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Chiral Sulfur-Containing 1,2-Disubstituted Ferrocenes

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Abstract: Enantiopure 1-*t*-butylsulfinyl-2-subsituted ferrocenes were synthesized in reactions of (*SR*,1*S*,2*R*)-1-*t*-butylsulfinyl-2-lithioferrocene (**11**) with various electrophiles in good yields. (*SR*,1*S*,2*R*)-1-*t*-Butylsulfinyl-2-formylferrocene (**19**), prepared this way, underwent complete stereoselective addition reactions with Grignard reagents under chelation controlled conditions with titanium tetraisopropoxide. 1,4–Addition reactions of selected α,β-unsaturated esters with cuprate reagents gave mixtures of two diastereomers. The lack of stereoselectivity in these 1,4-addition reactions is due presumably to the remote reactive site (C-3') and the flexibility of the side chain of the ester. A stereoselective cationic displacement reaction of (1*S*,2*R*,1'*S*)-1-(*t*-butylsulfonyl)-2-[α-(2-propenoyl)oxybenzyl]ferrocene (**44**) with 1-acetoxy-1,3-butadiene was found to produce (1*S*,2*R*,1'*S*)-1-(*t*-butylsulfonyl)-2-(5'-oxo-1'-phenyl-3'-pentenyl)ferrocene (**45**).

INTRODUCTION

A large number of ferrocenyl derivatives with planar or planar and central chirality have been designed in the quest for asymmetric synthesis (for example, hydrogenation of alkenes or ketones, hydrosilylation, cross-coupling reactions, or aldol condensation).[1] These recent successes in asymmetric catalysis involving chiral ferrocene ligands have increased the need for an easy access to chiral ferrocenyl molecules.[2]

The design and the preparation of chiral diphosphine ligands, particularly with C2-symmetry, are of great importance in the development of transition metal-catalyzed enantioselective reactions.[3] Meanwhile, the planar chiralities of ferrocene, which were found to provide excellent chiral environments, have received immense attention.[1,4] Chiral chelating phosphines derived from ferrocene constitute a unique class of asymmetric ligands.[5] Many of the compounds of this type known so far impart high enantioselectivities to several transition-metal-catalyzed reactions.[4a] One of the most widespread methods for preparing enantiopure or enantiomerically enriched planar-chiral ferrocene derivatives relies upon a diastereoselective *ortho*-lithiation and subsequent reaction with an appropriate electrophile. The most prominent example of this methodology is based on the pioneering work of Ugi and coworkers.[6] This strategy, which involves the use of stereogenic *ortho*-directing groups, has been further developed in more recent years by several research groups.[7–9] Our idea was to first synthesize a chiral ferrocenyl sulfoxide, and then use this sulfoxide moiety to regioselectively introduce a second functional group at C-2 of the ferrocene ring.[10]

A significant number of transition-metal complexes containing sulfoxides and sulfides has been reported.[11] However, relatively few chiral complexes containing sulfur have been described,[2,7,11a] and in most cases,

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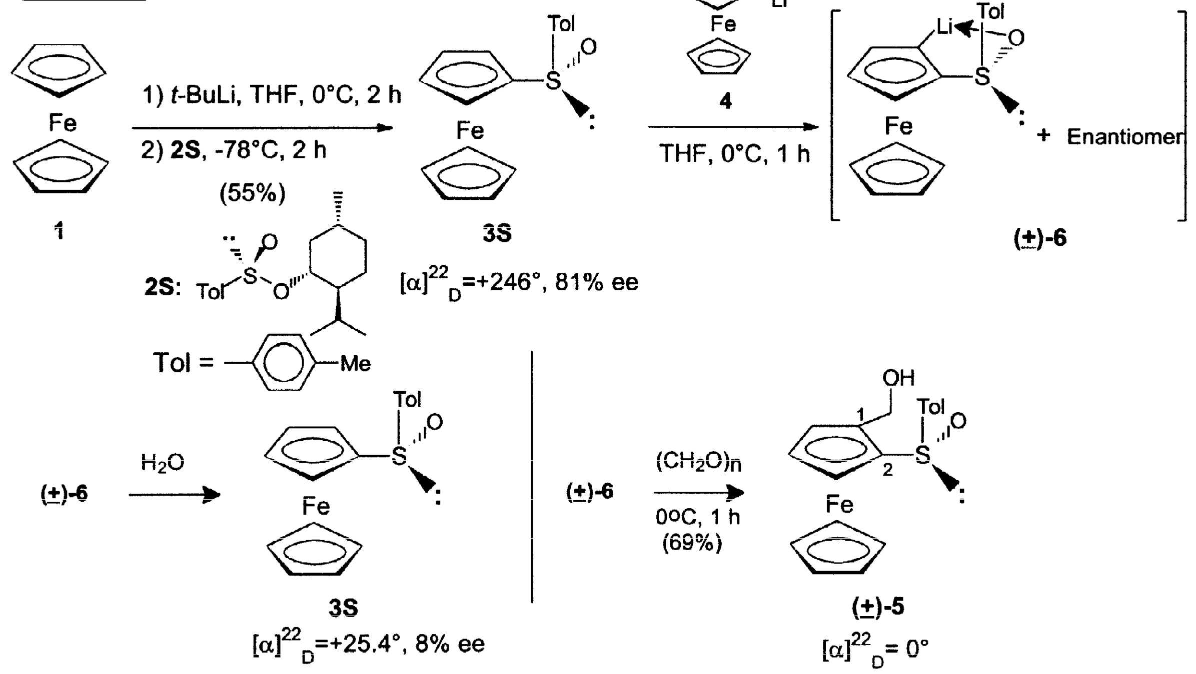
chiral sulfoxides were first synthesized and complexation with various transition-metals was then carried out.[7a,b,11a] Chiral transition-metal complexes containing sulfones have not been reported; indeed, asymmetric catalysis utilizing chiral transition-metal complexes containing sulfur is relatively rare.[7,11a] These observations, together with the attractive structural and chemical properties of ferrocene, prompted us to investigate the stereoselective synthesis of chiral 1,2-disubstituted ferrocenes containing sulfur, and to study their use in asymmetric synthesis.

RESULTS AND DISCUSSION

1. Enantioselective Synthesis of 1,2-Disubstituted Ferrocenes Containing Sulfur:

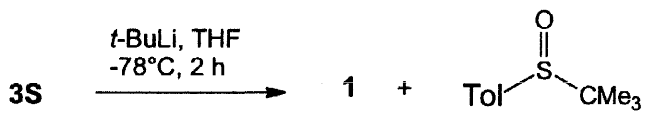
We first investigated the synthesis of enantiomerically pure ferrocenyl sulfoxide by direct sulfenylation of ferrocene (**1**) (Scheme 1) with *t*-butyllithium in THF at 0 °C followed by the addition of (*SS*)-*l*-menthyl *p*-tolylsulfinate (**2S**)[12,13] at -78 °C. (*SS*)-*p*-tolylsulfinylferrocene (**3S**) was isolated in 55% yield with a specific rotation of +246° (c=0.5, $CHCl_3$). Kagan and coworkers[7d] reported a similar reaction in which sulfinate **2S** was allowed to react with lithiated ferrocene at 0 °C, yielding sulfoxide **3S** with a specific rotation of +4° (c 0.9, $CHCl_3$) (*S*-configuration). However,[7e] when the reaction was carried out at -35 °C using sulfinate **2R** (the enantiomer of **2S**), a 75% yield of **3R** {87% ee; $[\alpha]_D$ = -257° (c 0.46, $CHCl_3$)} was reported. A later publication by Kagan and coworkers,[7f] reporting the synthesis of **3S** from the asymmetric oxidation of the corresponding sulfide, allowed us to determine that our product **3S** had an enantiomeric excess of 81%. We attributed this partial racemization process[7e] at -78°C to the nucleophilic attack of lithiated ferrocene on **3S** to provide **3R**. This assumption was confirmed (Scheme 1) when our 81% optically pure **3S** was treated with 1 equivalent of lithiated ferrocene in THF at 0 °C for 1 hour to give nearly racemized **3S** ($[\alpha]^{22}_D$ = +25.4°; 8% ee).[14] Furthermore, when the same reaction was carried out followed by the addition of paraformaldehyde at 0

Scheme 1



°C (Scheme 1), **sulfoxide alcohol 5** was isolated as a racemic mixture of a single diastereomer in 69% yield, $[\alpha]^{22}_D = 0°$ (based on 64% recovery of nearly racemic **3S**, $[\alpha]^{22}_D = +8°$, 3% ee). No other diastereomer of **5** was detected in the crude reaction product. Single-crystal X-ray analysis of **5** established the relative stereochemistry to be *SS**,1*S**,2*R**.[14] The racemization process is believed to result from nucleophilic attack of lithiated ferrocene (**4**) on the sulfur center of **3S**, to provide **3R**, and **4**.[15] Deprotonation of racemized **3** by **4** subsequently occurs (at a slower rate) diastereoselectively to give the lithiated anion (±)-**6** in which the lithium ion is chelated with the sulfoxide oxygen. Subsequent nucleophilic addition of anion (±)-**6** on paraformaldehyde generates (±)-**5**. In contrast to the reported[7e] C-2 deprotonation of ferrocenyl sulfoxides with various bases, such as *n*-BuLi or LDA, treatment of **3S** with *t*-BuLi in THF at -78 °C for 2 hours resulted in the formation of racemic *t*-butyl *p*-tolyl sulfoxide (**7**) (41%) and ferrocene (**1**) (84%) due to a nucleophilic displacement reaction at the sulfur center (Scheme 2).

Scheme 2



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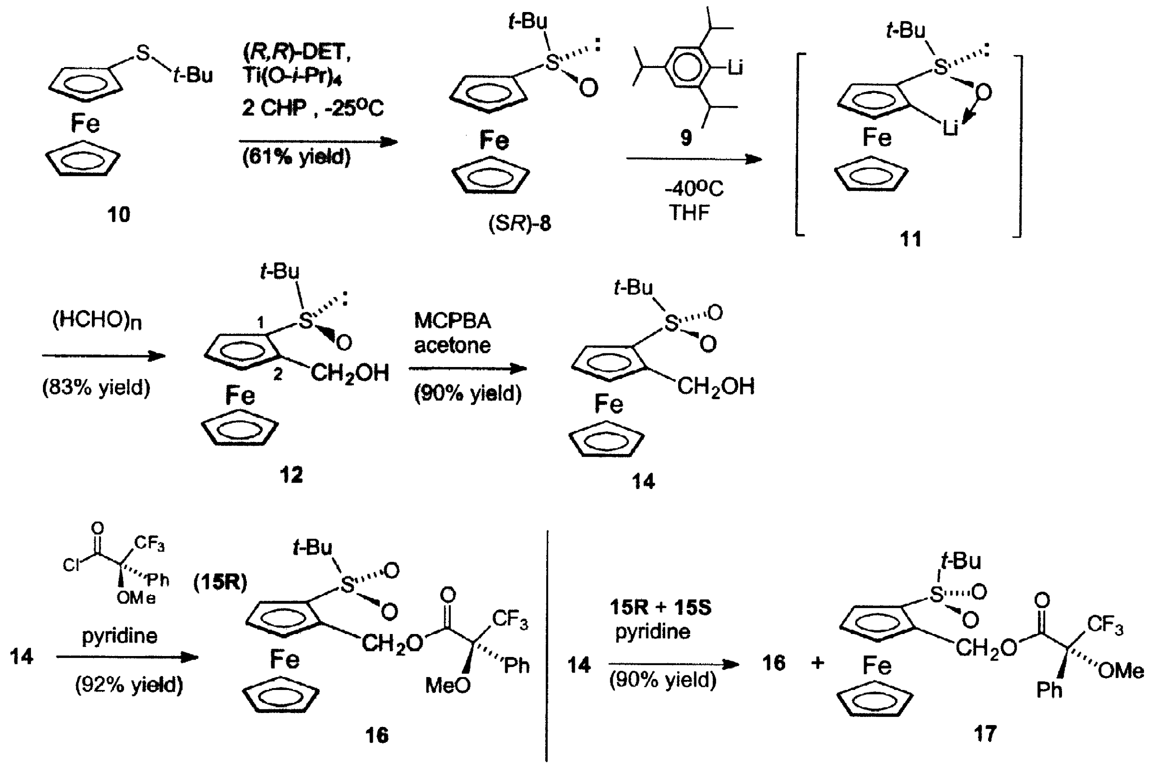
To avoid this displacement reaction, a bulkier sulfoxide, (*SR*)-(-)-*t*-butylsulfinylferrocene (**8**), and a more sterically hindered base, 2,4,6-triisopropylphenyllithium (**9**), were used. (*SR*)-*t*-Butylsulfinylferrocene (**8**) was prepared by Kagan's asymmetric oxidation[7f] (Scheme 3) of the corresponding sulfide **10** [L-(*R*,*R*)-diethyl tartrate, titanium tetraisopropoxide, H_2O, and cumene hydroperoxide (CHP) in CH_2Cl_2 at -25 °C for 72 hours]. The reaction was repeated a number of times, yielding the desired sulfoxide **8** in enantiomeric excesses ranging from 92% to 100%, based on the reported specific rotation of 95% optically pure sulfoxide **8** $[\alpha]^{22}_D = -339°$ (c 0.505; $CHCl_3$).[7f] The reaction is quite sensitive to temperature and reaction time, but after the ideal reaction conditions had been mastered sulfoxide **8** could reproducibly be obtained in enantiomeric excesses of 98% or above. Treatment of 100% ee sulfoxide **8** with the hindered base **9** in THF at -40 °C, followed by trapping of the corresponding lithiated anion **11** with paraformaldehyde afforded alcohol **12** in 83% yield along with 5% recovery of **8**. The absolute configuration of **12** was determined by single-crystal X-ray analysis[10] to be *SR*,1*S*,2*R*. The ^{1}H NMR spectrum of the crude product **12** showed no indication of the presence of its (*SR*,1*R*,2*S*)-isomer **13R** (see Scheme 4). The optical purity of alcohol **12** was confirmed to be >99% ee by the following correlations. Compound **12** was oxidized with MCPBA (90% yield) to sulfone **14** (Scheme 3), which was converted to ester **16** by treatment with Mosher's acid chloride **15R**. The ^{1}H NMR spectrum of crude **16** indicated only one set of signals. Treatment of **14** with racemic Mosher's acid chloride (±)-**15** afforded a 1:1 mixture of **16** and **17**, whose ^{1}H NMR spectrum displayed two distinct sets of signals. In particular, the C<u>H</u>$_2$OC=O of **16** appears as an AB quartet, one at 5.67 ppm and the other at 5.32 ppm. The resonances of the $CH_2OC{=}O$ of diastereomer **17** appeared at 5.58 ppm (doublet) and 5.36 ppm (doublet) (Figure 1). The ^{1}H NMR resonance of this $CH_2OC{=}O$ group was then used to verify the regioselectivity of the hydroxymethylation of sulfoxide **8**. Hence, 92% ee and 100% ee sulfoxide **8** were converted to the corresponding Mosher's derivatives, the optical purity of which was determined by analysis of the 5.30-5.70 ppm region (CH_2O signal) of the corresponding ^{1}H NMR spectra, as shown on Figure 1. The results indicate that the diastereomeric excesses of the Mosher's esters obtained correlate well with the optical purity of the

Scheme 3



starting sulfoxide **8**, meaning that the deprotonation reaction is highly diastereoselective and that the enantiomeric composition of the material is retained.

The rationale for the high diastereoselectivity of the lithiation reaction is that the lone pair of the oxygen atom of the sulfoxide is in a suitable position to form a donating bond to the lithium atom at C-2, stabilizing the 2-lithioisomer by the chelating effect with respect to the 3-lithio-compound or the 1'-isomer which has the lithium on the other cyclopentadienyl ring (Cp) so that the chelating effect does not exist. If one now considers that there is not much space at the interior-side of the ferrocene moiety (i.e., between the two rings), it seems convincing that the lone pair of the sulfoxide, and not the *t*-butyl group, will preferably occupy this space as depicted in structure **11** (the *t*-butyl group would have strong repulsive interactions with the hydrogen atoms of the second Cp ring). The selectivity of the deprotonation is likely due to a kinetic process. When deprotonation with 2,4,6-triisopropylphenyllithium (**9**) was carried out at higher temperature (-20 °C instead of -40 °C), **12** was isolated in 39% yield, 5% yield of one of C-2' diastereomers **13R**, and 52% recovery of **8** (Scheme 4). The absolute stereochemistry of **13R** was determined by single-crystal X-ray crystallography.[16] To account for the formation of **13R**, it was proposed that **11a** was presumably generated from proton exchange between **11** and residual **8** (which had not yet reacted with base **9**). It is also possible that **12a**, the -CH_2OLi form of **12**, undergoes a reversible reaction back to **11** and paraformaldehyde, which at higher temperature and over longer time would continue to provide **11a**, thus increasing the production of **13R**.

