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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.5b00185 • Publication Date (Web): 25 Feb 2015

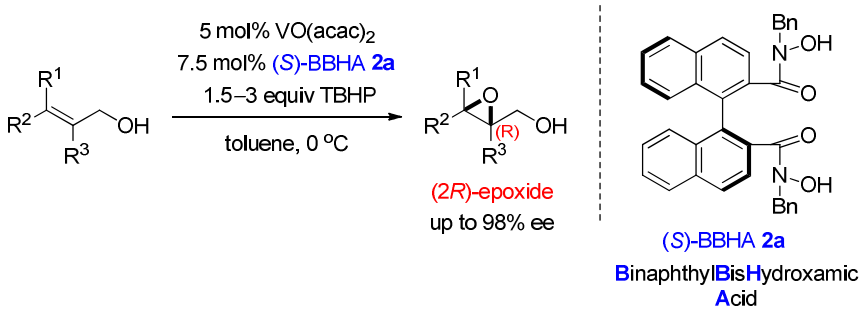
Asymmetric Epoxidation of Allylic Alcohols Catalyzed by Vanadium–Binaphthylbishydroxamic Acid Complex

Masahiro Noji,* Toshihiro Kobayashi, Yuria Uechi, Asami Kikuchi, Hisako Kondo, Shigeo Sugiyama, and Keitaro Ishii

Department of Life and Pharmaceutical Sciences, Meiji Pharmaceutical University, 2-522-1 Noshio, Kiyose, Tokyo 204-8588, Japan

mnoji@my-pharm.ac.jp

GRAPHICAL ABSTRACT



ABSTRACT: A vanadium–binaphthylbishydroxamic acid (BBHA) complex-catalyzed asymmetric epoxidation of allylic alcohols is described. The optically active binaphthyl-based ligands BBHA **2a** and **2b** were synthesized from (*S*)-1,1′-binaphthyl-2,2′-dicarboxylic acid and *N*-substituted-*O*-trimethylsilyl (TMS)-protected hydroxylamines via a one-pot, three-step procedure. The epoxidations of 2,3,3-trisubstituted allylic alcohols using the vanadium complex of **2a** were easily performed in toluene with a TBHP water solution to afford (2*R*)-epoxy alcohols in good to excellent enantioselectivities.

INTRODUCTION

The asymmetric epoxidation of allylic alcohols is an attractive method for the synthesis of chiral epoxy alcohols, which are useful chiral building blocks for the production of pharmaceuticals and agrochemicals.[1] The Katsuki–Sharpless asymmetric epoxidation of allylic alcohols is reliable method of obtaining synthetically useful chiral epoxy alcohols.[2] The epoxidation gives very high asymmetric induction for various types of allylic alcohols. The enantioselectivity depends only on the chirality of L-(+)-, or D-(−)-tartrates as ligands, independent of the structure of the allylic alcohols. Therefore, the absolute configuration of the products can be predicted. Although the epoxidation is conducted using commercially available titanium tetraisopropoxide, tartrate, and *tert*-butylhydroperoxide (TBHP) as an oxidizing agent, it requires strict anhydrous conditions.

Recently, the vanadium–chiral hydroxamic acid (V–HA) complex-catalyzed asymmetric epoxidation of allylic alcohols with TBHP has also become a highly potent approach to obtaining chiral epoxy alcohols. The advantage of the V–HA complex-catalyzed method is its simple reaction procedure, which can be conducted in aqueous TBHP solution, rather than under anhydrous conditions. Since the first report by Sharpless,[3] the V–HA complex-catalyzed system has been extensively studied for the last decade.[4–7] Yamamoto has reported C_2-symmetric cyclohexane diamine-based chiral bishydroxamic acid (BHA) ligands.[8] The vanadium–BHA system exhibited excellent enantioselectivities for a wide range of substituted allylic alcohols. The recent application of BHA ligands for Mo-, Zr-, Hf-, and W-catalyzed systems demonstrated that the C_2-symmetric chiral BHA ligand was very useful for asymmetric oxidations of sulfides, simple alkenes, homoallylic alcohols, and allylic amine derivatives.[9]

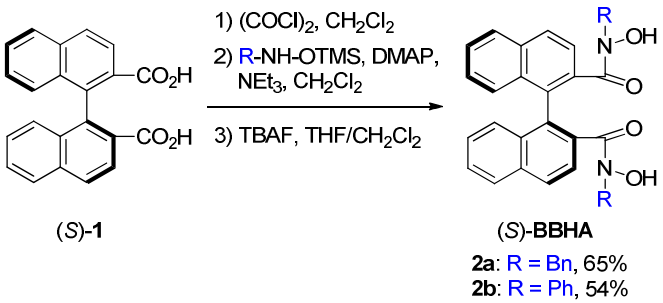
Axially chiral C_2-symmetric binaphthyl derivatives have been recognized as a privileged chiral ligand for many

enantioselective reactions.[10] The C_2-symmetric chiral auxiliaries minimize the possibility of diastereomeric interactions at the transition state and are therefore useful for obtaining high enantiomeric excesses and for elucidating the mechanism of asymmetric induction.[11] The steric bulkiness and structural rigidity of naphthalene rings would be effective for the production of large asymmetric space. The flexibility of the binaphthyl axis enable the chiral ligand to adapt a wide range of substrates. This *induced-fit* property[12] would also be a great advantage for the asymmetric reaction. Herein, we report the vanadium–binaphthylbishydroxamic acid (BBHA) complex-catalyzed asymmetric epoxidation of allylic alcohols.

RESULTS AND DISCUSSION

The BBHA ligands were synthesized via a one-pot, three-step procedure. The method involved (i) the preparation of the acid chloride of (*S*)-1,1′-binaphthyl-2,2′-dicarboxylic acid[13] (**1**) followed by (ii) the reaction of the *N*-substituted-*O*-TMS protected hydroxylamines and then (iii) the removal of the TMS groups from the amide. Chromatographic purification and recrystallization gave pure BBHA ligands **2a** and **2b** in 65% and 54% chemical yields from (*S*)-**1** (Scheme 1).

Scheme 1. Synthesis of binaphthylbishydroxamic acid (BBHA)



(*S*)-**1** (*S*)-**BBHA**

2a: R = Bn, 65%
2b: R = Ph, 54%

^{1}H NMR spectra of **2a** and **2b** in $CDCl_3$ at room temperature showed broad signals, probably because of the

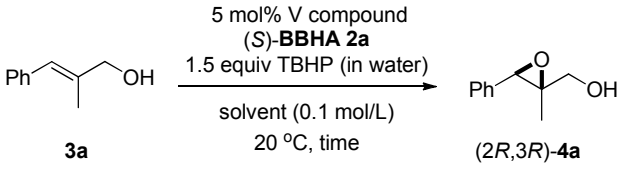
structural rigidity of the amide linkage and hydrogen bonding. Therefore, most of the ^{13}C NMR signals of **2a** and **2b** were not observed. NMR measurements at 80 °C improved the situation with regard to the broad signals in the ^{1}H and ^{13}C spectra of **2a** and **2b**. However, the structure assignments on the basis of the aromatic NMR signals remained difficult. Consequently, single-crystal X-ray diffraction analysis was used to ascertain the structure and conformation of BBHA ligands **2a** and **2b**.

A single crystal of **2a** was obtained by slow evaporation from toluene solution at room temperature. Similarly, a single crystal of **2b** was prepared from EtOH–THF solution. The molecular structures of **2a** and **2b** were determined by single-crystal X-ray diffraction analysis.[14] The crystal prepared from **2a** contained one toluene molecule per **2a**. The dihedral angle of the binaphthyl axis, C2-C1-C1′-C2′, of **2a** and **2b** was 85° and 70°, respectively. Intramolecular hydrogen bonds between the carbonyl oxygen and hydroxyl group were observed in both structures, and the oxygen–oxygen distances were 2.6–2.7 Å. In the crystal of **2a** with toluene, the hydroxamic acid moieties were transoid structures and the torsional angles of HO–N–C=O were 170° and 175°. In contrast, cisoid and transoid structures were observed in the crystal structure of **2b** and the torsional angles were 14° and 167°, respectively. The cisoid hydroxamic groups formed intramolecular stacking structures between the naphthalene and benzene rings.[15] BBHA **2a** appears to have a larger asymmetric space than **2b**, and we employed **2a** for initial examination of the asymmetric epoxidation.

