Experimental Section

General: Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for ^{1}H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts in $CDCl_3$ were reported downfield from TMS (= 0 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported downfield from TMS (= 0 ppm) or in the scale relative to $CHCl_3$ (77.00 ppm for ^{13}C NMR) as an internal reference. Chemical shifts in acetone-d_6 were reported in the scale relative to acetone (2.09 ppm for ^{1}H NMR and 30.6 ppm for ^{13}C NMR). Chemical shifts in DMSO-d_6 were reported in the scale relative to DMSO (2.49 ppm for ^{1}H NMR and 39.5 ppm for ^{13}C NMR). Optical rotations were measured on a JASCO P-1010 polarimeter. ESI mass spectra were measured on Waters micromass ZQ. EI mass spectra were measured on JEOL JMS-DX303 or JMS-BU20 Gcmate. The enantiomeric excess (ee) was determined by HPLC analysis. HPLC was performed on JASCO HPLC systems consisting of the following: pump, 880-PU or PU-980; detector, 875-UV or UV-970, measured at 254 nm or 280 nm; column, DAICEL CHIRALPAK AS, CHIRALPAK AS–H, DAICEL CHIRALPAK AD, DAICEL CHIRALPAK AD-H, DAICEL CHIRALCEL OD, DAICEL CHIRALCEL OD–H, DAICEL CHIRALCEL OJ–H; mobile phase, hexane–2-propanol; flow rate, 0.4–1.25 mL/min. Reactions were carried out in dry solvents under an argon atmosphere, unless otherwise stated. Ln(O-*i*-Pr)$_3$ was purchased from Kojundo Chemical Laboratory Co., LTD., 5-1-28, Chiyoda, Sakado-shi, Saitama 350-0214, Japan (fax: +(81)-492-84-1351). MS 4A (Molecular Sieve UOP type 4A, powder) was purchased from Fluka. Other reagents were purified by the usual methods.

第 1 部

第 2 章

Synthesis of the Epoxy Ketones 2a–2h, 4 and 6 Using La-(*R*)-BINOL-Ph$_3$As=O Complex. The epoxy ketones **2a–2h, 4 and 6** were prepared according to the general procedure. The compounds **2a–2c** and **2e–2h** were reported in ref 26a. The compound **4** was reported in ref 23b. The compound **6** was reported in ref 26d. For the known compound **2d**, see: *J. Chem. Soc., Perkin Trans. 1* **1996**, 343. The ees were determined by HPLC analysis. The absolute configurations were determined by comparing the measured optical rotations with the

reported ones.

General Procedure for the Catalytic Asymmetric Epoxidation of Enones Using La-(*R*)-BINOL-Ph_3As=O Complex (Table 2-2, entry 5). To a mixture of (*R*)-BINOL (7.2 mg, 0.025 mmol), triphenylarsine oxide (8.1 mg, 0.025 mmol) and MS 4A [500 mg; MS 4A was not dried (1000 mg/mmol of starting material).] in dry THF (2.5 mL) was added a solution of La(O-*i*-Pr)$_3$ (0.125 mL, 0.025 mmol, 0.2 M solution in THF) at room temperature. After being stirred for 1 h at the same temperature, TBHP (0.12 mL, 0.6 mmol, 5 M solution in decane) was added. After being stirred for 30 min, enone **1d** (73.1 mg, 0.5 mmol) was added directly and the mixture was stirred at room temperature. After 6 h, the reaction was quenched by addition of 2.5% aqueous critic acid solution (5 mL) at 0 °C and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 50:1) to give epoxy ketone **2d** (74,9 mg, 92%, 99.2% ee) as a colorless oil. The IR, ^{1}H NMR, ^{13}C NMR and mass were identical with those of an authentic sample. $[\alpha]_D^{25}$ +102° (*c* 1.0 $CHCl_3$); The enantiomeric excess of **2d** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 2/98, flow rate 1.25 mL/min, t_R 10.7 min (3*R*,4*S*)-isomer and 11.9 min (3*S*,4*R*)-isomer, detection at 254 nm).

***trans*-(2*S*,3*R*)-Epoxy-1,3-diphenylpropan-1-one (2a):** colorless oil; $[\alpha]_D^{25}$ +192° [*c* 1.0 $CHCl_3$(96% ee)]; The enantiomeric excess of **2a** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALCEL OD, *i*-PrOH/hexane 2/98, flow rate 1.0 mL/min, t_R 15.4 min (2*S*,3*R*)-isomer and 16.6 min (2*R*,3*S*)-isomer, detection at 254 nm).

***trans*-(2*S*,3*R*)-Epoxy-3-phenyl-1-(methoxymethoxy phenyl)propan-1-one (2b):** white powder; $[\alpha]_D^{25}$ +135° [*c* 1.03 $CHCl_3$(95% ee)]; The enantiomeric excess of **2b** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 1/9, flow rate 1.0 mL/min, t_R 11.0 min (2*S*,3*R*)-isomer and 13.3 min (2*R*,3*S*)-isomer, detection at 254 nm).

***trans*-(2*S*,3*R*)-Epoxy-4-methyl-1-phenylpentan-1-one (2c):** colorless oil; $[\alpha]_D^{25}$ –22.4° [*c* 1.47 $CHCl_3$(94% ee)]; The enantiomeric excess of **2c** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALCEL OD, *i*-PrOH/hexane 2/98, flow rate 1.0 mL/min, t_R 7.5 min (2*S*,3*R*)-isomer and 8.8 min (2*R*,3*S*)-isomer, detection at 254 nm).

***trans*-(3*S*,4*R*)-Epoxy-4-phenylbutan-2-one (2d):** colorless oil; $[\alpha]_D^{25}$ +102° [*c* 1.0 $CHCl_3$(99.2% ee)]; The enantiomeric excess of **2d** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 2/98, flow rate 1.25 mL/min, t_R

10.7 min (3*R*,4*S*)-isomer and 11.9 min (3*S*,4*R*)-isomer, detection at 254 nm).

***trans*-(3*S*,4*R*)-Epoxy-6-phenylhexan-2-one (2e):** colorless oil; $[\alpha]_D^{26}$ –23.1° [*c* 1.24 $CHCl_3$(92% ee)]; The enantiomeric excess of **2e** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 2/98, flow rate 1.0 mL/min, t_R 10.2 min (3*R*,4*S*)-isomer and 12.9 min (3*S*,4*R*)-isomer, detection at 254 nm).

***trans*-(3*S*,4*R*)-Epoxynonan-2-one (2f):** colorless oil; $[\alpha]_D^{25}$ –40.8° [*c* 0.75 $CHCl_3$(95% ee)]; The enantiomeric excess of **2f** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 1/100, flow rate 0.4 mL/min, t_R 15.6 min (3*R*,4*S*)-isomer and 17.5 min (3*S*,4*R*)-isomer, detection at 280 nm).

***trans*-(4*S*,5*R*)-Epoxy-2-methyl-5-phenylpentan-3-one (2g):** colorless oil; $[\alpha]_D^{25}$ +156° [*c* 1.0 $CHCl_3$(95% ee)]; The enantiomeric excess of **2g** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AS, *i*-PrOH/hexane 2/98, flow rate 1.0 mL/min, t_R 6.8 min (4*S*,5*R*)-isomer and 8.5 min (4*R*,5*S*)-isomer, detection at 254 nm).

***trans*-(4*S*,5*R*)-Epoxy-2,2-dimethyl-5-phenylpentan-3-one (2h):** white powder; $[\alpha]_D^{21}$ +227° [*c* 0.68 $CHCl_3$(98% ee)]; The enantiomeric excess of **2h** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, EtOH/hexane 5/95, flow rate 1.0 mL/min, t_R 8.2 min (4*R*,5*S*)-isomer and 11.2 min (4*S*,5*R*)-isomer, detection at 254 nm).

(*trans*,*trans*)-(2*S*,3*R*)-Epoxy-1-phenyl-4-octen-1-one (4): colorless oil; IR (neat) ν2963, 1690, 1234 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.4 Hz, 3H), 1.45 (sextet, *J* = 7.4 Hz, 2H), 2.10 (ddt, *J* = 1.5, 6.7, 7.4 Hz, 2H), 3.53 (dd, *J* = 2.0, 8.2 Hz, 1H), 4.17 (d, *J* = 2.0 Hz, 1H), 5.32 (ddt, J = 1.5, 8.2, 15.5 Hz, 1H), 6.06 (dt, *J* = 6.7, 15.5 Hz, 1H), 7.46–7.55 (m, 2H), 7.62 (tt, *J* = 1.3, 7.4 Hz, 1H), 7.98–8.04 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.0, 34.5, 59.0, 59.8, 125.4, 128.1, 128.7, 133.7, 135.4, 139.4, 193.8; MS *m/z* 216 [M^+]; $[\alpha]_D^{26}$ +51.2° [*c* 1.10 $CHCl_3$(96% ee)]; HRMS (M^+) Calcd for $C_{14}H_{16}O_2$ 216.1150. Found 216.1175. The enantiomeric excess of **4** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALCEL OD, *i*-PrOH/hexane 2/98, flow rate 1.0 mL/min, t_R 11.4 min (2*S*,3*R*)-isomer and 13.2 min (2*R*,3*S*)-isomer, detection at 254 nm).

***cis*-(3*S*,4*S*)-Epoxynonan-2-one (6):** colorless oil; $[\alpha]_D^{25}$ –36.0° [*c* 1.15 $CHCl_3$(59% ee)]; The enantiomeric excess of **6** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AS, *i*-PrOH/hexane 1/100, flow rate 0.5 mL/min, t_R 25.2 min (3*S*,4*S*)-isomer and 28.8 min (3*R*,4*R*)-isomer, detection at 280 nm).

Preparation of the Crystal of Labis[(*R*)-binaphthoxide]tris(triphenylarsine oxide) (12) for X-ray Analysis. To a stirred mixture of (*R*)-BINOL (28.6 mg, 0.1 mmol) and triphenylarsine oxide (96.6 mg, 0.3 mmol) in THF (0.5 mL) was added a solution of La(O-*i*-

$Pr)_3$ (0.5 mL, 0.1 mmol, 0.2 M solution in THF). After the reaction mixture was stirred for 1 h, the solution was concentrated to 0.125 M–0.15 M and kept at room temperature under argon. After 24 h, an X-ray grade crystal of Labis[(*R*)-binaphthoxide]tris(triphenylarsine oxide) (**12**) was grown.

Labis[(*R*)-binaphthoxide]tris(triphenylarsine oxide) (12): Collected at −100 °C, $C_{98}H_{80}O_9As_3La$ = 1765.37, clear, prism, Crystal System : trigonal, Lattice Type : Primitive, a = 17.6048(6) °*A*, c = 26.653(1) °*A*, V = 7153.9(5) °A^3, $P3_221$,[126] Z = 3, D = 1.229 g/cm^3, R(F) = 0.054, R_w(F) = 0.082, GOF = 1.85. Hydrogen atoms were included but not refined. THF x 1 and H_2O x 1 were incorporated in the crystal. Detailed information of data collection and solution and refinement of the structure are summarized in page 182 to 201.

General Conditions for Kinetic Experiments: To a mixture of (*R*)-BINOL (17.2 mg, 0.06 mmol), triphenylarsine oxide (19.3 mg, 0.06 mmol) and MS 4A [500 mg; MS 4A was not dried (1000 mg/mmol of starting material).] in dry THF was added an appropriate amount of La(O-*i*-Pr)$_3$ (0.2 M solution in THF). At this point, a total volume of the reaction mixture was set to 6.10 mL. After being stirred for 1 h at room temperature, TBHP (0.15 mL, 0.75 mmol, 5 M solution in decane) was added at 0 °C and the resulting mixture was stirred at the same temperature. After 30 min, **1a** (104.1 mg, 0.5 mmol) was added directly at 0 °C. Thus, the above mixture is calculated to contain 0.08 M **1a** and 0.12 M TBHP. Aliquots were taken at recorded times according to the following procedure. Approximately 0.7 mL of the reaction mixture was withdrawn with a syringe and was immediately introduced into a test tube containing approximately 1.0 mL of 2.5% aqueous critic acid solution and 1.5 mL of ether. The resulting mixture was thoroughly agitated, and the organic layer was withdrawn. After the solvent was evaporated *in vacuo*, the obtained crude residue was analyzed by ^{1}H NMR. Yields of the products were measured by comparison of integrated area of a proton at C-3 position of **1a** (7.81 ppm) and a value calculated as an average of the ones of protons at C-2 position (4.29 ppm) and C-3 position (4.07 ppm) of **2a**.

第 3 章

General Procedure for the Catalytic Asymmetric Epoxidation of Enones Using La-modified BINOL Complex (Table 3-2, entry 1). To a mixture of (*R*)-**16** (17.8 mg, 0.025 mmol) in dry THF (2.5 mL) was added a solution of La(O-*i*-Pr)$_3$ (0.125 mL, 0.025 mmol, 0.2 M solution in THF) at room temperature. After being stirred for 1 h at −20 °C, TBHP (0.15

mL, 0.6 mmol, ca. 4 M solution in toluene) was added. After being stirred for 30 min, enone **1a** (52.0 mg, 0.25 mmol) was added directly, and the mixture was stirred at the same temperature. After 24 h, the reaction was quenched by addition of 2.5% aqueous critic acid solution (5 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 30:1) to give epoxy ketone **2a** (55.5 mg, 99%, 87% ee) as a colorless oil.

第4章

Synthesis of the Acid Imidazolides 26a–p. The imidazolides **26a–26f** and **26h–26p** were prepared according to the general procedure. For the known compound **23a**, see: *Synlett.* **2001**, 637. For the known compounds **26e** and **26g**, see: *Synthesis.* **2000**, 123.

General Procedure for the Synthesis of β-Aryl-Substituted 4-Phenyl Imidazolides (Scheme 4-4). To a stirred solution of cinnamic acid (445 mg, 3 mmol) and 4-phenylimidazole (433 mg, 3 mmol) in DMF (15 ml) was added 1-ethyl-3-(dimethylaminopropyl)carbodiimide hydrochloride (719 mg, 3.75 mmol) at room temperature. After being stirred for 12 h at the same temperature, the reaction mixture was poured into saturated aqueous ammonium chloride. The resulting mixture was extracted with ethyl acetate (200 ml) and ether (100 ml), and the combined organic layers were washed with water successively. The organic layer was washed with brine, dried over Na_2SO_4, and then evaporated *in vacuo*. Successive washing of the residue with cold ether gave the imidazolide **26f** (734 mg, 90%) as a yellow solid.

General Procedure for the Synthesis of β-Aryl-Substituted 4-Phenyl Imidazolides (Scheme 4-4). 5-Phenyl-2-pentenoic acid (1.76 g, 10 mmol) was added in small portions to thionyl chloride (2 ml, 27.4 mmol) at room temperature. After being stirred for 30 min, the reaction mixture was heated to 50 °C and stirred until the evolution of HCl was ceased. The mixture was cooled to room temperature and concentrated to give crude acid chloride. To a stirred solution of 4-phenylimidazole (1.51 g, 10.5 mmol) in THF (30 ml) was added *n*-butyllithium (6.62 ml, 10 mmol, 1.51 M solution in hexane) at –78 °C. After being stirred for 40 min, THF (10 ml) solution of the crude acid chloride was added slowly to the reaction mixture at the same temperature. After 15 min, the reaction was quenched with saturated

aqueous sodium hydrogen carbonate and extracted with CH_2Cl_2 (2 x 50 ml). The combined organic layers were washed with brine, dried over $MgSO_4$. After concentration *in vacuo*, recrystallization of the obtained residue from CH_2Cl_2–Et_2O at room temperature afforded **26k** (2.3 g, 76%) as a white solid.

1-[(2*E*)-1-Oxo-3-phenyl-2-propenyl]-1*H*-benzoimidazole (26a): white solid; mp 233–234 °C; IR (KBr) ν3091, 1701, 1622, 1506, 1478, 1451, 1319, 1289, 1275, 1225, 1207, 1151, 994, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.24 (d, *J* = 15.3 Hz, 1H), 7.43–7.50 (m, 5H), 7.68–7.70 (m, 2H), 7.84 (d, *J* = 7.0 Hz, 1H), 8.11 (d, *J* = 15.3 Hz, 1H), 8.34 (d, *J* = 7.0 Hz, 1H), 8.57 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 115.7, 115.8, 120.6, 125.1, 125.8, 128.7 (x 2), 129.2 (x 2), 131.5, 131.9, 133.8, 140.7, 144.1, 148.9, 162.9; MS *m/z* 248 [M^+]; Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.24; H, 5.01; N, 11.05.

1-[(2*E*)-1-Oxo-3-phenyl-2-propenyl]-2-phenyl-1*H*-imidazole (26b): white-yellow solid; mp 92–92.5 °C; IR (KBr) ν3383, 1698, 1617, 1465, 1378, 1352, 1230, 1202, 1087, 995, 757, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.48 (d, *J* = 15.3 Hz, 1H), 7.17 (d, *J* = 1.6 Hz, 1H), 7.17-7.19 (m, 2H), 7.30–7.46 (m, 6H), 7.60–7.62 (m, 2H), 7.67 (d, 1.6 Hz, 1H), 7.82 (d, *J* = 15.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 118.5, 119.3, 128.4 (x 2), 128.6 (x 2), 128.9 (x 2), 129.2, 129.5 (x 2), 129.6, 131.3, 131.5, 133.7, 147.7, 148.1, 164.1; MS *m/z* 274 [M^+]; HRMS (M^+) Calcd for $C_{18}H_{14}N_2O$: 274.1106. Found 274.1104.

2-Methyl-1-[(2*E*)-1-oxo-3-phenyl-2-propenyl]-1*H*-imidazole (26c): white solid; mp 84–85 °C; IR (KBr) ν3392, 1709, 1618, 1404, 1286, 1254, 1134, 994, 775, 762, 679 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.73 (s, 3H), 6.96 (d, *J* = 1.6 Hz, 1H), 7.05 (d, *J* = 15.3 Hz, 1H), 7.39 (d, *J* = 1.6 Hz, 1H), 7.43–7.49 (m, 3H), 7.62–7.63 (m, 2H), 7.97 (d, *J* = 15.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 17.4, 116.7, 116.9, 128.4, 128.6 (x 2), 129.1 (x 2), 131.4, 133.8, 148.5, 149.0, 163.7; MS *m/z* 212 [M^+], HRMS (M^+) Calcd for $C_{13}H_{12}N_2O$: 212.0950. Found 212.0959.

4-Methyl-1-[(2*E*)-1-oxo-3-phenyl-2-propenyl]-1*H*-imidazole (26d): white solid; mp 145–148 °C; IR (KBr) ν3128, 1690, 1626, 1484, 1396, 1376, 1285, 1263, 1174, 987, 763 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (d, *J* = 1.2 Hz, 3H), 7.03 (d, *J* = 15.6 Hz, 1H), 7.33 (br-t, 1H), 7.44–7.47 (m, 3H), 7.63–7.65 (m, 2H), 8.04 (d, *J* = 15.6 Hz, 1H), 8.21 (d, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.6, 112.4, 115.0, 128.6 (x 2), 129.1 (x 2), 131.5, 133.7, 135.7, 140.7, 149.2, 161.5; MS *m/z* 212 [M^+]; HRMS (M^+) Calcd for $C_{13}H_{12}N_2O$: 212.0950. Found 212.0956.

1-[(2*E*)-1-Oxo-3-phenyl-2-propenyl]-4-phenyl-1*H*-imidazole (26f): white-yellow solid; mp 230–232 °C; IR (KBr) ν1687, 1621, 1495, 1395, 1290, 1236, 1188, 988, 753, 694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.11 (d, *J* = 15.6 Hz, 1H), 7.31–7.50 (m, 6H), 7.67–7.69 (m, 2H), 7.86–7.87 (m, 2H), 7.91 (d, 1.6 Hz, 1H), 8.11 (d, *J* = 15.6 Hz, 1H), 8.35 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR

($CDCl_3$) δ 111.2, 114.5, 125.5 (x 2), 128.1, 128.8 (x 2), 128.9 (x 2), 129.9 (x 2), 131.8, 132.4, 133.7, 136.3, 143.6, 150.0, 161.6; MS *m/z* 274 [M^+]; HRMS (M^+) Calcd for $C_{18}H_{14}N_2O$: 274.1106. Found 274.1102.

1-[(2*E*)-3-(4-Chlorophenyl)-1-oxo-2-propenyl]-4-phenyl-1*H*-imidazole (26h): white-yellow solid; mp 269–270 °C; IR (KBr) ν3127, 1697, 1620, 1492, 1409, 1390, 1190, 993, 980, 823, 784, 762, 694, 419 cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.27–7.31 (m, 1H), 7.40–7.43 (m, 2H), 7.58 (m, 2H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.90–7.92 (m, 2H), 7.98 (m, 2H), 8.01 (d, *J* = 15.6 Hz, 1H), 8.42 (s, 1H), 8.81 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 112.1, 117.1, 125.1 (x 2), 127.7, 128.8 (x 2), 129.2 (x 2), 131.0 (x 2), 132.8, 133.0, 136.1, 137.9, 142.4, 147.0, 161.8; MS *m/z* 308 [M^+]; HRMS (M^+) Calcd for $C_{18}H_{13}ClN_2O$: 308.0716. Found 308.0714.

1-[(2*E*)-3-(4-Bromophenyl)-1-oxo-2-propenyl]-4-methyl-1*H*-imidazole (26i): yellow solid; mp 203–205 °C; IR (KBr) ν3127, 1692, 1624, 1585, 1483, 1406, 1392, 1278, 1261, 1175, 987, 820, 781, 403 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (d, *J* = 1.2 Hz, 3H), 7.04 (d, *J* = 15.6 Hz, 1H), 7.33 (dd, *J* = 1.2, 1.2 Hz, 1H), 7.50–7.52 (m, 2H), 7.58–7.60 (m, 2H), 7.97 (d, *J* = 15.6 Hz, 1H), 8.24 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.6, 112.4, 115.5, 126.0, 130.0 (x 2), 132.4 (x 2), 132.6, 135.6, 140.7, 147.8, 161.3; MS *m/z* 292 [M+2], 290 [M^+]; Anal. Calcd for $C_{13}H_{11}BrN_2O$: C, 53.63; H, 3.81; N, 9.62. Found: C, 53.61; H, 3.91; N, 9.39.

1-[(2*E*)-3-(4-Methoxyphenyl)-1-oxo-2-propenyl]-4-phenyl-1*H*-imidazole (26j): white-yellow solid; mp 188–189 °C; IR (KBr) ν3120, 1695, 1621, 1560, 1572, 1511, 1294, 1250, 1174, 997, 978, 834, 766, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.88 (s, 3H), 6.96 (d, *J* = 15.6 Hz, 1H), 6.97 (m, 2H), 7.30–7.44 (m, 3H), 7.63 (m, 2H), 7.85–7.90 (m, 2H), 7.90 (d, *J* = 1.2 Hz, 1H), 8.06 (d, *J* = 15.6 Hz, 1H), 8.33 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.5, 111.2, 111.8, 114.7 (x 2), 125.4 (x 2), 126.5, 127.9, 128.7 (x 2), 130.8 (x 2), 132.7, 136.3, 143.6, 149.6, 161.9, 162.6; MS *m/z* 304 [M^+]; Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 75.01; H, 5.38; N, 9.09.

1-[(2*E*)-1-Oxo-5-phenyl-2-pentenyl]-4-phenyl-1*H*-imidazole (26k): white solid; mp 140–144 °C; IR (KBr) ν1698, 1635, 1496, 1396, 1196, 758, 697, 409 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.73 (ddd, *J* = 14.5, 7.4, 1.5 Hz, 2H), 2.90 (t, *J* = 7.4 Hz, 2H), 6.48 (dd, *J* = 15.3, 1.5 Hz, 1H), 7.21–7.44 (m, 9H), 7.76 (d, *J* = 1.2 Hz, 1H), 7.82 (m, 2H), 8.15 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 34.1, 34.4, 111.0, 119.6, 125.4 (x 2), 126.5, 127.9, 128.4 (x 2), 128.6 (x 2), 128.7 (x 2), 132.6, 136.3, 140.1, 153.9, 161.2; MS *m/z* 302 [M^+]; HRMS (M^+) Calcd for $C_{20}H_{18}N_2O$: 302.1419. Found 302.1418.

1-[(2*E*,6*Z*)-1-Oxo-2,6-octadienyl]-4-phenyl-1*H*-imidazole (26l): white solid; mp 96–102 °C; IR (KBr) ν3132, 3008, 1702, 1642, 1503, 1398, 1312, 1295, 1254, 1200, 978, 758, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64–1.66 (m, 3H), 2.32–2.35 (m, 2H), 2.45–2.49 (m, 2H),

5.39–5.41 (m, 1H), 5.55–5.59 (m, 1H), 6.56 (dt, J = 15.3, 1.5 Hz, 1H), 7.30–7.43 (m, 3H), 7.41 (dt, J = 15.3, 7.0 Hz, 1H), 7.82 (d, J = 1.2 Hz, 1H), 7.82–7.84 (m, 2H), 8.24 (d, J = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.9, 25.2, 32.8, 111.1, 119.1, 125.4 (x 2), 125.8, 127.9, 128.2, 128.7 (x 2), 132.6, 136.3, 143.7, 154.9, 161.3; MS *m/z* 266 [M^+]; HRMS (M^+) Calcd for $C_{17}H_{18}N_2O$: 266.1419. Found 266.1416.

1-[(2*E*,6*E*)-1-Oxo-2,6-octadienyl]-4-phenyl-1*H*-imidazole (26m): white-yellow solid; mp 112–119 °C; IR (KBr) ν 3133, 2934, 1698, 1635, 1499, 1395, 1293, 1253, 1201, 983, 964, 758, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.68 (dd, J = 6.1, 1.2 Hz, 3H), 2.23–2.27 (m, 2H), 2.42–2.47 (m, 2H), 5.40–5.45 (m, 1H), 5.49–5.56 (m, 1H), 6.56 (dt, J = 15.3, 1.5 Hz, 1H), 7.29–7.42 (m, 3H), 7.39 (dt, J = 15.3, 7.0 Hz, 1H), 7.82 (d, J = 1.2 Hz, 1H), 7.82–7.84 (m, 2H), 8.24 (d, J = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 17.9, 30.8, 32.9, 111.1, 119.0, 125.3 (x 2), 126.8, 127.9, 128.7 (x 2), 129.0, 132.5, 136.4, 143.6, 155.0, 161.3; MS *m/z* 266 [M^+]; HRMS (M^+) Calcd for $C_{17}H_{18}N_2O$: 266.1419. Found 266.1424.

1-[(2*E*,6*Z*)-1-Oxo-7-phenyl-2,6-heptadienyl]-4-phenyl-1*H*-imidazole (26n): white-yellow solid; mp 117–119 °C; IR (KBr) ν 3127, 1699, 1643, 1498, 1401, 1254, 1204, 758, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.52–2.56 (m, 2H), 2.61–2.65 (m, 2H), 5.65 (dt, J = 11.6, 7.0 Hz, 1H), 6.50 (dt, J = 15.3, 1.6 Hz, 1H), 6.54 (d, J = 11.6 Hz, 1H), 7.29–7.42 (m, 9H), 7.77 (d, J = 1.2 Hz, 1H), 7.81–7.83 (m, 2H), 8.17 (d, J = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.6, 32.9, 111.1, 119.3, 125.4 (x 2), 127.0, 127.9, 128.4 (x 2), 128.7 (x 2), 128.7 (x 2), 130.2, 130.6, 132.6, 136.4, 137.1, 143.7, 154.3, 161.2; MS *m/z* 328 [M^+]; HRMS (M^+) Calcd for $C_{22}H_{20}N_2O$: 328.1576. Found 328.1577.

1-[(2*E*)-1,7-Dioxo-2-octenyl]-4-phenyl-1*H*-imidazole (26o): white-yellow solid; IR (KBr) ν3136, 1707, 1697, 1637, 1316, 1295, 1252, 1199, 989, 858, 767, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.84 (tt, J = 7.0 Hz, 7.0 Hz, 2H), 2.16 (s, 3H), 2.38–2.42 (m, 2H), 2.54 (t, J = 7.0 Hz, 2H), 6.57 (dt, J = 15.3, 1.6 Hz, 1H), 7.30–7.43 (m, 3H), 7.38 (dt, J = 15.3, 7.0 Hz, 1H), 7.82 (d, J = 1.5 Hz, 1H), 7.82–7.84 (m, 2H), 8.25 (d, J = 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 30.0, 32.0, 42.4, 111.0, 119.3, 125.4 (x 2), 127.9, 128.7 (x 2), 132.5, 136.4, 143.7, 154.3, 161.2, 207.7; MS *m/z* 282 [M^+]; HRMS (M^+) Calcd for $C_{17}H_{18}N_2O_2$: 282.1368. Found 282.1365.

1-[(2*E*)-3-Cyclohexyl-1-oxo-2-propenyl]-1*H*-imidazole (26p): white solid; mp 147–149 °C; IR (KBr) ν3129, 2931, 2855, 1698, 1627, 1495, 1389, 1279, 1246, 1197, 1177, 987, 762, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.19–1.40 (m, 6H), 1.71–1.88 (m, 4H), 2.32–2.35 (m, 1H), 6.48 (dd, J = 15.3, 1.2 Hz, 1H), 7.30–7.43 (m, 3H), 7.36 (dd, J = 15.3, 7.0 Hz, 1H), 7.82 (d, J = 1.2 Hz, 1H), 7.82–7.84 (m, 2H), 8.24 (d, J = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.6, 25.8, 31.5, 41.3, 111.1, 116.4, 125.4 (x 2), 127.9, 128.7 (x 2), 132.6, 136.4, 143.7, 160.4, 161.7; MS *m/z* 280 [M^+]; HRMS (M^+) Calcd for $C_{18}H_{20}N_2O$: 280.1576. Found 280.1574.

Synthesis of the α,β–Epoxy Esters 25a, 25h–p Using the La–(*S*)-BINOL–Ph_3As=O Complex and Enantiomeric Analysis of 25a, 25h-p. The α,β–Epoxy Esters **25a**, **25h-p** were prepared according to the general procedure of catalytic asymmetric epoxidation of imidazolides except for the compoumnd **25j** due to the low stability against acidic conditions. Detailed experimental procedure for work-up and purification of **25j** is described below. The compound **25a** was reported in ref 11b and ref 47c. The compound **25j** was reported in ref 47d. For the known compound **25q**, see: *Tetrahedron Lett.* **1998**, *39*, 2071. The absolute configurations of **25a**, **25j** and **25q** were determined by comparing the measured optical rotations with the reported ones. The absolute configuration of **25k** was determined by comparing the measured optical rotation with the reported one (Calis, I.; Kuruüzüm, A.; Demirezer, L. O.; Sticher, O.; Ganci, W. *J. Nat. Prod.* **1999**, *62*, 1101.) after converting into the corresponding β-hydroxy ester. The absolute configurations of **25l** and **25m** were determined by comparing the measured optical rotation with the reported one (Rychnovsky, S. D.; Griesgraber, G. *J. Org. Chem.* **1992**, *57*, 1559.) after converting into methyl 3-hydroxyoctanoate.

