Supporting Information

Catalytic Asymmetric Epoxidation of α,β -Unsaturated Esters Using an Yttrium-Biphenyldiol Complex

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Experimental Procedures and Characterization of the Products

Experimental

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 ^1H NMR and 125.65 MHz for ^{13}C NMR. Chemical shifts in CDCl_3 were reported downfield from TMS (= 0 ppm) for ^1H 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. Optical rotations were measured on a JASCO P-1010 polarimeter. ESI mass spectra were measured on Waters micromass ZQ. 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 210 nm or 254 nm; column, DAICEL CHIRALPAK AS-H, DAICEL CHIRALPAK AD-H, DAICEL CHIRALSEL OD-H; mobile phase, hexane–2-propanol; flow rate, 0.4–1 mL/min. Reactions were carried out in dry solvents under an argon atmosphere, unless otherwise stated. $\text{Ln}(\text{O-}i\text{-Pr})_3$ 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 4A, powder) was purchased from Fluka. Other reagents were purified by the usual methods.

Scheme SI-1 Synthesis of 1d

2,2',6,6'-Tetrahydroxybiphenyl (6): 2,2',6,6'-tetrahydroxybiphenyl (**6**) was synthesized by following the literature. See: *J. Org. Chem.* **1987**, 52, 547.

(aS,R)-6,6'-[(Propylene)dioxy]biphenyl-2,2'-diol (8): (aS,R)-**8** was synthesized by the following literature. See: *Org. Lett.* **2000**, 2, 1319.

(aS,R)-2,2'-[Oxybis(ethylene)dioxy]-6,6'-[(propylene)dioxy]biphenyl (9): To a mixture of (aS,R)-**8** (600 mg, 2.4 mmol) and K₂CO₃ (720 mg, 5.52 mmol) in DMF (150 mL) at 80 °C was added a solution of 2-bromoethyl ether (553 μ L, 4.8 mmol) in DMF (4 mL) during 4 h by using syringe pump and stirred for 5 h at the same temperature. After the reaction mixture was cooled to room temperature, aqueous 1N HCl was added and the solution was extracted with benzene (3 times), washed with brine, and dried over Na₂SO₄. After concentration in *vacuo*, the residue was purified by flash chromatography (SiO₂, hexane/ethyl acetate = 20/1 to 4/1) to give (aS,R)-**9** (558.0 mg, 70%) as a white solid. IR (KBr) ν 2959, 2927, 2858, 1589, 1574, 1459, 1442, 1274, 1242, 1222, 1136, 1096, 1082, 838, 751, 723 cm⁻¹; ¹H NMR (CDCl₃) δ 1.22 (d, *J* = 6.4 Hz, 3H), 3.62-3.66 (m, 1H), 3.77-3.81 (m, 2H), 3.84-3.88 (m, 2H), 4.08-4.12 (m, 2H), 4.15-4.19 (m, 1H), 4.25-4.29 (m, 3H), 6.61-6.63 (m, 2H), 6.73-6.74 (m, 2H), 7.19-7.23 (m, 2H); ¹³C NMR (CDCl₃) δ 17.2, 69.7, 69.7, 72.5, 72.5, 78.9, 80.6, 107.4, 107.5, 114.8, 114.8, 117.8, 117.8, 129.2, 129.3, 156.2, 156.2, 160.0, 160.4 ESI-MS *m/z* 351 [M+Na⁺]; HR-MS [FAB(+)] calcd for C₁₉H₂₁O₅⁺ [M+H⁺]: 329.1389. Found 329.1387.

Synthesis of (S)-6,6'-[oxybis(ethylene)dioxy]biphenyl-2,2'-diol (1d): A solution of

LDBB in THF (0.34 M) was prepared by the reaction of Li (140 mg, 20 mmol) with 4,4'-di-*tert*-butylbiphenyl (16.9 mmol) in THF (50 mL) at 0 °C. To a reaction flask containing (a*S,R*)-**9** (656.0 mg, 2 mmol) at 0 °C was added the LDBB solution in THF (25 mL). After being stirred for 1 h, aqueous 1N HCl was added and the solution was extracted with ether (3 times), washed with brine, and dried over Na₂SO₄. After concentration in *vacuo*, the residue was purified by flash chromatography (SiO₂, hexane/ethyl acetate = 20/1 to 3/1) to give (*S*)-**1d** (426.3 mg, 74%, 98% ee) as a white solid.

