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Chiral ferrocene derivatives containing a 2,2′-bridged binaphthyl moiety

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Abstract

Ten novel chiral ferrocene derivatives including some of interest as auxiliaries in asymmetric catalysis such as aminophosphines **2a**–**2c** and aminoalcohols **20** and **21** were selectively prepared in yields of 56–82% either from the corresponding bromoamines **12a**,**b** and **18**, respectively, via metal–halogen exchange or from ferrocenylamine **6** via *ortho*-lithiation. All of them contained the C_2-symmetrical 3,5-dihydro-4*H*-dinaphth[2,1-c:1′,2′-e]azepine subunit as the chirality inducing fragment. Relative configurations were determined by crystal structure analyses of **2a** and **2b**.

1. Introduction

Within the plethora of chiral structures that have been tested as auxiliaries and ligands[1] in stoichiometric and catalytic asymmetric syntheses, it is noteworthy that two groups have attracted particular attention: due to their generally high enantioselection in various asymmetric transformations, atropisomeric biaryls (mostly binaphthyls)[2] and planar chiral ferrocene derivatives[3] are frequently applied in ligand design.

Since it is generally accepted that crucial requirements for high asymmetric induction are large chiral bias controlling the reaction volume, as well as defined catalyst geometry with only moderate conformational freedom, it appears that these features are being well met by the above-mentioned auxiliaries. Consequently, it should be worth investigating ligand structures which combine both types of stereogenic units in a single molecule. To the best of our knowledge, however, their synthesis has not been attempted. The present paper deals with a stereoselective access to various difunctional ferrocene derivatives bearing an atropisomeric 3,5-dihydroazepine substituent.

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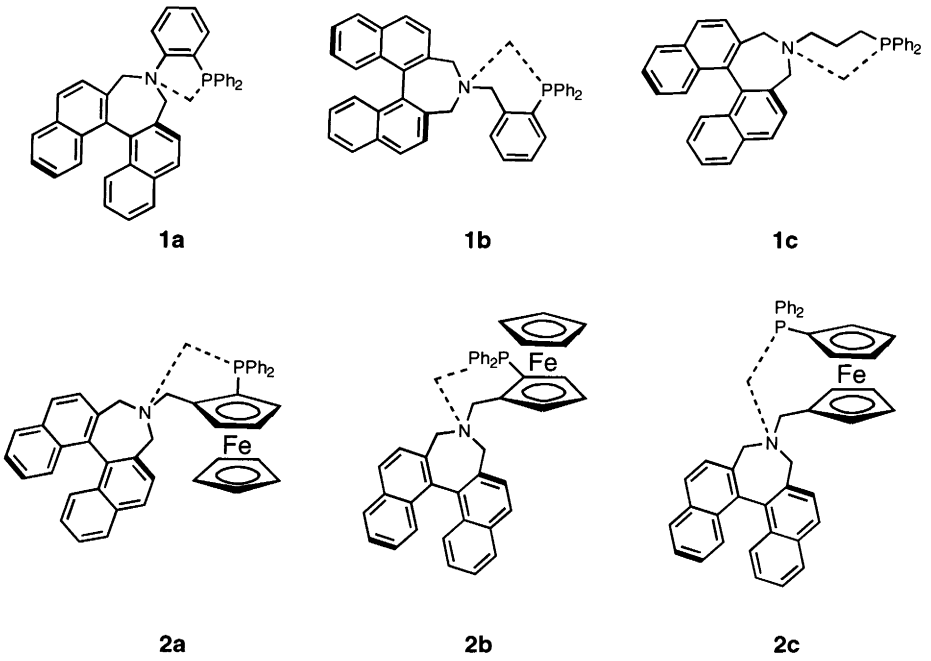
The original starting point for our interest in this class of ferrocene ligands was our previous work on binaphthyl-based aminophosphine ligands of type **1** which have proven their efficiency as chiral ligands in asymmetric carbon–carbon coupling reactions,[4] especially in allylic alkylations.[5] One structural parameter in catalytically active chelate complexes of type **1a–c** is the bite angle, governed by the rigidity and length of the P–N linkage (Fig. 1).[6]



1a **1b** **1c**

2a **2b** **2c**

Fig. 1.

As an extension to our work the introduction of a biscyclopentadienyl fragment was attempted for the following reasons: a ferrocene moiety, homo- or hetero-disubstituted, changes the bite angle in a chelate complex of **2a**, **2b** or **2c**, respectively, in comparison to phenylene- and benzylidene-bridged ligands **1a** and **1b**. Moreover, in the case of homoannular disubstitution (**2a**, **2b**), either the area above or below the basal plane, depending on the planar chirality of the ferrocene unit, is assumed to be sterically blocked in the derived square planar transition metal complexes. Both features may have important consequences with regard to catalytic activity as well as asymmetric induction, particularly in allylic substitution reactions.[7]

2. Results and discussion

The synthesis of **2a** proceeded straightforwardly[8] (Scheme 1). Mannich base **3** provided easy access to methiodide **4**.[9] Treatment of **4** with a mixture of aqueous ammonia and benzene at elevated temperatures afforded aminomethylferrocene **5** in 80% yield. This was dibenzylated with 2,2′-bis(bromomethyl)-1,1′-binaphthyl[10] to form the *N*-substituted dihydroazepine derivative **6** (79%). *ortho*-Lithiation and subsequent treatment with chlorodiphenylphosphine resulted in a mixture of three isomeric aminomonophosphines. Regardless of the lithiation conditions product **2a** was always formed predominantly. Small amounts of stereoisomer **2b** (8%) and of heteroannularly substituted product **2c** (7%) were isolated as by-products, which were found to be inseparable by chromatographic methods. Under optimized conditions

the more polar stereoisomer **2a** was formed in 65% yield for which the relative configuration (S_a*)(S_m*)[11] was determined by crystal structure analysis. Neither extended variation of the lithiation conditions nor attempted lithiation of the trimethylsilyl protected aminoferrocene **7,** carried out in order to obtain **2c** or **2b** selectively, were successful (Scheme 1):[12] only starting material could be isolated in the latter case. From this we suspect that the bulky trimethylsilyl substituent might restrict the rotation of the dihydroazepine subunit so much that it no longer adopts a suitable conformation for the stabilization of the *ortho*-lithiated intermediate.

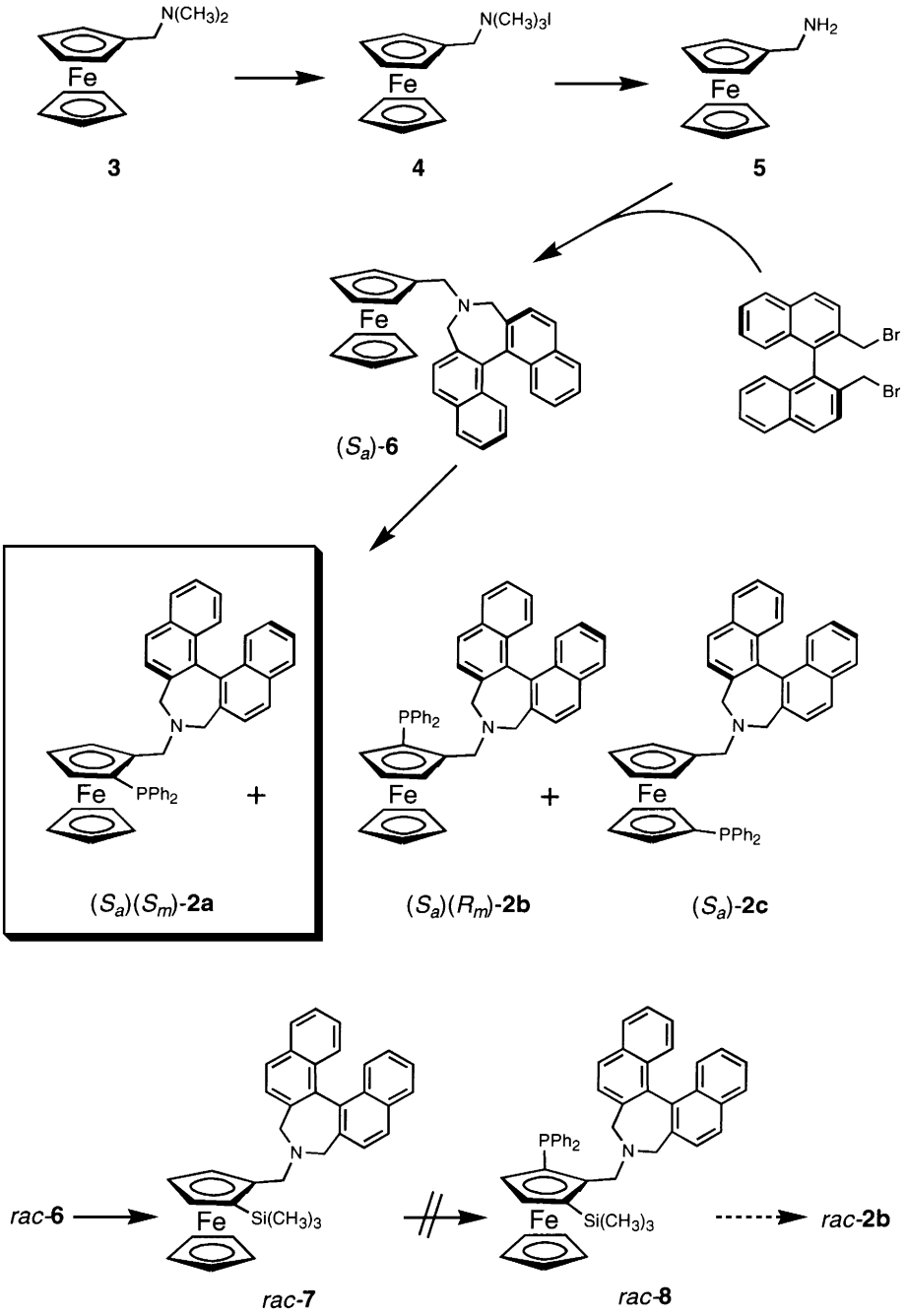
Since a method for selective access of both isomers of *ortho*-substituted ferrocene ligands, **2a** and **2b**, was desired due to their expected different behaviors in asymmetric induction, we decided to follow a more direct path via aminobromides **12a** and **12b** (Scheme 2). *ortho*-Lithiation of the Mannich base **3** followed by treatment with tributylboronate afforded aminoboronic acid **9** which was converted to aminobromide **10**. Modification of reported procedures[13] yielded **10** in 61% yield (from **3**). Aminolysis of the methiodide of **10** gave **11** (81%), which was alkylated in a similar manner to **5**, resulting in a chromatographically separable 1:1 mixture of stereoisomers **12a** and **12b** (82%). Halogen exchange using *s*-BuLi at room temperature followed by reaction with chlorodiphenylphosphine yielded exclusively either **2a** (77%) or **2b** (65%), respectively.

The relative configuration of stereoisomers **2a** and **2b**, and consequently of the precursors **12a** and **12b** as well, was determined via X-ray structure analyses (Figs. 2 and 3). For the less polar compound **2b**, eluted preferentially from a silica gel chromatography column, the (S_a*)(R_m*) configuration was found, while **2a**, the main product of the *o*-lithiation, showed the configuration (S_a*)(S_m*).

A similar concept was followed in the selective preparation of the hetero-substituted isomer **2c** (Scheme 3). Starting from 1,1′-dibromoferrocene **13**[14] the *mono*-lithio intermediate[14b,15] was treated with Eschenmoser's salt[16] to give Mannich compound **14** in 56% yield. The use of *n*-BuLi resulted in the formation of considerable amounts of quaternary ammonium salt **15** (33%). Both **15** and the methiodide of **14**, **16**, afforded on treatment with aqueous ammonia the primary amine **17**, which was isolated as a moderately stable brown oil (56–58%). Cyclization with 2,2′-bis(bromomethyl)-1,1′-binaphthyl gave **18** (78%) which was finally converted into aminophosphine **2c** (81%), from which a crystal structure could also be obtained (Fig. 4). On repeating the synthesis of **2a**–**2c** with enantiomerically pure (S_a)-2,2′-bis(bromomethyl)-1,1′-binaphthyl the enantiomers (S_a)(S_m)-**2a**, (S_a)(R_m)-**2b**, and (S_a)-**2c** were obtained with absolute configurations drawn in Schemes 1–3.

