A Synthesis Detour to Planar-Diastereoisomeric Ferrocene Derivatives around an Unexpected Rearrangement of *ortho*-Lithiated *Kagan*'s Template [*S*(*S*)]-(*p*-Tolylsulfinyl)ferrocene

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Usually, *ortho* lithiation of *Kagan*'s template **1** and quenching with electrophiles leads highly diastereoselectively to planar-chiral 1,2-disubstituted ferrocenes. Surprisingly, lithiation of **1** with lithium diisopropylamide (LDA) followed by addition of paraformaldehyde afforded regioisomer (+)-{[*S*(*S*)]-[4-(2-hydroxyethyl)phenyl]sulfinyl}ferrocene (**2**), which was converted to (+)-{[*S*(*S*)]-{4-{2-[(methylsulfonyl)oxy]ethyl}phenyl}sulfinyl}ferrocene (**3**) (*Scheme 1*). The desired diastereoisomer (*l*)-1-(hydroxymethyl)-2-(*p*-tolylsulfinyl)ferrocene (**5**) in turn could also be obtained by *ortho* lithiation of **1** with LDA but by quenching with DMF to yield aldehyde **4** first, which then was reduced with $NaBH_4$ to **5**. Finally, target compound (*l*)-1-[(dimethylamino)methyl]-2-(*p*-tolylsulfinyl)ferrocene (**6**) was obtained by substitution of the OH group of **5** under mild conditions or directly by *ortho* lithiation of **1** with lithio-2,4,6-triisopropylbenzene (=2,4,6-triisopropylphenyl)lithium; LTP) followed by quenching with *N*,*N*-dimethylmethyleneiminium chloride. At low temperatures, reaction of **1** with LDA leads, *via* the preferred diastereoisomeric transition state '*exo*'-**7** and under extrusion of a (diisopropylamine)lithium complex of type **8**, in a highly selective manner, to diastereoisomeric *ortho*-lithiated chelate (*l*)-**9** (*Scheme 2*). The reaction of **1** to **2** is explained by a rearrangement of (*l*)-**9** to {[*S*(*S*)][4-(lithiomethyl)phenyl]sulfinyl}ferrocene **10**, which is acid-catalyzed by coordinated diisopropylamine in complexes of type **8**. This rearrangement is not observed if LTP is used as base or, in case LDA is applied, if the electrophile is sufficiently reactive at low temperatures.

1. Introduction. – Robust mono- [1a,b] and bidentate [1c][2] planar-chiral ferrocenyl ligands gained a fundamental role in enantioselective catalysis over the past decade. This is documented by the industrially important *Syngenta* (*S*)-Metolachlor process [3], for example. Usually 1,2-disubstituted ferrocene derivatives are obtained *via ortho* lithiation of a ferrocene containing coordinating functionalities; R_2N-CR_2- and $RO-CR_2-$ are the most common types. Usually, alkyllithium reagents are used for this deprotonation reaction. Coordination of the lithium ion with the ligating substituent at the ferrocene guides the carbanion to the *ortho* position, where deprotonation can then occur under kinetic control, popularly defined as 'kinetic acidity'. This deprotonation can also occur under thermodynamic control, to which is

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popularly referred as 'thermodynamic acidity'[2]), if the pK_A value of the *ortho*-H-atom at the η^5-cyclopentadienyl (η^5-Cp) unit is lower than the one of the conjugate acid of the lithiating reagent. In this sense, the resulting chelation of the lithium ion with the coordinating group stabilizes the *ortho*-lithiated ferrocene, in the first case in a metastable or in the second in a truly thermodynamic fashion. To gain full benefit from these coordination effects, THF, Et_2O, or hexanes and mixtures thereof are the solvents of choice, which coordinate only in a labile fashion or not at all with the lithium ion. After *ortho* lithiation, quenching with an electrophile leads then to the desired 1,2-disubstituted planar-chiral ferrocene. Enantiomerically pure 1,2-disubstituted ferrocenes are usually obtained by resolution of diastereoisomers *via* a temporarily introduced chiral auxiliary as covalent substituent [4] and mostly established by diastereoselective *ortho* lithiation of a ferrocene template containing a 'diastereodirecting' chiral auxiliary group such as *Ugi*'s template (*R*)- or (*S*)-[1-(dimethylamino)-ethyl]ferrocene (FA) [2][3][5]. *Kagan*'s template {[*S*(*S*)]-*p*-tolylsulfinyl}ferrocene (**1**) [6] can also be *ortho*-lithiated with high diastereoselectivity, but BuLi, *sec*-BuLi, and *t*-BuLi cannot be used as bases, because they substitute the chiral sulfinyl group, which serves as the 'diastereodirecting' functionality. This can be avoided, if lithio-2,4,6-triisopropylbenzene (=(2,4,6-triisopropylphenyl)lithium; LTP) [6e,g] is used instead, which is sterically too bulky for a nucleophilic attack on the sulfinyl group. Compared to FA, the thermodynamic C–H acidities of the η^5-Cp moieties of **1** are enhanced to such an extent by the inherently strong electron-withdrawing sulfinyl group that also lithium diisopropylamide (LDA) can be used for *ortho* lithiation. Unfortunately, the use of LDA is limited by the electrophiles added later, which must be inert against LDA and diisopropylamine as well. Taking advantage of the aforementioned base incompatibility, the sulfinyl group of the resulting *ortho*-substituted {[*S*(*S*)]-*p*-tolylsulfinyl}ferrocene can be substituted by virtually any other electrophile by Li-exchange with ^{t}BuLi in a following step [6]. In this way *Kagan*'s template **1** offers a larger synthetic variety than FA, so we chose **1** for our quest for planar-chiral 1,2-disubstituted ferrocenyl ligands. Suitable synthetic pathways for the diastereoselective introduction of a (dimethylamino)methyl group in *ortho* position of **1** were investigated (*Scheme 1*), because the resulting (*l*)-1-[(dimethylamino)methyl]-2-(*p*-tolylsulfinyl)-ferrocene (**6**) is a very promising intermediate for the simple preparation of *Josiphos* analogs [2c–f]. Derivative **6** is also a prototype ligand for bidentate planar-chiral ferrocenyl ligands containing a chiral sulfinyl group as second donor functionality. Such sulfinyl groups can complex a metal by an O- or S-binding mode and are expected to show additional steric effects due to their important geometric asymmetry. Therefore, such ligands are very attractive for possible applications in enantioselective catalysis.

