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FULL PAPER

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Abstract: Few studies have been reported on the synthesis of ferrocenesulfonates up to now. Here, we describe the use of *ortho*-deprotometalation and "halogen dance" reactions to easily reach original derivatives. Further functionalizations using cross-coupling and metal/halogen exchange were also performed from iodinated derivatives. Finally, while the electrochemical properties of selected ferrocenesulfonates were evaluated and compared with the corresponding sulfonamide derivatives, halogen bonds were observed at the solid state for iodinated derivatives of ferrocenesulfonates.

Introduction

Since its discovery in 1952,[1] ferrocene has been established as one of the most important organometallics. Synthetic developments around this sandwich compound are inescapable. Indeed, due to the relative stability of ferrocene and an easy reversible one-electron oxidation process, derivatives have found applications in numerous fields including catalysis and material science.[2]

While many ferrocene derivatives functionalized with usual functional groups have heavily been studied, syntheses of ferrocenesulfonic acids remain scarce in the literature. The parent compound can be obtained by sulfonation of ferrocene, and be isolated either as the free acid,[3] or more conveniently as its ammonium[4] or 4-toluidinium sulfonate[5] salt.

Monosubstituted ferrocene sulfonic acids/sulfonates have been used as anion dopants in the formation of cationic polymers due to their good charge-discharge properties.[6] Their high electrocatalytic activity also made ferrocenesulfonates useful as mediators for detection (e.g. of sulfides),[7] and as electron carriers in redox enzyme catalysis.[7-8]

Few applications in catalysis have also been reported for phosphino derivatives of ferrocenesulfonic acid. Indeed, 2-phosphinoferrocenesulfonic acids appeared as an attractive class of ligands for chemists working in the field of catalysis, and in particular those in search of efficient ligands for palladium-catalyzed alkene (co)polymerization.[9] These original compounds can be easily prepared from 4-toluidinium ferrocenesulfonate by a deprotolithiation-trapping sequence involving its initial conversion into the corresponding lithium salt.[9]

Interestingly, *O*-alkyl 2-phosphinoferrocenesulfonates have also been identified as ligands for catalysis in water. They were for example employed as soluble catalysts, in the presence of a ruthenium source, in the *ortho*-arylation of (2-pyridyl)benzene.[10] Besides, their gold(I) complexes proved hydrophilic enough to catalyze the addition of carboxylic acids to non-activated internal alkynes in aqueous media.[11].

However, despite the potential applications of *O*-alkyl ferrocenesulfonates, very few studies have been dedicated to their functionalization. In 2002, Metallinos and Snieckus reported the enantioselective deprotometalation of *O*-isopropyl- and *O*-(2,4-dimethyl-3-pentyl)ferrocenesulfonates in the presence of *n*-, *iso*- or *sec*-butyllithium and (–)-sparteine. While moderate enantiomeric excesses (*ee*) were observed, the recourse to a double asymmetric induction from enantiopure *O*-menthylferrocenesulfonates led to diastereoisomeric ratios up to 91:9.[12] To our knowledge, this represents the only reported study dedicated to the functionalization of *O*-alkyl ferrocenesulfonates.

In continuation with our work dedicated to the synthesis of original polysubstituted ferrocenes,[13] we recently used tertiary sulfonamides to promote functionalization of the remaining positions of the substituted ferrocene cyclopentadienyl ring.[14] Here, we report how isopropylsulfonate can be used efficiently to direct not only deprotolithiation but also "halogen dance" reaction toward original ferrocene derivatives. While we mainly worked in racemic series, attempts to enantioselectively functionalize *O*-isopropylferrocenesulfonate are also presented.

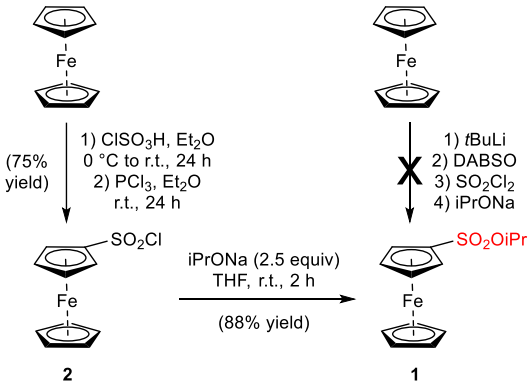
Results and Discussion

Synthesis of the functionalized ferrocenes

We first attempted the synthesis of *O*-isopropylferrocenesulfonate (**1**) from ferrocene by using a deprotometalation-trapping sequence. Indeed, Willis and co-workers showed the possible use of 1,4-diazabicyclo[2.2.2]octane-bis(sulfur dioxide) (DABSO) as a sulfur dioxide surrogate to intercept different organometallic compounds.[15] However, after treatment of ferrocenyllithium

(prepared by reacting ferrocene with *tert*-butyllithium)[16] with DABSO, conversion of the putative lithium sulfinate to ferrocenesulfonyl chloride (**2**) by using sulfuryl chloride, and addition of sodium isopropoxide, the expected sulfonate **1** could not be detected (Scheme 1, top right).

Therefore, we rather took advantage of our recently optimized one-pot synthesis of ferrocenesulfonyl chloride (**2**) following an efficient sulfonation-chlorination sequence (75% yield).[17] Similarly to a previously reported protocol,[12] we treated **2** with *in situ* prepared sodium isopropoxide in tetrahydrofuran (THF) and isolated the corresponding sulfonate **1** in 88% yield (Scheme 1, left and bottom).



Scheme 1. Synthesis of racemic 2-iodo-*O*-isopropylferrocenesulfonate (**3**) and "halogen dance" precursor **5**.

It is known that alkyl sulfonates behave as very efficient deprotometalation directing groups.[18] In addition, in the ferrocene series, the pK_a values calculated within DFT framework (see Experimental Section for computational details) for *O*-isopropylferrocenesulfonate (**1**; see Figure 1) show that the isopropylsulfonate function is more able to stabilize 2-lithioferrocenes when present at the position next to the metal than diisopropylcarboxamide (as already observed in the benzene series[19]), and even than dimethylsulfonamide.

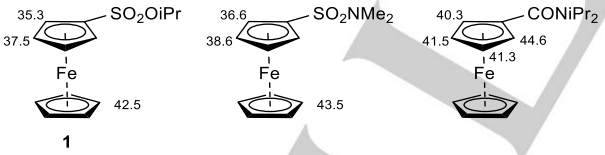
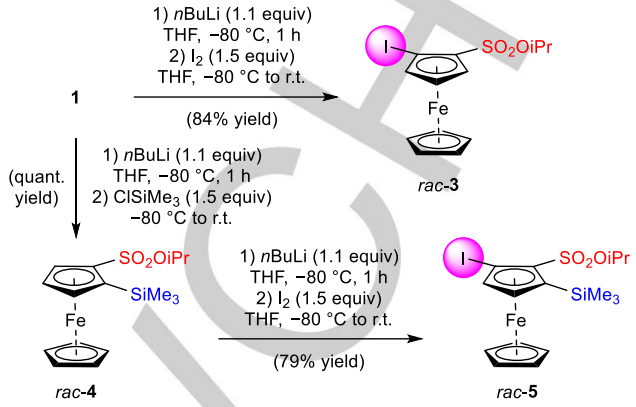


Figure 1. Calculated pK_a values of *O*-isopropylferrocenesulfonate (**1**), and comparison with *N*,*N*-dimethylferrocenesulfonamide[14] and more commonly used *N*,*N*-diisopropylferrocenecarboxamide.[20]

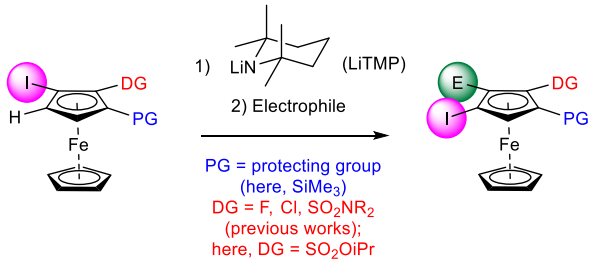
As a consequence, as shown by Metallinos and Snieckus from *O*-menthyl-2-(trimethylsilyl)ferrocenesulfonate,[12] and by Sierra, Cadierno and co-workers from *O*-isopropylferrocenesulfonate,[10-11] alkyllithiums (*n*- or *sec*-butyllithium) are basic enough to achieve the deprotonation of **1** in THF at −78 °C. Accordingly, reacting **1** with *n*-butyllithium in THF at −80 °C for 1 h followed by addition of molecular iodine led to the formation of the iodide **3** in 84% yield (Scheme 2, top). In order to progress toward original 1,3-disubstituted and 1,2,4-trisubstituted ferrocenes, the lithio intermediate was also intercepted by chlorotrimethylsilane to provide **4** in high yield. When this 2-silylated derivative **4** was subjected to a second metalation-iodination sequence, as above, the 1,2,3-trisubstituted ferrocene **5** was isolated in 79% yield (Scheme 2, bottom).



Scheme 2. Synthesis of racemic 2-iodo-*O*-isopropylferrocenesulfonate (**3**) and "halogen dance" precursor **5**.

"Halogen dance" is an elegant way to transfer a heavy halogen (in general iodine or bromine, the former being more appropriate) from a position of a (hetero)aromatic compound to another one.[21] The reaction, based on the conversion of a less stable arylmetal to a more stable one, is generally performed by means of hindered lithium amides such as lithium 2,2,6,6-tetramethylpiperidide (LiTMP) and lithium diisopropylamide.

