The Search for Benchrotrenes and Ferrocenes Containing a Chiral Sulfoximido Group: Preparation and Structural Properties

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Dedicated to Professor Dr. Ch. Elschenbroich (Marburg) on the occasion of his 60th birthday

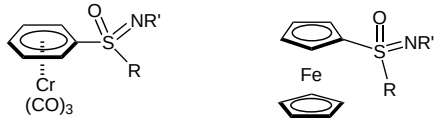
Abstract: Syntheses of chiral benchrotrene and ferrocene complexes bearing *N*-protected sulfonimidoyl moieties are reported. They are obtained by metal-catalyzed imination reactions starting from enantiopure sulfoxides. An X-ray structure analysis was carried out for one of the novel complexes confirming the stereospecificity of the imination process.

Key words: sulfoximines, imination of sulfoxides, metal catalysis, chromium transition metal complexes, iron transition metal complexes

Introduction

The synthesis of chiral ferrocene and benchrotrene complexes is of ongoing interest in organometallic chemistry because these compounds have found various applications in organic synthesis, catalytic processes and material sciences.[1] A few years ago, we initiated a program that focussed on the use of bidentate sulfoximines as chiral ligands for metal complexes, and we began to investigate their applications in several asymmetric catalytic transformations.[2,3]

In the course of these studies we became aware that sulfoximines containing an organometallic π-complex as backbone were unknown and thus decided to investigate the preparation of such compounds. For benchrotrenes and ferrocenes of such type, the respective target structures **A** and **B** are depicted in Figure 1. In this feature article we report on our recent results in this area.



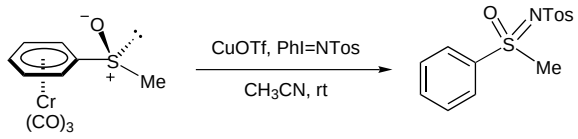
A **B**

Figure 1

Synthesis of Benchrotrenyl Sulfoximines

Tricarbonyl(η^6-arene)chromium(0) complexes became our prime targets because complexes like **A** were expected to be accessible from direct complexation of the respective aryl sulfoximines. However, despite numerous attempts to achieve this transformation including the use of hexacarbonyl chromium(0), tricarbonyl trisacetonitrilochromium(0) and tricarbonyl(η^6-naphthalene)chromium(0) (Kündig's reagent) as $Cr(CO)_3$ source, no products resulting from complexation were ever isolated. Only in a single case, when the thermal complexation of *N*,*S*-dimethyl *S*-phenyl sulfoximine and $Cr(CO)_6$ was stopped after a reaction time of 7 hours, traces of the expected product could be detected in the crude proton NMR spectrum. Similar observations have been reported by Gibson (née Thomas) who found that the direct complexation of alkylsulfinyl arenes in the presence of the mentioned tricarbonylchromium(0) sources gave the desired chromium complexes in yields of only 0–4%.[4] Here, the respective tricarbonyl(alkylsulfanyl-η^6-arene)chromium(0) complexes had to be generated from the alkylsulfanyl precursors by oxidation with dimethyldioxirane[4] or Kagan's modified Sharpless reagent.[5] Interestingly, the corresponding sulfonyl complexes could be obtained by the usual complexation procedure without any difficulty.[6]

After these unsuccessful attempts of direct sulfoximine complexation we decided to change strategy and to focus on iminations of known alkylsulfinyl-substituted arene chromium complexes. In particular, our attention was turned towards two recent procedures for copper(I)-catalyzed imination reactions of aromatic sulfides[7] and sulfoxides.[8] However, employing the conditions described for the conversion of sulfoxides into sulfoximines by use of copper(I) triflate, imination of tricarbonyl(methyl η^6-phenyl sulfoxide)chromium(0) (**1**)[5] led to green and cloudy reaction mixtures within seconds after the addition of the first portion of *N*-(*p*-toluenesulfonyl)iminophenyl-λ^3-iodane indicating an oxidative decomposition of the starting material by the hypervalent iodine. In accordance with this assumption, the product, which was isolated from this reaction after the usual workup, was identified as the uncomplexed sulfoximine **2** (Scheme 1).



1 **2**

Scheme 1

Biographical Sketches

Carsten Bolm was born in Braunschweig in 1960. He studied chemistry at the universities in Braunschweig and Madison, Wisconsin, and obtained his doctorate in 1987 under the guidance of Prof. Reetz in Marburg. After postdoctoral studies at MIT, Cambridge, with Prof. Sharpless, he worked in Basel with Prof. Giese to obtain his habilitation. In 1993 he became Professor of Organic Chemistry at the University of Marburg, and since 1996 he is full professor of Organic Chemistry at the RWTH Aachen. His awards include the Heinz-Maier-Leibnitz prize, the ADUC-Jahrespreis for habilitands, the annual prize for Chemistry of the Akademie der Wissenschaften zu Göttingen, the Otto-Klung prize, and the Otto-Bayer award.

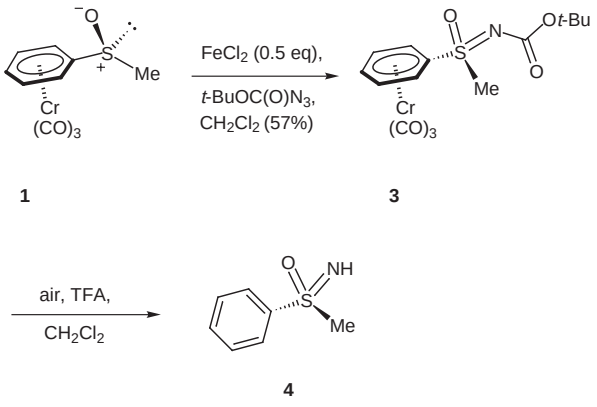
Kilian Muñiz was born in Hildesheim in 1970. He studied chemistry at the Universität Hannover (Germany), at Imperial College, London (UK) and at the Universidad de Oviedo (Spain) to obtain his Diploma in Chemistry in 1996. From 1996 to 1998 he worked on his PhD in the group of Prof. Bolm at the RWTH Aachen (Germany). Currently, he is a postdoctoral fellow with Prof. Noyori at Nagoya University (Japan). His research interests are in the area of organometallic chemistry with special focus on the synthesis of enantiomerically pure complexes and their behaviour in asymmetric transformations.

Núria Aguilar was born in Barcelona in 1971. She studied Chemistry at Universitat de Barcelona (Spain) and received her BSc and MSc degrees from this university in 1994 and 1995, respectively. Since 1995 she has been working in the group of Prof. Pericàs where she focussed on the stereoselective synthesis of chiral amino alcohols. During fall 1998 she joined the group of Prof. Bolm at the RWTH Aachen (Germany) as an exchange student. She was awarded her PhD earlier this year and is currently holding an academic position at the Organic Department of the Universitat de Barcelona.

Martin Kesselgruber was born in Mistelbach (Austria) in 1974. He studied Chemistry at the University of Technology Vienna (Austria) and received his MSc degree in 1998 under the guidance of Prof. Jordis. Currently he is carrying out his PhD studies within the research group of Prof. Bolm on the preparation of ferrocenyl sulfoximines and their application in asymmetric catalysis.

