Diastereoselective additions of organometallic reagents to \((S_{Fe})-2-p\)-tolylsulfanylferrocene carboxyaldehyde and to \((S_{Fe})-2-p\)-tolylsulfanyl ferrocenyl imines. Synthesis of new central and planar chiral ferrocenyl alcohols and amines

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Dedicated to Professor Binne Zwanenburg on his 70th birthday
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Abstract
Enantiomerically pure 2-hydroxyalkyl, 2-aminoalkyl and 2-iminoalkyl ferrocenyl \(p\)-tolylsulfides are easily prepared in good yields and with complete diastereocontrol from \((S)\)-(2-\(p\)-tolylthio)ferrocencarboxyaldehyde. This aldehyde provides also an easy access to the first enantiomerically pure planar chiral ferrocenyl cyanohydrin. The absolute configuration of the new stereocenters has been determined by single-crystal X-ray analysis.

Keywords: Planar chiral ferrocenyl aldehyde, planar chiral ferrocenyl imines, organometallic reagents

Introduction
The design and the synthesis of new ferrocenyl derivatives possessing planar and/or central chirality are of great importance in the development of new versatile and effective ligands as well as of useful chiral auxiliaries and building blocks1 for asymmetric synthesis. It is noteworthy that planar chiral ferrocenes have also found considerable applications in industrial processes.2

In general, the synthesis of enantiopure or enantiomerically enriched 1,2-disubstituted ferrocenes involves either a traditional resolution of racemic intermediates3 or a stereoselective
ortho-metallation step. The stereoselective ortho-metallation methods reported to date rely on a diastereoselective lithiation of ferrocenyl sulfoxides,\(^4\) acetals,\(^5\) amines,\(^6\) oxazolines,\(^7\) hydrazones,\(^8\) sulfoximines,\(^9\) azeptines,\(^10\) methylethers,\(^11\) methoxymethylpyrrolidines\(^{3b,12}\) and \(O\)-methylepheidrines\(^{13}\) or on an enantioselective lithiation of achiral ferrocenyl phosphinoxides,\(^{14}\) amides\(^{15}\) or amines\(^{16}\) using a chiral lithium amide or external chiral auxiliaries such as (-)-sparteine or cyclohexanediamine.

1,2-Disubstituted enantiomerically pure planar chiral ferrocenylaldehydes have been recently employed as precursors of more complex molecules,\(^{17}\) in particular the formyl group could be stereoselectively alkylated\(^{18}\) by reaction with organometallic reagents. Asymmetric additions of organometallic reagents to the \(C=\text{N}\) functional group are of great interest for the preparation of chiral amines and derivatives.\(^{19}\) Only few examples have been reported so far on the 1,2-addition of organometallic reagents to ferrocenyl imines. In particular chiral ferrocenyl amines possessing central chirality have been obtained \textit{via} highly stereoselective additions of organolithium\(^{20}\) or organozinc\(^{21}\) reagents to chiral ferrocenyl imines deriving from enantiomerically pure amines or by enantioselective addition of dialkylzinc reagents to achiral ferrocenyl imines in the presence of chiral ligands.\(^{22}\) Moreover, new planar chiral ferrocenyl diamines have been synthesized starting from \(2-(N,N\text{-dimethylaminomethy})\) ferrocencarboxaldehyde \textit{via} the corresponding imine.\(^{23}\)

As a part of our ongoing interest in sulfur containing compounds\(^{24}\) and in molecules bearing the sulfur and the ferrocene moiety,\(^{25}\) we have recently synthesized enantiomerically pure \(\beta\)-hydroxyalkyl, \(\beta\)-aminoalkyl and \(\beta\)-iminoalkyl ferrocenyl sulfides having only the central chirality. Some of these derivatives were successfully employed as ligands in palladium-catalyzed allylic substitution with asymmetric induction up to 99\%.\(^{26}\)

Herein we wish to report our results on the synthesis of 2-(hydroxyalkyl)- \(\text{I}\), 2-(aminoalkyl)-ferrocenyl \(p\)-tolylsulfides \(\text{2}\) with planar and central chirality, and 2-(iminoalkyl)-ferrocenyl \(p\)-tolylsulfides \(\text{3}\) with planar chirality taking advantage of (S)-(2-\(p\)-tolylthio) ferrocencarboxaldehyde \(\text{4}^{5b}\) as the key compound (Scheme 1). The enantiomerically pure \(\text{4}\) can react with organometallic reagents affording \(\text{I}\) and with amines allowing the preparation of ferrocenyl imines \(\text{3}\), which in turn may be converted into \(\text{2}\) by reaction with organometallic reagents thus introducing a new stereogenic center beside the planar chirality.

\begin{center}
\begin{tikzpicture}
  \node at (0,0) {2};
  \node at (2,0) {3};
  \node at (4,0) {4};
  \node at (6,0) {1};
  \node at (0,-1.5) {O};
  \node at (2,-1.5) {N};
  \node at (4,-1.5) {O};
  \node at (6,-1.5) {O};
  \node at (0,-3) {N};
  \node at (2,-3) {N};
  \node at (4,-3) {N};
  \node at (6,-3) {N};
  \node at (0,-4.5) {H};
  \node at (2,-4.5) {H};
  \node at (4,-4.5) {H};
  \node at (6,-4.5) {H};
  \node at (0,-6) {S\text{-}\(p\)-Tol};
  \node at (2,-6) {S\text{-}\(p\)-Tol};
  \node at (4,-6) {S\text{-}\(p\)-Tol};
  \node at (6,-6) {S\text{-}\(p\)-Tol};
  \node at (0,-7.5) {R^1 \cdot \bullet \cdot \text{R}^2};
  \node at (2,-7.5) {R^3 \cdot \bullet \cdot \text{R}^2};
  \node at (4,-7.5) {R^1 \cdot \bullet \cdot \text{R}'};
  \node at (6,-7.5) {R^1 \cdot \bullet \cdot \text{R'}\cdot \text{R'}\cdot \text{R'}\cdot \text{R'}\cdot \text{R'}\cdot \text{R'}\cdot \text{R'}};
\end{tikzpicture}
\end{center}
Results and Discussion

(S)-(2-p-Tolylthio)ferrocencarboxaldehyde $4^{5b}$ has been synthesized, beside a wide range of enantiopure $\alpha$-substituted ferrocenyl aldehydes, by Kagan et al. starting from ferrocencarboxaldehyde that could be readily transformed into the acetal of (S)-1,2,4-butanetriol. The enantio- and diastereomerically pure ferrocenyl acetal behaves as ortho-lithiation guide and the deprotonation can be stereoselectively directed to a single diastereotopic ortho-hydrogen (Scheme 2).

\begin{equation}
\begin{array}{c}
\text{Fe} \quad \text{O} \\
\text{O} \quad \text{MeO} \\
\text{HO} \quad \text{HO} \\
\text{HO} \\
1) \text{CH(OMe)$_3$} \\
2) \text{RX} \\
3) \text{NaH; Mel} \\
\end{array}
\end{equation}

