Synthesis and Characterization of Planar-Chiral Cyclopentadienyliron Complexes (*S*)- and (*R*)-{η^5-[1-Ph_2(OH)C-2-Me-4-PhC_5H_2]}$Fe(CO)_2R$ (R = C≡CPh, Me, SO_2Me)

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The first enantiomerically pure planar-chiral cyclopentadienyliron complexes, (*S*)- and (*R*)-η^5-$Cp^cFe(CO)_2R$ [Cp^c = 1-hydroxydiphenylmethyl-2-methyl-4-phenylcyclopentadienyl; R = C≡CPh (**6**), Me (**8**)], in which the locus of chirality is in the cyclopentadienyl center, were synthesized from $Cp^aFe(CO)_2I$ (**4a**: Cp^a = 1-(−)-menthoxycarbonyl-2-methyl-4-phenylcyclopentadienyl) and $Cp^bFe(CO)_2I$ (**4b**: Cp^b = 1-(+)-menthoxycarbonyl-2-methyl-4-phenylcyclopentadienyl) and were isolated as a diastereomerically pure form by fractional recrystallization. The molecular structures of **4a** and **4b**, including the absolute configuration, have been established by an X-ray crystallographic analysis based on the configuration of the (−)- and (+)-menthyl groups.

Introduction

There are a variety of stereoselective organic reactions including stereoselective polymerizations in which transition metal complexes act as effective catalytic or stoichiometric mediators.[1] In particular enantioselective reactions have been attracting much attention in terms of the asymmetric syntheses of new medical supplies and new functional materials, and many effective systems including practical applications have been established.[2] The development of such systems has been supported by the discovery of new optically active and reactive organometallic complexes. There are three types of optically active organometallic complexes: one bearing chiral ligands and others containing a metal-centered chirality or a planar chirality. Most known optically active organometallic complexes have chiral ligands such as chiral phosphines and amines, whereas there are relatively limited examples for the latter two types of chiral complexes.[3−6] Recently planar-chiral cyclopentadienyl−metal complexes have received attention because of their potential in catalysis for the stereoselective polymerization of vinyl monomers.[7]

Planar-chiral cyclopentadienyl−metal complexes are advantageous as catalytic and stoichiometric mediators for asymmetric organic reactions because the electron-donor/acceptor properties and steric bulk of the cyclopentadienyl ligands are easily altered, as seen in group 4 metallocene derivatives used as stereoselective polymerization catalysts.[7] Coordination of a cyclopentadienyl ligand to a metal atom is generally so strong that there is almost no chance of ligand association resulting in racemization. Planar chirality in organometallic complexes arises from the coordination of prochiral ligands such as unsymmetrically substituted cyclopentadienyls,[4] arenes,[5] and olefins[6] to a metal and is thus

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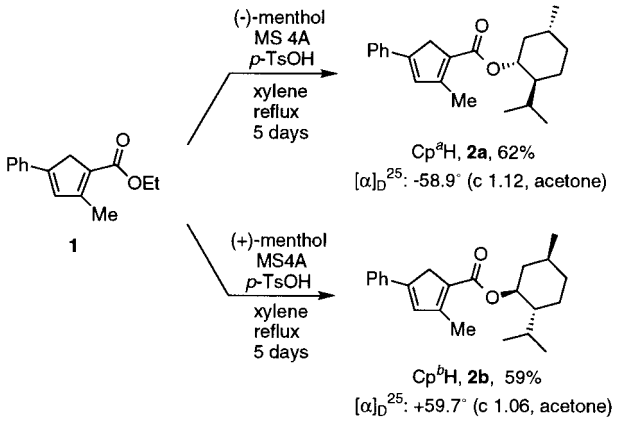
characteristic of metal complexes. Efforts have been directed to the synthesis of planar-chiral cyclopentadienyl−metal complexes, and several optically pure examples with a planar chirality have been isolated; however, they are limited to exceptionally stable complexes such as ferrocene and cymantrene derivatives.[8] Previously we reported the synthesis of planar-chiral cyclopentadienylcobalt,[9] -rhodium,[10] and -ruthenium[11] complexes and now report the synthesis of planar-chiral cyclopentadienyliron complexes with a three-legged "piano stool" structure. Iron complexes with a piano stool structure are known to exhibit a variety of reactivities in stoichiometric and catalytic reactions.[1,12] Indeed, the synthesis and reactivity of the first planar-chiral olefin−iron complexes, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-olefin})]^+$, in which the locus of planar chirality is the olefin center, have been studied extensively by Rosenblum and co-workers,[6a] who found that these complexes undergo enantioselective reactions with nucleophiles.[13]

Results and Discussion

Synthesis and Resolution of Planar-Chiral Di(carbonyl)(η^5-cyclopentadienyl)(iodo)iron. Recently we reported the optical resolution of racemic planar-chiral cyclopentadienyl−transition metal complexes by means of column chromatography using cyclodextrins and successfully isolated optically pure enantiomers of a planar-chiral cyclopentadienylrhodium complex.[14] Attempts to similarly obtain an enantiomerically pure iron analogue were unsuccessful. As a consequence of this, we tested a strategy based on resolution of diastereomers involving chiral cyclopentadienes. There are several methods for the selective synthesis of multisubstituted cyclopentadienes, but few for the synthesis of chiral cyclopentadienes.[4,15] Previously, we developed a convenient route to chiral cyclopentadienes involving an intramalecular Wittig reaction[16] between haloketones and phosphonium bromides to give selectively 1,2,4-trisubstituted cyclopentadienes with an ethyl ester group, which could be exchanged with chiral alcohols such as (−)-menthol.[9] By this method we prepared chiral 1,2,4-trisubstituted cyclopentadiene derivatives having a removable chiral auxiliary, as shown in Scheme 1. Thus, in the presence of a catalytic amount of toluene-*p*-sulfonic acid (*p*-TsOH), 1-ethoxycarbonyl-2-methyl-4-phenyl-1,3-cyclopentadiene (**1**), prepared by the intramolecular Wittig reaction, was allowed to react with (−)- and (+)-menthol in xylene under reflux. The alcohol-exchange reaction proceeded smoothly to give (−)-menthyl ester Cp^{a}H (**2a**) and (+)-menthyl ester Cp^{b}H (**2b**), respectively, which were purified by chromatography on silica and subsequent distillation.

Scheme 1



The planar-chiral cyclopentadienyliron complex, Cp^a-Fe(CO)$_2$I (**4a**), was synthesized from **2a** by a conventional method.[17] Heating **2a** with pentacarbonyliron in the presence of 2-norbornene as a hydrogen acceptor afforded a diastereomeric mixture of the di(carbonyl)(cyclopentadienyl)iron dimer, $[Cp^aFe(CO)_2]_2$ (**3a**), in a good yield. Refluxing **3a** with iodine in chloroform gave Cp^{a}Fe(CO)$_2$I (**4a**) in an almost quantitative yield (Scheme 2). The analysis of **4a** by high-performance liquid chromatography (HPLC) using a chiral column and 5:95 isopropyl alcohol/hexane as a mobile phase showed that **4a** consists of two diastereomers, (*S*)-**4a** and (*R*)-**4a**, in a ratio of 1:1. In the ^{1}H NMR spectrum of **4a**, one set of resonances due to the 3-proton on a cyclopentadienyl ring appeared at δ 5.95 and 5.85 with a ratio of 1:1, and one set of resonances assignable to the 5-proton on a cyclopentadienyl ring appeared at δ 6.38 and 6.31 with a ratio of 1:1, indicating that diastereomers (*S*)-**4a** and (*R*)-**4a** are clearly distinguished by ^{1}H NMR.

Fractional recrystallization of **4a** has been found to give diastereomerically pure complexes (Scheme 2). Thus, pure (*S*)-**4a** was isolated as dark purple needles by recrystallization from a mixture of 1:5 diethyl ether/hexane, while (*R*)-**4a** was obtained from the filtrate as a black oil with 87% diastereomer excess (de). The same procedure using chiral cyclopentadiene Cp^{b}H (**2b**) bearing a (+)-menthyl group afforded Cp^{b}Fe(CO)$_2$I (**4b**), and fractional recrystallization gave diastereomerically pure (*R*)-**4b** along with (*S*)-**4b** in 76% de. The four diastereomers were identified by IR and ^{1}H and ^{13}C NMR (see

