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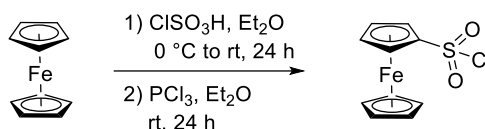
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Synthesis of ferrocenesulfonyl chloride, key intermediate toward ferrocenesulfonamides

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Large scale synthesis: 400 mmol
Purification by crystallization
65% yield - 74 g in one batch

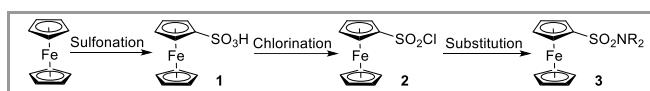


Abstract Ferrocenesulfonyl chloride is the key intermediate in the synthesis of ferrocenesulfonamides, a family of underexplored derivatives. Here, we report a one-pot synthesis of this compound able to easily deliver multigram quantities of product. While we also describe an original protocol for the synthesis of ferrocenesulfonamides, we highlight the reactivity difference between arene and ferrocene sulfonyl chlorides. Finally, we describe an example of diastereoselective deprotonation of chiral ferrocenesulfonamides.

Key words Ferrocene, sulfonyl chloride, sulfonamide, scale-up, diastereoselective deprotonation.

Although discovered seventy years ago, ferrocene still remains one of the most important organometallic scaffolds with multiple applications in all areas of chemistry.¹ This results from its three-dimensional structure, reversible redox behavior, planar chirality properties and high stability in various conditions. While many ferrocene derivatives have been the focus of detailed studies, ferrocenesulfonamides remain a class of compounds barely explored although promising applications have already been reported. They can be found in a few macrocycles acting as multielectron systems² or behaving as efficient ligands in catalysis.³ They have also been used to reach original *N*-heterocyclic carbenes, studied for their metal coordinating properties.⁴ Ferrocenesulfonamides are also interesting substrates toward sulfur-containing derivatives as described by Herberhold and Sato,⁵ or original materials as proposed by Wurm.⁶ Concerning the redox properties of ferrocenesulfonamide derivatives, they were exploited in a ferrous ions rhodamine-based sensor⁷ or in self-bleaching electrochromic devices.⁸ Applications in medicinal chemistry have also been reported with antibacterial penicillanic and cephalosporanic ferrocenesulfonamide derivatives.⁹ Finally, a few other reports were dedicated to specific structures and their study at the solid state.¹⁰

Whatever their applications, all the ferrocenesulfonamides described are prepared from bare ferrocene by sulfonation, chlorination and nucleophilic substitution (Scheme 1).



Scheme 1 Step order toward ferrocenesulfonamides.

Weinmayr and Nesmeyanov were the first to independently report the sulfonation of ferrocene using concentrated sulfuric acid and the dioxane- SO_3 complex, respectively, with the isolation of the ammonium $\mathbf{1}\cdot\text{NH}_3$ salt (78% yield) or dihydrate $\mathbf{1}\cdot\mathbf{2H}_2\mathbf{O}$ (62% yield).¹¹ Pauson then introduced the use of chlorosulfonic acid toward the same $\mathbf{1}\cdot\mathbf{2H}_2\mathbf{O}$ hydrate (60% yield)¹² while Schlögl reported a modification of its isolation protocol to deliver the *p*-toluidinium salt ($\mathbf{1}\cdot\mathbf{p}$ -toluidine, 92% yield).¹³ Since then, most of the studies involving ferrocenesulfonic acid relied on the protocols described by Pauson and Schlögl.

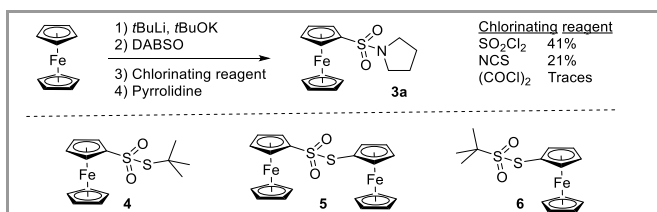
While the chlorination of $\mathbf{1}$ toward ferrocenesulfonyl chloride ($\mathbf{2}$) was first described by Nesmeyanov using phosphorus trichloride in 69% yield,^{11b, 14} Pauson later reported that phosphorus pentachloride and thionyl chloride were not suitable chlorinating reagents.¹² More recently, oxalyl chloride was used in the synthesis of $\mathbf{2}$, although different yields were reported under similar reaction conditions.^{4, 6} Interestingly, Slocum proposed a two-step one-pot protocol to convert ferrocene into $\mathbf{2}$ by the sequential use of chlorosulfonic acid and PCl_3 .¹⁵ Although the yield was lower than in the other approaches (23%), this protocol does not require the isolation of $\mathbf{1}$.

While all the syntheses of $\mathbf{1}$ and $\mathbf{2}$ employ similar reagents and conditions, the reported protocols to access the ferrocenesulfonamides $\mathbf{3}$ are more diverse. Indeed, some ferrocenesulfonamides were prepared with heating in the presence of an excess of amine at reflux of a given solvent^{9, 10b, 12,}

¹⁴ while others were obtained by performing reactions between 0 °C and 25 °C using various solvents.^{5d,13,15} Reactive amines such as methylaziridine can react with **2** at -30 °C⁶ while imidazole and benzimidazole require heating at acetonitrile reflux in the presence of an inorganic base.⁴ It can be finally noticed that 1,1'-bis(ferrocenesulfonyl) chloride reacts in a stepwise manner with an excess of amine, the second substitution being slower than the first one.^{10e}

While we recently described the synthesis of various polysubstituted ferrocenesulfonamides,¹⁶ we were limited by the low yielding synthesis of ferrocenesulfonyl chloride (**2**; 30% yield). With a view to developing a more efficient approach toward ferrocenesulfonamides, we decided to evaluate the use of 1,4-diazabicyclo[2.2.2]octane-bis(sulfur dioxide) (DABSO) in the ferrocene series. Indeed, Willis described the reaction of various organometallics with this surrogate of gaseous SO₂ toward sulfonamides,¹⁷ sulfones,¹⁸ sulfoxides¹⁹ and sulfenamides.²⁰

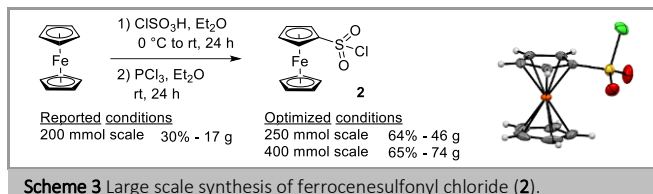
Therefore, we reacted ferrocenyllithium, obtained by treating ferrocene by *tert*-butyllithium in the presence of potassium *tert*-butoxide,²¹ with DABSO. After conversion of the intermediate sulfinate to **2** using sulfonyl chloride, the addition of pyrrolidine afforded the desired (*N*-pyrrolidino)sulfonylferrocene (**3a**) in a moderate 41% yield (Scheme 2). However, facing reproducibility troubles, we suspected the chlorinating reagent used to be incompatible with the oxidation-sensitive ferrocene. We therefore evaluated alternatives such as *N*-chlorosuccinimide²² and oxalyl chloride. While the former led to compound **3a** in a 21% yield, the use of the later only delivered low amounts of the thiosulfonates **4-6** (see SI for a putative reaction mechanism and for the solid-state structures of **5** and **6**).



