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Synthesis of Ferrocenesulfonyl Chloride: Key Intermediate toward Ferrocenesulfonamides

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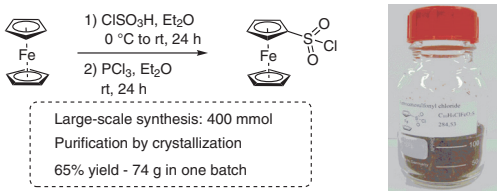

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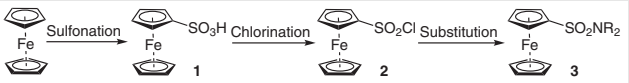
Abstract Ferrocenesulfonyl chloride is the key intermediate in the synthesis of ferrocenesulfonamides, a family of underexplored derivatives. A one-pot synthesis of this compound, able to easily deliver multigram quantities of product, is reported. An original protocol for the synthesis of ferrocenesulfonamides is described along with highlighting the reactivity difference between arene and ferrocenesulfonyl chlorides. Finally, an example of diastereoselective deprotolithiation of chiral ferrocenesulfonamides is described.

Key words ferrocene, sulfonyl chloride, sulfonamide, scale-up, diastereoselective deprotolithiation

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 systems[2] 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 ion rhodamine-based sensor[7] 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 1,4-dioxane·SO_3 complex, respectively, with the isolation of the ammonium **1·NH$_3$** salt (78% yield) or dihydrate **1·2H$_2$O** (62% yield).[11] Pauson then introduced the use of chlorosulfonic acid toward the same **1·2H$_2$O** hydrate (60% yield)[12] while Schlögl reported a modification of its isolation protocol to deliver the *p*-toluidinium salt (**1·*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 ferrocenesulfonic acid (**1**) toward ferrocenesulfonyl chloride (**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 **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 **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 **1**.

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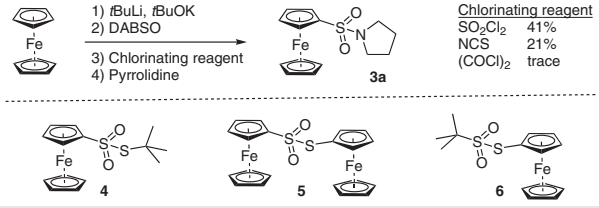
While all the syntheses of **1** and **2** employ similar reagents and conditions, the reported protocols to access the ferrocenesulfonamides **3** are more diverse. Indeed, some ferrocenesulfonamides were prepared with heating in the presence of an excess of amine at reflux of a given solvent[9,10b,12,14] 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 °C[6] 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]

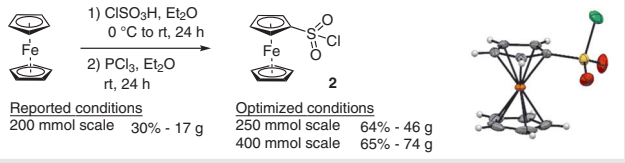
While we recently described the synthesis of various polysubstituted ferrocenesulfonamides,[16] we were limited by the low-yielding synthesis of ferrocenesulfonyl chloride (**2**; 30% yield). With a view to developing a more efficient approach toward ferrocenesulfonamides, we decided to evaluate the 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 SO_2 toward sulfonamides,[17] sulfones,[18] sulfoxides,[19] and sulfinamides.[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 sulfuryl 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*-chlorosuccinimide[22] 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

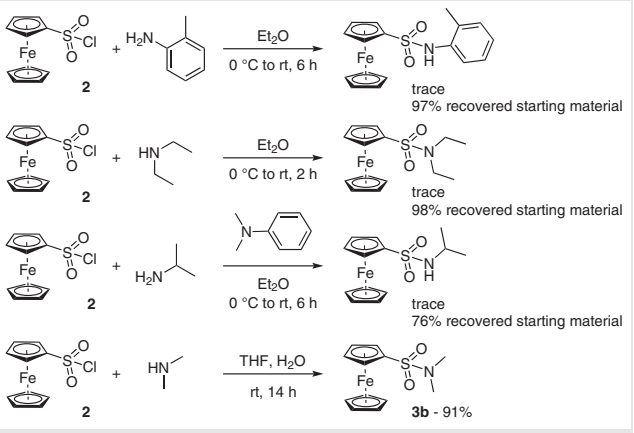
Therefore, to progress toward a practical large-scale synthesis of ferrocenesulfonyl chloride (**2**), we decided to focus our efforts on the one-pot protocol described by Slocum.[15] We reasoned that the main difference between the high-yielding protocol of Pauson[12] and the low-yielding from Slocum[15] 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 hours stirring at room temperature. After addition of phosphorus trichloride, another 24 hours stirring period is required before removal of volatiles under vacuum to give the crude product. While Slocum uses petroleum ether (bp 30–60 °C 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% yield; 74 and 80 g of **2** isolated, respectively).