Since our preliminary results in the ferrocene series using dialkylcarboxamides as directing groups (DG),[20,22] we have disclosed more appropriate substituents (fluorine,[23] chlorine[23a] and dialkylsulfonamides[14]) to direct "halogen dance" by exerting acidifying and/or coordinating effect(s) that stabilize the lithio product. These substituents are efficient when combined with a protecting group (PG) that avoids competitive deprotometalation at the otherwise free position next to the DG. Furthermore, as trimethylsilyl is not a DG for deprotometalation, both the free position next to the DG and the next one are protected from deprotonation (Scheme 3).



Scheme 3. General reaction scheme for a "Halogen dance" reaction.

That 2-iodo-*O*-isopropyl-5-(trimethylsilyl)ferrocenesulfonate (**5**) is a relevant substrate to attempt "halogen dance" was confirmed by a pK_a value between I and SO_2OiPr in **6** (30.7) lower than the one next to I in **5** (34.2) (see Figure 2), and by a lower Gibbs free energy of the corresponding anion for **6** compared to **5** (by 31 kJ mol^{-1}). In addition, when the pK_a values of 4-iodo-*O*-isopropyl-2-(trimethylsilyl)ferrocenesulfonate (**6**) were compared

with those of 4-iodo-*N*,*N*-dimethyl-2-(trimethylsilyl)ferrocenesulfonamide and 1-fluoro-4-iodo-2-(trimethylsilyl)ferrocene, which are substrates suitable to undertake "halogen dance", a lower pK_a value at the free position next to the alkyl sulfonate was recorded for **6**, making **5** even more promising than the corresponding dimethylsulfonamide and fluoride.

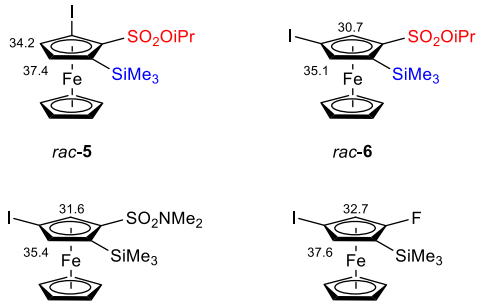
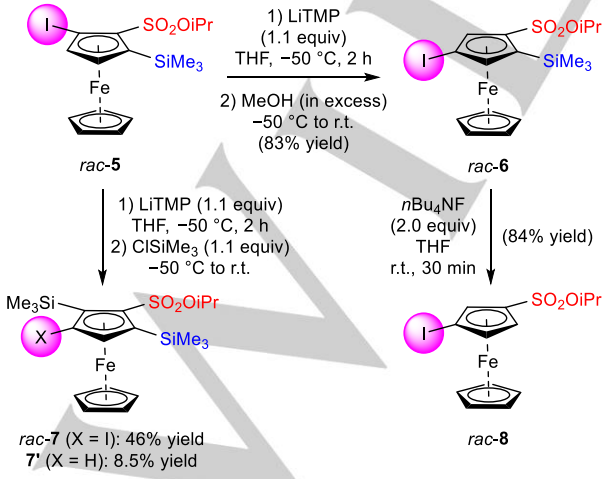


Figure 2. Calculated pK_a values of 2-iodo-*O*-isopropyl-5-(trimethylsilyl)ferrocenesulfonate (**5**) and 4-iodo-*O*-isopropyl-2-(trimethylsilyl)ferrocenesulfonate (**6**), and comparison with 4-iodo-*N*,*N*-dimethyl-2-(trimethylsilyl)ferrocenesulfonamide and 1-fluoro-4-iodo-2-(trimethylsilyl)ferrocene.[14]

The "halogen dance" reaction was thus performed, as described previously,[14,23] by treating the 1,2,3-trisubstituted ferrocene **5** with LiTMP (1.1 equiv) in THF at −50 °C for 2 h. After subsequent methanolysis, the expected 1,2,4-trisubstituted derivative **6** was isolated in 83% yield (Scheme 4, top). The same approach also allows for the synthesis of 1,2,3,4-tetrasubstituted ferrocenes containing an alkyl sulfonate, when an electrophile is introduced after the "halogen dance" step. This was exemplified, by using chlorotrimethylsilane to intercept the lithiated intermediate, during the synthesis of 3-iodo-*O*-isopropyl-2,5-bis(trimethylsilyl)ferrocenesulfonate (**7**). The product was isolated in a moderate 46% yield, partly due to the formation of *O*-isopropyl-2,5-bis(trimethylsilyl)ferrocenesulfonate (**7'**) (Scheme 4, left). The latter seems to result from a competitive iodine/lithium exchange between LiTMP and **5**, followed by electrophilic trapping, as already noticed previously.[24]

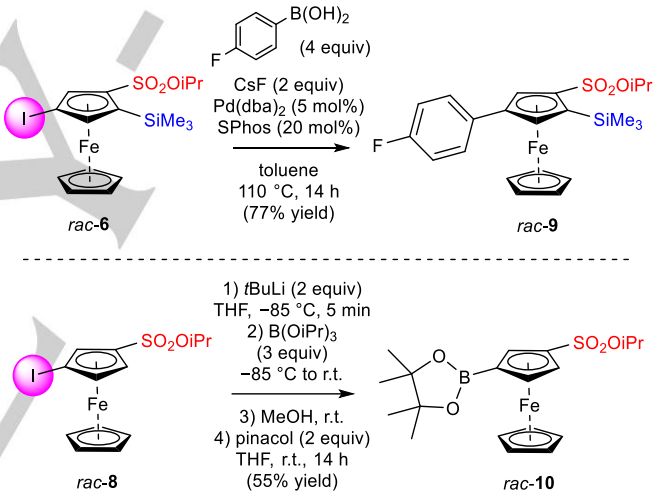


Scheme 4. Ferrocene "halogen dance" reaction from 1,2,3-trisubstituted **5** to 1,2,4-trisubstituted **6** and 1,2,3,4-tetrasubstituted **7**, and subsequent deprotection of **6** toward 1,3-disubstituted **8**.

Removal of the silyl protecting group, using tetrabutylammonium fluoride in THF at room temperature, finally furnished 3-iodo-*O*-isopropylferrocenesulfonate (**8**) in 84% yield (Scheme 4, right). This compound constitutes a new original 1,3-disubstituted ferrocene scaffold, prone for further functionalization.

From the iodinated derivatives of *O*-isopropylferrocenesulfonates, post-functionalizations can be considered. For example, 4-iodo-*O*-isopropyl-2-(trimethylsilyl)ferrocenesulfonate (**6**) was involved in a Suzuki-Miyaura cross-coupling with 4-fluorophenylboronic acid. Thus, in the presence of caesium fluoride, $Pd(dba)_2$ (dba = dibenzylideneacetone) and SPhos (2-(dicyclohexylphosphino)-2',6'-dimethoxybiphenyl), the 4-arylated product **9** was isolated in 77% yield (Scheme 5, top).

Iodine is also a suitable group to introduce molecular diversity through halogen/metal exchange. This was demonstrated from 3-iodo-*O*-isopropylferrocenesulfonate (**8**) upon treatment by *tert*-butyllithium and subsequent quenching with tri(isopropyl)borate. As pinacol boronic esters are more stable towards hydrolysis and easier to purify, trans-esterification with pinacol was finally done to isolate the product **10** in 55% yield (Scheme 5, bottom).

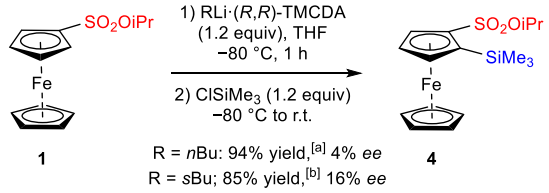


Scheme 5. Examples of post-functionalization (top: Suzuki-Miyaura cross-coupling; bottom: halogen/metal exchange followed by electrophilic trapping) to increase molecular diversity in the ferrocenesulfonate family.

Monosubstituted ferrocenes being prochiral substrates, several studies have been dedicated to their enantioselective deprotometalation with recourse to either alkyllithium-ligand chelates or chiral lithium amides.[25] The most successful achievements were reported from *N*,*N*-diisopropylferrocenecarboxamide by using *n*BuLi·(–)-sparteine (up to 99% *ee*)[26] or *n*BuLi·(+)-sparteine surrogate (92%),[27] from (dialkylaminomethyl)ferrocenes by using either *n*BuLi·(*R*,*R*)-*N*,*N*,*N'*,*N'*-tetramethylcyclohexane-1,2-diamine ((*R*,*R*)-TMCDA; up to 80% *ee*),[28] or isopropyllithium·(*R*,*R*)-TMCDA (up to 98%),[29] and from boron trifluoride-activated aminoferrocenes by using *n*BuLi·(*R*,*R*)-*N*,*N'*-dimethyl-*N*,*N'*-di(3-methylbutyl)cyclohexane-1,2-diamine (up to 80% *ee*).[30]

As regarding *O*-isopropylferrocenesulfonate (**1**), Metallinos and Snieckus attempted its enantioselective deprotolithiation by using *n*-, *iso*- or *sec*-butyllithium as their chelates with (–)-sparteine in ethers (Et_2O or *t*BuOMe), but always obtained

moderate results (*ee* < 58%).[12] We further tested both chelates *n*BuLi·(*R*,*R*)-TMCDA and *s*BuLi·(*R*,*R*)-TMCDA in THF at −80 °C for 1 h toward **1**, but low enantioselectivities were recorded (*ee* < 17%) after subsequent trapping of the lithio products by chlorotrimethylsilane (Scheme 6).