Scheme 2 Attempts to use DABSO in the synthesis of ferrocenesulfonamides.

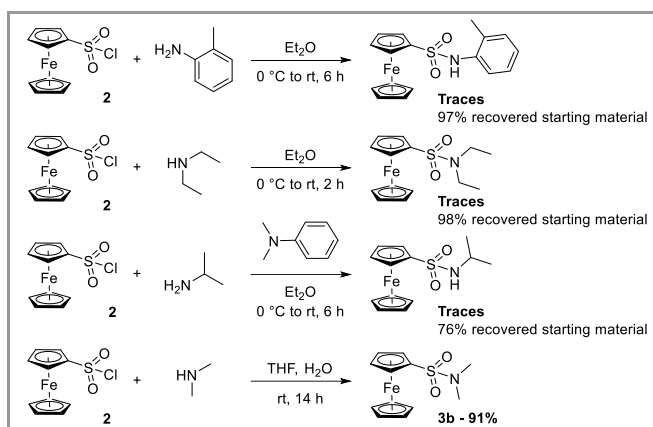
Therefore, to progress toward a practical large scale synthesis of ferrocenesulfonyl chloride (**2**), we decided to focus our efforts on the one-pot protocol described by Slocum.¹⁵ We reasoned that the main difference between the high-yielding protocol of Pauson¹² and the low-yielding from Slocum¹⁵ preferably lies in the sulfonation of ferrocene rather than in the chlorination step. While chlorosulfonic acid is employed in both protocols, the former used acetic anhydride, proposed to reduced competitive oxidation of ferrocene,^{11a} while the latter used diethyl ether. Keen to avoid the use of large amounts of acetic anhydride, we decided to keep diethyl ether as solvent but under more diluted reaction conditions. Furthermore, to avoid the use of anhydrous solvent, we used a slight excess of chlorosulfonic acid (1.2 equiv instead of 1.1). This led to an increase of the formation of **2** on a 250 mmol scale (46 g isolated, 64% yield, Scheme 3). Our optimized conditions involve the dropwise addition of chlorosulfonic acid onto an ice-cooled solution of ferrocene in diethyl ether followed by 24 h stirring at room temperature. After addition of phosphorus trichloride, another 24 h stirring period is required before removal of volatiles under vacuum to give the crude

product. While Slocum uses petroleum ether (30-60 °C boiling point fraction) to recrystallize **2**, we found that repeated trituration of the crude product with hot heptane, followed by crystallization, was a more efficient process. Pleasingly, we were able to conduct the reaction on a 400 mmol scale with reproducible results (reaction done two times in 65 and 71% yields; 74 and 80 g of **2** isolated, respectively).



Scheme 3 Large scale synthesis of ferrocenesulfonyl chloride (**2**).

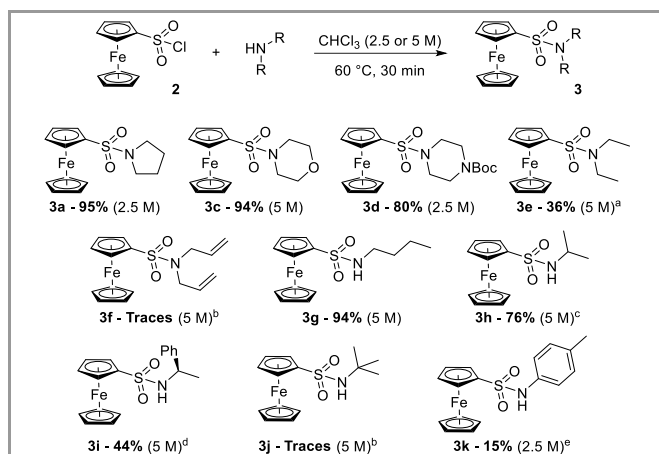
With the possibility to easily obtain large amounts of ferrocenesulfonyl chloride (**2**), we next focused our efforts on the synthesis of sulfonamides. Indeed, we were intrigued by the various reaction conditions described in the literature and by a report from Koppang on some low-yielding smooth reaction conditions.²³ Therefore, we reacted **2** with different amines under reaction conditions inspired from the literature (Scheme 4). However, in our hands, most of the reaction conditions applied only led to traces of expected product with various degrees of starting material recovery. The only successful conditions were the ones reported by Sato^{5c} for the synthesis of **3b** in a THF-water mixture (91% yield on a 26 mmol scale).



Scheme 4 Synthetic attempts toward ferrocenesulfonamides using protocols adapted from the literature. THF: tetrahydrofuran.

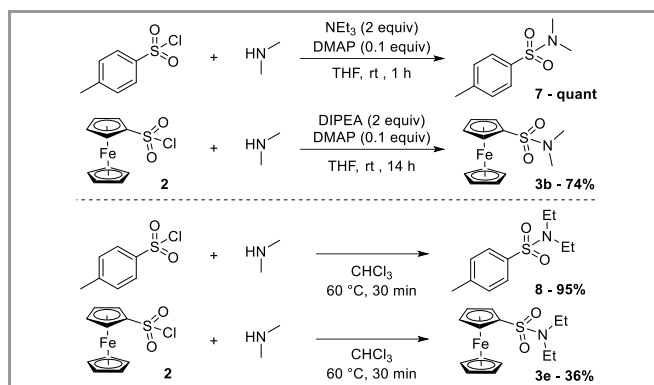
In search for harsher reaction conditions, **2** was reacted at 60 °C with a three-fold excess of morpholine in chloroform at a 5 molar concentration. Pleasingly, (*N*-morpholino)sulfonylferrocene (**3c**) was isolated in 94% yield after only 30 min (Scheme 5). As we recognized that such high concentration might be incompatible with some solid amines, we repeated the reaction by adding a solution of morpholine in chloroform, leading to a final 2.5 molar concentration, with similar results (96% yield). We next studied the scope of these new reaction conditions with various amines. Although pyrrolidine led to the sulfonamide **3a** in a similar 95% yield, it was found so reactive that the reaction needed to be done at a 2.5 molar concentration. For solubility reason, the same concentration was required when using Boc-protected piperazine to deliver **3d** in 80% yield, together with the recovery of 15% of unreacted **2**. However, moving to other acyclic secondary amines resulted in a major drop of the yield,

diethylamine leading to only 36% of **3e** while diallylamine was found unreactive in our conditions toward compound **3f**. Although primary amines were found more reactive, the yield of the sulfonamides **3** was strongly influenced by their steric hindrance. Indeed, while *n*-butylamine afforded **3g** in 94% yield, isopropylamine led to compound **3h** in 76% yield. A further drop in the yield was recorded with (*R*)- α -methylbenzylamine, even after 1 h of reaction (compound **3i**, 44% yield), while only traces of the sulfonamide **3j** were noticed using *tert*-butylamine. However, we found that increasing the reaction time favored the substitution as the sulfonamide **3i** was isolated in 85% yield after 4 h at 60 °C. Aromatic amine such as *p*-toluidine was also found to be poorly reactive as compound **3k** was only isolated in 15% yield. It should be noticed that the yields recorded are in good agreement with the nucleophilicity of the amine used. Indeed, Mayr reported the following order of reactivity for secondary and primary amines, respectively: pyrrolidine > morpholine > diethylamine and *n*-butylamine > isopropylamine > *tert*-butylamine.²⁴