Enantiomeric Enrichment of (*S*)-1d: To a reaction flask containing (*S*)-**1d** (225.6 mg, 0.78 mmol) and quinine (127.0 mg, 0.39 mmol) was added ethanol (1.56 mL). The solution was heated until the solution turned to clear and was settled for 12 h. To a mixture of aqueous 1N HCl and ether was added the obtained crystal of (*S*)-**1d**-quinine complex, stirred for 15 min at room temperature, and the solution was extracted with ether (2 times), washed with brine, and dried over Na₂SO₄. After concentration in *vacuo*, the residue was purified by flash chromatography (SiO₂, hexane/ethyl acetate = 20/1 to 3/1) to give (*S*)-**1d** (167.8 mg, 74%, 99% ee) as a white solid. (*S*)-**1d**: IR (KBr) ν 3387, 2929, 1600, 1579, 1459, 1254, 1187, 1131, 1087, 779 cm⁻¹; ¹H NMR (CDCl₃) δ 3.66 (dd, *J* = 12.7, 6.3 Hz, 2H), 3.75 (dd, *J* = 12.7, 5.6 Hz, 2H), 4.08 (dd, *J* = 12.2, 5.6 Hz, 2H), 4.23 (dd, *J* = 12.2, 6.3 Hz, 2H), 5.15 (br-s, 2H), 6.48 (d, *J* = 8.3 Hz, 2H), 6.62 (d, *J* = 8.3 Hz, 2H), 7.18 (dd, *J* = 8.3, 8.3 Hz, 1H), 7.19 (dd, *J* = 8.3, 8.3 Hz, 1H); ¹³C NMR (CDCl₃) δ 69.9, 72.0, 105.6, 108.7, 109.1, 130.1, 154.4, 157.4. The enantiomeric excess of (*S*)-**1d** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALCEL OD-H, *i*-PrOH/hexane 1/4, flow rate 1.0 mL/min, *t*_R 14.0 min ((*R*)-isomer) and 21.3 min ((*S*)-isomer), detection at 254 nm]; [α]_D²² +136.2 [c 0.89 CHCl₃ (99% ee)].

Synthesis of α,β -unsaturated esters **2**

α,β -Unsaturated esters were prepared by Horner-Emmons-Wadsworth reaction of corresponding aldehydes.

(*E*)-Methyl 3-phenylacrylate (**2a**). See: *J. Org. Chem.* **2004**, 69, 4216.

(*E*)-Ethyl 3-phenylacrylate (**2b**). See: *J. Org. Chem.* **2004**, 69, 4216.

(*E*)-Ethyl 3-(4-methylphenyl)acrylate (**2c**). See: *J. Am. Chem. Soc.* **1990**, 112, 4324.

(E)-Ethyl 3-(4-methoxyphenyl)acrylate (2d). See: *J. Org. Chem.* **2004**, 69, 4216.

(E)-Ethyl 3-(3-chlorophenyl)acrylate (2e). See: *J. Org. Chem.* **2002**, 67, 5320.

(E)-Ethyl 3-(4-chlorophenyl)acrylate (2f). See: *J. Am. Chem. Soc.* **2002**, 124, 8792.

(E)-Ethyl 3-(4-acetylphenyl)acrylate (2g). See: *J. Org. Chem.* **2003**, 68, 2929.

(E)-Ethyl 3-naphthalen-1-yl-acrylate (2h). See: *J. Org. Chem.* **1989**, 54, 3963.

(E)-Ethyl 3-naphthalen-2-yl-acrylate (2i). See: *Tetrahedron* **1996**, 52, 1943.

(E)-Ethyl 3-furan-3-yl-2-acrylate (2j). See: *J. Org. Chem.* **1998**, 63, 4489.

(E)-Ethyl 3-pyridin 3-yl-2-acrylate (2k). See: *J. Org. Chem.* **1994**, 59, 2537.

(E)-Ethyl 3-thiophene 3-yl-2-acrylate (2l). See: *Tetrahedron* **1989**, 45, 4103.