2. Results and Discussion. – The diastereoselective introduction of a hydroxymethyl group in **1** leading to (*l*)-1-(hydroxymethyl)-2-(*p*-tolylsulfinyl)ferrocene (**5**), followed

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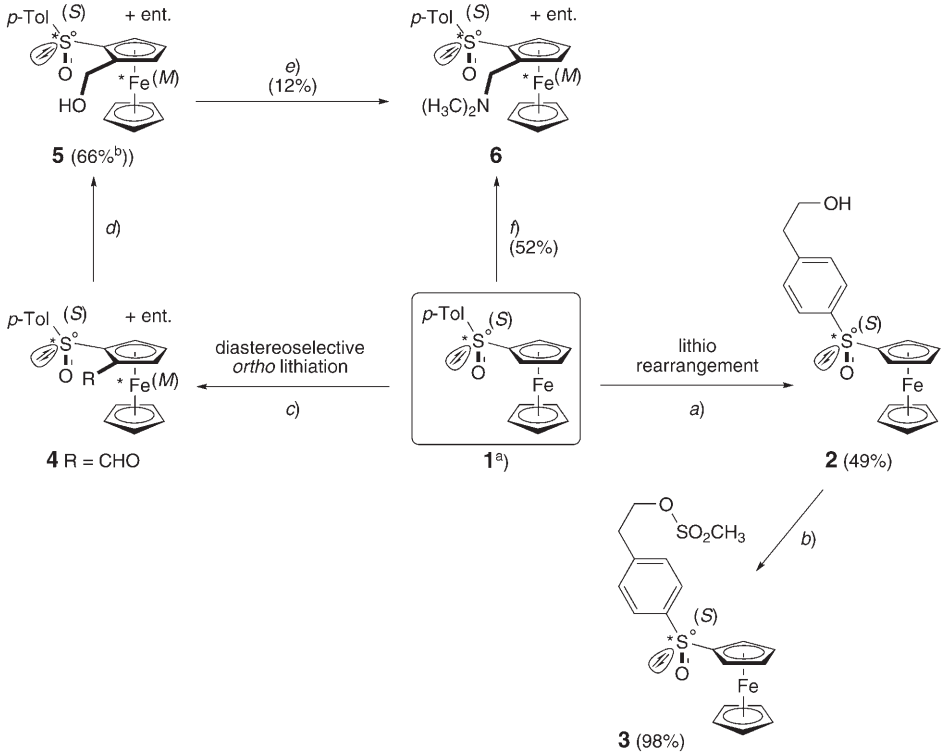
[2]) The authors wish to express their concerns about the terminologies 'kinetic' and 'thermodynamic' acidity, because 'acidity' as the dissociation capability of an acid (HA) into protons (H^+ resp. H_3O^+) and into the conjugate base (A^-) expressed by the pK_A value correlating to the H–A bond strength is by definition exclusively thermodynamic! Only for a common transparency, the authors finally decided to use these unfortunate terminologies.

Scheme 1



a) 1. LDA (2.0 equiv.)/THF, −78°; 2. $(H_2CO)_n$ (5.8 equiv.), −78° to r.t. *b*) $MeSO_2Cl$ (1.2 equiv.), Et_3N (1.5 equiv.), CH_2Cl_2, 0° to r.t. *c*) With racemate of **1**: 1. LDA (2.0 equiv.), THF, −78°; 2. DMF (5.8 equiv.), −78° to r.t. *d*) With not further purified crude **4**: $NaBH_4$ ('1.1 equiv.'), MeOH, r.t. *e*) 1. Addition *to* preformed phosphine adduct from PPh_3 (1.1 equiv.) + CBr_4 (1.2 equiv.), CH_2Cl_2, −70°; 2. $[Me_2N]_2CH_2$ (3.0 equiv.), $AgBF_4$ (1.2 equiv.), r.t. *f*) With racemate of **1**: 1. LTP (2.0 equiv.), THF, −78°; 2. $[Me_2N{=}CH_2]^+ Cl^-$ (4.2 equiv.), −78° to r.t.

[a]) In this and the following schemes, **1** refers to 86.4% e.e. of [*S*(*S*)]. [b]) Overall yield.

by linear functional-group interconversion, was anticipated first. Lithiation of **1** (86.4% enantiomeric excess (e.e.), [*S*(*S*)]) with LDA and reaction with paraformaldehyde did not lead to the expected 1,2-disubstituted ferrocene diastereoisomer **5** but exclusively to regioisomer (**2**) in 49% yield; some residual, not racemized **1** was recovered. This result is the more surprising because racemic **5** was obtained under similar reaction conditions, but using for *ortho* lithiation ferrocenyllithium (FcLi) [6e][3]) and LTP [6e,g] for analog 1,2-substituted ferrocenes instead. While LTP deprotonates irreversibly at the *ortho* position, diisopropylamine, the conjugate acid of LDA, is obviously not an

[3]) Note that FcLi is not an appropriate base for *ortho* lithiation of **1** because the sulfinyl group racemizes by an intermolecular exchange equilibrium with FcLi [6b,f]. Nevertheless, racemic **5** was obtained as pure (*l*)-diastereoisomer after 1 h reaction with paraformaldehyde at 0°.

innocent spectator in *ortho*-lithiation reactions. Both, the Me–C(4) group at the phenylsulfinyl part and the η^5-Cp units are in conjugation with the electron-withdrawing sulfinyl group of **1**, but this Me group is also in σ^*-π resonance with the benzene moiety, which is more electron-deficient than the η^5-Cp units[4]). Therefore, the thermodynamic C–H acidity of this Me group is even more enhanced than the ones of the η^5-Cp units. On the first hand, this Me group with three equivalent protons is expected to have also a three times higher statistical probability for proton abstraction, and in this way also a stronger kinetic acidity than the two diastereotopic positions at the η^5-Cp units. If so, then lithiation of **1** followed by electrophile quenching should lead generally to the Me–C(4)-functionalized isomer under kinetic and thermodynamic conditions as well, and independently from the base used. But this is not the case, so these alleged contradictions require a clarifying explanation (*Scheme 2*).

