Highly Selective Negishi Cross-Coupling Reaction of a Zinc-Metallated Ferrocenyl *p*-Tolyl Sulfoxide: New Chiral Ferrocene-Based Quinone Ligands

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A highly selective Negishi coupling of zinc-metallated ferrocenyl *p*-tolyl sulfoxide with aryl bromides was developed. With $Pd(PPh_3)_4$ as catalyst, a well-matched system in terms of reactivity of organometallic compound, aryl bromide, and catalyst, was obtained. The scope of the reaction was studied by the use of aryl bromides **7a**–**g**, which afforded high yields of coupling products. The reaction conditions for the preparation of ferrocenyl *p*-tolyl sulfoxide, according to the Andersen method, were optimised to give a yield of 80% and an enantiomeric excess of 98%. Target compound **1b** was obtained by deprotection of acetate-protected hydroquinone **8f**, employing sodium borohydride in dimethoxyethane, in a yield of 87%. Target compounds **2b** and **3b** decomposed during workup. The possibility of internal electron transfer, between the ferrocene moiety and the hydroquinone moiety, may account for this instability.

Introduction

Metal-mediated cross-coupling reactions have become useful and efficient methods for C−C bond formation.[1] The first metal-mediated cross-coupling reaction was reported in the early 1970s and during the last three decades a large number of palladium-, nickel- and copper-catalysed coupling reactions between an organometallic compound (of, e.g., zinc, magnesium, aluminium, zirconium, or boron) and an electrophile (e.g., an organohalide or a related compound) have been developed. The cross-coupling reactions proceed mostly with high selectivity and high yields. For palladium-catalysed reactions the choice of phosphane ligand has a profound influence on the outcome of the reaction. Electronic properties of the phosphane ligand as well as steric effects, which can be described in terms of the cone angle, govern the reactivity of the catalyst.[2] More recently, carbene ligands have been employed in palladium-catalysed cross-coupling reactions.[3] Ferrocene compounds are suitable for metal-mediated cross-coupling reactions as they can easily be lithiated and transformed into organometallic compounds.

Over the past two decades a large number of ferrocene ligands have been successfully used in asymmetric catalysis.[4−7] The fact that ferrocene structures can contain both central and planar chirality makes them especially interesting as chiral ligands. Kagan and co-workers have shown that the Andersen method of introducing chiral sulfoxides with high enantiomeric excess to aromatic compounds, by the use of menthyl *p*-toluenesulfinate, can be applied to ferrocene.[8,9] Furthermore, they showed that the chiral sulfoxide obtained by this methodology has a highly diastereoselective *ortho*-directing effect when a second substituent is introduced, giving rise to planar chirality. These sulfoxides have gained much interest as synthetic intermediates as the *p*-tolyl sulfoxide group can easily be replaced by lithium.[9−11] A few examples of ferrocenyl *p*-tolyl sulfoxides employed as ligands for transition-metal-catalysed reactions, have been reported.[12,13]

The palladium(II)-catalysed 1,4-oxidation of 1,3-dienes has been developed by our group and subjected to extensive studies.[14] Recently, efforts were made to develop an asymmetric version of this reaction. Since benzoquinone is needed in the 1,4-oxidation for the second nucleophilic attack on the intermediate, (π-allyl)palladium complex, and hence is in near proximity of the reaction centre, chiral benzoquinones are potential ligands for the asymmetric version. A molecular oxygen/(phthalocyanine)iron system[15] reoxidises hydroquinone to benzoquinone making it possible to use the chiral benzoquinone ligand in catalytic amounts. The ligand can be introduced either as the benzoquinone or the corresponding hydroquinone, depending on which is the most favourable to synthesise (Scheme 1).

The first generation of chiral benzoquinone ligands afforded a moderate enantioselectivity in the 1,4-diacetoxylation[16] and 1,4-dialkoxylation reactions.[17,18] The best chiral induction was obtained with benzoquinones substituted with chiral sulfoxides or chiral amino alcohols. Since ferrocene has been successfully used as a backbone in chiral ligands we decided to study ligands with a quinonylferro-

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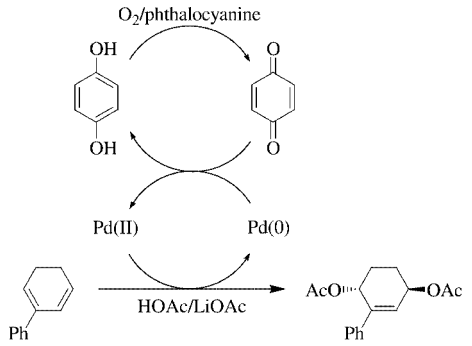


Scheme 1. Diacetoxylation using molecular oxygen/phthalocyanine to reoxidise hydroquinone

cenyl *p*-tolyl sulfoxide structure. We chose **1**, **2**, and **3** as target compounds (Figure 1). In these ferrocenyl *p*-tolyl sulfoxide compounds asymmetric induction may arise from the planar chirality or the central chirality of the sulfoxide. Target compound **1** is the simple benzoquinonyl-substituted ferrocenyl *p*-tolyl sulfoxide.

