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Enantioface-differentiating protonation with chiral γ-hydroxyselenoxides

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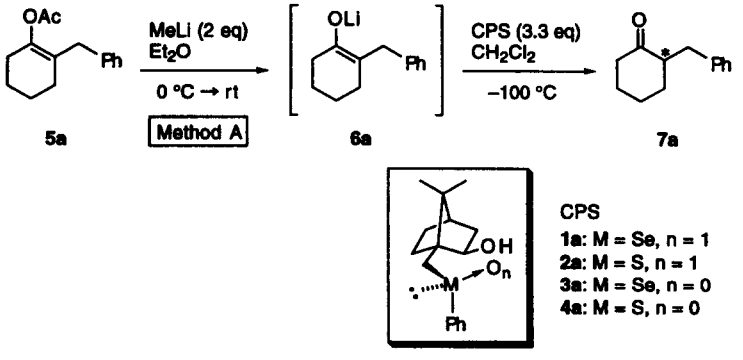
Abstract: Enantioface-differentiating protonation of achiral metal enolates of α-alkylcarbonyl compounds **7** has been developed using chiral γ-hydroxyselenoxides **1** as a proton source. Reaction of zinc bromide enolates of 2-benzyl- and 2-*n*-propylcyclohexanones with (S_{Se})-**1e** gave (*S*)-2-benzylcyclohexanone **7a** and (*R*)-2-*n*-propylcyclohexanone **7c** in high enantiomeric excess, respectively. Intramolecular hydrogen bonding of the selenoxide **1**, chelation effects between **1** and metal enolate, and 2-*exo*-hydroxy-10-bornyl-framework could contribute to this asymmetric induction. © 1997 Elsevier Science Ltd

Despite numerous studies on the application of optically active sulfoxides, few have investigated those of optically active selenoxides.[1] Such applications of chiral selenoxides have so far been limited to asymmetric [2,3]-sigmatropic rearrangements and asymmetric selenoxide eliminations.[2] The difficulty for studies of optically active selenoxides comes from their rapid inversion of configuration at the selenium atom. To avoid the racemization, an optically active selenoxide can be stabilized by steric protection[3] or intramolecular hydrogen bonding.[4] We have selected the 2-*exo*-hydroxy-10-bornyl group as a chiral ligand and developed a method for highly diastereoselective preparation of enantiomerically pure selenoxide **1** (Scheme 1).[5] Compound **1** is sterically protected by the bulky 10-bornyl group and configurationally stabilized by intramolecular hydrogen bonding[6] between the hydroxy group and seleninyl oxygen. Accordingly, the selenoxide **1** is stable at room temperature. Considering the characteristic γ-hydroxyselenoxide structure of **1**, the seleninyl group would chelate with a metal cation and the hydroxy group would act as a proton source. We report here that the γ-hydroxyselenoxides **1** can act as a chiral proton source (CPS) and the asymmetric protonation reaction with (S_{Se})-**1e** proceeded with up to 89% enantiomeric excess (ee).[7]



Scheme 1.

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Table 1. Enantioselective protonation of enolate **6a** with chiral chalcogen compounds **1a–4a**[a]

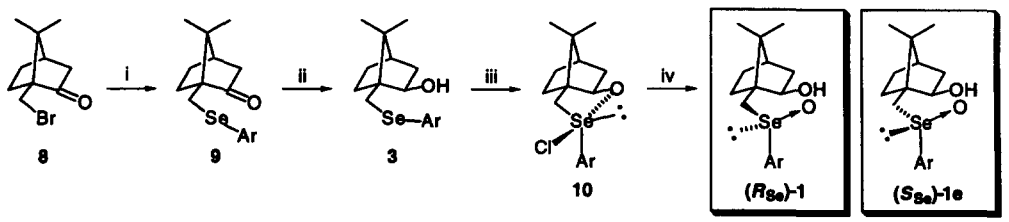
CPS			7a			
	M	n	yield (%)	$[\alpha]_D$	config.	ee (%)[b]
(R_{Se})-**1a**	Se	1	51[c]	+13.3	*R*	29
(R_S)-**2a**	S	1	35[c]	–5.8	*S*	13
3a	Se	0	53[c]	+2.7	*R*	6
4a	S	0	31[c]	–4.4	*S*	10

[a]Method A. [b]The ee was determined by HPLC analysis[8] and/or specific rotation.[9] [c]A mixture of unidentified compounds was also obtained.

Results and discussion

As a preliminary experiment, we examined enantioselective protonation of the lithium enolate of 2-benzylcyclohexanone **6a** with simple chalcogen compounds **1a–4a** as CPSs (Scheme 1 and Table 1). The reaction was carried out according to the method of Matsumoto and Ohta[8] (Method A): 2 equivalents of methyl lithium in Et_2O were added to a solution of the enolacetate **5a** in Et_2O at 0°C and the reaction mixture was stirred at room temperature to form **6a**. Then, 3.3 equivalents of a CPS in CH_2Cl_2 were added to the mixture at −100°C. After being stirred at −100°C for 10 min, the reaction was allowed to warm to room temperature. The reaction was quenched by addition of 0.2 M phosphate buffer (pH 6.8). Usual work-up and isolation gave 2-benzylcyclohexanone **7a**. The ee of the ketone **7a** was determined by HPLC analysis and/or calculated from the $[\alpha]_D$ value.[9] Asymmetric induction of the chalcogen compounds **2a–4a** was only 6–13% ee, whereas that of the selenoxide **1a** was 29% ee (Table 1). We thus set out to apply the selenoxide **1** as a CPS.

Enantiomerically pure selenoxides **1b–h** were synthesized as shown in Scheme 2. Reaction of bromocamphor **8** with lithium arylselenolate gave camphorselenides **9b–h** in 36–100% yield. Reduction of the carbonyl group of **9b–h** followed by the reaction of the resulting **3b–h** with *tert*-butyl hypochlorite gave chloroselenuranes **10b–h**. Treatment of **10b–h** with sodium hydrogen carbonate afforded diastereoselectively (R_{Se})-selenoxides **1b–h** in 7–46% yield from camphorselenides **9b–h**. The absolute configuration of stereogenic selenium centers in (R_{Se})-**1b–h** was determined by comparison of their spectral data with those of (R_{Se})-**1a**.[5]



b: Ar = 2-Py
c: Ar = 4-FC_6H_4
d: Ar = 4-MeC_6H_4
e: Ar = 4-$MeOC_6H_4$
f: Ar = 2,4-$(MeO)_2C_6H_3$
g: Ar = 4-MeO-2-MeC_6H_3
h: Ar = 2-MeC_6H_4

Scheme 2. *Reagent and conditions*: (i) ArSeLi, THF, reflux; (ii) $LiAlH_4$, Et_2O, −20°C; (iii) ^tBuOCl, MeOH-CH_2Cl_2, 0°C; (iv) aq. $NaHCO_3$.

Unexpectedly, we obtained (S_{Se})-selenoxide (S_{Se})-**1e** in 12% yield by treatment of enantiomerically pure (R_{Se})-**1e** with acetone at room temperature. The absolute configuration at the selenium atom in

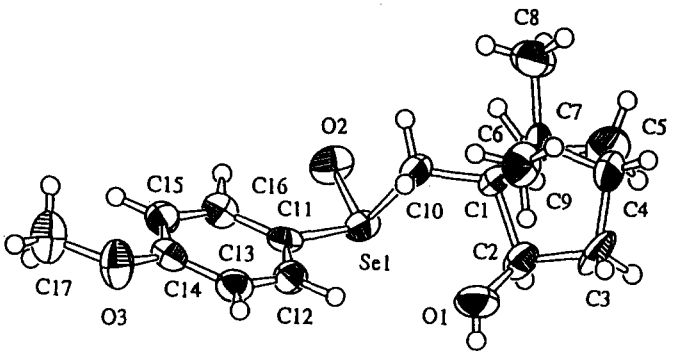


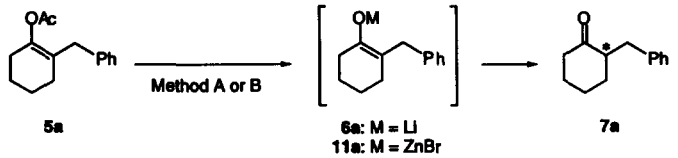
Figure 1. Perspective structure of (S_{Se})-**1e**.

Table 2. Mp and spectral data of (R_{Se})-**1a**,[5] (R_{Se})-**1e** and (S_{Se})-**1e**

	(R_{Se})-**1a**	(R_{Se})-**1e**	(S_{Se})-**1e**
mp, °C	133–135	129–130	127
$[\alpha]_D$	+134.0	+103.5	−174.8
CD, nm ([θ] x10^4)	251 (+5.90)	253 (+9.57)	254 (−8.20)
^{77}Se NMR, δ	852	851	869

(S_{Se})-**1e** is unequivocally established by X-ray crystallography (Figure 1). (S_{Se})-**1e** is stable at room temperature. Some spectral data of (R_{Se})-**1a**,[5] (R_{Se})- and (S_{Se})-**1e** are shown in Table 2.