i) Obviously the strong basicity of LDA (pK_A diisopropylamine > 35) does not determine the position of proton abstraction but only that the reaction itself can proceed (*Paths c* and *e* in *Scheme 2*). *ii*) It is reasonable to assume that the diastereoselectivity of the *ortho*-lithiation is driven by precomplexation of LDA *via* coordination of the sulfinyl O-atom of **1** with Li^+ in the sense of two possible conformational and diastereoisomeric transition states '*exo*'-**7** and '*endo*'-**7** (*Paths a* and *b* in *Scheme 2*). This precomplexation under kinetic control at $-78°$ is obviously strong enough to outflank the kinetic and the thermodynamic acidity of the Me–C(4) group: It increases the basicity of the N-atom of LDA and 'guides' it simultaneously and preferably closest to that diastereotopic *ortho*-H-atom of the η^5-Cp unit which allows then the *p*-tolyl group to adopt a sterically preferred '*exo*' position in this whole arrangement. This leads finally *via* transition state '*exo*'-**7** to the diastereoisomeric *ortho*-lithiated chelate (*l*)-**9** (*Path c* in *Scheme 2*) and finally by trapping with a strong electrophile to the corresponding *like* diastereoisomer **4** (*Path d* in *Scheme 2*). If very slow addition rates of LDA at $-78°$ are chosen, the formation of the sterically less preferable transition state '*endo*'-**7** leading to *ortho*-lithiated chelate (*u*)-**9** can be suppressed completely (*Path b* in *Scheme 2*). *iii*) *Seebach* and co-workers found in the deuteration of various compounds with LDA that the deuterium incorporation is sometimes incomplete because diisopropylamine is coordinated to Li-cations [7]. In such complexes of the general type **8** (*Path c* in *Scheme 2*), diisopropylamine is then transformed to a comparably strong acid, which can now act catalytically. Furthermore, it is also possible for diisopropylamine to coordinate to the corresponding *ortho*-lithioferrocene intermediate (*l*)-**9** in analogy to the known [Li(Fc)(tmeda)] complex (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine) [8], giving rise to an intramolecular active proton source. Therefore, *ortho* lithiation of *Kagan*'s template **1** becomes now reversible. Consistent with this explanation, we found that *ortho* lithiation of **1** followed by electrophile quenching never leads to complete conversion to the desired 1,2-disubstituted ferrocene, even when up to 4 equiv. of LDA are used. In other words, the formation of diastereoisomeric *ortho*-lithiated chelate (*l*)-**9** (also of (*u*)-**9** if addition of LDA is not performed slowly enough) is not an irreversible but only a metastable energy sink under these reaction conditions. *iv*) Paraformaldehyde as polyacetal is not

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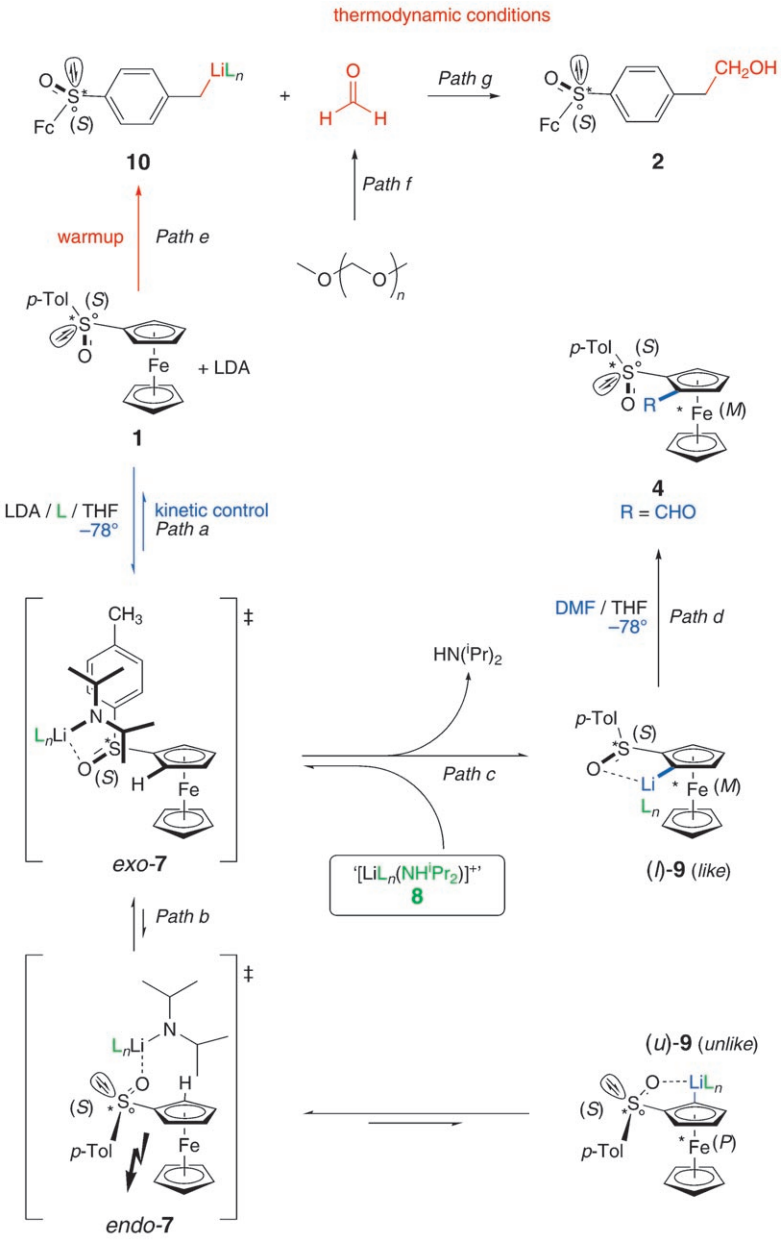
[4]) Note that ferrocene reacts $3 \cdot 10^6$ times faster than benzene in electrophilic aromatic substitution reactions.

Scheme 2. *Diastereoselective* ortho-*Lithiation of* Kagan's *Template* **1** (blue) *and Lithio Rearrangement* (red). Permutative ligand coordination around Li^+ is symbolized with L = THF, $^iPr_2N^-$, LDA, HN^iPr_2 (green).



well soluble, not reactive, and does not depolymerize when added at $-78°$. Reaching slowly thermodynamic conditions, (*l*)-**9** can now rearrange to the thermodynamically favored product **10** (*Path e* in *Scheme 2*) because reaction with an electrophile cannot occur at that moment. Later on, during warmup to room temperature and after decay of paraformaldehyde into its reactive carbonyl monomer (*Path f* in *Scheme 2*), base **10** is trapped to give finally **2** (*Path g* in *Scheme 2*). *v*) The diastereoselectivity of the *ortho* lithiation of *Ugi*'s template (*R*)- or (*S*)-FA is widely explained by an equilibrium of its corresponding *ortho*-lithiated diastereoisomers. In analogy to (*R*)- or (*S*)-FA, an equilibrium of (*l*)-**9** and (*u*)-**9** should be in favor of (*l*)-**9** due to the preferred '*exo*' position of the *p*-tolyl group with decreasing temperature, of course. If (*l*)- and (*u*)-**9** interconvert directly, then such an equilibrium must be trapped by the irreversible formation of the thermodynamically favored product **10**. This is not the case if *ortho* lithiation is not performed with LDA [6e], establishing that without the presence of complexed diisopropylamine, diastereoisomeric chelates of the type (*l*)- and (*u*)-**9** are not in an equilibrium. Therefore, such an explanation for the high diastereoselectivity of the *ortho* lithiation of *Kagan*'s template **1** must be questioned in favor of the previously discussed strong kinetic acidity of the *ortho*-H-atom at the η^5-Cp unit represented by the diastereomeric transition state '*exo*'-**7**.

