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Diastereo- and enantioselective synthesis of *anti*-1,3-mercapto alcohols from α,β-unsaturated ketones via tandem Michael addition–MPV reduction

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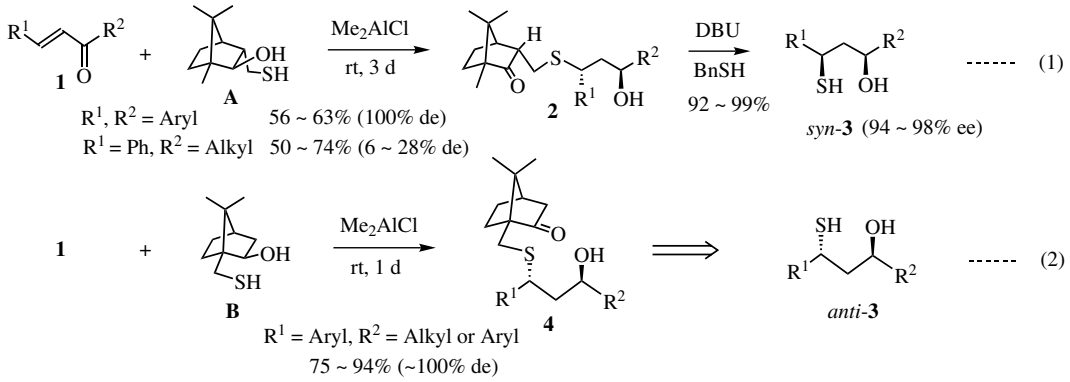
Abstract—A new and effective asymmetric synthesis of *anti*-1,3-mercapto alcohols **3** from α,β-unsaturated ketones **1** utilizing tandem Michael addition–Meerwein–Ponndorf–Verley (MPV) reduction is described. Transformation of the MPV products *anti*-**4** via the Wagner–Meerwein rearrangement was optimized under acidic or basic conditions to afford 1,3-mercapto alcohols *anti*-**3**, depending on the substituent R^2 of **4**.

1. Introduction

Chiral 1,3-oxathiane derivatives, prepared from optically active 1,3-mercapto alcohols, have been developed as chiral auxiliaries for asymmetric synthesis.[1] Optically active 1,3-mercapto alcohols are only available from natural sources[1] with little attention being given on their asymmetric synthesis. Therefore, asymmetric synthesis of 1,3-mercapto alcohols still remains as untouched research region. We have recently reported a new method for the asymmetric synthesis of 1,3-mercapto alcohols *syn*-**3** from α,β-unsaturated ketones **1** using the new chiral reagent **A** via a tandem Michael addition–Meerwein–Ponndorf–Verley (MPV) reduction,[2] as shown in Eq. 1 (Scheme 1). A characteristic of the above synthetic method was the elimination reaction with a base producing *syn*-1,3-mercapto alcohols **3**.[3] However, the tandem reaction proceeded in extremely low diastereoselectivity in the case of the substrate **1** having an alkyl substituent R^2. We report herein a new synthetic method of optically active *anti*-1,3-mercapto alcohols **3** via the known tandem Michael addition–MPV reduction using the chiral reagent **B**, as shown as Eq. 2 in Scheme 1.



Scheme 1.

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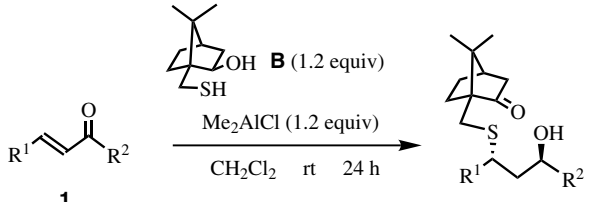
2. Results and discussion

The new strategy in Eq. 2 consists of a diastereoselective construction of two stereogenic centers by the tandem reaction using **B** and transformation of the resulting sulfide **4** into *anti*-1,3-mercapto alcohols **3** via a Wagner–Meerwein rearrangement as the key reaction. As previously reported of the use of the tandem reaction,[4] sulfide **4** can be obtained in high yield with short reaction time when compared to that of the tandem reaction using **A**, and furthermore, a different diastereomer *anti*-**3** of 1,3-mercapto alcohol can be obtained. First, we attempted the tandem reaction of various kinds of α,β-unsaturated ketones **1** using the chiral reagent **B** (1.2 equiv) and dimethylaluminum chloride (1.2 equiv) in dichloromethane at room temperature. The results of the tandem reaction are summarized in Table 1. The reaction of α,β-unsaturated ketones bearing an aromatic group on the β-carbon proceeded in nearly complete diastereoselectivity and in high yields (Table 1, entries 1–3). In the cases of α,β-unsaturated ketones possessing alkyl substituent R^1, the tandem reactions were maintained in high yields but the diastereoselectivities decreased significantly (58–81%) (Table 1, entries 4–6). However a propyl substituent at R^1 on the β-carbon, gave diastereomeric excesses over 90% de for products **4** (Table 1, entries 7–10). It was observed that the lowering of diastereoselectivity was correlated to the decreasing bulkiness of the R^1 group at the β-carbon.

Table 1. Tandem Michael–MPV reaction using **B** as a chiral reagent

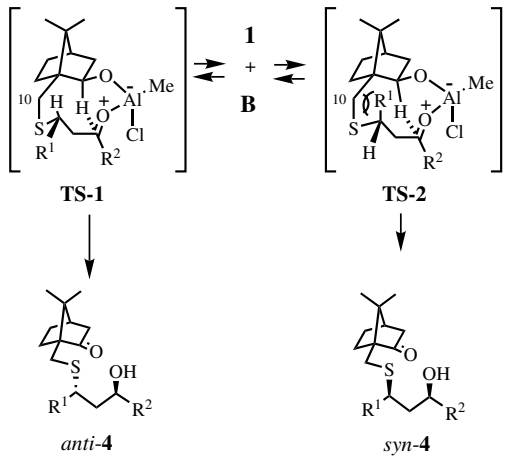


1 **4**

Entry	1			4	
		R^1	R^2	Yield (%)[a]	De (%)
1	**a**	Ph	Me	95	99
2	**b**	Ph	*i*-Pr	96	99
3	**c**	Ph	*c*-Hex	92	99
4	**d**	Me	Et	95	58
5	**e**	Et	Hex	93	81
6	**f**	Et	Oct	92	74
7	**g**	Pr	Me	88	92
8	**h**	Pr	Hex	81	95
9	**i**	Pr	Oct	81	94
10	**j**	Pr	Ph	82	90

[a] Isolated yields.

The above diastereochemical control can be interpreted based on dynamic kinetic resolution via a reversible Michael addition in the tandem reaction, as shown in Scheme 2.

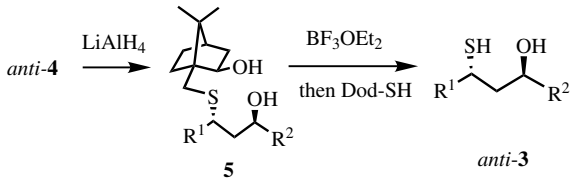


Scheme 2.

Namely, in the substrates having aromatic substituent R^1, a significant steric repulsion between the aromatic ring and the C-10 methylene protons on one diastereomer **TS-2** of the Michael adduct retarded the rate of the MPV reaction, whereas the other diastereomer **TS-1** without such steric repulsion proceeded smoothly to give the MPV product *anti*-**4**. In the cases of the substrates having an alkyl substituent R^1, the above mentioned steric repulsion would be smaller than those with the aromatic groups. Therefore, the MPV reduction through **TS-2** proceeded slowly to give *syn*-**4** and decreased the diastereoselectivities. Determination of the stereochemistry of *anti*-**4** and *syn*-**4** will be discussed in the Experimental section.

Next, we investigated the transformation of sulfide **4** into *anti*-1,3-mercapto alcohol **3**. Recently, we have developed a new asymmetric synthesis[5] of β-mercapto esters from α,β-unsaturated esters via a Michael addition of the chiral thiol **B** followed by a one-pot degradation of the adducts with boron trifluoride etherate ($BF_3{\cdot}OEt_2$) and odourless 1-dodecanethiol[6] (Dod-SH). This new method of transformation using sulfides **4** was applied for the 1,3-mercapto alcohols *anti*-**3**. As reported previously,[5] the transformation requires three steps, that is, reduction of the carbonyl group on **4**, a Wagner–Meerwein rearrangement and a thiol exchange reaction. The ketone *anti*-**4**, which was purified by HPLC, was diastereoselectively reduced with $LiAlH_4$ in THF at room temperature to give *exo*-alcohol **5**. The obtained crude diol **5** was then subsequently treated with $BF_3{\cdot}OEt_2$ and Dod-SH in CH_2Cl_2 at room temperature. The results are summarized in Table 2. By these transformations, the desired 1,3-mercapto alcohols *anti*-**3** were obtained in good yields (63–83%) and high enantiomeric excess (>97% ee) without epimerization (entries 1–10). However, in the case of $R^2 = Ph$ (entry 11), the substrate decomposed during the rearrangement reaction with $BF_3{\cdot}OEt_2$. Besides the expected Wagner–Meerwein rearrangement, formation of the stable benzyl cation by elimination of the hydroxyl group probably occurred under strongly acidic conditions. Therefore, we examined the reaction under basic conditions using trifluoromethansulfonic anhydride (Tf_2O) according to the

Table 2. Conversion of sulfides **4** into 1,3-mercapto alcohols *anti*-**3**



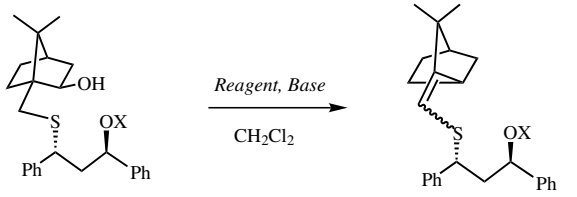
Entry	4			*anti*-3	
		R^1	R^2	Yield (%)[a]	Ee (%)[b]
1	**a**	Ph	Me	74	97
2	**k**	Ph	Et	79	99
3	**l**	Ph	Pr	67	99
4	**b**	Ph	*i*-Pr	78	98
5	**c**	Ph	*c*-Hex	72	98
6	**d**	Me	Et	79	98
7	**e**	Et	Hex	68	98
8	**f**	Et	Oct	63	98
9	**g**	Pr	Me	83	98
10	**h**	Pr	Hex	63	98
11	**m**	Ph	Ph	Decompose	

[a] Isolated yield.
[b] Enantiomeric excesses were determined by HPLC analysis using DAICEL CHIRALCEL OB or OD.

reports[7] by Martinez et al. (entries 1 and 2 in Table 3). Unfortunately, the reaction of **6m** derived from *anti*-**4m** did not proceed under both reaction conditions using either Et_3N or pyridine as the base. The reaction using Et_3N and MsCl instead of Tf_2O, afforded the desired rearrangement product **8m** in low yield (entry 3). Exchange of the protecting group from acetyl (Ac) **6m** to methoxymethyl (MOM) **7m** was also not effective (entry 4). In contrast to a small amine like Et_3N, the use of more bulky amines such as the Hünig base (*i*-Pr_2NEt) increased the yield from 13% to 41%. However, the use of even more bulky amines, that is, *i*-Bu_3N was not effective (entry 6). The optimal result was obtained by the treatment with Ms_2O and *i*-Pr_2NEt, with the desired rearrangement reaction proceeding successfully in a short reaction time (entry 7). Under the optimized reaction conditions, MPV products *anti*-**4j** and **m** were converted to vinyl sulfides **9j** and **m** in 80–86% overall yields (three steps).

Finally, we turned our attention to the conversion of vinyl sulfide **9m** into 1,3-mercapto alcohol *anti*-**3m** by a thiol exchange reaction using an odourless Dod-SH. After screening several Lewis acids and protic acids, we found that the use of *n*-Bu_2BOTf as a Lewis acid, which is more weak acid than $BF_3{\cdot}OEt_2$, was effective in giving the desired 1,3-mercapto alcohol *anti*-**3m** in 68% yield. Moreover, we studied an alternative conversion of vinyl sulfides **9j** and **m** by ozonolysis. Namely, vinyl sulfides **9j** and **m** were converted to thioformate **10j** and **m** by ozonolysis followed by reductive treatment with PPh_3.