The enantiomer of **13R** was unequivocally synthesized by stereoselective oxidation of sulfide **18** with 1 equivalent of MCPBA (Scheme 5) in THF at 25 °C. Compound (*SS*,1*S*,2*R*)-**13S** was isolated in 95% yield, and its TLC, ^{1}H and ^{13}C NMR spectra were different from those of **12**. Sulfide **18** was obtained from the

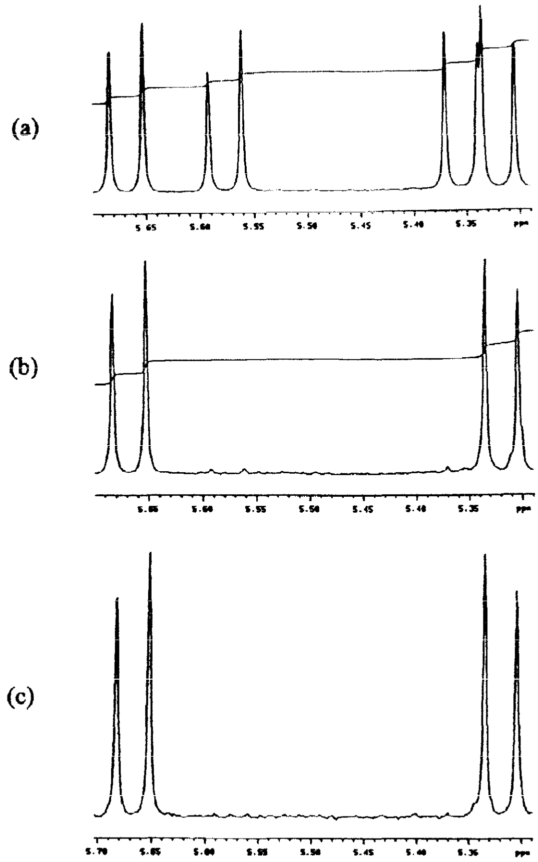
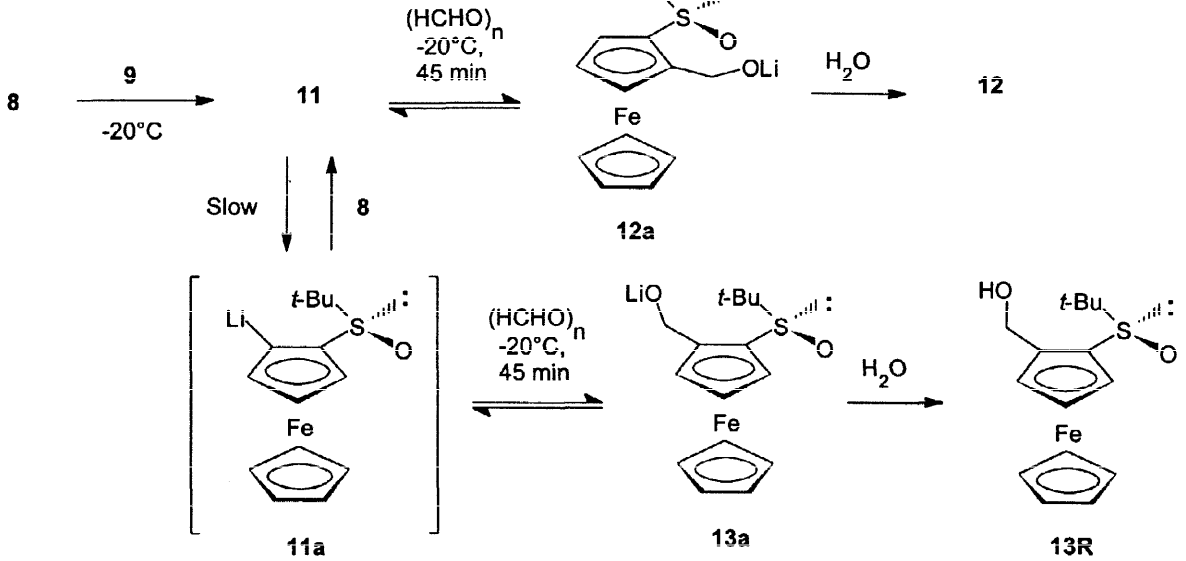


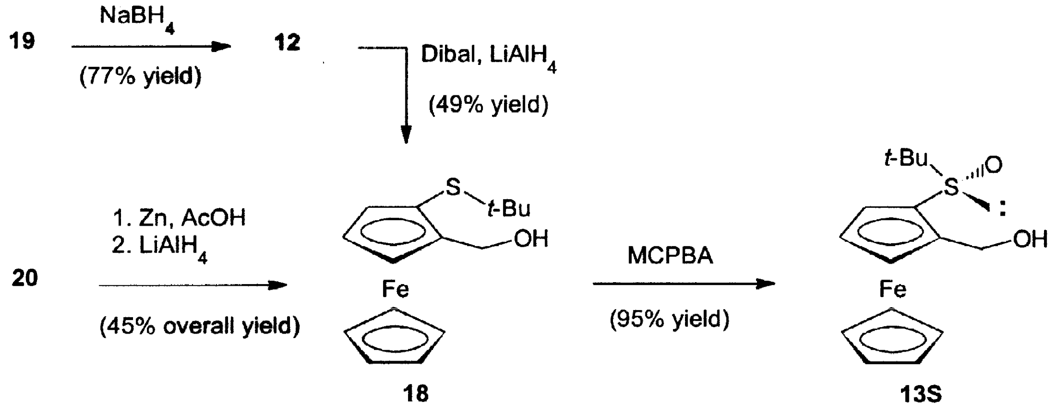
Figure 1. Portions of ^{1}H NMR spectra for **16** and **17** derived from (a) reaction of (±)-**15** and sulfone **14**; (b) reaction of (+)-(*R*)-**15** and 92% ee **14**; (c) reaction of (+)-(*R*)-**15** and 100% ee **14**.

reduction of **12** with DIBALH and LAH in diethyl ether at 25 °C (49% yield). DIBALH was used to prechelate the hydroxyl and sulfinyl moieties of **12**. Without the addition of DIBALH, LAH alone afforded only 25% yield of **18**. Reduction of **12** with Zn in AcOH was sluggish, and mainly starting material was recovered.

Scheme 4

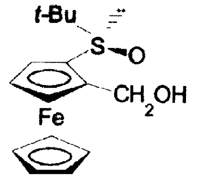
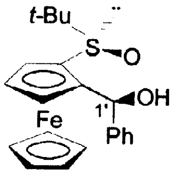
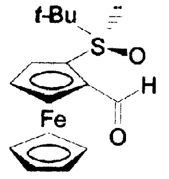
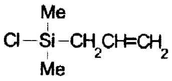
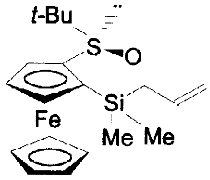
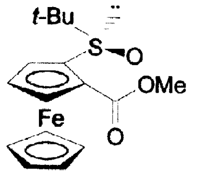
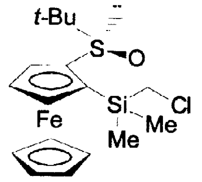
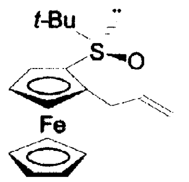
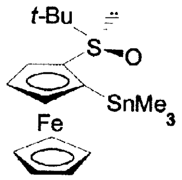
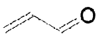
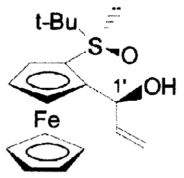
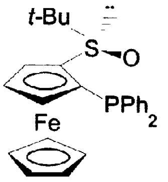
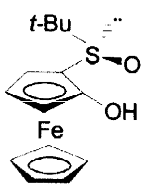


Scheme 5



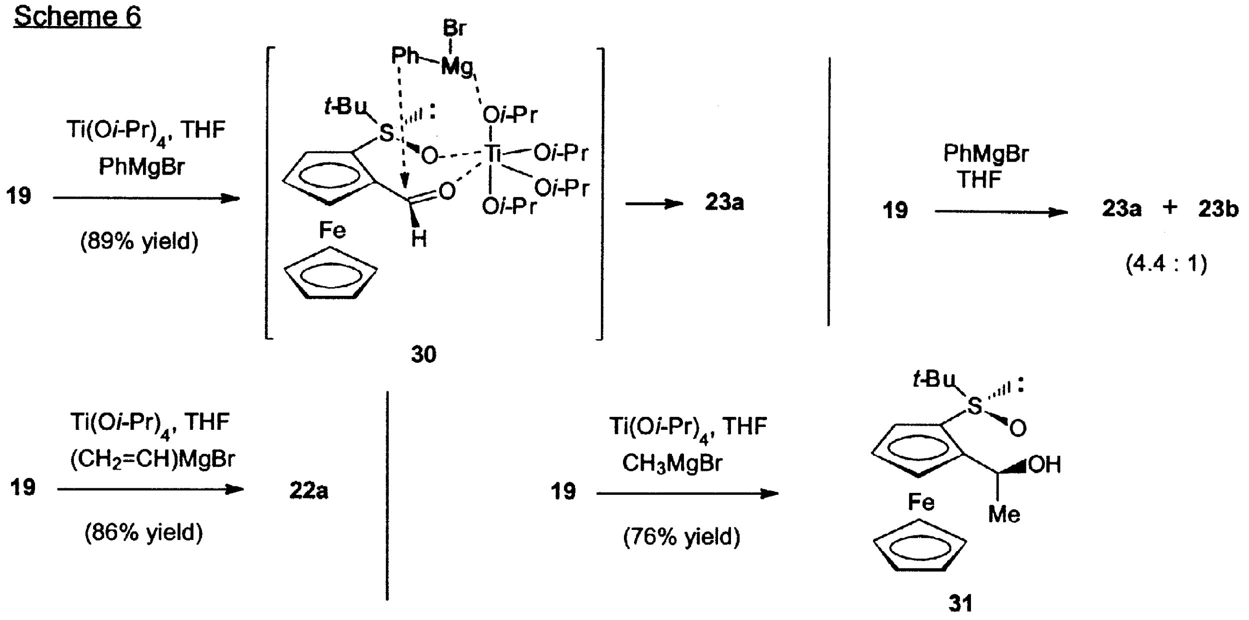
The regioselective alkylation of **8** prompted us to investigate the synthesis of other 1,2-disubstituted ferrocenes. Thus, reaction of anion **11** with electrophiles composed of carbon (ethyl formate, methyl chloroformate, allyl bromide, acrolein, benzaldehyde), silicon (allyldimethylsilyl chloride, chloromethyldimethylsilyl chloride), tin (trimethyltin chloride) and phosphorus (diphenylphosphinyl chloride) gave the corresponding adducts in very good yields as shown in Table 1. Bis(trimethylsilyl)peroxide (oxygen electrophile) provided only a 55% yield (18% of **8** was recovered). In all cases, only a single regioisomer was detected by ^{1}H NMR. In entries 5 and 6, pairs of diastereomers were produced at the C-1' center (carbon bears the hydroxyl group). The regiochemistry and optical purity of aldehyde **19** and ester **20** were determined by the following correlations (Scheme 5). Reduction of **19** with $NaBH_4$ in methanol at 25 °C furnished **12** (77% yield) whose ^{1}H and ^{13}C NMR spectra and specific rotation were identical to those of the sample obtained from the reaction of **8** with paraformaldehyde. Reduction of **20** to the corresponding sulfide with activated zinc in acetic acid at 25 °C (47% yield of sulfide **29**), followed by treatment with lithium aluminum hydride (LAH) in diethyl ether (96% yield) gave alcohol **18** whose spectra and specific rotation were identical to those obtained from the product of the reduction of sulfoxide **12** with DIBALH and LAH as mentioned above. The addition of lithiated anion **11** to acrolein at -85°C provided a 4:13 diastereomeric mixture **22a** and **22b** (21% and 69% yield, respectively; separated by column chromatography). However, when acrolein was added to the lithiated anion **11** at -78°C, the stereoselectivity was diminished: a 1:2 mixture of diastereomers **22a**:**22b** was isolated. Benzaldehyde (Entry 6) gave a 1:1 mixture of two isomers, **23a** and **23b** (75% yield). The absolute configurations of **22a** and **23a** were determined as followed. The sulfoxide and aldehyde moieties in substrate **19** have coordination abilities through their oxygen atoms and could potentially chelate with a transition-metal complex acceptor. Such chelation would bring the sulfoxide and carbonyl atoms together, thereby locking the molecule in a more restrained conformation, and potentially increasing the degree of stereoselectivity of the anion addition reaction onto the aldehyde moiety. This possibility was tested by using $Ti(O\text{-}i\text{-}Pr)_4$ as the chelating agent.[17] Thus, pre-chelation was effected by treating aldehyde **19** with $Ti(O\text{-}i\text{-}Pr)_4$ (1.3 equiv) in THF at 0 °C for 30 minutes (Scheme 6). After the reaction mixture was cooled to -78 °C, phenylmagnesium bromide was added and allowed to react from -78 to 0 °C over 3.5 hours. Compound (1'*S*)-**23a** was isolated in 89% yield as a single diastereomer. Compound **23b** was not detected by ^{1}H NMR analysis of the crude product. The stereochemistry of **23a** was determined by single-crystal X-ray analysis (Figure 2).[18] Without the addition of $Ti(O\text{-}i\text{-}Pr)_4$, **23a** and its 1'*R*-isomer **23b** were produced in a 4.4:1 ratio.

Table 1. Products and Yields of the Reactions of the Anion of **8** with Various Electrophiles.

Entry	Reagents	Product (% yield)[a]	Entry	Reagents	Product (% yield)[a]
1	$(CH_2O)_n$	 **12** (87%)	6	PhCHO	 + **23b** (isomer at C-1') **23a** (75%; 1:1)
2	EtO-CHO	 **19** (85%)	7	 $\mathrm{Cl{-}\underset{Me}{\overset{Me}{Si}}{-}CH_2CH{=}CH_2}$	 **24** (73%)
3	$Cl\text{-}CO_2Me$	 **20** (84%)	8	$ClSiMe_2CH_2Cl$	 **25** (85%)
4	$Br\text{-}CH_2CH{=}CH_2$	 **21** (84%)	9	Cl-$SnMe_3$	 **26** (86%)
5		 + **22b** (69% ; isomer at C-1') **22a** (21%)	10	Cl-PPh_2	 **27** (82%)
			11	$Me_3SiOOSiMe_3$	 **28** (55%)

(a) Isolated yields. Small amount of starting sulfoxide **8** (5~25%) was recovered.

Scheme 6



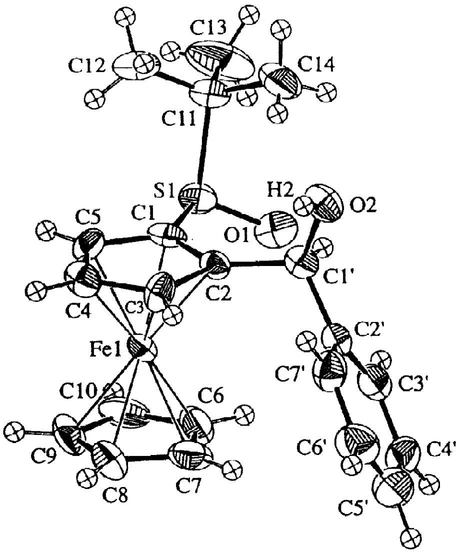


Figure 2. ORTEP drawing of X-ray crystallographically determined structure of **23a**.

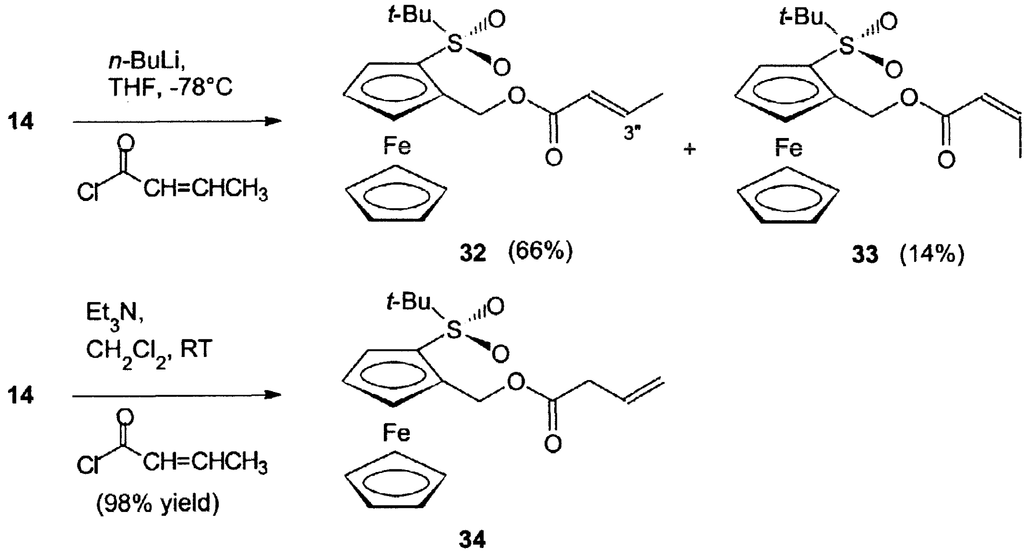
To account for this high stereoselectivity, it was proposed that the reaction occurred through transition state **30**, where the phenyl group attacks from the *si*-face of the aldehyde. Similarly, addition of **19** with Ti(O-*i*-Pr)$_4$ and vinylmagnesium bromide or methylmagnesium bromide afforded 86% yield of **22a** and 76% yield of **31**, respectively.

In summary, the stereoselective synthesis of enantiomerically pure 2-substituted 1-(*t*-butylsulfinyl)ferrocenes can be achieved in excellent yields by the reaction of 2-lithioferrocene **11** with various electrophiles. The addition of aldehyde **19** with a variety of Grignard reagents under chelation control is completely stereoselective.

2. *1,4-Addition Reactions of Sulfonylferrocenyl Esters:*

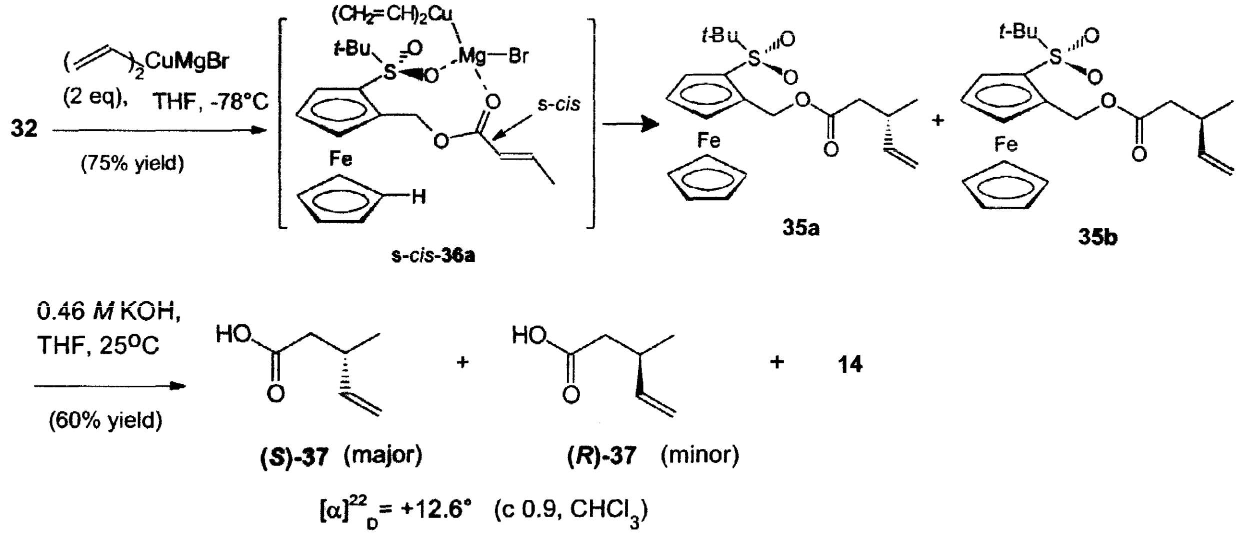
Since the sulfoxide moiety is relatively reactive towards strong nucleophile and electrophile, the asymmetric inductive properties of the chiral ferrocenyl sulfones were first investigated by studying the 1,4-addition of various alkyl and alkenyl cuprates to sulfonylferrocenyl ester **32**. Compound **32** was prepared (Scheme 7) in 66% yield along with 14% yield of the *cis*-isomer **33** by the reaction of alcohol **14** with *n*-BuLi in THF at -78 °C, followed by the addition of crotonyl chloride (this chloride consisted of a 4:1 mixture of *trans*- and *cis*-isomer). Treatment of **14** with Et_3N and crotonyl chloride in methylene chloride at 0 °C provided ester **34** (98% yield). The mechanism for the formation of **34** may involve *in situ* formation of vinyl ketene [$(CH_2=CH)CH=C=O$] followed by the addition of alcohol **14**. Ene ester **32** was subjected to 1,4-addition of bromomagnesium divinylcuprate in THF at -78 °C in the presence of dimethyl sulfide. Surprisingly, no reaction was observed when one equivalent of the cuprate reagent was used. Only when a second equivalent of the copper complex was added, did the reaction leading to **35** go to completion (Scheme 8). This observation suggested that the first equivalent of bromomagnesium divinylcuprate might serve as a chelating agent between the sulfonyl moiety and the carbonyl of the ene ester (as depicted in s-*cis*-**36a**), and the second equivalent being the actual reactive species. Since it was difficult to determine the stereoselectivity of the reaction solely on the basis of ^1H and ^{13}C NMR data, ester **35** was saponified (KOH, H_2O, THF) to sulfone alcohol **14** and carboxylic acid **37** {$[\alpha]^{22}_D = +12.6°$, c 0.9, $CHCl_3$}. The specific rotation of the latter had been reported[19a,b] (for *S*-**37**: lit.[19a] $[\alpha]^{22}_D = +13.55°$, c 3.3, $CHCl_3$; lit.[19b] $[\alpha]^{22}_D = +17.5°$; for *R*-**37**: lit.[19a] $[\alpha]^{22}_D = -13.97°$, c 2.9, $CHCl_3$). The determination of the optical purity based on the specific rotation of **37** proved difficult because of the relative volatility of the compound and the different specific rotation values reported. Furthermore, our specific rotation and the reported values were recorded at different concentrations. A method to determine the optical purity of our product **35** consisted in synthesizing a 1:1 mixture of two stereoisomers at C-3", **35a** and **35b**, and compare its ^1H NMR spectrum with that of 1,4-addition product **35** from **32**. Thus, methyl crotonate was treated with bromomagnesium divinylcuprate to give adduct **38**, which was then saponified (KOH in H_2O-THF) and esterified [**14**, *N,N'*-dicyclohexylcarbodiimide (DCC), Et_3N, CH_2Cl_2] to give **35ab** (Scheme 6). Its ^1H NMR spectrum did show two distinct sets of signals, assigned to the

Scheme 7

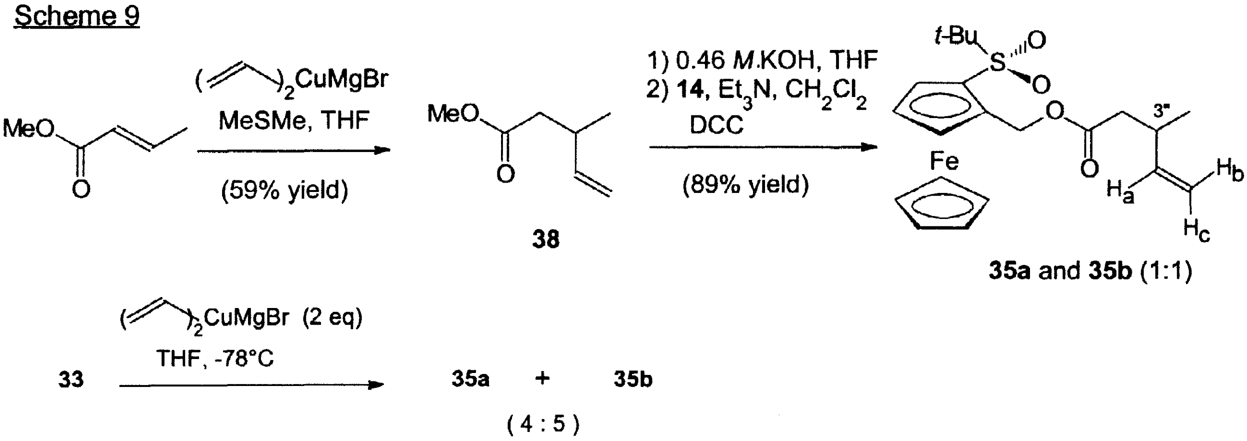


geminal vinylic protons H_B and H_C. The signals (two doublet of triplet) at 4.94 ppm (H_C) undoubtedly showed that the adduct, **35**, obtained from the asymmetric 1,4-addition of divinylcuprate on ene ester **32** was actually a mixture of two diastereomers in a ratio approaching 1.8:1 (28% ee). This result is in disagreement with the specific rotation; the $[\alpha]^{22}_D$ value of 12.6° would be 72% ee assumming that $[\alpha]^{22}_D$ of $+17.5^{\circ}$[19b] represents 100% optically purity.

