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Fluorosulfonylferrocene, (Trifluoromethylsulfonyl)ferrocene and New Ferrocenyl Sulfonates: Directed *ortho* Lithiation and New Anionic Thia-Fries Rearrangements at Ferrocene

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Dedicated to the 70th anniversary of the discovery of ferrocene

Ferrocenyl triflates are known to undergo anionic thia-Fries rearrangements at low temperature in high yields. In order to expand the scope of this reaction, ferrocenyl sulfonates and sulfonylferrocenes were prepared and their reactivity investigated. Treatment of ferrocenyl fluorosulfonate with lithium 2,2,6,6-tetramethylpiperidide gave rise to a new anionic thia-Fries rearrangement at ferrocene. The formation of a rare oxathiine was observed with ferrocenyl (pentafluorophenyl) sulfonate as a result of an *ortho* lithiation and a subsequent intramolecular nucleophilic aromatic substitution. In contrast to fluorinated ferrocenyl sulfonates, fluorosulfonylferrocene as well as (trifluoromethylsulfonyl)ferrocene underwent *ortho* lithiation under comparable reaction conditions.

Introduction

Directed *ortho* metalation (DOM), followed by treatment with an electrophile, is a powerful functionalisation tool in organic chemistry for the creation of new carbon-carbon and carbon-heteroatom bonds mostly at aromatic systems (Scheme 1).[1] This requires an *ortho* directing group (ODG) as in **1**, which preferably has a nucleophilic heteroatom for interaction with the lithium atom of an organolithium RLi shown in **2** and **3**.[2,3] The combination of complexation and inductive effects plays an important role leading Snieckus, Beak et al. to coin the term CIPE standing for a complex-induced proximity effect. The general mechanism can be summarized through an interaction of the aggregated alkyl lithium to the ODG, de-aggregation followed by *ortho* lithiation to **4**, and a final trapping by the electrophile resulting in **5**.[4]

Among the large number of existing ODGs, those containing sulfur-oxygen double bonds are among the more active ones: sulfones, sulfoxides, secondary and tertiary sulfonamides.[2] The use of the (trifluoromethyl)sulfonyl group of some arenes as an ODG was first reported in 2018 by Shibata et al.[5] The first observation of fluorosulfonylarenes to undergo *ortho*-lithiation has recently been reported by Barbasiewicz et al. in the context of the new anionic thia-Fries rearrangement of non-organometallic aryl fluorosulfonates.[6]

It deserves mention that Lang et al. reported some interesting phosphate derivatives to show similar *ortho* directing properties allowing for highly selective anionic phospho-Fries rearrangements.[7] However, due to the stronger electron withdrawal of sulfonate groups, these allow for the lithiation at temperatures as low as −78 °C making them more suitable for further study.

Focusing on organometallic derivatives, here we report on the new syntheses of (trifluoromethyl)sulfonylferrocene (**6**) and fluorosulfonylferrocene (**7**), and ferrocenyl (pentafluorophenyl) sulfonate (**9**) *ortho*-lithiations at these systems, as well as on the first anionic thia-Fries rearrangements at ferrocenyl fluorosulfonate (**8**) (Scheme 2).

Results and Discussion

The first anionic thia-Fries rearrangements at ferrocene derivatives were reported in 2010 starting with ferrocenyl triflate (**12**) and 1,1′-ferrocenediyl ditriflate. These rearrangements took place instantaneously at low temperatures in very high yields and, in the case of the latter, with full diastereoselectivity exclusively affording the *meso* product.[8] Later, it was found that ferrocenyl nonaflate undergoes the reaction as well, in comparably high yields.[9] A mechanistic study of these reactions has recently been published including a structural analysis of intermediate **13**, which leads to **14**.[10] These results raise the question in how far other ferrocenyl sulfonates, besides triflates or nonaflates, allow for similar rearrangements.

In a first attempt, ferrocenyl mesylate (**10**) and ferrocenyl tosylate (**11**) were treated with lithium diisopropylamide (LDA) in THF affording only ferrocenolate **15**, which was trapped by the addition of mesyl or tosyl chloride to afford **10** and **11** in

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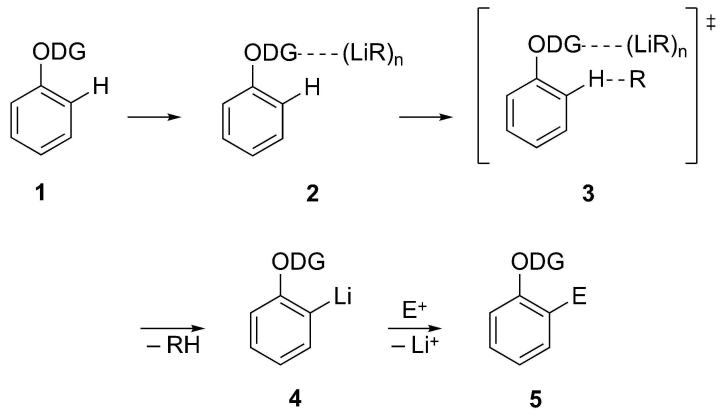
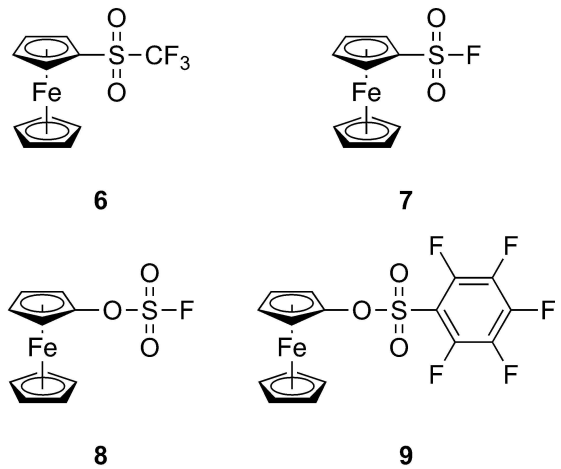


Scheme 1. Directed *ortho* lithiation general mechanism.

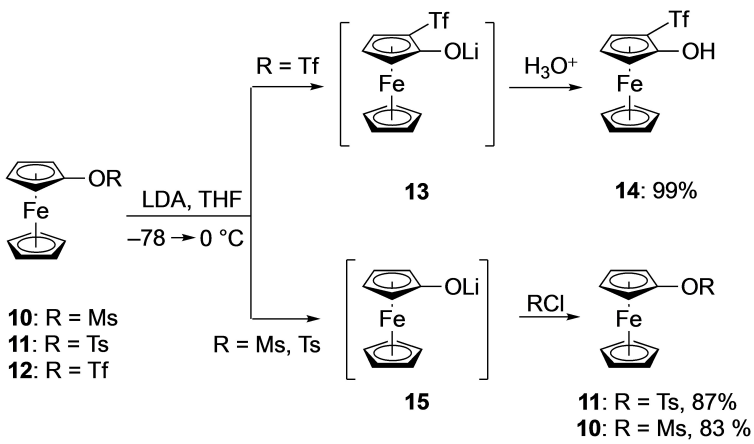


Scheme 2. Sulfonylferrocenes and ferrocenyl sulfonates.

83% and 87% yield, respectively (Scheme 3). Presumably, a methyl proton of the mesyl or the phenylog tosyl substituents was removed, allowing for the formation of the respective sulfene and ferrocenolate. In this context, it is of interest that Carreira et al. reported the treatment of methanesulfonates with lithium diisopropylamide in THF as a mild chemoselective deprotection method for mesylphenols.[11] Alternatively, a nucleophilic attack of the base at the sulfur atoms may be considered.

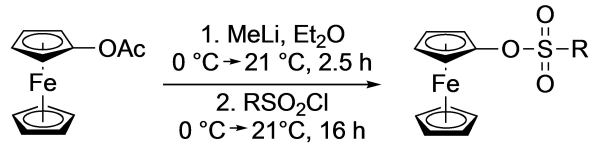
As the nature of the sulfonyl substituent appears to be critical for the course of the reaction, some other ferrocenyl arylsulfonates **9**, **17**–**20** were prepared in a similar fashion to that of ferrocenyl tosylate (**11**)[9] (Table 1) and tested for their suitability to undergo an anionic thia-Fries rearrangement upon treatment with LDA or with lithium 2,2,6,6-tetramethylpiperidide (LiTMP). However, none of them underwent an anionic thia-Fries rearrangement. While **17**, **19** and **20** reacted with the formation of ferrocenolate as indicated by electrophilic trapping or by TLC/MS analysis, no reaction was observed with the sterically highly crowded **18**.

Ferrocenyl (2,3,4,5,6-pentafluorophenyl) sulfonate (**9**) contains an even more electron withdrawing aryl substituent and lacks any hydrogen atoms at the sulfonyl substituent, which could possibly be abstracted leading to a sulfene derivative. **9** was thus expected to undergo an anionic thia-Fries rearrangement. When **9** was treated with LiTMP at −78 °C, the yellow

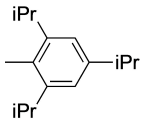
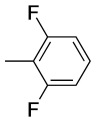
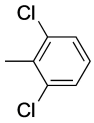


Scheme 3. Reactions of ferrocenyl sulfonates with LDA.

Table 1. Synthesis of ferrocenyl sulfonates **9**, **17**–**20**.



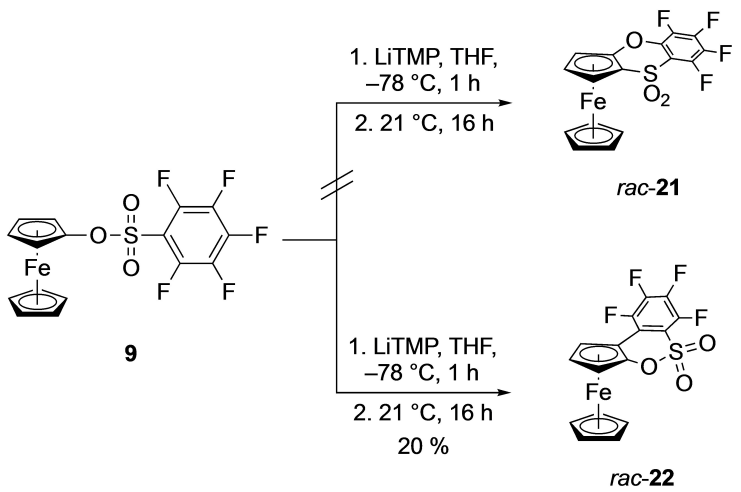
16 **9, 17 - 20**

Entry	R	Product	Yield [%]
1		**9**	50
2		**17**[12]	83
3		**18**	93
4		**19**	90
5		**20**	67

solution immediately turned purple. Subsequently, after stirring the solution at −78 °C for 1 h and then warming to 21 °C over 16 h, a red solid was obtained. The ferrocene-anellated 1,4-oxathiine-4,4-dioxide *rac*-**21** was thought to be the reaction product resulting from an anionic thia-Fries rearrangement followed by an intramolecular nucleophilic substitution. However, it turned out that after deprotonation, the rearrangement had not taken place, but instead was directly followed by an intramolecular nucleophilic aromatic substitution affording the ferrocene anellated 6,7,8,9-tetrafluorobenzo[*c*,*e*]-[1,2]oxathiine 5,5-dioxide *rac*-**22** as a red solid in 20% yield (Scheme 4). Crystallization of *rac*-**22** via slow evaporation of a solution of *rac*-**22** in ethyl acetate rendered single crystals suitable for X-ray analysis. Although only a low-quality X-ray structure analysis was obtained (see SI), it confirmed the identity of the compound *rac*-**22**. Fluorinated benzo[*c*,*e*][1,2]oxathiine 5,5-dioxides are rare. A small number of monofluorinated derivatives were obtained by radical reactions by Motherwell et al.[13,14] Only very recently Politanskaya et al. published some more highly fluorinated [1,4]-oxathiine-4,4-dioxide derivatives.[15] The formation of *rac*-**22** is explained by an *ortho* lithiation of **9** followed by an intramolecular nucleophilic aromatic substitution with a newly formed carbon-carbon bond.

