

Asymmetric Methoxyselenenylation of Alkenes with Chiral Ferrocenylselenium Reagents

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Asymmetric methoxyselenenylation of alkenes was studied using some chiral ferrocenylselenium compounds which were prepared from chiral ferrocenyl-substituted amine, sulfoxide, oxazoline, and pyrrolidine. The highest diastereoselectivity was observed using the chiral amino-substituted ferrocenylselenium triflates in the reaction with *trans*- β -methylstyrene in an excellent yield. The reaction with silyl enol ethers gave chiral α -seleno ketone with moderate to excellent selectivities. The β,γ -unsaturated ester may be converted into the optically active γ -alkoxy α,β -unsaturated ester using ammonium persulfate in the presence of a catalytic amount of the chiral diferrocenyl diselenide in low optical yields.

Introduction

Organoselenium compounds have become standard reagents for synthetic organic chemistry,¹ and attention has recently been drawn to their application to asymmetric synthesis.² Functionalizations of alkenes with selenium compounds offer attractive possibilities. One of the most important of these reactions is methoxyselenenylation, and the asymmetric variant of the reaction has been demonstrated by us³ and other research groups.^{4–6} Several chiral selenium compounds have been designed for asymmetric methoxyselenenylation; however, most of them have been prepared by multistep syntheses with low overall yields. We have reported the highly selective asymmetric methoxyselenenylation with a ferrocenyl-based chiral selenium compound which can be easily prepared from a chiral amino-substituted ferrocene.^{3a} Although this approach to enantiomeric pure compounds has undoubted value, its utility is hampered by the low yields of the products. We have improved the reaction with respect to yield and selectivity using a more

electrophilic selenium triflate as an electrophile. Several novel substituted ferrocenes with planar chirality have been proposed for asymmetric synthesis since our previous work was reported in 1993.⁷ We present here the usefulness of some chiral ferrocenylselenium compounds derived from chiral ferrocenes, in addition to the previous amino-substituted ferrocenylselenium compound, as a chiral inducer in asymmetric methoxyselenenylation.

Results and Discussion

Methoxyselenenylation with Simple Alkenes.

Treatment of the chiral ferrocenyl-substituted (*R*)-amine,⁸ (*S*)-sulfoxide,^{7c} (*S*)-oxazoline,^{7d} and (*S*)-methoxymethylpyrrolidine with *s*-BuLi followed by addition of elemental selenium, air oxidation, and recrystallization, respectively, afforded the corresponding diastereomerically pure (*R,S*;*R,S*)-diselenide-**1**,^{3a} (*R,S*;*R,S*)-diselenide-**2**, (*S,S*;*S,S*)-diselenide-**3**, and (*S,S*;*S,S*)-diselenide-**4** in 70–80% yields (Scheme 1). We abbreviate these diselenides as Fa*SeSeFa*, Fs*SeSeFs*, Fo*SeSeFo*, and Fp*SeSeFp*, respectively. Fa*SeSeFa* was initially treated with bromine in CH₂Cl₂ at –78 °C to yield the bromide Fa*SeBr, which was subsequently allowed to react with silver triflate or silver tetrafluoroborate to give the more electrophilic triflate Fa*SeOTf or tetrafluoroborate Fa*SeBF₄. Fa*SeOTf reacted with *trans*- β -methylstyrene at 0 °C for 5 h in the presence of methanol to give the β -methoxyselenium compound **6** as a single regioisomer (attack of methanol at the benzylic carbon) in high diastereoselectivity (96% de) with an excellent yield (99%). The diastereomeric excess (% de) in the crude adduct was determined by ¹H NMR (400 MHz) integra-

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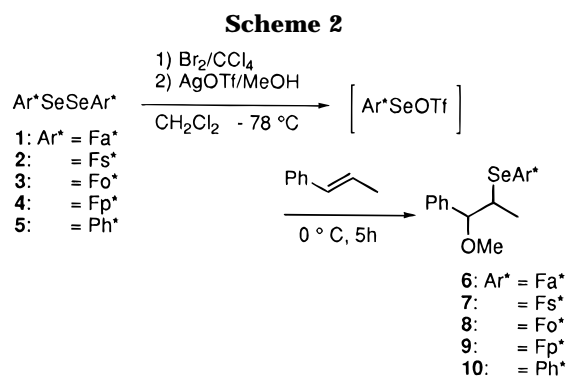
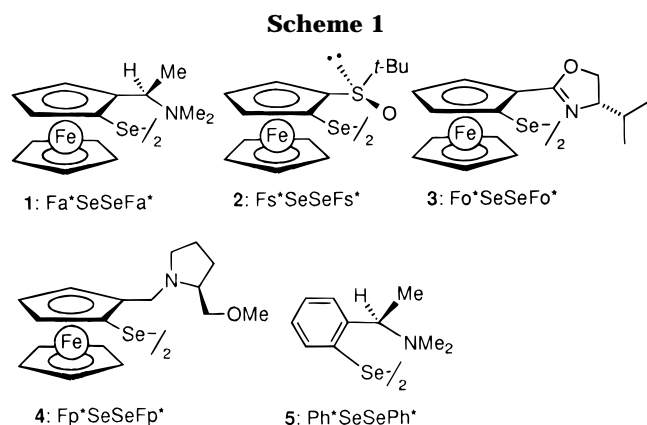


Table 1. Asymmetric Methoxyselenenylation of *trans*- β -Methylstyrene with Chiral Selenium Compounds Derived from Chiral Ferrocene Derivatives^a

entry	chiral ferrocenyl or aryl group	X	% isolated yield	% de ^b
1	Fa*	Br	20	98
2		OTf	99	96
3		BF ₄	99	89
4	Fs*	OTf	99	30
5	Fo*	OTf	99	66
6	Fp*	OTf	95	56
7	Ph*	OTf	99	28

^a Diselenide (0.50 mmol), Br₂ (0.60 mmol), AgOTf (1.2 mmol), alkene (2.0 mmol), MeOH (1.0 mL); 0 °C for 5 h. ^b Determined by ¹H NMR (400 MHz).

tion of the proton of the dimethylamino group and/or the methoxy group. When compared to those the corresponding bromide, the yields were remarkably increased, preserving a high diastereoselectivity. Diastereoselectivity of the reaction was as high as that with other recent chiral selenium compounds.^{4–6} Fa*SeBF₄ gave a somewhat lower diastereoselectivity than the triflate (89% ee). The diselenides **2**, Fs*SeSeFs*, **3**, Fo*SeSeFo*, and **4**, Fp*SeSeFp*, similarly converted into the corresponding selenium triflates, respectively, i.e., Fs*SeOTf, Fo*SeOTf, and Fp*SeOTf. They underwent methoxyselenenylation with *trans*- β -methylstyrene to give the corresponding adduct (**7–9**) in 30%, 66%, and 56% de, respectively (Scheme 2). These results of the reactions with the chiral electrophilic selenium reagents with *trans*- β -methylstyrene are shown in Table 1. It should be noted that all diastereoselectivities with these ferrocenylselenium reagents were higher than that with chiral (*R*)-2-(1-(dimethylamino)ethyl)phenylselenium triflate (**5**; Ph*SeOTf) (Table 1, entry 7).

