Synthesis of [*R*,*S*;*R*,*S*]- and [*S*,*R*;*S*,*R*]-Bis[2-[1-(dimethylamino)ethyl]ferrocenyl] Diselenides and Their Application to Asymmetric Selenoxide Elimination and [2,3]Sigmatropic Rearrangement

Yoshiaki Nishibayashi,† Jai Deo Singh,† Shin-ichi Fukuzawa,‡ and Sakae Uemura*,†

Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606–01, Japan, and Faculty of Science and Engineering, Chuo University, Bunkyo-ku, Tokyo 112, Japan

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Novel optically-active bis[2-[1-(dimethylamino)ethyl]ferrocenyl] diselenides ([*R*,*S*;*R*,*S*] and [*S*,*R*;*S*,*R*]), each of which possesses two axial and two central elements of chirality, have been prepared by lithiation of commercially available chiral [1-(dimethylamino)ethyl]ferrocenes, followed by reaction with elemental selenium and air oxidation, in 77–80% isolated yields. The structure of the [*S*,*R*;*S*,*R*]-bisferrocenyl diselenide has been fully characterized by X-ray crystallography. Six chiral ferrocenyl vinylic selenides and six chiral allylic ferrocenyl selenides have been newly prepared by reaction of the diselenides with the corresponding propiolate derivatives and allylic halides. The oxidation of the vinylic selenides with *m*-chloroperbenzoic acid in various organic solvents produces axially chiral allenecarboxylic esters via asymmetric selenoxide elimination in 27–59% chemical yields with high enantioselectivities (up to 89% ee). Similar treatment of the allylic selenides afforded the corresponding chiral allylic alcohols via asymmetric [2,3]sigmatropic rearrangement in 28–82% chemical yields with high enantioselectivities (up to 89% ee). The observed high enantioselectivities indicate that oxidation proceeds highly diastereoselectively, that the resultant chiral selenoxides are slow to racemize, and also that selenoxide elimination and [2,3]sigmatropic rearrangement proceed with little loss of optical activity.

Introduction

Organoselenium methodology is an established tool in synthetic organic chemistry,[1] and attention has recently been drawn to its application to asymmetric organic synthesis.[2] Asymmetric [2,3]sigmatropic rearrangement and selenoxide elimination involving chiral selenoxide intermediates have been reported by Davis,[3] Reich,[4] and ourselves.[5] There are two methods for preparing chiral selenoxides.[5] One is the enantioselective oxidation of prochiral selenides, and the other is the diastereoselective oxidation of selenides containing a chiral moiety. By the first method, almost complete stereoselective oxidation to chiral selenoxide was recently accomplished, and yet the application of such selenoxides to asymmetric induction has only been limited to [2,3]sigmatropic rearrangements leading to allylic alcohols in moderate enantiomeric excess (ee).[3] With the second method, Reich et al. described an interesting application using chiral [2.2]paracyclophane-substituted selenides and obtained the corresponding allylic alcohols with high chirality transfer via [2,3]sigmatropic rearrangement.[4]

Ferrocene and its derivatives are widely used as structural units in material science.[6] Chiral ferrocenyl phosphines are important compounds in the field of catalytic asymmetric synthesis.[7] We envisioned using a readily available chiral ferrocenyl group as an aryl substituent on selenoxides since an arylselenium moiety is easy to introduce. We report here on the preparation of two novel enantiomeric bisferrocenyl diselenides together with the X-ray structural elucidation of one of them and also on their application to asymmetric selenoxide elimination and [2,3]sigmatropic rearrangement, leading to chiral allenecarboxylic esters and allylic alcohols, respectively.[8]

Results and Discussion

Synthesis of Chiral Bisferrocenyl Diselenides. Treatment of commercial (*R*)-[1-(dimethylamino)ethyl]ferrocene, which can be easily prepared by the reported method,[9] with *sec*-butyllithium followed by addition of elemental selenium and air oxidation afforded a diastereomeric mixture of bis[2-[1-(dimethylamino)ethyl]ferrocenyl] diselenides that mostly consisted of the [*R*,*S*;*R*,*S*]-isomer in accordance with the reported[10] highly diastereoselective lithiation (94% de) of the ferrocene. After purification by column chromatography, the pure [*R*,*S*;*R*,*S*]-diselenide **2a** was obtained in 77% isolated

† Kyoto University.
‡ Chuo University.
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(2) For reviews: (a) Kamigata, N.; Shimizu, T. In *Reviews on Heteroatom Chemistry*; Oae, S., Ed.; MYU: Tokyo, 1991; Vol. 4, p 226. (b) Tomoda, S.; Usuki, Y.; Fujita, K.; Iwaoka, M. In *Reviews on Heteroatom Chemistry*; Oae, S., Ed.; MYU: Tokyo, 1991; Vol. 4, p 249.
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(6) For a review: Togni, A.; Hayashi, T. *Ferrocenes*; VCH: Weinheim, 1995; see also references therein.
(7) For example: Sawamura, M.; Ito, Y. *Chem. Rev.* **1992**, *92*, 867.
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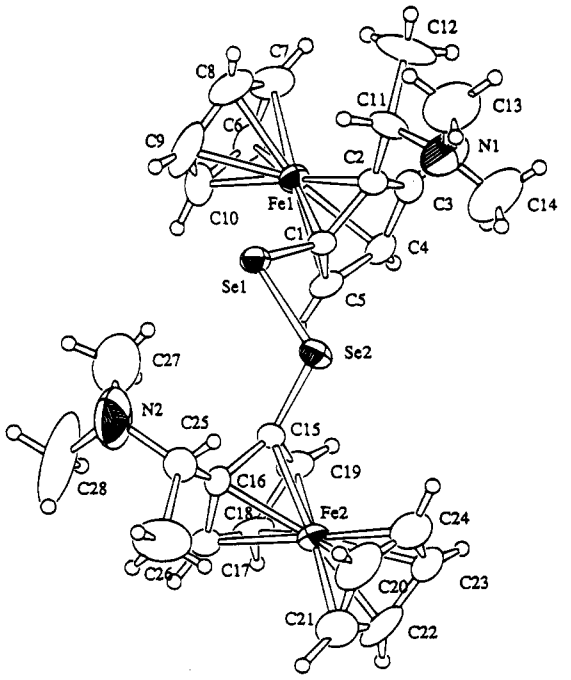
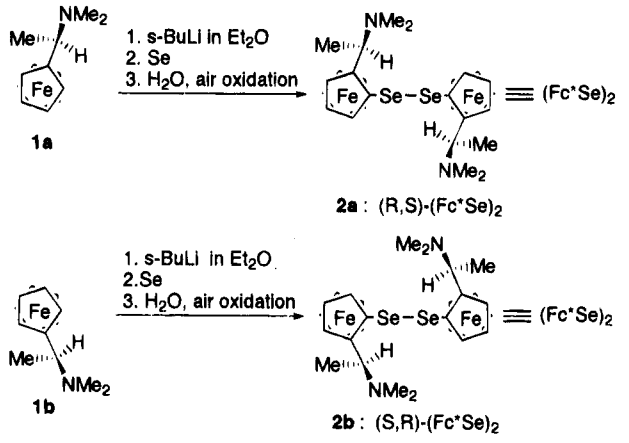


Figure 1. Crystal structure of **2b** (ORTEP, ellipsoids at the 30% probability level).