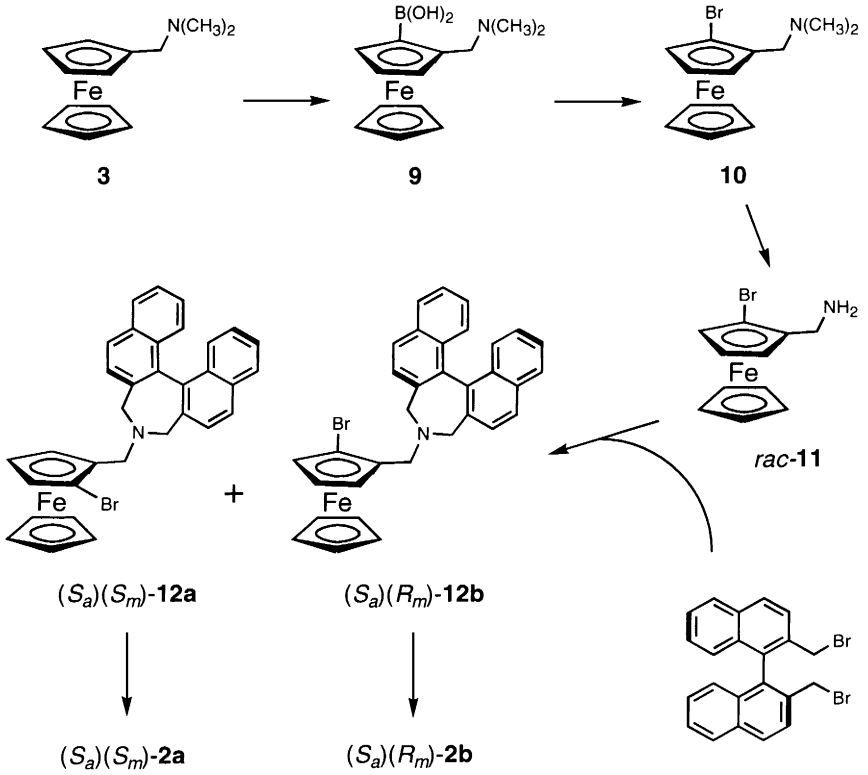
These stereoselective (via **6**) or stereospecific routes (via **12a**,**b**) to planar chiral ferrocene compounds with a C_2-symmetrical dinaphthdihydroazepine entity can be further extended to obtain numerous difunctionalized derivatives. To demonstrate the feasibility of this method, a group of chiral ferrocenyl compounds with and without a binaphthyl fragment has been synthesized, particularly those which are of interest from the viewpoint of chiral catalysis, either as ligands or as precursors for their synthesis (Scheme 4). Depending on the ease of separating diastereomeric products, either the halide–lithium exchange (procedure *B*) or *ortho*-lithiation protocol (procedure *A*) has been applied. For the latter case the completeness of the *ortho*-lithiation step was confirmed by analyzing the product mixture obtained after quenching with D_2O. Mass spectrometry revealed the formation of ≥97% of deuterated products from which the predominant isomer (S_a*)(R_m*)-**19** was obtained pure by recrystallization (Table 1). Under conditions similar to that outlined for **2a** and **2b**, aminoalcohols **20** and **21**, aminoaldehyde **22**, phenylthioether **23**, amino boronic acid **24**, and iodoamine **25** could be obtained in good yields (Table 1).

While aminoalcohols like **20** and **21** serve as efficient auxiliaries, for instance in the enantioselective addition of Et_2Zn to aldehydes,[17] the iodo compound **25** was effective in palladium-mediated coupling reactions. A Suzuki reaction[18] with benzene boronic acid afforded biaryl **26** (69%), while treatment of **25** with KCN/CuCN in refluxing THF[19] yielded aminonitrile **27** (82%) which was smoothly reduced with



Scheme 1.

AlH_3[20] to give diamine **28** (90%). Alternatively, the binaphthyl moiety can be removed with Ac_2O to leave planar chiral bromo or iodo acetates **29** and **30** only. These, in turn, may serve as precursors for the synthesis of various ferrocene derivatives. As examples, aldehydes **33** and **34** were prepared. In these cases the chiral auxiliary was recovered as its *N*-acetyl derivative in nearly quantitative yield (93–98%) which could be converted into the useful 3,5-dihydro-4*H*-dinaphth[2,1-c:1′,2′-e]azepine.[21]



Scheme 2.

2.1. X-Ray structure analyses

The crystal structures of **2a**, **2b** and **2c** have been determined in order to unambiguously establish their relative configurations and to learn more about the geometric variations of these novel ligands. Racemic compounds were used for this study. Crystallographic data are given in the Experimental section, selected structural parameters are listed in Table 2, and views of the molecules are shown in Figs. 2–4. It was previously found that (S_a)(S_m)-**2a** crystallized as an acetone solvate in the chiral monoclinic space group $P2_1$ with one molecule in the asymmetric unit.[8] The racemic form of **2a** described in the present work crystallizes in the non-chiral centrosymmetric space group $P2_1/c$ without solvent but with two independent molecules in the asymmetric unit, designated A- and B-molecules. Due to their similar appearance, only the A-molecule is depicted in Fig. 2a. In this structure for the ferrocenyl unit a staggered arrangement of the two cyclopentadienyl (Cp) rings with an interplanar angle of 4.2° is found. The *N*-methyl-dinaphthazepine moiety adopts a twisted chair conformation and is oriented off from the ferrocenyl group with *trans*-type torsion angles Fe–C6–C11–N=−162.5° and C6–C11–N–C13=167.7°. Thus, the lone pair of N is directed approximately towards the *exo*-oriented phenyl ring 1 of the PPh_2 group, whereas the lone pair of phosphorus is approximately perpendicular to the P···N vector (Fig. 2a). The two naphthyl groups are mutually inclined at 61.0° (Table 2). The C–N–C bridge imposes some strain on the binaphthyl system, causing a notable outward bending combined with some twist of the terminal parts of the naphthyl groups in response to their side-on contacts near C22 and C32 (C22–C32=3.22 Å, H22–H32=2.67 Å). Interplanar angles between the inner and outer C_6 rings of 3.2° for naphthyl-1 (C14–C33) and 0.3° for naphthyl-2 (C24–C33) are found. Further deviations from ideal geometry of the binaphthyl entity are caused by 1,8-*peri* interactions which cause several bond angle deformations

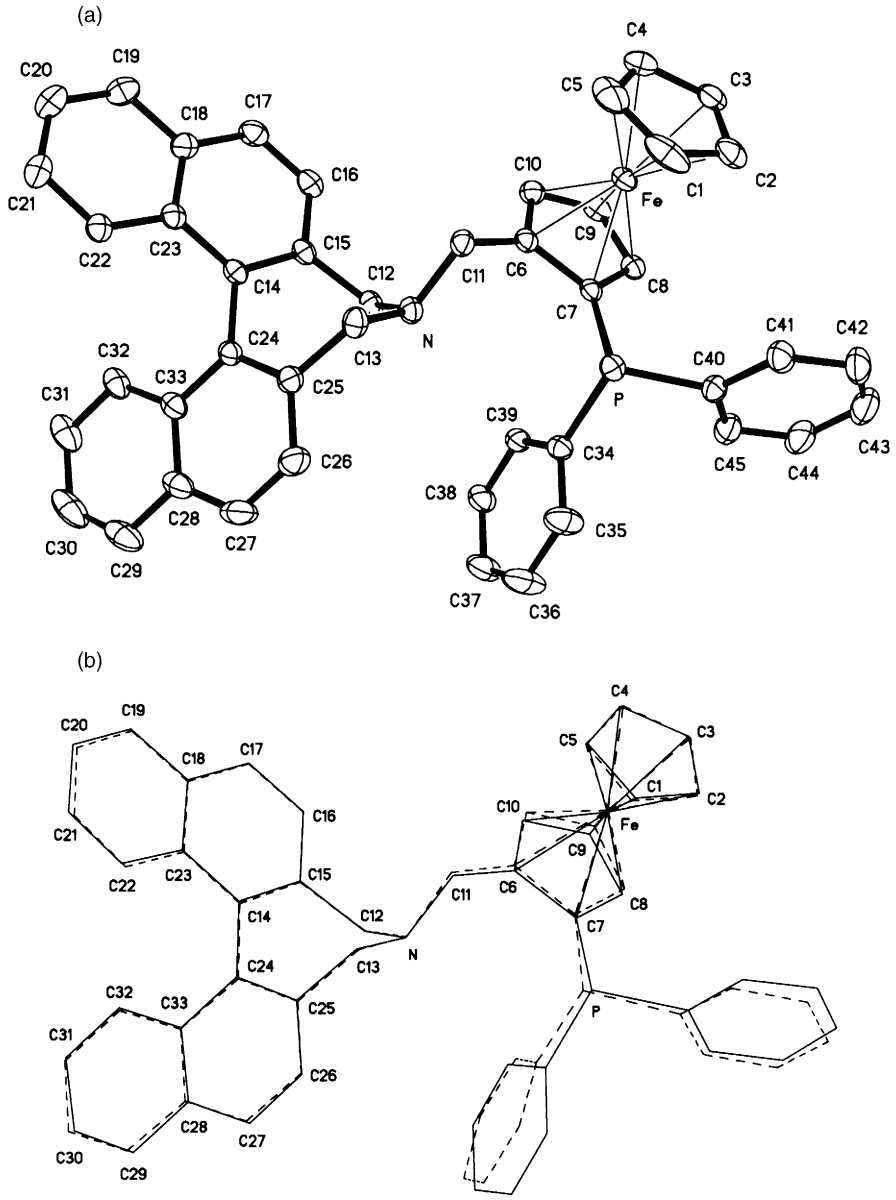


Fig. 2. (a) Thermal ellipsoid plot (20% ellipsoids) of the A-molecule in **2a**. Hydrogen atoms omitted. (b) Least-squares fitted superposition of A- and B-molecules in **2a**. View direction as in (a)

(see Table 2).[22] Some strain is also released by an out-of-plane bending of C12 and C13 from the benzene rings to which they are bonded (C12=0.189 Å, C13=0.094 Å; both displacements toward the ring center). The PPh_2 group adopts a conformation with one phenyl ring directed straight away from Fe (*exo*-orientation, Fe–C7–P1–C34=175.4°), and the second phenyl ring exposes its π-electrons to Fe (*endo*-orientation, Fe–C7–P–C40=−81.4°). The B-molecule of compound **2a** is very similar to the A-molecule (Table 2) except for some small but visible differences in torsion angles and dimensions depending on them (Fig. 2b). The background for the observed similarity of the two crystallographically independent molecules in **2a** is that the crystal lattice exhibits a pronounced pseudosymmetry with non-crystallographic local glide planes parallel to (001) at $z \approx \frac{1}{4}, \frac{3}{4}$, glide component a/2, which mutually relate

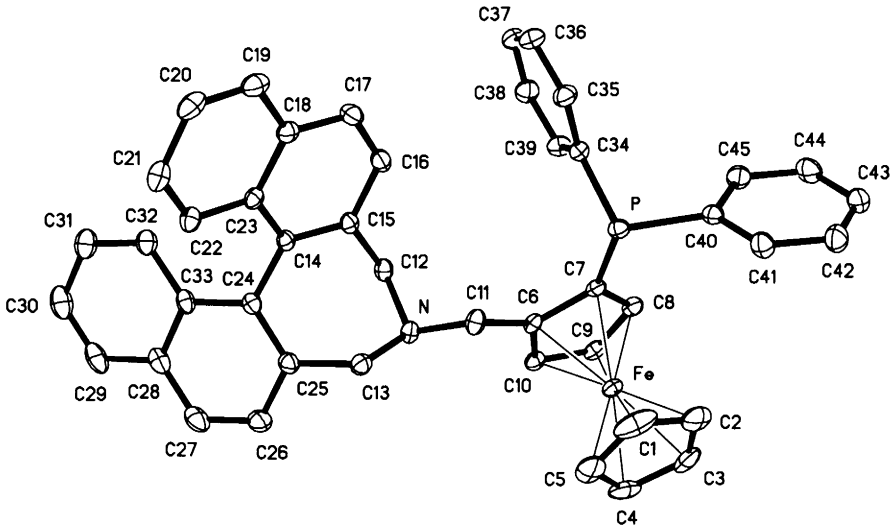
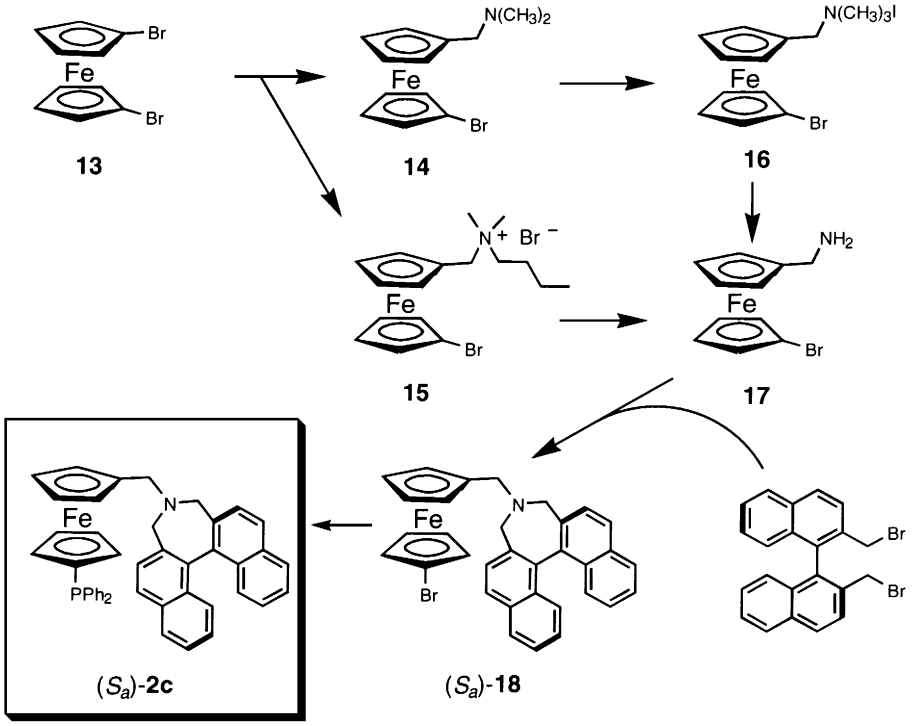


Fig. 3. Molecular structure of **2b** in crystalline state



Scheme 3.