In an attempt the increase the yield of *rac*-**22**, the reaction was repeated, more equivalents of base were used, and the solution was stirred at −78 °C for 5 h before bringing it to room temperature. The yield of red solid obtained did not change, but the NMR spectra showed two different compounds, which could not be separated. The new NMR peaks are similar in shape to the peaks of *rac*-**22**, apart from the ones at δ = 4.4 ppm, as shown in Figure 1. VT NMR measurements of *rac*-**22** did not show any changes in the spectra. It can only be speculated that the peaks belong to a small amount of *rac*-**21** formed in the reaction.

As mentioned above, Barbasiewicz et al. reported the anionic thia-Fries rearrangement of 2-chlorophenyl fluorosulfonate.[6] In the context of our earlier investigations on anionic thia-Fries rearrangements at ferrocene,[8,16] it was of interest to investigate if the rearrangement also took place at ferrocenyl fluorosulfonate (**8**). Based on Sharpless' sulfur(VI) exchange (SuFex) chemistry[17] De Borggraeve developed a very convenient procedure for the synthesis of aryl fluorosulfonates from phenols in the presence of a base and *ex situ* produced sulfuryl fluoride.[18] Following this, ferrocenyl acetate (**16**) was treated with potassium hydroxide in water followed by acid hydrolysis. Without isolation, the intermediate ferrocenol (**23**)



Scheme 4. Formation of ferrocene anellated 6,7,8,9-tetrafluorobenzo[*c*,*e*]-[1,2]oxathiine 5,5-dioxide *rac*-**22**.

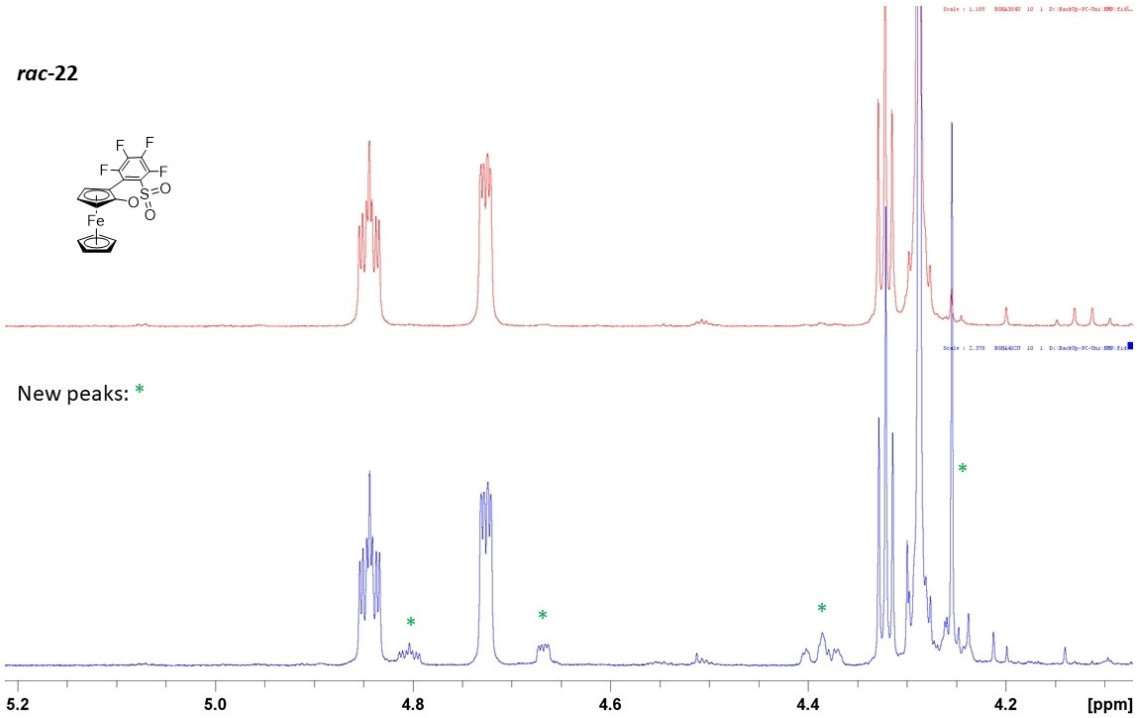
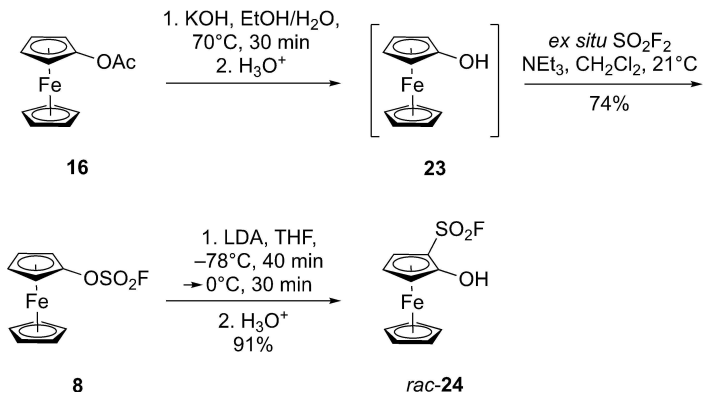


Figure 1. NMR stacking plot of *rac*-**22** and the red solid obtained when prolonging the first step of the reaction in the presence of an increased amount of base.

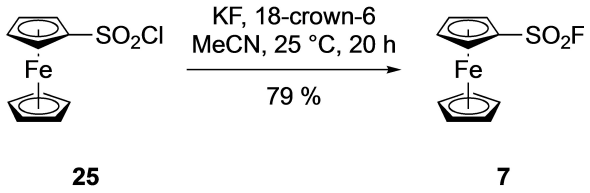
was treated with sulfuryl fluoride in the presence of triethylamine affording ferrocenyl fluorosulfonate (**8**) in 74% yield. The desired anionic thia-Fries rearrangement was finally realized by treatment of **8** with lithium diisopropylamide at −78 °C for 40 min followed by warming to 0 °C over 30 min and hydrolytic workup giving 2-(fluorosulfonyl)ferrocenol (*rac*-**24**), which was isolated as an oxygen sensitive compound not undergoing hydrolysis, in 91% yield (Scheme 5). This result confirms the propensity of the ferrocene system to undergo anionic thia-Fries rearrangements.

7 is only the third (fluorosulfonyl)ferrocene derivative reported so far. Nesmeyanov et al reported 1-carboxy- and 1-methoxycarbonyl-1′-(fluorosulfonyl)ferrocene in 1959.[19] These authors obtained the fluorosulfonyl group from the respective chlorosulfonyl derivative by treatment with KHF_2 in acetic acid. We tested a similar route starting from ferrocenylsulfonyl chloride (**25**) in acetonitrile,[20] however, this procedure led only to a very modest yield of 21% of fluorosulfonylferrocene (**7**). Application of a halogen exchange procedure originally applied for the synthesis of phenylsulfonyl fluoride[21] using potassium fluoride in the presence of 18-crown-6 in acetonitrile gave a much better yield of 79% of **7** (Scheme 6), whereas an attempt with tetrabutylammonium fluoride in THF failed.

In addition to **7**, we attempted the preparation of another ferrocenylsulfonyl derivative with an electron withdrawing substituent, namely (trifluoromethylsulfonyl)ferrocene (**6**). An



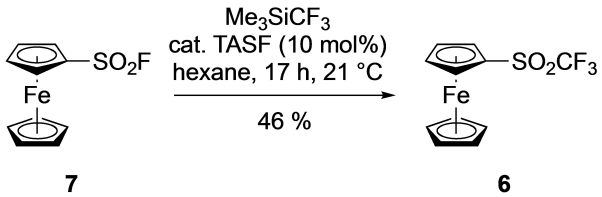
Scheme 5. Synthesis and anionic thia-Fries rearrangement of ferrocenyl fluorosulfonate (**8**).



25 **7**

Scheme 6. Synthesis of fluorosulfonylferrocene (**7**).

approach to prepare **6** by treatment of sulfonyl chloride **25** with copper(I) iodide and sodium trifluoroacetate in DMF failed,[22] and another attempt making use of the SuFEx protocol by Moses et al. treating sulfonyl fluoride **7** with KHF_2 and (trifluoromethyl)trimethylsilane (Ruppert's reagent) was also unsuccessful.[23] Finally, **6** was obtained in moderate yield of 46% following a route of Yagupolski et al.[24] by treatment of sulfonyl fluoride **7** with (trifluoromethyl)trimethylsilane in the presence of a catalytic amount (10 mol%) of tris (dimethylamino)sulfonium difluorotrimethylsilicate (TASF) (Scheme 7).



7 **6**

Scheme 7. Synthesis of (trifluoromethylsulfonyl)ferrocene (**6**). TASF = tris (dimethylamino)sulfonium difluorotrimethylsilicate.

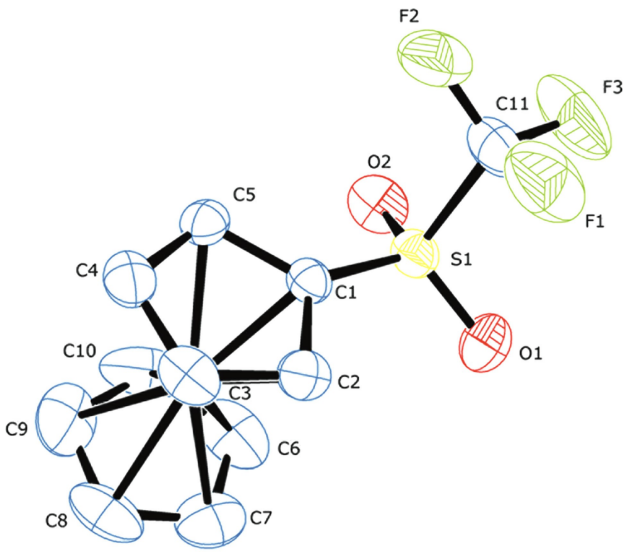


Figure 2. Structure of **6** in the crystal.[25] Selected bond lengths, centroid distances [pm] and angles [°] and dihedral angles [°]: S1-O1 143.1(3), S1-O2 142.9(3), S1-C11 182.7(4), S1-C1 171.7(3), C11-F1 131.6(5), C11-F2 130.9(5), C11-F3 131.6(5); Fe1-centroid (C1,C2,C3,C4,C5) 164.2, Fe1-centroid (C6,C7,C8,C9,C10) 165.1; C1-S1-O1 110.3°, C1-S1-C11 102.5°; C2-C1-S1-O1 14.3°.