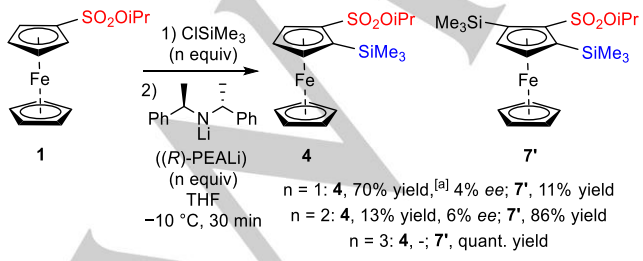


Scheme 6. Enantio-enriched deprotonation of **1** by using alkyllithium-(*R*,*R*)-TMCDA chelates. [a] Traces of **1** and **7'** were also detected in the crude. [b] **1** and **7'** were also obtained in 2 and 4% yield, respectively.

Besides alkyllithium-ligand chelates, chiral lithium amides can also be used to perform the enantioselective deprotometalation of prochiral ferrocenes. Such a possibility was investigated by Price and Simpkins in 1995 with moderate success.[31] The authors employed lithium bis[(*S*)-1-phenylethyl]amide [(*S*)-PEALi] in THF by using chlorotrimethylsilane in excess as *in situ* trap. While ferrocene diphenylphosphine oxide could be converted into its 2-silylated derivative in 54% *ee*, most of the tested ferrocenes either did not react (those substituted by CH_2OH, CH_2OMe, CH_2OCH_2OMe, PPh_2 and SPh) or only gave racemic mixtures (SO_2Ph, $CONiPr_2$).

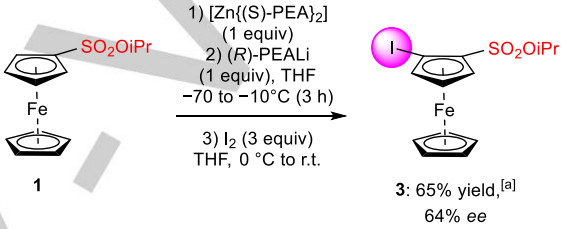
Because alkyl sulfonates are strong directing groups, we reasoned that the functionalization of **1** could work by this way. We therefore applied the procedure reported by Price and Simpkins, and added **1** to a mixture of lithium bis[(*R*)-1-phenylethyl]amide [(*R*)-PEALi] (1 equiv) and chlorotrimethylsilane (3 equiv) in THF at -80 °C. After 30 min at this temperature and subsequent hydrolysis, the 2-silylated derivative **4** was isolated in a low 7% yield and a moderate 20% *ee*, the rest being **1** (91% recovery) (result not shown).

In order to avoid unwanted trapping of the base by chlorotrimethylsilane, and to favor deprotonation,[32] we next treated a mixture of **1** and chlorotrimethylsilane (1 equiv) by (*R*)-PEALi in THF at −10 °C for 30 min before hydrolysis. This time, **4** was obtained in 70% yield, but in a low 4% *ee*. The 2,5-bis(trimethylsilyl) derivative **7',** formed competitively under these conditions (and isolated in 11% yield), became the major product by increasing the amount of chlorotrimethylsilane to 2 or 3 equivalents (Scheme 7).



Scheme 7. Attempts to enantioselectively deprotonate **1** by using (*R*)-PEALi in the presence of chlorotrimethylsilane as *in situ* trap. [a] Substrate **1** was also recovered (16% yield).

By following studies on the use of chiral lithium-zinc mixed amides and combinations to reach the same goal,[33] we showed in 2019 that zinc-based *in situ* traps generally give better results than chlorotrimethylsilane.[34] In particular, we evidenced [Zn{(*S*)-PEA}$_2$], *in situ* prepared from $ZnCl_2$·TMEDA and (*S*)-PEALi in a 1:2 ratio, as the best one to this purpose. Indeed, upon addition of (*S*)-PEALi (1 equiv) to a mixture of [Zn{(*S*)-PEA}$_2$] (1 equiv) and *N*,*N*-diisopropylferrocenecarboxamide in THF at −70 °C before slow warming to −10 °C (over 3 h) and iodolysis, the corresponding 2-iodo derivative was obtained in 96% yield and 69% *ee*. By applying comparable reaction conditions to *O*-isopropylferrocenesulfonate (**1**), the 2-iododerivative **3** was obtained in 65% yield and 64% *ee* (Scheme 8). Admittedly, we did not reach the 82% *ee* already reported from (–)-(1*R*,2*S*,5*R*)-*O*-menthylferrocenesulfonate by using *sec*-butyllithium·(–)-sparteine,[12] but we could get this result without recourse to double asymmetric induction.



Scheme 8. Attempts to enantioselectively deprotonate **1** by using (*R*)-PEALi in the presence of [(*R*)-PEA]$_2$Zn as *in situ* trap. [a] Substrate **1** was also recovered (26% yield).

Electrochemical characterization

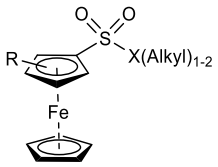
The electrochemical behavior of sulfur-containing ferrocene derivatives has been the subject of very few studies. In the course of a study on the use of alkylated potassium ferrocenesulfonates as electrocatalysts for sulfide detection, Lawrence and co-workers recorded in water the oxidation peak potentials of potassium 2,1'-dimethylferrocenesulfonate, and potassium 2-ethyl-, 2-butyl- and 2-*tert*-butylferrocenesulfonates. They evidenced a little effect of the chain length on the oxidation potential while the presence of a second alkyl group onto ferrocene logically led to a lower oxidation potential.[7]

In 1997, Kagan and co-workers studied by cyclic voltammetry the electrochemical properties of different ferrocene sulfides, sulfoxides and sulfones. In all cases, they recorded a one-electron reversible system, in accordance with the formation of stable ferricinium species. The $E_{1/2}$ values (*vs.* SCE) recorded in acetonitrile were found to be dependent on the number of oxygens at sulfur, with increasing ferrocene redox potentials from sulfides to sulfones (e.g., 0.450 V for Fc-SPh, 0.605 for Fc-S(O)Ph, 0.695 for Fc-S(O)$_2$Ph; Fc = ferrocenyl). Furthermore, the $E_{1/2}$ values were slightly dependent on the electron-withdrawing or -donating character of the substituent on sulfur (e.g., 0.450 V for Fc-SPh, 0.440 for Fc-S-4-tolyl, 0.471 V for Fc-4-chlorophenyl).[35]

Due to the lack of data on both *O*-alkylferrocenesulfonates and *N*,*N*-dialkylferrocenesulfonamides, we studied by cyclic voltammetry the electrochemical behavior of some of the *O*-isopropylferrocenesulfonates here synthesized, as well as *N*,*N*-dimethylferrocenesulfonamides[14,17] and (*N*-

pyrrolidino)sulfonylferrocenes[17] previously prepared, in order to compare their $E_{1/2}$ values (Table 1). The measurements were performed in dry, oxygen-free dichloromethane, at a concentration of 1 mM, with nBu$_4$NPF$_6$ (0.1 M) as the supporting electrolyte. For all the experiments, the working electrode was a glassy carbon disk (diameter 1.5 mm) which was polished (5 µm grain size) with a slurry of alumina and ethanol and rinsed with dichloromethane before to use. The reference electrode was Ag/AgCl separated from the solution by a glass frit, while the counter electrode was a glassy carbon rod.

Table 1. Electrochemical data (in V).[a]

Substrate	R	-X(Alkyl)$_{1-2}$								
		-OiPr					-NMe$_2$			
		Compound	E_{pa}	E_{pc}	$E_{1/2}$	i_{pa}/i_{pc}[b]	E_{pa}	E_{pc}	$E_{1/2}$	i_{pa}/i_{pc}[b]
	H	**1**	0.48	0.38	*0.43*	*0.99*	0.36	0.27	*0.31*	*1.04*
	2-I	**3**	0.59	0.50	*0.55*	*0.94*	0.50	0.42	*0.45*	*1.02*
	2-SiMe$_3$[c]	**4**	0.46	0.37	*0.41*	*1.10*	0.39	0.31	*0.33*	*1.02*
	2-I-5-SiMe$_3$	**5**	0.58	0.49	*0.53*	*0.96*	0.49	0.41	*0.44*	*1.01*
	4-I-2-SiMe$_3$	**6**	0.60	0.51	*0.55*	*0.93*	0.55	0.46	*0.51*	*1.04*
	3-I	**8**	0.62	0.52	*0.57*	*0.96*	0.56	0.47	*0.52*	*0.97*

[a] Potentials values given relative to FcH/FcH$^+$; scan rate = 50 mV·s^{-1}; nBu$_4$NPF$_6$ (0.1 M) in CH_2Cl_2; working electrode: glassy carbon; reference electrode: Ag/AgCl. [b] Corrected value, taking i_{pa}/i_{pc} for ferrocene (0.86) equal to 1. [c] The E_{pa}, E_{pc} and $E_{1/2}$ values for (trimethylsilyl)ferrocene are 0.08, 0.02 and 0.02 V, respectively.

In all cases, cyclic voltammograms were recorded at a scan rate of 50 mV·s^{-1}. Determination of the half-wave ($E_{1/2}$) potentials was carried out from a DPV (Differential Pulse Voltammetry) experiment which were recorded under the same reaction conditions. Thus, ferrocene (Fc-H) displayed a one-electron redox event at $E_{1/2}$ = 0.45 V.

Similarly, all compounds exhibited a one-electron reversible process at a scan rate of 50 mV·s^{-1} with a peak separation below 100 mV range (see Supporting information). In all cases studied, the ferrocenesulfonates were characterized by slightly higher redox potentials than the corresponding sulfonamides. This trend is in line with the lower pK_a values calculated for ferrocenesulfonates, indicating the better electron withdrawing properties of this group. When compared with the *N*,*N*-dimethylferrocenesulfonamides, the corresponding (*N*-pyrrolidino)sulfonylferrocenes (see Table S3 of the Supporting information) have slightly lower redox potentials.

