 (m, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 89.38, 77.16, 68.61, 68.61, 68.54, 68.47, 68.00, 66.30, 32.32, 26.21; MS (EI, 70 eV): *m*/*z* (%): 326 (*M*$^+$, 100), 255 (16), 135 (13), 121 (12); C$_{18}$H$_{22}$FeO$_2$ (326.22): calcd C 66.27, H 6.80; found C 66.41, H 6.91.

***(R,R)*-1,1′-Bis(*N*-methyl-2-pyrrolidinon-5-yl)ferrocene (24a)**: The diacetate **4g** (420 mg, 0.84 mmol) was treated with methylamine (40% in water, 6 mL) in MeOH/water according to general procedure E. Chromatography (CH$_2$Cl$_2$/MeOH 10:1) gave the dipyrrolidinone **24a** (90 mg, 28%), which was directly reduced to the dipyrrolidine **25a** (see below). Yellow oil; $[\alpha]_D$ = +327.5 (*c* = 0.91, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.24–4.04 (m, 10H), 2.53 (s, 6H), 2.49–2.09 (m, 8H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 173.90, 87.32, 70.08, 69.66, 68.64, 66.64, 59.19, 30.45, 27.41, 25.80.

***(R,R)*-1,1′-Bis(*N*-benzyl-2-pyrrolidinon-5-yl)ferrocene (24b)**: The diacetate **4g** (260 mg, 0.52 mmol) was treated with benzylamine (2 mL) in MeOH/water according to general procedure E. Chromatography (CH$_2$Cl$_2$/MeOH 40:1) gave the dipyrrolidinone **24b** (210 mg, 76%, *dl*:*meso* = 92:8). Yellow oil; $[\alpha]_D$ = +168.9 (*c* = 0.74, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3083 (w), 3029 (w), 2920 (m), 1682 (vs), 1413 (m), 1242 (m), 702 (m); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.31–7.21 (m, 6H), 7.10–7.08 (m, 4H), 4.88 (d, *J* = 15.1 Hz, 2H), 4.20–4.03 (m, 8H), 3.91–3.90 (m, 2H), 3.48 (d, *J* = 15.1 Hz, 2H), 2.60–2.15 (m, 8H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 173.82, 136.36, 128.21, 127.58, 126.98, 86.77, 70.46, 69.56, 68.36, 65.98, 55.93, 43.22, 30.48, 25.73 (*dl*); 70.33 (*meso*, separated signal); MS (EI, 70 eV): *m*/*z* (%): 532 (*M*$^+$, 100), 294 (64), 91 (47); C$_{32}$H$_{32}$FeN$_2$O$_2$ (532.46): calcd C 72.18, H 6.06, N 5.26; found C 71.89, H 6.18, N 5.13.

***(R,R)*-1,1′-Bis(*N*-methyl-2-pyrrolidinyl)ferrocene (25a)**: LiAlH$_4$ reduction of **24a** (70 mg, 0.18 mmol) afforded **25a** (53 mg, 84%, *dl*:*meso* 87:13). Yellow oil; $[\alpha]_D$ = +152.9 (*c* = 0.34, CHCl$_3$); IR (film): $\tilde{\nu}_{max}$ = 3080 (w), 2910 (s), 2760 (s), 1450 (m), 1210 (m), 1040 (m), 820 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.14–4.00 (m, 8H), 3.07–3.02 (m, 2H), 2.84 (t, *J* = 8.2 Hz, 2H), 2.25–2.14 (m, 4H), 2.13 (s, 6H), 2.05–1.72 (m, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 88.13, 70.38, 68.95, 67.94, 66.02, 65.50, 57.44, 40.00, 32.04, 22.32 (*dl*); 70.25, 68.82, 67.80, 65.40, 35.13 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 352 (*M*$^+$, 41), 321 (34), 294 (43), 268 (100), 205 (62), 148 (24), 121 (20), 84 (80); C$_{20}$H$_{28}$FeN$_2$ (352.30): calcd C 68.19, H 8.01, N 7.95; found C 67.94, H 7.98, N 8.15.

***(R,R)*-1,1′-Bis(*N*-benzyl-2-pyrrolidinyl)ferrocene (25b)**: The diacetate **12c** (250 mg, 0.52 mmol) was treated with benzylamine (2 mL) in MeOH/water according to general procedure E. Chromatography (hexanes/MTBE 1:1 with 5% NEt$_3$) gave the dipyrrolidine **25b** (248 mg, 95%, *dl*:*meso* = 92:8). LiAlH$_4$ reduction of **24b** (197 mg, 0.37 mmol) also afforded **25b** (114 mg, 61%). Yellow solid; m.p. 124–126°C; $[\alpha]_D$ = +153.6 (*c* = 0.74, CHCl$_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3058 (s), 3027 (w), 2936 (vs), 2781 (s), 1453 (m), 1107 (m), 1027 (m), 821 (m), 697 (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.25–7.13 (m, 10H), 4.22–4.21 (m, 2H), 4.12–4.11 (m, 2H), 4.07–4.06 (m, 4H), 3.92 (d, *J* = 12.8 Hz, 2H), 3.24 (t, *J* = 7.9 Hz, 2H), 2.99 (d, *J* = 12.8 Hz, 2H), 2.89–2.83 (m, 2H), 2.35–2.00 (m, 6H), 1.80–1.70 (m, 4H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 139.86, 128.72, 127.96, 126.50, 89.11, 70.45, 68.88, 67.76, 66.56, 63.67, 57.87, 53.84, 32.42, 22.25 (*dl*); 67.63, 63.55 (*meso*, separated signals); MS (EI, 70 eV): *m*/*z* (%): 504 (*M*$^+$, 60), 413 (18), 344 (25), 281 (46), 253 (15), 189 (23), 160 (32), 91 (100); C$_{32}$H$_{36}$FeN$_2$ (504.50): calcd C 76.19, H 7.19, N 5.55; found C 75.94, H 6.99, N 5.43.

***(R,R)*-1,1′-Bis(2-pyrrolidinyl)ferrocene (26)**: The dibenzylated diamine **25b** (100 mg, 0.20 mmol) was deprotected according to general procedure F to afford quantitatively the dipyrrolidine **26** (66 mg, > 90% pure). Yellow oil; $[\alpha]_D$ = +9.4 (*c* = 0.44, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 4.14–4.07 (m, 8H), 3.87–3.81 (m, 2H), 3.13–3.07 (m, 2H), 2.93–2.86 (m, 2H), 2.13–2.03 (m, 4H), 1.87–1.56 (m, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 92.43, 67.89, 67.86, 67.33, 66.56, 57.58, 46.85, 33.11, 25.79; C$_{18}$H$_{24}$FeN$_2$ (324.25): calcd C 66.68, H 7.46, N 8.64; found C 66.30, H 7.39, N 8.46.