Scheme 2

An alternative procedure, developed by us, for synthesizing aldehyde (S)-4 is based on the diastereoselective ortho-lithiation of (S)-ferrocenyl $p$-tolyl sulfoxide $5^{4c}$ (Scheme 3) with a sterically hindered base such as 2,4,6-triisopropylphenyllithium,$^{4b}$ followed by electrophilic trapping with ethyl formate. The obtained ($S_{Fe}, S_\alpha$)-2-p-tolylsulfinyl ferrocencarboxaldehyde 6 was directly reduced to the corresponding aldehyde (S)-4 by treatment with sodium iodide and trifluoroacetic anhydride in acetone.$^{27}$ The enantiopure aldehyde (S)-4 was obtained in 45% overall yield and showed spectroscopic and optical properties identical with the product obtained following the Kagan’s procedure.

\begin{equation}
\begin{array}{c}
\text{Fe} \quad \text{S-pTol} \\
\text{O} \\
\text{Li} \\
1) \text{Li} \\
2) \text{HCOOEt} \\
\end{array}
\end{equation}

Scheme 3

The reaction of aldehyde (S)-4 with organometallic reagents, namely Grignard reagents, organolithium derivatives, tetraallyltin, and with diethylaluminiumcyanide and trimethylsilyl cyanide afforded the corresponding secondary alcohols 1 in very good yields, very short reaction time (only few minutes) and high diastereoselectivity as determined by $^1$H-NMR spectra of the crude reaction mixture. Only one set of signals was detected in the reactions with methylmagnesium bromide (entry 1), vinylmagnesiumbromide (entry 3), tetraallyltin (entry 6),
diethylaluminiumcyanide (entry 7) and trimethylsilyl cyanide (entry 8). On the contrary the reaction with phenylmagnesiumbromide (entry 4), methyllithium (entry 2) and n-butyllithium (entry 5) showed two sets of signals. In these cases the two diastereoisomers could be separated by preparative thin layer chromatography.

**Table 1. Reaction of aldehyde (S)-4 with organometallic reagents**

<table>
<thead>
<tr>
<th>Entry</th>
<th>R'M</th>
<th>T (°C)</th>
<th>Solvent</th>
<th>Yield of 1 (%)</th>
<th>d.e.</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₃MgBr</td>
<td>-78</td>
<td>THF</td>
<td>a 87</td>
<td>&gt; 98</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CH₃Li</td>
<td>-78</td>
<td>THF</td>
<td>a 82</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CH₂=CHMgBr</td>
<td>-78</td>
<td>THF</td>
<td>b 76</td>
<td>&gt; 98</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PhMgBr</td>
<td>-78</td>
<td>THF</td>
<td>c 89</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>BuLi</td>
<td>-78</td>
<td>THF</td>
<td>d 85</td>
<td>82</td>
<td>In the presence of 10 mol% of ZnI₂.</td>
</tr>
<tr>
<td>6c</td>
<td>Sn(· · ··)₄</td>
<td>0</td>
<td>CH₂Cl₂</td>
<td>e 86</td>
<td>&gt; 98</td>
<td>In the presence of 10 mol% of Sc(OTf)₃.</td>
</tr>
<tr>
<td>7</td>
<td>Et₂AlCN</td>
<td>-78</td>
<td>THF</td>
<td>f 98</td>
<td>&gt; 98</td>
<td></td>
</tr>
<tr>
<td>8d</td>
<td>TMSCN</td>
<td>-50</td>
<td>CH₂Cl₂</td>
<td>g 98</td>
<td>&gt; 98</td>
<td></td>
</tr>
</tbody>
</table>

a Isolated yield.
b Determined by ¹H-NMR on the crude reaction mixture.
c In the presence of 10 mol% of Sc(OTf)₃.
d In the presence of 10 mol% of ZnI₂.

Although (R)-(+-)-ferrocenecyanohydrin acetate has been previously obtained²⁸ by Lipase catalyzed acylation of the racemic ferrocenecyanohydrin and (R)-(+-)-ferrocenecyanohydrin has been synthesized from formyl ferrocene employing the hydroxynitrile lyase from Hevea brasiliensis,²⁹ products 1f and 1g represent the first enantiomerically pure ferrocenecyanohydrins containing both the central and the planar chirality.

The absolute configuration of the new stereocenters has been determined by single-crystal X-ray analysis on the major diastereoisomer of product 1c³⁰ indicating (S)-configuration (Figure 1). We could therefore assign the (S,S₅c) configuration to products 1. This stereochemical outcome can be rationalized by an exo attack of the organometallic species on the less congested Si-face of the aldehyde away from the sterically hindered lower cyclopentadienyl ring (Figure 2). These results are in agreement with the assumption of Ugi³¹ and of Kagan.³²
Figure 1. X-ray crystal structure of $(S, S_{Fe})$-1c.

Figure 2. Exo attack of the organometallic species on aldehyde $(S)$-4.

Then we turned our attention to the preparation of planar chiral ferrocenyl imines 3 that was readily achieved by treatment of the aldehyde $(S)$-4 with the appropriate amine in the presence of powdered molecular sieves (4 Å) in toluene. The 2-iminoalkyl ferrocenyl $p$-tolyl sulfides 3a and 3b were obtained in excellent yields (Table 2) and were purified by crystallization from MeOH. The yield of product 3c was increased by reacting $(S)$-4 with TsNH$_2$ in the presence of TiCl$_4$ and Et$_3$N using CH$_2$Cl$_2$ as the solvent. Imines 3 were obtained as geometrically $(E)$-homogeneous compounds according to the $^1$H-NMR spectra. Moreover, they are very stable and in particular 3c could also be purified by column chromatography on silica gel.
Table 2. Synthesis of 2-iminoalkyl ferrocenyl $p$-tolylsulfides 3

\[
\begin{array}{cccccc}
\text{Entry} & R^2 & 3 & T (\degree \text{C}) & \text{Yield} (%)^a & E:Z^b \\
1 & \text{PMP} & a & 50 & 90 & > 98:2 \\
2 & \text{CH}_2\text{Ph} & b & 50 & 93 & > 98:2 \\
3 & \text{Ts} & c & 110^c & 41 & > 98:2 \\
4 & \text{Ts} & c & \text{r.t.}^d & 98 & > 98:2 \\
\end{array}
\]

^a Isolated yield.  
^b Determined by $^1$H-NMR on the crude reaction mixture.  
^c In the presence of a catalytic amount of $p$-toluensulfonic acid.  
^d Reaction performed with TiCl$_4$ in the presence of Et$_3$N using CH$_2$Cl$_2$ as the solvent.

The reactivity of ferrocenyl imines 3 with organometallic reagents and the possibility of obtaining 2-aminoalkyl ferrocenyl $p$-tolylsulfides 2 were tested upon derivatives 3a and 3c as model compounds.