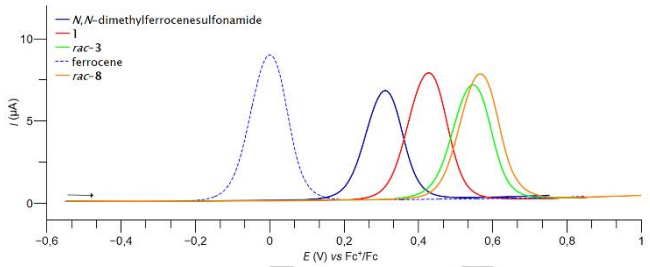


Figure 3. Differential pulse voltammograms for *N*,*N*-dimethylferrocenesulfonamide (blue line), **1** (red line), **3** (green line), ferrocene (dotted blue line) and **8** (orange line).

As one would have expected, addition of trimethylsilyl group onto both ferrocenesulfonate and -sulfonamides had a limited impact onto the measured redox potential. However, addition of iodine led to derivatives with a ferrocene backbone of lower electron density, this effect being more pronounced on 3-substituted than on 2-substituted ferrocenes (Figure 3).

We analyzed the impact of the substituent nature on the redox potential within linear free energy relationship methodology. It is known that half-wave potentials of relative compounds could be predicted by using Hammett constants of substituents.[36] In our case, the situation is tangled by multiple possible redox centers in ferrocenesulfonates and ferrocenesulfonamides.

The Hammett equation in its simple form was developed for six-membered rings, but not for five-membered or metallocene systems. Jaffé considered possible extensions of the Hammett equation, including 1) the effect of substituents in polysubstituted compounds can be expressed as the sum of the individual effects of the substituents in the corresponding monosubstituted compounds, and 2) for description of substituent effects in five-membered systems, the constants could be 'mixed' with different weights.[36a,37] Earlier, we showed that a vicinal substituent in triazoles affects the reaction center similarly to that of a *meta*-group in a benzene ring.[38]

Inspired by Ushijima *et al.* who proved half-wave potentials of (η5-cyclopentadienyl)(1,2-ethylenedithiolato)cobalt(III) complexes to be linearly dependent on the sum of the constants of the substituents,[36d] here we performed similar analysis for the sulfonates **1**, **3**-**5**, and their corresponding sulfonamides (the derivatives **6** and **8** were skipped due to the lack of σ constant suitable for the 1,3-disubstitution case). By using the above-mentioned approximations, we obtained the following best equations for the *O*-isopropylferrocenesulfonates:

$E_{1/2} = 0.87 + 0.34\Sigma\sigma_m$ (N = 4, r^2 = 0.997, rmse = 0.004),

and for the *N*,*N*-dimethylferrocenesulfonamides:

$E_{1/2} = 0.77 + 0.35\Sigma\sigma_m$ (N = 4, r^2 = 0.939, rmse = 0.022).

All Hammett constant values were taken from the work of Hansch *et al*.[39] So, there is a correlation between the nature of the substituent (electron-donating/electron-withdrawing) and the half-wave potential change (see Figure S1 of the Supporting information). Also, one can admit that ΔE is the same (−0.02 V) for the pairs of **1** and **4**, **3** and **5**, **8** and **6**, proving additivity.

Specific solid-state structures of the ferrocenesulfonates

Although most of the ferrocenesulfonates were solids, only the compounds **5**, **7** and **10** gave crystals suitable for X-ray diffraction

analysis (Figures 4-6). At the solid state, although similar C-Si, C-S and C-I bond lengths were observed for the compounds **5** and **7**, small differences were noticed in their geometry. Indeed, in **5**, both S=O bonds of the sulfonate are directed towards the iron with similar angles while in **7**, one oxygen is almost coplanar with the cyclopentadienyl (Cp) ring, the other one being more orientated towards the iron atom (47.7° angle). Furthermore, while one methyl attached to Si1 is coplanar with the Cp in both **5** and **7**, one methyl linked to Si2 is rotated by 8.9(3) ° in compound **7**, probably to reduce steric pressure on this tetrasubstituted ferrocene. Finally, an eclipsed conformation was observed for compound **5** (C10-Cg2···Cg1-C3 = 9.22 °, Cg1 being the centroid of the C1-C2-C3-C4-C5 ring and Cg2 the one of the C6-C7-C8-C9-C10 ring) while staggered for compound **7** (C9-Cg2···Cg1-C1 = 31.36 °). This differs from the previously reported ferrocenesulfonamide derivatives which were in an eclipsed conformation before and after the halogen 'dance' reaction.[14]

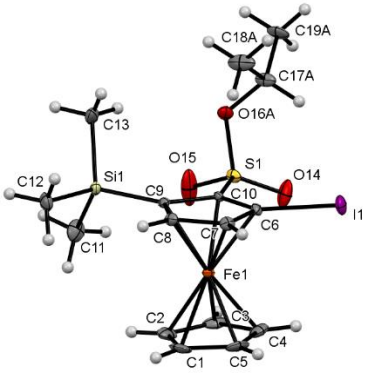


Figure 4. Molecular structure of compound *rac*-**5** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C9-Si1 = 1.884(4), C10-S1 = 1.744(3), C6-I1 = 2.091(4), C8-C9-Si1-C12 = -1.2(3), C6-C10-S1-O14 = 25.0(4), C9-C10-S1-O15 = -24.0(3).

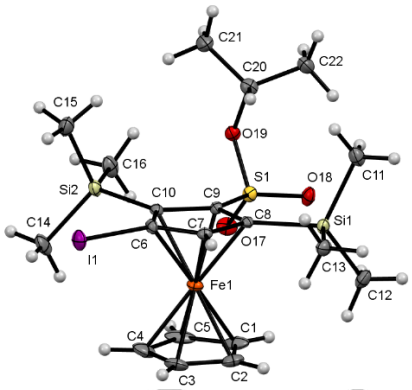


Figure 5. Molecular structure of compound *rac*-**7** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C8-Si1 = 1.891(3), C9-S1 = 1.758(3), C10-Si2 = 1.895(3), C6-I = 2.096(3), C7-C8-Si1-C13 = 0.7(2), C9-C10-Si2-C16 = 8.9(3), C8-C9-S1-O18 = -3.4(2), C10-C9-S1-O17 = -47.7(3).

Concerning the borylated ferrocene **10**, the two S=O bonds of the sulfonate are directed toward the iron atom, so as the boron atom with a dip angle α* between the centre of gravity of the substituted Cp ring, the C_{ipso} and the boron atom measured to 6.15 °. This lower value than the one observed for ferrocenylpinacolborane (8.55°)[40] suggests slightly increased interactions between the empty boron p orbital and the filled p orbital of the ipso carbon atom.

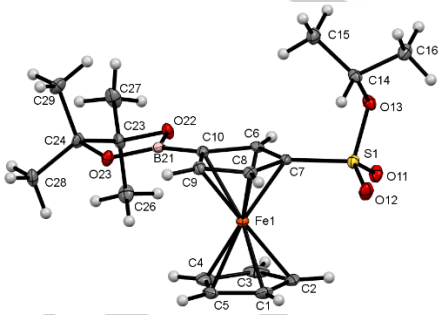


Figure 6. Molecular structure of compound *rac*-**10** at the solid state. Thermal ellipsoids shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: C7-S1 = 1.730 (4), C10-B21 = 1.553(3), C8-C7-S1-O12 = 16.5(4), C6-C7-S1-O11 = -28.2(4).

Finally, due to the presence of both iodine and sulfonate on the compounds **5** and **7**, halogen-chalcogen bonds were identified at the solid state (Figure 7). They result from the interaction between the σ-hole of the iodine atom and the lone pair of one oxygen of the sulfonate.[41] However, due to the different substitution patterns, different networks are observed: a zig-zag chain in the case of **5** and a linear one for **7**. Furthermore, as each enantiomer is involved into a different chain, two independent chains of halogen bonds exist for each compound. However, the bond lengths (I1···O14 3.193(4) and I1···O18 3.227(2) Å for **5** and **7**, respectively) and angles (S1-O14···I1 133.70(2) and O14···I1-C6 167.85(12) for **5**, S1-O18···I1 148.99(11) and O18···I1-C6 171.06(8) for **7**) are within the range of classical values.[14,42]

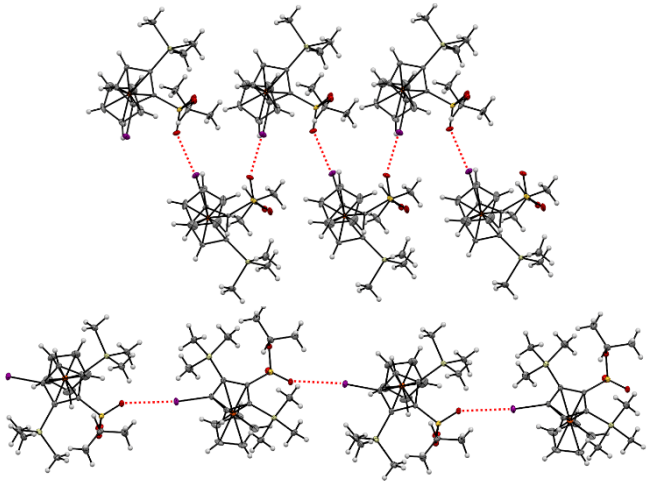


Figure 7. Halogen bonds network observed at the solid state for the compounds *rac*-**5** (top) and *rac*-**7** (bottom). Thermal ellipsoids shown at the 30% probability level.