Table 3. Wagner–Meerwein rearrangement of **6m** or **7m** to vinyl sulfides **8m** or **9m** under basic conditions

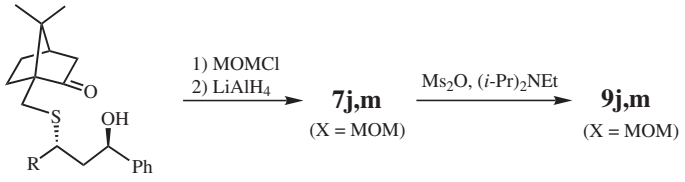


6m: X = Ac
7m: X = MOM

8m: X = Ac
9m: X = MOM

Entry	Substrate		Reagent (equiv)	Base (equiv)	Time	Temperature	Vinyl sulfide[a]	
		X						Yield (%)[b]
1	**6m**	Ac	Tf_2O (1.5)	Et_3N (2)	41 h	0 °C to rt		n.r.[c]
2	**6m**	Ac	Tf_2O (1.5)	Pyridine (neat)	24 h	0 °C to rt		n.r.[c]
3	**6m**	Ac	MsCl (10)	Et_3N (20)	30 min	0 °C	**8m**	11
4	**7m**	MOM	MsCl (10)	Et_3N (20)	30 min	0 °C	**9m**	13
5	**7m**	MOM	MsCl (10)	*i*-Pr_2NEt (20)	30 min	0 °C	**9m**	41
6	**7m**	MOM	MsCl (10)	*i*-Bu_3N (20)	30 min	0 °C	**9m**	n.r.[c]
7	**7m**	MOM	Ms_2O (10)	*i*-Pr_2NEt (20)	15 min	−10 °C	**9m**	88

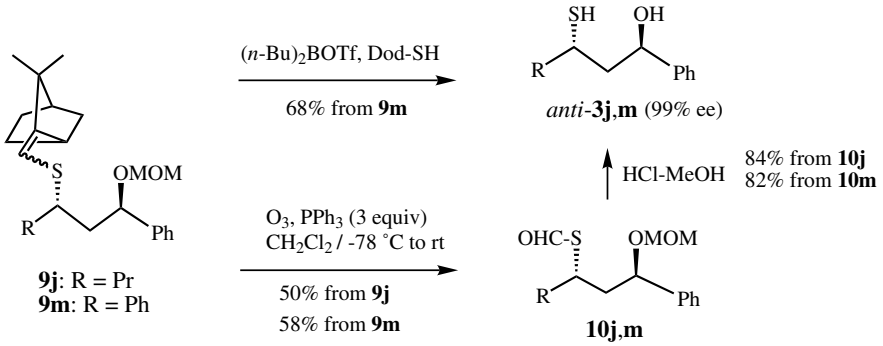
[a] A mixture of *E*- and *Z*-isomers.
[b] Isolated yield.
[c] No reaction.



anti-**4j**: R = Pr
anti-**4m**: R = Ph

7j (89%)
7m (98%)

9j (90%)
9m (88%)



Scheme 3. Conversion of vinyl sulfides **9** into 1,3-mercapto alcohols *anti*-**3**.

The thioformates **10j** and **m** can be regarded as the protected compound of 1,3-mercapto alcohols *anti*-**3j** and **m** on both the hydroxyl and the thiol groups. Indeed, the thioformates **10j** and **m** were easily deprotected to give 1,3-mercapto alcohols *anti*-**3j** and **m** by hydrolysis with HCl in MeOH. Having these reaction sequences should prove useful to afford, either the protected form of 1,3-mercapto alcohols or the free form 1,3-mercapto alcohols directly (Scheme 3).

3. Conclusions

In conclusion, we have developed a diastereo- and enantioselective synthesis of 1,3-mercapto alcohols from α,β-unsaturated ketones via a tandem Michael addition–MPV reduction using chiral reagent **B**. It was found that the magnitude of diastereoselectivity in the tandem reaction depends on the bulkiness of the R^1 group rather than the R^2 group, and more bulky R^1 group than Me or Et groups resulted in high diastereoselectivity (>90%). Transformation of *anti*-**4** to 1,3-mercapto alcohols *anti*-**3** was effectively achieved via the Wagner–Meerwein rearrangement and thiol exchange reaction under the acidic condition using $BF_3{\cdot}OEt_2$/Dod-SH system, except for the substrate with phenyl group at R^2. In the case if R^2 is phenyl, the transformation can be performed by the rearrangement using Ms_2O/*i*-Pr_2NEt followed by the thiol exchange reaction with *n*-Bu_2BOTf/Dod-SH, or alternatively, by the reductive ozonolysis of the vinyl sulfide intermediates and subsequent hydrolysis. Consequently, we were able to provide a new method for preparation of 1,3-mercapto alcohols *anti*-**3**, which was complementary to the previously reported method.[5]

4. Experimental

4.1. General

Melting points were taken on a micro hot-stage apparatus (Yanagimoto) and are uncorrected. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8300 diffraction grating infrared spectrophotometer. ^{1}H NMR spectra were obtained on a JEOL JNM-AL300, a Varian Unity INOVA-400 spectrometer with tetramethylsilane as an internal standard. ^{13}C NMR spectra were obtained on a Varian Unity INOVA-400 spectrometer with $CDCl_3$ as an internal standard. Mass spectra (MS) were determined on a JEOL JMS-SX 102A QQ or a JEOL JMS-GC mate mass spectrometer. Specific rotations were recorded on a Horiba SEPA-200 automatic digital polarimeter. Chiral HPLC analyses were performed with a Shimadzu LC-9A and LC-10A Liquid Chromatograph series using a Daicel chiral column (CHIRALCEL OB, OD). Their data were recorded with Shimadzu C-R6A Chromatopac. Flash column chromatography was performed with silica gel 60N (Kanto Chemical Co., Inc.). Kieselgel 60 F-254 plates (Merck) were used for thin layer chromatography (TLC). Preparative TLC (PTLC) was done with Kieselgel 60 F-254 plate (0.25 mm, Merck) or silica gel 60 F-254 plate (0.5 mm, Merk). When necessary, compounds were further purified by recycled HPLC (JAI LC-908) on a GPC column (JAIGEL 1H and 2H) after purification on silica gel. Some diastereomeric mixtures of **4** were separated by recycled HPLC (JAI LC-908) on SiO_2 gel column (Kusano Si-10) after purification on silica gel.

4.2. Materials

Toluene, diethyl ether, and tetrahydrofuran were distilled from sodium benzophenone ketyl, and dichloromethane from CaH_2, after 10 washing with water to remove methanol contaminants. Most of the reagents were obtained from Wako pure Chemical Industries, Ltd., Nakalai Tesque, Inc., Aldrich Chemical Inc. (*S*)-(+)-Camphorsulfonic acid monohydrate were commercially available. Dimethylaluminum chloride (hexane solution) was purchased from Kanto Chemical Co., Inc. α,β-Unsaturated ketones (**1a**, **1b**, **1c**, **1d**, **1g**, **1i**, **1k**, **1m**) are commercially available compounds. Other α,β-unsaturated ketones are known compound.

4.3. Synthesis of (−)-10-mercaptoisoborneol B

(−)-10-Mercaptoisoborneol **B** was prepared by Eliel's procedure[1a] from (*S*)-(+)-camphorsulfonic acid monohydrate. The enantiomeric excess of **B** was determined in our previous report.[4a,b]

4.4. A typical procedure for the tandem Michael–MPV reaction using B as a chiral reagent

To a dichloromethane solution (20 mL) of (−)-10-mercaptoisoborneol **B** (100 mg, 0.54 mmol) was added, dropwise, dimethylaluminum chloride (0.94 M hexane solution, 0.57 mL, 0.54 mmol) at 0 °C under a nitrogen atmosphere. After the reaction stirred for 30 min, a dichloromethane (5 mL) solution of an α,β-unsaturated ketone **1** (0.45 mmol) was added dropwise at 0 °C, and the mixture then stirred for 1 day at room temperature. The reaction mixture was quenched with sat. ammonium chloride aqueous solution. The aqueous layer was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (hexane/ethyl acetate = 7:1–10:1) gave products **4** in the yields shown in Table 1.

Characterization data for **4a**, **4k**, **4l**, **4m** can be referred to in our previous report.[4a,b]

Minor diastereomers for **4d**, **4e**, **4f**, **4g**, **4h**, **4i** could not be separated by HPLC, completely. Characterization data for minor diastereomers were shown ^{1}H NMR and MS, mainly.

4.4.1. (1*R*,3*R*)-4-Methyl-1-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]-1-phenyl-3-pentanol *anti*-4b. Pale yellow oil; $[\alpha]_D^{26} = +175.1$ (*c* 1.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.20 (m, 5H), 4.10 (dd, $J = 10.1$, 5.1 Hz, 1H), 3.77–3.64 (m, 1H), 2.62 (d, A part of AB, $J_{AB} = 13.2$ Hz, 1H), 2.32 (ddd, A part of AB, $J_{AB} = 18.4$ Hz, $J = 4.6$, 3.3 Hz, 1H), 2.20 (d, B part of AB, $J_{AB} = 13.2$ Hz, 1H), 2.20–2.16 (br s, 1H), 2.00–1.80 (m, 4H), 1.83 (d, B part of AB, $J_{AB} = 18.4$ Hz, 1H), 1.78–1.63 (m, 2H), 1.55–1.47 (m, 1H), 1.36–1.29 (m, 1H), 0.93 (d, $J = 6.8$ Hz, 3H), 0.91 (d, $J = 6.8$ Hz, 3H), 0.88 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.0, 143.9, 128.4 (2), 127.9 (2), 127.0, 73.8, 60.7, 49.2, 47.8, 43.3, 43.1, 41.3, 33.6, 27.6, 26.8, 26.7, 19.9, 19.8, 18.7, 17.5; IR ($CHCl_3$): 3501, 2964, 2878, 1736, 1599, 1491, 1470, 1452 cm^{-1}; MS (20 eV) *m*/*z*: 360 (M^+, 11), 273 (39), 185 (68), 176 (23), 151 (26), 133 (72), 105 (100), 91 (20), 73 (43), 55 (28); HRMS calcd for $C_{22}H_{32}O_2S$ (M^+): 360.2123, found 360.2117.

4.4.2. (1*R*,3*R*)-1-Cyclohexyl-3-[(1*S*,4*R*)-2-oxobornane-10-sulfenyl]-3-phenyl-1-propanol *anti*-4c. Pale yellow oil; $[\alpha]_D^{26} = +144.9$ (*c* 0.64, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.19 (m, 5H), 4.10 (dd, $J = 10.3$, 5.0 Hz, 1H), 3.75 (ddd, $J = 9.3$, 5.7, and 3.3 Hz, 1H), 2.62 (d, A part of AB, $J_{AB} = 13.2$ Hz, 1H), 2.32 (ddd, A part of AB, $J_{AB} = 18.3$ Hz, $J = 4.8$, 3.5 Hz, 1H), 2.20 (d, B part of AB, $J_{AB} = 13.2$ Hz, 1H), 2.03–1.96 (m, 3H), 1.96–1.79 (m, 6H), 1.81 (d, B part of AB, $J_{AB} = 18.3$ Hz, 1H), 1.54 (ddd, $J = 13.6$, 9.3, and 5.0 Hz, 1H), 1.38–1.28 (m, 2H), 1.27–1.00 (m, 7H), 0.88 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.2, 144.2, 128.6 (2), 128.1 (2), 127.2, 73.5, 61.0, 49.4, 48.0, 44.0, 43.5, 43.3, 41.7, 29.3, 28.3, 27.8, 27.0, 26.9, 26.7, 26.6, 26.4, 20.2, 20.1; IR ($CHCl_3$): 3649, 2929, 2854, 1735, 1601, 1452 cm^{-1}; MS (20 eV) *m*/*z*: 400 (M^+, 3), 382 (5), 299 (3), 273 (31), 231 (19), 216 (62), 199 (18), 185 (45), 151 (27), 133 (77), 105 (97), 95 (100), 83 (46), 67 (28), 55 (27); HRMS calcd for $C_{25}H_{36}O_2S$ (M^+): 400.2434, found 400.2436.