Gerhard Raabe was born in Obrighoven (Germany) in 1950. He studied chemistry and received his degrees from the RWTH Aachen (Diploma 1980, Dr.rer.nat. 1984, both with Prof. Fleischhauer). During a postdoctoral stay (1984/1985) with Prof. Michl at the University of Utah in Salt Lake City (USA) he worked on the matrix isolation of highly reactive silicon compounds. After additional postdoctoral work with Prof. Fleischhauer he left for a brief sojourn in industry (1987/1988). Since 1989 he is in charge of the X-ray structure division of the Department of Organic Chemistry at the RWTH Aachen. Working in the field of theoretical organic solid state chemistry he finished his Habilitation in 1998. His research interests concern various aspects of theoretical chemistry especially the structure of and the bonding in organic molecular crystals.

Imination of enantiomerically enriched complex **1** was finally achieved following a recent protocol by Bach and Körber who recommended the use of iron(II) chloride and *t*-butyloxycarbonyl azide.[9] Under modified reaction conditions sulfonimidoyl complex **3** was obtained in 67% chemical yield (Scheme 2).



1 **3** **4**

Scheme 2

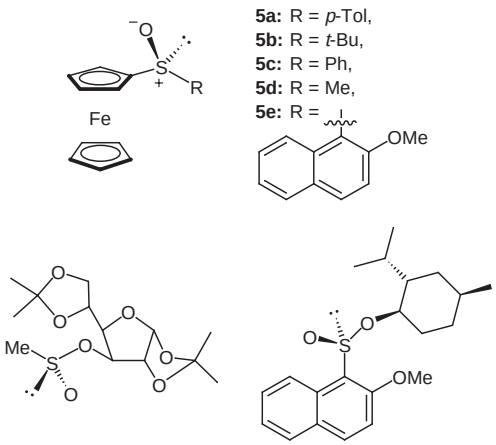
As expected, in the proton NMR spectrum the diastereotopic *ortho*-hydrogens can clearly be identified by their significant downfield shifts to δ = 5.80 and 4.98. This is in agreement with the data of the parent sulfoxide complexes for which comparable shifts were observed.[4,10]

In order to determine the stereochemical path of the imination of **2**, complex **3** was transformed into known *S*-methyl *S*-phenylsulfoximine (**4**) by one-pot treatment with iodine/air and TFA in order to remove both the chromium moiety and the Boc group simultaneously. GC-analysis of **4** revealed that the imination had been stereospecifically indeed.

Synthesis of Ferrocenyl Sulfoxides

Because direct complexation of sulfoximido precursors is not feasible in the case of ferrocenyl sulfoximines, sulfoxide imination occurred as the route of choice. Enantiopure ferrocenes **5a–d** were synthesized according to literature protocols from Kagan, Riant and co-workers employing either Kagan's asymmetric oxidation of the corresponding ferrocenyl sulfides[11] or reaction of lithio ferrocene with the respective diastereomerically pure sulfinyl precursors.[12] Application of an alternative system for enantioselective sulfide oxidation as recently reported from our laboratories[13] gave ferrocenyl methyl sulfoxide (**5d**) with only 39% *ee*. A very convenient route towards enantiopure **5d** was finally developed starting from the two methylsulfinates of diacetone-D-glucose which are readily accessible in diastereomerically pure form.[14] Thus, reaction of **6** having *S*-configuration at sulfur with in situ-generated ferrocenyl lithium yielded **1d** with 90% enantiomeric excess in 65% chemical yield. Consequently, use of (*R*)-**6** gave access to (*R*)-configurated ferrocenyl methyl sulfoxide (78% yield, 93% *ee*).

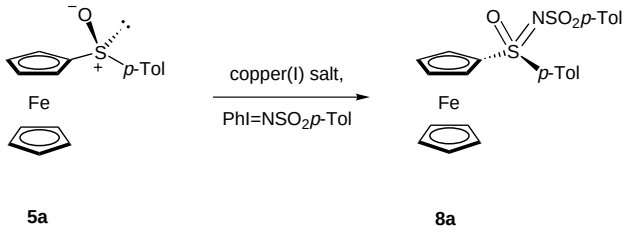
The novel ferrocenyl (2-methoxynaphthyl) sulfoxide (**5e)** was obtained in a similar fashion from the diastereomerically pure sulfinyl **7**.[15]



(*S*)-**6** **7**

Synthesis of Ferrocenyl Sulfoximines

At first, the synthesis of ferrocenylsulfoximines was attempted employing the well-studied *O*-mesitylensulfonylhydroxylamine (MSH) reagent,[16] but this procedure did not lead to the formation of any sulfoximine from the corresponding sulfoxide, and only starting material was isolated from the reaction mixture. Consequently, attention was again turned towards the mentioned copper triflate catalyzed imination[8] since it was assumed that in the case of ferrocenyl sulfoxides no oxidative decomposition should occur. Thus, ferrocene **5a** was submitted to imination, but under literature conditions the conversion remained very low. However, by changing the copper salt to Cu(I)PF_6 and by careful optimization of the reaction conditions, an increase in chemical yield was achieved. Representative data are summarized in Table 1.

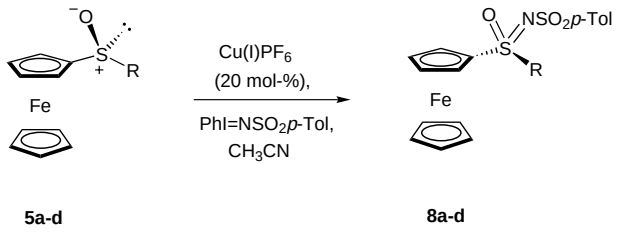


5a **8a**

Scheme 3

Subsequently, ferrocenyl sulfoxides **5a–d** were submitted to imination under the optimized reaction conditions using 20 mol% of Cu(I)PF_6 as catalyst and *N*-(*p*-toluene-

sulfonyl)iminophenyl-λ³-iodane as nitrene source in acetonitrile (Table 2).



Scheme 4

Table 1 Copper(I)-catalyzed[a] imination of ferrocenyl sulfoxide **5a**

Entry	Metal catalyst (mol %)	Solvent	Reaction Time [h]	Chemical Yield [%][c]
1	CuOTf[a] (5)	Toluene	50	8[d]
2	$CuPF_6$[b] (5)	Toluene	47	10[d]
3	$CuPF_6$ (5)	CH_3CN	46	20[d]
4	$CuPF_6$ (20)	CH_3CN	49	58

[a] $CuOTf(C_6H_6)_{0.5}$.
[b] $CuPF_6(CH_3CN)_4$.
[c] Isolated after column chromatography and/or recrystallization.
[d] As determined from the ^1H NMR spectrum of the crude reaction mixture.

Table 2 Copper(I)-catalyzed imination of ferrocenyl sulfoxides **5a**–**d**

Entry	Ferrocene	Rest R	Product	Reaction Time [h]	Chemical Yield [%][b]
1	**5a**	*p*-Tolyl	**8a**	49	53
2	**5b**	*t*-Butyl	**8b**	44	46
3	**5c**	Phenyl	**8c**	39	51
4	**5d**	Methyl	**8d**	53	43

[a] $CuPF_6(CH_3CN)_4$.
[b] Isolated after column chromatography and/or recrystallization.