Scheme 8

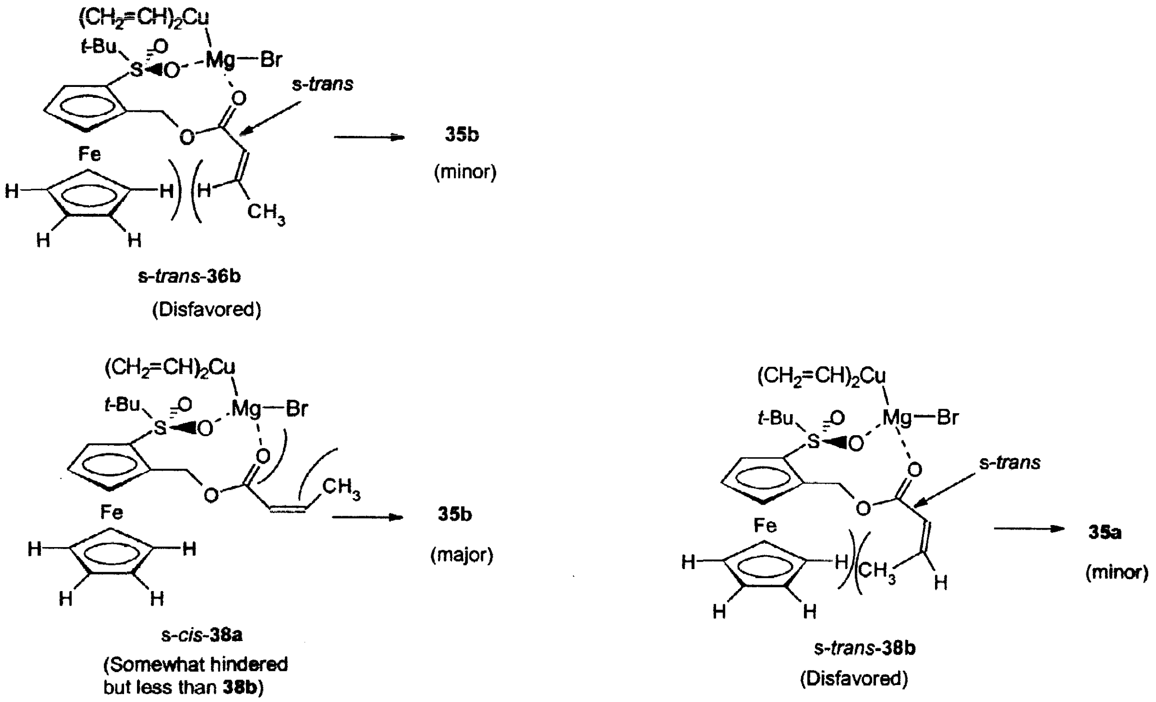


Scheme 9



Unexpectedly, when *cis*-ester **33** was subjected to the same reaction (Scheme 9), the desired product **35** was obtained with a reverse diastereomeric ratio; i.e. **35a** : **35b** ≃ 4:5 based on the relative intensities of the vinylic H_c signals of **35a** and **35b** on the ^1H NMR spectrum of the crude product. To account for these results, it was proposed that the reaction proceeded via transition state **36a** (Scheme 8), where the system is held intact by chelation of the sulfonyl moiety and the carbonyl of the ester with the cuprate reagent. In such an arrangement, the s-*cis* conformation **36a** of the ester should be favored over the s-*trans* conformation **36b** (Scheme 10) due to steric repulsion of the β–olefinic proton geminal to the methyl group with the cyclopentadienyl hydrogens. Attack of the second equivalent of cuprate reagent from the most open face of s-*cis*-**36a** would lead to **35a** as the major product. In the case of *cis*-ester **33**, these considerations still hold, except that the difference in steric interactions between s-*cis* (**38a**) and s-*trans* (**38b**) conformers is probably not as pronounced as in the *trans* ester **32** case. Both **38a** and **38b** show steric repulsion between the methyl group and carbonyl oxygen in the case of s-*cis* **38a**, and the methyl group and the cyclopentadienyl hydrogens in the case of s-*trans* **38b**. However, steric interactions seem less severe for **38a** (leading to **35b**) than for **38b** (leading to **35a**).

Scheme 10

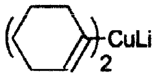
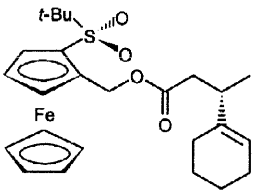
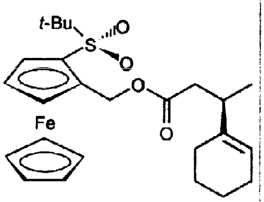
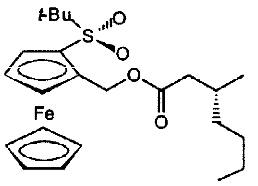
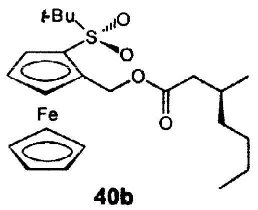
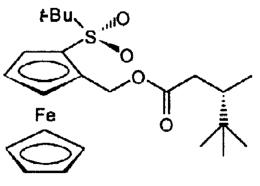
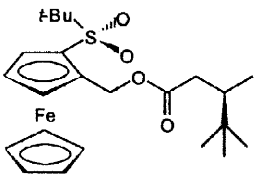


1,4-Addition to ester **32** with other cuprate reagents have been carried out and the corresponding adducts **39a-b** ~ **41a-b** have been isolated in good yields as mixtures of diastereomers (Table 2). The absolute stereochemistry at the newly created stereocenter was assumed to be of (*S*)-configuration (**39a**, **40a**, **41a**) based on the results obtained from ene ester **32** with vinylcuprate (Entry 1). The ratios of diastereomers were determined from the relative intensities of the CH_2O signals in the ^{1}H NMR spectra or $CH_2C{=}O$ signals in the ^{13}C NMR spectra for both diastereomers. For instance, one proton belongs to the CH_2O group of **39a** and **39b** appear at δ 5.33 (d) and 5.34 (d) ppm (^{1}H NMR), respective [for **41a** and **41b**: 5.33 (d) and 5.1 (d) ppm; for **40a** and **40b**; ^{13}C NMR: δ 41.9 and 41.8 ppm].

When cinnamoyl ester **42** [prepared from sulfonyl alcohol **14** and cinnamoyl chloride (Scheme 11)] was treated with bromomagnesium divinylcuprate or lithium divinylcuprate under various conditions (dimethyl sulfide or/and THF, ether were used and temperature ranges from -78 to 25 °C), no desired 1,4-adduct was isolated. The starting material **42** was recovered along with some sulfone **14** (product of the 1,2-addition reaction of the cuprate reagent with **42**). However when lithium dicyclohexenylcuprate was used (6 equiv.) and the reaction mixture was allowed to reach room temperature, the desired adduct **43** was obtained as a 1:1 mixture of diastereomers (based on the ^{1}H NMR spectrum of the crude product).

The inherent planar chirality of ene esters such as **32** and **33** allows the 1,4-addition of various cuprate reagents to occur with some stereoselectivity. The remoteness of the reactive center (the β-carbon of the ene

Table 2. Products and Yields of the 1,4-Addition Reactions of **32** and **33** with Various Cuprate Reagents.

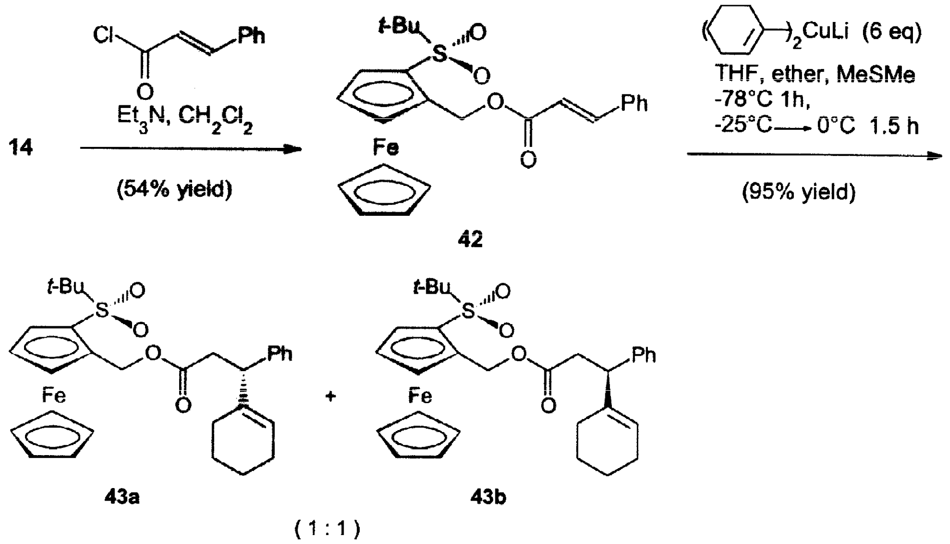
Entry	Ene Ester	Cuprate Reagent	Reaction conditions	Product (% yield)[a]
1	**32**	2 equiv $(CH_2{=}CH)_2CuMgBr$	THF, Me_2S -78°C, 0.5 h	**35a** + **35b** (75% ; 1.8:1)
2	**33**	2 equiv $(CH_2{=}CH)_2CuMgBr$	THF, Me_2S -78°C, 0.5 h; -45°C, 1 h	**35a** + **35b** (60% ; 4:5)
3	**32**		THF, Me_2S -78°C, 1 h	 **39a**  **39b** (77% ; 3:2)
4	**32**	2 equiv n-Bu_2CuLi	THF, Me_2S -50°C, 3 h	 **40a**  **40b** (75% ; 2:1)
5	**32**	2 equiv t-Bu_2CuLi	THF, Me_2S -78°C, 1.5 h	 **41a**  **41b** (100% ; 5.2:1)

(a) Isolated yields. A mixture of two inseparable diastereomers.

esters is five atoms away from the ferrocene moiety) and flexibility of the side-chain esters are two possible factors responsible for the lack of stereoselectivity.

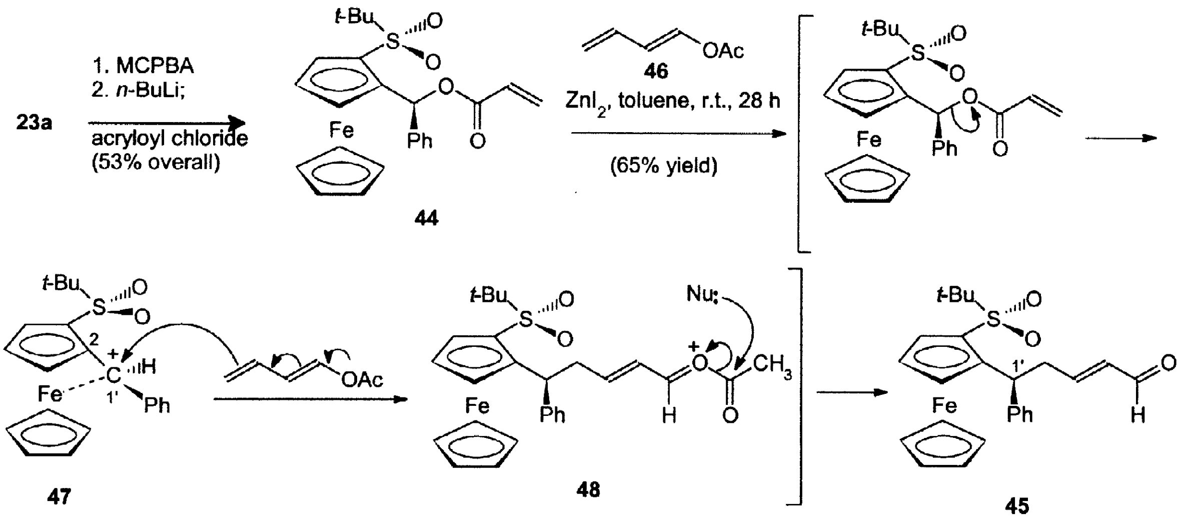
An interesting-cationic displacement reaction was found when ene ester **44** [prepared from the oxidation (MCPBA) of alcohol **23a** followed by acylation (n-BuLi, then acryloyl chloride)] was treated with 1-acetoxy-1,3-butadiene and 0.3 equiv of ZnI_2 in toluene at 25 °C. Enal **45** was obtained in 63% yield (Scheme 12). The proposed mechanism of its formation invokes the initial formation of a "chiral" ferrocenyl cation **47**, which is then attacked by nucleophile 1-acetoxy-1,3-butadiene. It is known that α-ferrocenylalkyl carbocations (carbocations on a position adjacent to the cyclopentadienyl ring) are particularly stable. It is believed that this stability arises from the direct participation of the iron atom in charge delocalization, which causes the two cyclopentadienyl rings to deviate from being parallel (tilt angle 4-5°) and leads to a bending of the substituent bearing the cationic center out of the plane of the ring, in the direction of the iron atom.[20] As a

Scheme 11



consequence of the special structure of such cations, rotation around the bond between the ring carbon and the cationic center is hindered because of its partial double bond character. Thus the cation exists as distinct diastereomers with only a low tendency towards rotation of C2-C1' bond. The leaving group of the α-ferrocenylalkyl/aryl compound departs in the direction away from the iron atom (*exo*), as there is little space between the two Cp rings and strong steric repulsion would be expected if the reaction were to occur at this side. Any entering nucleophile also attacks from the *exo*-side, which leads to net retention of configuration. Based on these considerations, the stereochemistry of compound **45** at C-1' was assumed to be the same as that of the starting ene ester **44** [(*S*)-configuration].

Scheme 12



CONCLUSION

Various enantiomerically pure 1,2-disubstituted ferrocenes were synthesized that contain a sulfinyl, sulfonyl, or sulfenyl moiety at C-1 and a carbon or heteroatom substituent at C-2 of the ferrocene ring.

Stereoselective addition of aldehyde **19** with a variety of Grignard reagents was found under chelation controlled conditions. The stereoselectivity of the 1,4-addition reactions of ene esters (**32, 33 and 42**) with cuprate reagents was studied and presumably the remoteness of the reactive site (C-3") and the flexibility of the side chain of the esters are responsible for the lack of stereoselectivity. In view of the study of the synthesis of planar-chiral 1,2-disubstituted ferrocenyl derivatives reported previously, the design and construction of a sulfenyl-alkoxy, -amino, or -phosphinoferrocenyl bidentate complexes along with their asymmetric catalytic reactions are currently under investigation.

EXPERIMENTAL SECTION

General Methods. All non-aqueous reactions were carried out under argon atmosphere unless specified otherwise. Nuclear magnetic resonance spectra were obtained at 400 MHz for ^{1}H and 100 MHz for ^{13}C in deuteriochloroform. ^{1}H NMR spectra are reported in ppm (δ units) downfield of internal reference tetramethylsilane (TMS), ^{13}C NMR spectra are reported in ppm (δ units) using chloroform ($CHCl_3$) as the standard (77 ppm). Infrared spectra are reported in wavenumbers (cm^{-1}). Mass spectra were obtained from a Hewlett Packard GC/HPLC 5989A mass spectrometer using either EI, CI or FAB (*m*-nitrobenzyl alcohol was used as the matrix). Rotations of optically active compounds were determined with a Perkin-Elmer 241 polarimeter. Davisil silica gel, grade 643 (200~425 mesh), was used for the flash chromatographic separations. E. Merck precoated TLC plates silica gel 60F-254 were used in preparative TLC plates. Solvents such as THF and diethyl ether for organometallic reactions were distilled over sodium and benzophenone under argon, and diisopropylamine was freshly distilled from CaH_2. Ferrocene, L-(*R*,*R*)-diethyl tartrate, cumene hydroperoxide, titanium tetraisopropoxide, *m*-chloroperbenzoic acid, methyl chloroformate, allyl bromide, acrolein, allyldimethylsilyl chloride, chloromethyldimethylsilyl chloride, trimethyltin chloride, diphenylphosphinyl chloride, *t*-BuLi, *n*-BuLi, phenylmagnesium bromide, methylmagnesium bromide, vinylmagnesium bromide, *trans*-crotonyl chloride (containing the *cis*-isomer), acryloyl chloride, and 1-acetoxy-1,3-butadiene were purchased from Aldrich.