Rearrangement product **2** (min. 86.4% e.e.) was then converted to mesylate derivative **3** in 98% yield (*Scheme 1*), which might be of interest as suitable electrophilic reagent for the introduction of terminal chiral ferrocenyl units on dendrimers [9], for instance. Crystals of **3** suitable for X-ray crystal-structure determination were obtained from a saturated CH_2Cl_2 solution with some drops of AcOEt (*Fig. 1*, *Table 1*). In this way, the rearrangement and trapping reaction of **1** to **2** is established beyond doubt.

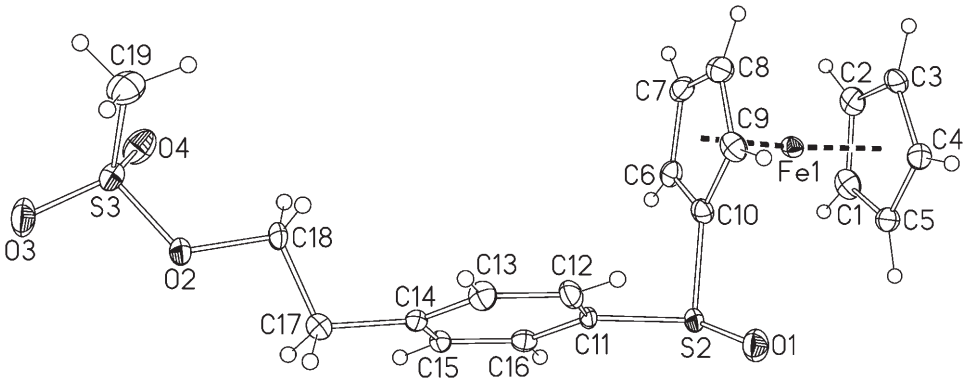


Fig. 1. *Thermal ellipsoid plot* (50% probality) *of the molecular structure of the chiral ferrocenyl derivative* **3** *obtained from unexpected product* **2**. For selected bond distances and angles, see *Table 1*.

Racemic aldehyde **4** was then obtained by *ortho* lithiation of racemic **1** followed by quenching with DMF. NMR Analysis of the crude product established that racemic **4** was obtained diastereoisomerically pure. This shows again that the regio- and coherently also the diastereoselectivity is only dependent on the electrophile's

Table 1. *Selected Bond Distances and Angles of* **3**

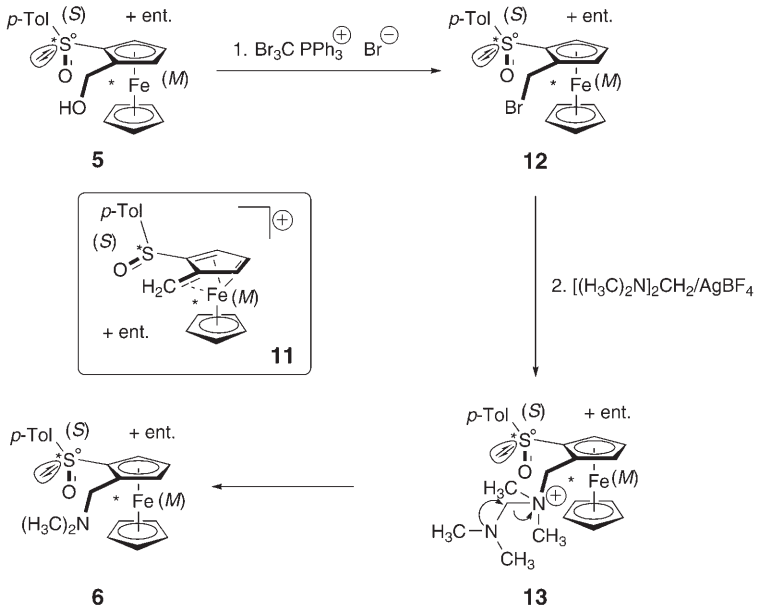
Distance	[Å]	Angle	[°]
S(2)–C(11)	1.797(2)	C(11)–S(2)–O(1)	106.91(9)
S(2)–O(1)	1.488(2)	C(10)–S(2)–O(1)	108.1(1)
S(2)–C(10)	1.777(2)	C(18)–O(2)–S(3)	119.3(2)
S(3)–O(2)	1.574(2)	O(3)–S(3)–O(4)	119.5(2)
S(3)–O(3)	1.429(2)	O(2)–S(3)–C(19)	103.3(2)
S(3)–O(4)	1.428(2)	C(10)–Fe(1)–C(1)	125.36(9)
S(3)–C(19)	1.758(2)	C(10)–Fe(1)–C(2)	158.83(9)
O(2)–C(18)	1.471(2)	C(10)–Fe(1)–C(3)	160.49(9)
C(10)–Fe(1)	2.028(2)	C(10)–Fe(1)–C(4)	126.57(9)
C(5)–Fe(1)	2.057(2)	C(10)–Fe(1)–C(5)	111.92(9)

reactivity at $-78°$ under otherwise identical reaction conditions (*Path d* in *Scheme 2*). Aldehyde **4** was previously also obtained by using LTP as base and ethyl formate as electrophile [6g]. Crude **4** was then directly reduced with $NaBH_4$ to **5** allowing then an easy removal of residual **1** from the previous product mixture by purification with column chromatography to obtain pure **5** in 66% overall yield (*Scheme 1*). Again, no epimerization of the chiral sulfinyl group was observed by NMR analysis of the crude product.