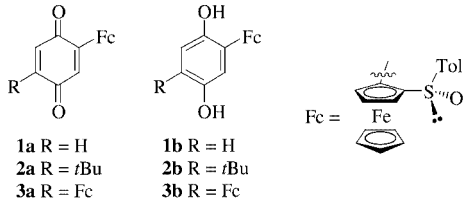


Figure 1. Target compounds **1**, **2**, and **3**

During the development of the first generation of chiral benzoquinone ligands it was found that certain structural features of the benzoquinone were favourable. The design of target molecules **2** and **3** was based on these observations. As the palladium atom can coordinate to both C=C double bonds of the benzoquinone ring one idea was to block the double bond farthest away from the chiral substituent forcing the palladium atom to coordinate to the C=C double bond closest to the asymmetric centre. A *tert*-butyl group was introduced but did not significantly affect the enantioselectivity. On the other hand, the yield of the 1,4-diacetoxylation product was very much improved, probably due to an increased stability of the benzoquinone ligand.[16] In target compound **2** a *tert*-butyl substituent is introduced in the 4-position. By introducing the same chiral substituents on both sides of the benzoquinone, creating a C_2-symmetric ligand, the palladium atom had the same steric environment whichever C=C double bond it coordinated. Indeed, an enhancement of the *ee* was observed.[17] In target compound **3** the ferrocenyl *p*-tolyl sulfoxide substituent is introduced in the 2- and 5-position of the benzoquinone, creating a C_2-symmetric quinone.

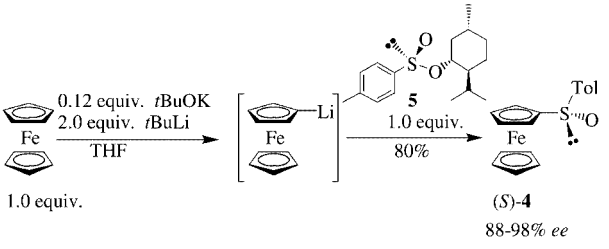
The bond between the ferrocenyl *p*-tolyl sulfoxide and the benzoquinone moiety can be introduced by, for example, copper-catalysed conjugate addition[19] or a metal-mediated cross-coupling reaction. The advantage of conjugate addition is that the quinone is formed in one step. However, with substituents on the benzoquinone ring, there might be problems with regioselectivity. Hence, we chose to use the cross-coupling alternative. In the plethora of modern cross-coupling reactions available, the Negishi cross-coupling reaction was chosen for two major reasons: first it has previously been successfully applied to protected hydroquinones in our laboratory,[20] and secondly Negishi cross-coupling reactions of (*S*)-ferrocenyl *p*-tolyl sulfoxide (**4**) with aryl iodides have been reported in the literature, in moderate yields.[9,11] The hydroquinones had to be protected when employed in the Negishi cross-coupling reaction. Ethers are the most widely used protective groups for phenols,[21] and are thus also suitable for hydroquinones. Esters are also important protective groups for phenol, but are less stable. We chose to work with methyl-, benzyl-, and acetate-protected hydroquinones.

In order to obtain target compounds **1**, **2**, and **3** we developed a highly efficient arylation of ferrocenyl *p*-tolyl sulfoxide by employing the Negishi cross-coupling reaction. In this publication we wish to report on the general application of these Negishi cross-coupling conditions in the reaction of ferrocenyl *p*-tolyl sulfoxide with aryl bromides, as well as the synthesis of compounds **1**, **2**, and **3**.

Results and Discussion

1. Preparation of (*S*)-Ferrocenyl *p*-Tolyl Sulfoxide

The preparation of (*S*)-ferrocenyl *p*-tolyl sulfoxide (**4**), by the Andersen method, was reported by Kagan and co-workers (Scheme 2).[9] Ferrocene is lithiated with *tert*-butyllithium. In order to obtain monolithiated ferrocene it is essential to perform the lithiation in the presence of potassium *tert*-butoxide, otherwise large amounts of the 1,1′-dilithiated ferrocene are formed.[22] Lithiated ferrocene is subsequently treated with (−)-(1*R*,3*R*,4*S*)-menthyl (*S*)-*p*-toluenesulfinate (**5**), yielding the desired product **4**.



Scheme 2. Synthesis of (*S*)-ferrocenyl *p*-tolyl sulfoxide (**4**)

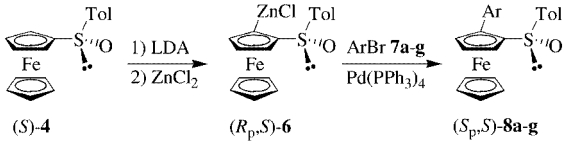
When using the published procedure we had difficulties in reproducing the reported yield, but by running the reaction under modified conditions we were actually able to improve the yield of **4** to 80%, compared to the yield of 69% reported in the literature. In the improved procedure, the reaction was performed in a more dilute system, preventing the lithiated ferrocene to precipitate. This resulted in a higher yield, as unchanged ferrocene otherwise was trapped

in the precipitate. Furthermore, we changed the stoichiometry according to Scheme 2. In the original procedure 2 equiv. of ferrocene compared to menthyl sulfinate **5** was used. We found that this was unnecessary and used 1 equiv. instead.

It is crucial to add the lithiated ferrocene to the menthyl sulfinate **5**, and not reversed, otherwise racemisation of the product takes place. Accordingly, the addition of the ferrocene was performed over a long period of time at −45 to −55 °C to prevent racemisation. Our method always gave slightly higher enantiomeric excess compared to the 83%, which is reported in the literature. We obtained 88−98% *ee*, probably due to the dilute system and lower temperature. Material with an enantiomeric excess of 88% was obtained by adding lithiated ferrocene at −45 °C for 1 h and material with an enantiomeric excess of 98% was obtained when a lower temperature of −55 °C and an addition time of 50 min was used.[23] It has recently been reported that very high enantiomeric excess can be obtained if the addition is performed at −78 °C, however in this case the yield was only 40% probably due to the absence of potassium *tert*-butoxide.[13] We chose to perform the reaction at temperatures above −60 °C, avoiding the precipitation of menthyl sulfinate **5** during the addition.