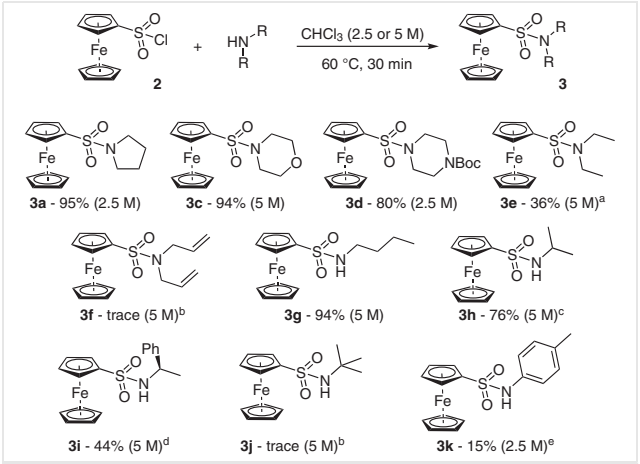
Scheme 3 Large-scale synthesis of ferrocenesulfonyl chloride (**2**)

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).

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 minutes (Scheme 5). As we recognized that such high concentration might be incompatible with some solid amines, the reaction was repeated 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



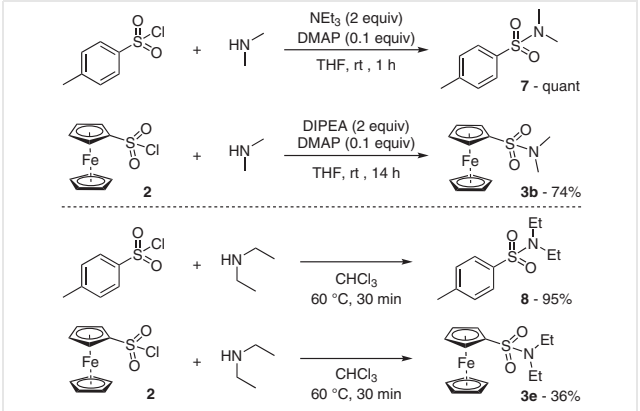
Scheme 4 Synthetic attempts toward ferrocenesulfonamides using protocols adapted from the literature



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.

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 hour 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 hours 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 noted 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]

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 minutes. 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).

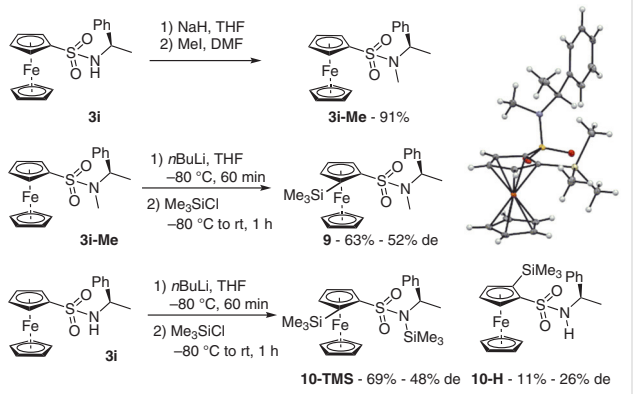


Scheme 6 Reactivity studies of *p*-tosyl chloride and ferrocenesulfonyl chloride (**2**). DIPEA: diisopropylethylamine; DMAP: 4-(dimethylamino)-pyridine.

As previously observed by Ziegler,[10e,g] 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 deprotolithiation 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 hour of contact. From **3i-Me**, the disubstituted ferrocene **9** was obtained in 63% yield with a moderate 52% diastereoselective excess (de), estimated from the ^{1}H 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** (69%, 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 ^{1}H 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 deprotolithiation of ferrocenesulfonamides **3i** and **3i-Me**

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 deprotolithiation 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.