A- with B-molecules and provide them with similar environments in slab-like portions of the structure. Dissimilar environments for A- and B-molecules at the boundaries of the slabs ($z \approx 0, \frac{1}{2}$) obviously cause their partial differences. It is worth noting that the acetone solvate of enantiopure **2a**[8] is similar in conformation (Fig. 2), although the spatial arrangement of the molecules in this compound is not related to the unsolvated crystalline **2a** described here.

Compound **2b** crystallizes in the triclinic centrosymmetric space group $P\bar{1}$ with one molecule in the

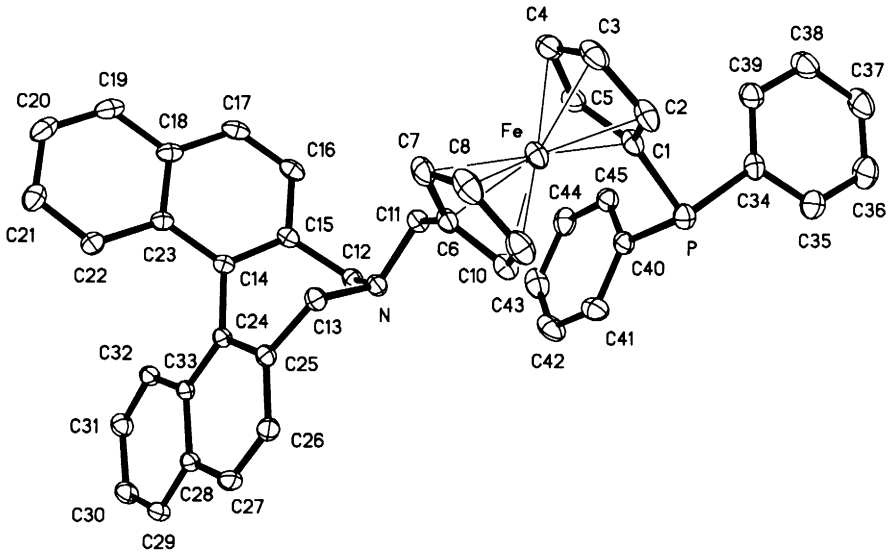


Fig. 4. Molecular structure of **2c**·$(CH_3)_2CO$ in crystalline state. Hydrogen atoms and acetone molecule omitted

asymmetric unit (Fig. 3). Many general features of **2a** are retained in this compound, e.g. bond length pattern, approximately staggered conformation of the Cp rings, strain distortion of the binaphthazepine unit, and orientation of PPh_2 relative to the ferrocenyl group. However, the *N*-methyl-binaphthazepine group adopts a significantly different orientation with Fe–C6–C11–N=−121.8° instead of the −162.5° and –155.9° for **2a**. Moreover, C6–C11–N–C13=151.5° is about 15° smaller than observed in **2a**. The two most obvious consequences are: the lone pair of nitrogen is now directed away from phosphorus and the P···N distance increased from ≈3.5 Å in **2a** to 4.68 Å in **2b**. As intramolecular steric hindrance of the amino and phosphino substituents cannot be invoked for explanation, these steric features must result from crystal packing.

Compound **2c** crystallizes from acetone as a relatively stable acetone solvate **2c**·$(CH_3)_2CO$ of space group $P\bar{1}$ with one molecule in the asymmetric unit. As shown in Fig. 4, the hetero-disubstituted isomer **2c** prefers a different conformation with eclipsed arrangement of the Cp rings. While the orientation of the PPh_2 group corresponds in principle to that of the foregoing compounds (see torsion angles involving P in Table 2), the *N*-methyl-dinaphthazepine group shows much distortion (see naphthyl bending angles in Table 2) and adopts a different orientation relative to the Cp ring. Again, crystal packing effects are considered responsible. The acetone molecules fill open gaps in the structure and are anchored via weak C–H···O hydrogen bond-like interactions to two aromatic CH groups with H···O distances of 2.67 and 2.80 Å.

In summary, the following main features can be deduced from the crystal structures of **2a**, **2b** and **2c**·$(CH_3)_2CO$: (i) the conformation of the ferrocenyl group varies between staggered and eclipsed; (ii) the orientation of the PPh_2 group at the ferrocenyl moiety is fairly constant, with one phenyl *exo*-oriented at Fe–C_{Cp}–P–C_{Ph} close to 180° and one phenyl *endo*-oriented with the π-electrons exposed to Fe; (iii) the dinaphthazepine unit shows distortions due to internal strain; and (iv) the orientation of the *N*-methyl-dinaphthazepine moiety relative to the ferrocenyl group varies widely by considerable rotational freedom of the C_{Cp}–CH_2–N bridge.

Table 1
Stereoselective synthesis of 2-substituted *N*-ferrocenylmethyl-3,5-dihydro-4*H*-dinaphthazepine derivatives

compound	yield[a] (*procedure*[b])	$[\alpha]_D^{20}$	mp.:
(S_a*)(S_m*)-**2a**	65 (*A*), 77 (*B*)	--	222-225 °C
(S_a)(S_m)-**2a**	65 (*A*)	-31.7	136-140 °C
(S_a*)(R_m*)-**2b**	65 (*B*)	--	255-260 °C
(S_a)(R_m)-**2b**	65 (*B*)	+207	foam
(S_a*)(S_m*)-**7**	69 (*A*)	--	foam
(S_a*)(R_m*)-**19**	84 (*A*)[c]	--	199-201 °C
(S_a*)(S_m*)-**20**	73 (*A*)	--	223-227 °C
(S_a)(S_m)-**20**	63 (*A*)	+95.0	foam
(S_a*)(S_m*)-**21**	70 (*A*)	--	256-258 °C
(S_a)(S_m)-**21**	69 (*A*)	-100.7	110-115 °C
(S_a)(S_m)-**22**	82 (*B*)	-80.5	foam
(S_a*)(S_m*)-**23**	75 (*A*)	--	112-116 °C
(S_a*)(R_m*)-**24**	64 (*A*)	--	225-235 °C (dec.)
(S_a)(S_m)-**25**	79 (*A*)	+58.9	114-119 °C

[a] isolated yield. [b] *Procedure A*: *via* stereoselective ortho lithiation of **6**; *Procedure B*: *via* halogen-lithium exchange from **12a** or **12b**, respectively, see Experimental. [c] mixture of isomers.

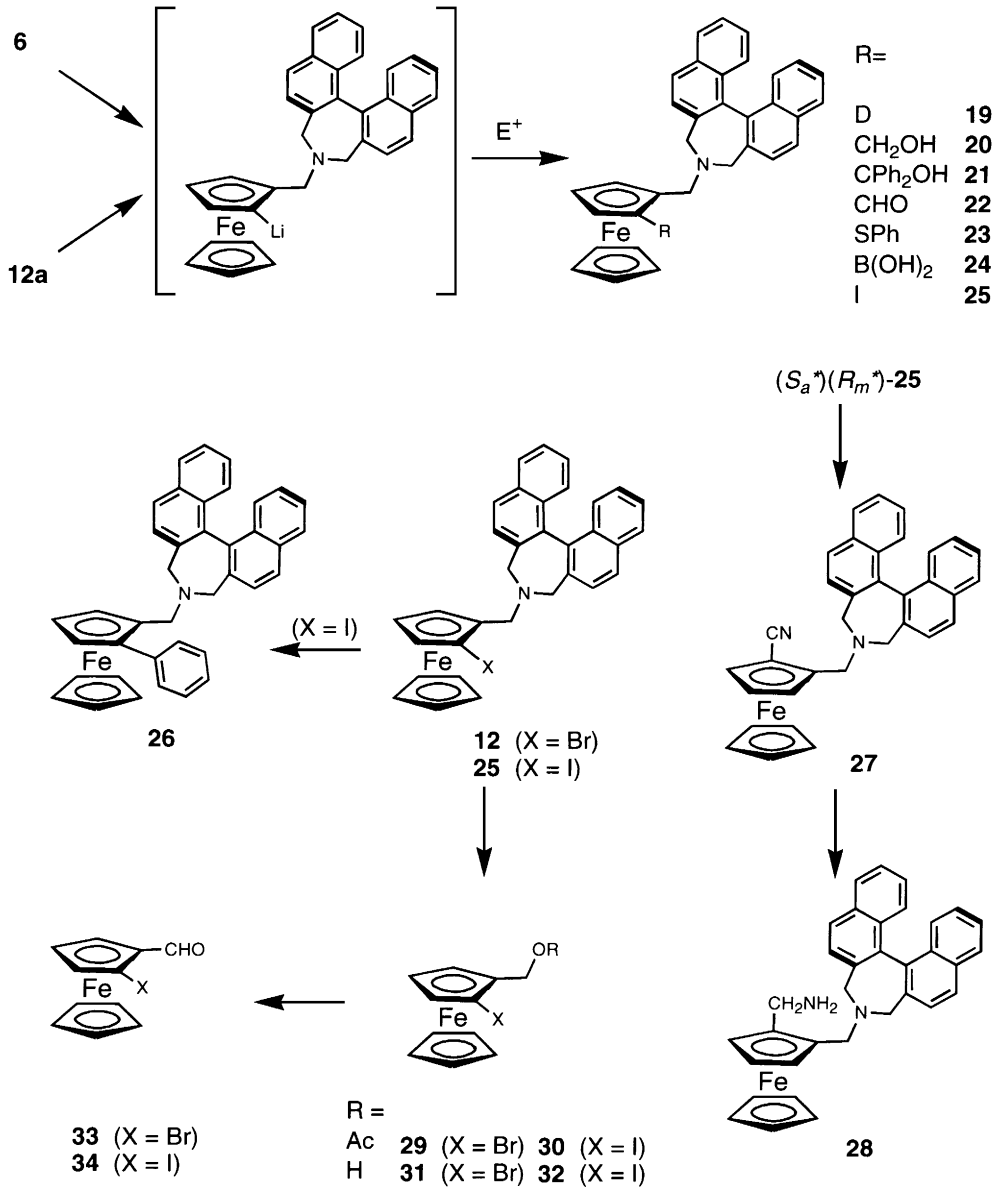
3. Conclusions

We report on a convenient preparation method for aminomethylferrocene **5** and bromoaminomethylferrocenes **11** and **17**, all of which represent versatile precursors for the synthesis of a novel class of chiral ferrocenylamines. From these intermediates a practical high-yielding access to various difunctionalized ligands including aminophosphines and aminoalcohols with defined metallocene chirality was explored, either by *ortho*-lithiation or halogen exchange protocol. The relative stereochemistry of the new ferrocenyl-binaphthyl donors was elucidated by X-ray structure analysis. The potential of new ligands as chiral inducers in asymmetric catalysis is currently under investigation and results will be reported in due course.

4. Experimental

4.1. General

Melting points: the Kofler melting point apparatus was uncorrected. NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400.13 MHz (^{1}H), 100.62 MHz (^{13}C), and 161.98 (^{31}P), respectively, or on a Bruker DPX 250 spectrometer at 250 MHz (^{1}H) and 62.90 MHz (^{13}C), respectively, in $CDCl_3$ if not otherwise noted; chemical shifts as δ values are reported in ppm; calibration: ^{1}H: tetramethylsilane or $CHCl_3$ (0.00 or 7.24 ppm); ^{13}C: $CHCl_3$ (77.00 ppm); ^{31}P: H_3PO_4 (85%, 0.00 ppm). Coupling patterns are designated as s(inglet), d(oublet), t(riplet), p(seudo), and b(road). ^{13}C NMR spectra were recorded



Scheme 4.

in a *J*-modulated mode; undesignated signals refer to CH resonances. In areas of both extreme signal overlapping and splitting due to PC-coupling (compound **2a**), an assignment was not possible; such signals of unclear relationships are underlined. MS: MAT 900, EI (70 eV) or FD. Optical rotations were measured using a Perkin–Elmer 241, thermostatted. Elemental analyses were performed at the Institute of Physical Chemistry (University of Vienna).