All ferrocenyl sulfoximines prepared by this modified imination procedure are air-stable, orange to brownish solids, which can easily be separated from unreacted ferrocenyl sulfoxides by column chromatography. No ferrocene-containing byproducts were detected and chemical yields are nearly quantitative based on the amounts of recovered starting material. On the other hand, neither a higher catalyst loading nor carrying out the reaction at higher reaction temperature led to an improvement in conversion.

The solid state structure of complex **8b** is shown in Figure 2.[17] In **8b**, the absolute configuration at sulfur S1 was determined to be *S*, which is in agreement with a stereospecific imination under retention of configuration as already described for the original catalytic system.[8]

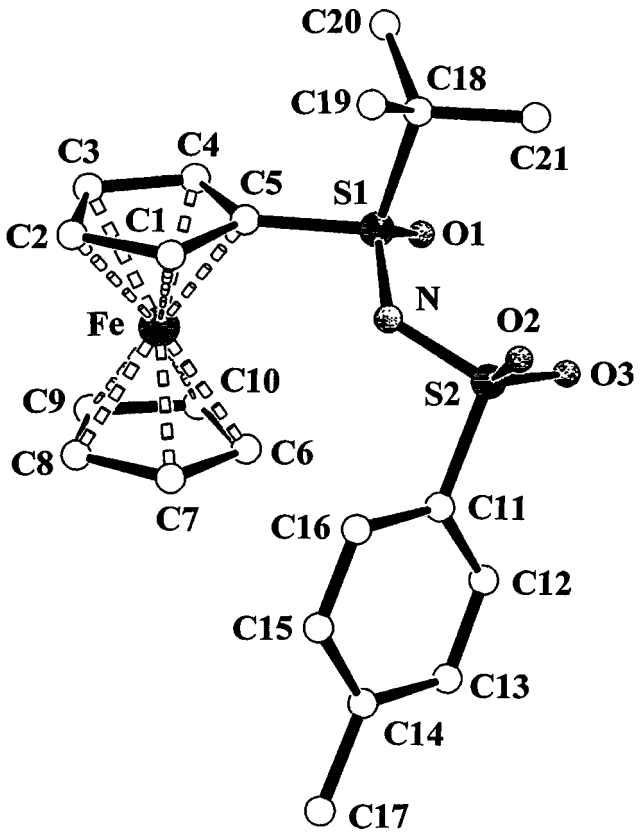


Figure 2 Selected bond lengths (Å) and angles (°) for **8b**: S1–C5 1.734(7), S1–O1 1.443(4), S1–C18 1.825(7), S1–N 1.542(5), N–S2 1.602(5), O1–S1–C5 109.7(3), O1–S1–C18 108.0(3), C5–S1–C18 105.4(3), O1–S1–N 120.8(2).

It is interesting to compare the structural features of this compound to those of related ferrocenyl sulfoxides.[12b,18] Apparently, the geometry around the sulfur atom and the bond lengths between the sulfur and the two attached carbon atoms are not altered significantly by the introduction of the imido moiety.

Moreover, as for all new compounds **8a–d** the proton NMR spectrum of **8b** contains two signals for either *ortho*-hydrogen on the substituted ferrocene ring displaying the diastereotopicity of these hydrogens. While the chemical shift of δ = 4.77 for the pro-S_p-hydrogen is only slightly changed relative to the δ = 4.69 in the parent ferrocenyl sulfoxide, the second *ortho*-hydrogen experiences a significant downfield shift from δ = 4.35 in **5b** to δ = 4.59 in **8b**. Such a displacement can be rationalized by the proximity of this hydrogen to the newly introduced imido group.

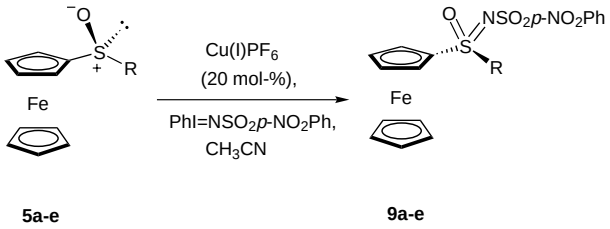
The imination of ferrocenyl sulfoxides can also be carried out employing *N*-(*p*-nitrophenylsulfonyl)iminophenyl-λ³-iodane as the nitrogen source. So far, examples for the use of this hypervalent iodane in catalytic transformation are still rare,[19,20] and to date none has been reported for the conversion of sulfides or sulfoxides.

Table 3 Copper(I)-catalyzed imination of ferrocenyl sulfoxides **5a–e**

Entry	Ferrocene	Rest R	Product	Reaction Time [h]	Chemical Yield [%][b]
1	**5a**	*p*-Tolyl	**9a**	41	69
2	**5b**	*t-Butyl*	**9b**	55	62
3	**5c**	Phenyl[a]	**9c**	48	66
4	**5d**	Methyl	**9d**	64	68
5	**5e**	2-Methoxy-naphthyl	**9e**	61	74

[a] Racemic material was used.
[b] Isolated after column chromatography and/or recrystallization.

The results for the synthesis of the *N*-nosyl-protected ferrocenylsulfoximines are given in Table 3.



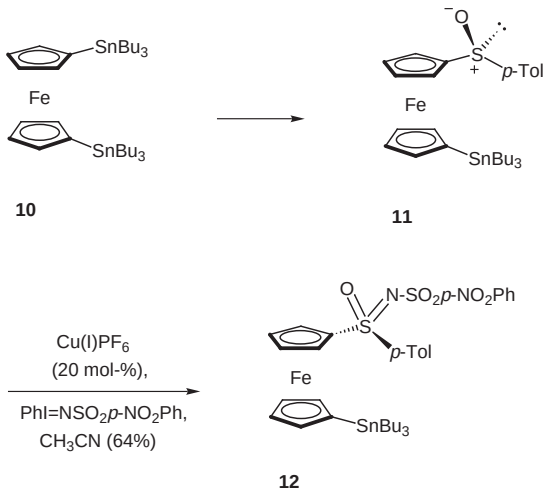
5a-e **9a-e**

Scheme 5

It is notable that this process of imidonosylation gives higher yields as in comparable cases where the tosyl precursor is employed. Such behavior has already been observed by Andersson in Cu-catalyzed aziridinations of alkenes.[19a]

Again, the product ferrocenes **9a–e** are air-stable, light yellow to orange solids that are generated without formation of ferrocene-containing byproducts. Their spectroscopic properties are similar to those of the tosyl derivatives including the distinct diastereotopicity of the *ortho*-hydrogens as clearly observed in the proton NMR spectra. For example, significant downfield shifts to δ = 4.79 and δ = 4.62 for the two *ortho*-protons of complex **9b** were detected.

Next, we wondered about a 1,1'-substitution pattern on the ferrocene. Such functionalization should allow future incorporation of ferrocenyl sulfoximines into dendritic structures or polymers via the "lower" cyclopentadienyl ring.[21,22] A tributyltin moiety was considered suitable for this purpose and thus, (1'-tributyltinferrocenyl)sulfoximine (**11**) was synthesized by transmetalation of 1,1'-bis(tributyltin)ferrocene (**10**) with 1.1 equiv. of butyllithium[23] followed by reaction of the resulting monolithiated complex with (–)-menthyl-(*S*)-*p*-tolyl sulfinate (Andersen's reagent[12c, 24]) to give sulfoxide **11** in excellent yield. Imination of this compound employing the conditions described above furnished sulfoximine **12** in the good chemical yield of 64% which is comparable to that of the 1'-unsubstituted complex **9a**.