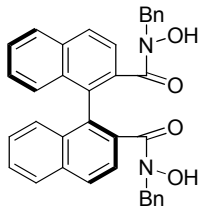
To optimize the epoxidation conditions using BBHA **2a**, allylic alcohol **3a** was used as a model substrate. The vanadium/ligand ratio, solvent, and vanadium compounds were investigated using 5 mol% of vanadium compound;

the results are reported in Table 1. A typical reaction procedure was as follows: BBHA **2a** and 5 mol% of vanadium compound were stirred in the solvent at 20 °C for 24 h, whereupon 1.5 equiv of TBHP water solution and then allylic alcohol **3a** were added. The mixture was stirred at 20 °C until the complete consumption of allylic alcohol **3a** or 24 h of reaction time. The reaction was then quenched by adding saturated aqueous Na_2SO_3 solution; subsequent extraction and chromatographic purification gave epoxy alcohols **4a** and recovered **3a**. The enantiomeric excess (ee) was determined by chiral-stationary-phase HPLC analysis. The absolute stereochemistry of (2*R*,3*R*)-**4a** was determined by comparison of the chiroptical property with the literature data.[16]

Table 1. Optimization of Vanadium/Ligand Ratio, Solvent, and Vanadium Compounds



3a (2*R*,3*R*)-**4a**



(*S*)-**BBHA 2a**

entry[a]	vanadium (5 mol%)	**BBHA 2a (mol%)**	solvent	time (h)	epoxide **4a** yield (%)	epoxide **4a** ee[b] (%)	recov. **3a** (%)
1	$VO(OEt)_3$	10	toluene	24	60	86	31
2	$VO(OEt)_3$	7.5	toluene	24	62	86	24
3	$VO(OEt)_3$	3	toluene	3	86	38	0
4	$VO(OEt)_3$	7.5	$CHCl_3$	9.5	83	80	4
5	$VO(OEt)_3$	7.5	CH_2Cl_2	24	78	84	8
6	$VO(OEt)_3$	7.5	EtOAc	24	64	85	20
7	$VO(OEt)_3$	7.5	CH_3CN	24	40	72	35
8	$VO(OEt)_3$	7.5	acetone	24	20	68	63
9	**$VO(acac)_2$**	**7.5**	**toluene**	**6**	**84**	**89**	**7**
10	$VO(acac)_2$	7.5	CH_2Cl_2	6	81	87	5
11	$VO(acac)_2$	7.5	EtOAc	24	62	83	21
12	$VO(O\textit{i}\text{-}Pr)_3$	7.5	toluene	24	65	87	26

[a]Complexation time was 24 h. [b]Determined by HPLC.

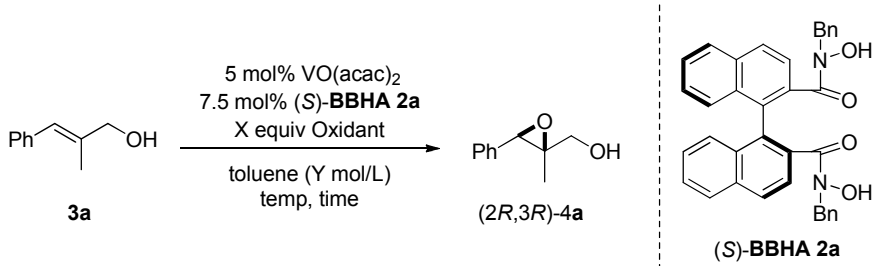
The vanadium/ligand ratio for the best asymmetric induction was examined via the reactions described in entries 1–3. Generally, one hydroxamic acid group (C=O–NOH) serves as one bidentate ligand using two oxygen atoms of

carbonyl and hydroxyl groups. Because BBHA **2a** has two hydroxamic acids and might be potentially tetradendate, we examined the optimum molar amount of BBHA for 5 mol% of $VO(OEt)_3$ (entries 1–3). The use of 10 mol% of **2a** (potentially 20 mol% of coordination sites for 5 mol% of $VO(OEt)_3$) and 7.5 mol% of **2a** (potentially 15 mol% of coordination sites for 5 mol% of $VO(OEt)_3$) gave better asymmetric induction of 86% ee (entries 1 and 2) than the quantities used in entry 3. Allylic alcohol **3a** was recovered in entries 1 and 2; thus, the reaction proceeded more slowly in the cases of entries 1 and 2 than in the case of entry 3. The vanadium excess condition in entry 3, $VO(OEt)_3$ 5 mol% and BBHA 3 mol% (potentially 6 mol% of coordination sites), appeared to produce ligand-free vanadium species, which resulted in racemic epoxy alcohol **4a** with improved yield and decreased enantioselectivity. We therefore chose the best ratio of 7.5 mol% BBHA for 5 mol% of vanadium.

Next, the solvent effect was examined using an excess–ligand condition: 5 mol% of $VO(OEt)_3$ and 7.5 mol% of BBHA **2a**. The epoxidation proceeded rapidly in $CHCl_3$ and CH_2Cl_2, moderately in toluene and EtOAc, and slowly in acetonitrile and acetone (entries 4–8). A considerable amount of allylic alcohol **3a** was recovered from the reactions in EtOAc, acetonitrile, and acetone. The best enantioselectivity was observed in toluene in the reaction involving $VO(OEt)_3$ (entries 2 and 4–7). A similar tendency was observed in the solvent screening reaction involving $VO(acac)_2$ (entries 9–11). $VO(acac)_2$ is an inexpensive, air-stable, and easy-to-handle solid reagent. Toluene was also the best solvent for the combination of **2a** and $VO(acac)_2$. A comparison of the vanadium compounds revealed that $VO(acac)_2$ exhibited slightly better enantioselectivity than $VO(OEt)_3$ or $VO(O\textit{i}\text{-}Pr)_3$ (entries 2, 9, and 12). Further optimization of reaction conditions was conducted with 5 mol% of $VO(acac)_2$ and 7.5 mol%

of BBHA **2a** in toluene. The complexation time, oxidant, concentration, and equivalents of TBHP were examined; the results are summarized in Table 2.

Table 2. Optimization of the Complexation Time, Oxidant, Reaction Temperature, and Equivalents of TBHP



entry	complexation time (h)	oxidant	conc. (Y mol/L)	oxidant (X equiv)	reaction temp. (°C)	reaction time (h)	epoxide **4a** yield (%)	epoxide **4a** ee[a] (%)	recov **3a** (%)
1	**24**	TBHP (in water)	0.1	1.5	20	6	84	89	7
2	**6**	TBHP (in water)	0.1	1.5	20	4	88	89	4
3	**3**	**TBHP (in water)**	0.1	1.5	20	4	**88**	**89**	1
4	3	**TBHP (in nonane)**	0.1	1.5	20	24	84	89	1
5	3	**CHP**	0.1	1.5	20	24	67	83	27
6	3	TBHP (in water)	**0.1**	1.5	**0**	**48**	**80**	**92**	10
7	3	TBHP (in water)	**0.25**	1.5	0	48	80	90	17
8	3	TBHP (in water)	**0.5**	1.5	0	48	77	90	21
9	3	TBHP (in water)	**1.0**	1.5	0	48	81	93	17
10	3	TBHP (in water)[e]	1.0	**3.0**	0	48	86	91	5
11	**3**	**TBHP (in water)**	**0.1**	**3.0**	**0**	**48**	**87**	**92**	**2**
12	3[b]	TBHP (in water)	0.1	3.0	0	24	93	89	0

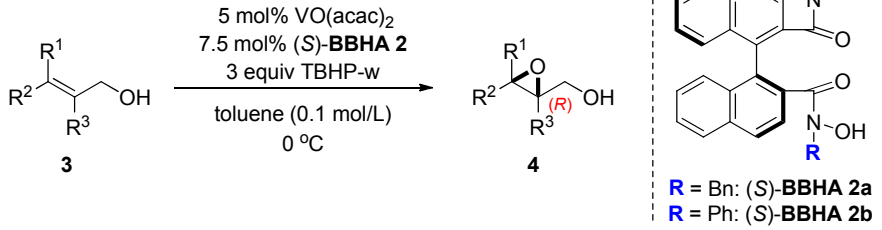
[a]Determined by HPLC. [b]5 mol% $VO(acac)_2$ and 5.5 mol% **BBHA 2a** was used.