4.4.3. (2*S*,4*S*)-2-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-4-hexanol *anti*-4d. Colorless oil; $[\alpha]_D^{23} = +69.4$ (*c* 0.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90–3.99 (m, 1H), 3.08 (ddq, $J = 11.0$, 6.8, and 4.2 Hz, 1H), 2.71 (d, A part of AB, $J_{AB} = 13.0$ Hz, 1H), 2.70–2.65 (br s, 1H), 2.62 (d, B part of AB, $J_{AB} = 13.0$ Hz, 1H), 2.36 (ddd, A part of AB, $J_{AB} = 18.3$ Hz, $J = 4.8$, 2.4 Hz, 1H), 2.09–1.94 (m, 3H), 1.88 (d, B part of AB, $J_{AB} = 18.3$ Hz, 1H), 1.68–1.37 (m, 6H), 1.35 (d, $J = 6.8$ Hz, 3H), 1.04 (s, 3H), 0.96 (t, $J = 7.5$ Hz, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.1, 70.3, 60.9, 47.9, 43.4 (2), 43.2, 39.7, 30.2, 27.4, 26.8, 26.7, 22.9, 20.11, 20.10, 10.1; IR ($CHCl_3$): 3695, 3004–2873, 1735, 1446, 1384, 1350, 1110 cm^{-1}; MS (20 eV) *m*/*z*: 284 (M^+, 47), 211 (34), 185 (100), 151 (27), 123 (13), 109 (26); HRMS calcd for $C_{16}H_{28}O_2S$ (M^+): 284.1810, found 284.1811.

4.4.4. (2*R*,4*S*)-2-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-4-hexanol *syn*-4d. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.90–3.79 (m, 0.4H), 3.68 (ddt, $J = 9.2$, 6.2, and 2.7 Hz, 0.6H), 3.08 (ddq, $J = 11.0$, 6.8, and 4.2 Hz, 0.4H), 2.94–2.86 (m, 0.6H), 2.87 (d, A part of AB, $J_{AB} = 12.8$ Hz, 0.6H), 2.62–2.48 (br s, 0.6), 2.71 (d, A part of AB, $J_{AB} = 13.0$ Hz, 0.4H), 2.70–2.65 (br, 0.4H), 2.62 (d, B part of AB, $J_{AB} = 13.0$ Hz, 0.4H), 2.50 (d, B part of AB, $J_{AB} = 12.8$ Hz, 0.6H), 2.37 (ddd, A part of AB, $J_{AB} = 18.4$ Hz, $J = 4.9$, 3.1 Hz, 0.6H) 2.36 (ddd, A part of AB, $J_{AB} = 18.3$ Hz, $J = 4.8$, 2.4 Hz, 0.4H), 2.09–1.93 (m, 3H), 1.88 (d, B part of AB, $J_{AB} = 18.3$ Hz, 0.4H), 1.87 (d, B part of AB, $J = 18.4$ Hz, 0.6H), 1.68–1.37 (m, 6H), 1.35 (d, $J = 6.8$ Hz, 1.2H), 1.32 (d, $J = 6.8$ Hz, 1.8H), 1.05 (s, 1.8H), 1.04 (s, 1.2H), 0.96 (t, $J = 7.5$ Hz, 3H), 0.91 (s, 1.8H), 0.90 (s, 1.2H); MS (70 eV) *m*/*z*: 284 (M^+, 3), 256 (3), 185 (10), 149 (10), 129 (9), 109 (14), 97 (28), 83 (100), 69 (63), 55 (86); HRMS calcd for $C_{16}H_{28}O_2S$ (M^+): 284.1810, found 284.1807.

4.4.5. (3*S*,5*S*)-3-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-5-undecanol *anti*-4e. Colorless oil; $[\alpha]_D^{21} = +50.6$ (*c* 0.61, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.00–3.91 (m, 1H), 2.89 (ddt, $J = 10.4$, 6.4, and 3.7 Hz, 1H), 2.82–2.78 (br s, 1H), 2.68 (d, A part of AB, $J_{AB} = 13.0$ Hz, 1H), 2.59 (d, B part of AB, $J_{AB} = 13.0$ Hz, 1H), 2.36 (ddd, A part of AB, $J_{AB} = 18.5$ Hz, $J = 4.6$, 2.2 Hz, 1H), 2.09–1.97 (m, 3H), 1.88 (d, B part of AB, $J_{AB} = 18.5$ Hz, 1H), 1.76–1.60 (m, 5H), 1.60–1.36 (m, 5H), 1.36–1.28 (m, 6H), 1.03 (s, 3H), 1.00 (t, $J = 7.3$ Hz, 3H), 0.89 (s, 3H), 0.88 (br t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.2, 68.9, 60.9, 47.9, 46.9, 43.3, 43.2, 41.2, 37.6, 31.8, 29.4, 29.2, 27.7, 26.8, 26.6, 25.8, 22.6, 20.14, 20.08, 14.1, 11.3; IR ($CHCl_3$): 3499, 3004, 2963, 2930, 2874, 2856, 1736, 1466, 1454, 1416, 1390, 1375, 1238 cm^{-1}; MS (70 eV) *m*/*z*: 354 (M^+, 9), 336 (1), 225

(25), 185 (100), 151 (34), 141(22), 123 (21), 113 (54), 81 (50), 69 (49), 55 (98); HRMS calcd for $C_{21}H_{38}O_2S$ (M^+): 354.2592, found 354.2588.

4.4.6. (3*S*,5*S*)-3-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-5-undecanol *syn*-4e. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80–3.72 (m, 1H), 3.00–2.90 (br s, 1H), 2.83 (d, A part of AB, $J_{AB} = 12.7$ Hz, 1H), 2.71–2.62 (m, 1H), 2.47 (d, B part of AB, $J_{AB} = 12.7$ Hz, 1H), 2.37 (ddd, A part of AB, $J_{AB} = 18.4$ Hz, $J = 4.8$, 3.1 Hz, 1H), 2.21–1.96 (m, 3H), 1.87 (d, B part of AB, $J_{AB} = 18.4$ Hz, 1H), 1.74–1.56 (m, 4H), 1. 56–1.22 (m, 12H), 1.05 (s, 3H), 1.00 (t, $J = 7.3$ Hz, 3H), 0.91 (s, 3H), 0.88 (br t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.6, 71.3, 60.7, 47.9, 47.5, 43.6, 43.1, 41.6, 38.0, 32.0, 29.3, 27.9, 26.9, 26.7, 26.4, 25.5, 22.6, 20.3, 20.2, 14.1, 11.1; MS (70 eV) m/z: 354 (M^+, 13), 225 (25), 185 (100), 151 (27), 141 (18), 123 (16), 113 (42), 95 (19), 81 (37), 69 (40), 55 (71); HRMS calcd for $C_{21}H_{38}O_2S$ (M^+): 354.2592, found 354.2589.

4.4.7. (3*S*,5*S*)-3-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-5-tridecanol *anti*-4f. Colorless oil; $[\alpha]_D^{21} = +26.4$ (c 1.84, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.00–3.89 (m, 1H), 2.89 (ddt, $J = 13.2$, 6.2, and 3.5 Hz, 1H), 2.84–2.76 (br, 1H), 2.68 (d, A part of AB, $J_{AB} = 13.0$ Hz, 1H), 2.59 (d, B part of AB, $J_{AB} = 13.0$ Hz, 1H), 2.36 (ddd, A part of AB, $J_{AB} = 18.5$ Hz, $J = 4.8$, 2.4 Hz, 1H), 2.09–1.97 (m, 3H), 1.88 (d, B part of AB, $J_{AB} = 18.5$ Hz, 1H), 1.73–1.36 (m, 10H), 1.34–1.20 (m, 10H), 1.03 (s, 3H), 1.00 (t, $J = 7.3$ Hz, 3H), 0.89 (s, 3H), 0.88 (br t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.2, 68.9, 60.9, 47.9, 46.9, 43.3, 43.2, 41.2, 37.6, 31.9, 30.2, 29.6, 29.3, 29.2 (2), 27.6, 26.8, 26.7, 25.8, 22.6, 20.1, 14.1, 11.3; IR ($CHCl_3$): 3665, 3009, 2963, 2930, 2874, 2856, 1739, 1466, 1452, 1417, 1391, 1375, 1236, 1051 cm^{-1}; MS (70 eV) m/z: 382 (M^+, 8), 225 (25), 213 (16), 185 (100), 141 (28), 123 (19), 109 (45), 95 (23), 81 (44), 69 (50), 55 (69); HRMS calcd for $C_{23}H_{42}O_2S$ (M^+): 382.2905, found 382.2897.

4.4.8. (3*R*,5*S*)-3-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-5-tridecanol *syn*-4f. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81–3.72 (m, 1H), 3.05–2.90 (br s, 1H), 2.83 (d, A part of AB, $J_{AB} = 12.8$ Hz, 1H), 2.71–2.63 (m, 1H), 2.47 (d, B part of AB, $J_{AB} = 12.8$ Hz, 1H), 2.37 (ddd, A part of AB, $J_{AB} = 18.4$ Hz, $J = 4.8$, 2.9 Hz, 1H), 2.13–1.94 (m, 3H), 1.87 (d, B part of AB, $J_{AB} = 18.4$ Hz, 1H), 1.75–1.56 (m, 4H), 1.56–1.20 (m, 16H), 1.05 (s, 3H), 1.00 (t, $J = 7.3$ Hz, 3H), 0.91 (s, 3H), 0.90 (br t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.6, 71.3, 60.7, 47.9, 47.5, 43.5, 43.1, 41.6, 38.0, 31.9, 29.7, 29.6, 29.3, 27.9, 26.9, 26.7, 26.3, 25.5, 22.7, 20.3, 20.2, 14.1, 11.1; MS (70 eV) m/z: 382 (M^+, 12), 225 (25), 213 (15), 185 (100), 141 (26), 123 (15), 109 (38), 95 (13), 81 (35), 69 (43), 55 (55); HRMS calcd for $C_{23}H_{42}O_2S$ (M^+): 382.2905, found 382.2908.

4.4.9. (2*S*,4*S*)-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-2-heptanol *anti*-4g. Colorless oil; $[\alpha]_D^{24} = +63.2$ (c 0.94, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.17 (ddq, $J = 9.5$, 6.2, and 2.4 Hz, 1H), 2.90–2.85 (br s, 1H), 2.93 (ddt, $J = 10.3$, 6.6, and 3.7 Hz, 1H), 2.69 (d, A part of AB, $J_{AB} = 13.2$ Hz, 1H), 2.59 (d, B part of AB, $J_{AB} = 13.2$ Hz, 1H), 2.36 (ddd, A part of AB, $J_{AB} = 18.5$ Hz, $J = 4.8$, 2.2 Hz, 1H), 2.10–1.94 (m, 3H), 1.88 (d, B part of AB, $J_{AB} = 18.5$ Hz, 1H), 1.69 (ddd, $J = 14.5$, 9.5, and 3.7 Hz, 1H), 1.66–1.34 (m, 7H), 1.21 (d, $J = 6.2$ Hz, 3H), 1.03 (s, 3H), 0.93 (t, $J = 7.3$ Hz, 3H), 0.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 219.3, 66.0, 62.0, 48.9, 46.1, 44.33, 44.25, 44.1, 39.7, 28.7, 27.8, 27.7, 24.5, 21.09, 21.07, 21.0, 15.0; IR ($CHCl_3$): 3666, 3003, 2966, 2930, 2873, 1735, 1466, 1454, 1416, 1391, 1375, 1236 cm^{-1}; MS (20 eV) m/z: 298 (M^+, 35), 211 (12), 183 (100), 151 (52), 123 (36), 109 (69), 81 (59), 67 (44), 55 (86); HRMS calcd for $C_{17}H_{30}O_2S$ (M^+): 298.1966, found 298.1969.