Scheme 5 Synthesis of ferrocenesulfonamides. a) 34% recovered starting material; b) 98% recovered starting material; c) 15% recovered starting material; d) 46% recovered starting material; e) 53% recovered starting material.

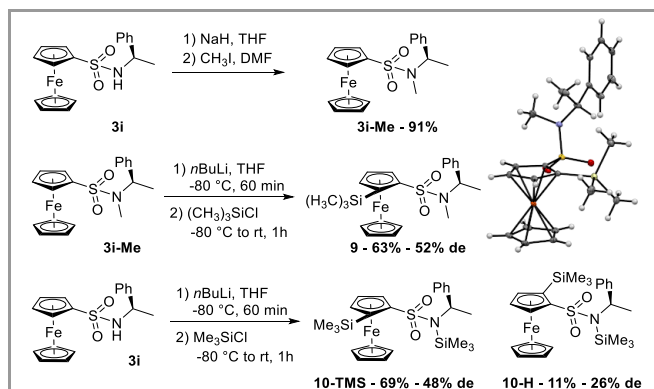
While the amine nucleophilicity plays an important role in the reaction outcome, we were also keen to compare the reactivity of ferrocenesulfonyl chloride (**2**) with more classical sulfonyl chloride such as the widely used *p*-tosyl chloride (Scheme 6).²⁵ Under smooth reaction conditions, the latter was converted into the sulfonamide **7** in a quantitative way after only one hour at room temperature. However, the use of ferrocenesulfonyl chloride (**2**) required prolonged reaction time to deliver **3b** in 74% yield. The reactivity difference between **2** and *p*-tosyl chloride was further highlighted when they were reacted with diethylamine in our new reaction conditions. While **3e** was formed in 36% yield, the sulfonamide **8** was obtained in 95% yield after 30 min. Although one could have suspected **2** to be less reactive than other aromatic sulfonyl chlorides, these results clearly show the difference between ferrocene and more classical aromatic compounds. This might result from both the electron-rich nature of ferrocene and unfavorable steric parameters, the approach of the nucleophile opposite to the leaving being probably disfavored by the unsubstituted cyclopentadienyl ring as observed at the solid state (Scheme 3).



Scheme 6 Reactivity studies of *p*-tosyl chloride and ferrocenesulfonyl chloride (**2**). DIPEA: Diisopropylethylamine; DMAP: 4-(dimethylamino)pyridine; THF: tetrahydrofuran.

As previously observed by Ziegler,^{10e, 10g} hydrogen bonds can be observed at the solid state. For the ferrocenesulfonamides bearing a free NH, a single string of hydrogen bonds linking all sulfonamide groups in compounds **3h** and **3k** was observed while two intermolecular hydrogen bonds link two sulfonamides in compound **3g** (see SI).

Finally, we were eager to evaluate the ability of chiral sulfonamides to direct a diastereoselective deprotonation in the ferrocene series (Scheme 7).²⁶ Therefore, we reacted the sulfonamides **3i** and **3i-Me** (obtained by deprotonation of **3i** with NaH and subsequent trapping with methyl iodide) with *n*-BuLi in THF at -80 °C and added trimethylsilyl chloride after 1 h of contact. From **3i-Me**, the disubstituted ferrocene **9** was obtained in 63% yield and a moderate 52% diastereoselective excess (*de*), estimated from the ¹H NMR spectrum. While 2-dimensional NMR experiments suggested the *S_p* configuration for the minor diastereoisomer (see SI), we found that the major isomer selectively crystallized from the mixture. The X-ray diffraction analysis allowed us to attribute the *R,R_p* configuration to the major isomer, thus validating the *S_p* configuration for the minor one, as suggested from NMR analysis. From **3i**, we isolated the two products **10-TMS** (71%, 48% *de*) and **10-H** (11%, 26% *de*). For **10-TMS**, although we were not able to grow crystals suitable for X-ray diffraction analysis, the ¹H NMR suggested the same configuration (*R,R_p*) as for **9** while we propose the other configuration (*R,S_p*) for the sulfonamide **10-H**. Although the most used chiral directing groups can lead to higher yields and diastereoselectivities,²⁷ these results highlight the ability of chiral sulfonamides to act in a similar way.



Scheme 7 Diastereoselective deprotonation of ferrocenesulfonamides **3i** and **3i-Me**. DMF: dimethylformamide; THF: tetrahydrofuran.

In conclusion, although we proved possible the use of DABSO to reach ferrocenesulfonamides, we focused our efforts on the large-scale synthesis of ferrocenesulfonyl chloride using a more classical route. Furthermore, we have described a new protocol for the synthesis of various ferrocenesulfonamides and identified its limitations in terms of both amine and ferrocenesulfonyl chloride reactivity. Finally, an example of diastereoselective deprotonation of chiral ferrocenesulfonamides was described with moderate but promising diastereoselectivity. Considering the already reported applications of ferrocenesulfonamides and our recent work toward their polysubstituted derivatives, we strongly believe that further important developments in this field could be expected.

General Considerations. Unless otherwise stated, all the reactions were performed under air using reagent grade solvents. Deprotonation experiments were performed under an argon atmosphere with anhydrous solvents using Schlenk techniques and THF distilled over sodium-benzophenone. Unless otherwise stated, all reagents were used without prior purification. *n*-Butyllithium was titrated before use,²⁸ *t*BuOK (99.99% quality) was purchased from Sigma-Aldrich and used without further purification. Room temperature (rt) refers to 25 °C. Column chromatography separations were achieved on silica gel (40–63 μm). For the purification of sulfonamides, 2% of CHCl₃ was added to the eluant at the beginning of the purification to avoid the precipitation of compound on silica. All Thin Layer Chromatographies (TLC) were performed on aluminum backed plates pre-coated with silica gel (Merck, Silica Gel 60 F254). They were visualized by exposure to UV light. PET refers to petroleum ether. Melting points were measured on a Kofler bench. IR spectra were taken on a Perkin-Elmer Spectrum 100 spectrometer. ¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectra were recorded either (i) on a Bruker Avance III spectrometer at 300 MHz and 75.4 MHz, or (ii) on a Bruker Avance III at 400 MHz and 100 MHz, or (iii) on a Bruker Avance III HD at 500 MHz and 126 MHz, respectively. ¹H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ¹³C chemical shifts are relative to the central peak of the solvent signal.²⁹ Cp refers to the unsubstituted cyclopentadienyl ring of ferrocene. The numbering used in this experimental section is defined in Supporting information.