Scheme 6

Unfortunately, compound **12** proved unstable during purification. Even when stored under argon partial decomposition occurred.

In summary, we have described the syntheses of the first enantiopure sulfoximines bearing benchrotrenyl and ferrocenyl backbones. We are currently investigating the removal of the *N*-protecting groups,[25] the incorporation of the ferrocenyl sulfoximido moiety into catalyst systems,[2] and we try to generate planar chiral derivatives starting from the *N*-protected ferrocenyl sulfoximines.[26,27]

All manipulations except workup and purification steps were performed in oven-dried glass ware under Ar using common Schlenk techniques. Chromium hexacarbonyl, ferrocene, butyllithium and tributyltin chloride were obtained from Merck-Schuchardt and used as received. Copper(I) triflate and copper(I) hexafluorophosphate were purchased from Aldrich and stored under Ar. THF, hexane, dibutyl ether and toluene were distilled from sodium/benzophenone ketyl radical under Ar. CH_2Cl_2 was distilled from CaH_2 under Ar. All other solvents were reagent grade and used as received. Sulfoxide complexes **1** and **5a–c** were obtained following literature protocols.[5,11,12] (*R*)- and (*S*)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosylmethanesulfinate,[14] (–)-menthyl-(*S*)-(2-methoxynaphthyl)sulfinate,[15] (–)-menthyl-(*S*)-(*p*-tolyl)sulfinate,[24] *N*-(*p*-toluenesulfonyl)iminophenyl-λ^3-iodane,[30] *N*-(*p*-nitrophenylsulfonyl)iminophenyl-λ^3-iodane[30] and *t*-butyloxycarbonyl azide[9] were synthesized according to literature protocols.

If not stated otherwise, "standard workup" refers to quenching the mixture with distilled water, followed by extraction with CH_2Cl_2 and washing of the organic layer with brine and water followed by drying of the combined organic phases with anhyd $MgSO_4$.

^{1}H NMR spectra were recorded at 300 MHz and chemical shifts are reported in ppm with internal referencing to TMS. Splitting pattern are designated as s (singlet), d (doublet), t (triplet), m (multiplet). ^{13}C NMR spectra were recorded at 75 MHz and chemical shifts are reported in ppm with internal referencing to TMS. Generally, spectra were recorded in $CDCl_3$; other solvents were used as indicated. Optical rotations were measured at r.t. Elemental analyses and HRMS were carried out at the Institutes of Organic and Inorganic Chemistry at RWTH Aachen, respectively. All new syntheses were

repeated at least twice in order to ensure reproduceability. Given yields are average values.

(*S*)-Methyl-(*S*)-phenyl-(*N*-*p*-tolylsulfonylsulfoximine (2)

A solution of (*S*)-tricarbonyl[methyl η^6-phenyl sulfoxide]chromium(0) (**1**) (106 mg, 0.384 mmol) and copper(I) triflate (28.5 mg, 0.077 mmol) in freshly distilled MeCN (10 mL) was treated portionwise with *N*-(*p*-toluenesulfonyl)iminophenyl-λ^3-iodane (172 mg, 0.461 mmol). The mixture was stirred for 2 days and the progress was monitored by tlc which showed complete consumption of starting material. Standard workup and purification by column chromatography (silica gel, Et_2O) gave the title compound (69.6 mg, 0.273 mmol, 71% yield) as a yellowish solid.

^{1}H NMR: δ = 2.37 (s, 3H); 3.40 (s, 3H); 7.22–7.29 (m, 2H); 7.55–7.58 (m, 2H); 7.65–7.69 (m, 1H); 7.81–7.83 (m, 2H); 7.96–7.98 (m, 2H).

^{13}C NMR: δ = 21.60; 46.60; 126.68; 127.51; 129.38; 129.80; 134.51; 138.26; 140.71; 142.98.

(*S*)-Tricarbonyl[η^6-*N*-*tert*-butyloxycarbonyl-*S*-methyl-*S*-phenylsulfoximine]chromium(0) (3)

In a well-dried Schlenk tube under Ar, **1** (200 mg, 0.72 mmol) and $FeCl_2$ (46 mg, 0.36 mmol) were dissolved in freshly distilled CH_2Cl_2 (10 mL) and stirred at r.t. *t*-Butyloxycarbonyl azide (115 mg, 0.796 mmol) was added dropwise and the mixture was stirred at r.t. for 29 h while the progress was monitored by tlc. Standard workup and column chromatography [silicagel, Et_2O, then Et_2O/MeOH (70/30)] gave a first fraction containing the title complex and a second containing unreacted starting material. After removal of the solvent, the title complex was obtained in form of a yellow solid [189 mg, 0. 483 mmol, 67% yield (98% based on recovered starting material)]. In order to avoid decomposition, the solid product was stored under argon at –24°C.

$[\alpha]_D$ = –33 (*c* = 0.35, CH_2Cl_2).

^{1}H NMR (C_6D_6): δ = 1.07 (s, 9H); 2.75 (s, 3H); 3.88–3.94 (m, 2H); 4.34–4.38 (m, 1H); 4.97–4.99 (m, 1H); 5.79–5.81 (m, 1H).

^{13}C NMR (C_6D_6): δ = 14.98; 27.54; 42.86; 85.54; 85.68; 91.33; 94.44; 94.60; 107.88; 229.46.

MS (EI, 70 eV): *m/z* (%) = 335 (M^+ – 2 CO, 4), (307 M^+ – 3 CO, 7), 251 (7), 200 (25), 182 (100), 156 (20), 124 (115), 94 (35), 77 (21), 57 (33).

IR (KBr): $\tilde{\nu}$ = 3019, 2978, 1984, 1966, 1920, 1895, 1659, 1367, 1307, 1279, 756 cm^{-1}.

(*S*)-*S*-Methyl-*S*-phenylsulfoximine (4)

A solution of **3** (160 mg, 0.41 mmol) in CH_2Cl_2 (10 mL)was treated with trifluoroacetic acid (1.0 mL) and exposed to air. After 4 hours, a small amount of iodine was added directly and the mixture was stirred for a further 28 h. The crude mixture was filtered through a pad of Kieselgur and diluted with H_2O. Subsequent acid/base extraction afforded a colourless solid (29.3 mg, 0.189 mmol, 46% yield).

^{1}H NMR: δ = 2.75 (s, 3H); 7.46–7.57 (m, 3H); 7.62–7.67 (m, 2H).

The enantiomeric excess of the product sample derived from **1** (ca. 90% *ee*[5]) was 89% and was determined by GC on chiral phase employing a Lipodex E column (50 m × 0.25 mm). Oven temperature: 160°C (isothermic); head column pressure: 75 kPa N_2; retention times: 54.15 min (*S*-enantiomer), 50.47 min (*R*-enantiomer).