Due to the strong electron-withdrawing sulfinyl group, the usual dissociation tendency of the OH group proved to be retarded for **5** compared to (hydroxymethyl)ferrocene. Of course, nucleophilic substitution of the OH group was desired, which is known to proceed in S_N1 fashion *via* (η^4:η^2)-fulvenium intermediates [2][10], but the corresponding intermediate **11** of that type is expected to be destabilized (*Scheme 3*). Therefore, activation of the OH group by esterification [2] was considered to be insufficient. If possible at all, nucleophilic substitution in glacial acetic acid [2][3] would presumably have led to epimerization of the chiral sulfinyl group. Having *Salzer* and co-worker's electrophilic activation of benzylic positions of (η^6-arene)tricarbonylchromium(0) complexes in mind [11], racemic **5** was activated *in situ* as bromide **12** with the preformed PPh_3/CBr_4 adduct (*Scheme 3*). Preformation was necessary to avoid reduction of the *p*-tolylsulfinyl to the corresponding *p*-tolylthio group by triphenylphosphine. No attempts were made to isolate **12**. Bromide **12** in turn was then treated *in situ* with $AgBF_4$ and *N,N,N′,N′*-tetramethylmethanediamine as synthetic equivalent for free dimethylamine to give, presumably *via* adduct **13**, the desired [(dimethylamino)methyl]ferrocene **6**. Again, only the *like* diastereoisomer of **6** could be detected in the crude product by NMR, but **6** was only obtained in 12% yield after chromatography with this method. To the best of our knowledge, this reaction is the first successful activation and substitution reaction at a fulvenic position of a 1,2-disubstituted ferrocene containing a strongly deactivating group.

This reaction was then finally complemented with the diastereoselective *ortho* lithiation of racemic **1** with LTP followed by quenching with *N,N*-dimethylmethyleneiminium chloride (*Eschenmoser*'s salt) [12] to diastereoisomerically pure racemic **6** (*Scheme 1*) in a more practicable yield of 52%. After addition of *Eschenmoser*'s salt to intermediate (*l*)-**9**, the deep orange color turned into clear yellow within minutes,

Scheme 3. *Presumable* in situ S_N1*-Type Reaction Pathway of* **5** *to* **6** via ($\eta^4:\eta^2$)*-Fulvenium Intermediate* **11**



demonstrating the strong electrophilic potential of *Eschenmoser*'s salt compared to DMF and to the polyacetal paraformaldehyde. After applying a trick (see *Exper. Part*), single crystals of racemic **6** suitable for X-ray crystal-structure determination could be obtained from a saturated AcOEt solution. The crystal examined contained both enantiomers of **6** (*Fig. 2*, *Table 2*). This confirms the diastereoselectivity of the *ortho* lithiation and the configurational integrity *vide infra*. Conclusively, now the method for preparing enantiomerically pure **6** is given.

3. Conclusion. – The rearrangement of *ortho*-lithiated intermediate (*l*)-**9** to the thermodynamically more stable base **10** can only occur if diisopropylamine complexes of type **8** are present as catalysts in the reaction solution. The following crucial issues should be considered for the preparation of diastereoisomerically pure 1,2-disubstituted ferrocenes *via ortho* lithiation of *Kagan*'s template **1**: *i*) if LDA is chosen as base, then *ortho* lithiation as well as electrophile quenching should be performed strictly at $-78°$; furthermore, the subjected electrophile should not only be inert against LDA and diisopropylamine but also highly reactive at this temperature. *ii*) If the electrophile does not fulfill these requirements, then *ortho* lithiation should preferably be performed with LTP. *iii*) Complementary, if functionalization of the Me–C(4) group is desired, lithiation must be performed with LDA and, before electrophile quenching, the reaction solution must warm up over a sufficient time scale to ensure rearrangement to intermediate **10**.

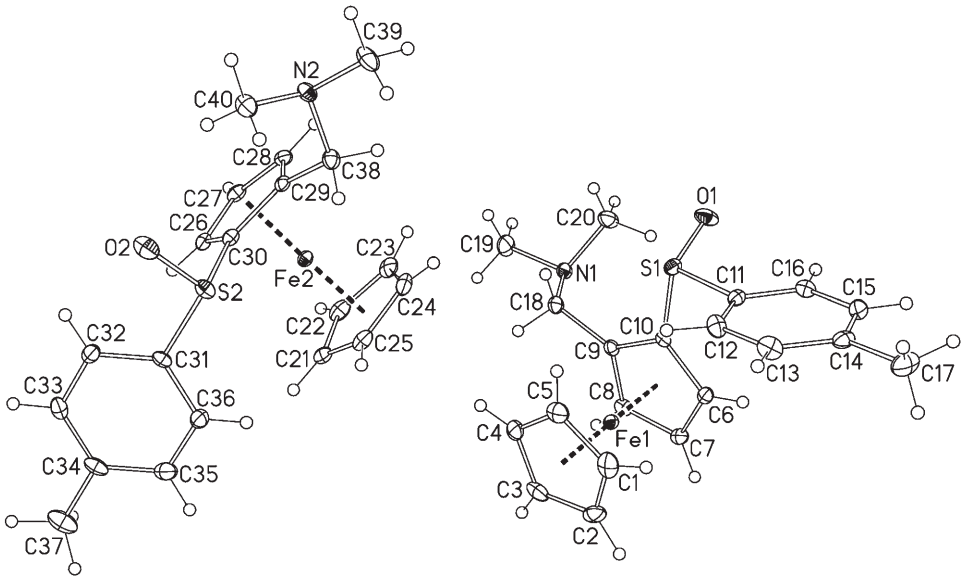


Fig. 2. *Thermal ellipsoid plot* (50% probality) *of the arrangement of the two symmetrically independent molecules representing the two enantiomers of* **6** (*like*) *as [*S(S),M*]-***6** (left) *and [*S(R),P*]-***6** (right). Note that due to the inversion center of space group $P\bar{1}$ (no. 2), the corresponding inversion image of this arrangement is also present in the unit cell. The two independent molecules differ only slightly in their conformations. For selected bond distances and angles, see *Table 2*.

Table 2. *Selected Bond Distances and Angles of racemic* **6**

Distance	[Å]	Angle	[°]
S(1)–C(11)	1.796(2)	C(11)–S(1)–O(1)	106.65(8)
S(1)–O(1)	1.496(2)	C(10)–S(1)–O(1)	106.91(8)
S(1)–C(10)	1.777(2)	C(9)–C(18)–N(1)	113.1(2)
C(18)–C(9)	1.506(3)	C(18)–N(1)–C(19)	109.8(2)
N(1)–C(18)	1.469(2)	C(18)–N(1)–C(20)	110.5(2)
N(1)–C(19)	1.458(2)		
N(1)–C(20)	1.462(2)		
S(2)–C(31)	1.792(2)	C(31)–S(2)–O(2)	106.60(8)
S(2)–O(2)	1.496(2)	C(30)–S(2)–O(2)	106.96(8)
S(2)–C(30)	1.779(2)	C(29)–C(38)–N(2)	113.4(2)
C(38)–C(29)	1.508(3)	C(38)–N(2)–C(39)	109.6(2)
N(2)–C(38)	1.477(2)	C(38)–N(2)–C(40)	110.6(2)
N(2)–C(39)	1.460(2)		
N(2)–C(40)	1.459(2)		