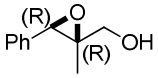
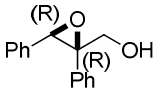
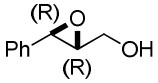
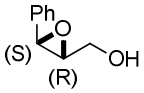
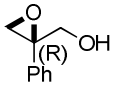
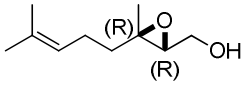
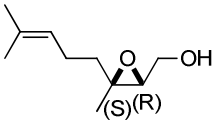
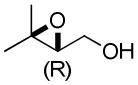
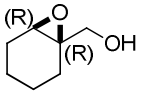
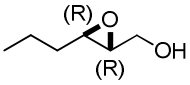
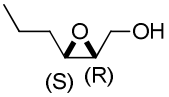
During the complexation process in toluene at 20 °C for 24 h (entry 1), dark-green toluene-insoluble $VO(acac)_2$ became a dark-purple solution with BBHA **2a**. Shorter complexation time was examined for convenience of epoxidation. Nearly the same change in color was observed at 3 h (entry 3), and the ee of the epoxide **4a** was the same as for 24 h. Three hours was sufficient for the complexation of **2a** to obtain the best enantioselectivity in toluene solution at 20 °C (entries 1−3). Hydroperoxide species were investigated (entries 3−5) under these complexation conditions. The use of a water solution or nonane solution of TBHP gave the same ee of 89%. The

use of the nonane solution of TBHP required a longer reaction time of 24 h for the consumption of allylic alcohol **3a** (entry 4). The epoxidation employing cumene hydroperoxide (CHP) in aromatic hydrocarbon proceeded more slowly, and the enantioselectivity slightly decreased (entry 5). Compared to the epoxidation at 20 °C (entry 3), reaction at the lower temperature of 0 °C improved the enantioselectivity to 92% ee (entry 6). Next, the substrate concentration and equivalents of TBHP were examined. Higher substrate concentrations (0.1 *vs*. 0.25−1 mol/L) did not improve the yields (entries 6 *vs*. 7−9), whereas excess TBHP (3 equiv) slightly improved the yields (entries 9−10). Under TBHP (3 equiv) conditions, no influence of substrate concentration on the yield and enantioselectivity was observed (entries 10 and 11). Based on the best epoxidation condition in entry 11 (87% yield, 92% ee), more ligand-efficient condition was re-examined. The molar ratio of $VO(acac)_2$/BBHA **2a** was changed from 5/7.5 to 5/5.5. Unfortunately, enantioselectivity was decreased to 89% ee, whereas the yield was increased to 93% in 24 h.

The substrate scope of the epoxidation was examined under the optimized reaction conditions (Table 2, entry11) using BBHA **2a** with a complexation time of 3 h. The results are summarized in Table 3. The ee was determined by chiral-stationary-phase HPLC analysis. For the HPLC analysis of aliphatic epoxy alcohols **4f**–**4k**, the epoxy alcohols were converted into benzoate derivatives. The absolute stereochemistry of the epoxide was determined by comparison of the chiroptical properties with the literature data.

Table 3. Epoxidation of Various Allylic Alcohols Using 5 mol% of $VO(acac)_2$ and 7.5 mol% of BBHA 2



entry	ligand	time	epoxide **4**			recov. **3** (%)
				configuration[a]	yield (%)	ee (%)[b]	
1	**2a**	2 d	**4a**		87	92	2
2	**2b**	2 d			84	16	3
3	**2a**	4 d	**4b**		95	87	1
4	**2a**	4 d	**4c**		29	82	39
5	**2a**	4 d	**4d**		18	89	70
6	**2a**	6 d	**4e**		20	21	0
7	**2b**	5 d			26	11[c]	14
8	**2a**	3 d	**4f**		89	98[d]	0
9	**2a**	3 d	**4g**		95	84[d]	0
10	**2a**	1 d	**4h**		60	80[d]	0
11	**2a**	1 d	**4i**		52	83[d]	0
12	**2a**	5 d	**4j**		75	80[d]	8
13	**2a**	5 d	**4k**		86	87[d]	14

[a]Determined by comparison of the chiroptical property with the literature data. [b]Deteremined by HPLC. [c]Major product was (*S*)-**4e**. [d]Determined by HPLC after benzoylation or *m*-toluoylation of the isolated products.

The epoxidation of trisubstituted allylic alcohols proceeded faster than the epoxidation of disubstituted allylic

alcohols (entries 1, 3 *vs*. entries 4−6 and entries 8−11 *vs.* entries 12−13). Although the chemical reactivity of the vanadium complex of BBHA **2b** was almost the same as the chemical reactivity of BBHA **2a**, enantioselectivity was low for the epoxidation of **3a** (entry 1−2). In the case of the epoxidation of geminal substituted allylic alcohol **3e**, the opposite enantiomer of (*S*)-**4e** was obtained when BBHA **2b** were used in the reaction (entries 6−7). The enantioselectivity of the epoxidation was better in the case of the reaction of trisubstituted allylic alcohols than in the case of disubstituted allylic alcohols (entries 1, 3 *vs*. entries 4−6). In the reaction of disubstituted allylic alcohols, enantioselectivity of the epoxidation increased in the order *geminal* < *trans* < *cis* with respect to the geometry of the olefin moiety (entries 4−6 and 12−13). Epoxidation of a bulky trisubstituted allylic alcohol, geraniol (**3f**), showed excellent enantioselectivity and gave epoxide **4f** in 98% ee (entry 8).[17] In the epoxidation of geraniol (**3f**) and nerol (**3g**), allylic alcohol moieties were predominantly epoxidized over the trisubstituted alkene moieties, and no over-oxidized products were obtained (entries 8 and 9). The epoxidation of low-molecular-weight allylic alcohol **3h** proceeded with good enantioselectivity to give epoxy alcohol **4h** (entry 10). The use of (*S*)-configured BBHA **2a** gave (2*R*)-epoxy alcohols as the major enantiomers in all cases.

CONCLUSIONS

We observed that binaphthyl-based BBHA **2a** was an effective ligand for the vanadium-catalyzed asymmetric epoxidation of allylic alcohols. The (*S*)-BBHA ligands were easily synthesized by the one-pot, three-step procedure from (*S*)-1,1′-binaphthyl-2,2′-dicarboxylic acid. The combination of the stable and inexpensive $VO(acac)_2$ and a TBHP water solution as the oxidant in toluene gave the epoxy alcohols in the best enantioselectivities. The reaction

proceeded faster for trisubstituted allylic alcohols than for disubstituted allylic alcohols. The enantioselectivity was better for trisubstituted allylic alcohols. The stereochemistry of the epoxy alcohols corresponded to (2*R*)-structures in all cases when (*S*)-BBHA **2a** was used for the epoxidation. Further study of the coordination structure and the mechanisms of asymmetric induction and further development of other BBHAs are in progress.

EXPERIMENTAL SECTION

General Experimental Methods. The epoxidations were conducted under air without anhydrous conditions. Reactions for the syntheses of BBHA ligands and allylic alcohols and for the benzoylation of epoxy alcohols were conducted in anhydrous conditions under argon atmosphere. All solvents and reagents were used as received. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were collected with spectrometers operating at 300 or 500 MHz for proton nuclei in the solvents indicated. ^{1}H chemical shifts are reported in δ ppm with tetramethylsilane (TMS) as an internal standard. ^{13}C{^{1}H} chemical shifts are reported relative to the central peak of $CDCl_3$ (77.0 ppm) or DMSO-d_6 (39.52). Infrared spectra were collected using an FT-IR spectrometer. Melting points were measured on a hot-plate melting-point apparatus and are uncorrected. High-resolution mass spectra were obtained on a double-focusing high-resolution magnetic-sector mass analyzer operating in a fast atom bombardment (FAB) mode or an electron impact (EI) mode. Optical rotation was measured on a polarimeter. Chromatographic purifications were performed on silica gel (40–50 μm, spherical) or alumina (activity III). The ee of the products was determined by chiral-stationary-phase HPLC on a chromatograph equipped with a Daicel CHIRALCEL OD-H or a CHIRALCEL OB-H column. (*Z*)-3-Phenyl-2-propen-1-ol[18] (*cis*-cinnamyl alcohol) (**3d**), 2-phenyl-2-propen-1-ol[19] (**3e**), and

1-cyclohexenylmethanol[20] (**3i**) were synthesized according to methods reported in the literature.