Using these selenoxides, we studied substituent effects on the enantioface-differentiating protonation (Scheme 3 and Table 3). All (R_{Se})-selenoxides **1** were quantitatively recovered without inversion of configuration. When the electron-withdrawing 2-pyridyl or 4-fluorophenyl group is substituted instead of the phenyl group, the ee of **7a** decreased. Next, we examined the selenoxides which have an electron-donating group on the aryl ring. In the case of the 4-tolyl or 4-anisyl group, the absolute configuration of the obtained enantiomer of **7a** turns to *S* and the ee of **7a** went up to 51% or 64%. Consequently, the enantioselectivity of this reaction has been improved by introduction of the electron-donating group to the aryl ring of a CPS.



Scheme 3. *Reagent and conditions*: Method A: (i) 2 eq. MeLi, Et_2O, 0°C then rt; (ii) 3.3 eq. **1**, CH_2Cl_2, −100°C. Method B: (i) 4 eq. MeLi, Et_2O, 0°C; (ii) 1.5 eq. $ZnBr_2$, 0°C then rt, (iii) 4.3 eq. **1**, CH_2Cl_2, −100°C.

We expected that introduction of an additional electron-donating group to the 4-anisyl ring would have more effect on the enantioselectivity. Contrary to our expectation, introduction of the additional 2-methoxy or 2-methyl group resulted in a change of the preferred configuration to *R* and a decrease of the ee (Scheme 3 and Table 4). In the case of the 2-tolyl group, the preferred enantiomer of **7a** turns to *S* and the ee was determined to be 21%. This may be due to steric hindrance of the 2-substituent in the transition state of the protonation.

Next, we searched for optimum reaction conditions (solvent, reaction temperature and equivalents

Table 3. Enantioselective protonation of enolate **6a** with (R_{Se})-selenoxides (R_{Se})-**1a–e**[a]

CPS		7a			
	Ar	yield (%)	$[\alpha]_D$	config.	ee (%)[b]
(R_{Se})-**1a**	Ph	51[c]	+13.3	*R*	29
(R_{Se})-**1b**	2-Py	76	+3.3	*R*	7
(R_{Se})-**1c**	4-FC_6H_4	68[c]	-0.2	—	0
(R_{Se})-**1d**	4-MeC_6H_4	70	-23.9	*S*	51
(R_{Se})-**1e**	4-$MeOC_6H_4$	47[c]	-29.9	*S*	64

[a]Method A. [b]The ee was determined by HPLC analysis[8] and/or specific rotation.[9] [c]A mixture of unidentified compounds was also obtained.

Table 4. Enantioselective protonation of enolate **6a** with (R_{Se})-Selenoxides (R_{Se})-**1e–h**[a]

CPS		7a			
	Ar	yield (%)	$[\alpha]_D$	config.	ee (%)[b]
(R_{Se})-**1e**	4-$MeOC_6H_4$	47[c]	–29.9	*S*	64
(R_{Se})-**1f**	2,4-$(MeO)_2C_6H_3$	72	+12.3	*R*	26
(R_{Se})-**1g**	4-MeO-2-MeC_6H_3	51[c]	+6.2	*R*	13
(R_{Se})-**1h**	2-MeC_6H_4	56[c]	–9.8	*S*	21

[a]Method A. [b]The ee was determined by HPLC analysis[8] and/or specific rotation.[9] [c]A mixture of unidentified compounds was also obtained.

Table 5. Examination of reaction conditions[a]

solvent	reaction temp. (°C)	(R_{Se})-**1e** equiv.	7a			
			yield(%)	$[\alpha]_D$	config.	ee (%)[b]
CH_2Cl_2	–100	3.3	47[c]	–29.9	*S*	64
THF	–100	3.3	61[c]	+4.4	*R*	9
toluene	–100	3.3	60[c]	–4.3	*S*	9
CH_2Cl_2	–20	3.3	45[c]	–1.6	*S*	3
CH_2Cl_2	–100	1.1	29[c]	–5.0	*S*	11

[a]Method A. [b]The ee was determined by HPLC analysis[8] and/or specific rotation.[9] [c]A mixture of unidentified compounds was also obtained.

of the CPS) using (R_{Se})-**1e** and lithium enolate **6a**. The best result was obtained when the reaction was carried out in CH_2Cl_2 at −100°C with 3.3 equivalents of the CPS (Scheme 3 and Table 5).

To examine the influence of the configuration of the seleninyl group on enantioface-differentiation, we performed this reaction with (S_{Se})-selenoxide (S_{Se})-**1e** (Scheme 3 and Table 6). Unexpectedly, this reaction also gave (*S*)-**7a** and showed about the same degree of enantioface-differentiation. That is, not only the chirality of the seleninyl group but also the 2-*exo*-hydroxy-10-bornyl group influences this asymmetric induction. In the case of (R_{Se})-**1e**, changing lithium of the enolate to zinc bromide,[10] the chemical yield of **7a** was improved to be 82%. The reaction with (S_{Se})-**1e** and the zinc bromide enolate **11a** worked well. Both ee and chemical yield went up to be 89% and 81%, respectively.

A typical procedure of Method B was as follows: 4 equivalents of MeLi in Et_2O were added to a solution of enolacetate of 2-benzylcyclohexanone **5a** in Et_2O at 0°C and the reaction mixture was stirred at 0°C for 5 min to form lithium enolate **6a**. 1.5 equivalents of $ZnBr_2$ were added and the

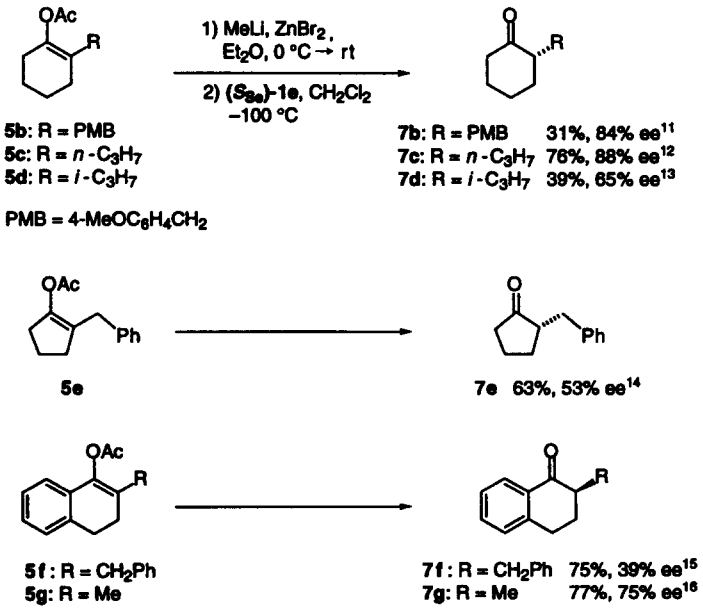
Table 6. Enantioselective protonation of enolate **6a** or **11a** with (R_{Se})- or (S_{Se})-selenoxide (R_{Se})- or (S_{Se})-**1e**

CPA	method	**7a**		
		yield (%)	config.	ee (%)[a]
(R_{Se})-**1e**	A	47[e]	*S*	64
(S_{Se})-**1e**[b]	A	35[e]	*S*	62
(R_{Se})-**1e**[c]	B	82	*S*	62
(S_{Se})-**1e**[d]	B	81	*S*	89

[a]The ee was determined by specific rotation[9] and HPLC analysis.[8] [b]R_{Se} : S_{Se} = 5 : 95. [c]R_{Se} : S_{Se} = 95 : 5. [d]R_{Se} : S_{Se} = 3 : 97. [e]A mixture of unidentified compounds was also obtained.

whole mixture was stirred at 0°C for 5 min then at room temperature for 20 min to yield zinc bromide enolate **11a**. To this was added a solution of 4.3 equivalents of a CPS in CH_2Cl_2 at −100°C. After 10 min stirring at −100°C, the reaction was allowed to warm to room temperature. Similar work-up to Method A and the purification gave 2-benzylcyclohexanone **7a**.

Next, we applied this enantioselective protonation to other enolacetates **5b–g** under the optimum reaction conditions with (S_{Se})-**1e** (Scheme 4). The absolute configuration of **7b–g** was determined by comparing the sign of specific rotation with reported ones.[11–16] The ee was determined by HPLC analysis for **7b**, **7c** and **7e–g** or specific rotation[13] for **7d**. Good results were obtained in the cases of the enolacetates **5b**, **5c** and **5g**. The ee and chemical yield of (*R*)-2-*n*-propylcyclohexanone (***R***)-**7c** were 88% and 76%, respectively.



Scheme 4.

The exact mechanism of the reaction remains uncertain. We suggest the following two reasons for this high degree of enantioface-differentiation: 1) intramolecular hydrogen bonding of the selenoxides **1** and chelation effects between **1** and metal enolate, and 2) steric effect of 2-*exo*-hydroxy-10-bornyl-framework.