As can be deduced from the results reported in Table 3 both imines 3a and 3c can be successfully allylated with tetraallyltin in the presence of catalytic amount of Sc(OTf)$_3$ affording the corresponding homoallylic amines 2a and 2b in good yields and very good diastereoselectivity (entries 1 and 2). The N-PMP ferrocenyl imine 3a does not react with Grignard reagents even in the presence of a Lewis acid as LiCl, MgBr$_2$ or Sc(OTf)$_3$ (entries 4-7); the reaction of 3a with MeLi occurs in very low yield (10%) and with 58% d.e. (entry 3). The N-tosyl ferrocenyl imine 3c shows a different behavior and readily reacts with methylmagnesium bromide, vinylvagnesium bromide and phenylmagnesiumbromide, in the presence of MgBr$_2$ or LiCl, the latter giving a very fast reaction and better results in term of yields. The amines 2e, 2f and 2g (entries 8, 10, 11, 13) bearing the central and the planar chirality were indeed obtained in good yields and good to very good diastereoselectivity. Product 2e was also obtained by reaction of 3c with MeLi (entry 9), but in lower yield reproducing the same behavior as observed in the case of the aldehyde 4.
Table 3. Synthesis of 2-aminoalkyl ferrocenyl \( p \)-tolylsulfides \( 2 \)

![Diagram](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>( R^2 )</th>
<th>( R^3M )</th>
<th>L. A.</th>
<th>Reaction Conditions</th>
<th>Yield of ( 2 ) (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>d.e.&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
</table>
| 1     | a    | Sn(\( \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot 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\cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \::
Table 4. Reaction with EtMgBr

<table>
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<tr>
<th>Entry</th>
<th>Reaction conditions</th>
<th>L.A.</th>
<th>Yield of 2 (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>d.e.&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Yield of 7 (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Ratio 2h:7b</th>
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<tr>
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<td>Cp&lt;sub&gt;2&lt;/sub&gt;ZrCl&lt;sub&gt;2&lt;/sub&gt;</td>
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</tr>
<tr>
<td>3</td>
<td>c EtMgBr 3 equiv /THF/r.t./48 h</td>
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<td>&gt;98</td>
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<tr>
<td>5</td>
<td>c EtMgBr 3 equiv /THF/r.t./30 min</td>
<td>Cp&lt;sub&gt;2&lt;/sub&gt;ZrCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>21</td>
<td>&gt;98</td>
<td>67</td>
<td>1:3</td>
</tr>
<tr>
<td>6</td>
<td>c EtMgBr 10 equiv THF/r.t./30 min</td>
<td>Cp&lt;sub&gt;2&lt;/sub&gt;ZrCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>30</td>
<td>&gt;98</td>
<td>60</td>
<td>1:2</td>
</tr>
<tr>
<td>7</td>
<td>c EtMgBr 25 equiv THF/r.t./30 min</td>
<td>Cp&lt;sub&gt;2&lt;/sub&gt;ZrCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>48</td>
<td>&gt;98</td>
<td>42</td>
<td>1.2:1</td>
</tr>
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</table>

The absolute configuration of the new stereocenters of amino derivatives 2 has been determined by single-crystal X-ray analysis on the major diastereoisomer of product 2g<sup>36</sup> indicating an (S)-configuration (Figure 3). We could therefore assign the (S,<i>S</i><sub>Fe</sub>) configuration to products 2. This result implies a similar behavior of the imine (S)-3 and the aldehyde (S)-4 toward the addition of organometallic reagents.

![Figure 3. X-ray crystal structure of (S,<i>S</i><sub>Fe</sub>)-2g.](image)
Conclusions

(S)-(2-p-Tolythio)ferrocenecarboxyaldehyde was found to be a very versatile compound that allowed the synthesis of a large variety of enantiomerically pure sulfur containing ferrocenyl derivatives. 2-Hydroxyalkyl, 2-aminoalkyl and 2-iminoalkyl ferrocenyl p-tolylsulfides were easily prepared in good yields and with complete diasterecontrol. Moreover (S)-(2-p-tolythio)ferrocenecarboxyaldehyde provides an easy access to the first enantiomerically pure planar chiral cyanohydrin. All these derivatives bear several functional groups, that make them attractive from a synthetic point of view, and contain different heteroatoms, useful for the coordination to a metal centers and for the preparation of new ligands for asymmetric catalysis.

Experimental Section

General Procedures. Melting points (uncorrected) were determined with a Büchi melting point apparatus. 1H NMR and 13C NMR spectra were recorded with a Varian Gemini 300 at 300 and 75 MHz, or a Varian Gemini 400 at 400 and 100 MHz respectively, using CDCl3 solutions of the samples. Chemical shifts (δ) are reported in ppm relative to CHCl3 (δ = 7.26 for 1H and δ = 77.0 for 13C). J values are given in Hz. 13C NMR spectral assignments were made by DEPT experiments. IR spectra were recorded on a Perkin-Elmer model 257 grating spectrometer. Mass spectra were obtained using a VG 7070-E spectrometer at an ionizing voltage of 70 eV or with an electrospray ionization source (ESIMS). All the ESIMS spectra were performed using MeOH as the solvent. [α]D values were measured with Perkin Elmer Polarimeter 341 and are given in 101degcm²g⁻¹. The originality of all compounds was checked by a CAS-on-line structure search. Reactions were conducted in oven-dried (120 °C) glassware under a positive Ar atmosphere. Transfer of anhydrous solvents or mixtures was accomplished with oven-dried syringes/septum techniques. THF was distilled from sodium/benzophenone prior to use and stored under Ar. CH2Cl2 was passed through basic alumina and distilled from CaH2 prior to use. Other solvents were purified by standard procedures. Light petroleum ether refers to the fraction with a bp 40-60 °C. The reactions were monitored by TLC, using silica gel plates (Baker-flex IB2-F). Column chromatography was performed with Merck silica gel 60 (70-230 mesh). Preparative thick layer chromatography was carried out on glass plates using a 1 mm layer of Merck silica gel 60 Pf 254. All chemicals were used as obtained or purified by distillation as needed. (S)-ferrocenyl p-tolyl sulfoxide 5⁴c and (S)-(2- p-tolylsulfanyl)ferrocenecarboxaldehyde 4⁵b were prepared following the literature procedure.

(S,S)-(2-(p-Tolylsulfinyl)-ferrocenecarboxaldehyde (6). A solution of of (S)-ferrocenyl p-tolyl sulfoxide 5 (0.2 g, 0.6 mmol) in dry THF (5 mL) cooled at-78 °C under argon atmosphere was transferred via cannula into a cooled solution of 2,4,6-triisopropylphenyllithium⁴b (1.2 mmol) in THF (5 mL) prepared from 1-bromo-2,4,6-triisopropylbenzene and t-BuLi at –
78 °C for 2.5 h. The resulting solution was warmed to –40 °C over 1.5h and then stirred at –
40 °C for another 1.5h. The solution was cooled again to –78 °C and freshly distilled ethyl
formate was added. After 10 min the reaction was quenched with acetic acid and the mixture was
concentrated under reduced pressure. The crude was diluted with Et₂O, washed with water, dried
(MgSO₄) and concentrated. Column chromatography (Light petroleum / Et₂O = 1:1) afforded 6
in 68% yield (140 mg). \( \delta_H \) (CDCl₃, 300MHz) 2.37 (3H, s, CH₃), 4.60 (5H, s, FcH), 4.71 (H br s,
FcH), 4.76 (1H, bs, FcH), 5.02 (1H, bs, FcH), 7.27 (2H, d, \( J = 8.0 \) Hz, ArH), 7.51 (2H, d, \( J = 8.4 
Hz, ArH), 10.49 (H, s, CHO).

\((S_Fc)-2-(p-Tolylsulfanyl)-ferrocenecarboxaldehyde \( (4) \). To a stirred solution of 6 (100 mg,
0.28 mmol) and NaI (105 mg, 0.70 mmol) in acetone (1.0 mL) at 0 °C under argon atmosphere, a
solution of trifluoroacetic anhydride (0.16 ml, 1.12 mmol) in acetone (1.0 mL) was slowly
added. After stirring for 30 min at 0 °C, the reaction mixture was concentrated in vacuo and
water (4 mL) was added. The mixture was extracted with CHCl₃ (3 x 5 mL) and the organic
layer was washed with a 10% solution of Na₂S₂O₃, dried and concentrated. The residue was
purified by chromatography on silica gel (light petroleum/EtOAc 2:3) giving 4 as a red solid
(62 mg, 65%).