Conclusion

Owing to the strong acidifying properties of alkyl sulfonate, we prepared original iodinated ferrocenesulfonates by using *ortho*-deprotolithiation and "halogen dance" reactions. Further functionalization using cross-coupling or iodine/lithium exchange was also successfully demonstrated. Although the use of alkyllithium·diamine chelates was ineffective to deliver enantio-enriched derivatives, we showed that chiral lithium amide, in combination with a suitable *in situ* trap, was able to give results close to those obtained by following a double asymmetric induction strategy. An electrochemical study of the most relevant compounds was further done, showing the better electron-withdrawing properties of the sulfonate when compared with the sulfonamides. Finally, as already observed in the ferrocenesulfonamide series, halogen bonds can also be present in iodinated derivatives of ferrocenesulfonates. Taking together, these results are expected to pave the way to the synthesis of polysubstituted derivatives tailored for applications.

Experimental Section

General Considerations. All reactions were performed under an argon atmosphere and by using anhydrous solvents in dried Schlenk tubes. THF was distilled on sodium-benzophenone prior to use. All organolithiated reagents were titrated before use.[43] Room temperature (r.t.) refers to 25 °C. 2,2,6,6-Tetramethylpiperidine was distilled on CaH_2 under reduced pressure, and stored on KOH pellets. Bis[(*R*)-1-phenylethyl]amine was stored on KOH pellets 24 h before use. (*R*,*R*)-TMCDA was prepared according to Jacobsen[44] and Alexakis.[45] Column chromatography separations were achieved on silica gel (40-63 µm). Thin layer chromatographies were performed on aluminum-backed plates pre-coated with silica gel (Merck, silica gel 60 F254). They were visualized upon exposure to UV light. Melting points were measured on a Kofler bench. IR spectra were taken on a Perkin-Elmer Spectrum 100 spectrometer. ^{1}H and ^{13}C{1H} Nuclear Magnetic Resonance (NMR) spectra were recorded either (a) on a Bruker Avance III spectrometer at 300 MHz and 75.4 MHz, respectively, or (b) on a Bruker Avance III HD at 500 MHz and 126 MHz, respectively. ^{1}H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ^{13}C chemical shifts are relative to the central peak of the solvent signal.[46] The numbering used in this experimental section is defined in Supporting information. **Safety considerations**. Due to its high pyrophoric character, *t*BuLi needs to be used only under inert conditions (anhydrous, nitrogen or argon atmosphere) and by people well trained to the manipulation of reactive organometallics.

Ferrocenesulfonyl chloride[17] and $ZnCl_2$·TMEDA[47] were prepared as described previously. *N*,*N*-Dimethylferrocenesulfonamide,[17] 2-iodo-*N*,*N*-dimethylferrocenesulfonamide,[14] *N*,*N*-dimethyl-2-(trimethylsilyl)ferrocenesulfonamide,[14] 2-iodo-*N*,*N*-dimethyl-5-(trimethylsilyl)ferrocenesulfonamide,[14] 4-iodo-*N*,*N*-dimethyl-2-(trimethylsilyl)ferrocenesulfonamide,[14] 3-iodo-*N*,*N*-dimethylferrocenesulfonamide,[14] and (*N*-pyrrolidino)sulfonylferrocene[17] were prepared in previous studies. The synthesis of 1-(*N*-pyrrolidino)sulfonyl-2-(trimethylsilyl)ferrocene is described in the experimental part.

Crystallography

The X-ray diffraction data were collected for the compound *rac*-**5** on a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector and for the compounds *rac*-**7** and *rac*-**10** on a APEXII Kappa-CCD Bruker AXS diffractometer equipped with CCD plate detector, by using Mo-Kα radiation (λ = 0.71073 Å; multilayer monochromator for the D8 VENTURE Bruker AXS diffractometer and graphite monochromator for the APEXII Kappa-CCD Bruker AXS diffractometer). The structure of *rac*-**5** was solved by direct methods using the *SIR97* program,[48] and then refined with full-matrix least-squares methods based on F^2 (*SHELXL*).[49] The structures of *rac*-**7** and *rac*-**10** were solved by dual-space algorithm using the *SHELXT* program,[50] and then refined with full-matrix least-square methods based on F^2 (*SHELXL*).[49] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except hydrogen atoms linked to nitrogen atoms that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. The molecular diagrams were generated by MERCURY 2020.3.0.

*O-Isopropylferrocenesulfonate (**1**)*. The procedure was inspired by a previously reported protocol.[12] To a suspension of NaH (60% dispersion in oil, 2.70 g, 62.5 mmol, 2.50 equiv) in THF (100 mL) at 0 °C was added isopropanol (4.80 mL, 3.76 g, 62.5 mmol, 2.50 equiv) dropwise. After addition, the reaction mixture was warmed to room temperature and stirred for 15 min. A solution of ferrocenesulfonyl chloride (7.09 g, 20.0 mmol, 1.00 equiv) in THF (20 mL) was added dropwise and the reaction mixture was then stirred for 2 h at room temperature. Saturated aqueous NH_4Cl (50 mL) was added, layers were separated, and the aqueous layer was extracted with AcOEt (2 x 50 mL). The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography over silica gel, eluting with petroleum ether-AcOEt 70:30 to give the title product **1** in 88% yield (6.80 g) as an orange solid: Rf (petroleum ether-AcOEt 90:10) = 0.31; mp 69-70 °C (lit.[12] 66-68 °C); IR (ATR) ν 772, 823, 834, 880, 893, 910, 1001, 1011, 1027, 1093, 1105, 1156, 1181, 1203, 1259, 1332, 1342, 1367, 1377, 1390, 1413, 1464, 1688, 2934, 2973, 3114 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.23 (d, 6H, *J* = 6.2 Hz, Me), 4.40 (s, 5H, Cp), 4.42 (t, 2H, *J* = 1.6 Hz, H3 and H4), 4.69 (sept, 1H, *J* = 6.2 Hz, C*H*Me$_2$), 4.70 (t, 2H, *J* = 1.6 Hz, H2 and H5) ppm; ^{13}C{1H} NMR ($CDCl_3$) δ 23.0 ($2CH_3$), 69.2 (2CH, C2 and C5), 71.0 (2CH, C3 and C4), 71.1 (5CH, Cp), 76.5 (CH, *C*HMe$_2$), 84.3 (C, C1, *C*SO_3iPr) ppm. These data are as reported previously.[12]

General procedure 1. *n*BuLi (1.4 M in hexanes, 1.10 equiv) was added dropwise to a solution of the required substrate (1.00 equiv) in THF (0.15 M) at −80 °C and the reaction mixture was stirred at the same temperature for 1 h. The suitable electrophile (1.50 equiv), pure for liquids or in solution for solids, was added and the reaction was warmed to room temperature. Saturated aqueous $Na_2S_2O_3$ when iodine is used as electrophile, or NH_4Cl instead, was added. Layers were separated, and the aqueous layer was extracted with AcOEt. The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography over silica gel (eluent given in product description) to give the title product.

*2-Iodo-O-isopropylferrocenesulfonate (**3**, racemic mixture).* It was prepared by following the general procedure 1, starting from *O*-isopropylferrocenesulfonate (**1**; 924 mg, 3.00 mmol) and using iodine (1.14 g) as the electrophile in THF (6 mL). It was isolated (eluent: petroleum ether-AcOEt 10:1) in 84% yield (1.09 g) as an orange solid: Rf (petroleum ether-AcOEt 90:10) = 0.31; mp 82-85 °C; IR (ATR) ν 764, 829, 877, 913, 932, 1002, 1028, 1058, 1096, 1108, 1151, 1161, 1201, 1341, 1362, 1376, 1388, 1411, 1463, 1681, 2981, 3106 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (d, 3H, *J* = 6.3 Hz, Me), 1.29 (d, 3H, *J* = 6.3 Hz, Me), 4.39 (s, 5H, Cp), 4.44 (t, 1H, *J* = 2.6 Hz, H4), 4.67 (dd, 1H, *J* = 2.5 and 1.5 Hz, H3), 4.78 (sept, 1H, *J* = 6.3 Hz, C*H*Me$_2$), 4.81 (dd, 1H, *J* = 2.7 and 1.5 Hz, H5) ppm; ^{13}C{1H} NMR ($CDCl_3$) δ 22.9 (CH_3), 23.2 (CH_3), 37.2 (C, C2, C-I), 71.0 (CH, C5), 71.7 (CH, C4), 74.1 (5CH, Cp), 77.2 (CH, *C*HMe$_2$), 79.6 (CH, C3), 86.0 (C, C1, *C*SO_3iPr) ppm; MS (EI, 70 eV): 434 [M], 392 [M-iPr+H]. Anal. Calcd for $C_{13}H_{15}FeIO_3S$ (434.07): C, 35.97; H, 3.48; S, 7.39. Found: C, 36.10; H, 3.57; S, 7.10.