The moderate yield may be explained by difficulties in the purification of **6**. Many attempts to separate residual **7** and **6** by column chromatography failed. Both compounds crystallize from hexane and both compounds sublime at 50 °C/1.0 mbar. Finally, pure **6** was obtained by stirring the mixture of **7** and **6** in dioxane/water (1:1) in the presence of potassium phosphate for 16 h at 85 °C causing hydrolysis of **7**. Crystals of **6** suitable for a crystal structure analysis were obtained by crystallization from hexane at −30 °C over 7 d (Figure 2).

(Trifluoromethylsulfonyl)ferrocene (**6**) crystallizes in a monoclinic crystal system [space group P $2_1/n$ (14)]. The cyclopentadienyl ligands adopt an almost eclipsed conformation (eclipsed angle 7.8°), and the trifluoromethylsulfonyl substituent points away from the unsubstituted cyclopentadienyl ring almost perpendicularly (C2-C1-S1-C11 98.8°).

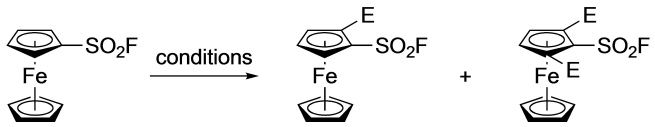
Next, we investigated in how far fluorosulfonylferrocene (**7**) and (trifluoromethylsulfonyl)ferrocene (**6**) are prone to *ortho* lithiation. Initial experiments with **7** and LiTMP showed that a reaction took place, however, products obtained by quench with acetyl chloride were not stable enough for the isolation of pure products. Replacing acetyl chloride with the less reactive 2,6-dimethoxybenzoyl chloride afforded mono-substitution product *rac*-**26** in 16% yield with no di-substitution product being observed in addition to 74% of recovered **7**. Higher yields were achieved with iodomethane as the electrophile. When 1.3 equiv. of LiTMP were used, 60% of the mono-substitution product *rac*-**27** was obtained in addition to 10% of di-substitution product **28** and 19% of starting material **7**. Increasing the amount of LiTMP to 3.0 equiv. afforded an improved yield of *rac*-**27** of 72% in addition to 9% of **28** and 10% of starting material **7** indicating higher chemoselectivity (Table 2).

The *ortho* lithiation of (trifluoromethylsulfonyl)ferrocene (**6**) was tested by treatment with 1.3 equiv. of LiTMP and iodomethane as the electrophile and gave the mono-substitution product *rac*-**29** in 51% yield in addition to di-substitution product **30** (5%) and starting material **6** (6%) (Scheme 8). The chromatographic separation of the product mixture was problematic and caused some product loss. It is interesting to note that Shibata et al. did not observe di-substitution products in the respective reactions of (trifluoromethylsulfonyl) benzene.[5]

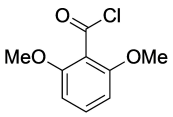
In the course of the investigations, it was observed that ferrocenylsulfonyl chloride (**25**) is remarkably resistant against hydrolysis, presumably as a result of the electron rich ferrocenyl group. Therefore, we became interested in a possible *ortho* lithiation of this compound. Treatment of **25** with LiTMP under the usual reaction conditions with carbon dioxide as the electrophile resulted, however, in the formation of ferrocenyl sulfonamide **31** in 91% yield in addition to a side product (most likely **32a**, 4% yield) (Scheme 9). The reaction shows the remarkable difference in the reactivity of the sulfonyl chloride **25** and the sulfonyl fluoride **7**.

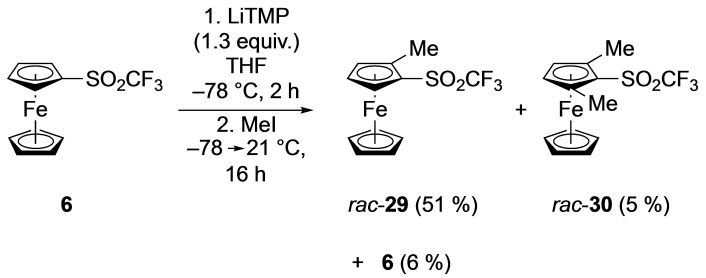
After analysis of the NMR and IR spectra of the side product, constitution **32a** was considered. The ESI mass spectrum shows a peak at $m/z = 344$ corresponding to $[M + {}^{23}Na]^+$ for compound **32a**. However, there is also a signal at $m/z = 663$, which

Table 2. *ortho* Lithiation of fluorosulfonylferrocene (**7**).



7 *rac*-**26**: E = 2,6-$(MeO)_2C_6H_3C(O)$ *rac*-**27**: E = Me **28**: E = Me

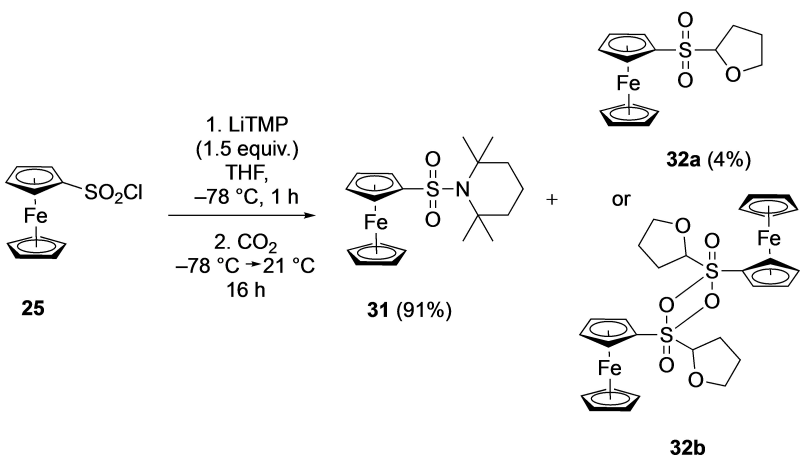
Entry	Conditions	Electrophile E	Product (Yield) mono-substitution	Product (Yield) di-substitution	Recovery of **7**
1	LiTMP (1.1 equiv.), THF, −78 °C, 1 h. After electrophile addition −78 °C (15 min)→22 °C (30 min)		*rac*-**26** (16%)	–	74%
2	LiTMP (1.3 equiv.), THF, −78 °C, 2 h. After electrophile addition −78 °C (15 min)→21 °C (30 min)	MeI	*rac*-**27** (60%)	**28** (10%)	19%
3	LiTMP (3.0 equiv.), THF, −78 °C, 2 h. After electrophile addition −78 °C (15 min)→21 °C (30 min)	MeI	*rac*-**27** (72%)	**28** (9%)	10%



6 *rac*-**29** (51 %) *rac*-**30** (5 %)

+ **6** (6 %)

Scheme 8. *ortho* Lithiation of (trifluoromethylsulfonyl)ferrocene (**6**).



25 **31** (91%) **32b**

Scheme 9. Formation of sulfonamide **31** and side product **32a** or **32b**.

corresponds to $[M+^{23}Na]^+$ for cyclodimer **32b**, which cannot easily be distinguished from **32a** by standard NMR measurements. In both cases, the presence of tetrahydrofuranyl substituents can be explained by a lithiation at C2 of a THF molecule followed by reaction with **25** forming (ferrocenyl)(2-tetrahydrofuranyl)sulfone (**32a**). A [2+2] cyclodimerization of **32a** leading to **32b** would, to our knowledge, be unprecedented and might have taken place under the conditions of the mass spectrometric analysis. In this context the observation may be of interest that the ratio of **32a** and **32b** seems to be concentration dependent.

In order to test the feasibility of (trifluoromethylsulfonyl) ferrocenes for Suzuki-Miyaura coupling reactions, we applied the optimized reaction conditions by Moran et al.[26] However, the reaction of (trifluoromethylsulfonyl)ferrocene (**6**) with 4-(trifluoromethyl)phenylboronic acid (**35**) gave a yield of only 7% of **36** (Scheme 10). The coupling reaction using 2-methoxy (trifluoromethylsulfonyl)ferrocene (*rac*-**33**) gave 3% yield of *rac*-**37**, and no coupling product *rac*-**38** was obtained with acetoxy (trifluoromethylsulfonyl)ferrocene (*rac*-**34**).[8]

Conclusions

We described the syntheses of several new ferrocenyl sulfonates and sulfonyl ferrocenes. The effective *ortho* lithiation of ferrocenyl fluorosulfonate (**8**) allowed the anionic thia-Fries rearrangement at ferrocene to take place in high yields whilst the *ortho* lithiation at ferrocenyl (2,3,4,5,6-pentafluorobenzene) sulfonate (**9**) followed by intramolecular nucleophilic aromatic substitution led to the formation of a rare ferrocene-annellated [1,2]oxathiin *rac*-**22**. Fluorosulfonylferrocene (**7**) proved to be a good substrate for *ortho* lithiation and will possibly enable future SuFEx reactions at ferrocene. The *ortho* lithiation of (trifluoromethylsulfonyl)ferrocene (**6**) was also demonstrated to be effective.

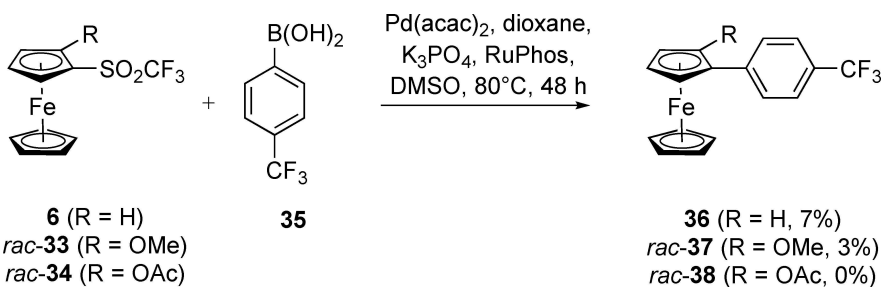
Experimental Section

General: All reactions were carried out in an inert atmosphere (Argon) using the Schlenk technique. THF, diethyl ether and hexane were dried at reflux over sodium/benzophenone, dichloromethane by stirring over calcium hydride, and diisopropylamine (DIPA) by stirring over potassium hydroxide. All solvents were freshly distilled before use. Acetonitrile, dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) were purchased from commercial suppliers and used without further purification. When necessary, deuterated chloroform was dried by heating at reflux over CaH_2 and distilled in an inert atmosphere. IR: Fourier transform infrared spectrophotometer Shimadzu IRAffinity 1S with quest ATR unit (32 scans). Signal intensities: strong (s), medium (m), weak (w), broad (br). High resolution electron ionization (HR-EI) mass spectra were measured using a Micromass GCT spectrometer with direct insertion probe, 70 eV electron ionization energy and 250 °C source temperature. High resolution electrospray ionization (HR-ESI) mass spectra were measured using a Waters LCT Premier instrument with Alliance 2695 HPLC (Waters), 2700 V capillary voltage, 650 l/h desolvation gas and 250 °C desolvation temperature. NMR: Bruker Ascend (^{1}H: 600.1 MHz, ^{13}C: 150.9 MHz) with Avance NEO Console at 298 K, Ascend (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz, ^{19}F: 376.5 MHz) with Avance III Console or Ascend with Avance III HD Console and Ultrashield (^{1}H: 500.1 MHz, ^{13}C: 125.8 MHz) with Avance-III HD console. The chemical shift of the residual solvent signal of the deuterated solvent ($CDCl_3$, ^{1}H: $\delta = 7.26$ ppm, ^{13}C: 77.16 ppm; C_6D_6, ^{1}H: $\delta = 7.16$ ppm, ^{13}C: 128.06 ppm) was used as the internal standard. ^{19}F NMR: Spectrometer frequency for ^{1}H was multiplied by 0.94094008 and the resulting value entered as the spectrometer frequency for ^{19}F according to the IUPAC convention.[27] Cp′ refers to the unsubstituted cyclopentadienyl ligand (C_5H_5). Melting points (m.p.) were measured using Electrothermal IA 9000 Series Melting Point Apparatus. Medium pressure liquid chromatography (MPLC): Büchi Chromatography Pump 688, Büchi gradient Former B687, Büchi Fraction collector B684 and a Knauer UV detector K-2501.