General procedure G for diphosphines 27 and 28: The diacetate (0.46 mmol) was dissolved in acetic acid (4 mL) under argon. Diphenylphosphine (930 mg, 5 mmol) was added and the reaction heated to 40°C for 3 h. The solid that formed was evaporated in vacuum (0.7 mm Hg, 2 h) and dissolved in THF (10 mL). An excess of BH$_3$ · SMe$_2$ (10 M, 0.8 mL) was added and the mixture stirred for 1 h at room temperature. Unreacted borane was destroyed by slow addition of MeOH (2 mL; **caution**: gas evolution!). After concentration to 2 mL the crude reaction mixture was directly purified by column chromatography (CH_2Cl_2/hexanes 1:1) to provide the diphosphine complexed to borane.

(*R,R*)-1,1′-Bis(*α*-(diphenylphosphino)phenylmethyl)ferrocene (diborane complex) (27): The diacetate **12e** (220 mg, 0.46 mmol) was treated with diphenylphosphine (930 mg, 5.0 mmol) to provide the protected diphosphine **27** (244 mg, 70%). Yellow solid; m.p. 242–244 °C; $[\alpha]_D = -63.5$ ($c = 0.05$, $CHCl_3$); IR (KBr): $\tilde{\nu}_{max} = 3054$ (w), 3027 (w), 2401 (s), 1436 (s), 1065 (s), 739 (s); ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 7.65–7.14$ (m, 30H), 4.31 (d, $J = 14.9$ Hz, 2H), 3.64–3.63 (m, 2H), 3.41–3.38 (m, 4H), 3.11–3.10 (m, 2H), 2.0–0.0 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 137.23$, 133.92 (d, $J = 8.5$ Hz), 132.78 (d, $J = 8.2$ Hz), 131.24 (d, $J = 2.1$ Hz), 130.79 (d, $J = 2.2$ Hz), 130.01 (d, $J = 5.4$ Hz), 128.61 (d, $J = 5.2$ Hz), 128.24 (d, $J = 14.5$ Hz), 118.14 (d, $J = 14.5$ Hz), 127.98, 127.69 (d, $J = 53$ Hz), 127.33 (d, $J = 1.5$ Hz), 84.99 (d, $J = 3.8$ Hz), 70.84 (d, $J = 1.1$ Hz), 69.62 (d, $J = 1.0$ Hz), 69.36, 68.19, 47.10 (d, $J = 26.7$ Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 24.4$; MS (EI, 70 eV): *m/z* (%): 733 ([$M^+ - 2BH_3$], 9), 549 (100), 395 (53), 364 (57), 183 (32); $C_{48}H_{46}B_2FeP_2$ (762.31): calcd C 75.63, H 6.35; found C 75.26, H 6.66.

(*R,R*)-1,1′-Bis(*α*-(diphenylphosphino)phenylmethyl)ruthenocene (diborane complex) (28): The diacetate **13** (396 mg, 0.75 mmol) was treated with diphenylphosphine (930 mg, 5.0 mmol) to provide the protected diphosphine **28** (204 mg, 34%). Pale yellow solid; m.p. >260 °C; $[\alpha]_D = +11.3$ ($c = 0.16$, $CHCl_3$); IR (KBr): $\tilde{\nu}_{max} = 3059$ (w), 3026 (w), 2874 (w), 2399 (vs), 1435 (s), 1105 (m), 1067 (s), 815 (m), 738 (s), 692 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.52–7.10$ (m, 30H), 4.15 (d, $J = 15.5$ Hz, 2H), 4.13–4.12 (m, 2H), 3.80–3.79 (m, 2H), 3.76–3.75 (m, 2H), 3.59–3.58 (m, 2H), 1.50–0.50 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 138.78$, 133.68 (d, $J = 8.4$ Hz), 132.85 (d, $J = 8.3$ Hz), 131.16 (d, $J = 2.2$ Hz), 130.82 (d, $J = 2.2$ Hz), 129.71 (d, $J = 5.2$ Hz), 128.74 (d, $J = 14.1$ Hz), 128.50 (d, $J = 9.7$ Hz), 128.20 (d, $J = 9.7$ Hz), 127.72, 127.10 (d, $J = 1.0$ Hz), 89.74 (d, $J = 5.6$ Hz), 74.01 (d, $J = 1.4$ Hz), 72.65 (d, $J = 1.3$ Hz), 71.95, 70.36, 46.35 (d, $J = 26.6$ Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 24.3$; MS (EI, 70 eV): *m/z* (%): 804 (1), 802 (1), 594 (47), 410 (100), 369 (18), 186 (38), 108 (69); $C_{48}H_{46}B_2P_2Ru$ (807.53): calcd C 71.39, H 5.74; found C 71.23, H 5.52.

(*R,R*)-1,1′-Bis(*α*-thioacetophenylmethyl)ferrocene (29): The diacetate **12e** (56 mg, 0.12 mmol) was dissolved in acetic acid (3 mL) and KSAc (114 mg, 1.0 mmol) was added. The mixture was heated to 50 °C for 3 h. After cooling to room temperature volatile matter was removed in vacuum and the residue dissolved in water (10 mL) and ether (30 mL). The organic layer was washed with water (10 mL) and dried. Concentration and chromatography of the residue (hexanes/MTBE 10:1) gave the dithioacetate **29** (60 mg, 97%, *dl*:*meso* = 90:10). Glassy yellow solid; $[\alpha]_D = -130$ ($c = 1.35$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 2970$ (m), 2930 (m), 2830 (w), 1680 (vs), 1455 (w), 1355 (m), 1110 (vs), 950 (s), 830 (s), 710 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.31–7.17$ (m, 10H), 5.57 (s, 2H), 4.08–4.07 (m, *dl*)/4.02–4.01 (m, *meso*)/4.00–3.98 (m)/3.95–3.94 (m, *meso*)/3.86–3.85 (m, *dl*, 8H total), 2.27 (s, *dl*)/2.26 (s, *meso*, 6H total); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 193.93$, 142.12, 128.29, 128.00, 127.25, 89.82, 69.43, 69.36, 69.21, 68.65, 47.76, 30.22 (*dl*); 128.03, 69.28, 68.89 (*meso*, separated signals); MS (EI, 70 eV): *m/z* (%): 514 (M^+, 53), 440 (6), 396 (30), 364 (27), 285 (100), 208 (33), 154 (84), 43 (45); $C_{28}H_{26}FeO_2S_2$ (514.48): calcd C 65.37, H 5.09; found C 65.28, H 5.10.

General procedure H for the aminophosphines 30 and 31: The diamine (1.04 mmol) was dissolved in Et_2O (5 mL) and BuLi (1.6 M in hexanes, 3 mL, 4.1 mmol) was added within 10 min. After 10–30 min the color changed from yellow to red. After 6 h diphenylchlorophosphine (1.55 g, 7.0 mmol) was added at such a rate that the exothermic reaction did not cause the solvent to boil. After the addition was complete the resulting suspension was stirred for 4 h at room temperature and hydrolyzed by addition of saturated aqueous $NaHCO_3$ (10 mL). A precipitate formed at this stage was dissolved by adding ether (20 mL) or a small amount of CH_2Cl_2. After separation of the phases the aqueous layer was extracted with ether (20 mL). The combined organic layers were dried and concentrated, and the residue purified by column chromatography without delay (otherwise rapid decomposition of the crude product was observed).