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Scheme 2

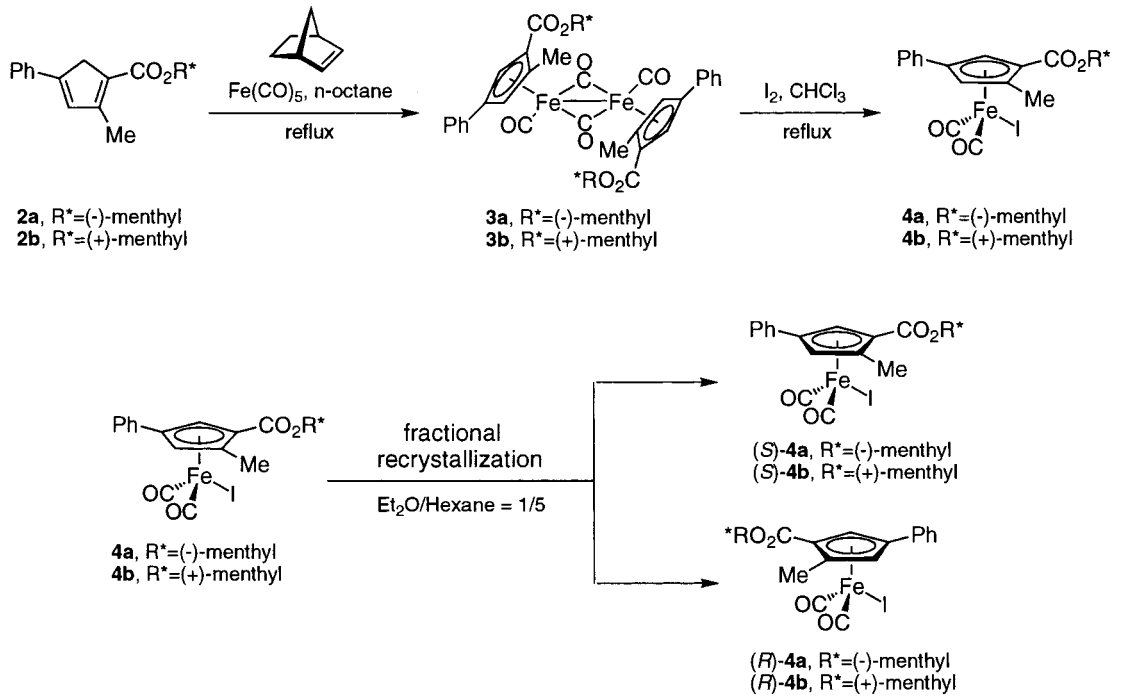

Table 1. Planar-Chiral Enantiomers $[\eta^5\text{-}C_5H_2(1\text{-}CO_2R^*)(2\text{-}Me)(4\text{-}Ph)]Fe(CO)_2Y$

complex	Y	R*	decomp (°C)	$[\alpha]_D^{25}$ (deg)[a]
(*S*)-**4a**	I	(−)-mentyl	136.0−136.5	+93 (*c* 0.073)
(*R*)-**4b**	I	(+)-mentyl	136.0−136.5	−92 (*c* 0.074)
(*S*)-**5a**	C≡CPh	(−)-mentyl	44.0−46.5	+164 (*c* 0.115)
(*R*)-**5b**	C≡CPh	(+)-mentyl	43.5−45.5	−164 (*c* 0.157)
(*S*)-**7a**	CH_3	(−)-mentyl	oil	+69.3 (*c* 0.113)
(*R*)-**7b**	CH_3	(+)-mentyl	oil	−68.8 (*c* 0.124)

[a] In CH_2Cl_2.

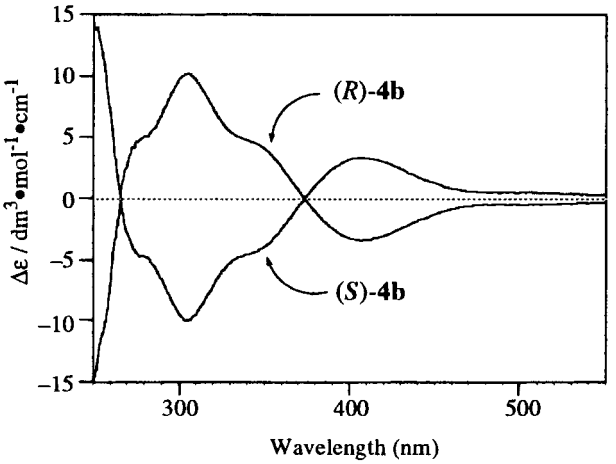

Figure 1. CD spectra of enantiomers (*S*)-**4a** and (*R*)-**4b** (in CH_2Cl_2).

Experimental Section). Complexes (*S*)-**4a** and (*R*)-**4b** exhibited almost the same absolute value but an opposite sign for the $[\alpha]_D$ (Table 1) and showed circular dichroism (CD) spectra with mirror symmetry (Figure 1), indicating (*S*)-**4a** and (*R*)-**4b** to be a pair of enantiomers. The absolute configuration of the planar-chiral complexes was established by X-ray structural analyses (vide infra).

Remove of the Chiral Auxiliary on the Cyclopentadienyl Ligand and Synthesis of Enantiomeric Planar-Chiral (η^5-cyclopentadienyl)di(carbonyl)methyliron and -ethynyliron. Converting enantiomeric complexes (*S*)-**4a** and (*R*)-**4b** into enantiomers possessing only planar chirality by removing the chiral auxiliaries, (−)- and (+)-menthyl groups, was attempted via hydrolysis because the ethyl ester of a planar-chiral cobalticinium analogue easily undergoes hydrolysis in acidic media to give a carboxylic acid.[18] However a similar treatment of **4** resulted in the formation of a complex mixture that did not yield a carboxylic acid derivative. Next we transformed **4** to a stable acetylide complex, $Cp^aFe(CO)_2(C{\equiv}CR)$, by the treatment with an ethynyltin derivative in the presence of a palladium catalyst in DMF at room temperature.[19] Thus, from the reactions of (*S*)-**4a** and (*R*)-**4b** with $PhC{\equiv}CSnBu_3$ we obtained iron acetylides $Cp^aFe(CO)_2C{\equiv}CPh$ ((*S*)-**5a**) and $Cp^bFe(CO)_2C{\equiv}CPh$ ((*R*)-**5b**) in 87 and 88% yield, respectively, as orange solids. Both acetylides showed a C≡C stretching absorption at 2112 cm^{-1} in the IR. Signals due to the C≡C group in (*S*)-**5a** and (*R*)-**5b** appeared at δ 115.3 (α-C) and 92.8 (β-C) in the ^{13}C NMR. These data as well as the optical rotation and melting points indicated that (*S*)-**5a** and (*R*)-**5b** maintain their planar chirality and are a pair of iron acetylide enantiomers (Table 1).

To remove the menthyl group on the cyclopentadienyl ligand, **5** was reacted with 2.4 equiv of phenyllithium at −78 °C in ether, which afforded planar-chiral cyclopentadienyliron acetylide complexes, $Cp^cFe(CO)_2C{\equiv}CPh$, (*S*)-**6** and (*R*)-**6**, in 55 and 52%, respectively, from (*S*)-**5a** and (*R*)-**5b** (Scheme 3). On reaction with phenyllithium, the menthyl ester group was converted to a (hydroxy)diphenylmethyl group; the conversion has been confirmed by IR and NMR. Complex (*S*)-**6** exhibits an optical rotation with the same absolute value but opposite sign as (*R*)-**6** (Table 2), indicating (*S*)-**6** and

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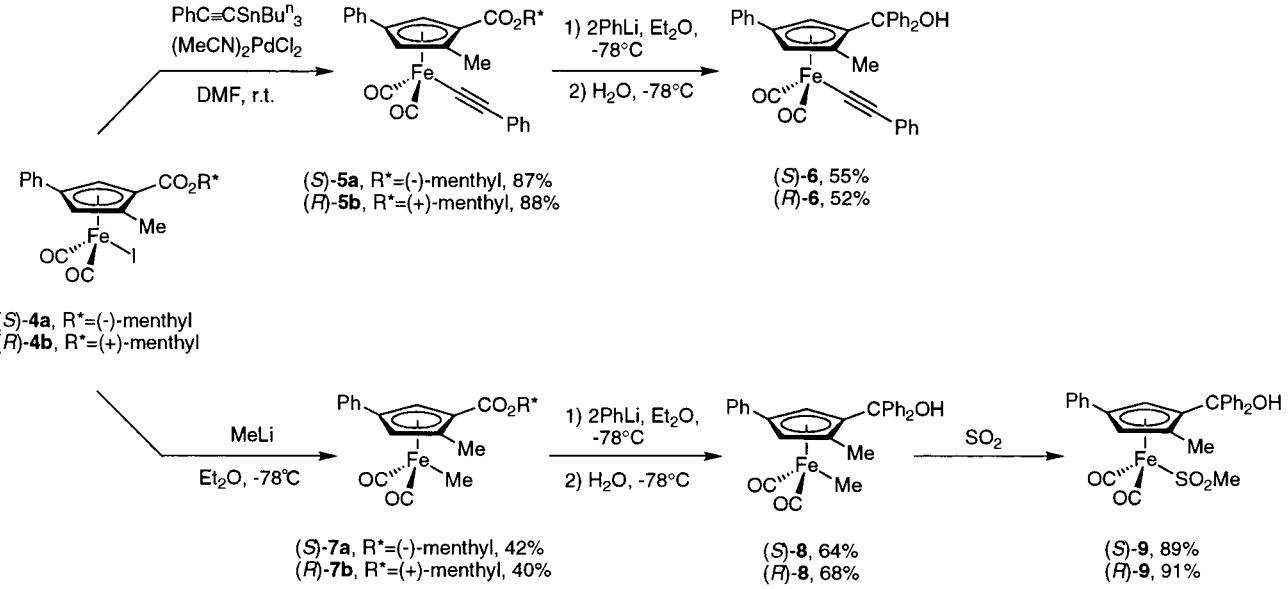
Scheme 3[a]



[a] The absolute structures of all the complexes are shown in an *S*-form.

Table 2. Planar-Chiral Enantiomers [η^5-C_5H_2(1-CPh_2OH)(2-Me)(4-Ph)]Fe(CO)$_2$R

complex	R	decomp (°C)	$[\alpha]_D^{25}$ (deg)[a]
(*S*)-**6**	C≡CPh	171.5−172.0	+221 (*c* 0.102)
(*R*)-**6**	C≡CPh	171.5−172.0	−221 (*c* 0.100)
(*S*)-**8**	Me	163.0−164.0	+126 (*c* 0.100)
(*R*)-**8**	Me	163.0−164.0	+126 (*c* 0.105)
(*S*)-**9**	SO_2Me	192.0−192.5	+255 (*c* 0.107)
(*R*)-**9**	SO_2Me	192.0−192.5	−255 (*c* 0.101)

[a] In CH_2Cl_2.