General Procedure for the Catalytic Asymmetric Epoxidation of Carboxylic Acid Imidazolides Using the La–BINOL–Ph_3As=O Complex (Table 4-4, entry 1). To a mixture of (*S*)-BINOL (7.2 mg, 0.025 mmol), triphenylarsine oxide (8.1 mg, 0.025 mmol) and MS 4A (250 mg; MS 4A was not dried (1000 mg/mmol of starting material).) in dry THF (2.5 mL) was added a solution of La(O-*i*-Pr)$_3$ (0.125 mL, 0.025 mmol, 0.2 M solution in THF) at room temperature. After being stirred for 45 min at the same temperature, TBHP (0.12 mL, 0.6 mmol, 5 M solution in decane) was added. After being stirred for 10 min, imidazolide **26f** (68.6 mg, 0.25 mmol) was added directly and the mixture was stirred at room temperature. After the starting material was consumed completely, excess MeOH (0.5 mL) was added to the reaction mixture and the resulting mixture was stirred for 3 h, and then quenched by addition of 1% aqueous critic acid solution (2.5 mL) at 0 °C. The mixture was extracted with ethyl acetate (2 x 10 mL) and the combined organic layers were washed with 2% aqueous sodium thiosulfate (5 mL) and brine (5 mL), and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 50:1) to give epoxy ester **25a** (38.5 mg, 86%) as a colorless oil. The enantiomeric excess of **25a** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 2/98, flow rate 0.4 mL/min, t_R 30.3 min (2*S*,3*R*)-isomer and 34.3 min (2*R*,3*S*)-isomer, detection at 254 nm).

Methyl (2*R*,3*S*)-3-Phenyloxiranecarboxylate (25a): white-solid; $[\alpha]_D^{24}$ −111.8° [*c* 1.17, $CHCl_3$ (92% ee)]. The enantiomeric excess of **25a** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 2/98, flow rate 0.4 mL/min, t_R 28.6 min (2*S*,3*R*)-isomer and 30.6 min (2*R*,3*S*)-isomer, detection at 254 nm).

Methyl (2*R*,3*S*)-3-(4-Chlorophenyl)oxiranecarboxylate (25h): white-yellow solid; mp 59–62 °C; IR (neat) ν3034, 1753, 1496, 1427, 1340, 1213, 1090, 834, 802, 728 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.47 (dd, *J* = 1.9, 1.5 Hz, 1H), 3.83 (s, 3H), 4.08 (d, *J* = 1.5 Hz, 1H), 7.21–7.23 (m, 2H), 7.33–7.35 (m, 2H); ^{13}C NMR ($CDCl_3$) δ52.7, 56.6, 57.3, 127.1 (x 2), 128.9 (x 2), 133.4, 134.9, 168.3; MS *m/z* 212 [M^+], 155; HRMS (M^+) Calcd for $C_{10}H_9ClO_3$: 212.0240. Found 212.0246; $[\alpha]_D^{23}$ −148.7° [*c* 1.03, $CHCl_3$ (93% ee)]. The enantiomeric excess of **25h** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALCEL OD, *i*-PrOH/hexane 1/9, flow rate 0.5 mL/min, t_R 14.7 min (major-isomer) and 17.7 min (minor-isomer), detection at 254 nm).

Methyl (2*R*,3*S*)-3-(4-Bromophenyl)oxiranecarboxylate (25i): white-yellow solid; mp 74–75 °C; IR (neat) ν3033, 1752, 1493, 1425, 1339, 1214, 1071, 832, 801, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.47 (d, *J* = 1.4 Hz, 1H), 3.83 (s, 3H), 4.07 (d, *J* = 1.4 Hz, 1H), 7.15–7.17 (m, 2H), 7.49–7.51 (m, 2H); ^{13}C NMR ($CDCl_3$) δ52.7, 56.6, 57.4, 123.1, 127.4 (x 2), 131.9 (x 2), 134.0, 168.3; MS *m/z* 257 [M+2], 255 [M^+], 200, 198; Anal. Calcd for $C_{10}H_9BrO_3$: C, 46.72; H, 3.53. Found: C, 46.47; H, 3.57; $[\alpha]_D^{25}$ −118.0° [*c* 0.79, $CHCl_3$ (89% ee)]. The enantiomeric excess of **25i** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALCEL OD, *i*-PrOH/hexane 1/9, flow rate 0.5 mL/min, t_R 15.1 min (major-isomer) and 18.8 min (minor-isomer), detection at 254 nm).

Methyl (2*R*,3*S*)-3-(4-Methoxyphenyl)oxiranecarboxylate (25j): Because of the instability of the compound **25j** against acidic conditions, special work-up and purification method was necessary to minimize the decomposition of **25j** to the corresponding α,β-dihydroxy ester. After the conversion of the peroxy ester to the methyl ester **25j**, the reaction mixture was cooled at 0 °C, diluted with ethyl acetate (5 mL), and then quenched by addition of aqueous 0.01 M HCl solution (10 mL) to the mixture. The resulting mixture was poured into water (5 mL) and extracted with ethyl acetate (2 x 15 mL). The combined organic layers were washed with 2% aqueous sodium thiosulfate (5 mL) and brine (5 mL), and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (neutral SiO_2, hexane/ethyl acetate/triethylamine 200:10:1) to give **25j** in 80% isolated yield as a colorless oil. $[\alpha]_D^{25}$ −144.8° [*c* 0.63, $CHCl_3$ (91% ee)]. The enantiomeric excess of **25j** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALCEL OD, *i*-PrOH/hexane 1/9, flow rate 1.0 mL/min, t_R 8.5 min (2*R*,3*S*)-isomer and 12.1 min (2*S*,3*R*)-

isomer, detection at 254 nm).

Methyl (2*R*,3*S*)-3-(2-Phenylethyl)oxiranecarboxylate (25k): colorless oil; IR (neat) ν3027, 2952, 1752, 1453, 1291, 1029, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.86–2.01 (m, 2H), 2.73–2.86 (m, 2H), 3.20 (ddd, *J* = 6.4, 4.6, 1.8 Hz, 1H), 3.21 (4.07 (d, *J* = 1.8 Hz, 1H), 3.76 (s, 3H), 7.18–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ31.9, 33.2, 52.4, 53.1, 57.8, 126.3, 128.3 (x 2), 128.6 (x 2), 140.5, 169.5; MS *m/z* 206 [M^+]; HRMS (M^+) Calcd for $C_{12}H_{14}O_3$: 206.0943. Found 206.0945; $[\alpha]_D^{25}$ –33.5° [*c* 0.82, $CHCl_3$ (83% ee)]. The enantiomeric excess of **25k** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 2/98, flow rate 1.0 mL/min, t_R 9.7 min (2*R*,3*S*)-isomer and 10.7 min (2*S*,3*R*)-isomer, detection at 254 nm).

Methyl (2*R*,3*S*)-3-[(3*Z*)-3-Pentenyl]oxiranecarboxylate (25l): colorless oil; IR (neat) ν3015, 2953, 1755, 1446, 1291, 1206, 1030, 711 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62 (ddd, *J* = 6.7, 1.8, 0.9 Hz, 3H), 1.64–1.73 (m, 2H), 2.21–2.25 (m, 2H), 3.18 (ddd, *J* = 6.1, 5.2, 1.8 Hz, 1H), 3.25 (d, *J* = 1.8 Hz, 1H), 3.78 (s, 3H), 5.36–5.42 (m, 1H), 5.44–5.56 (m, 1H); ^{13}C NMR ($CDCl_3$) δ12.7, 23.0, 31.3, 52.4, 53.0, 58.1, 125.4, 128.4, 169.7; MS *m/z* 149, 137, 121; HRMS (M–1) Calcd for $C_9H_{13}O_3$: 169.0865. Found 169.0861; $[\alpha]_D^{21}$ –14.8° [*c* 1.09, $CHCl_3$ (86% ee)]. The enantiomeric excess of **25l** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALCEL OD, *i*-PrOH/hexane 1/9, flow rate 0.5 mL/min, t_R 14.5 min (minor-isomer) and 23.7 min (major-isomer), detection at 254 nm) after conversion to the corresponding 4-methoxybenzyl ester.

Methyl (2*R*,3*S*)-3-[(3*E*)-3-Pentenyl]oxiranecarboxylate (25m): colorless oil; IR (neat) ν2938, 2856, 1755, 1448, 1291, 1206, 1029, 968, 471 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62 (dd, *J* = 6.1 Hz, 1.2 Hz, 3H), 1.60–1.73 (m, 2H), 2.12–2.20 (m, 2H), 3.17 (ddd, *J* = 6.1, 5.2, 1.8 Hz, 1H), 3.25 (d, *J* = 1.8 Hz, 1H), 3.78 (s, 3H), 5.36–5.42 (m, 1H), 5.44–5.56 (m, 1H); ^{13}C NMR ($CDCl_3$) δ17.8, 28.7, 31.4, 52.4, 53.0, 58.1, 126.4, 129.3, 169.7; MS *m/z* 149, 137, 121, 120; HRMS (M–C_3H_5) Calcd for $C_6H_9O_3$: 129.0552. Found 129.0562; $[\alpha]_D^{23}$ –21.2° [*c* 0.9, $CHCl_3$ (79% ee)]. The enantiomeric excess of **25m** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 1/9, flow rate 0.5 mL/min, t_R 14.5 min (minor-isomer) and 20.4 min (major-isomer), detection at 254 nm) after conversion to the corresponding 4-methoxybenzyl ester.

Methyl (2*R*,3*S*)-3-[(3*Z*)-4-Phenyl-3-butenyl]oxiranecarboxylate (25n): colorless oil; IR (neat) ν3019, 2952, 1753, 1446, 1291, 1206, 1029, 770, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70–1.84 (m, 2H), 2.49–2.54 (m, 2H), 3.19 (ddd, *J* = 6.4, 4.9, 1.9 Hz, 1H), 3.25 (d, *J* = 1.9 Hz, 1H), 3.76 (s, 3H), 5.65 (dt, *J* = 11.6, 7.3 Hz, 1H), 6.48 (d, *J* = 11.6 Hz, 1H), 7.22–7.26 (m, 2H), 7.32–7.35 (m, 3H); ^{13}C NMR ($CDCl_3$) δ24.8, 31.6, 52.4, 52.9, 57.9, 126.8, 128.2 (x 2),

128.7 (x 2), 130.2, 130.4, 137.1, 169.5; MS *m/z* 232 [M$^+$]; HRMS (M$^+$) Calcd for $C_{14}H_{16}O_3$: 232.1099. Found 232.1098; $[\alpha]_D^{22}$ –13.7° [*c* 0.54, $CHCl_3$ (82% ee)]. The enantiomeric excess of **6o** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALCEL OD, *i*-PrOH/hexane 1/9, flow rate 0.5 mL/min, t_R 14.9 min (minor-isomer) and 25.8 min (major-isomer), detection at 254 nm).

Methyl (2*R*,3*S*)-3-(4-Oxopentyl)oxiranecarboxylate (25o): colorless oil; IR (neat) ν2955, 1751, 1714, 1488, 1361, 1293, 1207 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.49–1.58 (m, 1H), 1.69–1.82 (m, 3H), 2.15 (s, 1H), 2.52 (t, *J* = 7.3 Hz, 2H), 3.16 (ddd, *J* = 6.7, 4.0, 1.8 Hz, 1H), 3.22 (d, *J* = 1.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$) δ19.8, 30.0, 30.6, 42.6, 52.4, 52.6, 58.1, 169.5, 208.0; MS *m/z* 186 [M$^+$]; HRMS (M$^+$) Calcd for $C_9H_{14}O_4$: 186.0892. Found 186.0888; $[\alpha]_D^{22}$ –10.3° [*c* 0.26, $CHCl_3$ (81% ee)]. The enantiomeric excess of **25o** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALCEL OD, *i*-PrOH/hexane 1/3, flow rate 0.5 mL/min, t_R 19.7 min (minor-isomer) and 30.3 min (major-isomer), detection at 254 nm) after conversion to the corresponding 4-methoxybenzyl ester.

Methyl (2*R*,3*S*)-3-Cyclohexyloxiranecarboxylate (25p): colorless oil; $[\alpha]_D^{25}$ –24.8° [*c* 1.27, $CHCl_3$ (88% ee)]. The enantiomeric excess of **25p** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 1/9, flow rate 0.5 mL/min, t_R 15.5 min (2*S*,3*R*)-isomer and 17.5 min (2*R*,3*S*)-isomer, detection at 254 nm) after conversion to the corresponding 4-methoxybenzyl ester.

Experimental Procedures and Spectral and Analytical Data for the Compounds 22 and 24a.

***tert*-Butyl 3-Phenyl-2-peroxypropenoate (22):** The compound **22** could be prepared from **26g** in good yield according to the general procedure for catalytic asymmetric epoxidation of imidazolides. orange oil; IR (neat) ν2987, 1756, 1634, 1450, 1366, 1305, 1189, 1103, 979, 839, 762 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 9H), 6.42 (d, *J* = 16.2 Hz, 1H), 7.40 (m, 3H), 7.54 (m, 2H), 7.76 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.2 (x 3), 83.7, 113.2, 128.2 (x 2), 128.9 (x 2), 130.7, 134.1, 146.0, 165.3; MS *m/z* 220 [M$^+$]; HRMS (M$^+$) Calcd for $C_{13}H_{16}O_3$: 220.1099. Found 220.1101.

***tert*-Butyl (2*R*,3*S*)-3-Phenylperoxyglycidate (24a):** To a mixture of (*S*)-BINOL (7.2 mg, 0.025 mmol), triphenylarsine oxide (8.1 mg, 0.025 mmol) and MS 4A (250 mg; MS 4A was not dried (1000 mg/mmol of starting material).) in dry THF (2.5 mL) was added a solution of La(O-*i*-Pr)$_3$ (0.125 mL, 0.025 mmol, 0.2 M solution in THF) at room temperature. After being stirred for 45 min at the same temperature, TBHP (0.12 mL, 0.6 mmol, 5 M solution in

decane) was added. After being stirred for 10 min, imidazolide **26f** (68.6 mg, 0.25 mmol) was added directly and the mixture was stirred at room temperature. After 3.5 h, the reaction was quenched by addition of 1% aqueous critic acid solution (2.5 mL) at 0 °C. The mixture was extracted with ethyl acetate (2 x 10 mL) and the combined orgaic layers were washed with brine (5 mL), and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 50:1) to give **24a** (51.0 mg, 86%) as a white solid: mp 86–88 °C; IR (neat) ν2983, 1787, 1458, 1419, 1367, 1248, 1187, 1131, 752, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (s, 9H), 3.52 (d, J = 2.0 Hz, 1H), 4.14 (d, J = 2.0 Hz, 1H), 7.23–7.28 (m, 2H), 7.33–7.39 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 26.1 (x 3), 54.9, 58.1, 84.5, 125.8 (x 2), 128.7 (x 2), 129.2, 134.4, 165.8; MS *m/z* 236 [M^+]; $[\alpha]_D^{27}$ –167.2° [*c* 0.75 $CHCl_3$(94% ee)]; HRMS (M^+) Calcd for $C_{13}H_{16}O_4$: 236.1049. Found 236.1055.

Experimental Procedures and Spectral and Analytical Data for the Compounds 30, 31, 34, 35, and 36. The compounds **30**, **31**, **34**, **35**, and **36** were synthesized according to the following procedures. For the known compound **30**, see: *Tetrahedron Lett.* **1997**, *38*, 1235. For the known compound **31**, see: *Synth Commn.* **1997**, *27*, 1731.

(2*R*,3*S*)-3-Phenyl-*N*-(phenylmethyl)oxiranecarboxamide (30): To a mixture of (*S*)-BINOL (14.3 mg, 0.05 mmol), triphenylarsine oxide (16.1 mg, 0.05 mmol) and MS 4A (500 mg; MS 4A was not dried (1000 mg/mmol of starting material).) in dry THF (5 mL) was added a solution of La(O-*i*-Pr)$_3$ (0.25 mL, 0.05 mmol, 0.2 M solution in THF) at room temperature. After being stirred for 60 min at the same temperature, TBHP (0.24 mL, 0.6 mmol, 5 M solution in decane) was added. After being stirred for 10 min, imidazolide **26f** (137.1 mg, 0.5 mmol) was added directly and the mixture was stirred at room temperature. After the starting material was consumed completely, excess 40% aq. CH_3NH_2 (0.43 mL, 5 mmol) was added to the reaction mixture and the resulting mixture was stirred for 3 h, and then quenched by addition of 2% aqueous critic acid solution (5 mL) at 0 °C. The mixture was extracted with ethyl acetate (2 x 10 mL) and the combined organic layers were washed with water (5 mL) and brine (5 mL), and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 5:1) to give epoxy amide **30** (81.2 mg, 92%) as a white solid: mp 136–139 °C; IR (KBr) ν 3266, 3068, 1656, 1558, 1458, 1425, 1254, 1080, 746, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ3.57 (d, J = 2.0 Hz, 3H), 3.39 (d, J = 2.0 Hz, 1H), 4.45 (dd, J = 14.7, 5.8 Hz, 1H), 4.49 (dd, J = 14.7, 6.1 Hz, 1H), 6.58 (br-s, 1H), 7.24–7.37 (m, 10H); ^{13}C NMR ($CDCl_3$) δ43.0, 59.0, 59.1, 125.8 (x 2), 127.8 (x 2), 127.8, 128.7 (x 2), 128.8 (x 2), 129.1, 134.8, 137.5, 167.3; MS *m/z* 253

[M^+]; HRMS (M^+) Calcd for $C_{16}H_{15}NO_2$: 253.1103. Found 253.1094; $[\alpha]_D^{24}$ –78.3° [*c* 1.31 $CHCl_3$(95% ee)].

(2*R*,3*S*)-3-Phenyloxiranecarboxaldehyde (31): To a stirred solution of **24a** (32.4 mg, 0.137 mmol) in toluene (1.4 mL) was added dropwise sodium bis(2-methoxyethoxy)aluminum hydride (Red-Al®, 86 μL, 0.069 mmol, 0.8 M in toluene) at –78 °C. After being stirred for 2 h at the same temperature, the reaction was quenched by addition of $Na_2SO_4 \cdot 10H_2O$ followed by aqueous NH_4Cl solution, extracted with dichloromethane, and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by preparative thin-layer chromatography (SiO_2, hexane/ethyl acetate 4:1) to give **31** (14.3 mg, 70%) as a colorless oil. IR (neat) ν 3431, 1637, 1094 cm^{-1}; ^1H NMR ($CDCl_3$) δ3.45 (dd, *J* = 6.1, 1.8 Hz, 1H), 4.17 (d, *J* = 1.8 Hz, 1H), 7.29–7.39 (m, 5H), 9.20 (d, *J* = 6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ56.6, 62.9, 125.7 (x 2), 128.8 (x 2), 129.2, 134.2, 196.8; MS *m/z* 148 [M^+], 147 [M–1], 119 [M–CHO]; HRMS (M^+) Calcd for $C_9H_8O_2$: 148.0524. Found 148.0522; $[\alpha]_D^{23}$ +14.3° [*c* 0.48 $CHCl_3$(94% ee)].

(2*R*,3*S*)-3-Phenethyloxirane-2-carbaldehyde (34): To a stirred solution of **33** (37.5 mg, 0.135 mmol) in toluene (2.5 ml) was added DIBAH (0.134 ml, 0.135 mmol, 1.01 M solution in toluene) at –78 °C. After being stirred for 2 h at the same temperature, 2.5 ml of a 20% aqueous potassium sodium tartrate was added. The reaction mixture was allowed to warm to room temperature and stirred vigorously for 3 h. The aqueous layer was extracted with CH_2Cl_2 (2 x 10 ml) and the combined organic layers were washed with brine, and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 15:1) to give **34** (16.8 mg, 71%) as a colorless oil: IR (neat) n 2927, 1728, 1496, 1455, 1117, 748, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.96–2.01 (m, 2H), 2.76–2.87 (m, 2H), 3.12 (dd, *J* = 6.1, 1.8 Hz, 1H), 3.25 (dt, *J* = 11.1, 1.8 Hz, 1H), 7.18–7.32 (m, 5H), 8.99 (d, *J* = 6.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 32.0, 32.9, 56.1, 59.2, 126.4, 128.3 (x 2), 128.6 (x 2), 140.2, 198.0; MS *m/z* 147 [M^+–CHO]; $[\alpha]_D^{25}$ +45.8° [*c* 0.8, $CHCl_3$ (84% ee)].

Ethyl (4*R*,5*S*)-4,5-Epoxy-3-oxo-5-phenylpentanoate (35): To a stirred solution of ethyl acetate (16.8 μL, 0.172 mmol) in THF (0.86 mL) was added LHMDS (0.138 mL, 0.138 mmol, 1M solution in THF) at –78 °C. After the mixture was stirred for 15 min, THF solution of **24a** (20.4 mg, 0.086 mmol in 1 mL of THF) was added slowly over 5 min at the same temperature. After 30 min, the resulting mixture was quenched with aqueous saturated ammonium chloride (2.5 mL), diluted with H_2O (2.5 mL) and then extracted with ethyl acetate (2 x 10 mL). The combined organic layers were washed with 2% aqueous aqueous sodium thiosulfate (5 mL) and brine (5 mL), and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 25:1) to give **35** (15.5

mg, 77%) as a colorless oil. IR (neat) ν3446, 2983, 1743, 1717, 1658, 1414, 1233, 1029, 752, 697 cm^{-1}; ^1H NMR ($CDCl_3$) β-ketoester: δ 1.29 (t, *J* = 7.0 Hz, 3H), 3.52 (s, 2H), 3.61 (d, *J* = 1.8 Hz, 1H), 4.08 (d, *J* = 1.8 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 7.27–7.39 (m, 5H); enol: δ1.31 (t, *J* = 7.0 Hz, 3H), 3.38 (d, *J* = 1.6 Hz, 1H), 4.07 (d, *J* = 1.6 Hz, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 5.31 (s, 1H), 7.27–7.39 (m, 5H), 12.0 (s, 1H); ^{13}C NMR ($CDCl_3$) β-ketoester: δ14.1, 44.2, 58.0, 61.7, 63.1, 125.7 (x 2), 128.6, 128.7 (x 2), 134.6, 166.5, 198.4; enol: δ 14.2, 59.2, 59.2, 60.5, 90.1, 125.7 (x 2), 128.8, 129.2 (x 2), 135.6, 171.0, 172.3; MS *m/z* 234 [M^+]; HRMS (M^+) Calcd for $C_{13}H_{14}O_4$: 234.0892. Found 234.0891; $[\alpha]_D^{23}$ –57.8° [*c* 0.7 $CHCl_3$(94% ee)].

Ethyl (4*R*,5*S*)-4,5-Epoxy-3-oxo-5-phenethylpentanoate (36): To a stirred solution of ethyl acetate (0.292 ml, 2.93 mmol) in THF (5 ml) was added LHMDS (2.34 ml, 2.34 mmol, 1.0 M solution in THF) at –78 °C. After being stirred for 30 min, THF (4 ml) solution of **33** (310 mg, 1.17 mmol) was added to the reaction mixture, and the reaction was stirred for 30 min at the same temperature. After being warmed up to 0 °C, the reaction was diluted with ethyl acetate and quenched with saturated aqueous ammonium chloride. The water layer was extracted with ethyl acetate (10 ml) and the combined organic layers were washed with brine, and then dried over Na_2SO_4. After evaporation of the organic solvent under reduced pressure, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 30:1 to 15:1) to give γ,δ-epoxy β-keto ester **36** (260 mg, 85%, ~7:1 mixture of the β-keto ester and the corresponding enol) as a pale yellow oil: IR (neat) ν2983, 2932, 1718, 1654, 1454, 1319, 1226, 1030, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (t, *J* = 7.0 Hz, 3H), 1.93–2.00 (m, 2H), 2.74–2.86 (m, 2H), 3.16 (dt, *J* = 1.8, 5.3 Hz, 1H), 3.29 (d, *J* = 1.8 Hz, 1H), 3.31 (d, *J* = 16.2 Hz, 1H), 3.35 (d, *J* = 16.2 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 7.18–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.0, 31.9, 33.4, 43.8, 57.7, 59.6, 61.6, 126.3, 128.3 (x 2), 128.6 (x 2), 140.2, 166.6, 199.9; MS *m/z* 262 [M^+]; $[\alpha]_D^{21}$ +19.0° [*c* 0.78, $CHCl_3$ (84% ee)].

第5章

Synthesis of the α,β-Unsaturated Amides 37a–o. All of the α,β-unsaturated amides were prepared from the corresponding acid chlorides and amines. For the known compounds **37i**, see: *Bull. Chem. Soc. Jpn.* **1976**, *49*, 493. For the known compound **37k**, see: *J. Org. Chem.* **1991**, *56*, 553. For the known compound **37l**, see: *Tetrahedron* **2001**, 31, 8705. For the known compound **37m**, see: *Synth. Commn.* **2001**, *31*, 1201. For the known compound **37o**, see: *Tetrahedron* **1989**, *45*, 4415. For the known compound **44** and **48**, see: *Chem. Eur. J.* **2004**, *10*,

1527.

5-Phenyl-pent-2-enoic acid methylamide (37a): white yellow solid; IR (KBr) ν 3303, 2924, 1668, 1624, 1557, 1498, 1454, 1410, 1353, 1159 959, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.49 (ddt, *J* = 7.6, 7.0, 1.1 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.85 (d, *J* = 4.9 Hz, 1H), 5.53 (br-s, 1H), 5.76 (dt, *J* = 15.3, 1.1 Hz, 1H), 6.85 (dt, *J* = 15.3, 7.0 Hz, 1H), 7.16–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 26.2, 33.7, 34.6, 124.0, 126.1, 128.3 (x 2), 128.4 (x 2), 141.0, 143.2, 166.5; ESI-MS *m/z* 212 [M+Na^+], 189 [M+H^+]; Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.15; H, 8.06; N, 7.38.

5-Phenyl-pent-2-enoic acid benzylamide (37c): white-yellow solid; IR (KBr) ν 3224, 3061, 1661, 1615, 1557, 1452, 1424, 1337, 1266, 1221, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.49 (ddt, *J* = 1.5, 7.0, 7.8 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 4.52 (d, *J* = 5.8 Hz, 2H), 5.75 (br-t, 1H), 5.79 (dt, *J* = 15.3, 1.5 Hz, 1H), 6.91 (dt, J = 15.3, 7.0 Hz, 1H), 7.15–7.43 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 33.8, 34.6, 43.6, 123.9, 126.1, 127.5, 127.9 (x 2), 128.3 (x 2), 128.4 (x 2), 128.7 (x 2), 138.3, 141.0, 144.0, 165.7; ESI-MS *m/z* 288 [M+Na^+]; Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.50; H, 7.40; N, 5.20.

5-Phenyl-pent-2-enoic acid allylamide (37d): white solid; IR (KBr) ν 3295, 3061, 3027, 2921 1670, 1625, 1549, 1452, 1360, 1253, 990, 917 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.50 (ddt, *J* = 1.5, 7.0, 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 3.93 (ddd, *J* = 1.3, 1.5, 4.1 Hz, 2H), 5.13 (ddt, *J* = 1.5, 10.2, 1.3 Hz, 1H), 5.18 (ddt, *J* = 1.5, 17.1, 1.5 Hz, 1H), 5.80 (dt, *J* = 15.2, 1.5 Hz, 1H), 5.85 (ddt, *J* = 10.2, 17.1, 4.1 Hz, 1H), 6.89 (dt, *J* = 15.2, 7.0 Hz, 1H), 7.10–7.43 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 33.8, 34.6, 41.9, 116.5, 126.1, 128.4 (x 2), 128.4 (x 2), 134.2, 141.0, 143.8, 165.6; ESI-MS *m/z* 238 [M+Na^+], 216 [M+H^+]; Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.18; H, 7.98; N, 6.43.

5-Phenyl-pent-2-enoic acid cyclohexylamide (37e): white solid; IR (KBr) ν 3299, 3065, 3027, 2921, 2851, 1669 1626, 1545, 1445 1350, 1220, 978, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09–1.21 (m, 3H), 1.34–1.42 (m, 2H), 1.60–1.72 (m, 3H), 1.92–1.95 (m, 2H), 2.48 (ddt, *J* = 1.6, 7.0, 8.0 Hz, 2H), 2.75 (t, *J* = 8.0 Hz, 2H), 3.83 (m, 1H), 5.74 (dt, *J* = 15.3, 1.6 Hz, 1H), 6.85 (dt, *J* = 15.3, 7.0 Hz, 1H), 7.16–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.8 (x 2), 25.6 (x 2), 33.2 (x 2), 33.8, 34.6, 48.1, 124.5, 126.1, 128.3 (x 2), 128.4 (x 2), 141.1, 143.1, 164.9; ESI-MS *m/z* 280 [M+Na^+], 258 [M+H^+]; Anal. Calcd for $C_{12}H_{15}NO$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.03; H, 8.95 N, 5.31.

5-Phenyl-pent-2-enoic acid *tert*-butylamide (37f): white solid; IR (KBr) ν 3259, 3067, 2959, 1663, 1627, 1557, 1450, 1361, 1227, 975, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (s, 9H), 2.47 (ddd, *J* = 7.8, 6.7, 1.6 Hz, 2H), 2.75 (t, *J* = 7.8 Hz, 2H), 5.24 (s, 1H), 5.71 (dt, *J* = 15.3,

1.6 Hz, 1H), 6.82 (dt, J = 15.3, 6.7 Hz, 1H), 7.16–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 28.9 (x 3), 33.7, 34.7, 51.2, 125.2, 126.0, 128.3 (x 2), 128.4 (x 2), 141.1, 142.6, 165.2; ESI-MS *m/z* 254 [M+Na$^+$], 232 [M+H$^+$]; Anal. Calcd for $C_{12}H_{15}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.69; H, 8.90; N, 5.89.

5-Phenyl-pent-2-enoic acid dimethylamide (37g): yellow oil; IR (neat) ν 3472, 3025, 2928, 1660, 1616, 1495, 1454, 1395, 1141, 749, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.52 (ddt, J = 1.5, 7.0, 7.6 Hz, 2H), 2.77 (t, J = 7.6 Hz, 2H), 2.98 (s, 6H), 6.21 (dt, J = 15.0, 1.5 Hz, 1H), 6.88 (dt, J = 15.0, 7.0 Hz, 1H), 7.16–7.28 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 34.1, 34.6, 121.0, 125.9, 128.3 (x 2), 128.3 (x 2), 141.0, 144.6, 166.7; ESI-MS *m/z* 226 [M+Na$^+$], 204 [M+H$^+$]; HRMS (M$^+$) Calcd for $C_{13}H_{17}NO$: 203.1310. Found 203.1300.