Synthesis of BBHA 2a and 2b. *N*-Benzyl-*O*-(trimethylsilyl)hydroxylamine To a solution of *N*-benzylhydroxylamine hydrochloride (2.82 g, 17.5 mmol), DMAP (109 mg, 877 μmol), and triethylamine (29.2 mL, 210 mmol) in CH_2Cl_2 (175 mL) was added TMSCl (7.97 mL, 63.1 mmol) at 0 °C. The mixture was gradually warmed to room temperature and stirred for 18 h. Saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with CH_2Cl_2 (100 mL × 3). The combined organic layer was washed with sat. NaCl (100 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated, and the residue was purified by bulb-to-bulb distillation (160 °C, 11-12 Pa) to give a colorless oil (3.26 g, 94%): ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.36–7.26 (5H, m), 5.21 (1H, bs), 4.01 (2H, s), 0.11 (9H, s);[21] IR (neat) cm^{-1}: 3255 (m), 2958 (m), 1604 (m), 1249 (s), 880 (m), 843 (m), 749 (m), 698 (m); EI-MS (70 eV) *m/z* (relative intensity): 195 (M^+, 76), 180 (22), 151 (12), 102 (20), 91 (100), 75 (46).

***N*-Phenyl-*O*-(trimethylsilyl)hydroxylamine** To a solution of *N*-phenylhydroxylamine (2.09 g, 19.2 mmol), DMAP (104 mg, 852 μmol), and triethylamine (11.4 mL, 82.0 mmol) in CH_2Cl_2 (110 mL) was added TMSCl (5.56 mL, 44.0 mmol) at −20 °C. The mixture was gradually warmed to room temperature and stirred for 30 h. Saturated aqueous $NaHCO_3$ was added, and the mixture was extracted with *n*-hexane/Et_2O = 1:2 (150 mL × 3). The combined organic layer was washed with sat. NaCl (100 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure at a temperature below 15 °C, and the residue was dried under vacuum. The crude product was then used without further purification.

(*S*)-*N*,*N*′-Dibenzyl-1,1′-binaphtyl-2,2′-biscarbohydroxamic acid (2a) To a solution of

(*S*)-1,1′-binaphthyl-2,2′-dicarboxylic acid **1** (1.50 g, 4.38 mmol) in CH_2Cl_2 (44 mL) were added oxalyl chloride (3.82 mL, 43.8 mmol) and DMF (100 μL) at 0 °C. The mixture was gradually warmed to room temperature. After gas generation ceased (4 h), the mixture was concentrated under reduced pressure and dried under vacuum. The residue was dissolved in CH_2Cl_2 (44 mL). *N*-Benzyl-*O*-(trimethylsilyl)hydroxylamine (2.66 g, 13.7 mmol), triethylamine (3.65 mL, 26.3 mmol), and DMAP (27.0 mg, 221 μmol) were added at 0 °C, and the mixture was brought to room temperature and stirred for 15 h.

The mixture was cooled to 0 °C, whereupon tetrabutylammonium fluoride (1 mol/L in THF, 17.5 mL, 17.5 mmol) was added, and the resulting mixture was stirred for 3.5 h. Water (100 mL) was added, and the mixture was extracted with CH_2Cl_2 (150 mL × 3). The combined organic layer was washed with sat. NaCl (100 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, 1–50% EtOAc/*n*-hexane + 15% THF) and recrystallization from *n*-hexane and $CHCl_3$ (1:1) to give **2a** as colorless needles (1.58 g, 65%): R_f = 0.20 (silica gel, EtOAc/*n*-hexane/THF = 1:4:1); mp 199–202 °C; ^{1}H NMR (500 MHz, DMSO-d_6, 80°C) δ: 9.96 (2H, s), 8.10 (2H, d, J = 8.6 Hz), 8.02 (2H, d, J = 8.3 Hz), 7.60 (2H, d, J = 8.6 Hz), 7.51 (2H, ddd, J = 8.3, 7.0, 1.2 Hz), 7.26 (2H, ddd, J = 8.6, 7.1, 1.3 Hz), 7.17 (2H, d, J = 8.6 Hz), 7.14 (2H, d, J = 7.4 Hz), 7.12–7.06 (4H, m), 6.71 (4H, br), 4.58 (2H, d, J = 15.6 Hz), 4.51 (2H, d, J = 15.6 Hz); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6, 80°C) δ: 168.4, 135.5, 133.8, 132.6, 132.3, 131.9, 127.6, 127.4, 127.3, 126.8, 126.7, 126.4, 126.3, 125.9, 123.7, 51.2; IR (KBr) cm^{-1}: 3198 (br), 2905 (br), 1609 (s), 1481 (s), 1445 (m), 1421 (m), 1348 (s), 1245 (s), 1147 (s), 819 (s), 755 (s), 628 (m), 488 (m); EI-MS (70 eV) *m/z* (relative intensity): 552 (M^+, 75),

430 (78), 281 (84), 252 (47), 91 (100); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{36}H_{28}N_2O_4$ 552.2049; Found 552.2054; Anal. Calcd for $C_{36}H_{28}N_2O_4$: C, 78.24; H, 5.11; N, 5.07. Found: C, 78.14; H, 5.37; N, 5.07; $[\alpha]_D^{21}$ −117 (*c* 0.496, $CHCl_3$).

(*S*)-*N*,*N*′-Diphenyl-1,1′-binaphtyl-2,2′-biscarbohydroxamic acid (2b) To a solution of (*S*)-1,1′-binaphthyl-2,2′-dicarboxylic acid **1** (1.00 g, 2.92 mmol) in CH_2Cl_2 (30 mL) was added oxalyl chloride (2.50 mL, 29.2 mmol) and DMF (100 μL) at 0 °C. The mixture was gradually warmed to room temperature. After gas generation ceased (1.5 h), the mixture was concentrated under reduced pressure, and dried under vacuum. The residue was dissolved in CH_2Cl_2 (30 mL). *N*-Phenyl-*O*-(trimethylsilyl)hydroxylamine (1.59 g, 8.76 mmol), triethylamine (2.43 mL, 17.5 mmol), and DMAP (22.2 mg, 182 μmol) were added at 0 °C and the resulting mixture was brought to room temperature and stirred for 20 h. The mixture was cooled to 0 °C, whereupon tetrabutylammonium fluoride (1 mol/L in THF, 11.7 mL, 11.7 mmol) was added, and the resulting mixture was stirred for 3.5 h. Water (100 mL) was added, and the mixture was extracted with CH_2Cl_2 (150 mL × 3). The combined organic layer was washed with sat. NaCl (100 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, 2–50% EtOAc/*n*-hexane + 15% THF) and recrystallization from *n*-hexane and CH_2Cl_2 (2:1) to give **2b** as colorless prisms (828 mg, 54%): R_f = 0.16 (silica gel, EtOAc/*n*-hexane/THF = 1:4:1); mp 119–123 °C; ^{1}H NMR (500 MHz, DMSO-d_6, 80 °C) δ: 10.41 (2H, s), 8.03 (2H, d, *J* = 8.6 Hz), 7.98 (2H, d, *J* = 8.3 Hz), 7.69 (2H, d, *J* = 8.6 Hz), 7.52 (2H, ddd, *J* = 8.0, 6.8, 1.3 Hz), 7.32 (2H, ddd, *J* = 8.3, 6.7, 1.2 Hz), 7.25–7.16 (10H, m), 7.11–7.06 (2H, m); ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6, 80°C) δ: 167.9, 140.5, 134.0, 132.5, 132.3, 132.1, 127.8, 127.8, 127.3, 126.9, 126.3, 125.8, 125.4,

123.9, 121.5; IR (KBr) cm^{-1}: 3149 (br), 3065 (br), 2918 (br), 2856 (Br), 1617 (s), 1589 (s), 1490 (s), 1389 (m), 828 (m), 754 (m), 680 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 524 (M^+, 2), 492 (12), 416 (13), 400 (14), 372 (23), 325 (11), 281 (100), 252 (40); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{36}H_{28}N_2O_4$ 552.2049; Found 552.2054; Anal. Calcd for $C_{34}H_{24}N_2O_4$: C, 77.85; H, 4.61; N, 5.34. Found: C, 77.71; H, 4.68; N, 5.21; $[\alpha]_D^{21}$ +12.1 (*c* 0.444, $CHCl_3$).