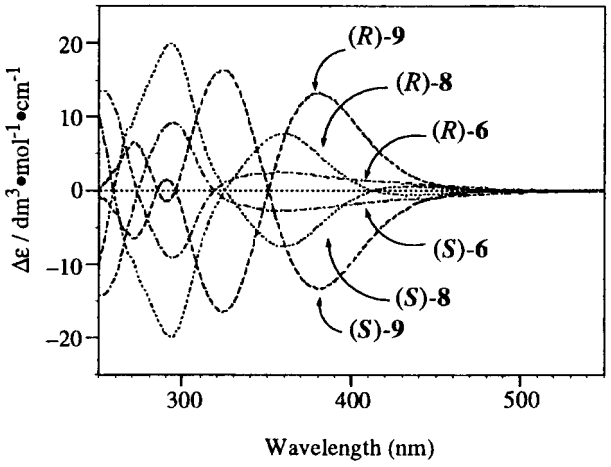


Figure 2. CD spectra of enantiomers (*S*)- and (*R*)-**6**, **8,** and **9** (in CH_2Cl_2).

(*R*)-**6** to be a pair of enantiomers, which is supported by the CD spectra as shown in Figure 2. It should be noted that the chirality in **6** originates from only planar chirality based on the cyclopentadienyliron moiety.

In the next step, we attempted the synthesis of reactive planar-chiral iron complexes which may be useful in organic syntheses. Such complexes may contain iron−alkyl, and we reacted **4** directly with alkyllithium to synthesize planar-chiral iron−alkyl complexes. Thus, we treated (*S*)-**4a** and (*R*)-**4b** with 1.1 equiv of methyllithium in diethyl ether at −78 °C and obtained planar-chiral cyclopentadienyliron methyl complexes, Cp^{a}Fe(CO)$_2$Me, (*S*)-**7a,** and Cp^{b}Fe(CO)$_2$Me, (*R*)-**7b,** as yellow oils in 42 and 40% yield, respectively. Methyliron complexes (*S*)-**7a** and (*R*)-**7b** showed signals due to the Fe−Me at δ 0.13 in ^{1}H NMR and δ −16 in ^{13}C NMR. Complexes (*S*)-**7a** and (*R*)-**7b** were treated with phenyllithium to remove the menthyl group, affording planar-chiral cyclopentadienyliron methyl Cp^c-Fe(CO)$_2$Me, (*S*)-**8** and (*R*)-**8**, in 64 and 68% yield, respectively, as orange-yellow crystals. No exchange of the methyl group on the iron with a phenyl group was seen. The optical measurements indicated (*S*)-**8** and (*R*)-**8** to be a pair of enantiomers having only planar chirarity (Table 2).

Reaction of Planar-Chiral Di(carbonyl)(η^5-cyclopentadienyl)ethyliron with Sulfur Dioxide. The optically pure complexes (*S*)-**8** and (*R*)-**8** were reacted with sulfur dioxide by condensing SO_2 on solid (*S*)-**8** in a flask at −78 °C.[20] The complex dissolved in the liquid sulfur dioxide to form a red solution. After 10 min, sulfur dioxide was slowly evaporated at room temperature to leave a yellow solid. Purification by alumina chromatography afforded a planar-chiral cyclopentadienyliron methylsulfinato complex, Cp^{c}Fe(CO)$_2$SO$_2$Me, (*S*)-**9**, in good yield (Scheme 3). Similar treatment of (*R*)-**8** with sulfur dioxide gave (*R*)-**9**. These methylsulfinato complexes were formed by the insertion of sulfur dioxide into the iron−methyl bond without racemization of the planar chirality (Table 2) and were identified by spectral analyses (see Experimental Section).

Molecular Structure of (*S*)-4a, (*R*)-4b, and (*S*)-8. To establish the absolute configuration of planar-chiral cyclopentadienyliron complexes, X-ray crystallographic studies of (*S*)-**4a** and (*R*)-**4b** have been performed. Recrystallization of (*S*)-**4a** and (*R*)-**4b** from diethyl ether/hexane gave dark purple single-crystals suitable for an X-ray crystallographic analysis. The molecular structures of (*S*)-**4a** and (*R*)-**4b** are illustrated in Figure 3 together with atom-labeling schemes. The structural parameters and crystal data are summarized in Tables 3 and 4, respectively. The cyclopentadienyl rings (C(1)−

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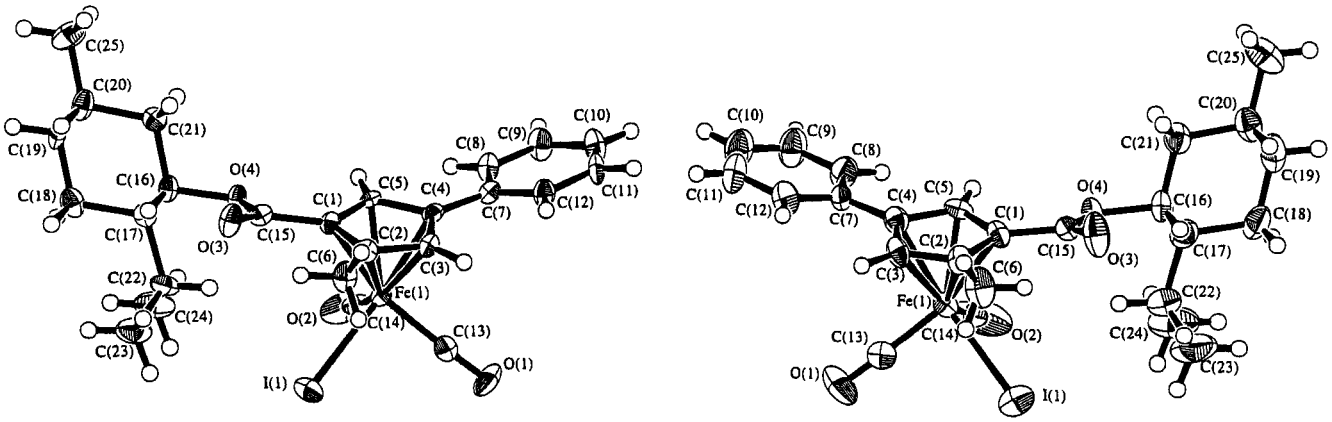

Figure 3. ORTEP drawings of the molecular structures of (*S*)-**4a** (right) and (*R*)-**4b** (left) (ellipsoids drawn at 50% probability level).

Table 3. Structural Parameters

	(*S*)-**4a**	(*R*)-**4b**	(*S*)-**8**
	Distances (Å)		
Fe(1)−I(1) or −C(28)	2.599(1)	2.5999(1)	2.058(7)
Fe(1)−C(1)	2.093(7)	2.093(5)	2.136(6)
Fe(1)−C(2)	2.162(7)	2.164(5)	2.123(6)
Fe(1)−C(3)	2.144(7)	2.136(6)	2.103(6)
Fe(1)−C(4)	2.107(7)	2.106(6)	2.133(7)
Fe(1)−C(5)	2.069(6)	2.079(5)	2.098(6)
Fe(1)−C(13)	1.772(9)	1.784(6)	1.753(8)
Fe(1)−C(14)	1.784(9)	1.780(6)	1.740(8)
O(1)−C(13)	1.122(9)	1.123(7)	1.143(8)
O(2)−C(14)	1.091(10)	1.127(7)	1.151(8)
O(3)−C(15)	1.193(8)	1.186(6)	1.435(8)
C(1)−C(2)	1.421(9)	1.433(7)	1.461(8)
C(2)−C(3)	1.409(9)	1.407(7)	1.422(8)
C(3)−C(4)	1.436(8)	1.445(7)	1.433(8)
C(4)−C(5)	1.422(9)	1.434(7)	1.432(8)
C(5)−C(1)	1.428(9)	1.420(7)	1.417(9)
C(1)−C(15)	1.485(9)	1.489(7)	1.513(9)
C(2)−C(6)	1.49(1)	1.481(7)	1.480(9)
C(4)−C(7)	1.477(9)	1.476(7)	1.459(9)
	Angles (deg)		
C(13)−Fe(1)−I(1) or −C(28)	91.3(3)	91.7(2)	85.6(4)
C(14)−Fe(1)−I(1) or −C(28)	88.7(3)	88.0(2)	84.6(3)
C(13)−Fe(1)−C(14)	91.9(4)	92.9(3)	96.0(4)
Fe(1)−C(13)−O(1)	176.6(9)	177.2(6)	177.6(8)
Fe(1)−C(14)−O(2)	177.7(8)	178.1(6)	176.9(7)
C(1)−C(2)−C(3)	107.9(6)	107.0(4)	106.9(6)
C(2)−C(3)−C(4)	109.1(6)	109.7(4)	110.4(6)
C(3)−C(4)−C(5)	106.6(6)	106.1(4)	105.3(6)
C(4)−C(5)−C(1)	108.6(6)	108.4(4)	110.9(5)
C(5)−C(1)−C(2)	107.8(6)	108.7(4)	106.5(6)
C(1)−C(2)−C(6)	127.1(7)	131.0(4)	127.8(6)
C(3)−C(2)−C(6)	124.9(6)	125.2(5)	125.0(6)
C(3)−C(4)−C(7)	126.5(7)	126.4(5)	127.9(6)
C(5)−C(4)−C(7)	126.6(6)	127.1(5)	126.9(5)
C(5)−C(1)−C(15)	126.2(6)	126.6(5)	127.2(5)
C(2)−C(1)−C(15)	125.6(7)	124.4(5)	126.3(6)
C(1)−C(15)−O(3)	123.1(7)	123.9(5)	110.7(5)
	Dihedral Angle between Planes (deg)		
Cp ring C(1)−C(5) and phenyl ring C(7)−C(12)	13.94	15.75	5.29
	Distance between Atom and Plane (Å)		
Fe(1) and Cp ring C(1)−C(5)	1.733	1.731	1.730