*O-Isopropyl-2-(trimethylsilyl)ferrocenesulfonate (**4**, racemic mixture).* It was prepared by following the general procedure 1, starting from *O*-isopropylferrocenesulfonate (**1**; 2.15 g, 7.00 mmol) and using chlorotrimethylsilane (1.30 mL, 1.14 g) as the electrophile. It was isolated (eluent: petroleum ether-AcOEt 15:1) in a quantitative yield (2.60 g) as an

orange oil: Rf (petroleum ether-AcOEt 90:10) = 0.50; IR (ATR) ν 660, 693, 762, 823, 874, 919, 960, 1004, 1039, 1069, 1099, 1143, 1161, 1199, 1246, 1284, 1346, 1411, 1467, 1681, 2900, 2956, 2982, 3107 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.35 (s, 9H, $SiMe_3$), 1.13 (d, 3H, J = 6.2 Hz, CH*Me*$_2$), 1.32 (d, 3H, J = 6.2 Hz, CH*Me*$_2$), 4.36 (dd, 1H, J = 2.4 and 1.1 Hz, H3), 4.39 (s, 5H, Cp), 4.53 (t, 1H, J = 2.4 Hz, H4), 4.71 (sept, 1H, J = 6.2 Hz, C*H*Me$_2$), 4.89 (dd, 1H, J = 2.4 and 1.1 Hz, H5) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$) δ 0.7 ($3CH_3$, $SiMe_3$), 22.7 (CH_3, CH*Me*$_2$), 23.3 (CH_3, CH*Me*$_2$), 71.0 (5CH, Cp), 72.3 (CH, C4), 73.5 (C, C2, *C*-$SiMe_3$), 73.9 (CH, C5), 75.9 (CH, *C*HMe$_2$), 78.4 (CH, C3), 88.6 (C, C1, *C*SO_3iPr) ppm. These data are as reported previously.[12]

*2-Iodo-O-isopropyl-5-(trimethylsilyl)ferrocenesulfonate (**5**, racemic mixture).* It was prepared by following the general procedure 1, starting from *O*-isopropyl-2-(trimethylsilyl)ferrocenesulfonate (**4**; 2.50 g, 6.60 mmol) and using iodine (2.52 g) as the electrophile in THF (15 mL). It was isolated (eluent: petroleum ether-AcOEt 15:1) in 79% yield (2.65 g) as an orange solid: Rf (petroleum ether-AcOEt 90:10) = 0.70; mp 125-126 °C; IR (ATR) ν 690, 763, 821, 839, 879, 891, 915, 964, 1003, 1074, 1100, 1128, 1145, 1167, 1204, 1242, 1344, 1377, 1412, 1465, 1679, 2898, 2949, 2980, 3090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.34 (s, 9H, $SiMe_3$), 1.28 (d, 3H, J = 6.2 Hz, CH*Me*$_2$), 1.31 (d, 3H, J = 6.2 Hz, CH*Me*$_2$), 4.40 (s, 5H, Cp), 4.41 (d, 1H, J = 2.3 Hz, H4), 4.81 (d, 1H, J = 2.3 Hz, H3), 4.84 (sept, 1H, J = 6.2 Hz, C*H*Me$_2$) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$) δ 0.7 ($3CH_3$, $SiMe_3$), 23.0 (CH_3), 23.1 (CH_3), 41.5 (C, C2, C-I), 74.1 (5CH, Cp), 76.1 (C, C5, *C*-$SiMe_3$), 76.3 (CH, *C*HMe$_2$), 78.9 (CH, C4), 81.7 (CH, C3), 89.8 (C, C1, *C*SO_3iPr) ppm. Anal. Calcd for $C_{16}H_{23}FeIO_3SSi$ (506.25): C, 37.96; H, 4.58; S, 6.33. Found: C, 38.04; H, 4.57; S, 6.37. *Crystal data for **5**.* $C_{16}H_{23}FeIO_3SSi$, M = 506.24, T = 150(2) K, monoclinic P 1 $2_1/a$ 1 (I.T.#14), a = 14.1732(19), b = 8.0466(9), c = 18.201(2) Å, β = 108.601(5) °, V = 1967.3(4) Å^3, Z = 4, d = 1.709 g·cm^{-3}, μ = 2.513 mm^{-1}. A final refinement on F^2 with 4509 unique intensities and 230 parameters converged at $\omega R(F^2)$ = 0.0919 ($R(F)$ = 0.0394) for 3953 observed reflections with $I > 2\sigma(I)$. CCDC 2084907.

General procedure 2. *n*BuLi (1.4 M in hexanes, 1.10 equiv) was added dropwise to a solution of 2,2,6,6-tetramethylpiperidine (1.10 equiv) in THF (0.55 M) at −15 °C. After 15 min, the reaction mixture was cooled to −50 °C and 2-iodo-*O*-isopropyl-5-(trimethylsilyl)ferrocenesulfonate (**5**) was added in one portion. The reaction was stirred at the same temperature for 2 h before the desired electrophile was added. The reaction mixture was warmed to room temperature and aqueous HCl (1 M, 10 mL) was added. The reaction mixture was extracted with AcOEt (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography over silica gel (eluent given in product description) to give the title product.

*4-Iodo-O-isopropyl-2-(trimethylsilyl)ferrocenesulfonate (**6**, racemic mixture).* It was prepared by following the general procedure 2, starting from 2-iodo-*O*-isopropyl-5-(trimethylsilyl)ferrocenesulfonate (**5**; 506 mg, 1.00 mmol) and using methanol in excess (1 mL) as the electrophile. It was isolated (eluent: petroleum ether-AcOEt 95:5) in 83% yield (421 mg) as an orange solid: Rf (petroleum ether-AcOEt 90:10) = 0.72; mp 64-65 °C; IR (ATR) ν 663, 693, 755, 825, 870, 910, 982, 1005, 1054, 1096, 1111, 1161, 1212, 1247, 1277, 1304, 1327, 1341, 1377, 1453, 1464, 1661, 2899, 2954, 2980, 3096 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.34 (s, 9H, $SiMe_3$), 1.17 (d, 3H, J = 6.2 Hz, CH*Me*$_2$), 1.34 (d, 3H, J = 6.2 Hz, CH*Me*$_2$), 4.40 (s, 5H, Cp), 4.56 (s, 1H, H3), 4.73 (sept, 1H, J = 6.2 Hz, C*H*Me$_2$), 5.13 (s, 1H, H5) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$) δ 0.5 ($3CH_3$, $SiMe_3$), 22.8 (CH_3, CH*Me*$_2$), 23.3 (CH_3, CH*Me*$_2$), 40.1 (C, C4, C-I), 74.0 (5CH, Cp), 75.4 (C, C2, *C*-$SiMe_3$), 76.4 (CH, *C*HMe$_2$), 79.3 (CH, C5), 84.6 (CH, C3), 89.3 (C, C1, *C*SO_3iPr) ppm. Anal. Calcd for $C_{16}H_{23}FeIO_3SSi$ (506.25): C, 37.96; H, 4.58; S, 6.33. Found: C, 38.16; H, 4.71; S, 6.16.

*3-Iodo-O-isopropyl-2,5-bis(trimethylsilyl)ferrocenesulfonate (**7**, racemic mixture).* It was prepared by following the general procedure 2, starting from 2-iodo-*O*-isopropyl-5-(trimethylsilyl)ferrocenesulfonate (**5**; 380 mg, 0.75 mmol) and using chlorotrimethylsilane (105 µL, 89.6 mg, 0.82 mmol, 1.10 equiv) as the electrophile. It was isolated (eluent: petroleum ether-Et_2O 98:2) in 46% yield (200 mg) as an orange solid: Rf (petroleum ether-AcOEt 90:10) = 0.78; mp 91-93 °C; IR (ATR) ν 669, 691, 761, 820, 829, 839, 878, 912, 940, 1002, 1097, 1167, 1209, 1244, 1310, 1325, 1345, 1376, 1388, 1413, 1469, 2899, 2958 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.36 (s, 9H, $SiMe_3$), 0.56 (s, 9H, $SiMe_3$), 1.21 (d, 3H, J = 6.3 Hz, CH*Me*$_2$), 1.39 (d, 3H, J = 6.3 Hz, CH*Me*$_2$), 4.38 (s, 5H, Cp), 4.75 (s, 1H, H4), 4.83 (sept, 1H, J = 6.3 Hz, C*H*Me$_2$) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$) δ 1.2 ($3CH_3$, $SiMe_3$), 2.8 ($3CH_3$, $SiMe_3$), 23.0 (CH_3, CH*Me*$_2$), 23.5 (CH_3, CH*Me*$_2$), 51.1 (C, C3, C-I), 74.1 (5CH, Cp), 75.9 (CH, *C*HMe$_2$), 76.9 (C, C2, *C*-$SiMe_3$), 80.7 (C, C5, *C*-$SiMe_3$), 89.1 (CH, C4), 93.8 (C, C1, *C*SO_3iPr) ppm. Anal. Calcd for $C_{19}H_{31}FeIO_3SSi_2$ (578.43): C, 39.45; H, 5.40; S, 5.54. Found: C, 39.13; H, 5.53; S, 5.49. *Crystal data for **7**.* $C_{19}H_{31}FeIO_3SSi_2$, M = 578.43, T = 150(2) K, monoclinic P $2_1/n$ (I.T.#14), a = 11.0820(6), b = 17.2810(9), c = 13.2452(6) Å, β = 109.287(2) °, V = 2394.2(2) Å^3, Z = 4, d = 1.605 g·cm^{-3}, μ = 2.123 mm^{-1}. A final refinement on F^2 with 5449 unique intensities and 252 parameters converged at $\omega R(F^2)$ = 0.0654 ($R(F)$ = 0.0324) for 4385 observed reflections with $I > 2\sigma(I)$. CCDC 2084908.