4.4.10. (2*S*,4*R*)-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-2-heptanol *syn*-4g. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.04–3.95 (m, 1H), 3.10–2.96 (br s, 1H), 2.83 (d, A part of AB, $J_{AB} = 12.7$ Hz, 1H), 2.74–2.65 (m, 1H), 2.47 (d, B part of AB, $J_{AB} = 12.7$ Hz, 1H), 2.37 (ddd, A part of AB, $J_{AB} = 18.4$ Hz, $J = 4.6$, 2.9 Hz, 1H), 2.12–1.94 (m, 3H), 1.87 (d, B part of AB, $J_{AB} = 18.4$ Hz, 1H), 1.76–1.62 (m, 2H), 1.60–1.34 (m, 6H), 1.20 (d, $J = 6.2$ Hz, 3H), 1.05 (s, 3H), 0.92 (t, $J = 7.3$ Hz, 3H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.6, 67.5, 60.7, 47.9, 45.5, 43.8, 43.5, 43.1, 37.6, 26.9, 26.7, 26.1, 23.8, 20.3, 20.2, 19,9, 14.0; MS (70 eV) m/z: 298 (M^+, 13), 185 (43), 151 (17), 123 (17), 109 (34), 95 (29), 83 (98), 69 (91), 55 (100); HRMS calcd for $C_{17}H_{30}O_2S$ (M^+): 298.1966, found 298.1971.

4.4.11. (4*S*,6*S*)-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-6-dodecanol *anti*-4h. Colorless oil; $[\alpha]_D^{26} = +48.8$ (c 1.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.00–3.88 (m, 1H), 2.93 (ddt, $J = 10.1$, 6.4, and 3.5 Hz, 1H), 2.86–2.82 (br s, 1H), 2.69 (d, A part of AB, $J_{AB} = 13.0$ Hz, 1H), 2.58 (d, B part of AB, $J_{AB} = 13.0$ Hz, 1H), 2.36 (ddd, A part of AB, $J_{AB} = 18.4$ Hz, $J = 4.8$, 2.2 Hz, 1H), 2.09–1.97 (m, 3H), 1.88 (d, B part of AB, $J_{AB} = 18.4$ Hz, 1H), 1.71–1.43 (m, 11H), 1.37–1.22 (m, 7H), 1.03 (s, 3H), 0.92 (t, $J = 7.3$ Hz, 3H), 0.89 (br t, $J = 7.1$ Hz, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.2, 68.9, 60.9, 47.9, 45.0, 43.3, 43.1, 41.5, 38.7, 37.6, 31.8, 29.4, 27.5, 26.8, 26.6, 25.8, 22.6, 20.2, 20.1 (2), 14.1, 14.0; IR ($CHCl_3$): 3690, 2939, 1733, 1458, 1234 cm^{-1}; MS (70 eV) m/z: 368 (M^+, 4), 239 (9), 185 (44), 136 (12), 122 (18), 109 (25), 97 (30), 81 (36), 69 (64), 55 (100); HRMS calcd for $C_{22}H_{40}O_2S$ (M^+): 368.2749, found 368.2745.

4.4.12. (4*R*,6*S*)-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-6-dodecanol *syn*-4h. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80–3.72 (m, 1H), 3.03–2.90 (br s, 1H), 2.83 (d, A part of AB, $J_{AB} = 12.7$ Hz, 1H), 2.74–2.67 (m, 1H), 2.47 (d, B part of AB, $J_{AB} = 12.7$ Hz, 1H), 2.37 (ddd, A part of AB, $J_{AB} = 18.4$ Hz, $J = 4.8$, 3.1 Hz, 1H), 2.12–1.94 (m, 3H), 1.87 (d, B part of AB, $J_{AB} = 18.4$ Hz, 1H), 1.73–1.25 (m, 18H), 1.05 (s, 3H), 0.92 (t, $J = 7.3$ Hz,

3H), 0.90 (s, 3H), 0.88 (br t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.7, 71.3, 60.7, 47.9, 45.5, 43.5, 43.1, 42.1, 38.0, 37.5, 31.8, 29.4, 26.9, 26.7, 26.2, 25.5, 22.6, 20.3, 20.2, 19.9, 14.1, 14.0; MS (70 eV) m/z: 368 (M^+, 2), 185 (6), 152 (10), 124 (10), 111 (16), 98 (31), 84 (90), 69 (49), 55 (100); HRMS calcd for $C_{22}H_{40}O_2S$ (M^+): 368.2749, found 368.2744.

4.4.13. (4*S*,6*S*)-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-6-tetradecanol *anti*-4i. Colorless oil; $[\alpha]_D^{25} = +42.5$ (c 2.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.00–3.91 (m, 1H), 2.93 (ddt, $J = 10.1$, 6.4, and 3.5 Hz, 1H), 2.84–2.78 (br s, 1H), 2.69 (d, A part of AB, $J_{AB} = 12.8$ Hz, 1H), 2.58 (d, B part of AB, $J_{AB} = 12.8$ Hz, 1H), 2.36 (ddd, A part of AB, $J_{AB} = 18.4$ Hz, $J = 4.8$, 2.2 Hz, 1H), 2.09 (m, 3H), 1.88 (d, B part of AB, $J_{AB} = 18.4$ Hz, 1H), 1.70–1.34 (m, 10H), 1.32–1.24 (m, 12H), 1.04 (s, 3H), 0.92 (t, $J = 7.1$ Hz, 3H), 0.89 (s, 3H), 0.88 (br t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.1, 68.9, 60.9, 47.9, 44.9, 43.3, 43.1, 41.5, 38.7, 37.6, 31.9, 29.7, 29.5, 29.2, 27.5, 26.8, 26.6, 25.8, 22.6, 20.2, 20.1 (2), 14.1, 14.0; IR ($CHCl_3$): 3510, 2959, 2930, 2874, 3856, 1736, 1466, 1454, 1416, 1391, 1373 cm^{-1}; MS (70 eV) m/z: 396 (M^+, 9), 368 (1), 239 (23), 227 (15), 211 (18), 194 (9), 185 (100), 167 (12), 151 (27), 141 (33), 109 (41), 98 (31), 83 (70), 69 (73), 55 (99); HRMS calcd for $C_{24}H_{44}O_2S$ (M^+): 396.3062, found 396.3058.

4.4.14. (4*R*,6*S*)-4-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-6-tetradecanol *syn*-4i. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80–3.72 (m, 1H), 3.10–2.92 (br s, 1H), 2.83 (d, A part of AB, $J_{AB} = 12.8$ Hz, 1H), 2.71 (quintet, $J = 7.1$ Hz, 1H), 2.47 (d, B part of AB, $J_{AB} = 12.8$ Hz, 1H), 1.37 (ddd, A part of AB, $J_{AB} = 18.4$ Hz, $J = 4.8$, 2.9 Hz, 1H), 2.12–1.98 (m, 3H), 1.87 (d, B part of AB, $J_{AB} = 18.4$ Hz, 1H), 1.72–1.63 (m, 2H), 1.63–1.20 (m, 20H), 1.05 (s, 3H), 0.92 (t, $J = 7.1$ Hz, 3H), 0.91 (s, 3H), 0.88 (br t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.7, 71.3, 60.7, 47.9, 45.5, 43.5, 43.1, 42.5, 38.0, 37.5, 31.9, 29.7, 29.6, 29.3, 26.9, 26.7, 26.2, 25.5, 22.7, 20.3, 20.2, 19.9, 14.1, 14.0; MS (70 eV) m/z: 396 (M^+, 12), 239 (25), 227 (15), 185 (100), 151 (25), 141 (31), 123 (15), 109 (37), 81 (39), 69 (49), 55 (63); HRMS calcd for $C_{24}H_{44}O_2S$ (M^+): 396.3062, found 396.3058.

4.4.15. (1*R*,3*S*)-3-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-1-phenyl-1-hexanol *anti*-4j. Colorless oil; $[\alpha]_D^{22} = +53.6$ (c 1.16, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.31 (m, 4H), 7.27–7.23 (m, 1H), 5.12 (dt, $J = 9.8$, 3.5 Hz, 1H), 3.14 (d, $J = 4.0$ Hz, 1H), 3.00–2.93 (m, 1H), 2.74 (d, A part of AB, $J_{AB} = 12.9$ Hz, 1H), 2.61 (d, B part of AB, $J_{AB} = 12.9$ Hz, 1H), 2.37 (ddd, A part of AB, $J_{AB} = 18.4$ Hz, $J = 4.9$, 2.5 Hz, 1H), 2.09–1.95 (m, 4H), 1.89 (d, B part of AB, $J_{AB} = 18.4$ Hz, 1H), 1.78–1.36 (m, 7H), 1.05 (s, 3H), 0.91 (s, 3H), 0.91 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.2, 144.9, 128.3 (2), 127.1, 125.6 (2), 71.4, 60.9, 47.9, 45.0, 44.1, 43.4, 43.2, 38.6, 27.6, 26.9, 26.8, 20.2, 20.1, 20.0, 14.0; IR ($CHCl_3$): 3502, 3031, 3022, 3010, 2960, 2933, 2873, 1735, 1602, 1494, 1454, 1415, 1298, 1280 cm^{-1}; MS (70 eV) m/z: 360 (M^+, 2), 342 (12), 176 (66), 159 (97), 133 (100), 129 (59), 117 (96), 105 (59), 91 (41), 77 (27), 67 (18), 55 (16); HRMS calcd for $C_{22}H_{32}O_2S$ (M^+): 360.2123, found 360.2125.

4.4.16. (1*R*,3*R*)-3-[(1*S*,4*R*)-2-Oxobornane-10-sulfenyl]-1-phenyl-1-hexanol *syn*-4j. Colorless oil; $[\alpha]_D^{22} = +31.1$ (c 0.96, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41–7.32 (m, 4H), 7.29–7.24 (m, 1H), 4.93–4.90 (m, 1H), 3.12 (d, $J = 2.6$ Hz, 1H), 2.85 (d, A part of AB, $J_{AB} = 12.6$ Hz, 1H), 2.69–2.61 (m, 1H), 2.47 (d, B part of AB, $J_{AB} = 12.6$ Hz, 1H), 2.38 (ddd, A part of AB, $J_{AB} = 18.3$ Hz, $J = 4.7$, 2.9 Hz, 1H), 2.14–1.88 (m, 5H), 1.88 (d, B part of AB, $J_{AB} = 18.3$ Hz, 1H), 1.63–1.35 (m, 6H), 1.07 (s, 3H), 0.92 (s, 3H), 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 217.7, 144.6, 128.4 (2), 127.5, 125.9 (2), 73.5, 60.7, 47.9, 45.0, 43.9, 43.5, 43.1, 37.4, 26.9, 26.7, 26.2, 20.4, 20.2, 19.9, 13.9; IR ($CHCl_3$): 3421, 3033, 3014, 3004, 2989, 2960, 2933, 2893, 1735, 1602, 1494, 1456, 1415, 1390, 1373, 1317, 1299, 1280 cm^{-1}; MS (70 eV) m/z: 360 (M^+, 1), 342 (6), 176 (41), 159 (53), 133 (71), 129 (100), 117 (66), 105 (51), 91 (41), 77 (39), 67 (29), 55 (27); HRMS calcd for $C_{22}H_{32}O_2S$ (M^+): 360.2123, found 360.2119.