2. Negishi Cross-Coupling Reactions between Aryl Bromides and Zinc-Metallated (*S*)-Ferrocenyl *p*-Tolyl Sulfoxide

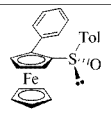
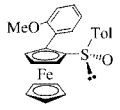
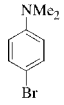
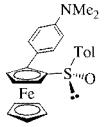
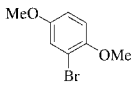
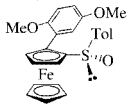
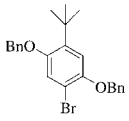
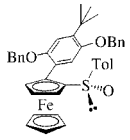
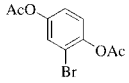
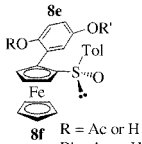
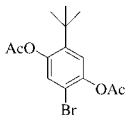
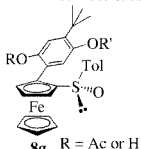
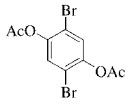
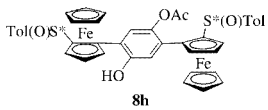
Kagan and co-workers showed that (*S*)-ferrocenyl *p*-tolyl sulfoxide (**4**) can be selectively *ortho*-lithiated by LDA employing the chiral sulfoxide as an *ortho*-directing substituent.[8] We used Kagan's procedure to lithiate (*S*)-ferrocenyl *p*-tolyl sulfoxide (**4**), which was followed by metal exchange with an excess (2.6 equiv.) of thoroughly dried $ZnCl_2$. Compound **6** was subjected to cross-coupling reactions with aryl bromides **7a**−**g** in THF at 60 °C for 18 h in the presence of 6 mol % $Pd(PPh_3)_4$, giving the products **8a**−**g** in high yields (Scheme 3, Table 1).



a Ar = phenyl
b Ar = 2-methoxyphenyl
c Ar = 4-(dimethylamino)phenyl
d Ar = 2,5-dimethoxyphenyl
e Ar = 2,5-dibenzyloxy-4-*tert*-butylphenyl
f Ar = 2,5-diacetoxyphenyl
g Ar = 2,5-diacetoxy-4-*tert*-butylphenyl

Scheme 3. Synthesis of compounds **8a**−**g** by Negishi cross-coupling reaction

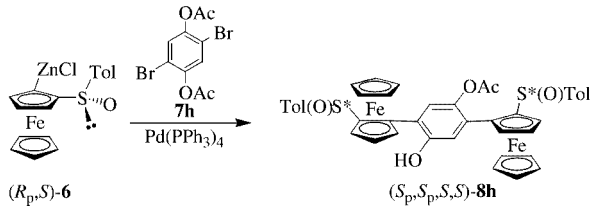
Table 1. Negishi cross-coupling reactions between (*S*)-ferrocenyl *p*-tolyl sulfoxide (**4**) and aryl bromides **7a**−**h**; the reactions were performed in THF at 60 °C on a 0.31−5.6 mmol scale

Entry	Electrophile	Catalyst[a]	Product	Yield (%)[b]
1	 **7a**	A	 **8a**	88
2	 **7b**	A	 **8b**	85
3	 **7c**	A	 **8c**	88
4	 **7d**	A	 **8d**	90
5	 **7e**	A	 **8e**	70
6[c]	 **7f**	A	 **8f** R = Ac or H, R' = Ac or H	63 (85)[d]
7[c]	 **7g**	A	 **8g** R = Ac or H, R' = Ac or H	92
8	 **7h**	B	 **8h**	41
9[c]	**7f**	C	**8f**	42
10[c]	**7f**	D	**8f**	44

[a] Catalyst A = 6 mol % $Pd(PPh_3)_4$, catalyst B = 10 mol % $Pd(PPh_3)_4$, catalyst C = 8.5 mol % tris(2-furyl)phosphane and 4 mol % $Pd(dba)_2$, catalyst D = 8.5 mol % tris(*o*-tolyl)phosphane and 4 mol % $Pd(dba)_2$. [b] Isolated yields. [c] Isolated **8f** also contained one of the two monoacetate-protected hydroquinones. [d] The total yield of **8f** and the two monoacetate-protected hydroquinones was calculated from ^1H NMR spectrum of the crude reaction mixture to be 85%. [e] Isolated **8g** also contained the two monoacetate-protected hydroquinones.

The Negishi cross-coupling reactions between compound **6** and bromobenzene (**7a**), 2-bromoanisole (**7b**), 4-bromo-*N*,*N*-dimethylaniline (**7c**), and 1-bromo-2,5-dimethoxybenzene (**7d**) gave the desired products in 85−90% yield (Table 1, Entries 1−4). With benzyl-protected hydroquinone **7e**, a yield of 70% was obtained (Table 1, Entry 5) and the more bulky substituents may account for the lower yield in this case. The Negishi cross-coupling reaction between acetate-protected hydroquinone **7f** and zinc compound **6** resulted in a mixture of the two monoacetate-protected hydroquinones and the desired product **8f** in a total yield of 85%, as the acetoxy-substituted hydroquinone was

not stable during the reaction. This partial hydrolysis is not a serious problem, since deprotection of the hydroquinone was the following step. However, one of the partially deprotected hydroquinones could not be separated from the starting material **4**, resulting in a lower isolated yield of 63% (Table 1, Entry 6).[24] The Negishi cross-coupling reaction between acetate-protected hydroquinone **7g** and zinc compound **6** was performed with good results and the desired product **8g** and the two monoacetate-protected hydroquinones could be separated from the starting material in a combined isolated yield of 92% (Table 1, Entry 7). To obtain target compound **3b** the Negishi cross-coupling reaction was performed between 2,5-diacetoxy-1,4-dibromobenzene (**7h**) and zinc compound **6** (Scheme 4). When 6 mol % of $Pd(PPh_3)_4$ was used as catalyst a very low yield was obtained. Increasing the amount of catalyst loading to 10 mol % and prolonging the reaction time to 48 h afforded **8h** in a moderate yield of 41% (Table 1, Entry 8). Surprisingly, none of the diacetate-protected product could be detected.