C(5)) of (*S*)-**4a** and (*R*)-**4b** are planar and the Fe−C (cyclopentadienyl ring) distances are in the range 2.069(6)−2.162(7) and 2.079(5)−2.164(5) Å with averages of 2.115 and 2.116 Å, respectively, which are in the normal region found for an η^5-pentamethylcyclopentadienyliron complex.[21] The distances between the Cp ring and Fe atom are 1.733 Å for (*S*)-**4a** and 1.731 Å for (*R*)-**4b**. These also lie in the normal range. The Fe(1)−I(1) bond lengths of 2.599(1) for (*S*)-**4a** and 2.5999(1) for (*R*)-**4b** are in the normal range of related iron iodide complexes.[21] The dihedral angles between the Cp ring and the phenyl ring (C(7)−C(12)) of (*S*)-**4a** and (*R*)-**4b** are 13.94° and 15.75°, respectively. The coordination geometry of (*S*)-**4a** and (*R*)-**4b** is best described as a distorted octahedron with an η^5-cyclopentadienyl ligand occupying three facial coordination sites, C(13)−Fe(1)−I(1), C(14)−Fe(1)−I(1), and C(13)−Fe(1)−C(14), and interligand bond angles approximate to 90° ((*S*)-**4a** 91.3(3)°, 88.7(3)°, and 91.9(4)°; (*R*)-**4b** 91.7(2)°, 88.0(2)°, and 92.9(3)°). Based on the known configuration of the (−)-menthyl group, the absolute configuration around the Cp−M moiety has been determined to be *S* for (*S*)-**4a**. Similarly, on the basis of the known configuration of the (+)-menthyl group, the absolute configuration has been determined to be *R* for (*R*)-**4b**. Therefore, complexes (*S*)-**5a**, (*S*)-**6**, (*S*)-**7a**, (*S*)-**8**, and (*S*)-**9**, which are derived from (*S*)-**4a** and exhibit a positive optical rotation, must possess an *S* stereochemistry, while (*R*)-**5b**, (*R*)-**6**, (*R*)-**7b**, (*R*)-**8**, and (*R*)-**9** from (*R*)-**4b** have an *R* configuration.

Similarly, recrystallization of (*S*)-**8** from diethyl ether/hexane gave orange-yellow single crystals suitable for an X-ray crystallographic analysis. Figure 4 depicts an ORTEP drawing of the molecular structure of (*S*)-**8** together with an atom-labeling scheme. The Cp ring (C(1)−C(5)) is planar and the Fe−C (cyclopentadienyl ring) distance is in the range 2.098(6)−2.133(7) Å with an average of 2.116 Å, which is in the normal region found for an η^5-pentamethylcyclopentadienyliron complex.[21] The distance between the Cp ring and the Fe atom is 1.730 Å. This also lies in the normal range. The Fe(1)−C(28) bond length is 2.058(7) Å and almost the same value in comparison with the (η^5-cyclopentadienyl)iron−methyl complex of 2.066(6) Å.[22] The dihedral angles between the Cp ring and three phenyl rings (C(7)−C(12), C(16)−C(21), and C(22)−C(27)) are 5.29°, 81.51°, and 71.73°, respectively. The coordination geometry of (*S*)-**8** is also described as a distorted octahedron. The interligand bond angles, C(13)−Fe(1)−C(28), C(14)−Fe(1)−C(28), and C(13)−Fe(1)−C(14) are 85.6(4)°, 84.6(3)°, and 96.0(4)°, respectively.

(21) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watoson, D. G.; Taylor, R. *J. Chem. Soc., Dalton. Trans.* **1989**, S1.
(22) Brunner, H.; Hammer, B. *Organometallics* **1983**, *2*, 1595.

Table 4. Crystal Data of (*S*)-4a, (*R*)-4b, and (*S*)-8

	(*S*)-**4a**	(*R*)-**4b**	(*S*)-**8**
empirical formula	$C_{25}H_{29}O_4IFe$	$C_{25}H_{29}O_4IFe$	$C_{28}H_{24}O_3Fe$
molecular weight	576.23	576.23	464.34
color	dark purple	dark purple	orange
crystal size (mm)	0.60 × 0.10 × 0.10	0.50 × 0.23 × 0.05	0.35 × 0.25 × 0.15
habit	prismatic	prismatic	prismatic
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
a (Å)	13.303(2)	13.310(3)	10.655(1)
b (Å)	24.403(2)	24.182(4)	22.222(2)
c (Å)	7.621(2)	7.572(4)	9.934(1)
V (Å^3)	2473(7)	2437(1)	2352(4)
Z value	4	4	4
D(calcd) (g cm^{-3})	1.547	1.570	1.311
F(000)	1160.00	1160.00	968.00
μ (cm^{-1})	18.84	19.13	6.67
diffractometer	Rigaku AFC5R	Rigaku AFC5R	Rigaku AFC5R
λ (Mo Kα radiation) (Å)	0.71069	0.71069	0.71069
monochromator	graphite	graphite	graphite
temperature (°C)	20.0	−70.0	−75.0
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan rate (deg min^{-1})	8.0	8.0	16.0
scan range (deg)	0.70 + 0.35 tan θ	0.58 + 0.30 tan θ	0.79 + 0.30 tan θ
method	Patterson	Patterson	Patterson
no. of reflns measd	4094	3205	3047
no. of obsns ($I > 3.00\sigma(I)$)	2425	2699	1985
no. of variables	280	280	290
R	0.043	0.044	0.051
R_w	0.049	0.047	0.063
goodness of fit	1.13	1.24	1.13
max peak in final diff map (e Å^{-3})	0.71	1.10	0.33
min peak in final diff map (e Å^{-3})	−0.54	−0.69	−0.37

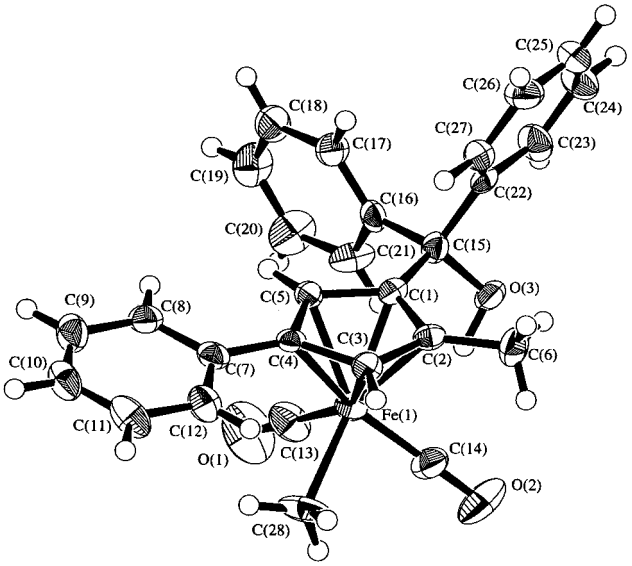

Figure 4. ORTEP drawing of the molecular structure of (*S*)-**8** (ellipsoids drawn at 50% probability level).

In conclusion, we have synthesized several novel planar-chiral cyclopentadienyliron complexes by using chiral cyclopentadienes and successfully isolated them in an optically pure form. The molecular structures of (*S*)-**4a**, (*R*)-**4b,** and (*S*)-**8** including the absolute configurations have been established by a single-crystal X-ray structural analysis. The complexes described herein provide the first examples of optically pure planar-chiral (η^5-cyclopentadienyl)iron complexes with a piano stool structure in which the locus of planar chirality is the cyclopentadienyl center.

Experimental Sections

General. All reactions were carried out under an atmosphere of nitrogen or argon, but the workup was performed in air. Melting and decomposition points are corrected. ^{1}H and ^{13}C NMR spectra were measured in acetone-d_6 or CD_3Cl with $SiMe_4$ as an internal standard and recorded on a JEOL JNM-LA400 (400 MHz) spectrometer. Chemical shifts are given in ppm. IR and mass spectra were taken on Perkin-Elmer system 2000 FT-IR and JEOL JMS-600H instruments, respectively. Optical rotations were measured on a JASCO DIP-1000 polarimeter, and a JASCO J-725 spectropolarimeter was used for the measurement of CD spectra. Optical purity was determined by HPLC using a DAICEL chiral cell OD column. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University. Diethyl ether and THF were distilled over benzophenone ketyl under argon just before use. Dichloromethane was dried over calcium hydride and then distilled. 1-Ethoxycarbonyl-2-methyl-4-phenylcyclopentadiene (**1**) and 1-(−)-menthoxycarbonyl-2-methyl-4-phenylcyclopentadiene (**2a**, $[\alpha]_D^{25}$: −58.9° (*c* 1.12, acetone)) were prepared by the method previously reported.[9,15] All other chemicals available commercially were used without further purification.