Unless otherwise stated, all the reactions were performed under air using reagent grade solvents. Deprotolithiation experiments were performed under an argon atmosphere with anhydrous solvents using Schlenk technics and THF distilled over Na/benzophenone. Unless otherwise stated, all reagents were used without prior purification. *n*-BuLi 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 $CHCl_3$ was added to the eluent at the beginning of the purification to avoid the precipitation of compound on silica gel. All TLC analyses were performed on aluminum-backed plates precoated with silica gel (Merck, Silica Gel 60 F254). They were visualized by exposure to UV light. PE refers to petroleum ether. Melting points were measured on a Kofler bench. IR spectra were taken on a Perkin-Elmer Spectrum 100 spectrometer. ^{1}H and ^{13}C 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. ^{1}H chemical shifts (δ) are given in ppm relative to the solvent residual peak and ^{13}C chemical shifts are relative to the central peak of the solvent signal.[29] Cp refers to the unsubstituted cyclopentadienyl ring of ferrocene. The numbering used in this experimental section is defined in the Supporting Information.

Ferrocenesulfonyl Chloride (2)[30]

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

$ClSO_3H$ (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 Et_2O (1.3 L). After addition, the dark reaction mixture was allowed to warm to rt and stirred for 24 h. PCl_3 (80.4 mL, 126 g, 920 mmol, 2.30 equiv) was added dropwise to the reaction mixture at rt and the 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 was extracted, the initial solids evolved to a gummy blue-green paste, which can be scrapped with a spatula for a better extraction. **Caution**: If a heat gun is used, attention must be paid to avoid hot spots as thermal decomposition might happen if the crude product becomes dry. The heptane solutions were allowed to cool slowly to rt and the resulting red crystals were filtered using a sintered glass funnel (porosity 3). The solids were washed with a small amount of cold pentane and allowed to dry under high vacuum to give the title product **2** as a red solid; yield: 74.3 g (65%); R_f = 0.40 (PE/EtOAc 90:10); mp 99–100 °C.

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

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.45 (s, 5 H, Cp), 4.60 (t, *J* = 1.75 Hz, 2 H, H3 and H4), 4.85 (t, *J* = 1.75 Hz, 2 H, H2 and H5).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 68.6 (2 × CH, C2 and C5), 71.9 (5 × CH, Cp), 72.3 (2 × CH, C3 and C4), 94.2 (C, C1, CSO_2Cl).

Analytical data analogous to those reported previously.[12]

Ferrocenesulfonamides; General Procedure

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 $CHCl_3$ (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 1 M HCl (20 mL) was added and the reaction mixture was extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), filtered over cotton wool, and concentrated under vacuum to give the product. This was purified by column chromatography over silica gel, using PE/EtOAc (proportions given for each product) to give the title product.

(*N*-Pyrrolidino)sulfonylferrocene (3a)[30]

From Ferrocene by Using DABSO and SO_2Cl_2: *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 mixture was stirred at –40 °C for 1h. SO_2Cl_2 (0.90 mL, 1.50 g, 10.0 mmol, 2.20 equiv) was added dropwise and the mixture 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 mixture was stirred at rt for 3 h. Aq 1 M HCl (1 M, 50 mL) was added and the mixture was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$), filtered over cotton wool, and concentrated under vacuum to give the product. This was purified by column chromatography over silica gel using PE/EtOAc (80:20) to give the product, which was recrystallized to give the title product **3a** as a yellow solid; yield: 658.0 mg (41%).

From Ferrocenesulfonyl Chloride: By following the general procedure, using pyrrolidine (1.50 mL) and $CHCl_3$ (2.40 mL), **3a** was obtained after column chromatography (PE/EtOAc, 50:50) as a yellow solid; yield: 1.81 g (95%); R_f = 0.25 (PE/EtOAc 70:30); mp 216 °C.