Scheme 1. Synthesis of Chiral Bisferrocenyl Diselenides



yield (Scheme 1). Similarly, starting from commercial (*S*)-[1-(dimethylamino)ethyl]ferrocene, we prepared the corresponding pure [*S*,*R*;*S*,*R*]-diselenide **2b** in 80% isolated yield. We abbreviate these diselenides as (*R*,*S*)- and (*S*,*R*)-(Fc*Se)$_2$, respectively. The structure of **2b** was fully characterized by X-ray crystallography, and its absolute configuration was clarified to be *S*,*R* where configuration around the ferrocene axis is *R* (Figure 1).[11] Representative crystallographic data of **2b** are presented in Table 1. The torsional angle of C(1)−Se(1)−Se(2)−C(15) is 94.1° which is larger than that of 84.8° of bis[2-[(dimethylamino)methyl]ferrocenyl] diselenide,[12] probably due to the greater steric bulkiness resulting from introduction of one additional methyl group. Although interaction between Se and N atoms was observed in some ortho N-containing, functional group-substituted benzeneselenium compounds,[13] no such interaction was found in **2b**; the atomic distances between Se and N atoms were 3.98 Å (Se(1)−N(1)) and 4.12 Å (Se(2)−N(2)) and larger than the sum of their van der Waals radii (3.54 Å). In accordance with this fact, the methyl protons of the dimethylamino group appeared as a singlet peak in the ^{1}H-NMR spectrum.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2b

Bond Distances			
Se(1)−Se(2)	2.347(2)		
Se(1)−C(1)	1.88(1)	Se(2)−C(15)	1.89(1)
C(1)−C(2)	1.45(1)	C(15)−C(16)	1.44(1)
C(2)−C(11)	1.51(1)	C(16)−C(25)	1.51(2)
C(11)−C(12)	1.52(2)	C(25)−C(26)	1.59(2)
C(11)−N(1)	1.46(2)	C(25)−N(2)	1.51(2)
Bond Angles			
Se(2)−Se(1)−C(1)	100.7(3)	Se(1)−Se(2)−C(15)	100.6(3)
C(1)−C(2)−C(11)	127(1)	C(15)−C(16)−C(25)	106(1)
C(2)−C(11)−N(1)	113(1)	C(16)−C(25)−N(2)	121(1)
C(2)−C(11)−C(12)	109(1)	C(16)−C(25)−C(26)	107(1)
C(11)−N(1)−C(13)	114(1)	C(25)−N(2)−C(27)	113(1)
C(11)−N(1)−C(14)	130(1)	C(25)−N(2)−C(28)	103(1)

Asymmetric Selenoxide Elimination Leading to Chiral Allenecarboxylic Esters. We attempted to use these diselenides for asymmetric organic synthesis by using methodologies characteristic of organoselenium compounds such as selenoxide elimination and [2,3]-sigmatropic rearrangement.[1] First, we chose allenic compounds as target molecules and tried to prepare chiral allenecarboxylic esters by asymmetric selenoxide elimination. Optically-active allenes having axial chirality are important synthetic intermediates for various biologically active compounds.[14] However, the methods for asymmetric synthesis of axially chiral allenes reported so far are limited to a few cases such as [3,3]Claisen[15] and [2,3]Wittig rearrangements[16] of optically-active propargyl ethers and copper-catalyzed alkylations of optically-active propargyl compounds.[17]

Six novel chiral ferrocenyl vinylic selenides (**4**) were prepared by addition of the chiral ferrocenylselenium anion derived from **2** to ethyl propiolate derivatives (**3**) (51−92% isolated yield). All the produced selenides had the (*Z*)-configuration (Scheme 2).[18] The oxidation of **4** was carried out with 1 molar equiv of *m*-chloroperbenzoic acid (MCPBA) under various conditions. The chiral selenoxides formed suffered in situ selenoxide elimination to afford axially chiral allenecarboxylic esters (**5**) in moderate chemical yields with high enantioselectivities (Scheme 2). The ee of the products was determined by HPLC using a Daicel Chiralcel OJ column. The absolute configuration was determined by comparing the optical rotation with literature data.[19] The results are summarized in Table 2. The highest ee was obtained when **4b** (R′ = CH_3) was oxidized by MCPBA in CH_2Cl_2 in the presence of 4 Å molecular sieves at −78 °C for 1 h and then at −20 °C for 70 h (43% isolated yield; 89% ee). The

(11) The same result has been obtained with chiral ferrocenylphosphines: Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138.

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(15) Henderson, M. A.; Heathcock, C. H. *J. Org. Chem.* **1988**, *53*, 4736.