Petroleum ether (PE), CH_2Cl_2, $CHCl_3$, and ethyl acetate (EA) were distilled. THF was distilled from potassium benzophenone ketyl, diethylether from $LiAlH_4$, and DMF from CaH_2 under reduced pressure. Triethylamine was filtered over alumina (activity I), *n*-BuLi was used as a 1.6 molar solution in hexane (Aldrich), *s*-BuLi as a 1.3 molar solution in cyclohexane (Fluka). Chlorodiphenylphosphine and chlorotrimethylsilane were distilled and stored under argon. Racemic and enantiomerically pure

Table 2
Selected geometric parameters [Å, °] of the crystal structures of **2a**, **2b**, and **2c**·$(CH_3)_2CO$

	2a A-molecule	**2a** B-molecule	**2b**	**2c**·$(CH_3)_2CO$
<Fe-C>$_{Cp(1)}$	2.044(3)	2.046(3)	2.036(3)	2.047(2)
<Fe-C>$_{Cp(2)}$	2.048(2)	2.050(2)	2.051(2)	2.049(2)
<C-C>$_{Cp(1)}$	1.404(5)	1.400(4)	1.381(4)	1.421(3)
<C-C>$_{Cp(2)}$	1.424(3)	1.424(3)	1.424(3)	1.419(3)
angle Cp(1)/Cp(2)	4.2(2)	4.4(2)	3.6(2)	0.9(2)
Fe-C6-C11-N	-162.5(2)	-155.9(2)	-121.8(2)	159.7(1)
C6-C11-N-C12	-66.4(3)	-69.6(2)	-84.2(2)	179.3(2)
C6-C11-N-C13	167.7(2)	165.8(2)	151.5(2)	54.3(2)
Fe-C7-P-C34 [a)]	175.4(1)	175.1(1)	-173.4(1)	178.5(1)
Fe-C7-P-C40 [a)]	-81.4(2)	-81.5(2)	80.7(1)	74.0(2)
C7-P-C34-C35 [a)]	-179.9(2)	-166.4(2)	159.6(2)	162.9(2)
C7-P-C40-C41 [a)]	97.2(2)	97.1(2)	-106.2(2)	-115.8(2)
angle naphtyl-1/naphthyl-2 [b)]	61.0(1)	60.9(1)	61.4(1)	67.3(1)
bending angle naphthyl-1 [c)]	3.2(1)	5.2(2)	6.4(1)	5.1(1)
bending angle naphthyl-2 [c)]	0.25(2)	1.5(2)	1.8(2)	5.4(1)
N···P (non-bonding)	3.593(2)	3.424(2)	4.679(3)	5.855(3)
deformations attributed to 1,8-*peri* interactions:				
C22-C24	3.051(4)	3.013(4)	3.005(3)	3.009(3)
C32-C14	3.008(4)	3.012(4)	3.011(3)	2.996(3)
H22-C24	2.736	2.692	2.680	2.688
H32-C14	2.683	2.694	2.689	2.670
C14-C22	2.511(3)	2.505(3)	2.512(3)	2.511(3)
C24-C32	2.504(4)	2.508(4)	2.516(3)	2.506(3)
C17-C19	2.472(4)	2.486(5)	2.491(4)	2.479(4)
C27-C30	2.480(6)	2.489(6)	2.470(4)	2.476(3)

[a)] for **2c**·$(CH_3)_2CO$ C1 instead of C7.
[b)] angle sensitive to bending of naphthyl groups, in particular for **2c**·$(CH_3)_2CO$.
[c)] angle between the least squares planes of the inner and the terminal C_6 ring of the naphthyl group.

2,2′-bis(bromomethyl)-1,1′-binaphthyl,[10] 1-dimethylaminomethylferrocene-2-boronic acid,[13] and 1,1′-dibromoferrocene[14] were prepared according to reported procedures. Column chromatography was performed on silica gel Si 60, 25–40 μm (Merck) or alumina, activity II–III, 63–200 μm (Merck). All the other chemicals were of analytical grade and used without further purification.

4.2. Aminomethylferrocene **5**

Methiodide **4** (2.012 g, 5.23 mmol) was suspended in a mixture of concentrated aqueous ammonia (30 ml) and benzene (60 ml). This was heated in a pressure tube or steel autoclave with glass liner to 100°C with vigorous stirring. The progress of the reaction could be followed visually since the color intensity of the aqueous phase decreased while that of the organic phase increased. The reaction was found to be complete after 24–48 h. The organic layer was separated and evaporated. The product was purified by Kugelrohr distillation; yield: 898 mg (80%) of **5**.[23]

4.3. N-*Ferrocenylmethyl-3,5-dihydro-4*H-*dinaphth[2,1-c:1′,2′-e]azepine* **6**

Aminomethylferrocene **5** (1.027 g, 4.77 mmol), 2,2′-bis(bromomethyl)-1-1′-binaphthyl (2.099 g, 4.77 mmol), and triethylamine (2.64 ml, 4 equiv.) were dissolved in 60 ml of benzene (p.a.) in a Schlenk tube and degassed. The reaction mixture was heated to reflux for 18 h under argon and the progress of the reaction was monitored via TLC (SiO_2, EA:PE=30:70). The solvent was removed in vacuo and the residue was partitioned between CH_2Cl_2 (50 ml) and water (50 ml). The organic phase was separated, washed with water and brine, and dried (K_2CO_3). After evaporation of the solvent the crude product was chromatographed on silica gel (column: 35×2 cm, EA:PE=30:70) to give 1.855 g (79%) of **6** as a yellow powder; mp: 185–195°C (dec.). ^{1}H NMR (250 MHz) δ: 3.12 (2H, d, *J*=12.4 Hz), 3.39 (1H, d, *J*=12.3 Hz), 3.50 (1H, d, *J*=12.3 Hz), 3.69 (2H, d, *J*=12.4 Hz), 4.10 (5H, s), 4.11 (1H, m), 4.17 (1H, m), 4.19 (1H, m), 4.38 (1H, m), 7.24 (2H, bpt, *J*=7.5 Hz), 7.44 (4H, m), 7.53 (2H, d, *J*=8.5 Hz), 7.93 (4H, bd, *J*≈8.0 Hz). ^{13}C NMR (62.9 MHz) δ: 54.98 (CH_2), 55.21 (CH_2), 68.11, 68.18, 68.58 (5×CH), 70.30 (2×CH), 84.39 (C), 125.36, 125.68, 127.46, 127.90, 128.19, 128.27, 131.39 (C), 133.10 (C), 133.47 (C), 135.06 (C). MS (FD) *m/z*: 493.3 (100%, M^+). Anal. calcd for $C_{33}H_{27}FeN$: C, 80.33; H, 5.52; N, 2.84; Fe, 11.32; found: C, 80.12; H, 5.49; N, 2.68.

In a similar way, (S_a)-**6** was obtained from (S_a)-2,2′-bis(bromomethyl)-1,1′-binaphthyl as a foam; $[\alpha]_D^{20}$ –7.0 (*c* 0.53, CH_2Cl_2).

4.4. (S_a*)(S_m*)- and (S_a)(S_m)-N-*(1-Diphenylphosphino-2-ferrocenylmethyl)-3,5-dihydro-4*H-*dinaphth-[2,1-c:1′,2′-e]azepine* ***2a*** *(procedure* A*)*

To a suspension of amine **6** (200 mg, 0.41 mmol) in degassed ether (10 ml) was added a solution of *s*-BuLi (0.93 ml, 1.2 mmol) at room temperature under argon. This was stirred for 4 h to give a slightly turbid red–brown solution of mono-lithiated products. The mixture was cooled to −78°C and chlorodiphenylphosphine (265 mg, 1.2 mmol, 215 μl) was introduced by a microliter syringe. After a few minutes the color changed to pale yellow, whereupon the cooling bath was removed and a heavy yellow precipitate formed at room temperature. Water (5 ml) and EA (10 ml) were added and the mixture was stirred for 0.5 h. The organic layer was separated, washed with water and brine, and evaporated. The residue was subjected to column chromatography (SiO_2, 35×2 cm, EA:PE:Et_3N=19:80:1) to give two fractions: (A) 40 mg (8% of **2b**, 7% of **2c**, according to NMR integration); followed by (B) 179 mg (65%) of **2a** which crystallized from acetone as orange–red crystals; mp: 222–225°C (dec.). The use of *n*-BuLi instead of *s*-BuLi gave a similar product composition but incomplete conversion; lithiation at 0°C or rt, >10 h, afforded **2a** in 55–58% yield. ^{1}H NMR (400 MHz) δ: 2.66 (2H, bd, *J*=12.0 Hz), 3.44 (1H, bd, *J*≈13.7 Hz), 3.45 (2H, d, *J*=12.0 Hz), 3.76 (1H, dd, *J*=13.7, 1.5 Hz), 3.80 (1H, bs), 4.03 (5H, s), 4.32 (1H, pt, *J*=2.5 Hz), 4.65 (1H, bs), 6.87 (3H, m), 7.14 (2H, m), 7.22 (2H, m), 7.32 (2H, d, *J*=7.9 Hz), 7.34–7.44 (7H, m), 7.58 (2H, m), 7.85 (2H, d, *J*=8.4 Hz), 7.92 (2H, d, *J*=8.4 Hz). ^{13}C NMR (62 MHz,

320 K) δ: 52.90 (CH_2, d, J=7.4 Hz), 53.90 (CH_2), 68.86, 69.75 (5×CH, d, J=1 Hz), 71.76 (d, J=4.6 Hz), 72.91 (d, J=4.0 Hz), 77.80 (C, d, J=8.8 Hz), 91.15 (C, d, J=24.1 Hz), 125.12, 125.47, 127.36, 127.44, 127.46, 127.49, 127.88 (d, J=5.0 Hz), 128.04, 128.20, 128.75, 131.45 (C), 132.76 (d, J=18.5 Hz), 133.08 (C), 133.93 (C), 134.87 (C), 135.00 (d, J=20.4 Hz), 138.21 (C, d, J=9.2 Hz), 139.84 (C, d, J=8.7 Hz). ^{31}P NMR (162 MHz) δ: −21.89 (s). MS (FD) *m/z*: 677.5 (100%, M^+). Anal. calcd for $C_{45}H_{36}FeNP$: C, 79.77; H, 5.35; N, 2.07; P, 4.57; found: C, 79.54; H, 5.61; N, 1.93; P, 4.81.

Similarly, (S_a)(S_m)-**2a** was obtained from (S_a)-**6**; mp: 136–140°C. $[\alpha]_D^{20}$ −31.7 (*c* 0.7, CH_2Cl_2).

4.5. (S_a)(S_m*)-N-(2-Trimethylsilyl-1-ferrocenylmethyl)-3,5-dihydro-4H-dinaphth[2,1-c:1′,2′-e]-azepine **7***

Procedure *A* was applied with chlorotrimethylsilane (3 equiv.) as the electrophile. The residue was subjected to column chromatography (SiO_2, 35×2 cm, EA:PE=10:90) to give 69% of **7** as a yellow foam. ^{1}H NMR (400 MHz) δ: 0.26 (9H, s), 2.98 (2H, d, J=12.6 Hz), 3.10 (1H, d, J=12.6 Hz), 3.58 (2H, d, J=12.6 Hz), 3.62 (1H, d, J=12.6 Hz), 4.11 (1H, m), 4.11 (5H, s), 4.34 (1H, pt, J=2.5 Hz), 4.48 (1H, m), 7.26 (2H, m), 7.45 (2H, m), 7.48 (2H, bd, J=8.0 Hz), 7.52 (2H, d, J=8.5 Hz), 7.95 (4H, d, J=8.5 Hz). ^{13}C NMR (100.6 MHz) δ: −0.02 (CH_3), 53.46 (CH_2), 53.97 (CH_2), 68.79 (5×CH), 60.09, 72.75 (C), 73.94, 74.78, 90.24 (C), 125.24, 125.62, 127.45, 127.74, 128.13, 128.24, 131.40 (C), 133.00 (C), 133.84 (C), 134.98 (C). MS (FD) *m/z*: 565 (100%, M^+). Anal. calcd for $C_{36}H_{35}FeNSi$: C, 76.45; H, 6.24; N, 2.48; found: C, 76.67; H, 6.47; N, 2.34.

*4.6. 1-Bromo-2-dimethylaminomethylferrocene **10***

To a suspension (the use of an ultrasonic bath is recommended) of aminoboronic acid **9** (5.74 g, 20 mmol) in 160 ml of distilled water was added dropwise a solution of cupric bromide (11.50 g, 50 mmol) in 120 ml of water with stirring. The mixture was warmed up to 60–65°C and kept at this temperature for 2 h. After cooling 400 ml of water and 400 ml of ether were added. To destroy the yellow copper complex sufficient concentrated aqueous ammonia solution (20–50 ml) was added slowly and the resulting yellow organic phase was separated from the dark blue aqueous phase. The latter was repeatedly extracted with ether until no further coloration of the organic phase was observed. The combined extracts were washed with diluted ammonia until no coloration was detected and, finally, with water and brine, and dried with K_2CO_3. Evaporation of the solvent afforded a red oil which was chromatographed on alumina (column 25×3 cm). Ether eluted the product which solidified upon storage in a refrigerator. With MeOH/ether small amounts of starting material could be recovered. ^{1}H NMR revealed minor impurities of dimethylaminomethylferrocene (1–2%). No attempts have been made to remove this impurity since the product was found to be sufficiently pure for the next step; yield: 5.795 g (90%).[13] ^{1}H NMR (250 MHz) δ: 2.25 (6H, s), 3.38 (1H, d, J=13.0 Hz), 3.50 (1H, d, J=13.0 Hz), 4.13 (1H, m), 4.17 (5H, s), 4.25 (1H, dd, J=2.7, 1.4 Hz), 4.46 (1H, dd, J=2.5, 1.4 Hz). ^{13}C NMR (62.9 MHz) δ: 44.96 (CH_3), 56.99 (CH_2), 66.44, 68.27, 70.19, 71.08 (5×CH), 80.78 (C), 82.35 (C). MS (20°C) *m/z*: 323/321 (22/24%, M^+), 279/277 (17/16%), 243 (96%).