Synthesis of Allylic Alcohols. (*E*)-2,3-Diphenyl-2-propen-1-ol (3b)[22] A mixture of (*E*)-2,3-diphenyl-2-propennoic acid (3.02 g, 13.4 mmol) and powdered KOH (1.24 g, 18.7 mmol) in DMSO (40 mL) was stirred at room temperature for 1 h. The mixture was cooled to 0 °C, whereupon MeI (1.25 mL, 20.1 mmol) was added, and the resulting mixture was stirred at room temperature for 42 h. Water (100 mL) was added, and the mixture was extracted with *n*-hexane/EtOAc (1:1) (100 mL × 3). The combined organic layer was washed with water (100 mL × 3), dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, 0–4% EtOAc/*n*-hexane) to give methyl (*E*)-2,3-diphenyl-2-propennoate (2.97 g, 92%) as a colorless solid: R_f = 0.22 (silica gel, EtOAc/*n*-hexane = 1:40); ^1H NMR (300 MHz, $CDCl_3$) δ: 7.85 (1H, s), 7.40–7.33 (3H, m), 7.23–7.12 (5H, m), 7.03 (2H, d, *J* = 5.5 Hz), 3.79 (3H, s).

To a solution of (*E*)-2,3-diphenyl-2-propennoate (2.67 g, 11.2 mmol) in Et_2O (22 mL) was added DIBAL solution (0.98 mol/L in hexanes, 25.2 mL, 46.2 mmol) at 0 °C over 20 min. The mixture was warmed to room temperature and stirred for 4 h. The mixture was then re-cooled to 0 °C, and water (100 mL) was carefully added, followed by brine (50 mL). The white solid that formed was dissolved by the addition of 2 mol/L aqueous HCl. The resulting

mixture was extracted with Et_2O (150 mL × 3). The combined organic layer was washed with brine (100 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, 5–32% EtOAc/*n*-hexane) to give allylic alcohol **3b** (2.13 g, 90%) as a colorless oil: R_f = 0.20 (silica gel, EtOAc/*n*-hexane = 1:4); ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.37–7.28 (3H, m), 7.28–7.19, (2H, m), 7.16–7.06 (3H, m), 7.20–6.94 (2H, m), 6.69 (1H, s), 4.47 (2H, d, J = 2.9 Hz), 1.64 (1H, br); EI-MS (70 eV) *m*/*z* (relative intensity): 210 (M^+, 100), 191 (13), 178 (40), 165 (14), 105 (69), 91 (33), 77 (11); IR (KBr) cm^{-1}: 3262 (m), 1445 (m), 1091 (m), 1071 (m), 1004 (m), 916 (m), 694 (m).

Typical Procedure for the Asymmetric Epoxidation: Epoxidation of 3a (Table 3, Entry 1). A mixture of $VO(acac)_2$ (6.62 mg, 25.0 μmol) and BBHA **2a** (20.7 mg, 37.5 μmol) in toluene (5.00 mL) was stirred at 20 °C for 3 h. To the resulting dark-purple solution, TBHP in water (70 %, 206 μL, 1.5 mmol, 3.0 equiv) was added at 0 °C; the resulting mixture was stirred for 10 min. Allylic alcohol **3a** (74.6 mg, 500 μmol) was added, and the reaction was monitored by TLC. Saturated aqueous Na_2SO_3 solution was added. The mixture was stirred for 30 min and extracted with Et_2O or EtOAc (5 mL × 5). The combined organic layer was dried over $MgSO_4$ and filtered. The filtrate was concentrated under vacuum. The crude product was purified by column chromatography (silica gel, 5−40% EtOAc/*n*-hexane) to give epoxy alcohol **4a** as colorless needles (72.3 mg, 87%). HPLC analysis of **4a** indicated 92% ee. To isolate the volatile aliphatic epoxy alcohols (**4h**, **4j**, **4k**), a partially concentrated solution of crude epoxy alcohols, mostly in toluene, was charged directly to the column for chromatography. Al_2O_3 (activity III) was used instead of silica gel for the purification of epoxy alcohols **4d**, **4f**, **4g**, **4h**, **4i**, **4j**, and **4k**.

Benzoylation and *m*-Toluoylation of Aliphatic Epoxy Alcohols (4f−4k). To a CH_2Cl_2 (0.25 mol/L) solution of epoxy alcohol **4f−4k** (1 equiv), DMAP (2 mol%), and NEt_3 (3 equiv) was added RCOCl (1.2 equiv) at 0 °C. The mixture was gradually warmed to room temperature and stirred for 5 h. Saturated aqueous $NaHCO_3$ was added, and the organic layer was extracted with CH_2Cl_2. The extracts were dried over $MgSO_4$, filtered, and concentrated. The crude ester was purified by column chromatography (silica gel, EtOAc/*n*-hexane or EtOAc/*n*-hexane/CH_2Cl_2) to give esters of **4f−4h-benzoyl** and **4i−4k-toluoyl**.

(2*R*,3*R*)-(2-Methyl-3-phenyloxiran-2-yl)methanol (4a) Purified by silica gel column chromatography (5–40% EtOAc/*n*-hexane) to give 72.3 mg (87%) of colorless needles: mp 50–52 °C (lit.[23] 52–53 °C); R_f = 0.13 (silica gel, EtOAc/*n*-hexane = 1:4); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37–7.27 (5H, m), 4.21 (1H, s), 3.85 (1H, dd, *J* = 12.6, 2.8 Hz), 3.75 (1H, dd, *J* = 12.6, 8.2 Hz), 2.04 (1H, br), 1.09 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 135.6, 128.9, 127.6, 126.4, 65.0, 63.6, 60.2, 13.4; IR (KBr) cm^{-1}: 3424 (m), 1451 (m), 1094 (m), 1070 (m), 851 (m), 740 (m), 699 (m), 554 (m), 507 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 164 (M^+, 7), 145 (10), 131 (22), 107 (100), 90 (71), 79 (39), 77 (25), 58 (13); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{10}H_{12}O_2$ 164.0837; Found 164.0843; $[\alpha]_D^{25}$ +13.6 (*c* 1.28, $CHCl_3$, 92% ee), (lit.[16] $[\alpha]_D^{25}$ −16.9 [*c* 2.0, $CHCl_3$, (2*S*,3*S*)-epoxide, >98% ee]); HPLC conditions: OD-H, *n*-hexane/2-propanol = 95/5, 0.4 mL/min, 210 nm, 28.2 min (2*S*,3*S*), minor, 36.0 min (2*R*,3*R*), major.[8a]

(2*R*,3*R*)-(2,3-Diphenyloxiran-2-yl)methanol (4b) Purified by silica gel column chromatography (4–40% EtOAc/*n*-hexane) to give 107.3 mg (95%) of colorless solid: mp 66–69 °C (lit.[23] 115–116 °C); R_f = 0.13 (silica gel, EtOAc/*n*-hexane = 1:6); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.23–7.15 (5H, m), 7.12–7.09 (3H, m), 7.05–7.01 (2H, m),

4.51 (1H, s), 4.06–4.00 (2H, m), 2.06 (1H, t, J = 6.7 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 134.7, 134.4, 128.3, 127.8, 127.71, 127.66, 127.5, 126.6, 69.1, 65.0, 60.8; IR (KBr) cm^{-1}: 3401 (m), 1496 (m), 1455 (m), 1093 (m), 1036 (m), 1004 (m), 908 (m), 754 (m), 700 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 226 (M^+, 6), 195 (26), 167 (51), 152 (9), 120 (100), 105 (27), 91 (72), 77 (22); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{15}H_{14}O_2$ 226.0994; Found 226.0992; $[\alpha]_D^{28}$ –65.4 (*c* 1.97, $CHCl_3$, 87% ee), $[\alpha]_D^{18}$ –55.6 (*c* 1.08, CH_2Cl_2, 87% ee), [lit.[2a] (+)-(2*S*,3*S*)-epoxide (>95% ee) was reported.]; HPLC conditions: OD-H, *n*-hexane/2-propanol= 95/5, 1 mL/min, 210 nm, 13.5 min (2*S*,3*S*), minor, 15.7 min (2*R*,3*R*), major.[8a,23]