*O-Isopropyl-2,5-bis(trimethylsilyl)ferrocenesulfonate (**7'**).* This bis-silylated compound was also isolated in 8.5% yield (29 mg) as an orange solid: Rf (petroleum ether-AcOEt 90:10) = 0.72; mp 69-70 °C; IR (ATR) ν 753, 818, 829, 872, 907, 1003, 1080, 1096, 1111, 1131, 1163, 1206, 1242, 1283, 1320, 1386, 1411, 1452, 2901, 2954, 2987 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.37 (s, 18H, $SiMe_3$), 1.31 (d, 6H, J = 6.2 Hz, CH*Me*$_2$), 4.37 (s, 5H, Cp), 4.48 (s, 2H, H3 and H4), 4.94 (sept, 1H, J = 6.2 Hz, C*H*Me$_2$) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$) δ 1.1 ($6CH_3$, $SiMe_3$), 23.4 ($2CH_3$, CH*Me*$_2$), 71.1 (5CH, Cp), 74.8 (CH, *C*HMe$_2$), 77.9 (2C, C2 and C5, *C*-$SiMe_3$), 80.3 (2CH, C3 and C4), 93.1 (C, C1, *C*SO_3iPr) ppm. Anal. Calcd for $C_{19}H_{32}FeO_3SSi_2$ (452.54): C, 50.43; H, 7.13; S, 7.08. Found: C, 50.33; H, 7.11; S, 7.15.

*3-Iodo-O-isopropylferrocenesulfonate (**8**, racemic mixture).* Tetrabutylammonium fluoride (1.0 M in THF, 1.60 mL, 1.60 mmol, 2.00 equiv) was added to a solution of 4-iodo-*O*-isopropyl-2-(trimethylsilyl)ferrocenesulfonate (**6**; 405 mg, 0.80 mmol, 1.00 equiv) in THF (2.5 mL) at room temperature and the reaction mixture was stirred for 30 min. Water (10 mL) was added and the reaction mixture was extracted with AcOEt (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography over silica gel, by using petroleum ether-AcOEt 95:5 as eluent, to give the title product **8** in 84% yield (293 mg) as an orange oil: Rf (petroleum ether-AcOEt 90:10) = 0.46; IR (ATR) ν 655, 729, 764, 828, 872, 913, 1004, 1033, 1044, 1097, 1161, 1208, 1362, 1388, 1414, 1467, 1675, 2257, 2938, 2983, 3108 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (d, 3H, J = 6.2 Hz, Me), 1.26 (d, 3H, J = 6.2 Hz, Me), 4.43 (s, 5H, Cp), 4.67 (dd, 1H, J = 1.7 and 1.2 Hz, H4), 4.71 (dd, 1H, J = 1.7 and 1.2 Hz, H5), 4.71 (sept, 1H, J = 6.2 Hz, C*H*Me$_2$), 4.97 (t, 1H, J = 1.2 Hz, H2) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$) δ 23.0 ($2CH_3$), 38.6 (C, C3, C-I), 70.1 (CH, C5), 74.1 (5CH, Cp), 75.0 (CH, C2), 77.1 (CH, *C*HMe$_2$), 77.6 (CH, C4), 85.2 (C, C1, *C*SO_3iPr) ppm. Anal. Calcd for $C_{13}H_{15}FeIO_3S$ (434.07): C, 35.97; H, 3.48; S, 7.39. Found: C, 36.19; H, 3.64; S, 7.12.

*4-(4-Fluorophenyl)-O-isopropyl-2-(trimethylsilyl)ferrocenesulfonate (**9**, racemic mixture).* 4-Iodo-*O*-isopropyl-2-(trimethylsilyl)ferrocenesulfonate (**6**; 126 mg, 0.25 mmol, 1.00 equiv), 4-fluorophenylboronic acid (140 mg, 1.00 mmol, 4.00 equiv), $Pd(dba)_2$ (7.20 mg, 12.5 µmol, 5 mol%), SPhos (20.5 mg, 50.0 µmol, 20 mol%) and CsF (75.9 mg, 0.50 mmol, 2.00 equiv) were placed in a dried Schlenk tube, subjected to three cycles of vacuum/argon. Toluene (2.00 mL) was added, and the reaction mixture was stirred overnight at 110 °C (external temperature) in a pre-heated oil bath. The reaction mixture was cooled to room temperature and was diluted with water (10 mL). The reaction mixture was extracted with AcOEt (2 x 10 mL), the combined organic layers were dried over $MgSO_4$, filtrated on cotton wool, and concentrated under reduced pressure on a rotary evaporator to give the crude product. This was purified by column chromatography over silica gel, eluting with petroleum ether-AcOEt 95:5 to give the title product **9** in 77% yield (92 mg) as an orange solid: Rf (petroleum ether-AcOEt 90:10) = 0.58; mp 104-105 °C; IR (ATR) ν 659, 695, 767, 822, 833, 878, 917, 964, 990, 1003, 1033, 1074, 1100, 1109,

1138, 1167, 1204, 1230, 1242, 1343, 1377, 1412, 1457, 1526, 1607, 2900, 2957, 2980, 3091 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.39 (s, 9H, $SiMe_3$), 1.19 (d, 3H, J = 6.3 Hz, CHMe_2), 1.36 (d, 3H, J = 6.3 Hz, CHMe_2), 4.26 (s, 5H, Cp), 4.74 (d, 1H, J = 1.2 Hz, H3), 4.79 (sept, 1H, J = 6.3 Hz, CHMe$_2$), 5.31 (d, 1H, J = 1.2 Hz, H5), 7.04 (t, 2H, J = 8.6 Hz, H3' and H5'), 7.48 (dd, 2H, J = 8.6 and 5.3 Hz, H2' and H6') ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$) δ 0.7 ($3CH_3$, $SiMe_3$), 22.9 (CH_3, CHMe_2), 23.4 (CH_3, CHMe_2), 71.5 (CH, C5), 72.7 (5CH, Cp), 74.5 (C, C2, C-$SiMe_3$), 76.0 (CH, C3 or CHMe$_2$), 76.1 (CH, C3 or CHMe$_2$), 89.0 (C; C1, CSO$_3$iPr or C4, C-C_6H_4-4-F), 89.1 (C; C1, CSO$_3$iPr or C4, C-C_6H_4-4-F), 115.8 (2CH, J = 21.5 Hz, C3' and C5'), 127.8 (2CH, J = 8.0 Hz, C2' and C6'), 132.4 (C, J = 3.0 Hz, C1'), 162.1 (C, J = 246.9 Hz, C4') ppm; $^{19}F\{1H\}$ NMR ($CDCl_3$) δ -114.9 ppm. Anal. Calcd for $C_{22}H_{27}FFeO_3SSi$ (474.44): C, 55.70; H, 5.74; S, 6.76. Found: C, 55.74; H, 6.16; S, 6.63.

*O-Isopropyl-3-[4,4,5,5-tetramethyl-2-(1,3,2-dioxaborolyl)]ferrocenesulfonate (**10**, racemic mixture).* *t*BuLi (1.6 M in pentane, 0.80 mL, 1.30 mmol, 2.00 equiv) was added to a solution of 3-iodo-*O*-isopropylferrocenesulfonate (**8**; 282 mg, 0.65 mmol, 1.00 equiv) in THF (3.5 mL) at −85 °C. The reaction mixture was stirred at the same temperature for 5 min before triisopropylborate (450 µL, 367 mg, 1.95 mmol, 3.00 equiv) was added dropwise. The reaction mixture was stirred at −85 °C for 15 min before being warmed to room temperature. Methanol (2 mL) was added, and the reaction was stirred for 1 h. Volatiles were removed under reduced pressure, pinacol (154 mg, 1.30 mmol, 2.00 equiv) and THF (6.5 mL) were added, and the reaction mixture was stirred at room temperature for 15 min before volatiles were removed under reduced pressure. THF (6.5 mL) was added and the reaction mixture was stirred at room temperature for 14 h. Volatiles were removed under reduced pressure to give the crude product. This was purified by column chromatography over silica gel, eluting with petroleum ether-AcOEt 85:15, to give the title product **10** in 55% yield (156 mg) as an orange solid: Rf (petroleum ether-AcOEt 80:20) = 0.39; mp 105-107 °C; IR (ATR) ν 671, 691, 707, 766, 827, 853, 874, 920, 964, 1003, 1058, 1096, 1108, 1141, 1159, 1198, 1279, 1334, 1347, 1479, 1500, 1678, 2943, 2986, 3091 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (d, 3H, J = 6.3 Hz, CHMe_2), 1.24 (d, 3H, J = 6.3 Hz, CHMe_2), 1.34 (s, 12H, Me-pinacol), 4.38 (s, 5H, Cp), 4.63 (dd, 1H, J = 2.3 and 1.1 Hz, H4), 4.69 (sept, 1H, J = 6.3 Hz, CHMe$_2$), 4.85 (dd, 1H, J = 2.3 and 1.1 Hz, H5), 4.96 (t, 1H, J = 1.1 Hz, H2) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$) δ 22.9 (CH_3, CHMe_2), 23.0 (CH_3, CHMe_2), 24.9 ($2CH_3$, CMe_2-pinacol), 25.1 ($2CH_3$, CMe_2-pinacol), 71.6 (5CH, Cp), 72.6 (CH, C5), 74.9 (CH, C2), 76.3 (CH, C4), 76.6 (CH, CHMe$_2$), 83.9 (2C, CMe$_2$-pinacol), 87.5 (C, C1, CSO$_3$iPr) ppm; ^{11}B NMR ($CDCl_3$) δ 32.3 (br s) ppm. Anal. Calcd for $C_{19}H_{27}BFeO_5S$ (434.13): C, 52.57; H, 6.27; S, 7.38. Found: C, 52.65; H, 6.38; S, 7.30. *Crystal data for **10**.* $C_{19}H_{27}BFeO_5S$, M = 434.12, T = 150(2) K, orthorhombic, $P\,2_1\,2_1\,2_1$ (I.T.#19), a = 7.4269(4), b = 12.2846(5), c = 22.7194(9) Å, V = 2072.84(16) Å^3, Z = 4, d = 1.391 g·cm^{-3}, μ = 0.854 mm^{-1}. A final refinement on F^2 with 4733 unique intensities and 251 parameters converged at $\omega R(F^2)$ = 0.0818 ($R(F)$ = 0.0401) for 4213 observed reflections with $I > 2\sigma(I)$. CCDC 2084909.