Ferrocenyl methanesulfonate (10): At −78 °C a solution of methyllithium in hexane (1.6 M, 3.1 mL, 6.2 mmol) was added to ferrocenyl acetate[12] (**16**, 500 mg, 2.1 mmol) in diethyl ether (10 mL). The reaction mixture was stirred for 30 min and warmed to 0 °C. Methanesulfonyl chloride (0.48 mL, 6.2 mmol) was added dropwise, and the solution was stirred for 30 min. After warming to 21 °C the mixture was stirred for another 30 min. After addition of water (25 mL) the mixture was extracted with ethyl acetate (3× 40 mL). The collected organic layers were dried with magnesium sulfate and the solvent removed at reduced pressure. After purification by column chromatography (3×30 cm, SiO_2, petroleum ether/dichloromethane 9:1) ferrocenyl mesylate (**10**, 410 mg, 1.5 mmol, 71%) was obtained as an orange/yellow solid (m.p. 63 −64 °C).

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 3.00$ (s, 3H, CH_3), 4.01 + 4.48 (AA′BB′, $J = 1.8$ Hz, 2×2H, Cp), 4.30 (s, 5H, Cp′) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): $\delta = 36.5$ (CH_3), 61.6 ($C_{Cp}H$), 64.2 ($C_{Cp}H$), 70.1 (Cp′), 116.7 ($C_{Cp}O$) ppm. IR: $\tilde{\nu} = 3113$ (w), 3037 (w), 2941 (w), 1436 (m), 1375 (m), 1170 (s), 1018 (m), 921 (m), 806 (s), 761 (m), 592 (m), 522 (m), 482 (s) cm^{-1}. HRMS (ESI, MeCN): Calcd. for $C_{11}H_{12}FeO_3S$ [M^+] 279.9857, found 279.9849.

Ferrocenyl (4-methylphenyl)sulfonate (11):[9] At −78 °C a solution of methyllithium in hexane (1.6 M, 3.1 mL, 6.2 mmol) was added to ferrocenyl acetate[12] (**16**, 607 mg, 2.5 mmol) in diethyl ether (15 mL) and stirred at −78 °C for 5 min. After slowly warming to 21 °C the mixture was stirred for another 2 h. At 0 °C, a solution of 4-toluenesulfonyl chloride (711 mg, 3.7 mmol) in THF (5 mL) was added dropwise, the solution was slowly warmed to 21 °C and stirred for 30 min. After addition of water (15 mL) the mixture was extracted with dichloromethane (3×20 mL). The collected organic layers were dried with magnesium sulfate, and the solvent removed at reduced pressure. After purification through column chromatography (3×30 cm, SiO_2, petroleum ether/dichloromethane 8:2) ferrocenyl tosylate (**11**, 835 mg, 2.3 mmol, 94%) was obtained as an



6 (R = H)
rac-**33** (R = OMe)
rac-**34** (R = OAc)

35

36 (R = H, 7%)
rac-**37** (R = OMe, 3%)
rac-**38** (R = OAc, 0%)

Scheme 10. Suzuki coupling of (trifluoromethylsulfonyl)ferrocene derivatives. RuPhos = 2-Dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl.

orange solid (m.p. 95–96 °C), identified by comparison with literature data (^{1}H NMR, ^{13}C NMR, MS).[9]

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 2.43$ (s, 3H, CH_3), 3.87 + 4.17 (AA′BB′, $J = 2.0$ Hz, 2×2H, Cp), 4.23 (s, 5H, Cp′), 7.29 + 7.66 (AA′BB′, $J = 8.2$ Hz, 2×2H, C_6H_4) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): $\delta = 21.8$ (CH_3), 62.0 ($C_{Cp}H$), 63.9 ($C_{Cp}H$), 69.9 (Cp′), 116.5 ($C_{Cp}O$), 128.7 ($C_{Ar}H$), 129.7 ($C_{Ar}H$), 132.1 ($C_{Ar}S$), 145.3 ($C_{Ar}CH_3$). HRMS (ESI, MeCN): Calcd. for $C_{17}H_{16}FeO_3SNa$ [M^+ + Na] 379.0067, found 379.0067.

Ferrocenyl benzenesulfonate (17):[11] At 0 °C methyllithium in hexane (1.6 M, 0.90 mL, 1.5 mmol) was added to ferrocenyl acetate[11] (**16**, 294 mg, 1.2 mmol) in diethyl ether (10 mL). The reaction mixture was slowly warmed to 22 °C and stirred for 2.5 h. At 0 °C, benzenesulfonyl chloride (254 mg, 1.5 mmol) in diethyl ether (5 mL) was added dropwise, and the solution was slowly warmed to 22 °C and stirred for 16 h. After addition of water (10 mL) the mixture was extracted with dichloromethane (3× 10 mL). The collected organic layers were dried with magnesium sulfate and the solvent removed at reduced pressure. After purification by column chromatography (3×30 cm, SiO_2, petroleum ether/ethyl acetate 95:5 to 8:2) ferrocenyl benzenesulfonate (**17**, 342 mg, 1.0 mmol, 83 %) was obtained as a yellow solid (m.p. 89 °C).

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 3.87$ (s, 2H, $C_{Cp}H$), 4.16 (s, 2H, $C_{Cp}H$), 4.23 (s, 5H, Cp′), 7.50 (m, 2H, SCCCH), 7.64 (m, 1H, SCCCCH), 7.78 (m, 2H, SCCH) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): $\delta =$ 61.9 ($C_{Cp}H$), 64.0 ($C_{Cp}H$), 69.9 (Cp′), 116.6 ($C_{Cp}O$), 128.7 ($C_{Ph}H$), 129.1 ($C_{Ph}H$), 134.2 ($C_{Ph}H$), 135.1 (SC) ppm. IR: $\tilde{\nu} = 3105$ (w), 3082 (w), 1448 (m), 1441 (m), 1398 (w), 1371(s), 1337 (w), 1310(w), 1227 (w), 1182 (s), 1173 (s), 1105 (w), 1090 (m), 1024 (m), 1001 (m), 926 (s), 831 (w), 795 (s), 754 (s), 733 (s), 704 (m), 682 (s), 613 (s), 575 (s), 550 (s), 498 (s), 486 (s), 424 (w) cm^{-1}. HRMS (EI): Calcd. for $C_{16}H_{14}FeO_3S$ [M^+] 342.0013, found 342.0018.

Ferrocenyl (2,4,6-triisopropylbenzene)sulfonate (18): At 0 °C methyllithium in hexane (1.6 M, 2.00 mL, 3.2 mmol) was added to ferrocenyl acetate[11] (**16**, 517 mg, 2.1 mmol) in diethyl ether (15 mL). The reaction mixture was slowly warmed to 22 °C and stirred for 2.5 h. At 0 °C 2,4,6-triisopropylbenzenesulfonyl chloride (962 mg, 3.18 mmol) in Et_2O (5 mL) was added dropwise, the solution was slowly warmed to 21 °C and stirred for 2 h. After addition of water (25 mL) the mixture was extracted with dichloromethane (3×25 mL). The collected organic layers were washed with water (25 mL) and dried with magnesium sulfate. The solvent was removed at reduced pressure. After purification by column chromatography [20×3 cm, SiO_2 (deactivated with Et_3N), *tert*-butyl methyl ether] 2,4,6-triisopropylbenzenesulfonyl ferrocene (**18**, 921 mg, 2.0 mmol, 93 %) was obtained as a yellow solid (m.p. 144 °C).

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.21$ (d, $^3J = 6.8$ Hz, 12H, SCCCHCH_3), 1.27 (d, $^3J = 6.9$ Hz, 6H, SCCCHCCHCH_3), 2.92 (sept, $^3J = 6.9$ Hz, 1H, SCCCHCC*H*CH$_3$), 3.87 + 4.10 (AA′BB′, $J = 1.9$ Hz, 2×2H, $C_{Cp}H$), 4.04 (sept, $^3J = 6.8$ Hz, 2H, SCCC*H*CH$_3$), 4.23 (s, 5H, Cp′), 7.17 (s, 2H, SCCCH) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): $\delta =$ 23.5 (SCCCHCCH*C*H$_3$), 24.6 (SCCCHCC*H*CH$_3$), 29.6 (SCC*C*HCH$_3$), 34.2 (SCCCHCCHCH$_3$), 62.0 ($C_{Cp}H$), 63.9 ($C_{Cp}H$), 69.7 (Cp′), 115.8 ($C_{Cp}O$), 123.7 (SCC*C*H), 129.2 (SC), 151.3 (SC*C*), 154.1 (SCCCH*C*) ppm. IR: $\tilde{\nu} =$ 2957 (w), 2926 (w), 1595 (w), 1439 (w), 1425 (w), 1410 (w), 1226 (w), 1180 (s), 1107 (w), 1038 (w), 922 (m), 777 (s), 756 (m), 721 (m), 663 (m), 559 (m), 550 (m), 482 (s) cm^{-1}. HRMS (ESI, MeCN): Calcd. for $C_{25}H_{32}FeO_3S$ [M^+] 468.1422, found 468.1422; calcd. for $C_{25}H_{32}FeO_3SNa$ [M^+ + Na] 491.1319, found 491.1317.