Fa*SeOTf was revealed to be most effective for high selectivity; therefore, we applied this compound to various alkenes in this reaction (Scheme 3). The results of

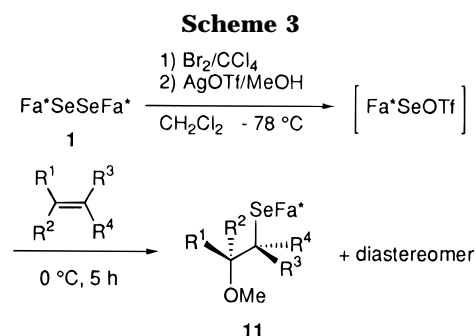


Table 2. Asymmetric Methoxyselenenylation of Alkenes with a Chiral Ferrocenylselenium Triflate (Fa*SeOTf)^a

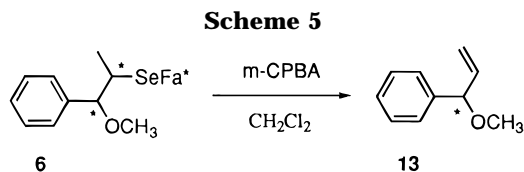
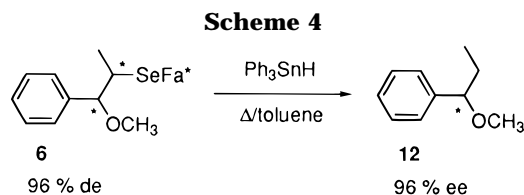
entry	alkene	% isolated yield	% de ^b
1	styrene	97	35
2	<i>o</i> -methylstyrene	99	47
3	<i>m</i> -methylstyrene	97	35
4	α -methylstyrene	99	15
5	<i>trans</i> - β -methylstyrene	99	96
6	<i>cis</i> -2-butene ^c	96	50
7	<i>trans</i> -2-butene ^c	96	96
8	cyclopentene	96	73
9	cyclohexene	99	60
10	1-methylcyclohexene	96	96
11	1-phenylcyclohexene	99	93
12	3,3-dimethyl-1-butene	96	21

^a Diselenide (0.50 mmol), Br₂ (0.60 mmol), AgOTf (1.2 mmol), alkene (2.0 mmol), MeOH (1.0 mL); 0 °C for 5 h. ^b Determined by ¹H NMR (400 MHz). ^c 20 mmol of alkene was used.

the reaction of Fa*SeOTf with alkenes are summarized in Table 2. With styrene and substituted styrenes, the adducts were obtained as a single regioisomer (Markovnikov adduct; methanol attacks at the more substituted carbon) in high yields, but the facial selectivity was lower than that with β -methylstyrene (entries 1–4). The selectivity was not improved even if the reaction was carried out at lower temperature (–78 °C). The reaction with *cis*-2-butene gave only 50% de (entry 6), while with *trans*-2-butene a high de value (96% de) was obtained (entry 7). With cyclopentene and cyclohexene, we obtained the *trans* adduct with moderate de values (60–73% de) (entries 8–9). On the basis of these results, *cis*-alkenes tend to give less diastereoselectivity than that with *trans*-alkenes.^{5d} On the other hand, with 1-substituted cyclohexenes, higher selectivities could be achieved than with cyclohexene; 1-methylcyclohexene and 1-phenylcyclohexene gave only Markovnikov adducts in 96% and 93% de, respectively (entries 10–11). These results suggest that a sterically large group in an alkene is necessary to achieve a high facial selectivity. However, the reaction with sterically crowded 3,3-dimethyl-1-butene afforded the poor selectivity (21% de) (entry 12).

Reaction Mechanism. We confirmed the absolute configuration of the adduct from methoxyselenenylation of *trans*- β -methylstyrene with Fa*SeOTf. Reductive removal of the chiral organoselenium group of the diastereomeric mixture of the adduct (**6**) (96% de) by triphenyltin hydride in refluxing toluene gave methyl 1-phenyl-1-propyl ether (**12**) in 70% yield (Scheme 4).⁹ The enantiomeric excess was determined by HPLC analysis using a chiral column (Daicel, Chiralcel OD column) compared with authentic samples. The (*S*)-configured methyl ether was formed in 96% ee from the

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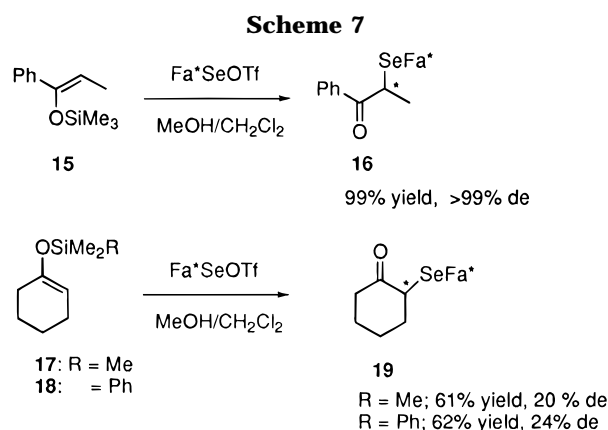
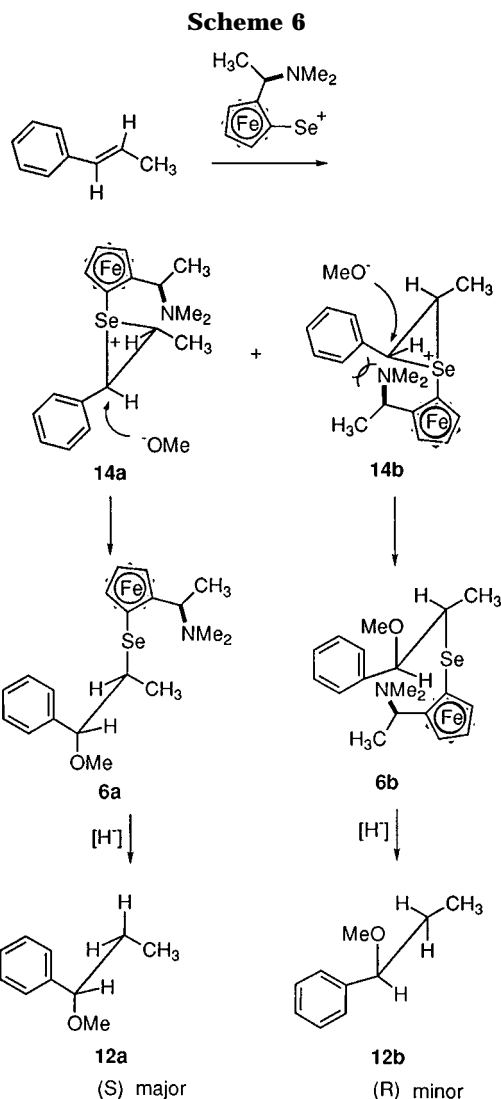
reaction with the (*R,S*)-chiral ferrocenylselenium reagent. The enantiomeric excess found was consistent with the diastereomeric excess in the β -methoxyselenium compound, while the (*R*)-configured methyl ether was revealed to be formed with the (*S,R*)-chiral ferrocenylselenium reagent.