1-(N-Pyrrolidino)sulfonyl-2-(trimethylsilyl)ferrocene (racemic mixture). *n*BuLi (1.4 M in hexanes, 0.80 mL, 1.10 mmol, 1.10 equiv) and, 15 min later, a solution of (*N*-pyrrolidino)sulfonylferrocene (319 mg, 1.00 mmol, 1.00 equiv) in THF (6 mL) were added to a solution of *N,N,N',N'*-tetramethylethylenediamine (0.16 mL, 128 mg, 1.10 mmol, 1.10 equiv) in THF (2 mL) at −80 °C. After 1 h at this temperature, chlorotrimethylsilane (0.19 mL, 163 mg, 1.50 mmol, 1.50 equiv) was added at −80 °C, and the mixture was stirred for 15 min. The reaction mixture was warmed to room temperature and aqueous HCl (1 M, 10 mL) was added. The reaction mixture was extracted with AcOEt (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography over silica gel (eluent: petroleum ether-AcOEt 80:20; Rf = 0.47) to give the title product in 60% yield (230 mg) as an orange solid: mp 92 °C; IR (ATR) ν 655, 717, 702, 755, 814, 826, 954, 1007, 1047, 1076, 1108, 1135, 1108, 1185, 1222, 264, 1248, 1327, 1731, 2875, 2957, 3420 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.35 (s, 9H, $SiMe_3$), 1.72-1.83 (m, 4H, NCH_2CH_2), 3.08-3.23 (m, 4H, NCH_2), 4.29 (dd, 1H, J = 2.6 and 1.4 Hz, H3), 4.39 (s, 5H, Cp), 4.50 (t, 1H, J = 2.4 Hz, H4), 4.80 (dd, 1H, J = 2.3 and 1.4 Hz, H5) ppm; $^{13}C\{1H\}$ NMR ($CDCl_3$) δ 1.1 ($3CH_3$, $SiMe_3$), 25.4 ($2CH_2$, NCH_2CH_2), 47.7 ($2CH_2$, NCH_2), 70.8 (5CH, Cp), 72.4 (CH, C4), 72.7 (CH, C5), 73.5 (C, C2, C-$SiMe_3$), 77.5 (CH, C3), 90.7 (C, C1, C-SO_2-N-pyrrolidino) ppm. Anal. Calcd for $C_{17}H_{25}FeNO_2SSi$ (391.38): C, 52.17; H, 6.44; N, 3.58; S, 8.19. Found: C, 52.29; H, 6.64; S, 7.98.

Deprotonation of *O*-isopropylferrocenesulfonate (1) with *s*BuLi·TMCDA by using chlorotrimethylsilane as electrophile. *s*BuLi (1.1 M in cyclohexane-hexane 92:8, 1.10 mL, 1.20 mmol, 1.20 equiv) was added dropwise to a solution of (*R,R*)-TMCDA (204 mg, 1.20 mmol, 1.20 equiv) in Et_2O (6 mL) at −80 °C. After 15 min at this temperature, a solution of *O*-isopropylferrocenesulfonate (**1**; 308 mg, 1.00 mmol, 1.00 equiv) in Et_2O (4 mL) was added dropwise and the reaction mixture was stirred at the same temperature for 1 h. Chlorotrimethylsilane (152 µL, 130 mg, 1.20 mmol, 1.20 equiv) was added and the reaction mixture was warmed to room temperature. Aqueous HCl (1 M, 10 mL) was added, and the reaction mixture was extracted with AcOEt (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography, using petroleum ether-AcOEt 100:10 to 80:20 to give the title product **4** as an orange oil in 85% yield (323 mg). The *ee* (16%) was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 98:2, 0.7 mL·min^{-1}, 20 °C, λ = 220 nm, t (major) = 17.03 min, t (minor) = 19.68 min. The bis-silylated product **7'** was also obtained as an orange solid in 4% yield (21 mg).

Deprotonation of *O*-isopropylferrocenesulfonate (1) with PEALi by using chlorotrimethylsilane as *in situ* trap. *n*BuLi (1.4 M in hexanes, 715 µL, 1.00 mmol, 1.00 equiv) was added dropwise to a solution of (*R*)-PEAH (228 µL, 225 mg, 1.00 mmol, 1.00 equiv) in THF (6 mL) at −15 °C. After 5 min at this temperature, this solution was cannulated onto a solution of *O*-isopropylferrocenesulfonate (**1**; 308 mg, 1.00 mmol, 1.00 equiv) and chlorotrimethylsilane (127 µL, 109 mg, 1.00 mmol, 1.00 equiv) in THF (6 mL) at −15 °C. After addition, the reaction mixture was warmed to −10 °C and stirred for 30 min. Aqueous HCl (1M, 10 mL) was added, and the reaction mixture was extracted with AcOEt (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography, using petroleum ether-AcOEt 90:10 to 80:20 to give the title product **4** as an orange oil in 70% yield (266 mg). The *ee* (4%) was determined by HPLC analysis on a Chiralpak IC-3 column, hexane-isopropanol 98:2, 0.7 mL·min^{-1}, 20 °C, λ = 220 nm, t (major) = 16.98 min, t (minor) = 19.60 min. The bis-silylated product **7'** was also obtained as an orange solid in 11% yield (49 mg).

Deprotonation of *O*-isopropylferrocenesulfonate (1) with PEALi by using $(PEA)_2Zn$ as *in situ* trap. *n*BuLi (1.4 M in hexanes, 1.43 mL, 2.00 mmol, 2.00 equiv) was added dropwise to a solution of (*R*)-PEAH (457 µL, 450 mg, 2.00 mmol, 2.00 equiv) in THF (6 mL) at −15 °C. After 5 min at this temperature, $ZnCl_2$·TMEDA (252 mg, 1.00 mmol, 1.00 equiv) was added in one portion and the reaction mixture was stirred for 15 min. *O*-Isopropylferrocenesulfonate (**1**; 308 mg, 1.00 mmol, 1.00 equiv) was added in one portion at the same temperature, and the reaction mixture was stirred for another 15 min. A cooled (−70 °C) solution of (*R*)-PEALi (prepared by adding *n*BuLi (714 µL, 1.00 mmol, 1.00 equiv) dropwise to a solution of (*R*)-PEAH (229 µL, 225 mg, 1.00 mmol, 1.00 equiv) in THF (6 mL) at −15 °C and stirring for 5 min) was then added at −70 °C by cannula. After addition, the reaction mixture was slowly warmed to −10 °C over a period of 3 h. A solution of iodine (761 mg, 3.00 mmol, 3.00 equiv) in THF (4 mL) was added and the reaction mixture was stirred for 1 h at room temperature. A saturated aqueous solution of $Na_2S_2O_3$ (10 mL) was added to the reaction mixture which was extracted with AcOEt (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtrated, and concentrated under reduced pressure to give the crude product. This was purified by column chromatography, using petroleum ether-AcOEt 90:10 to 80:20 to give an inseparable mixture (366 mg) of title product **3** and starting material **1** in a 29:71 ratio. The *ee* (64%) was determined by HPLC

analysis on a Chiralpak IA-3 column, hexane-isopropanol 99:1, 0.4 mL·min^{-1}, 20 °C, λ = 220 nm, t (**1**) = 41.27 min, t (minor) = 31.46 min, t (major) = 36.97 min.

Electrochemical measurements. Cyclic voltammetry was performed in CH_2Cl_2 containing nBu$_4$NPF$_6$ (0.1 M) as supporting electrolyte. An aqueous Ag/AgCl reference electrode, a Pt counter electrode and a glassy carbon working electrode were used.

Computational details. All electronic structure calculations were performed by using Gaussian 09 package.[51] Full geometry optimization of the considered species was carried out by using the CAM-B3LYP hybrid functional.[52] Vibrational frequencies were calculated to establish the nature of the stationary points and to derive thermochemical corrections for enthalpies and free energies. The LANL2DZ basis set[53] with the effective core potential was used for Fe and I, while the 6-31G(d) basis set[54] was applied to the rest of the atoms. The latter was replaced by 6-311+G(d,p) set for single point energies. The pK_a values were obtained from the Gibbs free energy of the homodesmic reaction. This approach was successfully applied in the ferrocene series earlier.[13e,14,20,23a] The polarizable continuum model (IEF-PCM)[55] was used to account for solvation effects with a default parameters of THF to simulate the reaction conditions.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Ferrocene • Alkyl sulfonate • Chirality • Lithium • Halogen dance

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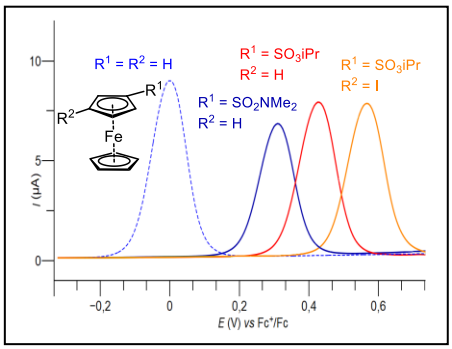

Original 2- or 3-substituted, 2,4- or 2,5-disubstituted, and 2,3,5-trisubstituted ferrocenesulfonates were obtained from *O*-isopropylferrocenesulfonate by applying deprotolithiation, “halogen dance” reaction, Suzuki-Miyaura cross-coupling and halogen/metal exchange to this series. Enantioselective deprotometalation was also attempted. Compared with *N*,*N*-dialkylferrocenesulfonamides, the corresponding *O*-isopropylferrocenesulfonates proved slightly more difficult to oxidize.

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