(SS)-(p-Toluenesulfinyl)ferrocene (3S). To a cold (0 °C) solution of 0.759 g (4 mmol) of ferrocene (**1**) in 6 mL of THF under argon was added 2.0 mL (3.4 mmol; 1.7 *M* solution in pentane) of *t*-BuLi. After the solution was stirred at 0 °C for 2 h, it was cooled to -78 °C and then transferred into a cold (-78 °C) solution of 1 g (3.4 mmol) of (-)-(*S*)-*l*-menthyl *p*-toluenesulfinate (**2S**) in 5 mL of THF. The resulting solution was stirred at -78 °C for 2 h, poured into 100 mL of brine, and extracted three times with 100 mL portion of CH_2Cl_2. The combined CH_2Cl_2 extracts were dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using hexane-diethyl ether as eluant to give sulfoxide **3S** which was recrystallized from diethyl ether and hexane to give 0.606 g (55% yield) of pure **3S**; mp. 118-119 °C (dec.); $[\alpha]^{22}_D = +246°$ (c = 0.5, $CHCl_3$); 81% ee based on the value of +305° for the 100% pure sample reported by Kagan and coworkers.[7f] ^{1}H NMR ($CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.25 (d, *J* = 8.0 Hz, 2 H, Ar-H), 4.61 (dt, *J* = 2.4, 1.2 Hz, 1 H, Cp-H), 4.37 (s, 5 H, Cp'-H), 4.35 (m, 2 H, Cp-H), 4.32 (dt, *J* = 3.6, 1.2 Hz, 1 H, Cp-H), 2.37 (s, 3 H, *p*-Me); ^{13}C NMR ($CDCl_3$) δ 142.3 (s, Ar), 140.2 (s, Ar), 129.0 (d, 2 C, Ar), 123.6 (d, 2 C, Ar), 94.0 (s, Cp), 69.3 (d, 5 C, Cp'), 67.2 (d, 2 C, Cp), 64.6 (d, 2 C, Cp), 20.8 (q, Me); MS *m/z* FAB 324 (M+).

Reaction of (SS)-p-toluenesulfinylferrocene (3S) with t-BuLi. Formation of ferrocene (1) and t-butyl p-tolylsulfoxide (7). To a cold (-78 °C) solution of 60 mg (0.185 mmol) of 3S {$[\alpha]^{22}_{D}$ = +233°; 76% ee} in 1 mL of THF was added 0.2 mL (0.315 mmol; 1.7 *M* in pentane) of *t*-BuLi dropwise. After the reaction was stirred for 2 h at -78 °C, it was diluted with 20 mL of water at -78 °C, warmed to 25 °C and extracted with CH_2Cl_2 three times (50 mL each). The combined extracts were dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using diethyl ether/hexane as eluant to give 29 mg (85% yield) of ferrocene (2) and 15 mg (42% yield) of 7. A small amount of unidentifiable material was also isolated from the column chromatographic separation. Compound 7: $[\alpha]^{22}_{D}$ = +1.0° (c 1.5, acetone); Lit.[21] +161° (*R*-configuration). ^{1}H NMR ($CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.28 (d, *J* = 8.0 Hz, 2 H, Ar-H), 2.41 (s, 3 H, *p*-Me), 1.16 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 141.5 (s, Ar), 136.7 (s, Ar), 129.1 (d, 2 C, Ar), 126.3 (d, 2 C, Ar), 55.6 (s, CS), 22.7 (q, 3 C, t-Bu), 21.4 (q, Me); MS *m/z* CI 197 (M+1).

Racemization of 3S with lithiated ferrocene. To a cold (0 °C) solution of 13 mg (0.07 mmol) of ferrocene (1) in 0.3 mL of THF was added 35 μL (0.06 mmol) of *t*-BuLi (1.7 *M* in pentane). After the solution was stirred at 0 °C for 2 h, a cold (0 °C) solution of 16 mg (0.05 mmol) of 3S ($[\alpha]^{22}_{D}$ = +246°; 81% ee) in 0.2 mL of THF was added via cannula and the resulting solution was stirred at 0 °C for 1 h. The solution was poured into 25 mL of brine, extracted with 75 mL of diethyl ether, and then twice with methylene chloride (30 mL each). The combined organic extracts were dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane and diethyl ether as eluant to give 13 mg of ferrocene (100%) and 15 mg (94%) of 3S. Compound 3S: $[\alpha]^{22}_{D}$ = +26.8°; 8% ee.

(SS,1S*,2R*)-1-(Hydroxymethyl)-2-(p-toluenesulfinyl)ferrocene [(±)-5].* To a cold (0 °C) solution of 0.208 g (1.12 mmol) of ferrocene (1) in 2 mL of THF was added a solution of 0.56 mL (0.96 mmol) of *t*-BuLi (1.7 *M* in pentane). After the solution was stirred at 0 °C for 2 h, a cold (0 °C) solution of 0.26 g (0.80 mmol) of sulfoxide 3S (81% ee) in 2 mL of THF was added and the resulting solution was stirred for 1 h, after which time it was transferred via cannula into a cold (0 °C) solution of 30 mg (0.96 mmol) of paraformaldehyde in 2 mL of THF. After stirring at 0 °C for 1 h, the solution was diluted with brine, and extracted three times with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether-diethyl ether as eluant to give 70 mg (69% yield, based on recovered 3) of (±)-5 and 167 mg (64%) of nearly racemic 3. Recrystallization of *(±)-5* from a mixture of petroleum ether and ether gave yellow crystals (mp 52-54°C) suitable for X-ray analysis.[14] Compound (±)-5: $[\alpha]^{22}_{D}$ = 0°; ^{1}H NMR ($CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 2 H, Ph-H), 7.25 (d, *J* = 8.2 Hz, 2 H, Ph-H), 4.74 (t, *J* = 6.2 Hz, 1 H, OH), 4.49 (s, 5 H, Cp'-H), 4.44 (broad s, 1 H, Cp-H), 4.38 (broad s, 1 H, Cp-H), 4.27 (t, *J* = 2.4 Hz, 1 H, Cp-H), 4.15 (d, *J* = 6.2 Hz, 2 H, CH_2-O), 2.36 (s, 3 H, *p*-Me); ^{13}C NMR ($CDCl_3$) δ 141.5 (s, 2 C, Tol), 130.0 (d, 2 C, Tol), 124.1 (d, 2 C, Tol), 91.0 (s, Cp), 89.0 (s, Cp), 72.3 (d, Cp), 70.0 (d, 5 C, Cp'), 69.5 (d, Cp), 64.9 (d, Cp), 57.8 (t, CO), 21.7 (q, Me); MS *m/z* FAB 354 (M+). Anal. Calcd for $C_{18}H_{18}FeO_2S$: C, 61.03; H, 5.12. Found: C, 60.87; H, 5.41.

2,4,6-Triisopropylphenyllithium (9). Preparation of 1-bromo-2,4,6-triisopropylbenzene:[22] [The reaction was performed in the dark: the apparatus (100 mL three-necked flask and dropping funnel) was wrapped in aluminum foil]. To a cold (-5 ~ 0 °C) solution of 6.675 g (32.72 mmol) of 1,3,5-triisopropylbenzene and 164 mg (2.94 mmol) of iron metal in 3.25 mL of CCl_4 was added dropwise a solution of 5.23 g (1.70 mL; 32.72 mmol) of bromine in 3.40 mL of CCl_4. After the addition of bromine was over, the reaction was allowed to slowly reach room temperature and was kept at this temperature overnight. The mixture was washed successively with 50 mL of water, 50 mL of 1 *N* NaOH and 2 × 50 mL of H_2O (or until the aqueous washings were neutral). The organic layer was dried ($MgSO_4$) and concentrated. The crude product was distilled under reduced pressure to give 9.130 g (98% yield) of colorless oil. Bp: 110°C/0.75 mm Hg.

To a cold (-78 °C) solution of 130 mg (0.46 mmol) of 1-bromo-2,4,6-triisopropylbenzene in 1.2 mL of THF was added 0.55 mL (0.92 mmol) of *t*-BuLi (1.7 *M* solution in pentane) dropwise. The resulting mixture was stirred at -78 °C for 2.5 h, and was used immediately.

(SR)-(-)-t-Butylsulfinylferrocene (8).[7f] To a stirred solution of 1.879 g (9.12 mmol) of L-(*R,R*)-diethyl tartrate in 8.75 mL of CH_2Cl_2 at 27 °C, 1.3 mL (4.56 mmol) of Ti(O-*i*-Pr)$_4$ was added. The resulting mixture was stirred at 27 °C for 6 min, after which time 82 μL (4.56 mmol) of distilled water was added. The resulting solution was stirred at 27 °C for 25 min, then cooled to -23 °C and a solution of 1.25 g (4.56 mmol) of *t*-butylsulfenylferrocene (**10**)[7d] in 5.1 mL of CH_2Cl_2 was added via cannula. The resulting solution was stirred at -23 °C for 30 min, after which time a cold (-23 °C) solution of 1.35 mL (9.12 mmol) of cumene hydroperoxide in 3.9 mL of CH_2Cl_2 was added dropwise via syringe. After the addition, stirring was stopped and the solution was stored at -25 °C for 72 h. The reaction solution was poured into a solution of 11.6 g of ferrous sulfate heptahydrate and 3.9 g of citric acid in 135 mL of water, 64 mL of diethyl ether and 64 mL of dioxane. The resulting mixture was stirred at 25 °C for 45 min and transferred into a separatory funnel. The aqueous layer was extracted three times with diethyl ether (200 mL and 2 × 100 mL). The combined organic layers were stirred with 125 mL of 2 *N* NaOH at 25 °C for 1 h. After separation of the two layers on a separatory funnel, the aqueous layer was extracted with 50 mL of diethyl ether. The combined organic layers were dried ($MgSO_4$) and concentrated to give 2.698 g of dark orange oil. Column chromatographic separation on a silica gel column of the crude product afforded 0.9517 g (72% yield) of sulfoxide **8** and 11 mg (8.9 % recovery) of sulfide **10**. Recrystallization of sulfoxide **8** from a mixture of diethyl ether/petroleum ether gave 0.738 g (61% yield) of yellow needles: mp. 149-150 °C; $[\alpha]^{22}_D = -357.8°$ (c 0.505, $CHCl_3$); ~100% ee; Lit.[7f] $[\alpha]^{22}_D = -339°$ (c 0.505, $CHCl_3$); *R*-configuration, 95% ee. IR (in CH_2Cl_2) ν 3080, 2950, 1630, 1040 cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.68 (m, 1 H, Cp-H), 4.41 (m, 2 H, Cp-H), 4.38 (s, 5 H, Cp'-H), 4.35 (m, 1 H, Cp-H), 1.12 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 86.4 (s, CS, Cp), 70.0 (d, 5 C, Cp'), 69.9 (d, Cp), 69.6 (d, Cp), 69.4 (d, Cp), 65.3 (d, Cp), 54.9 (s, C-S), 22.7 (q, 3 C, Me). MS *m/z* CI 291 (M+1).

(SR,1S,2R)-1-(t-Butylsulfinyl)-2-(hydroxymethyl)ferrocene (12). To a cold (-78 °C) solution of 0.70 mmol (2.03 equiv) of 2,4,6-triisopropylphenyllithium in 1.3 mL of THF under argon was added via cannula a cold (-78 °C) solution of 100 mg (0.345 mmol) of (S*R*)-(-)-**8** in 2.5 mL of THF. The resulting solution was warmed to -40 °C over 1.5 h, then stirred at this temperature for another 1.5 h after which time the characteristic orange color of the ferrocenyl anion appeared. A cold (-40 °C) suspension of 23 mg (0.767 mmol) of paraformaldehyde in 1 mL of THF was then added via cannula. The resulting mixture was allowed to reach -5 °C over 15 min and stirred at this temperature for 45 min. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with 20 mL of brine. The aqueous layer was extracted with three 40-mL portions of CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to

give 288 mg of brownish oil. Column chromatographic separation of the crude product on silica gel using hexane/diethyl ether as eluant afforded 90.9 mg of **12** (83% yield) as an orange oil and 5 mg (5% recovery) of **8**. Recrystallization of **12** from diethyl ether gave yellow crystals, mp. 89~90 °C; $[\alpha]^{22}_D$= -147.5° (c 0.495, $CHCl_3$), and a crystal of this material was subjected to single-crystal X-ray diffraction analysis.[10] TLC: R_f value is 0.2 in ether:hexane = 3:1; IR (in CH_2Cl_2) ν 3250, 3080, 2960, 1630, 1455, 1040, 1005, 820 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.62 (dd, J = 11.0, 1.0 Hz, 1 H, OH), 4.53 (dd, J = 13.4, 1.0 Hz, 1 H, CH_2O), 4.49 (s, 5 H, Cp'), 4.39 (m, 2 H, Cp), 4.32 (t, J = 2.4 Hz, 1 H, Cp), 4.08 (dd, J = 13.4, 11.0 Hz, 1 H, CH_2O), 1.19 (s, 9 H, *t*-Bu). ^{13}C NMR ($CDCl_3$) δ 91.2 (s, Cp), 82.6 (s, Cp), 72.5 (d, Cp), 71.1 (d, Cp), 71.0 (d, 5 C, Cp'), 68.6 (d, Cp), 59.3 (t, CO), 57.1 (s, CS), 23.4 (q, 3 C, Me); MS *m/z* FAB 320 (M+, 50%), 303, 264, 246 (100%), 181, 138, 131. Anal. Calcd for $C_{15}H_{20}FeO_2S$: C, 56.26; H, 6.29. Found: C, 56.38; H, 6.41.

(SR,1S,2R)-1-(t-Butylsulfinyl)-2-(hydroxymethyl)ferrocene (12) and (SR,1R,2S)-1-(t-Butylsulfinyl)-2-(hydroxymethyl)ferrocene (13R). To a cold (-78 °C) solution of 0.38 mmol (1.1 equiv) of 2,4,6-triisopropylphenyllithium in 1.0 mL of THF under argon was added via cannula a cold (-78 °C) solution of 101 mg (0.35 mmol) of (S*R*)-(-)-**8** in 2.0 mL of THF. The resulting solution was warmed to -45~-40 °C over 1.5 h and then stirred at this temperature for another 1.5 h. The reaction mixture was allowed to reach -20 °C and was stirred at this temperature for 1 h, then cooled to -40 °C. A cold (-40 °C) suspension of 14 mg (0.455 mmol; 1.3 eq) of paraformaldehyde in 1 mL of THF was then added via cannula. The resulting mixture was allowed to reach 5 °C over 3.3 h. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with 30 mL of brine. The aqueous layer was extracted with four 50-mL portions of CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated to give 229 mg of brownish oil. Column chromatographic separation of the crude product on silica gel using hexane/diethyl ether as eluant afforded 44 mg (39% yield) of **12** and 6 mg (5% yield) of **13R**, along with 52.5 mg (52% recovery) of starting material **8**. Compound **13R** was recrystallized from diethyl ether and was subjected to X-ray single crystal analysis.[16] Compound **13R**: TLC: R_f value is 0.05 in ether:hexane = 3:1; mp. 165 °C (dec.); $[\alpha]^{22}_D$ = -165° (c 0.1, CH_2Cl_2). ^1H NMR $CDCl_3$ δ 4.73 (dd, J = 2.7, 1.6 Hz, 1 H, Cp-H), 4.53 (dd, J = 12.5 Hz, 3.7 Hz, 1 H, CH-O), 4.48 (dd, J = 2.7 Hz, 1.6 Hz, 1 H, Cp-H), 4.44 (t, J = 2.7 Hz, 1 H, Cp-H), 4.40 (s, 5 H, Cp'-H), 4.37 (dd, J = 12.5, 7.2 Hz, 1 H, CH-O), 1.79 (dd, J = 7.2, 3.7 Hz, 1 H, OH), 1.16 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 90.9 (s, Cp), 86.7 (s, Cp), 70.5 (d, 5 C, Cp'), 69.9 (d, Cp), 69.2 (d, Cp), 66.1 (d, Cp), 59.0 (t, C-O), 56.0 (s, C-S), 23.0 (q, t-Bu). Anal. Calcd for $C_{15}H_{20}FeO_2S$: C, 56.26; H, 6.29. Found: C, 56.42; H, 6.33.

(1S,2R)-1-(t-Butylthio)-2-(hydroxymethyl)ferrocene (18) from the reduction of sulfinyl alcohol (12) with DIBALH and LiAlH$_4$. To a cold (0 °C) solution of 110 mg (0.34 mmol) of **12** in 2.5 mL of THF was added 0.70 mL (1.03 mmol; 3 equiv) of DIBALH (1.5 *M* in toluene). The resulting solution was stirred at 0 °C for 15 min and 1 h at 25 °C. A solution of 130 mg (3.39 mmol; 10 equiv) of $LiAlH_4$ in 7.4 mL of diethyl ether was added and the resulting solution was stiired overnight. The reaction mixture was diluted (carefully) with 25 mL of water, acidified with 1 *N* HCl until the aluminum complex disappears (~ 15 mL). The aqueous layer was extracted three times with diethyl ether (100 mL and 2 x 25 mL). The combined organic layers were washed with 50 mL of brine, dried ($MgSO_4$), and concentrated to give 92 mg of a yellow oil. The crude product was column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl

ether as eluant to give 50 mg (49% yield) of sulfide **18**. Mp. 45~46 °C; $[\alpha]^{22}_D$ = +61.7° (c 1.05 CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 4.52 (d, *J* = 12 Hz, 1 H, CH_2O), 4.40 (d, *J* = 12 Hz, 1 H, CH_2O), 4.38 (d, *J* = 2.4 Hz, 2 H, Cp-H), 4.25 (t, *J* = 2.4 Hz, 1 H, Cp-H), 4.19 (s, 5 H, Cp'-H), 1.21 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 91.9 (s, Cp), 77.3 (d, Cp), 75.7 (s, Cp), 70.1 (d, 5 C, Cp'), 69.5 (d, Cp), 68.9 (d, Cp), 59.8 (t, C-O), 46.3 (s, C-S), 31.0 (q, 3 C, Me). Anal. Calcd for $C_{15}H_{20}FeOS$: C, 59.22; H, 6.63. Found: C, 58.92; H, 6.75.

*(1S,2R)-1-(t-Butylthio)-2-(hydroxymethyl)ferrocene (18) from the reduction of sulfinyl alcohol **12** with $LiAlH_4$.* To a solution of 124 mg (0.385 mmol) of **12** in 3 mL of THF was added 59 mg (1.55 mmol; 4 equiv) of $LiAlH_4$. The resulting solution was stirred at 25 °C overnight, diluted with water (carefully), acidified with 1 *N* HCl, and extracted three times with diethyl ether. The combined organic extract was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 18 mg (25% yield) of sulfide alcohol **18** and 48 mg (39% recovery) of **12**.

*(SS,1S,2R)-1-(t-Butylsulfinyl)-2-(hydroxymethyl)ferrocene (13S) from the oxidation of sulfide **18**.* To a solution of 18.5 mg (0.0609 mmol) of sulfide **18** in 1 mL of THF at 25 °C was added 18.8 mg (0.106 mmol; 55% pure, from Aldrich) of *m*-chloroperbenzoic acid in 1 mL of THF and the solution was stirred at 25 °C for 0.5 hour, diluted with aqueous $Na_2S_2O_3$ and $NaHCO_3$ solutions, and extracted with diethyl ether three times. The combined diethyl ether layers were washed with brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using hexane/ether as eluant to give 18.5 mg (95% yield) of **13S**. TLC: R_f value is 0.05 in ether:hexane = 3:1; mp. 165 °C (dec.); $[\alpha]^{22}_D$ = +165° (c 0.1, CH_2Cl_2). The ^{1}H and ^{13}C NMR spectra were identical to that of **13R**.

(SR,1S,2R)-1-(t-Butylsulfinyl)-2-(hydroxymethyl)ferrocene (12) from the reduction of (19). To a solution of 89 mg (0.28 mmol) of aldehyde **19** in 12 mL of methanol was added 10 mg (0.28 mmol) of $NaBH_4$. The resulting solution was stirred at 25 °C for 30 min and was evaporated to dryness on rotary evaporator. The residue was diluted with 75 mL of diethyl ether and washed with 50 mL of water. The aqueous layer was extraxted twice with diethyl ether (30 mL each) and the combined organic extracts were dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 69 mg (77% yield) of **12**. $[\alpha]^{22}_D$= -148.3° (c 0.665, $CHCl_3$).