Scheme 4. Synthesis of compound **8h** by the Negishi cross-coupling reaction

The partial deprotection of the acetate-protected hydroquinones **8f**−**h** may decrease if the reaction could proceed at a lower temperature. $Pd(PPh_3)_4$ needs high temperatures to work effectively, although other palladium catalysts work fine at room temperature. It has been reported that Negishi cross-coupling reactions with ferrocenyl *p*-tolyl sulfoxide and aryl iodides have been performed using tris(2-furyl)-phosphane as a ligand at room temperature as well as in refluxing THF, to give the desired products **8a**−**c** in moderate yields.[9,11] To investigate the influence of phosphane ligand on the product distribution and yield the Negishi cross-coupling reaction was performed with acetoxy-protected hydroquinone **7f** and zinc compound **6** in the presence of tris(2-furyl)phosphane/$Pd(dba)_2$ (2.1:1) and tris(*o*-tolyl)phosphane/$Pd(dba)_2$ (2.1:1). The reactions were performed at room temperature for 20 h. In the case of tris(2-furyl)phosphane no reaction was observed. In the case of tris(*o*-tolyl)phosphane some product was detected and, indeed, less partially deprotected product was obtained. However, as the conversion in both cases was unsatisfactory the temperature was increased to 60 °C for 18 h, resulting in 42 and 44% isolated yield, respectively, of the diacetate and one of the monoacetates **8f** (Table 1, Entries 9 and 10). Comparing this with the isolated yield of 63% employing $Pd(PPh_3)_4$ (vide supra), implies that the latter catalyst is more efficient than the palladium(0) complexes with tris(2-furyl)phosphane or tris(*o*-tolyl)phosphane as ligands in the Negishi cross-coupling reaction obtaining **8f**.

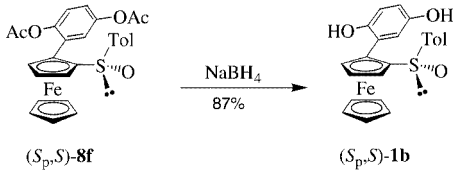
The yields obtained in Table 1 were considerably higher than those previously reported for compounds **8a**−**c** by the Negishi cross-coupling reactions between (*S*)-ferrocenyl *p*-tolyl sulfoxide (**4**) and aryl iodides using tetrakis[tris(2-furyl)phosphane]palladium as a catalyst,[9,11] even though we used the less reactive aryl bromides. This can be explained by the use of $Pd(PPh_3)_4$. In the case of aryl bromides **7a**−**g**, compound **6**, and $Pd(PPh_3)_4$ the system can be considered well-matched with respect to reactivity, resulting in high yields of the products **8a**−**g**. On the other hand, application of the same reaction conditions to aryl bromide **7h** did not result in such a well-matched system. Hence, increased catalyst loading and longer reaction time was needed to obtain a moderate yield in the latter case.

The Negishi cross-coupling reactions were performed employing compound **4**, with an enantiomeric excess of 88%.[23] Consequently, if no racemisation occurred compounds **8a**−**h** would also be obtained with an enantiomeric excess of 88%. The enantiomers of compound **8e** and of the diacetate of compound **8g** were successfully separated on a Daicel Chiracel OD-H column confirming the enantiomeric excess of 88%. Compound **8e** was crystallised in diethyl ether increasing the enantiomeric excess to > 99%. Furthermore, the deprotection of compound **8f** yielded compound **1b** with an *ee* of 88% (vide infra). It can therefore be concluded that the Negishi cross-coupling reaction occurred without any racemisation of the sulfoxide.

3. Deprotection of the Hydroquinones

Deprotection of the methyl-protected compound **8d** proved to be more difficult than expected. As it is known that sulfoxides racemise under acidic conditions,[25,26] we wanted to avoid acidic deprotection methods. Furthermore, methods applying high temperatures were avoided. Attempts to employ either cerium(IV) ammonium nitrate (CAN)[27] or BBr_3 [28] for deprotection resulted in decomposition. Compound **8d** was more prone to decompose than the similar, 2-ferrocenyl-1,4-dimethoxybenzene, which has been reported to undergo deprotection by BBr_3 without decomposition.[29] So far we had only regarded the ferrocene moiety as an interesting structural feature and not considered the possibility of the iron atom being oxidised. This is probably what happens with CAN, which acts by oxidative demethylation oxidising the hydroquinone to the benzoquinone in situ. The Lewis acid properties of BBr_3 might also facilitate the oxidation of Fe^{II} to Fe^{III}. A possible way of avoiding decomposition might be to employ reductive conditions during deprotection. Consequently, our attention turned to the benzyl-protected hydroquinone **8e**, which can be deprotected by catalytic hydrogenation. The attempted deprotection using H_2 in the presence of Pd/C, gave only one of the monodeprotected hydroquinones, probably for steric reasons. Attempted deprotection with TMS iodide[30] resulted in decomposition. We then turned our attention to acetate as hydroxy protecting group, as this can be easily removed by saponification. Attempts were made to deprotect the

acetate-protected hydroquinone **8f** under mildly basic conditions, using sodium bicarbonate.[31] Unfortunately, these efforts resulted in decomposition. Another strategy was tried, in which sodium borohydride was used in dimethoxyethane at 40 °C for 48 h.[32] Under these reductive conditions the desired compound **1b** was obtained in 87% yield (Scheme 5). The workup was performed under argon as the product turned out to be sensitive towards decomposition in solution, when exposed to air. The material was crystallised in pentane/ethyl acetate, increasing the enantioselectivity from 88% *ee* to >99% *ee*.