**General procedure for the reaction with Grignard reagents**

To a solution of \((S)-4 \) (0.5 mmol) in dry THF cooled at –78 °C under argon atmosphere, a
solution of the Grignard reagent (1.5 mmol) was slowly added. The colour of the solution
immediately change from red to yellow/orange and a TLC analysis (hexane/EtOAc 4:1) showed
the complete disappearance of the starting aldehyde. The reaction mixture was quenched at –
78 °C with saturated NH₄Cl solution and extracted with Et₂O. The organic layer was dried over
magnesium sulfate and concentrated under reduced pressure. The diastereomeric ratio was
determined by \(^1\)H and \(^1\)C NMR spectra on the reaction mixture and then the final derivative was
isolated by column chromatography eluent (eluent hexane/EtOAc 4:1).

\((1S)-1-[\(SFc\)-2-(p-Tolylsulfanyl)-ferrocenyl]ethanol \( (1a) \). Following the general procedure and
using a 3.0 M solution in THF of MeMgBr, the final product was obtained after chromatography
as a yellow solid in 87 % yield. M.p. 93 – 95 (Et₂O) (dec). \( \delta_H \) (CDCl₃, 300MHz) 2.25 (3H, s, CH₃),
2.34 (1H, s, OH), 4.36 (6H, br s, FcH + CHOH), 4.53 (2H br s, FcH), 4.64 (1H, br s, FcH), 6.91 (2H, d, \( J = 
8.4 \) Hz, ArH), 6.99 (2H, d, \( J = 8.4 \) Hz, ArH). \( \delta_C \) (CDCl₃, 75MHz) 20.4, 22.7 (CH₃),
64.5, 68.2, 69.2, 69.75, 70.55 (CH), 90.6, 93.9 (C), 125.0,
129.8 (ArCH), 140.5, 141.5 (ArC). \( \nu_{max}(CCl₄) \) 3437 cm⁻¹. ESI-MS \( m/z \) 352 (M⁺); 375 (M⁺ +Na).
\([\alpha]_{20}^{D} +19.5 \) (c 0.645 CHCl₃). Anal. Calcd. for C₁₉H₂₀FeOS (352.06): C, 64.76; H, 5.72. Found:
C, 65.01; H, 5.61.

\((1S)-1-[\(SFc\)-2-(p-Tolylsulfanyl)-ferrocenyl]-2-propen-1-ol \( (1b) \). Following the general procedure and
using a 1.0 M solution in THF of vinylMgBr, the final product was obtained after chromatography
as a yellow solid in 81% yield. M.p. 112 –114 °C (Et₂O). \( \delta_H \) (CDCl₃, 300MHz) 2.25 (3H, s, CH₃),
2.50 (1H, s, OH) 4.31 (5H, s, FcH), 4.40 (1H, m, FcH), 4.47 (2H, m, FcH),
4.92 (1H, dt, m, \( J = 10.3 \), \( J = 1.4 \) Hz, Hₐ-CH₂=), 5.02 (1H, bd, \( J = 6.3 \) Hz, CHOH), 5.07 (1H, dt,
\[ J = 17.0, J = 1.4 \text{ Hz}, \text{ H}_2\text{-CH} = \), 5.54 (1H, 4d, \( J = 17.0, J = 10.3, J = 6.3 \text{ Hz}, \text{ CH} = \), 6.95 (4H, m, ArH). \( \delta_C \) (CDCl\textsubscript{3}, 75MHz) 20.8 (CH\textsubscript{3}), 67.5, 68.7, 69.2, 70.0, 75.5 (CH) 115.0 (CH\textsubscript{2}), 126.5, 129.3 (ArCH), 135.0 (ArC), 138.9 (CH). \( \nu_{\text{max}} \) (CCl\textsubscript{4}) 3611 cm\textsuperscript{-1}. ESI-MS \( m/z \) 387 (M++Na). [\( \alpha \)]\textsubscript{D}\textsuperscript{20} +108 (c 0.51 in CHCl\textsubscript{3}). Anal. Calcd. for C\textsubscript{20}H\textsubscript{20}FeOS (364.06): C, 65.92; H, 5.53. Found: C, 65.78; H, 5.62.

(1\textsuperscript{S})-1-[\( \text{SFc} \)-2-(\( \text{p}-\text{Tolylsulfanyl} \)-ferrocenyl](phenyl)methanol (1c). Following the general procedure and using a 1.0 M solution in THF of PhMgBr, the final product was obtained as a mixture of two diastereoisomers with a d.e. 96% (calculated by \( ^1\text{H-NMR} \) on the crude mixture). The two diastereoisomers could be isolated by preparative TLC (hexane/EtOAc = 15:1). The major diastereoisomer was fully characterized and crystallized by MeOH affording crystals suitable for X-ray analysis.

(1\textsuperscript{S})-1c. M.p. 107 – 108 °C (MeOH). \( \delta_H \) (CDCl\textsubscript{3}, 300MHz) 2.21 (3H, s, CH\textsubscript{3}), 2.64 (1H, br s, OH) 4.39 (5H, s, FcH), 4.46 (1H, m, FcH), 4.51 (2H, m, FcH), 5.61 (1H, br s, CH), 6.69 (2H, d, \( J = 8.0 \text{ Hz}, \text{ ArH} \), 6.82 (2H, d, \( J = 8.0 \text{ Hz}, \text{ ArH} \), 7.12 (2H, m, ArH), 7.19 (3H, m, ArH). \( \delta_C \) (CDCl\textsubscript{3}, 75MHz) 20.8 (CH\textsubscript{3}), 67.7, 68.8, 70.3, 70.45, 75.6, (CH), 77.2, 97.6 (FcC), 126.4, 126.5, 127.2, 127.95, 129.1 (ArCH), 134.7, 135.4, 142.2, 142.3 (ArC). \( \nu_{\text{max}} \) (CCl\textsubscript{4}) 3577 cm\textsuperscript{-1}. ESI-MS \( m/z \) 437 (M++Na). [\( \alpha \)]\textsubscript{D}\textsuperscript{20} +38 (c 0.51 in CHCl\textsubscript{3}). Anal. Calcd. for C\textsubscript{24}H\textsubscript{22}FeOS (414.07): C, 69.55; H, 5.35. Found: C, 65.69; H, 5.22.

(1\textsuperscript{S}) and (1\textsuperscript{R})-1-[\( \text{SFc} \)-2-(\( \text{p}-\text{Tolylsulfanyl} \)-ferrocenyl]-1-pentanol ((1\textsuperscript{S})-1d and (1\textsuperscript{R})-1d). To a solution of (\( S \))-4 (170 mg, 0.5 mmol) in dry THF cooled at –78 °C under argon atmosphere, a solution of \( n \)-BuLi (1.6M, 0.5 mL, 0.75 mmol) was slowly added. The colour of the solution immediately change from red to yellow and a TLC analysis (light petroleum/Et\textsubscript{2}O = 3/1) showed the complete disappearance of the starting aldehyde. The reaction mixture was quenched at –78 °C with water and extracted with Et\textsubscript{2}O. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR spectra of the crude reaction mixture showed the presence of a mixture of diastereoisomers in a 10:1 ratio (de =82%). Chromatography of the crude yielded as the major \( R \) product the major diastereoisomer in 78 % yield (155 mg) as orange/yellow viscous oil and as the second \( R \) product the minor diastereoisomer in 7 % yield (15 mg) as a yellow oil.