4.5. A typical procedure for the conversion of sulfides *anti*-4 into 1,3-mercapto alcohols *anti*-3 under acidic conditions

To a suspension of lithium aluminum hydride (0.75 mmol) in tetrahydrofuran (1 mL) was added dropwise a solution of *anti*-**4** (0.25 mmol) in tetrahydrofuran (3 mL) at 0 °C, and the reaction mixture then stirred for 2 h at room temperature under a nitrogen atmosphere. The reaction mixture was diluted diethyl ether, and quenched with sat. sodium sulfate aqueous solution at 0 °C, and dried over magnesium sulfate, filtrated, and concentrated in vacuo to give a crude diol. To a solution of a crude diol in dichloromethane (3 mL) was added $BF_3{\cdot}OEt_2$ (0.25 mmol), and the resulting mixture stirred at room temperature under a nitrogen atmosphere for 2.5 h until all starting material had disappeared on TLC analysis. If any starting material remained, additional $BF_3{\cdot}OEt_2$ (0.05–0.13 mmol) was added. 1-Dodecanethiol (Dod-SH) (5.0 mmol) was then added and the resultant mixture stirred for 5.5 h at room temperature. At this stage, if the reaction has gone to completion, the additional $BF_3{\cdot}OEt_2$ (0.13 mmol) was added. The reaction mixture was poured into water, and extracted with ethyl acetate. The combined organic layers were washed with brine, and dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (hexane/ethyl acetate = 10:1) gave *anti*-**3** in the yields shown in Table 2.

4.5.1. (1*R*,3*S*)-1-Mercapto-1-phenyl-3-butanol *anti*-3a. Colorless oil; $[\alpha]_D^{24} = +121.8$ (c 0.59, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.30 (m, 4H), 7.26–7.22 (m, 1H), 4.23 (dt, $J = 9.5$, 5.7 Hz, 1H), 4.05 (ddq, $J = 8.6$, 6.1, and 4.0 Hz, 1H), 2.04 (ddd, A part of AB,

$J_{AB} = 14.1$ Hz, $J = 8.6$, 5.7 Hz, 1H), 1.93 (ddd, B part of AB, $J_{AB} = 14.1$ Hz, $J = 9.5$, 4.0 Hz, 1H), 1.93 (d, $J = 5.7$ Hz, 1H), 1.57 (br s, 1H), 1.25 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 128.7 (2), 127.2, 126.7 (2), 65.8, 48.3, 40.8, 23.8; IR ($CHCl_3$): 3610, 3008, 2970, 2931, 1600, 1492, 1454, 1377, 1126 cm^{-1}; MS (70 eV) m/z: 182 (M^+, 10), 164 (21), 148 (14), 123 (10), 105 (100), 91 (14), 77 (20); HRMS calcd for $C_{10}H_{14}OS$ (M^+): 182.0765, found 182.0773. [97% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25×0.46); eluent: hexane/isopropanol = 10/1; flow rate: 1.0 mL/min; Temp.: 26 °C; detector: 254 nm, (−): 9.6 min, (+): 11.5 min].

4.5.2. (1*R*,3*R*)-1-Mercapto-4-methyl-1-phenyl-3-pentanol *anti*-3b. Colorless oil; $[\alpha]_D^{24} = +125.5$ (c 1.49, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.29 (m, 5H), 4.28 (dt, $J = 9.0$, 5.9 Hz, 1H), 3.73 (dt, $J = 7.5$, 5.3 Hz, 1H), 2.02–1.92 (m, 2H), 1.89 (d, $J = 5.9$ Hz, 1H), 1.70 (septet d, $J = 6.9$, 5.3 Hz, 1H), 1.65–1.50 (br s, 1H), 0.94 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 128.7 (2), 127.2, 126.8 (2), 74.2, 43.6, 41.2, 33.9, 18.9, 17.5; IR ($CHCl_3$): 3622, 3065, 2964, 2912, 2897, 2876, 1601, 1493, 1468, 1452, 1389, 1369 cm^{-1}; MS (20 eV) m/z: 210 (M^+, 5), 192 (12), 176 (7), 158 (7), 133 (71), 105 (100), 91 (24), 73 (33), 55 (26); HRMS calcd for $C_{12}H_{18}OS$ (M^+): 210.1078, found 210.1076. [99% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25×0.46); eluent: hexane/isopropanol = 9/1; flow rate: 0.2 mL/min; Temp.: 27 °C; detector: 254 nm, (−): 27.9 min, (+): 35.0 min].

4.5.3. (1*R*,3*R*)-1-Cyclohexyl-3-mercapto-3-phenyl-1-propanol *anti*-3c. Colorless oil; $[\alpha]_D^{26} = +128.3$ (c 0.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.21 (m, 5H), 4.29 (dt, $J = 9.0$, 6.0 Hz, 1H), 3.75–3.68 (br m, 1H), 2.05–1.90 (m, 2H), 1.88 (d, $J = 6.0$ Hz, 1H), 1.86–1.63 (m, 5H), 1.60–1.56 (br s, 1H), 1.42–1.31 (m, 1H), 1.30–0.98 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 128.7 (2), 127.1, 126.8 (2), 73.7, 44.0, 43.7, 41.2, 29.1, 27.9, 26.4, 26.2, 26.1; IR ($CHCl_3$): 3601, 3007, 2930, 2855, 1495, 1450, 1387, 1238, 1223 cm^{-1}; MS (20 eV) m/z: 250 (M^+, 2), 232 (15), 216 (12), 198 (23), 169 (7), 155 (12), 133 (86), 105 (93), 95 (70), 77 (56), 55 (100); HRMS calcd for $C_{15}H_{22}OS$ (M^+): 250.1391, found 250.1386. [99% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25×0.46); eluent: hexane/isopropanol = 50/1; flow rate: 0.5 mL/min; Temp.: 26 °C; detector: 254 nm, (−): 13.7 min, (+): 17.3 min].

4.5.4. (2*S*,4*S*)-2-Mercapto-4-hexanol *anti*-3d. Colorless oil; $[\alpha]_D^{24} = +63.3$ (c 0.26, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80–3.78 (m, 1H), 3.27–3.16 (m, 1H), 1.70 (ddd, $J = 14.3$, 9.9, and, 3.8 Hz, 1H), 1.67–1.63 (br m, 1H), 1.56–1.45 (m, 3H), 1.49 (d, $J = 6.8$ Hz, 1H), 1.38 (d, $J = 6.8$ Hz, 3H), 0.96 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 71.0, 47.3, 32.5, 30.6, 26.8, 9.9; IR ($CHCl_3$): 3620, 2968, 2926, 2878, 1456, 1377 cm^{-1}; MS (20 eV) m/z: 134 (M^+, 12), 132 (32), 116 (65), 100 (68), 83 (100), 69 (76), 55 (46); HRMS calcd for $C_6H_{14}OS$ (M^+): 134.0765, found 134.0770.

4.5.5. (3*S*,5*S*)-3-Mercapto-5-undecanol *anti*-3e. Colorless oil; $[\alpha]_D^{26} = +28.8$ (c 1.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99–3.89 (m, 1H), 3.05–2.97 (m, 1H), 1.77–1.63 (m, 3H), 1.62–1.42 (m, 5H), 1.42–1.22 (m, 7H), 1.34 (d, $J = 7.3$ Hz, 1H), 1.02 (t, $J = 7.3$ Hz, 3H), 0.90 (br t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.4, 45.6, 39.5, 38.0, 32.9, 31.8, 29.3, 25.6, 22.6, 14.1, 11.5; IR ($CHCl_3$): 3620, 3007, 2963, 2932, 2874, 2858, 1460, 1379 cm^{-1}; MS (20 eV) m/z: 204 (M^+, 10), 186 (42), 170 (28), 157 (73), 141 (35), 129 (65), 115 (82), 97 (100), 88 (96), 75 (88), 55 (54); HRMS calcd for $C_{11}H_{24}OS$ (M^+): 204.1548, found 204.1552.

4.5.6. (3*S*,5*S*)-3-Mercapto-5-tridecanol *anti*-3f. Colorless oil; $[\alpha]_D^{26} = +27.8$ (c 1.06, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.98–3.89 (m, 1H), 3.04–2.94 (m, 1H), 1.73–1.64 (m, 3H), 1.62–1.41 (m, 5H), 1.36–1.24 (m, 11H), 1.34 (d, $J = 7.3$ Hz, 1H), 1.02 (t, $J = 7.3$ Hz, 3H), 0.89 (br t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.4, 45.6, 39.5, 38.0, 32.9, 31.8, 29.6, 29.5, 29.2, 25.7, 22.6, 14.1, 11.5; IR ($CHCl_3$): 3690, 2961, 2930, 2856, 1458, 1437 cm^{-1}; MS (20 eV) m/z: 232 (M^+, 10), 214 (17), 198 (8), 185 (28), 167 (22), 157 (28), 167 (22), 157 (28), 141 (38), 129 (8), 115 (33), 98 (90), 83 (100), 69 (53), 58 (62); HRMS calcd for $C_{13}H_{28}OS$ (M^+): 232.1861, found 232.1857.

4.5.7. (2*S*,4*S*)-4-Mercapto-2-heptanol *anti*-3g. Colorless oil; $[\alpha]_D^{24} = +32.6$ (c 1.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.15 (ddq, $J = 9.5$, 6.4, and 2.9 Hz, 1H), 3.09–2.99 (m, 1H), 1.76 (ddd, $J = 14.3$, 9.5, and 3.5 Hz, 1H), 1.65–1.40 (m, 6H), 1.37 (d, $J = 7.1$ Hz, 1H), 1.23 (d, $J = 5.5$ Hz, 3H), 0.92 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 65.5, 47.7, 42.0, 37.5, 24.1, 20.1, 13.7; IR ($CHCl_3$): 3647, 2999, 2930, 1456 cm^{-1}; MS (20 eV) m/z: 148 (M^+, 10), 146 (50), 130 (13), 114 (37), 97 (100), 83 (63), 71 (27), 55 (65); HRMS calcd for $C_7H_{16}OS$ (M^+): 148.0922, found 148.0916.

4.5.8. (4*S*,6*S*)-4-Mercapto-6-dodecanol *anti*-3h. Colorless oil; $[\alpha]_D^{23} = +26.7$ (c 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.99–3.90 (m, 1H), 3.12 (m, 1H), 1.73 (ddd, $J = 14.3$, 9.9, and 3.3 Hz, 1H), 1.68–1.40 (m, 9H), 1.40–1.28 (m, 7H), 1.36 (d, $J = 7.3$ Hz, 1H), 0.92 (t, $J = 7.1$ Hz, 3H), 0.90 (br t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 69.4, 46.0, 42.2, 38.0, 31.9, 29.6, 29.2, 25.7, 22.7, 20.2, 14.1, 13.8; IR ($CHCl_3$): 3630, 2958, 2931, 2858, 1458, 1379 cm^{-1}; MS (20 eV) m/z: 218 (M^+, 10), 200 (37), 184 (20), 167 (25), 157 (79), 141 (35), 129 (83), 113 (63), 102 (69), 97 (100), 89 (87), 81 (50), 69 (59), 55 (67); HRMS calcd for $C_{12}H_{26}OS$ (M^+): 218.1704, found 218.1707.

4.5.9. (1*R*,3*S*)-1-Mercapto-1-phenyl-3-pentanol *anti*-3k. Colorless oil; $[\alpha]_D^{23} = +120.9$ (c 0.88, $CHCl_3$); ^{1}H NMR

(400 MHz, $CDCl_3$): δ 7.36–7.29 (m, 4H), 7.25–7.21 (m, 1H), 4.28 (dt, $J = 8.8$, 6.0 Hz, 1H), 3.83 (tt, $J = 7.5$, 4.9 Hz, 1H), 1.99 (m, 2H), 1.91 (d, $J = 6.0$ Hz, 1H), 1.59 (br s, 1H), 1.58–1.44 (m, 2H), 0.97 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 128.7 (2), 127.2, 126.7 (2), 70.9, 46.2, 40.9, 30.5, 9.8; IR ($CHCl_3$): 3616, 2968, 2935, 2879, 1600, 1492, 1454 cm^{-1}; MS (70 eV) m/z: 196 (M^+, 4), 178 (16), 162 (8), 136 (22), 123 (13), 105 (100), 91 (14), 77 (13), 59 (38); HRMS calcd for $C_{11}H_{16}OS$ (M^+): 196.0922, found 196.0915. [99% ee, chiral HPLC analysis; DAICEL CHIRALCEL OB (25×0.46); eluent: hexane/isopropanol = 100/1; flow rate: 0.5 mL/min; Temp.: 25 °C; detector: 254 nm, (−): 35.5 min, (+): 39.6 min].