(2*R*,3*R*)-(3-Phenyloxiran-2-yl)methanol (4c) Purified by silica gel column chromatography (5–40% EtOAc/*n*-hexane) to give 21.9 mg (29%) of colorless oil: R_f = 0.15 (silica gel, EtOAc/*n*-hexane = 1:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37–7.25 (5H, m), 4.04 (1H, ddd, J = 12.8, 5.2, 2.5 Hz), 3.92 (1H, d, J = 2.2 Hz), 3.79 (1H, dd, J = 12.8, 7.6, 4.0 Hz), 3.22 (1H, dt, J = 4.0, 2.0 Hz), 2.09 (1H, dd, J = 7.7, 5.5 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 136.7, 128.5, 128.3, 125.7, 62.4, 61.3, 55.6; IR (KBr) cm^{-1}: 3439 (m), 1464 (m), 1398 (m), 1069 (m), 929 (m), 768 (m), 700 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 150 (M^+, 15), 132 (30), 119 (27), 107 (100), 91 (95), 90 (84), 79 (41); HRMS (EI) *m*/*z*: M^+ Calcd for $C_9H_{10}O_2$ 150.0681; Found 150.0680; $[\alpha]_D^{24}$ +37.2 (*c* 0.340, $CHCl_3$, 82% ee), (lit.[16] $[\alpha]_D^{25}$ −49.6 [*c* 2.4, $CHCl_3$, (2*S*,3*S*)-epoxide, 98% ee]); HPLC conditions: OD-H, *n*-hexane/2-propanol= 90/10, 0.5 mL/min, 210 nm, 24.5 min (2*S*,3*S*), minor, 27.1 min (2*R*,3*R*), major.[8a]

(2*R*,3*S*)-(3-Phenyloxiran-2-yl)methanol (4d) Purified by Al_2O_3 column chromatography (10–100% EtOAc/*n*-hexane) to give 13.9 mg (18%) of colorless oil: R_f = 0.15 (silica gel, EtOAc/*n*-hexane = 1:3), 0.20 (Al_2O_3,

EtOAc/*n*-hexane = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37–7.25 (5H, m), 4.19 (1H, d, J = 4.3 Hz), 3.57–3.52 (1H, m), 3.48–3.42 (2H, m), 1.57 (1H, br); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 134.7, 128.3, 127.9, 126.2, 60.5, 58.5, 57.0; IR (neat) cm^{-1}: 3391 (br), 1496 (m), 1454 (s), 1041 (s), 894 (m), 745 (S), 700 (S); EI-MS (70 eV) *m*/*z* (relative intensity): 150 (M^+, 4), 132 (31), 119 (28), 107 (100), 90 (85), 79 (41), 51 (11); HRMS (EI) *m*/*z*: M^+ Calcd for $C_9H_{10}O_2$ 150.0681; Found 150.0678; $[\alpha]_D^{21}$ +35.0 (*c* 0.344, $CHCl_3$, 89% ee), (lit.[24] $[\alpha]_D^{25}$ −50 [*c* 3.3, $CHCl_3$, (2*S*,3*R*)-epoxide, 78% ee]); HPLC conditions: OD-H, *n*-hexane/2-propanol= 90/10, 0.5 mL/min, 210 nm, 19.5 min (2*R*,3*S*), major, 24.8 min (2*S*,3*R*), minor.[8a]

(*R*)-(2-Phenyloxiran-2-yl)methanol (4e) Purified by silica gel column chromatography (5–40% EtOAc/*n*-hexane) to give 17.4 mg (20%) of colorless oil: TLC R_f = 0.14 (silica gel, EtOAc/*n*-hexane = 1:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40–7.30 (5H, m), 4.10 (1H, d, J = 12.5 Hz), 4.00 (1H, d, J = 12.5 Hz), 3.26 (1H, d, J = 5.5 Hz), 2.82 (1H, d, J = 5.5 Hz), 2.12 (1H, br); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 137.3, 128.5, 128.1, 126.0, 63.1, 60.4, 52.5; IR (neat) cm^{-1}: 3420 (br, s), 2926 (m), 1496 (m), 1448 (m), 1044 (m), 1024 (m), 761 (s), 699 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 150 (M^+, 3), 120 (92), 105 (23), 91 (100), 77 (20); HRMS (FAB) *m*/*z*: $[M+H]^+$ Calcd for $C_9H_{11}O_2$, 151.0759; Found, 151.0761; $[\alpha]_D^{22}$ +5.19 (*c* 0.233, $CHCl_3$, 21% ee), (lit.[25] $[\alpha]_D^{25}$ +27.4 [*c* 1.3, $CHCl_3$, (2*R*)-epoxide, 77% ee]); HPLC conditions: OD-H, *n*-hexane/2-propanol= 90/10, 1 mL/min, 210 nm, 9.4 min (2*S*), minor, 11.8 min (2*R*), major.[8a]

(2*R*,3*R*)-Geraniol-2,3-epoxide (4f) Purified by Al_2O_3 column chromatography (7–60% EtOAc/*n*-hexane) to give 76.5 mg (89%) of colorless oil: R_f = 0.13 (Al_2O_3, EtOAc/*n*-hexane = 3:7), 0.20 (silica gel, EtOAc/*n*-hexane = 1:3); ^{1}H

NMR (500 MHz, $CDCl_3$) δ: 5.11–5.05 (1H, m), 3.83 (1H, ddd, *J* = 11.9, 7.8, 4.6 Hz), 3.68 (1H, ddd, *J* = 11.6, 6.7, 4.6 Hz), 2.98 (1H, dd, *J* = 6.7, 4.3 Hz), 2.09 (2H, q, *J* = 7.6 Hz), 1.94 (1H, dd, *J* = 7.0, 4.9 Hz), 1.74–1.65 (1H, m), 1.69 (3H, d, *J* = 0.9 Hz), 1.61 (3H, s), 1.48 (1H, ddd, *J* = 13.8, 9.2, 7.1 Hz), 1.30 (3H, s); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 132.1, 123.3, 62.9, 61.4, 61.1, 38.5, 25.6, 23.7, 17.6, 16.7; IR (neat) cm^{-1}: 3419 (br, s), 2968 (s), 1451 (s), 1384 (s), 1036 (s), 865 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 170 (M^+, 1), 152 (3), 139 (5), 121 (7), 109 (100), 95 (26), 82 (46), 69 (67); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{10}H_{18}O_2$ 170.1307; Found 170.1303; $[\alpha]_D^{25}$ +4.93 (*c* 1.44, $CHCl_3$, 98% ee), (lit.[16] $[\alpha]_D^{25}$ –5.3 [*c* 3.0, $CHCl_3$, (2*S*,3*S*)-epoxide, 91% ee]).

(2*R*,3*R*)-2,3-Epoxygeranyl benzoate (**4f-benzoyl**) Purified by silica gel column chromatography (1–10% EtOAc/*n*-hexane) to give 99.6 mg (86% based on 422 μmol **4f**) of colorless oil: R_f = 0.27 (silica gel, EtOAc/*n*-hexane = 1:15); ^1H NMR (500 MHz, $CDCl_3$) δ: 8.11–8.07 (2H, m), 7.59–7.56 (1H, m), 7.47–7.42 (2H, m), 5.15–5.09 (1H, m), 4.59 (1H, dd, *J* = 12.2, 4.5 Hz), 4.27 (1H, dd, *J* = 11.9, 7.1 Hz), 3.13 (1H, dd, *J* = 6.7, 4.0 Hz), 2.23–2.09 (2H, m), 1.75–1.67 (1H, m), 1.70 (3H, d, *J* = 0.9 Hz), 1.62 (3H, s) 1.60–1.53 (1H, m), 1.38 (3H, s); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 166.4, 133.1, 132.5, 129.8, 129.7, 128.4, 123.2, 63.7, 61.0, 60.8, 33.3, 25.7, 24.2, 22.0, 17.6; IR (neat) cm^{-1}: 2967 (s), 1723 (s), 1451 (s), 1272 (s), 1109 (m), 712 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 274 (M^+, 1), 256 (1), 192 (14), 134 (9), 105 (100), 77 (18); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{17}H_{22}O_3$ 274.1569; Found 274.1572; $[\alpha]_D^{25}$ +15.1 (*c* 1.71, $CHCl_3$, 98% ee), (lit.[26] $[\alpha]_D^{27}$ –13.8 [*c* 1.0, $CHCl_3$, (2*S*,3*S*)-epoxide, 99% ee]); HPLC conditions: OD-H, *n*-hexane/2-propanol= 99/1, 1 mL/min, 254 nm, 10.3 min (2*R*,3*R*), major, 15.7 min (2*S*,3*S*), minor.