Intramolecular hydrogen bonding between the hydroxy group and seleninyl-oxygen of **1** as well as chelation between **1** and the metal enolate probably make the transition state rigid as shown in

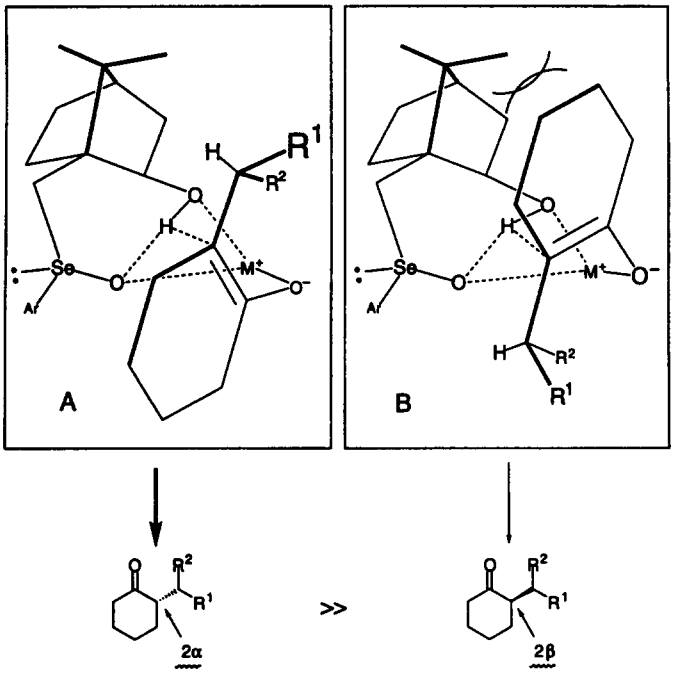
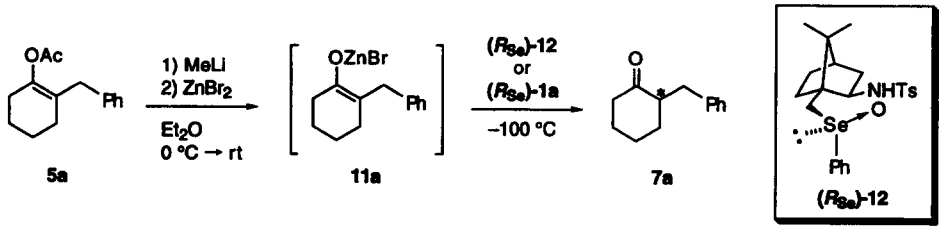


Figure 2.

Figure 2. X-Ray analysis showed that an intramolecular hydrogen bond is not present in crystallline states of (S_{Se})-**1e** (Figure 1). However, its presence was supported by a 3270 cm^{-1} absorption of the FT-IR spectrum of a highly dilute (0.005 M) $CHCl_3$ solution of (S_{Se})-**1e**. A 3270 cm^{-1} absorption was also detected in FT-IR spectrum of a 0.005 M $CHCl_3$ solution of (R_{se})-**1e**. As a result, attack of the proton of (S_{Se})-**1e** to C-2 of **11a** from its *si*-face (transition state B) is unfavored because of steric repulsion between the methyl group of the bornyl moiety and the cyclohexene ring of the enolate. On the other hand, *re*-face attack (transition state A) is free from such steric interaction, resulting in the preferential formation of (*S*)-**7a**. This mechanism was also supported by the fact that the reaction with (S_{Se})-**1e** and (R_{Se})-**1e** gave the same product, (*S*)-**7a**.

To support the effect of hydrogen bonding, we carried out the protonation reaction of zinc bromide enolate **11a** with (R_{Se})-4-toluenesulfonamide (R_{Se})-**12**[17] (Scheme 5 and Table 7). By IR spectra, intramolecular hydrogen bonding of the NH group of (R_{Se})-**12** was shown to be weaker than that of the OH group.[18] The ee decreased to 4%.



Scheme 5.

In conclusion, we have developed the asymmetric protonation with stable chiral γ-hydroxyselenoxides **1**. Recently, much attention has been paid to an enantioselective protonation

Table 7. Enantioselective protonation of enolate **11a** with (R_{Se})-**1a** or (R_{Se})-**12**

	7a		
CPS	yield (%)	config.	ee (%)[b]
(R_{Se})-**1e**	82	*S*	62
(R_{Se})-**1a**	57[c]	*S*	40
(R_{Se})-**12**	70	*R*	4

[a]Method B. [b]The ee was determined by HPLC analysis.[8] [c]A mixture of unidentified compounds was also obtained.

and there have been some reports which are successful for the asymmetric induction of simple enolates.[8,19] Our present method would provide a new entry to this research field.

Experimental

Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. Microanalyses were performed by Microanalysis Center of Toyama Medical & Pharmaceutical University. Spectroscopic measurements were carried out with the following instruments: optical rotations, JASCO DIP-140 digital polarimeter; circular dichroism spectra (CD), JASCO J-500 C spectrometer; IR, Perkin Elmer 1600 Series FTIR; mass spectra (MS) and high resolution mass spectra (HRMS), JEOL JMS D-200; ^{1}H NMR, Varian Gemini 300 (300 MHz) and Varian Unity 500 (500 MHz) for solutions in $CDCl_3$ with Me_4Si as an internal standard; ^{13}C NMR, Varian Gemini 300 (75 MHz) for solutions in $CDCl_3$ with Me_4Si as an internal standard. The chemical shifts from Me_4Si were calculated based on $CDCl_3$; ^{77}Se NMR, Varian Unity 500 (95 MHz) for solutions in $CDCl_3$ with $(MeSe)_2$ as an external standard. The chemical shifts from Me_2Se were calculated based on $(MeSe)_2$.[20] Column chromatography, flash column chromatography and preparative TLC (PLC) were performed on Kieselgel 60 (Merck, Art. 7734, Art. 9385 and Art. 7748, respectively).

Typical procedure for preparation of (1S)-10-(arylselenenyl)camphor **9**

To a solution of 4-bromoanisole (5.61 g, 30.0 mmol) in dry THF (60 mL) was added ^{t}BuLi (1.7 M in pentane, 35.3 mL, 60.0 mmol) at −78°C under an Ar atmosphere and the whole mixture was stirred at the same temperature for 2 h. Se powder (2.37 g, 30.0 mmol) was added to the mixture and the reaction temperature was allowed to rise to room temperature with stirring. After all Se powder was dissolved, 10-bromocamphor[21] (4.62 g, 20.0 mmol) was added in one portion to the mixture and the whole mixture was refluxed for 12 h. After the solvent was evaporated, Et_2O (150 mL) and brine (80 mL) were added to the residue. The organic layer was separated and the aqueous layer was extracted with Et_2O (100 mL×2). The combined organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was subjected to column chromatography (hexane/Et_2O 15:1) to give the selenide **9e** (6.48 g, 96%). Selenides **9b–d** and **9f–h** were prepared similarly (36–100%).

(1S)-10-[(4-Methoxyphenyl)selenenyl]camphor **9e**

Pale yellow oil: $[\alpha]_D^{26}$ −56.2 (*c* 1.27, MeOH); IR (neat) 2959, 1738, 1590, 1490, 1283, 1245, 1174, 1130 cm^{-1}; ^{1}H NMR δ: 0.89 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 1.35–1.41 (m, 1H), 1.66–1.73 (m, 1H), 1.86–1.99 (m, 3H), 2.08–2.11 (m, 1H), 2.38 (ddd, *J*=18.1, 4.9, and 2.2 Hz, 1H, 3-*exo*-H), 2.68 (d, *J*=12.6 Hz, 1H, 10-H), 3.20 (d, *J*=12.1 Hz, 1H, 10-H), 3.79 (s, 3H, OCH_3), 6.78–6.83 (m, 2H, ArH×2), 7.48–7.52 (m, 2H, ArH×2); ^{13}C NMR δ: 20.1 (CH_3), 20.3 (CH_3), 26.9 (CH_2), 27.0 (CH_2), 28.0 (CH_2), 43.3 (CH_2), 43.7 (CH), 48.3 (C), 55.4 (CH_3), 61.5 (C), 114.9 (CH×2), 122.7 (C), 135.5 (CH×2), 159.3 (C), 217.5 (C); MS *m/z*: 338 (M^+) (^{80}Se); Anal. Calcd for $C_{17}H_{22}O_2Se$: C, 60.53; H, 6.57. Found: C, 60.51; H, 6.68.

(1S)-10-[(2-Pyridyl)selenenyl]camphor ***9b***

Pale yellow oil: yield 77%: $[\alpha]_D^{26}$ −98.5 (*c* 1.13, MeOH); IR (neat) 2960, 1740, 1452, 1109 cm^{-1}; ^1H NMR δ: 0.94 (s, 3H, CH_3), 1.10 (s, 3H, CH_3), 1.32–1.39 (m, 1H), 1.63–1.70 (m, 1H), 1.86–1.99 (m, 3H), 2.12–2.14 (m, 1H), 2.41 (ddd, *J*=18.1, 5.0, and 2.2 Hz, 1H, 3-*exo*-H), 3.25 (d, *J*=12.6 Hz, 1H, 10-H), 3.49 (d, *J*=12.1 Hz, 1H, 10-H), 6.99 (ddd, *J*=7.1, 4.9, and 1.1 Hz, 1H, ArH), 7.31–7.34 (m, 1H, ArH), 7.38–7.44 (m, 1H, ArH), 8.43 (ddd, *J*=4.9, 1.6, and 1.1 Hz, 1H, ArH); ^{13}C NMR δ: 20.0 (CH_3), 20.3 (CH_3), 21.3 (CH_2), 26.8 (CH_2), 27.8 (CH_2), 43.3 (CH_2), 43.9 (CH), 48.4 (C), 61.5 (C), 120.2 (CH), 125.5 (CH), 135.8 (CH), 149.9 (CH), 156.2 (C), 218.0 (C); MS *m/z*: 309 (M^+) (^{80}Se); HRMS found M^+ 309.0645, $C_{15}H_{19}NO^{80}Se$ requires M^+ 309.0630.