Procedures

Ferrocenesulfonyl chloride (2)

[CAS Reg. No. 33010-70-7]

Chlorosulfonic acid (31.9 mL, 55.9 g, 480 mmol, 1.20 equiv) was added dropwise to an ice-cold solution of ferrocene (74.4 g, 400 mmol, 1.00 equiv) in diethyl ether (1.3 L). After addition, the dark reaction mixture was allowed to warm to rt and stirred for 24 h. Phosphorus trichloride (80.4 mL, 126 g, 920 mmol, 2.30 equiv) was added dropwise to the reaction mixture at rt and the reaction mixture was then stirred at rt for 24 h. Volatiles were removed under vacuum to give the crude product as dark solids which were scrapped with a spatula and kept under high vacuum for 10 min. Heptane (320 mL) was added and the mixture was heated at 90 °C. After 10 min at this temperature, the red-colored heptane was transferred to a hot flask which was allowed to cool to rt. The extraction process was repeated until most of ferrocenesulfonyl chloride was extracted. Depending on the exact amount of heptane, the temperature, the contact time and the size of the solids, 2 to 4 extractions could be required. As ferrocenesulfonyl chloride is extracted, the initial solids evolve to a gummy blue-green paste which can be scrapped with a spatula for a better extraction. **Caution:** if a heat gun is used, pay attention to avoid hot spots as thermal decomposition might happen if the crude product becomes dry. Let the heptane solutions slowly cool to rt and filter the resulting red crystals using a sintered glass funnel (porosity 3). Wash the solids with a small amount of cold pentane and let it dry under high vacuum to give the title product **2** as a red solid (74.3 g, 65%); *R*_f = 0.40 (PET-EtOAc 90:10); mp 99–100 °C. CCDC 2063540.

Analytical data analogous to those reported previously.¹²

IR (film): 817, 831, 889, 1003, 1015, 1031, 1109, 1141, 1203, 1371, 1395, 1413, 1734, 2234, 3113 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 4.45 (s, 5H, Cp), 4.60 (t, 2H, *J* = 1.75 Hz, H3 and H4), 4.85 (t, 2H, *J* = 1.75 Hz, H2 and H5).

¹³C NMR (126 MHz, CDCl₃): δ = 68.6 (2CH, C2 and C5), 71.9 (5CH, Cp), 72.3 (2CH, C3 and C4), 94.2 (C, C1, C-SO₂Cl).

General procedure for the synthesis of ferrocenesulfonamides.

The required amine (18.0 mmol, 3.00 equiv) was added dropwise to a solution of compound **2** (1.70 g, 6.00 mmol, 1.00 equiv) in CHCl₃ (1.2 or 2.4 mL) at 60 °C. After addition, the reaction mixture was stirred at the same temperature for 30 min before being cooled to rt. Aq. HCl (1 M, 20 mL) was added and the reaction mixture was extracted with CH₂Cl₂. The combined organic layers were dried over MgSO₄, filtrated over cotton wool and concentrated under vacuum to give the product. This was purified by column chromatography over SiO₂, using PET-EtOAc (proportions given for each product) to give the title product.

(*N*-Pyrrolidino)sulfonylferrocene (3a)

From ferrocene by using DABSO and sulfonyl chloride. *t*BuLi (1.5 M, 6.60 mL, 10.0 mmol, 2.00 equiv) was added dropwise to a solution of ferrocene (930 mg, 5.00 mmol, 1.00 equiv) and *t*BuOK (56.0 mg, 0.50 mmol, 0.10 equiv) in THF (45 mL) at -80 °C. After addition, the reaction mixture was stirred at the same temperature for 1 h before being cannulated onto a suspension of DABSO (2.60 g, 10.0 mmol, 2.20 equiv) in THF (45 mL) at -40 °C. After addition, the reaction mixture was stirred at -40 °C for 1 h. Sulfonyl chloride (0.90 mL, 1.50 g, 10.0 mmol, 2.20 equiv) was added dropwise and the reaction was warmed to rt and stirred for 1 h. Pyrrolidine (4.20 mL, 3.60 g, 50.0 mmol, 10.0 equiv) was added dropwise and the reaction mixture was stirred at rt for 3 h. Aq. HCl (1 M, 50 mL) was added and the reaction mixture was extracted with ethyl acetate. The combined organic layers were dried over MgSO₄, filtrated over cotton wool and concentrated under vacuum to give the product. This was purified by column chromatography over SiO₂, using PET-EtOAc (80:20) to give the product which was recrystallized to give the title product **3a** as a yellow solid (658.0 mg, 41%).

By following the general procedure, using pyrrolidine (1.50 mL) and CHCl₃ (2.40 mL), **3a** was obtained after column chromatography (PET-EtOAc, 50:50) as a yellow solid (1.81 g, 95%); *R*_f = 0.25 (PET-EtOAc 70:30); mp 216 °C. CCDC 2063541.

IR (film): 656, 718, 755, 818, 832, 944, 959, 1002, 1045, 1077, 1113, 1135, 1149, 1188, 1217, 1246, 1259, 1301, 1327, 1340, 1412, 1453, 2859, 2900, 2960, 3104 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 1.67–1.72 (m, 4H, NCH₂CH₂), 3.13 (t, 4H, *J* = 6.6 Hz, NCH₂CH₂), 4.37 (t, 2H, *J* = 1.65 Hz, H3 and H4), 4.40 (s, 5H, Cp), 4.62 (t, 2H, *J* = 1.65 Hz, H2 and H5).

¹³C NMR (75 MHz, CDCl₃): δ = 25.3 (2CH₂, NCH₂CH₂), 48.0 (2CH₂, NCH₂), 69.0 (2CH, C2 and C5), 70.6 (2CH, C3 and C4), 70.8 (5CH, Cp), 83.8 (C, C1, C-SO₂-*N*-pyrrolidino).

N,N-Dimethylferrocenesulfonamide (3b)

[CAS Reg. No. 63453-42-9]

A solution of NaOH (4.80 g, 120 mmol, 4.80 equiv) in water (20 mL) was added to a solution of dimethylamine hydrochloride (10.2 g, 125 mmol, 5.00 equiv) in water (100 mL). The resulting aqueous solution of dimethylamine was added to a solution of compound **2** (7.33 g, 26.0 mmol, 1.00 equiv) in THF (150 mL) at rt. After addition, the reaction was stirred overnight at rt. Layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over MgSO₄, filtrated over cotton wool and concentrated under vacuum to give the product. This was purified by recrystallization from heptane-CHCl₃ to give the title product **3b** as a yellow solid (6.93 g, 91%); *R*_f = 0.50 (PET-EtOAc 70:30); mp 172 °C. CCDC 2063542.