(2*R*,3*S*)-Nerol-2,3-epoxide (**4g**) Purified by Al_2O_3 column chromatography (7–60% EtOAc/*n*-hexane) to give 80.5

mg (95%) of colorless oil: R_f = 0.16 (Al_2O_3, EtOAc/*n*-hexane = 3:7), 0.21 (silica gel, EtOAc/*n*-hexane = 1:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.12–5.06 (1H, m), 3.84–3.77 (1H, m), 3.67–3.62 (1H, m), 2.97 (1H, dd, *J* = 7.0, 4.3 Hz), 2.40 (1H, br), 2.18–2.02 (2H, m),1.69 (3H, s), 1.70–1.63 (1H, m), 1.62 (3H, s), 1.48 (1H, ddd, *J* = 13.7, 10.1, 7.0 Hz), 1.34 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 132.4, 123.3, 64.3, 61.5, 61.2, 33.1, 25.6, 24.1, 22.1, 17.5; IR (neat) cm^{-1}: 3419 (br, s), 2968 (s), 1450 (s), 1380 (s), 1034 (s), 865 (m); FAB-MS (glycerol) *m*/*z*: 171 $[M+H]^+$; HRMS (FAB) *m*/*z*: $[M+H]^+$ Calcd for $C_{10}H_{19}O_2$ 171.1385; Found 171.1387; $[\alpha]_D^{25}$ +17.8 (*c* 1.42, $CHCl_3$, 84% ee), (lit.[27] $[\alpha]_D$ +15.4 [*c* 3.3, $CHCl_3$, (2*R*,3*S*)-epoxide, 70% ee]).

(2*R*,3*S*)-2,3-Epoxyneryl benzoate (**4g-benzoyl**) Purified by silica gel column chromatography (1–10% EtOAc/*n*-hexane) to give 97.3 mg (88% based on 402 μmol **4g**) of colorless oil: R_f = 0.29 (silica gel, EtOAc/*n*-hexane = 1:15); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09–8.06 (2H, m), 7.59–7.55 (1H, m), 7.46–7.43 (2H, m), 5.15–5.10 (1H, m), 4.59 (1H, dd, *J* = 11.9, 4.0 Hz), 4.28 (1H, dd, *J* = 11.9, 7.1 Hz), 3.13 (1H, dd, *J* = 8.0, 5.3 Hz), 2.23–2.10 (2H, m), 1.73–1.65 (1H, m), 1.70 (3H, d, *J* = 0.9 Hz), 1.62 (3H, s), 1.59–1.53 (1H, m), 1.38 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 166.4, 133.1, 132.5, 129.8, 129.7, 128.4, 123.2, 63.7, 61.0, 60.8, 33.3, 25.6, 24.2, 22.0, 17.6; IR (neat) cm^{-1}: 2967 (m), 1722 (s), 1451 (m), 1272 (s), 1109 (m), 712 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 274 (M^+, 0.2), 191 (5), 134 (9), 105 (100), 77 (22); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{17}H_{22}O_3$ 274.1569; Found 274.1572; $[\alpha]_D^{26}$ +19.1 (*c* 1.25, $CHCl_3$, 84% ee); HPLC conditions: OD-H, *n*-hexane/2-propanol = 99.7/0.3, 1 mL/min, 230 nm, 11.3 min (2*S*,3*R*), minor, 16.7 min (2*R*,3*S*), major.[28]

(2*R*)-(3,3-Dimethyloxiran-2-yl)methanol (**4h**) Purified by Al_2O_3 column chromatography (8–66%

EtOAc/*n*-hexane) to give 30.7 mg (60%) of colorless oil: R_f = 0.16 (Al_2O_3, EtOAc/*n*-hexane = 1:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.83 (1H, dd, *J* = 12.2, 1.2 Hz), 3.67 (1H, dd, *J* = 12.2, 7.1 Hz), 2.99 (1H, dd, *J* = 6.7, 4.3 Hz), 2.89 (1H, br), 1.35 (3H, s), 1.31 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 63.9, 61.3, 58.8, 24.7, 18.7; IR (neat) cm^{-1}: 3419 (br, s), 1456 (s), 1380 (s), 1033 (s), 858 (m); FAB-MS (glycerol) *m*/*z*: 103 ([M+H]$^+$); HRMS (FAB) *m*/*z*: [M+H]$^+$ Calcd for $C_5H_{11}O_2$ 103.0759; Found 103.0757; $[\alpha]_D^{22}$ +13.0 (*c* 0.417, $CHCl_3$, 80% ee), (lit.[29] $[\alpha]_D^{25}$ −19.4 [*c* 0.40, $CHCl_3$, (2*S*)-epoxide, 86% ee]).

(2*R*)-(3,3-Dimethyloxiran-2-yl)methyl benzoate (4h-benzoyl) Purified by silica gel column chromatography (0–4% EtOAc/*n*-hexane + 2% CH_2Cl_2) to give 40.7 mg (66% based on 300 μmol **4h**) of colorless oil: R_f = 0.09 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09–8.06 (2H, m), 7.60–7.55 (1H, m), 7.47–7.43 (2H, m), 4.59 (1H, dd, *J* = 12.2, 4.3 Hz), 4.28 (1H, dd, *J* = 12.2, 6.7 Hz), 3.14 (1H, dd, *J* = 6.7, 4.3 Hz), 1.390 (3H, s), 1.387 (3H, s); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 166.4, 133.1, 129.8, 129.7, 128.4, 63.9, 60.6, 58.2, 24.6, 19.0; IR (neat) cm^{-1}: 2965 (m), 1722 (s), 1453 (m), 1273 (m), 1113 (m), 711 (m); FAB-MS (*m*-nitrobenzylalcohol) *m*/*z*: 207 ([M+H]$^+$); HRMS (FAB) *m*/*z*: [M+H]$^+$ Calcd for $C_{12}H_{15}O_3$ 207.1021; Found 207.1029; $[\alpha]_D^{22}$ +22.2 (*c* 0.573, $CHCl_3$, 80% ee), (lit.[30] $[\alpha]_D^{25}$ –22.2 [*c* 1.00, $CHCl_3$, (*S*)-epoxide, 90% ee]); HPLC conditions: OB-H, *n*-hexane/2-propanol = 90/10, 1 mL/min, 230 nm, 12.5 min (2*S*), minor, 16.3 min (2*R*), major.

(1*R*,6*R*)-7-Oxabicyclo[4.1.0]heptan-1-ylmethanol (4i) Purified by Al_2O_3 column chromatography (7–60% EtOAc/*n*-hexane) to give 33.7 mg (52%) of colorless oil: R_f = 0.16 (Al_2O_3, EtOAc/*n*-hexane = 1:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.68 (1H, d, *J* = 11.9 Hz), 3.59 (1H, dd, *J* = 12.2, 7.9 Hz), 3.26 (1H, d, *J* = 3.4 Hz), 1.98 (1H, dt, *J* =

15.6, 7.5 Hz), 1.99–1.77 (3H, m), 1.74–1.66 (1H, m), 1.53–1.42 (2H, m), 1.33–1.22 (2H, m); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 64.5, 60.1, 55.8, 25.3, 24.4, 19.9, 19.6; IR (neat) cm^{-1}: 3418 (s), 2937 (s), 1434 (m), 1109 (m), 1069 (m), 1034 (m), 917 (m), 835 (m); FAB-MS (glycerol) *m*/*z*: 129 ($[M+H]^+$); HRMS (FAB) *m*/*z*: $[M+H]^+$ Calcd for $C_7H_{13}O_2$ 129.0916; Found 129.0915; $[\alpha]_D^{24}$ +9.64 (*c* 0.512, $CHCl_3$, 81% ee), (lit.[16] $[\alpha]_D^{25}$ −22.8 [*c* 2.6, $CHCl_3$, (*S*,*S*)-epoxide, 93% ee]).

(1*R*,6*R*)-7-Oxabicyclo[4.1.0]heptan-1-ylmethyl 3-methylbenzoate (4i-toluoyl) Purified by silica gel column chromatography (0–4% EtOAc/*n*-hexane + 2% CH_2Cl_2) to give 43.9 mg (71% based on 251 μmol **4i**) of colorless oil: R_f = 0.09 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:40:1); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.87–7.83 (2H, m), 7.38 (1H, d, *J* = 7.9 Hz), 7.33 (1H, t, *J* = 7.7 Hz), 4.46 (1H, d, *J* = 11.9 Hz), 4.18 (1H, d, *J* = 11.9 Hz), 3.21 (1H, d, *J* = 3.4 Hz), 2.41 (3H, s), 2.05–1.95 (2H, m), 1.91–1.84 (2H, m), 1.54–1.44 (2H, m), 1.36–1.23 (2H, m); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 166.4, 138.2, 138.9, 130.2, 129.8, 128.3, 126.9, 68.4, 57.8, 56.7, 25.5, 24.3, 21.3, 19.7, 19.5; IR (neat) cm^{-1}: 2938 (s), 1719 (s), 1590 (m), 1436 (m), 1274 (m), 1197 (s), 1083 (m), 1001 (m), 744 (s); EI-MS (20 eV) *m*/*z* (relative intensity): 246 (M^+, 0.5), 119 (100); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{15}H_{18}O_3$ 246.1256; Found 246.1254; Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.23; H, 7.40; $[\alpha]_D^{21}$ +11.8 (*c* 0.624, $CHCl_3$) (81% ee); HPLC conditions: OB-H, *n*-hexane/2-propanol = 90/10, 1 mL/min, 230 nm, 9.6 min (*S*,*S*), minor, 14.2 min (*R*,*R*), major.