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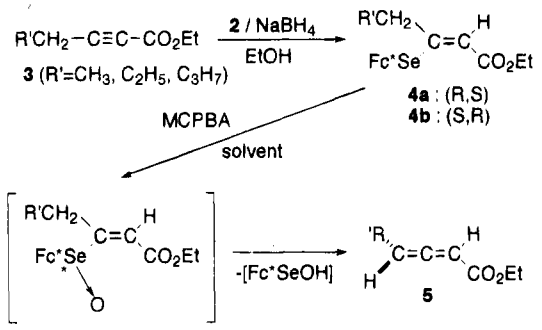
Table 2. Asymmetric Synthesis of Allenecarboxylic Esters (5)[a]

run	substrate	conditions: solvent	conditions: time (h) (temp (°C))	yield[b] (%)	ee[c] (%)	config
1	**4a** (R′ = CH_3)	CH_2Cl_2[d]	1 (−78) → 70 (−20)	47	83	*R*
2	**4a** (R′ = C_2H_5)	CH_2Cl_2[d]	1 (−78) → 70 (−20)	38	75	*R*
3	**4a** (R′ = C_3H_7)	CH_2Cl_2[d]	1 (−78) → 70 (−20)	45	79	*R*
4	**4b** (R′ = CH_3)	MeOH	19 (0)	35	30	*S*
5	**4b** (R′ = CH_3)	Et_2O	22 (0)	21	16	*S*
6	**4b** (R′ = CH_3)	CH_2Cl_2	24 (0)	52	39	*S*
7	**4b** (R′ = CH_3)	CH_2Cl_2	45 (−20)	33	43	*S*
8	**4b** (R′ = CH_3)	CH_2Cl_2	1 (−78) → 46 (−20)	48	70	*S*
9	**4b** (R′ = CH_3)	CH_2Cl_2[d]	1 (−78) → 70 (−20)	43	89	*S*
10	**4b** (R′ = C_2H_5)	CH_2Cl_2[d]	1 (−78) → 70 (−20)	59	82	*S*
11	**4b** (R′ = C_3H_7)	CH_2Cl_2[d]	1 (−78) → 70 (−20)	52	85	*S*

[a] All the reactions were carried out in 0.20 mmol scale. [b] Isolated yield. [c] Determined by HPLC. [d] In the presence of 4 Å molecular sieves (powder).

Scheme 2. Asymmetric Selenoxide Elimination Leading to Chiral Allenecarboxylic Esters

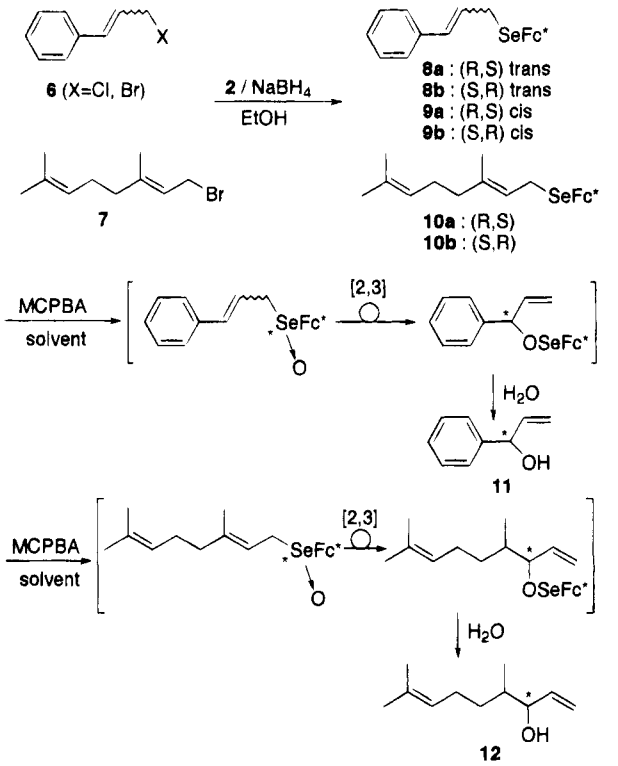


reaction temperature had a remarkable effect upon stereoselectivity. As shown in Table 2, the low temperature was essential for obtaining high selectivity. Chiral selenoxides, key intermediates in this asymmetric reaction, are known to racemize easily with even a small amount of water,[20,21] and in fact, the addition of 4 Å molecular sieves to the reaction system much improved the stereoselectivity. In other solvents such as methanol and diethyl ether, both yield and ee were lower compared to the values with CH_2Cl_2. Starting from the (*R*,*S*)- and (*S*,*R*)-isomers of **4**, we produced (*R*)- and (*S*)-isomers of the corresponding **5**. This is the first example of asymmetric selenoxide elimination leading to chiral allenecarboxylic esters, which have previously only been prepared by optical resolution of the corresponding racemic acids.[22] This method is also superior to other methods[15-17] for obtaining chiral allenecarboxylic esters because chiral alkynyl compounds are not required as starting substrates.

Asymmetric [2,3]Sigmatropic Rearrangement Leading to Chiral Allylic Alcohols. Next, we attempted to apply the chiral diselenides **2** to asymmetric [2,3]sigmatropic rearrangements to produce chiral allylic alcohols, since we had already been successful with enantioselective [2,3]sigmatropic rearrangments via chiral selenoxides.[5a]

Four novel chiral cinnamyl ferrocenyl selenides (**8a,b** and **9a,b**) and two chiral geranyl (*trans*-3,7-dimethyl-2,6-octadienyl) ferrocenyl selenides (**10a,b**) were prepared in 43−67% yield from diselenides (**2**) and (*E*)- and (*Z*)-cinnamyl halides and geranyl bromide, respectively

Scheme 3. Asymmetric [2,3]Sigmatropic Rearrangement Leading to Chiral Allylic Alcohols



(Scheme 3). Treatment of these selenides with 1 molar equiv of MCPBA at 0 or −78 °C for 1 h in various solvents afforded optically-active 1-phenyl-2-propen-1-ol (**11**) and linalool (**12**) in moderate to good chemical yields with high enantioselectivities (Scheme 3, Table 3). The ee value and the configuration[23] of **11** were determined by HPLC using a Daicel Chiralcel OJ column. The ee and configuration of **12** were determined by ^{1}H-NMR using Eu(tfc)$_3$.[4,24] The highest ee was obtained when **8a** was oxidized in MeOH at 0 °C (60% isolated yield; 89% ee). From (*R*,*S*)- and (*S*,*R*)-ferrocenyl selenides (**8a** and **9a**; **8b** and **9b**) were obtained (*R*)- and (*S*)-allylic alcohols

(20) Davis, F. A.; Billmers, J. M.; Stringer, O. D. *Tetrahedron Lett.* **1983**, 3191.
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(23) The racemic 1-phenyl-2-propen-1-ol (**11**) was prepared from benzaldehyde and vinylmagnesium bromide, while (*S*)-**11** was prepared by kinetic resolution of racemic **11** as reported: Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.
(24) We determined the optical purity of **12** by ^{1}H-NMR. Commercial (*R*)-(−)-linalool (ca. 30% ee) was analyzed with Eu(tfc)$_3$. The doublet peak initially appeared at δ 5.23 shifted and was separated two doublets at δ 5.85 and δ 5.78 by addition of a suitable amount of Eu(tfc)$_3$. The former larger doublet was assigned to the (*R*)-enantiomer.