5-Phenyl-1-pyrolidin-1-yl-pent-2-en-1-one (37h): yellow oil; IR (neat) ν 3476, 3025, 2927, 2875, 1652, 1455, 1415, 1341, 751, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.84–1.90 (m, 4H), 2.51 (ddt, J = 1.0, 7.1, 7.7 Hz, 2H), 2.76 (t, J = 7.7 Hz, 2H), 3.46 (m, 4H), 6.08 (dt, J = 15.4, 1.0, Hz, 1H), 6.94 (dt, J = 15.4, 7.1 Hz, 1H), 7.17–7.28 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.1, 25.9, 33.9, 34.5, 45.5, 46.2, 122.2, 125.7, 128.1 (x 2), 128.2 (x 2), 140.9, 144.0, 164.5; ESI-MS *m/z* 252 [M+Na$^+$], 230 [M+H$^+$]; HRMS (M$^+$) Calcd for $C_{15}H_{19}NO$: 229.1467. Found 229.1466.

7-Phenyl-hept-2-enoic acid methylamide (37i): white solid; IR (KBr) ν 3301, 3026, 2931, 2855, 1627, 1159, 977, 746, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.46–1.51 (m, 2H), 1.61–1.67 (m, 2H), 2.17–2.21 (m, 2H), 2.61 (t, J = 7.6 Hz, 2H), 2.86 (d, J = 4.0 Hz, 3H), 5.51 (br-s, 1H), 5.73 (d, J = 15.3 Hz, 1H), 6.81 (dt, J= 6.7, 15.3 Hz, 1H), 7.15–7.19 (m, 3H), 7.23–7.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.2, 27.8, 30.9, 31.8, 35.6, 123.4, 125.7, 128.2 (x 2), 128.3 (x 2), 142.2, 144.4, 166.9; ESI-MS *m/z* 240 [M+Na$^+$], 218 [M+H$^+$]; HRMS (M$^+$) Calcd for $C_{14}H_{19}NO$: 217.1467. Found 217.1468.

***N*-Benzyl-3-cyclohexyl-acrylamide (37k):** white solid; IR (KBr) ν 3287, 3065, 3032, 2915, 2851, 1666, 1625, 1548, 1337, 1238, 985, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07–1.30 (m, 6H), 1.63–1.73 (m, 4H), 2.09–2.14 (m, 1H), 4.48 (d, J = 3.3 Hz, 2H), 5.72 (d, J = 15.3 Hz, 1H), 6.82 (dd, J = 15.3, 6.7 Hz, 1H), 7.24–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.7, 25.9, 31.9, 40.2, 43.6, 120.8, 127.5, 127.9, 128.7, 138.3, 150.3, 166.2; ESI-MS *m/z* 266 [M+Na$^+$], 244 [M+H$^+$]; HRMS (M$^+$) Calcd for $C_{16}H_{21}NO$: 243.1623. Found 243.1618.

3-(4-Fluro-phenyl)-*N*-methyl-acrylamide (37n): white solid; IR (KBr) ν 3262, 3077, 1660, 1613, 1567, 1509, 1342, 1224, 1160, 985, 831, 509 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.92 (d, J = 4.6 Hz, 3H), 5.65 (br-s, 1H), 6.28 (d, J = 15.5 Hz, 1H), 7.00–7.04 (m, 2H), 7.43–7.46 (m, 2H), 7.56 (d, J = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.4, 115.7 (d, J = 21.7 Hz) (x 2), 120.4, 129.4 (d, J = 8.2 Hz) (x 2), 131.0, 139.4, 163.43 (d, J = 250 Hz) (x 2), 166.72; ESI-MS *m/z* 202 [M+Na$^+$], 180 [M+H$^+$]; HRMS (M$^+$) Calcd for $C_{10}H_{10}FNO$: 179.0746. Found 179.0745

Synthesis of the α,β–Epoxy Amides 38a–o Using the Sm–(*S*)-BINOL–Ph_3As=O Complex and Enantiomeric Analysis of 38a–o. The α,β–epoxy amides **38a–o** were prepared according to the general procedure of catalytic asymmetric epoxidation of α,β-unsaturated amides. For the known compound **37k**, see: *J. Org. Chem.* **1985**, *50*, 5696. For the known compound **38b**, see: *J. Chem. Soc. Perkin Trans 1* **1988**, 2663. For the known compound **38l**, see: *J. Am. Chem. Soc.* **2001**, *123*, 9474. For the known compound **38m**, see: *Tetrahedron Lett.* **1998**, *39*, 1017. For the compound **45** and **49**, see: *Chem. Eur. J.* **2004**, *10*, 1527. The absolute configurations of **38b** and **38l** were determined by comparing the measured optical rotations with the reported ones. The absolute configurations of **38a**, **38c**, **38g** and **38k** were determined by comparing the measured optical rotations with the authentic samples, which were prepared from the corresponding α,β–epoxyperoxy esters.

General Procedure for the Catalytic Asymmetric Epoxidation of β-Alkyl Substituted α,β-Unsaturated Amides Using the Sm–BINOL–Ph_3As=O Complex (Table 5-7, entry 1). To a mixture of (*S*)-BINOL (14.3 mg, 0.05 mmol), triphenylarsine oxide (16.1 mg, 0.05 mmol) and MS 4A [500 mg (1000 mg/mmol of starting material); MS 4A was not dried.] in dry THF (5 mL) was added a solution of $Sm(O\text{-}i\text{-}Pr)_3$ (0.5 mL, 0.05 mmol, 0.1 M solution in THF) at room temperature. After being stirred for 45 min at the same temperature, TBHP (0.12 mL, 0.6 mmol, 5 M solution in decane) was added. After being stirred for 10 min, amide **37a** (94.6 mg, 0.5 mmol) was added directly and the mixture was stirred at room temperature. After complete consumption of the starting material (8 h), the reaction mixture was diluted with ethyl acetate (20 mL) and quenched with 2% aqueous citric acid (5 mL). The water layer was extracted with ethyl acetate (10 mL), the combined organic layers were washed with brine (10 ml) and dried over sodium sulphate. After concentration in *vacuo*, the residue was purified by flash chromatography (SiO_2, hexane/ethyl acetate = 4/1 to 3/1) to give epoxy amide **38a** (101.9 mg, 99%) as a white yellow solid. IR (KBr) ν 3294, 3124, 1656, 1580, 1450, 1267, 902, 742, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80–1.81 (m, 1H), 1.99–2.06 (m, 4H), 2.73–2.83 (m, 2H), 2.79 (d, J = 5.0 Hz, 3H), 2.96(ddd, J =6.6, 4.3, 2.1 Hz, 1H), 3.23 (d, J = 2.1 Hz, 1H), 6.09 (br-s, 1H), 7.19–7.23 (m, 3H), 7.27–7.33 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.7, 32.0, 33.7, 55.7, 59.2, 126.5, 128.6 (x 2), 128.8 (x 2), 140.7, 169.2; ESI-MS *m/z* 228 [M+Na^+]; HRMS (M^+) Calcd for $C_{12}H_{15}NO_2$: 205.1103. Found 205.1111. The enantiomeric excess of **38a** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 0.6 mL/min, t_R 26.0 min ((*2S,3R*)-isomer) and 35.5 min ((*2R,3S*)-isomer), detection at 254 nm]; $[\alpha]_D^{27}$ +12.2° [*c* 1.50 $CHCl_3$(>99% ee)].

(*2R,3S*)-3-Phenethyl-oxirane-2-carboxlic acid benzylamide (38c): white solid; IR (KBr) ν 3262, 3054, 1654, 1566, 1495, 1454, 1423, 1223, 900, 719, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.83–1.89 (m, 1H), 1.98–2.05 (m, 1H), 2.73–2.83 (m, 2H), 2.99 (ddd, *J* = 6.5, 4.6, 2.1 Hz, 1H), 3.30 (d, *J* = 2.1 Hz, 1H), 4.38 (dd, *J* = 14.7, 5.8 Hz, 1H), 4.42 (dd, *J* = 14.7, 5.8 Hz, 1H), 6.39 (br-s, 1H), 7.05–7.37 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 31.8, 33.4, 42.8, 55.4, 59.0, 126.2, 127.6, 127.7 (x 2), 128.3 (x 2), 128.6 (x 2), 128.7 (x 2), 137.6, 140.4, 168.2; ESI-MS *m/z* 304 [M+Na^+]; HRMS (M^+) Calcd for $C_{18}H_{19}NO_2$: 281.1416. Found 281.1421. The enantiomeric excess of **38c** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 0.8 mL/min, t_R 28.4 min ((*2S,3R*)-isomer) and 50.5 min ((*2R,3S*)-isomer), detection at 254 nm]; $[\alpha]_D^{25}$ –20.1° [*c* 0.97 $CHCl_3$(>99% ee)].

(*2R,3S*)-3-Phenethyl-oxirane-2-carboxlic acid allylamide (38d): colorless oil; IR (KBr) ν3298, 3027, 2925, 1666, 1538, 1454, 1261, 905, 700cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.83–1.90 (m, 1H), 1.98–2.06 (m, 1H), 2.73–2.83 (m, 2H), 2.97–3.01 (m, 1H), 3.27 (d, *J* = 2.0 Hz, 1H), 3.78–3.91 (m, 2H), 5.11–5.18 (m, 2H), 5.78 (ddd, *J* = 17.0, 10.0, 5.5 Hz, 1H), 6.21 (br-s, 1H), 7.17–7.23 (m, 3H), 7.30 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 31.8, 33.3, 41.0, 55.4, 59.0, 116.6, 126.2, 128.2 (x 2), 128.5 (x 2), 133.5, 140.4, 168.1; ESI-MS *m/z* 254 [M+Na^+]; HRMS (M^+) Calcd for $C_{14}H_{17}NO_2$: 231.1259. Found 231.1262. The enantiomeric excess of **38d** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 0.8 mL/min, t_R 16.2 min (minor isomer) and 26.4 min (major isomer), detection at 254 nm]; $[\alpha]_D^{26}$ –4.05° [*c* 4.2 $CHCl_3$(98% ee)].

(*2R,3S*)-3-Phenethyl-oxirane-2-carboxlic acid cyclohexylamide (38e): white solid; IR (KBr) ν 3295, 3063, 3027, 2930, 2850, 1653, 1540, 1497, 1450, 1314, 1123, 1105, 899, 739, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07–1.19 (m, 3H), 1.31–1.38 (m, 2H), 1.58–1.72 (m, 2H), 1.79–1.91 (m, 2H), 1.98–2.04 (m, 1H), 2.73–2.83 (m, 2H), 2.94 (ddd, *J* = 6.5, 4.6, 2.2 Hz, 1H), 3.23 (d, *J* = 2.2 Hz, 1H), 3.69–3.76 (m, 1H), 5.95 (d, *J* = 7.0 Hz, 1H), 7.18–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ24.7 (x 2), 25.4, 31.8, 32.9, 33.0, 33.4, 47.6, 55.5, 59.1, 126.2, 128.3 (x 2), 128.5 (x 2), 140.5, 167.4; ESI-MS *m/z* 296 [M+Na^+]; HRMS (M^+) Calcd for $C_{17}H_{23}NO_2$: 273.1729. Found 273.1723. The enantiomeric excess of **38e** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 0.5 mL/min, t_R 24.1 min (minor isomer) and 48.2 min (major isomer), detection at 254 nm]; $[\alpha]_D^{28}$ +0.77° [*c* 0.78 $CHCl_3$(>99% ee)].

(*2R,3S*)-3-Phenethyl-oxirane-2-carboxlic acid *tert*-butylamide (38f): colorless oil; IR (neat) ν 3312, 3063, 3026, 2968, 1667, 1537, 1496, 1479, 1455, 1364, 1223, 896, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, 9H), 1.81–1.89 (m, 1H), 1.99–2.06 (m, 1H), 2.73–2.84 (m,

2H), 2.93 (ddd, J = 6.5, 4.6, 2.2 Hz, 1H), 3.14 (d, J = 2.2 Hz, 1H), 5.88 (s, 1H), 7.19–7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ28.6 (x2) 31.9, 33.4, 50.9, 55.8, 59.1, 126.2, 128.3 (x 2), 128.6 (x 2), 140.6, 167.5; ESI-MS *m/z* 270 [M+Na$^+$]; HRMS (M$^+$) Calcd for $C_{15}H_{21}NO_2$: 247.1572. Found 247.1576. The enantiomeric excess of **38f** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 0.5 mL/min, t_R 9.5 min (minor isomer) and 13.7 min (major isomer), detection at 254 nm]; $[\alpha]_D^{25}$ +6.8° [*c* 0.78 $CHCl_3$(99% ee)].

(*2R,3S*)-3-Phenethyl-oxirane-2-carboxlic acid dimethylamide (38g): colorless oil; IR (neat) ν 3480, 3025, 2930, 1652, 1496, 1455, 1398, 1264, 1154, 752, 701 cm^1; ^{1}H NMR ($CDCl_3$) δ 1.98 (ddd, J = 7.9, 7.0, 5.8 Hz, 2H), 2.76 (dt, J = 14.0, 7.9, Hz, 1H), 2.86 (dt, J = 14.0, 7.0 Hz, 1H), 2.94 (s, 3H), 2.97 (s, 3H), 3.19 (dt, J = 2.1, 5.8 Hz, 1H), 3.32 (d, J = 2.1 Hz, 1H), 7.18–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 31.9, 33.3, 35.7, 36.2, 53.8, 57.5, 126.2, 128.4 (x 2), 128.5 (x 2), 140.8, 167.2; ESI-MS *m/z* 242 [M+Na$^+$]; HRMS (M$^+$) Calcd for $C_{13}H_{17}NO_2$: 219.1259. Found 219.1257. The enantiomeric excess of **38g** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 0.5 mL/min, t_R 42.8 min ((*2S,3R*)-isomer) and 51.8 min ((*2R,3S*)-isomer), detection at 254 nm]; $[\alpha]_D^{26}$ –25.8° [*c* 0.97 $CHCl_3$(99% ee)].

(*2R,3S*)-(3-Phenethyl-oxiranyl)-pyrrolidin-1-yl-methanone (38h): colorless oil; IR (neat) ν 3481, 2972, 2875, 1650, 1455, 1415, 1341, 910, 751, 701 cm^1; ^{1}H NMR ($CDCl_3$) δ 1.78–2.05 (m, 6H), 2.75 (ddd, J = 14.1, 8.3, 7.9 Hz, 1H), 2.87 (ddd, J = 14.1, 8.2, 5.8 Hz, 1H), 3.16–3.21 (m, 1H), 3.18 (d, J = 2.1 Hz, 1H), 3.23 (dt, J = 2.1, 5.7 Hz, 1H), 3.43–3.52 (m, 3H), 7.18–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$) δ23.8, 26.1, 32.0, 33.2,45.6, 46.2, 54.1, 57.4, 126.1, 128.4 (x 2), 128.5 (x 2), 140.8, 165.8; ESI-MS *m/z* 268 [M+Na$^+$]; HRMS (M$^+$) Calcd for $C_{15}H_{19}NO_2$: 245.1416. Found 245.1415. The enantiomeric excess of **38h** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/1, flow rate 0.5 mL/min, t_R 30.9 min (minor isomer) and 43.5 min (major isomer), detection at 254 nm]; $[\alpha]_D^{26}$ –32.1° [*c* 0.77 $CHCl_3$(>99% ee)].

(*2R,3S*)-3-(4-Phenyl-butyl)-oxirane-2-carboxlic acid methylamide (38i): white solid; IR (neat) ν 3277, 3107, 3026, 2936, 2853, 1662, 1567, 1451, 1412, 1268, 1162, 893, 749, 697 cm^1; ^{1}H NMR ($CDCl_3$) δ 1.48–1.74 (m, 6H), 2.62 (t, J = 7.3 Hz, 2H), 2.79 (d, J = 5.2 Hz, 3H), 2.92 (dt, J = 6.0, 2.1 Hz, 1H), 3.22 (d, J = 2.1 Hz, 1H), 6.11 (br-s, 1H), 7.15–7.18 (m, 3H), 7.23–7.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.2, 25.4, 31.0, 31.6, 35.7, 55.4, 59.6, 125.8, 128.3 (x 2) , 128.4 (x 2), 142.1, 169.2; ESI-MS *m/z* 256 [M+Na$^+$]; HRMS (M$^+$) Calcd for $C_{14}H_{19}NO_2$: 233.1416. Found 233.1415. The enantiomeric excess of **38i** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4,

flow rate 1.0 mL/min, t_R 13.5 min (minor isomer) and 24.7 min (major isomer), detection at 254 nm]; $[\alpha]_D^{25}$ +21.8° [*c* 1.29 $CHCl_3$(>99% ee)].

(*2R,3S*)-3-Propyl-oxirane-2-carboxlic acid benzylamide (38j): white solid; IR (KBr) ν 3223, 3065, 2954, 1654, 1560, 1451, 1257, 1030, 907, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (t, *J* = 7.1 Hz, 3H), 1.47–1.66 (m, 4H), 2.95 (m, 1H), 3.27 (d, *J* = 2.1 Hz, 1H), 4.42 (d, *J* = 6.1 Hz, 2H), 5.80 (s, 1H), 7.26–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ13.7, 19.0, 33.7, 42.8, 55.4, 59.6, 127.6, 127.7 (x 2), 128.8 (x 2), 137.6, 168.5; ESI-MS *m/z* 242 [M+Na^+]; HRMS (M^+) Calcd for $C_{13}H_{17}NO_2$: 219.1259. Found 219.1264. The enantiomeric excess of **38j** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 0.5 mL/min, t_R 26.3 min (minor isomer) and 41.5 min (major isomer), detection at 254 nm]; $[\alpha]_D^{22}$ –1.78° [*c* 0.56 $CHCl_3$(94% ee)].

(*2R,3S*)-3-Cyclohexyl-oxirane-2-carboxlic acid benzylamide (38k): The enantiomeric excess of **38k** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 0.5 mL/min, t_R 27.6 min ((*2R,3S*)-isomer) and 68.0 min ((*2S,3R*)-isomer), detection at 254 nm]; $[\alpha]_D^{27}$ –4.14° [*c* 0.29 $CHCl_3$(>99% ee)].

General Procedure for the Catalytic Asymmetric Epoxidation of β-Aryl Substituted α,β-Unsaturated Amides Using the Sm–BINOL–Ph_3As=O Complex (Table 5-7, entry 15). To a stirred mixture of MS 4A [250 mg (1000 mg/mmol of starting material); MS 4A was dried for 3 h at 180 °C under reduced pressure.] was added (*S*)-BINOL (7.2 mg, 0.025 mmol) and triphenylarsine oxide (8.1 mg, 0.025 mmol) as a THF solution (2.5 mL), and then Sm(O-*i*-Pr)$_3$ (0.25 mL, 0.025 mmol, 0.1 M solution in THF) was added to the reaction mixture at room temperature. After being stirred for 45 min at the same temperature, TBHP (0.077 mL, 0.6 mmol, 3.9 M solution in toluene) was added. After being stirred for 10 min, **37b** (40.3 mg, 0.25 mmol) was added directly and the mixture was stirred at room temperature. After complete consumption of the starting material (18 h), the reaction mixture was diluted with ethyl acetate (10 ml) and quenched with 2% citric acid (2.5 ml). The water layer was extracted with ethyl acetate (10 mL), the combined organic layers were washed with brine (5 ml) and dried over sodium sulphate. After concentration in *vacuo*, the residue was purified by flash chromatography (SiO_2, hexane/ethyl acetate = 4/1 to 3/1) to give epoxy amide **38b** (42.3 mg, 95%) as a white yellow solid. The enantiomeric excess of **38b** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 1.0 mL/min, t_R 17.4 min ((*2S,3R*)-isomer) and 31.1 min ((*2R,3S*)-isomer), detection at 254 nm]; $[\alpha]_D^{26}$ –50.8° [*c* 0.76 $CHCl_3$(>99% ee)].

(*2R,3S*)-3-Phenyl-oxirane-2-carboxlic acid benzylamide (38l): The enantiomeric excess of **38l** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 1.0 mL/min, t_R 25.0 min ((*2S,3R*)-isomer) and 62.2 min ((*2R,3S*)-isomer), detection at 254 nm]; $[\alpha]_D^{25}$ –86.1° [*c* 0.62 $CHCl_3$(>99% ee)].

(*2R,3S*)-3-Phenyl-oxirane-2-carboxlic acid dimethylamide (38m): The enantiomeric excess of **38m** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/1, flow rate 0.5 mL/min, t_R 23.3 min (minor isomer) and 28.5 min (major isomer), detection at 254 nm]; $[\alpha]_D^{26}$ –109.4° [*c* 1.09 $CHCl_3$(>99% ee)].

(*2R,3S*)-3-(4-Fluro-phenyl)-oxirane-2-carboxlic acid methylamide (38n): white solid; IR (KBr) ν 3300, 3121, 1652, 1578, 1509, 1413, 1219, 1155, 887, 841, 554, 528 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.87 (d, *J* = 5.2 Hz, 3H), 3.50 (d, *J* = 2.1 Hz, 1H), 3.86 (d, *J* = 2.1 HZ, 1H), 6.25 (br-s, 1H), 7.04–7.07 (m, 2H), 7.23–7.27 (m, 2H); ^{13}C NMR ($CDCl_3$) δ25.6, 58.5, 58.9, 115.7 (d, *J* = 21.6 Hz) (x 2), 127.5 (d, *J* = 9.3 Hz) (x 2), 130.72 (d, *J* = 3.1 Hz), 163.1 (d, *J* = 248 Hz), 167.8; ESI-MS *m/z* 218 [M+Na^+]; HRMS (M^+) Calcd for $C_{10}H_{10}FNO_2$: 195.0696. Found 195.0704. The enantiomeric excess of **38n** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 1.0 mL/min, t_R 20.5 min (minor isomer) and 40.0 min (major isomer), detection at 254 nm]; $[\alpha]_D^{26}$ +39.7° [*c* 0.64 $CHCl_3$(99% ee)].

(*2R,3S*)-3-*p*-Tolyl-oxirane-2-carboxlic acid methylamide (38o): white solid; ^1H NMR ($CDCl_3$) δ 2.34 (s, 3H), 2.85 (d, *J* = 5.0 Hz, 3H), 3.52 (d, *J* = 2.0 Hz, 1H), 3.83 (d, *J* = 2.0 Hz, 1H), 6.34 (s, 1H), 7.12–7.16 (m, 4H); ^{13}C NMR ($CDCl_3$) δ21.2, 25.5, 58.9, 59.1, 125.7 (x 2), 129.2 (x 2), 131.8, 138.9, 168.2; ESI-MS *m/z* 214 [M+Na^+]; HRMS (M^+) Calcd for $C_{11}H_{13}NO_2$: 191.0946. Found 191.0940. The enantiomeric excess of **38o** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 1.0 mL/min, t_R 18.7 min (minor isomer) and 37.9 min (major isomer), detection at 254 nm]; $[\alpha]_D^{27}$ –53.4° [*c* 1.31 $CHCl_3$(>99% ee)].

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第 6 章

Experimental Procedures and Spectral and Analytical Data for New Compounds for the Synthetic Pathway to (+)-Decursin (51) and Related Natural Products (–)-Prantschimgin (55), (+)-Decursinol (53), (+)-Marmesin (56) and (–)-Peucedanol (54).

6-Hydroxy-7-(methoxymethoxy)chromen-2-one (65b): To a stirred suspension of esculetin (**56**) (520.5 mg, 2.92 mmol) and potassium carbonate (605 mg, 4.38 mmol) in DMF (14.6 mL) was added methoxymethyl chloride (0.443 mL, 5.84 mmol) at –20 °C. After being stirred for 13 h at the same temperature, the reaction mixture was diluted with H_2O (10 mL) and then 1N HCl was added at 0 °C until the yellow solution turned to clear. The resulting solution was extracted with ethyl acetate (3 x 20 mL) and washed with H_2O successively. The combined aqueous layers were extracted with ether (2 x 30 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4 and then evaporated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 9:2 to 2:1) to give MOM ether **65b** (555.3 mg 85%) as a yellow solid. IR (KBr) ν3157, 1686, 1558, 1287, 1142 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.41 (s, 3H), 5.28 (s, 3H), 6.27 (d, J = 9.5 Hz, 1H), 7.05 (s, 1H), 7.06 (s, 1H), 7.91 (d, J = 9.5 Hz, 1H), 9.49 (s, 1H); ^{13}C NMR (DMSO-d_6) δ 56.0, 94.6, 103.5, 112.7, 112.7, 113.3, 144.1, 144.3, 147.7, 148.5, 160.5; MS *m/z* 222 [M^+]; HRMS (M^+) Calcd for $C_{11}H_{10}O_5$: 222.0528. Found 222.0532.

7-(Methoxymethoxy)-6-(trifluoromethanesulfonyl)chromen-2-one (66b): To an ice-cooled suspension of **65b** (114.4 mg, 0.497 mmol) in CH_2Cl_2 (5 mL) was added diisopropylethylamine (0.261 mL, 1.5 mmol) and the mixture was stirred for 10 min at 0 °C. After the solution was cooled to –30 °C, trifluoromethansulfonic anhydride (0.126 mL, 0.75 mmol) was added dropwise. The reaction mixture was stirred for 2 h at 0 °C and then saturated aqueous sodium hydrogen carbonate (10 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL), the combined organic layers were washed with brine and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 8/1) to give **66b** (158 mg, 90%) as a white solid. IR (KBr) ν1743, 1624, 1426, 1214, 1131, 937 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.54 (s, 3H), 5.33 (s, 2H), 6.38 (d, J = 9.5 Hz, 1H), 7.27 (s, 1H), 7.37 (s, 1H), 7.63 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 56.9, 95.4, 104.7, 112.6, 115.5, 118.7 (q, J = 320 Hz), 120.8, 135.5, 142.0, 151.9, 154.3, 159.8; MS *m/z* 354 [M^+]; Anal. Calcd for $C_{12}H_9F_3O_7S$: C, 40.68; H, 2.56. Found: C,

40.84; H, 2.78.

6-Formyl-7-(methoxymethyl)chromen-2-one (71b): A solution of **66b** (70.8 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), DPPP (12.4 mg, 0.03 mmol) and triethylsilane (0.096 mL, 0.6 mmol) in DMF (2 mL) was stirred for 5 h at 60 °C under CO atmosphere (15 atm). The reaction mixture was poured into H_2O (10 mL) and extracted with ethyl acetate (2 x 20 mL). The combined organic layers were washed with H_2O (4 x 10 mL) and brine (10 mL), dried over Na_2SO_4 and then evaporated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 5/1) to give **71b** (36.5 mg, 78%) as a white solid. Moreover **71b** was obtained in 82% yield when 20 mol % of $Pd(OAc)_2$ was used. IR (KBr) ν 1734, 1672, 1608, 1377, 1128, 1077, 971 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.55 (s, 3H), 3.57 (s, 2H), 6.35 (d, J = 9.5 Hz, 1H), 7.16 (s, 1H), 7.69 (d, J = 9.5 Hz, 1H), 8.01 (s, 1H), 10.45 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 56.9, 95.0, 103.1, 113.4, 115.1, 122.6, 128.8, 143.2, 159.2, 159.7, 161.8, 187.8; MS *m/z* 234 [M^+]; HRMS (M^+) Calcd for $C_{12}H_{10}O_5$ 234.0528. Found 234.0532.

7-(Methoxymthoxy)-6-(3-oxo-1-butenyl)chromen-2-one (57b): A solution of **71b** (106.4 mg, 0.454 mmol) and 1-triphenylphosphoranylidene-2-propanone **73** (180.8 mg, 0.568 mmol) in THF (4.5 mL) was stirred for 50 h at 60 °C. After the reaction mixture was cooled to room temperature, H_2O (10 mL) was added and the solution was extracted with ethyl acetate (3 x 15 mL), washed with brine (10 mL) and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 2.5/1) to give enone **57b** (116.6 mg, 94%) as a mixture of *trans*- and *cis*-isomer (11:1). *Cis*-isomer (11.3 mg, 0.0412 mmol) separated by flash column chromatography (SiO_2, hexane/ethyl acetate 4/1) could be isomerized by treating with DBU (0.3 mL) in CH_2Cl_2 (2.7 mL) at 40 °C for 2 days. After the reaction was quenched by addition of saturated aqueous ammonium chloride (10 mL), the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL), the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and then evaporated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 4/1) to give *trans*-isomer (9.2 mg, 81%) as a yellow solid. IR (KBr) ν 1739, 1665, 1618, 1384, 1168, 1134, 959 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H), 3.52 (s, 3H), 5.33 (s, 2H), 6.32 (d, J = 9.5 Hz, 1H), 6.77 (d, J = 16.5 Hz, 1H), 7.14 (s, 1H), 7.65 (d, J = 9.5 Hz, 1H), 7.66 (s, 1H), 7.83 (d, J = 16.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 27.6, 56.7, 94.9, 102.9, 113.4, 114.7, 121.4, 127.2, 128.3, 136.6, 142.9, 156.6, 158.6, 160.3, 198.3; MS *m/z* 274 [M^+]; Anal. Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.42; H, 5.22.

6-[(1*R*,2*S*)-1,2-Epoxy-3-oxobutyl]-7-(methoxymethyl)chromen-2-one (57b): To a mixture of (*R*)-BINOL (7.2 mg, 0.025 mmol), triphenylarsine oxide (8.1 mg, 0.025 mmol) and MS 4A [250 mg; MS 4A was not dried (1000 mg/mmol of starting material).] in dry THF (3.4 mL)

was added La(O-*i*-Pr)$_3$ (0.125 mL, 0.025 mmol, 0.2 M solution in THF) at room temperature and the mixture was stirred for 1 h, and then TBHP (0.1 mL, 0.5 mmol, 5 M soluiton in decane) was added. After being stirred for 30 min, enone **57b** (68.5 mg, 0.25 mmol) was added directly and the mixture was stirred at room temperature. After 5 h, the reaction was quenched by addition of 2.5% aqueous critic acid (5 mL) at 0 °C and extracted with ethyl acetate (3 x 10 mL), the combined organic layers were washed with brine (10 mL) and then dried with Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 4/1) to give epoxy ketone **52b** (65.0 mg, 90%, 93% ee) as a white solid. The enantiomeric excess of this product was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 1/9, flow rate 1.0 mL/min, t_R 28.4 min (1*S*,2*R*)-isomer and 36.0 min (1*R*,2*S*)-isomer, detection at 254 nm). The ee of **52b** could be increased by recrystallization. To a suspension of **52b** (148 mg, 93% ee) in hexane (12 mL) was added acetone at 50 °C until **52b** was dissolved into the solvent completely. The solution was cooled slowly and kept at room temperature. In the meantime, a total of 6 mL of hexane was added in some portions. After 24 h, optically pure **52b** was obtained as a needle-like crystal (113 mg, 76 %, >99% ee). IR (KBr) ν 1736, 1716, 1625, 1379, 1132, 961 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 3H), 3.38 (d, *J* = 1.8 Hz, 1H), 3.50 (s, 3H), 4.33 (d, *J* = 1.8 Hz, 1H), 5.33 (s, 2H), 5.28 (d, *J* = 8.0 Hz, 1H), 5.29 (d, *J* = 8.0 Hz, 1H), 6.30 (d, *J* = 9.5 Hz, 1H), 7.10 (s, 1H), 7.28 (s, 1H), 7.61 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 24.8, 53.1, 56.5, 62.8, 94.7, 102.2, 113.1, 114.2, 121.7, 124.4, 142.9, 155.4, 158.2, 160.4, 203.8; MS *m/z* 290 [M$^+$]; $[\alpha]_D^{22}$ +1.9° [*c* 1.0 $CHCl_3$(>99% ee)]; Anal. Calcd for $C_{15}H_{14}O_6$: C, 62.07; H, 4.86. Found: C, 61.94; H, 4.98.