Synthesis of 1-(+)-Menthoxycarbonyl-2-methyl-4-phenyl-1,3-cyclopentadiene (2b). To a solution of trisubstituted cyclopentadiene **1** (11.4 g, 50.0 mmol) in xylene (150 mL) were added (+)-menthol (23.4 g, 150 mmol) and toluene-*p*-sulfonic acid (0.30 g, 1.5 mmol). The solution gradually turned from yellow to black and was refluxed for 5 days by a Soxhlet's method using MS 4A. After the reaction mixture was cooled to room temperature, the solvent was evaporated in vacuo. The residual oil was added on a column of silica gel and eluted with a mixture of 1:9 diethyl ether/hexane. Alcohol-exchange product **2b** was isolated from the first yellow band as an orange-red oil. Then, purification by distillation in vacuo gave 10.0 g (59%) of **2b** as an orange-red oil, bp, 190−195 °C; 0.40 mmHg. IR (neat, cm^{-1}): 1693 (CO). Mass (EI): *m*/*z* 338 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.80 (3H, d, J = 7.1 Hz, menthyl−CH_3), 0.92 (3H, d, J = 6.3 Hz, menthyl−CH_3), 0.93 (3H, d, J = 7.3 Hz, menthyl−CH_3), 0.87−0.97 (1H, m, menthyl−CH), 1.00−1.13 (2H, m, menthyl−CH_2), 1.43−1.57 (2H, m, menthyl−CH_2), 1.69−1.74 (2H, m, menthyl−CH_2), 1.97 (1H, quint. d, J = 6.8 and 2.7 Hz, menthyl−CH), 2.09−2.14 (1H, m, menthyl−CH), 2.40 (3H, t, J = 2.4 Hz, Cp−CH_3), 3.71 (2H, t, J = 2.4 Hz, Cp), 4.82 (1H, td, J = 10.8 and 4.4 Hz,

O-menthyl−CH), 6.76 (1H, s, Cp), 7.24−7.28 (1H, m, *p*-Ph), 7.32−7.37 (2H, m, *o*-Ph), 7.55−7.57 (2H, m, *m*-Ph). Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.62; H,8.93. Found: C, 81.80; H,8.83. $[\alpha]_D^{25}$: +59.7° (*c* 1.06, acetone).

Synthesis of Bis(η^5-1-(−)-menthoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)tetra(carbonyl)diiron (3a). To a solution of Cp^{a}H (**2a**) (20.3 g, 60.0 mmol) in *n*-octane (200 mL) was added pentacarbonyliron (17.6 g, 90.0 mmol) and 2-norbornene (5.93 g, 63.0 mmol).[16] The solution turned from yellow to black and was refluxed for 16 h. After the reaction mixture was cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was then dissolved in dichloromethane and filtered with a glass filter. The filtrate was concentrated to 20 mL, and *n*-hexane was slowly added. The brown precipitate of **3a** thus formed was collected, washed with hexane, and dried under vacuum: 19.4 g, 72% yield. IR (KBr, cm^{-1}): 1999, 1959 (terminal CO), 1796 (bridging CO), 1714 (ester CO). Mass (FAB): *m*/*z* 899 (M$^+$). Anal. Calcd for $C_{50}H_{58}O_8Fe_2$: C, 66.82; H, 6.51. Found: C, 67.01; H, 6.24.

Synthesis of Bis(η^5-1-(+)-menthoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)tetra(carbonyl)diiron (3b). A mixture of Cp^{b}H (**2b**) (20.3 g, 60.0 mmol), pentacarbonyliron (17.6 g, 90.0 mmol), and 2-norbornene (5.93 g, 63.0 mmol) in *n*-octane (200 mL) was treated as described for **3a**. A similar workup gave 18.3 g (68%) of **3b** as a brown powder. IR (KBr, cm^{-1}): 1999, 1960 (terminal CO), 1795 (bridging CO), 1715 (ester CO). Mass (FAB): *m*/*z* 899 (M$^+$). Anal. Calcd for $C_{50}H_{58}O_8Fe_2$: C, 66.82; H, 6.51. Found: C, 66.93; H, 6.72.

Synthesis and Resolution of Iodo(η^5-1-(−)-menthoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)di(carbonyl)iron (4a). A mixture of [Cp^{a}Fe(CO)$_2$]$_2$ (**3a**) (13.5 g, 15.0 mmol) and iodine (5.71 g, 22.5 mmol) in chloroform (400 mL) was refluxed for 1.5 h.[16] The solvent was removed, and then the residue was chromatographed on silica gel. After unreacted iodine was eluted out with 2:1 dichloromethane/hexane, a black band with dichloromethane was collected to give a mixture of diastereomers (*S*)-**4a** and (*R*)-**4a** (15.6 g, 90%). Pure (*S*)-**4a** was isolated by recrystallization three times from 5:1 hexane/diethyl ether as black-purple needles (6.74 g, 39%), while (*R*)-**4a** was obtained from the filtrate as a black oil (6.57 g, 38%) with 87% de.

(*S*)-**4a**: IR (KBr, cm^{-1}): 2038, 1997 (terminal CO), 1715 (ester CO). ^{1}H NMR (400 MHz, acetone-d_6): δ 0.81 (3H, d, J = 6.8 Hz, menthyl−CH$_3$), 0.93 (3H, d, J = 7.3 Hz, menthyl−CH$_3$), 0.95 (3H, d, J = 7.3 Hz, menthyl−CH$_3$), 0.88−1.00 (1H, m, menthyl−CH), 1.09−1.22 (2H, m, menthyl−CH$_2$), 1.51−1.61 (2H, m, menthyl−CH$_2$), 1.76 (2H, dt, J = 13.7 and 3.2 Hz, menthyl−CH$_2$), 2.04−2.10 (1H, m, menthyl−CH), 2.22 (1H, quint. d, J = 6.8 and 2.4 Hz, menthyl−CH), 2.55 (3H, s, Cp−CH$_3$), 4.93 (1H, td, J = 11.0 and 4.4 Hz, O-menthyl−CH), 5.95 (1H, d, J = 2.0 Hz, Cp), 6.38 (1H, d, J = 2.0 Hz, Cp), 7.42−7.48 (3H, m, Ph), 7.77−7.79 (2H, m, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ 14.74, 16.35, 21.30, 22.38 (CH$_3$), 23.63 (menthyl−CH$_2$), 26.54, 32.22 (menthyl−CH), 34.93, 41.85 (menthyl−CH$_2$), 48.10 (menthyl−CH), 75.86 (O-menthyl−CH), 82.43, 85.27, 88.63, 96.73, 108.85 (Cp), 127.51, 129.87 (Ph), 130.31 (*p*-Ph), 130.96 (*ipso*-Ph), 164.94 (ester CO), 214.42, 214.56 (terminal CO). Mass (FAB): *m*/*z* 576 (M$^+$). Anal. Calcd for $C_{25}H_{29}O_4IFe$: C, 52.10; H, 5.08; I, 22.02. Found: C, 51.82; H, 5.02; I, 22.22.

(*R*)-**4a**: IR (KBr, cm^{-1}): 2038, 1997 (terminal CO), 1715 (ester CO). ^{1}H NMR (400 MHz, acetone-d_6): δ 0.81 (3H, d, J = 6.8 Hz, menthyl−CH$_3$), 0.93 (3H, d, J = 7.3 Hz, menthyl−CH$_3$), 0.95 (3H, d, J = 7.3 Hz, menthyl−CH$_3$), 0.91−1.00 (1H, m, menthyl−CH), 1.10−1.22 (2H, m, menthyl−CH$_2$), 1.51−1.58 (2H, m, menthyl−CH$_2$), 1.74−1.77 (2H, m, menthyl−CH$_2$), 2.04−2.10 (1H, m, menthyl−CH), 2.22 (1H, quint. d, J = 6.8 and 2.4 Hz, menthyl−CH), 2.57 (3H, s, Cp−CH$_3$), 4.93 (1H, td, J = 11.0 and 4.4 Hz, O-menthyl−CH), 5.85 (1H, d, J = 2.0 Hz, Cp), 6.31 (1H, d, J = 2.0 Hz, Cp), 7.43−7.48 (3H, m, Ph), 7.75−7.77 (2H, m, Ph). Mass (FAB): *m*/*z* 576 (M$^+$).

Synthesis and Resolution of Iodo(η^5-1-(+)-menthoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)di(carbonyl)iron (4b). A mixture of [Cp^{b}Fe(CO)$_2$]$_2$ (**3b**) (10.8 g, 12.0 mmol) and iodine (4.57 g, 18.0 mmol) in chloroform (350 mL) was treated as described for **4a**, giving a mixture of diastereomers (*S*)-**4b** and (*R*)-**4b** as a black-purple solid in 93% yield. Pure (*R*)-**4b** was isolated by recrystallization three times from 5:1 hexane/diethyl ether as black-purple needles (4.84 g, 35%), while (*S*)-**4b** was obtained from the filtrate as a black oil (5.95 g, 43%) with 76% de.

(*R*)-**4b**: IR (KBr, cm^{-1}): 2038, 1997 (terminal CO), 1715 (ester CO); ^{1}H NMR (400 MHz, acetone-d_6): δ 0.81 (3H, d, J = 6.8 Hz, menthyl−CH$_3$), 0.92 (3H, d, J = 7.3 Hz, menthyl−CH$_3$), 0.94 (3H, d, J = 7.3 Hz, menthyl−CH$_3$), 0.89−0.99 (1H, m, menthyl−CH), 1.08−1.21 (2H, m, menthyl−CH$_2$), 1.49−1.60 (2H, m, menthyl−CH$_2$), 1.71−1.77 (2H, m, menthyl−CH$_2$), 2.04−2.09 (1H, m, menthyl−CH), 2.21 (1H, quint. d, J = 6.8 and 2.4 Hz, menthyl−CH), 2.54 (3H, s, Cp−CH$_3$), 4.93 (1H, td, J = 11.0 and 4.4 Hz, O-menthyl−CH), 5.94 (1H, d, J = 2.0 Hz, Cp), 6.38 (1H, d, J = 2.0 Hz, Cp), 7.41−7.47 (3H, m, Ph), 7.76−7.78 (2H, m, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ 14.75, 16.35, 21.31, 22.39 (CH$_3$), 23.63 (menthyl−CH$_2$), 26.54, 32.22 (menthyl−CH), 34.93, 41.85 (menthyl−CH$_2$), 48.10 (menthyl−CH), 75.86 (O-menthyl−CH), 82.43, 85.27, 88.64, 96.73, 108.85 (Cp), 127.51, 129.88 (Ph), 130.31 (*p*-Ph), 130.95 (*ipso*-Ph), 164.94 (ester CO), 214.42, 214.56 (terminal CO). Mass (FAB): *m*/*z* 576 (M$^+$). Anal. Calcd for $C_{25}H_{29}O_4IFe$: C, 52.10; H, 5.08; I, 22.02. Found: C, 52.13; H, 4.83; I, 21.83.