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}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.67–1.72 (m, 4 H, 2 × NCH_2CH_2), 3.13 (t, *J* = 6.6 Hz, 4 H, 2 × NCH_2CH_2), 4.37 (t, *J* = 1.65 Hz, 2 H, H3 and H4), 4.40 (s, 5 H, Cp), 4.62 (t, *J* = 1.65 Hz, 2 H, H2 and H5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.3 (2 × CH_2, NCH_2CH_2), 48.0 (2 × CH_2, NCH_2), 69.0 (2 × CH, C2 and C5), 70.6 (2 × CH, C3 and C4), 70.8 (5 CH, Cp), 83.8 (C, C1, CSO_2N-pyrrolidino).

N,*N*-Dimethylferrocenesulfonamide (3b)[30]

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

A solution of NaOH (4.80 g, 120 mmol, 4.80 equiv) in H_2O (20 mL) was added to a solution of dimethylamine hydrochloride (10.2 g, 125 mmol, 5.00 equiv) in H_2O (100 mL). The resulting aqueous solution of Me_2NH 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 mixture was stirred overnight at rt. Layers were separated and the aqueous layer was extracted with EtOAc. The combined organic layers were dried ($MgSO_4$), filtered over cotton wool, and concentrated under vacuum to give the product. This was purified by recrystallization from heptane/$CHCl_3$ to give the title product **3b** as a yellow solid; yield: 6.93 g (91%); R_f = 0.50 (PE/EtOAc 70:30); mp 172 °C.

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}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.59 [s, 6 H, $N(CH_3)_2$], 4.39 (s, 2 H, H3 and H4), 4.41 (s, 5 H, Cp), 4.59 (s, 2 H, H2 and H5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 38.0 [2 × CH_3, $N(CH_3)_2$], 69.2 (2 × CH, C2 and C5), 70.7 (2 × CH, C3 and C4), 70.8 (5 × CH, Cp), 82.3 (C, C1, CSO_2NMe_2).

Analytical data analogous to those reported previously.[5c]

(*N*-Morpholino)sulfonylferrocene (3c)[30]

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

By following the general procedure, using morpholine (1.60 mL) and $CHCl_3$ (1.20 mL), **3c** was obtained after column chromatography (PE/EtOAc 50:50) as an orange solid; yield: 1.90 g (94%); R_f = 0.13 (PE/EtOAc 70:30); mp 208 °C.

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}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.90 (t, *J* = 4.7 Hz, 4 H, 2 × NCH_2), 3.70 (t, *J* = 4.4 Hz, 4 H, 2 × OCH_2), 4.42 (s, 7 H, H3, H4, and Cp), 4.56 (t, *J* = 1.65 Hz, 2 H, H2 and H5).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 46.0 (2 × CH_2, NCH_2), 66.1 (2 × CH_2, OCH_2), 69.3 (2 × CH, C2 and C5), 70.9 (5 × CH, Cp), 71.0 (2 × CH, C3 and C4), 82.2 (C, C1, CSO_2N-morpholino).

Analytical data analogous to those reported previously.[31]

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

By following the general procedure, a solution of *N*-Boc-piperazine (3.35 g) in $CHCl_3$ (1.20 mL) was added to compound **2** in $CHCl_3$ (1.20 mL). Product **3d** was obtained after column chromatography (PE/EtOAc 80:20 to 70:30) as a yellow solid; yield: 2.09 g (80%); R_f = 0.46 (PE/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}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.40 (s, 9 H, *t*-C_4H_9), 2.87 (t, *J* = 5.0 Hz, 4 H, 2 × CH_2NSO_2), 3.46 (t, *J* = 5.0 Hz, 4 H, 2 × CH_2NBoc), 4.40 (t, *J* = 1.9 Hz, 2 H, H3 and H4), 4.41 (s, 5 H, Cp), 4.55 (t, *J* = 1.9 Hz, 2 H, H2 and H5).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.4 (3 × CH_3, *t*-C_4H_9), 42.9 (2 × CH_2, CH_2NBoc), 45.9 (2 × CH_2, CH_2CH_2NBoc), 69.2 (2 × CH, C2 and C5), 70.9 (5 × CH, Cp), 71.0 (2 × CH, C3 and C4), 80.4 (C, CMe_3), 82.5 (C, C1, CSO_2N).

N,*N*-Diethylferrocenesulfonamide (3e)

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

By following the general procedure, using Et_2NH (1.90 mL) and $CHCl_3$ (1.20 mL), **3e** was obtained after column chromatography (PE/EtOAc 90:10; R_f = 0.30) as an orange solid; yield: 701 mg (36%); mp 88–89 °C.