(1S)-10-[(4-Fluorophenyl)selenenyl]camphor ***9c***

Pale yellow oil: yield 100%: $[\alpha]_D^{26}$ −41.5 (*c* 1.20, MeOH); IR (neat) 2959, 1741, 1487, 1221 cm^{-1}; ^1H NMR δ: 0.90 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.36–1.43 (m, 1H), 1.66–1.74 (m, 1H), 1.88–2.01 (m, 3H), 2.10–2.13 (m, 1H), 2.40 (ddd, *J*=18.7, 4.9, and 2.2 Hz, 1H, 3-*exo*-H), 2.71 (d, *J*=12.1 Hz, 1H, 10-H), 3.23 (d, *J*=12.1 Hz, 1H, 10-H), 6.93–6.99 (m, 2H, ArH×2), 7.51–7.55 (m, 2H, ArH×2); ^{13}C NMR δ: 20.1 (CH_3), 20.3 (CH_3), 26.7 (CH_2), 26.9 (CH_2), 28.0 (CH_2), 43.3 (CH_2), 43.6 (CH), 48.3 (C), 61.5 (C), 116.3 (d, $J_{C\text{-}F}$=21.8 Hz, CH×2), 127.1 (d, $J_{C\text{-}F}$=3.4 Hz, C) 135.2 (d, $J_{C\text{-}F}$=6.9 Hz, CH×2), 162.3 (d, $J_{C\text{-}F}$=247.4 Hz,CF), 217.5 (C); MS *m/z*: 326 (M^+) (^{80}Se); HRMS found M^+ 326.0577, $C_{16}H_{19}FO^{80}Se$ requires M^+ 326.0584.

(1S)-10-[(4-Methylphenyl)selenenyl]camphor ***9d***

Pale yellow oil: yield 100%: $[\alpha]_D^{26}$ −46.0 (*c* 1.25, MeOH); IR (neat) 2959, 1741, 1489, 1040, 803 cm^{-1}; ^1H NMR δ: 0.90 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.35–1.41 (m, 1H), 1.66–1.73 (m, 1H), 1.86–1.99 (m, 3H), 2.09–2.12 (m, 1H), 2.32 (s, 3H, CH_3), 2.39 (ddd, *J*=18.1, 4.9, and 2.2 Hz, 1H, 3-*exo*-H), 2.73 (d, *J*=12.1 Hz, 1H, 10-H), 3.23 (d, *J*=12.1 Hz, 1H, 10-H), 7.07 (d, *J*=7.7 Hz, 2H, ArH×2), 7.43–7.45 (m, 2H, ArH×2); ^{13}C NMR δ: 20.1 (CH_3), 20.3 (CH_3), 21.2 (CH_3), 25.9 (CH_2), 27.0 (CH_2), 27.9 (CH_2), 43.3 (CH_2), 43.6 (CH), 48.3 (C), 61.5 (C), 128.9 (C), 130.0 (CH×2), 133.1 (CH×2), 136.8 (C), 217.5 (C); MS *m/z*: 322 (M^+) (^{80}Se); HRMS found M^+ 322.0816, $C_{17}H_{22}O^{80}Se$ requires M^+ 322.0834.

(1S)-10-[(2,4-Dimethoxyphenyl)selenenyl]camphor ***9f***

Yellow oil: yield 60%: $[\alpha]_D^{26}$ −66.0 (*c* 1.05, MeOH); IR (neat) 2958, 1739, 1592, 1463, 1301, 1209, 1160, 1065, 1033 cm^{-1}; ^1H NMR δ: 0.90 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.33–1.40 (m, 1H), 1.63–1.71 (m, 1H), 1.88 (d, *J*=18.1 Hz, 1H, 3-*endo*-H), 1.92–2.04 (m, 2H), 2.07–2.10 (m, 1H), 2.38 (ddd, *J*=18.1, 4.9, and 2.2 Hz, 1H, 3-*exo*-H), 2.72 (d, *J*=12.1 Hz, 1H, 10-H), 3.12 (d, *J*=12.1 Hz, 1H, 10-H), 3.79 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.41–6.45 (m, 2H, ArH×2), 7.39–7.42 (m, 1H, ArH); ^{13}C NMR δ: 20.3 (CH_3×2), 23.6 (CH_2), 27.0 (CH_2), 27.7 (CH_2), 43.3 (CH_2), 43.6 (CH), 48.3 (C), 55.6 (CH_3), 56.0 (CH_3), 61.4 (C), 99.0 (CH), 105.3 (CH), 111.5 (C), 134.6 (CH), 159.7 (C), 160.8 (C), 217.7 (C); MS *m/z*: 368 (M^+) (^{80}Se); Anal. Calcd for $C_{18}H_{24}O_3Se$: C, 58.86; H, 6.58. Found: C, 58.84; H, 6.69.

(1S)-10-[(4-Methoxy-2-methylphenyl)selenenyl]camphor ***9g***

Pale yellow oil: yield 100%: $[\alpha]_D^{30}$ −49.1 (*c* 1.44, $CHCl_3$); IR (neat) 2958, 1740, 1592, 1477, 1292, 1238, 1162, 1060 cm^{-1}; ^1H NMR δ: 0.90 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 1.36–1.42 (m, 1H), 1.69–1.75 (m, 1H), 1.89 (d, *J*=18.1 Hz, 1H, 3-*endo*-H), 1.96–2.00 (m, 2H), 2.10–2.12 (m, 1H), 2.39 (ddd, *J*=18.1, 4.9, and 2.2 Hz, 1H, 3-*exo*-H), 2.47 (s, 3H, CH_3), 2.59 (d, *J*=12.1 Hz, 1H, 10-H), 3.13 (d, *J*=12.1 Hz, 1H, 10-H), 3.78 (s, 3H, OCH_3), 6.66 (dd, *J*=8.8 and 2.7 Hz, 1H, ArH), 6.77 (d, *J*=2.7 Hz, 1H, ArH), 7.49 (d, *J*=8.8 Hz, 1H, ArH); ^{13}C NMR δ: 20.2 (CH_3), 20.3 (CH_3), 23.3 (CH_3), 25.7 (CH_2), 27.0 (CH_2), 27.8 (CH_2), 43.3 (CH_2), 43.6 (CH), 48.3 (C), 55.3 (CH_3), 61.4 (C), 112.1 (CH),

115.8 (CH), 123.6 (C), 135.7 (CH), 142.1 (C), 159.3 (C), 217.6 (C); MS *m/z*: 352 (M^+) (^{80}Se); HRMS found M^+ 352.0955, $C_{18}H_{24}O_2{}^{80}Se$ requires M^+ 352.0940.

(1S)-10-[(2-Methylphenyl)selenenyl]camphor **9h**

Yellow oil: yield 36%: $[\alpha]_D{}^{26}$ −51.1 (*c* 0.64, MeOH); IR (neat) 2958, 1741, 1463, 1040, 746 cm^{-1}; ^1H NMR δ: 0.93 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.36–1.42 (m, 1H), 1.66–1.73 (m, 1H), 1.91 (d, *J*=18.1 Hz, 1H, 3-*endo*-H), 1.97–2.05 (m, 2H), 2.10–2.12 (m, 1H), 2.37–2.44 (m, 1H), 2.42 (s, 3H, CH_3), 2.74 (d, *J*=11.5 Hz, 1H, 10-H), 3.21 (d, *J*=12.1 Hz, 1H, 10-H), 7.01–7.16 (m, 3H, ArH×3), 7.46–7.49 (m, 1H, ArH); ^{13}C NMR δ: 20.28 (CH_3), 20.31 (CH_3), 22.6 (CH_3), 24.2 (CH_2), 27.3 (CH_2), 27.9 (CH_2), 43.3 (CH_2), 43.7 (CH), 48.4 (C), 61.4 (C), 126.66 (CH), 126.70 (CH), 126.9 (C), 130.0 (CH), 131.6 (CH), 139.4 (C), 217.6 (C); MS *m/z*: 322 (M^+) (^{80}Se); HRMS found M^+ 322.0841, $C_{17}H_{22}O^{80}Se$ requires M^+ 322.0834.

*Typical procedure for preparation of (1S, R_{Se})-10-(arylseleninyl)-2-*exo*-borneol* **1**

To a suspension of $LiAlH_4$ (541 mg, 14.2 mmol) in dry Et_2O (60 mL) was added a solution of selenide **9e** (4.00 g, 11.9 mmol) in dry Et_2O (15 mL) at −20°C under an Ar atmosphere in the period of 20 min. The whole mixture was stirred at −20°C for 40 min. Saturated aqueous NH_4Cl (16 mL) was added to the mixture and the whole mixture was stirred for 10 min. After removal of insoluble matter through a Celite pad, the organic layer was separated. The aqueous layer was extracted with Et_2O (50 mL×3). The combined organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was subjected to column chromatography (hexane/Et_2O 18:1) to give the hydroxyselenide **3e** (3.57 g) as an yellow oil.