(*S*)-**4b**: IR (KBr, cm^{-1}): 2039, 1998 (terminal CO), 1715 (ester CO). ^{1}H NMR (400 MHz, acetone-d_6): δ 0.81 (3H, d, J = 6.8 Hz, menthyl−CH$_3$), 0.93 (3H, d, J = 7.3 Hz, menthyl−CH$_3$), 0.95 (3H, d, J = 7.3 Hz, menthyl−CH$_3$), 0.88−1.00 (1H, m, menthyl−CH), 1.09−1.22 (2H, m, menthyl−CH$_2$), 1.51−1.61 (2H, m, menthyl−CH$_2$), 1.76 (2H, dt, J = 13.7 and 3.2 Hz, menthyl−CH$_2$), 2.04−2.10 (1H, m, menthyl−CH), 2.22 (1H, quint. d, J = 6.8 and 2.4 Hz, menthyl−CH), 2.58 (3H, s, Cp−CH$_3$), 4.93 (1H, td, J = 11.0 and 4.4 Hz, O-menthyl−CH), 5.85 (1H, d, J = 2.0 Hz, Cp), 6.31 (1H, d, J = 2.0 Hz, Cp), 7.43−7.48 (3H, m, Ph), 7.75−7.77 (2H, m, Ph). Mass (FAB): *m*/*z* 576 (M$^+$).

Synthesis of (*S*)-(η^5-1-(−)-Menthoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)di(carbonyl)phenylethynyliron ((*S*)-5a). To a solution of Cp^{a}Fe(CO)$_2$I [(*S*)-**4a**] (2.31 g, 4.01 mmol) and tri-*n*-butylstannylethnylbenzene (1.88 g, 4.81 mmol) in DMF (150 mL) was added 5 mol % of $(CH_3CN)_2PdCl_2$ with stirring.[18] The solution immediately turned dark, and the stirring was continued at ambient temperature. After 18 h, diethyl ether (200 mL) was added to the reaction mixture, followed by a saturated aqueous solution (400 mL) of potassium fluoride. The mixture was stirred rapidly for 30 min, while argon was bubbled through the solution and then filtered by vacuum suction through a column tube covered with a Celite pad. The aqueous phase was discarded, the solution was washed with water, and the aqueous phase was back-extracted with diethyl ether. The combined ether extracts were dried over anhydrous sodium sulfate and filtered. Celite (40 g) was added to the filtrate, and then the mixture was evaporated to dryness in vacuo. The residue was added to a column of silica gel and eluted with a mixture of 1:9 hexane/ethyl acetate. The coupled product, (*S*)-**5a**, was isolated from the orange-red band as an orange solid (1.92 g, 87%). IR (KBr, cm^{-1}): 2112 (C≡C), 2039, 1997 (terminal CO), 1715 (ester CO). ^{1}H NMR (400 MHz, acetone-d_6): δ 0.78 (3H, d, J = 6.8 Hz, menthyl−CH$_3$), 0.87 (3H, d, J = 7.1 Hz, menthyl−CH$_3$), 0.88 (3H, d, J = 6.6 Hz, menthyl−CH$_3$), 0.89−0.94 (1H, m, menthyl−CH), 1.08−1.20 (2H, m, menthyl−CH$_2$), 1.43−1.55 (2H, m, menthyl−CH$_2$), 1.69−1.74 (2H, m, menthyl−CH$_2$), 2.04−2.09 (1H, m, menthyl−CH), 2.15 (1H, quint. d, J = 6.8 and 2.7 Hz, menthyl−CH), 2.38 (3H, s, Cp−CH$_3$), 4.91 (1H, td, J = 11.0 and 4.4 Hz,

O-menthyl−CH), 5.98 (1H, d, J = 2.0 Hz, Cp), 6.42 (1H, d, J = 2.0 Hz, Cp), 7.05−7.10 (1H, m, Ph), 7.16−7.23 (4H, m, Ph), 7.37−7.46 (3H, m, Ph), 7.77−7.80 (2H, m, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ 14.13, 16.40, 21.24, 22.30 (CH_3), 23.71 (menthyl−CH_2), 26.75, 32.16 (menthyl−CH), 32.16, 41.73 (menthyl−CH_2), 48.14 (menthyl−CH), 75.58 (O-menthyl−CH), 83.70, 86.89, 87.47 (Cp), 92.82 (FeC≡*C*), 99.79, 111.29 (Cp), 115.31 (Fe*C*≡C), 125.83, 127.32, 128.57 (Ph), 129.53 (*ipso*-Ph), 129.74, 129.83 (Ph), 131.86 (*ipso*-Ph), 131.96 (Ph), 165.23 (ester CO), 212.83, 213.12 (terminal CO). Mass (FAB): *m*/*z* 551 (M^+). Anal. Calcd for $C_{33}H_{34}O_4Fe$: C, 72.00; H, 6.23. Found: C, 72.03; H, 6.10.

Synthesis of (*R*)-(η^5-1-(+)-Menthoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)di(carbonyl)phenylethynyliron ((*R*)-5b). To a solution of Cp^{b}Fe(CO)$_2$I [(*S*)-**4b**] (1.73 g, 3.00 mmol) and tri-*n*-butylstannylethnylbenzene (1.41 g, 4.60 mmol) in DMF (150 mL) was added 5 mol % of $(CH_3CN)_2PdCl_2$ with stirring. After 19 h, the reaction mixture was treated as discribed for (*S*)-**5a**, yielding 1.45 g (88%) of (*R*)-**5b** as an orange powder. IR (KBr, cm^{-1}): 2112 (C≡C), 2040, 1997 (terminal CO), 1715 (ester CO). ^{1}H NMR (400 MHz, acetone-d_6): δ 0.77 (3H, d, J = 6.8 Hz, menthyl−CH_3), 0.87 (3H, d, J = 7.1 Hz, menthyl−CH_3), 0.87 (3H, d, J = 6.6 Hz, menthyl−CH_3), 0.84−0.89 (1H, m, menthyl−CH), 1.13 (2H, quint, J = 11.8 Hz, menthyl−CH_2), 1.48−1.54 (2H, m, menthyl−CH_2), 1.69−1.74 (2H, m, menthyl−CH_2), 2.04−2.07 (1H, m, menthyl−CH), 2.14 (1H, quint. d, J = 6.8 and 2.7 Hz, menthyl−CH), 2.37 (3H, s, Cp−CH_3), 4.90 (1H, td, J = 11.0 and 4.4 Hz, O-menthyl−CH), 5.98 (1H, d, J = 2.0 Hz, Cp), 6.43 (1H, d, J = 2.0 Hz, Cp), 7.04−7.09 (1H, m, Ph), 7.12−7.22 (4H, m, Ph), 7.36−7.45 (3H, m, Ph), 7.75−7.81 (2H, m, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ 14.12, 16.39, 21.24, 22.28 (CH_3), 23.86 (menthyl−CH_2), 26.75, 32.16 (menthyl−CH), 34.93, 41.73 (menthyl−CH_2), 48.15 (menthyl−CH), 75.59 (O-menthyl−CH), 83.73, 86.90, 87.49 (Cp), 92.80 (FeC≡*C*), 99.81, 111.27 (Cp), 115.31 (Fe*C*≡C), 125.84, 127.32, 128.58 (Ph), 129.54 (*ipso*-Ph), 129.74, 129.83 (Ph), 131.85 (*ipso*-Ph), 131.97 (Ph), 165.24 (ester CO), 212.84, 213.13 (terminal CO). Mass (FAB): *m*/*z* 551 (M^+). Anal. Calcd for $C_{33}H_{34}O_4Fe$: C, 72.00; H, 6.23. Found: C, 72.15; H, 6.22.

Synthesis of (*S*)-(η^5-1-Hydroxydiphenylmethyl-2-methyl-4-phenylcyclopentadienyl)di(carbonyl)phenylethynyliron ((*S*)-6). To a solution of Cp^{a}Fe(CO)$_2$C≡CPh [(*S*)-**5a**] (0.870 g, 1.58 mmol) in diethyl ether (50 mL) at −78 °C was added dropwise a solution of 1.8 M phenyllithium (2.1 mL, 2.4 equiv) in 7:3 cyclohexane/diethyl ether. The temperature was maintained at −78 °C, while the solution was stirred for 1 h. Then, to the solution was added dropwise water (20 mL) at −78 °C, and the reaction mixture was warmed to room temperature. The aqueous phase was discarded, the solution was washed with water, and the aqueous phase was back-extracted with diethyl ether. The combined ether extracts were dried over anhydrous sodium sulfate and filtered. The solvent was evaporated to dryness in vacuo, and (−)-menthol formed was removed from the residue by sublimation at 50 °C in vacuo. The residue dissolved in diethyl ether (5 mL) was then transferred to a chromatographic column packed with silica gel and eluted with a mixture of 1:9 hexane/diethyl ether. The product, (*S*)-**6**, was isolated as a yellow powder (0.478 g, 55%). IR (KBr, cm^{-1}): 2101 (C≡C), 2039, 1991 (terminal CO). ^{1}H NMR (400 MHz, acetone-d_6): δ 1.98 (3H, s, Cp−CH_3), 5.29 (1H, d, J = 2.0 Hz, Cp), 6.04 (1H, d, J = 2.0 Hz, Cp), 6.20 (1H, s, OH), 7.15−7.19 (1H, m, Ph), 7.25−7.29 (2H, m, Ph), 7.31−7.40 (11H, m, Ph), 7.45−7.47 (2H, m, Ph), 7.56−7.59 (4H, m, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ 13.71 (Cp−CH_3), 78.67 (COH), 87.01, 87.84 (Cp), 93.65 (FeC≡*C*), 96.50, 108.12, 110.19 (Cp), 119.43 (Fe*C*≡C), 126.54, 126.79, 127.90, 128.09, 128.20, 128.22, 128.58, 128.75, 128.92, 129.40, 129.74, 131.77 (Ph), 132.25, 146.37, 146.81 (*ipso*-Ph), 213.41, 213.64 (terminal CO). Mass (FAB): *m*/*z* 551 (M^+). Anal. Calcd for $C_{35}H_{26}O_3Fe$: C, 76.10; H, 4.81. Found: C, 76.12; H, 4.70.