Analytical data analogous to those reported previously.^{5c}

IR (film): 655, 675, 701, 717, 754, 825, 845, 950, 1000, 1030, 1047, 1070, 1108, 1136, 1165, 1222, 1264, 1318, 1336, 1391, 1446, 1488, 1580, 2849, 2960, 3057, 3418 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 2.59 (s, 6H, NMe₂), 4.39 (s, 2H, H3 and H4), 4.41 (s, 5H, Cp), 4.59 (s, 2H, H2 and H5).

¹³C NMR (75 MHz, CDCl₃): δ = 38.0 (2CH₃, NMe₂), 69.2 (2CH, C2 and C5), 70.7 (2CH, C3 and C4), 70.8 (5CH, Cp), 82.3 (C, C1, C-SO₂NMe₂).

(*N*-Morpholino)sulfonylferrocene (3c)

[CAS Reg. No. 63453-44-1]

By following the general procedure, using morpholine (1.60 mL) and CHCl₃ (1.20 mL), **3c** was obtained after column chromatography (PET-EtOAc, 50:50) as an orange solid (1.90 g, 94%); *R*_f = 0.13 (PET-EtOAc 70:30); mp 208 °C. CCDC 2063543.

Analytical data analogous to those reported previously.³⁰

IR (film): 656, 719, 755, 819, 943, 959, 1002, 1046, 1077, 1112, 1148, 1188, 1246, 1259, 1327, 1340, 1412, 1453, 1719, 2860, 2901, 2960, 3104 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 2.90 (t, 4H, *J* = 4.7 Hz, NCH₂), 3.70 (t, 4H, *J* = 4.4 Hz, OCH₂), 4.42 (s, 7H, H₃, H₄ and Cp), 4.56 (t, 2H, *J* = 1.65 Hz, H₂ and H₅).

¹³C NMR (126 MHz, CDCl₃): δ = 46.0 (2CH₂, NCH₂), 66.1 (2CH₂, OCH₂), 69.3 (2CH, C₂ and C₅), 70.9 (5CH, Cp), 71.0 (2CH, C₃ and C₄), 82.2 (C, C₁, C-SO₂-*N*-morpholino).

(*N'*-tert-Butoxycarbonyl-*N*-piperazino)sulfonylferrocene (3d)

By following the general procedure, a solution of *N*-Boc-piperazine (3.35 g) in CHCl₃ (1.20 mL) was added to compound **2** in CHCl₃ (1.20 mL). **3d** was obtained after column chromatography (PET-EtOAc, 80:20 to 70:30) as a yellow solid (2.09 g, 80%); *R*_f = 0.46 (PET-EtOAc 70:30); mp 194-196 °C.

IR (film): 730, 768, 822, 859, 924, 999, 1018, 1054, 1093, 1126, 1146, 1166, 1188, 1251, 1284, 1307, 1323, 1348, 1362, 1391, 1426, 1453, 1682, 2865, 2970 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 1.40 (s, 9H, *t*Bu), 2.87 (t, 4H, *J* = 5.0 Hz, CH₂NSO₂), 3.46 (t, 4H, *J* = 5.0 Hz, CH₂NBoc), 4.40 (t, 2H, *J* = 1.9 Hz, H₃ and H₄), 4.41 (s, 5H, Cp), 4.55 (t, 2H, *J* = 1.9 Hz, H₂ and H₅).

¹³C NMR (75 MHz, CDCl₃): δ = 28.4 (3CH₃, *t*Bu), 42.9 (2CH₂, CH₂-NBoc), 45.9 (2CH₂, CH₂CH₂-NBoc), 69.2 (2CH, C₂ and C₅), 70.9 (5CH, Cp), 71.0 (2CH, C₃ and C₄), 80.4 (C, CMe₃), 82.5 (C, C₁, C-SO₂N).

***N,N*-Diethylferrocenesulfonamide (3e)**

[CAS Reg. No. 63495-23-8]

By following the general procedure, using diethylamine (1.90 mL) and CHCl₃ (1.20 mL), **3e** was obtained after column chromatography (PET-EtOAc, 90:10; *R*_f = 0.30) as an orange solid (701 mg, 36%); mp 88-89 °C.

Analytical data analogous to those reported previously.¹⁵

IR (film): 796, 814, 928, 1017, 1067, 1105, 1134, 1182, 1324, 1336, 1356, 1383, 1412, 1467, 2937, 2979, 3108, 3684 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 1.08 (t, 6H, *J* = 7.1 Hz, CH₂Me), 3.10 (q, 4H, *J* = 7.1 Hz, CH₂Me), 4.34 (s, 2H, H₃ and H₄), 4.40 (s, 5H, Cp), 4.59 (s, 2H, H₂ and H₅).

¹³C NMR (126 MHz, CDCl₃): δ = 14.0 (2CH₃, Et), 42.0 (2CH₂, Et), 68.5 (2CH, C₂ and C₅), 70.2 (2CH, C₃ and C₄), 70.7 (5CH, Cp), 87.7 (C, C₁, C-SO₂NEt₂).

***N*-Butylferrocenesulfonamide (3g)**

By following the general procedure, using *n*-butylamine (1.80 mL) and CHCl₃ (1.20 mL), **3g** was obtained after column chromatography (PET-EtOAc, 80:20; *R*_f = 0.43) as an orange solid (1.82 g, 94%); mp 102-103 °C. CCDC 2063544.

IR (film): 741, 819, 845, 866, 909, 980, 1000, 1021, 1055, 1083, 1108, 1116, 1144, 1190, 1225, 1260, 1320, 1336, 1391, 1413, 1426, 1467, 1659, 2872, 2953, 3253 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 0.85 (t, 3H, *J* = 7.3 Hz, Me), 1.28 (sext, 2H, *J* = 7.2 Hz, CH₂Me), 1.41 (quint, 2H, *J* = 7.2 Hz, CH₂CH₂Me), 2.91 (q, 2H, *J* = 6.8 Hz, CH₂(CH₂)₂Me), 4.06 (t, 1H, *J* = 6.2 Hz, NH), 4.37 (t, 2H, *J* = 1.9 Hz, H₃ and H₄), 4.40 (s, 5H, Cp), 4.63 (t, 2H, *J* = 1.9 Hz, H₂ and H₅).

¹³C NMR (126 MHz, CDCl₃): δ = 13.7 (CH₃, Bu), 19.9 (CH₂, CH₂Me), 31.7 (CH₂, CH₂CH₂Me), 43.1 (CH₂, CH₂(CH₂)₂Me), 68.7 (2CH, C₂ and C₅), 70.5 (2CH, C₃ and C₄), 70.9 (5CH, Cp), 87.8 (C, C₁, C-SO₂NHBu).