(*aR,a′R*)-2,2′-Bis(*α*-*N,N*-dimethylaminoethyl)-(*S,S*)-1,1′-bis(diphenylphosphino)ferrocene (30a): Diamine **17a** (340 mg, 1.04 mmol) was lithiated (*n*BuLi, 4.1 mmol, 6 h) and treated with diphenylchlorophosphine (1.55 g, 7.0 mmol). Chromatography (hexanes/ethyl acetate 2:1) afforded the aminophosphine **30a** (200 mg, 29%). Yellow solid; $[\alpha]_D = -435$ ($c = 1.0$, $CHCl_3$); IR (KBr): $\tilde{\nu}_{max} = 3050$ (w), 2930 (w), 2770 (m), 1432 (m), 1094 (m), 739 (m), 696 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.42–7.37$ (m, 4H), 7.30–7.20 (m, 16H), 4.45–4.44 (m, 2H), 4.25–4.24 (m, 2H), 4.20–4.16 (m, 2H), 3.15–3.14 (m, 2H), 1.80 (s, 12H), 1.35 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 140.87$ (d, $J = 7.2$ Hz), 138.30 (d, $J = 9.4$ Hz), 134.71 (d, $J = 22.0$ Hz), 131.96 (d, $J = 7.2$ Hz), 128.39, 127.72 (d, $J = 7.7$ Hz), 127.05 (d, $J = 6.8$ Hz), 126.77, 98.17 (d, $J = 23.0$ Hz), 76.74 (d, $J = 9.4$ Hz), 72.63 (d, $J = 6.0$ Hz), 72.43 (d, $J = 4.1$ Hz), 70.70 (d, $J = 3.7$ Hz), 56.53 (d, $J = 7.0$ Hz), 38.64, 8.78; ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = -23.1$; MS (EI, 70 eV): *m/z* (%): 696 (M^+, 45), 651 (25), 636 (100), 608 (17), 574 (31), 466 (40), 325 (18), 72 (46). Value of optical rotation and ^1H NMR data are in good agreement with literature data.[28]

(*aR,a′R*)-2,2′-Bis(*α*-*N,N*-dimethylaminohexyl)-(*S,S*)-1,1′-bis(diphenylphosphino)ferrocene (30b): Diamine **17b** (169 mg, 0.38 mmol) was lithiated (*t*BuLi, 2.3 mmol, 18 h) and treated with diphenylchlorophosphine (880 mg, 4.0 mmol). Chromatography (hexanes/MTBE 15:1 with 1% NEt_3) afforded the diastereomerically pure aminophosphine **30b** (122 mg, 39%, >96% ee). Yellow solid; m.p. 189–191 °C; HPLC (OD, 1% *i*PrOH, 1.0 mL/min, 254 nm): t_R/min = 3.69 (*aRa′R,SS*), 3.91 (*aSa′S,RR*); $[\alpha]_D = -357$ ($c = 0.78$, $CHCl_3$); IR (KBr): $\tilde{\nu}_{max} = 3069$ (w), 3050 (w), 2925 (s), 2854 (w), 2821 (w), 2776 (w), 1432 (s), 824 (w), 735 (m), 696 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.25–7.03$ (m, 20H), 4.39–4.38 (m, 2H), 4.08–4.06 (m, 2H), 3.90–3.86 (m, 2H), 2.93 (s, 2H), 2.00–1.92 (m, 2H), 1.88-1.78 (m, 2H), 1.77 (s, 12H), 1.55–1.20 (m, 12H), 0.93 (t, $J = 6.5$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 140.60$ (d, $J = 6.9$ Hz), 138.39 (d, $J = 9.0$ Hz), 134.94 (d, $J = 22.4$ Hz), 132.04 (d, $J = 18.7$ Hz), 128.49, 127.89 (d, $J = 8.0$ Hz), 127.17 (d, $J = 6.6$ Hz), 126.91, 98.26 (d, $J = 24.0$ Hz), 76.24 (d, $J = 8.8$ Hz), 73.02 (d, $J = 5.0$ Hz), 72.11 (d, $J = 5.5$ Hz), 70.63, 61.04 (d, $J = 7.4$ Hz), 39.61, 32.75, 30.71, 28.62, 22.79, 14.14; ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = -23.3$; MS (EI, 70 eV): *m/z* (%): 808 (M^+, 63), 763 (32), 748 (42), 720 (32), 706 (88), 647 (15), 382 (47), 362 (14), 319 (21), 128 (100); $C_{50}H_{62}FeN_2P_2$ (808.85): calcd C 74.25, H 7.72, N 3.46; found C 74.22, H 7.80, N 3.36. Data for *meso*-**30b** (from racemic **17b**): IR (KBr): $\tilde{\nu}_{max} = 3068$ (w), 3050 (w), 2926 (s), 2854 (s), 2813 (m), 2771 (m), 1432 (s), 826 (m), 748 (s), 698 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.65–7.60$ (m, 4H), 7.40–7.30 (m, 6H), 7.20–7.05 (m, 10H), 4.38 (s, 2H), 3.85 (s, 2H), 3.72–3.70 (m, 2H), 3.48 (s, 2H), 1.65 (s, 12H), 1.27–1.05 (m, 16H), 0.98–0.90 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 140.58$ (d, $J = 7.1$ Hz), 139.10 (d, $J = 9.2$ Hz), 135.67 (d, $J = 22.7$ Hz), 132.10 (d, $J = 18.5$ Hz), 129.99, 128.09 (d, $J = 8.0$ Hz), 127.30 (d, $J = 6.6$ Hz), 127.05, 97.37 (d, $J = 24.4$ Hz), 75.93 (d, $J = 9.3$ Hz), 74.26 (d, $J = 5.4$ Hz), 72.47, 70.43, 60.32 (d, $J = 8.0$ Hz), 39.55, 32.12, 29.55, 27.95, 22.74, 14.16; ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = -23.6$; MS (EI, 70 eV): *m/z* (%): 808 (M^+, 18), 762 (7), 746 (15), 718 (100), 533 (7), 382 (46), 359 (43), 319 (19), 128 (27); $C_{50}H_{62}FeN_2P_2$ (808.85): calcd C 74.25, H 7.72, N 3.46; found C 74.13, H 7.89, N 3.75. As by-product the monophosphorylated diamine ((*aR,a′R*)-2,1′-bis(*α*-*N,N*-dimethylaminoethyl)-(*S*)-1-(diphenylphosphino)ferrocene, 83 mg, 35%) was isolated; yellow oil; $[\alpha]_D = -120$ ($c = 1.11$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3060$ (w), 2920 (vs), 2860 (s), 2820 (w), 2780 (m), 1435 (s), 1030 (m), 820 (m), 740 (s), 695 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.65–7.60$ (m, 2H), 7.35–7.33 (m, 3H), 7.19–7.13 (m, 5H), 4.31 (s, 1H), 4.20 (t, $J = 2.3$ Hz, 1H), 4.02–4.01 (m, 1H), 3.98–3.93 (m, 1H), 3.87–3.86 (m, 1H), 3.85–3.83 (m, 3H), 2.34 (dd, $J = 10.6$, 3.3 Hz, 1H), 1.80 (s, 6H), 1.77 (s, 6H), 1.82–1.25 (m, 16H), 0.98–0.91 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 141.28$ (d, $J = 7.4$ Hz), 139.20 (d, $J = 9.6$ Hz), 135.72 (d, $J = 22.35$ Hz), 132.02 (d, $J = 18.6$ Hz), 128.89, 128.06 (d, $J = 8.0$ Hz), 127.22 (d, $J = 6.7$ Hz), 126.91, 96.75 (d, $J = 23.7$ Hz), 85.56, 76.29 (d, $J = 8.7$ Hz), 72.55 (d, $J = 5.7$ Hz), 71.70, 70.37, 70.07 (d, $J = 4.2$ Hz), 68.99, 67.60, 61.82, 61.50 (d, $J = 6.4$ Hz), 40.26, 39.43, 32.55, 32.21, 31.25, 28.77, 28.29, 27.01, 22.75, 22.71, 14.17, 14.14; ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = -22.7$; MS (EI, 70 eV): *m/z* (%): 624 (M^+, 32), 579 (64), 564 (48), 536 (56), 522 (100), 465 (38), 350 (23), 178 (70), 128 (75); $C_{38}H_{53}FeN_2P$ (624.67): calcd C 73.07, H 8.55, N 4.48; found C 72.83, H 8.60, N 4.58.