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

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.08 (t, *J* = 7.1 Hz, 6 H, 2 × CH_2CH_3), 3.10 (q, *J* = 7.1 Hz, 4 H, 2 × CH_2Me), 4.34 (s, 2 H, H3 and H4), 4.40 (s, 5 H, Cp), 4.59 (s, 2 H, H2 and H5).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.0 (2 × CH_3, Et), 42.0 (2 × CH_2, Et), 68.5 (2 × CH, C2 and C5), 70.2 (2 × CH, C3 and C4), 70.7 (5 × CH, Cp), 87.7 (C, C1, CSO_2NEt_2).

Analytical data analogous to those reported previously.[15]

N-Butylferrocenesulfonamide (3g)[30]

By following the general procedure, using $BuNH_2$ (1.80 mL) and $CHCl_3$ (1.20 mL), **3g** was obtained after column chromatography (PE/EtOAc 80:20; R_f = 0.43) as an orange solid; yield: 1.82 g (94%); mp 102–103 °C.

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}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.28 (sext, *J* = 7.2 Hz, 2 H, CH_2Me), 1.41 (quint, *J* = 7.2 Hz, 2 H, CH_2CH_2Me), 2.91 [q, *J* = 6.8 Hz, 2 H,$CH_2(CH_2)_2$Me], 4.06 (t, *J* = 6.2 Hz, 1 H, NH), 4.37 (t, *J* = 1.9 Hz, 2 H, H3 and H4), 4.40 (s, 5 H, Cp), 4.63 (t, *J* = 1.9 Hz, 2 H, H2 and H5).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.7 (CH_3, Bu), 19.9 (CH_2, CH_2Me), 31.7 (CH_2, CH_2CH_2Me), 43.1 [CH_2, $CH_2(CH_2)_2$Me], 68.7 (2 × CH, C2 and C5), 70.5 (2 × CH, C3 and C4), 70.9 (5 × CH, Cp), 87.8 (C, C1, CSO_2NHBu).

N-Isopropylferrocenesulfonamide (3h)[30]

By following the general procedure, using *i*-$PrNH_2$ (1.60 mL) and $CHCl_3$ (1.20 mL), **3h** was obtained after column chromatography (PE/EtOAc 80:20; R_f = 0.35) as an orange solid; yield: 1.40 g (76%); mp 165–166 °C.

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

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05 [d, *J* = 6.1 Hz, 6 H, $CH(CH_3)_2$], 3.44 (oct, *J* = 6.1 Hz, 1 H, $CHMe_2$), 4.07 (br d, *J* = 6.1 Hz, 1H, NH), 4.37 (s, 2 H, H3 and H4), 4.39 (s, 5 H, Cp), 4.64 (s, 2 H, H2 and H5).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 24.0 [2 × CH_3, $CH(CH_3)_2$], 46.1 (CH, $CHMe_2$), 68.6 (2 × CH, C2 and C5), 70.5 (2 × CH, C3 and C4), 70.9 (5 × CH, Cp), 89.1 (C, C1, CSO_2NH*i*Pr).

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

By following the general procedure, using (*R*)-α-methylbenzylamine (2.30 mL) and $CHCl_3$ (1.20 mL), **3i** was obtained after column chromatography (PE/EtOAc 80:20; R_f = 0.28) as an orange solid; yield: 981 mg (44%). The reaction was also performed for 4 h starting from 12.0 mmol of compound **2**; yield: 3.79 g (85%); mp 111–112 °C; $[\alpha]_D$ +50.0 (*c* 0.01 in $CHCl_3$).

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}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.41 (d, *J* = 6.6 Hz, 3 H, CH_3), 4.24 (s, 1 H, H3 or H4), 4.30 (s, 1 H, H3 or H4), 4.36 (s, 5 H, Cp), 4.42 (s, 1 H, H2 or H5), 4.45 (quint, *J* = 6.6 Hz, 1 H, CHMe), 4.56 (s, 1 H, H2 or H5), 4.61 (d, *J* = 5.9 Hz, 1 H, NH), 7.14 (d, *J* = 7.5 Hz, 2 H, H2′ and H6′), 7.17–7.24 (m, 3 H, H3′, H4′, and H5′).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 23.8 (CH_3, $CHCH_3$), 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 (5 × CH, Cp), 88.6 (C, C1, CSO_2NHR), 126.3 (2 × CH, C2′ and C6′), 127.6 (CH, C4′), 128.6 (2 × CH, C3′ and C5′), 142.6 (C, C1′).