To a solution of **3e** (1.45 g, 4.3 mmol) in CH_2Cl_2/MeOH (2:1, 8 mL) was added ^{t}BuOCl (0.488 mL, 4.3 mmol) at 0°C. After 5 min stirring at 0°C, the mixture was diluted with CH_2Cl_2 (8 mL) and saturated aqueous $NaHCO_3$ (8 mL). After 5 min stirring, the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (10 mL×3) and the combined organic phase was dried over $MgSO_4$. The residual oil obtained after evaporation of the solvent was purified by flash column chromatography (benzene/AcOEt/MeOH 7:3:0.5) followed by recrystallization from CH_2Cl_2/hexane to give the selenoxide **1e** (597 mg, 35% from **9e**). Selenoxides **1b–d** and **1f–h** were prepared similarly (7–46% from **9**).

*(1S, R_{Se})-10-[(4-Methoxyphenyl)seleninyl]-2-*exo*-borneol (R_{se})-1e*

Colorless prisms: mp 129–130°C (CH_2Cl_2/hexane); $[\alpha]_D{}^{28}$+103.5 (*c* 1.07, $CHCl_3$); CD ($CHCl_3$) 253 nm ($[\theta]$+9.57×10^4); IR (KBr) 3135, 2938, 1591, 1493, 1301, 1248, 1077, 1028 cm^{-1}; ^1H NMR δ: 0.79 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.17–1.25 (m, 1H), 1.55–1.95 (m, 6H), 2.61 (d, *J*=12.1 Hz, 1H, 10-H), 3.34 (d, *J*=12.1 Hz, 1H, 10-H), 3.86 (s, 3H, OCH_3), 4.14 (ddd, *J*=7.7, 3.8, and 3.8 Hz, 1H, 2-H), 5.38 (d, *J*=3.3 Hz, 1H, OH), 7.07 (d, *J*=8.8 Hz, 2H, ArH×2), 7.66 (d, *J*=8.8 Hz, 2H, ArH×2); ^{77}Se NMR δ: 850.52; MS *m/z*: 338 (M^+−18) (^{80}Se); Anal. Calcd for $C_{17}H_{24}O_3Se$: C, 57.47; H, 6.80. Found: C, 57.44; H, 6.71.

*(1S,R_{Se})-10-[(2-Pyridyl)seleninyl]-2-*exo*-borneol (R_{se})-1b*

Colorless prisms: yield 46% from **9b**: mp 127–128°C (CH_2Cl_2/hexane); $[\alpha]_D{}^{28}$+133.1 (*c* 1.08, $CHCl_3$); IR (KBr) 3173, 2950, 1573, 1559, 1417, 1079 cm^{-1}; ^1H NMR δ: 0.83 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 1.19–1.26 (m, 1H), 1.52–1.59 (m, 1H), 1.69–1.89 (m, 5H), 3.03 (d, *J*=12.1 Hz, 1H, 10-H), 3.33 (d, *J*=11.5 Hz, 1H, 10-H), 4.11–4.16 (m, 1H, 2-H), 5.23 (d, *J*=3.3 Hz, 1H, OH), 7.45 (dd, *J*=7.7 and 4.9 Hz, 1H, ArH), 7.96 (dt, *J*=7.7 and 1.6 Hz, 1H, ArH), 8.15 (d, *J*=8.2 Hz, 1H, ArH), 8.63 (d, *J*=4.9 Hz, 1H, ArH); MS *m/z*: 327 (M^+) (^{80}Se); Anal. Calcd for $C_{15}H_{21}NO_2Se$: C, 55.22; H, 6.48; N, 4.29. Found: C, 55.05; H, 6.44; N, 4.10.

*(1S,R$_{Se}$)-10-[(4-Fluorophenyl)seleninyl]-2-*exo*-borneol (**R$_{se}$**)-**1c***

Colorless needles: yield 7% from **9c**: mp 137–138°C (benzene); $[\alpha]_D^{28}$+117.6 (*c* 1.40, $CHCl_3$); IR (KBr) 3241, 2950, 1585, 1489, 1078 cm^{-1}; ^1H NMR δ: 0.81 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.19–1.27 (m, 1H), 1.53–1.91 (m, 6H), 2.65 (d, *J*=12.1 Hz, 1H, 10-H), 3.35 (d, *J*=12.1 Hz, 1H, 10-H), 4.12–4.17 (m, 1H, 2-H), 5.24 (d, *J*=3.3 Hz, 1H, OH), 7.24–7.31 (m, 2H, ArH×2), 7.72–7.78 (m, 2H, ArH×2); ^{77}Se NMR δ: 852.98; MS *m/z*: 344 (M^+) (^{80}Se); Anal. Calcd for $C_{16}H_{21}FO_2Se$: C, 55.98; H, 6.16. Found: C, 55.90; H, 6.08.

*(1S,R$_{Se}$)-10-[(4-Methylphenyl)seleninyl]-2-*exo*-borneol (**R$_{se}$**)-**1d***

Colorless columns: yield 19% from **9d**: mp 127°C (CH_2Cl_2/Et_2O); $[\alpha]_D^{28}$+125.7 (*c* 1.00, $CHCl_3$); IR (KBr) 3284, 2951, 2874, 1079, 1050 cm^{-1}; ^1H NMR δ: 0.80 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.18–1.27 (m, 1H), 1.53–1.71 (m, 2H), 1.75–1.90 (m, 4H), 2.44 (s, 3H, CH_3), 2.62 (d, *J*=12.1 Hz, 1H, 10-H), 3.35 (d, *J*=12.1 Hz, 1H, 10-H), 4.12–4.18 (m, 1H, 2-H), 5.37 (d, *J*=3.3 Hz, 1H, OH), 7.38 (d, *J*=8.2 Hz, 2H, ArH), 7.63 (d, *J*=8.2 Hz, 2H, ArH); ^{13}C NMR δ: 20.1 (CH_3), 20.6 (CH_3), 21.6 (CH_3), 27.4 (CH_2), 32.0 (CH_2), 38.6 (CH_2), 45.6 (CH), 48.7 (C), 52.3 (C), 57.0 (CH_2), 77.5 (CH), 125.9 (CH×2), 130.7 (CH×2), 137.2 (C), 142.2 (C); ^{77}Se NMR δ: 850.58; MS *m/z*: 340 (M^+) (^{80}Se); Anal. Calcd for $C_{17}H_{24}O_2Se$: C, 60.18; H, 7.13. Found: C, 60.09; H, 7.17.

*(1S,R$_{Se}$)-10-[(2,4-Dimethoxyphenyl)seleninyl]-2-*exo*-borneol (**R$_{se}$**)-**1f***

Colorless columns: yield 22% from **9f**: mp 137–138°C (Et_2O/hexane); $[\alpha]_D^{28}$+239.5 (*c* 0.51, $CHCl_3$); IR (KBr) 3202, 2949, 1585, 1289, 1208, 1026 cm^{-1}; ^1H NMR δ: 0.81 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 1.19–1.26 (m, 1H), 1.57–1.74 (m, 2H), 1.78–1.87 (m, 4H), 2.95 (d, *J*=12.1 Hz, 1H, 10-H), 3.14 (d, *J*=11.5 Hz, 1H, 10-H), 3.86 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 4.13–4.19 (m, 1H, 2-H), 5.44 (d, *J*=3.3 Hz, 1H, OH), 6.50 (d, *J*=2.8 Hz, 1H, ArH), 6.74 (dd, *J*=8.8 and 2.2 Hz, 1H, ArH), 7.79 (d, *J*=8.8 Hz, 1H, ArH); MS *m/z*: 368 (M^+-18) (^{80}Se); Anal. Calcd for $C_{18}H_{26}O_4Se$: C, 56.10; H, 6.80. Found: C, 55.84; H, 6.60.

*(1S, R$_{Se}$)-10-[(4-Methoxy-2-methylphenyl)seleninyl]-2-*exo*-borneol (**R$_{se}$**)-**1g***

Colorless needles: yield 13% from **9g**: mp 123°C (Et_2O); $[\alpha]_D^{30}$+139.0 (*c* 0.68, $CHCl_3$); IR (KBr) 3216, 2946, 1593, 1464, 1317, 1245, 1078, 1046 cm^{-1}; ^1H NMR δ: 0.80 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.18–1.28 (m, 1H), 1.55–1.92 (m, 6H), 2.41 (s, 3H, CH_3), 2.70 (d, *J*=12.1 Hz, 1H, 10-H), 3.21 (d, *J*=12.1 Hz, 1H, 10-H), 3.80 (s, 3H, OCH_3), 4.15–4.20 (m, 1H, 2-H), 5.43 (d, *J*=3.3 Hz, 1H, OH), 6.79 (d, *J*=2.2 Hz, 1H, ArH), 7.00 (dd, *J*=8.8 and 2.2 Hz, 1H, ArH), 7.93 (d, *J*=8.8 Hz, 1H, ArH); MS *m/z*: 370 (M^+) (^{80}Se); Anal. Calcd for $C_{18}H_{26}O_3Se$: C, 58.54; H, 7.09. Found: C, 58.25; H, 7.07.