(E)-Ethyl 5-phenylpent-2-enoate (2m): colorless oil; IR (neat) ν 1720, 1654, 1267, 1197, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.27 (t, $J = 7.0$ Hz, 3H), 2.49-2.54 (m, 2H), 2.76 (t, $J = 8.0$ Hz, 2H), 4.17 (q, $J = 7.0$ Hz, 2H), 5.83 (dt, $J = 15.5, 2.0$ Hz, 1H), 7.00 (dt, $J = 15.5, 7.0$ Hz, 1H), 7.17-7.21 (m, 3H), 7.27-7.30 (m, 2H); ^{13}C NMR (CDCl_3) δ 14.2, 33.9, 34.3, 60.14, 121.8, 126.1, 128.2, 128.4, 140.7, 148.0, 166.5; ESI-MS m/z 227 [$\text{M}+\text{Na}^+$]; HR-MS [FAB(+)] calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2^+$ [$\text{M}+\text{H}^+$]: 205.1229. Found 205.1232.

(2E, 5Z)-Ethyl 6-phenylhexa-2,5-dienote (2n): colorless oil; IR (neat) ν 1720, 1654, 1266, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.28 (t, $J = 7.5$ Hz, 3H), 2.34 (dt, $J = 7.5, 6.8$ Hz, 2H), 2.50 (dt, $J = 7.5, 6.8$ Hz, 2H), 4.17 (q, $J = 7.0$ Hz, 2H), 5.62 (m, 1H), 5.83 (d, $J = 16.0$ Hz, 1H), 6.47 (d, $J = 11.5$ Hz, 1H), 6.96 (m, 1H), 7.21-7.35 (m, 5H); ^{13}C NMR (CDCl_3) δ 14.2, 26.9, 32.3, 60.2, 121.8, 126.7, 128.1, 128.6, 129.9, 130.8, 137.2, 148.0, 166.5; ESI-MS m/z 253 [$\text{M}+\text{Na}^+$]; HR-MS [FAB(+)] calcd for $\text{C}_{15}\text{H}_{19}\text{O}_2^+$ [$\text{M}+\text{H}^+$]: 231.1385. Found 231.1381.

(E)-Ethyl 7-oxo-7-phenylhept-2-enoate (2o): colorless oil; IR (neat) ν 1718, 1686, 1367, 1201, 691 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.28 (t, $J = 7.0$ Hz, 3H), 1.90-1.96 (m, 2H),

2.29-2.34 (m, 2H), 3.00 (t, $J = 7.5$ Hz, 2H), 4.18 (q, $J = 7.0$ Hz, 2H), 5.84-5.88 (m, 1H), 6.97 (dt, $J = 14.5, 7.5$ Hz, 1H), 7.45-7.48 (m, 2H), 7.54, (m, 1H), 7.94 (m, 2H); ^{13}C NMR (CDCl_3) δ 14.2, 22.3, 31.4, 37.4, 60.2, 121.2, 127.9, 128.6, 133.1, 136.7, 148.15, 166.51, 199.47; ESI-MS m/z $[\text{M}+\text{Na}^+]$ 269; HR-MS [FAB(+)] calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3^+$ $[\text{M}+\text{H}^+]$: 247.1334. Found 247.1336.

(E)-Ethyl 5-(4-methoxybenzyloxy)pent-2-enoate (2p): colorless oil; IR (neat) 1717, 1512, 1247, 1095, 820 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.28 (t, $J = 7.5$ Hz, 3H), 2.49 (dd, $J = 13.0, 6.5$ Hz, 2H), 3.55 (t, $J = 6.5$ Hz, 2H), 3.80 (s, 3H), 4.18 (q, 7.5 Hz, 2H), 4.45 (s, 2H), 5.88 (dt, $J = 16.0, 2.0$ Hz, 1H), 6.88 (m, 2H), 6.96 (dt, $J = 16.0, 7.0$ Hz, 1H), 7.25 (m, 2H); ^{13}C NMR (CDCl_3) δ 14.3, 32.6, 55.2, 60.2, 67.9, 72.7, 113.8, 122.8, 129.31, 130.1, 145.6, 159.2, 166.4; ESI-MS m/z 287 $[\text{M}+\text{Na}^+]$; HR-MS [FAB(+)] calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4^+$ $[\text{M}^+]$: 264.1362. Found 264.1364, for $\text{C}_{15}\text{H}_{21}\text{O}_4^+$ $[\text{M}+\text{H}^+]$: 265.1447. Found 265.1439.