We propose the strong kinetic acidity of the *ortho*-H-atom at the η^5-Cp unit as main reason for the high diastereoselectivity of the *ortho* lithiation of **1** and not an interconversion equilibrium of the diastereoisomeric chelate intermediates (*l*)- and (*u*)-**9**. This strong kinetic acidity is given by a synergism of a simultaneous increase of the N-atom basicity of precomplexed LDA and the preferable conformational '*exo*-

guidance' of the base to the *ortho*-H-atom as represented by the diastereomeric transition state '*exo*'-**7**. To suppress the formation of the undesired chelate intermediate (*u*)-**9** completely, slow addition rates of LDA to **1** have to be chosen. For practical reasons, *ortho* lithiation of **1** with LTP is recommended to be performed by slow inverse addition, but due to the steric bulk of the base, complete diastereoselectivity is also ensured here. Based simply upon different electrophile reactivities and base variations, these estimations are qualitative in nature in the scope of our more synthesis-orientated work. However, they clearly indicate that the mechanistic discussion of the highly diastereoselective *ortho* lithiation of chiral ferrocene templates has to be continued.

The *in situ* activation and nucleophilic substitution of the OH group of **5** might be developed further into a general procedure for the preparation of various bidentate planar-chiral ferrocenyl ligands containing a chiral sulfinyl group as second donor functionality.

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Experimental Part

1. *General.* All reactions were carried out under dry N_2 by using conventional *Schlenk* and septum techniques. Liquid reagents were generally added with disposable plastic syringes, but reagent solns. freshly prepared prior to use were transferred to reaction solns. from a *Schlenk* tube by using a double canula with N_2 overpressure. All workups were performed in air. Solvents and chemicals were purchased from *Acros*, *Aldrich*, *Strem*, and *Merck*. Solvents and amines were dried and distilled under N_2 prior to use: THF over sodium/benzophenone; MeOH over magnesium; CH_2Cl_2, $^iPr_2NH$, and Et_3N over CaH_2. The actual concentrations of the alkyllithium reagents were determined by inverse titration of diphenylacetic acid prior to use. All other chemicals were used as received. LTP was prepared from 1-bromo-2,4,6-triisopropylbenzene [6e] in a slightly modified fashion (see *Exper. 6*). *Kagan*'s template **1** was prepared as published [6b,d]. The enantiomeric excess (e.e.) of **1** was determined by HPLC [6b], and the e.e. of the resulting diastereoisomeric **2** and **3** referenced to it as starting material. We did not achieve a satisfactory separation of the enantiomers of **2** and **3** by HPLC on various chiral stationary phases. *N,N,N′,N′*-Tetramethylmethanediamine was prepared according to [12a] and distilled from CaH_2 under N_2 prior to use. *Eschenmoser*'s salt *N,N*-dimethylmethyleneiminium chloride was prepared by *Danishefsky*'s method [12c], but the isolated product contained also polymeric $\{Me_2N[CH_2NMe_2]_nCH_2NMe_2\}Cl$, which does react in the same way. Flash column chromatography (FC): silica gel *F 60* from *Fluka* or *Merck*. Thin layer chromatography (TLC): *Merck F-60* silica plates with a 364-nm fluorescence indicator. Melting points: *Büchi 530* melting point apparatus; not corrected. Polarimetric measurements: *Perkin-Elmer-341* polarimeter. NMR Spectra: *Jeol FT-JNM-EX 270* (270 MHz) and *Bruker AMX-300* (300 MHz) spectrometers; in deuterated solvents and referenced to the residual proton signal of the particular solvent. Mass Spectra: *Varian MAT-212* spectrometer; in *m/z* (rel. %). Elemental analyses: *Carlo-Erba* elemental analyzer, model 1108.

2. *(+)-{[S(S)]-[4-(2-Hydroxyethyl)phenyl]sulfinyl}ferrocene* (**2**). An LDA soln. prepared from $^iPr_2NH$ (8.00 ml, 56.92 mmol) in THF (20 ml) at $-20°$ with 1.58M ^{t}BuLi in pentane (31.00 ml, 48.97 mmol) was transferred dropwise within 15 min to a well stirred soln. of **1** (7.82 g, 24.12 mmol; 86.4% e.e.) in THF (120 ml) at $-78°$. The soln. turned slowly deep orange and was stirred 90 min at

– 78° (→ deep orange suspension). To this suspension was added in one portion solid paraformaldehyde (4.21 g, 140.13 mmol), and the mixture was stirred for 16 h in the cooling bath slowly defrosting to r.t. (→ yellow suspension). The suspension was poured into brine saturated with NH_4Cl and extracted twice with AcOEt. The combined org. layer was dried ($MgSO_4$) and concentrated: 9.02 g of crude **2** as solid orange foam containing also starting material **1** (by NMR). The crude product was purified by FC (substance applied in a silica gel matrix, hexanes/AcOEt 1:3): 4.17 g (49%; R_f 0.13 (TLC)) of **2** and 151 mg (2%; R_f 0.43 (TLC)) of recovered of **1**. **2**. M.p. 139–140°. $[\alpha]_D^{23} = +231.3$ (CH_2Cl_2, $c = 0.0029$; 86.4% e.e.). ^{1}H-NMR ($CDCl_3$, 270 MHz): 7.52 (*d*, $^3J = 8.1$, 2 H_o of C_6H_4); 7.28 (*d*, $^3J = 8.1$, 2 H_m of C_6H_4); 4.59 (*m*, 1 H, Cp); 4.34–4.31 (*s* and *m*, 8 H, Cp and Cp′); 3.82 (*t*, $^3J = 6.6$, CH_2CH_2OH); 2.85 (*t*, $^3J = 6.6$, CH_2CH_2OH); 1.82 (br. *s*, OH). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 68 MHz): 143.91 (C_{ipso} of C_6H_4); 141.74 (C_p of C_6H_4); 129.56 (C_m of C_6H_4); 124.42 (C_o of C_6H_4); 94.13 (C(1) of Cp); 70.04 (Cp); 69.94 (Cp and Cp′); 67.92 (Cp); 64.99 (Cp); 63.19 (CH_2CH_2OH); 38.96 (CH_2CH_2OH). FAB-MS: 186 (43, Fc^+ with respect to ^{56}Fe), 339 (26, $[M-O]^+$ with respect to ^{56}Fe), 355 (100, M^+ with respect to ^{56}Fe). A correct elementary analysis could not be obtained.