(*aR,a′R*)-2,2′-Bis(*α*-*N,N*-dimethylaminophenylmethyl)-(*S,S*)-1,1′-bis(diphenylphosphino)ferrocene (30c): Diamine **17c** (216 mg, 0.48 mmol) was lithiated (*n*BuLi, 1.8 mmol, 6 h) and treated with diphenylchlorophosphine (900 mg, 4.1 mmol). Chromatography (hexanes/MTBE 2:1) afforded the diastereomerically pure aminophosphine **30c** (225 mg, 57%, >98% *ee*). Yellow solid; m.p. 245–246 °C; HPLC (OD, 5% *i*PrOH, 1.0 mL/min, 254 nm): t_R/min = 5.08 (*aRa′R,SS*), 5.86 (*aSa′S,RR*); $[\alpha]_D = -331$ ($c = 1.99$,

$CHCl_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3090 (w), 3064 (w), 3030 (w), 2951 (m), 2856 (w), 2811 (m), 2764 (s), 1450 (s), 1006 (s), 814 (m), 737 (s), 703 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35 – 7.10 (m, 30 H), 4.52 (s, 2 H), 4.39 (s, 2 H), 3.29 (s, 2 H), 3.15 (s, 2 H), 1.51 (s, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 139.99, 139.68 (d, J = 6.8 Hz), 137.84 (d, J = 10.1 Hz), 134.77 (d, J = 23.0 Hz), 132.38 (d, J = 13.4 Hz), 128.55, 128.49, 127.97 (d, J = 8.0 Hz), 127.92, 127.44 (d, J = 7.0 Hz), 127.30, 126.59, 98.09 (d, J = 22.5 Hz), 76.51 (d, J = 10.0 Hz), 73.13, 72.88 (d, J = 5.2 Hz), 71.57, 68.27 (d, J = 10.1 Hz), 42.00; ^{31}P NMR ($CDCl_3$, 162 MHz): δ = – 23.9; MS (EI, 70 eV): m/z (%): 820 (M^+, 11), 773 (40), 732 (12), 437 (100), 394 (33), 239 (19), 183 (29), 134 (38); $C_{52}H_{50}FeN_2P_2$ (820.78): calcd C 76.10, H 6.14, N 3.41; found C 76.22, H 6.35, N 3.42.

(*αR,α′R*)-2,2′-Bis(*α-N,N*-dimethylamino(2-naphtyl)methyl)-(*S,S*)-1,1′-bis(diphenylphosphino)ferrocene (**30 d**): Diamine **17 d** (193 mg, 0.35 mmol) was lithiated (*n*BuLi, 1.23 mmol, 6 h) and treated with diphenylchlorophosphine (420 mg, 1.9 mmol). Chromatography (hexanes/MTBE 5:1 with 0.5% NEt_3) afforded the diastereomerically pure aminophosphine **30 d** (100 mg, 31%, > 98% *ee*). Yellow solid; HPLC (OD, 2% *i*PrOH, 0.9 mL min^{-1}, 215 nm): t_R/min = 5.67 (*αRα′R,SS*), 7.01 (*αSα′S,RR*); $[\alpha]_D$ = – 407 (c = 0.79, $CHCl_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3054 (w), 2819 (w), 2775 (w), 1432 (m), 827 (m), 739 (m), 698 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.84 – 7.80 (m, 2 H), 7.70 – 7.66 (m, 2 H), 7.59 (s, 2 H), 7.54 – 7.48 (m, 4 H), 7.35 – 7.14 (m, 20 H), 6.93 – 6.87 (m, 4 H), 4.72 – 4.71 (m, 2 H), 4.43 – 4.42 (m, 2 H), 3.37 – 3.36 (m, 2 H), 3.22 (s, 2 H), 1.46 (s, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 139.82 (d, J = 6.6 Hz), 137.94 (d, J = 10.4 Hz), 134.77 (d, J = 23.0 Hz), 133.02, 132.50 (d, J = 19.8 Hz), 132.27, 128.55, 128.07 – 127.24 (m), 126.41, 125.67, 125.24, 97.52 (d, J = 22.1 Hz), 76.64 (d, J = 4.5 Hz), 73.68 (d, J = 3.5 Hz), 73.33 (d, J = 5.7 Hz), 71.65 (d, J = 4.1 Hz), 68.42 (d, J = 9.1 Hz), 41.67; ^{31}P NMR ($CDCl_3$, 162 MHz): δ = – 24.5; MS (EI, 70 eV): m/z (%): 920 (M^+, 22), 874 (100), 831 (31), 487 (72), 444 (32), 184 (37); $C_{60}H_{54}FeN_2P_2$ (920.90): calcd C 78.26, H 5.91, N 3.04; found C 78.14, H 5.78, N 2.92.