The oxidative removal of the selenium moiety by *m*-chloroperbenzoic acid (*m*-CPBA) readily converted **6** into the optically active allyl methyl ether (**13**) in a good yield (Scheme 5). The absolute configuration of the major isomer of **13** was determined as (*S*) which was consistent with the above reductive removal result.

Scheme 6 illustrates the possible reaction mechanism of the reaction. The first step of the reaction involves the electrophilic attack of the selenium moiety to the carbon-carbon double bond to form the seleniranium cation intermediate.^{5d} In this step the diastereoselectivity should be determined and the two diastereomers (**14a** and **14b**) would be formed. The second step, ring opening of the seleniranium cation by MeO^- , is not responsible for the diastereoselectivity. When (*R,S*)- Fa^*SeOTf is used as an electrophile, **14b** is more hindered than **14a**; steric repulsion between the phenyl and the ferrocenyl groups in **14b** should exist. Thus, the formation of **14a** is more favorable than **14b** and then leads to the major diastereomer of β -methoxyselenium compound (**6a**) which gives methyl (*S*)-1-phenyl-1-propyl ether (**12a**) after reductive removal of the selenium moiety.

Reaction with Silyl Enol Ethers. Asymmetric methoxyselenenylation with a silyl enol ether may lead to a chiral α -seleno ketone.¹⁰ The reaction of Fa^*SeOTf with (*Z*)-1-phenyl-1-(trimethylsiloxy)-1-propene (**15**) and methanol yielded the α -ferrocenylseleno ketone **16** in excellent diastereoselectivity (>99% de) in high yield, while 1-(trimethylsiloxy)-1-cyclohexene (**17**) gave the α -ferrocenylselenocyclohexanone **19** in lower selectivity (23% de). Replacement of the trimethyl group by a dimethylphenyl group (**18**) resulted in almost the same degree of selectivity (24% de) (Scheme 7). These results were consistent with the diastereoselectivities observed in the reaction with *trans*- β -methylstyrene and cyclohexene.

Catalytic Asymmetric Conversion of Alkenes into Allylic Ethers. We finally applied the diselenide **1** to the catalytic asymmetric oxidation of a β,γ -unsaturated ester (**20–21**) and *trans*- β -methylstyrene into the optically active allylic ethers.¹¹ The catalytic reaction was carried out using ammonium persulfate in the presence

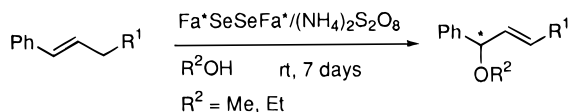


of a catalytic amount of $\text{Fa}^*\text{SeSeFa}^*$ in alcohol at room temperature for 7 days. The allylic ethers (**23**, $\text{R}^1 = \text{R}^2 = \text{Me}$, or **24**, $\text{R}^1 = \text{R}^2 = \text{Et}$) were produced from 4-phenyl-3-butenic acid ester in 17–22% ee with 70–78% yield (Scheme 8). The reaction with *trans*- β -methylstyrene gave the product in only 4% ee with 35% yield although methoxyselenenylation with the alkene provides excellent selectivity. Surprisingly, when this catalytic oxidation was carried out using sulfoxide-substituted diferrocenyl diselenide ($\text{Fs}^*\text{SeSeFs}^*$) as a catalyst, the vinylic ether was produced instead of the allylic ether (Scheme 9). The mechanism for the reaction has not been clarified yet, but sulfoxide or sulfone may participate in the reaction.

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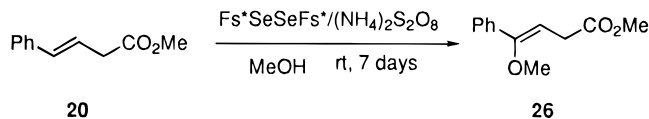
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Scheme 8



20: R ¹ = CO ₂ Me	23: R ¹ = CO ₂ Me, R ² = Me	17 % ee
21: = CO ₂ Et	24: = CO ₂ Et, R ² = Et	22 % ee
22: = H	25: = H, R ² = Me	4% ee

Scheme 9



Experimental Section

General. ¹H and ¹³C NMR spectra were recorded in CDCl₃, and the chemical shifts are reported in δ units downfield from Me₄Si as an internal standard. Gas chromatography analyses were carried out using a chiral capillary column (G-TA, Asteck, 0.25 mm, 30 m) and helium as the carrier gas. HPLC analyses were performed on a Dical Chiralcel OD column (0.46 mm, 25 cm) eluting with 2-propanol/*n*-hexane (1/9). Elemental analyses were carried out in the Microanalytical Laboratory at Chuo University.

Materials. The chiral ferrocenyl diselenides (**1–4**) were prepared by regioselective *o*-lithiation of the parent chiral ferrocenes followed by reaction with elemental selenium according to the reported method.⁷

Preparation of Diselenide (2, Fs*SeSeFs*). After lithiation of (*R*)-ferrocenyl *tert*-butyl sulfoxide (>99% ee) (1.47 g, 2.0 mmol) in tetrahydrofuran with *n*-butyllithium (2.5 mmol) at 0 °C under nitrogen, selenium powder (0.24 g, 3.0 mmol) was added portionwise, and the resulting mixture was stirred at 0 °C for 15 min and then at room temperature for 3 h. The mixture was poured into water, and then oxygen was bubbled through the solution for 1 h at room temperature. [*R,S;R,S*]-Bis[2-(*tert*-butylsulfinyl)ferrocenyl] diselenide (**2**) was isolated by column chromatography on silica gel eluted with hexane/ethyl acetate (1/1): red solid; yield, 1.09 g, 1.48 mmol, 74%; mp 170–172 °C dec; IR (KBr) 3080, 2958, 1632, 1471, 1362, 1176, 1107, 1030, 822, 572, 508, 475 cm⁻¹; [α]_D²⁵ = +1385 (*c* = 1.0, CHCl₃); ¹H NMR (CDCl₃) δ 1.22 (s, 18H), 4.37 (s, 10H), 4.2–4.8 (m, 6H); ¹³C NMR δ 23.5, 56.8, 70.0, 70.1, 70.2, 72.3, 75.1, 82.9. Anal. Calcd for C₂₈H₃₄O₂S₂Se₂Fe₂: C, 45.67; H, 4.65. Found: C, 45.52; H, 4.51.

[*S,S;S,S*]-Bis[(4-isopropyl-2-oxazolin-2-yl)ferrocenyl] diselenide (**3, Fo*SeSeFo***): red solid; yield, 1.08 g, 1.44 mmol, 72%; mp 192–194 °C dec; IR (KBr) 2962, 1650, 1457, 1355, 1222, 1209, 1135, 974, 824, 770, 756, 742, 728 cm⁻¹; [α]_D²⁵ = -1186 (*c* = 1.0, CHCl₃); ¹H NMR (CDCl₃) δ 1.03 (d, 6H, *J* = 6.9 Hz), 1.08 (d, 6H, *J* = 6.8 Hz), 1.85 (oct, 2H, *J* = 6.8 Hz), 4.01–4.09 (m, 2H), 4.18 (s, 10H), 4.1–4.2 (m, 2H), 4.27 (t, 2H, *J* = 2.5 Hz), 4.32 (dd, 2H, *J* = 8.3, 9.5 Hz), 4.6–4.7 (m, 4H); ¹³C NMR δ 18.4, 18.6, 32.6, 69.1, 69.9, 70.0, 71.4, 71.5, 72.4, 73.7, 78.8, 165.2. Anal. Calcd for C₃₂H₃₆N₂O₂-Fe₂Se₂: C, 51.23; H, 4.84; N, 3.73. Found: C, 50.98; H, 4.84; N, 3.81.