(1S,2R)-1-(t-Butylsulfonyl)-2-(hydroxymethyl)ferrocene (14). To a solution of 66 mg (0.206 mmol) of **12** in 6 mL of distilled acetone were added 65 mg (0.206 mmol) of *m*-chloroperbenzoic acid (55%) at 25 °C. The solution was stirred at 30 °C for 0.5 h. The reaction mixture was evaporated to dryness on a rotary evaporator, diluted with methylene chloride (50 mL), washed with 1 *N* NaOH (25 mL), and the aqueous layer was extracted twice with CH_2Cl_2 (50 mL each). The combined organic extracts were dried ($MgSO_4$), and concentrated to give 82 mg of a brown oil. Column chromatographic separation on silica gel using a mixture of petroleum ether/diethyl ether as eluant gave 63 mg (90% yield) of **14** as a yellow oil; $[\alpha]^{22}_D$ = +79.3° (c = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 4.61 (dd, *J* = 2.4, 1.5 Hz, 1 H, Cp-H), 4.55 (dd, *J* = 13.0, 2.7 Hz, 1 H, CH_2-O), 4.52 (s, 6 H, Cp'-H unsubstituted + Cp-H), 4.44 (dd, *J* = 2.4, 2.4 Hz, 1 H, Cp-H), 4.32 (dd, *J* = 13.0, 9.7 Hz, 1 H, CH_2-O), 3.18 (dd, *J* = 9.7, 2.7 Hz, 1 H, OH), 1.32 (s, 9 H, *t*-Bu). ^{13}C NMR ($CDCl_3$) δ 91.2 (s, CS, Cp), 81.1 (s, CO, Cp), 73.1 (d, Cp), 72.9 (d, Cp), 71.3 (d, 5 C, Cp'), 69.4 (d, Cp), 59.8 (s, C-S), 58.7 (t, C-O),

23.5 (q, 3 C, Me); MS *m/z* CI 337 (M+1). Anal. Calcd for $C_{15}H_{20}FeO_3S$: C, 53.58; H, 6.00. Found: C, 53.35; H, 6.17.

*The following experimental procedure for the preparation of Mosher derivative from alcohol **14** is representative.*

*(1S,2R,4'S)-1-(t-Butylsulfonyl)-2-{[α–methoxy-α–(trifluoromethyl)phenylacetoxy]methyl}ferrocene (**16**).* To a solution of 17.6 mg (0.05 mmol) of **14** in 0.5 mL of pyridine was added 30 μL (0.15 mmol) of (+)-(*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (**15R**) at 25 °C. The solution was stirred at 45 °C for 21 h. The reaction mixture was diluted in 200 mL of diethyl ether and washed with 30 mL of 1 *N* HCl. The organic layer was then washed with 30 mL of aqueous $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated. The ^1H NMR spectrum of the crude product indicated only one isomer (this result indicated that the optical purity of the starting hydroxy sulfone was > 99% ee) of the ester based on the chemical shift of the $C\underline{H}_2OCO$. Column chromatographic separation of the crude product on silica gel using petroleum ether/diethyl ether as eluent afforded **16** in 92% yield as a yellow oil. ^1H NMR ($CDCl_3$) δ 7.42 (d, *J* = 7.0 Hz, 2 H, Ph), 7.34 (m, 3 H, Ph), 5.67 (d, *J* = 12.5 Hz, 1 H, CH_2O), 5.32 (d, *J* = 12.5 Hz, 1 H, CH_2O), 4.65 (dd, *J* = 2.4, 1.5 Hz, 1 H, Cp-H), 4.62 (dd, *J* = 2.4, 1.5 Hz, 1 H, Cp-H), 4.50 (t, J = 2.4 Hz, 1 H, Cp-H), 4.42 (s, 5 H, Cp'-H), 3.54 (s, 3 H, OMe), 1.13 (s, 9 H, *t*-Bu). ^{13}C NMR ($CDCl_3$) δ 166.4 (s, CO), 132.2 (s, Ph), 129.5 (d, Ph), 128.3 (d, Ph), 127.2 (d, Ph), 123.3 (q, *J* = 287 Hz, CF_3), 82.2 (s, Cp), 73.6 (d, Cp), 73.5 (d, Cp), 71.6 (d, 5 C, Cp'), 71.4 (s, Cp), 70.8 (d, Cp), 61.8 (q, OMe), 59.2 (s, CPh), 55.5 (s, CS), 23.3 (q, 3 C, Me). MS *m/z* FAB 552 (M+).

Reaction of (1S,2R)-1-(t-butylsulfonyl)-2-(hydroxymethyl)ferrocene (14) with (±)-(15). Formation of the two diastereomeric Mosher's esters (16) and (17). Reaction conditions similar to above were followed but using (±)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride [(±)-**15**]. The two diastereomeric esters **16** and **17** (90% yield) are inseparable by TLC or silica gel column chromatography. ^1H NMR ($CDCl_3$) δ 7.5 ~ 7.3 (m, 10 H, 2 Ph), 5.67 (d, *J* = 12.5 Hz, 1 H, CH_2O of isomer **16**), 5.58 (d, *J* = 12.5 Hz, 1 H, CH_2O of isomer **17**), 5.35 (d, *J* = 12.5 Hz, 1 H, CH_2O of isomer **17**), 5.32 (d, *J* = 12.5 Hz, 1 H, CH_2O of isomer **16**), 4.65 (dd, *J* = 2.4, 1.5 Hz, 2 H, Cp of isomers **16** and **17**), 4.62 (dd, *J* = 2.4, 1.5 Hz, 1 H, Cp of isomer **16**), 4.54 (t, *J* = 2.4 Hz, 1 H, Cp of isomer **17**), 4.50 (m, 2 H, Cp of isomers **16** and **17**), 4.42 (s, 10 H, 2 Cp), 3.54 (s, 3 H, OMe of isomer **16**), 3.50 (s, 3 H, OMe of isomer **17**), 1.18 (s, 9 H, *t*-Bu of isomer **17**), 1.13 (s, 9 H, *t*-Bu of isomer **16**).

*The following experiment serves as the general procedure for the preparation of 1,2-disubstituted ferrocene from sulfoxide **8**.*

(SR,1S,2R)-1-(t-Butylsulfinyl)-2-formylferrocene (19). A cold (-78 °C) solution of 228 mg (0.786 mmol) of **8** in 5 mL of THF was cannulated into a cold (-78 °C) solution of 1.56 mmol (2 equiv) of 2,4,6-triisopropylphenyllithium in 2.5 mL of THF. After stirring at -78 °C for 10 min, the solution was warmed to -40 °C and stirred at this temperature for 1.5 h. After the solution was cooled to -78 °C, 0.65 mL (10 equiv) of freshly distilled ethyl formate was added. The orange color of the ferrocenyl anion disappeared to become yellow immediately. After 10 min, the reaction mixture was diluted with 90 μL (2 equiv) of acetic acid. The reaction mixture was concentrated on rotary evaporator, the residue was diluted with 50 mL of ether and washed with 30 mL of water. The aqueous layer was extracted three times with ether (75 mL each). The

combined organic extracts were dried ($MgSO_4$), concentrated, and column chromatographed immediately (to minimize decomposition of the desired product) on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 213 mg of **19** (85% yield) and 33.4 mg (14% recovery) of sulfoxide **8**. Recrystallization of **19** from diethyl ether and hexane gave yellow crystals, mp. 130-131 °C; $[\alpha]^{22}_D$ = -1020.4° (c 0.5, diethyl ether); ^1H NMR ($CDCl_3$) δ 10.65 (s, 1 H, CHO), 5.10 (t, J = 1.8 Hz, 1 H, Cp-H), 4.72 (d, J = 1.8 Hz, 2 H, Cp-H), 4.52 (s, 5 H, Cp'-H), 1.17 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 194.1 (s, C=O), 95.5 (s, Cp), 75.1 (d, Cp), 73.1 (d, Cp), 71.8 (d, 5 C, Cp'), 70.0 (s, Cp), 69.5 (d, Cp), 55.7 (s, CS), 23.0 (q, 3 C, Me); MS m/z FAB 318 (M+); Anal. Calcd for $C_{15}H_{18}FeO_2S$: C, 56.62; H, 5.70. Found: C, 56.39; H, 6.03.

(SR,1S,2R)-1-(t-Butylsulfinyl)-2-(methoxycarbonyl)ferrocene (20). Following a similar reaction conditions as described above, the anion of 106 mg (0.36 mmol) of **8** was reacted with 62 μL (0.80 mmol) of methyl chloroformate (in 1 mL of THF) at -78 °C for 0.5 h. After dilution with 20 mL of brine, the aqueous layer was extracted three times with CH_2Cl_2 (75 mL each). The combined organic layers were dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and ether as eluant to give 105 mg (84% yield) of **20** as a yellow solid and 8 mg (7.5% recovery) of **8**. The compound is unstable and decomposes upon standing at room temperature in solution. The pure compound (solid form) can be stored at -20 °C (freezer) for several days. Due to its instability, no elemental analysis was performed. $[\alpha]^{22}_D$ = -184.2° (c 0.5, $CHCl_3$). IR (CH_2Cl_2) ν 3100, 2950, 1720, 1700, 1440, 1265, 1240, 1145, 1068, 1002, 820 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.02 (d, J = 2.5 Hz, 1 H, Cp-H), 4.60 (d, J = 2.5 Hz, 1 H, Cp-H), 4.55 (t, J = 2.5 Hz, 1 H, Cp-H), 4.47 (s, 5 H, Cp'-H), 3.83 (s, 3 H, OMe), 1.23 (s, 9 H, *t*-Bu). ^{13}C NMR ($CDCl_3$) δ 169.3 (s, C=O), 87.4 (s, Cp), 75.3 (d, Cp), 74.6 (d, Cp), 71.9 (d, 5 C, Cp'), 71.7 (s, Cp), 71.3 (d, Cp), 56.5 (s, CS), 51.8 (q, MeO), 24.0 (q, 3 C, *t*-Bu). MS *m/z* CI 349 (M+1).

Sulfoxide **20** was reduced with zinc in acetic acid to the corresponding sulfide **29** which is a stable compound.

(SR,1S,2R)-1-(t-Butylsulfinyl)-2-(2-propenyl)ferrocene (21). The anion of 55 mg (0.19 mmol) of **8** was reacted with 33 μL (0.38 mmol) of freshly distilled allyl bromide at -78 °C, and warmed to -40 °C and allowed to reach 0 °C over 1 h (the reaction was monitored by TLC analysis, which did not show any changes after warming and stirring the solution at 25°C). The reaction mixture was quenched with 20 mL of brine and extracted with 75 mL of diethyl ether and two 50 mL portions of CH_2Cl_2. The combined organic layer was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel to give 52.4 mg of **21** (84% yield) and 2.8 mg (5 % recovery) of **8**. Compound **21**: $[\alpha]^{22}_D$ = -419.1° (c 0.8, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 6.05 (dddd, J = 18.9, 10.1, 7.5, 6.3 Hz, 1 H, CH=), 5.13 (ddt, J = 18.9, 1.8, 1.6 Hz, 1 H, CH_2=), 5.08 (ddt, J = 10.1, 1.6, 1.2 Hz, 1 H, CH_2=), 4.37 (s, 5 H, Cp'-H), 4.27 (m, 3 H, Cp-H), 3.84 (ddt, J = 16.4, 6.3, 1.8 Hz, 1 H, CH_2), 3.23 (ddt, J = 16.4, 7.5, 1.2 Hz, 1 H, CH_2), 1.19 (s, 9 H, *t*-Bu). ^{13}C NMR ($CDCl_3$) δ 136.7 (d, CH=), 116.0 (t, CH_2=), 88.0 (s, Cp), 81.9 (s, Cp), 70.6 (d, 5 C, Cp'), 70.4 (d, Cp), 70.1 (d, Cp), 68.5 (d, Cp), 56.3 (s, CS), 31.5 (t, CH_2), 23.5 (q, 3 C, Me). MS m/z FAB 330 (M+, 40%), 274 (100%), 256, 226, 191, 155, 136, 121. Anal. Calcd for $C_{17}H_{22}FeOS$: C, 61.82; H, 6.71. Found: C, 61.65; H, 6.93.

(SR,1S,2R,1'S)-1-(t-Butylsulfinyl)-2-(1-hydroxy-2-propenyl)ferrocene (22a) and (SR,1S,2R,1'R)-1-(t-butylsulfinyl)-2-(1-hydroxy-2-propenyl)ferrocene (22b). The anion of 101 mg (0.35 mmol) of **8** was

reacted with 58 µL (0.86 mmol) of freshly distilled acrolein (acrolein was dissolved in 1 mL of THF) at -85 °C for 10 min. After which time the characteristic orange color of ferrocenyl anion **11** had disappeared (indicating that the reaction was nearly complete). The reaction mixture was diluted with 20 mL of brine and extracted three times with CH_2Cl_2 (40 mL each). The combined organic extract was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether / diethyl ether as eluant to give 84 mg (69% yield) of **22b**, 25 mg (21% yield) of **22a** and 9 mg (9% recovery) of **8**. Compound **22b** (less polar isomer): $[\alpha]^{22}_D$= -256.7° (c 0.4, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 6.48 (s, 1 H, OH), 6.10 (ddd, *J* = 17.1, 10.1, 6.7 Hz, 1 H, CH=), 5.42 (dt, *J* = 17.1, 1.4 Hz, 1 H, CH_2=), 5.30 (dd, *J* = 10.1, 1.4 Hz, 1 H, CH_2=), 4.94 (dd, *J* = 6.7, 1.4 Hz, 1 H, CH-O), 4.51 (s, 5 H, Cp'-H), 4.41 (t, *J* = 2.0 Hz, 1 H, Cp-H), 4.32 (d, *J* = 2.0 Hz, 2 H, Cp-H), 1.22 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 138.8 (d, CH=), 116.6 (t, CH_2=), 93.9 (s, Cp), 81.6 (s, Cp), 72.4 (d), 71.5 (d), 70.7 (d, 5 C, Cp'), 68.4 (d), 68.3 (d), 57.2 (s, C-S), 23.3 (q, *t*-Bu); Anal. Calcd for $C_{17}H_{22}FeO_2S$: C, 58.97; H, 6.40. Found: C, 58.61; H, 6.51. Compound **22a** (more polar isomer): $[\alpha]^{22}_D$= -107.5° (c 0.4, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 6.01 (ddd, *J* = 16.5, 10.4, 7.0 Hz, 1 H, CH=), 5.78 (dd, *J* = 7.0, 0.9 Hz, 1 H, CH-O), 5.34 (d, *J* = 16.5 Hz, 1 H, CH_2=), 5.15 (t, *J* = 6.1 Hz, 1 H, Cp-H), 5.08 (dd, *J* = 10.4, 0.9 Hz, 1 H, CH_2=), 4.43 (s, 5 H, Cp'-H), 4.37-4.34 (m, 2 H, Cp-H), 1.19 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 141.61 (d, CH=), 114.11 (t, CH_2=), 93.08 (s, Cp), 82.36 (s, Cp), 71.43 (d, 5 C, Cp'), 71.27 (d), 70.93 (d), 69.82 (d), 69.53 (d), 57.17 (s, C-S), 24.04 (q, *t*-Bu); MS m/z FAB 346 (M+).

(SR,1S,2R)-2-(Allyldimethylsilyl)-1-(t-butylsulfinyl)ferrocene (24). After the anion of 98 mg (0.34 mmol) of **8** was reacted with 100 mg (0.68 mmol) of freshly distilled allyldimethylsilyl chloride (the silyl chloride was dissolved in 1 mL of THF) at -80 °C for 45 min, 20 mL of brine was added and the mixture was diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The aqueous layer was extracted three times with CH_2Cl_2 (75 mL each). The combined organic layer was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 96 mg of **24** (73% yield) and 24.5 mg (25% recovery) of **8**. Compound **24**: $[\alpha]^{22}_D$ = -70.4° (c 1.85, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 5.83 (ddt, *J* = 17.1, 10.4, 8.0 Hz, 1 H, CH=), 4.89 (d, *J* = 17.1 Hz, 1 H, CH_2=), 4.86 (d, *J* = 10.1 Hz, 1H, CH_2=), 4.52 (d, *J* = 1.8 Hz, 2 H, Cp-H), 4.33 (s, 5 H, Cp'-H), 4.32 (t, *J* = 1.8 Hz, 1 H, Cp-H), 1.94 (dd, *J* = 13.1, 8.0 Hz, 1 H, CH_2Si), 1.87 (dd, *J* = 13.1, 8.0 Hz, 1 H, CH_2Si), 1.15 (s, 9 H, *t*-Bu), 0.42 (s, 3 H, MeSi), 0.37 (s, 3 H, MeSi). ^{13}C NMR ($CDCl_3$) δ 135.9 (d, CH=), 112.9 (t, CH_2=), 91.6 (s, Cp), 77.0 (d, Cp), 72.4 (d, Cp), 70.7 (d, Cp), 70.3 (d, 5 C, Cp'), 70.0 (s, Cp), 56.1 (s, CS), 25.8 (t, CH_2Si), 23.5 (q, 3 C, Me), -0.0 (q, MeSi), -0.7 (q, MeSi). MS m/z FAB 388 (M+), 347, 290. Anal. Calcd for $C_{19}H_{28}FeOSSi$: C, 58.75; H, 7.27. Found: C, 58.69; H, 7.41.

(SR,1S,2R)-1-(t-Butylsulfinyl)-2-[(chloromethyl)dimethylsilyl]ferrocene (25). Similar reaction conditions were carried out starting with 52 mg (0.18 mmol) of **8** and 56 mg (0.40 mmol) of (chloromethyl)dimethylsilyl chloride to give 60 mg (85% yield) of **25** and 7 mg (13% recovery) of **8**. Compound **25**: mp. 62-63 °C; $[\alpha]^{22}_D$ = -60.6° (c 0.6, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 4.57 (t, *J* = 2.4 Hz, 1 H, Cp-H), 4.55 (dd, *J* = 2.4, 1.2 Hz, 1 H, Cp-H), 4.37 (dd, *J* = 2.4, 1.2 Hz, 1 H Cp-H), 4.34 (s, 5 H, Cp'-H), 3.24 (d, *J* = 13.4 Hz, 1 H, CH_2Cl), 3.14 (d, *J* = 13.4 Hz, 1 H, CH_2Cl), 1.13 (s, 9 H, *t*-Bu), 0.52 (s, 3 H, MeSi), 0.47 (s, 3 H, MeSi). ^{13}C NMR ($CDCl_3$) δ 91.5 (s, Cp), 76.9 (d, Cp), 72,9 (d, Cp), 70.5 (d, Cp), 70.4 (d, 5 C, Cp'), 67.1 (s, Cp), 56.2 (s, CS), 32.7 (t, CH_2Cl), 23.3 (q, 3 C, Me), -0.9 (q, MeSi), -1.2 (q, MeSi). MS m/z FAB 398, 397, 396 (M+, 20%), 340

(100%), 323, 292, 243, 217, 167, 133. Anal. Calcd for $C_{17}H_{25}ClFeOSSi$: C, 51.45; H, 6.35. Found: C, 51.73; H, 6.59.

(SR,1S,2S)-1-(t-Butylsulfinyl)-2-(trimethylstannyl)ferrocene (26). The anion of 66 mg (0.23 mmol) of **8** was reacted with 100 mg (0.51 mmol) of trimethyltin chloride (the tin chloride was dissolved in 1 mL of THF) at -78 °C for 10 min, and -30 °C for 20 min. After the addition of 20 mL of brine and 30 mL of aqueous $NaHCO_3$, the mixture was extracted with 75 mL of ether and twice with CH_2Cl_2 (50 mL each), and the combined organic extract was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 89 mg (86% yield) of **26** as yellow solids and 6.6 mg (10% recovery) of **8**. Compound **26**: mp. 60-61 °C; $[\alpha]^{D}_{22}$= -93.1° (c 0.75, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 4.53 (t, J = 2.4 Hz, 1 H, Cp-H), 4.49 (dd, J = 2.4, 0.7 Hz, 1 H, Cp-H), 4.29 (s, 5 H, Cp'-H), 4.27 (dd, J = 2.4, 0.7 Hz, 1 H Cp-H), 0.32 (s, 9 H, *t*-Bu), 0.32 (s, 9 H, MeSn), 0.32 (d, J = 55 Hz, Me-Sn^{119}); ^{13}C NMR ($CDCl_3$) δ 90.5 (s, Cp), 75.6 (d, Cp), 73.2 (d, Cp), 69.8 (d, 5 C, Cp'), 69.4 (d, Cp), 66.8 (s, Cp), 55.5 (s, CS), 23.0 (q, 3 C, Me), -5.6 (q, 3 C, Me_3Sn). MS m/z FAB 452, 453 (M+ and isotope), 437, 438 (M-Me, 100%), 382, 381, 349, 348, 300, 217, 165, 121. Anal. Calcd for $C_{17}H_{26}FeOSSn$: C, 45.07; H, 5.78. Found: C, 44.85; H, 6.02.