Table 3. Asymmetric Synthesis of Allylic Alcohols (11 and 12)[a]

run	substrate 8–10	conditions: solvent	conditions: time (h) (temp (°C))	yield[b] (%)	ee[c] (%)	config
1	**8a**	MeOH	1 (0)	60	89	*R*
2	**8a**	CH_2Cl_2	1 (0)	39	65	*R*
3	**8a**	Et_2O	1 (0)	58	68	*R*
4	**8a**	CCl_4	1 (0)	16	87	*R*
5	**8a**	MeOH	1 (−78)	38	88	*R*
6	**8a**	CH_2Cl_2	1 (−78)	30	89	*R*
7	**8a**	Et_2O	1 (−78)	44	76	*R*
8	**8a**	toluene	1 (−78)	28	76	*R*
9	**8b**	MeOH	1 (0)	83	72	*S*
10	**9a**	MeOH	1 (0)	37	84	*R*
11	**9b**	MeOH	1 (0)	56	67	*S*
12	**10a**	MeOH	1 (0)	45	83[d]	*S*
13	**10b**	MeOH	1 (0)	51	77[d]	*R*

[a] All the reactions were carried out in 0.20 mmol scale. The product is **11** from **8** and **9** and **12** from **10**. [b] Isolated yield. [c] Determined by HPLC. [d] Determined by ^{1}H-NMR using Eu(tfc)$_3$.

(**11**), respectively. In contrast to the oxidation of vinylic selenides described above, the reaction temperature did not have a marked effect upon the stereochemical result and methanol was the solvent of choice. The fact that methanol produces high ee values indicates a fast sigmatropic rearrangement of the intermediate chiral ferrocenyl selenoxides, since it is known that racemization of optically-active selenoxides occurs readily in methanol.[21] To date, only one example of an asymmetric [2,3]-sigmatropic rearrangement of a chiral allylic aryl selenoxide in which a [2.2]paracyclophane derivative was employed as the chiral selenium substituent has been reported.[4] Our method can be used complementarily since chiral diselenides **2** are readily accessible and a high ee value results.

The Steric Course of Asymmetric Selenoxide Elimination and [2,3]Sigmatropic Rearrangement. In order to clarify the steric course of these highly stereoselective reactions, we carried out the following experiments. First, we prepared two (*R*,*S*)-ferrocenyl sulfides, methyl ferrocenyl sulfide (**13**, R′ = CH_3) and *p*-tolyl ferrocenyl sulfide (**13**, R′ = *p*-Tol), from (*R*)-[(dimethylamino)ethyl]ferrocene and the corresponding disulfide (Scheme 4).[25] Each sulfide was oxidized with 1.5 equiv of MCPBA at various temperatures for 2 h in CH_2Cl_2. The corresponding sulfoxides (**14**) were obtained in high chemical yields with high diastereoselectivities ((*S*)-configuration at sulfur atom), as reported.[26] The results are summarized in Table 4. In the case of **13** (R′ = CH_3), highly diastereoselective oxidation (60–62% de) occurred at low temperatures (−78 to −20 °C), while the selectivity was quite low (35–0% de) at higher temperatures (0–25 °C). On the other hand, in the case of **13** (R′ = *p*-Tol), an almost completely diastereoselective oxidation occurred (>99% de) at either −20 or −78°C to give (*S*,*R*,*S*)-sulfoxide **14** (R′ = *p*-Tol). It is worth noting that the sulfide having the bulkier R′ group showed the higher diastereoselectivity in this oxidation. This high diastereoselectivity may not be due to the chirality of the substituent on the ferrocene ring but rather to the axial chirality of the ferrocene.[27]

Considering these results, we propose the course of oxidation of vinylic selenides (**4a**) shown in Scheme 5.

Scheme 4. Asymmetric Oxidation of (*R*,*S*)-Ferrocenyl Sulfides

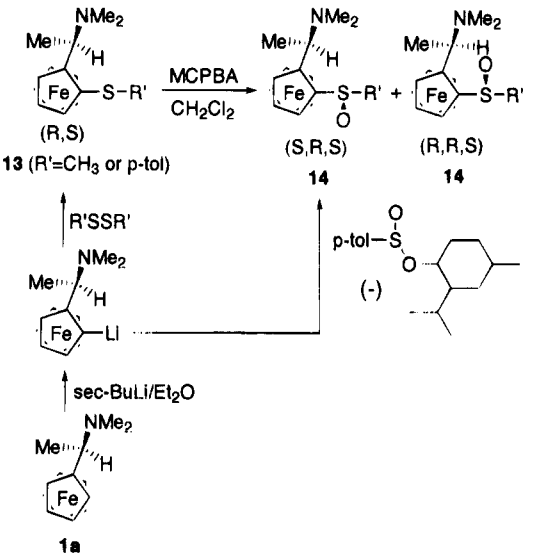

Table 4. Asymmetric Oxidation of 13[a]

run	sulfides R′	temp (°C)	yield[b] (%)	de[c] (%)	config[d]
1	CH_3	−78	94	62	*S*
2	CH_3	−20	97	60	*S*
3	CH_3	0	95	35	*S*
4	CH_3	25	90	0	
5	*p*-Tol	−78	62	>99	*S*
6	*p*-Tol	−20	75	>99	*S*

[a] All the reactions were carried out in 0.20 mmol scale. The product was the sulfoxide **14**. [b] Isolated yield. [c] Determined by ^{1}H-NMR. [d] Configuration at sulfur center.

Highly diastereoselective oxidation similar to that of the sulfide case is expected to occur to give a vinyl ferrocenyl selenoxide (**15**) of (*S*)-configuration (step i ≫ step ii). Next, the selenoxide oxygen abstracts a prochiral methylene proton in the more stable transition state. In this case, transition state **17** should be more stable than **18** because the methyl group at the allylic position is favored to take the position anti to the bulky (dimethylamino)-ethyl substituent on the chiral ferrocenyl moiety. (*R*)-Allene is obtained from **17** (step iii) and (*S*)-allene from **18** (step iv), and (*R*)-allene was obtained as the major product, as expected.