4.5.10. (1*R*,3*S*)-1-Mercapto-1-phenyl-3-hexanol *anti*-3l. Colorless oil; $[\alpha]_D^{23} = +105.8$ (*c* 0.76, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.29 (m, 4H), 7.26–7.21 (m, 1H), 4.27 (dt, $J = 8.1$, 6.0 Hz, 1H), 3.90 (quintet, $J = 5.9$ Hz, 1H), 2.02–1.94 (m, 2H), 1.90 (d, $J = 6.0$ Hz, 1H), 1.56 (br s, 1H), 1.52–1.31 (m, 4H), 0.94 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 128.7 (2), 127.2, 126.7 (2), 69.4, 46.7, 40.9, 39.9, 18.7, 14.0; IR ($CHCl_3$): 3618, 3064–2873, 1600, 1492, 1465, 1454, 1434, 1380 cm^{-1}; MS (20 eV) m/z: 210 (M^+, 9), 192 (19), 176 (27), 159 (24), 133 (39), 123 (16), 105 (100), 91 (12); HRMS calcd for $C_{12}H_{18}OS$ (M^+): 210.1078, found 210.1077. [99% ee, chiral HPLC analysis; DAICEL CHIRALCEL OB (25×0.46); eluent: hexane/isopropanol = 50/1; flow rate: 0.5 mL/min; Temp.: 27 °C; detector: 254 nm, (−): 21.4 min, (+): 25.6 min].

4.6. Determination of the enantiomeric excess of 1,3-mercapto alcohols 3d, 3e, 3f, 3g, 3h

The enantiomeric excesses of **3d**, **3e**, **3f**, **3g**, **3h** were determined by chiral HPLC analyses of their *S*-, *O*-benzoylated compounds **11d**, **11e**, **11f**, **11g**, **11h**, respectively.

4.6.1. General procedure for benzoylation of 1,3-mercapto alcohols. To a pyridine solution (3 mL) of *anti*-**3** (0.70 mmol) was added benzoic anhydride (4.2 mmol) and 4-dimethylaminopyridine (0.04 mmol), and the reaction mixture was stirred at room temperature under a nitrogen atmosphere for 2 h. The reaction mixture was quenched with a sat. sodium hydrogen carbonate aqueous solution, and the aqueous layer was extracted with hexane. The organic layer was dried over sodium sulfate, and concentrated in vacuo to give crude material. Purification of the crude material by silica gel column chromatography (hexane/ethyl acetate = 20:1) gave benzoylated compounds **11**.

4.6.1.1. (2*S*,4*S*)-2-Benzoylthiohex-4-yl benzoate 11d. 92% yield. Colorless oil; $[\alpha]_D^{22} = +66.8$ (*c* 1.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.02 (m, 2H), 7.90–7.86 (m, 2H), 7.58–7.50 (m, 2H), 7.43–7.36 (m, 4H), 5.30–5.21 (m, 1H), 3.95–3.84 (m, 1H), 2.11 (ddd, A part of AB, $J_{AB} = 14.5$ Hz, $J = 7.9$, 6.0 Hz, 1H), 2.06 (ddd, B part of AB, $J_{AB} = 14.5$ Hz, $J = 8.1$, 4.8 Hz, 1H), 1.85–1.72 (m, 2H), 1.47 (d, $J = 7.0$ Hz, 3H), 0.98 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 166.1, 137.2, 133.1, 132.7, 130.6 (2), 129.6 (2), 128.5 (2), 128.2 (2), 127.1, 73.7, 40.2, 36.4, 27.2, 21.9, 9.3; IR ($CHCl_3$): 2970–2927, 1712, 1658, 1600, 1581, 1450 cm^{-1}; MS (20 eV) m/z: 342 (M^+, 0.5), 220 (24), 204 (18), 187 (29), 115 (31), 105 (100), 77 (8); HRMS calcd for $C_{20}H_{22}O_3S$ (M^+): 342.1280, found 342.1290. [99% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25×0.46); eluent: hexane/isopropanol = 50/1; flow rate: 0.5 mL/min; Temp.: 28 °C; detector: 254 nm, (+): 11.8 min, (−): 14.9 min].

4.6.1.2. (3*S*,5*S*)-3-Benzoylthioundec-5-yl benzoate 11e. 97% yield. Colorless oil; $[\alpha]_D^{25} = +38.3$ (*c* 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.01 (m, 2H), 7.91–7.86 (m, 2H), 7.54–7.50 (m, 2H), 7.45–7.37 (m, 4H), 5.34–5.25 (m, 1H), 3.83 (ddt, $J = 9.0$, 7.5, and 5.3 Hz, 1H), 2.15 (ddd, A part of AB, $J_{AB} = 14.5$ Hz, $J = 8.6$, 5.3 Hz, 1H), 2.01 (ddd, B part of AB, $J_{AB} = 14.5$ Hz, $J = 9.0$, 4.2 Hz, 1H), 1.91–1.65 (m, 4H), 1.45–1.20 (m, 8H), 1.03 (t, $J = 7.1$ Hz, 3H), 0.88–0.82 (br t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 166.1, 137.3, 133.1, 132.7, 130.7, 129.6 (2), 128.4 (2), 128.2 (2), 127.2 (2), 72.8, 42.7, 38.5, 34.5, 31.7, 29.2, 28.4, 25.1, 22.5, 14.1, 11.2; IR ($CHCl_3$): 2961, 2932, 2860, 1711, 1659, 1601, 1581, 1450, 1276 cm^{-1}; MS (20 eV) m/z: 412 (M^+, 0.4), 290 (19), 274 (6), 257 (11), 206 (4), 185 (31), 169 (6), 152 (43), 122 (26), 105 (100), 82 (10), 68 (7), 55 (2); HRMS calcd for $C_{25}H_{32}O_3S$ (M^+): 412.2072, found 412.2076. [99% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25×0.46); eluent: hexane/isopropanol = 200/1; flow rate: 0.5 mL/min; Temp.: 28 °C; detector: 254 nm, (+): 11.6 min, (−): 14.5 min].

4.6.1.3. (3*S*,5*S*)-3-Benzoylthiotridec-5-yl benzoate 11f. 94% yield. Colorless oil; $[\alpha]_D^{26} = +34.7$ (*c* 0.91, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.00 (m, 2H), 7.91–7.86 (m, 2H), 7.58–7.50 (m, 2H), 7.45–7.37 (m, 4H), 5.34–5.25 (m, 1H), 3.82 (ddt, $J = 8.9$, 7.3, and 5.3 Hz, 1H), 2.15 (ddd, A part of AB, $J_{AB} = 14.5$ Hz, $J = 8.6$, 5.3 Hz, 1H), 2.01 (ddd, B part of AB, $J_{AB} = 14.5$ Hz, $J = 8.9$, 4.0 Hz, 1H), 1.89–1.65 (m, 4H), 1.35–1.18 (m, 12H), 1.03 (t, $J = 7.3$ Hz, 3H), 0.86 (br t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 166.1, 137.3, 133.1, 132.7, 130.7, 129.6 (2), 128.4 (2), 128.2 (2), 127.2 (2), 72.7, 42.7, 38,5, 34.5, 31.8, 29.5 (2), 29.4, 29.2, 28.4, 25.1, 22.6, 14.1; IR ($CHCl_3$): 2957, 2928, 2856, 1711, 1659, 1601, 1581, 1450, 1315, 1277 cm^{-1}; MS (20 eV) m/z: 440 (M^+, 0.4), 318 (16), 302 (5), 285 (12), 213 (29), 197 (7), 180 (36), 157 (5), 122 (13), 105 (100), 82 (20), 68 (12), 57 (3); HRMS calcd for $C_{27}H_{36}OS$ (M^+): 440.2385, found 440.2390. [99% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25×0.46); eluent: hexane/isopropanol = 200/1; flow rate: 0.5 mL/min; Temp.: 28 °C; detector: 254 nm, (+): 12.6 min, (−): 14.8 min].

4.6.1.4. (2*S*,4*S*)-4-Benzoylthiohept-2-yl benzoate 11g. 96% yield. Colorless oil; $[\alpha]_D^{26} = +74.3$ (*c* 0.54, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.02 (m, 2H), 7.91–7.87 (m, 2H), 7.57–7.50 (m, 2H), 7.44–7.37 (m, 4H),

5.34–5.28 (m, 1H), 3.96–3.88 (m, 1H), 2.21 (ddd, A part of AB, $J_{AB} = 14.5$ Hz, $J = 8.8$, 5.2 Hz, 1H), 1.96 (ddd, B part of AB, $J_{AB} = 14.5$ Hz, $J = 9.0$, 4.2 Hz, 1H), 1.79–1.70 (m, 2H), 1.58–1.44 (m, 2H), 1.41 (d, $J = 6.2$ Hz, 3H), 0.94 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 166.1, 137.2, 133.1, 132.7, 130.7, 129.5 (2), 128.5 (2), 128.2 (2), 127.2 (2), 69.4, 41.1, 40.9, 37.5, 20.4, 20.0, 13.8; IR ($CHCl_3$): 3065, 2961, 2934, 2874, 1713, 1659, 1601, 1582, 1450, 1281 cm^{-1}; MS (70 eV) m/z: 356 (M^+, 0.6), 251 (2), 234 (20), 218 (9), 192 (16), 129 (30), 105 (100), 96 (10), 55 (4); HRMS calcd for $C_{21}H_{24}O_3S$ (M^+): 356.1446, found 356.1438. [99% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25 × 0.46); eluent: hexane/isopropanol = 50/1; flow rate: 0.1 mL/min; Temp.: 26 °C; detector: 254 nm, (+): 48.0 min, (−): 50.9 min].

4.6.1.5. (4*S*,6*S*)-4-Benzoylthiododec-6-yl benzoate 11h. 96% yield. Colorless oil; $[\alpha]_D^{24} = +32.7$ (c 0.61, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.00 (m, 2H), 7.90–7.85 (m, 2H), 7.56–7.49 (m, 2H), 7.44–7.36 (m, 4H), 5.33–5.25 (m, 1H), 3.92–3.82 (m, 1H), 2.14 (ddd, A part of AB, $J_{AB} = 14.4$ Hz, $J = 8.6$, 5.1 Hz, 1H), 2.00 (ddd, B part of AB, $J_{AB} = 14.4$ Hz, $J = 9.0$, 4.0 Hz, 1H), 1.80–1.60 (m, 4H), 1.62–1.22 (m, 10H), 0.91 (t, $J = 7.3$ Hz, 3H), 0.85 (br t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.4, 166.1, 137.3, 133.1, 132.7, 130.7, 129.6 (2), 128.4 (2), 128.2 (2), 127.2 (2), 72.7, 41.0, 39.0, 37.6, 34.5, 31.7, 29.2, 25.1, 22.5, 20.0, 14.1, 13.8; IR ($CHCl_3$):2959, 2931, 2872, 2860, 1711, 1659, 1601, 1581, 1450, 1466, 1379, 1362, 1315, 1277, 1176, 1115 cm^{-1}; MS (20 eV) m/z: 426 (M^+, 0.4), 304 (13), 288 (5), 271 (10), 262 (8), 199 (31), 166 (30), 129 (8), 105 (100), 96 (13), 82 (10), 67 (7), 55 (3); HRMS calcd for $C_{26}H_{34}O_3S$ (M^+): 426.2229, found 426.2236. [99% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25 × 0.46); eluent: hexane/isopropanol = 200/1; flow rate: 0.5 mL/min; Temp.: 27 °C; detector: 254 nm, (+): 12.0 min, (−): 13.8 min].