(SR,1S,2R)-1-(t-Butylsulfinyl)-2-(diphenylphosphino)ferrocene (27). The anion of 357 mg (1.23 mmol) of **8** was reacted with 0.45 mL (2.46 mmol) of chlorodiphenylphosphine (freshly distilled) at -78 °C, and 25 °C for 1.7 h (the reaction was monitored by TLC). After adding 5 mL of methanol to the reaction solution, 20 mL of aqueous $NaHCO_3$ was added and the mixture was extracted with diethyl ether three times. The combined extract was washed with brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of hexane, toluene and diethyl ether as eluant to give 480 mg (82% yield) of **27** and 50 mg (14% recovery) of sulfoxide **8**. Compound **27**: yellow solids (the compound could be stored as the solid form under argon in the freezer for long period of time without decomposition, however, when kept in methylene chloride solution, the material decomposed at room temperature); mp. 162-163 °C (dec.); $[\alpha]^{22}_{D}$ = -303.3° (c 3.25, benzene); ^1H NMR (benzene-d6) δ 7.70 (m, 2 H, Ph), 7.19 (t, J = 6.8 Hz, 2 H, Ph), 7.05 (m, 6 H, Ph), 4.34 (broad s, 1 H, Cp-H), 4.25 (s, 1 H, Cp-H), 4.16 (broad s, 1 H, Cp-H), 4.13 (s, 5 H, Cp'-H), 0.98 (s, 9 H, t-Bu); ^{13}C NMR (benzene-d6; C-H decoupled) δ 142.3 (d, J_{CP} = 16.5 Hz, 2 C, Ph), 140.2 (d, J = 17.8 Hz, 2 C, Ph), 136.3 (d, J = 23.5 Hz, 4 C, Ph), 133.6 (d, J = 19.7 Hz, 4 C, Ph), 91.8 (d, J = 21 Hz, 1 C, C-P, Cp), 78.2 (d, J = 29 Hz, 1 C, C-S, Cp), 75.5 (d, J = 5.7 Hz, 1 C, Cp), 73.7 (d, J = 4.2 Hz, 1 C, Cp), 72.6 (d, J = 5 Hz, 1 C, Cp), 72.2 (s, 5 C, Cp'), 55.9 (s, CS), 24.2 (s, 3 C, Me); Anal. Calcd for $C_{26}H_{27}FeOPS$: C, 65.83; H, 5.74. Found: C, 65.77; H, 5.91.

(SR,1S,2R)-1-(t-Butylsulfinyl)-2-hydroxyferrocene (28). The anion of 65 mg (0.22 mmol) of **8** was reacted with 150 mg (0.84 mmol) of bis(trimethylsilyl)peroxide[23] at -40 °C for 10 min, and -20 °C for 1 h (the reaction was monitored by TLC). After addition of 20 mL of aqueous $NaHCO_3$, the mixture was extracted with 75 mL of ether and twice with methylene chloride (50 mL each). The combined organic layer was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 37 mg of **28** (55% yield) as yellow solids and 12 mg (18% recovery) of **8**. Compound **28**: mp 122-124 °C (dec.); $[\alpha]^{22}_{D}$ = -136.7° (c 0.9, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.75 (s, 1 H,

OH), 4.37 (s, 5 H, Cp'-H), 4.34 (t, J = 1.8 Hz, 1 H, Cp-H), 3.96 (d, J =1.8 Hz, 2 H, Cp-H), 1.23 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 125.5 (s, C-O, Cp), 71.0 (d, 5 C, Cp'), 65.5 (s, CS, Cp), 62.6 (d, Cp), 61.8 (d, Cp), 59.1 (d, Cp), 56.9 (s, CS), 22.5 (q, 3 C, Me); Anal. Calcd for $C_{14}H_{18}FeO_2S$: C, 54.91; H, 5.93. Found: C, 54.63; H, 6.21.

(SR,1S,2R,1'S)-1-(t-Butylsulfinyl)-2-(α-hydroxybenzyl)ferrocene (23a) and (SR,1S,2R,1'R)-1-(t-butylsulfinyl)-2-(α-hydroxybenzyl)ferrocene (23b). The anion of 106 mg (0.36 mmol) of **8** was reacted with 93 μL (97 mg, 0.91 mmol) of freshly distilled benzaldehyde (the aldehyde was dissolved in 1 mL of THF) at -78 °C 10 min. The characteristic orange color of the ferrocenyl anion **11** had disappeared. The reaction mixture was diluted with 15 mL of brine, extraction with diethyl ether (50 mL) and CH_2Cl_2 (3 × 50 mL), the combined organic extract was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether / diethyl ether as eluant to give 108 mg (75% yield) of a 1:1 mixture of diastereomeric products, **23a** and **23b**. Since the ^{1}H and ^{13}C NMR spectra of **23a** are the same as those listed in the next experiment, only spectra of **23b** are reported here (signals for **23a** have been removed); **23b**: ^{1}H NMR ($CDCl_3$) δ 7.44 (d, J = 7.9 Hz, 2 H, Ph), 7.39 (t, J = 8.0 Hz, 2 H, Ph), 7.32 (t, J = 8.0 Hz, 1 H, Ph), 6.61 (s, 1 H, OH), 5.62 (d, J = 8.5 Hz, 1 H, <u>CH</u>-OH), 4.51 (s, 5H, Cp-H), 4.48 (s, 5 H, Cp-H), 4.41 (dd, J = 2.6, 1.5 Hz, 1 H, Cp-H), 4.18 (t, J = 2.6 Hz, 1 H, Cp-H), 3.50 (dd, J = 2.6, 1.5 Hz, 1H, Cp-H), 1.28 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 146.1 (s, 1 C, Ph), 127.9 (d, 2 C, Ph), 127.4 (d, 1 C, Ph), 127.2 (d, 2 C, Ph), 88.4 (s, Cp), 87.0 (s, Cp), 74.0 (d, Cp), 71.1 (d, Cp), 70.8 (d, 5 C, Cp'), 69.0 (d, Cp), 68.0 (d, C-O), 57.2 (s, C-S), 23.4 (q, 3 C, Me) (the assignment was based on pure **23a** obtained from **19**).

(SR,1S,2R,1'S)-1-(t-Butylsulfinyl)-2-(α-hydroxybenzyl)ferrocene (23a). From 19. To a cold (0 °C) solution of 267 mg (0.902 mmol) of **19** in 15 mL of THF was added 0.35 mL (1.17 mmol) of titanium tetraisopropoxide. The solution was stirred at 0 °C for 30 min, cooled to -78 °C and 0.90 mL (1.8 mmol) of phenylmagnesium bromide (2 *M* solution in THF) was added. The resulting solution was warmed to 0 °C over 3.5 h. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with diethyl ether and washed with brine and then $NaHCO_3$ solution. The aqueous layer was extracted once with 100 mL of diethyl ether and then twice with CH_2Cl_2 (75 mL and 30 mL). The combined organic extract was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluent to give 317.9 mg (89% yield) of **23a** as a yellow solid; mp. 137 ~ 139 °C; $[\alpha]^{22}_D$ = -45.3° (c 0.8, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.44 (d, J = 7.9 Hz, 2 H, Ph), 7.25 (dd, J = 7.3, 7.9 Hz, 2 H, Ph), 7.16 (t, J = 7.3 Hz, 1 H, Ph), 6.38 (d, J = 8.5 Hz, 1 H, OH), 5.62 (d, J = 8.5 Hz, 1 H, <u>CH</u>-OH), 4.48 (s, 6 H, 1Cp + unsubstituted Cp'), 4.41 (t, J = 2.4 Hz, 1 H, Cp), 4.37 (dd, J = 2.4, 1.5 Hz, 1 H, Cp), 0.87 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 144.8 (s, Ph), 127.7 (d, Ph), 126.5 (d, Ph), 125.8 (d, Ph), 94.2 (s, Cp), 81.8 (s, Cp), 72.7 (d, Cp), 71.2 (d, 5 C, Cp'), 70.9 (d, Cp), 69.8 (d, Cp), 68.9 (d, CH-O), 56.8 (s, CS), 23.1 (q, 3 C, Me). MS m/z CI 397 (M+1). Anal. Calcd for $C_{21}H_{24}FeO_2S$: C, 63.64; H, 6.10. Found: C, 63.41; H, 6.33.

Reaction of aldehyde 19 with phenylmagnesium chloride. Formation of 23a and 23b. To a cold (-78 °C) solution of 16.8 mg (0.053 mmol) of aldehyde **19** in 2 mL of THF was added 29 μL (0.058 mmol) of phenylmagnesium chloride (2.0 *M* in THF). After stirring at -78 °C for 1 h, the reaction mixture was diluted with 25 ml of brine and extracted with diethyl ether (50 mL) and CH_2Cl_2 (3 × 30 mL). The combined organic layer was dried ($MgSO_4$) and concentrated to give 35 mg of crude yellow oil. ^1H NMR analysis of this crude mixture showed a 4.4:1 diastereomeric mixture of **23a** and **23b**.

*(1S,2R)-1-(t-Butylthio)-2-(hydroxymethyl)ferrocene (18) from the reduction of methyl ester **20**.* To a solution of 55 mg (0.166 mmol) of **20** in 4 mL of diethyl ether under argon was added 19 mg (0.497 mmol) of $LiAlH_4$ at 0 °C. The solution was stirred at 0 °C for 15 min and then at 25 °C for 4 h, and then diluted with diethyl ether and water (carefully added). The water layer was extracted twice with diethyl ether (40 mL) and the combined ether extracts were washed with brine, dried ($MgSO_4$), concentrated to give 48 mg (96% yield) of alcohol **18**.

(1S,2R)-1-(t-Butylthio)-2-(methoxycarbonyl)ferrocene (29). To a solution of 118 mg (0.34 mmol) of **20** in 10 mL of acetic acid was added 150 mg of activated zinc dust. The suspension was stirred vigorously at 25 °C for 2 days. The reaction was diluted with methylene chloride, filtered through Celite, concentrated to remove solvents, diluted with 200 mL of diethyl ether, and washed with 1 *N* NaOH solution. The aqueous layer was extracted twice with diethyl ether (75 mL each) and the combined ether layer was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 53 mg (47% yield) of sulfide **29** and 3.5 mg (3% recovery) of sulfoxide **20**. Sulfide **29**: $[\alpha]^{22}_D = -65.0°$ (c 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 4.92 (dd, *J* = 2.6, 1.6 Hz, 1 H, Cp-H), 4.57 (dd, *J* = 2.6, 1.6 Hz, 1 H, Cp-H), 4.47 (t, *J* = 2.6 Hz, 1 H, Cp-H), 4.23 (s, 5 H, Cp'-H), 3.82 (s, 3 H, OMe), 1.22 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 171.0 (s, C=O), 81.4 (d, Cp), 78.4 (s, Cp), 73.9 (s, Cp), 72.8 (d, Cp), 71.3 (d, 5 C, Cp'), 71.1 (d, Cp), 51.3 (q, OMe), 46.1 (s, C-S), 30.6 (q, 3 C, Me); MS m/z FAB 332 (M+; 80%), 301, 276 (100%), 245, 216, 152, 121. Anal. Calcd for $C_{16}H_{20}FeO_2S$: C, 57.84; H, 6.07. Found: C, 57.97; H, 6.33.

(SR,1S,2R,1'S)-1-(t-Butylsulfinyl)-2-(1-hydroxy-2-propenyl)ferrocene (22a). From 19. To a cold (0 °C) solution of 27 mg (0.08 mmol) of **19** in 1.5 mL of THF was added 35 μL (0.12 mmol) of titanium tetraisopropoxide. The solution was stirred at 0 °C for 30 min, cooled to -78 °C and 0.24 mL (0.24 mmol) of vinylmagnesium bromide (1 *M* solution in THF) was added. The resulting solution was warmed to 0 °C over 3.5 h. After completion of the reaction (monitored by TLC), the reaction mixture was diluted with diethyl ether and washed with brine and then $NaHCO_3$ solution. The aqueous layer was extracted once with 30 mL of diethyl ether and then twice with CH_2Cl_2 (30 mL each). The combined organic extract was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluent to give 24 mg (86% yield) of **22a**. Optical rotation and spectral data were the same as those obtained from sulfoxide **8**.

(SR,1S,2R,1'S)-1-(t-Butylsulfinyl)-2-(1-hydroxyethyl)ferrocene (31). From 19. To a cold (0 °C) solution of 98 mg (0.31 mmol) of **19** in 10 mL of THF was added 0.12 mL (0.4 mmol) of titanium tetraisopropoxide. The solution was stirred at 0 °C for 30 min, cooled to -78 °C and 0.31 mL (0.62 mmol) of methylmagnesium bromide (2 *M* solution in THF) was added. The resulting solution was warmed to 0 °C over 3 h. The reaction mixture was diluted with diethyl ether and washed with brine and then $NaHCO_3$ solution. The aqueous layer was extracted twice with CH_2Cl_2 (30 mL each). The combined organic extract was dried ($MgSO_4$),

concentrated, and column chromatographed on silica gel using petroleum ether and diethyl ether (7:1) as eluent to give 79 mg (76% yield) of **31**; mp. 77 ~ 78 °C; $[\alpha]^{22}_D$ = -83° (c 2.2, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 5.31 (d, *J* = 7 Hz, 1 H, OH), 5.01 (pent, *J* = 7 Hz, 2 Hz, 1 H, CH-O), 4.41 (t, *J* = 2.4 Hz, 1 H, Cp-H), 4.35 (s, 5 H, Cp'), 4.3 ~ 4.34 (m, 2 H, Cp), 1.47 (d, *J* = 7 Hz, 3 H, Me), 1.23 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 94.9 (s, Cp), 83.2 (s, Cp), 71.3 (d, 5 C, Cp'), 69.8 (d, Cp), 69.1 (d, Cp), 68.8 (d, Cp), 65.5 (d, C-O), 57.2 (s, C-S), 24.2 (q, Me), 23.9 (q, 3 C, Me); MS m/z FAB 334 (M+). Anal. Calcd for $C_{16}H_{22}FeO_2S$: C, 57.49; H, 6.63. Found: C, 57.57; H, 6.45.

(1S,2R)-1-(t-Butylsulfonyl)-2-[trans-(2-butenoyl)oxymethyl]ferrocene (32) and (1S,2R)-1-(t-butylsulfonyl)-2-[cis-(2-butenoyl)oxymethyl]ferrocene (33). To a cold (-78 °C) solution of 122 mg (0.51 mmol) of **14** in 8 mL of THF was added dropwise 0.32 mL (0.51 mmol) of *n*-BuLi (1.6 *M* in hexanes). The resulting mixture was stirred at -78 °C for 10 min, and 54 µL of distilled crotonyl chloride (0.56 mmol; a 4:1 mixture of *trans* and *cis*) was added. The solution was stirred for 20 min at -78 °C, and 30 min at 0 °C. The reaction mixture was quenched with 50 mL of $NaHCO_3$ and the aqueous layer was extracted twice with diethyl ether (100 mL and 50 mL). The combined organic extracts were dried ($MgSO_4$), concentrated and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 97 mg (66%) of *trans*-crotonate ester **32** and 21 mg (14%) of *cis*-crotonate ester **33** as yellow oils. *Trans*-crotonate ester **32**: mp. 91-92 °C; $[\alpha]^{22}_D$ = -45.3° (c 0.7, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 6.95 (dq, *J* = 15.6, 7.0 Hz, 1 H, CH=), 5.79 (dq, *J* = 15.6, 1.8 Hz, 1 H, CH=), 5.34 (d, *J* = 12.2 Hz, 1 H, CH_2-O), 5.22 (d, *J* = 12.2 Hz, 1 H, CH_2-O), 4.64 (dd, *J* = 2.4, 1.5 Hz, 1 H, Cp-H), 4.61 (dd, *J* = 2.4, 1.5 Hz, 1 H, Cp-H), 4.47 (t, *J* = 2.4 Hz, 1 H, Cp-H), 4.46 (s, 5 H, Cp'-H), 1.87 (dd, *J* = 7.0, 1.8 Hz, 3 H, CH_3), 1.32 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 166.0 (s, C=O), 145.0 (d, CH=), 122.4 (d, CH=), 83.8 (s, Cp), 82.1 (s, Cp), 73.8 (d, Cp), 73.4 (d, Cp), 71.5 (d, 5 C, Cp'), 70.5 (d, Cp), 59.7 (t, C-O), 59.3 (s, C-S), 23.6 (q, 3 C, *t*-Bu), 18.0 (q, CH_3). Anal. Calcd for $C_{19}H_{24}FeO_4S$: C, 56.44; H, 5.98. Found: C, 56.17; H, 6.25. *Cis*-crotonate ester **33**: $[\alpha]^{22}_D$= -13.8° (c 0.6, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 6.34 (qd, *J* = 11.6, 7.0 Hz, 1 H, CH=), 5.73 (qd, *J* = 11.6, 1.8 Hz, 1 H, CH=), 5.33 (d, *J* = 12.5 Hz, 1 H, CH_2O), 5.21 (d, *J* = 12.5 Hz, 1 H, CH_2O), 4.64 (dd, *J* = 2.4, 1.7 Hz, 1 H, Cp), 4.62 (dd, *J* = 2.7, 1.7 Hz, 1 H, Cp-H), 4.47 (dd, *J* = 2.7, 2.4 Hz, 1 H, Cp-H), 4.46 (s, 5 H, Cp'-H), 2.15 (dd, *J* = 7.0, 1.8 Hz, 1 H, CH_3), 1.31 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 165.9 (s, C=O), 145.7 (d, CH=), 120.2 (d, CH=), 83.9 (s, Cp), 82.1 (s, Cp), 73.7 (d, Cp), 73.3 (d, Cp), 71.5 (d, 5 C, Cp'), 70.5 (d, Cp), 59.4 (t, C-O), 59.3 (s, C-S), 23.5 (q, 3 C, *t*-Bu), 15.4 (q, CH_3); MS m/z FAB 404 (M+).