The proposed steric course of asymmetric [2,3]sigmatropic rearrangement, using (*R*,*S*)-(*E*)-allylic selenide **8a** as a substrate, is depicted in Scheme 6. The oxidation will similarly give the (*S*)-allylic selenoxide which may rearrange via endo and exo transition states.[3] The endo transition state leading to (*R*)-allylic alcohol **11** should be more stable than the exo one because the steric repulsion between the styryl and Fc* moieties is larger in the exo transition state. This is consistent with the considerations proposed by Davis in the enantioselective [2,3]sigmatropic rearrangement using his oxidants.[3]

The following features are essential to successful asymmetric induction: (1) a highly stereoselective oxidation to selenoxide, (2) no or slow racemization of the chiral selenoxide intermediate, and (3) an almost complete asymmetric induction from the selenoxide to the products.

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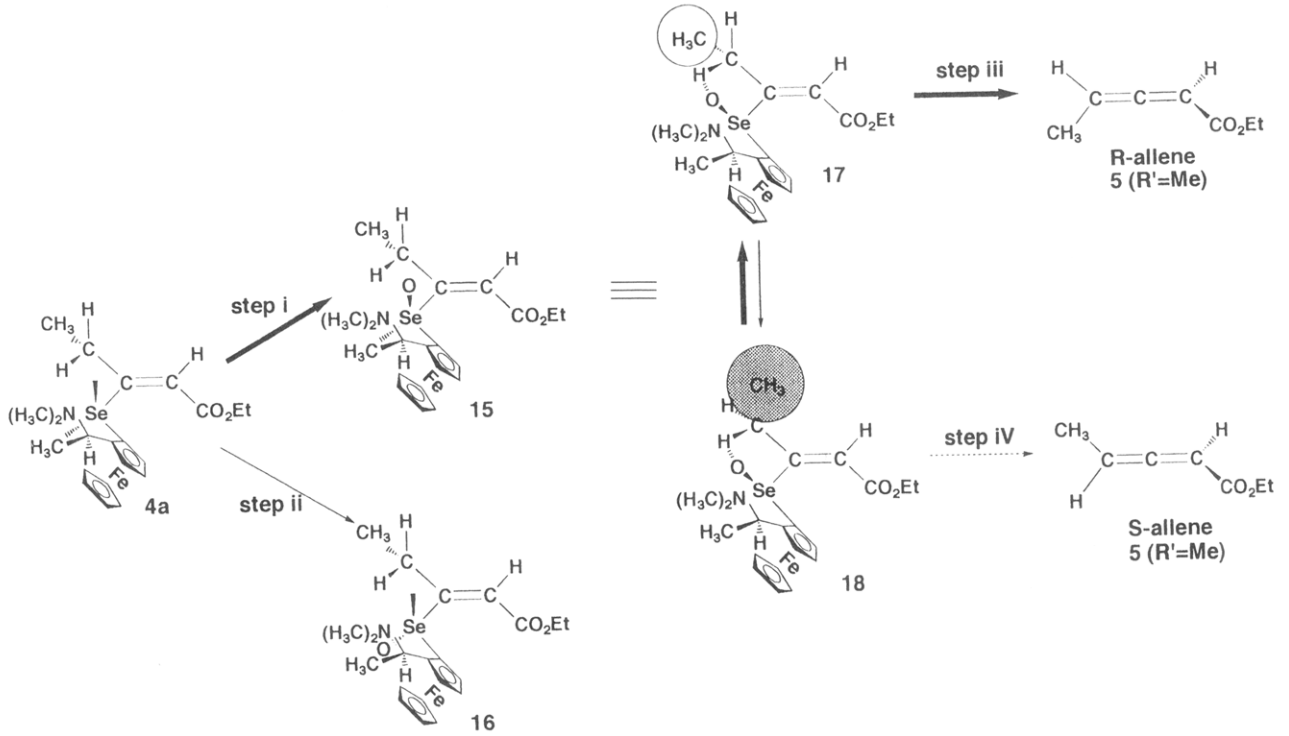
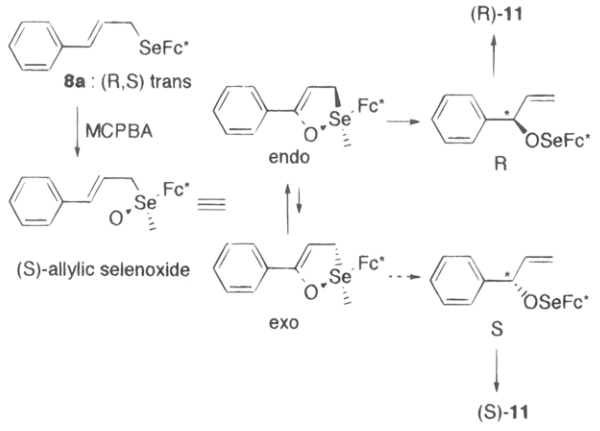
(26) Herrmann, R.; Hübener, G.; Ugi, I. *Tetrahedron* **1985**, *41*, 941.

(27) Shimazaki, M.; Takahashi, M.; Komatsu, H.; Ohta, K.; Kajii, K.; Kodama, Y. *Synthesis* **1992**, 555. The oxidation of (*R*)-2-[1-(dimethylamino)ethyl]phenyl ethyl sulfide with MCPBA afforded the corresponding sulfoxide of only 18% de.

Scheme 5. A Model for Stereoselection in Selenoxide Elimination



Scheme 6. The Steric Course for [2,3]Sigmatropic Rearrangement Leading to Chiral Allylic Alcohols



In conclusion, two chiral bisferrocenyl diselenides having axial as well as central chirality have been newly prepared and shown to be good reagents for asymmetric synthesis of chiral allenes and allylic alcohols by selenoxide elimination and [2,3]sigmatropic rearrangement, respectively. We have explained the steric course of these highly stereoselective reactions by considering the highly diastereoselective oxidation of sulfides to sulfoxides under similar conditions. We are making efforts to apply these novel reagents to other asymmetric reactions.[28]

Experimental Section

General. ^{1}H- and ^{13}C-NMR spectra were measured from $CDCl_3$ solutions. Melting points are uncorrected. GLC analyses were performed on a 1 m × 3 mm stainless steel column packed with 20% PEG on Shimalite and a 25 m HiCap-CBP-10-S25 capillary column with flame-ionization detectors and N_2 as carrier gas. Column chromatographies on Al_2O_3 were performed with ICN Alumina N, Akt. I (hexane and hexane/ethyl acetate as eluents). Preparative TLC to isolate all the allenecarboxylic esters (**5**) was carried out using 5 cm × 10 cm silicagel 70 Plate-Wako PLC plates. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Solvents were distilled from CaH_2 or $LiAlH_4$ and stored over 4 Å molecular sieves under N_2. Commercial MCPBA (70% purity) was used without further purification. Eu(tfc)$_3$ was purchased from Aldrich Chemical Co., Inc.