3. *(+)-{[S(S)]-{4-{2-[(Methylsulfonyl)oxy]ethyl}phenyl}sulfinyl}ferrocene* (**3**). To a stirred soln. of **2** (4.036 g, 11.39 mmol; 86.4% e.e.) and Et_3N (2.30 ml, 1.670 g, 16.50 mmol) in CH_2Cl_2 (70 ml) at 0°, mesyl chloride (1.10 ml, 1.592 g, 13.90 mmol) was added dropwise. The red clear soln. was stirred for 12 h in the cooling bath defrosting to r.t. The soln. was poured into a sat. $NaHCO_3$ soln. and the lower org. phase washed once with brine, dried ($MgSO_4$), and concentrated to afford 4858 mg (99%) of nearly pure **3** which was purified by FC (substance applied in eluent, AcOEt): 4.837 g (98%) of **3** as yellow microcrystals. Crystallization from CH_2Cl_2 and some drops AcOEt gave crystals suitable for X-ray analysis. M.p. 111°. $[\alpha]_D^{23} = +199.6$ (CH_2Cl_2, $c = 0.0027$; 86.4% e.e.). ^{1}H-NMR ($CDCl_3$, 270 MHz): 7.56 (*d*, $^3J = 8.1$, 2 H_o of C_6H_4); 7.30 (*d*, $^3J = 8.1$, 2 H_m of C_6H_4); 4.57 (*m*, 1 H, H–C(2) or H–C(5) of Cp); 4.39 (*t*, $^3J = 6.7$, CH_2CH_2O); 4.37–4.31 (*s* and *m*, Cp′ and H–C(3), H–C(4), and H–C(5), or H–C(2), H–C(3), and H–C(4) of Cp); 3.06 (*t*, $^3J = 6.7$, CH_2CH_2O); 2.83 (*s*, Me). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 68 MHz): 145.06 (C_{ipso} of C_6H_4); 139.10 (C_p of C_6H_4); 129.49 (C_m of C_6H_4); 124.54 (C_o of C_6H_4); 94.27 (C(1) of Cp); 70.08 (Cp); 69.95 (CH_2CH_2O and Cp′); 69.49 (Cp); 67.92 (Cp); 64.84 (Cp); 37.41 (Me); 35.39 (CH_2CH_2O). FD-MS (pos.; CH_2Cl_2): 433 (100, M^+ with respect to ^{56}Fe). Anal. calc. for $C_{19}H_{20}FeO_4S_2$ (432.34): C 52.78, H 4.66, S 14.83; found: C 52.88, H 4.80, S 14.63.

4. *rac-(1)-1-Formyl-2-[(4-methylphenyl)sulfinyl]ferrocene* (**4**) *and* rac-*(1)-1-(Hydroxymethyl)-2-[(4-methylphenyl)sulfinyl]ferrocene* (**5**). *a*) *Crude* **4**. To racemic **1** (7.212 g, 22.24 mmol) in THF (100 ml) at – 78°, a freshly prepared LDA soln. from ^{i}Pr$_2$NH (7.00 ml, 5.040 g, 49.81 mmol) and 1.69M ^{t}BuLi in pentane (26.00 ml, 43.93 mmol) in THF (20 ml, at – 20°) was transferred dropwise within 15 min. The soln. turned slowly to a deep orange suspension and was stirred for 130 min at – 78°. The suspension was quenched at – 78° with DMF (10.00 ml, 128.61 mmol), and after 5 min stirring, the suspension turned into a clear orange soln., which was stirred overnight defrosting slowly to r.t. inside the cooling bath. The soln. was poured into brine and extracted once with AcOEt, the org. layer washed five times with brine to remove all DMF, dried ($MgSO_4$), and concentrated: 7.448 g (95%) of diastereoisomerically pure racemic **4** containing **1**. The crude product can be purified by FC (substance applied in a silica gel matrix, hexanes/AcOEt 1:2; R_f(**1**) 0.40 and R_f(**4**) 0.28 (TLC), but contained still traces of **1**, and the yield dropped to 74% in another batch, so the crude product was directly taken to the next step and purified then. Spectroscopic data of **4**: in full agreement with the ones reported [6g].

b) *Pure* **5**. All of the crude product **4** from above was dissolved in MeOH (160 ml), and then $NaBH_4$ (841 mg, 22.23 mmol) was added in portions under a stream of N_2 to the well stirred soln. at r.t. The soln. was stirred for another 20 min until foaming and H_2 evolution ceased. After quenching with AcOEt (2 ml) and concentration, the residue was dissolved in AcOEt again and the soln. washed once with brine, dried ($MgSO_4$), and concentrated to give 7.358 g (93%) of racemic **5** as a brown oil containing small amounts of **1** but no **4**. The crude product was purified by FC (substance applied in a silica gel matrix, gradient elution with Et_2O/CH_2Cl_2 1:0 (→ impurities and **1**) and then with Et_2O/CH_2Cl_2 1:0, 3:1, 1:1 (→ **5**): 644 mg (9%; R_f 0.32 (TLC)) **1** and 5.167 g (66% overall ; R_f 0.19 (TLC)) of racemic **5** as yellow microcrystalline powder. Spectroscopic data of **5**: in full agreement with the ones reported [6e].

5. rac-*(1)-1-[(Dimethylamino)methyl]-2-[(4-methylphenyl)sulfinyl]ferrocene* (**6**). *a*) *From* **5**. To a clear soln. of PPh_3 (2.940 g, 11.21 mmol) in CH_2Cl_2 (20 ml), CBr_4 (3.957 g, 11.93 mmol) was added at