(*αR,α′R*)-2,2′-Bis(*α-N,N*-dimethylaminophenylmethyl)-(*S,S*)-1,1′-bis(diphenylphosphino)ruthenocene (31): Diamine **18** (663 mg, 1.33 mmol) was lithiated (*n*BuLi, 5.34 mmol, 6 h) and treated with diphenylchlorophosphine (1.6 g, 7.3 mmol). Chromatography (hexanes/MTBE 3:1) afforded the diastereomerically pure aminophosphine **31** (473 mg, 43%, > 98% *ee*). Colorless solid; HPLC (OD, 2% *i*PrOH, 0.9 mL/min, 215 nm): t_R/min = 5.93 (*αRα′R,SS*), 7.20 (*αSα′S,RR*); $[\alpha]_D$ = – 183 (c = 0.52, $CHCl_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3053 (w), 2946 (w), 2771 (m), 1434 (m), 1015 (m), 741 (s), 698 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.27 – 7.05 (m, 30 H), 4.40 (s, 2 H), 4.25 (d, J = 5.6 Hz, 2 H), 3.40 – 3.36 (m, 4 H), 1.67 (s, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 144.63, 138.83 (d, J = 38.7 Hz), 138.72 (d, J = 39.5 Hz), 134.51 (d, J = 22.6 Hz), 132.73 (d, J = 18.9 Hz), 128.31 (d, J = 5.9 Hz), 127.80, 127.72, 127.60 (d, J = 5.0 Hz), 126.57, 103.81 (d, J = 25.6 Hz), 82.20 (d, J = 13.2 Hz), 76.26 (d, J = 5.0 Hz), 75.61, 74.67, 68.21 (d, J = 12.4 Hz), 43.78; ^{31}P NMR ($CDCl_3$, 162 MHz): δ = – 24.2; MS (EI, 70 eV): m/z (%): 821 (M^+, 100), 806 (36), 778 (17), 746 (10), 593 (5), 517 (5), 134 (59); $C_{48}H_{50}N_2P_2Ru$ (817.95): calcd C 70.48, H 6.16, N 3.42; found C 70.71, H 6.13, N 3.21.

General procedure I for the palladium complexes 32 and 33: The aminophosphine (0.15 mmol) and $PdCl_2(MeCN)_2$ (40.1 mg, 0.15 mmol) were suspended in toluene (4 mL) and stirred for 12 h at room temperature. A slow change in color from yellow to deep red was observed. Removal of the solvent in vacuum gave a quantitative yield of the palladium complex.

(*αR,α′R*)-2,2′-Bis(*α-N,N*-dimethylaminophenylmethyl)-(*S,S*)-1,1′-bis(diphenylphosphino)ferrocenepalladium(II) chloride (32 c): From aminophosphine **30 c** (127 mg, 0.15 mmol) and $PdCl_2(MeCN)_2$ (40.1 mg, 0.15 mmol). Red powder; m.p. 176 °C (decomp.); $[\alpha]_D$ = – 130 (c = 0.69, $CHCl_3$); IR (KBr): $\tilde{\nu}_{max}$ = 3055 (w), 2950 (m), 2860 (w), 2818 (w), 2773 (w), 1436 (s), 1093 (m), 743 (s), 692 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.17 (s, 4 H), 7.99 (s, 4 H), 7.42 – 7.32 (m, 12 H), 7.20-7.14 (m, 6 H), 6.81 (s, 4 H), 4.34 (s, 2 H), 4.11 (s, 2 H), 3.04 (s, 2 H), 2.32 (s, 2 H), 1.52 (s, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 143.51, 136.74 (t, J = 6.7 Hz), 135.84 (t, J = 4.6 Hz), 132.53 (d, J = 57.1 Hz), 131.63, 130.62, 129.05 (d, J = 55.2 Hz), 128.07, 127.44, 127.30, 127.02, 99.03, 77.99, 76.46 (d, J = 17.4 Hz), 72.73 (d, J = 55.5 Hz), 72.07, 64.07, 42.92; ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 40.0; MS (EI, 70 eV): m/z (%): 262 (43), 183 (22), 72 (33), 57 (65), 43 (100); $C_{52}H_{50}Cl_2FeN_2P_2Pd$ (998.10): calcd C 62.58, H 5.05, N 2.81; found C 62.54, H 5.15, N 2.50.

(*αR,α′R*)-2,2′-Bis(*α-N,N*-dimethylamino(2-naphthyl)methyl)-(*S,S*)-1,1′-bis(diphenylphosphino)ferrocenepalladium(II) chloride (**32 d**): From aminophosphine **30 d** (127 mg, 0.138 mmol) and $PdCl_2(MeCN)_2$ (35.7 mg, 0.138 mmol). The red powder obtained was used in the asymmetric cross-coupling reaction without further purification. IR (KBr): $\tilde{\nu}_{max}$ = 3053 (w), 2944 (w), 2773 (w), 1436 (s), 1093 (m), 743 (s), 692 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.40 – 8.30 (m, 4 H), 8.10 – 8.04 (m, 4 H), 7.80 – 7.31 (m, 22 H), 7.25 – 7.21 (m, 2 H), 7.10 – 7.09 (m, 2 H), 4.49 – 4.48 (m, 2 H), 4.24 – 4.23 (m, 2 H), 3.29 (s, 2 H), 2.18 – 2.17 (m, 2 H), 1.60 (s, 12 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 141.14, 137.29, 137.20, 137.10, 136.01, 135.94, 135.88, 132.76, 132.31, 131.85, 130.74, 129.33 (d, J = 54.9 Hz), 128.43, 128.35, 128.27, 127.89, 127.74, 127.44, 127.35, 126.24, 126.18, 125.87, 125.74, 99.09, 78.52, 76.83 (d, J = 10.7 Hz), 72.43, 71.76 (d, J = 26.9 Hz), 64.43, 43.17; ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 39.3; MS (EI, 70 eV): m/z (%): 262 (40), 78 (20), 44 (100).

The palladium complexes **32 a**, **32 b**, and **33** were obtained from the corresponding aminophosphines according to general procedure I and were found to be mixtures of coordination isomers. They were used for the asymmetric cross-coupling reactions without further purification.

General procedure J for asymmetric cross-coupling: The vinyl bromide (2.5 mmol) and the Grignard reagent (5.0 mmol) were added to the palladium complex (25 µmol) (and in some cases a zinc halide (10 mmol)) at – 78 °C. The reaction mixture was warmed to 0 °C and stirred at this temperature for 20 h. The resulting suspension was poured into 10% hydrochloric acid (30 mL) and extracted with hexanes (3 × 40 mL). The combined organic layers were dried and concentrated, and the residue distilled under reduced pressure. As an alternative a purification by column chromatography was carried out.