(2*R*,3*R*)-(3-Propyloxiran-2-yl)methanol (4j) Purified by Al_2O_3 column chromatography (7–60% EtOAc/*n*-hexane) to give 43.9 mg (75%) of colorless oil: R_f = 0.14 (Al_2O_3, EtOAc/*n*-hexane = 3:7); ^1H NMR (500 MHz, $CDCl_3$) δ: 3.91

(1H, d, J = 12.6 Hz), 3.63 (1H, d, J = 12.2 Hz), 2.96 (1H, td, J = 5.7, 2.4 Hz), 2.92 (1H, dt, J = 4.3, 2.4 Hz), 1.85 (1H, br), 1.58–1.42 (4H, m), 0.97 (3H, t, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 61.7, 58.4, 55.8, 33.6, 19.2, 13.7; IR (neat) cm^{-1}: 3419 (br, s), 2961 (s), 1665 (m), 1382 (m), 1223 (m), 1065 (m), 1045 (m), 901 (m), 854 (m); FAB-MS (glycerol) *m*/*z*: 107 ($[M+H]^+$); HRMS (FAB) *m*/*z*: $[M+H]^+$ Calcd for $C_6H_{13}O_2$, 117.0916; Found, 117.0918; $[\alpha]_D^{23}$ +27.0 (*c* 0.694, $CHCl_3$, 80% ee), (lit.[31] $[\alpha]_D^{25}$ −46.6 [*c* 1.0, $CHCl_3$, (2*S*,3*S*)-epoxide, 96.8% ee]).

(2*R*,3*R*)-(3-Propyloxiran-2-yl)methyl 3-methylbenzoate (4j-toluoyl) Purified by silica gel column chromatography (0–4% EtOAc/*n*-hexane + 2% CH_2Cl_2) to give 44.4 mg (50% based on 378 μmol **4j**) of colorless oil: R_f = 0.14 (silica gel, EtOAc/*n*-hexane/CH_2Cl_2 = 1:40:1); ^1H NMR (500 MHz, $CDCl_3$) δ: 7.88 (1H, d, J = 0.7 Hz), 7.86 (1H, d, J = 7.9 Hz), 7.37 (1H, d, J = 7.7 Hz), 7.33 (1H, t, J = 7.7 Hz), 4.59 (1H, dd, J = 12.0, 3.4 Hz), 4.18 (1H, dd, J = 12.0, 6.0 Hz), 3.10 (1H, ddd, J = 5.7, 3.4, 2.2 Hz), 2.93 (1H, td, J = 5.7, 2.2 Hz), 2.40 (3H, s), 1.62–1.42 (4H, m), 0.97 (3H, t, J = 7.3 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 166.4, 138.1, 133.9, 130.2, 129.6, 128.2, 126.8, 65.1, 56.5, 55.3, 33.5, 21.2, 19.1, 13.8; IR (neat) cm^{-1}: 2960 (s), 1721 (s), 1276 (m), 1199 (m), 1106 (m), 1082 (m), 745 (m); EI-MS (70 eV) *m*/*z* (relative intensity): 234 (M^+, 1), 191 (1), 136 (4), 119 (100), 91 (17); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{14}H_{18}O_3$ 234.1256; Found 234.1258; $[\alpha]_D^{20}$ +31.7 (*c* 0.550, $CHCl_3$, 80% ee); HPLC conditions: OB-H, *n*-hexane/2-propanol = 98/2, 0.5 mL/min, 230 nm, 30.4 min (2*R*,3*R*), major, 34.8 min (2*S*,3*S*), minor.[8a]

(2*R*,3*S*)-(3-Propyloxiran-2-yl)methanol (4k) Purified by Al_2O_3 column chromatography (7–60% EtOAc/*n*-hexane) to give 50.5 mg (86%) of colorless oil: R_f = 0.14 (Al_2O_3, EtOAc/*n*-hexane = 3:7); R_f = 0.14 (silica gel, EtOAc/*n*-hexane = 1:3); ^1H NMR (500 MHz, $CDCl_3$) δ: 3.85 (1H, dd, J = 12.2, 4.0 Hz), 3.67 (1H, dd, J = 12.2, 7.0

Hz), 3.16 (1H, dt, *J* = 4.3, 2.1 Hz), 3.07–3.01 (1H, m), 1.59–1.41 (4H, m), 2.37 (1H, br), 0.98 (3H, t, *J* = 7.0 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 60.9, 57.1, 56.9, 29.9, 19.9, 13.8; IR (neat) cm^{-1}: 3408 (br, s), 2962 (s), 1465 (m), 1042 (s), 914 (m), 858 (m), 829 (m), 768 (m); FAB-MS (glycerol) *m*/*z*: 117 ($[M+H]^+$). HRMS (FAB) *m*/*z*: $[M+H]^+$ Calcd for $C_6H_{13}O_2$ 117.0916; Found 117.0919; $[\alpha]_D^{22}$ +2.87 (*c* 0.757, $CHCl_3$, 87% ee), (lit.[32] $[\alpha]_D^{21.5}$ −4.99 [*c* 3.64, $CHCl_3$, (2*S*,3*R*)-epoxide, 85.8% ee]).

(2*R*,3*S*)-(3-Propyloxiran-2-yl)methyl 3-methylbenzoate (4k-toluoyl) Purified by silica gel column chromatography (0–4% EtOAc/*n*-hexane + 2% CH_2Cl_2) to give 50.9 mg (50% based on 435 μmol **4k**) of colorless oil: R_f = 0.16 (EtOAc/*n*-hexane/CH_2Cl_2 = 1:40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.89 (1H, d, *J* = 0.6 Hz), 7.88 (1H, d, *J* = 7.6 Hz), 7.38 (1H, d, *J* = 7.9 Hz), 7.33 (1H, t, *J* = 7.6 Hz), 4.58 (1H, dd, *J* = 11.9, 4.3 Hz), 4.28 (1H, dd, *J* = 12.2, 7.0 Hz), 3.32 (1H, dt, *J* = 7.0, 3.5 Hz), 3.08 (1H, td, *J* = 6.1, 4.3 Hz), 2.41 (3H, s), 1.64–1.46 (4H, m), 1.01 (3H, t, *J* = 7.2 Hz); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ: 166.6, 138.2, 133.9, 130.3, 129.7, 128.3, 126.9, 63.3, 56.4, 53.8, 30.0, 21.2, 19.9, 13.9; IR (neat) cm^{-1}: 2961 (s), 1721 (s), 1457 (m), 1278 (s), 1199 (s), 1107 (m), 1083 (m), 745 (s); EI-MS (70 eV) *m*/*z* (relative intensity): 234 (M^+, 1), 119 (100), 91 (16); HRMS (EI) *m*/*z*: M^+ Calcd for $C_{14}H_{18}O_3$ 234.1256; Found 234.1259; $[\alpha]_D^{21}$ +14.2 (*c* 0.793, $CHCl_3$, 87% ee); HPLC conditions: OB-H, *n*-hexane/2-propanol = 99.8/0.2, 1 mL/min, 230 nm, 19.4 min (2*R*,3*S*), major, 28.4 min (2*S*,3*R*), minor.[9f]

AUTHOR INFORMATION

Corresponding Author

*E-mail: mnoji@my-pharm.ac.jp.

ACKNOWLEDGEMENTS

M.N. thanks Mr. Kubota and Ms. Ohashi for their technical assistance.

ASSOCIATED CONTENT

Supporting Information

NMR spectra, HPLC charts, X-ray crystal structure details. This material is available free of charge via the Internet at http://pubs.acs.org.

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