*4.7. 2-Aminomethyl-1-bromoferrocene **11***

The methiodide of **10** (1.752 g, 4.00 mmol)[7] was slurried in concentrated aqueous ammonia (100 ml) and benzene (50 ml) in a glass tube which fitted tightly in a stainless steel autoclave. The autoclave was closed and heated to 110°C for 12 h with vigorous stirring. After cooling, the reaction mixture was

transferred to a separatory funnel and diluted with 200 ml of ether. The organic phase was separated and the aqueous phase was sufficiently extracted with ether (2×50 ml). The combined extracts were washed with water and brine, and dried (K_2CO_3). Concentration in vacuo left a red oil which was purified by chromatography (Al_2O_3, column 40×2.5 cm, MeOH:$CHCl_3$=5:95→10:90). The first fraction contained a small amount of an orange-colored side product which was discarded. The main band (with considerable tailing) contained the desired product. The product was found to be moderately stable and should be used as soon as possible; storage in a deep freezer is recommended; yield: 0.956 g (86%) of **11**, red oil, solidifying in a deep freezer. ^{1}H NMR (250 MHz) δ: ~1.40 (2H, bs), 3.56 (1H, d, *J*=14.4 Hz), 3.71 (1H, d, *J*=14.4 Hz), 4.05 (1H, pt, *J*=2.5 Hz), 4.14 (1H, m), 4.15 (5H, s), 4.39 (1H, dd, *J*=2.5, 1.4 Hz). ^{13}C NMR (62.9 MHz) δ: 40.48 (CH_2), 65.78, 66.02, 70.11, 70.87 (5×CH), 79.13 (C), 88.48 (C). MS (30°C) *m*/*z*: 293/295 (100/97%, M^+). HRMS: calcd for $C_{11}H_{12}BrFeN$: 292.9501; found: 292.9506.

4.8. (S_a)(S_m*)-, (S_a)(S_m)-, (S_a*)(R_m*)-, and (S_a)(R_m)-N-(1-Bromo-2-ferrocenylmethyl)-3,5-dihydro-4H-dinaphth[2,1-c:1′,2′-e]azepine **12a**, **12b***

A solution of the bromoamine **11** (945 mg, 3.21 mmol), 2,2′-bis(bromomethyl)-1,1′-binaphthyl (1.49 g, 3.37 mmol, 1.05 equiv.), and triethylamine (1.300 g, 12.84 mmol, 4 equiv., 1.79 ml) in 50 ml of benzene was prepared in a 80 ml Schlenk tube. This was degassed and the reaction was heated to reflux under argon for 20–24 h. TLC showed, at this time, complete consumption of the starting material. Benzene was removed in vacuo and the residue was partitioned between CH_2Cl_2 and water (200 ml each). The organic layer was washed with water and brine, and dried (Na_2SO_4). After removal of the solvent the stereoisomers were separated on silica gel (column 60×2 cm, EA:PE=15:85). A small amount of red-colored by-product was eluted first and discarded. This was followed by 759 mg (41%) of **12b** and subsequently 750 mg (41%) of **12a**. Only racemic compounds could be obtained crystalline, enantiomeric products remained as yellow foams.

(S_a)(R_m*)*-**12b**: mp: 186–190°C. ^{1}H NMR (400 MHz) δ: 3.20 (2H, d, *J*=12.3 Hz), 3.42 (1H, d, *J*=13.3 Hz), 3.70 (2H, d, *J*=12.3 Hz), 3.77 (1H, d, *J*=13.3 Hz), 4.09 (1H, pt, *J*=2.7 Hz), 4.13 (5H, s), 4.25 (1H, dd, *J*=2.5, 1.5 Hz), 4.47 (1H, dd, *J*=2.5, 1.5 Hz), 7.24 (2H, ddd, *J*=8.4, 6.9, 1.5 Hz), 7.44 (4H, m), 7.62 (2H, d, *J*=8.4 Hz), 7.94 (4H, bd, *J*=8.4 Hz). ^{13}C NMR (100.6 MHz) δ: 53.69 (CH_2), 55.50 (CH_2), 66.41, 68.55, 70.18, 71.23 (5×CH), 80.08 (C), 83.79 (C), 125.33, 125.64, 127.46, 128.09, 128.20, 128.24, 131.37 (C), 133.11 (C), 133.65 (C), 135.02 (C). MS (FD) *m/z*: 571/573 (95/100%, M^+). Anal. calcd for $C_{33}H_{26}BrFeN$: C, 69.25; H, 4.58; N, 2.45; found: C, 69.18; H, 4.70; N, 2.28.

(S_a)(R_m)-**12b**: $[\alpha]_D^{20}$ –33.0 (c 1.14, CH_2Cl_2).

(S_a)(S_m*)*-**12a**: mp: 208–212°C. ^{1}H NMR (400 MHz) δ: 3.25 (2H, d, *J*=12.3 Hz), 3.59 (1H, d, *J*=13.0 Hz), 3.64 (1H, d, *J*=13.0 Hz), 3.69 (2H, d, *J*=12.3 Hz), 4.13 (1H, pt, *J*=2.7 Hz), 4.15 (5H, s), 4.39 (1H, m), 4.43 (1H, m), 7.24 (2H, bpt, *J*~7.4 Hz), 7.44 (4H, m), 7.53 (2H, d, *J*=8.4 Hz), 7.93 (4H, bd, *J*=8.4 Hz). ^{13}C NMR (100.6 MHz) δ: 53.20 (CH_2), 55.04 (CH_2), 66.57, 68.44, 70.30, 71.15 (5×CH), 80.78 (C), 83.39 (C), 125.31, 125.64, 127.48, 127.79, 128.26, 128.28, 131.38 (C), 133.09 (C), 133.65 (C), 134.99 (C). MS (FD) *m/z*: 571/573 (95/100%, M^+). Anal. calcd for $C_{33}H_{26}BrFeN$: C, 69.25; H, 4.58; N, 2.45; found: C, 68.92; H, 4.61; N, 2.31.

(S_a)(S_m)-**12a**: $[\alpha]_D^{20}$ +46.1 (*c* 1.17, CH_2Cl_2).

4.9. (S_a)(R_m*) and (S_a)(R_m) N-(1-Diphenylphosphino-2-ferrocenylmethyl)-3,5-dihydro-4H-dinaphth-[2,1-c:1′,2′-e]azepine **2b** (procedure B)*

A slurry of (racemic) bromoamine **12b** (262 mg, 0.46 mmol) — a solution in the case of optically active starting material — in 10 ml of ether was prepared in a 80 ml Schlenk tube and degassed. A solution of *s*-BuLi (0.74 ml, 0.96 mmol, 2.1 equiv.) was added and the resulting red–brown solution was stirred for 1 h at rt. During this time the color faded and the solution became slightly turbid. Chlorodiphenylphosphine (507 mg, 2.3 mmol, 5 equiv., 0.42 ml) was added at 0°C and a light yellow precipitate formed immediately. After 1 h stirring at room temperature and 10 min refluxing TLC indicated complete conversion of the starting material. Water (10 ml) and CH_2Cl_2 (50 ml) were added in sequence to the stirred mixture. The organic layer was separated, washed with water and brine, and dried (Na_2SO_4). After removal of the solvent chromatographic purification on silica gel (column 30×2 cm, EA:PE=15:85) afforded 201 mg (65%) of **2b**. Only the racemic ligand could be obtained in crystalline state; mp: 255–260°C; the optically active product remained as a yellow foam. ^{1}H NMR (400 MHz) δ: 2.99 (2H, d, *J*=12.3 Hz), 3.30 (1H, d, *J*=12.8 Hz), 3.53 (2H, d, *J*=12.3 Hz), 3.88 (1H, bs), 3.93 (5H, s), 4.08 (1H, dd, *J*=12.8, 1.6 Hz), 4.24 (1H, bm), 4.36 (1H, bs), ~7.20 (5H, m), ~7.30 (4H, m), ~7.39 (7H, m), 7.62 (2H, m), 7.83 (2H, d, *J*=8.5 Hz), 7.90 (2H, d, *J*=8.0 Hz). ^{13}C NMR (100.6 MHz) δ: 54.93 (CH_2, d, *J*=7.8 Hz), 55.61 (CH_2), 69.20, 69.62 (5×CH), 71.78 (d, *J*=4.1 Hz), 73.06 (d, *J*=4.1 Hz), ~76.6 (C), 125.18, 125.52, 127.43, 127.54, 127.83 (d, *J*=6.5 Hz), 127.84, 127.97, 128.03 (d, *J*=7.9 Hz), 128.18, 128.99, 131.33 (C), 132.46 (d, *J*=17.8 Hz), 132.97 (C), 134.09 (C), 134.82 (C), 135.26 (d, *J*=21.8 Hz), ~138.14 (C, d, *J*~7 Hz), ~140.52 (C, d, *J*~8.4 Hz), one signal due to (C) was not observed. ^{31}P NMR (162 MHz) δ: −22.00 (s). MS (210°C) *m/z*: 677.2 (37%, M^+). Anal. calcd for $C_{45}H_{36}FeNP$: C, 79.77; H, 5.35; N, 2.07; P, 4.57; found: C, 79.44; H, 5.60; N, 1.88; P, 4.82.

(S_a)(R_m)-**2b**: $[\alpha]_D^{20}$ +207 (*c* 0.6, CH_2Cl_2).

4.10. (S_a)(S_m*)- and (S_a)(S_m)-N-(1-Diphenylphosphino-2-ferrocenylmethyl)-3,5-dihydro-4H-dinaphth[2,1-c:1′,2′-e]azepine **2a***

This compound was prepared analogously to **2b** on using **12b** instead of **12a** (procedure *B*); yield: 77%. The product was found to be identical with the main product of the *ortho*-lithiation of **6**.

*4.11. 1-Bromo-1′-dimethylaminomethylferrocene **14***

1,1′-Dibromoferrocene **13** (3.44 g, 10 mmol) was dissolved in dry THF (40 ml), degassed, and cooled to −78°C. Using a syringe a solution of *n*-BuLi (6.3 ml, 10 mmol) was slowly added through a rubber septum and the dark orange solution was first stirred at −78°C for 30 min and then at −25°C for 10 min. Solid *N*,*N*-dimethylmethyleneiminium iodide (Eschenmoser's salt, 2.04 g, 11 mmol) was added at the same temperature and stirring was continued for another 30 min. Then the mixture was allowed to reach room temperature overnight. Water (40 ml) and EA (100 ml) were added to the reaction mixture while stirring. After complete dissolution of the precipitate the organic layer was separated and the aqueous layer was extracted with EA (2×20 ml). The combined extracts were washed with saturated NaCl solution and dried (K_2CO_3). After evaporation of the solvent the residue was purified by column chromatography (Al_2O_3, 15×3 cm, EA:PE:Et_3N=20:79:1). After elution of small amounts of less polar impurities the product was eluted, which, upon concentration, gave a brown oil of moderate stability; yield: 1.792 g (56%) of **14**. Elution with $CHCl_3$ containing increasing amounts of MeOH afforded the butylammonium bromide of the main product **15** as a crystalline orange solid; yield: 1.509 g (33%). Compound **14**: ^{1}H

NMR (250 MHz) δ: 2.16 (6H, s), 3.28 (2H, s), 4.03 (2H, m), 4.16 (4H, s), 4.30 (2H, m). ^{13}C NMR (62.9 MHz) δ: 44.84 (CH_3), 58.41 (CH_2), 67.60, 70.61, 70.66, 72.61, 77.98 (C), 85.07 (C). MS (80°C) *m/z*: 321/323 (100%), 277/279 (77%). HRMS: calcd for $C_{13}H_{16}BrFeN$: 320.9816; found: 320.9811.

4.12. 1-Bromo-1′-ferrocenylmethyltrimethylammonium iodide ***16***

A solution of 1-bromo-1′-dimethylaminomethylferrocene **14** (1.78 g, 5.53 mmol) in acetonitrile (15 ml) was cooled to 0°C and methyl iodide (3.42 ml, 55 mmol) was added dropwise over a period of 10 min. Stirring was continued at room temperature for 1 h. Slow addition of ether (70 ml) precipitated **16** as a yellow powder which was collected, washed with ether, and air-dried; yield 2.463 g (96%). The product was pure enough to be used without further purification in the next step.

4.13. 1-Aminomethyl-1′-bromoferrocene ***17***

The methiodide **16** (2.00 g 4.31 mmol) or the corresponding butylammonium salt **15** (4 mmol), concentrated aqueous ammonia (100 ml, 25%), and benzene (50 ml) were placed in a steel autoclave with glass insert and heated to 110°C with stirring for 12 h. After cooling the organic phase was separated and the aqueous phase was extracted with EA (2×50 ml). The combined extracts were washed with water and brine, and dried (K_2CO_3). After evaporation of the solvent the residue was purified by column chromatography (Al_2O_3, 15×3 cm, $CHCl_3$:MeOH=95:5) to give 0.706 g (56%) **17** as a brown, moderately stable oil (58% from **15**). ^{1}H NMR (250 MHz) δ: ca. 1.50 (2H, bs), 3.57 (2H, s), 4.05 (2H, pt, *J*=1.9 Hz), 4.15 (4H, s), 4.33 (2H, pt, *J*=1.8 Hz). ^{13}C NMR (62.9 MHz) δ: 40.51 (CH_2), 67.35, 69.52, 70.09, 70.45, 77.91 (C), 92.50 (C). MS (40°C) *m/z*: 293/295 (90/100%), 214 (21%). HRMS: calcd for $C_{11}H_{12}BrFeN$: 292.9502; found: 292.9511.