[*S,S;S,S*]-Bis[(2-(methoxymethyl)pyrrolidin-1-yl)methyl]ferrocenyl diselenide (**4, Fp*SeSeFp***): orange solid; yield, 1.14 g, 1.46 mmol, 73%; mp 110–114 °C dec; IR (KBr) 3417, 3096, 3072, 2970, 2926, 2882, 2806, 1633, 1449, 1351, 1121, 999, 816 cm⁻¹; [α]_D²⁵ = -312 (*c* = 0.49, CHCl₃); ¹H NMR (CDCl₃) δ 1.5–1.8 (m, 3H), 1.8–2.0 (m, 1H), 1.85 (ddd, 1H, *J* = 9.3, 7.3, 2.0 Hz), 2.7–2.8 (m, 1H), 3.01 (ddd, 1H, 8.6, 7.0, 1.7 Hz), 3.28 (dd, 1H, 8.0, 6.9 Hz), 3.41 (s, 3H), 3.53 (dd, 1H, 7.0, 4.7 Hz), 4.06 (s, 10H), 4.2–4.5 (m, 2H); ¹³C NMR δ 22.6, 28.5, 53.8, 54.1, 59.0, 61.6, 67.8, 67.9, 68.3, 70.0, 70.1, 76.3, 83.8. Anal. Calcd for C₃₄H₄₆N₂O₂Fe₂Se₂: C, 52.20; H, 5.67; N, 3.56. Found: C, 51.97; H, 5.95; N, 3.56.

(*R,R*)-Bis[2-(1-(*N,N*-Dimethylamino)ethyl)phenyl] diselenide (**5, Ph*SeSePh***): orange oil; yield, 0.64 g, 1.40

mmol, 70%; IR (KBr) 3055, 2973, 2938, 2861, 2824, 2780, 1738, 1585, 1456, 1370, 953, 776 cm⁻¹; [α]_D²⁵ = +151.8 (*c* = 1.03, CHCl₃); ¹H NMR (CDCl₃) δ 1.35 (d, 3H), 2.26 (s, 6H), 3.78 (q, 1H, *J* = 6.7 Hz), 7.1–7.3 (m, 3H), 7.8–7.9 (m, 1H); ¹³C NMR δ 14.1, 41.0, 63.6, 125.9, 126.2, 127.6, 131.5, 133.3, 144.1. Anal. Calcd for C₂₀H₂₈N₂Se₂: C, 52.87; H, 6.21; N, 6.17. Found: C, 52.91; H, 6.22; N, 6.14.

Asymmetric Methoxyselenenylation of Alkenes with a Chiral Ferrocenyl Diselenide. Typical experimental procedure for the asymmetric methoxyselenenylation of an alkene is as follows. To a CH₂Cl₂ solution (2.0 mL) of (*R,S*)-**1** (335 mg, 0.50 mmol) at -78 °C was added a CCl₄ (1.0 mL) solution of bromine (96 mg, 0.60 mmol) slowly over a period of 20 min. After 30 min, a methanol solution of silver triflate (308 mg, 1.2 mmol) was added. The resulting heterogeneous mixture was stirred at -78 °C for 30 min. Then *trans*-β-methylstyrene (2.0 mmol) was added to the resulting solution at -78 °C, and the solution was warmed to 0 °C and stirred for 5 h. The mixture was treated with an aqueous solution of NaHCO₃, extracted with CH₂Cl₂ (20 mL × 2), and dried (K₂CO₃). Evaporation of the solvent left a dark brown residue which was subjected to preparative TLC (Al₂O₃; hexane/ethyl acetate = 4/1). A diastereomeric mixture of (*R,S*)-2-(1-(dimethylamino)ethyl)ferrocenyl 3-methoxy-3-phenyl-2-propyl selenide (**6**) was obtained as a yellow oil. The diastereomeric excess was determined by ¹H NMR: major diastereomer δ 1.20 (d, 3H, *J* = 7.0 Hz), 1.32 (d, 3H, *J* = 6.8 Hz), 2.18 (s, 6H), 3.28 (s, 3H), 3.53 (dq, 1H, *J* = 3.9, 7.0 Hz), 4.03 (q, 1H, *J* = 6.8 Hz), 4.10 (s, 5H), 4.14–4.23 (m, 4H, including CHOCH₃), 7.1–7.3 (m, 5H); ¹³C NMR δ 9.4, 14.1, 39.8, 44.5, 56.8, 57.4, 67.5, 67.9, 69.8, 70.0, 71.3, 76.3, 84.7, 95.7, 127.0, 127.9, 128.1, 140.4. Minor diastereomer (distinct signals): ¹H NMR δ 2.20 (s, N(CH₃)₂), 3.33 (s, OCH₃). Anal. Calcd for C₂₄H₃₁NOFeSe: C, 59.50; H, 6.40; N, 2.89. Found: C, 59.22; H, 6.49; N, 2.76.

(*R,S*)-2-(*tert*-Butylsulfinyl)ferrocenyl 3-Methoxy-3-phenyl-2-propyl Selenide (**7**). The title compound was obtained as a mixture of diastereomers by the reaction of Fs*SeOTf with *trans*-β-methylstyrene and methanol. Major diastereomer: ¹H NMR δ 1.25 (s, 9H), 1.37 (d, 3H, *J* = 7.1 Hz), 3.32 (s, 3H), 4.3–4.4 (m, 9H including CHOCH₃), 7.20–7.50 (m, 5H). Minor diastereomer (distinct signals): ¹H NMR δ 1.30 (s, *t*-Bu), 1.40 (d, CH₃CH, *J* = 7.1 Hz), 3.32 (s, OCH₃). Anal. Calcd for C₂₄H₃₁-OFe₂SSe: C, 55.72; H, 5.84. Found: C, 55.88; H, 5.93.

(*S,S*)-2-(4-Isopropyl-2-oxazolin-2-yl)ferrocenyl 3-Methoxy-3-phenyl-2-propyl Selenide (**8**). The title compound was obtained as a mixture of diastereomers by the reaction of Fo*SeOTf with *trans*-β-methylstyrene and methanol. Major diastereomer: ¹H NMR δ 1.01 (d, 3H, *J* = 6.9 Hz), 1.07 (d, 3H, *J* = 6.8 Hz), 1.26 (d, 3H, *J* = 7.1 Hz), 1.88 (oct, 1H, *J* = 6.6 Hz), 3.31 (s, 3H), 3.4–3.50 (m, 1H), 3.9–4.8 (m, 7H, including CHOCH₃), 4.20 (s, 5H), 7.20–7.40 (m, 5H); ¹³C NMR δ 15.9, 18.2, 18.8, 32.5, 45.4, 57.6, 69.4, 69.9, 71.0, 71.2, 72.5, 72.6, 74.3, 76.9, 86.5, 126.8, 127.3, 128.1, 140.0, 164.5. Minor diastereomer (distinct signals): ¹H NMR δ 0.94 (d, one of CH₃ in CH(CH₃)₂, *J* = 6.8 Hz), 1.02 (d, CH(CH₃)₂, *J* = 6.8 Hz), 1.29 (d, *J* = 6.9 Hz, CH₃CH), 1.84 (oct, CH(CH₃)₂, *J* = 6.6 Hz), 3.25 (s, OCH₃); ¹³C NMR δ 15.6, 18.0, 18.7, 32.4, 45.1, 57.4, 69.5, 71.2, 72.3, 85.8. Anal. Calcd for C₂₆H₃₁NFeO₂Se: C, 59.56; H, 5.96; N, 2.67. Found: C, 59.88; H, 5.83; N, 2.59.