***N*-Isopropylferrocenesulfonamide (3h)**

By following the general procedure, using isopropylamine (1.60 mL) and CHCl₃ (1.20 mL), **3h** was obtained after column chromatography (PET-EtOAc, 80:20; *R*_f = 0.35) as an orange solid (1.40 g, 76%); mp 165-166 °C. CCDC 2063545.

IR (film): 819, 879, 905, 1003, 1022, 1107, 1128, 1191, 1300, 1385, 1435, 1463, 2959, 3236 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 1.05 (d, 6H, *J* = 6.1 Hz, CHMe₂), 3.44 (oct, 1H, *J* = 6.1 Hz, CHMe₂), 4.07 (br d, 1H, *J* = 6.1 Hz, NH), 4.37 (s, 2H, H₃ and H₄), 4.39 (s, 5H, Cp), 4.64 (s, 2H, H₂ and H₅).

¹³C NMR (126 MHz, CDCl₃): δ = 24.0 (2CH₃, CHMe₂), 46.1 (CH, CHMe₂), 68.6 (2CH, C₂ and C₅), 70.5 (2CH, C₃ and C₄), 70.9 (5CH, Cp), 89.1 (C, C₁, C-SO₂NHiPr).

(*R*)-*N*-(1-phenylethyl)ferrocenesulfonamide (3i)

By following the general procedure, using (*R*)- α -methylbenzylamine (2.30 mL) and CHCl₃ (1.20 mL), **3i** was obtained after column chromatography (PET-EtOAc, 80:20; *R*_f = 0.28) as an orange solid (981 mg, 44%). When the reaction was performed for 4 h starting from 12.0 mmol of compound **2**, the title product **3i** was obtained (3.79 g, 85%); mp 111-112 °C.

IR (film): 757, 783, 814, 836, 862, 920, 959, 1001, 1021, 1059, 1096, 1133, 1191, 1318, 1336, 1388, 1412, 1437, 1455, 1495, 1606, 2988, 3245 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 1.41 (d, 3H, *J* = 6.6 Hz, Me), 4.24 (s, 1H, H₃ or H₄), 4.30 (s, 1H, H₃ or H₄), 4.36 (s, 5H, Cp), 4.42 (s, 1H, H₂ or H₅), 4.45 (quint, 1H, *J* = 6.6 Hz, CHMe), 4.56 (s, 1H, H₂ or H₅), 4.61 (d, 1H, *J* = 5.9 Hz, NH), 7.14 (d, 2H, *J* = 7.5 Hz, H_{2'} and H_{6'}), 7.17-7.24 (m, 3H, H_{3'}, H_{4'} and H_{5'}).

¹³C NMR (126 MHz, CDCl₃): δ = 23.8 (CH₃, Me), 53.6 (CH, CHMe), 68.4 (CH, C₂ or C₅), 69.0 (CH, C₂ or C₅), 70.4 (CH, C₃ or C₄), 70.5 (CH, C₃ or C₄), 70.8 (5CH, Cp), 88.6 (C, C₁, C-SO₂NHR), 126.3 (2CH, C_{2'} and C_{6'}), 127.6 (CH, C_{4'}), 128.6 (2CH, C_{3'} and C_{5'}), 142.6 (C, C_{1'}).

[α]_D = +50.0 (c 0.01 in CHCl₃).

***N*-(4-tolyl)ferrocenesulfonamide (3k)**

[CAS Reg. No. 115417-89-5]

By following the general procedure, a solution of *p*-toluidine (1.93 g) in CHCl₃ (1.20 mL) was added to compound **2** in CHCl₃ (1.20 mL). **3k** was obtained after column chromatography (PET-EtOAc, 90:10 to 80:20) as an orange solid (330 mg, 15%); *R*_f = 0.17 (PET-EtOAc 90:10); mp 174-175 °C. CCDC 2063546.

Analytical data analogous to those reported previously.³¹

IR (film): 773, 814, 889, 915, 1020, 1057, 1107, 1131, 1192, 1220, 1278, 1299, 1326, 1392, 1457, 1508, 1614, 2988, 3236 cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 2.28 (s, 3H, Me), 4.30 (t, 2H, *J* = 1.9 Hz, H₃ and H₄), 4.37 (s, 5H, Cp), 4.49 (t, 2H, *J* = 1.9 Hz, H₂ and H₅), 6.32 (br s, 1H, NH), 6.94 (d, 2H, *J* = 8.2 Hz, H_{2'} and H_{6'}), 7.04 (d, 2H, *J* = 8.2 Hz, H_{3'} and H_{5'}).

¹³C NMR (126 MHz, CDCl₃): δ = 21.0 (CH₃, tolyl), 69.0 (2CH, C₂ and C₅), 70.6 (2CH, C₃ and C₄), 70.9 (5CH, Cp), 86.8 (C, C₁, C-SO₂NHtolyl), 122.7 (2CH, C_{2'} and C_{6'}), 129.9 (2CH, C_{3'} and C_{5'}), 134.3 (C, C_{1'} or C_{4'}), 135.4 (C, C_{1'} or C_{4'}).

***N,N*-4-Trimethylbenzenesulfonamide (7)**

[CAS Reg. No. 599-69-9]

A solution of dimethylamine in THF (2 M, 15.0 mL, 30.0 mmol, 1.50 equiv) was added to a solution of *p*-tosyl chloride (3.81 g, 20.0 mmol, 1.00 equiv) and triethylamine (5.60 mL, 4.05 g, 40.0 mmol, 2.00 equiv) in THF (50 mL). After addition, the reaction mixture was stirred at rt for 1 h before volatiles were removed under vacuum. The residue was dissolved in ethyl acetate and the organic phase was washed with aq. HCl (1 M), NaHCO₃ (sat.), dried over MgSO₄, filtrated over cotton wool and concentrated under vacuum to give the title product **7** as a white solid (3.98 g, quant.); *R*_f = 0.33 (PET-EtOAc 80:20); mp 79-80 °C.

Analytical data analogous to those reported previously.³²

IR (film): 721, 801, 814, 824, 954, 1054, 1091, 1159, 1188, 1264, 1290, 1309, 1332, 1381, 1455, 1472, 1596, 2875, 3037 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 2.43 (s, 3H, Me), 2.68 (s, 6H, NMe₂), 7.33 (d, 2H, *J* = 8.2 Hz, H₃ and H₅), 7.65 (d, 2H, *J* = 8.2 Hz, H₂ and H₆).

¹³C NMR (100 MHz, CDCl₃): δ = 21.6 (CH₃, Me), 38.1 (2CH₃, NMe₂), 127.9 (2CH, C₂ and C₆), 129.7 (2CH, C₃ and C₅), 132.6 (C, C₁, C-SO₂N), 143.6 (C, C₄).