Ferrocenyl (2,6-difluorobenzene)sulfonate (19): At 0 °C methyllithium in hexane (1.6 M, 2.20 mL, 3.5 mmol) was added to ferrocenyl acetate[12] (**16**, 860 mg, 3.5 mmol) in diethyl ether (15 mL). At 0 °C 2,6-difluorobenzenesulfonyl chloride (0.48 mL, 749 mg, 3.5 mmol) was added dropwise, and the reaction mixture was slowly warmed to 21 °C and stirred for 2 h. After addition of water (25 mL) the mixture was extracted with dichloromethane (3× 25 mL). The collected organic layers were washed with water (25 mL) and dried with magnesium sulfate. The solvent was removed at reduced pressure. After purification by column chromatography [3×20 cm, SiO_2 (deactivated with Et_3N), petroleum ether/ethyl acetate 100:0 gradient to 6:4] ferrocenyl (2,6-difluorobenzene)sulfonate (**19**, 1194 mg, 3.2 mmol, 90 %) was obtained as an orange solid (m.p. 114 °C).

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 3.91 + 4.34$ (AA′BB′, $J = 2.0$ Hz, 2× 2H, $C_{Cp}H$), 4.27 (s, 5H, Cp′), 7.04 (m, $J = 8.4$ Hz, 2H, SCCCH), 7.59 (m, $J = 8.5$, $J = 5.8$, 1H, SCCCHC*H*) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): $\delta = 61.3$ ($C_{Cp}H$), 64.1 ($C_{Cp}H$), 70.1 (Cp′), 113.3 (m, SCCCH*C*H), 116.7 ($C_{Cp}O$), 136.4 (t, $^3J_{F,C} = 11$ Hz, SCCC*H*), 160.23 (dd, $^1J_{F,C} = 263$ Hz, $^3J_{F,C} = 3$ Hz, CF) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta =$ −104.3 (s) ppm. IR: $\tilde{\nu} = 3113$ (w), 3082 (w), 1609 (m), 1587 (m), 1564 (w), 1470 (s), 1440 (m), 1412 (w), 1391 (s), 1292 (w), 1242 (m), 1229 (w), 1188 (s), 1105 (m), 1053 (w), 1024 (m), 1005 (s), 928 (m), 816 (s), 795 (s), 772 (m), 716 (m), 644 (m), 600 (m), 557 (m), 540 (s), 501 (m), 482 (s), 426 (w), 411 (w) cm^{-1}. HRMS (ESI, MeCN): Calcd. for $C_{16}H_{12}F_2FeO_3SNa$ [M^+ + Na] 400.9722, found 400.9728.

Ferrocenyl (2,6-dichlorobenzene)sulfonate (20): At 0 °C methyllithium in hexane (1.6 M, 2.22 mL, 3.6 mmol) was added to ferrocenyl acetate[12] (**18**, 866 mg, 3.6 mmol) in diethyl ether (30 mL). The reaction mixture was slowly warmed to 21 °C and stirred for 2.5 h. At 0 °C 2,6-dichlorobenzenesulfonyl chloride (871 mg, 3.6 mmol) in diethyl ether (5 mL) was added dropwise, and the solution was slowly warmed to 21 °C and stirred for 2 h. After addition of water (30 mL) the mixture was extracted with dichloromethane (3×30 mL). The collected organic layers were washed with water (30 mL) and dried with magnesium sulfate, and the solvent was removed at reduced pressure. After purification by column chromatography [3×20 cm, SiO_2 (deactivated with Et_3N), petroleum ether/ethyl acetate 100:0 gradient to 6:4] ferrocenyl (2,6-dichlorobenzene)sulfonate (**20**, 958 mg, 2.3 mmol, 67 %) was obtained as a yellow solid (m.p. 117 °C).

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 3.90$ (s, 2H, $C_{Cp}H$), 4.27 (s, 5H, Cp′), 4.32 (s, 2H, $C_{Cp}H$), 7.39 (m, 1H, SCCCHC*H*), 7.47 (m, 2H, SCCCH) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, HSQC, HMBC): $\delta = 61.2$ ($C_{Cp}H$), 64.1 ($C_{Cp}H$), 70.1 (Cp′), 116.6 ($C_{Cp}O$), 131.5 (SCCCH), 131.9 (SC), 133.9 (SCCCH*C*H), 136.7 (SCCCl) ppm. IR: $\tilde{\nu} = 3102$ (w), 1560 (m), 1427 (s), 1410 (m), 1383 (s), 1368 (m), 1223 (w), 1188 (s), 1159 (w), 1132 (w), 1105 (w), 1028 (m), 1020 (m), 920 (m), 835 (m), 802 (m), 783 (s), 741 (m), 714 (m), 613 (s), 584 (s), 557 (m), 511 (m), 498 (m), 480 (s), 442 (m), 407 (m) cm^{-1}. HRMS (ESI, MeCN): Calcd. for $C_{16}H_{12}Cl_2FeO_3SNa$ [M^+ + Na] 432.9131, found 432.9129.

Ferrocenyl (2,3,4,5,6-pentafluorobenzene)sulfonate (9): At 0 °C methyllithium in hexane (1.6 M, 1.65 mL, 2.6 mmol) was added to ferrocenyl acetate[12] (**16**, 645 mg, 2.6 mmol) in diethyl ether (30 mL). The reaction mixture was slowly warmed to 21 °C and stirred for 2.5 h. At 0 °C 2,3,4,5,6-pentafluorobenzenesulfonyl chloride (0.39 mL, 704 mg, 2.6 mmol) was added dropwise, and the solution was slowly warmed to 21 °C and stirred for 2 h. After addition of water (30 mL) the mixture was extracted with dichloromethane (3×30 mL). The collected organic layers were washed with water (30 mL) and dried with magnesium sulfate. The solvent was removed at reduced pressure. After purification by column chromatography eluted with PE:EtOAC [3×20 cm, SiO_2 (deactivated with Et_3N), petroleum ether/ethyl acetate 8:2] ferrocenyl 2,3,4,5,6-pentafluorobenzenesulfonate (**9**, 571 mg, 1.3 mmol, 50 %) was obtained as a yellow solid (m.p. 132 °C).

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 3.97 + 4.38$ (AA′BB′, $J = 2.0$ Hz, 2× 2H, $C_{Cp}H$), 4.31 (Cp′) ppm. $^{13}C\{^1H\}$ NMR (150.9 MHz, $CDCl_3$, HSQC, HMBC): $\delta = 61.2$ ($C_{Cp}H$), 64.5 ($C_{Cp}H$), 70.3 (Cp′), 111.6 (m, SC), 117.0 ($C_{Cp}O$), 138.0 (m, $^1J_{C,F} = 256.8$ Hz, SCCCF), 145.2 (m, $^1J_{C,F} = 261.2$ Hz, SCCCCF) ppm, 145.3 (m, $^1J_{C,F} = 261.2$ Hz, SCCF) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -132.9$ (m, SCCF), −142.0 (m, SCCCCF), −157.7 (m, SCCCF) ppm. IR: $\tilde{\nu} = 3103$ (w), 1643 (m), 1522 (m), 1501 (s), 1435 (m), 1404 (m), 1304 (m), 1219 (m), 1184 (s), 1105 (s), 1020 (m), 993 (s), 922 (s), 868 (m), 810 (s), 698 (m), 608 (s), 588 (s), 575 (m), 488 (s), 438 (m) cm^{-1}. HRMS (ESI, MeCN): Calcd. for $C_{16}H_{12}Cl_2FeO_3SNa$ [M^+] 431.9542, found 431.9541.

Ferrocene anellated 6,7,8,9-tetrafluorobenzo[*c,e*]-[1,2]oxathiine 5,5-dioxide (*rac*-22): At −78 °C LiTMP [prepared from butyllithium in hexane (2.5 M, 0.26 mL, 0.6 mmol) and 2,2,6,6-tetramethylpiperidine (0.16 mL, 1.0 mmol) in THF (1.5 mL)] was added dropwise to ferrocenyl 2,3,4,5,6-pentafluorobenzenesulfonate (**9**, 278 mg, 0.6 mmol) in THF (70 mL). The initially yellow solution immediately turned purple. The solution was stirred at −78 °C for 2 h and then slowly warmed to 21 °C. After stirring for 16 h water (70 mL) was added, and the solution was extracted with ethyl acetate (3×70 mL). The collected organic layers were dried with magnesium sulfate and the solvent removed at reduced pressure. After purification by column chromatography [3×30 cm, SiO_2 (deactivated with Et_3N), petroleum ether/ethyl acetate 95:5 gradient to 65:35] ferrocene anellated 6,7,8,9-tetrafluorobenzo[*c,e*]-[1,2]oxathiine 5,5-dioxide (rac-**22**, 54 mg, 0.2 mmol, 20%) was obtained as a red solid [m.p. 160 °C (dec.)].

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 4.29$ (Cp′), 4.32 (t, $^3J = 2.8$ Hz, 1H, $C_{Cp}H$), 4.73 (m, 1H, $C_{Cp}H$), 4.84 (m, 1H, $C_{Cp}H$) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$, HSQC, HMBC, HMQC): $\delta = 59.3$ ($C_{Cp}H$), 60.8 (m, $C_{Cp}C_{Ph}$), 63.3 (d, $J_{C-F} = 8.9$ Hz, $C_{Cp}H$), 64.6 (d, $J_{C-F} = 1.8$ Hz, $C_{Cp}H$), 72.1 (Cp′), 115.5 (dt, $^2J_{C-F} = 12.6$ Hz, $^3J_{C-F} = 4.3$ Hz, SCCF), 118.1 ($C_{Cp}O$), 122.5 (dd, $^2J_{C-F} = 15.8$ Hz, $^3J_{C-F} = 4.3$ Hz, SCCC), 138.9 (dddd, $^1J_{C-F} = 258.6$ Hz, $^2J_{C-F} = 16.3$ Hz, $^2J_{C-F} = 13.2$ Hz, $^3J_{C-F} = 2.9$ Hz, $C_{Ar}F$), 143.4 (ddd, $^1J_{C-F} = 254.5$ Hz, $^2J_{C-F} = 11.7$ Hz, $^3J_{C-F} = 3.9$ Hz, $C_{Ar}F$), 144. 3 (dddd, $^1J_{C-F} = 261.9$ Hz, $^2J_{C-F} = 16.0$ Hz, $^2J_{C-F} = 12.5$ Hz, $^3J_{C-F} = 3.6$ Hz, $C_{Ar}F$), 145.4 (dddd, $^1J_{C-F} = 261.3$ Hz, $^2J_{C-F} = 13.0$ Hz, $^3J_{C-F} = 3.7$ Hz, $^3J_{C-F} = 3.2$ Hz, $C_{Ar}F$) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = -134.66$ (m, $C_{Ar}F$), −139.11 (m, $C_{Ar}F$), −146.33 (m, $C_{Ar}F$), −154.06 (m, $C_{Ar}F$) ppm. IR: $\tilde{\nu} = 3121$ (w), 1632 (w), 1603 (w), 1504 (s), 1466 (m), 1418 (s), 1385 (s, C–F), 1368 (m), 1300 (m)1248 (w), 1188 (s, C–F), 1125 (m), 1098 (m), 1049 (m), 999 (s), 866 (s), 827 (s), 806 (m), 783 (s), 768 (m), 689 (s), 608 (m), 579 (s), 523 (m), 490 (s), 461 (s), 436 (m) cm^{-1}. HRMS (EI): Calcd. for $C_{16}H_8F_4FeO_3S$ [M^+] 411.9480, found 411.9479.