Preparation of Bisferrocenyl Diselenides [(Fc*Se)$_2$] 2. After lithiation of commercial (*R*)-(+)-*N*,*N*-dimethyl(1-ferrocenylethyl)amine (**1a**) (5.14 g, 20 mmol) with *s*-BuLi (22 mmol) in dry diethyl ether (50 mL) at 0 °C under N_2, selenium powder (1.58 g, 20 mmol) was added portionwise, and the resulting mixture was stirred for 3 h at 0 °C. The mixture was poured into water, and then air was bubbled through the solution for 5 h at room temperature. [*R*,*S*;*R*,*S*]-Bisferrocenyl diselenide **2a** (red solid, mp 98−100 °C (hexane)) was isolated in 77% yield (5.13 g, 7.7 mmol) by column chromatography on active alumina with ethyl acetate as an eluent (Scheme 1). Similarly, [*S*,*R*;*S*,*R*]-bisferrocenyl diselenide **2b** (red solid, mp 103 °C (hexane)) was prepared in 80% isolated yield (5.30 g, 7.9 mmol) from the (*S*)-(−)-(ferrocenylethyl)amine (**1b**).

[*R*,*S*;*R*,*S*]-Bisferrocenyl diselenide 2a: ^{1}H-NMR δ 4.27−4.51 (6H, m), 4.08 (10H, s), 3.85 (2H, q, J = 6.87 Hz), 2.19 (12H, s), 1.44 (6H, d, J = 6.87 Hz); ^{13}C-NMR δ 75.5 (d), 70.5 (s), 70.5 (s), 70.3 (d), 69.0 (d), 68.4 (d), 57.0 (d), 41.5 (q), 16.4 (q); $[\alpha]^{22}_D$ −650 (*c* 1.06, $CHCl_3$). Anal. Calcd for $C_{28}H_{36}N_2Fe_2Se_2$: C, 50.18; H, 5.41; N, 4.18. Found: C, 49.91; H, 5.36; N, 4.18.

[*S*,*R*;*S*,*R*]-Bisferrocenyl diselenide 2b: $[\alpha]^{23}_D$ +650 (*c* 1.70, $CHCl_3$). Anal. Calcd for $C_{28}H_{36}N_2Fe_2Se_2$: C, 50.18; H, 5.41; N, 4.18. Found: C, 50.01; H, 5.48; N, 4.05.

X-ray Structure Determination of 2b (Figure 1, Table 1).[29] Data for **2b** (an orange crystal, grown in *n*-hexane) of $C_{28}H_{36}N_2Fe_2Se_2$ were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) and a 12 kW rotating anode generator. Crystal

(28) Nishibayashi, Y.; Singh, J. D.; Segawa, K.; Fukuzawa, S.; Uemura, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1375. Chiral bisferrocenyl diselenide acted as a chiral ligand in Rh(I)-catalyzed hydrosilylation of acetophenone with diphenylsilane (up to 85% ee).

(29) The author has deposited atomic coordinates, thermal parameters, bond distances, and bond angles for the X-ray structure of **2b** with the Cambridge Crystallographic Data Centre. These data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

data for **2b** are as follows: orthorhombic, space group $P2_12_12_1$; a = 15.128(4) Å, b = 17.754(3) Å, c = 10.771(4) Å; V = 2892(1) Å^3; Z = 4; D_{calcd} = 1.54 g cm^{-3}; Mo Kα = 35.37 cm^{-1}; total of 4643 reflections within 2θ = 60.1°. The final R value was 0.048 (R_w = 0.055). The structure was solved by the direct method (SAPI91). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were geometrically calculated or taken from a difference Fourier map.

Preparation of Ferrocenyl Vinylic Selenides (4). In a two-necked 50 mL round bottom flask containing a magnetic stirring bar were placed (Fc*Se)$_2$ (640 mg, 0.96 mmol) and $NaBH_4$ (129 mg, 3.40 mmol) under N_2. Ethanol (10 mL) was added to the flask at 0 °C. The mixture became homogeneous after being stirred for 0.5 h at rt. An ethanol (3 mL) solution of ethyl 2-pentynoate (**3**, R′ = CH_3) (278 mg, 2.2 mmol) was then added, and the mixture was stirred at rt for 5 d. The mixture was washed with brine (200 mL) and then extracted with CH_2Cl_2 (50 mL × 3). The extract was dried over $MgSO_4$ and evaporated to leave a yellow solid of **4a** (R′ = CH_3) which was purified by column chromatography on alumina with hexane/ethyl acetate (7/3) as an eluent: yield 440 mg (60% based on (Fc*Se)$_2$).

4a (R′ = CH_3): yellow solid; mp 89–91 °C; ^{1}H-NMR δ 6.07 (1H, t, J = 1.35 Hz), 4.28–4.37 (3H, m), 4.24 (2H, q, J = 7.29 Hz), 4.15 (5H, s), 3.89 (1H, q, J = 6.75 Hz), 2.31 (2H, m), 2.04 (6H, s), 1.32 (3H, t, J = 7.02 Hz), 1.26 (3H, d, J = 6.75 Hz), 0.95 (3H, t, J = 7.29 Hz); ^{13}C-NMR δ 170.1 (s), 168.1 (s), 111.3 (d), 95.5 (s), 77.1 (d), 70.2 (d), 68.7 (d), 68.5 (d), 60.2 (t), 56.8 (d), 40.0 (q), 30.3 (t), 27.7 (s), 14.7 (q), 13.5 (q), 10.1 (q); yield 60%. Anal. Calcd for $C_{28}H_{29}NO_2FeSe$: C, 54.56; H, 6.32; N, 3.03. Found: C, 54.16; H, 6.31; N, 3.00.

4b (R′ = CH_3): yellow solid; mp 90–92 °C; yield 50%. Anal. Calcd for $C_{28}H_{29}NO_2FeSe$: C, 54.56; H, 6.32; N, 3.03. Found: C, 54.20; H, 6.33; N, 2.95.