***N,N*-Diethyl-4-methylbenzenesulfonamide (8)**

[CAS Reg. No. 649-15-0]

By following the general procedure, using diethylamine (1.90 mL) and CHCl₃ (1.20 mL), **8** was obtained after column chromatography (PET-EtOAc, 80:20 to 70:30) as a white solid (1.29 g, 95%); *R*_f = 0.49 (PET-EtOAc 80:20); mp 60-61 °C.

Analytical data analogous to those reported previously.³³

IR (film): 713, 777, 815, 928, 1013, 1072, 1087, 1155, 1200, 1306, 1330, 1354, 1375, 1467, 1495, 1598, 2936, 2976 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.11 (t, 6H, *J* = 7.1 Hz, CH₂Me), 2.40 (s, 3H, Me), 3.22 (q, 4H, *J* = 7.1 Hz, CH₂Me), 7.27 (d, 2H, *J* = 8.3 Hz, H₃ and H₅), 7.68 (d, 2H, *J* = 8.3 Hz, H₂ and H₆).

¹³C NMR (100 MHz, CDCl₃): δ = 14.3 (2CH₃, Et), 21.6 (CH₃, Me), 42.1 (2CH₂, Et), 127.2 (2CH, C₂ and C₆), 129.7 (2CH, C₃ and C₅), 137.6 (C, C₁, C-SO₂N), 143.0 (C, C₄).

(*R*)-*N*-Methyl-*N*-(1-phenylethyl)ferrocenesulfonamide (3i-Me)

Sodium hydride (60% in oil, 651 mg, 15.0 mmol, 3.00 equiv) was added portionwise to a solution of compound **3i** (1.84 g, 5.00 mmol, 1.00 equiv) in anhydrous THF (50 mL) under argon before being warmed to rt and stirred for 1 h. The reaction mixture was cooled to 0 °C, methyl iodide (965

μL , 2.20 g, 15.0 mmol, 3.00 equiv) and dimethylformamide (10 mL) were added. After addition, the reaction was warmed to rt and stirred for 2 h. NH_4Cl (sat.) was added dropwise to the reaction mixture which was then extracted with ethyl acetate. The combined organic layers were washed with water, brine, dried over MgSO_4 , filtrated over cotton wool and concentrated under vacuum to give the crude product. This was purified by column chromatography over SiO_2 , using PET-EtOAc (80:20) to give the title product **3i-Me** as an orange solid (1.75 g, 91%); $R_f = 0.59$ (PET-EtOAc 80:20); mp 128-129 °C.

IR (film): 709, 767, 785, 827, 893, 913, 979, 1018, 1028, 1046, 1107, 1126, 1154, 1188, 1325, 1336, 1381, 1413, 1455, 2982, 3101 cm^{-1} .

^1H NMR (500 MHz, CDCl_3): $\delta = 1.28$ (d, 3H, $J = 7.0$ Hz, *CHMe*), 2.47 (s, 3H, NMe), 4.37-4.39 (m, 2H, H3 and H4), 4.43 (s, 5H, Cp), 4.62 (quint, 1H, $J = 1.2$ Hz, H2 or H5), 4.65 (quint, 1H, $J = 1.2$ Hz, H2 or H5), 5.16 (q, 1H, $J = 7.0$ Hz, *CHMe*), 7.23-7.25 (m, 1H, H4'), 7.28-7.31 (m, 4H, H2', H3', H5' and H6').

^{13}C NMR (126 MHz, CDCl_3): δ (ppm) 15.2 (CH_3 , *MeCHPh*), 28.3 (CH_3 , NMe), 54.9 (CH, *CHMe*), 68.6 (CH, C2 or C5), 68.7 (CH, C2 or C5), 70.4 (CH, C3 or C4), 70.5 (CH, C3 or C4), 70.9 (5CH, Cp), 87.8 (C, C1, C-SO₂N), 127.4 (2CH, C2' and C6'), 127.5 (CH, C4'), 128.4 (2CH, C3' and C5'), 140.4 (C, C1').

$[\alpha]_D^{25} = +56.3$ (c 0.01 in CHCl_3).

(R)-N-Methyl-N-(1-phenylethyl)-2-(trimethylsilyl)ferrocenesulfonamide (9)

*n*BuLi (1.4 M, 1.30 mL, 1.80 mmol, 1.50 equiv) was added dropwise to a solution of **3i-Me** (460 mg, 1.20 mmol, 1.00 equiv) in anhydrous THF (6 mL) at -80 °C under argon. After addition, the reaction mixture was stirred at the same temperature for 1 h before trimethylsilyl chloride (228 μL , 195 mg, 1.8 mmol, 1.50 equiv) was added. After addition, the reaction mixture was warmed to rt and stirred for a further 15 min. NH_4Cl (sat.) was added dropwise to the reaction mixture which was then extracted with ethyl acetate. The combined organic layers were washed with brine, dried over MgSO_4 , filtrated over cotton wool and concentrated under vacuum to give the crude product. This was purified by column chromatography over SiO_2 , using PET-EtOAc (10:1) to give the title product **9** (3.2:1 diastereoisomeric mixture) as an orange solid (345 mg, 63%, 52% *de*); $R_f = 0.70$ (PET-EtOAc 10:1); mp 90-92 °C. CCDC 2063549.

IR (film): 713, 760, 784, 827, 858, 929, 957, 988, 1029, 1046, 1109, 1125, 1139, 1167, 1189, 1243, 1280, 1312, 1329, 1357, 1385, 1414, 1450, 1498, 1686, 2948, 3092 cm^{-1} .

In the NMR description below, * was used to spot the signals of the minor diastereoisomer.

^1H NMR (500 MHz, CDCl_3): $\delta = 0.36$ and 0.37^* (s, 9H, FcSiMe_3), 1.25 and 1.42* (d, 3H, $J = 7.1$ Hz, and d, 3H, $J = 6.9$ Hz, respectively; *CHMe*), 2.46* and 2.51 (s, 3H, NMe), 4.32-4.33* (m, 1H, H3), 4.40* and 4.41 (s, 5H, Cp), 4.53* and 4.54 (t, 1H, $J = 2.4$ Hz, H4), 4.81* and 4.82 (dd, 1H, $J = 2.3$ and 1.4 Hz, and dd, 1H, $J = 2.2$ and 1.5 Hz, respectively; H5), 5.13 and 5.18* (q, 1H, $J = 7.1$ Hz, and q, 1H, $J = 6.9$ Hz, respectively; *CHMe*), 7.23-7.31* (m, 5H; H2', H3', H4', H5' and H6').

^{13}C NMR (126 MHz, CDCl_3): $\delta = 1.1$ and 1.2^* (3CH_3 , SiMe_3), 15.0 and 16.0* (CH_3 , *MeCHPh*), 28.4 and 28.6* (CH_3 , NMe), 54.2 and 54.6* (CH, *CHMe*), 70.9 and 71.0* (5CH, Cp), 72.3 and 72.5* (CH, C5), 72.6 and 72.7* (CH, C4), 73.0 and 73.3* (C, C2, *C-SiMe}_3*), 77.4 and 77.4* (CH, C3), 93.5 and 93.5* (C, C1, C-SO₂N), 127.5* (5CH, C2', C3', C4', C5' and C6'), 140.1* and 140.4 (CH, C1').