Ferrocenyl fluorosulfonate (8): Water (40 mL) was added to a solution of ferrocenyl acetate[12] (**16**, 737 mg, 3.0 mmol) in ethanol (5 mL) followed by addition of potassium hydroxide (847 mg, 15.1 mmol). The mixture was stirred for 30 min at 70 °C. After cooling to 21 °C, the mixture was acidified by addition of oxygen free 37% aq. HCl under pH control until pH 6. Dichloromethane (3× 40 mL) was added, and the mixture was intensely stirred for 2 min. After phase separation, the organic layers were collected with a syringe and filtered into a Schlenk flask (250 mL) through a P4 frit covered with a 5 cm thick layer of magnesium sulfate. After solvent removal at reduced pressure the remaining solid was redissolved in dichloromethane (60 mL), and triethylamine (0.84 mL, 611 mg, 6.0 mmol) was added. The Schlenk flask was connected through its side arm to another Schlenk flask (25 mL) containing 1,1-sulfonyldiimidazole (898 mg, 4.5 mmol) and potassium fluoride (702 mg, 12.1 mmol). With stirring, trifluoroacetic acid (3.0 mL) was added. Immediate sulfuryl fluoride gas formation was observed. Both Schlenk flasks were stirred for 16 h. Then the small Schlenk flask was exchanged for another one, containing more 1,1-sulfonyldiimidazole (299 mg, 1.5 mmol) and potassium fluoride (351 mg, 6.0 mmol). With stirring, trifluoroacetic acid (1.0 mL) was added, and both flasks were stirred for 16 h.[18] The stoppers were removed to release the residual pressure and the Schlenk flasks were stirred for more 15 min to ensure that all sulfuryl fluoride had evaporated into to the fume hood. The content of the bigger Schlenk flask was transferred to a round bottomed flask, and Celite® (ca. 125 mL) was added. After solvent removal at reduced pressure the crude product was purified by column chromatography [3×25 cm, SiO_2 (deactivated with Et_3N), petroleum ether/ethyl acetate 9:1] affording ferrocenyl fluorosulfonate (**8**) as a yellow oil (632 mg, 2.2 mmol, 74%), which solidified upon standing over night (m.p. 38 °C).

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 4.06 + 4.55$ (AA′BB′, $J = 2.0$ Hz, 2× 2H, $C_{Cp}H$), 4.34 (Cp′) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): $\delta = 60.8$ (d, $^4J_{C,F} = 0.8$ Hz, $C_{Cp}H$), 64.3 ($C_{Cp}H$), 70.4 (Cp′), 119.8 ($C_{Cp}O$) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = 35.1$ (OSO_2F) ppm. IR: $\tilde{\nu} = 3109$ (w), 1456 (s), 1431 (s), 1366 (w), 1234 (s), 1207 (s), 1105 (m), 1020 (m), 1001 (m), 926 (s), 874 (s), 835 (s), 800 (s), 791 (s), 716 (m), 604 (m), 567 (m), 544 (m), 488 (s), 463 (s), 440 (m), 420 (m) cm^{-1}. HRMS (EI): Calcd. for $C_{10}H_9FFeO_3S$ [M^+] 283.9606, found 283.9605.

2-Hydroxyferrocenesulfonyl fluoride (*rac*-24): At −78 °C LDA [prepared from butyllithium (2.5 M, 0.26 mL, 0.7 mmol) in hexane and diisopropylamine (0.28 mL, 2.0 mmol)] in THF (3 mL) was added dropwise to ferrocenyl fluorosulfonate (**8**, 187 mg, 0.7 mmol) in THF (5 mL). The initially yellow solution slowly turned orange. The solution was stirred for 40 min at −78 °C, warmed to 0 °C and stirred for another 30 min. The orange solution slowly turned red. The solution was acidified by addition of oxygen free 37% aq. HCl under pH control until pH 6. Water (15 mL) and dichloromethane (3×20 mL) were added, and the mixture was intensely stirred for 2 min. After phase separation, the organic layers were collected with a syringe and filtered into a Schlenk flask through a P4 frit covered with a 5 cm thick layer of magnesium sulfate. The solvent was removed at reduced pressure, and the remaining yellow oil was redissolved in hexane (3×20 mL) and transferred into another Schlenk flask. The solvent was removed at reduced pressure affording 2-hydroxyferrocenesulfonyl fluoride (*rac*-**24**, 171 mg, 0.6 mmol, 91%) as an air sensitive yellow solid (m.p. 60 °C, dec.).

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 4.29$ (s, 1H, $C_{Cp}H$), 4.42 (s, 5H, Cp′), 4.51 (s, 1H, $C_{Cp}H$), 4.64 (s, 1H, $C_{Cp}H$), 5.06 (br. s, 1H, OH) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): $\delta = 61.0$ ($C_{Cp}H$), 62.4 ($C_{Cp}H$), 63.5 (d, $^2J_{C-F} = 38.5$ Hz, $C_{Cp}S$), 65.6 ($C_{Cp}H$), 72.4 (Cp′), 122.3 ($C_{Cp}O$) ppm. ^{19}F NMR (376.5, $CDCl_3$): $\delta = 68.92$ (SO_2F) ppm. IR: $\tilde{\nu} = 3505$ (m), 3107 (w), 2924 (w), 2853 (w), 1495 (m), 1414 (w), 1383 (s), 1346 (m), 1287 (m), 1219 (m), 1190 (s), 1161 (s), 1109 (m), 1092 (m), 1030 (m), 1007 (m), 908 (w), 829 (m), 802 (m), 748 (s), 683 (m), 646 (s), 613 (s), 544 (s), 486 (s), 473 (s), 419 (m) cm^{-1}. HRMS (EI): Calcd. for $C_{10}H_9FFeO_3S$ [M^+] 283.9606, found 283.9599.

Fluorosulfonylferrocene (7): Chlorosulfonylferrocene[20] (**25**, 533 mg, 1.8 mmol), anhydrous potassium fluoride (435 mg, 7.5 mmol) and 18-crown-6 (15 mg, 0.06 mmol) in anhydrous acetonitrile (7 mL) were vigorously stirred for 20 h. After addition of water (20 mL) the mixture was extracted with dichloromethane (3× 20 mL). The collected organic layers were dried with magnesium sulfate, and the solvent was removed under reduced pressure. After purification by column chromatography [3×30 cm, SiO_2 (deactivated with Et_3N), petroleum ether/ethyl acetate 7:3)] fluorosulfonylferrocene (**7**, 398 mg, 1.5 mmol, 79%) was obtained as an orange/yellow solid (m.p. 77 °C).

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 4.44$ (s, 5H, Cp′), 4.58 + 4.83 (AA′BB′, $J = 2.0$ Hz, 2×2H, $C_{Cp}H$) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): $\delta = 70.0$ ($C_{Cp}H$), 71.7 (Cp′), 72.6 ($C_{Cp}H$), 77.9 (d, $^2J_{C-F} = 39.2$ Hz, CSO_2F) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): $\delta = 68.2$ (SO_2F) ppm. IR: $\tilde{\nu} = 3121$ (w), 1396 (s), 1383 (m), 1213 (s), 1161 (s), 1109 (w), 1018

(m), 899 (w), 868 (w), 772 (m), 721 (s), 642 (s), 623 (m), 611 (s), 525 (m), 471 (s), 417 (w) cm^{-1}. HRMS (EI): Calcd. for $C_{10}H_9FFeO_2S$ [M^+] 267.9657, found 267.9653.

(Trifluoromethyl)sulfonylferrocene (6): (Trifluoromethyl)–trimethylsilane (269 mg, 0.28 mL, 1.9 mmol) in hexane (10 mL) was slowly added dropwise to a mixture of ferrocenylsulfonyl fluoride (**7**, 507 mg, 1.9 mmol) and tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF, 52 mg, 0.19 mmol) in hexane (25 mL). The mixture was stirred at 21 °C for 17 h and filtered through a patch of silica. This procedure was repeated two more times with the resulting mixture of **7** and **6** not being separable by chromatography, crystallization, or sublimation. The mixture of **7** and **6** was dissolved in 1,4-dioxane (10 mL). After addition of water (10 mL) and K_3PO_4 (803 mg, 3.78 mmol), the mixture was stirred at 85 °C (oil bath temperature) for 16 h. The mixture was extracted with petroleum ether (3×10 mL). After drying the collected organic layers with magnesium sulfate the solvent was evaporated at reduced pressure. After purification by column chromatography [3×20 cm, SiO_2 (deactivated with Et_3N), petroleum ether/ethyl acetate 85:15)] (trifluoromethyl)sulfonylferrocene (**6**, 278 mg, 0.9 mmol, 46%) was obtained as an orange solid (m.p. 69 °C).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.51 (s, 5H, Cp′), 4.66 + 4.80 (AA′BB′, J = 1.9 Hz, 2×2H, C_{Cp}H) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): δ = 71.4 (Cp′), 71.7 (d, $^4J_{C,F}$ = 0.5 Hz, C_{Cp}H), 73.7 (C_{Cp}H), 76.6 (q, $^3J_{C,F}$ = 2.1 Hz, C_{Cp}S), 119.40 (q, $^1J_{C,F}$ = 325.2 Hz, CF_3) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = −79.5 (SO_2CF_3) ppm. IR: $\tilde{\nu}$ = 3121 (w), 1414 (w), 1350 (s), 1211 (s), 1192 (s), 1175 (s), 1103 (s), 1061 (w), 1034 (m), 1018 (m), 899 (w), 826 (s), 760 (m), 642 (m), 621 (s), 554 (m), 532 (w), 480 (s), 434 (s) cm^{-1}. HRMS (EI): Calcd. for $C_{11}H_9F_3FeO_2S$ [M^+] 317.9625, found 317.9625.

Crystal structure analysis:[25] CCDC 2106432. Single crystals suitable for X-ray crystallographic analysis were obtained by crystallization from hexane at −30 °C over 7 d. $C_{11}H_9F_3FeO_2S$, prismatic orange crystal, M_r = 318.09 g.mol^{-1}, crystal system monoclinic, space group P 2$_1$/n (14), a = 9.8033(13) Å, b = 9.2232(14) Å, c = 13.541 (2) Å, α = 90°, β = 102.494(5)°, γ = 90°. V = 1195.4(3) Å^3, Z = 4, d_{calc} = 1.768 g cm^{-3}, μ = 1.464 mm^{-1}, crystal size 0.43×0.29×0.28 mm^3, F(000) = 640, Bruker SMART X2S diffractometer, graphite crystal monochromator, T = 200 K, Mo–Ka radiation (λ = 0.71073 Å), 2.69 ≤ θ ≤ 27.54°, index ranges −12 ≤ h ≤ 12, −11 ≤ k ≤ 11, −17 ≤ l ≤ 17, reflections collected/unique 2754/2003, numerical absorption correction, structure solution and refinement with SHELXL-2018/3,[28] parameters/restrains 163/0, R_1 = 0.0523 [I > 2σ(I)], wR_2 = 0.1062 (all data), S = 1.060, finals maximum/minimum difference electron density 0.424/−0.458 eÅ^{-3}.