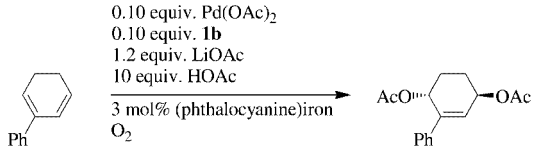


Scheme 5. Synthesis of target compound **1b**

The synthetic route to compound **1b** was applied to the synthesis of target compounds **2b** and **3b**. However, both compounds decomposed during workup. The unsuccessful attempts to isolate compound **2b** and **3b** might be due to the instability of the desired compound under the reaction and workup conditions, but it might also be a consequence of the inherent properties of compounds **1**, **2**, and **3**, which all showed some degree of instability. It is known that ferrocene is easily oxidised to the ferrocenium cation, which can decompose to cyclopentadienol in the presence of oxygen.[33,34] Since the quinone moiety is directly bound to ferrocene an internal electron-transfer can take place, yielding the ferrocenium cation.[35,36]

4. Application to the Asymmetric 1,4-Oxidation Reaction

The 1,4-diacetoxylation reaction was performed on 2-phenyl-1,3-cyclohexadiene, using compound **1b** as a chiral quinone ligand (Scheme 6). This gave the desired product in 60% conversion with a *trans*/*cis* selectivity of 80:20. However, analysis by chiral HPLC showed that the *trans* product was of 7% *ee*. This can be due to the structure of compound **1b**, but it may also be a result of the instability of the compound regarding oxidative conditions, thus not surviving the 1,4-oxidation reaction. The ligand could not be recovered after the reaction. As the reaction was performed with 10 mol % of catalyst, a conversion of 60% implies that the catalytic system was active through 6 catalytic cycles. It cannot be ruled out that decomposition products of **1b** containing a benzoquinone ring could act as ligand and give a poor enantioselectivity. Further studies of this reaction under modified conditions and studies of ligand **1b** in related transition-metal-catalysed transformations will be pursued.



Scheme 6. Diacetoxylation reaction using **1b** as a chiral quinone ligand

Conclusion

We have developed a highly selective Negishi cross-coupling reaction of zinc-metallated ferrocenyl *p*-tolyl sulfoxide with aryl bromides. A well-matched system in terms of reactivity of organometallic compound, aryl bromide, and catalyst was created using $Pd(PPh_3)_4$ as catalyst. The applicability of the reaction was demonstrated by the high-yielding coupling reaction of aryl bromides **7a**−**g**. The cross-coupling reaction with aryl bromide **7h** was not as well-matched and resulted in a lower yield. Furthermore, we have optimised the reaction conditions for the preparation of (*S*)-ferrocenyl *p*-tolyl sulfoxide, according to the Andersen method, and obtained a yield of 80% and an enantiomeric excess of 98%. The acetate-protected hydroquinone **8f** was deprotected by treatment with sodium borohydride in dimethoxyethane yielding target compound **1b** in 87% yield. Target compounds **2b** and **3b** decomposed during workup. The possibility of internal electron transfer, between the ferrocene moiety and the hydroquinone moiety may account for this instability.

After the completion of this work we became aware of a recent publication describing similar couplings as those given in Table 1 but with aryl iodides and tris(2-furyl)phosphane/$Pd(dba)_2$ as catalyst.[37]

Experimental Section

General Remarks: ^1H (400 or 300 MHz) and ^{13}C (100 or 75 MHz) NMR spectra were recorded with a Varian Mercury spectrometer. Chemical shifts (δ) are reported in ppm, using residual solvent resonance or tetramethylsilane as internal standard. IR spectra were obtained using a Perkin−Elmer 1600 FT-IR instrument, and the samples were examined on NaBr plates. Only the strongest/structurally most significant peaks (cm^{-1}) are listed. HPLC was performed with a Waters liquid chromatograph using a Daicel Chiracel OD-H column. Optical rotation was obtained with a Perkin−Elmer 241 Polarimeter. Mass spectra were recorded with a MALDI-TOF apparatus. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. **7e** was prepared from the corresponding hydroquinone by deprotonation and treatment with benzyl chloride under standard conditions. **7f**, **7g**, and **7h** were prepared from the corresponding hydroquinones by treatment with acetyl chloride under standard conditions. Spectral data for **7e**,[38] **7f**,[39] **7g**,[40] and **7h**[41] were in agreement with those reported in the literature. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl prior to use. Zinc chloride was dried at 140 °C in vacuo overnight prior to use. (−)-(1*R*,3*R*,4*S*)-Menthyl (S_S)-*p*-toluenesulfin-

ate,[26] $Pd(PPh_3)_4$,[42] and $Pd(dba)_2$[43] were prepared according to literature procedures. All reactions were performed under argon.

(*S*)-Ferrocenyl *p*-Tolyl Sulfoxide (4): Ferrocene (4.00 g, 21.5 mmol) and potassium *tert*-butoxide (0.294 g, 2.58 mmol) were dissolved in 180 mL of THF and cooled to −78 °C. *tert*-Butyllithium (25.3 mL, 1.7 M, 43.0 mmol) was added dropwise over 40 min. The reaction mixture was kept at −78 °C for 1.5 h and at room temperature for 1 h, after which the solution was cooled to −55 °C. (−)-(1*R*,3*R*,4*S*)-Menthyl (S_S)-*p*-toluenesulfinate (6.34 g, 21.5 mmol) was dissolved in 110 mL of THF and cooled to −55 °C. The lithiated ferrocene was transferred dropwise to the menthyl sulfinate by cannula over 50 min. After 1 h at −55 °C, water was added. The material was extracted with diethyl ether and the combined organic phases were washed with brine and water and dried with sodium sulfate. The solvent was removed in vacuo and the material was purified by column chromatography (petroleum ether/diethyl ether), yielding 5.60 g (80%) of **4** as a yellow solid, with 98% *ee*. Analytical data are in agreement with those reported in the literature.[13]