4a (R′ = C_2H_5): yellow solid; mp 65–67 °C; ^{1}H-NMR δ 6.07 (1H, t, J = 1.35 Hz), 4.28–4.37 (3H, m), 4.24 (2H, q, J = 7.29 Hz), 4.15 (5H, s), 3.89 (1H, q, J = 6.75 Hz), 2.30 (2H, m), 2.04 (6H, s), 1.36 (2H, m), 1.32 (3H, t, J = 7.02 Hz), 1.26 (3H, d, J = 6.75 Hz), 0.74 (3H, t, J = 7.29 Hz); ^{13}C-NMR δ 168.5 (s), 161.7 (s), 111.7 (d), 95.2 (s), 76.8 (d), 70.2 (s), 69.9 (d), 68.4 (d), 68.2 (d), 59.9 (t), 56.4 (d), 39.7 (q), 38.8 (t), 22.1 (t), 14.4 (q), 13.5 (q), 9.8 (q); yield 92%. Anal. Calcd for $C_{29}H_{31}NO_2FeSe$: C, 55.48; H, 6.56; N, 2.94. Found: C, 55.22; H, 6.64; N, 2.71.

4b (R′ = C_2H_5): yellow solid; mp 63–65 °C; yield 51%. Anal. Calcd for $C_{29}H_{31}NO_2FeSe$: C, 55.48; H, 6.56; N, 2.94. Found: C, 55.27; H, 6.75; N, 2.65.

4a (R′ = C_3H_7): yellow oil; ^{1}H-NMR δ 6.07 (1H, t, J = 1.35 Hz), 4.28–4.37 (3H, m), 4.24 (2H, q, J = 7.29 Hz), 4.15 (5H, s), 3.89 (1H, q, J = 6.75 Hz), 2.27 (2H, m), 2.04 (6H, s), 1.32 (3H, t, J = 7.02 Hz), 1.29 (2H, m), 1.26 (3H, d, J = 6.75 Hz), 1.13 (2H, m), 0.76 (3H, t, J = 7.29 Hz); ^{13}C-NMR δ 168.8 (s), 167.7 (s), 111.8 (d), 95.2 (s), 76.9 (d), 70.3 (s), 69.9 (d), 68.4 (d), 68.3 (d), 59.9 (t), 56.5 (d), 39.8 (q), 36.7 (t), 31.3 (t), 22.3 (t), 14.5 (q), 13.8 (q); 10.0 (q); yield 44%. Anal. Calcd for $C_{30}H_{33}NO_2FeSe$: C, 56.34; H, 6.78; N, 2.86. Found: C, 56.05; H, 6.91; N, 2.82.

4b (R′ = C_3H_7): yellow oil; yield 59%. Anal. Calcd for $C_{30}H_{33}NO_2FeSe$: C, 56.34; H, 6.78; N, 2.86. Found: C, 56.21; H, 6.53; N, 2.98.

Synthesis of Allenecarboxylic Esters (5). To a dry CH_2Cl_2 (1 mL) solution of **4b** (R′ = CH_3) (61 mg, 0.20 mmol) containing a small amount of 4 Å molecular sieves (powder) was added dropwise a dry CH_2Cl_2 (1 mL) solution of MCPBA (70% purity, 35 mg, 0.22 mmol) at −78 °C under N_2. The resulting mixture was stirred for 1 h and then at −20 °C for 70 h. The mixture was poured into brine (50 mL) and extracted with CH_2Cl_2 (30 mL × 3). The extract was dried over $MgSO_4$ and evaporated to leave a pale yellow semisolid which was purified by TLC (SiO_2, hexane/EtOAc = 9/1 as an eluent) to afford (*S*)-ethyl 2,3-pentadienoate **5** (R′ = CH_3) of 89% ee as a pale yellow oil in 43% chemical yield (7.2 mg). The ee value of the product was determined by HPLC on a Daicel Chiralcel OJ column. Compound **5** obtained from **4a** showed negative rotation, meaning (*R*)-configuration.[19,30]

5 (R′ = CH_3): pale yellow oil; ^{1}H-NMR δ 5.57 (2H, m), 4.19 (2H, q, J = 7.29 Hz), 1.78 (3H, dd, J = 3.51 Hz), 1.28 (3H, t, J = 7.29 Hz).

5 (R′ = C_2H_5): pale yellow oil; ^{1}H-NMR δ 5.65 (2H, m), 4.19 (2H, q, J = 7.29 Hz), 2.10–2.22 (2H, m), 1.28 (3H, t, J = 7.29 Hz), 1.07 (3H, t, J = 7.29 Hz).

5(R′ = C_3H_7): pale yellow oil; ^{1}H-NMR δ 5.59 (2H, m), 4.19 (2H, q, J = 7.29 Hz), 2.07–2.16 (2H, m), 1.49 (3H, q, J = 7.29 Hz), 1.28 (3H, q, J = 7.29 Hz), 0.96 (3H, t, J = 7.29 Hz).

Preparation of Allylic Ferrocenyl Selenides 8–10. Compound **8a** was prepared by the reaction of commercial *trans*-cinnamyl bromide (500 mg, 2.54 mmol) with (*R*,*S*)-(Fc*Se)$_2$ (640 mg, 0.96 mmol) and $NaBH_4$ (150 mg, 3.97 mmol) in EtOH (10 mL) at reflux for 3 h under N_2. Similar workup as in the case of **4** afforded a viscous red oil which was purified by column chromatography on alumina with hexane/ethyl acetate (9/1) as an eluent: yield 565 mg (65% based on (Fc*Se)$_2$). Compound **8b** was similarly prepared by using (*S*,*R*)-(Fc*Se)$_2$. Compounds **9a,b** were synthesized by the reaction of *cis*-cinnamyl chloride (containing ca. 5% of the trans isomer), which was prepared by the reported method,[3] with the corresponding (Fc*Se)$_2$. A simple chromatographic separation afforded pure **9a** and **9b**. Commercial geranyl bromide **7** was used for the preparation of compounds **10**.

8a: red oil; ^{1}H-NMR δ 7.2–7.4 (5H, m), 6.1–6.3 (2H, m), 4.1–4.3 (3H, m), 4.09 (5H, s), 4.00 (1H, q, J = 6.75 Hz), 3.64–3.71 (1H, m), 3.30–3.45 (1H, m), 2.16 (6H, s), 1.35 (3H, d, J = 6.75 Hz); ^{13}C-NMR δ 137.9 (s), 131.8 (d), 129.0 (d), 127.7 (d), 127.6 (d), 126.8 (d), 126.7 (d), 94.9 (s), 76.5 (d), 72.8 (s), 70.4 (d), 68.3 (d), 57.5 (d), 40.7 (q), 32.0 (t), 11.8 (q). Anal. Calcd for $C_{23}H_{27}NFeSe$: C, 61.08; H, 6.02; N, 3.10. Found: C, 61.28; H, 5.97; N, 3.30.