Synthesis of (*R*)-(η^5-1-Hydroxydiphenylmethyl-2-methyl-4-phenylcyclopentadienyl)di(carbonyl)phenylethynyliron ((*R*)-6). To a solution of Cp^{b}Fe(CO)$_2$*C*≡CPh [(*R*)-**5b**] (0.671 g, 1.22 mmol) in diethyl ether (40 mL) at −78 °C was added dropwise a solution of 1.8 M phenyllithium (1.6 mL, 2.4 equiv) in 7:3 cyclohexane/diethyl ether. The reaction mixture was treated as described for (S)-**6**, yielding 0.349 g (52%) of (*R*)-**6** as a yellow powder. IR (KBr, cm^{-1}): 2101 (C≡C), 2040, 1991 (terminal CO). ^{1}H NMR (400 MHz, acetone-d_6): δ 1.98 (3H, s, Cp−CH_3), 5.30 (1H, d, J = 2.0 Hz, Cp), 6.04 (1H, d, J = 2.0 Hz, Cp), 6.20 (1H, s, OH), 7.15−7.19 (1H, m, Ph), 7.25−7.29 (2H, m, Ph), 7.30−7.39 (11H, m, Ph), 7.45−7.47 (2H, m, Ph), 7.56−7.59 (4H, m, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ 13.71 (Cp−CH_3), 78.67 (COH), 87.02, 87.85 (Cp), 93.65 (FeC≡*C*), 96.50, 108.12, 110.20 (Cp), 119.43 (Fe*C*≡C), 126.54, 126.80, 127.90, 128.10, 128.20, 128.22, 128.60, 128.75, 128.93, 129.40, 129.74, 131.77 (Ph), 132.26, 146.37, 146.82 (*ipso*-Ph), 213.42, 213.64 (terminal CO). Mass (FAB): *m*/*z* 551 (M^+). Anal. Calcd for $C_{35}H_{26}O_3Fe$: C, 76.10; H, 4.81. Found: C, 76.37; H, 4.76.

Synthesis of (*S*)-(η^5-1-(−)-Menthoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)di(carbonyl)methyliron ((*S*)-7a). To a solution of Cp^{a}Fe(CO)$_2$I [(*S*)-**4a**] (2.31 g, 4.01 mmol) in diethyl ether (30 mL) at −78 °C was added dropwise a solution of 1.14 M methyllithium (4.0 mL, 1.15 equiv) in diethyl ether. The solution was stirred at room temperature for 3 h. The reaction mixture was quenched with water at −78 °C and extracted with diethyl ether. The ether extracts were transferred to a chromatographic column packed with silica gel and eluted with a mixture of 5:1 hexane/diethyl ether. Two bands were collected. Product (*S*)-**7a** was isolated from the first yellow band as a yellow oil (0.78 g, 42%), and the second black one was unreacted Cp^{a}Fe(CO)$_2$I [(*S*)-**4a**] (0.56 g, 24%). IR (KBr, cm^{-1}): 2015, 1965 (terminal CO), 1714 (ester CO). ^{1}H NMR (400 MHz, acetone-d_6): δ 0.13 (3H, s, Fe−CH_3), 0.80 (3H, d, J = 6.8 Hz, menthyl−CH_3), 0.92 (3H, d, J = 6.8 Hz, menthyl−CH_3), 0.93 (3H, d, J = 6.6 Hz, menthyl−CH_3), 0.91−0.98 (1H, m, menthyl−CH), 1.07−1.19 (2H, m, menthyl−CH_2), 1.49−1.55 (2H, m, menthyl−CH_2), 1.71−1.75 (2H, m, menthyl−CH_2), 2.02−2.04 (1H, m, menthyl−CH), 2.07 (1H, quint. d, J = 6.8 and 2.7 Hz, menthyl−CH), 2.18 (3H, s, Cp−CH_3), 4.86 (1H, td, J = 11.0 and 4.4 Hz, O-menthyl−CH), 5.59 (1H, d, J = 2.0 Hz, Cp), 6.02 (1H, d, J = 2.0 Hz, Cp), 7.30−7.34 (1H, m, Ph), 7.37−7.41 (2H, m, Ph), 7.62 (2H, d, J = 7.1 Hz, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ −16.05 (Fe−CH_3), 13.14, 16.37, 21.21, 22.35 (CH_3), 23.76 (menthyl−CH_2), 26.79, 32.21 (menthyl−CH), 34.97, 41.88 (menthyl−CH_2), 48.17 (menthyl−CH), 75.01 (O-menthyl−CH), 83.52, 87.04, 87.04, 100.55, 107.60 (Cp), 126.81, 129.04, 129.66 (Ph), 133.03 (*ipso*-Ph), 166.01 (ester CO), 216.93, 216.97 (terminal CO). Mass (FAB): *m*/*z* 464 (M^+). Anal. Calcd for $C_{26}H_{32}O_4Fe$: C, 67.25; H, 6.95. Found: C, 67.41; H, 7.02.

Synthesis of (*R*)-(η^5-1-(+)-Menthoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)di(carbonyl)methyliron ((*R*)-7b). To a solution of Cp^{b}Fe(CO)$_2$I [(*R*)-**4b**] (4.61 g, 8.00 mmol) in diethyl ether (60 mL) at −78 °C was added dropwise a solution of 1.14 M methyllithium (8.0 mL, 1.15 equiv) in diethyl ether. The reaction mixture was treated as described for (*S*)-**6a**, yielding 1.49 g (40%) of (*R*)-**6b** as a yellow oil and 1.29 g (28%) of unreacted Cp^{b}Fe(CO)$_2$I. IR (KBr, cm^{-1}): 2014, 1965 (terminal CO), 1714 (ester CO). ^{1}H NMR (400 MHz, acetone-d_6): δ 0.13 (3H, s, Fe−CH_3), 0.80 (3H, d, J = 7.1 Hz, menthyl−CH_3), 0.92 (3H, d, J = 6.8 Hz, menthyl−CH_3), 0.93 (3H, d, J = 6.6 Hz, menthyl−CH_3), 0.91−0.98 (1H, m, menthyl−CH), 1.07−1.19 (2H, m, menthyl−CH_2), 1.48−1.55 (2H, m, menthyl−CH_2), 1.71−1.76 (2H, m, menthyl−CH_2), 2.02−2.04 (1H, m, menthyl−CH), 2.07 (1H, quint. d, J = 6.8 and 2.7 Hz, menthyl−CH), 2.18 (3H, s, Cp−CH_3), 4.86 (1H, td, J = 11.0 and 4.4 Hz, O-menthyl−CH), 5.58 (1H, d, J = 2.0 Hz, Cp), 6.01 (1H, d, J = 2.0 Hz, Cp), 7.30−7.34 (1H, m, Ph), 7.37−7.41 (2H, m, Ph), 7.62 (2H, d, J = 7.3 Hz, Ph). ^{13}C NMR (100

MHz, acetone-d_6): δ −16.00 (Fe−CH_3), 13.12, 16.33, 21.20, 22.35 (CH_3), 23.70 (menthyl−CH_2), 26.74, 32.18 (menthyl−CH), 34.92, 41.84 (menthyl−CH_2), 48.12 (menthyl−CH), 74.93 (O-menthyl−CH), 83.42, 86.96, 87.00, 100.48, 107.61 (Cp), 126.77, 129.01, 129.64 (Ph), 132.99 (*ipso*-Ph), 165.97 (ester CO), 216.91, 216.94 (terminal CO). Mass (FAB): *m*/*z* 464 (M^+). Anal. Calcd for $C_{26}H_{32}O_4Fe$: C, 67.25; H, 6.95. Found: C, 67.28; H, 6.71.