(*S*)-*S*-Ferrocenyl *S*-Methyl Sulfoxide (5c)

Procedure A

Titanium tetraisopropoxide (15 μL; 0.05 mmol) was added to a solution of (*S*,*S*)-4,4'-bis(3-hydroxy-estra-1,3,5(10),6,8-pentane) (50 mg, 0.1 mmol) in 2.5 mL of freshly distilled THF under argon. The deep red solution was stirred for 5 min at r.t. before distilled H_2O (27 μL, 1.5 mmol) was added. After stirring for 55 min, ferrocenyl methyl sulfide (100 mg, 0.5 mmol) was added and stirring was continued for 30 min before the mixture was cooled to 0°C. At this temperature, a solution of TBHP (70% in H_2O, 75 μL, 0.55 mmol) was added and the mixture was stirred for 22.5 h before it was submitted to standard workup. The crude product was purified by column chromatography [silica gel, EtOAc/hexanes (70/30), then EtOAc, then THF] to yield the title compound in form of a dark highly viscous oil (94.0 mg, 0. 435 mmol, 87% yield).

Procedure B

A solution of ferrocenyl tributylstannane (663 mg, 1.395 mmol) in freshly distilled THF (20 mL) at –78°C was treated dropwise with BuLi (0.97 mL, 1.6M in hexane, 1.55 mmol). The mixture was stirred for 45 min and then transferred dropwise via cannula into a second solution of (*S*)-**6** (500 mg, 1.55 mmol) in freshly distilled THF (20 mL) at –78°C. The resulting yellow solution was maintained at –78°C for 10 min before quenching. Standard workup and column chromatography [silica gel, hexanes/*i*-PrOH (90/10)] afforded the title complex (250 mg, 1.01 mmol, 65.3% yield) in form of an orange solid. HPLC revealed an enantiomeric excess of 90%. The product could be recrystallized from hexane at r.t. to yield the title complex with 96% *ee*.

^{1}H NMR: δ = 2.76 (s, 3H); 4.35 (s, 5H); 4.35–4.49 (m, 3H); 4.69–4.72 (m, 1H).

^{13}C NMR: δ = 42.34; 66.06; 66.36; 69.85; 70.09; 70.16; 93.01.

The enantiomeric excess of the respective product samples was determined by chiral HPLC on solid phase employing a Daicel CHIRACEL OD-H column. Eluent: hexane/i-PrOH (97/3); flow rate: 0.4 $mLmin^{-1}$; retention times: 127.5 (*S*-enantiomer), 137.5 (*R*-enantiomer).

(*S*)-Ferrocenyl (2-Methoxy)naphthyl Sulfoxide (5e)

A solution of ferrocenyl tributylstannane (760 mg, 1.60 mmol) in freshly distilled THF (10 mL) at –78°C was treated dropwise with BuLi (1.00 ml, 1.60 mmol, 1.6 M solution in hexane). The mixture was stirred for 45 min and then transferred dropwise via cannula into a second solution of (–)-menthyl-(*S*)-(2-methoxynaphthyl)sulfinate (550 mg, 1.52 mmol) in freshly distilled THF (20 mL) at –78°C. The resulting yellow solution was maintained at –78°C for 2 h before warmed to –40°C over a period of 4 h. Standard workup and column chromatography [silica gel, Et_2O/hexanes (70/30)] afforded the title complex (512 mg, 1.31 mmol, 86% yield) in form of a yellow solid.

$[\alpha]_D$ = +297 (*c* = 0.3, CH_2Cl_2).

^{1}H NMR: δ = 4.00 (s, 3H); 4.14–4.19 (m, 2H); 4.32 (s, 5H); 4.33–4.37 (m, 1H); 4.98–5.00 (m, 1H); 7.20 (d, *J* = 9.1 Hz, 1H); 7.32–7.39 (m, 1H); 7.46–7.53 (m, 1H); 7.76 (dd, *J* = 0.8, 8.3 Hz, 1H); 7.88 (d, *J* = 9.1 Hz, 1H); 8.98 (d, *J* = 8.8 Hz, 1H).

^{13}C NMR: δ = 56.57; 67.24; 67.71; 69.21; 69.46; 69.56; 91.76; 112.58; 123.71; 124.06; 127.18; 128.01; 128.29; 129.90; 131.35; 133.74; 155.57.

MS (EI, 70 eV): *m/z* (%) = 392 (M+2, 8), 392 (M+1, 25), 390 (M^+, 100), 324 (37), 295 (25), 233 (28), 121 (29).

IR (KBr): $\tilde{\nu}$ = 1617, 1589, 1504, 1464, 1427, 1333, 1270, 1248, 1150, 1046, 1021, 816, 751 cm^{-1}.

Anal. $C_{21}H_{18}FeO_2S$ (390.27): calcd C, 64.63; H, 4.65; found C, 64.63; H, 4.80.

General Procedure for the Imination of Ferrocenyl Sulfoxides 5a–d by Means of Hypervalent *N*-(*P*-Toluenesulfonyl)iminophenyl-λ³-iodane

The ferrocenyl sulfoxide and the copper catalyst were placed in a dry schlenk flask under Ar and were dissolved in freshly distilled MeCN (10 mL per mmol of substrate). The solution was stirred at r.t. while *N*-(*p*-toluenesulfonyl)iminophenyl-λ³-iodane (1.2 mmol per 1 mmol of substrate) was added in small portions over a period of 2 h. The mixture was then sealed and stirred at r.t. Conversion was monitored by tlc and after 48–60 h the mixture was filtered through a G3 frit followed by standard workup.

The crude mixtures were purified as stated below.

(*S*)-*N*-*p*-Tolylsulfonyl-*S*-*p*-tolyl-*S*-ferrocenylsulfoximine (8a)

Following the general procedure detailed above, (*S*)-*S*-ferrocenyl *S*-*p*-tolyl sulfoxide **5a** (549 mg, 1.695 mmol) was reacted with *N*-(*p*-toluenesulfonyl)iminophenyl-λ³-iodane (697 mg, 1.87 mmol) in the presence of copper(I) hexafluorophosphate (126 mg, 0.339 mmol). Purification by column chromatography (silica gel, CH_2Cl_2) yielded the title complex (443 mg, 0.899 mmol, 53% yield) in form of an orange solid. Recrystallization from hexane/Et_2O afforded a light brown solid.

$[\alpha]_D$ = –245 (c = 0.4, CH_2Cl_2).

^{1}H NMR: δ = 2.37 (s, 3H); 2.38 (s, 3H); 4.29 (s, 5H); 4.37–4.39 (m, 1H); 4.41–4.45 (m, 1H); 4.50–4.53 (m, 1H); 4.90–4.92 (m, 1H); 7.23–7.26 (m, 4H); 7.75–7.79 (m, 2H); 7.88–7.91 (m, 2H).

^{1}H NMR (C_6D_6): δ = 1.48 (s, 3H); 1.55 (s, 3H); 3.42–3.44 (m, 1H); 3.52–3.55 (m, 1H); 3.83 (s, 3H); 4.05–4.06 (m, 1H); 4.51–4.53 (m, 1H); 6.41 (d, *J* = 8.3 Hz, 2H); 6.54 (d, *J* = 8.2 Hz, 2H); 7.74 (d, *J* = 8.3 Hz, 2H); 8.27 (d, *J* = 8.2 Hz, 2H).

^{13}C NMR (C_6D_6): δ = 21.21; 21.26; 67.48; 70.01; 70.73; 71.03; 71.32; 90.59; 126.29; 126.81; 128.84; 129.58; 138.33; 141.24; 142.14; 143.89.

MS (EI, 70 eV): *m/z* (%) = 493 (M, 100), 428 (91), 91 (42).

IR (KBr): $\tilde{\nu}$ = 1318, 1242, 1151, 1090, 1061, 547 cm^{-1}.