4.7. A typical procedure for conversion of sulfides *anti*-4 into vinyl sulfides 9 through a Wagner–Meerwein rearrangement under basic conditions

To a solution of *anti*-**4** (1.4 mmol) in tetrahydrofuran (5 mL) was added *N*,*N*-diisopropylethylamine (41 mmol) and chloromethyl methyl ether (14 mmol). The reaction mixture was refluxed for 5 h under a nitrogen atmosphere. The mixture was poured into water, and neutralized with 1 M HCl, and extracted with ethyl acetate. The combined organic layer was washed with brine, and dried over magnesium sulfate, filtered, and concentrated in vacuo to give a crude material. Subsequently, to a suspension of lithium aluminum hydride (1.0 mmol) in tetrahydrofuran (2 mL) was added dropwise a solution of the above crude material in tetrahydrofuran (6 mL) at 0 °C, and the reaction mixture stirred for 2 h at room temperature under a nitrogen atmosphere. The reaction mixture was diluted diethyl ether, and quenched with sat. sodium sulfate aqueous solution at 0 °C, and then dried over magnesium sulfate, and filtrated, concentrated in vacuo to give a crude diol derivative. Purification of the residue by silica gel column chromatography (hexane/ethyl acetate = 15:1) gave **7** in the yields shown in Table 3.

4.7.1.1. (1*R*,3*S*)-1-Methoxymethoxy-3-[(1*S*,2*R*,4*R*)-2-hydroxybornane-10-sulfenyl]-1-phenylhexane 7j. Colorless oil; $[\alpha]_D^{26} = +71.6$ (c 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.25 (m, 5H), 4.96 (dd, $J = 9.9$, 3.3 Hz, 1H), 4.55 (d, A part of AB, $J_{AB} = 6.6$ Hz, 1H), 4.52 (d, B part of AB, $J_{AB} = 6.6$ Hz, 1H), 3.95–3.92 (br m, 1H), 3.39 (s, 3H), 2.92–2.84 (m, 1H), 2.84 (d, $J = 2.9$ Hz, 1H), 2.69 (d, A part of AB, $J_{AB} = 10.4$ Hz, 1H), 2.54 (d, B part of AB, $J_{AB} = 10.4$ Hz, 1H), 2.07 (ddd, $J = 14.8$, 9.9, and 3.8 Hz, 1H), 1.83–1.42 (m, 10 H), 1.28–1.21 (m, 1H), 1.07 (s, 3H), 1.06–1.02 (m, 1H), 0.93 (t, $J = 7.3$ Hz, 3H), 0.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 128.5 (2), 127.6, 126.6 (2), 94.8, 76.7, 76.4, 56.0, 51.9, 47.6, 45.1, 43.3, 43.2, 39.0, 38.1, 31.0, 29.3, 27.2, 20.7, 20.0, 19.9 14.0; IR ($CHCl_3$):3519, 3006, 2989, 2956, 2881, 1602, 1492, 1465, 1454, 1388, 1369, 1309, 1284, 1199, 1095, 1033, 914 cm^{-1}; MS (20 eV) m/z:406 (M^+, 3), 343 (51), 326 (20), 223 (29), 158 (43), 129 (100), 105 (48), 91 (21), 77 (6); HRMS calcd for $C_{24}H_{38}O_3S$ (M^+):406.2542, found 406.2549.

4.7.1.2. (1*R*,3*R*)-1-Methoxymethoxy-3-[(1*S*,2*R*,4*R*)-2-hydroxybornane-10-sulfenyl]-1,3-diphenylpropane 7m. Colorless oil; $[\alpha]_D^{23} = +128.3$ (c 1.26, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37–7.22 (m, 10H), 4.84 (dd, $J = 8.9$, 4.8 Hz, 1H), 4.55 (d, A part of AB, $J_{AB} = 6.6$ Hz, 1H), 4.52 (d, B part of AB, $J_{AB} = 6.6$ Hz, 1H), 3.92 (dd, $J = 9.5$, 5.5 Hz, 1H), 3.86–3.83 (br m, 1H), 3.39 (s, 3H), 2.56 (d, A part of AB, $J_{AB} = 10.8$ Hz, 1H), 2.51 (d, $J = 2.9$ Hz, 1H), 2.36 (ddd, A part of AB, $J_{AB} = 14.3$ Hz, $J = 8.9$, 5.5 Hz, 1H), 2.23 (d, B part of AB, $J_{AB} = 10.8$ Hz, 1H), 2.14 (ddd, B part of AB, $J_{AB} = 14.3$ Hz, $J = 9.5$, 4.8 Hz, 1H), 1.77–1.56 (m, 4H), 1.33–1.26 (m, 1H), 1.15–1.08 (m, 1H), 1.02–0.95 (m, 1H), 0.97 (s, 3H), 0.68 (s, 3H); IR ($CHCl_3$): 3529, 3028, 3012, 2954, 2823, 1600, 1492, 1454, 1369 cm^{-1}; MS (70 eV) m/z: 440 (M^+, 1), 422 (2), 360 (14), 275 (8), 222 (21), 192 (49), 165 (13), 134 (73), 105 (100), 91 (39), 77 (41); HRMS calcd for $C_{27}H_{36}O_3S$ (M^+): 440.2385, found 440.2382.

To a solution of **7** (0.4 mmol) and *N*,*N*-diisopropylethylamine (10.6 mmol) in dichloromethane (3 mL) was added a solution of methanesulfonic anhydride (3.5 mmol) in dichloromethane (2 mL) at −10 °C. The reaction mixture was stirred for 15 min at −10 °C. It was then poured into water, and neutralized with 1 M HCl, and extracted with ethyl acetate. The combined organic layers were washed with brine, and dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (hexane/ethyl acetate = 100:1) gave **9j**,**m** in the yields shown in Table 3.

4.7.2.1. (1*R*,4*S*)-3-[(1*R*,3*S*)-1-Methoxymethoxy-1-phenylhexylsulfanylmethylene]-2,2-dimethyl-bicyclo[2.2.1]-heptane 9j. Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.23 (m, 5H), 5.60 (s, 0.09H), 5.39 (s, 0.91H), 4.93 (dd, $J = 9.6$, 3.9 Hz, 1H), 4.55 (d, A part of AB,

$J_{AB} = 6.7$ Hz, 1H), 4.54 (d, B part of AB, $J_{AB} = 6.7$ Hz, 1H), 3.36 (s, 3H), 3.15 (br, 1H), 2.40–2.80 (m, 1H), 2.07–1.98 (m, 1H), 1.92 (br d, $J = 2.4$ Hz, 1H), 1.80–1.35 (m, 8H), 1.28–1.13 (m, 3H), 1.03 (s, 3H), 1.01 (s, 3H), 0.93–0.88 (m, 3H); IR ($CHCl_3$): 2958, 2893, 2871, 1602, 1492, 1456, 1382, 1361, 1097, 1033 cm^{-1}; MS (70 eV) m/z: 388 (M^+, 52), 343 (14), 223 (42), 136 (77), 117 (43), 105 (100), 91 (68), 77 (23), 55 (32); HRMS calcd for $C_{24}H_{36}O_2S$ (M^+): 388.2436, found 388.2430.

4.7.2.2. (1*R*,4*S*)-3-[(1*R*,3*R*)-3-Methoxymethoxy-1,3-diphenylpropylsulfanylmethylene]-2,2-dimethyl-bicyclo[2.2.1]heptane 9m. Colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 7.36–7.17 (m, 10.0H), 5.42 (s, 0.1H), 5.21 (s, 0.9H), 4.78–4.66 (m, 1.0H), 4.54–4.48 (m, 2.0H), 3.87 (dd, $J = 8.2$, 6.9 Hz, 0.9H), 3.75 (dd, $J = 8.2$, 6.9 Hz, 0.1H), 3.34 (s, 2.7H), 3.33 (s, 0.3H), 3.01 (d, $J = 3.4$ Hz, 0.9H), 2.56–2.12 (m, 2.2H), 1.85–1.80 (m, 0.9H), 1.62–1.45 (m, 3.0H), 1.35–1.26 (m, 1.0H), 1.18–0.76 (m, 2.0H), 0.93 (s, 2.7H), 0.88 (s, 2.7H), 0.79 (s, 0.3H), 0.77 (s, 0.3H); IR ($CHCl_3$): 3028, 2954, 2889, 2823, 1600, 1492, 1454, 1380, 1361 cm^{-1}; MS (70 eV) m/z: 422 (M^+, 32), 360 (25), 345 (11), 212 (38), 193 (35), 151 (100), 134 (42), 121 (54), 105 (83), 91 (54), 77 (35); HRMS calcd for $C_{27}H_{34}O_2S$ (M^+): 422.2279, found 422.2281.

4.8. A typical procedure for conversion of vinyl sulfides 9 into thioformate 10 by ozonolysis

A solution of **9** (0.04 mmol) in dichloromethane (15 mL) was bubbled through with ozone until the solution was changed blue at −78 °C. The reaction mixture was then stirred at −78 °C for 30 min. After 30 min, ozone was displaced with oxygen, followed by nitrogen. The reaction mixture was added dropwise to a solution of triphenylphosphine (0.13 mmol) in dichloromethane (1 mL) at −78 °C, with the resulting mixture then stirred for 1 h at −78 °C. After 1 h, the reaction mixture was allowed to warm to room temperature, and stirred overnight. The reaction mixture was concentrated in vacuo to give a crude material. The crude material was purified by preparative TLC (hexane/ethyl acetate = 5:1) to give **10** in the yields shown in Scheme 1.

4.8.1. (1*R*,3*S*)-*S*-(3-Methoxymethoxy-1-phenylhexyl) thioformate 10j. Colorless oil; $[\alpha]_D^{21} = +77.5$ (c 1.14, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 10.18 (s, 1H), 7.36–7.25 (m, 5H), 4.71 (dd, $J = 10.3$, 2.9 Hz, 1H), 4.51 (d, A part of AB, $J_{AB} = 3.4$ Hz, 1H), 4.50 (d, B part of AB, $J_{AB} = 3.4$ Hz, 1H), 4.02 (dddd, $J = 10.6$, 7.3, 5.8, and 3.6 Hz, 1H), 3.32 (s, 3H), 2.16 (dddd, A part of AB, $J_{AB} = 14.9$ Hz, $J = 10.3$, 3.6, and 1.1 Hz, 1H), 1.81 (ddd, B part of AB, $J_{AB} = 14.9$ Hz, $J = 10.6$, 2.9 Hz, 1H), 1.71–1.58 (m, 2H), 1.50–1.36 (m, 2H), 0.92 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.9, 141.7, 128.5 (2), 127.8, 126.6 (2), 94.6, 75.7, 56.1, 43.0, 39.8, 38.4, 19.8, 13.8; IR ($CHCl_3$): 3009, 2960, 2933, 2893, 2875, 2844, 2827, 1666, 1602, 1492, 1465, 1456, 1348, 1149, 1095, 1033, 1024, 916 cm^{-1}; MS FAB(+) m/z: 305 (M^++Na, 36); HRMS calcd for $C_{15}H_{22}O_3SNa$ (M^++Na): 305.1187, found 305.1191.

4.8.2. (1*R*,3*R*)-*S*-(3-Methoxymethoxy-1,3-diphenylpropyl) thioformate 10m. Colorless oil; $[\alpha]_D^{23} = +219.0$ (c 0.32, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 10.10 (d, $J = 0.8$ Hz, 1H), 7.37–7.23 (m, 10H), 4.95 (dd, $J = 9.6$, 6.0 Hz, 1H), 4.62 (dd, $J = 8.8$, 4.9 Hz, 1H), 4.49 (s, 2H), 3.31 (s, 3H), 2.49 (dddd, A part of AB, $J_{AB} = 14.5$ Hz, $J = 8.8$, 6.0, and 0.8 Hz, 1H), 2.28 (ddd, B part of AB, $J_{AB} = 14.5$ Hz, $J = 9.5$, 4.9 Hz, 1H); IR ($CHCl_3$): 3004, 2950, 2827, 1670, 1600, 1492, 1454, 1346 cm^{-1}; MS (20 eV) m/z: 316 (M^+, 0.2), 271 (11), 225 (28), 209 (19), 193 (28), 151 (100), 105 (86), 77 (8); HRMS calcd for $C_{18}H_{20}O_3S$ (M^+): 316.1133, found 316.1112.