(*S,S*)-2-(2-(Methoxymethyl)pyrrolidin-1-yl)methylferrocenyl 3-Methoxy-3-phenyl-2-propyl Selenide (**9**). The title compound was obtained as a mixture of diastereomers by the reaction of Fp*SeOTf with *trans*-β-methylstyrene and methanol. Major diastereomer: ¹H NMR (CDCl₃) δ 1.5–1.8 (m, 3H), 1.8–2.0 (m, 1H), 1.85 (ddd, 1H, *J* = 9.3, 7.3, 2.0 Hz), 2.7–2.8 (m, 1H), 3.01 (ddd, 1H, 8.6, 7.0, 1.7 Hz), 3.28 (dd, 1H, 8.0, 6.9 Hz), 3.25 (s, 3H), 3.35 (s, 3H), 3.53 (dd, 1H, 7.0, 4.7 Hz), 4.06 (s, 10H), 4.2–4.5 (m, 2H); ¹³C NMR δ 13.4, 22.5, 29.0, 44.4, 54.1, 54.3, 57.6, 58.9, 63.3, 68.2, 69.6, 69.7, 71.4, 72.0, 76.6, 84.0, 88.9, 126.7, 127.0, 127.8, 140.0. Minor diastereomer (distinct signals): ¹H NMR δ 3.40 (s, OCH₃); ¹³C NMR δ 13.6, 45.1. Anal. Calcd for C₂₇H₃₅NFeO₂Se: C, 60.00; H, 6.53; N, 2.59. Found: C, 60.18; H, 6.53; N, 2.59.

(*R,S*)-2-(1-(Dimethylamino)ethyl)phenyl 3-Methoxy-3-phenyl-2-propyl Selenide (**10**). The title compound was obtained as a mixture of diastereomers by the reaction of

Ph*SeOTf with *trans*- β -methylstyrene and methanol. Major diastereomer: $^1\text{H NMR } \delta$ 1.27 (d, 3H, $J = 6.5$ Hz), 1.38 (d, 3H, $J = 7.0$ Hz), 2.19 (s, 6H), 3.29 (s, 3H), 3.4–3.5 (m, 1H), 3.85 (q, 1H, $J = 6.5$ Hz), 4.38 (d, 1H, $J = 4.3$ Hz), 7.0–7.5 (m, 9H); $^{13}\text{C NMR } \delta$ 16.1, 17.9, 42.5, 45.0, 57.6, 63.3, 86.3, 126.9–147.0 (several aromatic peaks). Minor diastereomer (distinct signals): $^1\text{H NMR } \delta$ 1.29 (d, SeCHCH_3 , $J = 6.5$ Hz), 1.33 (d, CHCH_3 , $J = 7.0$ Hz), 2.21 (s, $\text{N}(\text{CH}_3)_2$), 3.32 (s, OCH_3), 3.88 (q, $\text{CHN}(\text{CH}_3)_2$, $J = 6.5$ Hz), 4.49 (d, CHOCH_3 , $J = 4.3$ Hz); $^{13}\text{C NMR } \delta$ 16.0, 18.2, 42.6, 45.2, 63.4. Anal. Calcd for $\text{C}_{20}\text{H}_{27}\text{NOSe}$: C, 55.57; H, 6.30; N, 3.24. Found: C, 55.75; H, 6.39; N, 3.20.

(*R,S*)-2-(1-(Dimethylamino)ethyl)ferrocenyl 2-Methoxy-2-phenylethyl Selenide. The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with styrene and methanol. Major diastereomer: $^1\text{H NMR } \delta$ 1.33 (d, 3H, $J = 6.8$ Hz), 2.08 (s, 6H), 2.94 (dd, 1H, $J = 8.3, 11.7$ Hz), 3.07 (dd, 1H, $J = 4.7, 12.2$ Hz), 3.25 (s, 3H), 3.96 (q, 1H, $J = 6.8$ Hz), 4.10 (s, 5H), 4.1–4.4 (m, 4H, including CHOCH_3), 7.20–7.40 (m, 5H); $^{13}\text{C NMR } \delta$ 11.1, 36.1, 40.0, 56.8, 56.9, 67.5, 69.83, 71.9, 73.0, 75.3, 82.7, 94.5, 126.5, 127.7, 128.3, 141.5. Minor diastereomer (distinct signals): $^1\text{H NMR } \delta$ 1.34 (d, CHCH_3 , $J = 6.8$ Hz), 2.14 (s, $\text{N}(\text{CH}_3)_2$), 2.89 (dd, $J = 5.1, 11.5$ Hz, CHSeFa^*), 3.24 (s, OCH_3), 4.00 (q, $\text{CHN}(\text{CH}_3)_2$, $J = 6.8$ Hz); $^{13}\text{C NMR } \delta$ 10.9, 83.8, 94.0. Anal. Calcd for $\text{C}_{23}\text{H}_{29}\text{NOFeSe}$: C, 58.74; H, 6.22; N, 2.98. Found: C, 58.51; H, 6.26; N, 2.80.

(*R,S*)-2-(1-(Dimethylamino)ethyl)ferrocenyl 2-Methoxy-2-*o*-tolylethyl Selenide. The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with *o*-methylstyrene and methanol. Major diastereomer: $^1\text{H NMR } \delta$ 1.32 (d, 3H, $J = 6.8$ Hz), 2.04 (s, 6H), 2.13 (s, 3H), 2.86 (dd, 1H, $J = 9.5, 12.4$ Hz), 3.01 (dd, 1H, $J = 3.9, 12.5$ Hz), 3.27 (s, 3H), 3.97 (q, 1H, $J = 6.8$ Hz), 4.10 (s, 5H), 4.1–4.7 (m, 4H, including CHOCH_3), 7.00–7.40 (m, 4H); $^{13}\text{C NMR } \delta$ 11.0, 18.9, 35.2, 40.0, 56.7, 56.9, 67.6, 69.7, 71.9, 73.1, 74.7, 79.6, 94.4, 125.6, 126.0, 127.1, 130.3, 135.4, 139.3. Minor diastereomer (distinct signals): $^1\text{H NMR } \delta$ 1.35 (d, CHCH_3 , $J = 6.8$ Hz), 2.12 (s, $\text{N}(\text{CH}_3)_2$), 2.29 (s, *o*- CH_3), 2.92 (dd, CHCH_2 , $J = 4.7, 11.7$ Hz), 3.12 (dd, CHCH_2 , $J = 9.3, 12.0$ Hz), 3.99 (q, $\text{CHN}(\text{CH}_3)_2$, $J = 6.8$ Hz); $^{13}\text{C NMR } \delta$ 11.3, 18.7, 35.7, 40.1, 80.1, 93.4. Anal. Calcd for $\text{C}_{24}\text{H}_{31}\text{NOFeSe}$: C, 59.50; H, 6.40; N, 2.89. Found: C, 59.15; H, 6.52; N, 2.71.