General Procedure for the Catalytic Asymmetric Epoxidation of α,β -Unsaturated Esters Using the Y–Biphenyldiol **1d** – $\text{Ph}_3\text{As}=\text{O}$ Complex.

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.] biphenyldiol **1d** was added (7.2 mg, 0.025 mmol) and triphenylarsine oxide (8.1 mg, 0.025 mmol) as a THF solution (1.125 mL), and then $\text{Y}(\text{O}-i\text{-Pr})_3$ (0.125 mL, 0.025 mmol, 0.2 M solution in THF) was added to the reaction mixture at room temperature. After being stirred for 45 min at the same temperature, TBHP (0.375 mL, 1.5 mmol, 4.0 M solution in toluene) was added. After being stirred for 10 min, **2b** (220.3mg, 1.25 mmol) was added directly and the mixture was stirred at room temperature. After complete consumption of the starting material (36 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 Na_2SO_4 . After concentration in *vacuo*, the residue was purified by flash chromatography (SiO_2 , hexane/ethyl acetate = 100/1 to 50/1) to give epoxy ester **3b** (212.7 mg, 89%) as a clear oil. The enantiomeric excess of **3b** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 2/98, flow rate 0.4 mL/min, t_R 31.5 min ((2*S*,3*R*)-isomer) and 38.0 min ((2*R*,3*S*)-isomer), detection at 254 nm]; $[\alpha]_D^{24} -158.8$ [c 1.06 CHCl_3 (99% ee)]. lit. $[\alpha]_D^{25} +160.1$ [c 1.15, CHCl_3 , (96% ee (2*S*,3*R*)-isomer)]. See: *J. Am. Chem. Soc.* **2002**, 124, 8792.

Methyl (2*R*,3*S*)-3-phenyloxirane-2-carboxylate (3a): The enantiomeric excess of **3a** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 2/98, flow rate 0.4 mL/min, t_R 31.6 min ((2*S*,3*R*)-isomer) and 38.0 min ((2*R*,3*S*)-isomer), detection at 254 nm]; $[\alpha]_D^{20}$ -132.6 [c 0.44 CHCl₃ (99% ee)]. lit. $[\alpha]_D^{25}$ -111.8 [c 1.17, CHCl₃, (92% ee)]. See: *J. Am. Chem. Soc.* **2001**, 123, 9474.

Ethyl (2*R*,3*S*)-3-(4-methylphenyl)oxirane-2-carboxylate (3c): The enantiomeric excess of **3c** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1.0 mL/min, t_R 7.5 min (minor) and 8.8 min (major), detection at 254 nm]; $[\alpha]_D^{24}$ -174.4 [c 1.14 CHCl₃ (98% ee)]. See: *J. Am. Chem. Soc.* **2002**, 124, 8792.

Ethyl (2*R*,3*S*)-3-(4-methoxyphenyl)oxirane-2-carboxylate (3d): The enantiomeric excess of **3d** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALCEL OD-H, *i*-PrOH/hexane 5/95, flow rate 1.0 mL/min, t_R 8.9 min ((2*R*,3*S*-isomer)) and 10.4 min ((2*S*,3*R*)-isomer), detection at 254 nm]; $[\alpha]_D^{23}$ -153.3 [c 1.11 CHCl₃ (99% ee)]. lit. $[\alpha]_D^{25}$ +143.2 [c 1.15 CHCl₃ (90% ee (2*S*,3*R*)-isomer)]. See: *J. Am. Chem. Soc.* **2002**, 124, 8792.