6-[(1*R*,2*S*)-1,2-Epoxy-3-hydroxy-3-metylbutyl]-7-(methoxymethoxy)chromen-2-one (77): To a stirred solution of dry **52b** (200 mg, 0.689 mmol) in THF (13,8 mL) was added MeMgBr (0.893 mL, 0.757 mmol, 0.848 M solution in THF) over 5 min at –78 °C. The reaction mixture was stirred for 15 min and then quenched by addition of saturated aqueous ammonium chloride (10 mL). The mixture was extracted with ethyl acetate (2 x 15 mL), the combined organic layers were washed with brine (10 mL), and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 2/1) to give **77** (160.5 mg, 76 %) as a colorless oil and recovered starting material (40.7 mg, 20%). The enantiomeric excess of this product was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 1/9, flow rate 0.5 mL/min, t_R 13.5 min (1*R*,2*S*)-isomer and 16.6 min (1*S*,2*R*)-isomer) after conversion of the hydroxyl group into trimethylsilyl ether. IR (neat) ν 3460, 2973, 1730, 1623, 1376, 1274, 1155, 1130, 1073, 973 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 3H), 1.40 (s, 3H), 1.90 (s, 1H), 2.86 (d, *J* =

2.1 Hz, 1H), 3.50 (s, 3H), 4.26 (d, J = 2.1 Hz, 1H), 5.28 (d, J = 10.7 Hz, 1H), 5.30 (d, J = 10.7 Hz, 1H), 6.28 (d, J = 9.5 Hz, 1H), 7.07 (s, 1H), 7.31 (s, 1H), 7.61 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 24.9, 27.7, 51.0, 56.4, 67.9, 68.5, 94.5, 101.9, 113.1, 114.1, 123.9, 124.4, 143.1, 155.1, 157.9, 160.8; MS *m/z* 306 [M^+]; $[\alpha]_D^{22}$ –31.3° [*c* 0.83 $CHCl_3$(>99% ee)]; HRMS (M^+) Calcd for $C_{16}H_{18}O_6$ 306.1103. Found 306.1115.

6-[(2*S*)-2,3-Dihydroxy-3-metylbutyl]-7-(methoxymethoxy)chromen-2-one (74): To a stirred suspension of sodium borohydride (11 mg, 0,293 mmol) in THF (4 mL) was added BH_3·THF complex (0.216 mL, 0,234 mmol, 1,08 M solution in THF) at 0 °C. The resulting mixture was stirred for 10 min and then THF solution of **77** (36 mg, 0.117 mmol, 1.2 mL) was added to the reaction mixture at the same temperature. After being stirred for 1 h, the reaction mixture was diluted with ethyl acetate (5 mL) and then saturated aqueous ammonium chloride (5 mL) was added. The aqueous layer was extracted with ethyl acetate (10 mL x 2), and the combined organic layers were washed with brine (5 mL) and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 4/5) to give diol **74** (26.8 mg, 74%) as a white solid. IR (KBr) ν3267, 2979, 1730, 1619, 1165, 1132, 1090, 1064, 976 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 3H), 1.33 (s, 3H), 2.08 (s, 1H), 2.28 (d, J = 4.0 Hz, 1H), 2.57 (dd, J = 10.4, 14.1 Hz, 1H), 3.03 (dd, J = 1.9, 14.1 Hz, 1H), 3.50 (s, 3H), 3.65 (ddd, J = 1.9, 10.4, 14.1 Hz, 1H), 5.27 (s, 2H), 6.26 (d, J = 9.5 Hz, 1H), 7.07 (s, 1H), 7.34 (s, 1H), 7.62 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.6, 26.4, 32.7, 56.5, 72.9, 77.8, 94.7, 102.1, 113.0, 113.8, 125.4, 129.7, 143.2, 154.5, 158.1, 161.1; MS *m/z* 308 [M^+]; $[\alpha]_D^{22}$ –55.1° (*c* 0.76 $CHCl_3$); Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.33; H, 6.54. Found: C, 62.10; H, 6.55.

(–)-Peucedanol (54): To a stirred solution of **74** (27.2 mg, 0.088 mmol) in THF (2.2 mL) and H_2O (1.7 mL) was added conc. HCl (0.5 mL) at 35 °C and the reaction mixture was stirred for 17 h at the same temperature. After being cooled to room temperature, the resulting mixture was extracted with CH_2Cl_2 (5 mL x 2), washed with brine (5 mL) and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, MeOH/CH_2Cl_2 1/40) to give (–)-peucedanol (**54**) (21.4 mg, 92%) as a white solid. IR (KBr) ν3385, 2976, 1708, 1628, 1577, 1387, 1147 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 1.24 (s 3H), 1.25 (s, 3H), 2.68 (dd, J = 10.1, 14.4 Hz, 1H), 2.79 (s(b), 2H), 3.02 (dd, J = 1.8, 14.4 Hz, 1H), 3.65 (dd, J = 1.8, 10.1 Hz, 1H), 6.13 (d, J = 9.5 Hz, 1H), 6.71 (s, 1H), 7.41 (s, 1H), 7.81 (J = 9.5 Hz, 1H); ^{13}C NMR (acetone-d_6) δ 25.5, 25.6, 33.9, 72.8, 80.4, 103.9, 112.8, 113.0, 125.9, 131.4, 144.7, 155.7, 160.9, 161.3; MS *m/z* 264 [M^+]; $[\alpha]_D^{25}$ –38.8° (*c* 0.57 EtOH); Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.70; H, 6.31.

6-[(2*S*)-2,3-Dihydroxy-3-methylbutyl]-7-(trifluoromethanesulfonyl)chromen-2-one (79):

To an ice-cooled solution of **54** (70.5 mg, 0.267 mmol) and diisopropylethylamine (0.116 mL, 0.667 mmol) in CH_2Cl_2 (7.5 mL) was added trifluoromethansulfonic anhydride (0.05 mL, 0.297 mmol) dropwise and the mixture was stirred for 10 min at the same temperature. After the reaction was quenched by addition of saturated aqueous sodium hydrogen carbonate (5 mL), the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL), and the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and then evaporated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 1/1) to give **79** (97.5 mg, 92%) as a white solid. IR (KBr) ν 3497, 3402, 1698, 1426, 1248, 1223, 1137, 887 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 3H), 1.35 (s, 3H), 1.80 (s, 1H), 2.29 (d, J = 4.6 Hz, 1H), 2.70 (dd, J = 11.0, 14.3 Hz, 1H), 3.05 (dd, J = 1.6, 14.3 Hz, 1H), 3.65 (ddd, J = 1.6, 4.6, 11.0 Hz, 1H), 6.47 (d, J = 9.5 Hz, 1H), 7.29 (s, 1H), 7.62 (s, 1H), 7.68 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.5, 26.6, 31.9, 73.0, 77.4, 110.2, 117.8, 118.5 (q, J = 320 Hz), 118.6, 129.0, 131.4, 142.3, 149.5, 153.0, 159.5; MS *m/z* 396 [M^+]; $[\alpha]_D^{23}$ –17.3° (*c* 0.53 $CHCl_3$); Anal. Calcd for $C_{15}H_{15}F_3O_7S$: C, 45.46; H, 3.81. Found: C, 45.21; H, 3.79.

(+)-Marmesin (56): To a stirred solution of **79** (51.7 mg, 0.1305 mmol), $Pd(OAc)_2$ (2.94 mg, 0.0131 mmol), DPPF (14.5 mg, 0.0262 mmol) in toluene (3 mL) was added Na(O-*t*-Bu) (0.415 mL, 0.196 mmol, 0.427 M solution in THF) at room temperature. After being stirred for 1 h at 90 °C, the reaction mixture was poured into H_2O (5 mL), the aqueous layer was extracted with ethyl acetate (2 x 10 mL), the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and then evaporated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 2/1) to give (+)-marmesin (**56**) (25.6 mg, 80%) as a white solid. IR (KBr) ν3480, 2979, 1704, 1631, 1572, 1269, 1138, 962, 948 cm^{-1}; ^1H NMR ($CDCl_3$) δ1.24 (s, 3H), 1.37 (s, 3H), 1.83 (s, 1H), 3.19 (dd, J = 9.5, 15.9 Hz, 1H), 3.25 (dd, J = 8.3, 15.9 Hz, 1H), 4.74 (dd, J = 8.3, 9.5 Hz, 1H), 6.21 (d, J = 9.5 Hz, 1H), 6.73 (s, 1H), 7.22 (s, 1H), 7.59 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ24.3, 26.1, 29.5, 71.6, 91.1, 97.9, 112.2, 112.7, 123.4, 125.1, 143.7, 155.6, 161.4, 163.1; MS *m/z* 246 [M^+]; $[\alpha]_D^{23}$ +21.7° (*c* 0.9 $CHCl_3$) (lit.[21] ($[\alpha]_D^{23}$ +20.3°); Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.01; H, 5.89.

(–)-Prantschimgin (55): To a stirred solution of **56** (9.9 mg, 0.04 mmol) and DMAP (12.2 mg, 0.1 mmol) in THF (1 mL) was added LHMDS (0.05 mL, 0.05 mmol, 1 M solution in THF) at –40 °C. After the reaction mixture was stirred for 15 min at the same temperature, senecioyl chloride (0.022mL, 0.2 mmol) was added. The stirred solution was warmed up to room temperature for 2 h and then quenched by addition of saturated aqueous sodium hydrogen carbonate (1 mL). After dilution with ethyl acetate (2 mL), the aqueous layer was extracted with ethyl acetate (2 x 4 mL), the combined organic layers were washed with brine

(4 mL) and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 5/1 to 2:1) to give (–)-prantschimgin (**55**) (9.5 mg, 72%) as a white solid. IR (KBr) ν2922, 1717, 1706, 1626, 1267, 1228, 1123 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53 (s, 3H), 1.60 (s, 3H), 1.85 (d, J = 1.2 Hz, 3H), 2.10 (d, J = 1.2 Hz, 3H), 3.23 (m, 2H), 5.14 (dd, J = 8.0, 9.5 Hz, 1H), 5.55 (t, J = 1.2 Hz, 1H), 6.21 (d, J = 9.5 Hz, 1H), 6.74 (s, 1H), 7.21 (s, 1H), 7.59 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.1, 21.3, 22.3, 27.4, 29.6, 81.3, 88.7, 98.0, 112.3, 112.7, 117.0, 123.2, 124.6, 143.6, 155.8, 156.6, 161.4, 163.5, 165.8; MS *m/z* 328 [M^+]; $[\alpha]_D^{25}$ –34.6° (*c* 0.72 $CHCl_3$); HRMS (M^+) Calcd for $C_{19}H_{20}O_5$ 328.1311. Found 328.1315.

6-[(2*S*)-3-Hydroxy-3-metyl-2-(triethylsilyloxy)butyl]-7-(trifluoromethanesulfonyl)chromen-2-one (81a): To an ice-cooled solution of **79** (13.5 mg, 0.034 mmol) and imidazol (9.3 mg, 0.136 mmol) in CH_2Cl_2 (1.2 mL) was added chlorotriethylsilane (0.017mL, 0.102 mmol). The reaction mixture was stirred for 12 h at room temperature and then saturated aqueous sodium hydrogen carbonate (2 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (2 x 4 mL), the combined organic layers were washed with brine (4 mL) and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 5/1) to give **81a** (15.9 mg, 92%) as a colorless oil. The enantiomeric excess of this product was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALCEL OD, *i*-PrOH/hexane 2/98, flow rate 0.3 mL/min, t_R 25.0 min (2*R*)-isomer and 26.9 min (2*S*)-isomer). IR (KBr) ν3495, 2958, 2879, 1748, 1425, 1218, 1140, 1101, 1065, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.19–0.35 (m, 6H), 0.79 (t, J = 7.9 Hz, 9H), 1.25 (s, 3H), 1.26 (s, 3H), 1.90 (s, 1H), 2.69 (dd, J = 10.1, 14.0 Hz, 1H), 3.11 (dd, J = 2.5, 14.0 Hz, 1H), 3.80 (dd, J = 2.5, 10.1 Hz, 1H), 6.49 (d, J = 9.5 Hz, 1H), 7.31 (s, 1H), 7.47 (s, 1H), 7.67 (d, J = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ5.0 (x 3), 6.8 (x 3), 24.3, 26.3, 33.7, 73.0, 79.3, 110.1, 118.0, 118.3, 118.6 (q, J = 320 Hz), 129.2, 132.1, 141.8, 149.7, 153.0, 159.4; MS m/z 481 [M^+-CH_2CH_3]; $[\alpha]_D^{22}$ –18.2° [*c* 0.79 $CHCl_3$(>99% ee)]; Anal. Calcd for $C_{15}H_{15}F_3O_7S$: C, 45.46; H, 3.81. Found: C, 45.21; H, 3.79.

(*S*)-7,8-Dihydro-8,8-dimetyl-7-triethylsilyloxy-6*H*-pyrano[3,2-*g*]chromen-2-one (82): A solution of **81a** (22.3 mg, 0.0437 mmol), $Pd(OAc)_2$ (1.00 mg, 0.00437mmol), (*S*)-tol-BINAP (3.56 mg, 0.00524 mmol) and K_2CO_3 (9.0 mg, 0.0655 mmol) in toluene (1.5 mL) was stirred for 16 h at 80 °C. After being cooled to room temperature, the reaction mixture was poured into H_2O (3 mL), and the aqueous layer was extracted with ethyl acetate (2 x 5 mL), and the combined organic layers were washed with brine (5 mL), dried over Na_2SO_4 and then evaporated *in vacuo*. The residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 15/1) to give triethylsilyl ether **82** (14.3 mg, 91%) as a white solid. IR

(KBr) ν3422, 2956, 1737, 1627, 1561, 1458, 1389, 1299, 1116 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.64 (q, *J* = 8.0Hz, 6H), 0.97 (t, *J* = 8.0Hz, 9H), 1.24 (s, 3H), 1.40 (s, 3H), 2.75 (dd, *J* = 8.9, 16.2 Hz, 1H), 2.94 (dd, *J* = 5.2, 16.2 Hz, 1H), 3.84 (dd, *J* = 5.2, 8.9 Hz, 1H), 6.20 (d, *J* = 9.5 Hz, 1H), 6.74 (s, 1H), 7.13 (s, 1H), 7.57 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ5.0 (x 3), 6.8 (x 3), 20.0, 26.2, 31.7, 70.0, 78.6, 104.5, 112.5, 113.0, 117.8, 128.4, 143.2, 154.2, 156.7, 161.4; MS *m/z* 360 [M^+]; $[\alpha]_D^{22}$ +110.0° (*c* 1.6 $CHCl_3$); Anal. Calcd for $C_{20}H_{28}O_4Si$: C, 66.63; H, 7.83. Found: C, 66.90; H, 7.91.

(+)-Decursinol (53): To a stirred solution of triethylsilyl ether **82** (6.3 mg, 0.0175 mmol) in THF (1 mL) was added tetrabutylammonium fluoride (0.05 mL, 0.05 mmol, 1 M solution in THF) at room temperature. After being stirred for 10 min, the reaction mixture was quenched by addition of saturated aqueous ammonium chloride (1 mL). The aqueous layer was extracted with ethyl acetate (3 mL x 2), and the combined organic layers were washed with brine (3 mL) and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 2/1) to give (+)-decursinol (**53**) (4.1 mg, 95%) as a white solid. The enantiomeric excess of this product was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD, *i*-PrOH/hexane 1/9, flow rate 1.0 mL/min, t_R 26.5 min (*S*)-isomer and 34.9 min (*R*)-isomer). IR (KBr) ν3452, 1703, 1628, 1562, 1392, 1141, 1072, 821 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (s, 3H), 1.39 (s, 3H), 1.98 (s, 1H), 2.84 (dd, *J* = 5.8, 17.1 Hz, 1H), 3.11 (dd, *J* = 4.6, 17.1 Hz, 1H), 3.87 (dd(b), *J* = 4.6, 5.8 Hz, 1H), 6.22 (d, *J* = 9.5 Hz, 1H), 6.78 (s, 1H), 7.18 (s, 1H), 7.57 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ22.1, 25.0, 30.7, 69.2, 78.2, 104.8, 113.0, 113.3, 116.4, 129.0, 143.1, 154.2, 156.5, 161.3; MS *m/z* 246 [M^+]; $[\alpha]_D^{22}$ +6.8° [*c* 0.65 $CHCl_3$(>99% ee)] (lit.[18b] $[\alpha]_D^{26}$ +10.8°); Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.11; H, 6.02.

(+)-Decursin (51): This compound was obtained from (+)-decursinol (**53**) (4.2 mg, 0.017 mmol) and senecioyl chloride in the same manner as (–)-plantschimgin. (+)-Decursin (**51**) (4.6 mg, 83%) was obtained as a colorless oil. IR (neat) ν 2981, 2933, 1731, 1627, 1565, 1391, 1299, 1281, 1227, 1135 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (s, 3H), 1.38 (s, 3H), 1.88 (d, *J* = 1.0 Hz, 3H), 2.14 (d, *J* = 1.0 Hz, 3H), 2.86 (dd, *J* = 4.9, 17.1 Hz, 1H), 3.19 (dd, *J* = 4.6, 17.1 Hz, 1H), 5.08 (dd, *J* = 4.6, 4.9 Hz, 1H), 5.66 (s(b), 1H), 6.22 (d, *J* = 9.5 Hz, 1H), 6.79 (s, 1H), 7.14 (s, 1H), 7.57 (d, *J* = 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 20.4, 23.2, 25.0, 27.5, 27.9, 69.2, 76.8, 104.7, 112.8, 113.3, 115.6, 116.0, 128.7, 143.1, 154.2, 156.5, 158.5, 161.3, 165.8; MS *m/z* 328 [M^+]; $[\alpha]_D^{24}$ +135.2° (*c* 0.66 $CHCl_3$) (lit.[18c] $[\alpha]_D^{15}$ +172.9°); HRMS (M^+) Calcd for $C_{19}H_{20}O_5$ 328.1311. Found 328.1317.

Catalytic Asymmetric Synthesis of β–Aryl α–Hydroxy Esters 83a, 83h, 83j, and 83r-t Using One-Pot Tandem Process. β–Aryl α–hydroxy esters were prepared according to the general procedure. For the known compound **83a**, see: *Synthesis* **2000**, 1608. For the known compound **83j**, see: *ACH-Models Chem.* **1998**, *135*, 625. For the known compound **83a**, see: *Synthesis* **2000**, 1608. For the compound **83r**, see: *Shanhai Yike Daxue Xuebao* 1989, 16, 135. For the known compound **83s**, see: *Angew. Chem. Int. Ed.* **2001**, *40*, 2906. For the known compound **83t**, see: *Tetrahedron Lett.* **1994**, *35*, 5205.

General Procedure for the One-Pot Tandem Catalytic asymmetric Epoxidation–Methanolysis–Pd-Catalyzed Epoxide Opening Process (Table 7-3, entry 1). To a mixture of (*S*)-BINOL (7.2 mg, 0.025 mmol), triphenylphosphine oxide (20.9 mg, 0.075 mmol) and MS 4A (250 mg; MS 4A was not dried (1000 mg/mmol of starting material).) in dry THF (2.5 mL) was added a solution of La(O-*i*-Pr)$_3$ (0.125 mL, 0.025 mmol, 0.2 M solution in THF) at room temperature. After being stirred for 45 min at the same temperature, TBHP (0.12 mL, 0.6 mmol, 5 M solution in decane) was added. After being stirred for 10 min, imidazolide **26f** (68.6 mg, 0.25 mmol) was added directly and the mixture was stirred at room temperature. After the starting material was consumed completely (2 h), excess MeOH (1.25 mL) was added to the reaction mixture and the resulting mixture was stirred for 4 h. Pd-C (10%, 13.3 mg, 0.0125 mmol) was added directly and the reaction mixture was stirred under hydrogen atmosphere (1 atm) for 1 h. After dilution with ethyl acetate (10 mL), the resulting mixture was filtered through a short pad of celite, and then quenched with 2% citric acid (2.5 mL). The water layer was extracted with ethyl acetate (10 mL), the combined organic layers were washed with brine (5 mL) and dried over Na_2SO_4. After concentration in *vacuo*, the residue was purified by flash chromatography (SiO_2, hexane/acetone = 20:1) to give α-hydroxy ester **83a** (39.0 mg, 87%) as a colorless oil. The enantiomeric excess of **83a** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 2/98, flow rate 0.5 mL/min, t_R 40.7 min ((*2R*)-isomer) and 44.1 min ((*2S*)-isomer), detection at 254 nm]; $[\alpha]_D^{27}$ +73.0° [*c* 1.0 $CHCl_3$(95% ee)].

1-[(2*E*)-3-(4-Fluorophenyl)-1-oxo-2-propenyl]-4-phenyl-1*H*-imidazole (26r): white yellow solid; IR (KBr) ν 3120, 1693, 1624, 1599, 1509, 1395, 1231, 1192, 993, 832 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.28–7.43 (m, 5H), 7.67 (d, *J* = 15.0 Hz, 1H), 7.89–7.94 (m, 2H); 8.03 (d, *J* = 15.0 Hz, 1H), 8.03–8.06 (m, 2H), 8.43 (d, *J* = 1.2 Hz, 1H), 8.82 (d, *J* = 1.2 Hz, 1H); EI-MS

m/z 292 [M$^+$].

1-[(2*E*)-3-(2-Naphthyl)-1-oxo-2-propenyl]-4-phenyl-1*H*-imidazole (26s): white yellow solid; IR (KBr) ν 3409, 1692, 1621, 1400, 1192, 1080, 991 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.29–7.32 (m, 1H), 7.41–7.44 (m, 2H), 7.59–7.64 (m, 2H), 7.83 (d, *J* = 15.4 Hz, 1H), 7.93–8.06 (m, 5H); 8.19 (d, *J* = 15.4 Hz, 1H), 8.17–8.20 (m, 1H), 8.41 (s, 1H), 8.48 (d, *J* = 1.2 Hz, 1H), 8.87 (d, *J* = 1.2 Hz, 1H); EI-MS *m/z* 324 [M$^+$].

1-[(2*E*)-3-(3-Pyridyl)-1-oxo-2-propenyl]-4-phenyl-1*H*-imidazole (26t): yellow solid; IR (KBr) ν 3409, 1698, 1627, 1498, 1398, 1192, 771, 694 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.19 (d, *J* = 15.6 Hz, 1H), 7.33–7.36 (m, 1H), 7.42–7.47 (m, 3H), 7.86–7.89 (m, 2H), 7.91 (d, *J* = 1.2 Hz, 1H), 8.10 (d, *J* = 15.6 Hz, 1H), 8.36 (d, *J* = 1.2 Hz, 1H); 8.72 (dd, *J* = 4.9, 1.5 Hz, 1H), 8.91 (d, *J* = 1.9 Hz, 1H); EI-MS *m/z* 275 [M$^+$].

Catalytic Asymmetric Synthesis of β–Aryl α–Hydroxy Amides 85a–g Using One-Pot Tandem Process. β–Aryl α–Hydroxy Amides **85a–g** were prepared according to the general procedure of one pot tandem catalytic asymmetric epoxidation–Pd-catalyzed epoxide opening process. For the known compound **85a**, see: *Tetrahedron Lett.* **1984**, *25*, 329. For the known compound **85b**, see: *J. Chem. Soc. Perkin Trans 1* **1999**, 1295. For the known compound **85d**, see: *J. Orgmet. Chem.* **1989**, *370*, 81. For the known compound **85e**, see: *Tetrahedron* **1998**, *54*, 5041. The absolute configurations of **85a, 85b,** and **85d** were determined by comparing the measured optical rotation with the authentic samples, which were prepared from the corresponding α,β–epoxyperoxy ester **24a**.

General Procedure for the Synthesis of β–Aryl α–Hydroxy Amides Starting from α,β–Unsaturated Carboxylic Acid Imidazolides (Table 7-4, entry 1). To a mixture of (*S*)-BINOL (7.2 mg, 0.025 mmol), triphenylphosphine oxide (20.9 mg, 0.075 mmol) and MS 4A (250 mg; MS 4A was not dried (1000 mg/mmol of starting material).) in dry THF (2.5 mL) was added a solution of La(O-*i*-Pr)$_3$ (0.125 mL, 0.025 mmol, 0.2 M solution in THF) at room temperature. After being stirred for 45 min at the same temperature, TBHP (0.12 mL, 0.6 mmol, 5 M solution in decane) was added. After being stirred for 10 min, imidazolide **26f** (68.6 mg, 0.25 mmol) was added directly and the mixture was stirred at room temperature. After the starting material was consumed completely (2 h), aq. CH_3NH_2 (43 μL, 0.5 mmol) was added to the reaction mixture and the resulting mixture was stirred at room temperature. After complete consumption of the starting material (1 h), Pd-C (10%, 13.3 mg, 0.0125 mmol) and MeOH (1.3 mL) were added directly and the reaction mixture was stirred under hydrogen atmosphere (1 atm) for 1 h. After dilution with ethyl acetate (10 mL), the resulting

mixture was filtered through a short pad of celite, and then quenched with 2% citric acid (2.5 mL). The water layer was extracted with ethyl acetate (10 mL), the combined organic layers were washed with brine (5 mL) and dried over sodium sulphate. After concentration in *vacuo*, the residue was purified by flash chromatography (SiO_2, hexane/ethyl acetate = 1/1 to 1/3) to give α-hydroxy amide **85a** (38.5 mg, 87%) as a white yellow solid. The enantiomeric excess of **85a** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 1.0 mL/min, t_R 14.5 min ((2*R*)-isomer) and 28.5 min ((2*S*)-isomer), detection at 254 nm]; $[\alpha]_D^{22}$ +96.5° [*c* 0.95 $CHCl_3$(95% ee)].

General Procedure for the Synthesis of β–Aryl α–Hydroxy Amides Starting from α,β–Unsaturated Amides (Table 7-6, entry 1). To a stirred mixture of MS 4A [250 mg (1000 mg/mmol of starting material); MS 4A was dried for 3 h at 180 °C under reduced pressure.] was added (*S*)-BINOL (7.2 mg, 0.025 mmol) and triphenylphosphine oxide (20.9 mg, 0.075 mmol) as a THF solution (2.5 mL), and then Sm(O-*i*-Pr)$_3$ (0.25 mL, 0.025 mmol, 0.1 M solution in THF) was added to the reaction mixture at room temperature. After being stirred for 45 min at the same temperature, TBHP (0.077 mL, 0.6 mmol, 3.9 M solution in toluene) was added. After being stirred for 10 min, **37b** (40.3 mg, 0.25 mmol) was added directly and the mixture was stirred at room temperature. After complete consumption of the starting material (21 h), Pd-C (10%, 13.3 mg, 0.0125 mmol) and MeOH (1.3 mL) were added directly and the reaction mixture was stirred under hydrogen atmosphere (1 atm) for 2 h. After dilution with ethyl acetate (10 mL), the resulting mixture was filtered through a short pad of celite, and then quenched with 2% citric acid (2.5 mL). The water layer was extracted with ethyl acetate (10 mL), the combined organic layers were washed with brine (5 mL) and dried over sodium sulphate. After concentration in *vacuo*, the residue was purified by flash chromatography (SiO_2, hexane/ethyl acetate = 1/1 to 1/3) to give α-hydroxy amide **85a** (43.4 mg, 97%, 97% ee) as a white yellow solid.

(2*R*)-2-Hydroxy-*N*-benzyl-3-phenyl-propionamide (85b): The enantiomeric excess of **85b** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS, *i*-PrOH/hexane 1/4, flow rate 1.0 mL/min, t_R 13.5 min ((2*R*)-isomer) and 26.5 min ((2*S*)-isomer), detection at 254 nm]; $[\alpha]_D^{24}$ +70.7° [*c* 1.28 $CHCl_3$(98% ee)].

(2*R*)-2-Hydroxy-*N*-cyclohexyl-3-phenyl-propionamide (85c): white solid; IR (KBr) ν 3387, 3276, 2940, 2918, 2853, 1620, 1536, 1105, 1092, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01–1.18 (m, 3H), 1.29–1.38 (m, 2H), 1.58–1.86 (m, 5H), 2.80 (d, *J* = 4.8 Hz, 1H), 2.92 (dd, *J* = 14.1, 8.0 Hz, 1H), 3.18 (dd, *J* = 14.1, 4.6 Hz, 1H), 3.74 (m, 1H), 4.25 (ddd, *J* = 8.0, 4.6, 4.0 Hz, 1H),

6.28 (d, J = 7.3 Hz, 1H), 7.24–7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.7, 25.4, 32.9 (x 2), 41.0, 47.8, 72.6, 126.9, 128.6 (x 2), 129.6 (x 2), 136.8, 171.5; EI-MS *m/z* 247 [M^+]; HRMS (M^+) Calcd for $C_{15}H_{21}NO_2$: 247.1572. Found 247.1578. The enantiomeric excess of **85c** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS, *i*-PrOH/hexane 1/4, flow rate 1.0 mL/min, t_R 7.5 min ((*2R*)-isomer) and 15.7 min ((*2S*)-isomer), detection at 254 nm]; $[\alpha]_D^{26}$ +60.8° [*c* 0.87 $CHCl_3$(94% ee)].

(*2R*)-2-Hydroxy-*N,N*-dimethyl-3-phenyl-propionamide (85d): The enantiomeric excess of **85d** was determined by chiral stationary-phase HPLC analysis after converting into the corresponding triethylsilyl ether. [DAICEL CHIRALCEL OD-H, *i*-PrOH/hexane 2/98, flow rate 1.0 mL/min, t_R 9.1 min ((*2S*)-isomer) and 13.3 min ((*2R*)-isomer), detection at 254 nm]; $[\alpha]_D^{25}$ –24.4° [*c* 1.21 $CHCl_3$(99% ee)].

(*2R*)-2-Hydroxy-*N*-(2-hydroxyethyl)-3-phenyl-propionamide (85e): The enantiomeric excess of **85e** was determined by chiral stationary-phase HPLC analysis after converting into the corresponding bis(triethylsilyl) ether. [DAICEL CHIRALCEL OD-H, *i*-PrOH/hexane 2/98, flow rate 0.5 mL/min, t_R 10.0 min ((*2S*)-isomer) and 25.3 min ((*2R*)-isomer), detection at 254 nm]; $[\alpha]_D^{26}$ +69.8° [*c* 0.44 $CHCl_3$(94% ee)].