(1\textsuperscript{S})-1d. \( \delta_H \) (CDCl\textsubscript{3}, 300MHz) 0.70 (3H, t, \( J = 7.1 \text{ Hz}, \text{ CH}_3 \)), 1.00 – 1.47 (6H, m, (CH\textsubscript{2})\textsubscript{3}), 2.10 (1H, br s, OH), 2.24 (3H, s, CH\textsubscript{3}) 4.30 (5H, s, FcH), 4.34 (1H, m, FcH), 4.46 (1H, m, FcH), 4.51 (1H, m, FcH), 4.58 (1H, brd, \( J = 7.0 \text{ Hz}, \text{ CHO} \)), 6.93 (2H, d, \( J = 8.0 \text{ Hz}, \text{ ArH} \), 6.98 (2H, d, \( J = 8.0 \text{ Hz}, \text{ ArH} \)). \( \delta_C \) (CDCl\textsubscript{3}, 75MHz) 13.8 (CH\textsubscript{3}), 20.8. 22.35, 27.8 (CH\textsubscript{2}), 37.6 (CH), 68.75, 67.8, 68.4, 69.8, 75.4 (CH), 126.4, 129.3 (ArCH), 134.9, 136.0 (ArC). \( \nu_{\text{max}} \) (CCl\textsubscript{4}) 3590 cm\textsuperscript{-1}. ESI-MS \( m/z \) 417 (M\textsuperscript{++Na}). [\( \alpha \)]\textsubscript{D}\textsuperscript{20} +5.7 (c 0.51 in CHCl\textsubscript{3}). Exact mass Calcd. for C\textsubscript{22}H\textsubscript{26}FeOS: 394.1054. Found: 394.1078.

(1\textsuperscript{R})-1d. \( \delta_H \) (CDCl\textsubscript{3}, 300MHz) 0.90 (3H, t, \( J = 7.0 \text{ Hz}, \text{ CH}_3 \)), 1.20 – 1.80 (6H, m, (CH\textsubscript{2})\textsubscript{3}), 1.98 (1H, brd, \( J = 4.3 \text{ Hz}, \text{ OH} \)), 2.24 (3H, s, CH\textsubscript{3}) 4.23 (5H, s, FcH), 4.33 (1H, m, FcH), 4.38 (1H, m, FcH), 4.45 (1H, m, FcH), 4.64 (1H, m, CHO\textsubscript{2}), 6.69 (4H, m, ArH). \( \delta_C \) (CDCl\textsubscript{3}, 75MHz) 14.0 (CH\textsubscript{3}), 22.5, 28.7, 30.2 (CH\textsubscript{2}), 35.6 (CH), 68.6, 68.7, 69.1, 70.1, 75.75 (CH), 125.9,
129.6 (ArCH), 136.4, 138.7 (ArC). $\nu_{\text{max}}$ (CCl$_4$) 3588 cm$^{-1}$; ESI-MS $m/z$ 417 (M$^\text{+}$+Na). [$\alpha$]$^{20}_D$ $-7.4$ (c 0.50 in CHCl$_3$).

(S)-1-[($S$)-2-$p$-Tolylsulfanyl]-ferrocenyl]-3-buten-1-ol (1e). To a solution of ($S$)-4 (170 mg, 0.5 mmol) in dry CH$_2$Cl$_2$ and of catalytic amounts of Sc(OTf)$_3$ (28 mg, 0.05 mmol) cooled at 0 °C under argon atmosphere, tetraallyltin (0.13 mL, 0.55 mmol) was added. The reaction was stirred at 0°C per 0.5 h and then quenched by adding water at the same temperature. The organic layer was separated, dried over magnesium sulfate and concentrated under reduced pressure. The $^1$H and $^{13}$C NMR spectra of the crude reaction mixture showed the presence of a single diastereoisomer. Chromatography on silica gel yielded the desired compound in 86% yield as a yellow viscous oil. $\delta$$_H$ (C$_6$D$_6$, 300MHz) 1.85 (3H, s, CH$_3$), 2.01 (1H, s, OH) 2.15 (2H, m, CH$_2$), 3.86 (1H, m, FcH), 3.98 (5H, s, FcH), 4.24 (1H, m, FcH), 4.26 (1H, m, FcH), 4.80 (2H, m, CH$_2$=CHOH), 5.80 (1H, m, CH=) 6.68 (2H, d, $J$ = 8.0 Hz, ArH), 7.00 (2H, d, $J$ = 8.0 Hz, ArH). $\delta$$_C$ (C$_6$D$_6$, 75MHz) 20.55 (CH$_3$), 43.25 (CH$_2$), 67.4, 67.9, 68.5, 70.2, 75.6 (CH), 74.8, 96.7 (FcC), 117.2 (CH$_2$), 126.5, 129.5 (ArCH), 134.8 (ArC), 135.1 (CH), 137.1 (ArC). $\nu_{\text{max}}$ (CCl$_4$) 3577 cm$^{-1}$.

ESI-MS $m/z$ 378 (M$^+$), 401 (M$^+$+Na). [$\alpha$]$^{20}_D$ $+33.7$ (c 0.55 in CHCl$_3$). Exact mass Calcd. for C$_{21}$H$_{22}$FeOS: 378.0741. Found: 378.0721.

(S)-4-$p$-Tolylsulfanyl]ferrocene cyanohydrin (1f). To a solution of (S)-4 (170 mg, 0.5 mmol) in dry THF cooled at –78 °C under argon atmosphere, a solution of the Et$_2$AlCN (1.0 M in Toluene, 2.5 mL, 2.5 mmol) was slowly added. The colour of the solution immediately changed from red to yellow. The reaction mixture was quenched at –78 °C with water and extracted with Et$_2$O. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The $^1$H and $^{13}$C NMR spectra of the crude reaction mixture showed the presence of a single diastereoisomer and a chemical purity major of 97%. M.p. 80 °C (EtOAc). $\delta$$_H$ (C$_6$D$_6$, 300MHz) 1.78 (3H, s, CH$_3$), 2.40 (1H, s, OH), 3.69 (1H, m, FcH), 3.90 (5H, s, FcH), 4.03 (1H, m, FcH), 4.07 (1H, m, FcH), 6.63 (2H, d, $J$ = 8.4 Hz, ArH), 6.92 (2H, d, $J$ = 8.4 Hz, ArH). $\delta$$_C$ (C$_6$D$_6$, 75MHz) 20.6 (CH$_3$), 43.25 (CH$_2$), 67.4, 67.9, 68.5, 70.2, 75.6 (CH), 74.8, 88.4, 88.7 (FcC), 118.6 (CN), 127.0, 130.0 (ArCH), 135.6, 135.7 (ArC). $\nu_{\text{max}}$ (CCl$_4$) 3440 cm$^{-1}$.

ESI-MS $m/z$ 386 (M$^+$+Na). [$\alpha$]$^{20}_D$ $+394$ (c 0.50 CHCl$_3$). Anal. Calcd. for C$_{19}$H$_{17}$FeNOS (363.04): C, 62.80; H, 4.72; N, 3.86. Found: C, 62.69; H, 4.89; N 3.91.