N-(4-Tolyl)ferrocenesulfonamide (3k)[30]

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

By following the general procedure, a solution of *p*-toluidine (1.93 g) in $CHCl_3$ (1.20 mL) was added to compound **2** in $CHCl_3$ (1.20 mL). Product **3k** was obtained after column chromatography (PE/EtOAc 90:10 to 80:20) as an orange solid; yield: 330 mg (15%); R_f = 0.17 (PE/EtOAc 90:10); mp 174–175 °C.

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

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.28 (s, 3 H, CH_3), 4.30 (t, *J* = 1.9 Hz, 2 H, H3 and H4), 4.37 (s, 5 H, Cp), 4.49 (t, *J* = 1.9 Hz, 2 H, H2 and H5), 6.32 (br s, 1 H, NH), 6.94 (d, *J* = 8.2 Hz, 2 H, H2′ and H6′), 7.04 (d, *J* = 8.2 Hz, 2 H, H3′ and H5′).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 21.0 (CH_3, ArCH_3), 69.0 (2 × CH, C2 and C5), 70.6 (2 × CH, C3 and C4), 70.9 (5 × CH, Cp), 86.8 (C, C1, CSO_2NHtolyl), 122.7 (2 × CH, C2′ and C6′), 129.9 (2 × CH, C3′ and C5′), 134.3 (C, C1′ or C4′), 135.4 (C, C1′ or C4′).

Analytical data analogous to those reported previously.[32]

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

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

A solution of Me_2NH 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 Et_3N (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 EtOAc and the organic phase was washed with 1 M aq HCl, sat. aq $NaHCO_3$, dried ($MgSO_4$), filtered over cotton wool, and concentrated under vacuum to give the title product **7** as a white solid; yield: 3.98 g (quant); R_f = 0.33 (PE/EtOAc 80:20); mp 79–80 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, ArCH_3), 2.68 [s, 6 H, $N(CH_3)_2$], 7.33 (d, *J* = 8.2 Hz, 2 H, H3 and H5), 7.65 (d, *J* = 8.2 Hz, 2 H, H2 and H6).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6 (CH_3, ArCH_3), 38.1 [2 × CH_3, $N(CH_3)_2$], 127.9 (2 × CH, C2 and C6), 129.7 (2 × CH, C3 and C5), 132.6 (C, C1, CSO_2N), 143.6 (C, C4).

Analytical data analogous to those reported previously.[33]

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

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

By following the analogous procedure as above for **7**, using Et_2NH (1.90 mL) and $CHCl_3$ (1.20 mL), **8** was obtained after column chromatography (PE/EtOAc 80:20 to 70:30) as a white solid; yield: 1.29 g (95%); R_f = 0.49 (PE/EtOAc 80:20); mp 60–61 °C.

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

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (t, *J* = 7.1 Hz, 6 H, 2 × CH_2CH_3), 2.40 (s, 3 H, ArCH_3), 3.22 (q, *J* = 7.1 Hz, 4 H, CH_2Me), 7.27 (d, *J* = 8.3 Hz, 2 H, H3 and H5), 7.68 (d, *J* = 8.3 Hz, 2 H, H2 and H6).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 (2 × CH_3, Et), 21.6 (CH_3, ArCH_3), 42.1 (2 × CH_2, Et), 127.2 (2 × CH, C2 and C6), 129.7 (2 × CH, C3 and C5), 137.6 (C, C1, CSO_2N), 143.0 (C, C4).