(*2R*)-(2-Hydroxy-3-phenyl-propionylamino)-acetic acid methyl ester (85f): white solid; IR (KBr) ν 3392, 1748, 1658, 1533, 1214, 1088, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) 2.86 (dd, J = 14.1, 8.9 Hz, 1H), 2.96 (br-s, 1H), 3.23 (dd, J = 14.1, 3.7 Hz, 1H), 3.74 (dd, J = 2.4, 1.2 Hz, 1H), 3.97 (ddd, J = 18.3, 5.5, 2.4 Hz, 1H), 4.06 (ddd, J = 18.3, 5.8, 1.2 Hz, 1H), 4.31–4.35 (m, 1H), 7.10 (br-s, 1H), 7.24–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 40.7 (x 2), 52.4, 72.9, 126.9, 128.6 (x 2), 129.5 (x 2), 136.9, 170.2, 173.2; EI-MS *m/z* 237 [M^+]; The enantiomeric excess of **85f** was determined by chiral stationary-phase HPLC analysis after converting into the corresponding triethylsilyl ether. [DAICEL CHIRALCEL OD, *i*-PrOH/hexane 2/98, flow rate 1.0 mL/min, t_R 13.7 min ((*2S*)-isomer) and 24.9 min ((*2R*)-isomer), detection at 254 nm]; $[\alpha]_D^{25}$ +75.0° [*c* 0.62 $CHCl_3$(95% ee)].

(*2R*)-3-(4-Fluro-phenyl)-2-hydroxy-*N*-methyl-propionamide (85g): white solid; IR (KBr) ν 3296, 1669, 1638, 1514, 1415, 1232, 1159, 1100, 818 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.78 (d, J = 5.0 Hz, 2H), 2.84 (dd, J = 14.0, 8.2 Hz, 1H), 3.16 (dd, J = 14.0, 4.0 Hz, 1H), 4.25 (dd, J = 8.2, 4.0 Hz, 1H), 6.01 (s, 1H), 6.97–7.01 (m, 2H), 7.18–7.27 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.7, 40.0, 72.8, 115.3 (d, J = 20.6 Hz) (x 2), 131.0 (d, J = 8.3 Hz) (x 2), 132.6 (d, J = 3.1 Hz), 161.9 (d, J = 250 Hz), 173.3; ESI-MS *m/z* 220 [M+Na^+]; HRMS (M^+) Calcd for $C_{10}H_{12}FNO_2$: 197.0852. Found 197.0857. The enantiomeric excess of **85g** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 1.0 mL/min, t_R 15.7 min ((*2R*)-isomer) and 25.8 min ((*2S*)-isomer), detection at 254 nm];

$[\alpha]_D^{27}$ +84.6° [*c* 0.73 $CHCl_3$(99% ee)].

(*2R*)-2-Hydroxy-*N*-methyl-3-*p*-tolyl-propionamide (85h): white solid; IR (KBr) ν 3351, 2923, 1628, 1541, 1412, 1329, 1081, 805, 473 cm^1; ^1H NMR ($CDCl_3$) δ 2.33 (s, 3H), 2.81 (d, *J* = 5.0 Hz, 3H), 2.83 (dd, *J* = 14.0, 8.3 Hz, 1H), 3.19 (dd, *J* = 14.0, 4.0 Hz, 1H), 4.26 (dd, *J* = 8.3, 4.0 Hz, 1H), 6.52 (s, 1H), 7.13 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.0, 25.7, 40.5, 72.9, 129.3 (x 2), 129.4 (x 2), 133.6, 136.6, 173.3; ESI-MS *m/z* 216 [M+Na^+]; HRMS (M^+) Calcd for $C_{11}H_{15}NO_2$: 193.1103. Found 193.1104. The enantiomeric excess of **85h** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD, *i*-PrOH/hexane 1/4, flow rate 1.0 mL/min, t_R 11.2 min (major isomer) and 24.3 min (minor isomer), detection at 254 nm]; $[\alpha]_D^{26}$ +72.7° [*c* 0.66 $CHCl_3$(97% ee)].

Experimental Procedure for the Synthesis of 96a Using One Pot Tandem Catalytic Asymmetric Epoxidation–Peptide Coupling–Pd-Catalyzed Epoxide Opening Process (Scheme 7-5). To a mixture of (*S*)-BINOL (7.2 mg, 0.025 mmol), triphenylphosphine oxide (20.9 mg, 0.075 mmol) and MS 4A [250 mg (1000 mg/mmol of starting material); MS 4A was not dried.] in dry THF (2.5 mL) was added a solution of La(O-*i*-Pr)$_3$ (0.125 mL, 0.025 mmol, 0.2 M solution in THF) at room temperature. After being stirred for 45 min at the same temperature, TBHP (0.12 mL, 0.6 mmol, 5 M solution in decane) was added. After being stirred for 10 min, α,β-unsaturated imidazolide **26f** (68.6 mg, 0.25 mmol) was added directly and the mixture was stirred at room temperature. After complete consumption of the starting material (3 h), L-leucine methyl ester (0.06 mL, 0.375 mmol) and hexafluoroacetone hydrate (0.44 mL, solvent ratio: THF/hexafluoroacetone = 6/1) was added. After the resulting mixture was stired for 48 h at the same temperature, Pd-C (10%, 13.3 mg, 0.0125 mmol) and MeOH (1.3 mL) were added directly and the reaction mixture was stirred under hydrogen atmosphere (1 atm) for 4 h. After dilution with ethyl acetate (10 mL), the resulting mixture was filtered through a short pad of celite, and then quenched with 2% citric acid (2.5 mL). The water layer was extracted with ethyl acetate (10 mL), the combined organic layers were washed with brine (5 mL) and dried over sodium sulphate. After concentration in *vacuo*, the residue was purified by flash chromatography (SiO_2, hexane/ethyl acetate = 10/1 to 3/1) to give roughly purified **96a**. The diastereomeric ratio was determined by measuring ^1H NMR of this sample in C_6D_6. The crude sample was further purified by flash chromatography (SiO_2, hexane/ethyl acetate = 2/1) to give **96a** (54.2 mg, 74%) as a white solid. IR (KBr) ν 3348, 2955, 1722, 1645, 1529, 1437, 1296, 1260, 1092, 742, 696, 497 cm^{-1}; ^1H NMR ($CDCl_3$) δ0.90 (d, *J* = 5.5 Hz, 3H), 0.92 (d, *J* = 5.1 Hz, 3H), 1.49–1.65 (m, 3H), 2.44 (br-s, 1H), 2.88 (dd, *J* = 14.0, 8.8 Hz, 1H), 3.22 (dd, *J* = 14.0, 4.2 Hz, 1H), 3.73 (s, 3H), 4.30 (dd, *J* = 8.5, 4.2

Hz, 1H), 4.61 (ddd, J = 9.0, 8.6, 5.0 Hz, 1H), 6.75 (d, J = 8.6 Hz, 1H), 7.22–7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ21.8, 22.7, 24.8, 40.8, 41.5, 50.3, 52.3, 72.8, 127.1, 128.8 (x 2), 129.4 (x 2), 136.6, 172.3, 173.0; ESI-MS *m/z* 316 [M+Na$^+$]; HRMS (M$^+$) Calcd for $C_{16}H_{23}NO_4$: 293.1627. Found 293.1624. The enantiomeric excess of **96a** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 0.5 mL/min, t_R 12.9 min (major isomer) and 31.3 min (minor isomer), detection at 254 nm]; $[\alpha]_D^{25}$ +51.2° [*c* 0.68 $CHCl_3$(99% ee)].

(*2S*)-2-((*2S*)-Hydroxy-3-phenyl-propionylamino)-4-methyl-pentanoic acid methyl ester (L-3-phenyllactyl-L-Leu-OMe) (96b): white solid; IR (KBr) ν 3373, 3187, 2956, 1752, 1657, 1542, 1269, 1236, 1194, 1151, 1092, 706, 596 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ0.86 (d, J = 4.9 Hz, 3H), 0.88 (d, J = 4.9 Hz, 3H), 1.40–1.49 (m, 2H), 1.54-1.59 (m, 1H), 2.90 (dd, J = 14.0, 7.6 Hz, 1H), 3.18 (dd, J = 14.0, 4.0 Hz, 1H), 3.69 (s, 3H), 4.33 (dd, J = 7.6, 4.0 Hz, 1H), 4.57 (ddd, J = 8.9, 8.3, 5.2 Hz, 1H), 6.84 (d, J = 8.3 Hz, 1H), 7.21–7.24 (m, 3H), 7.27–7.30 (m, 2H); ^{13}C NMR ($CDCl_3$) δ21.8, 22.8, 24.6, 40.5, 41.3, 50.2, 52.3, 72.7, 126.9, 128.6 (x 2), 129.6 (x 2), 136.7, 172.5, 173.4; ESI-MS *m/z* 316 [M+Na$^+$]; HRMS (M$^+$) Calcd for $C_{16}H_{23}NO_4$: 293.1627. Found 293.1621. The enantiomeric excess of **96b** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 0.5 mL/min, t_R 11.9 min (minor isomer) and 13.7 min (major isomer), detection at 254 nm]; $[\alpha]_D^{26}$ –66.9° [*c* 1.06 $CHCl_3$(99% ee)].

Synthesis of D-Hpla-D-Leu Fragment (Synthetic Intermediate for Aeruginosin 298-A)

1-(4-Phenylimidazol-1-yl)-3-[4-(triisopropylsilanyloxy)phenyl]propenone (98). 1-Ethyl-3-(dimethylaminopropyl)carbodiimide hydrochloride (3.29 g, 17.2 mmol, 1.1 equiv) was added to a stirred solution of 4-hydroxycinnamic acid (2.19 g, 15.6 mmol) and 4-phenylimidazole (2.25 g, 15.6 mmol, 1.0 equiv) in DMF (62 mL, 0.25 M) at room temperature. After stirring for 12 h at the same temperature, triethylamine (3.3 mL, 23.4 mmol, 1.5 equiv) and triisopropylsilyl chloride (4.6 mL, 17.2 mmol, 1.1 equiv) were added to the reaction mixture at 4° C. After stirring for 2 h at room temperature, the reaction mixture was quenched by the addition of saturated aqueous ammonium chloride. The resulting mixture was extracted with diethyl ether (x 2). The combined organic layers were washed with saturated aqueous ammonium chloride followed by brine and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (silica gel, 10% EtOAc in hexane). The resulting yellow solid was washed with diisopropyl ether to afford imidazolide **98** (5.70 g, 82%, 2 steps) as a yellow solid. R_f= 0.34 (silica gel, EtOAc–hexane, 1:3); mp 127.5–128° C;

IR (KBr) ν 2866, 1698, 1624, 1597, 1509, 1394, 1265, 1193, 832 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08–1.15 (m, 18 H; TIPS), 1.25–1.33 (m, 3H; TIPS), 6.95 (d, *J* = 8.5 Hz, 2H; H-6, H-8), 6.95 (d, *J* = 15.5 Hz, 1H; H-2), 7.32 (t, *J* = 7.0 Hz, 1H; H-4"), 7.43 (t, *J* = 7.0 Hz, 2H; H-3", H-5"), 7.58 (d, *J* = 8.5 Hz, 2H; H-5, H-9), 7.86 (d, *J* = 7.0 Hz, 2H; H-2", H-5"), 7.91 (s, 1H; H-5'), 8.05 (d, *J* = 15.5 Hz, 1H; H-3), 8.39 (s, 1H; H-2'); ^{13}C NMR ($CDCl_3$) δ 12.7 (x 3; TIPS), 17.9 (x 6; TIPS), 111.2 (C-5'), 111.8 (C-2), 120.6 (x 2; C-6, C-8), 125.4 (x 2; C-2", C-6"), 126.7 (C-1"), 127.9 (C-4"), 128.7 (x 2; C-3", C-5"), 130.7 (x 2; C-5, C-9), 132.7 (C-4), 136.3 (C-2"), 143.6 (C-4'), 149.7 (C-3), 159.7 (C-7), 161.9 (C-1); MS [ESI (+)] *m/z* 447 ($M+H^+$); Anal. Calcd for $C_{27}H_{34}N_2O_2Si$: N 6.27, C 72.60, H 7.67; Found N 6.23, C 72.61, H 7.85.

(2*R*,3*S*)-3-[4-(Triisopropylsilanyloxy)phenyl]oxirane-2-carboperoxoic acid *tert*-butyl ester (101). A solution of La(O-*i*-Pr)$_3$ (0.2 M in THF, 5.0 mL, 1.0 mmol, 10 mol %) was added to a mixture of (*S*)-BINOL (286 mg, 1.0 mmol, 10 mol %), triphenylphosphine oxide (835 mg, 3.0 mmol, 30 mol %) and MS 4A (10 g) in dry THF (100 mL, 0.1 M) at room temperature. After stirring for 45 min at the same temperature, a solution of TBHP (5.0 M in decane, 4.8 mL, 24 mmol, 2.4 mol equiv) was added at 4 °C. After stirring for 10 min at the same temperature, imidazolide **98** (4.47 g, 10 mmol, 1.0 equiv) was added directly and the mixture was stirred at room temperature for 90 min. The reaction was quenched by the addition of 1% aqueous citric acid solution at 4 °C. The mixture was extracted with ethyl acetate (x 2) and the combined organic layers were washed with 2% aqueous sodium thiosulfate followed by brine, and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (silica gel, 5% EtOAc in hexane) to give epoxy peroxyester **101** (3.88 g, 95%) as a pale yellow oil. R_f = 0.57 (silica gel, EtOAc–hexane, 1:3); $[\alpha]_D^{25}$ –108° (*c* 1.8, $CHCl_3$, 94% ee); IR (neat) ν 2945, 2868, 1788, 1610, 1515, 1270, 1128, 1107, 911 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05–1.12 (m, 18H; TIPS), 1.22–1.30 (m, 3H; TIPS), 1.36 (s, 9H; *t*-Bu), 3.53 (d, *J* = 1.5 Hz, 1H; H-2), 4.09 (d, *J* = 1.5 Hz, 1H; H-3), 6.87 (d, *J* = 8.5 Hz, 2H; H-6, H-8), 7.14 (d, *J* = 8.5 Hz, 2H; H-5, H-9); ^{13}C NMR ($CDCl_3$) δ 12.6 (x 3; TIPS), 17.9 (x 6; TIPS), 26.1 (x 3; *t*-Bu), 54.9 (C-3), 58.2 (C-2), 84.5 (*t*-Bu), 120.2 (x 2; C-6, C-8), 126.5 (C-4), 127.1 (x 2; C-5, C-9), 157.1 (C-7), 166.0 (C-1); MS [ESI (+)] *m/z* 431 ($M+Na_+$); Anal. Calcd for $C_{22}H_{36}O_5Si$: C 64.67, H 8.88; Found C 64.40, H 8.66. The enantiomeric excess of **101** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/9, flow rate 0.5 mL/min, t_R 22.5 min (2*S*,3*R*)-isomer and 36.7 min (2*R*,3*S*)-isomer, detected at 254 nm] after conversion to the corresponding methyl amide **102**.

Synthesis of HO-D-Hpla(TIPS)-D-Leu-O-*t*-Bu (97). A solution of **106** (2.55 equiv, 1.38 mmol, 2 equiv) in THF (1.0 M, 1.4 mL) was added to **101** at room temperature. After stirring

for 24 h, 10% Pd-C (37 mg, 0.034 mmol, 5 mol %) was added to the reaction directly and argon was replaced with hydrogen (1 atm). After stirring for 24 h, the mixture was filtered thorough Cerite pad and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, 20 to 40% EtOAc in hexane) to give **97** (308 mg, 88%) as a white solid with recovery of excess amine **106** (82%). mp 108–110 °C; R_f = 0.14 (silica gel, EtOAc–hexane, 1:3); $[\alpha]_D^{24}$ +43.6° (*c* 2.1, $CHCl_3$); IR (KBr) ν 3269, 2946, 2868, 1729, 1649, 1508, 1265, 1151, 918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03–1.10 (m, 18H; TIPS), 1.20–1.28 (m, 3H; TIPS), 1.45 (s, 9H; *t*-Bu), 1.40–1.50 (m, 1H; H-4 (Leu)), 1.50–1.60 (m, 2H; H-3 (Leu)), 2.57 (br-s, 1H; OH (Hpla)), 2.87 (dd, *J* = 14.0, 7.0 Hz, 1H; H-3 (Hpla)), 3.12 (dd, *J* = 14.0, 3.5 Hz, 1H; H-3 (Hpla)), 4.28–4.30 (m, 1H; H-2 (Hpla)), 4.47 (dd, *J* = 14.0, 9.0 Hz, 1H; H-2 (Leu)), 6.81 (d, *J* = 8.5 Hz, 2H; H-6, H-8 (Hpla)), 6.84 (s, 1H; NH (Leu)), 7.08 (d, *J* = 8.5 Hz, 2 H; H-5, H-9 (Hpla)); ^{13}C NMR ($CDCl_3$) δ 12.6 (x 3; TIPS), 17.9 (x 6; TIPS), 22.0 (C-5' (Leu)), 22.8 (C-5 (Leu)), 24.8 (C-4 (Leu)), 28.0 (x 3; *t*-Bu), 39.7 (C-3 (Hpla)), 41.7 (C-3 (Leu)), 50.9 (C-2 (Leu)), 72.8 (C-2 (Hpla)), 81.9 (*t*-Bu), 120.0 (x 2; C-6, C-8 (Hpla)), 128.7 (C-4 (Hpla)), 130.5 (x 2; C-5, C-9 (Hpla)), 155.1 (C-7 (Hpla)), 172.0 (C-1 (Hpla)), 172.4 (C-1 (Leu)); MS [ESI (+)] *m/z* 530 ($M+Na^+$); Anal. Calcd for $C_{28}H_{49}NO_5Si$: N 2.76, C 66.23, H 9.73; Found N 2.75 C 65.99, H 9.69.

第 8 章

Synthesis of the β–Aryl β–Hydroxy Amides 107 and 110l-o. β–Aryl β–hydroxy amides **107** and **110l-o** were prepared according to the general procedure. For the known compound **110l**, see: *Tetrahedron* **1999**, 55, 5017. For the known compound **110n**, see: *Gazz. Chim. Ital.* **1962**, *92*, 501.

General Procedure for the β–Selective Epoxide Opening of β–Aryl-Substituted α,β–Epoxy Amides Using Red-Al and Crown Ether (Table 8-4, entry 8). To a solution of amide **30** (53.1 mg, 0.3 mmol) and 15-crown-5 (72 μL, 1.2 equiv) in dry DME (1.5 mL) was added a solution of Red-Al (105 μL, 1.2 equiv, 65% solution in toluene) at –40° C. After stirring for 1 h at the same temperature, the mixture was warmed to room temperature and stirred for 1.5 h. After complete consumption of the starting material, the solution was quenched by the addition of MeOH (0.5 mL) and diluted with ethyl acetate (10 mL). The organic layer was washed with saturated aqueous NH_4Cl, brine and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flush column chromatography (SiO_2,

hexane/ethyl acetate = 4:1 to hexane/ethyl acetate 4:1 + 5% MeOH) to give the corresponsing β–hydroxy amides **107** (46.9 mg, 87%, β–OH:α–OH = 18:1) as a white solid. The desired isomer was isolated by preparative thin-layer chromatography.

(3*R*)-3-Phenyl-3-hydroxypropionoic acid methyl amide (107). The enantiomeric excess of **107** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AS-H, *i*-PrOH/Hexane 1/2, flow rate 1.0 mL/min, t_R 15.9 min (minor) and 19.1 min (major), detection at 254 nm); $[\alpha]_D^{24}$ +26.8° (*c* 0.58, MeOH, 99% ee), lit. $[\alpha]_D^{25}$ +28.3° (*c* 1.25, MeOH, >99% ee). See: *Tetrahedron: Asymmetry* **1998**, *9*, 1637.

(3*R*)-3-(4-Fluorophenyl)-3-hydroxypropionoic acid methyl amide (110m): white solid; IR (KBr) ν 3304, 1642, 1512, 1231 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.48–2.56 (m, 2H), 2.81 (d, *J* = 5.0 Hz, 3H), 4.32 (d, *J* = 2.8Hz, 1H), 5.08 (br-d, *J* = 8.5 Hz, 1H), 5.74 (br-s, 1H), 7.01–7.05 (m, 2H), 7.31–7.35 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.2, 44.5, 70.3, 115.2 (d, *J* = 21.6 Hz) (x 2), 127.3 (d, *J* = 8.1 Hz) (x 2), 138.8, 162.2 (d, *J* = 234.8 Hz), 172.3; ESI-MS *m/z* 220 [M+Na+]; $[\alpha]_D^{23}$ +68.1° (*c* 0.71, $CHCl_3$, 99% ee).

Synthesis of the β–Alkyl β–Hydroxy Amides 112a-k. β–Alkyl β–hydroxy amides **112a-k** were prepared according to the general procedure. For the known compound **112a**, see: *J. Molecular Catalysys B* **2001**, *11*, 893.

General Procedure for the β–Selective Epoxide Opening of β–Alkyl-Substituted α,β–Epoxy Amides Using DIBAL (Table 8-7, entry 1). To a solution of amide **38a** (41.0 mg, 0.2 mmol) in dry DME (2.0 mL) was added a solution of DIBAL (220 μL, 2.2 equiv, 1 M solution in toluene) at 0° C. After stirring for 1 h at the same temperature, the solution was quenched by the addition of MeOH (0.5 mL) and diluted with ethyl acetate (10 mL). The solution was washed with saturated aqueous NH_4Cl, brine and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flush column chromatography (SiO_2, hexane/ethyl acetate = 4:1 to hexane/ethyl acetate = 4:1 + 5% MeOH) to give the corresponding β–hydroxy amides **112a** (39.1 mg, 94%, β–OH:α–OH = 22:1) as a white solid. The desired isomer was isolated by preparative thin-layer chromatography.

(3*S*)-3-Hydroxy-5-phenylpentanoic acid methyl amide (112a). The enantiomeric excess of **112a** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK OD-H, *i*-PrOH/Hexane 1/4, flow rate 0.3 mL/min, t_R 13.1 min (minor isomer), 15.1 min (major isomer), detection at 254nm); $[\alpha]_D^{23}$ +6.2° (*c* 0.90, $CHCl_3$, 99% ee).

(*3S*)-*3*-Hydroxy-5-phenylpentanoic acid benzyl amide (112c): white solid; IR (KBr) ν 3295, 2911, 1640, 1545, 1081, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72–1.75 (m, 1H), 1.80–1.87 (m, 1H), 2.33 (dd, *J* = 15.2, 8.6 Hz, 1H), 2.39 (dd, *J* = 15.2, 2.6 Hz, 1H), 2.69 (ddd, *J* = 14.0, 9.3, 7.0 Hz, 1H), 2.81 (ddd *J* = 14.0, 9.5, 5.0 Hz, 1H), 3.77 (m, 1H), 4.02 (s, 1H), 4.26 (d, *J* = 5.8 Hz, 2H), 6.09 (s, 1H), 7.16–7.34 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 31.8, 38.4, 42.4, 43.5, 67.9, 125.9, 127.6, 127.8 (x 2), 128.8(x 2), 137.8, 141.8 ,172.1; ESI-MS *m/z* 306 [M+Na^+]; $[\alpha]_D^{25}$ +7.9° (*c* 0.94, $CHCl_3$, 99% ee).

(3*S*)-Hydroxy-5-phenylpentanoic acid allyl amide (112d): white solid; IR (KBr) ν 3309, 2913, 1641, 1548, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.73–1.76 (m, 1H), 1.80–1.88 (m, 1H), 2.31 (dd, *J* = 15.3, 8.9 Hz, 1H), 2.38 (dd, *J* = 15.3, 2.8 Hz, 1H), 2.68 (ddd, *J* = 13.7, 9.1, 7.0 Hz, 1H), 2.81 (ddd, *J* = 13.7, 9.5, 5.0 Hz, 1H), 3.87 (m, 1H), 4.02 (br-s, 1H), 5.13 (d, *J* = 10.0 Hz, 1H), 5.18 (d, *J* = 17.5 Hz, 1H) 5.80 (ddt, *J* = 17.5, 10.0, 5.5 Hz, 1H), 6.08 (br-s, 1H), 7.16–7.28 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 31.7, 38.5, 41.7, 42.3, 67.9, 116.5, 125.8, 128.4 (x 2), 128.4 (x 2), 133.8, 141.7, 172.2; ESI-MS *m/z* 256 [M+Na^+], $[\alpha]_D^{23}$ +6.8° (*c* 1.10, $CHCl_3$, 98% ee).

(3*S*)-3-Hydroxy-5-phenyl-pentanoic acid cyclohexyl amide (112e): white solid; IR (KBr) ν 3322, 2939, 2855, 1637, 1542, 1453 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08–1.19 (m, 3H), 1.32–1.40 (m, 2H), 1.60–1.72 (m, 4H), 1.80–1.91 (m, 3H), 2.25 (dd, *J* = 15.1, 8.2 Hz, 1H), 2.31 (dd, *J* = 15.1, 2.8 Hz, 1H), 2.69 (ddd, *J* = 13.9, 8.2, 5.3 Hz, 1H), 2.82 (ddd, *J* = 13.9, 9.6, 4.6 Hz 1H), 3.73–3.80 (m, 1H), 4.00 (m, 2H), 5.52 (br-s, 1H), 7.17–7.30 (m 5H); ^{13}C NMR ($CDCl_3$) δ 24.8 (x 2), 25.4, 31.8, 33.1 (x 2), 38.5, 42.4, 48.2, 67.9, 125.8, 128.4 (x 2), 128.5 (x 2), 141.9, 171.4; ESI-MS *m/z* 298 [M+Na^+]; $[\alpha]_D^{25}$ +5.6° (*c* 0.86, $CHCl_3$, 99% ee).

(3*S*)-3-Hydroxy-5-phenylpentanoic acid *tert*-butyl amide (112f): yellow oil; IR (neat) ν 3317, 2966, 1645, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (s, 9H), 1.66–1.73 (m, 1H), 1.79–1.87 (m, 1H) 2.21 (dd, *J* = 15.3, 8.5 Hz, 1H), 2.26 (dd, *J* = 15.3, 3.1 Hz, 1H), 2.67 (ddd *J* = 12.8, 9.8, 7.0 Hz, 1H), 2.70 (ddd *J* = 12.8, 9.8, 5.2 Hz, 1H), 3.99 (m, 1H), 4.10 (br-s, 1H), 5.52 (br-s, 1H), 7.16–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 28.7 (x 3), 31.8, 38.4, 42.9, 51.4, 67.9, 125.8, 128.4 (x 2), 128.4 (x 2), 141.9, 171.9; ESI-MS *m/z* 272 [M+Na^+], 250 [M+H^+]; $[\alpha]_D^{23}$ +5.1° (*c* 1.14, $CHCl_3$, 99% ee).

(3*S*)-3-Hydroxy-7-phenylheptanoic acid methyl amide (112i): white solid; IR (KBr); ν 3333, 2930, 2852, 1646, 1559, 1407 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35–1.68 (m, 6H), 2.23 (dd *J* = 15.2, 9.1 Hz, 1H), 2.32 (dd *J* = 15.2, 2.5 Hz, 1H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.81 (d, *J* = 4.9 Hz, 3H), 3.72 (br-s, 1H), 3.97 (m, 1H), 5.85 (br-s,1H), 7.12–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.1, 26.1, 31.3, 35.8, 36.7, 42.2, 68.5, 125.6, 128.2 (x 2), 128.4 (x 2), 142.5, 173.0; ESI-MS *m/z* 258 [M+Na^+], 236 [M+H^+]; $[\alpha]_D^{25}$ +18.0° (*c* 0.77, $CHCl_3$, 99% ee).

(3*R*)-3-cyclohexyl-3-hydroxypropionic acid benzyl amide (112k): white solid; IR (KBr) ν 3293, 2914, 2851, 1646, 1561, 1447 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96–1.05 (m, 2H), 1.09–1.25 (m, 3H), 1.34–1.40 (m, 1H), 1.65–1.67 (m, 2H), 1.74–1.77 (m, 2H), 1.83–1.86 (m, 1H), 2.32 (dd, *J* = 15.1, 9.3 Hz, 1H), 2.39 (dd, *J* = 15.1, 2.5 Hz, 1H), 3.44 (d, *J* = 3.8 Hz, 1H), 3.76–3.79 (m, 1H), 4.45 (d, *J* = 5.5 Hz, 2H), 6.22 (s, 1H), 7.26–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 26.0, 26.1, 26.4, 28.2, 28.8, 39.7, 43.3, 43.5, 72.8, 127.5, 127.7 (x 2), 128.7 (x 2), 138.0, 172.7; ESI-MS *m/z* 284 [M+Na^+]; $[\alpha]_D^{23}$ +25.5° (*c* 0.98, $CHCl_3$, 99% ee).

第 9 章

Catalytic Asymmetric Synthesis of *Syn*- and *Anti*-3,5-Dihydroxy Esters.

For the known compound **121**, **122**, and **123**, see: *Chem. Pharm. Bull.* **1990**, *38*, 2890.

General Procedure for the Conversion of α,β-Epoxy Methyl Amides to α,β-Epoxy Methyl Ester. Martin Sulfurane (983 mg, 1.46 mmol) and **38a** (100 mg, 0.487 mmol) were combined in a grove box, and then dissolved in dry THF (4.8 mL). After being stirred for 3 h at room temperature, NaOMe (0.334 mL, 1.46 mmol, 25 wt % solution in MeOH) was added to the reaction mixture. After being stirred for 30 min, the reaction was diluted with ethyl acetate and quenched with saturated aqueous ammonium chloride. The aqueous layer was extracted with ethyl acetate (2 x 10 mL) and the combined organic layers were washed with brine, and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 20:1 to 3:1) to give **25k** [65 mg, 65% (conv. 98%)] as a pale yellow oil, with recovery of **7** (34 mg, 34%). The enantiomeric excess of **25k** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 2/98, flow rate 1.0 mL/min, t_R 8.9 min (2*R*,3*S*)-isomer and 10.3 min (2*S*,3*R*)-isomer, detection at 254 nm); $[\alpha]_D^{25}$ –39.9° (*c* 0.82, $CHCl_3$, 99% ee).

Ethyl (4*R*,5*S*)-4,5-Epoxy-3-oxo-5-phenethylpentanoate (36): See the experimental section for chapter 4.

Ethyl (5*S*)-5-Hydroxy-3-oxo-7-phenylheptanoate (123): To a stirred suspension of $NaBH_4$ (39 mg, 1.03 mmol) in EtOH (0.72 mL) was added PhSeSePh (161.4 mg, 0.517 mmol) at 0 °C, and then the mixture was stirred at room temperature. After 30 min, an EtOH solution of **36** (45.2 mg, 0.172 mmol in 1 mL of EtOH) was added slowly, and the yellow solution was stirred for 30 min. After the starting material was consumed completely, the reaction was diluted with ethyl acetate, washed with brine, and the organic layer was dried over Na_2SO_4.

After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 4:1) to give **123** (38.5 mg, 85%) as a pale yellow oil. $[\alpha]_D^{23}$ +9.35° [*c* 1.25, $CHCl_3$ (99% ee)].