Anal. $C_{24}H_{23}FeNO_3S_2$ (493.42): calcd C, 58.42; H, 4.70; N, 2.84; found C, 58.35; H, 4.78; N, 2.55.

(*S*)- *S*-*t*-Butyl-*S*-ferrocenyl-*N*-*p*-tolylsulfonylsulfoximine (8b)

Following the general procedure detailed above, (*S*)-*S*-*t*-butyl *S*-ferrocenyl sulfoxide (**5b)** (234 mg, 0.77 mmol) was reacted with *N*-(*p*-toluenesulfonyl)iminophenyl-λ³-iodane (317 mg, 0.85 mmol) in the presence of copper(I) hexafluorophosphate (68 mg, 0.154 mmol). Purification by column chromatography [silica gel, CH_2Cl_2/acetone (95/5)] yielded the title complex (162 mg, 0.35 mmol, 46% yield) in form of a yellow to orange solid.

Suitable crystals of complex **22** for X-ray structure determination were grown from a solution in CH_2Cl_2/hexane at r.t.

$[\alpha]_D$ = –189 (c = 0.15, CH_2Cl_2).

^{1}H NMR: δ = 1.25 (s, 9H); 2.40 (s, 3H); 4.42 (s, 5H); 4.49–4.50 (m, 2H); 4.57–4.61 (m, 1H); 4.75–4.80 (m, 1H); 7.26–7.30 (m, 2H); 7.95–7.98 (m, 2H).

^{13}C NMR: δ = 21.20; 23.24, 64.84; 69.07; 70.89; 72.55; 85.05; 126.07; 126.13; 128.89; 141.79; 141.83.

MS (EI, 70 eV): *m/z* (%) = 459 (M, 1), 264 (48), 210 (66), 97 (83), 91 (100), 57 (88).

IR (KBr): $\tilde{\nu}$ = 1302, 1233, 1151, 1115, 1090, 545 cm^{-1}.

Anal. $C_{21}H_{25}FeNO_3S_2$ (459.41): calcd C, 54.90; H, 5.48; N, 3.05; found C, 54.75; H, 5.52; N, 3.05.

(*S*)-*S*-Ferrocenyl-*S*-phenyl-*N*-*p*-tolylsulfonysulfoximine (8c)

Following the general procedure detailed above, (*S*)-*S*-ferrocenyl-*S*-phenyl sulfoxide **5c** (85 mg, 0.274 mmol) was reacted with *N*-(*p*-toluenesulfonyl)iminophenyl-λ³-iodane (113 mg, 0.303 mmol) in the presence of copper(I) hexafluorophosphate (20 mg, 0.054 mmol). Purification by column chromatography [silica gel, CH_2Cl_2/acetone (95/5)] yielded the title complex (67 mg, 0.140 mmol, 51% yield) in form of an orange to brownish solid.

$[\alpha]_D$ = –71 (c = 0.1, CH_2Cl_2).

^{1}H NMR: δ = 2.37 (s, 3H); 4.30 (s, 5H); 4.38–4.40(m, 1H); 4.44–4.46 (m, 1H); 4.52–4.54 (m, 1H); 4.92–4.93 (m, 1H); 7.21–7.25 (m, 2H); 7.42–7.47 (m, 2H); 7.50–7.55 (m, 1H); 7.86–7.90 (m, 2H).

^{13}C NMR: δ = 21.65; 68.05; 70.61; 71.21; 71.90; 90.60; 126.71; 127.18; 129.32; 133.21; 141.55; 142.61.

MS (EI, 70 eV): *m/z* (%) = 479 (M$^+$, 100), 414 (73), 310 (9), 121 (14), 91 (14), 66 (29).

IR (KBr): $\tilde{\nu}$ = 1319, 1242, 1152, 1090, 1060, 1030, 805, 757, 524 cm^{-1}.

Anal. $C_{23}H_{21}FeNO_3S_2$ (479.03): calcd C, 57.62; H, 4.42; N, 2.92; found C, 57.38; H, 4.54; N, 2.99.

(*S*)-*S*-Ferrocenyl-*S*-methyl-*N*-*p*-tolylsulfonylsulfoximine (8d)

Following the general procedure detailed above, (*S*)-ferrocenyl methyl sulfoxide **5d** (265 mg, 1.07 mmol) was reacted with *N*-(*p*-toluenesulfonyl)iminophenyl-λ³-iodane (439 mg, 1.18 mmol) in the presence of copper(I) hexafluorophosphate (79 mg, 0.213 mmol). Purification by column chromatography [silica gel, CH_2Cl_2/acetone (90/10)] followed by recrystallisation from hexane/diethylether yielded the title complex (192 mg, 0.460 mmol, 43% yield) in form of an orange solid.

$[\alpha]_D$ = –112 (c = 0.1, CH_2Cl_2).

^{1}H NMR: δ = 2.56 (s, 3H); 3.68 (s, 3H); 4.43 (s, 5H); 4.61–4.67 (m, 2H); 4.82–4.85 (m, 1H); 4.98–5.01 (m, 1H); 7.43–7.48 (m, 2H); 8.10–8.14 (m, 2H).

^{13}C NMR: δ = 21.22; 47.12; 67.89; 70.09; 70.67; 71.37; 88.18; 126.17; 129.00; 141.11; 142.35.

MS (EI, 70 eV): *m/z* (%) = 417 (M$^+$, 93), 352 (100), 225 (18), 129 (18), 121 (37), 91 (47), 65 (23), 56 (41).

IR (KBr): $\tilde{\nu}$ = 1314, 1230, 1151, 1091, 1053, 1030, 717, 537 cm^{-1}.

Anal. $C_{18}H_{19}FeNO_3S_2$ (417.33): calcd C, 51.80; H, 4.59; N, 3.36; found C, 51.44; H, 4.78; N, 3.18.

General Procedure for the Imination of Ferrocenyl Sulfoxides 5a–e by Means of Hypervalent *N*-(*P*-Nitrophenylsulfonyl)iminophenyl-λ³-iodane

The ferrocenyl sulfoxide and the copper catalyst were placed in a dry schlenk flask Ar and were dissolved in freshly distilled MeCN (10 mL per mmol of substrate). The solution was stirred at r.t. while *N*-(*p*-nitrophenylsulfonyl)iminophenyl-λ³-iodane (1.4 mmol per 1 mmol of substrate) was added in small portions over a period of 2 h. The mixture was then sealed and stirred at r.t. Conversion was monitored by tlc and after 48–60 h the mixture was filtered through a G3 frit followed by standard workup.

The crude mixtures were purified as stated below.

(*S*)-*S*-Ferrocenyl-*N*-*p*-nitrophenylsulfonyl-*S*-*p*-tolylsulfoximine (9a)

Following the general procedure detailed above, **5a** (400 mg, 1.24 mmol) is reacted with *N*-(*p*-nitrophenylsulfonyl)iminophenyl-λ³-iodane (590 mg, 1.49 mmol) in the presence of copper(I) hexafluorophosphate (90.3 mg, 0.248 mmol). Purification by column chromatography [silica gel, CH_2Cl_2/acetone (95/5)] yielded the title

complex (448.3 mg, 0.856 mmol, 69% yield) in form of an orange solid.

$[\alpha]_D$ = –85 (c = 0.9, CH_2Cl_2).