Analytical data analogous to those reported previously.[34]

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

NaH (60% in mineral 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 anhyd THF (50 mL) under argon before being warmed to rt and stirred for 1 h. The reaction mixture was cooled to 0 °C, then MeI (965 µL, 2.20 g, 15.0 mmol, 3.00 equiv) and DMF (10 mL) were added. After addition, the reaction mixture was warmed to rt and stirred for 2 h. Sat aq NH_4Cl was added dropwise to the reaction mixture, which was then extracted with EtOAc. The combined organic layers were washed with H_2O, brine, dried ($MgSO_4$), filtered over cotton wool, and concentrated under vacuum to give the crude product. This was purified by column chromatography over silica gel using PE/EtOAc (80:20) to give the title product **3i-Me** as an orange solid; yield: 1.75 g (91%); R_f = 0.59 (PE/EtOAc 80:20); mp 128–129 °C; $[\alpha]_D$ +56.3 (*c* 0.01 in $CHCl_3$).

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, $CDCl_3$): δ = 1.28 (d, *J* = 7.0 Hz, 3 H,CHCH_3), 2.47 (s, 3 H, NCH_3), 4.37–4.39 (m, 2 H, H3 and H4), 4.43 (s, 5 H, Cp), 4.62 (quint, *J* = 1.2 Hz, 1 H, H2 or H5), 4.65 (quint, *J* = 1.2 Hz, 1 H, H2 or H5), 5.16 (q, *J* = 7.0 Hz, 1 H, C*H*Me), 7.23–7.25 (m, 1 H, H4′), 7.28–7.31 (m, 4 H, H2′, H3′, H5′, and H6′).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 15.2 (CH_3, CH_3CHPh), 28.3 (CH_3, NCH_3), 54.9 (CH, *C*HMe), 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 (5 × CH, Cp), 87.8 (C, C1, CSO_2N), 127.4 (2 × CH, C2′ and C6′), 127.5 (CH, C4′), 128.4 (2 × CH, C3′ and C5′), 140.4 (C, C1′).

(*R*)-*N*-Methyl-*N*-(1-phenylethyl)-2-(trimethylsilyl)ferrocenesulfonamide (9)[30]

*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 anhyd THF (6 mL) at –80 °C under argon. After addition, the reaction mixture was stirred at the same temperature for 1 h before Me_3SiCl (228 µL, 195 mg, 1.8 mmol, 1.50 equiv) was added. After addition, the mixture was warmed to rt and stirred for a further 15 min. Sat. aq NH_4Cl was added dropwise to the mixture, which was then extracted with EtOAc. The combined organic layers were washed with brine, dried ($MgSO_4$), filtered over cotton wool, and concentrated under vacuum to give the crude product. This was purified by column chromatography over silica gel using PE/EtOAc (10:1) to give the title product **9** (3.2:1 diastereoisomeric mixture) as an orange solid; yield: 345 mg (63%); 52% de; R_f = 0.70 (PE/EtOAc 10:1); mp 90–92 °C;$[\alpha]_D$ +136.6 (*c* 0.01 in $CHCl_3$).

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, * is used to spot the signals of the minor diastereoisomer.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.36 and 0.37* [s, 9 H, $FcSi(CH_3)_3$], 1.25 and 1.42* (d, *J* = 7.1 Hz, and d, *J* = 6.9 Hz, 3 H, respectively; CHCH_3), 2.46* and 2.51 (s, 3 H, NCH_3), 4.32–4.33* (m, 1 H, H3), 4.40* and 4.41 (s, 5 H, Cp), 4.53* and 4.54 (t, *J* = 2.4 Hz, 1 H, H4), 4.81* and 4.82 (dd, *J* = 2.3, 1.4 Hz, and dd, *J* = 2.2, 1.5 Hz, 1 H, respectively; H5), 5.13 and 5.18* (q, *J* = 7.1 Hz, and q, *J* = 6.9 Hz, 1 H, respectively; C*H*Me), 7.23–7.31* (m, 5 H, H2′, H3′, H4′, H5′, and H6′).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 1.1 and 1.2* [3 × CH_3, $Si(CH_3)_3$], 15.0 and 16.0* (CH_3, CH_3CHPh), 28.4 and 28.6* (CH_3, NCH_3), 54.2 and 54.6* (CH, *C*HMe), 70.9 and 71.0* (5 × CH, 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, CSO_2N), 127.5* and 128.4* (5 × CH, C2′, C3′, C4′, C5′ and C6′), 140.1* and 140.4 (CH, C1′).