(S_p,*S*)-1-Phenyl-2-(*p*-tolylsulfinyl)ferrocene (8a). General Procedure for the Negishi Cross-Coupling Reactions: (*S*)-Ferrocenyl *p*-tolyl sulfoxide (**4**) (0.270 g, 0.833 mmol) was dissolved in 5 mL of THF and cooled to −78 °C. LDA [prepared prior to use by treating diisopropylamine (0.152 mL, 1.08 mmol) with *n*BuLi (0.750 mL, 1.6 M, 1.20 mmol) in 2 mL of THF] was added to the ferrocenyl *p*-tolyl sulfoxide solution over 30 min. The mixture was kept at −78 °C for another 30 min. Zinc chloride (0.300 g, 2.20 mmol) was dissolved in 5 mL of THF and cooled to −78 °C. The lithiated ferrocene compound was transferred to the zinc chloride solution by cannula over 30 min. The reaction mixture was kept at −78 °C for 1 h and at room temperature for 1 h. Bromobenzene (0.126 g, 0.800 mmol) and $Pd(PPh_3)_4$ (54 mg, 0.047 mmol) were dissolved in 3 mL of THF. The zinc compound was added by cannula and the resulting solution was heated to 60 °C. After 18 h, saturated aqueous ammonium chloride solution was added. The material was extracted with dichloromethane. The combined organic phases were washed with water, dried with sodium sulfate and the solvent was removed in vacuo. Column chromatography (pentane/ethyl acetate) yielded 0.281 g (88%) of **8a** as an orange solid. Analytical data corresponds with previously published data.[37]

(S_p,*S*)-1-(2-Methoxyphenyl)-2-(*p*-tolylsulfinyl)ferrocene (8b): The Negishi cross-coupling reaction was performed according to the General Procedure described for compound **8a**. (*S*)-Ferrocenyl *p*-tolyl sulfoxide (0.270 g, 0.833 mmol) was treated with LDA [diisopropylamine (0.152 mL, 1.08 mmol), *n*BuLi (0.750 mL, 1.6 M, 1.20 mmol)] and zinc chloride (0.300 g, 2.20 mmol). The zinc compound obtained was added to 2-bromoanisole (125 mg, 0.670 mmol) and $Pd(PPh_3)_4$ (54 mg, 0.047 mmol). Column chromatography (pentane/ethyl acetate) yielded 0.245 g (85%) of **8b** as an orange solid. Analytical data corresponds with previously published data.[37]

(S_p,*S*)-1-[4-(Dimethylamino)phenyl]-2-(*p*-tolylsulfinyl)ferrocene (8c): The Negishi cross-coupling reaction was performed according to the General Procedure described for compound **8a**. (*S*)-Ferrocenyl *p*-tolyl sulfoxide (0.133 g, 0.411 mmol) was treated with LDA [diisopropylamine (75 μL, 0.53 mmol), *n*BuLi (0.360 mL, 1.6 M, 0.575 mmol)] and zinc chloride (0.148 g, 1.09 mmol). The zinc compound obtained was added to 4-bromo-*N*,*N*-dimethylaniline (75 mg, 0.36 mmol) and $Pd(PPh_3)_4$ (27 mg, 0.023 mmol). Column chromatography (pentane/ethyl acetate) yielded 0.14 g (88%) of **8c** as an orange solid. Analytical data corresponds with previously published data.[8]

(S_p,*S*)-1-(2,5-Dimethoxyphenyl)-2-(*p*-tolylsulfinyl)ferrocene (8d): The Negishi cross-coupling reaction was performed according to the General Procedure described for compound **8a**. (*S*)-Ferrocenyl *p*-tolyl sulfoxide (100 mg, 0.309 mmol) was treated with LDA [diisopropylamine (56 μL, 0.41 mmol), *n*BuLi (0.270 mL, 1.6 M, 0.433 mmol)] and zinc chloride (0.112 g, 0.819 mmol). The zinc compound obtained was added to 1-bromo-2,5-dimethoxybenzene (64 mg, 0.30 mmol) and $Pd(PPh_3)_4$ (20 mg, 0.018 mmol). Column chromatography (pentane/ethyl acetate) yielded 0.123 g (90%) of **8d** as an orange solid. ^{1}H NMR ($CDCl_3$, 300 Hz): δ = 2.41 (s, 3 H), 3.66 (s, 3 H), 3.89 (s, 3 H), 4.17 (s + m, 6 H), 4.42 (m, 1 H), 4.80 (m, 1 H), 6.77 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H), 6.82 (dd, $^3J_{H,H}$ = 9.0, $^4J_{H,H}$ = 3.0 Hz, 1 H), 7.26 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.63 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.70 (d, $^4J_{H,H}$ = 3.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 Hz): δ = 21.5, 56.0, 56.3, 68.6, 69.2, 71.1, 74.0, 86.1, 93.7, 112.6, 114.0, 119.1, 124.8, 125.5, 129.2, 140.6, 141.1, 151.7, 153.2 ppm. IR (neat): $\tilde{\nu}$ = 3082 cm^{-1}, 2931, 1608, 1583, 1505, 1466, 1435, 1222, 1179, 1082, 1042, 809, 732 cm^{-1}. MS (*m*/*z*): calcd. for $C_{25}H_{25}FeO_3S$ [M$^+$ + H] 461.0874; found 461.0901. $[\alpha]_D^{25}$ = +8.74 (*c* = 0.103, acetone).