(*S*)-3-Phenyl-1-butene (**34 a**): Reaction of vinyl bromide (213 mg, 2.0 mmol) and 1-phenylethylmagnesium chloride (11.0 mL, 0.36 M in Et_2O, 4.0 mmol) with palladium complex **31 c** (10 mg, 10 µmol) as catalyst provided **34 a** (214 mg, 81%, 63% *ee*) after chromatography (hexanes). A reaction with addition of ZnI_2 (4 equiv) also gave **34 a** (86%, 82% *ee*). Colorless liquid; GC (CB, 50 kPa, 80 °C): t_R/min = 11.78 (*R*), 11.92 (*S*); $[\alpha]_D$ = + 4.77 (c = 16.16, $CHCl_3$); IR (film): $\tilde{\nu}_{max}$ = 3055 (w), 3030 (w), 2960 (m), 2870 (w), 1640 (s), 1600 (s), 1495 (m), 1455 (m), 1370 (s), 910 (s), 755 (m), 700 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.32 – 7.17 (m, 5 H), 6.00 (ddd, J = 17.0, 10.5, 6.5 Hz, 1 H), 5.09 – 4.98 (m, 2 H), 3.50 (quin, J = 6.7 Hz, 1 H), 1.34 (d, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 145.55, 143.24, 128.39, 127.22, 126.10, 113.09, 43.17, 20.71; MS (EI, 70 eV): m/z (%): 132 (M^+, 25), 117 (100), 91 (48); $C_{10}H_{12}$ (132.21): calcd C 90.85, H 9.15; found C 90.61, H 9.31.

(*S*)-(*E*)-1,3-Diphenyl-1-butene (**34 b**): Reaction of β-bromostyrene (458 mg, 2.5 mmol) and 1-phenylethylmagnesium chloride (13.9 mL, 0.36 M in Et_2O, 5.0 mmol) with palladium complex **31 c** (25 mg, 25 µmol) as catalyst provided **34 b** (452 mg, 87%, 93% *ee*) after chromatography (hexanes). A reaction with addition of $ZnCl_2$ (4 equiv) also gave **34 b** (82%, 29% *ee*). Colorless liquid; b.p. 120 °C (Kugelrohr, 0.7 mm Hg); HPLC (OD, 0.25% *i*PrOH, 0.9 mL min^{-1}, 215 nm): t_R/min = 7.41 (*S*), 8.05 (*R*); $[\alpha]_D$ = – 39.3 (c = 2.51, $CHCl_3$); – 34.2 (c = 2.60, benzene); IR (film): $\tilde{\nu}_{max}$ = 3030 (w), 2970 (w), 1600 (w), 1495 (m), 1450 (m), 1375 (w), 965 (s), 745 (s), 695 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.51 – 7.30 (m, 10 H), 6.61 – 6.49 (m, 2 H), 3.83 – 3.74 (m, 1 H), 1.62 (d, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 145.58, 137.56, 135.19, 128.55, 128.44, 127.26, 127.00, 126.18, 126.13, 42.52, 21.19; MS (EI, 70 eV): m/z (%): 208 (M^+, 84), 193 (71), 178 (23), 130 (19), 115 (88), 105 (100), 91 (46); $C_{16}H_{16}$ (208.30): calcd C 92.26, H 7.74; found C 92.49, H 7.50.

(*S*)-(*E*)-4-Phenyl-2-pentene (**34 c**): Reaction of (*E*)-1-bromo-1-propene (107 mg, 0.88 mmol) and 1-phenylethylmagnesium chloride (5.5 mL, 0.36 M in Et_2O, 2.0 mmol) with palladium complex **31 c** (5 mg, 5 µmol) as catalyst provided **34 c** (88 mg, 68%, 65% *ee*) after chromatography (hexanes). (The enantiomeric excess was determined by $RuCl_3/NaIO_4$ cleavage and esterification of the resulting 2-phenylpropionic acid with (*S*)-methyl mandelate;[33] the crude derivatization product was analyzed by NMR.) Colorless liquid; $[\alpha]_D$ = + 10.2 (c = 0.98, $CHCl_3$); IR (film): $\tilde{\nu}_{max}$ = 3030 (w), 2970 (s), 2880 (w), 1600 (w), 1495 (m), 1440 (s), 1375 (m), 1015 (m), 695 (s), 770 (s), 700 (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36 – 7.31 (m, 2 H), 7.27-7.19 (m, 3 H), 5.70 – 5.62 (m, 1 H), 5.54 – 5.46 (m, 1 H), 3.45 (quin, J = 6.9 Hz, 1 H), 1.73 – 1.70 (m, 3 H), 1.39 – 1.36 (m, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 146.47, 136.27, 128.32, 127.13, 125.90, 123.61, 42.35, 21.47, 17.87; MS (EI, 70 eV): m/z (%): 146 (M^+, 44), 131 (100), 115 (27), 91 (62), 77 (28); $C_{11}H_{14}$ (146.23): calcd C 90.35, H 9.65; found C 90.16, H 9.52.

(*S*)-(*E*)-7-Chloro-2-phenyl-3-heptene (**34 d**): Reaction of (*E*)-1-bromo-5-chloro-1-pentene (183 mg, 1.00 mmol) and 1-phenylethylmagnesium chloride (5.5 mL, 0.36 M in Et_2O, 2.0 mmol) with palladium complex **31 c** (10 mg, 10 µmol) as catalyst provided **34d** (135 mg, 65 %, 11 % *ee*) after chromatography (hexanes/MTBE 50:1). (The enantiomeric excess was determined by $RuCl_3/NaIO_4$ cleavage and esterification of the resulting 2-phenylpropionic acid with (*S*)-methyl mandelate;[33] the crude derivative was analyzed by NMR.) Colorless liquid; $[\alpha]_D = +3.8$ ($c = 1.25$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3020$ (w), 2950 (s), 1600 (m), 1480 (m), 1445 (s), 1370 (w), 960 (s), 905 (m), 700 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.38-7.32$ (m, 2H), 7.27–7.21 (m, 3H), 5.72 (ddt, $J = 15.3$, 6.7, 1.3 Hz, 1H), 5.47 (dtd, $J = 15.4$, 6.7, 1.3 Hz, 1H), 3.56 (t, $J = 6.6$ Hz, 2H), 3.48 (quin, $J = 6.9$ Hz, 1H), 2.22 (q, $J = 6.9$ Hz, 2H), 1.88 (quin, $J = 6.8$ Hz, 2H), 1.41 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 146.10$, 136.60, 128.34, 127.08, 127.04, 125.97, 44.30, 42.23, 32.24, 29.56, 21.45; MS (EI, 70 eV): *m/z* (%): 208 (M^+, 24), 193 (8), 131 (100), 117 (21), 105 (46), 91 (35); $C_{13}H_{17}Cl$ (208.73): calcd C 74.81, H 8.21; found C 74.82, H 8.37.