^{1}H NMR: δ = 2.39 (s, 3H); 4.29 (s, 5H); 4.41–4.44 (m, 1H); 4.47–4.50 (m, 1H); 4.51–4.53 (m, 1H); 4.91–4.93 (m, 1H); 7.26–7.29 (m, 2H); 7.73–7.70 (m, 2H); 8.16–8.21 (m, 2H); 8.28–8.33 (m, 2H).

^{13}C NMR: δ = 21.61; 67.80; 70.34; 71.09; 71.62; 72.02; 90.34; 123.92; 126.99; 128.00; 130.05; 137.98; 144.83; 149.50; 149.83.

MS (EI, 70 eV): *m/z* (%) = 524 (M^+, 1), 346 (1), 340 (9), 308 (4), 204 (20), 85 (68), 83 (100), 77 (24).

IR (KBr): ν = 1527, 1349, 1331, 1305, 1239, 1174, 1156, 1090, 1055, 1030, 1013, 766 cm^{-1}.

Anal. $C_{23}H_{20}FeN_2O_5S_2$ (524.39): calcd C, 52.68; H, 3.84; N, 5.34; found C, 52.51; H, 4.09; N, 5.33.

(*S*)-*S*-*t*-Butyl-*S*-ferrocenyl-*N*-*p*-nitrophenylsulfonylsulfoximine (9b)

Following the general procedure detailed above, **5b** (120 mg, 0.41 mmol) was reacted with *N*-(*p*-nitrophenylsulfonyl)iminophenyl-λ^3-iodane (200 mg, 0.492 mmol) in the presence of copper(I) hexafluorophosphate (31 mg, 0.083 mmol). Purification by column chromatography [silica gel, CH_2Cl_2/acetone (95/5)] yielded the title complex (124.6 mg, 0.25 mmol, 62% yield) in form of an orange solid.

$[\alpha]_D$ = –131 (c = 0.15, CH_2Cl_2).

^{1}H NMR (CD_2Cl_2): δ = 1.22 (s, 9H); 4.49 (s, 5H); 4.54–4.59 (m, 2H); 4.61–4.63 (m, 1H); 4.78–4.80 (m, 1H); 8.26 (d, *J* = 9.1 Hz, 2H); 8.36 (d, *J* = 9.1 Hz, 2H).

^{13}C NMR (CD_2Cl_2): δ = 23.32; 65.47; 69.33; 71.37; 71.42; 71.67; 72.97; 84.78; 124.01; 127.74; 149.39; 150.28.

MS (EI, 70 eV): *m/z* (%) = 490 (M^+, 13), 434 (50), 322 (59), 233 (47), 217 (68), 202 (53), 138 (56), 56 (100).

IR (KBr): $\tilde{\nu}$ = 3103, 1528, 1347, 1329, 1235, 1156, 1098, 658 cm^{-1}.

Anal. $C_{20}H_{22}FeN_2O_5S_2$ (490.38): calcd C, 48.99; H, 4.52; N, 5.71; found C, 48.89; H, 4.55; N, 5.79.

***N*-*S*-ferrocenyl-*p*-nitrophenylsulfonyl-*S*-phenylsulfoximine (9c)**

Following the general procedure detailed above, **5c** (150 mg, 0.48 mmol) was reacted with *N*-(*p*-nitrophenylsulfonyl)iminophenyl-λ^3-iodane (234 mg, 0.578 mmol) in the presence of copper(I) hexafluorophosphate (36 mg, 0.096 mmol). Purification by column chromatography [silica gel, CH_2Cl_2/acetone (95/5)] followed by recrystallization from hexane/Et_2O yielded the title complex (161.6 mg, 0.317 mmol, 66% yield) in form of an orange solid.

^{1}H NMR (CD_2Cl_2): δ = 4.22 (s, 5H); 4.24–4.39 (m, 1H); 4.44–4.48 (m, 2H); 4.84–4.85 (m, 1H); 7.38–7.46 (m, 2H); 7.49–7.56 (m, 1H); 7.75–7.78 (m, 2H); 8.02–8.07 (m, 2H); 8.18–8.23 (m, 2H).

^{13}C NMR (CD_2Cl_2): δ = 68.54; 71.08; 71.69; 72.45; 72.90; 124.55; 127.49; 128.47; 129.94; 134.18; 141.18; 150.16; 150.30.

MS (EI, 70 eV): *m/z* (%) = 510 (M^+, 100), 445 (38).

IR (KBr): $\tilde{\nu}$ = 1526, 1346, 1326, 1300, 1229, 1162, 1089, 1045, 1006, 733 cm^{-1}.

HRMS for $C_{22}H_{18}FeN_2O_5S_2$: calcd 510.0007; found 510.0007.

(*S*)-*S*-Ferrocenyl-*S*-methyl-*N*-*p*-nitrophenylsulfonylsulfoximine (9d)

Following the general procedure detailed above, **5d** (210 mg, 0.905 mmol) was reacted with *N*-(*p*-nitrophenylsulfonyl)iminophenyl-λ^3-iodane (439 mg, 1.09 mmol) in the presence of copper(I) hexafluorophosphate (67.4 mg, 0.18 mmol). Purification by column chromatography [silica gel, CH_2Cl_2/acetone (95/5)] followed by recrystallization from hexane/Et_2O yielded the title complex (275.7 mg, 0.615 mmol, 68% yield) in form of an orange solid.

$[\alpha]_D$ = –90 (c = 0.1, CH_2Cl_2).

^{1}H NMR (CD_2Cl_2): δ = 3.57 (s, 3H); 4.26 (s, 5H); 4.47–4.55 (m, 2H); 4.62–4.64 (m, 1H); 4.83–4.85 (m, 1H); 8.28 (d, *J* = 9.0 Hz, 2H); 8.37 (d, *J* = 9.0 Hz, 2H).

^{13}C NMR (CD_2Cl_2): δ = 47.77; 68.10; 70.34; 71.01; 71.97; 72.06; 87.92; 124.09; 127.95; 149.66; 149.77.

MS (EI, 70 eV): *m/z* (%) = 448 (M^+, 100), 383 (56), 121 (13).

IR (KBr): $\tilde{\nu}$ = 1530, 1351, 1325, 1306, 1224, 1170, 1153, 1108, 1093, 1069, 1053, 980, 855 cm^{-1}.

HRMS for $C_{17}H_{16}FeN_2O_5S_2$: calcd 447.9850; found 447.9851.

(*S*)-*S*-Ferrocenyl-*S*-(2-methoxynaphthyl)-*N*-*p*-nitrophenylsulfonylsulfoximine (9e)

Following the general procedure detailed above, **5e** (100 mg, 0.26 mmol) was reacted with *N*-(*p*-nitrophenylsulfonyl)iminophenyl-λ^3-iodane (124 mg, 0.31 mmol) the presence of copper(I) hexafluorophosphate (19 mg, 0.051 mmol). Purification by column chromatography [silica gel, CH_2Cl_2/acetone (95/5)] followed by a second chromatographic purification [silica gel, EtOAc/hexanes (30/70)] in order to remove some nosyl amide byproduct yielded the title complex (113.5 mg, 0.192 mmol, 74% yield) in form of an orange solid.

$[\alpha]_D$ = +69 (c = 0.2, CH_2Cl_2).