4.9. A typical procedure for hydrolysis of thioformate 10 to 1,3-mercapto alcohols *anti*-3

A solution of **10** (0.21 mmol) in methanol (5 mL) was adjusted to pH 1 with *concd* HCl, and stirred at 55 °C overnight. The mixture was neutralized with sat. sodium hydrogen carbonate aqueous solution and the solvent removed in vacuo. Water was added to this residue, and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (hexane/ethyl acetate = 7:1) gave *anti*-**3** in the yields shown in Scheme 3.

4.9.1. (1*R*,3*S*)-3-Mercapto-1-phenyl-1-hexanol *anti*-3j. Colorless oil; $[\alpha]_D^{23} = +45.2$ (c 1.53, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.25 (m, 5H), 5.06 (dd, $J = 10.1$, 2.9 Hz, 1H), 3.15–3.06 (m, 1H), 2.13 (br s, 1H), 2.09 (ddd, A part of AB, $J_{AB} = 14.3$ Hz, $J = 10.1$, 3.5 Hz, 1H), 1.69–1.38 (m, 4H), 1.67 (ddd, B part of AB, $J_{AB} = 14.3$ Hz, $J = 10.7$, 2.9 Hz, 1H), 1.43 (d, $J = 7.7$ Hz, 1H), 0.91 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 128.5 (2), 127.5, 125.6 (2), 71.8, 48.3, 41.9, 37.6, 20.1, 13.7; IR ($CHCl_3$): 3600, 3008, 2960, 2933, 2910, 2873, 1602, 1492, 1465, 1456, 1436, 1309, 1280, 1002 cm^{-1}; MS (70 eV) m/z: 210 (M^+, 6), 208 (10), 192 (48), 176 (21), 159 (100), 145 (26), 129 (36), 117 (85), 105 (71), 91 (20), 55 (9); HRMS calcd for $C_{12}H_{18}OS$ (M^+): 210.1078, found 210.1076. [99% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25×0.46); eluent: hexane/isopropanol = 50/1; flow rate: 1.0 mL/min; Temp.: 26 °C; detector: 254 nm, (+): 16.1 min, (−): 18.8 min].

4.9.2. (1*R*,3*R*)-3-Mercapto-1,3-diphenyl-1-propanol *anti*-3m. Colorless oil; $[\alpha]_D^{25} = +105.7$ (c 0.77, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–7.21 (m, 10H), 4.90–4.86 (br m, 1H), 4.18 (ddd, $J = 9.4$, 6.1, and 5.8 Hz, 1H), 2.40 (ddd, A part of AB, $J_{AB} = 14.2$ Hz, $J = 8.8$, 5.8 Hz, 1H), 2.21 (ddd, B part of AB, $J_{AB} = 14.2$ Hz, $J = 9.4$, 4.7 Hz, 1H), 2.03 (br s, 1H), 1.97 (d, $J = 6.1$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 143.9, 128.8 (2), 128.6 (2), 127.9, 127.3, 126.8 (2), 125.9 (2), 72.2, 48.3, 40.6; IR ($CHCl_3$): 3602, 3064, 3035, 3006, 1602, 1494, 1454, 1053 cm^{-1}; MS (70 eV) m/z: 244 (M^+, 2), 226 (15), 210 (69), 122 (27), 105 (96), 104 (100), 91 (16), 51 (29);

HRMS calcd for $C_{15}H_{16}OS$ (M^+): 244.0922, found 244.0924. [99% ee, chiral HPLC analysis; DAICEL CHIRALCEL OD (25×0.46); eluent: hexane/isopropanol = 50/1; flow rate: 1.0 mL/min; Temp.: 25 °C; detector: 254 nm, (−): 32.4 min, (+):37.8 min].

4.10. A procedure for the conversion of vinyl sulfide 9m into 1,3-mercapto alcohol *anti*-3m using an *n*-Bu_2BOTf/Dod-SH system

To a solution of **9m** (13 mg, 0.03 mmol) and Dod-SH (71 μL, 0.30 mmol) in dichloromethane (1 mL) was added dropwise dibutylboron triflate (1.0 M dichloromethane, 30 μL, 0.03 mmol) at −30 °C. The reaction mixture was stirred at −30 °C for 1.5 h under a nitrogen atmosphere. After 1.5 h, the reaction mixture was allowed to warm to room temperature, and stirred at room temperature for 3.5 h. The reaction mixture was poured into water and then extracted with ethyl acetate. The combined organic layer was washed with brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification of the residue by preparative TLC (hexane/ethyl acetate = 5:1) gave the title compound (*anti*-**3m**) (5 mg, 68%).

4.11. Determination of the absolute configuration of major isomer *anti*-4

Previously, we determined the absolute configuration of the major isomer by the following procedure. A compound *anti*-**4a** was converted into crystalline sulfone by oxidation using Oxone®. The absolute configuration of this sulfone was determined by X-ray crystallographic analysis.[4a,b]

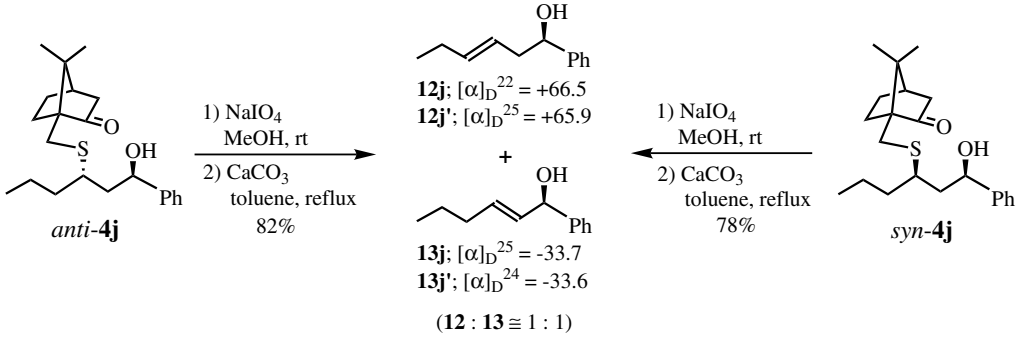
4.12. Determination of the absolute configuration of minor isomer *syn*-4

Each of the diastereomers *anti*-**4j** and *syn*-**4j** were separated by HPLC. Absolute configuration of the minor isomer was determined by the following sequence (Scheme 4). Compound *anti*-**4j** was oxidized to the sulfoxide, and the sulfoxide subsequently converted into the homoallylic alcohol **12j** (known compound[8]) and allylic alcohol **13j**. Compounds **12j′** and **13j′** obtained from *syn*-**4j** by the same method were identical to **12j** and **13j**, respectively. Consequently, the absolute configuration of the minor isomer *syn*-**4j** was determined.

4.12.1. A typical procedure for conversion into homoallylic alcohol 12j and allylic alcohol 13j from 4j. To a solution of *anti*- (or *syn*-) **4j** (0.44 mmol) in methanol (10 mL) was added sodium periodate (0.67 mmol), and stirred at room temperature overnight. The reaction mixture was filtered, and the solvent removed in vacuo. The residue was added water, and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography (hexane/ethyl acetate = 1:1) gave a sulfoxide (quantitative yield). Subsequently, to a solution of this sulfoxide (0.44 mmol) in toluene (20 mL) was added calcium carbonate (1.09 mmol), and refluxed overnight. The reaction mixture was filtered, and the solvent removed in vacuo to give a crude product. The crude product was then purified with silica gel column chromatography (hexane/ethyl acetate = 8:1) to give a mixture of **12j** and **13j** (70–82%, **12j**:**13j**≅1:1). The mixture of **12j** and **13j** was separated into each compound by HPLC.

4.12.1.1. (3*E*,1*R*)-1-Phenylhex-3-en-1-ol 12j. Colorless oil; $[\alpha]_D^{22} = +66.5$ (*c* 0.74, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.37–7.26 (m, 5H), 5.67–5.59 (m, 1H), 5.44–5.36 (m, 1H), 4.68 (br dd, *J* = 7.0, 5.4 Hz, 1H), 2.51–2.35 (m, 2H), 2.08 (br, 1H), 2.04 (quintet, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 136.7, 128.3 (2), 127.3, 125.8 (2), 124.4, 73.4, 42.8, 25.6, 13.7; IR ($CHCl_3$): 3602, 3006, 2966, 2933, 2873, 2850, 1602, 1494, 1454, 1436, 1382, 1315 cm^{-1}; MS FAB(+) *m*/*z*: 199 (M^++Na, 27); HRMS calcd for $C_{12}H_{16}ONa$ (M^++Na): 199.1099, found 199.1102.

4.12.1.2. (3*E*,1*R*)-1-Phenylhex-3-en-1-ol 12j′. Colorless oil; $[\alpha]_D^{25} = +65.9$ (*c* 0.36, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.37–7.24 (m, 5H), 5.69–5.59 (m, 1H), 5.45–5.36 (m, 1H), 4.68 (ddd, *J* = 8.0, 4.6, and 2.2 Hz, 1H), 2.51–2.36 (m, 2H), 2.07 (br, 1H), 2.04 (quintet, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 136.8, 128.3 (2),



Scheme 4.

127.4, 125.8 (2), 124.4, 73.4, 42.8, 25.6, 13.7; IR ($CHCl_3$): 3600, 3006, 2966, 2933, 2873, 2850, 1602, 1494, 1454, 1434, 1382, 1315 cm^{-1}; MS FAB(+) m/z: 199 (M^++Na, 21); HRMS calcd for $C_{12}H_{16}ONa$ (M^++Na): 199.1099, found 199.1103.

4.12.1.3. (2*E*,1*R*)-1-Phenylhex-2-en-1-ol 13j. Colorless oil; $[\alpha]_D^{25} = -33.7$ (c 0.84, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.25 (m, 5H), 5.76 (dt, $J = 15.2$, 6.4 Hz, 1H), 5.66 (ddt, $J = 15.2$, 6.6, and 1.1 Hz, 1H), 5.16 (d, $J = 6.6$ Hz, 1H), 2.03 (br q, $J = 7.2$ Hz, 2H), 1.91 (br, 1H), 1.42 (sextet, $J = 7.5$ Hz, 2H), 0.90 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 132.6, 132.4, 128.4 (2), 127.5, 126.1 (2), 75.2, 34.2, 22.2, 13.7; IR ($CHCl_3$): 3600, 3006, 2962, 2931, 2873, 1666, 1602, 1492, 1454, 1379, 968 cm^{-1}; MS (20 eV) m/z: 176 (M^+, 23), 158 (42), 133 (86), 129 (100), 105 (26), 91 (11), 55 (16); HRMS calcd for $C_{12}H_{16}O$ (M^+): 176.1201, found 176.1204.

4.12.1.4. (2*E*,1*R*)-1-phenylhex-2-en-1-ol 13j′. Colorless oil; $[\alpha]_D^{24} = -33.6$ (c 0.60, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.25 (m, 5H), 5.76 (dt, $J = 15.2$, 6.4 Hz, 1H), 5.66 (ddt, $J = 15.2$, 6.6, and 1.1 Hz, 1H), 5.16 (d, $J = 6.6$ Hz, 1H), 2.03 (br q, $J = 7.2$ Hz, 2H), 1.93 (br, 1H), 1.42 (sextet, $J = 7.5$ Hz, 2H), 0.90 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 132.6, 132.4, 128.4 (2), 127.4, 126.1 (2), 75.2, 34.2, 22.2, 13.7; IR ($CHCl_3$): 3600, 3006, 2962, 2931, 2873, 1666, 1602, 1492, 1454, 1379, 968 cm^{-1}; MS (20 eV) m/z: 176 (M^+, 18), 158 (40), 133 (73), 129 (100), 105 (24), 91 (8), 55 (14); HRMS calcd for $C_{12}H_{16}O$ (M^+): 176.1201, found 176.1193.

References and notes

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