(*R,S*)-2-(1-(Dimethylamino)ethyl)ferrocenyl 2-Methoxy-2-*m*-tolylethyl Selenide. The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with *m*-methylstyrene and methanol. Major diastereomer: $^1\text{H NMR } \delta$ 1.33 (d, 3H, $J = 6.8$ Hz), 2.08 (s, 6H), 2.32 (s, 3H), 2.92 (dd, 1H, $J = 9.0, 11.9$ Hz), 3.08 (dd, 1H, $J = 4.6, 12.2$ Hz), 3.25 (s, 3H), 3.96 (q, 1H, $J = 6.8$ Hz), 4.10 (s, 5H), 4.1–4.4 (m, 4H, including CHOCH_3), 7.00–7.30 (m, 4H); $^{13}\text{C NMR } \delta$ 11.1, 21.4, 36.0, 40.1, 56.8, 56.9, 67.4, 72.0, 73.0, 74.9, 82.7, 94.4, 123.6, 127.2, 128.1, 128.3, 137.9, 141.4. Minor diastereomer (distinct signals): $^1\text{H NMR } \delta$ 1.34 (d, CHCH_3 , $J = 6.8$ Hz), 2.14 (s, $\text{N}(\text{CH}_3)_2$), 2.35 (s, *m*- CH_3), 2.88 (dd, CHCH_2 , $J = 5.1, 11.7$ Hz), 3.02 (dd, CHCH_2 , $J = 9.0, 11.7$ Hz), 3.99 (q, $\text{CHN}(\text{CH}_3)_2$, $J = 6.8$ Hz); $^{13}\text{C NMR } \delta$ 11.0, 21.3, 36.8, 40.0, 83.8, 93.9. Anal. Calcd for $\text{C}_{24}\text{H}_{31}\text{NOFeSe}$: C, 59.50; H, 6.40; N, 2.89. Found: C, 59.37; H, 6.60; N, 2.84.

(*R,S*)-2-(1-(Dimethylamino)ethyl)ferrocenyl 2-Methyl-2-methoxy-2-phenylethyl Selenide. The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with α -methylstyrene and methanol. Major diastereomer: $^1\text{H NMR } (\text{CDCl}_3) \delta$ 1.32 (d, 3H, $J = 6.9$ Hz), 1.67 (s, 3H), 2.07 (s, 6H), 3.12 (s, 3H), 3.14 (d, 1H, $J = 12.0$ Hz), 3.31 (d, 1H, $J = 8.8$ Hz), 3.92 (q, 1H, $J = 6.8$ Hz), 4.06 (s, 5H), 4.1–4.2 (m, 3H), 7.2–7.4 (m, 5H); $^{13}\text{C NMR}$ major diastereomer δ 11.5, 23.9, 40.0, 42.6, 50.8, 56.8, 67.3, 67.5, 69.7, 73.2, 74.8, 78.9, 94.1, 126.2, 127.0, 128.1, 144.3. Minor diastereomer (distinct signals): $^1\text{H NMR } \delta$ 1.33 (d, CHCH_3 , $J = 6.9$ Hz), 1.69 (s, CCH_3), 2.11 (s, $\text{N}(\text{CH}_3)_2$), 3.11 (s, OCH_3), 3.22 (d, CCH_2Se , $J = 11.3$ Hz), 3.34 (d, CCH_2Se , $J = 9.5$ Hz), 3.98 (q, $\text{CHN}(\text{CH}_3)_2$, $J = 6.8$ Hz); $^{13}\text{C NMR } \delta$ 11.3, 24.2, 40.1, 42.4, 56.7, 78.8, 94.0. Anal. Calcd for $\text{C}_{24}\text{H}_{31}\text{NOFeSe}$: C, 59.50; H, 6.40; N, 2.89. Found: C, 59.26; H, 6.58; N, 2.71.

(*R,S*)-2-(1-(Dimethylamino)ethyl)ferrocenyl 2-Methoxy-3,3-dimethyl-1-butyl Selenide. The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with 3,3-dimethyl-1-butene and methanol. Major diastereomer: $^1\text{H NMR } \delta$ 1.10 (s, 9H), 1.30 (d, 3H, $J = 6.8$ Hz), 2.10 (s, 6H), 3.15 (s, 3H), 3.32 (dd, 1H, $J = 3.0, 6.8$ Hz), 3.51 (dd, 1H, $J = 3.2, 11.2$ Hz), 3.58 (dd, 1H, $J = 6.8, 11.2$ Hz), 4.05 (q, 1H, $J = 6.8$ Hz), 4.10 (s, 5H), 4.1–4.4 (m, 3H); $^{13}\text{C-NMR}$ major diastereomer δ 9.5, 29.0, 29.3, 34.4, 39.8, 56.8, 57.9, 58.4, 67.6, 68.2, 69.9, 73.4, 75.7, 94.9. Minor diastereomer (distinct signals): $^1\text{H NMR } \delta$ 1.04 (s, $\text{C}(\text{CH}_3)_3$), 1.31 (d, CHCH_3 , $J = 6.8$ Hz), 2.12 (s, $\text{N}(\text{CH}_3)_2$), 3.06 (dd, CHOCH_3), 3.26 (s, OCH_3), 3.74 (dd, CHCH_2 , $J = 6.1, 10.5$ Hz), 3.83 (dd, CHCH_2 , $J = 3.2, 6.1$ Hz), 3.99 (q, $\text{CHN}(\text{CH}_3)_2$, $J = 6.8$ Hz); $^{13}\text{C NMR } \delta$ 9.6, 35.3, 39.9, 55.4, 59.6, 95.7. Anal. Calcd for $\text{C}_{21}\text{H}_{33}\text{NOFeSe}$: C, 56.00; H, 7.33; N, 3.11. Found: C, 55.99; H, 7.43; N, 3.02.

***trans*-(*R,S*)-2-(1-(Dimethylamino)ethyl)ferrocenyl 2-Methoxycyclohexyl Selenide.** The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with cyclohexene and methanol. Major diastereomer: $^1\text{H NMR } \delta$ 1.2–2.0 (m, 8H), 1.32 (d, 3H, $J = 6.8$ Hz), 2.12 (s, 6H), 3.2–3.3 (m, 2H), 3.29 (s, 3H), 3.96 (q, 1H, $J = 6.8$ Hz), 4.09 (s, 5H), 4.2–4.4 (m, 3H); $^{13}\text{C NMR } \delta$ 10.3, 22.7, 24.9, 29.0, 29.9, 39.9, 46.4, 55.9, 56.6, 67.6, 67.7, 69.8, 71.9, 76.3, 82.0, 94.7. Minor diastereomer (distinct signals): $^1\text{H NMR } \delta$ 2.10 (s, $\text{N}(\text{CH}_3)_2$), 3.37 (s, OCH_3), 3.98 (q, $\text{CHN}(\text{CH}_3)_2$, $J = 6.8$ Hz); $^{13}\text{C NMR } \delta$ 10.8, 23.6, 25.5, 30.4, 31.5, 46.1, 56.0, 83.2, 95.2. Anal. Calcd for $\text{C}_{21}\text{H}_{31}\text{NOFeSe}$: C, 56.25; H, 6.92; N, 3.13. Found: C, 56.06; H, 6.94; N, 3.07.