***rac*-2-(2,6-Dimethoxybenzoyl)ferrocenesulfonyl fluoride (*rac*-26)**: At −78 °C LiTMP [prepared from butyllithium in hexane (2.5 M, 0.52 mL, 1.3 mmol) and 2,2,6,6-tetramethylpiperidine (0.24 mL, 201 mg, 1.4 mmol)] in THF (3 mL) was added dropwise to a solution of ferrocenesulfonyl fluoride (**7**, 318 mg, 1.2 mmol) in THF (7 mL). The initial yellow colour changed immediately to orange/red. After stirring for 1 h at −78 °C, 2,6-dimethoxybenzoyl chloride (286 mg, 1.42 mmol) was added at −78 °C, and the solution was stirred for 15 min before it was slowly warmed to 22 °C followed by stirring for 30 min. After addition of water (10 mL), dichloromethane (3× 10 mL) was added, and the mixture was intensely stirred for 2 min. After phase separation, the organic layers were collected with a syringe and filtered through a P4 frit covered with a 5 cm thick layer of magnesium sulfate into a Schlenk flask. The solvent was removed at reduced pressure. After purification by column chromatography (30×3 cm, SiO_2 (deactivated with Et_3N), petroleum ether/ethyl acetate 6:4) *rac*-2-(2,6-dimethoxybenzoyl) – ferrocenesulfonyl fluoride (*rac*-**26**, 82 mg, 0.2 mmol, 16%) was obtained as an orange solid (m.p. 90 °C, dec.).

^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.78 (s, 6H, OCH_3), 4.52 (s, 5H, Cp′), 4.71, (t, ^3J = 2.8 Hz, 1H, C_{Cp}H), 4.92 (m, 1H, C_{Cp}H), 5.18 (m, 1H, C_{Cp}H), 6.60 (d, ^3J = 8.4 Hz, 2H, C_{Ar}H), 7.34 (t, ^3J = 8.4 Hz, 1H, C_{Ar}H) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): δ = 55.9 (OMe), 72.6 (C_{Cp}H), 73.6 (Cp′), 76.6 (d, $^3J_{C,F}$ = 0.9 Hz, C_{Cp}H), 78.2 (d, $^4J_{C,F}$ = 1.3 Hz, C_{Cp}H), 78.9 (d, $^2J_{C,F}$ = 37.1 Hz, CSO_2F), 81.9 (C_{Cp}C), 104.2 (C_{Ar}H), 118.8 C_{Ar}CO), 131.5 (C_{Ar}H), 157.6 (C_{Ar}O), 194.9 (C=O) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = 65.8 (SO_2F) ppm. IR: $\tilde{\nu}$ = 3123 (w), 3013 (w), 2926 (w), 2845 (w), 1661 (s), 1595 (s), 1472 (s), 1443 (s), 1391 (s), 1373 (m), 1341 (m), 1285 (m), 1246 (s), 1206 (s), 1105 (s), 1049 (m), 1030 (m), 1016 (m), 1005 (m), 907, (w), 876 (m), 837 (m), 827 (m), 779 (s), 752 (s), 741 (s), 718 (s), 650 (m), 629 (s), 604 (m), 571 (m), 532 (m), 507 (m), 463 (s), 420 (m) cm^{-1}. HRMS (ESI, MeCN): Calcd. for $C_{19}H_{17}FFeO_5SNa$ [M^+Na] 455.0028, found 455.0037.

***rac*-2-Methylferrocenesulfonyl fluoride (*rac*-27) and 2,5-Dimethylferrocenesulfonyl fluoride (28)**: At −78 °C LiTMP [prepared from butyllithium in hexane (2.5 M, 1.04 mL, 2.6 mmol) and 2,2,6,6-tetramethylpiperidine (0.47 mL, 391 mg, 2.8 mmol)] in THF (3 mL) was added dropwise to ferrocenesulfonyl fluoride **7** (232 mg, 0.9 mmol) in THF (5 mL). The yellow colour changed immediately to red. After stirring at −78 °C for 2 h iodomethane (2.0 M solution in *tert*-butyl methyl ether, 1.38 mL, 2.8 mmol) was added, and the solution was slowly warmed to 21 °C and stirred for another 1 h. After addition of water (10 mL) the solution was extracted with ethyl acetate (3×10 mL). After drying the collected organic layers with magnesium sulfate the solvent was removed at reduced pressure. Column chromatography [MPLC, Büchi, 20×3 cm, SiO_2, petroleum ether/ethyl acetate 100:0 gradient to 45:55 (v:v) in 60 min, flow: 20 mL/min] afforded two products.

I: **28** (24 mg, 0.08 mmol, 9%), yellow solid (m.p. 133–134 °C). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.21 (s, 6H, CH_3), 4.27 (s, 5H, Cp′), 4.34 (s, 2H, C_{Cp}H) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): δ = 13.8 (CH_3), 72.0 (C_{Cp}H), 72.6 (Cp′), 76.5 (d, $^2J_{C,F}$ = 36.8 Hz, CSO_2F), 86.7 ($C_{Cp}CH_3$) ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ = 70.4 (SO_2F) ppm. IR: $\tilde{\nu}$ = 2997 (w), 2967 (w), 2853 (w), 1452 (m), 1414 (w), 1393 (s), 1375 (s), 1341 (m), 1196 (s), 1107 (m), 1088 (m), 1042 (m), 1003 (m), 966 (w), 856 (w), 839 (m), 827 (m), 737 (s), 654 (s), 629 (m), 557 (s), 525 (m), 486 (s), 471 (s) cm^{-1}. HRMS (EI): Calcd. for $C_{12}H_{13}FFeO_2S$ [M^+] 295.9970, found 295.9972.

II: *rac*-**27** (175 mg, 0.6 mmol, 72%), yellow solid (m.p. 71 °C). ^{1}H NMR (400.1 MHz, C_6D_6): δ = 1.98 (s, 3H, CH_3), 3.71 (ABX, J = 2.6 Hz, 1H, C_{Cp}H), 3.78 (ABX, 1H, C_{Cp}H), 3.96 (s, 5H, Cp′), 4.51 (ABX, J = 2.7, 1.6 Hz) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): 12.9 (CH_3), 69.8 (C_{Cp}H), 70.5 (C_{Cp}H), 72.1 (Cp′), 74.3 (C_{Cp}H), 77.6 (d, $^2J_{C,F}$ = 39.0 Hz, CSO_2F), 85.8 ($C_{Cp}CH_3$) ppm. ^{19}F NMR (376.5 MHz, C_6D_6): δ = 69.0 (SO_2F) ppm. IR: $\tilde{\nu}$ = 3125 (w), 2965 (w), 2924 (w), 1452 (w), 1393 (s), 1371 (m), 1337 (w), 1244 (m), 1200 (s), 1171 (w), 1107 (w), 1090 (w), 1034 (w), 1020 (w), 1003 (w), 962 (w), 862 (w), 831 (m), 814 (m), 733 (s), 665 (m), 640 (m), 608 (s), 523 (m), 484 (s), 471 (s), 420 (m), 413 (m) cm^{-1}. HRMS (EI): Calcd. for $C_{11}H_{11}FFeO_2S$ [M^+] 281.9813, found 281.9814.

***rac*-2-Methyl-1-(trifluoromethylsulfonyl)ferrocene (*rac*-29) and 2,5-dimethyl-1-(trifluoromethylsulfonyl)ferrocene (30)**: At −78 °C LiTMP [prepared from butyllithium in hexane (2.5 M, 0.23 mL, 0.57 mmol) and 2,2,6,6-tetramethylpiperidine (0.11 mL, 93 mg, 0.7 mmol)] in THF (3 mL) was added dropwise to (trifluoromethylsulfonyl)ferrocene (**6**, 140 mg, 0.4 mmol) in THF (3 mL). The yellow colour changed immediately to red. The solution was stirred at −78 °C for 2 h. Iodomethane (2.0 M in *tert*-butyl methyl ether, 0.33 mL, 0.7 mmol) was added and the solution was slowly warmed to 21 °C and stirred for another 1 h. After addition of water (10 mL) the solution was extracted with ethyl acetate (3×10 mL). After drying the collected organic layers with magnesium sulfate the solvent was removed at reduced pressure. Column chromatography [MPLC, Büchi, 20×3 cm, SiO_2, petroleum ether/ethyl acetate 100:0

gradient to 45:55 in 60 min, flow: 20 mL/min] afforded two fractions.

I: **30** (8 mg, 0.02 mmol, 5%), yellow oil. ^{1}H NMR (600.3 MHz, C_6D_6): $\delta = 2.02$ (s, 6H, CH_3), 3.79 (s, 2H, $C_{Cp}H$), 3.99 (s, 5H, $C_{Cp'}H$) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6, HSQC, HMBC): 13.9 (CH_3), 72.5 (Cp′), 73.3 ($C_{Cp}H$), 73.9 (q, $^3J = 2.1$ Hz, $C_{Cp}S$), 88.2 ($C_{Cp}CH_3$), 120.6 (q, $^1J_{C,F} = 325.7$ Hz, CF_3) ppm. ^{19}F NMR (376.5, $CDCl_3$): $\delta = -80.3$(SO_2CF_3) ppm. IR: $\tilde{\nu} = 3100$ (w), 2967 (w), 2932 (w), 1730 (w), 1460 (w), 1449 (w), 1381 (w), 1350 (s), 1335 (m), 1275 (m), 1207 (s), 1182 (s), 1138 (s), 1109 (m), 1067 (s), 1040 (m), 1003 (m), 968 (w), 895 (w), 864 (m), 826 (s), 760 (m), 664 (w), 642 (s), 615 (m), 565 (s), 557 (s), 527 (m), 496 (s), 482 (s), 449 (s) cm-1. HRMS (EI): Calcd. for $C_{13}H_{13}F_3FeO_2S$ [M^+] 345.9938, found 345.9944.

II: *rac*-**29** (75 mg, 0.2 mmol, 51%), yellow oil. ^{1}H NMR (600.3 MHz, $CDCl_3$): $\delta = 2.18$ (s, 3H, CH_3), 4.43 (s, 5H, Cp′), 4.52 (ABX, $J = 2.6$ Hz, 1H, $C_{Cp}H$), 4.55 (ABX, 1H, $C_{Cp}H$), 4.71 (ABX, $J = 2.6$, 1.6 Hz, 1H, $C_{Cp}H$) ppm. ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, HSQC, HMBC): $\delta = 12.9$ (CH_3), 71.2 ($C_{Cp}H$), 71.9 (Cp′), 72.3 ($C_{Cp}H$), 75.0 (q, $^3J = 2.0$ Hz, $C_{Cp}S$), 75.6 ($C_{Cp}H$), 87.9 ($C_{Cp}CH_3$), 119.64 (q, $^1J_{C,F} = 325.3$ Hz, CF_3) ppm. ^{19}F NMR (376.5, $CDCl_3$): $\delta = -79.7$ (SO_2CF_3) ppm. IR: $\tilde{\nu} = 3102$ (w), 2928 (w), 1450 (w), 1377 (w), 1352 (s), 1242 (s), 1211 (s), 1126 (s), 1109 (m), 1082 (s), 1036 (m), 1018 (m), 1005 (m), 964 (w), 829 (m), 812 (m), 760 (m), 664 (m), 644 (m), 613 (s), 557 (s), 534 (w), 484 (s), 444 (m) cm^{-1}. HRMS (EI): Calcd. for $C_{12}H_{11}F_3FeO_2S$ [M^+] 331.9781, found 331.9770.