^{1}H NMR: δ = 3.73 (s, 3H); 4.21–4.40 (m, 1H); 4.44 (s, 5H); 4.45–4.48 (m, 1H); 4.51–4.55 (m, 1H); 5.12–5.13 (m, 1H); 7.01 (d, *J* = 9.0 Hz, 1H); 7.42–7.47 (m, 1H); 7.59–7.66 (m, 1H); 7.74–7.76 (m, 1H); 7.91 (d, *J* = 8.8 Hz, 2H); 7.96 (d, *J* = 9.1 Hz, 1H); 8.06 (d, *J* = 8.9 Hz, 2H); 9.17 (d, *J* = 9.1 Hz, 1H).

^{13}C NMR: δ = 56.34; 68.30; 70.27; 71.16; 71.36; 72.02; 93.27; 112.27; 118.96; 123.32; 123.82; 124.77; 127.94; 128.85; 129.20; 131.58; 137.50; 149.16; 149.28; 157.19.

MS (EI, 70 eV): *m/z* (%) = 590 (M^+, 100), 525 (7), 233 (11), 115 (10).

IR (KBr): $\tilde{\nu}$ = 3433, 3095, 1527, 1510, 1351, 1328, 1302, 1253, 1220, 1154, 1106, 1085, 1042, 976, 823, 769, 747, 603 cm^{-1}.

HRMS for $C_{27}H_{22}FeN_2O_6S_2$: calcd 590.0269; found 590.0268.

(*S*)-*S*-*p*-Tolyl *S*-(1'-Tributylstannylferrocenyl) Sulfoxide (11)

A solution of 1,1'-bis(tributylstannyl)ferrocene **10** (1.80 g, 2.44 mmol) in freshly distilled THF (20 mL) under Ar was cooled to –78°C. At this temperature, BuLi (1.68 mL, 2.69 mmol, 1.6-M solution in hexane) was added dropwise via syringe and the resulting mixture was stirred for a further 90 min before it was added via cannula to a precooled solution of of (–)-menthyl-(*S*)-(*p*-tolyl)sulfinate (1.30 g, 4.40 mmol) in THF (40 mL). The mixture was allowed to reach –30°C within 3 h before it was worked up under standard conditions. The crude product was purified by column chromatography [silica gel, Et_2O/hexanes (50/50)] to afford the title compound (1.42 g, 2.32 mmol, 95% yield) as a deep red oil that was stored under Ar at –24°C.

$[\alpha]_D$ = +116 (*c* = 2.0, CH_2Cl_2).

^{1}H NMR: δ = 0.91 (t, *J* = 7.1 Hz, 9H); 1.03 (t, *J* = 8.0 Hz, 6H); 1.35 (dt, *J* = 7.1, 8.0 Hz, 6H), 1.50–1.61 (m, 6H); 2.36 (s, 3H); 4.17–4.21 (m, 2H); 4.21–4.24 (m, 1H); 4.26–4.29 (m, 2H); 4.57–4.63 (m, 3H); 7.21–7.25 (m, 2H); 7.50–7.54 (m, 2H).

^{13}C NMR: δ = 9.94; 13.42; 21.07; 27.08; 28.86; 64.72; 67.31; 69.64; 69.76; 70.92; 72.21; 75.92; 75.98; 93.88; 124.05; 129.29; 140.64; 142.75.

MS (EI, 70 eV): *m/z* (%) = 613 (M^+, 2), 575(100), 541 (13), 434 (7), 314 (8), 211(4).

IR (KBr): $\tilde{\nu}$ = 2955, 2925, 2870, 2852, 1493, 1463, 1419, 1378, 1161, 1084, 1049, 1028, 830, 809, 755 cm^{-1}.

HRMS for $C_{29}H_{41}FeOSSn$: calcd 613.1249; found 613.1258.

(*S*)-*N*-*p*-Nitrophenylsulfonyl-*S*-*p*-tolyl-*S*-(1'-tributylstannylferrocenyl)sulfoximine (12)

Following the procedure given above, a reaction of ferrocene **11** (400 mg, 0.65 mmol) with *N*-(*p*-nitrophenylsulfonyl)-iminophenyl-λ^3-iodane (316 mg, 0.78 mmol) in the presence of copper(I) hexafluorophosphate (49 mg, 0.13 mmol) yielded a crude brown oil after standard workup. Purification by column chromatography [silica gel, CH_2Cl_2/acetone (90/10)] followed by a second chromatography [silica gel, Et_2O/hexanes (20/80)] afforded the title compound (338 mg, 0.416 mmol, 64% yield) as a deep red oil that was stored under Ar at –24°C.

$[\alpha]_D$ = –49 (*c* = 0.7, CH_2Cl_2).

^1H NMR: δ = 0.91 (t, *J* = 7.1 Hz, 9H); 1.00 (t, *J* = 8.0 Hz, 6H); 1.33 (dt, *J* = 7.1, 7.9 Hz, 6H), 1.46–1.58 (m, 6H); 2.39 (s, 3H);); 4.09–4.12 (m, 2H); 4.30–4.33 (m, 1H); 4.37–4.40 (m, 1H); 4.44–4.49 (m, 3H); 4.86–4.87 (m, 1H); 7.29–7.32 (m, 2H); 7.74 (d, *J* = 8.6 Hz, 2H); 8.19 (d, *J* = 9.1 Hz, 2H); 8.31 (d, *J* = 9.1 Hz, 2H).

^{13}C NMR: δ = 10.22; 13.70; 21.61; 27.30; 29.09; 67.54; 69.98; 71.63; 72.07; 73.00; 73.96; 77.13; 77.29; 90.06; 123.89; 127.00; 128.05; 130.04; 138.23; 144.74; 149.50; 149.91.

MS (EI, 70 eV): *m/z* (%) = 613 (M^+, 2), 556 (100), 541 (13), 434 (7), 314 (8), 91 (8).

IR (KBr): $\tilde{\nu}$ = 2956, 2926, 1530, 1349, 1332, 1307, 1241, 1180, 1158, 1092, 1065, 1051, 730, 657 cm^{-1}.

HRMS for $C_{31}H_{37}FeN_2O_5S_2Sn$ (M – C_4H_9): calcd 757.0515; found 757.0524.

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Supporting information available: A complete reproduction of the spectral characterization (^1H and ^{13}C NMR) for all new ferrocene compounds is available from the authors upon request.

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(17) *Crystallographic data* for **8b**: $C_{21}H_{25}S_2O_3NFe$; M_w: 459.41; triclinic, space group *P*1, *a* = 6.305(1), *b* = 9.504(2), *c* = 9.927(2) Å, α = 69.81(2), β = 76.46(2), γ = 72.48(2) °, *V* = 526.7 $Å^3$, *Z* = 1. 3230 independent reflections measured at 225 K on a CAD4 Enraf-Nonius diffractometer. MoKα radiation. The final full-matrix least-squares refinement including 2875 reflections with $I > 2\sigma(I)$ and 251 variables yields *R* = 0.052

and R_w = 0.063 (w = σ^{-2}).[28] The absolute configuration of **8b** as depicted in Figure 2 was determined by calculation of Flack's absolute structure parameter [X_{abs} = –0.069(69)].[29] Crystallographic data (excluding structure factors) for the structure have been deposited at the Cambridge Crystallographic Data Centre CCDC 118720 Copies of the data can be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK; e-mail: deposit@chemcrys.cam.ac.uk.

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