(*S*)-(*E*)-2,4-Diphenyl-2-pentene (34e): Reaction of (*E*)-1-bromo-2-phenyl-1-propene (138 mg, 0.70 mmol) and 1-phenylethylmagnesium chloride (4.0 mL, 0.36 M in Et_2O, 1.4 mmol) with palladium complex **31c** (6 mg, 6 µmol) as catalyst provided **34e** (81 mg, 52 %, 59 % *ee*) after distillation. Colorless liquid; b.p. 120 °C (Kugelrohr, 0.7 mm Hg); HPLC (OD, 0.25 % *i*PrOH, 0.9 mL/min, 215 nm): t_R/min = 6.80 (*S*), 7.34 (*R*); $[\alpha]_D = -50.9$ ($c = 1.48$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3030$ (w), 2970 (m), 2870 (w), 1600 (m), 1495 (s), 1450 (s), 1380 (m), 1020 (m), 760 (s), 700 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.52-7.30$ (m, 10H), 6.04 (dd, $J = 9.3$, 1.4 Hz, 1H), 3.97 (dq, $J = 9.2$, 7.0 Hz, 1H), 2.03 (d, $J = 1.4$ Hz, 3H), 1.54 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 146.55$, 143.77, 133.92, 133.42, 128.44, 128.13, 126.97, 126.67, 125.92, 125.78, 38.70, 22.39, 16.06; MS (EI, 70 eV): *m/z* (%): 222 (M^+, 61), 207 (70), 129 (100), 105 (42), 91 (55), 77 (25); $C_{17}H_{18}$ (222.33): calcd C 91.84, H 8.16; found C 91.62, H 8.03.

2-Methyl-3-phenyl-1-butene (34f): Reaction of 2-bromopropene (200 mg, 1.65 mmol) and 1-phenylethylmagnesium chloride (7.5 mL, 0.36 M in Et_2O, 2.7 mmol) with palladium complex **31c** (7.5 mg, 7.5 µmol) as catalyst provided **34f** (80 mg, 33 %, racemic) after distillation. Colorless liquid; b.p. 70 °C (Kugelrohr, 13 mbar); GC (CB, 50 kPa, 80 °C): t_R/min = 19.35, 19.54; IR (film): $\tilde{\nu}_{max} = 3020$ (w), 2960 (m), 1645 (w), 1450 (s), 1375 (w), 890 (m). ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.40-7.24$ (m, 5H), 4.97 (s, 1H), 4.93 (s, 1H), 3.46 (q, $J = 7.0$ Hz, 1H), 1.68 (s, 3H), 1.45 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 149.16$, 145.14, 128.25, 127.40, 126.04, 109.85, 46.54, 21.31, 20.00; $C_{11}H_{14}$ (146.23): calcd C 90.35, H 9.65; found C 90.50, H 9.66.

(*R*)-(*E*)-1-Phenyl-3-methyl-1-pentene (34g): Reaction of *β*-bromostyrene (342 mg, 1.87 mmol) and *sec*-butylmagnesium chloride (4.8 mL, 0.83 M in Et_2O, 4.0 mmol) with palladium complex **31c** (5 mg, 5 µmol) as catalyst provided **34g** (260 mg, 75 %, 15 % *ee*) after distillation. (The enantiomeric excess was determined by $RuCl_3/NaIO_4$ cleavage and esterification of the resulting 2-methylbutyric acid with (*S*)-methyl mandelate;[33] the crude derivatization product was analyzed by ^1H NMR (200 MHz, C_6D_6): major diastereomer: $\delta = 6.18$ (s); minor diastereomer: $\delta = 6.16$ (s).) Colorless liquid; $[\alpha]_D = -3.5$ ($c = 4.39$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3020$ (w), 2950 (s), 2925 (s), 2870 (m), 1600 (w), 1490 (m), 1450 (s), 1375 (w), 960 (s), 740 (s), 690 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.38-7.27$ (m, 4H), 7.23–7.16 (m, 1H), 6.35 (d, $J = 15.9$ Hz, 1H), 6.10 (dd, $J = 15.9$, 7.8 Hz, 1H), 2.21 (sept, $J = 7.0$ Hz, 1H), 1.42 (quin, $J = 7.0$ Hz, 2H), 1.08 (d, $J = 6.8$ Hz, 3H), 0.92 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 138.00$, 136.65, 128.42, 128.22, 126.72, 125.97, 38.89, 29.82, 20.17, 11.79; MS (EI, 70 eV): *m/z* (%): 160 (M^+, 24), 131 (100), 145 (8), 115 (15), 91 (48), 77 (6); $C_{12}H_{16}$ (160.26): calcd C 89.94, H 10.06; found C 89.71, H 10.20.

(*E*)-8-Chloro-3-methyl-4-octene (34h): Reaction of (*E*)-1-bromo-5-chloro-1-pentene (341 mg, 1.86 mmol) and *sec*-butylmagnesium chloride (4.8 mL, 0.83 M in Et_2O, 4.0 mmol) with palladium complex **31c** (10 mg, 10 µmol) as catalyst provided **34h** (223 mg, 75 %, racemic) after chromatography (hexanes). (The enantiomeric excess was determined by $RuCl_3/NaIO_4$ cleavage and esterification of the resulting 2-methylbutyric acid with (*S*)-methyl mandelate;[33] the crude derivative was analyzed by ^1H NMR (200 MHz, C_6D_6): major diastereomer: $\delta = 6.18$ (s); minor diastereomer: $\delta = 6.16$ (s).) Colorless liquid; IR (film): $\tilde{\nu}_{max} = 2950$ (s), 2930 (s), 2870 (m), 1450 (m), 1370 (w), 960 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 5.37-5.24$ (m, 2H), 3.54 (t, $J = 6.7$ Hz, 2H), 2.17–2.10 (m, 2H), 1.97 (sept, $J = 6.8$ Hz, 1H), 1.84 (quin, $J = 7.3$ Hz, 2H), 1.33–1.22 (m, 2H), 0.95 (d, $J = 6.8$ Hz, 3H), 0.83 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 137.87$, 126.36, 44.29, 38.39, 32.46, 29.76, 29.64, 20.32, 11.69; MS (EI, 70 eV): *m/z* (%): 162 (M^+, 4), 160 (M^+, 14), 133 (11), 131 (34), 95 (21), 83 (54), 70 (36), 55 (100), 41 (47); $C_9H_{17}Cl$ (160.69): calcd C 67.27, H 10.66; found C 67.20, H 10.91.