***trans*-(*R,S*)-2-(1-(Dimethylamino)ethyl)ferrocenyl 2-Methyl-2-methoxycyclohexyl Selenide.** The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with 1-methyl-1-cyclohexene and methanol. Major diastereomer: $^1\text{H NMR } \delta$ 1.26 (s, 3H), 1.32 (d, 3H, $J = 6.9$ Hz), 1.3–1.8 (m, 8H), 2.13 (s, 6H), 3.03 (s, 3H), 3.53 (dd, 1H, $J = 2.9, 7.3$ Hz), 3.99 (q, 1H, $J = 6.8$ Hz), 4.10 (s, 5H), 4.1–4.4 (m, 3H); $^{13}\text{C NMR } \delta$ 9.7, 22.1, 22.7, 24.4, 30.6, 34.3, 39.9, 48.2, 51.9, 56.8, 67.3, 69.8, 69.9, 73.2, 76.1, 95.3. Minor diastereomer (distinct signals): $^1\text{H NMR } \delta$ 2.11 (s, $\text{N}(\text{CH}_3)_2$), 3.25 (s, OCH_3). Anal. Calcd for $\text{C}_{22}\text{H}_{33}\text{NOFeSe}$: C, 57.14; H, 7.14; N, 3.03. Found: C, 56.87; H, 7.15; N, 3.04.

***trans*-(*R,S*)-2-(1-(Dimethylamino)ethyl)ferrocenyl 2-Methoxy-2-phenylcyclohexyl Selenide.** The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with 1-phenyl-1-cyclohexene and methanol. Major diastereomer: $^1\text{H NMR } \delta$ 1.25 (d, 3H, $J = 6.5$ Hz), 1.3–2.6 (m, 8H), 2.13 (s, 6H), 2.81 (s, 3H), 3.74 (t, 1H, $J = 2.4$ Hz), 3.90 (s, 5H), 3.9–4.2 (m, 4H, including $\text{CHN}(\text{CH}_3)_2$), 7.2–7.5 (m, 5H); $^{13}\text{C NMR } \delta$ 10.0, 20.9, 22.2, 25.5, 30.2, 39.9, 49.9, 56.1, 56.8, 66.6, 67.2, 69.5, 72.8, 75.4, 80.1, 94.5, 126.8, 127.5, 127.6, 143.8. Minor diastereomer (distinct signals): $^1\text{H NMR } \delta$ 1.18 (d, CHCH_3 , $J = 6.5$ Hz), 2.06 (s, $\text{N}(\text{CH}_3)_2$), 2.88 (s, OCH_3); $^{13}\text{C NMR } \delta$ 9.9, 21.2, 24.8, 25.0, 39.8, 51.2, 56.5, 78.7. Anal. Calcd for $\text{C}_{27}\text{H}_{35}\text{NOFeSe}$: C, 61.83; H, 6.68; N, 2.67. Found: C, 61.78; H, 6.89; N, 2.53.

***trans*-(*R,S*)-2-(1-(Dimethylamino)ethyl)ferrocenyl 2-Methoxycyclopentyl Selenide.** The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with cyclopentene and methanol. Major diastereomer: $^1\text{H NMR } \delta$ 1.32 (d, 3H, $J = 6.8$ Hz), 1.5–2.1 (m, 6H), 2.14 (s, 6H), 2.99 (s, 3H), 3.6–3.7 (m, 1H), 3.8–3.9 (m, 1H), 4.02 (q, 1H, $J = 6.8$ Hz), 4.08 (s, 5H), 4.2–4.4 (m, 3H); $^{13}\text{C-NMR } \delta$ 9.9, 23.7, 31.1, 31.2, 39.9, 45.8, 56.0, 56.8, 67.7, 67.9, 69.8, 71.8, 75.9, 89.1, 95.3. Minor diastereomer (distinct signals): $^1\text{H NMR } \delta$ 2.12 (s, $\text{N}(\text{CH}_3)_2$), 3.22 (s, OCH_3), 3.94 (q, $\text{CHN}(\text{CH}_3)_2$, $J = 6.8$ Hz); $^{13}\text{C NMR } \delta$ 10.3, 22.9, 31.3, 31.6, 40.0, 46.7, 56.4, 56.7, 87.7, 94.2. Anal. Calcd for $\text{C}_{20}\text{H}_{29}\text{NOFeSe}$: C, 55.30; H, 6.68; N, 3.23. Found: C, 55.06; H, 6.70; N, 3.13.

***erythro*-(*R,S*)-2-(1-(Dimethylamino)ethyl)ferrocenyl 3-Methoxy-2-butyl Selenide.** The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with *cis*-2-butene and methanol. Major diastereomer: $^1\text{H NMR } \delta$ 1.21 (d, 3H, $J = 6.1$ Hz), 1.23 (d, 3H, $J = 7.3$ Hz), 1.32 (d, 3H, $J = 6.8$ Hz), 2.13 (s, 6H), 3.17 (s, 3H), 3.3–

3.4 (m, 1H), 3.58 (dq, 1H, $J = 3.7, 7.3$ Hz), 4.02 (q, 1H, $J = 6.8$ Hz), 4.08 (s, 5H), 4.2–4.4 (m, 3H); ^{13}C NMR δ 9.8, 14.5, 16.2, 39.8, 41.3, 56.1, 56.8, 67.5, 67.8, 69.8, 71.5, 75.8, 79.5, 95.3. Minor diastereomer (distinct signals): ^1H NMR δ 1.19 (d, SeCHCH_3 , $J = 5.9$ Hz), 1.24 (d, $\text{CH}_3\text{OCHCH}_3$, $J = 6.9$ Hz), 1.31 (d, CHCH_3 , $J = 6.8$ Hz), 2.11 (s, $\text{N}(\text{CH}_3)_2$), 3.30 (s, OCH_3), 3.49 (dq, $J = 1.2, 6.1$ Hz), 3.99 (q, $\text{CHN}(\text{CH}_3)_2$, $J = 6.8$ Hz); ^{13}C NMR δ 10.2, 14.3, 16.9, 39.9, 43.8, 56.2, 56.7, 80.1, 94.8. Anal. Calcd for $\text{C}_{19}\text{H}_{29}\text{NOFeSe}$: C, 54.05; H, 6.92; N, 3.32. Found: C, 53.87; H, 6.94; N, 3.27.

threo-(R,S)-2-(1-(Dimethylamino)ethyl)ferrocenyl 3-Methoxy-2-butyl Selenide. The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with *trans*-2-butene and methanol. Major diastereomer: ^1H NMR δ 1.12 (d, 3H, $J = 6.5$ Hz), 1.28 (d, 3H, $J = 6.9$ Hz), 1.31 (d, 3H, $J = 6.8$ Hz), 2.11 (s, 6H), 3.26 (s, 3H), 3.3–3.4 (m, 2H), 3.99 (q, 1H, $J = 6.8$ Hz), 4.10 (s, 5H), 4.2–4.4 (m, 3H); ^{13}C NMR major diastereomer δ 9.6, 15.8, 16.7, 39.7, 44.5, 56.6, 56.7, 67.4, 67.8, 69.7, 71.7, 76.4, 79.2, 95.2. Minor diastereomer (distinct signals): ^1H NMR δ 1.18 (d, SeCHCH_3 , $J = 6.0$ Hz), 1.24 (d, $\text{CH}_3\text{OCHCH}_3$, $J = 7.1$ Hz), 2.10 (s, $\text{N}(\text{CH}_3)_2$), 3.39 (s, OCH_3); ^{13}C NMR δ 17.1, 39.8, 80.4. Anal. Calcd for $\text{C}_{19}\text{H}_{29}\text{NOFeSe}$: C, 54.05; H, 6.92; N, 3.32. Found: C, 54.13; H, 6.98; N, 3.27.