2,2,6,6-Tetramethyl-1-(ferrocenylsulfonyl)piperidine (31) and 32 (a or b): At −78 °C LiTMP [prepared from butyllithium in hexane (2.5 M, 0.61 mL, 1.5 mmol) and 2,2,6,6-tetramethylpiperidine (0.30 mL, 252 mg, 1.8 mmol)] in THF (4 mL) was added dropwise to chlorosulfonylferrocene (**25**, 363 mg, 1.3 mmol) in THF (8 mL). The orange/brown solution changed very quickly and shortly to green upon addition of LiTMP and then changed to yellow. The solution was stirred at −78 °C for 1 h. A small piece of dry ice was added to the solution at −78 °C and it was slowly warmed to 21 °C. The mixture was stirred for 1 h. After addition of water (20 mL) the solution was extracted with ethyl acetate (3×30 mL). After drying the collected organic layers with magnesium sulfate, the solvent was removed at reduced pressure. Column chromatography [MPLC, Büchi, 20×3 cm, SiO_2, petroleum ether/ethyl acetate 100:0 gradient to 0:100 (v:v) in 40 min, flow: 30 mL/min] afforded two fractions.

I: **31** (452 mg, 1.2 mmol, 91%), yellow solid (m.p. 139 °C). ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.47$ (m, 4H, $NCCH_2$ 1.53 (m, 2H, $NCCH_2CH_2$), 1.59 (s, 12H, CH_3), 4.28 + 4.67 (AA′BB′, $J = 1.9$ Hz, 2x2H, $C_{Cp}H$), 4.36 (s, 5H, Cp′) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta = 16.7$ ($NCCH_2$), 31.2 (CH_3), 44.5 ($NCCH_2CH_2$), 60.5 (NC), 69.2 ($C_{Cp}H$), 69.2 ($C_{Cp}H$), 71.0 (Cp′), 96.3 ($C_{Cp}S$) ppm. IR: $\tilde{\nu} = 3013$ (w), 2970 (w), 2940 (w), 2866 (w), 1466 (w), 1443 (w), 1410 (w), 1387 (w), 1360 (w), 1321 (s), 1240 (m), 1184 (m), 1126 (s), 1105 (m), 1092 (w), 988 (m), 970 (m), 912 (s), 889 (m), 847 (w), 826(m), 816 (m), 777 (m), 652 (s), 627 (s), 573 (m), 505 (m), 490 (m), 473 (s), 442 (m) cm^{-1}. HRMS (ESI, MeCN): Calcd. for $C_{19}H_{27}FeNO_2SNa$ [M^+Na] 412.1010, found 412.1007.

II: **32a** (17 mg, 0 .05 mmol, 4%) or **32b** (17 mg, 0.03 mmol, 4%), yellow solid (m.p. 60 °C). ^{1}H NMR (500.1 MHz, $CDCl_3$): $\delta = 1.90$ (m, 1H, CH_2), 2.05 (m, 1H, CH_2), 2.24 (m, 1H, CH_2), 2.54 (m, 1H, CH_2), 3.95 (m, 1H, O-CH_2), 4.03 (m, 1H, O-CH_2), 4.45 (s, 5H, Cp′), 4.46 (m, 1H, $C_{Cp}H$), 4.48 (m, 1H, $C_{Cp}H$), 4.64 (m, 1H, $C_{Cp}H$), 4.71 (m, 1H, $C_{Cp}H$), 4.76 (dd, $J = 8.2$ Hz, $J = 3.9$ Hz, 1H, OCHS) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 25.1$ (CH_2), 26.4 (CH_2), 70.16 ($C_{Cp}H$), 70.7 (Cp′), 71.0 (O-CH_2), 71.2($C_{Cp}H$), 71.5 ($C_{Cp}H$), 71.7 ($C_{Cp}H$), 84.1 ($C_{Cp}S$), 94.2 (OCHS) ppm. IR: $\tilde{\nu} = 3111$ (w), 2986 (w), 2882 (w), 1447 (w), 1410 (w), 1364 (w), 1290 (s), 1231 (w), 1186 (m), 1123 (m), 1107 (w), 1088 (w), 1061 (s), 1028 (m), 1020 (m), 1005 (w), 951 (w), 923 (w), 901 (w), 883 (w), 851 (w), 822 (s), 768 (m), 712 (w), 677 (m), 646 (m), 592 (w), 552 (m), 511 (m), 482 (s), 467 (s), 447 (s) cm^{-1}. HRMS (ESI, MeCN): Calcd. for $C_{28}H_{32}Fe_2O_6S_2$ (**32a**) [M^+] 320.0170, found 320.0175. (**32b**) [M^+Na] 663.0237, found 663.0235.

[4-(Trifluoromethyl)phenyl]ferrocene (36):[29] Trifluoromethylsulfonyl ferrocene (**6**) (203 mg, 0.6 mmol), 4-(trifluoromethyl)-phenylboronic acid (**35**) (182 mg, 1.0 mmol), K_3PO_4 (408 mg, 1.9 mmol), palladium(II) acetylacetonate [$Pd(acac)_2$] (9 mg, 0.03 mmol) and 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (RuPhos) (61 mg, 0.1 mmol) were suspended in 1,4-dioxane (2 mL). Dimethyl sulfoxide (30 mL) was added, and the mixture was stirred for 48 h at 80 °C. After addition of water (10 mL) the mixture was extracted with dichloromethane (8×10 mL). After drying the collected organic layers with magnesium sulfate, the solvent was removed at reduced pressure. After purification by column chromatography (30×3 cm, SiO_2, petroleum ether/ethyl acetate 9:1) [4-(trifluoromethyl)phenyl]ferrocene (**36**, 15 mg, 0.05 mmol, 7%) was obtained as a red solid. (m.p. 140 °C).

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 4.05$ (s, 5H, Cp′), 4.38 + 4.69 (AA′BB′, $J = 1.5$ Hz, 2×2H, $C_{Cp}H$), 7.54 (AA′BB′, $J = 13.8$ Hz, $J = 8.6$ Hz, 4H, $C_{Ph}H$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): $\delta = 67.0$ ($C_{Cp}H$), 69.8 ($C_{Cp}H$), 69.9 (Cp′), 83.4 ($C_{Cp}C$), 124.6 (q, $^1J_{C,F} = 271.6$ Hz, CF_3), 125.4 (q, $^3J_{C,F} = 3.9$ Hz, $C_{Ph}H$), 126.1 ($C_{Ph}H$), 127.8 (q, $^2J_{C,F} = 32.3$ Hz, $C_{Ph}CF_3$), 143.9 (d, $^5J = 1.4$ Hz, $C_{Ph}C_{Cp}$) ppm. ^{19}F NMR (376.5, $CDCl_3$): $\delta = -62.35$ ppm (CF_3). IR: $\tilde{\nu} = 1614$ (m), 1518 (w, 1531 (w), 1420 (m), 1391 (w), 1325 (s), 1283 (m), 1192 (m), 1157 (m), 1105 (s), 1090 (s), 1063 (s), 1038 (m), 1015 (m), 1001 (m), 957 (w), 889 (m), 856 (m), 841 (s), 812 (s), 687 (m), 644 (m), 592 (m), 501 (s), 480 (m), 447 (s) cm^{-1}. HRMS (EI): Calcd. for $C_{17}H_{13}F_3Fe$ [M^+] 330.0319, found 330.0319.

2-Methoxy-1-[4-(trifluoromethyl)phenyl]ferrocene (*rac*-37): 2-Methoxy-1-(trifluoromethylsulfonyl) ferrocene (**6**) (75 mg, 0.2 mmol), 4-(trifluoromethyl)phenylboronic acid (**35**) (60 mg, 0.3 mmol), K_3PO_4 (136 mg, 0.6 mmol), palladium(II) acetylacetonate [$Pd(acac)_2$] (3 mg, 0.01 mmol) and 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl (RuPhos) (19 mg, 0.04 mmol) were suspended in 1,4-dioxane (2 mL). Dimethyl sulfoxide (10 mL) was added, and the mixture was stirred for 72 h at 95 °C. The reaction mixture was filtered through Celite® and rinsed with dichloromethane (20 mL). After removing the solvent at reduced pressure, the crude product was purified by column chromatography (30×3 cm, SiO_2, petroleum ether/ethyl acetate 10:1), and 2-methoxy-1-[4-(trifluoromethyl)phenyl]ferrocene (*rac*-**37**, 2 mg, 0.01 mmol, 3%) was obtained as an orange-red solid (m.p. 76 °C).

^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 3.79$ (s, 3H, OCH_3), 4.02 (ABC, $J = 2.7$ Hz, 1H, $C_{Cp}H$), 4.26 (ABC, $J = 2.5$ Hz, $J = 1.7$ Hz 1H, $C_{Cp}H$), 4.36 (ABC, $J = 2.5$ Hz, $J = 1.7$ Hz 1H, $C_{Cp}H$), 7.54 (d, $J = 8.2$ Hz, 2H, $C_{Cp}H$), 7.81 (d, $J = 8.2$ Hz, 2H, $C_{Cp}H$) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, HSQC, HMBC): $\delta = 54.2$ ($C_{Cp}H$), 58.0 (OCH_3), 61.5 ($C_{Cp}H$), 62.7 ($C_{Cp}H$), 70.2 (Cp′), 72.5 ($C_{Cp}C$), 124.7 (q, $^1J_{C,F} = 271.6$ Hz, CF_3), 125.1 7 (q, $^3J_{C,F} = 3.8$ Hz, $C_{Ph}H$), 125.7 ($C_{Cp}O$), 127.5 ($C_{Ph}H$), 127.6 (q, $^2J_{C,F} = 32.2$ Hz, $C_{Ph}CF_3$), 142.8 (q, $^5J_{C,F} = 1.3$ Hz, $C_{Ph}C_{Cp}$) ppm. ^{19}F NMR (376.5, $CDCl_3$): $\delta = -62.39$ ppm (CF_3). IR: $\tilde{\nu} = 3092$ (w), 2934 (w), 2860 (w), 1713 (w), 1614 (m), 1572 (w), 1531 (w), 1481 (m), 1452 (w), 1423 (w), 1406 (m), 1321 (s), 1300 (m), 1227 (m), 1161 (m), 1117 (s), 1103 (s), 1069 (s), 1047 (m), 1016 (m), 1001 (m), 953 (w), 845 (m), 818 (m), 799 (m), 775 (w), 700 (m), 642 (m), 604 (m), 525 (m), 496 (m), 465 (m), 442 (m) cm^{-1}. HRMS (EI): Calcd. for $C_{18}H_{15}F_3FeO$ [M^+] 360.0424, found 360.0422.

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Conflict of Interest

The authors declare no conflict of interest.

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