Ethyl (2*R*,3*S*)-3-(3-chlorophenyl)oxirane-2-carboxylate (3e): colorless oil; IR (neat) ν 2984, 1748, 1444, 1286, 1202, 1028, 786, 687 cm⁻¹; ¹H NMR (CDCl₃) δ 1.32 (t, J = 7.2 Hz, 3H), 3.46 (d, J = 1.7 Hz, 1H), 4.07 (d, J = 1.7 Hz, 1H), 4.24-4.32 (m, 2H), 7.18 (ddd, J = 6.7, 3.1, 1.8 Hz, 1H), 7.27-7.30 (m, 3H); ¹³C NMR (CDCl₃) δ 13.9, 56.5, 56.9, 61.7, 123.9, 125.6, 128.9, 129.8, 134.5, 137.0, 167.6; ESI-MS m/z 249 [M+Na⁺]; HR-MS [FAB(+)] calcd for C₁₁H₁₂O₃Cl⁺ [M+H⁺]: 227.0475. Found 227.0476. The enantiomeric excess of **3e** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 2/98, flow rate 0.4 mL/min, t_R 28.1 min (major) and 31.2 min (minor), detection at 254 nm]; $[\alpha]_D^{23}$ -157.9 [c 1.69 CHCl₃(99% ee)].

Ethyl (2*R*,3*S*)-3-(4-chlorophenyl)oxirane-2-carboxylate (3f): The enantiomeric excess of **3f** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALCEL OD-H, *i*-PrOH/hexane 2/98, flow rate 1.0 mL/min, t_R 8.7 min (major) and 9.6 min (minor), detection at 254 nm]; $[\alpha]_D^{23}$ -155.7 [c 1.37 CHCl₃(99% ee)]. See: *J. Am. Chem. Soc.* **2002**, 124, 8792.

Ethyl (2R,3S)-3-(4-acetylphenyl)oxirane-2-carboxylate (3g): colorless oil; IR (neat) ν 2984, 1748, 1685, 1266, 1202, 1026 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.34 (t, $J = 7.2$ Hz, 3H), 2.61 (s, 3H), 3.51 (d, $J = 1.8$ Hz, 1H), 4.16 (d, $J = 1.8$ Hz, 1H), 4.16-4.34 (m, 2H), 7.40 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.40 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.96 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.96 (dd, $J = 8.3, 1.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 14.0, 26.6, 56.8, 57.2, 61.8, 125.9, 128.5, 137.4, 140.1, 167.6, 197.3; ESI-MS m/z $[\text{M}+\text{Na}^+]$; HR-MS [FAB(+)] calcd for $\text{C}_{13}\text{H}_{15}\text{O}_4^+$ $[\text{M}+\text{H}^+]$: 235.0970. Found 235.0968. The enantiomeric excess of **3g** 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 14.8 min (major) and 16.3 min (minor), detection at 254 nm]; $[\alpha]_D^{23}$ -164.4 [c 0.46 CHCl_3 (89% ee)].

Ethyl (2R,3S)-3-naphthalen-1-yl-oxirane-2-carboxylate (3h): colorless oil; IR (neat) ν 3059, 2982, 1748, 1200, 800, 776 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.36 (t, $J = 7.2$ Hz, 3H), 3.52 (d, $J = 1.7$ Hz, 1H), 4.34-4.36 (m, 2H), 4.72 (d, $J = 1.7$ Hz, 1H), 7.44 (m, 4H), 7.40 (dd, $J = 8.3, 1.8$ Hz, 1H), 7.82 (m, 1H), 7.88 (m, 1H), 8.04 (m, 1H); ^{13}C NMR (CDCl_3) δ 14.9, 55.9, 56.2, 61.8, 122.5, 122.7, 125.3, 126.1, 126.6, 128.7, 128.9, 131.0, 131.1, 133.2, 168.4; ESI-MS m/z 265 $[\text{M}+\text{Na}^+]$; HR-MS [FAB(+)] calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3^+$ $[\text{M}+\text{H}^+]$: 243.1021. Found 243.1025. The enantiomeric excess of **3h** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1.0 mL/min, t_R 7.3 min (minor) and 8.9 min (major), detection at 254 nm]; $[\alpha]_D^{23}$ +16.1 [c 0.85 CHCl_3 (97% ee)].