Ethyl (3*S*,5*S*)-3,5-Dihydroxy-7-phenylheptanoate (121): To a stirred solution of **123** (25.2 mg, 0.095 mmol) in THF (0.6 mL) and MeOH (0.15 mL) was added $BEt_2(OMe)$ (0.104 mL, 0.104 mmol in THF solution) at –78 °C and the mixture was stirred at the same temperature. After 1 h, $NaBH_4$ (4.5 mg, 0.119 mmol) was added and the reaction was kept stirring for 3 h at –78 °C, then for 1 h at –20 °C. The reaction was quenched with water and the aqueous layer was extracted with ethyl acetate (2 x 10 mL). The combined organic layers were washed with brine, and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was azeotroped a few times with MeOH and the obtained crude residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 3:1) to give *syn*-3,5-dihydroxy ester **121** [20.0 mg, 79% isolated yield, (*syn*:*anti* = >20:1)] as a colorless oil. $[\alpha]_D^{22}$ +4.63° [*c* 0.67, $CHCl_3$ (99% ee)]. The enantiomeric excess of **121** was determined after conversion of **121** into the corresponding acetonide-protected compound **125** (dimethoxypropane, cat. TsOH, rt, 98%). Compound **125**: IR (neat) ν2991, 2940, 1737, 1496, 1455, 1380, 1199, 1167, 1028, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29–7.26 (m, 3H), 7.19–7.17 (m, 2H), 4.29–4.24 (m, 1H), 4.18–4.11 (m, 2H), 3.84–3.78 (m, 1H), 2.74 (ddd, *J* = 5.2, 9.0, 14.0 Hz, 1H), 2.65 (ddd, *J* = 8.0, 8.3, 14.0 Hz, 1H), 2.52 (dd, *J* = 6.9, 15.4 Hz, 1H), 2.36 (dd, *J* = 6.3, 15.4 Hz, 1H), 1.787–1.79 (m, 1H), 1.72–1.54 (m, 3H), 1.43 (s, 3H), 1.40 (s, 3H), 1.25 (dt, *J* = 0.6, 7.2 Hz, 3H),; ^{13}C NMR ($CDCl_3$) δ 171.0, 141.9, 128.5 (x 2), 128.3 (x 2), 125.8, 98.8, 67.6, 66.0, 60.4, 41.5, 37.8, 36.5, 31.0, 30.1, 19.7, 14.2; MS *m/z* 306 [M^+]. The enantiomeric excess of **125** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALCEL OJ-H, *i*-PrOH/hexane 1/99, flow rate 1.0 mL/min, t_R 14.4 min (3*R*,5*R*)-isomer and 17.7 min (3*S*,5*S*)-isomer, detection at 254 nm); $[\alpha]_D^{23}$ –27.4° [*c* 1.08, $CHCl_3$ (99% ee)].

Ethyl (3*R*,5*S*)-3,5-Dihydroxy-7-phenylheptanoate (122): To a stirred solution of tetramethylammonium triacetoxyborohydride (235 mg, 0.906 mmol) in anhydrous acetonitrile (0.5 mL) was added acetic acid (0.5 mL) and the mixture was stirred at room temperature for 30 min. The mixture was cooled to 0 °C, and an acetonitrile solution of **123** (40.0 mg, 0.151 mmol in 0.5 mL of acetonitrile) was added. The mixture was stirred at the same temperature for 3 h. The reaction was quenched with 0.5 N aqueous sodium potassium tartrate and the mixture was diluted with CH_2Cl_2, washed with saturated aqueous Na_2CO_3. The aqueous layer was back extracted with CH_2Cl_2 (4 x 5 mL), and the combined organic layers were washed with saturated aqueous Na_2CO_3. The aqueous layer was back extracted with CH_2Cl_2 (4 x 5 mL), and the conbined organic layers were dried with Na_2SO_4. After concentration *in vacuo*,

the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 3:1) to give a mixture of *syn*- and *anti*-3,5-dihydroxy ester **121** and **122** [36.3 mg, 89%, (*syn*:*anti* = 1:9)]. The mixture fraction was purified by preparative thin-layer chromatography and **122** was isolated as a white solid (30.0 mg, 80%). $[\alpha]_D^{21}$ –15.5° [*c* 0.89, $CHCl_3$ (99% ee)]. The enantiomeric excess of **122** was determined after conversion of **122** into the corresponding acetonide-protected compound **126** (dimethoxypropane, cat. TsOH, rt, 96%). Compound **126**: IR (neat) ν2986, 2937, 1738, 1496, 1455, 1380, 1224, 1187, 1025, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29–7.26 (m, 3H), 7.19–7.16 (m, 2H), 4.29–4.25 (m, 1H), 4.17–4.11 (m, 2H), 3.79–3.75 (m, 1H), 2.77 (ddd, *J* = 5.5, 9.5, 13.8 Hz, 1H), 2.61 (ddd, *J* = 7.2, 8.9, 13.8 Hz, 1H), 2.50 (dd, *J* = 8.3, 15.3 Hz, 1H), 2.41 (dd, *J* = 5.2, 15.3 Hz, 1H), 1.88–1.82 (m, 1H), 1.76–1.59 (m, 3H), 1.38 (s, 3H), 1.33 (s, 3H), 1.25 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 170.9, 141.9, 128.4 (x 2), 128.3 (x 2), 125.8, 100.6, 65.6, 63.5, 60.4, 40.8, 37.9, 37.4, 31.6, 24.7, 24.6, 14.2; MS *m/z* 306 [M^+]. The enantiomeric excess of **126** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALCEL OJ-H, *i*-PrOH/hexane 2/98, flow rate 1.0 mL/min, t_R 8.7 min (3*R*,5*S*)-isomer and 11.6 min (3*S*,5*R*)-isomer, detection at 254 nm); $[\alpha]_D^{22}$ +17.4° [*c* 0.70, $CHCl_3$ (99% ee)].

Catalytic Asymmetric Synthesis of 128a and 128b.

Catalytic Asymmetric Epoxidation of α,β-Unsaturated Amides 133 to 135.

1-Morpholin-4-yl-7-phenyl-hept-2-en-1-one (133): pale yellow oil; IR (neat) 2926, 2855, 1658, 1620, 1432, 1268, 1230, 1116, 975, 749, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29–7.26 (m, 2H), 7.19–7.15 (m, 3H), 6.89 (dt, *J* = 15.0, 7.0 Hz, 1H), 6.17 (d, *J* = 15.0 Hz, 1H), 3.67–3.39 (m, 8H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.25–2.21 (m, 2H), 1.68–1.62 (m, 2H), 1.54–1.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 165.6, 146.9, 142.2, 128.3 (x 2), 128.2 (x 2), 125.7, 119.5, 66.8 (x 2), 46.0, 42.2, 36.7, 32.4, 31.0, 27.8; EI-MS *m/z* 273 [M^+].

1-Morpholin-4-yl-[(*2S,3R*)-3-(4-phenyl-butyl)-oxiranyl]-methanone (135): colorless oil; IR (neat) ν 2928, 2857, 1659, 1465, 1274, 1239, 749, 701 cm^1; ^1H NMR ($CDCl_3$) δ7.29–7.26 (m, 2H), 7.19–7.16 (m, 3H), 3.69–3.56 (m, 8H), 3.33 (d, *J* = 2.1 Hz, 1H), 3.15 (ddd, *J* = 6.4, 4.6, 2.1 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.72–1.48 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 166.1, 142.1, 128.3 (x 2), 128.3 (x 2), 125.8, 66.7 (x 2), 58.2, 53.9, 45.3, 42.3, 35.7, 31.4, 31.0, 25.4; EI-MS *m/z* 289 [M^+]. The enantiomeric excess of **135** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AS-H, *i*-PrOH/hexane 1/4, flow rate 1.0 mL/min, t_R 32.3 min (2*S*,3*R*)-isomer and 58.1 min (2*R*,3*S*)-isomer, detection at 254 nm];

$[\alpha]_D^{24}$ +20.0° (*c* 0.79 $CHCl_3$, 99% ee).

Synthetic Routes towards γ,δ-Epoxy β-Keto Amide 132

Route A: via α,β–Epoxy Ester 134

(2*S*,3*R*)-3-(4-Phenyl-butyl)-oxirane-2-carboxylic acid methyl ester (134): Martin Sulfurane (1020 mg, 1.52 mmol) and **38i** (100 mg, 0.487 mmol) were combined in a grove box, and then dissolved in dry THF (5 mL). After being stirred for 3 h at room temperature, NaOMe (0.347 mL, 1.52 mmol, 25 wt % solution in MeOH) was added to the reaction mixture. After being stirred for 30 min, the reaction was diluted with ethyl acetate and quenched with saturated aqueous ammonium chloride. The aqueous layer was extracted with ethyl acetate (2 x 10 mL) and the combined organic layers were washed with brine, and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 20:1 to 3:1) to give **134** [84.3 mg, 71% (conv. 97%)] as a pale yellow oil, with recovery of **38i** (31.7 mg, 27%). IR (neat) ν 3025, 2935, 2858, 1755, 1453, 1291, 1250, 1030, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34 (m, 2H), 7.24 (m, 3H), 3.84 (s, 3H), 3.29 (d, *J* = 2 Hz, 1H), 3.22 (ddd, *J* = 6, 5, 2 Hz, 1H), 2.69 (t, *J* = 7.5 Hz, 2H), 1.78-1.55 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 169.7, 142.1, 128.34 (x 2), 128.29 (x 2), 125.8, 58.4, 52.9, 52.4, 35.7, 31.3, 31.0, 25.3; EI-MS *m/z* 234 [M^+]. The enantiomeric excess of **15** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 1/99, flow rate 1.0 mL/min, t_R 12.1 min (2*R*,3*S*)-isomer and 14.0 min (2*S*,3*R*)-isomer, detection at 254 nm]; $[\alpha]_D^{24}$ +24.6° (*c* 1.68, $CHCl_3$, 99% ee). The absolute stereochemistry was determined by Mosher's method after conversion to the corresponding β-hydroxy ester. Detailed data are referred in the Suporting Information of the following report: Tosaki, S.; Nemoto, T.; Ohshima, T.; Shibasaki, M. *Org. Lett.* **2003**, *5*, 495.

γ,δ-Epoxy β-keto amide (132): To a stirred solution of *N*-methoxy-*N*-methylacetoamide (0.361 mL, 3.40 mmol) in THF (14 mL) was added LHMDS (3.20 mL, 3.20 mmol, 1.0 M solution in THF) at –78 °C. After being stirred for 20 min, a THF solution of **134** (398 mg, 1.70 mmol in 7 mL of THF) was added to the reaction mixture at the same temperature. The reaction was slowly warmed to –30 °C over a period of 2 h. The reaction was quenched with saturated aqueous ammonium chloride. The aqueous layer was extracted with ethyl acetate (2 x 10 mL) and the combined organic layers were washed with brine, and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 3:1) to give **132** (464 mg, 89%) as a pale yellow oil. IR (neat) ν 2936, 2858, 1724, 1643, 1454, 1359, 1185, 1009, 749, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.27 (m, 2H),

7.17 (m, 3H), 3.66 (s, 3H), 3.59 (d, J = 16 Hz, 1H), 3.41 (d, J = 16 Hz, 1H), 3.30 (d, J = 1.5 Hz, 1H), 3.20 (s, 3H), 3.15 (m, 1H), 2.62 (t, J = 7.5 Hz, 2H) 1.74–1.46 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 200.9, 167.6, 142.0, 128.34 (x 2), 128.29 (x 2), 125.8, 61.3, 59.6, 58.1, 42.3, 35.6, 32.1, 31.6, 30.9, 25.3; EI-MS *m/z* 305 [M^+]; $[\alpha]_D^{26}$ –21.1° (*c* 0.87, $CHCl_3$, 99% ee).

Route B: via α,β–Epoxy Amide 135

γ,δ-Epoxy β-keto amide (132): To a stirred solution of *N*-methoxy-*N*-methylacetoamide (28 μL, 0.263 mmol) in THF (0.75 mL) was added LHMDS (0.25 mL, 0.25 mmol, 1.0 M solution in THF) at –78 °C. After being stirred for 20 min, a THF solution of **135** (30.5 mg, 0.105 mmol in 0.4 mL of THF) was added to the reaction mixture at the same temperature. The reaction was slowly warmed to –50 °C over a period of 1 h and stirred for 70 h. The reaction was quenched with saturated aqueous ammonium chloride. The aqueous layer was extracted with ethyl acetate (2 x 5 mL) and the combined organic layers were washed with brine, and dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 3:1) to give **132** [19.3 mg, 60% (conv. 85%)] as a pale yellow oil, with recovery of **135** (8.7 mg, 29%).

Total Synthesis of 128a and 128b.

δ-Hydroxy β-keto amide (136): To a stirred suspension of $NaBH_4$ (227mg, 6.00 mmol) in EtOH (5 mL) was added PhSeSePh (936 mg, 3.00 mmol) at 0 °C. The reaction was allowed to warm to room temperature, and then stirred for 20 min. An EtOH solution of **132** (305 mg, 1.00 mmol in 3 mL of EtOH) was added to the reaction mixture. After being stirred for 10 min, the reaction was diluted with ethyl acetate and poured into water. The aqueous layer was extracted with ethyl acetate (2 x 10 mL) and the combined organic layers were washed with brine, and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 1:2) to give the corresponding δ-hydroxy β-keto amide **136** (259 mg, 84%) as a pale yellow oil. IR (neat) ν3429, 2934, 1715, 1650, 1454, 1194, 749, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.28 (m, 2H), 7.18 (m, 3H), 4.08 (m, 1H), 3.68 (s, 3H) 3.61 (s, 2H), 3.22 (s, 3H), 2.72–2.62 (m, 4H), 1.68–1.39 (m, 6H); ^{13}C NMR ($CDCl_3$): δ204.8, 167.8, 142.5, 128.3 (x 2), 128.2 (x 2), 125.6, 67.5, 61.4, 49.8, 48.2, 36.3, 35.8, 32.0, 31.3, 25.1; EI-MS *m/z* 307 [M^+]; $[\alpha]_D^{27}$ –18.8° (*c* 1.21, $CHCl_3$, 99% ee)

Benzyliden acetal of β,δ-hydroxy amide (138b): To a stirred solution of δ-hydroxy β-keto amide **136** (69.1 mg, 0.225 mmol) in THF (1.3 mL) and MeOH (0.44 mL) was added $BEt_2(OMe)$ (0.45 mL, 0.45 mmol, 1.0 M solution in THF) at –78 °C. After being stirred for 15

min, $NaBH_4$ (30 mg, 0.79 mmol) was added and stirred for 5 h at the same temperature. The reaction was quenched with water and the aqueous layer was extracted with ethyl acetate (2 x 10 mL). The combined organic layers were washed with brine, and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was azeotroped a few times with MeOH to give crude diol **137**. To a solution of the crude **137** in toluene (1.0 mL) was added benzaldehyde dimethyl acetal (0.084 mL, 0.563 mmol) and PPTS (2.8 mg, 0.011 mmol) at room temperature, and then the mixture was allowed to reflux. After being stirred for 10 h, the reaction was diluted with ether and poured into saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ether (2 x 5 mL) and the combined organic layers were washed with brine, and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 5:1) to give **138b** (66.2 mg, 74% in 2 steps) as a yellow oil. IR (neat) ν2936, 2857, 1661, 1454, 1343, 1120, 1026, 752, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.48 (m, 2H), 7.36–7.27 (m, 5H), 7.18 (m, 3H), 5.56 (s, 1H), 4.38 (m, 1H), 3.85 (m, 1H) 3.68 (s, 3H), 3.20 (s, 3H), 2.98 (dd, J = 17.5, 5.5 Hz, 1H) 2.63 (t, J = 7.5 Hz, 2H), 2.55 (dd, J = 17.5, 6 Hz, 1H), 1.81–1.40 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 171.4, 142.6, 138.7, 128.5 (x 2), 128.4 (x 2), 128.2 (x 2), 128.1 (x 2), 126.1, 125.6, 100.6, 76.6, 73.5, 61.4, 38.2, 37.0, 35.8, 35.7, 32.0, 31.4, 24.7; EI-MS *m/z* 397 [M^+]. The enantiomeric excess of **138b** was determined by chiral stationary-phase HPLC analysis (DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 1/9, flow rate 1.0 mL/min, t_R 7.9 min (3*S*, 5*S*)-isomer and 10.0 min (3*R*, 5*R*)-isomer, detection at 254 nm); $[\alpha]_D^{27}$ +21.8° (*c* 0.92, $CHCl_3$, 99% ee).

Homoallylketone (131b): To a stirred solution of **138b** (77.9 mg, 0.196 mmol) in THF (1.6 mL) was added allylmagnesium bromide (0.39 mL, 0.39 mmol, 1M solution in Et_2O) at 0 °C. After being stirred for 30 min at the same temperature, the reaction was quenched with saturated aqueous ammonium chloride. The aqueous layer was extracted with ethyl acetate (2 x 4 mL) and the combined organic layers were washed with brine, and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 20:1) to give **131b** (64.2 mg, 87%) as a colorless oil. IR (neat) ν2934, 2857, 1715, 1454, 1346, 1128, 1026, 921, 752, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45 (m, 2H), 7.37–7.29 (m, 5H), 7.18 (m, 3H), 5.92 (ddt, 17.5, 10.5, 7 Hz, 1H), 5.53 (s, 1H), 5.20 (dd, J =10.5, 1.5 Hz, 1H), 5.14 (dd, J = 17.5, 1.5 Hz, 1H), 4.32 (m, 1H), 3.83 (m, 1H), 3.24 (ddd, J = 7, 1.5, 1.5 Hz, 2H), 2.89 (dd, J = 16, 6.5 Hz, 1H), 2.63 (t, J = 7.5 Hz, 2H), 2.57 (dd, J = 16, 6 Hz, 1H), 1.72–1.35 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 206.4, 142.5, 138.5, 130.1, 128.6 (x 2), 128.4 (x 2), 128.2 (x 2), 128.1 (x 2), 126.0, 125.6, 119.1, 100.5, 76.6, 73.0, 48.8, 48.2, 36,7, 35.8, 35.6, 31.4, 24.6; MS *m/z* 378 [M^+]; $[\alpha]_D^{30}$ –2.1° (*c* 1.36, $CHCl_3$, 99% ee)

Homoallylalcohol (139b): To a stirred solution of **131b** (22.2 mg, 0.0586 mmol) in THF (0.6

mL) was added L-Selectride (0.117 mL, 0.117 mmol, 1.0 M solution in THF) at −100 °C. After being stirred for 2 h at the same temperature, the reaction was quenched with H_2O_2 (30 wt. % solution in water) and 1 M NaOH. The mixture was allowed to warm to room temperature and diluted with ether. The aqueous layer was extracted with ether (2 x 3 mL) and the combined organic layers were washed with 2% aqueous $Na_2S_2O_3$, brine, and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 10:1) to give **139b** [13.3 mg, 60%, conv. 97%, inseparable mixture of *syn* and *anti* diastereomers (7:1)] as a colorless oil.

IR (neat) ν3522, 2935,2857, 1454, 1342, 1104, 1026, 914, 752, 698 cm^{-1}; ^1H NMR ($CDCl_3$) *syn* : δ 7.46 (m, 2H), 7.36–7.27 (m, 5H), 7.18 (m, 3H), 5.84 (ddt, J = 17.5, 10.5, 7 Hz), 5.55 (s, 1H), 5.12 (m, 2H), 4.08 (m, 1H), 3.97 (m, 1H), 3.82 (m, 1H), 2.63 (t, J = 7.5 Hz, 2H), 2.26 (m, 2H), 1.80–1.43 (m, 10H); ^{13}C NMR ($CDCl_3$) *syn* : δ 142.5, 138.3, 134.7, 128.7 (x 2), 128.4 (x 2), 128.3 (x 2), 128.2 (x 2), 126.0, 125.6, 117.6, 100.6, 77.3, 76.8, 70.4, 42.0, 37.1, 35.8, 35.6, 31.4, 24.6; MS *m/z* 380 [M^+]; $[\alpha]_D^{23}$ −0.93° (*c* 1.40, $CHCl_3$, 99% ee, 7:1 mixture of *syn* and *anti* diastereomers)

Acryloyl ester (140): To a stirred solution of **139b** (21.1mg, 0.0554 mmol) in CH_2Cl_2 (0.55 mL) was added acryloyl chloride (9.0 μL, 0.11 mmol) and *i*-Pr_2NEt (20 mL, 0.115 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was diluted with ether and poured into saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ether and the combined organic layers were washed with brine, and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 25:1) to give **140** (21.8 mg, 91%, inseparable mixture of *syn* and *anti* diastereomers) as a colorless oil. IR (neat) ν2934, 2857, 1721, 1404, 1194, 1026, 699 cm^{-1}; ^1H NMR ($CDCl_3$) *syn*-isomer: δ 7.40 (m, 2H), 7.28–7.18 (m, 5H), 7.10 (m, 3H), 6.30 (dd, J = 17.5, 1.5 Hz, 1H), 6.01 (dd, J = 17.5, 10.5 Hz, 1H), 5.73 (dd, J = 10.5, 1.5 Hz, 1H), 5.70 (ddt, J = 17.5, 10.5, 7 Hz, 1H), 5.40 (s, 1H), 5.14 (m, 1H), 5.02 (m, 2H), 3.83 (m, 1H), 3.70 (m, 1H), 2.55 (t, J = 7.5 Hz, 2H), 2.00 (m, 1H), 1.70 (m, 1H), 1.63–1.29 (m, 8H); ^{13}C NMR ($CDCl_3$) *syn*-isomer: δ 165.7, 142.6, 138.7, 133.2, 130.7, 128.6 (x 2), 128.5, 128.4 (x 2), 128.2 (x 2), 128.1 (x 2), 126.1, 125.6, 118.2, 100.6, 76.6, 74.0, 70.4, 39.8, 38.9, 36.8, 35.8, 35.7, 31.4, 24.7; MS *m/z* 434 [M^+]; $[\alpha]_D^{23}$ +4.6° (*c* 1.09, $CHCl_3$, 99% ee, mixture of *syn* and *anti* diastereomers)

α,β-Unsaturated lactone (141): 140 (19.9 mg, 0.0458 mmol) was dissolved in 6.5 mL of CH_2Cl_2. After degassing, Grubbs's catalyst (1.5 mg, 1.8 μmol) was added to the mixture at room temperature. The reaction was allowed to reflux for 9 h. After the solvent being removed, the obtained residue was purified by flash column chromatography (SiO_2,

hexane/ethyl acetate 4:1) to give **141** (15.7 mg, 84%, separable mixture of *syn* and *anti* diastereomers) as a colorless oil. *Syn*-isomer (**141β**): IR (neat) ν 2929, 2857, 1730, 1245, 1119, 1026, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.46 (m, 2H), 7.38–7.24 (m, 5H), 7.18 (m, 3H), 6.90 (m, 1H), 6.04 (dd, *J* = 10.0, 1.5 Hz, 1H), 5.52 (s, 1H), 4.68 (m, 1H), 4.16 (m, 1H), 3.83 (m, 1H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.55–2.39 (m, 2H), 2.22 (m, 1H), 1.92 (m, 1H), 1.73–1.43 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 164.3, 145.3, 142.5, 138.6, 128.6 (x 2), 128.4 (x 2), 128.2 (x 2), 128.1 (x 2), 126.0, 125.6, 121.2, 100.5, 77.2, 74.6, 72.5, 40.3, 36.5, 35.8, 35.7, 31.4, 29.3, 24.7; MS *m/z* 406 [M^+]; $[\alpha]_D^{27}$ -47.6° (*c* 1.21, $CHCl_3$, 99% ee).

Natural Products 128a and 128b: 141β (9.0 mg, 0.022 mmol) was dissolved in 0.5 mL of an 80 % solution of AcOH and the solution was heated to 60 °C. After being stirred for 5 h, the reaction was diluted with ethyl acetate and then poured into saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, and then dried over Na_2SO_4. After concentration *in vacuo*, crude diol was obtained. To a stirred solution of the crude diol in CH_2Cl_2 (0.2 mL) was added triethyl orthoacetate (10 μL, 0.055 mmol) and PPTS (0.5 mg, 2 μmol) at room temperature. After the reaction being stirred until all of the starting material was consumed (1 h), water (1 μL) was added to the reaction and the mixture was stirred for 1 h. The reaction mixture was directly purified by flash column chromatography (SiO_2, hexane/ethyl acetate 1:1) to give **128a** and **128b** (6.0 mg, 76% in 2 steps) as a yellow oil. IR (neat) ν 3453, 2933, 1730, 1375, 1246, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) **128a**: δ 7.27 (m, 2H), 7.18 (m, 3H), 6.89 (m, 1H), 6.02 (d, *J* = 9.5 Hz, 1H), 4.95 (m, 1H), 4.65 (m, 1H), 3.89 (m, 1H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.41 (m, 2H), 2.20–1.31 (m, 10H), 2.04 (s, 3H); ^1H NMR ($CDCl_3$) **128b**: δ 7.27 (m, 2H), 7.18 (m, 3H), 6.89 (m, 1H), 6.02 (d, *J* = 9.5 Hz, 1H), 5.23 (m, 1H), 4.51 (m, 1H), 3.70 (m, 1H), 2.62 (t, *J* = 7.5 Hz, 2H), 2.42–2.22 (m, 2H), 2.20–1.31 (m, 10H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$) **128a**: δ 171.3, 163.8, 145.2, 142.3, 128.4 (x 2), 128.3 (x 2), 125.7, 121.3, 76.7, 72.4, 67.1, 42.3, 41.7, 35.7, 34.6, 31.1, 29.4, 24.8, 21.3; ^{13}C NMR ($CDCl_3$) **128b**: 171.3, 163.8, 144.7, 142.3, 128.4 (x 2), 128.3 (x 2), 125.7, 121.4, 75.1, 69.2, 69.0, 41.7, 39.3, 37.7, 35.8, 31.3, 29.2, 25.0, 21.3; MS *m/z* 360 [M^+]; $[\alpha]_D^{26}$ –29.7° (*c* 0.60, MeOH, 99% ee, mixture of synthetic **128a** and **128b**) ; lit. $[\alpha]_D$ +35° (*c* 0.05, MeOH) for **128a** and $[\alpha]_D$ +35° (*c* 0.05, MeOH) for **128b**.

Diacetate (142): To a stirred solution of a mixture of **128a** and **128b** (2.4 mg, 6.7 μmol) in pyridine (0.1 mL) was added Ac_2O (2.5 μL, 0.027 mmol) and catalytic amount of DMAP. After being stirred for 30 min, the reaction mixture was diluted with ethyl acetate and the solution was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with 1N HCl, brine, and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by preparative thin-

layer chromatography (SiO_2, hexane/ethyl acetate 1:2) to give **142** (2.4 mg, 89%) as a yellow oil. IR (neat) ν2931, 1730, 1372, 1240, 1038 cm^{-1}; ^1H NMR ($CDCl_3$) δ7.27 (m, 2H), 7.18 (m, 3H), 6.88 (m, 1H), 6.01 (dd, *J* = 9.75, 2 Hz, 1H), 5.04 (m, 1H), 4.93 (m, 1H), 4.48 (m, 1H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.45–2.27 (m, 2H), 2.06 (s, 3H), 2.04 (s, 3H), 2.16–1.78 (m, 4H), 1.62 (m, 4H), 1.34 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 170.8, 170.7, 163.8, 144.7, 142.3, 128.4 (x 2), 128.3 (x 2), 125.7, 121.4, 74.9, 70.8, 67.9, 39.03, 38.98, 35.7, 34.1, 31.1, 29.1, 24.7, 21.2, 21.2; MS *m/z* 402 [M^+].

In confirmation of the stereochemistry, minor isomer (**141α**) was also converted to the corresponding diacetate by the same procedure.

141α: IR (neat) ν2930, 2857, 1724, 1248, 1120, 1026, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ7.46 (m, 2H), 7.37–7.27 (m, 5H), 7.19 (m, 3H), 6.88 (ddd, *J* = 10, 5.5, 3 Hz, 1H), 6.03 (dd, *J* = 10, 1.5 Hz, 1H), 5.50 (s, 1H), 4.80 (m, 1H), 4.23 (m, 1H), 3.82 (m, 1H), 2.63 (t, *J* = 7.5 Hz, 2H), 2.36 (m, 2H), 1.94 (m, 1H), 1.86 (m, 1H), 1.73–1.37 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 164.4, 145.1, 142.6, 138.7, 128.6 (x 2), 128.4 (x 2), 128.3 (x 2), 128.2 (x 2), 126.1, 125.6, 121.4, 100.4, 76.7, 74.0, 72.0, 41.6, 37.2, 35.8, 35.7, 31.4, 30.0, 24.7; MS *m/z* 406 [M^+]; $[\alpha]_D^{27}$ –2.1° (*c* 0.28, $CHCl_3$, 99% ee)

***syn, anti*-Diastereomer of 142**: IR (neat) ν2931, 1731, 1373, 1240, 1023 cm^{-1}; ^1H NMR ($CDCl_3$) δ7.27 (m, 2H), 7.19 (m, 3H), 6.85 (ddd, *J* = 10, 5.5, 3 Hz, 1H), 6.02 (dd, *J* = 10, 1.5 Hz, 1H), 5.14 (m, 1H), 4.92 (m, 1H), 4.48 (m, 1H), 2.60 (t, *J* = 7.5 Hz, 2H), 2.35–2.31 (m, 2H), 2.10–1.78 (m, 4H), 2.04 (s, 3H), 2.04 (s, 3H), 1.60 (m, 4H), 1.32 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 170.8, 170.3, 163.6, 144.5, 142.3, 128.4 (x 2), 128.3 (x 2), 125.7, 121.6, 74.5, 70.7, 68.0, 39.4, 38.8, 35.7, 34.0, 31.1, 29.6, 24.7, 21.22, 21.18 ; MS *m/z* 402 [M^+].