α -(R,S)-2-(((1-(Dimethylamino)ethyl)ferrocenyl)seleno)propiofenone (16). The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with (*Z*)-1-phenyl-1-(trimethylsilyloxy)-1-propene and methanol. Major diastereomer: ^1H NMR δ 1.25 (d, 3H, $J = 6.8$ Hz), 1.54 (d, 3H, $J = 6.8$ Hz), 2.21 (s, 6H), 3.51 (br s, 1H), 3.85 (t, 1H, $J = 2.5$ Hz), 3.93 (s, 5H), 4.05 (q, 1H, $J = 6.8$ Hz), 4.15 (br s, 1H), 5.10 (q, 1H, $J = 6.8$ Hz), 7.0–7.6 (m, 5H); ^{13}C NMR δ 8.1, 16.2, 39.8, 57.2, 67.6, 68.2, 69.6, 69.8, 71.5, 76.7, 96.0, 127.7, 129.1, 132.1, 136.8, 199.4. Anal. Calcd for $\text{C}_{23}\text{H}_{27}\text{NOFeSe}$: C, 58.99; H, 5.81; N, 2.99. Found: C, 58.72; H, 5.89; N, 3.07.

(R,S)-2-(1-(Dimethylamino)ethyl)ferrocenyl 2-Oxacyclohexyl Selenide (19). The title compound was obtained as a mixture of diastereomers by the reaction of Fa^*SeOTf with 1-(trimethylsilyloxy)-1-cyclohexene and methanol. Major diastereomer: ^1H NMR δ 1.27 (d, 3H, $J = 6.8$ Hz), 1.4–2.8 (m, 8H), 2.08 (s, 6H), 3.06 (dd, 1H, $J = 6.1, 12.4$ Hz), 3.98 (q, 1H, $J = 6.8$ Hz), 4.10 (s, 5H), 4.2–4.4 (m, 3H); ^{13}C NMR major diastereomer δ 9.0, 24.2, 26.5, 33.2, 37.5, 39.5, 52.6, 56.8, 67.6, 68.2, 69.7, 70.8, 75.7, 94.2, 209.5. Minor diastereomer (distinct signals): ^1H NMR δ 1.31 (d, CHCH_3 , $J = 6.6$ Hz), 2.10 (s, $\text{N}(\text{CH}_3)_2$), 3.10 (dd, COCHSe , $J = 6.1, 12.5$ Hz), 3.96 (q, $\text{CHN}(\text{CH}_3)_2$, $J = 6.8$ Hz); ^{13}C NMR δ 10.1, 22.3, 27.0, 34.7, 38.0, 39.8, 52.7, 56.9, 95.3, 208.2; IR (CHCl_3) 1693 cm^{-1} ($\text{C}=\text{O}$). Anal. Calcd for $\text{C}_{20}\text{H}_{27}\text{NOFeSe}$: C, 55.57; H, 6.30; N, 3.24. Found: C, 55.54; H, 6.30; N, 3.24.

Catalytic Asymmetric Conversion of Alkenes into Allylic Ethers. The following is the typical procedure for the

oxidation of alkenes with ammonium persulfate in the presence of $\text{Fa}^*\text{SeSeFa}^*$. In a 50-mL two-neck round bottom flask containing a magnetic stirrer bar were placed $\text{Fa}^*\text{SeSeFa}^*$ (67 mg, 0.10 mmol) and ammonium persulfate (0.46 g, 2.0 mmol). A methanol (15 mL) solution of methyl 4-phenyl-3-propenoate (0.18 g, 1.0 mmol) was added to the flask at room temperature, and the resulting homogeneous mixture was stirred at this temperature for 7 days. Water was added to the mixture, and the aqueous layer was extracted with three portions of diethyl ether (20 mL) and dried over MgSO_4 . Evaporation of the solvent left a pale yellow oil which was subjected to column chromatography on silica gel; hexane/diethyl ether (10/1) eluted *trans*-methyl 4-methoxy-4-phenyl-2-butenate (**23**). The optical purity of the product was determined by GC using a chiral capillary column (Astec G-TA, 30 m): ^1H NMR (CDCl_3) δ 3.32 (s, 3H), 3.72 (s, 3H), 4.78 (dd, 1H, $J = 1.7, 5.6$ Hz), 6.09 (dd, 1H, $J = 1.7, 15.6$ Hz), 6.96 (dd, 1H, $J = 5.6, 15.6$ Hz), 7.2–7.4 (m, 5H). ^{13}C NMR δ 51.4, 56.6, 82.3, 120.3, 126.9, 128.1, 128.6, 138.7, 147.4, 166.6. Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.89; H, 6.84. Found: C, 69.54; H, 6.30.

trans-Ethyl 4-ethoxy-4-phenyl-2-butenate (24): ^1H -NMR (CDCl_3) δ 1.22 (t, 3H, $J = 7.1$ Hz), 1.27 (t, 3H, $J = 7.1$ Hz), 3.47 (m, 2H), 4.17 (q, 2H, $J = 7.3$ Hz), 4.89 (dd, 1H, $J = 1.5, 5.3$ Hz), 6.08 (dd, 1H, $J = 1.5, 15.6$ Hz), 6.97 (dd, 1H, $J = 5.3, 15.6$ Hz), 7.2–7.4 (m, 5H); ^{13}C NMR δ 14.0, 15.1, 60.3, 64.3, 80.5, 120.6, 126.9, 128.0, 128.5, 139.3, 147.6, 166.2. Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3$: C, 71.77; H, 7.74. Found: C, 71.54; H, 7.30.

Methyl 4-methoxy-4-phenyl-3-butenate (26): ^1H NMR (CDCl_3) δ 3.34 (d, 2H, $J = 7.1$ Hz), 3.52 (s, 3H), 3.72 (s, 3H), 5.41 (t, 1H, $J = 7.1$ Hz), 7.2–7.5 (m, 5H); ^{13}C NMR δ 31.1, 51.8, 58.4, 105.2, 126.3, 128.3, 128.4, 135.0, 156.9, 172.5. Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.89; H, 6.84. Found: C, 69.54; H, 6.30.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of diferrocenyl diselenides, **2–4**, β -methoxyalkyl or arylferrocenyl selenides, and α -seleno ketones (49 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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