Ethyl (2R,3S)-3-naphthalen-2-yl-oxirane-2-carboxylate (3i): white solid; IR (KBr) ν 2985, 1749, 1369, 1316, 1235, 1207, 1022, 907, 867, 831, 809, 783, 755 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.32 (t, $J = 7.3$ Hz, 3H), 3.60 (d, $J = 1.5$ Hz, 1H), 4.25-4.33 (m, 3H), 7.29 (d, $J = 8.1, 1.4$ Hz, 1H), 7.46-7.49 (m, 2H), 7.79-7.81 (m, 4H); ^{13}C NMR (CDCl_3) δ 14.0, 56.7, 58.1, 61.7, 122.3, 125.8, 126.4, 126.5, 127.7, 127.7, 128.5, 132.2, 132.9, 133.4, 168.1; ESI-MS m/z 265 $[\text{M}+\text{Na}^+]$; HR-MS [FAB(+)] calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3^+$ $[\text{M}+\text{H}^+]$: 243.1021. Found 243.1022. The enantiomeric excess of **3i** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 2/98, flow rate 0.4 mL/min, t_R 39.8 min (minor) and 48.7 min (major), detection at 254 nm]; $[\alpha]_D^{24}$ -170.3 [c 1.50 CHCl_3 (99% ee)].

Ethyl (2R,3S)-3-furan-3-yl-oxirane-2-carboxylate (3j): white-yellow solid; IR (KBr) ν 3141, 2985, 1731, 1424, 1308, 1164, 1026, 903, 876, 774 cm^{-1} ; ^1H NMR

(CDCl₃) δ 1.33 (t, J = 7.0 Hz, 3H), 3.58 (d, J = 2.0 Hz, 1H), 4.04 (d, J = 2.0 Hz, 1H), 4.24-4.32 (m, 2H), 6.29 (dd, J = 1.8, 0.6 Hz, 1H), 7.40-7.41 (m, 1H), 7.57 (m, 1H); ¹³C NMR (CDCl₃) δ 14.1, 51.8, 55.4, 61.8, 107.7, 120.9, 142.1, 143.9, 168.3; ESI-MS m/z 205 [M+Na⁺]; HR-MS [FAB(+)] calcd for C₉H₁₁O₄⁺ [M+H⁺]: 183.0657. Found 183.0654. The enantiomeric excess of **3j** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 5/95, flow rate 1.0 mL/min, t_R 9.1 min (major) and 10.2 min (minor), detection at 210 nm]; [α]_D²³ -93.8 [c 0.83 CHCl₃ (92% ee)].

Ethyl (2*R*,3*S*)-3-pyridin-3-yl-oxirane-2-carboxyate (3k): yellow oil; IR (neat) ν 2984, 1747, 1288, 1204, 1025, 893, 799, 712 cm⁻¹; ¹H NMR (CDCl₃) δ 1.34 (t, J = 7.2 Hz, 3H), 3.56 (d, J = 1.7 Hz, 1H), 4.16 (d, J = 1.7 Hz, 1H), 4.26-4.34 (m, 2H), 7.32 (ddd, J = 7.9, 4.9, 0.7 Hz, 1H), 7.58 (ddd, J = 7.9, 1.8, 1.8 Hz, 1H), 8.60-8.62 (m, 2H); ¹³C NMR (CDCl₃) δ 13.8, 55.6, 56.3, 61.7, 123.3, 130.6, 132.8, 147.8, 150.0, 167.4; ESI-MS m/z 216 [M+Na⁺]; HR-MS [FAB(+)] calcd for C₁₀H₁₂O₃N⁺ [M+H⁺]: 194.0817. Found 194.0818. The enantiomeric excess of **3k** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALPAK AD-H, *i*-PrOH/hexane 1/1, flow rate 1.0 mL/min, t_R 7.4 min (major) and 8.6 min (minor), detection at 254 nm]; [α]_D²⁴ -153.2 [c 0.85 CHCl₃ (98% ee)].

Ethyl (2*R*,3*S*)-3-thiophen-3-yl-oxirane-2-carboxyate (3l): The enantiomeric excess of **3l** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALCEL OD-H, *i*-PrOH/hexane 5/95, flow rate 1.0 mL/min, t_R 10.8 min (minor) and 26.5 min (major), detection at 254 nm]; [α]_D²³ -139.0 [c 0.98 CHCl₃ (93% ee)]. See: *J. Heterocyclic Chem.* **1964**, *11*, 242.