(S_p,*S*)-1-[2,5-Bis(benzyloxy)-4-*tert*-butylphenyl]-2-(*p*-tolylsulfinyl)-ferrocene (8e): The Negishi cross-coupling reaction was performed according to the General Procedure described for compound **8a**. (*S*)-Ferrocenyl *p*-tolyl sulfoxide (**7**) (0.268 g, 0.827 mmol) was treated with LDA [diisopropylamine (0.151 mL, 1.08 mmol), *n*BuLi (0.724 mL, 1.6 M, 1.16 mmol)] and zinc chloride (0.299 g, 2.19 mmol). The zinc compound obtained was added to 1,4-bis(benzyloxy)-2-bromo-5-*tert*-butylbenzene (0.340 g, 0.800 mmol) and $Pd(PPh_3)_4$ (54 mg, 0.048 mmol) in THF. Column chromatography (pentane/ethyl acetate) yielded 0.37 g (70%) of **8e** as an orange-coloured solid. The material was crystallised in diethyl ether, increasing the enantioselectivity from 88% *ee* to > 99% *ee*. The enantioselectivity was measured by HPLC analysis using a Daicel Chiracel OD-H-column, hexane/2-propanol (90:10), 0.5 mL/min, room temp. (R_p,*R*): 18.5 min; (S_p,*S*): 22.9 min. ^{1}H NMR ($CDCl_3$, 400 Hz): δ = 1.42 (s, 9 H), 2.36 (s, 3 H,), 3.97 (s, 5 H), 4.17 (m, 1 H), 4.36 (m, 1 H), 4.61 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H), 4.65 (d, $^2J_{H,H}$ = 11.6 Hz, 1 H), 4.83 (m, 1 H), 5.36 (d, $^2J_{H,H}$ = 12.8 Hz, 1 H), 5.40 (d, $^2J_{H,H}$ = 12.8 Hz, 1 H), 6.80 (s, 1 H), 7.16 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 7.27−7.47 (m, 10 H), 7.56 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H), 7.69 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 Hz): δ = 21.4, 29.8, 35.0, 68.8, 68.9, 70.6, 70.9, 72.2, 74.1, 85.4, 93.4, 114.3, 118.6, 122.6, 125.2, 126.7, 127.5, 127.67, 127.75, 128.3, 128.6, 128.9, 137.6, 138.4, 138.5, 140.4, 140.6, 150.3, 151.6 ppm. IR (neat): $\tilde{\nu}$ = 3032 cm^{-1}, 2956, 2867, 1513, 1494, 1443, 1398, 1358, 1202, 1107, 1126, 1082, 1026, 909, 809, 732, 696 cm^{-1}. MS (*m*/*z*): calcd. for $C_{41}H_{40}FeO_3S$ [M$^+$] 668.2048; found 668.2046. $[\alpha]_D^{25}$ = +80.1 (*c* = 0.450, acetone).

(S_p,*S*)-1-(2,5-Diacetoxyphenyl)-2-(*p*-tolylsulfinyl)ferrocene and Monoacetate (8f): The Negishi cross-coupling reaction was performed according to the General Procedure described for compound **8a**. (*S*)-Ferrocenyl *p*-tolyl sulfoxide (1.80 g, 5.56 mmol) was treated with LDA [diisopropylamine (1.01 mL, 7.22 mmol), *n*BuLi (4.86 mL, 1.6 M, 7.78 mmol)] and zinc chloride (1.51 g, 11.1 mmol). The zinc compound obtained was added to 1,4-diacetoxy-2-bromobenzene (1.46 g, 5.34 mmol) and $Pd(PPh_3)_4$ (0.449 g, 0.389 mmol). Column chromatography (pentane/ethyl acetate) yielded 1.75 g (63%) of **8f** as an orange solid, which contained the desired product together with one of the monoprotected hydroquinones. The compounds were separated by column chromatography (dichloromethane/diethyl ether) to give analytical samples. **8f (Diacetate):** ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.06 (s, 3 H), 2.37 (s, 6 H), 4.25 (s, 5 H), 4.39 (m, 1 H), 4.45 (m, 1 H), 4.54 (m, 1 H,), 6.94 (d, $^3J_{H,H}$ =

8.7 Hz, 1 H), 7.01 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 2.7 Hz, 1 H), 7.20 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.50 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 8.00 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 20.9, 21.37, 21.39, 69.1, 69.5, 71.3, 72.1, 84.1, 95.0, 121.2, 123.0, 125.0, 127.4, 129.0, 129.1, 140.4, 140.8, 146.4, 147.3, 169.2, 169.3 ppm. IR (neat): $\tilde{\nu}$ = 3085 cm^{-1}, 1762, 1454, 1369, 1211, 1169, 1040, 918, 731cm^{-1}. MS (*m*/*z*): calcd. for $C_{27}H_{25}FeO_5S$ [M^+ + H], 517.0772; found, 517.0669. $[\alpha]_D^{25}$ = −8.83 (*c* = 0.200, CH_2Cl_2).

(S_p,*S*)-1-(2,5-Diacetoxy-4-*tert*-butylphenyl)-2-(*p*-tolylsulfinyl)-ferrocene and Monoacetates (8g): The Negishi cross-coupling reaction was performed according to the General Procedure described for compound **8a**. (*S*)-Ferrocenyl *p*-tolyl sulfoxide (0.268 g, 0.827 mmol) was treated with LDA [diisopropylamine (0.151 mL, 1.08 mmol), *n*BuLi (0.724 mL, 1.6 M, 1.16 mmol)] and zinc chloride (0.299 g, 2.19 mmol). The zinc compound obtained was added to 1,4-diacetoxy-2-bromo-5-*tert*-butylbenzene (0.263 g, 0.800 mmol) and $Pd(PPh_3)_4$ (54 mg, 0.047 mmol). Column chromatography (pentane/ethyl acetate) yielded 0.420 g (92%) of **8g** as an orange solid, which contained the diacetate product **8g** together with the two monoacetates. The compounds were separated by column chromatography (pentane/ethyl acetate) to give analytical samples. **8g (Diacetate):** 88% *ee*. The enantioselectivity was measured by HPLC analysis using a Daicel Chiracel OD-H column, hexane/2-propanol (90:10), 0.5 mL/min, room temp. (S_p,*S*): 23.2 min; (R_p,*R*): 31.3 min. ^{1}H NMR (CD_3CN, 300 Hz): δ = 1.37 (s, 9 H), 2.11 (s, 3 H), 2.42 (s, 3 H), 2.43 (s, 3 H), 3.98 (m, 1 H), 4.19 (s, 5 H), 4.50 (m, 1 H), 4.61 (m, 1 H), 7.09 (s, 1 H), 7.40 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.71 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.84 (s, 1 H) ppm. ^{13}C NMR (CD_3CN, 75 Hz): δ = 21.1, 21.5, 22.0, 30.3, 35.3, 68.9, 70.8, 72.2, 72.9, 84.6, 95.7, 122.7, 126.3, 127.7, 130.4, 130.6, 141.3, 142.7, 143.0, 146.8, 147.4, 170.6, 170.9 ppm. IR (neat): $\tilde{\nu}$ = 2965 cm^{-1}, 1760, 1440, 1366, 1207, 1161, 1042, 1014, 917, 731 cm^{-1}. MS (*m*/*z*): calcd. for $C_{31}H_{32}FeO_5S$ [M^+] 572.1320; found 572.1375. $[\alpha]_D^{25}$ = +33.9 (*c* = 0.192, acetone).