Synthesis of (*S*)-(η^5-1-Hydroxydiphenylmethyl-2-methyl-4-phenylcyclopentadienyl)di(carbonyl)methyliron ((*S*)-8). To a solution of Cp^{a}Fe(CO)$_2$Me [(*S*)-**7a**] (0.470 g, 1.01 mmol) in diethyl ether (30 mL) at −78 °C was added dropwise a solution of 1.8 M phenyllithium (1.4 mL, 2.5 equiv) in 7:3 cyclohexane/diethyl ether. The temperature was maintained at −78 °C, while the solution was stirred for 1 h. Then, to the solution was added dropwise water (10 mL) at −78 °C, and the reaction mixture was warmed to room temperature. The aqueous phase was discarded, and the solution was washed with water. The ether extracts were dried over anhydrous sodium sulfate and filtered. The solvent was evaporated to dryness in vacuo, and (−)-menthol formed was removed from the residue by sublimation at 50 °C in vacuo. The residue dissolved in diethyl ether (5 mL) was then transferred to a chromatographic column packed with silica gel and eluted with a mixture of 10:1 hexane/diethyl ether. Two bands were collected, the first of which was unreacted Cp^{a}Fe(CO)$_2$Me (0.093 g, 20%); the second one is product. (*S*)-**8** was isolated by recrystallization from a mixture of diethyl ether−hexane as orange-yellow crystals (0.299 g, 64%). IR (KBr, cm^{-1}): 1997, 1935 (terminal CO). ^{1}H NMR (400 MHz, acetone-d_6): δ −0.03 (3H, s, Fe−CH_3), 1.89 (3H, s, Cp−CH_3), 4.72 (1H, d, J = 2.0 Hz, Cp), 5.26 (1H, d, J = 2.0 Hz, Cp), 5.31 (1H, s, OH), 7.21−7.24 (1H, m, Ph), 7.28−7.38 (10H, m, Ph), 7.41−7.44 (2H, m, Ph), 7.47−7.49 (2H, m, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ −17.65 (Fe−CH_3), 13.55 (Cp−CH_3), 78.74 (COH), 87.44, 90.39, 94.92, 101.38, 110.42 (Cp), 126.31, 128.07, 128.09, 128.18, 128.26, 128.44, 128.44, 128.70, 129.43 (Ph), 133.68, 147.13, 147.24 (*ipso*-Ph), 218.35, 218.89 (terminal CO). Mass (FAB): *m*/*z* 464 (M^+). Anal. Calcd for $C_{28}H_{24}O_3Fe$: C, 72.43; H, 5.21. Found: C, 72.53; H, 5.14.

Synthesis of (*R*)−(η^5-1-Hydroxydiphenylmethyl-2-methyl-4-phenylcyclopentadienyl)di(carbonyl)methyliron ((*R*)-8). To a solution of Cp^{b}Fe(CO)$_2$Me [(*R*)-**7b**] (0.741 g, 1.60 mmol) in diethyl ether (50 mL) at −78 °C was added dropwise a solution of 1.8 M phenyllithium (2.2 mL, 2.5 equiv) in 7:3 cyclohexane/diethyl ether. The reaction mixture was treated as discribed for (*S*)-**8**, yielding 0.503 g (68%) of (*R*)-**8** as orange-yellow crystals and 0.151 g (20%) of unreacted Cp^{b}Fe(CO)$_2$Me. IR (KBr, cm^{-1}): 1996, 1934 (terminal CO). ^{1}H NMR (400 MHz, acetone-d_6): δ −0.03 (3H, s, Fe−CH3), 1.89 (3H, s, Cp−CH_3), 4.72 (1H, d, J = 2.0 Hz, Cp), 5.28 (1H, d, J = 2.0 Hz, Cp), 5.31 (1H, s, OH), 7.22−7.26 (1H, m, Ph), 7.30−7.39 (10H, m, Ph), 7.42−7.44 (2H, m, Ph), 7.47−7.50 (2H, m, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ −17.65 (Fe−CH_3), 13.55 (Cp−CH_3), 78.76 (COH), 87.45, 90.04, 94.97, 101.41, 110.43 (Cp), 126.33, 128.08, 128.10, 128.20, 128.28, 128.45, 128.45, 128.72, 129.44 (Ph), 133.70, 147.14, 147.26 (*ipso*-Ph), 218.36, 218.90 (terminal CO). Mass (FAB): *m*/*z* 464 (M^+). Anal. Calcd for $C_{28}H_{24}O_3Fe$: C, 72.43; H, 5.21. Found: C, 72.40; H, 5.25.

Synthesis of (*S*)-(η^5-1-Hydroxydiphenylmethyl-2-methyl-4-phenylcyclopentadienyl)di(carbonyl)methylsulfonyliron ((*S*)-9). Sulfur dioxide was condensed into a flask containing Cp^{c}Fe(CO)$_2$Me [(*S*)-**8**] (0.105 g, 0.226 mmol) at −78 °C.[19] The temperature was maintained at −78 °C, while the red solution was stirred for 10 min. The reaction mixture was gradually warmed to room temperature, and sulfur dioxide was evaporated. The residue dissolved in dichloromethane (5 mL) was chromatographed on silica gel. After removing a small amount of byproducts eluted with dichloromethane, a yellow band eluting with a mixture of 1:1 dichloromethane/methanol was collected. Product (*S*)-**9** was isolated from the yellow band as a yellow powder (0.106 g, 89%). IR (KBr, cm^{-1}): 2048, 2001 (terminal CO), 1179 (SO). ^{1}H NMR (400 MHz, acetone-d_6): δ 1.94 (3H, s, Cp−CH_3), 2.88 (3H, s, SO_2CH_3), 5.51 (1H, d, J = 2.0 Hz, Cp), 5.91 (1H, d, J = 2.0 Hz, Cp), 7.21 (1H, s, OH), 7.27−7.41 (9H, m, Ph), 7.47−7.49 (2H, m, Ph), 7.55−7.57 (2H, m, Ph), 7.67−7.69 (2H, m, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ 13.85 (Cp−CH_3), 58.98 (SO_2CH_3), 77.80 (COH), 85.20, 88.00, 98.37, 109.88, 111.90 (Cp), 127.53, 127.95, 128.14, 128.14, 128.20, 128.67, 128.76, 129.90, 130.29 (Ph), 130.39, 147.09, 147.19 (*ipso*-Ph), 211.41, 212.12 (terminal CO). Mass (FAB): *m*/*z* 529 (M^+). Anal. Calcd for $C_{28}H_{24}O_5SFe$: C, 63.65; H, 4.58; S, 6.07. Found: C, 63.85; H, 4.60; S, 5.89.

Synthesis of (*R*)-(η^5-1-Hydroxydiphenylmethyl-2-methyl-4-phenylcyclopentadienyl)di(carbonyl)methylsulfonyliron ((*R*)-9). Sulfur dioxide was condensed into a flask containing Cp^{c}Fe(CO)$_2$Me [(*R*)-**8**] (0.113 g, 0.243 mmol) at −78 °C. The red solution was treated as discribed for (*S*)-**9**, yielding 0.116 g (91%) of (*R*)-**9** as a yellow powder. IR (KBr, cm^{-1}): 2048, 2002 (terminal CO), 1179 (SO). ^{1}H NMR (400 MHz, acetone-d_6): δ 1.94 (3H, s, Cp−CH_3), 2.88 (3H, s, SO_2CH_3), 5.51 (1H, d, J = 2.0 Hz, Cp), 5.91 (1H, d, J = 2.0 Hz, Cp), 7.21 (1H, s, OH), 7.27−7.42 (9H, m, Ph), 7.47−7.49 (2H, m, Ph), 7.55−7.57 (2H, m, Ph), 7.67−7.69 (2H, m, Ph). ^{13}C NMR (100 MHz, acetone-d_6): δ 13.85 (Cp−CH_3), 58.97 (SO_2CH_3), 77.81 (COH), 85.22, 88.02, 98.39, 109.89, 111.92 (Cp), 127.54, 127.97, 128.16, 128.16, 128.21, 128.69, 128.77, 129.92, 130.30 (Ph), 130.40, 147.11, 147.20 (*ipso*-Ph), 211.43, 212.14 (terminal CO). Mass (FAB): *m*/*z* 529 (M^+). Anal. Calcd for $C_{28}H_{24}O_5SFe$: C, 63.65; H, 4.58; S, 6.07. Found: C, 63.96; H, 4.81; S, 5.94.

Data Collection. Complexes (*S*)-**4a**, (*R*)-**4b,** and (*S*)-**8** were recrystallized from diethyl ether/hexane. Cell constants were determined on a Rigaku AFC5R four-circle automated diffractometer from setting angles of 25 reflections in the range 30.0° < 2θ < 40.0°. The crystal parameters along with data collection details are summarized in Table 4. Data collection was carried out on a Rigaku AFC5R diffractometer. Intensities were measured by the ω−2θ scan method using Mo Kα radiation (λ = 0.71069). A scan rate for (*S*)-**4a** and (*R*)-**4b** of 8.0° min^{-1} was used, and for (*S*)-**8,** 16.0° min^{-1}. Throughout the data collection, the intensities of the three standard reflections were measured every 150 reflections as a check of the stability of the crystals, and no decay was observed.

A total of 4094 independent intensities were measured for (*S*)-**4a**, 3025 for (*R*)-**4b,** and 3047 for (*S*)-**8**. Of these, there are, respectively, 2245 ($I > 3.00\sigma(I)$), 2699 ($I > 3.00\sigma(I)$), and 1985 ($I > 3.00\sigma(I)$) unique reflections, which were used in the solutions and refinements of the structures. Intensities were corrected for Lorentz and polarization effects and for absorption.

Determination of the Structures. The structures were solved by heavy-metal Patterson methods (DIRDIF92 PATTY) and expanded using Fourier techniques. Hydrogen atoms were calculated at the ideal positions with the C−H distance of 0.95 Å. Hydrogen atoms were included but not refined. The final refinement converged to R = 0.043 and R_w = 0.049 for (*S*)-**4a**, R = 0.044 and R_w = 0.047 for (*R*)-**4b**, and R = 0.051 and R_w = 0.063 for (*S*)-**8**, respectively. Final difference Fourier syntheses showed peaks at heights up to 0.33−1.10 e Å^{-3}.

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Supporting Information Available: Tables of X-ray crystallographic data for complexes (*S*)-**4a**, (*R*)-**4b,** and (*S*)-**8.** This material is available free of charge via the Internet at http://pubs.acs.org.

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