Ethyl (2*R*,3*S*)-3-(2-phenylethyl)oxirane-2-carboxylate (3m): colorless oil; IR (neat) ν 1749, 1454, 1370, 1198, 1030, 803 cm⁻¹; ¹H NMR (CDCl₃) δ 1.29 (t, J = 7.0 Hz, 3H), 1.86-2.01 (m, 2H), 2.73-2.76 (m, 2H), 3.16-3.22 (m, 2H), 4.17-4.25 (m, 2H), 7.18-7.22 (m, 3H), 7.28-7.31 (m, 2H); ¹³C NMR (CDCl₃) δ 14.1, 31.9, 33.2, 53.2, 57.8, 61.5, 126.2, 128.3, 140.5, 169.1; ESI-MS m/z 243 [M+Na⁺]; HR-MS [FAB(+)] calcd for C₁₃H₁₇O₂⁺ [M+H⁺]: 221.1178 Found 221.1178. The enantiomeric excess of **3m** 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 8.8 min ((2*R*,3*S*-isomer)) and 9.3 min ((2*S*,3*R*-isomer), detection at 254 nm]; [α]_D²² -39.4 [c 1.29 CHCl₃ (91% ee)].

Ethyl (2R,3S)-3-[(3Z)-4-phenyl-3-butenyl]oxirane-2-carboxylate (3n): colorless oil; IR (neat) ν 1748, 1446, 1197, 1094 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.28 (t, $J = 7.0$ Hz, 3H), 1.68-1.85 (m, 2H), 2.08-2.54 (m, 2H), 3.18 (ddd, $J = 6.0, 4.5, 2.0$ Hz 1H), 3.23 (m, 2H), 4.16-4.27 (d, $J = 2.0$ Hz, 1H), 5.65 (dt, $J = 11.5, 7.5$ Hz, 2H), 6.48 (d, $J = 11.5$ Hz, 1H), 7.21-7.25 (m, 3H), 7.32-7.35 (m, 2H); ^{13}C NMR (CDCl_3) δ 14.1, 24.8, 31.6, 53.0, 57.9, 61.5, 126.8, 128.2, 128.6, 130.1, 130.5, 137.1, 169.1; ESI-MS m/z 269 $[\text{M}+\text{Na}^+]$; HR-MS $[\text{FAB}(+)]$ calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3^+$ $[\text{M}+\text{H}^+]$: 247.1335 Found 247.1336. The enantiomeric excess of **3n** was determined by chiral stationary-phase HPLC analysis [DAICEL CHIRALCEL OD-H, *i*-PrOH/hexane 2/98, flow rate 1.0 mL/min, t_R 10.0 min (minor) and 23.1 min (major), detection at 254 nm]; $[\alpha]_D^{22}$ -13.1 [c 1.04 CH_2Cl_2 (93% ee)].

Ethyl (2R,3S)-3-(4-oxo-4-phenylbutyl)oxirane-2-carboxylate (3o): colorless oil; IR (neat) ν 1748, 1685, 1200, 691 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.30 (t, $J = 7.0$ Hz, 3H), 1.60-1.67 (m, 1H), 1.81-1.98 (m, 3H), 3.07 (t, $J = 7.0$ Hz 2H), 3.19-3.22 (m, 1H), 3.24 (d, $J = 2.0$ Hz, 1H), 4.18-4.29 (m, 2H), 7.45-7.48 (m, 2H), 7.55-7.58 (m, 1H), 7.95-7.97 (m, 2H); ^{13}C NMR (CDCl_3) δ 14.1, 20.2, 30.7, 37.4, 52.8, 58.1, 61.6, 127.9, 133.1, 136.7, 169.1, 199.4; ESI-MS m/z 285 $[\text{M}+\text{Na}^+]$; HR-MS $[\text{FAB}(+)]$ calcd for $\text{C}_{15}\text{H}_{19}\text{O}_4^+$ $[\text{M}+\text{H}^+]$: 263.1283 Found 263.1279. The enantiomeric excess of **3o** 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 35.4 min (minor) and 38.0 min (major), detection at 254 nm]; $[\alpha]_D^{22}$ -25.2 [c 0.98 CHCl_3 (92% ee)].