– 65° in one portion (→ immediately yellowish soln. and white precipitation). This suspension was stirred for 20 min outside the cooling bath defrosting to r.t. The resulting clear soln. was canuled to a soln. of racemic **5** (3.481 g, 9.83 mmol) in CH_2Cl_2 (30 ml) at – 70°, and the *Schlenk* tube with the phosphine adduct was washed out twice with a total of 10 ml of CH_2Cl_2. The washing solns. were transferred to the orange reaction soln., which was stirred for 26 h outside the cooling bath at r.t. The soln. was concentrated to half its volume by blowing off the solvent with N_2. Then *N*,*N*,*N*′,*N*′-tetramethylmethanediamine (4.00 ml, 29.32 mmol) and thereafter $AgBF_4$ (2.283 g, 11.73 mmol) were added in this order (→ AgBr precipitation). After 5 min stirring at r.t., the suspension was poured into brine, the mixture extracted twice with CH_2Cl_2, and the combined org. layer dried ($MgSO_4$), and concentrated to give 8.856 g of crude product as a complex mixture containing diastereoisomerically pure **6** (by NMR). The crude product was purified twice by FC (substance applied in a silica gel matrix, gradient elution with hexanes/AcOEt + 10% Et_3N 1:1, then 2:1): 462 mg (12%) of **6** (free of triphenylphosphine oxide) as a red oil solidifying on standing. Single crystals suitable for X-ray-analysis were obtained by mixing the purified product with AcOEt and with a few drops of hexanes and CH_2Cl_2 to a red slime, by adding one sand corn, and by leaving the mixture at r.t. for several days. M.p. 100° (racemate). ^{1}H-NMR ($CDCl_3$, 270 MHz): 7.63 (*d*, ^3J = 8.3, 2 H_o of C_6H_4); 7.27 (*d*, ^3J = 8.3, 2 H_m of C_6H_4); 4.52 (*m*, 1 H, Cp); 4.28 (*m*, 1 H, Cp); 4.18 (*s*, 5 H, Cp′); 4.15 (*m*, 1 H, Cp); 3.56 (*d*, ^2J = 13.3, 1 H, CH_2); 3.49 (*d*, ^2J = 13.3, 1 H, CH_2); 2.39 (*s*, 3 H, *Me*C_6H_4); 2.08 (*s*, Me_2N). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75 MHz): 141.57 (C_{ipso} of C_6H_4); 141.16 (C_p of C_6H_4); 129.05 (C_m of C_6H_4); 125.01 (C_o of C_6H_4); 91.64 (C(2) of Cp); 85.34 (C(1) of Cp); 72.21 (Cp); 70.29 (Cp′); 68.89 (Cp); 68.35 (Cp); 56.03 (CH_2); 44.87 (Me_2N); 21.17 (*Me*C_6H_4). FD-MS (pos.; CH_2Cl_2/AcOEt): 382 (100, M^+ with respect to ^{56}Fe). Anal. calc. for $C_{20}H_{23}FeNOS$ (381.32): C 63.00, H 6.08, N 3.67, S 8.41; found: C 62.96, H 6.16, N 3.84, S 8.19.

b) *From* **1**. To a stirred soln. of 1-bromo-2,4,6-triisopropylbenzene (1.809 g, 6.39 mmol) in THF (15 ml), 1.72M ^{t}BuLi in pentane (7.40 ml, 12.77 mmol) was added dropwise at – 78° within 7 min. The soln. was stirred for 4 h at – 78° (→ orange and LiBr precipitation). The – 78° cold soln. of (2,4,6-triisopropylphenyl)lithium (LTP) was directly used. To the freshly prepared LTP soln., a soln. of racemic **1** (1.033 g, 3.186 mmol) in THF (25 ml), held at *ca.* – 40°, was transferred dropwise within 15 min. The suspension was stirred defrosting to – 40° inside the cooling bath within 2 h (→ deep red and clear soln.) The soln. was cooled again to – 78°, and solid *N*,*N*-dimethylmethyleneiminium chloride (1.245 g, 13.307 mmol) was added in one portion. The suspension was stirred inside the cooling bath for 15 h slowly defrosting to r.t. Then the soln. was poured into brine and extracted twice with AcOEt, and the combined org. layer dried ($MgSO_4$) and concentrated to give 2.541 g of crude product as a deep red oil containing diastereoisomerically pure racemic **6**, 1,3,5-triisopropylbenzene, and some **1** (by NMR). The crude product was purified by FC (gradient elution with hexanes/AcOEt + 10% Et_3N 3:1 (→ impurities and **1**: R_f(**1**) 0.50 (TLC)) then with 1:1, and finally with 1:2 (→ **6**): 630 mg (52% yield) of racemic **6**. TLC: R_f 0.21.

6. *Crystal Structure Determination*[5]). Crystal parameters, data collection, and structure refinement details are summarized in *Table 3*. Intensity data were collected at 100 K on a *Bruker-Nonius-KappaCCD* diffractometer (MoK_α radiation, λ 0.71073 Å, graphite monochromator). All structures were solved by direct methods [13][14] and refined by full-matrix least-squares procedures on F^2. For **3**, the absolute configuration was determined by anomalous dispersion effects (least-square procedures, f' and f'') [14a,b]. All non-H-atoms were refined with anisotropic displacement parameters. Absorption corrections were performed by using either a numerical *Gauss* integration [14c] or on the basis of multiple scans with SADABS [13c]. The positions of all H-atoms were taken from a difference *Fourier* synthesis and were refined with a fixed common isotropic displacement parameter. The asymmetric unit of **6** contains two symmetry-independent molecules differing slightly in their conformation, the two enantiomers of the *like* diastereoisomer being present due to the centro symmetry of the space group.

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[5]) CCDC-603699 (for **3**) and CCDC-603700 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

Table 3. *Crystallographic Data of* **3** *and Racemic* **6**. Measured at 100 K.

	3	**6**
Empirical formula	$C_{19}H_{20}FeO_4S_2$	$C_{20}H_{23}FeNOS$
M_r	432.34	381.30
Color, shape	orange, irregular	orange, irregular
Crystal size [mm]	$0.21 \times 0.10 \times 0.07$	$0.23 \times 0.18 \times 0.14$
Crystal system	orthorhombic	triclinic
Space group	$P2_12_12_1$ (no. 19)	$P\bar{1}$ (no. 2)
a [Å]	7.977(1)	7.6883(7)
b [Å]	14.900(2)	7.7400(4)
c [Å]	15.213(2)	29.575(2)
α, β, γ [°]	90, 90, 90	86.231(6), 85.435(8), 89.663(6)
V [Å^3]	1808.2(4)	1750.6(2)
Z	4	4
ρ [g/cm^3] (calc.)	1.588	1.447
μ [mm^{-1}]	1.087	0.987
F (000)	896	800
Abs. corr.	multiple scans (SADABS)	numerical (*Gauss* integration)
T_{min}; T_{max}	0.843; 0.930	0.836; 0.904
2θ range [°]	$7.4 \leq 2\theta \leq 56.0$	$6.1 \leq 2\theta \leq 57.4$
Coll. refl.	52022	47120
Indep. refl.	4372	8984
Obs. refl. ($I_0 \geq 2\sigma(I)$)	3987	6781
No. ref. param.	295	571
wR_2 (all data)	0.0582	0.0793
R_1 ($I_0 \geq 2\sigma(I)$)	0.0278	0.0352
GooF (on F^2)	1.048	1.021
absolute structure parameter	0.03(2)	–
Max.; min. res. electr. density	0.583; −0.331	0.472; −0.529

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