(1*S*,2*S*,3*R*)-1,3-Diphenyl-1,2-butanediol (35): AD-mix (Aldrich, 2.52 g) was dissolved in water (9 mL) and *tert*-butanol (9 mL) and the solution cooled to 0 °C. Methanesulfonic amide (174 mg) and the olefin **34b** (378 mg, 1.82 mmol) were added. Rapid stirring was continued for 24 h at 0 °C. Solid Na_2SO_5 (2.0 g) was added. After 30 min the reaction mixture was partitioned between water (20 mL) saturated aqueous NH_4Cl (20 mL) and ether (40 mL). The aqueous phase was extracted with ether (2 × 40 mL) and the combined organic layers dried and concentrated. The residue was purified by column chromatography (hexanes/MTBE 3:1) to provide the diol **35** (373 mg, 85 %) containing 10 % of the (1*R*,2*R*,3*R*)-diastereomer. Colorless solid; m.p. 128–129 °C; $[\alpha]_D = +8.9$ ($c = 0.73$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3290$ (s), 3029 (w), 2906 (w), 1494 (m), 1452 (m), 1121 (m), 1025 (s), 765 (m), 699 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.34-7.20$ (m, 10H), 4.53 (t, $J = 5.3$ Hz, minor)/4.48 (t, $J = 4.6$ Hz, major, 1H total), 3.89–3.84 (m, minor)/3.80–3.75 (m, major, 1H total), 2.90–2.81 (m, 1H), 2.66–2.64 (m, 1H), 2.26–2.20 (m, 1H), 1.35 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 144.55$, 141.76, 128.44, 128.28, 127.58, 126.52, 126.35, 80.02, 73.77, 41.55, 15.96 (major); 142.94, 141.53, 128.53, 128.31, 127.74, 126.79, 126.24, 79.28, 74.42, 19.30 (minor, separated signals); MS (EI, 70 eV): *m/z* (%): 242 (M^+, 2), 208 (3), 193 (4), 108 (100), 91 (24), 79 (27); $C_{16}H_{18}O_2$ (242.32): calcd C 79.31, H 7.49; found C 79.36, H 7.74.

(1*S*,2*S*,3*R*)-1,2-Epoxy-1,3-diphenylbutane (36): Under argon the diol **35** (347 mg, 1.43 mmol) was dissolved in CH_2Cl_2 (2 mL) and treated with trimethyl orthoformate (0.23 mL) and trimethylsilyl chloride (0.24 mL). After 2 h the volatiles were removed in vacuum and the residue was dissolved in MeOH (10 mL). Addition of K_2CO_3 (300 mg) was followed by 6 h of rapid stirring. The suspension was then poured into a mixture of saturated aqueous $NaHCO_3$ (40 mL) and water (40 mL) and extracted with ether (2 × 80 mL). The combined organic layers were dried, concentrated and the residue purified by column chromatography (hexanes/MTBE 25:1) to provide the epoxide **36** (250 mg, 78 %) as a 90:10 mixture of diastereomers. Colorless oil; $[\alpha]_D = -41.4$ ($c = 3.67$, $CHCl_3$); IR (film): $\tilde{\nu}_{max} = 3030$ (w), 2950 (m), 1605 (m), 1495 (m), 1460 (s), 885 (s), 760 (s), 695 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.38-7.24$ (m, 10H), 3.75 (d, $J = 7.7$ Hz, 1H), 3.15–3.09 (m, 1H), 2.96 (quin, $J = 7.0$ Hz, minor)/2.85 (quin, $J = 7.0$ Hz, major, 1H total), 1.50 (d, $J = 7.0$ Hz, major)/1.42 (d, $J = 7.2$ Hz, minor, 3H total); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 142.53$, 137.46, 128.55, 128.35, 127.98, 127.28, 126.75, 125.51, 67.09, 58.22, 42.05, 17.49 (major); 142.60, 137.57, 128.51, 128.40, 127.45, 66.87, 57.46, 41.59, 17.12 (minor, separated signals); MS (EI, 70 eV): *m/z* (%): 224 (M^+, 7), 167 (41), 118 (100), 105 (39), 91 (30); $C_{16}H_{16}O$ (224.30): calcd C 85.68, H 7.19; found C 85.74, H 7.14.

(2*R*,4*R*)-2,4-Diphenyl-3-pentanol (37): Under argon copper(I) cyanide (0.90 g, 10 mmol) was suspended in Et_2O (25 mL) and cooled to 0 °C. Within 15 min MeLi (1.61 M in Et_2O, 6.2 mL) was added dropwise. After 30 min at 0 °C the mixture was cooled to −78 °C. The epoxide **36** (179 mg, 0.80 mmol) in Et_2O (2 mL) was added. After 5 min $BF_3 \cdot OEt_2$ (0.17 mL) was added dropwise over 5 min. The yellow suspension was stirred 30 min at −78 °C and then brought to 0 °C for 2 h. Saturated aqueous NH_4Cl (40 mL) was added. Extraction with ether (3 × 100 mL) was followed by drying of the combined organic layers. The concentrated crude product was purified by column chromatography (hexanes/MTBE 8:1) to provide the diastereomerically pure alcohol **37** (130 mg, 68 %, > 98 % *ee*). Colorless solid; m.p. 80–81 °C; HPLC (OD, 5 % *i*PrOH, 0.9 mL min^{-1}, 215 nm): t_R/min = 6.79 (*SS*), 7.32 (*meso-s*), 8.58 (*RR*), 10.35 (*meso-r*); $[\alpha]_D = -0.95$ ($c = 1.68$, $CHCl_3$); IR (KBr): $\tilde{\nu}_{max} = 3569$ (s), 3059 (w), 3027 (m), 2962 (s), 2932 (m), 2874 (m), 1601 (m), 1493 (s), 1452 (s), 1377 (m), 968 (s), 764 (s), 701 (vs); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.40-7.26$ (m, 10H), 3.86 (t, $J = 6.0$ Hz, 1H), 2.90 (quin, $J = 7.0$ Hz, *dl*)/2.81 (quin, $J = 6.7$ Hz, *meso-r*, 2H total), 1.64–1.62 (m, *meso-r*)/1.40–1.30 (m, 7H total); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 145.38$, 143.40, 128.44, 128.38, 128.37, 127.87, 126.56, 126.28, 79.93, 42.87, 42.57, 19.03, 15.27 (*dl*); 145.19, 128.57, 127.52, 126.35, 80.65, 42.32, 15.42 (*meso-r*); MS (EI, 70 eV): *m/z* (%): 240 (M^+, 3), 135 (23), 106 (100), 91 (55), 77 (20), 43 (41); $C_{17}H_{20}O$ (240.35): calcd C 84.96, H 8.39; found C 84.75, H 8.58. A small amount of *meso-s* **37** was isolated: colorless oil; IR (film): $\tilde{\nu}_{max} = 3570$ (s), 3060 (w), 3030 (w), 2960 (s), 2930 (m), 2875 (w), 1605 (w), 1495 (m), 1450 (s), 1385 (m), 1115 (m), 965 (m), 765 (s), 700 (s); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.35-7.27$ (m, 10H), 3.87-3.81 (m, 1H), 2.79 (quin, $J = 6.9$ Hz, 2H), 1.39 (d, $J = 7.0$ Hz, 6H), 1.36-1.34 (m, 1H); ^{13}H NMR ($CDCl_3$, 75 MHz): $\delta = 143.38$, 128.52, 128.34, 126.49, 79.86, 42.96, 19.34; MS (EI, 70 eV): *m/z* (%): 240 (M^+, 3), 135 (32), 106 (100), 91 (48), 43 (27); $C_{17}H_{20}O$ (240.35): calcd C 84.96, H 8.39; found C 84.93, H 8.51.

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