*4.14. (±)- and (S$_a$)-*N*-(1′-Bromo-1-ferrocenylmethyl)-3,5-dihydro-4*H*-dinaphth[2,1-c:1′,2′-e]azepine* ***18***

A solution of the bromoamine **17** (455 mg, 1.55 mmol), 2,2′-bis(bromomethyl)-1,1′-binaphthyl (715 mg, 1.63 mmol, 1.05 equiv.), and triethylamine (627 mg, 6.2 mmol, 4 equiv., 864 μl) in benzene (30 ml) was prepared in an 80 ml Schlenk tube and degassed. The reaction was heated to reflux under argon for 10–12 h. At this time, TLC showed complete consumption of the starting material. Benzene was removed in vacuo and the residue was partitioned between CH_2Cl_2 and water (50 ml each). The organic layer was washed with water and brine, and dried (Na_2SO_4). After removal of the solvent the residue was chromatographed (Al_2O_3 column, 20×2 cm, EA:PE=15:85) to give 0.689 g (78%) of **18**. The product crystallized from ether to give yellow needles; mp: 153–157°C. ^{1}H NMR (400 MHz) δ: 3.13 (2H, d, *J*=12.6 Hz), 3.39 (1H, d, *J*=12.6 Hz), 3.53 (1H, d, *J*=12.5 Hz), 3.68 (2H, d, *J*=12.6 Hz), 4.04 (2H, m), 4.18 (1H, m), 4.20 (1H, m), 4.25 (1H, m), 4.31 (1H, m), 4.33 (1H, m), 4.39 (1H, m), 7.24 (2H, m), 7.43 (4H, m), 7.53 (2H, d, *J*=8.0 Hz), 7.93 (4H, bd, *J*=8.5 Hz). ^{13}C NMR (100.6 MHz) δ: 54.38 (CH_2), 55.07 (CH_2), 67.70, 67.73, 70.68, 70.71, 70.79 (2×CH), 72.62, 72.88, 78.11 (C), 85.90 (C), 125.38, 125.70, 127.46, 127.87, 128.22, 128.28, 131.40 (C), 133.12 (C), 133.47 (C), 135.06 (C). MS (170°C) *m/z*: 573/571 (100/90%). Anal. calcd for $C_{33}H_{26}BrFeN$: C, 69.25; H, 4.58; N, 2.45; found: C, 70.27; H, 4.52; N, 2.38.

Cyclization of **17** with (*S*)-2,2′-bis(bromomethyl)-1,1′-binaphthyl afforded (*S*$_a$)-**18**: mp: 177−180°C; $[\alpha]_D^{20}$ −6.7 (*c* 0.995, CH_2Cl_2).

*4.15. (±)- and (S_a)-N-(1′-Diphenylphosphino-1-ferrocenylmethyl)-3,5-dihydro-4*H*-dinaphth-[2,1-c:1′,2′-e]azepine* ***2c***

A slurry of bromoamine **18** (572 mg, 1 mmol) in 15 ml of ether was prepared in an 80 ml Schlenk tube, degassed, and cooled to −20°C. To this was added a solution of *n*-BuLi (1.31 ml, 2 mmol) at the same temperature and stirring was continued for 30 min. Chlorodiphenylphosphine (880 mg, 4 mmol, 4 equiv., 0.72 ml) was added to the resulting dark orange solution, whereupon the color changed to light yellow and a precipitate formed. The mixture was allowed to reach room temperature during 2 h and water (20 ml) and CH_2Cl_2 (50 ml) were added in sequence to the stirred mixture. The organic layer was separated, washed with water and brine, and dried with Na_2SO_4. After removal of the solvent chromatographic purification on alumina (column 30×2 cm, EA:PE:Et_3N=10:89:1→20:79:1) afforded **2c**. The racemate crystallized from CH_2Cl_2/acetone in orange plates; mp: 209–211°C; enantiomers remained as pale yellow foam; yield: 551 mg (81%) of **2c**. ^{1}H NMR (400 MHz) δ: 3.05 (2H, d, *J*=12.1 Hz), 3.11 (1H, d, *J*=12.0 Hz), 3.23 (1H, d, *J*=12.6 Hz), 3.60 (2H, d, *J*=12.1 Hz), 4.03 (3H, m), 4.10 (2H, m), 4.31 (3H, m), 7.20–7.47 (16H, m), 7.49 (2H, d, *J*=8.0 Hz), 7.93 (4H, m). ^{13}C NMR (100.6 MHz) δ: 54.71 (CH_2), 54.97 (CH_2), 69.38, 69.40, 71.30, 71.42 (2×CH, d, *J*=3.8 Hz), 71.49, 73.46 (d, *J*=13.8 Hz), 73.48 (d, *J*=15.3 Hz), 76.13 (C, d, *J*=6.1 Hz), 85.04 (C), 125.36, 125.68, 127.45, 127.86, ≈128.13 (2×CH, d, J≈7.4 Hz), 128.17, 128.25, 128.43, 128.50, 131.38 (C), 133.09 (C), 133.44 (d, *J*=20.7 Hz), 133.51 (C), 133.64 (d, *J*=19.9 Hz), 135.03 (C), 139.13 (C, d, *J*=8.4 Hz), 139.22 (C, d, *J*=9.9 Hz). ^{31}P NMR (162 MHz) δ: −15.67 (s). MS (230°C) *m/z*: 677.3 (100%). Anal. calcd for $C_{45}H_{36}FeNP$: C, 79.77; H, 5.35; N, 2.07; P, 4.57; found: C, 78.58; H, 5.31; N, 1.97; P, 4.79.

Similarly, (S_a)-**2c** was obtained from (S_a)-**18**; $[\alpha]_D^{20}$ −33 (*c* 0.8, CH_2Cl_2).

4.16. (S_a)(R_m*)-N-(2-Deuterio-1-ferrocenylmethyl)-3,5-dihydro-4*H*-dinaphth[2,1-c:1′,2′-e]azepine* ***19***

Procedure *A* was applied with D_2O (20 equiv.) as the electrophile. For work-up and chromatography see **6**. A mixture of deuterated isomers with a deuterium content >97% (MS) was obtained in 84% yield. Recrystallization from Et_2O left a crystalline yellow powder which obviously represents the main product (S_a*)(R_m*)-**19**; mp: 199–201°C. ^{1}H and ^{13}C NMR spectra of **6** and **19** are superimposable with one exception: the integration of the multiplet at 4.18 ppm corresponds to 2H in **6** but 1H in **19**.

4.17. (S_a)(S_m*)- and (S_a)(S_m)-N-(1-Ferrocenylmethyl-2-hydroxymethyl)-3,5-dihydro-4*H*-dinaphth-[2,1-c:1′,2′-e]azepine* ***20***

Procedure *A* was applied with paraformaldehyde (3 equiv.) as the electrophile. After evaporation the residue was chromatographed (column 70×2 cm, SiO_2, EA:PE:Et_3N=29:70:1) to give 763 mg (73%) of the aminoalcohol as a yellow powder; mp: 223–227°C. ^{1}H NMR (400 MHz) δ: 3.06 (2H, d, *J*=12.5 Hz), 3.14 (1H, d, *J*=13.1 Hz), 3.65 (2H, d, *J*=12.5 Hz), 3.70 (1H, d, *J*=13.1 Hz), 4.00 (5H, s), 4.07 (1H, pt, *J*=2.5 Hz), 4.12 (1H, d, *J*=11.9 Hz), 4.24 (1H, m), 4.35 (1H, m), 4.87 (1H, d, *J*=11.9 Hz), 7.24 (2H, m), 7.44 (4H, m), 7.55 (2H, d, *J*=8.5 Hz), 7.93 (2H, d, *J*=7.6 Hz), 7.95 (2H, d, *J*=8 Hz). ^{13}C NMR (100.6 MHz) δ: 52.24 (CH_2), 53.11 (CH_2), 60.26 (CH_2), 65.63, 69.03 (5×CH), 69.94, 71.01, 84.40 (C), 88.19 (C), 125.58, 125.87, 127.41, 127.67, 128.30, 128.51, 131.38 (C), 132.58 (C), 133.22 (C), 135.15 (C). MS (190°C) *m/z*: 523 (23%, M^+). Anal. calcd for $C_{34}H_{29}FeNO$: C, 78.02.; H, 5.58.; N, 2.67; found: C, 76.94; H, 5.89; N, 2.62.

Similarly, (S_a)(S_m)-**20** was obtained from (S_a)-**6** as a foam; $[\alpha]_D^{20}$ +95.0 (*c* 1.0, CH_2Cl_2).

4.18. (S_a)(S_m*)- and (S_a)(S_m)-N-(1-Diphenylhydroxymethyl-2-ferrocenylmethyl)-3,5-dihydro-4H-dinaphth[2,1-c:1′,2′-e]azepine* ***21***

Procedure *A* was applied with benzophenone (3.1 equiv.) as the electrophile. After evaporation the residue was chromatographed (EA:PE=10:90) to give 70% of the aminoalcohol **21** as a yellow powder; mp: 256–258°C. ^{1}H NMR (400 MHz) δ: 2.59 (2H, d, *J*=12.3 Hz), 3.02 (1H, d, *J*=13.6 Hz), 3.48 (2H, bd, J∼12.3 Hz), 3.89 (1H, d, *J*=13.6 Hz), 3.90 (1H, m), 3.95 (5H, s), 4.17 (1H, pt, *J*=2.5 Hz), 4.26 (1H, m), 6.86 (1H, bpt, *J*=7.3 Hz), 6.95 (2H, bpt, *J*=7.5 Hz), 7.17 (2H, bd, *J*=7.5 Hz), 7.19–7.28 (3H, m), 7.36 (2H, pt, *J*=7.5 Hz), 7.38 (2H, bd, *J*=8.5 Hz), 7.43 (2H, bpt, *J*=7.8 Hz), 7.48 (2H, d, *J*=8.5 Hz), 7.64 (2H, bd, *J*=7.5 Hz), 7.90 (2H, d, *J*=8.0 Hz), 7.91 (2H, bd, *J*=8.0 Hz), ∼8.1 (1H, bs). ^{13}C NMR (100.6 MHz) δ: 53.24 (CH_2, b), 54.48 (CH_2), 65.77, 69.90 (5×CH), 70.73, 70.96, 77.94 (C), 80.94 (C), 96.96 (C), 125.48, 125.74, 126.30, 126.33, 127.10, 127.17, 127.20, 127.25, 127.37, 127.58, 128.26, 128.37, 131.26 (C), 132.78 (C), 133.15 (C), 134.96 (C), 147.29 (C), 149.79 (C). MS (FD, 230°C) *m/z*: 675.3 (100%, M^+). Anal. calcd for $C_{46}H_{37}FeNO$: C, 81.77; H, 5.52; N, 2.07; found: C, 80.88; H, 5.81; N, 1.99.

Similarly, (S_a)(S_m)-**21** was obtained from (S_a)-**6**; mp: 110−115°C; $[\alpha]_D^{20}$ –100.7 (*c* 1.0, CH_2Cl_2).

4.19. (S_a)(S_m*)- and (S_a)(S_m)-N-(2-Ferrocenylmethyl-1-formyl)-3,5-dihydro-4H-dinaphth-[2,1-c:1′,2′-e]azepine* ***22***

Compound **12a** was subjected to procedure *B* using DMF (6 equiv.) as the electrophile. After evaporation the residue was filtered over a short column (15×2 cm, SiO_2, Et_2O) to give 82% of the aldehyde **22** as an orange foam. ^{1}H NMR (400 MHz) δ: 3.16 (2H, d, *J*=12.3 Hz), 3.51 (1H, d, *J*=13.1 Hz), 3.70 (2H, d, *J*=12.3 Hz), 3.88 (1H, d, *J*=13.1 Hz), 4.23 (5H, s), 4.61 (1H, pt, *J*=2.5 Hz), 4.79 (1H, m), 4.82 (1H, m), 7.24 (2H, ptd, *J*=7.7, 1.3 Hz), 7.44 (4H, m), 7.51 (2H, d, *J*=8.0 Hz), 7.93 (2H, bd, *J*∼8.5 Hz), 7.94 (2H, d, *J*=8.5 Hz), 10.13 (1H, s). ^{13}C NMR (100.6 MHz) δ: 52.26 (CH_2), 54.57 (CH_2), 69.98, 70.26 (5×CH), 71.66, 75.76, 78.09 (C), 88.08 (C), 125.38, 125.71, 127.44, 127.73, 128.26, 128.29, 131.39 (C), 133.09 (C), 133.33 (C), 135.03 (C), 193.44. MS (180°C) *m/z*: 521 (27%, M^+). Anal. calcd for $C_{34}H_{27}FeNO$: C, 78.32; H, 5.22; N, 2.69; found: C, 78.03; H, 5.45; N, 2.47.

Similarly, (S_a)(S_m)-**22** was obtained from (S_a)(S_m)-**12a** as a foam; $[\alpha]_D^{20}$ −80.5 (*c* 0.42, CH_2Cl_2).