$[\alpha]_D^{25} = +136.6$ (c 0.01 in CHCl_3).

(R)-N-(1-phenylethyl)-N,2-bis(trimethylsilyl)ferrocenesulfonamide (10-TMS) and (R)-N-(1-phenylethyl)-2-(trimethylsilyl)ferrocenesulfonamide (10-H)

*n*BuLi (1.4 M, 2.60 mL, 3.60 mmol, 3.00 equiv) was added dropwise to a solution of **3i** (443 mg, 1.20 mmol, 1.00 equiv) in anhydrous THF (8 mL) at -80 °C under argon. After addition, the reaction mixture was stirred at the same temperature for 1 h before trimethylsilyl chloride (457 μL , 391 mg, 3.60 mmol, 3.00 equiv) was added. After addition, the reaction mixture was warmed to rt and stirred for a further 15 min. NH_4Cl (sat.) was added dropwise to the reaction mixture which was then extracted with ethyl acetate. The combined organic layers were washed with brine, dried over MgSO_4 , filtrated over cotton wool and concentrated under vacuum to give the crude product. This was purified by column chromatography over SiO_2 , using PET-EtOAc (15:1). The title product **10-TMS** (2.8:1 diastereoisomeric mixture) was isolated as an orange solid (427 mg, 69%, 48% *de*); $R_f = 0.66$ (PET-EtOAc 15:1); mp 127-130 °C.

IR (film): 750, 784, 822, 837, 907, 970, 1003, 1025, 1042, 1068, 1101, 1122, 1136, 1190, 1245, 1281, 1315, 1381, 1410, 1448, 1498, 2956 cm^{-1} .

In the NMR description below, * was used to spot the signals of the minor diastereoisomer.

^1H NMR (500 MHz, CDCl_3): $\delta = 0.11^*$ and 0.14 (s, 9H, NSiMe_3), 0.30^* and 0.31 (s, 9H, FcSiMe_3), 1.17 and 1.73^* (d, 3H, $J = 7.2$ Hz, and d, 3H, $J = 6.9$ Hz, respectively; *CHMe*), 4.28* and 4.33 (dd, 1H, $J = 2.4$ and 1.4 Hz, respectively; H3), 4.42* and 4.42 (s, 5H, Cp), 4.55 and 4.57^* (t, 1H, $J = 2.4$ Hz, H4), 4.59* and 4.69 (q, 1H, $J = 6.9$ Hz, and q, 1H, $J = 7.2$ Hz, respectively; *CHMe*), 4.79 and 4.92^* (dd, 1H, $J = 2.4$ and 1.4 Hz, and dd, 1H, $J = 2.3$ and 1.4 Hz, respectively; H5), 7.01* and 7.48 (d, 2H, $J = 7.5$ Hz, and d, 2H, $J = 8.1$ Hz, respectively; H2' and H6'), 7.10-7.12* and 7.30 (m, 2H, and t, 2H, $J = 7.5$ Hz, respectively; H3' and H5'), 7.10-7.12* and 7.22 (m, 1H, and t, 1H, $J = 7.5$ Hz, respectively; H4').

^{13}C NMR (126 MHz, CDCl_3): $\delta = 1.1^*$ and 1.1 (3CH_3 , FcSiMe_3), 3.1^* and 3.2 (3CH_3 , NSiMe_3), 18.3 and 20.2^* (CH_3 , *MeCHPh*), 53.7 and 54.0^* (CH, *CHMe*), 70.9 and 71.0^* (5CH, Cp), 72.1 and 72.2^* (CH, C5), 72.9^* and 72.9 (CH, C4), 75.1 and 75.3 (C, C2, *C-SiMe}_3*), 77.0 and 77.3^* (CH, C3), 94.2^* and 94.8 (C, C1, C-SO₂N), 126.7^* and 127.2 (2CH, C2' and C6'), 126.8* and 127.0 (CH, C4'), 128.1* and 128.2 (C3' and C5'), 142.3 and 142.6^* (C, C1').

$[\alpha]_D^{25} = +111.2$ (c 0.01 in CHCl_3).

The title product **10-H** (1.7:1 diastereoisomeric mixture) was similarly isolated as an orange oil (59.0 mg, 11%, 26% *de*); $R_f = 0.15$ (PET-EtOAc 15:1).

IR (film): 731, 755, 782, 822, 910, 948, 966, 1002, 1041, 1068, 1084, 1108, 1119, 1147, 1191, 1245, 1319, 1377, 1411, 1455, 1495, 1605, 2955, 3274 cm^{-1} .

In the NMR description below, * was used to spot the signals of the minor diastereoisomer.

^1H NMR (500 MHz, CDCl_3): $\delta = 0.28$ and 0.37^* (s, 9H, FcSiMe_3), 1.29* and 1.46 (d, 3H, $J = 6.9$ Hz, and d, 3H, $J = 6.7$ Hz, respectively; *CHMe*), 4.23 and 4.33-4.34* (dd, 1H, $J = 2.4$ and 1.4 Hz, and m, 1H, respectively; H3), 4.34 and 4.38^* (s, 5H, Cp), 4.41* and 4.46 (quint, 1H, $J = 7.3$ Hz, and quint, 1H, $J = 6.7$ Hz, respectively; *CHMe*), 4.33-4.34 and 4.50^* (m, 1H, and t, 1H, $J = 2.4$ Hz, respectively; H4), 4.58 and 4.81^* (dd, 1H, $J = 2.3$ and 1.5 Hz, and dd, 1H, $J = 2.2$ and 1.4 Hz, respectively; H5), 7.00-7.02 and 7.22-7.25* (m, 2H; H2' and H6'), 7.15-7.19 and 7.22-7.25* (m, 1H, H4'), 7.15-7.19 and 7.28-7.32* (m, 2H; H3' and H5').

^{13}C NMR (126 MHz, CDCl_3): $\delta = 0.8$ and 1.0^* (3CH_3 , FcSiMe_3), 23.2* and 24.0 (CH_3 , *MeCHPh*), 53.2* and 53.6 (CH, *CHMe*), 70.8 and 70.9^* (5CH, Cp), 71.8 and 72.2^* (CH, C4), 71.8 and 72.4^* (C, C2, *C-SiMe}_3*), 73.6* and 73.8 (CH, C5), 77.8 and 77.9^* (CH, C3), 92.6 and 92.9^* (C, C1, C-SO₂N), 126.3 and 126.3* (2CH, C2' and C6'), 127.6 and 127.6^* (CH, C4'), 128.6 and 128.7^* (C3' and C5'), 142.4 and 142.9^* (C, C1').

$[\alpha]_D^{25} = +43.7$ (c 0.01 in CHCl_3).

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