(S_p,S_p,*S*,*S*)-2,5-Bis[2-(*p*-toluenesulfinyl)ferrocenyl]-1,4-hydroquinone Monoacetate (8h): The Negishi cross-coupling reaction was performed according to the General Procedure described for compound **8a**. (*S*)-Ferrocenyl *p*-tolyl sulfoxide (0.175 g, 0.540 mmol) was treated with LDA [diisopropylamine (83 μL, 0.59 mmol), *n*BuLi (0.388 mL, 1.6 M, 0.621 mmol)] and zinc chloride (0.195 g, 1.43 mmol). The zinc compound obtained was added to 1,4-diacetoxy-2,5-dibromobenzene (95 mg, 0.27 mmol) and $Pd(PPh_3)_4$ (62 mg, 0.054 mmol). The reaction was performed at 60 °C for 48 h. Column chromatography (pentane/ethyl acetate) yielded 86 mg (41%) of **8h** as an orange solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.06 (s, 3 H), 2.32 (s, 3 H), 2.47 (s, 3 H), 4.13 (s, 5 H), 4.18 (m, 1 H), 4.43 (m, 1 H), 4.49 (m, 1 H), 4.55 (m, 2 H), 4.57 (s, 5 H), 4.67 (m, 1 H), 6.62 (s, 1 H), 7.09 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.27 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.38 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 7.61 (s, 1 H), 7.81 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H), 9.41 (s, 1 H) ppm. ^{13}C NMR (CD_3CN, 75 MHz): δ = 21.3, 21.5, 21.6, 69.0, 70.6, 70.9, 71.3, 72.2, 72.4, 73.1, 75.0, 84.7, 85.2, 93.6, 95.8, 123.5, 124.3, 125.9, 126.5, 128.3, 129.6, 130.47, 130.48, 140.5, 141.4, 142.7, 142.76, 142.80, 152.8, 170.7 ppm. IR (neat): $\tilde{\nu}$ = 3400 cm^{-1}, 2922, 1755, 1698, 1447, 1208, 1173, 1035, 811 cm^{-1}. MS (*m*/*z*): calcd. for $C_{42}H_{36}Fe_2NaO_5S_2$ [M^+ + Na] 819.0601; found 819.0823. $[\alpha]_D^{25}$ = +45.9 (*c* = 0.630, acetonitrile).

(S_p,*S*)-1-(2,5-Dihydroxyphenyl)-2-(*p*-tolylsulfinyl)ferrocene (1b): Compound **8f** together with one of the two monoacetate-protected hydroquinones (0.200 g, 0.388 mmol) was dissolved in 12 mL of dimethoxyethane. Sodium borohydride (0.220 g, 5.82 mmol) was added and the reaction mixture was heated to 40 °C. After 48 h, saturated aqueous ammonium chloride solution was added. The material was extracted with diethyl ether. The combined organic phases were washed with water, dried with sodium sulfate and the solvent was removed in vacuo. Column chromatography under argon (pentane/ethyl acetate) yielded 0.146 g (87%) of **1b** as a yellow solid. The material was crystallised in pentane/ethyl acetate, increasing the enantioselectivity from 88% *ee* to > 99% *ee*. The enantioselectivity was measured by HPLC analysis using a Daicel Chiracel OD-H column, hexane/2-propanol (60:40), 0.5 mL/min, room temp. (R_p,*R*): 12.0 min; (S_p,*S*): 19.3 min. ^{1}H NMR ([D_6]acetone, 300 MHz): δ = 2.36 (s, 3 H), 4.34 (m, 1 H), 4.39 (s, 5 H), 4.55 (m, 1 H), 4.64 (m, 1 H), 6.68 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 3.0 Hz, 1 H), 6.75 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H), 6.98 (d, $^4J_{H,H}$ = 3.0 Hz, 1 H), 7.29 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.53 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H), 7.82 (br. s, 1 H), 8.44 (br. s, 1 H) ppm. ^{13}C NMR ([D_6]acetone, 300 MHz): δ = 21.3, 69.8, 70.4, 71.8, 75.0, 86.9, 92.9, 116.7, 120.2, 120.4, 124.7, 125.9, 130.2, 140.8, 142.2, 148.9, 151.1 ppm. IR (neat): $\tilde{\nu}$ = 3271 cm^{-1}, 1697, 1493, 1463, 1432, 1247, 1208, 1002, 812, 784 cm^{-1}. MS (*m*/*z*): calcd. for $C_{23}H_{20}FeO_3S$ [M^+] 432.0483; found 432.0479. $[\alpha]_D^{25}$ = +164 (*c* = 0.255, acetone).

Supporting Information: ^{1}H and ^{13}C NMR spectra of compounds **1b**, **8d**, **8e**, **8f**, **8g**, and **8h** (see footnote on the first page of this article).

Acknowledgments

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