4.20. (S_a)(S_m*)- and (S_a*)(R_m*)-N-(2-Ferrocenylmethyl-1-phenylthio)-3,5-dihydro-4H-dinaphth-[2,1-c:1′,2′-e]azepine* ***23***

Procedure *A* was applied with PhSSPh (2.5 equiv.) as the electrophile. Evaporation of the solvent under vacuum left the crude product mixture which was separated by chromatography (SiO_2, EA:PE=30:70). After elution of small amounts of by-products the minor isomer with (S_a*)(R_m*)-configuration (7%) was eluted followed by the main product with (S_a*)(S_m*)-configuration (75%) with pronounced tailing. While the (S_a*)(R_m*)-isomer was only 90% pure and remained as an oil, the (S_a*)(S_m*)-isomer crystallized in yellow prisms from Et_2O/MeOH; mp: 112–116°C. *(S_a*)(R_m*)*-Isomer: ^{1}H NMR (400 MHz) δ: 3.08 (2H, d, *J*=12.0 Hz), 3.33 (1H, d, *J*=13.4 Hz), 3.59 (2H, d, *J*=12.1 Hz), 3.88 (1H, d, *J*=13.4 Hz), 4.17 (5H, s), 4.29 (1H, pt, *J*=2.7 Hz), 4.46 (1H, m), 4.47 (1H, m), 7.00 (1H, m), 7.10 (2H, m), 7.18–7.25 (4H, m), 7.37–7.43 (6H, m), 7.84 (2H, d, *J*=8.0 Hz), 7.89 (2H, d, *J*=8.5 Hz). ^{13}C NMR (100.6 MHz) δ: 53.27 (CH_2), 55.34 (CH_2), 68.96, 70.26 (5×CH), 71.97, 75.84, 76.27 (C), 88.81 (C), 124.92, 125.23, 125.56, 126.40, 127.42, 127.85, 128.10, 128.18, 128.52, 131.31 (C), 133.00 (C), 133.86 (C), 134.86 (C), 140.53 (C). *(S_a*)(S_m*)*-Isomer: ^{1}H NMR (400 MHz) δ: 2.81 (2H, d, *J*=12.0 Hz), 3.43 (2H, d, *J*=12.0 Hz), 3.57 (1H, d, *J*=12.5 Hz), 3.62 (1H, d, *J*=12.5 Hz), 4.18 (5H, s), 4.34 (1H, pt, *J*=2.7 Hz), 4.46 (1H, dd, *J*=2.5,

1.5 Hz), 4.64 (1H, dd, *J*=2.5, 1.5 Hz), 6.74 (3H, m), 6.99 (2H, m), 7.22 (2H, m), 7.33 (2H, d, *J*=8.0 Hz), 7.38 (2H, bd, *J*=8.5 Hz), 7.42 (2H, m), 7.87 (2H, d, *J*=8.0 Hz), 7.91 (2H, d, *J*=8.5 Hz). ^{13}C NMR (100.6 MHz) δ: 52.35 (CH_2), 54.67 (CH_2), 68.72, 70.23 (5×CH), 71.40, 75.54, 77.57 (C), 89.13 (C), 125.14, 125.21, 125.52, 127.48, 127.55, 127.71, 128.05, 128.08, 128.20, 131.35 (C), 133.00 (C), 133.74 (C), 134.84 (C), 139.47 (C). MS (220°C) *m/z*: 601 (100%, M^+). Anal. calcd for $C_{39}H_{31}FeNS$: C, 77.87; H, 5.19; N, 2.33; S, 5.33; found: C, 77.08; H, 5.33; N, 2.29.

4.21. (S$_a$)(R$_m$*)-N-(2-Borono-1-ferrocenylmethyl)-3,5-dihydro-4H-dinaphth[2,1-c:1′,2′-e]azepine* **24**

Procedure *A* was applied with $B(OCH_3)_3$ (3 equiv.) as the electrophile. The crude product was chromatographed on SiO_2. After removal of by-products (EA:PE, 30:70) the product was eluted with EA:MeOH (95:5) to yield 64% of the boronic acid **24** as a yellow powder; mp: 225–235°C (dec.). ^{1}H NMR (400 MHz, in $CDCl_3/D_2O$) δ: 3.05 (2H, d, *J*≈11.5 Hz), 3.16 (1H, d, *J*=13.1 Hz), 3.69 (2H, d, *J*≈11.5 Hz), 3.94 (1H, d, *J*=13.1 Hz), 4.13 (5H, s), 4.38 (1H, pt, *J*=2.6 Hz), 4.45 (1H, m), 4.52 (1H, m), 7.25 (2H, m), 7.41–7.56 (6H, m), 7.94 (2H, d, *J*=7.6 Hz), 7.94 (2H, d, *J*=8.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3/D_2O$) δ: 54.05 (CH_2), 69.54 (5×CH), 69.91, 73.87, 75.65, 87.06 (C), 125.69, 125.94, 127.39, 127.52, 128.33, 128.69, 131.35 (C), 133.71 (C), 135.18 (C). Two signals due to (CH_2), (C) could not be detected. MS (280°C) *m/z*: 493 (85%, $M^+-B(OH)_2$). Anal. calcd for $C_{33}H_{28}BFeNO_2$: C, 73.78; H, 5.25; N, 2.61; found: C, 74.05; H, 5.51; N, 2.45.

4.22. (S$_a$)(S$_m$*)-, (S$_a$)(S$_m$)-, (S$_a$*)(R$_m$*)-, and (S$_a$)(R$_m$)-N-(2-Ferrocenylmethyl-1-iodo)-3,5-dihydro-4H-dinaphth[2,1-c:1′,2′-e]azepine* **25**

Procedure *A* was applied with ICH_2CH_2I (3 equiv.) as the electrophile. Removal of the solvent under vacuum afforded the crude product mixture which was separated by chromatography (SiO_2, EA:PE=20:80). After elution of small amounts of iodide and excess of ICH_2CH_2I the minor isomer with (S_a*)(R_m*)-configuration (8%) was eluted followed by the main product with *(*S_a*)(*S_m*)-configuration (79%) displaying significant tailing. While *(*S_a*)(*R_m*)-**25** was only 89% pure and remained as an oil, (S_a*)(S_m*)-**25** was obtained crystalline; yellow prisms; mp: 114–119°C.

(S_a*)(*R_m*)-Isomer: ^{1}H NMR (400 MHz) δ: 3.20 (2H, d, *J*=12.4 Hz), 3.42 (1H, d, *J*=13.4 Hz), 3.68 (1H, d, *J*=13.4 Hz), 3.69 (2H, d, *J*=12.4 Hz), 4.09 (5H, s), 4.18 (1H, pt, *J*=2.5 Hz), 4.29 (1H, m), 4.46 (1H, m), 7.24 (2H, m), 7.41–7.46 (4H, m), 7.60 (2H, d, *J*=8.5 Hz), 7.93 (4H, d, *J*=8.5 Hz). ^{13}C NMR (100.6 MHz) δ: 45.16 (C), 55.64 (CH_2), 68.77, 69.12, 71.62 (5×CH), 74.70, 86.17 (C), 125.34, 125.65, 127.47, 128.12, 128.21, 128.24, 131.39 (C), 133.12 (C), 133.66 (C), 135.02 (C). One signal due to CH_2 is missing.

(S_a*)(*S_m*)-Isomer: ^{1}H NMR (400 MHz) δ: 3.23 (2H, d, *J*=12.4 Hz), 3.48 (1H, d, *J*=13.1 Hz), 3.59 (1H, d, *J*=13.1 Hz), 3.69 (2H, d, *J*=12.4 Hz), 4.11 (5H, s), 4.24 (1H, pt, *J*=2.5 Hz), 4.43 (1H, m), 4.46 (1H, m), 7.24 (2H, m), 7.41–7.46 (4H, m), 7.54 (2H, d, *J*=8.5 Hz), 7.93 (4H, m). ^{13}C NMR (100.6 MHz) δ: 46.16 (C), 54.42 (CH_2), 54.89 (CH_2), 68.97, 69.03, 71.58 (5×CH), 74.88, 85.87 (C), 125.30, 125.64, 127.47, 127.80, 128.26, 128.28, 131.39 (C), 133.09 (C), 133.67 (C), 135.00 (C). MS (200°C) *m/z*: 619 (100%, M^+). Anal. calcd for $C_{33}H_{26}FeIN$: C, 64.00; H, 4.23; N, 2.26; found: C, 63.81; H, 4.34; N, 2.13.

Similarly, (S_a)(S_m)-**25** was obtained from (S_a)-**6**; $[\alpha]_D^{20}$ +58.9 (*c* 1.109, CH_2Cl_2).

*4.23. (S_a)(S_m)-N-(2-Ferrocenylmethyl-1-phenyl)-3,5-dihydro-4H-dinaphth[2,1-c:1′,2′-e]azepine **26***

To 5 ml of toluene were added iodoamine **25** (310 mg, 0.5 mmol), a solution of phenylboronic acid (122 mg, 1.0 mmol) in EtOH p.a. (0.3 ml), and 2 molar Na_2CO_3 solution (1.05 ml, 2.1 mmol). The mixture was degassed and a catalytic amount of $Pd(PPh_3)_4$ (~10 mg) was added. The mixture was refluxed for 20 h with vigorous stirring. At this time, TLC did not show any starting material. EA (20 ml) and water (10 ml) were added and the organic phase was washed with water and brine, and dried with Na_2SO_4. After evaporation of the solvent the product was purified by chromatography (SiO_2, 25×2 cm, EA:PE, 20:80) to give 196 mg (69%) of the biaryl **26** as a crystalline orange solid. Recrystallization from CH_2Cl_2/PE afforded an analytically pure sample; mp: 248–253°C (dec.), $[\alpha]_D^{22}$ –67.5 (*c* 1.02, CH_2Cl_2). ^{1}H NMR (400 MHz) δ: 3.14 (2H, d, *J*=12.6 Hz), 3.43 (1H, d, *J*=13.1 Hz), 3.59 (1H, d, *J*=13.1 Hz), 3.82 (2H, d, *J*=12.5 Hz), 4.05 (5H, s), 4.33 (1H, pt, *J*=2.5 Hz), 4.54 (1H, m), 4.58 (1H, m), 7.20–7.29 (3H, m), 7.35 (2H, bt, *J*~7.5 Hz), 7.43–7.49 (4H, m), 7.63 (2H, d, *J*=8.5 Hz), 7.92 (2H, bd, *J*~7.5 Hz), 7.96 (2H, d, *J*=8.0 Hz), 7.99 (2H, d, *J*=8.0 Hz). ^{13}C NMR (100.6 MHz) δ: 52.30 (CH_2), 53.73 (CH_2), 67.07, 70.17 (5×CH), 70.87, 72.17, 82.38 (C), 88.31 (C), 125.33, 125.71, 125.99, 127.45, 127.78, 127.90, 128.25, 128.28, 129.25, 131.44 (C), 133.06 (C), 133.71 (C), 135.07 (C), 138.93 (C). MS (200°C) *m/z*: 568.9 (82%, M^+). Anal. calcd for $C_{39}H_{31}FeN$: C, 82.25; H, 5.49; N, 2.46; found: C, 82.03; H, 6.00; N, 2.41.

4.24. (S_a)(R_m*)-N-(1-Cyano-2-ferrocenylmethyl)-3,5-dihydro-4H-dinaphth[2,1-c:1′,2′-e]azepine **27***

(*S*a*)(*R*m*)-**25** (619 mg, 1 mmol) was dissolved in 10 ml of absolute THF and KCN (195 mg, 3 equiv.) and a catalytic amount of CuCN (10 mg) were added. The mixture was degassed, after which $Pd(PPh_3)_4$ (115 mg, 10 mol%) was added and the reaction was refluxed for 24 h (TLC). Usual workup with CH_2Cl_2 and chromatography (25×2 cm, SiO_2, EA:PE=20:80) afforded 423 mg (82%) of **27** which crystallized from EtOH; mp: 240–245°C (dec.). ^{1}H NMR (400 MHz) δ: 3.20 (2H, d, *J*=12.4 Hz), 3.52 (1H, d, *J*=13.1 Hz), 3.65 (2H, d, *J*=12.4 Hz), 3.72 (1H, d, *J*=13.1 Hz), 4.27 (5H, s), 4.35 (1H, pt, *J*=2.8 Hz), 4.51 (1H, m), 4.68 (1H, m), 7.24 (2H, td, *J*=7.8, 1.0 Hz), 7.41–7.46 (4H, m), 7.61 (2H, d, *J*=8.5 Hz), 7.93 (2H, bd, *J*=8.3 Hz), 7.95 (2H, d, *J*=8.0 Hz). ^{13}C NMR (100.6 MHz) δ: 53.29 (CH_2), 55.39 (CH_2), 70.40, 71.21 (5×CH), 71.60, 72.52, 88.85 (C), 120.00 (C), 125.40, 125.71, 127.45, 127.93, 128.29, 128.40, 131.37 (C), 133.16 (C), 133.28 (C), 135.00 (C). One signal due to (C) is missing. MS (200°C) *m/z*: 518 (100%, M^+). Anal. calcd for $C_{34}H_{26}FeN_2$: C, 78.77; H, 5.05; N, 5.40; found: C, 77.89; H, 5.18; N, 5.26

4.25. (S_a)(S_m*)-N-(2-Aminomethyl-1-ferrocenylmethyl)-3,5-dihydro-4H-dinaphth[2,1-c:1′,2′-e]-azepine **28***