(S)-2-$p$-Tolylsulfanyl]ferrocene trimethylsilyl cyanohydrin (1g). To a solution of of (S)-4 (170 mg, 0.5 mmol) in dry CH$_2$Cl$_2$ at –50°C under argon atmosphere, a catalytic amount of ZnI$_2$ and TMSCN (60 mg, 0.6 mmol) were added. The colour of the solution immediately changed from red to yellow. The reaction mixture was quenched with water. The organic layer was separated, dried over magnesium sulfate and concentrated under reduced pressure affording a yellow/brown oil. The $^1$H and $^{13}$C NMR spectra of the crude reaction mixture showed the presence of a single diastereoisomer and a chemical purity major of 97%. $\delta$$_H$ (C$_6$D$_6$, 300MHz) 0.06 (9H, s, SiMe$_3$), 1.79 (3H, s, CH$_3$), 3.77 (1H, m, FcH), 3.98 (5H, s, FcH), 4.13 (1H, m, FcH), 4.14 (1H, m, FcH), 5.14 (1H, s, CH), 6.67 (2H, d, $J$ = 8.0 Hz, ArH), 7.01 (2H, d, $J$ = 8.0 Hz, ArH). $\delta$$_C$ (C$_6$D$_6$, 75MHz) 0.52 (SiMe$_3$), 20.6 (CH$_3$), 59.2, 69.3, 71.0, 71.2, 76.4 (CH), 87.2, 89.2 (FcC), 119.0 (CN), 127.0, 129.7, 135.2 (ArCH), 136.2 (ArC). $\nu_{\text{max}}$ (CCl$_4$) 1250 cm$^{-1}$. 
ESI-MS m/z 458 (M^+Na). [α]_D^{20} +12 (c 0.025 CHCl_3). Exact mass Calcd. for C_{22}H_{25}FeNOSSi: 435.0775. Found: 435.0715.

N-(4-Methoxyphenyl)-N-{(E)-(S)-2-[(p-tolylsulfanyl)ferrocenyl]methylidene}amine (3a). To a stirred solution of (S)-4 (340 mg, 1.0 mmol) and 4-anisidine (135 mg, 1.1 mmol) in dry toluene under argon atmosphere, dry powdered MS (4 Å) (1 g) were added. The mixture was heated at 50°C overnight and then filtered and concentrated under reduced pressure. An ¹H-NMR spectrum of the crude showed the complete conversion of the aldehyde(S)-4 and the presence of 3a with a purity of about 90%. Crystallisation from boiling MeOH afforded 3a in 85% yield. M.p 133 – 135 °C (MeOH). δ_H (C_6D_6, 300MHz) 1.77 (3H, s, CH_3), 3.12 (3H, s, CH_3), 3.91 (5H, s, FcH), 4.01 (1H, m, FcH), 4.32 (1H, m, FcH), 5.25 (1H, d, J = 8.0 Hz, ArH), 6.56 (2H, d, J = 8.0 Hz, ArH), 6.59 (2H, d, J = 8.0 Hz, ArH), 6.97 (2H, d, J = 8.0 Hz, ArH), 7.11 (2H, d, J = 8.0 Hz, ArH), 8.82 (1H, s, CH). δ_C (C_6D_6, 75MHz) 20.6, 55.25 (CH_3), 69.5, 71.2, 71.7, 72.9 (CH), 86.4, 87.7 (FcC), 114.9, 122.1, 127.2, 129.85 (ArCH), 135.6, 146.2 (ArC), 157.2 (CHN). ν_{max}(CCl_4) 1620 cm⁻¹. ESI-MS m/z 441 (M^+H), 464 (M^+Na). [α]_{20}^{D} +910 (c 0.30 CHCl_3). Anal. Calcd. for C_{25}H_{23}FeNOS (441.085): C, 68.02; H, 5.25; N, 3.17. Found: C, 68.25; H, 5.15; N 3.41.

N-Benzyl -N-{(E)-(SFc)-2-[(p-tolylsulfanyl)ferrocenyl]methylidene}amine (3b). To a stirred solution of (S)-4 (340 mg, 1.0 mmol) and benzylamine (1.1 mmol) in dry toluene under argon atmosphere, dry powdered MS (4 Å) (1 g) were added. The mixture was heated at 50°C overnight and then filtered and concentrated under reduced pressure. An ¹H-NMR spectrum of the crude showed the complete conversion of the aldehyde(S)-4 and the presence of 3b with a purity of about 93%. Crystallization from boiling MeOH afforded 3b in 89% yield. M.p 123 – 125 °C (MeOH). δ_H (C_6D_6, 300MHz) 1.79 (3H, s, CH_3), 3.89 (5H, s, FcH), 4.0 (1H, m, FcH), 4.31 (1H, m, FcH), 4.33 (2H, d, J = 13.5 Hz, H_a-CH_2), 4.45 (2H, d, J = 13.5 Hz, H_b-CH_2), 5.13 (1H, m, FcH), 6.67 (2H, d, J = 8.7 Hz, ArH), 6.63-7.11 (5H, m, ArH), 7.16 (2H, m, ArH), 8.57 (H, s, CHN). δ_C (C_6D_6, 75MHz) 21.4 (CH_3), 66.4 (CH_2), 69.9, 71.7, 72.0, 77.9 (FcCH), 79.2, 84.4 (FcC) 127.2, 127.6, 129.0, 129.3, 130.6 (ArCH), 135.7,138.0, 141.3 (ArC), 160.8 (CHN). ν_{max}(CCl_4) 1641cm⁻¹. ESI-MS m/z 426 (M^+H). [α]_{20}^{D} +386 (c 0.315 CHCl_3). Anal. Calcd. for C_{25}H_{23}FeNS (425.09): C, 70.59; H, 5.45; N, 3.29. Found: C, 70.35; H, 5.35; N 3.38.

N-{(E)-(SFc)-2-(p-Tolylsulfanyl)ferrocenyl}methylidene]benzenesulfonamide (3c). Method A. To a stirred solution of (S)-4 (340 mg, 1.0 mmol) and p-toluenesulfonamide (171 mg, 1.1 mmol) in dry toluene under argon atmosphere, dry powdered MS (4 Å) (1 g) and a catalytic amount of p-toluenesulfonic acid were added. The mixture was heated at reflux overnight and then filtered and concentrated under reduced pressure. Chromatography on silical gel column (Light petroleum/EtOAc 3:1) afforded 3c in 41% yield. M.p 120 – 123 °C (MeOH). δ_H (CDCl_3, 400MHz) 2.27 (3H, s, CH_3), 2.41 (3H, s, CH_3), 4.25 (5H, s, FcH), 4.85 (1H, m, FcH), 4.89 (1H, m, FcH), 5.16 (1H, m, FcH), 6.94 (2H, d, J = 8.3 Hz, ArH), 6.99 (2H, d, J = 8.3 Hz, ArH), 7.29 (2H, d, J = 8.0 Hz, ArH), 7.99 (2H, d, J = 8.0 Hz, ArH) 9.29 (1H, s, CH). δ_C (CDCl_3, 100MHz) 20.9 21.6 (CH_3), 70.1, 71.8, 74.6, 80.7 (CH), 77.5, 84.0 (FcC), 127.5, 127.7, 129.7 (ArCH), 135.1, 136.0, 144.0 (ArC), 172.4 (CHN). ν_{max}(CCl_4) 1160, 1330, 1581 cm⁻¹. ESI-MS m/z 512 (M^+Na). CD λ_{max} (Δε): 293 (25.4), 383 (-3.4), 501 (14.8) (c 1.02 10⁻⁴ M, CHCl_3).
Method B. TiCl₄ (0.5 mL, 0.5 mmol, 1M toluene), was added dropwise to a stirred ice-cooled solution of (S)-4 (340 mg, 1.0 mmol), p-toluenesulfonylamine (172 mg, 1.0 mmol) and Et₃N (0.4 mL, 3.0 mmol) in dry CH₂Cl₂ (15 mL) under argon atmosphere. The mixture was stirred for 1h at room temperature and then quenched with water. The organic layer was separated dried (MgSO₄) and concentrated in vacuo. Imine 3c was obtained in quantitative yield as a red solid (482 mg) and could be used without any further purification. Chromatography on silica gel column (Light petroleum/EtOAc 3:1) for analytical aim afforded 3c in 85% yield.