*(1S,R$_{Se}$)-10-[(2-Methylphenyl)seleninyl]-2-*exo*-borneol (**R$_{se}$**)-**1h***

Colorless columns: yield 35% from **9h**: mp 127–129°C (CH_2Cl_2/hexane); $[\alpha]_D^{27}$+157.1 (*c* 1.48, $CHCl_3$); IR (KBr) 3264, 2942, 1454, 1075, 1042 cm^{-1}; ^1H NMR δ: 0.80 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.19–1.28 (m, 1H), 1.57–1.68 (m, 3H), 1.76–1.91 (m, 3H), 2.44 (s, 3H, CH_3), 3.20 (d, *J*=12.1 Hz, 1H, 10-H), 3.75 (d, *J*=12.1 Hz, 1H, 10-H), 4.16–4.21 (m, 1H, 2-H), 5.36 (d, *J*=3.3 Hz, 1H, OH), 7.26 (d, *J*=6.0 Hz, 1H, ArH), 7.41–7.52 (m, 2H, ArH×2), 8.04 (dd, *J*=7.7 and 1.6 Hz, 1H, ArH); ^{13}C NMR δ: 20.28 (CH_3), 20.31 (CH_3), 22.6 (CH_3), 24.2 (CH_2), 27.3 (CH_2), 27.9 (CH_2), 43.3 (CH_2), 43.7 (CH), 48.4 (C), 61.4 (C), 126.66 (CH), 126.70 (CH), 126.9 (C), 130.0 (CH), 131.6 (CH), 139.4 (C), 217.6 (C); MS *m/z*: 340 (M^+) (^{80}Se); Anal. Calcd for $C_{17}H_{24}O_2Se$: C, 60.18; H, 7.13. Found: C, 60.28; H, 7.06.

*Preparation of (1S,S$_{Se}$)-10-[(4-methoxyphenyl)seleninyl]-2-*exo*-borneol (**S$_{Se}$**)-**1e** from (**R$_{Se}$**)-**1e***

A solution of (*R*$_{Se}$)-selenoxide (***R*$_{Se}$**)-**(1e)** (107 mg, 0.30 mmol) in acetone (3 mL) was stored at room temperature for 24 h. The crystals appeared were collected by filtration, washed with a small amount of Et_2O, and dried under reduced pressure to give (*S*$_{Se}$)-selenoxide (***S*$_{Se}$**)-**(1e)** (13 mg, 12%)

as colorless needles. mp 127°C (acetone); $[\alpha]_D^{28}$ −174.8 (*c* 1.00, CH_2Cl_2); CD ($CHCl_3$) 254 nm ([θ] -8.20×10^4); IR (KBr) 3134, 2940, 1591, 1493, 1302, 1248, 1173, 1077, 1028 cm^{-1}; ^1H NMR δ: 0.65–0.74 (m, 1H), 0.79 (s, 3H, CH_3), 0.80–1.07 (m, 1H), 1.15 (s, 3H, CH_3), 1.15–1.25 (m, 1H), 1.53–1.71 (m, 3H), 1.77–1.85 (m, 3H), 2.73 (d, *J*=13.2 Hz, 1H, 10-H), 3.42 (d, *J*=13.2 Hz, 1H, 10-H), 3.87 (s, 3H, OCH_3), 3.97–4.02 (m, 1H, 2-H), 4.75 (d, *J*=3.3 Hz, 1H, OH), 7.07 (d, *J*=8.8 Hz, 2H, ArH×2), 7.66 (d, *J*=8.8 Hz, 2H, ArH×2); ^{13}C NMR δ: 20.5 (CH_3), 20.6 (CH_3), 27.6 (CH_2), 32.0 (CH_2), 38.6 (CH_2), 40.1 (CH), 45.1 (CH), 53.0 (C), 54.4 (C), 54.6 (CH_2), 55.7 (CH_3), 77.4 (CH), 115.4 (CH×2), 127.7 (CH×2), 130.3 (C), 162.2 (C); ^{77}Se NMR δ: 869.46; MS *m/z*: 356 (M^+) (^{80}Se), 338 (M^+-18) (^{80}Se); Anal. Calcd for $C_{17}H_{24}O_3Se$: C, 57.47; H, 6.80. Found: C, 57.17; H, 6.79.

Crystallographic data for (S_{Se})-**1e**

Orthorhombic, space group, $P2_12_12_1$ with *a*=11.449(6) Å, *b*=21.572(6) Å, *c*=6.665(4) Å, V=1645(1) $Å^3$, and Z=4 (d_{calcd}=1.434 g cm^{-3}), μ (MoKα)=22.89 cm^{-1} absorption corrected by ω scans; 2210 unique reflections; 1264 with $I>3.00\sigma(I)$ were used in refinement; *R*=4.4%, R_W=4.5%. The authors have deposited atomic coordinates for (S_{Se})-**1e** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ (UK).

*(1S)-10-(Phenylthio)-2-*exo-*borneol* **4a**

To a suspension of NaH (60%, 68 mg, 1.70 mmol) in dry benzene (8 mL) was added a solution of thiophenol (160 μL, 1.56 mmol) in dry DMF (2 mL) at 0°C under an Ar atmosphere and the whole mixture was stirred at the same temperature for 5 min. A solution of 10-bromoisoborneol (331 mg, 1.42 mmol) in dry DMF (4 mL) was added to the mixture in a period of 2 min. The reaction mixture was stirred at 60°C for 2.5 h. After cooling to room temperature, 1 N HCl (20 mL) was added to the reaction mixture. The resulting mixture was extracted with AcOEt (20 mL×3) and the combined organic layer was dried over $MgSO_4$. The residue obtained after evaporation of the solvent was subjected to column chromatography (hexane to hexane/AcOEt 12:1) to give the sulfide **4a** (372 mg, 100%) as a colorless oil. $[\alpha]_D^{24}$ −35.1 (*c* 2.44, $CHCl_3$); IR (neat) 3463, 2952, 1480, 1438, 1071 cm^{-1}; ^1H NMR δ: 0.88 (s, 3H, CH_3), 1.01–1.09 (m, 1H), 1.09 (s, 3H, CH_3), 1.22 (ddd, *J*=13.0, 9.0, and 3.5 Hz, 1H), 1.5–1.9 (m, 5H), 2.19 (br, 1H, OH), 2.95 (d, *J*=11.0 Hz, 1H, 10-H), 3.23 (d, *J*=11.0 Hz, 1H, 10-H), 3.9–4.0 (m, 1H, 2-H), 7.15–7.40 (m, 5H, ArH×5); MS *m/z*: 262 (M^+); HRMS found M^+ 262.1390, $C_{16}H_{22}OS$ requires M^+ 262.1353.

(1S, R_S*)-10-(Phenylsulfinyl)-2-*exo-*borneol* **2a**

To a solution of sulfide **4a** (338 mg, 1.29 mmol) in dry CH_2Cl_2 (5 mL) was added dropwise a solution of *m*-CPBA (80%, 307 mg, 1.42 mmol) in dry CH_2Cl_2 (10 mL) at −78°C under an Ar atmosphere in a period of 20 min. The whole mixture was stirred and the reaction temperature was allowed to rise to room temperature. After 4 h, Et_2O (50 mL) was added to the mixture and the organic layer was washed with 5% aqueous $Na_2S_2O_3$ (50 mL) followed by saturated aqueous $NaHCO_3$ (50 mL). The organic layer was dried over $MgSO_4$ and the solvent was evaporated. The residue was subjected to column chromatography (hexane/Et_2O 6:1) to give the sulfoxide (R_S)-**2a** (319 mg, 89%) as colorless columns. mp 134–136°C (hexane); $[\alpha]_D^{24}$ −119.3 (*c* 1.49, $CHCl_3$); IR (KBr) 3373, 2954, 1303, 1136, 1078 cm^{-1}; ^1H NMR δ: 0.80 (s, 3H, CH_3), 1.05 (s, 3H, CH_3), 1.25 (m, 1H), 1.65–1.9 (m, 6H), 2.38 (d, *J*=13.0 Hz, 1H, 10-H), 3.36 (d, *J*=13.0 Hz, 1H, 10-H), 4.13 (d, *J*=3.0 Hz, 1H, OH), 4.20 (ddd, *J*=8.0, 4.0, and 3.0 Hz, 1H, 2-H), 7.5–7.75 (m, 5H, ArH×5); MS *m/z*: 278 (M^+); Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.03; H, 7.96%. Found: C, 68.85; H, 8.05.

Typical procedure for preparation of 2-alkylcyclohexanones **7a,b**

To a solution of LDA [made from diisopropylamine (1.24 g, 12.2 mmol) and *n*-BuLi (1.63 M in hexane 7.5 mL, 12.2 mmol)] in dry THF (22 mL) was added a solution of cyclohexanone (1.00 g, 10.2 mmol) in dry THF (3 mL) at −78°C under Ar atmosphere and the whole mixture was stirred at the same

temperature for 10 min. Benzyl bromide (3.49 g, 20.4 mmol) was added to the reaction mixture at 30°C and the whole mixture was stirred at the same temperature for 20 min. After cooling, the mixture was poured into cooled saturated aqueous $NaHCO_3$ (27 mL) and extracted with hexane (10 mL×3). The organic layer was washed with H_2O (10 mL×1), 5% HCl (10 mL×2), H_2O (10 mL×1), and saturated aqueous $NaHCO_3$ (10 mL×1) and dried over $MgSO_4$. The residue obtained after evaporation of the solvent was subjected to column chromatography (hexane/Et_2O 40:1) to give 2-benzylcyclohexanone **7a**[22] (1.20 g, 63%) as a colorless oil. 2-(4-Methoxy-phenyl)methylcyclohexanone **7b** was similarly prepared from cyclohexanone and 4-bromoanisole.