A suspension of $LiAlH_4$ (114 mg, 3 mmol) in 10 ml of Et_2O was cooled to –5°C and powdered $AlCl_3$ (133 mg, 1.0 mmol) was added to give a milky suspension. After 20 min of stirring a solution of the nitrile **27** (259 mg, 0.5 mmol) in THF (5 ml) was added dropwise and the mixture was stirred at 0°C for 30 min. Excess of the reducing agent was decomposed by careful addition of wet Et_2O, followed by water (10 ml). To increase the volume of the organic phase, 10 ml of EA and two pellets of NaOH were added. This mixture was shaken strongly and then passed through a short pad of Celite (3 cm). The filtrate was washed with 2×10 ml of EA and the organic phase was separated, washed with water and brine, and dried (K_2CO_3). After removal of the solvent the product was found to be pure by NMR; addition of EtOH induced the crystallization; yield: 234 mg (90%), mp: 176–185°C . ^{1}H NMR (400 MHz) δ: 3.11 (2H, d, *J*=12.3 Hz), 3.16 (1H, d, *J*=12.1 Hz), 3.46 (1H, d, *J*=14.1 Hz), 3.56 (2H, d, *J*=12.3 Hz), 3.81 (1H, d, *J*=14.1 Hz), 3.90 (1H, m), 3.95 (1H, pt, *J*=2.5 Hz), 3.99 (1H, d, *J*=12.1 Hz), 4.03 (s, 5H), 4.17 (1H,

m), 7.24 (2H, m), 7.41–7.48 (6H, m), 7.91 (2H, d, *J*=8.0 Hz), 7.93 (2H, d, *J*=8.0 Hz). ^{13}C NMR (100.6 MHz) δ: 40.77 (CH_2), 55.07 (CH_2), 55.74 (CH_2), 65.54, 68.81 (5×CH), 68.91, 70.77, 83.27 (C), 90.12 (C), 125.33, 125.69, 127.36, 127.54, 128.21, 128.24, 131.33 (C), 133.03 (C), 133.70 (C), 134.95 (C). MS (170°C) *m/z*: 522 (29%, M^+). HRMS: calcd for $C_{34}H_{30}FeN_2$: 522.1758; found: 522.1779.

*4.26. (S$_m$)-2-Acetoxymethyl-1-bromoferrocene **29** and (S$_m$)-2-acetoxymethyl-1-iodoferrocene **30***

Bromoamine (S_a)(S_m)-**12a** (572 mg, 1.0 mmol) or iodoamine (S_a)(S_m)-**25** (619 mg, 1.0 mmol) was dissolved in toluene p.a. (1 ml), and acetic anhydride (2 ml) and acetic acid (1 ml) were added. The solution was degassed and stirred at 95°C for 16 h under Ar. After removing the bulk of the solvent and excess of the reagent in vacuo, the obtained brown oil was subjected to column chromatography (25×1 cm, SiO_2, EA:PE=30:70) to give 313 mg (93%) of acetate (S_m)-**29** or 338 mg (88%) of (S_m)-**30**. On increasing the solvent polarity to 50–80% EA, 93–97% of *N*-acetyl-3,5-dihydro-4*H*-dinaphth[2,1-c:1′,2′-e]azepine was eluted.

(S_m)-**29**: orange oil. ^{1}H NMR (250 MHz) δ: 2.03 (3H, s), 4.14 (1H, bpt, *J*∼2.8 Hz), 4.18 (5H, s), 4.28 (1H, dd, *J*=2.5, 1.4 Hz), 4.47 (1H, m), 4.93 (1H, d, *J*=12.2 Hz), 5.04 (1H, d, *J*=12.2 Hz). ^{13}C NMR (62.9 MHz) δ: 20.85 (CH_3), 61.29 (CH_2), 67.09, 68.35, 70.92, 71.11 (5×CH), 80.05 (C), 80.08 (C), 170.79 (C). MS (20°C) *m/z*: 336/338 (35/34%, M^+). HRMS: calcd for $C_{13}H_{13}{}^{79}BrFeO_2$: 335.9448, found: 335.9460. $[\alpha]_D{}^{22}$ +8.0 (*c* 3.13, CH_2Cl_2).

(S_m)-**30**: orange oil. ^{1}H NMR (250 MHz) δ: 2.03 (3H, s), 4.15 (5H, s), 4.24 (1H, pt, *J*=2.6 Hz), 4.34 (1H, dd, *J*=2.7, 1.4 Hz), 4.46 (1H, dd, J =2.5, 1.4 Hz), 4.85 (1H, d, *J*=12.1 Hz), 5.02 (1H, d, *J*=12.1 Hz). ^{13}C NMR (62.9 MHz) δ: 20.87 (CH_3), 44.55 (C), 62.93 (CH_2), 69.05, 69.61, 71.54 (5×CH), 75.50, 82.71 (C), 170.79 (C). MS: (20°C) m/z: 384 (72%, M^+). HRMS: calcd for $C_{13}H_{13}FeIO_2$: 383.9310; found: 383.9328. $[\alpha]_D{}^{20}$ –2.6 (*c* 3.02, CH_2Cl_2) [Ref. 24 $[\alpha]_D$ –3.1 (*c* 0.75, $CHCl_3$)].

*4.27. (S$_m$)-1-Bromo-2-hydroxymethylferrocene **31** and (S$_m$)-2-hydroxymethyl-1-iodoferrocene **32***

The ester (S_m)-**29** (304 mg, 0.9 mmol) or (S_m)-**30** (346 mg, 0.9 mmol) was dissolved in THF (10 ml). Water (10 ml), a pellet of NaOH, and finally 5 ml of MeOH were added and the mixture was stirred at 55–60°C for 1 h. After this time, TLC did not show any starting material. Ether (20 ml) was added and the organic phase was washed with water and brine, and dried (Na_2SO_4). The crude product was chromatographed on SiO_2 (25×2 cm, EA:PE=30:70) to yield carbinols (S_m)-**31** (91%) and (S_m)-**32** (∼100%) as low melting yellow crystalline solids.

(S_m)-**31**: mp: 84–93°C. ^{1}H NMR (250 MHz) δ: 1.65 (1H, bt, *J*=5.9 Hz), 4.11 (1H, pt, *J*=2.5 Hz), 4.18 (5H, s), 4.24 (1H, dd, *J*=2.6, 1.5 Hz), 4.40 (1H, dd, *J*=12.3, 5.9 Hz), 4.45 (1H, dd, *J*=12.4, 5.9 Hz), 4.55 (1H, dd, *J*=12.2, 5.9 Hz). ^{13}C NMR (62.9 MHz) δ: 59.74 (CH_2), 66.53, 66.97, 70.61, 70.90 (5×CH), 79.37 (C), one signal due to (C) is missing. MS (20°C) *m/z*: 294/296 (40/37%, M^+). HRMS: calcd for $C_{11}H_{11}{}^{79}BrFeO$: 293.9343; found: 293.9354. $[\alpha]_D{}^{20}$ –22.4 (*c* 1.12, CH_2Cl_2).

(S_m)-**32**: mp: 88–91°C. ^{1}H NMR (250 MHz) δ: 1.72 (1H, bs), 4.15 (5H, s), 4.21 (1H, pt, *J*=2.5 Hz), 4.30 (1H, dd, *J*=2.7, 1.4 Hz), 4.35 (1H, d, *J*=12.3 Hz), 4.44 (1H, m), 4.47 (1H, d, *J*=12.6 Hz). ^{13}C NMR (62.9 MHz) δ: 43.77 (C), 61.27 (CH_2), 67.68, 69.03, 71.29 (5×CH), 75.02, 88.12 (C). MS (30°C) *m/z*: 342 (100%, M^+). HRMS: calcd for $C_{11}H_{11}FeIO$: 341.9204; found: 341.9192. $[\alpha]_D{}^{20}$ –20.2 (*c* 2.22, CH_2Cl_2) [Ref. 24 $[\alpha]_D$ –24.1 (*c* 0.50, $CHCl_3$)].

4.28. (S_m)-1-Bromo-2-formylferrocene **33** and (S_m)-2-formyl-1-iodoferrocene **34**

To a solution of the carbinol *(S_m)*-**31** (207 mg, 0.7 mmol) or *(S_m)*-**32** (239 mg, 0.7 mmol) in 10 ml of $CHCl_3$ was added MnO_2 (activated, ca. 0.6–0.8 g) and the mixture was stirred at room temperature until TLC indicated complete conversion (0.5–1 h). The mixture was filtered over a short pad (2 cm) of Celite which was sufficiently washed with CH_2Cl_2. After evaporation of the solvent the crude aldehyde was chromatographed on a short column (10×2 cm, EA:PE=30:70) to give aldehydes *(S_m)*-**33** (92%) and *(S_m)*-**34** (86%) as dark red low melting solids.

(S_m)-**33**: mp: 56–60°C. ^{1}H NMR (250 MHz) δ: 4.28 (5H, s), 4.55 (1H, bpt, *J*=2.7 Hz), 4.77 (1H, m), 4.79 (1H, m), 10.16 (1H, s). ^{13}C NMR (62.9 MHz) δ: 66.61, 71.14, 72.15 (5×CH), 74.95, 75.56 (C), 80.06 (C), 192.84. MS (20°C) *m/z*: 292/294 (73/77%, M^+). HRMS: calcd for $C_{11}H_9{}^{79}BrFeO$: 291.9186; found: 291.9193. $[\alpha]_D{}^{20}$ +718 (*c* 0.194, CH_2Cl_2).

(S_m)-**34**: ^{1}H NMR (250 MHz) δ: 4.25 (5H, s), 4.66 (1H, bpt, *J*=2.6 Hz), 4.80 (1H, dd, *J*=2.6, 1.4 Hz), 4.87 (1H, dd, *J*=2.7, 1.4 Hz), 10.01 (1H, s). ^{13}C NMR (62.9 MHz) δ: 41.85 (C), 67.70, 72.60 (5×CH), 73.70, 76.73 (C), 79.59, 194.45. MS (30°C) *m/z*: 340 (100%, M^+). HRMS: calcd for $C_{11}H_9FeIO$: 339.9047; found: 339.9048. $[\alpha]_D{}^{20}$ +531 (*c* 0.30, CH_2Cl_2) [Ref. 24 $[\alpha]_D$ +544 (*c* 0.2, $CHCl_3$) calculated for enantiomeric pure compound].

4.29. X-Ray structure analyses

Crystal data for (±)-**2a**: $C_{45}H_{36}FeNP$, *M*=677.57, monoclinic, space group $P2_1/c$, *a*=15.935(4), *b*=21.314(6), *c*=21.125(6) Å, α=90°, β=102.03(2)°, γ=90°, *U*=7017(3) Å^3, *Z*=8, D_c=1.283 Mg/m^3, *T*=300(2) K, μ=0.51 mm^{-1}, λ=0.71073 Å, *F*(000)=2832, orange block (0.6×0.4×0.3 mm). Data were collected on a Siemens SMART 3-circle diffractometer with a CCD area detector and graphite monochromatized Mo Kα radiation by recording 4×606 ω-scan frames ($\Delta\omega$=0.3°, *t*=10–30 sec) covering a complete sphere of the reciprocal space, θ_{max}=25°. Corrections for absorption applied. Structure solution by direct methods, refinement by full-matrix least-squares on F^2 (SHELX-97).[25] Data/restraints/parameters=12188/0/866; final *R*1=0.0549, *wR*2=0.1033 (all data). CCDC 182/135454.

Crystal data for (±)-**2b**: $C_{45}H_{36}FeNP$, *M*=677.57, triclinic, space group $P\bar{1}$, *a*=10.790(4), *b*=11.606(5), *c*=14.832(6) Å, α=69.56(1)°, β=74.86(1)°, γ=85.35(1)°, *U*=1680(1) Å^3, *Z*=2, D_c=1.339 Mg/m^3, *T*=300(2) K, μ=0.53 mm^{-1}, λ=0.71073 Å, *F*(000)=708, orange prism (0.38×0.12×0.08 mm). Data collected on a Siemens SMART diffractometer (see above), θ_{max}=25°. Corrections for absorption applied. Structure solution by the Patterson method, refinement by full-matrix least-squares on F^2, data/restraints/parameters=5862/0/433; final *R*1=0.0525, *wR*2=0.0828 (all data). CCDC 182/135455.

Crystal data for (±)-**2c**·$(CH_3)_2CO$ (acetone solvate): $C_{48}H_{42}FeNOP$, *M*=735.65, triclinic, space group $P\bar{1}$, *a*=9.515(4), *b*=10.487(4), *c*=20.499(8) Å, α=90.92(2)°, β=96.62(2)°, γ=111.14(2)°, *U*=1891(1) Å^3, *Z*=2, D_c=1.292 Mg/m^3, *T*=299(2) K, μ=0.48 mm^{-1}, λ=0.71073 Å, *F*(000)=772, orange plate (0.50×0.34×0.12 mm). Data collected on a Siemens SMART diffractometer (see above), θ_{max}=27°. Corrections for absorption applied. Structure solution by direct methods, refinement by full-matrix least-squares on F^2, data/restraints/parameters=8232/0/471; final *R*1=0.0593, *wR*2=0.0977 (all data). CCDC 182/135456.

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