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

10-TMS

*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 anhyd THF (8 mL) at –80 °C under argon. After addition, the reaction mixture was stirred at the same temperature for 1 h before Me_3SiCl (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. Sat. aq NH_4Cl was added dropwise to the mixture, which was then extracted with EtOAc. The combined organic layers were washed brine, dried ($MgSO_4$), filtered over cotton wool, and concentrated under vacuum to give the crude product. This was purified by column chromatography over silica gel using PE/EtOAc (15:1). The title product **10-TMS** (2.8:1 diastereoisomeric mixture) was isolated as an orange solid; yield: 427 mg (69%); 48% de; R_f = 0.66 (PE/EtOAc 15:1); mp 127–130 °C; $[\alpha]_D$ +111.2 (*c* 0.01 in $CHCl_3$).

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, * is used to spot the signals of the minor diastereoisomer.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.11* and 0.14 [s, 9 H, $NSi(CH_3)_3$], 0.30* and 0.31 [s, 9 H, $FcSi(CH_3)_3$], 1.17 and 1.73* (d, *J* = 7.2 Hz, and d, *J* = 6.9 Hz, 3 H, respectively, CHCH_3), 4.28* and 4.33 (dd, *J* = 2.4, 1.4 Hz, 1 H, H3), 4.42* and 4.42 (s, 5 H, Cp), 4.55 and 4.57* (t, *J* = 2.4 Hz, 1 H, H4), 4.59* and 4.69 (q, *J* = 6.9 Hz, and q, *J* = 7.2 Hz, 1 H, respectively; C*H*Me), 4.79 and 4.92* (dd, *J* = 2.4, 1.4 Hz, and dd, *J* = 2.3, 1.4 Hz, 1 H, respectively, H5), 7.01* and 7.48 (d, *J* = 7.5 Hz and d, *J* = 8.1 Hz, 2 H, respectively, H2′ and H6′), 7.10–7.12* and 7.30 (m and t, *J* = 7.5 Hz, 2 H, respectively, H3′ and H5′), 7.10–7.12* and 7.22 (m and t, *J* = 7.5 Hz, 1 H, respectively, H4′).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 1.1* and 1.1 [3 × CH_3, $FcSi(CH_3)_3$], 3.1* and 3.2 [3 × CH_3, $NSi(CH_3)_3$], 18.3 and 20.2* (CH_3, CH_3CHPh), 53.7 and 54.0* (CH, *C*HMe), 70.9 and 71.0* (5 × CH, 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, CSO_2N), 126.7* and 127.2 (2 × CH, 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′).

10-H

The title product **10-H** (1.7:1 diastereoisomeric mixture) was similarly isolated as an orange oil; yield: 59.0 mg (11%); 26% de; R_f = 0.15 (PE/EtOAc 15:1); $[\alpha]_D$ +43.7 (*c* 0.01 in $CHCl_3$).

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, * is used to spot the signals of the minor diastereoisomer.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.28 and 0.37* [s, 9 H, $FcSi(CH_3)_3$], 1.29* and 1.46 (d, *J* = 6.9 Hz, and d, *J* = 6.7 Hz, 3 H, respectively; CHCH_3), 4.23 and 4.33–4.34* (dd, *J* = 2.4, 1.4 Hz, and m, 1 H, respectively, H3), 4.34 and 4.38* (s, 5 H, Cp), 4.41* and 4.46 (quint, *J* = 7.3 Hz, and quint, *J* = 6.7 Hz, 1 H, respectively; C*H*Me), 4.33–4.34 and 4.50* (m

and t, J = 2.4 Hz, 1 H, respectively, H4), 4.58 and 4.81* (dd, J = 2.3, 1.5 Hz, and dd, J = 2.2, 1.4 Hz, 1 H, respectively, H5), 7.00–7.02 and 7.22–7.25* (m, 2 H, H2′ and H6′), 7.15–7.19 and 7.22–7.25* (m, 1 H, H4′), 7.15–7.19 and 7.28–7.32* (m, 2 H, H3′ and H5′).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 0.8 and 1.0* [3 × CH_3, FcSi(CH_3)$_3$], 23.2* and 24.0 (CH_3, CH_3CHPh), 53.2* and 53.6 (CH, *C*HMe), 70.8 and 70.9* (5 × CH, 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, CSO_2N), 126.3 and 126.3* (2 × CH, 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′).

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

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