2-Benzylcyclohexanone 7a

Colorless oil: IR (neat) 3050, 2950, 2880, 1710, 1600, 1500, 1450, 1320, 1220, 1130, 730, 700 cm^{-1}; ^1H NMR δ: 1.26–1.43 (m, 1H), 1.50–1.88 (m, 3H), 1.98–2.12 (m, 2H), 2.27–2.61 (m, 4H), 3.24 (dd, *J*=13.7 and 4.4 Hz, 1H), 7.14–7.22 (m, 3H), 7.25–730 (m, 2H); MS *m/z*: 188 (M^+).

2-(4-Methoxyphenyl)methylcyclohexanone 7b

Colorless oil: yield 36%: IR (neat) 2935, 1749, 1511, 1248, 1223, 756 cm^{-1}; ^1H NMR δ: 1.28–1.40 (m, 1H), 1.51–1.75 (m, 2H), 1.80–1.86 (m, 1H), 1.98–2.09 (m, 2H), 2.26–2.54 (m, 4H), 3.16 (dd, *J*=14.0 and 4.7 Hz, 1H), 3.78 (s, 3H), 6.82 (d, *J*=8.8 Hz, 2H), 7.07 (d, *J*=8.8 Hz, 2H); ^{13}C NMR δ: 25.2 (CH_2), 28.2 (CH_2), 33.5 (CH_2), 34.7 (CH_2), 42.3 (CH_2), 52.8 (CH), 55.4 (CH_3), 113.8 (CH×2), 132.4 (CH×2), 132.4 (C), 158.0 (C), 213.0 (C); MS *m/z*: 218 (M^+); HRMS found M^+ 218.1328, $C_{14}H_{18}O_2$ requires M^+ 218.1306.

Typical procedure for preparation of 2-propylcyclohexanone 7c and 2-isopropylcyclohexanone 7d

MeLi (1.09 M in Et_2O 11.0 mL, 12.0 mmol)] was introduced into a reaction vessel at 0°C and Et_2O was removed under reduced pressure. DME (40 mL) was added to the residue and the mixture was stirred at 0°C for 5 min. A solution of 1-(trimethylsiloxy)cyclohexene (1.70 g, 10.0 mmol) in DME (4 mL) was added dropwise to the mixture at 0°C. After being stirred at room temperature for 20 min, to this was added 1-iodopropane (3.40 g, 20.0 mmol) and the whole mixture was stirred for an additional 1.5 h. After cooling to 0°C, brine (30 mL) was added to the reaction mixture and extracted with Et_2O (50 mL×3). The combined organic layer was washed with saturated NH_4Cl (50 mL×1) and dried over $MgSO_4$. The residue obtained after evaporation of the solvent was subjected to column chromatography (hexane/Et_2O 30:1) to give 2-propylcyclohexanone **7c**[22] (368 mg, 26%) as a colorless oil. 2-Isopropylcyclohexanone **7d** was similarly prepared from 1-(trimethylsiloxy)cyclohexene and 2-iodopropane in DME/HMPA (8:1).

2-Propylcyclohexanone 7c

Colorless oil: IR (neat) 2933, 2862, 1710, 1449, 917 cm^{-1}; ^1H NMR δ: 0.90 (t, *J*=7.1 Hz, 3H), 1.12–1.45 (m, 4H), 1.57–1.89 (m, 4H), 1.99–2.13 (m, 2H), 2.23–2.42 (m, 3H); ^{13}C NMR δ: 14.4 (CH_3), 20.5 (CH_2), 25.0 (CH_2), 28.2 (CH_2), 31.8 (CH_2), 34.0 (CH_2), 42.1 (CH_2), 50.7 (CH), 213.8 (C); MS *m/z*: 140 (M^+); HRMS found M^+ 140.1181, $C_9H_{16}O$ requires M^+ 140.1200.

2-Isopropylcyclohexanone 7d

Colorless oil: yield 27%: IR (neat) 2936, 2867, 1708, 1448, 1121 cm^{-1}; ^1H NMR δ: 0.84 (d, *J*=2.8 Hz, 3H), 0.86 (d, *J*=3.3 Hz, 3H), 1.46–2.36 (m, 10H); ^{13}C NMR δ: 19.1 (CH_3), 21.2 (CH_3), 24.4 (CH_2), 26.4 (CH), 28.1 (CH_2), 29.3 (CH_2), 42.1 (CH_2), 57.3 (CH), 213.6 (C); MS *m/z*: 140 (M^+); HRMS found M^+ 140.1205, $C_9H_{16}O$ requires M^+ 140.1200.

2-Benzylcyclopentanone 7e

2-Benzylcyclopentanone **7e** was prepared from ethyl 2-oxocyclopentanecarboxylate according to the literature.[23] colorless oil: yield 58%: IR (neat) 3207, 2901, 1751, 1369, 1210, 1179, 1032, 702

cm^{-1}; ^1H NMR δ: 1.54 (ddd, *J*=22.5, 11.0, and 6.6 Hz, 1H), 1.64–1.79 (m, 1H), 1.89–2.00 (m, 1H), 2.03–2.16 (m, 2H), 2.29–2.38 (m, 2H), 2.53 (dd, *J*=13.7 and 9.9 Hz, 1H), 3.15 (dd, *J*=13.7 and 4.4 Hz, 1H), 7.15–7.30 (m, 5H); ^{13}C NMR δ: 20.7 (CH_2), 29.3 (CH_2), 35.7 (CH_2), 38.3 (CH_2), 51.1 (CH), 126.3 (CH), 128.5 (CH×2), 129.0 (CH×2), 140.1 (C), 220.3 (C); MS *m/z*: 174 (M^+); HRMS found M^+ 174.1035, $C_{12}H_{14}O$ requires M^+ 174.1044.

Typical procedure for preparation of 3,4-dihydro-2-alkylnaphthalenones 7f,g

To a solution of LDA [made from diisopropylamine (1.11 g, 11.0 mmol) and *n*-BuLi (1.72 M in hexane 6.4 mL, 11.0 mmol)] in dry THF (10 mL) was added a solution of α-tetralone (1.46 g, 10.0 mmol) in dry THF (1 mL) at −78°C under Ar atmosphere and the whole mixture was stirred at the same temperature for 20 min. Iodomethane (3.49 g, 20.4 mmol) was added to the reaction mixture at room temperature and the whole mixture was stirred at the same temperature for 30 min. After cooling, H_2O (15 mL) was added to the reaction mixture and extracted with Et_2O (50 mL×3). The combined organic layer was washed with H_2O (40 mL×1), saturated NH_4Cl (40 mL×1), and brine (40 mL×1) and dried over $MgSO_4$. The residue obtained after evaporation of the solvent was subjected to column chromatography (hexane/Et_2O 30:1) to give 3,4-dihydro-2-methylnaphthalenone **7g** (776 mg, 49%) as a pale yellow oil. 2-Benzylketone **7f** was similarly prepared from α-tetralone and benzyl brimide. The ketone **7f** could not be separated from impurities, therefore it was used for the next reaction as a mixture of **7f** and impurities.

3,4-Dihydro-2-methylnaphthalenone 7g

Pale yellow oil: IR (neat) 2963, 1685, 1602, 1457, 1229, 968, 909, 737 cm^{-1}; ^1H NMR δ: 1.27 (d, *J*=7.1 Hz, 3H), 1.81–1.95 (m, 1H), 2.20 (dq, *J*=13.2 and 4.4 Hz, 1H), 2.53–2.65 (m, 1H), 2.92–3.10 (m, 2H), 7.24 (dd, *J*=7.1 and 7.1 Hz, 1H), 7.30 (dd, *J*=7.1 and 7.1 Hz, 1H), 7.45 (ddd, *J*=7.1, 1.1, and 1.1 Hz, 1H), 8.03 (d, *J*=7.1 Hz, 1H); ^{13}C NMR δ: 15.6 (CH_3), 29.0 (CH_2), 31.5 (CH_2), 42.8 (CH), 126.7 (CH), 127.5 (CH), 128.9 (CH), 132.5 (C), 133.2 (CH), 144.4 (C), 201.0 (C); MS *m/z*: 160 (M^+); HRMS found M^+ 160.0928, $C_{11}H_{12}O$ requires M^+ 160.0888.

Typical procedure for preparation of enol acetate 5

To a 30 mL flask were added CCl_4 (8 mL), Ac_2O (3.36 g, 33.0 mmol), 2-benzylcyclohexanone **7a** (1.17 g, 62.2 mmol), and 60% aqueous $HClO_4$ (2 drops). The flask was stoppered and set aside at room temperature for 3 h. The reaction mixture was poured into a cooled (0°C) mixture of saturated aqueous $NaHCO_3$ (5 mL) and hexane (5 mL). The mixture was neutralized with solid $NaHCO_3$ (ca. 8 g) with vigorous stirring at 0°C. The organic layer was separated and the aqueous phase was extracted with hexane (5 mL×2). The combined organic layer was dried over $MgSO_4$. The residue obtained after evaporation of the solvent was subjected to column chromatography (hexane/Et_2O 30:1) to give 2-benzylcyclohex-1-enyl acetate **5a**[22] (1.18 g, 82%) as a colorless oil.

2-Benzylcyclohex-1-enyl acetate 5a

Colorless oil: IR (neat) 3020, 2930, 2850, 1750, 1700, 1600, 1490, 1450, 1370, 1220, 1080, 700 cm^{-1}; ^1H NMR δ: 1.55–1.61 (m, 2H), 1.68–1.75 (m, 2H), 1.92–1.96 (m, 2H), 2.14 (s, 3H), 2.17–2.22 (m, 2H), 3.27 (s, 2H), 7.15–7.20 (m, 3H), 7.27–7.30 (m, 2H); MS *m/z*: 230 (M^+).