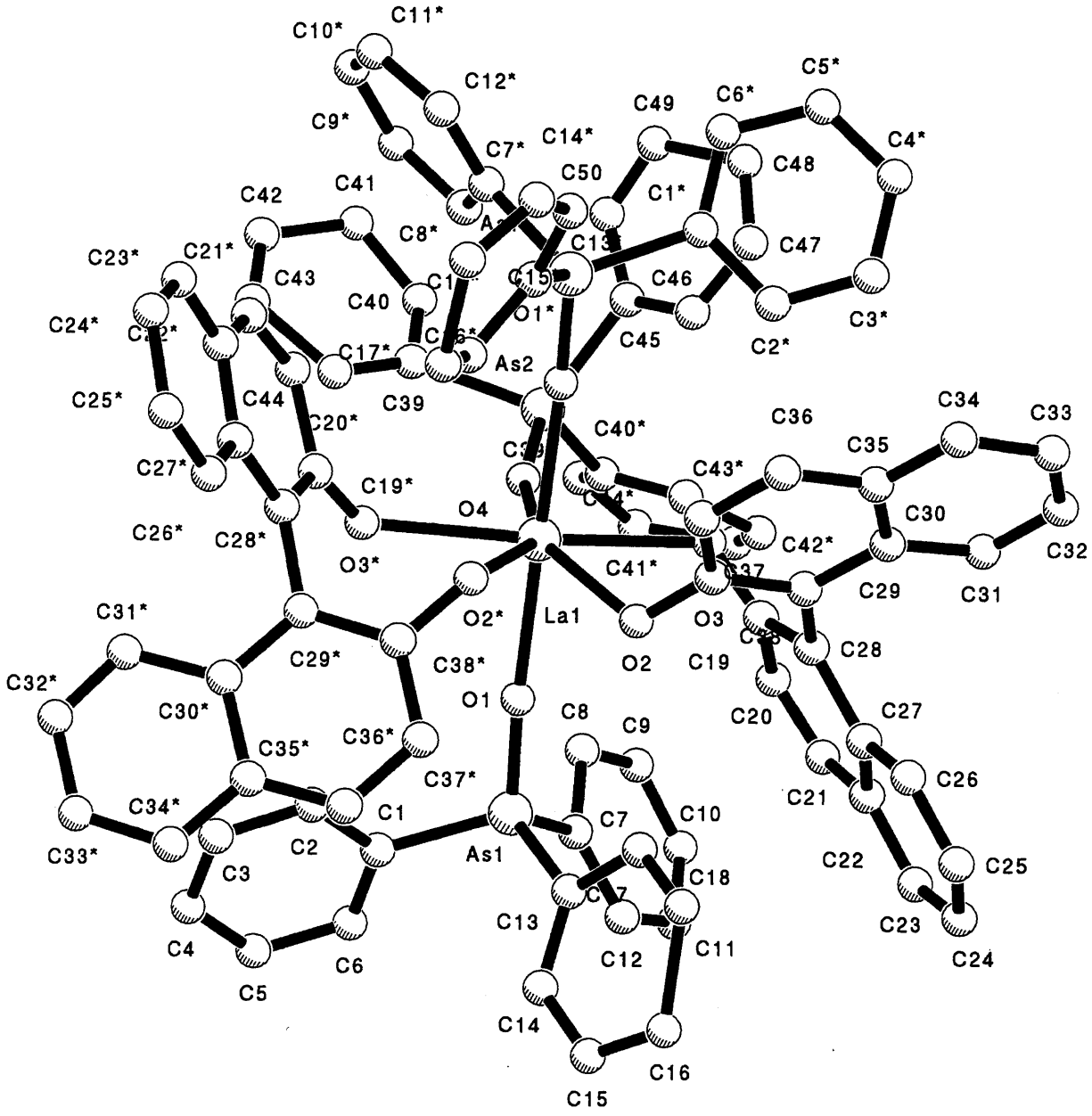
Catalytic Asymmetric Synthesis of the Intermediate for Use in Aimi's Total Synthesis of Strictifolione 129.

2-([4*R*,6*S*]-2,2-Dimethyl-6-phenethyl-[1,3]dioxan-4-yl)-ethanol (143): To a stirred solution of **2** (22.8 mg, 0.086 mmol) in dimethoxypropane (0.6 mL) was added TsOH (1.6 mg, 0.008 mmol) at room temperature. After 2 h, the reaction was diluted with ethyl acetate (10 mL). The solution was washed with saturated aqueous $NaHCO_3$ and brine, and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 30:1) to give the corresponding acetonide-

protected compound (25.2 mg, 96%). To a suspension of lithium aluminum hydride (6.6 mg, 0.175 mmol) in THF (0.3 mL) was added a THF solution of the acetonide-protected compound (22.4 mg, 0.073 mmol in 0.7 mL of THF) at 0 °C. After being stirred for 1 h, the reaction was quenched with excess MeOH, and diluted with ethyl acetate. The mixture was washed with 0.1N aqueous HCl, saturated aqueous $NaHCO_3$, brine, and then dried over Na_2SO_4. After concentration *in vacuo*, the residue was purified by flash column chromatography (SiO_2, hexane/ethyl acetate 2:1) to give alcohol **143** as a colorless oil (18.6 mg, 96%). $[\alpha]_D^{23}$ +23.1° (*c* 1.07, $CHCl_3$, 99% ee). lit. (ref. 124b); $[\alpha]_D^{25}$ +24.9° (*c* 1.70, $CHCl_3$).

X-ray Data for 12

Structure of **12**



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Refinement using reflections with F^2^ > 3.0 sigma(F^2^). The weighted R-factor
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O(5)	O	-0.738(2)	-0.184(2)	-0.8208(9)	0.34(1)	Uani 1.00 d . . .
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C(4)	C	-0.1122(6)	0.2983(5)	-1.0420(3)	0.059(2)	Uani 1.00 d . . .
C(5)	C	-0.0529(7)	0.3640(6)	-1.0112(4)	0.068(3)	Uani 1.00 d . . .
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C(7)	C	-0.0246(5)	0.3198(6)	-0.8346(3)	0.058(2)	Uani 1.00 d . . .
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C(9)	C	0.0983(8)	0.3208(9)	-0.7944(5)	0.106(4)	Uani 1.00 d . . .
C(10)	C	0.1283(8)	0.4039(9)	-0.7773(4)	0.095(4)	Uani 1.00 d . . .
C(11)	C	0.0799(9)	0.4444(8)	-0.7885(4)	0.103(4)	Uani 1.00 d . . .
C(12)	C	0.0031(8)	0.4041(6)	-0.8172(4)	0.086(3)	Uani 1.00 d . . .
C(13)	C	-0.2096(5)	0.2967(6)	-0.8467(3)	0.053(2)	Uani 1.00 d . . .
C(14)	C	-0.2059(10)	0.3701(9)	-0.8691(4)	0.159(4)	Uani 1.00 d . . .
C(15)	C	-0.248(1)	0.413(1)	-0.8517(6)	0.216(5)	Uani 1.00 d . . .
C(16)	C	-0.302(1)	0.380(1)	-0.8122(6)	0.227(5)	Uani 1.00 d . . .
C(17)	C	-0.3298(7)	0.2766(9)	-0.7927(4)	0.100(4)	Uani 1.00 d . . .
C(18)	C	-0.2697(6)	0.2505(6)	-0.8082(3)	0.063(2)	Uani 1.00 d . . .
C(19)	C	-0.2102(5)	0.1048(6)	-0.7240(3)	0.051(2)	Uani 1.00 d . . .
C(20)	C	-0.1255(5)	0.1861(7)	-0.7208(3)	0.063(2)	Uani 1.00 d . . .
C(21)	C	-0.1183(7)	0.2567(7)	-0.7021(3)	0.073(3)	Uani 1.00 d . . .
C(22)	C	-0.1888(6)	0.2659(6)	-0.6846(3)	0.061(2)	Uani 1.00 d . . .
C(23)	C	-0.1786(9)	0.3454(7)	-0.6674(4)	0.089(3)	Uani 1.00 d . . .
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C(25)	C	-0.3322(9)	0.2755(7)	-0.6493(4)	0.094(4)	Uani 1.00 d . . .
C(26)	C	-0.3443(6)	0.1983(6)	-0.6667(3)	0.064(2)	Uani 1.00 d . . .
C(27)	C	-0.2710(6)	0.1914(5)	-0.6839(3)	0.056(2)	Uani 1.00 d . . .
C(28)	C	-0.2813(5)	0.1079(6)	-0.7029(3)	0.049(2)	Uani 1.00 d . . .
C(29)	C	-0.3718(5)	0.0274(4)	-0.7040(3)	0.044(2)	Uani 1.00 d . . .
C(30)	C	-0.4100(5)	0.0000(5)	-0.6667(3)	0.047(2)	Uani 1.00 d S . .
C(31)	C	-0.3812(6)	0.0165(5)	-0.6104(3)	0.059(2)	Uani 1.00 d . . .
C(32)	C	-0.4270(7)	-0.0248(6)	-0.5694(3)	0.073(3)	Uani 1.00 d . . .
C(33)	C	-0.5094(7)	-0.0992(7)	-0.5724(4)	0.079(3)	Uani 1.00 d . . .
C(34)	C	-0.5461(6)	-0.1336(5)	-0.6185(3)	0.065(2)	Uani 1.00 d . . .
C(35)	C	-0.5030(5)	-0.0937(5)	-0.6632(3)	0.054(2)	Uani 1.00 d . . .
C(36)	C	-0.5365(5)	-0.1260(5)	-0.7102(3)	0.052(2)	Uani 1.00 d . . .

C(37)	C	-0.4931(5)	-0.0847(5)	-0.7532(3)	0.053(2)	Uani 1.00 d . . .
C(38)	C	-0.4099(5)	-0.0067(5)	-0.7510(3)	0.043(2)	Uani 1.00 d . . .
C(39)	C	-0.0066(5)	-0.0694(6)	-0.8788(3)	0.058(2)	Uani 1.00 d . . .
C(40)	C	0.0456(8)	-0.0994(8)	-0.8687(5)	0.114(3)	Uani 1.00 d . . .
C(41)	C	0.044(1)	-0.171(1)	-0.8950(8)	0.223(7)	Uani 1.00 d . . .
C(42)	C	0.0017(9)	-0.187(1)	-0.9464(6)	0.142(5)	Uani 1.00 d . . .
C(43)	C	-0.0460(9)	-0.1521(7)	-0.9569(4)	0.092(4)	Uani 1.00 d . . .
C(44)	C	-0.0542(8)	-0.0884(8)	-0.9200(5)	0.102(4)	Uani 1.00 d . . .
C(45)	C	-0.0824(7)	-0.1190(8)	-0.7636(5)	0.032(3)	Uani 0.50 d P . .
C(46)	C	-0.1494(7)	-0.1241(9)	-0.7318(4)	0.032(3)	Uani 0.50 d P . .
C(47)	C	-0.175(1)	-0.182(1)	-0.6965(7)	0.062(5)	Uani 0.50 d P . .
C(48)	C	-0.152(2)	-0.236(2)	-0.6928(9)	0.109(8)	Uani 0.50 d P . .
C(49)	C	-0.096(2)	-0.245(2)	-0.738(1)	0.128(10)	Uani 0.50 d P . .
C(50)	C	-0.072(2)	-0.182(2)	-0.7671(10)	0.113(9)	Uani 0.50 d P . .
C(51)	C	-0.781(2)	-0.123(2)	-0.8226(7)	0.211(9)	Uani 1.00 d . . .
C(52)	C	-0.741(2)	-0.100(2)	-0.7897(8)	0.31(1)	Uani 1.00 d . . .
C(53)	C	-0.765(2)	-0.149(2)	-0.7547(7)	0.31(1)	Uani 1.00 d . . .
C(54)	C	-0.811(2)	-0.231(2)	-0.7812(8)	0.35(1)	Uani 1.00 d . . .
H(1)	H	-0.2260	0.1528	-0.9559	0.0606	Uiso 1.00 calc . . .
H(2)	H	-0.2251	0.1779	-1.0432	0.0678	Uiso 1.00 calc . . .
H(3)	H	-0.1065	0.3059	-1.0774	0.0699	Uiso 1.00 calc . . .
H(4)	H	-0.0096	0.4180	-1.0258	0.0816	Uiso 1.00 calc . . .
H(5)	H	-0.0122	0.3988	-0.9378	0.0558	Uiso 1.00 calc . . .
H(6)	H	0.0000	0.2152	-0.8333	0.0976	Uiso 1.00 calc S . .
H(7)	H	0.1318	0.2935	-0.7868	0.1285	Uiso 1.00 calc . . .
H(8)	H	0.1811	0.4344	-0.7585	0.1141	Uiso 1.00 calc . . .
H(9)	H	0.0998	0.5024	-0.7763	0.1216	Uiso 1.00 calc . . .
H(10)	H	-0.0300	0.4329	-0.8240	0.1038	Uiso 1.00 calc . . .
H(11)	H	-0.1721	0.3919	-0.8992	0.1910	Uiso 1.00 calc . . .
H(12)	H	-0.2410	0.4640	-0.8679	0.2602	Uiso 1.00 calc . . .
H(13)	H	-0.3222	0.4151	-0.7948	0.2703	Uiso 1.00 calc . . .
H(14)	H	-0.3815	0.2401	-0.7737	0.1212	Uiso 1.00 calc . . .
H(15)	H	-0.2697	0.2013	-0.7923	0.0760	Uiso 1.00 calc . . .
H(16)	H	-0.0740	0.1867	-0.7330	0.0760	Uiso 1.00 calc . . .
H(17)	H	-0.0608	0.3065	-0.6999	0.0885	Uiso 1.00 calc . . .
H(18)	H	-0.1214	0.3970	-0.6678	0.1067	Uiso 1.00 calc . . .
H(19)	H	-0.2397	0.4060	-0.6378	0.1248	Uiso 1.00 calc . . .
H(20)	H	-0.3825	0.2792	-0.6367	0.1149	Uiso 1.00 calc . . .
H(21)	H	-0.4019	0.1475	-0.6677	0.0766	Uiso 1.00 calc . . .
H(22)	H	-0.3245	0.0666	-0.6071	0.0704	Uiso 1.00 calc . . .
H(23)	H	-0.4027	-0.0022	-0.5372	0.0869	Uiso 1.00 calc . . .
H(24)	H	-0.5403	-0.1263	-0.5421	0.0943	Uiso 1.00 calc . . .
H(25)	H	-0.6023	-0.1859	-0.6198	0.0782	Uiso 1.00 calc . . .

H(26)	H	-0.5919	-0.1790	-0.7127	0.0628	Uiso 1.00 calc . . .
H(27)	H	-0.5191	-0.1079	-0.7853	0.0638	Uiso 1.00 calc . . .
H(28)	H	0.0871	-0.0724	-0.8423	0.1348	Uiso 1.00 calc . . .
H(29)	H	0.0669	-0.2043	-0.8814	0.2674	Uiso 1.00 calc . . .
H(30)	H	0.0087	-0.2244	-0.9695	0.1696	Uiso 1.00 calc . . .
H(31)	H	-0.0761	-0.1654	-0.9884	0.1110	Uiso 1.00 calc . . .
H(32)	H	-0.0908	-0.0637	-0.9267	0.1205	Uiso 1.00 calc . . .
H(33)	H	-0.1733	-0.0871	-0.7364	0.0391	Uiso 0.50 calc P . .
H(34)	H	-0.2161	-0.1826	-0.6730	0.0733	Uiso 0.50 calc P . .
H(35)	H	-0.1625	-0.2729	-0.6627	0.1100	Uiso 0.50 calc P . .
H(36)	H	-0.0788	-0.2893	-0.7385	0.1219	Uiso 0.50 calc P . .
H(37)	H	-0.0485	-0.1930	-0.7966	0.1159	Uiso 0.50 calc P . .

loop_
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_atom_site_aniso_U_22
_atom_site_aniso_U_33
_atom_site_aniso_U_12
_atom_site_aniso_U_13
_atom_site_aniso_U_23

La(1)	0.0284(2)	0.0361(3)	0.0394(2)	0.0181	0.0021(1)	0.0042
As(1)	0.0390(3)	0.0358(3)	0.0379(3)	0.0169(2)	0.0007(3)	0.0040(3)
As(2)	0.0304(6)	0.0582(8)	0.0451(8)	0.0251(5)	-0.0061(6)	-0.0057(6)
O(1)	0.043(2)	0.042(2)	0.053(3)	0.018(2)	0.010(2)	0.013(2)
O(2)	0.039(2)	0.061(3)	0.038(2)	0.020(2)	0.007(2)	-0.001(2)
O(3)	0.065(3)	0.097(3)	0.036(3)	0.056(2)	0.006(2)	0.000(2)
O(4)	0.043(3)	0.076(6)	0.051(4)	0.0381	0.001(2)	0.0014
O(5)	0.26(2)	0.27(2)	0.36(3)	0.05(2)	-0.03(2)	0.06(2)
O(6)	0.46(4)	0.35(2)	0.34(2)	0.11(3)	0.00(2)	-0.22(2)
C(1)	0.050(4)	0.044(3)	0.039(3)	0.026(3)	-0.001(3)	-0.003(3)
C(2)	0.044(4)	0.062(4)	0.044(4)	0.025(3)	-0.007(3)	-0.007(4)
C(3)	0.058(4)	0.062(5)	0.051(5)	0.029(3)	-0.001(4)	-0.003(4)
C(4)	0.080(5)	0.055(4)	0.048(4)	0.038(4)	-0.003(4)	-0.002(4)
C(5)	0.086(6)	0.048(4)	0.065(5)	0.029(4)	0.022(5)	0.013(4)
C(6)	0.055(4)	0.044(4)	0.033(4)	0.019(3)	0.008(3)	0.003(3)
C(7)	0.040(4)	0.067(5)	0.043(4)	0.010(4)	-0.002(3)	0.015(4)
C(8)	0.051(5)	0.115(8)	0.064(5)	0.031(5)	-0.004(4)	0.029(5)
C(9)	0.081(6)	0.141(9)	0.100(8)	0.059(6)	-0.004(6)	0.050(7)
C(10)	0.071(7)	0.107(9)	0.074(7)	0.019(6)	-0.019(6)	0.007(7)
C(11)	0.104(10)	0.086(8)	0.058(6)	0.002(7)	-0.008(6)	-0.006(6)
C(12)	0.090(8)	0.046(5)	0.077(6)	0.000(5)	-0.028(6)	0.005(5)
C(13)	0.074(5)	0.075(4)	0.030(3)	0.051(3)	0.000(3)	0.004(3)

C(14)	0.316(9)	0.225(7)	0.077(6)	0.240(5)	0.077(7)	0.070(6)
C(15)	0.398(10)	0.298(8)	0.15(1)	0.322(5)	0.151(9)	0.124(8)
C(16)	0.346(10)	0.48(1)	0.087(9)	0.375(6)	0.033(9)	0.05(1)
C(17)	0.096(6)	0.181(9)	0.062(6)	0.097(5)	0.005(5)	-0.008(7)
C(18)	0.071(4)	0.090(5)	0.052(5)	0.058(3)	-0.012(4)	-0.014(4)
C(19)	0.044(4)	0.070(5)	0.034(4)	0.026(3)	0.007(3)	0.005(3)
C(20)	0.033(3)	0.097(6)	0.048(4)	0.025(4)	0.003(3)	0.018(5)
C(21)	0.058(5)	0.067(6)	0.047(4)	-0.004(5)	-0.006(4)	0.009(5)
C(22)	0.049(5)	0.049(5)	0.060(5)	0.007(4)	-0.014(4)	0.006(4)
C(23)	0.112(9)	0.067(6)	0.063(6)	0.026(6)	-0.022(6)	-0.005(5)
C(24)	0.15(1)	0.057(6)	0.090(7)	0.043(6)	-0.032(8)	-0.022(5)
C(25)	0.146(10)	0.046(5)	0.080(7)	0.039(5)	0.013(7)	-0.012(5)
C(26)	0.086(5)	0.053(4)	0.061(5)	0.041(3)	0.010(5)	-0.002(4)
C(27)	0.068(5)	0.043(4)	0.043(4)	0.016(4)	-0.012(4)	-0.001(3)
C(28)	0.045(4)	0.052(4)	0.041(4)	0.017(3)	0.009(3)	0.009(4)
C(29)	0.048(3)	0.043(3)	0.050(4)	0.029(2)	0.012(3)	0.007(3)
C(30)	0.056(4)	0.039(3)	0.052(4)	0.027(3)	0.018(3)	0.004(3)
C(31)	0.086(5)	0.055(4)	0.039(4)	0.038(4)	0.019(4)	0.008(3)
C(32)	0.117(7)	0.066(5)	0.041(4)	0.050(4)	0.016(5)	0.005(4)
C(33)	0.098(6)	0.067(5)	0.080(6)	0.048(4)	0.032(5)	0.025(5)
C(34)	0.077(5)	0.051(4)	0.068(5)	0.033(3)	0.034(4)	0.009(4)
C(35)	0.056(4)	0.030(3)	0.075(5)	0.021(3)	0.026(4)	0.015(4)
C(36)	0.052(4)	0.037(4)	0.067(5)	0.022(3)	0.020(4)	0.003(3)
C(37)	0.040(4)	0.042(4)	0.072(5)	0.017(3)	0.005(4)	-0.009(4)
C(38)	0.042(3)	0.046(3)	0.041(4)	0.023(3)	0.003(3)	-0.005(3)
C(39)	0.037(4)	0.052(4)	0.074(5)	0.015(3)	-0.001(4)	-0.020(4)
C(40)	0.164(7)	0.155(6)	0.095(7)	0.135(4)	-0.051(6)	-0.063(6)
C(41)	0.158(9)	0.34(1)	0.26(2)	0.189(8)	-0.11(1)	-0.20(1)
C(42)	0.121(8)	0.22(1)	0.13(1)	0.118(7)	0.006(8)	-0.049(9)
C(43)	0.116(9)	0.075(7)	0.075(7)	0.040(6)	-0.015(6)	0.006(6)
C(44)	0.104(7)	0.082(6)	0.129(9)	0.053(5)	-0.058(6)	-0.019(6)
C(45)	0.018(5)	0.029(6)	0.043(7)	0.009(4)	0.002(5)	0.001(5)
C(46)	0.023(5)	0.051(7)	0.017(5)	0.014(4)	-0.004(4)	0.006(5)
C(47)	0.050(7)	0.074(9)	0.08(1)	0.047(5)	0.018(8)	0.010(9)
C(48)	0.06(1)	0.12(2)	0.10(2)	0.02(1)	0.02(1)	0.04(1)
C(49)	0.09(2)	0.13(2)	0.14(2)	0.04(1)	-0.01(2)	0.05(2)
C(50)	0.08(2)	0.13(2)	0.09(2)	0.03(1)	-0.02(1)	0.02(2)
C(51)	0.29(2)	0.29(2)	0.13(1)	0.21(1)	-0.06(1)	-0.01(1)
C(52)	0.51(4)	0.18(2)	0.19(2)	0.14(2)	-0.21(2)	-0.06(2)
C(53)	0.29(3)	0.46(4)	0.11(1)	0.14(3)	-0.09(2)	-0.12(2)
C(54)	0.38(4)	0.20(3)	0.12(1)	-0.10(3)	-0.02(2)	0.02(2)

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_computing_cell_refinement              'P'
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_computing_structure_solution           SIR92
_computing_structure_refinement         'teXsan Ver. 1.10'
_computing_publication_material         'teXsan Ver. 1.10'
_computing_molecular_graphics           ?
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_geom_bond_atom_site_label_2
_geom_bond_distance
_geom_bond_site_symmetry_1
_geom_bond_site_symmetry_2
_geom_bond_publ_flag
 La(1)      O(1)       2.365(5)   . . yes
 La(1)      O(1)       2.365(5)   . 6_556 yes
 La(1)      O(2)       2.684(6)   . . yes
 La(1)      O(2)       2.684(6)   . 6_556 yes
 La(1)      O(3)       2.437(5)   . . yes
 La(1)      O(3)       2.437(5)   . 6_556 yes
 La(1)      O(4)       2.391(8)   . . yes
 As(1)      O(1)       1.657(5)   . . yes
 As(1)      C(1)       1.902(7)   . . yes
 As(1)      C(7)       1.922(8)   . . yes
 As(1)      C(13)      1.874(9)   . . yes
 As(2)      As(2)      1.254(3)   . 6_556 yes
 As(2)      O(4)       1.663(7)   . . yes
 As(2)      C(39)      2.039(9)   . . yes
 As(2)      C(39)      1.896(9)   . 6_556 yes
 As(2)      C(45)      1.97(1)    . . yes
 O(2)       C(38)      1.316(9)   . . yes
 O(3)       C(19)      1.29(1)    . . yes
 O(5)       C(51)      1.59(4)    . . yes
 O(5)       C(52)      1.71(4)    . . yes
 O(5)       C(54)      1.54(4)    . . yes
 C(1)       C(2)       1.43(1)    . . yes
 C(1)       C(6)       1.38(1)    . . yes
 C(2)       C(3)       1.39(1)    . . yes
 C(3)       C(4)       1.40(1)    . . yes
 C(4)       C(5)       1.38(1)    . . yes
 C(5)       C(6)       1.40(1)    . . yes
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C(7)	C(8)	1.42(2)	. . yes
C(7)	C(12)	1.39(1)	. . yes
C(8)	C(9)	1.44(2)	. . yes
C(9)	C(10)	1.36(2)	. . yes
C(10)	C(11)	1.39(2)	. . yes
C(11)	C(12)	1.40(2)	. . yes
C(13)	C(14)	1.39(2)	. . yes
C(13)	C(18)	1.41(1)	. . yes
C(14)	C(15)	1.37(2)	. . yes
C(15)	C(16)	1.34(2)	. . yes
C(16)	C(17)	1.71(2)	. . yes
C(17)	C(18)	1.41(2)	. . yes
C(19)	C(20)	1.46(1)	. . yes
C(19)	C(28)	1.40(1)	. . yes
C(20)	C(21)	1.28(2)	. . yes
C(21)	C(22)	1.41(2)	. . yes
C(22)	C(23)	1.40(2)	. . yes
C(22)	C(27)	1.38(1)	. . yes
C(23)	C(24)	1.36(2)	. . yes
C(24)	C(25)	1.41(2)	. . yes
C(25)	C(26)	1.35(1)	. . yes
C(26)	C(27)	1.43(1)	. . yes
C(27)	C(28)	1.48(1)	. . yes
C(28)	C(29)	1.513(10)	. . yes
C(29)	C(30)	1.41(1)	. . yes
C(29)	C(38)	1.40(1)	. . yes
C(30)	C(31)	1.45(1)	. . yes
C(30)	C(35)	1.46(1)	. . yes
C(31)	C(32)	1.34(1)	. . yes
C(32)	C(33)	1.39(1)	. . yes
C(33)	C(34)	1.38(1)	. . yes
C(34)	C(35)	1.40(1)	. . yes
C(35)	C(36)	1.38(1)	. . yes
C(36)	C(37)	1.37(1)	. . yes
C(37)	C(38)	1.422(10)	. . yes
C(39)	C(40)	1.30(2)	. . yes
C(39)	C(44)	1.32(1)	. . yes
C(40)	C(41)	1.42(2)	. . yes
C(41)	C(42)	1.51(2)	. . yes
C(42)	C(43)	1.30(2)	. . yes
C(43)	C(44)	1.55(2)	. . yes
C(45)	C(46)	1.42(2)	. . yes
C(45)	C(50)	1.21(3)	. . yes

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 C(46)      C(47)      1.29(2)    . . yes
 C(47)      C(48)      1.22(4)    . . yes
 C(48)      C(49)      1.61(4)    . . yes
 C(49)      C(50)      1.26(4)    . . yes
 C(51)      C(52)      1.07(3)    . . yes
 C(52)      C(53)      1.19(4)    . . yes
 C(53)      C(54)      1.44(4)    . . yes
#------------------------------------------------------------------------------
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_geom_angle_site_symmetry_3
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   O(1)       La(1)      O(1)       174.9(3)   . 1_555 6_556 yes
   O(1)       La(1)      O(2)       83.4(2)    . 1_555 1_555 yes
   O(1)       La(1)      O(2)       92.0(2)    . 1_555 6_556 yes
   O(1)       La(1)      O(3)       92.2(2)    . 1_555 1_555 yes
   O(1)       La(1)      O(3)       88.3(2)    . 1_555 6_556 yes
   O(1)       La(1)      O(4)       92.5(1)    . 1_555 1_555 yes
   O(1)       La(1)      O(2)       92.0(2)    . 6_556 1_555 yes
   O(1)       La(1)      O(2)       83.4(2)    . 6_556 6_556 yes
   O(1)       La(1)      O(3)       88.3(2)    . 6_556 1_555 yes
   O(1)       La(1)      O(3)       92.2(2)    . 6_556 6_556 yes
   O(1)       La(1)      O(4)       92.5(1)    . 6_556 1_555 yes
   O(2)       La(1)      O(2)       52.6(2)    . 1_555 6_556 yes
   O(2)       La(1)      O(3)       70.1(2)    . 1_555 1_555 yes
   O(2)       La(1)      O(3)       121.5(2)   . 1_555 6_556 yes
   O(2)       La(1)      O(4)       153.7(1)   . 1_555 1_555 yes
   O(2)       La(1)      O(3)       121.5(2)   . 6_556 1_555 yes
   O(2)       La(1)      O(3)       70.1(2)    . 6_556 6_556 yes
   O(2)       La(1)      O(4)       153.7(1)   . 6_556 1_555 yes
   O(3)       La(1)      O(3)       168.3(3)   . 1_555 6_556 yes
   O(3)       La(1)      O(4)       84.2(1)    . 1_555 1_555 yes
   O(3)       La(1)      O(4)       84.2(1)    . 6_556 1_555 yes
   O(1)       As(1)      C(1)       110.0(3)   . 1_555 1_555 yes
   O(1)       As(1)      C(7)       109.7(3)   . 1_555 1_555 yes
   O(1)       As(1)      C(13)      109.8(3)   . 1_555 1_555 yes
   C(1)       As(1)      C(7)       110.0(3)   . 1_555 1_555 yes
   C(1)       As(1)      C(13)      108.3(3)   . 1_555 1_555 yes
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C(7)	As(1)	C(13)	108.9(4)	. 1_555 1_555 yes
As(2)	As(2)	O(4)	67.8(1)	. 6_556 1_555 yes
As(2)	As(2)	C(39)	65.3(3)	. 6_556 1_555 yes
As(2)	As(2)	C(39)	77.7(3)	. 6_556 6_556 yes
As(2)	As(2)	C(45)	175.2(4)	. 6_556 1_555 yes
O(4)	As(2)	C(39)	105.9(3)	. 1_555 1_555 yes
O(4)	As(2)	C(39)	112.5(3)	. 1_555 6_556 yes
O(4)	As(2)	C(45)	113.5(4)	. 1_555 1_555 yes
C(39)	As(2)	C(39)	109.5(5)	. 1_555 6_556 yes
C(39)	As(2)	C(45)	110.0(5)	. 1_555 1_555 yes
C(39)	As(2)	C(45)	105.4(5)	. 6_556 1_555 yes
La(1)	O(1)	As(1)	176.0(3)	. 1_555 1_555 yes
La(1)	O(2)	C(38)	120.4(5)	. 1_555 1_555 yes
La(1)	O(3)	C(19)	124.1(5)	. 1_555 1_555 yes
La(1)	O(4)	As(2)	157.8(1)	. 1_555 1_555 yes
La(1)	O(4)	As(2)	157.8(1)	. 1_555 6_556 yes
As(2)	O(4)	As(2)	44.3(2)	. 1_555 6_556 yes
C(51)	O(5)	C(52)	37(1)	. 1_555 1_555 yes
C(51)	O(5)	C(54)	80(2)	. 1_555 1_555 yes
C(52)	O(5)	C(54)	75(2)	. 1_555 1_555 yes
As(1)	C(1)	C(2)	116.1(5)	. 1_555 1_555 yes
As(1)	C(1)	C(6)	122.0(5)	. 1_555 1_555 yes
C(2)	C(1)	C(6)	121.5(7)	. 1_555 1_555 yes
C(1)	C(2)	C(3)	119.1(7)	. 1_555 1_555 yes
C(2)	C(3)	C(4)	119.2(7)	. 1_555 1_555 yes
C(3)	C(4)	C(5)	120.7(8)	. 1_555 1_555 yes
C(4)	C(5)	C(6)	121.7(8)	. 1_555 1_555 yes
C(1)	C(6)	C(5)	117.6(7)	. 1_555 1_555 yes
As(1)	C(7)	C(8)	116.5(7)	. 1_555 1_555 yes
As(1)	C(7)	C(12)	119.7(8)	. 1_555 1_555 yes
C(8)	C(7)	C(12)	123.3(9)	. 1_555 1_555 yes
C(7)	C(8)	C(9)	114(1)	. 1_555 1_555 yes
C(8)	C(9)	C(10)	123(1)	. 1_555 1_555 yes
C(9)	C(10)	C(11)	118(1)	. 1_555 1_555 yes
C(10)	C(11)	C(12)	122(1)	. 1_555 1_555 yes
C(7)	C(12)	C(11)	117(1)	. 1_555 1_555 yes
As(1)	C(13)	C(14)	120.3(7)	. 1_555 1_555 yes
As(1)	C(13)	C(18)	118.3(7)	. 1_555 1_555 yes
C(14)	C(13)	C(18)	121.4(9)	. 1_555 1_555 yes
C(13)	C(14)	C(15)	125(1)	. 1_555 1_555 yes
C(14)	C(15)	C(16)	119(1)	. 1_555 1_555 yes
C(15)	C(16)	C(17)	117(1)	. 1_555 1_555 yes
C(16)	C(17)	C(18)	113(1)	. 1_555 1_555 yes