8b: red oil; yield 54%. Anal. Calcd for $C_{23}H_{27}NFeSe$: C, 61.08; H, 6.02; N, 3.10. Found: C, 61.32; H, 6.10; N, 2.96.

9a: red oil; ^{1}H-NMR δ 7.2–7.4 (5H, m), 6.41 (1H, d, J = 11.3 Hz), 5.83–5.94 (1H, m), 4.3–4.5 (3H, m), 4.09 (5H, s), 4.00 (1H, q, J = 6.75 Hz), 3.65 (2H, m), 2.14 (6H, s), 1.33 (3H, d, J = 6.75 Hz); ^{13}C-NMR δ 136.8 (s), 131.7 (d), 129.8 (d), 128.9 (d), 128.1 (d), 128.0 (d), 126.8 (d), 94.6 (s), 75.5 (d), 75.0 (d), 73.1 (s), 69.9 (d), 57.1 (d), 39.9 (q), 27.4 (t), 10.7 (q); yield 53%. Anal. Calcd for $C_{23}H_{27}NFeSe$: C, 61.08; H, 6.02; N, 3.10. Found: C, 60.85; H, 6.25; N, 2.99.

9b: red oil; yield 67%. Anal. Calcd for $C_{23}H_{27}NFeSe$: C, 61.08; H, 6.02; N, 3.10. Found: C, 61.11; H, 5.85; N, 3.26.

10a: red oil; ^{1}H-NMR δ 5.36 (1H, m), 5.09 (1H, m), 4.31 (1H, t, J = 1.89 Hz), 4.18 (2H, m), 4.08 (5H, s), 3.98 (1H, q, J = 7.02 Hz), 3.40 (2H, m), 2.14 (6H, s), 1.69 (3H, s), 1.60 (3H, s), 1.51 (3H, s), 2.01–2.07 (4H, m), 1.35 (3H, d, J = 7.02 Hz); ^{13}C-NMR δ 138.2 (s), 131.5 (s), 124.2 (d), 121.1 (d), 93.8 (s), 75.4 (d), 73.0 (s), 69.8 (d), 67.6 (d), 56.9 (d), 40.3 (q), 39.7 (t), 31.6 (d), 27.1 (t), 26.6 (t), 25.7 (q), 17.7 (q), 15.8 (q), 11.8 (q); yield 43%. Anal. Calcd for $C_{24}H_{35}NFeSe$: C, 61.03; H, 7.47; N, 2.97. Found: C, 61.28; H, 7.61; N, 2.72.

10b: red oil; yield 58%. Anal. Calcd for $C_{24}H_{35}NFeSe$: C, 61.03; H, 7.47; N, 2.97. Found: C, 60.92; H, 7.21; N, 3.05.

1-Phenyl-2-propen-1-ol (11) and Linalool (12). To a dry CH_2Cl_2 (1 mL) solution of **8a** (90 mg, 0.20 mmol) containing a small amount of 4 Å molecular sieves (powder) was added dropwise a dry CH_2Cl_2 (1 mL) solution of MCPBA (70% purity, 38 mg, 0.22 mmol) at −78 °C under N_2, and the resulting mixture was stirred for 1 h. The mixture was poured into saturated aqueous Na_2CO_3 solution (50 mL) and extracted with *n*-hexane (30 mL × 3). The extract was dried over $MgSO_4$ and evaporated to leave a yellow oil which was purified by column chromatography (SiO_2, hexane/EtOAc = 9/1 as an eluent) to afford (*R*)-1-phenyl-2-propen-1-ol (**11**) of 89% ee in 30% chemical yield (7.2 mg). The ee value and the configuration of the product were determined by HPLC on a Daicel Chiralcel OJ column: ^{1}H-NMR δ 7.26–7.40 (5H, m), 6.00–6.12 (1H, m), 5.36 (1H, d, J = 17.0 Hz), 5.18–5.22 (2H, m), 1.8–2.1 (1H, br).

(30) Racemic **5** was prepared by the reported method from acyl chloride and ethyl(triphenylphosphoranylidene)propionate: Lang, R. W.; Hansen, H. J. *Org. Synth.* **1984**, *62*, 202.

Similarly, linalool (**12**) was obtained: ^{1}H-NMR δ 5.91 (1H, dd, J = 17.5 and 11.0 Hz), 5.22 (1H, d, J = 17.5 Hz), 5.1 (1H, m), 5.06 (1H, d, J = 11.0 Hz), 2.0 (2H, m), 1.69 (3H, s), 1.60 (3H, s), 1.5 (2H, m), 1.28 (3H, s).

Preparation of Chiral Ferrocenyl Methyl Sulfide (13, R′ = CH$_3$), Ferrocenyl *p*-Tolyl Sulfide (13, R′ = *p*-Tol), and Ferrocenyl *p*-Tolyl Sulfoxide (14). These two sulfides and one sulfoxide were prepared by literature methods.[25,26] (*R*,*S*)-**13** (R′ = CH$_3$): yield 51%. (*R*,*S*)-**13** (R′ = *p*-Tol): yield 43%. (*S*,*R*,*S*)-**14**: yield 21%.

Oxidation of Chiral Ferrocenyl Sulfide (13) with MCPBA. A typical experimental procedure is as follows. To a dry CH_2Cl_2 (1 mL) solution of **13** (R′ = CH$_3$) (61 mg, 0.20 mmol) was added dropwise a dry CH_2Cl_2 (1 mL) solution of MCPBA (70% purity, 52 mg, 0.30 mmol) at −78 °C under N_2, and the resulting mixture was stirred for 3 h. The mixture was poured into a saturated aqueous Na_2CO_3 solution (50 mL) and extracted with CH_2Cl_2 (30 mL × 3). The extract was dried over $MgSO_4$ and evaporated to leave a yellow oil which was purified by short column chromatography (alumina, hexane/EtOAc = 7/3 as an eluent) to afford the corresponding sulfoxides **14** in 94% chemical yield (61 mg). The de value was determined by ^{1}H-NMR, and its configuration was assigned by comparison with the literature.[26] The corresponding sulfones were not detected at all.

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