Ethyl (2R,3S)-3-[2-(4-Methoxybenzyloxy)ethyl]oxirane-2-carboxylate (3p): colorless oil; IR (neat) ν 2929, 1748, 1612, 1370, 819 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.29 (t, $J = 7.0$ Hz, 3H), 1.82 (ddd, $J = 14.5, 11.5, 5.5$ Hz, 1H), 1.95-2.02 (m, 1H), 3.27 (d, $J = 1.9$ Hz 1H), 3.30 (ddd, $J = 6.0, 4.5, 2.0$ Hz, 1H), 3.80 (s, 1H), 4.17-4.28 (m, 2H), 4.44 (dd, $J = 14.0, 11.5$ Hz, 2H), 6.86-6.89 (m, 2H), 7.24-7.27 (m, 2H); ^{13}C NMR (CDCl_3) δ 13.2, 31.0, 52.1, 54.3, 55.3, 60.6, 65.1, 71.9, 112.9, 128.3, 129.2, 158.3, 168.2; ESI-MS m/z 303 $[\text{M}+\text{Na}^+]$; HR-MS $[\text{FAB}(+)]$ calcd for $\text{C}_{15}\text{H}_{20}\text{O}_5^+$ $[\text{M}^+]$: 280.1311. Found 280.1311, for $\text{C}_{15}\text{H}_{21}\text{O}_5^+$ $[\text{M}+\text{H}^+]$: 281.1389. Found 281.1386. The enantiomeric excess of **3p** 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 20.1 min (major) and 21.3 min (minor), detection at 254 nm]; $[\alpha]_D^{22}$ -13.7 [c 2.95 CHCl_3 (96% ee)].

SI-1 Catalytic Asymmetric Epoxidation of **2a** Using RE-(S)-BINOL-Ph₃As=O complex:
Central Metal Effects

RE-(S)-BINOL-Ph₃As=O (1:1:1)
complex (10 mol %)
TBHP (1.2 eq)
THF (0.1 M)
MS4A (activated), rt, 72 hr

2a → **3a**

entry	RE	yield of 3a (%)	ee of 3a (%)
1	Pr	24	88
2	Sm	7	ND
3	Gd	5>	ND
4	Y	36	95

SI-2 Catalytic Asymmetric Epoxidation of **2a** Using RE-(S)-BINOL-Ph₃As=O complex:
Central Metal Effects

RE-**1d**-Ph₃As=O (1:1:1)
complex (X mol %)
TBHP (1.2 eq)
THF (0.1 M)
MS4A (activated), rt

2a → **3a** **4a**: R=*i*-Pr
5a: R=*t*-Bu

entry	RE	time (h)	yield of 3a (%)	yield of 4a and 5a (%)	ee of 3a (%)
1	La	65		trace	ND
2	Sm	50	21	3	95
3	Gd	65	57	6	99
4	Y	65	77	12	99

SI-3 Catalytic Asymmetric Epoxidation of **2a Using Y-(S)-BINOL-Ph₃As=O complex:**
Effects of concentration and amounts of TBHP

entry	R ¹	TBHP (X eq)	Conc. of 2 (Y M)	time (h)	yield of 3 (%)	yield of 4 and 5 (%)	recovery of 2 (%)	ee of 3 (%)
1	Me	1.05	0.5	65	77	5	10	99
2	Me	1.2	1.0	50	77	12	11	99
3	Me	1.2	1.0	65	81	8	4	99
4	Et	1.05	1.0	65	81	-	13	99
5	Et	1.2	1.0	36	89	1	10	99
6	Et	1.2	1.5	65	72	-	20	95

S1-4 Determination of the absolute configurations of **3a, **3b**, **3d**, and **3m****

The absolute configurations of **3a**, **3b**, and **3d** were determined by comparing the optical rotations with the reported values.

The absolute configuration of **3m** was determined by comparing the measured optical rotations with an authentic sample, which were prepared from the corresponding α,β -epoxy methyl ester **3q**. Determination of the absolute configuration of **3m** is shown in Scheme SI-2.

Scheme SI-2.