(1S,2R)-1-(t-Butylsulfonyl)-2-[(3-butenoyl)oxymethyl]ferrocene (34). To a cold (0 °C) solution of 114 mg (0.34 mmol) of **14** in 3 mL of CH_2Cl_2 was added 0.2 mL (1.44 mmol) of Et_3N and 65 µL (0.68 mmol) of crotonyl chloride. The resulting solution was stirred at 0 °C for 10 min, and at 25 °C for 15 min. The reaction mixture was diluted with 50 mL of CH_2Cl_2 and washed with 75 ml of saturated aqueous solution of $NaHCO_3$. The aqueous layer was extracted twice with diethyl ether (50 mL each). The combined organic extract was washed with 50 mL of brine, dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 135 mg (98.5 % yield) of **34**. $[\alpha]^{22}_D$ = -37.2° (c 1.5, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 5.88 (ddt, *J* = 16.4, 10.9, 7.0 Hz, 1 H, CH=), 5.30 (d, *J* = 12.4 Hz, 1 H, CH_2O), 5.19 (d, *J* = 12.4 Hz, 1 H, CH_2O), 5.15 (dq, *J* = 16.4, 1.4 Hz, 1 H, CH_2=), 5.14 (dq, *J* = 10.9, 1.4 Hz, 1 H, CH_2=), 4.64 (dd, *J* = 2.5, 1.4 Hz, 1 H, Cp-H), 4.59 (dd, *J* = 2.5, 1.4 Hz, 1 H, Cp-H), 4.48 (t, *J* = 2.5

Hz, 1 H, Cp-H), 4.45 (s, 5 H, Cp'-H), 3.05 (dt, *J* = 7.0, 1.4 Hz, 2 H, $CH_2C{=}O$), 1.31 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 170.9 (C=O), 130.0 (d, CH=), 118.6 (t, CH_2=), 83.3 (s, Cp), 82.1 (s, Cp), 73.7 (d, Cp), 73.4 (d, Cp), 71.5 (d, 5 C, Cp'), 70.6 (d, Cp), 60.2 (t, C-O), 59.3 (C-S), 39.1 (t, CH_2), 23.5 (q, CH_3); MS m/z FAB 404 (M+).

The following experiment serves as the general procedure for the 1,4-addition reactions of ferrocenylesters (32, 33, and 42).

(1S,2R)-1-(t-Butylsulfonyl)-2-[(3S)-3-methyl-4-pentenoyloxymethyl]ferrocene (35a) and (1S,2R)-1-(t-butylsulfonyl)-2-[(3R)-3-methyl-4-pentenoyloxymethyl]ferrocene (35b) from 32. Preparation of bromomagnesium divinylcuprate: A solution of divinylcuprate reagent was prepared by adding 0.18 mL (0.163 mmol) of vinylmagnesium bromide (1 *M* in THF) to a -20 °C suspension of 22 mg (0.081 mmol) of cuprous iodide - dimethylsulfide complex in 4 mL of THF. The black reaction mixture was stirred at -20 °C for 30 min and was ready for use.

To a -78 °C solution of 15 mg (0.037 mmol) of **32** in 1 mL of THF was added 2 mL of the -20 °C cuprate solution. The resulting solution was stirred at -78 °C for 10 min, after which time another 2 mL of cuprate solution was added. The reaction mixture was stirred at -78 °C for 30 min. (The reaction was monitored by TLC, and an additional equivalent of cuprate reagent was added whenever necessary). The reaction mixture was quenched with 20 mL of NH_4Cl/NH_4OH (4/1) solution and the resulting two-phase solution was vigorously stirred at 25 °C for 30 min. The aqueous layer was extracted successively with 50 mL of diethyl ether and twice with CH_2Cl_2 (50 mL each). The combined organic extract was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 13 mg (75% yield) of the 1,4-adducts **35** as an inseparable mixture of diastereomers (**35a** and **35b**) in a ratio of 1.8:1 (based on the ^{1}H NMR spectrum of the crude product). $[\alpha]^{22}_D = -37.0°$ (c 0.5, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 5.74 (ddd, *J* = 17.2, 10.3, 7.0 Hz, 1 H, CH=; **35a** and **35b**), 5.32 (d, J = 12.4 Hz, 1 H, CH_2-O; **35a** and **35b**), 5.15 (d, *J* = 12.4 Hz, 1 H, CH_2-O, **35a** and **35b**), 5.00 (dt, *J* = 17.2, 1.4 Hz, 1 H, H_B of CH_2=; **35b**), 4.99 (dt, J = 17.2, 1.4 Hz, 1 H, H_B of CH_2=; **35a**), 4.95 (dt, *J* = 10.3, 1.4, Hz, 1 H, H_C of CH_2=; **35a**), 4.93 (dt, *J* = 10.3, 1.4, Hz, 1 H, H_C of CH_2=; **35b**), 4.64 (broad dd, *J* = 2.4, 1.5 Hz, 1 H, Cp-H; **35a** and **35b**), 4.59 (broad dd, *J* = 2.4, 1.5 Hz, 1 H, Cp-H; **35a** and **35b**), 4.47 (t, *J* = 2.4 Hz, 1 H, Cp-H; **35a** and **35b**), 4.45 (s, 5 H, Cp'-H; **35a** and **35b**), 2.65 (heptet-doublet, *J* = 7.0, 1.4 Hz, 1 H, CH; **35a** and **35b**), 2.32 (dd, *J* = 15.0, 7.0 Hz, 1 H, $CH_2C{=}O$; **35a** and **35b**), 2.22 (dd, *J* = 15.0, 7.0 Hz, 1 H, $CH_2C{=}CO$; **35a** and **35b**), 1.31 (s, 9 H, *t*-Bu; **35a** and **35b**), 1.03 (d, *J* = 7.0 Hz, 3 H, CH_3; **35a** and **35b**); ^{13}C NMR ($CDCl_3$) (mixture of two isomers) δ 173.4 (s, C=O), 142.3 (d, CH=), 113.5 (t, CH_2=), 82.7 (s, Cp), 82.1 (s, Cp), 73.7 (d, Cp), 73.4 (d, Cp), 71.6 (d, 5 C, Cp'), 70.7 (d, Cp), 59.9 (t, C-O), 59.3 (s, C-S), 41.2 (t, $CH_2C{=}O$), 34.3 (d, CH), 25.6 (q, 3 C, *t*-Bu), 19.7 (q, CH_3); MS m/z FAB 432 (M+).

(1S,2R)-1-(t-Butylsulfonyl)-2-[(3S)-3-methyl-4-pentenoyloxymethyl]ferrocene (35a) and (1S,2R)-1-(t-butylsulfonyl)-2-[(3R)-3-methyl-4-pentenoyloxymethyl]ferrocene (35b) from cis-crotonyl ester 33. A mixture of 5 mg (0.012 mmol) of ene ester **33** and 4 equiv of bromomagnesium divinylcuprate was allowed to react at -78°C for 0.5 h, and -50 ~ -45 °C for 1 h. The reaction mixture was quenched with 25 mL of NH_4Cl/NH_4OH (4/1) solution and the resulting two-phase solution was vigorously stirred at 25 °C for 30 min. The aqueous layer was extracted successively with 50 mL of diethyl ether and three times with CH_2Cl_2 (25 mL each). The combined organic extract was dried ($MgSO_4$), concentrated, and column chromatographed on

silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 7 mg (60% yield) of the 1,4-adducts **35** as an inseparable mixture of diastereomers (**35a** : **35b**) in a ratio of 4:5 (based on the ^{1}H NMR spectrum of the crude product).

(+)-(S)-3-Methyl-4-pentenoic acid (37). To a solution of 75 mg (0.171 mmol) of ester **35a** and **35b** (1.8:1) in 2 mL of THF was added 0.7 mL of 0.46 *M* KOH (0.31 mmol). The reaction mixture was monitored by TLC [eluant: petroleum ether/diethyl ether (1/2)]. Additions of 2 mL of THF and 2.4 mL of 0.46 *M* KOH were added in small amounts periodically over 72 h. After 95 h, the reaction was complete. The mixture was diluted with 75 mL of H_2O and extracted with 100 mL of diethyl ether. The aqueous layer was washed twice with diethyl ether (50 mL each) and the combined organic layers (200 mL) were washed with 25 mL of 1 *M* NaOH. The combined aqueous layer was acidified to pH ~ 3 with 1 *N* HCl and extracted three times with CH_2Cl_2 (50 mL each). The combined extract was dried ($MgSO_4$), concentrated by distillation of CH_2Cl_2 under normal pressure, and purified by silica gel column chromatography using a gradient mixture of petroleum ether and diethyl ether as eluant to give 11.4 mg (60% yield) of desired product (*S*)-**37**. $[\alpha]^{22}_D$ = +12.6° (c 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.79 (ddd, *J* = 17.4, 10.4, 7.0 Hz, 1 H, CH=), 4.99 (d, *J* = 17.4 Hz, 1 H, CH_2=), 4.93 (d, *J* = 10.4 Hz, 1 H, CH_2=), 2.73 (heptet, *J* = 7.0 Hz, 1 H, CH), 2.44 (dd, *J* = 16.2, 7.0 Hz, 1 H, CH_2C=O), 2.33 (dd, *J* = 16.2, 7.0 Hz, 1 H, CH_2C=O), 1.01 (d, *J* = 7.0 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 165.5 (s, C=O), 142.1 (d, CH=), 113.6 (t, CH_2=), 41.0 (d, CH), 34.1 (t, CH_2), 19.7 (q, CH_3).

(±)-Methyl 3-methyl-4-pentenoate (38). To a cold (-20 °C) suspension of 5.220 g (20.67 mmol) of cuprous iodide - dimethyl sulfide complex in 50 mL of diethyl ether was added 41.30 mL (20.65 mmol) of a 1.0 *M* solution of vinylmagnesium bromide in THF. After 10 minutes, 50 mL of dimethyl sulfide were added. The resulting black suspension was stirred at -20 °C for 30 min and used as such. To a cold (-50 °C) solution of 1.80 mL (1.700g, 0.017 mol) of methyl crotonate in 20 mL of THF was added a cold (-10 °C) solution of the above cuprate reagent. The resulting solution was allowed to reach -10 °C over 45 min, and was stirred at this temperature for 2.5 h. The reaction mixture was diluted with 400 mL of a 4/1 mixture of NH_4Cl/NH_4OH. The resulting blue solution was stirred at 25 °C for 45 min, after which time 200 mL of diethyl ether was added. After separation of the two layers, the blue aqueous layer was extracted with 300 mL of diethyl ether and 100 mL of CH_2Cl_2. The combined organic extract was dried ($MgSO_4$), concentrated by distillation of the solvent at atmospheric pressure, and column chromatographed on silica gel using a gradient mixture of petroleum ether / diethyl ether as eluant to give 1.279 g (59% yield) of **38** as a colorless oil and 0.272 g (16% recovery) of methyl crotonate. Compound **38**:[24] ^{1}H NMR ($CDCl_3$) δ 5.77 (ddd, *J* = 17.2, 10.4, 7.0 Hz, 1 H, CH=), 5.02 (dt, *J* = 17.2, 1.4 Hz, 1 H, CH_2=), 4.95 (dt, *J* = 10.4, 1.4 Hz, 1 H, CH_2=), 3.66 (s, 3 H, MeO), 2.68 (heptet, *J* = 7.0 Hz, 1 H, CH), 2.36 (dd, *J* = 15.0, 7.0 Hz, 1 H, CH_2C=O), 2.26 (dd, *J* = 15.0, 7.0 Hz, 1 H, CH_2C=O), 1.05 (d, *J* = 7.0 Hz, 3 H, CH_3).

Racemic 3-methyl-4-pentenoic acid. To a solution of 185 mg (1.44 mmol) of methyl 3-methyl-4-pentenoate (**38**) in 3 mL of THF was added 3 mL (4.5 mmol) of a 1.5 *M* aqueous solution of KOH. After stirring at 25 °C for 65 h, 55 °C for 12 h, the reaction was then diluted with 50 mL of diethyl ether. The mixture was transferred to a separatory funnel, and was washed with 50 mL of 4 *N* NaOH. The aqueous layer was extracted with 25 mL of diethyl ether. The combined ether extract was washed with 10 mL of 4 *N* NaOH.

The combined aqueous layer was acidified to pH~3 with 4 *N* HCl, and were then extracted three times with CH_2Cl_2 (50 mL and 2 × 20 mL). The combined organic extract was dried ($MgSO_4$) and concentrated by distillation of the solvent at atmospheric pressure to give 147 mg (89% yield) of the acid. ^{1}H NMR ($CDCl_3$) δ 5.79 (ddd, *J* = 17.4, 10.4, 7.0 Hz, 1 H, CH=), 4.99 (d, *J* = 17.4 Hz, 1 H, CH_2=), 4.93 (d, *J* = 10.4 Hz, 1 H, CH_2=), 2.73 (heptet, *J* = 7.0 Hz, 1 H, CH), 2.44 (dd, *J* = 16.2, 7.0 Hz, 1 H, CH_2C=O), 2.33 (dd, *J* = 16.2, 7.0 Hz, 1 H, CH_2C=O), 1.01 (d, *J* = 7.0 Hz, 3 H, CH_3); MS m/z EI 114 (M+).

*A 1:1 mixture of **35a** and **35b**.* To a solution of 53 mg (0.16 mmol) of sulfone **14** in 2.5 mL of CH_2Cl_2 was added 486 mg (2.35 mmol) of DCC, along with 75 μL (54 mg; 0.54 mmol) of Et_3N and a solution of 50 mg (0.44 mmol) of racemic 3-methyl-4-pentenoic acid in 1.5 mL of CH_2Cl_2. The resulting solution was stirred at 25 °C for 15 h. A total of 20 mL of brine was added and the mixture was extracted three times with CH_2Cl_2 (50 mL each). The combined organic extract was dried ($MgSO_4$) and concentrated to give 72 mg of crude product, the ^{1}H NMR spectrum of which revealed two distinct sets of signals (in a 1:1 ratio) for **35a** and **35b**.

*(1S,2R)-1-(t-Butylsulfonyl)-2-[(3S-(cyclohex-1-enyl)-butanoyl)oxymethyl]ferrocene (**39a**) and (1S,2R)-1-(t-butylsulfonyl)-2-[(3R-(cyclohex-1-enyl))-butanoyloxymethyl]ferrocene (**39b**).* Preparation of lithium dicyclohexenylcuprate: To a cold (-78 °C) solution of 200 mg (1.24 mmol) of 1-bromocyclohexene in 3 mL of diethyl ether was added 1.5 mL (2.48 mmol) of *t*-BuLi (1.7 *M* in pentane). The solution was stirred at -78 °C for 1 h and then added via cannula to a -30 °C suspension of 150 mg (0.60 mmol) of cuprous iodide-dimethyl sulfide complex in 1.5 mL of diethyl ether. After 10 min of stirring at -30 °C, 3 ml of dimethyl sulfide was added and the resulting solution was stirred for another 30 min at -30 °C and then cooled to -50 °C prior to use.

To a -78 °C solution of 29 mg (0.072 mmol) of ester **32** in 1 mL of diethyl ether was added 3 mL (3 equiv) of the above cuprate solution (-50 °C). The resulting mixture was stirred at -78 °C for 1 h, after which time 100 mL of a 4/1 mixture of NH_4Cl and NH_4OH was added. The solution was warmed to 25 °C and stirred for 30 min. The blue aqueous layer was extracted successively with 100 mL of diethyl ether and 50 mL of methylene chloride. The combined organic extract was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 27 mg (77% yield) of the 1,4-adducts **39** as an inseparable mixture of diastereomers **39a** : **39b** in a ratio 3:2 (based on the ^{1}H NMR spectrum of the crude product) along with 1 mg (3% recovery) of **32**. Compounds **39**: $[\alpha]^{22}_D$= -34.0° (c 1.2, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 5.41 (broad t, *J* = 3.7 Hz, 1 H, CH=; **39b**), 5.38 (broad t, *J* = 3.7 Hz, 1 H, CH=; **39a**), 5.34 (d, *J* = 12.4 Hz, 1 H, CH_2O; **39b**), 5.33 (d, *J* = 12.4 Hz, 1 H, CH_2O; **39a**), 5.12 (d, *J* = 12.4 Hz, 1 H, CH_2O; **39a** and **39b**), 4.63 (dd, *J* = 2.5, 1.6 Hz, 1 H, Cp-H; **39a** and **39b**), 4.58 (dd, *J* = 2.5, 1.6 Hz, 1 H, Cp-H; **39a** and **39b**), 4.46 (t, *J* = 2.5 Hz, 1 H, Cp-H; **39a** and **39b**), 4.45 (s, 5 H, Cp'-H; **39a** and **39b**), 2.50 (sextet, *J* = 7.4 Hz, 1 H, CH; **39a** and **39b**), 2.40 (dd, *J* = 14.5, 7.4 Hz, 1 H, CH_2C=O; **39b**), 2.39 (dd, *J* = 14.5, 7.4 Hz, 1 H, CH_2C=O; **39a**), 2.20 (dd, *J* = 14.5, 7.4 Hz, 1 H, CH_2C=O; **39a** and **39b**), 1.95 (m, 2 H, CH_2C=; **39a** and **39b**), 1.88 (m, 2 H, CH_2C=; **39a** and **39b**), 1.61-1.48 (m, 4 H, 2 CH_2; **39a** and **39b**), 1.32 (s, 9 H, *t*-Bu; **39a** and **39b**), 1.00 (d, *J* = 6.9 Hz, 3 H, CH_3; **39a** and **39b**); ^{13}C NMR ($CDCl_3$) δ 172.5 (s, C=O; **39a**), 140.4 (s, C=; **39a**), 120.7 (d, CH=; **39a**), 83.8 (s, Cp; **39a**), 82.0 (s, Cp; **39a**), 73.7 (d, Cp; **39a**), 73.7 (d, Cp; **39a**), 71.5 (d, 5 C, Cp'; **39a**), 70.5 (d, Cp; **39a**), 59.6 (t, C-O; **39a**), 59.3 (s, C-S; **39a**), 40.4 (t, CH_2C=; **39a**), 37.9 (t, CH_2C=; **39a**), 25.5 (t, CH_2; **39a**), 25.1 (t, CH_2; **39a**), 23.5 (q, 3 C, *t*-Bu; **39a**), 22.9 (t,

CH_2; **39a**), 22.5 (t, CH_2; **39a**), 19.32 (q, CH_3; **39a**); MS m/z FAB 486 (M+). Anal. Calcd for $C_{25}H_{34}FeO_4S$: C, 61.73; H, 7.05. Found: C, 61.51; H, 7.44.

(1S,2R)-1-(t-Butylsulfonyl)-2-[(3S)-3-methylheptanoyloxymethyl]ferrocene (40a) and (1S,2R)-1-(t-butylsulfonyl)-2-[(3R)-3-methylheptanoyloxymethyl]ferrocene (40b). Preparation of the cuprate reagent: To a -40 °C suspension of 120 mg (0.47 mmol) of cuprous iodide-dimethyl sulfide complex in 1.2 mL of diethyl ether was added 0.6 mL (0.95 mmol) of *n*-BuLi (1.6 *M* in hexanes). After stirring for 10 min at -40 °C, 2 mL of dimethyl sulfide was added, and the resulting solution was stirred at -35 °C for 30 min.