2-(4-Methoxyphenyl)cyclohex-1-enyl acetate 5b

Colorless oil: yield 100%, IR (neat) 2934, 2837, 1750, 1511, 1248, 1223, 1176, 1037, 816 cm^{-1}; ^1H NMR δ: 1.54–1.60 (m, 2H), 1.67–1.75 (m, 2H), 1.90–1.95 (m, 2H), 2.15 (s, 3H), 2.15–2.19 (m, 2H), 3.21 (s, 2H), 3.79 (s, 3H), 6.82 (d, *J*=8.8 Hz, 2H), 7.08 (d, *J*=8.8 Hz, 2H); ^{13}C NMR δ: 21.1 (CH_3), 22.5 (CH_2), 23.1 (CH_2), 27.2 (CH_2), 27.6 (CH_2), 35.4 (CH_2), 55.3 (CH_3), 113.8 (CH×2), 123.7 (C), 129.8 (CH×2), 131.6 (C), 142.9 (C), 158.0 (C), 169.6 (C); MS *m/z*: 260 (M^+); HRMS found M^+ 260.1374, $C_{16}H_{20}O_3$ requires M^+ 260.1411.

2-Propylcyclohex-1-enyl acetate **5c**[22]

Colorless oil: yield 54%, IR (neat) 2934, 1752, 1369, 1223, 1200, 1109 cm^{-1}; ^1H NMR δ: 0.86 (t, *J*=7.7 Hz, 3H), 1.32–1.38 (m, 2H), 1.40–1.72 (m, 4H), 1.89 (br t, *J*=7.7 Hz, 2H), 2.01–2.06 (m, 2H), 2.09–2.14 (m, 2H), 2.12 (s, 3H); ^{13}C NMR δ: 14.2 (CH_3), 20.7 (CH_2), 21.0 (CH_3), 22.7 (CH_2), 23.3 (CH_2), 27.3 (CH_2), 27.9 (CH_2), 32.4 (CH_2), 124.4 (C), 142.3 (C), 169.5 (C); MS *m/z*: 182 (M^+); HRMS found M^+ 182.1337, $C_{11}H_{18}O_2$ requires M^+ 182.1306.

2-Isopropylcyclohex-1-enyl acetate **5d**

Colorless oil: yield 73%, IR (neat) 2961, 2934, 1754, 1369, 1221, 1180, 1120, 1069 cm^{-1}; ^1H NMR δ: 0.92 (d, *J*=7.1 Hz, 6H), 1.58–1.72 (m, 4H), 1.99–2.03 (m, 2H), 2.06–2.13 (m, 2H), 2.13 (s, 3H), 2.70 (septet, *J*=7.1 Hz, 1H); ^{13}C NMR δ: 20.3 (CH_3×2), 21.1 (CH_3), 22.3 (CH_2), 22.6 (CH_2), 23.1 (CH_2), 27.2 (CH), 27.4 (CH_2), 129.3 (C), 140.6 (C), 169.6 (C); MS *m/z*: 182 (M^+); HRMS found M^+ 182.1300, $C_{11}H_{18}O_2$ requires M^+ 182.1306.

2-Benzylcyclopent-1-enyl acetate **5e**

Colorless oil: yield 36%: IR (neat) 3028, 2963, 2878, 1738, 1496, 1453, 1154, 912, 730, 699 cm^{-1}; ^1H NMR δ: 1.61–1.94 (m, 2H), 2.14 (s, 3H), 2.18–2.22 (m, 2H), 2.50–2.55 (m, 2H), 3.31 (s, 2H), 7.15–7.30 (m, 5H); ^{13}C NMR δ: 19.9 (CH_2), 21.0 (CH_3), 31.17 (CH_2), 31.22 (CH_2), 33.2 (CH_2), 125.6 (C), 126.2 (CH), 128.5 (CH×2), 128.8 (CH×2), 138.2 (C), 145.1 (C), 169.2 (C); MS *m/z*: 216 (M^+); HRMS found M^+ 216.1176, $C_{14}H_{16}O_2$ requires M^+ 216.1149.

3,4-Dihydro-2-benzylnaphthalenyl acetate **5f**

Pale yellow oil: yield 13% (from α-tetralone): IR (neat) 3205, 2934, 1757, 1206, 1066, 909, 738 cm^{-1}; ^1H NMR δ: 2.26 (t, *J*=7.7 Hz, 2H), 2.33 (s, 3H), 2.79 (t, *J*=7.7 Hz, 2H), 3.49 (br s, 2H), 7.05–7.31 (m, 9H); ^{13}C NMR δ: 20.8 (CH_3), 26.5 (CH_2), 27.8 (CH_2), 36.8 (CH_2), 120.8 (CH), 126.49 (CH), 126.54 (CH), 126.7 (CH), 127.49 (CH), 127.54 (CH), 128.6 (CH), 129.1 (CH×2), 130.9 (C), 135.8 (C), 138.9 (C), 141.1 (C), 160.4 (C); MS *m/z*: 278 (M^+); HRMS found M^+ 278.1299, $C_{19}H_{18}O_2$ requires M^+ 278.1306.

3,4-Dihydro-2-methylnaphthalenyl acetate **5g**

Pale yellow oil: yield 59%: IR (neat) 2932, 1756, 1369, 1207, 1134, 1073, 767, 738 cm^{-1}; ^1H NMR δ: 1.76 (s, 3H), 2.31 (s, 3H), 2.39 (t, *J*=8.0 Hz, 2H), 2.86 (t, *J*=8.0 Hz, 2H), 7.00 (d, *J*=6.0 Hz, 1H), 7.09–7.16 (m, 3H); ^{13}C NMR δ: 17.0 (CH_3), 20.7 (CH_3), 27.6 (CH_2), 29.0 (CH_2), 120.2 (CH), 124.3 (C), 126.5 (CH), 127.1 (CH), 131.1 (C), 135.4 (C), 140.2 (C), 169.0 (C); MS *m/z*: 202 (M^+); HRMS found M^+ 202.0988, $C_{13}H_{14}O_2$ requires M^+ 202.0933.

Typical procedure for asymmetric protonation

Method A. To a solution of the enolacetate **5a** (71 mg, 0.31 mmol) in dry Et_2O (3 mL) was added MeLi (1.08 M in Et_2O, 568 μL, 0.61 mmol) or MeLi–LiBr (1.08 M in Et_2O, 568 μL, 0.41 mmol) at 0°C under an Ar atmosphere. After being stirred for 20 min at room temperature, the mixture was cooled to −100°C. To this was added a solution of the chiral proton source **1e** (360 mg, 1.01 mmol) in dry CH_2Cl_2 (3 mL) and stirred at −100°C for an additional 10 min. The reaction temperature was allowed to warm to −10°C in a period of 1 h. To this was added 0.2 M phosphate buffer (pH 6.8, 5 mL) and the organic layer was separated. The aqueous phase was extracted with CH_2Cl_2 (10 mL×3) and the combined organic layer was dried over $MgSO_4$. The residue obtained after evaporation of the solvent was subjected to column chromatography (Et_2O) followed by PTLC (hexane/Et_2O 4:1) to give 2-benzylcyclohexanone **7a**.

Method B. To a solution of the enolacetate **5a** (24 mg, 0.10 mmol) in dry Et_2O (1 mL) was added MeLi (1.09 M in Et_2O, 375 μL, 0.41 mmol) at 0°C under an Ar atmosphere. After being stirred for 5 min at 0°C, $ZnBr_2$ (35 mg, 0.15 mmol, preheated at 200°C for 2 h) was added to this mixture at 0°C.

After being stirred for 5 min at 0°C and then 20 min at room temperature, the mixture was cooled to −100°C. To this was added a solution of the chiral proton source **1e** (156 mg, 0.44 mmol) in dry CH_2Cl_2 (2 mL) and stirred at −100°C for an additional 10 min. The reaction temperature was then allowed to warm to −10°C over a period of 1 h. Similar work-up to Method A gave 2-benzylcyclohexanone **7a**. Asymmetric protonation of **7b–g** was performed similarly. All the spectral data (^1H NMR, IR, and MS) of **7a–g** were in full agreement with those of the racemates. Ee, chemical yield, $[\alpha]_D$, and absolute configuration of **7** are shown in Tables 1 and 3–7 and Scheme 4. The absolute configuration of the ketones **7** was determined by comparing the sign of optical rotation with reported one.[11–16] The enantiomeric excess (ee) of **7** was determined by HPLC analysis and/or optical rotation. The analysis was carried out with CHIRALCEL OJ (eluent: hexane/^{i}PrOH 96:4, flow rate: 1.0 mL/min) for the ketones **7a**[8] and **7b,f**, with CHIRALCEL OB for the ketone **7c** (eluent: hexane/^{i}PrOH 99:1, flow rate: 0.5 mL/min), with CHIRALCEL AS for the ketone **7e** (eluent: hexane/^{i}PrOH 96:4, flow rate: 1.0 mL/min) and with CHIRALCEL AS for the ketone **7g** (eluent: hexane/^{i}PrOH 99:1, flow rate: 0.5 mL/min).

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