N-(4-Methoxyphenyl)-N-{(1S)-1-[2-(SFc)(p-tolylsulfanyl)ferrocenyl]-3-butenyl}amine (2a). (Table 3 entry 1) To a stirred solution of 3a (110 mg, 0.25 mmol) and of a catalytic amounts of Sc(OTf)₃ (14 mg, 0.025 mmol) in dry CH₂Cl₂ cooled at 0°C under argon atmosphere, tetraallyltin (0.07 mL, 0.275 mmol) was added. The reaction was stirred at 0°C per 18 h and then quenched by adding water at the same temperature. The organic layer was extracted washed, dried over magnesium sulfate and concentrated under reduced pressure. The ¹H and ¹³C NMR spectra of the crude reaction mixture showed the presence of a single diastereoisomer. Chromatography on silica gel yielded the desired compound in 72% yield (70 mg, 0.14 mmol) as a viscous yellow/orange oil. δH (CDCl₃, 400MHz) 2.11 (1H, m, Ha-CH₂), 2.26 (3H, s, CH₃), 2.33 (1H, m, Hb-CH₂), 3.77 (3H, s, CH₃), 4.17 (5H, s, FcH), 4.33 (2H, m, FcH), 4.49 (2H, m, FcH and CHN), 5.03 (1H, bd, NH) 4.77 (1H, dm, J = 17 Hz, Ha-CH₂=), 4.88 (1H, dm, J = 10 Hz, Hb-CH₂=), 5.55 (1H, m, CH=), 6.77 (2H, d, J = 8.8 Hz, ArH), 6.84 (2H, d, J = 8.8 Hz, ArH), 6.96 (2H, d, J = 8.4 Hz, ArH), 6.99 (2H, d, J = 8.4 Hz, ArH). δC (CDCl₃, 100MHz) 20.85 (CH₃), 40.73 (CH₂), 51.9 (CHN), 55.8 (CH₃), 67.3, 68.2, 70.2 (FcCH), 74.8 (FcC), 75.4 (FcCH), 95.5 (FcC), 114.99, 115.06 (ArCH), 117.5 (CH₂=), 126.1, 129.4 (ArCH), 134.4 (CH=), 134.8, 136.5, 142.0, 152.2 (ArC). νmax (CCl₄) 3399 cm⁻¹. ESI-MS m/z 484 (M⁺+H) 506 (M⁺+Na). [α]D +85 (c 0.40 CHCl₃).

N-{(1S)-1-[2-(SFc)p-tolylsulfanyl)ferrocenyl]-3-butenyl}p-toluenesulfonamide (2b). (Table 3 entry 2) To a stirred solution of 3c (125 mg, 0.25 mmol) and of a catalytic amounts of Sc(OTf)₃ (14 mg, 0.025 mmol) in dry CH₂Cl₂ cooled at −15 °C under argon atmosphere, tetraallyltin (0.07mL, 0.275 mmol) was added. The reaction was stirred at −15 °C for 32 h and then quenched by adding water at the same temperature. The organic layer was extracted washed, dried over magnesium sulfate and concentrated under reduced pressure. The ¹H and ¹³C NMR spectra of the crude reaction mixture showed the presence of a single diastereoisomer. Chromatography on silica gel yielded the desired compound in 88% yield (93 mg, 0.18 mmol) as a yellow solid. M.p 65 – 67 °C (MeOH). δH (CDCl₃, 400MHz) 1.89 (2H, m, CH₂), 2.22 (3H, s, CH₃), 2.42 (3H, s, CH₃), 4.21 (1H, m, FcH), 4.27 (5H, s, FcH), 4.32 (1H, m, FcH), 4.47 (1H, m, FcH), 4.54 (1H, dm, J = 17 Hz, H₃-CH₂=), 4.63 (1H, m, CHN) 4.86 (1H, dm, J = 10 Hz, H₃-CH₂= and 1H, bs, NH) 5.27 (1H, m, CH=), 6.85 (2H, d, J = 8.2 Hz, ArH), 6.95 (2H, d, J = 8.2 Hz, ArH), 7.33 (2H, d, J = 8.0 Hz, ArH), 7.85 (2H, d, J = 8.0 Hz, ArH). δC (CDCl₃, 100MHz) 20.8, 21.5(CH₃), 39.5 (CH₂), 51.5, 67.8, 68.6, 70.7, 75.9 (CH), 92.8 (C), 119.3 (CH₂), 125.6,
127.1, 129.4, 129.8 (ArCH), 132.1 (CH), 134.7, 136.4, 138.3, 143.5 (ArC). \( \nu_{\text{max}}(\text{CCl}_4) \) 3345, 1337, 1165 cm\(^{-1}\). ESI-MS \( m/z \) 554 (M\(^{+}\)+Na). \([\alpha]^{20}_D \) - 72.9 (c 0.45 CHCl\(_3\)). Anal. Calcd. for C\(_{28}\)H\(_{29}\)FeNO\(_2\)S\(_2\) (531.10): C, 63.27; H, 5.50; N, 2.64. Found: C, 63.42; H, 5.39; N 2.81.

**General procedure for the reaction of imines 3a and 3c with Grignard reagents in the presence a Lewis Acid (Table 3)**

To a solution of imine 3a or 3c (0.2 mmol) and a Lewis Acid (MgBr\(_2\) or LiCl) (0.4 mmol) in dry THF (10 mL) cooled at 0 °C under argon atmosphere, a solution of the Grignard reagent (0.6 mmol) was slowly added. The solution was stirred at the temperature reported in the Table 3. The reaction was followed by TLC analysis and then quenched with saturated NH\(_4\)Cl solution and extracted with Et\(_2\)O. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure. The diastereomeric ratio was determined by \(^1\)H- and \(^{13}\)C-NMR spectra on the reaction mixture and then the final derivative was isolated by column chromatography (hexane/EtOAc 3:1).