C(13)	C(18)	C(17)	119.8(10)	. 1_555 1_555 yes
O(3)	C(19)	C(20)	121.3(8)	. 1_555 1_555 yes
O(3)	C(19)	C(28)	123.0(7)	. 1_555 1_555 yes
C(20)	C(19)	C(28)	115.6(9)	. 1_555 1_555 yes
C(19)	C(20)	C(21)	121.8(9)	. 1_555 1_555 yes
C(20)	C(21)	C(22)	125.0(9)	. 1_555 1_555 yes
C(21)	C(22)	C(23)	123.0(9)	. 1_555 1_555 yes
C(21)	C(22)	C(27)	117.3(10)	. 1_555 1_555 yes
C(23)	C(22)	C(27)	119(1)	. 1_555 1_555 yes
C(22)	C(23)	C(24)	121(1)	. 1_555 1_555 yes
C(23)	C(24)	C(25)	119(1)	. 1_555 1_555 yes
C(24)	C(25)	C(26)	120(1)	. 1_555 1_555 yes
C(25)	C(26)	C(27)	120.1(10)	. 1_555 1_555 yes
C(22)	C(27)	C(26)	118.9(9)	. 1_555 1_555 yes
C(22)	C(27)	C(28)	119.2(9)	. 1_555 1_555 yes
C(26)	C(27)	C(28)	121.8(7)	. 1_555 1_555 yes
C(19)	C(28)	C(27)	120.6(7)	. 1_555 1_555 yes
C(19)	C(28)	C(29)	120.0(8)	. 1_555 1_555 yes
C(27)	C(28)	C(29)	119.1(8)	. 1_555 1_555 yes
C(28)	C(29)	C(30)	122.1(7)	. 1_555 1_555 yes
C(28)	C(29)	C(38)	118.2(6)	. 1_555 1_555 yes
C(30)	C(29)	C(38)	119.7(6)	. 1_555 1_555 yes
C(29)	C(30)	C(31)	122.5(7)	. 1_555 1_555 yes
C(29)	C(30)	C(35)	119.7(7)	. 1_555 1_555 yes
C(31)	C(30)	C(35)	117.8(7)	. 1_555 1_555 yes
C(30)	C(31)	C(32)	120.5(8)	. 1_555 1_555 yes
C(31)	C(32)	C(33)	121.8(9)	. 1_555 1_555 yes
C(32)	C(33)	C(34)	120.4(9)	. 1_555 1_555 yes
C(33)	C(34)	C(35)	121.4(8)	. 1_555 1_555 yes
C(30)	C(35)	C(34)	118.0(8)	. 1_555 1_555 yes
C(30)	C(35)	C(36)	118.3(7)	. 1_555 1_555 yes
C(34)	C(35)	C(36)	123.7(7)	. 1_555 1_555 yes
C(35)	C(36)	C(37)	122.2(7)	. 1_555 1_555 yes
C(36)	C(37)	C(38)	120.6(8)	. 1_555 1_555 yes
O(2)	C(38)	C(29)	120.8(6)	. 1_555 1_555 yes
O(2)	C(38)	C(37)	119.7(7)	. 1_555 1_555 yes
C(29)	C(38)	C(37)	119.5(7)	. 1_555 1_555 yes
As(2)	C(39)	As(2)	36.9(2)	. 1_555 6_556 yes
As(2)	C(39)	C(40)	111.4(8)	. 1_555 1_555 yes
As(2)	C(39)	C(44)	121.4(9)	. 1_555 1_555 yes
As(2)	C(39)	C(40)	130.5(8)	. 6_556 1_555 yes
As(2)	C(39)	C(44)	103.9(9)	. 6_556 1_555 yes
C(40)	C(39)	C(44)	123(1)	. 1_555 1_555 yes

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   C(39)      C(40)      C(41)      123(1)     . 1_555 1_555 yes
   C(40)      C(41)      C(42)      114(1)     . 1_555 1_555 yes
   C(41)      C(42)      C(43)      118(1)     . 1_555 1_555 yes
   C(42)      C(43)      C(44)      121(1)     . 1_555 1_555 yes
   C(39)      C(44)      C(43)      115(1)     . 1_555 1_555 yes
   As(2)      C(45)      C(46)      116(1)     . 1_555 1_555 yes
   As(2)      C(45)      C(50)      121(1)     . 1_555 1_555 yes
   C(46)      C(45)      C(50)      119(1)     . 1_555 1_555 yes
   C(45)      C(46)      C(47)      116(1)     . 1_555 1_555 yes
   C(46)      C(47)      C(48)      123(1)     . 1_555 1_555 yes
   C(47)      C(48)      C(49)      118(2)     . 1_555 1_555 yes
   C(48)      C(49)      C(50)      109(3)     . 1_555 1_555 yes
   C(45)      C(50)      C(49)      128(3)     . 1_555 1_555 yes
   O(5)       C(51)      C(52)      77(2)      . 1_555 1_555 yes
   O(5)       C(52)      C(51)      64(2)      . 1_555 1_555 yes
   O(5)       C(52)      C(53)      85(2)      . 1_555 1_555 yes
   C(51)      C(52)      C(53)      116(3)     . 1_555 1_555 yes
   C(52)      C(53)      C(54)      98(1)      . 1_555 1_555 yes
   O(5)       C(54)      C(53)      84(1)      . 1_555 1_555 yes
#------------------------------------------------------------------------------
loop_
_geom_torsion_atom_site_label_1
_geom_torsion_atom_site_label_2
_geom_torsion_atom_site_label_3
_geom_torsion_atom_site_label_4
_geom_torsion
_geom_torsion_site_symmetry_1
_geom_torsion_site_symmetry_2
_geom_torsion_site_symmetry_3
_geom_torsion_site_symmetry_4
_geom_torsion_publ_flag
   La(1)   O(1)    As(1)   C(1)    148(4)    1_555 1_555 1_555 1_555 yes
   La(1)   O(1)    As(1)   C(7)    -90(4)    1_555 1_555 1_555 1_555 yes
   La(1)   O(1)    As(1)   C(13)   29(4)     1_555 1_555 1_555 1_555 yes
   La(1)   O(1)    As(1)   C(1)    148(4)    1_555 6_556 6_556 6_556 yes
   La(1)   O(1)    As(1)   C(7)    -90(4)    1_555 6_556 6_556 6_556 yes
   La(1)   O(1)    As(1)   C(13)   29(4)     1_555 6_556 6_556 6_556 yes
   La(1)   O(2)    C(38)   C(29)   -84.7(8)  1_555 1_555 1_555 1_555 yes
   La(1)   O(2)    C(38)   C(37)   95.2(8)   1_555 1_555 1_555 1_555 yes
   La(1)   O(2)    C(38)   C(29)   -84.7(8)  1_555 6_556 6_556 6_556 yes
   La(1)   O(2)    C(38)   C(37)   95.2(8)   1_555 6_556 6_556 6_556 yes
   La(1)   O(3)    C(19)   C(20)   90.5(8)   1_555 1_555 1_555 1_555 yes
   La(1)   O(3)    C(19)   C(28)   -89.9(8)  1_555 1_555 1_555 1_555 yes
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La(1)	O(3)	C(19)	C(20)	90.5(8)	1_555 6_556 6_556 6_556 yes
La(1)	O(3)	C(19)	C(28)	-89.9(8)	1_555 6_556 6_556 6_556 yes
La(1)	O(4)	As(2)	As(2)	-180.0	1_555 1_555 1_555 6_556 yes
La(1)	O(4)	As(2)	C(39)	-125.7(3)	1_555 1_555 1_555 1_555 yes
La(1)	O(4)	As(2)	C(39)	114.6(4)	1_555 1_555 1_555 6_556 yes
La(1)	O(4)	As(2)	C(45)	-5.0(5)	1_555 1_555 1_555 1_555 yes
La(1)	O(4)	As(2)	As(2)	180.0	1_555 1_555 6_556 1_555 yes
La(1)	O(4)	As(2)	C(39)	114.6(4)	1_555 1_555 6_556 1_555 yes
La(1)	O(4)	As(2)	C(39)	-125.7(3)	1_555 1_555 6_556 6_556 yes
La(1)	O(4)	As(2)	C(45)	-5.0(5)	1_555 1_555 6_556 6_556 yes
As(1)	O(1)	La(1)	O(1)	-52(4)	1_555 1_555 1_555 6_556 yes
As(1)	O(1)	La(1)	O(2)	-26(4)	1_555 1_555 1_555 1_555 yes
As(1)	O(1)	La(1)	O(2)	-78(4)	1_555 1_555 1_555 6_556 yes
As(1)	O(1)	La(1)	O(3)	43(4)	1_555 1_555 1_555 1_555 yes
As(1)	O(1)	La(1)	O(3)	-148(4)	1_555 1_555 1_555 6_556 yes
As(1)	O(1)	La(1)	O(4)	127(4)	1_555 1_555 1_555 1_555 yes
As(1)	C(1)	C(2)	C(3)	-172.9(7)	1_555 1_555 1_555 1_555 yes
As(1)	C(1)	C(6)	C(5)	174.0(7)	1_555 1_555 1_555 1_555 yes
As(1)	C(7)	C(8)	C(9)	175.6(7)	1_555 1_555 1_555 1_555 yes
As(1)	C(7)	C(12)	C(11)	-174.0(8)	1_555 1_555 1_555 1_555 yes
As(1)	C(13)	C(14)	C(15)	170(1)	1_555 1_555 1_555 1_555 yes
As(1)	C(13)	C(18)	C(17)	176.5(7)	1_555 1_555 1_555 1_555 yes
As(2)	As(2)	C(39)	C(40)	70(1)	1_555 6_556 1_555 1_555 yes
As(2)	As(2)	C(39)	C(44)	-124.4(8)	1_555 6_556 1_555 1_555 yes
As(2)	As(2)	C(39)	C(40)	-129.7(8)	1_555 6_556 6_556 6_556 yes
As(2)	As(2)	C(39)	C(44)	69.8(9)	1_555 6_556 6_556 6_556 yes
As(2)	As(2)	C(45)	C(46)	133(4)	1_555 6_556 6_556 6_556 yes
As(2)	As(2)	C(45)	C(50)	-26(5)	1_555 6_556 6_556 6_556 yes
As(2)	O(4)	La(1)	O(1)	-145.7(2)	1_555 1_555 1_555 1_555 yes
As(2)	O(4)	La(1)	O(1)	34.3(2)	1_555 1_555 1_555 6_556 yes
As(2)	O(4)	La(1)	O(2)	-65.5(3)	1_555 1_555 1_555 1_555 yes
As(2)	O(4)	La(1)	O(2)	114.5(3)	1_555 1_555 1_555 6_556 yes
As(2)	O(4)	La(1)	O(3)	-53.8(2)	1_555 1_555 1_555 1_555 yes
As(2)	O(4)	La(1)	O(3)	126.2(2)	1_555 1_555 1_555 6_556 yes
As(2)	O(4)	As(2)	C(39)	-65.4(4)	1_555 1_555 6_556 1_555 yes
As(2)	O(4)	As(2)	C(39)	54.3(3)	1_555 1_555 6_556 6_556 yes
As(2)	O(4)	As(2)	C(45)	175.0(5)	1_555 1_555 6_556 6_556 yes
As(2)	C(39)	As(2)	O(4)	59.5(2)	1_555 1_555 6_556 1_555 yes
As(2)	C(39)	As(2)	C(39)	-58.0(3)	1_555 1_555 6_556 6_556 yes
As(2)	C(39)	As(2)	C(45)	-176.3(4)	1_555 1_555 6_556 6_556 yes
As(2)	C(39)	C(40)	C(41)	-145(1)	1_555 1_555 1_555 1_555 yes
As(2)	C(39)	C(44)	C(43)	157.0(8)	1_555 1_555 1_555 1_555 yes
As(2)	C(39)	As(2)	O(4)	-55.8(2)	1_555 6_556 6_556 1_555 yes

As(2)	C(39)	As(2)	C(39)	65.7(4)	1_555 6_556 6_556 1_555 yes
As(2)	C(39)	As(2)	C(45)	-178.9(4)	1_555 6_556 6_556 6_556 yes
As(2)	C(39)	C(40)	C(41)	176(1)	1_555 6_556 6_556 6_556 yes
As(2)	C(39)	C(44)	C(43)	-167.5(8)	1_555 6_556 6_556 6_556 yes
As(2)	C(45)	C(46)	C(47)	177(1)	1_555 1_555 1_555 1_555 yes
As(2)	C(45)	C(50)	C(49)	179(2)	1_555 1_555 1_555 1_555 yes
O(1)	La(1)	O(2)	C(38)	145.0(5)	1_555 1_555 1_555 1_555 yes
O(1)	La(1)	O(2)	C(38)	-37.3(5)	1_555 1_555 6_556 6_556 yes
O(1)	La(1)	O(3)	C(19)	-29.4(6)	1_555 1_555 1_555 1_555 yes
O(1)	La(1)	O(3)	C(19)	145.5(6)	1_555 1_555 6_556 6_556 yes
O(1)	As(1)	C(1)	C(2)	-33.0(8)	1_555 1_555 1_555 1_555 yes
O(1)	As(1)	C(1)	C(6)	153.6(7)	1_555 1_555 1_555 1_555 yes
O(1)	As(1)	C(7)	C(8)	-25.6(8)	1_555 1_555 1_555 1_555 yes
O(1)	As(1)	C(7)	C(12)	146.8(7)	1_555 1_555 1_555 1_555 yes
O(1)	As(1)	C(13)	C(14)	154.6(9)	1_555 1_555 1_555 1_555 yes
O(1)	As(1)	C(13)	C(18)	-24.0(7)	1_555 1_555 1_555 1_555 yes
O(2)	La(1)	O(2)	C(38)	-117.4(6)	1_555 1_555 6_556 6_556 yes
O(2)	La(1)	O(3)	C(19)	52.7(6)	1_555 1_555 1_555 1_555 yes
O(2)	La(1)	O(3)	C(19)	64.3(6)	1_555 1_555 6_556 6_556 yes
O(2)	C(38)	C(29)	C(28)	2(1)	1_555 1_555 1_555 1_555 yes
O(2)	C(38)	C(29)	C(30)	-178.5(7)	1_555 1_555 1_555 1_555 yes
O(2)	C(38)	C(37)	C(36)	179.4(8)	1_555 1_555 1_555 1_555 yes
O(3)	La(1)	O(2)	C(38)	50.2(5)	1_555 1_555 1_555 1_555 yes
O(3)	La(1)	O(2)	C(38)	-131.1(5)	1_555 1_555 6_556 6_556 yes
O(3)	La(1)	O(3)	C(19)	-121.8(6)	1_555 1_555 6_556 6_556 yes
O(3)	C(19)	C(20)	C(21)	-177.1(8)	1_555 1_555 1_555 1_555 yes
O(3)	C(19)	C(28)	C(27)	174.2(7)	1_555 1_555 1_555 1_555 yes
O(3)	C(19)	C(28)	C(29)	0(1)	1_555 1_555 1_555 1_555 yes
O(4)	La(1)	O(2)	C(38)	62.6(6)	1_555 1_555 1_555 1_555 yes
O(4)	La(1)	O(2)	C(38)	62.6(6)	1_555 1_555 6_556 6_556 yes
O(4)	La(1)	O(3)	C(19)	-121.8(6)	1_555 1_555 1_555 1_555 yes
O(4)	La(1)	O(3)	C(19)	-121.8(6)	1_555 1_555 6_556 6_556 yes
O(4)	As(2)	As(2)	C(39)	120.8(3)	1_555 1_555 6_556 1_555 yes
O(4)	As(2)	As(2)	C(39)	-120.8(3)	1_555 1_555 6_556 6_556 yes
O(4)	As(2)	As(2)	C(45)	-107(4)	1_555 1_555 6_556 6_556 yes
O(4)	As(2)	C(39)	C(40)	174.5(7)	1_555 1_555 1_555 1_555 yes
O(4)	As(2)	C(39)	C(44)	14.0(9)	1_555 1_555 1_555 1_555 yes
O(4)	As(2)	C(39)	C(40)	129(1)	1_555 1_555 6_556 6_556 yes
O(4)	As(2)	C(39)	C(44)	-65.0(8)	1_555 1_555 6_556 6_556 yes
O(4)	As(2)	C(45)	C(46)	27(1)	1_555 1_555 1_555 1_555 yes
O(4)	As(2)	C(45)	C(50)	-132(1)	1_555 1_555 1_555 1_555 yes
O(4)	As(2)	As(2)	C(39)	-120.8(3)	1_555 6_556 1_555 1_555 yes
O(4)	As(2)	As(2)	C(39)	120.8(3)	1_555 6_556 1_555 6_556 yes

O(4)	As(2)	As(2)	C(45)	-107(4)	1_555 6_556 1_555 1_555 yes
O(4)	As(2)	C(39)	C(40)	129(1)	1_555 6_556 1_555 1_555 yes
O(4)	As(2)	C(39)	C(44)	-65.0(8)	1_555 6_556 1_555 1_555 yes
O(4)	As(2)	C(39)	C(40)	174.5(7)	1_555 6_556 6_556 6_556 yes
O(4)	As(2)	C(39)	C(44)	14.0(9)	1_555 6_556 6_556 6_556 yes
O(4)	As(2)	C(45)	C(46)	27(1)	1_555 6_556 6_556 6_556 yes
O(4)	As(2)	C(45)	C(50)	-132(1)	1_555 6_556 6_556 6_556 yes
O(5)	C(51)	C(52)	C(53)	70(4)	1_555 1_555 1_555 1_555 yes
O(5)	C(52)	C(53)	C(54)	30(3)	1_555 1_555 1_555 1_555 yes
O(5)	C(54)	C(53)	C(52)	-34(3)	1_555 1_555 1_555 1_555 yes
C(1)	As(1)	C(7)	C(8)	95.6(7)	1_555 1_555 1_555 1_555 yes
C(1)	As(1)	C(7)	C(12)	-92.1(8)	1_555 1_555 1_555 1_555 yes
C(1)	As(1)	C(13)	C(14)	34.5(10)	1_555 1_555 1_555 1_555 yes
C(1)	As(1)	C(13)	C(18)	-144.2(6)	1_555 1_555 1_555 1_555 yes
C(1)	C(2)	C(3)	C(4)	-3(1)	1_555 1_555 1_555 1_555 yes
C(1)	C(6)	C(5)	C(4)	1(1)	1_555 1_555 1_555 1_555 yes
C(2)	C(1)	As(1)	C(7)	-153.9(7)	1_555 1_555 1_555 1_555 yes
C(2)	C(1)	As(1)	C(13)	87.1(7)	1_555 1_555 1_555 1_555 yes
C(2)	C(1)	C(6)	C(5)	0(1)	1_555 1_555 1_555 1_555 yes
C(2)	C(3)	C(4)	C(5)	5(1)	1_555 1_555 1_555 1_555 yes
C(3)	C(2)	C(1)	C(6)	0(1)	1_555 1_555 1_555 1_555 yes
C(3)	C(4)	C(5)	C(6)	-4(1)	1_555 1_555 1_555 1_555 yes
C(6)	C(1)	As(1)	C(7)	32.6(9)	1_555 1_555 1_555 1_555 yes
C(6)	C(1)	As(1)	C(13)	-86.3(8)	1_555 1_555 1_555 1_555 yes
C(7)	As(1)	C(13)	C(14)	-85.2(9)	1_555 1_555 1_555 1_555 yes
C(7)	As(1)	C(13)	C(18)	96.2(7)	1_555 1_555 1_555 1_555 yes
C(7)	C(8)	C(9)	C(10)	-2(1)	1_555 1_555 1_555 1_555 yes
C(7)	C(12)	C(11)	C(10)	0(1)	1_555 1_555 1_555 1_555 yes
C(8)	C(7)	As(1)	C(13)	-145.8(7)	1_555 1_555 1_555 1_555 yes
C(8)	C(7)	C(12)	C(11)	-2(1)	1_555 1_555 1_555 1_555 yes
C(8)	C(9)	C(10)	C(11)	0(1)	1_555 1_555 1_555 1_555 yes
C(9)	C(8)	C(7)	C(12)	3(1)	1_555 1_555 1_555 1_555 yes
C(9)	C(10)	C(11)	C(12)	1(1)	1_555 1_555 1_555 1_555 yes
C(12)	C(7)	As(1)	C(13)	26.5(8)	1_555 1_555 1_555 1_555 yes
C(13)	C(14)	C(15)	C(16)	4(2)	1_555 1_555 1_555 1_555 yes
C(13)	C(18)	C(17)	C(16)	16(1)	1_555 1_555 1_555 1_555 yes
C(14)	C(13)	C(18)	C(17)	-2(1)	1_555 1_555 1_555 1_555 yes
C(14)	C(15)	C(16)	C(17)	11(2)	1_555 1_555 1_555 1_555 yes
C(15)	C(14)	C(13)	C(18)	-10(2)	1_555 1_555 1_555 1_555 yes
C(15)	C(16)	C(17)	C(18)	-22(1)	1_555 1_555 1_555 1_555 yes
C(19)	C(20)	C(21)	C(22)	2(1)	1_555 1_555 1_555 1_555 yes
C(19)	C(28)	C(27)	C(22)	3(1)	1_555 1_555 1_555 1_555 yes
C(19)	C(28)	C(27)	C(26)	-173.8(8)	1_555 1_555 1_555 1_555 yes

C(19)	C(28)	C(29)	C(30)	-117.2(9)	1_555	1_555	1_555	1_555	yes
C(19)	C(28)	C(29)	C(38)	61(1)	1_555	1_555	1_555	1_555	yes
C(20)	C(19)	C(28)	C(27)	-6(1)	1_555	1_555	1_555	1_555	yes
C(20)	C(19)	C(28)	C(29)	179.9(7)	1_555	1_555	1_555	1_555	yes
C(20)	C(21)	C(22)	C(23)	175.8(10)	1_555	1_555	1_555	1_555	yes
C(20)	C(21)	C(22)	C(27)	-5(1)	1_555	1_555	1_555	1_555	yes
C(21)	C(20)	C(19)	C(28)	3(1)	1_555	1_555	1_555	1_555	yes
C(21)	C(22)	C(23)	C(24)	178(1)	1_555	1_555	1_555	1_555	yes
C(21)	C(22)	C(27)	C(26)	179.7(8)	1_555	1_555	1_555	1_555	yes
C(21)	C(22)	C(27)	C(28)	2(1)	1_555	1_555	1_555	1_555	yes
C(22)	C(23)	C(24)	C(25)	0(1)	1_555	1_555	1_555	1_555	yes
C(22)	C(27)	C(26)	C(25)	2(1)	1_555	1_555	1_555	1_555	yes
C(22)	C(27)	C(28)	C(29)	177.6(8)	1_555	1_555	1_555	1_555	yes
C(23)	C(22)	C(27)	C(26)	-1(1)	1_555	1_555	1_555	1_555	yes
C(23)	C(22)	C(27)	C(28)	-179.1(8)	1_555	1_555	1_555	1_555	yes
C(23)	C(24)	C(25)	C(26)	1(1)	1_555	1_555	1_555	1_555	yes
C(24)	C(23)	C(22)	C(27)	0(1)	1_555	1_555	1_555	1_555	yes
C(24)	C(25)	C(26)	C(27)	-2(1)	1_555	1_555	1_555	1_555	yes
C(25)	C(26)	C(27)	C(28)	-179.5(9)	1_555	1_555	1_555	1_555	yes
C(26)	C(27)	C(28)	C(29)	0(1)	1_555	1_555	1_555	1_555	yes
C(27)	C(28)	C(29)	C(30)	68(1)	1_555	1_555	1_555	1_555	yes
C(27)	C(28)	C(29)	C(38)	-112.5(8)	1_555	1_555	1_555	1_555	yes
C(28)	C(29)	C(30)	C(31)	0(1)	1_555	1_555	1_555	1_555	yes
C(28)	C(29)	C(30)	C(35)	177.8(8)	1_555	1_555	1_555	1_555	yes
C(28)	C(29)	C(38)	C(37)	-177.0(8)	1_555	1_555	1_555	1_555	yes
C(29)	C(30)	C(31)	C(32)	-179.3(9)	1_555	1_555	1_555	1_555	yes
C(29)	C(30)	C(35)	C(34)	-179.9(8)	1_555	1_555	1_555	1_555	yes
C(29)	C(30)	C(35)	C(36)	-1(1)	1_555	1_555	1_555	1_555	yes
C(29)	C(38)	C(37)	C(36)	0(1)	1_555	1_555	1_555	1_555	yes
C(30)	C(29)	C(38)	C(37)	1(1)	1_555	1_555	1_555	1_555	yes
C(30)	C(31)	C(32)	C(33)	-1(1)	1_555	1_555	1_555	1_555	yes
C(30)	C(35)	C(34)	C(33)	0(1)	1_555	1_555	1_555	1_555	yes
C(30)	C(35)	C(36)	C(37)	2(1)	1_555	1_555	1_555	1_555	yes
C(31)	C(30)	C(29)	C(38)	-179.1(8)	1_555	1_555	1_555	1_555	yes
C(31)	C(30)	C(35)	C(34)	-1(1)	1_555	1_555	1_555	1_555	yes
C(31)	C(30)	C(35)	C(36)	177.4(8)	1_555	1_555	1_555	1_555	yes
C(31)	C(32)	C(33)	C(34)	0(1)	1_555	1_555	1_555	1_555	yes
C(32)	C(31)	C(30)	C(35)	2(1)	1_555	1_555	1_555	1_555	yes
C(32)	C(33)	C(34)	C(35)	1(1)	1_555	1_555	1_555	1_555	yes
C(33)	C(34)	C(35)	C(36)	-179.3(10)	1_555	1_555	1_555	1_555	yes
C(34)	C(35)	C(36)	C(37)	-179.2(9)	1_555	1_555	1_555	1_555	yes
C(35)	C(30)	C(29)	C(38)	0(1)	1_555	1_555	1_555	1_555	yes
C(35)	C(36)	C(37)	C(38)	-1(1)	1_555	1_555	1_555	1_555	yes

C(39) As(2) As(2) C(39) 118.5(5) 1_555 1_555 6_556 6_556 yes
C(39) As(2) As(2) C(45) 131(4) 1_555 1_555 6_556 6_556 yes
C(39) As(2) C(39) As(2) -58.0(3) 1_555 1_555 6_556 6_556 yes
C(39) As(2) C(39) C(40) 12(1) 1_555 1_555 6_556 6_556 yes
C(39) As(2) C(39) C(44) 177.6(8) 1_555 1_555 6_556 6_556 yes
C(39) As(2) C(45) C(46) 145.8(9) 1_555 1_555 1_555 1_555 yes
C(39) As(2) C(45) C(50) -14(1) 1_555 1_555 1_555 1_555 yes
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C(39) As(2) As(2) C(45) 12(4) 1_555 6_556 1_555 1_555 yes
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C(39) As(2) C(39) C(40) -63.9(7) 1_555 6_556 6_556 6_556 yes
C(39) As(2) C(39) C(44) 135.5(10) 1_555 6_556 6_556 6_556 yes
C(39) As(2) C(45) C(46) -96.2(9) 1_555 6_556 6_556 6_556 yes
C(39) As(2) C(45) C(50) 103(1) 1_555 6_556 6_556 6_556 yes
C(39) C(40) C(41) C(42) -21(2) 1_555 1_555 1_555 1_555 yes
C(39) C(44) C(43) C(42) -3(1) 1_555 1_555 1_555 1_555 yes
C(40) C(39) As(2) C(45) 51.5(9) 1_555 1_555 1_555 1_555 yes
C(40) C(39) As(2) C(45) -105(1) 1_555 1_555 6_556 6_556 yes
C(40) C(39) C(44) C(43) -1(1) 1_555 1_555 1_555 1_555 yes
C(40) C(41) C(42) C(43) 16(2) 1_555 1_555 1_555 1_555 yes
C(41) C(40) C(39) C(44) 14(2) 1_555 1_555 1_555 1_555 yes
C(41) C(42) C(43) C(44) -5(2) 1_555 1_555 1_555 1_555 yes
C(44) C(39) As(2) C(45) -109.1(9) 1_555 1_555 1_555 1_555 yes
C(44) C(39) As(2) C(45) 59.3(9) 1_555 1_555 6_556 6_556 yes
C(45) As(2) As(2) C(45) 144(8) 1_555 1_555 6_556 6_556 yes
C(45) C(46) C(47) C(48) 7(2) 1_555 1_555 1_555 1_555 yes
C(45) C(50) C(49) C(48) -3(3) 1_555 1_555 1_555 1_555 yes
C(46) C(45) C(50) C(49) 19(3) 1_555 1_555 1_555 1_555 yes
C(46) C(47) C(48) C(49) 8(3) 1_555 1_555 1_555 1_555 yes
C(47) C(46) C(45) C(50) -22(2) 1_555 1_555 1_555 1_555 yes
C(47) C(48) C(49) C(50) -11(3) 1_555 1_555 1_555 1_555 yes
C(51) O(5) C(52) C(53) -122(3) 1_555 1_555 1_555 1_555 yes
C(51) O(5) C(54) C(53) 61(2) 1_555 1_555 1_555 1_555 yes
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C(52) C(51) O(5) C(54) -78(2) 1_555 1_555 1_555 1_555 yes
C(53) C(52) O(5) C(54) -29(2) 1_555 1_555 1_555 1_555 yes

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loop_

_geom_contact_atom_site_label_1

_geom_contact_atom_site_label_2

_geom_contact_distance

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_geom_contact_site_symmetry_1
_geom_contact_site_symmetry_2
_geom_contact_publ_flag
 La(1)     O(2)     2.684(6)   . . ?
 La(1)     O(2)     2.684(6)   . 6_556 ?
 O(6)      C(49)    3.37(5)    . 4_556 ?
 O(6)      C(15)    3.54(3)    . 4_656 ?
 C(5)      C(35)    3.53(1)    . 2_545 ?
 C(10)     C(23)    3.49(2)    . 5_556 ?
 C(10)     C(22)    3.57(1)    . 5_556 ?
 C(14)     C(25)    3.36(2)    . 2_545 ?
 C(15)     C(25)    3.52(2)    . 2_545 ?
 C(31)     C(42)    3.56(2)    . 3_554 ?
 C(40)     C(51)    3.51(3)    . 1_455 ?
 C(41)     C(51)    3.38(3)    . 1_455 ?
#------------------------------------------------------------------------------
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