To a -78 °C solution of 28 mg (0.07 mmol) of ester **32** in 1 mL of ether was added 1.9 mL (3 equiv) of the above cuprate solution. After the resulting solution was stirred at -78 °C for 1 h and -50 °C for 3 h, 100 mL of a 4/1 mixture of saturated aqueous NH_4Cl/NH_4OH solutions was added. The mixture was allowed to reach 25 °C and was stirred for 30 min. The blue aqueous layer was extracted successively with 100 mL of ether and 50 mL of methylene chloride. The combined organic layer was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 24 mg (75% yield) of the 1,4-adducts **40** as an inseparable mixture of diastereomers **40a** and **40b** in a ratio of 2:1 (based on the ^{1}H NMR spectrum of the crude product), 3 mg (10% recovery) of **32**, and 2 mg of sulfone **14**. Compound **40**: $[\alpha]^{22}_D = -29.7°$ (c 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 5.32 (d, $J = 12.3$ Hz, 1 H, CH_2O; major isomer **40a**), 5.31 (d, $J = 12.3$ Hz, 1 H, CH_2O; minor isomer **40b**), 5.15 (d, $J = 12.3$ Hz, 1 H, CH_2O), 5.14 (d, $J = 12.3$ Hz, 1 H, CH_2O; **40a**), 4.63 (dd, $J = 2.7$, 1.6 Hz, 1 H, Cp-H; **40a** and **40b**), 4.59 (dd, $J = 2.7$, 1.6 Hz, 1 H, Cp-H; **40a** and **40b**), 4.47 (t, $J = 2.7$ Hz, 1 H, Cp-H; **40a** and **40b**), 4.45 (s, 5 H, Cp'-H; **40a** and **40b**), 2.27 (dd, $J = 14.6$, 6.5 Hz, 1 H, $CH_2C{=}O$; **40b**), 2.26 (dd, $J = 14.6$, 6.5 Hz, 1 H, $CH_2C{=}O$; **40a**), 2.06 (dd, $J = 14.6$, 6.5 Hz, 1 H, $CH_2C{=}O$; **40a**), 2.05 (dd, $J = 14.6$, 6.5 Hz, 1 H, $CH_2C{=}O$; **40b**), 1.91 (octet, $J = 6.5$ Hz, 1 H, CH; **40a** and **40b**), 1.31 (s, 9 H, *t*-Bu; **40a** and **40b**), 1.29-1.15 (series of multiplets, 6 H, 3 CH_2; **40a** and **40b**), 0.90 (d, $J = 6.5$ Hz, 3 H, CH_3; **40a** and **40b**), 0.87 (t, $J = 6.5$ Hz, CH_3; **40a** and **40b**); ^{13}C NMR ($CDCl_3$) δ 172.9 (s, C=O), 83.8 (s, Cp), 82.1 (s, Cp), 73.7 (d, Cp), 73.4 (d, Cp), 71.5 (d, 5 C, Cp'), 70.2 (d, Cp), 59.7 (t, C-O), 59.3 (s, C-S), 41.9 (t, $CH_2C{=}O$ for **40a**), 41.8 (t, $CH_2C{=}O$ for **40b**), 36.4 (d, CH), 30.3 (t, CH_2), 29.1 (t, CH_2), 23.5 (q, 3 C, *t*-Bu), 22.8 (t, CH_2), 19.7 (q, CH_3), 14.0 (q, CH_3).

(1S,2R)-1-(t-Butylsulfonyl)-2-[(3S-t-butyl)-butanoyloxymethyl]ferrocene (41a) and (1S,2R)-1-(t-butylsulfonyl)-2-[(3R-t-butyl)-butanoyloxymethyl]ferrocene (41b). Preparation of the cuprate reagent: To a -30 °C suspension of 138 mg (0.55 mmol) of cuprous iodide-dimethyl sulfide complex in 1.3 mL of diethyl ether was added 0.65 mL (1.10 mmol) of *t*-BuLi (1.7 *M* in pentane). After stirring at -30 °C for 10 min, 2 mL of dimethyl sulfide was added and the resulting mixture was stirred at -30 °C for 30 min.

To a -78 °C solution of 26 mg (0.064 mmol) of ester **32** in 1 mL of diethyl ether was added 1.4 mL (3 equiv) of the above cuprate solution (-30 °C). The reaction mixture was stirred at -78 °C for 1.5 h, allowed to reach -40 °C, stirred from -40 to -20 °C over 1 h, and stirred at -20 °C for 30 min. A total of 100 mL of aqueous solution of NH_4Cl/NH_4OH (4:1) was added at -20 °C. The solution was allowed to reach 25 °C and was stirred for 30 min. The blue aqueous layer was extracted successively with 100 mL of diethyl ether and twice with methylene chloride (25 mL each). The combined organic extract was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 30 mg (100% yield) of 1,4-adducts **41** as an inseparable mixture of two diastereomers (**41a** and

41b) in a 5.2:1 ratio. ^{1}H NMR (CDCl$_3$) δ 5.33 (d, J = 12.4 Hz, 1 H, CH$_2$O; major isomer **41a**), 5.31 (d, J = 12.4 Hz, 1 H, CH$_2$O; **41b**), 5.16 (d, J = 12.4 Hz, 1 H, CH$_2$-O; **41b**), 5.14 (d, J = 12.4 Hz, 1 H, CH$_2$-O; **41a**), 4.64 (dd, J = 2.6, 1.5 Hz, 1 H, Cp-H; **41a** and **41b**), 4.59 (dd, J = 2.6, 1.5 Hz, 1H, Cp-H; **41a** and **41b**), 4.48 (t, J = 2.6 Hz, 1 H, Cp-H; **41a** and **41b**), 4.45 (s, 5 H, Cp'-H; **41a** and **41b**), 2.44 (dd, J = 14.4, 3.2 Hz, 1 H, CH$_2$C=O; **41a** and **41b**), 1.91 (dd, J = 14.4, 10.8 Hz, 1 H, CH$_2$C=O; **41b**), 1.90 (dd, J = 14.4, 10.8 Hz, 1 H, CH$_2$C=O; **41a**), 1.77 (dqd, J = 10.8, 6.7, 3.2 Hz, 1 H, CH; **41a** and **41b**), 1.32 (s, 9 H, *t*-Bu; **41a** and **41b**), 0.85 (d, J = 6.7 Hz, 3 H, CH$_3$; **41a** and **41b**); ^{13}C NMR (CDCl$_3$) δ 174.0 (s, C=O), 83.9 (s, Cp), 82.2 (s, Cp), 73.9 (d, Cp), 73.6 (d, Cp), 71.7 (d, 5 C, Cp'), 70.8 (d, Cp), 60.0 (t, C-O), 59.5 (s, CS), 40.2 (t, CH$_2$), 37.7 (d, CH), 32.9 (s, CMe$_3$), 27.3 (q, 3 C, Me), 23.8 (q, 3 C, Me), 15.2 (q, Me); MS m/z FAB 462 (M+). Anal. Calcd for $C_{23}H_{34}FeO_4S$: C, 59.74; H, 7.41. Found: C, 59.58; H, 7.57.

(1S,2R)-1-(t-Butylsulfonyl)-2-[trans-(3-phenyl-2-propenoyl)oxymethyl]ferrocene (42). To a cold (0 °C) solution of 120 mg (0.36 mmol) of alcohol **14** in 2 mL of CH$_2$Cl$_2$ was added 0.2 mL (1.44 mmol) of Et$_3$N and a solution of 119 mg (0.72 mmol) of *trans*-cinnamoyl chloride in 2 mL of CH$_2$Cl$_2$ via cannula. The resulting solution was stirred at 0 °C for 10 min, then at 25 °C for 48 h. The reaction mixture was washed with 10 mL of saturated aqueous solution of NaHCO$_3$ and extracted twice with CH$_2$Cl$_2$ (50 mL each). The combined organic layer was washed with brine (10 mL), dried (MgSO$_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether and diethyl ether as eluant to give 91 mg (54% yield) of ester **42** as yellow solids, along with 29 mg (24 % recovery) of starting alcohol **14**. Ester **42**: mp 185-187 °C; $[\alpha]^{22}_D$ = -68.8° (c 1.55, CH$_2$Cl$_2$); ^{1}H NMR (CDCl$_3$) δ 7.66 (d, J = 16.0 Hz, 1 H, CH=), 7.50 (m, 2 H, Ph), 7.38 (m, 3 H, Ph), 6.37 (d, J = 16.0 Hz, 1 H, CH=), 5.41 (d, J = 12.3 Hz, 1 H, CH$_2$O), 5.32 (d, J = 12.3 Hz, 1 H, CH$_2$O), 4.67 (d, J = 2.4 Hz, 1 H, Cp-H), 4.66 (d, J = 2.4 Hz, 1 H, Cp-H), 4.50 (t, J = 2.4 Hz, 1 H, Cp-H), 4.48 (s, 5 H, Cp'-H), 1.34 (s, 9 H, *t*-Bu); ^{13}C NMR (CDCl$_3$) δ 166.4 (s, C=O), 145.1 (d, CH=), 134.2 (s, Ph), 130.4 (d, CH=), 128.9 (d, 2 C, Ph), 128.0 (d, 2 C, Ph), 117.7 (d, Ph), 83.7 (s, Cp), 82.2 (s, Cp), 73.9 (d, Cp), 73.4 (d, Cp), 71.6 (d, 5 C, Cp'), 70.6 (d, Cp), 60.1 (t, C-O), 59.3 (s, C-S), 23.6 (q, 3 C, *t*-Bu); MS m/z FAB 466 (M+). Anal. Calcd for $C_{24}H_{26}FeO_4S$: C, 61.81; H, 5.62. Found: C, 61.56; H, 5.73.

(1S,2R)-1-(t-Butylsulfonyl)-2-[(3S–(cyclohex-1-enyl)-3-phenylpropanoyl)oxymethyl]ferrocene (43a) and (1S,2R)-1-(t-butylsulfonyl)-2-[(3R–(cyclohex-1-enyl)-3-phenyl propanoyl)oxymethyl]ferrocene (43b). Preparation of the cuprate reagent: To a cold (-78 °C) solution of 275 mg (1.71 mmol) of 1-bromocyclohexene in 3.2 mL of THF was added 2.0 mL (3.42 mmol) of *t*-BuLi (1.7 *M* in pentane). The resulting solution was stirred at -78 °C for 1 h, then transferred via cannula into a cold (-30 °C) suspension of 205 mg (0.81 mmol) of cuprous iodide - dimethyl sulfide complex in 2 mL of diethyl ether. After stirring for 10 min at -30 °C, 7 mL of dimethyl sulfide was added to the greenish brown solution. The reaction mixture was stirred at -30 °C for 30 min and was used as such.

To a cold (-78 °C) solution of 26 mg (0.056 mmol) of ester **42** in 3 mL of THF, were added 6 mL (6 equiv.) of the above cuprate solution (-30°C). The reaction mixture was warmed to -25 °C and allowed to reach 0 °C over 1.5 h, after which time TLC analysis indicated that the reaction was complete. The reaction mixture was quenched with 100 ml of a 4/1 mixture of aqueous NH$_4$Cl / NH$_4$OH solutions and stirred at 25 °C for 30 min. After extraction with diethyl ether (100 mL) and CH$_2$Cl$_2$ (50 mL), the combined organic layer was dried (MgSO$_4$) and concentrated to give 48 mg of crude product as a yellow oil. ^{1}H NMR analysis of this crude mixture revealed a 1:1 mixture of **43a** and **43b**. Column chromatographic separation using a gradient mixture of hexane and ether as eluant gave 29 mg (95% yield) of **43a** and **43b**. The NMR chemical shift assignment is arbitrary. ^{1}H NMR ($CDCl_3$) δ 7.28-7.12 (m, 10 H, Ph-H), 5.57 (broad s, 2 × 1 H, 2 × CH=), 5.30 (d, J = 12.0 Hz, 1 H, CH_2O of **43a**), 5.28 (d, J = 12.0 Hz, 1 H, CH_2O of **43b**), 5.07 (d, J = 12.0 Hz, 1 H, CH_2O of **43a**), 5.06 (d, J = 12.0 Hz, 1 H, CH_2O of **43b**), 4.60 (m, overlap, 2 H, 2 Cp-H), 4.45 (m, overlap, 2 H, 2 Cp-H), 4.42 (s, 5 H, Cp-H of **43a**), 4.41 (s, 5 H, Cp'-H of **43b**), 4.38 (m, overlap, 2 H, 2 Cp-H), 3.68 (t, J = 8.0 Hz, 1 H, CH of **43a**), 3.66 (t, J = 8.5 Hz, 1 H, CH of **43b**), 2.79 (dd, J = 15.0, 8.0 Hz, 1 H, CHCO of **43a**), 2.78 (dd, J = 15.0, 8.0 Hz, 1 H, CHCO of **43b**), 2.65 (dd, J = 15.0, 8.0 Hz, 1 H, CHCO of **43a**), 2.61 (dd, J = 15.0, 8.0 Hz, 1 H, CHCO of **43b**), 2.20-2.10 (m, 8 H, CH_2C=), 1.28 (s, 18 H, *t*-Bu). ^{13}C NMR ($CDCl_3$) δ 172.3, 172.2 (s, C=O), 142.8 (s, C=), 138.9 (s, Ph), 128.54, 128.50 (d, 2 C, Ph), 127.9, 127.8 (d, 2 C, Ph), 126.7 (d, CH=), 121.8 (d, Ph), 83.9, 83.8 (s, Cp), 82.0, 81.96 (s, Cp), 74.0, 73.7 (d, Cp), 73.4 (d, Cp), 71.7, 71.7 (d, 5 C, Cp'), 70.7 (d, Cp), 59.9, 59.9 (t, C-O), 59.4 (s, CS), 48.8 (d, CH), 39.2, 39.1 (t), 27.44, 27.40 (t), 25.4 (t), 23.7 (q, 3 C, t-Bu), 23.0, 22.6 (t), 19.3 (t). MS m/z FAB 548 (M+). Anal. Calcd for $C_{30}H_{36}FeO_4S$: C, 65.69; H, 6.62. Found: C, 65.41; H, 6.89.

(1S,2R,1'S)-1-(t-Butylsulfonyl)-2-(α-hydroxybenzyl)ferrocene (44A). To a solution of 27 mg (0.068 mmol) of sulfoxide **23a** in 3 mL of acetone was added 26 mg (0.082 mmol) of *m*-chloroperbenzoic acid (55%). The resulting solution was stirred at 30 °C for 20 min, diluted with 1 *N* NaOH (10 mL) and brine (10mL), and extracted with diethyl ether (50 mL) and twice with CH_2Cl_2 (30 mL each). The combined organic extract was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether / diethyl ether as eluant to give 28 mg (100% yield) of sulfone **44A** as a yellow oil. $[\alpha]^{22}{}_D$ = +101.6 (c 0.8, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.51 (d, J = 7.3 Hz, 2 H, Ph-H), 7.34 (t, J = 7.3 Hz, 2 H, Ph-H), 7.25 (t, J = 7.3 Hz, 1 H, Ph-H), 5.84 (d, J = 7.3 Hz, 1 H, OH), 4.59 (dd, J = 2.1, 1.9 Hz, 1 H, Cp-H), 4.51 (dd, J = 2.1, 1.9 Hz, 1 H, Cp-H), 4.48 (t, J = 2.1 Hz, 1 H, Cp-H), 4.35 (s, 5 H, Cp'-H), 4.01 (d, J = 7.3 Hz, 1 H, CH), 1.32 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 144.0 (s, Ph), 128.1 (d, Ph), 127.3 (d, Ph), 126.3 (d, Ph), 94.2 (s, Cp), 81.2 (s, Cp), 72.7 (d, Cp), 72.7 (d, Cp), 71.9 (d, 5 C, Cp'), 70.7 (d, Cp), 70.0 (d, C-O), 60.2 (s, C-S), 23.6 (q, *t*-Bu); MS m/z FAB 412 (M+).

(1S,2R,1'S)-1-(t-Butylsulfonyl)-2-[α-(2-propenoyl)oxybenzyl]ferrocene (44). To a cold (-78 °C) solution of 140 mg (0.34 mmol) of sulfone **44A** in 4 mL of THF was added 0.23 mL (0.37 mmol) of *n*-BuLi (1.6 *M* in hexanes). The resulting solution was stirred at this temperature for 15 minutes and 33μL of freshly distilled acryloyl chloride was added. The resulting mixture was stirred at -78°C for 20 min, allowed to reach 0 °C, and stirred at 0 °C for 30 min. The reaction mixture was diluted with 10 mL of brine and extracted with diethyl ether (30 mL) and three times with CH_2Cl_2 (30 mL each). The combined organic extract was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether / diethyl ether as eluant to give 84 mg of **44** (53 % yield) and 12 mg (9% recovery) of starting sulfone **44A**. Ester **44**: mp 177-179 °C; $[\alpha]^{22}{}_D$ = +21.7° (c 0.65, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.65 (d, J = 7.3 Hz, 2 H, Ph), 7.43 (t, J = 7.3 Hz, 2 H, Ph), 7.34 (t, J = 7.3 Hz, 1 H, Ph), 7.09 (s, 1 H, CHO), 6.32 (dd, J = 17.4, 1.5 Hz, 1 H, CH_2=), 6.02 (dd, J = 17.4, 10.4 Hz, 1 H, CH=), 5.74 (dd, J = 10.4, 1.5 Hz, 1 H, CH_2=), 4.66 (dd, J = 2.7, 1.7 Hz, 1 H, Cp-H), 4.60 (dd, J = 2.7, 1.5 Hz, 1 H, Cp), 4.52 (t, J = 2.7 Hz, 1 H, Cp), 4.06 (s, 5 H, Cp'-H), 1.31 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 164.4 (s, C=O), 141.1 (s, Ph), 131.0 (t, CH_2=), 128.2 (d, 2 C, Ph),

128.2 (d), 128.1 (d), 127.2 (d, 2 C, Ph), 89.1 (s, Cp), 81.4 (s, Cp), 72.6 (d, Cp), 72.6 (d, Cp), 72.0 (d, 5 C, Cp'), 72.0 (d, Cp), 70.8 (d, C-O), 59.5 (s, C-S), 23.4 (q, 3 C, *t*-Bu); MS m/z FAB 466 (M+). Anal. Calcd for $C_{24}H_{26}FeO_4S$: C, 61.81; H, 5.62. Found: C, 61.75; H, 5.89.

(1S,2R,1'S)-1-(t-Butylsulfonyl)-2-(5'-oxo-1'-phenyl-3'-pentenyl)ferrocene (45). A solution of 17 mg (0.036 mmol) of sulfone **44**, 8 mg (0.072 mmol) of 1-acetoxy-1,3-butadiene, and 4 mg (0.012 mmol) of dry ZnI_2 in 0.5 mL of toluene was stirred at 25 °C until TLC analysis indicated that the reaction was complete (31 h). The reaction mixture was diluted with diethyl ether (10 mL) and washed with 10 mL of brine. The aqueous layer was extracted twice with CH_2Cl_2 (30 mL each). The combined organic layer was dried ($MgSO_4$), concentrated, and column chromatographed on silica gel using a gradient mixture of petroleum ether/ diethyl ether as eluant to give 11 mg (65% yield) of aldehyde **45**. $[\alpha]^{22}_D = -5°$ (c 0.1, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 9.30 (d, *J* = 7.9 Hz, 1 H, CHO), 7.55 (d, *J* = 7.5 Hz, 2 H, Ph), 7.43 (t, *J* = 7.5 Hz, 2 H, Ph), 7.31 (t, *J* = 7.5 Hz, 1 H, Ph), 6.46 [ddd, *J* = 15.5 (indicating trans-C=C), 8.2, 6.7 Hz, 1 H, CH=], 5.94 [dd, *J* = 15.5 (indicating trans-C=C), 7.9 Hz, 1 H, CH=], 4.54 (dd, *J* = 2.7, 1.5 Hz, 1 H, Cp-H), 4.51 (dd, *J* = 2.7, 1.5 Hz, 1 H, Cp-H), 4.46 (t, *J* = 2.7 Hz, 1 H, Cp), 4.30 (dd, *J* = 12.0, 3.4 Hz, 1 H, CH-Ph), 3.84 (s, 5 H, Cp'-H), 2.97 (ddd, *J* = 16.0, 12.0, 6.7 Hz, 1 H, CH_2C=), 2.63 (ddd, *J* = 16.0, 8.2, 3.4 Hz, 1 H, CH_2C=), 1.38 (s, 9 H, *t*-Bu); ^{13}C NMR ($CDCl_3$) δ 193.8 (d, CHO), 155.2 (d, CH=), 144.6 (s, Ph), 133.8 (d, CH=), 128.6 (d, 2 C, Ph), 128.4 (d, 2 C, Ph), 127.2 (d, 1 C, Ph), 97.3 (s, Cp), 94.1 (s, Cp), 71.7 (d, 5 C, Cp'), 70.7 (d, Cp), 69.9 (d, Cp), 69.4 (d, Cp), 59.4 (s, C-S), 41.8 (d, CH), 40.1 (t, CH_2), 23.7 (q, 3 C, *t*-Bu); MS m/z FAB 464 (M+). Anal. Calcd for $C_{25}H_{28}FeO_3S$: C, 64.66; H, 6.08. Found: C, 64.38; H, 6.29.

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