\( N\{-\{1(S)-1-[2-(SFc)-p-Tolylsulfanyl)ferrocenyl]ethyl\}p-toluenesulfonamide \} \) (2e). (Table 3 entry 8). Following the general procedure using imine 3c (98 mg), MgBr\(_2\) (74 mg) and a 3.0 M solution in THF of MeMgBr (0.2 mL), the final product was obtained in 18 h at 0°C after chromatography as a yellow solid in 78 % yield. The d.e. was found >98% on the crude \(^1\)H-NMR. M.p 150 – 151 °C (Et\(_2\)O). \( \delta_H \) (CDCl\(_3\), 300MHz) 0.94 (3H, d, J = 6.4 Hz, CH\(_3\)), 2.11 (3H, s, CH\(_3\)), 2.29 (3H, s, CH\(_3\)), 4.08 (5H, s, FcH), 4.14 (1H, m, FcH), 4.16- 4.23 (2H, 2m, CHN, FcH), 4.31 (1H, m, FcH), 4.86 (1H, d, J = 4.8 Hz, NH), 6.72 (2H, d, J = 8.3 Hz, ArH), 6.83 (2H, d, J = 8.3 Hz, ArH), 7.17 (2H, d, J = 8.3 Hz, ArH), 7.78 (2H, d, J = 8.3 Hz, ArH). \( \delta_C \) (CDCl\(_3\), 75MHz) 20.9, 21.6, 29.7 (CH\(_3\)), 48.3, 66.9, 68.9, 70.5, 75.7 (CH), 79.2 95.4, (C), 126.2, 127.3, 129.6, 129.8 (ArCH), 135.1, 136.1, 137.8, 143.5 (ArC). \( \nu_{\text{max}}(\text{CCl}_4) \) 3331 cm\(^{-1}\). ESI-MS \( m/z \) 528 (M\(^{+}\)+Na). \([\alpha]^{20}_D \) +3 (c 0.54 CHCl\(_3\)). Anal. Calcd. for C\(_{26}\)H\(_{27}\)FeNO\(_2\)S\(_2\) (505.08): C, 61.78; H, 5.38; N, 2.77. Found: C, 61.52; H, 5.24; N 2.99.

\( N\{-\{1(S)-1-[2-(SFc)-p-Tolylsulfanyl)ferrocenyl]-2-propenyl\}p-toluenesulfonamide \} \) (2f). (Table 3 entry 10). Following the general procedure using imine 3c (98 mg) MgBr\(_2\) (74 mg) and a 1.0 M solution in THF of vinylMgBr (0.6 mL), the final product was obtained in 48 h at r.t. after chromatography as a yellow solid in 36 % yield and as a single diastereoisomer beside 39 % of the recovered imine 3c. M.p 62 – 63 °C (Et\(_2\)O). \( \delta_H \) (CDCl\(_3\), 300MHz) 2.12 (3H, s, CH\(_3\)), 2.29 (3H, s, CH\(_3\)), 4.12 (1H, m, FcH), 4.14 (5H, s, FcH), 4.19 (1H, m, FcH), 4.32 (1H, m, FcH), 4.56 (1H, m, CHN), 4.60 (2H, m, CH=), 4.57 (1H, d, J = 4.6 Hz, NH), 5.50 (1H, 4d, J = 17.3, J = 9.6, J = 7.6 Hz, CH=), 6.69 (2H, d, J = 7.9 Hz, ArH), 6.82 (2H, d, J = 7.9 Hz, ArH), 7.12 (2H, d, J = 8.2 Hz, ArH), 7.60 (2H, d, J = 8.2 Hz, ArH). \( \delta_C \) (CDCl\(_3\), 100MHz) 20.8, 21.5(CH\(_3\)), 54.8 (CHN), 68.5, 68.9, 71.5, 75.8 (FcCH), 77.2, 92.5 (Fcc), 116.35 (CH=), 126.6, 127.5, 129.3, 129.4 (ArCH), 135.0, 135.3, 137.4, 143.3 (ArC). \( \nu_{\text{max}}(\text{CCl}_4) \) 1160, 1336, 3331 cm\(^{-1}\). ESI-MS \( m/z \) 540 (M\(^{+}\)+Na). \([\alpha]^{20}_D \) +17 (c 0.44 CHCl\(_3\)). Anal. Calcd. for C\(_{27}\)H\(_{27}\)FeNO\(_2\)S\(_2\) (517.08): C, 62.67; H, 5.26; N, 2.71. Found: C, 62.79; H, 5.41; N 2.95.
$N$-\{1(S)-1-[2-(S$_{R_e}$)-(p-Tolylsulfanyl)ferrocenyl]-2-propenyl\}p-toluenesulfonamide (2f). (Table 3 entry 11). Following the general procedure using imine 3c (98 mg), LiCl (17 mg) and a 1.0 M solution in THF of vinylMgBr (0.6 mL), the final product was obtained in 5 min after chromatography as a yellow solid in 97 % yield. The d.e. was find 96% on the crude $^1$H-NMR.

$N$-\{1(S)-1-[2-(S$_{R_e}$)-(p-Tolylsulfanyl)ferrocenyl]-2-propenyl\}p-toluenesulfonamide (2g). (Table 3 entry 13). Following the general procedure using imine 3c (98 mg), LiCl (17 mg) and a 1.0 M solution in THF of vinylMgBr (0.2 mL), the final product was obtained in 20 min. The d.e. was find 77% on the crude $^1$H-NMR. The two diastereoisomers were separated by chromatography on preparative TLC that afforded as the higher R$_f$ product the minor diastereoisomer in 13% yield and as the second R$_f$ product the major diastereoisomer in 84% yield. M.p 107 – 109 °C (MeOH).

$N$-\{1(S)-1-[2-(S$_{R_e}$)-(p-Tolylsulfanyl)ferrocenyl]-2-propenyl\}p-toluenesulfonamide (2h). (Table 4 entry 3). Following the general procedure using imine 3c (98 mg) MgBr$_2$ (74 mg) and a 3.0 M solution in THF of EtMgBr (0.2 mL), after 48 h at r.t. the column chromatography afforded a fraction containing product 2h as a single diastereoisomer and product 7b a 1:3 ratio in a 35% yield. The separation of the two product was attempted by preparative thin layer chromatography and afford as the first R$_f$ fraction a mixture of 2h and 7 in a 1:1 ratio and as the second R$_f$ fraction product 7 with a purity of 90%.

$N$-\{1(S)-1-[2-(S$_{R_e}$)-(p-Tolylsulfanyl)ferrocenyl]-2-propenyl\}p-toluenesulfonamide (2h). (Table 4 entry 4). Following the general procedure using imine 3c (98 mg), LiCl (17 mg) and a 3.0 M solution in THF of EtMgBr (0.3 mL), after 18 h at r.t. the column chromatography afforded as the first R$_f$ fraction a mixture containing product 2h and product 7b in a 1:1 ratio in 62% yield and as the second R$_f$ fraction the unreacted imine 3c in 20% yield.
General procedure for the reaction of imine 3c with EtMgBr in the presence of Cp$_2$ZrCl$_2$ (Table 4, entries 5-7)

To a solution of imine 3c (98 mg, 0.2 mmol) and Cp$_2$ZrCl$_2$ (6 mg, 0.02 mmol) in dry THF (5 mL) under argon atmosphere, the EtMgBr (3M in THF) was added and the reaction mixture was stirred until disappearance of the starting imine. The reaction was quenched with 5% NaOH (1.5 mL) and then diluted with water and extracted with Et$_2$O. The combined organic layer were dried (MgSO$_4$) and concentrated. Chromatography of the crude reaction mixture furnished a fraction containing the alkylated product 2h and the reduction product 7b in variable ratio depending on the amount of EtMgBr used. (3 equivalents of EtMgBr: ratio 2h : 7b = 1:3 total yield 88%; 10 equivalents of EtMgBr: ratio 2h : 7b = 1:2 total yield 89%; 25 equivalents of EtMgBr: ratio 2h : 7b = 1.2:1 total yield 89%)

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References

30. CCDC 219884 contains the supplementary crystallographic data for 1c. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
36. CCDC 222560 contains the supplementary crystallographic data for 1c. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).