Supporting Information

Dyanamic Ligand Exchange of the Lanthanide Complex Leading to Structural and Functional Transformation: One-Pot Sequential Catalytic Asymmetric Epoxidation-Regioselective Epoxide Opening Process

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General: Reactions were monitored by thin-layer chromatography carried out on 0.25 mm Merk silica gel plates (60F-254). Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform infrared spectrophotometer. In situ IR spectra were recorded on a ReactIR 4000 instrument from ASI Applied Systems fitted with DiComp probe. 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 and calibrated using residual undeuterated solvent as an internal reference. Optical rotations were measured on a JASCO P-1010 polarimeter. ESI mass spectra were measured on Waters micromass ZQ. FAB mass spectra were measured on a JEOL JMS-MS700V in positive ion mode. 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; column, DAICEL CHIRALPAK AD-H, DAICEL CHIRALPAK AS-H, DAICEL CHIRALCEL OJ-H; mobile phase, hexane–2-propanol.

Reagents: 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 type 4A, powder) was purchased from Fluka and used without any prior activation. Decane solution of *tert*-butyl hydroperoxide (TBHP) was purchased from Aldrich Chemical Laboratory Co., LTD., and used as received. Dry tetrahydrofuran (THF) was purchased from KANTO CHEMICAL CO., INC. Other reagents were purified by standard methods.

Caution! Although we have not encountered any incident, the experiments with metal and organic azide should be performed with extreme caution.

Detailed Experimental Results, Experimental Procedures and Characterization of the Products:

1. ESI-MS Study

Figure S-1. ESI-MS analysis of the mixture of Sm-(*S*)-BINOL-Ph₃As=O (1:1:1) complex **1** and Me₃SiN₃.

C₅₄H₄₅As₃N₆O₃Sm⁺
Exact Mass: 1202.04
Mol. Wt.: 1201.10

C₇₂H₆₀As₄N₆O₄Sm⁺
Exact Mass: 1524.07
Mol. Wt.: 1523.33

2. In Situ IR Study

Procedure for *Figure 1A*

2-Necked flask equipped with ReactIR DiComp probe and a magnetic stirring bar were charged with a THF solution (2 mL) of Me_3SiN_3 (0.053 mL, 0.40 mmol). $\text{Sm}(\text{O-}i\text{-Pr})_3$ (0.100 mL, 0.02 mmol, 0.2 M solution in THF) was added at 25 °C and IR scan was started (the spectra were acquired 128 scans per spectrum at resolution 8, scan rate: every 2 min). The reaction mixture was stirred at the same temperature and IR scan was continued for 60 min.

Procedure for *Figure 1B*

2-Necked flask equipped with ReactIR DiComp probe and a magnetic stirring bar were charged with a mixture of (*S*)-BINOL (7.2 mg, 0.025 mmol), triphenylarsine oxide (8.1 mg, 0.025 mmol), and MS 4A [500 mg (1000 mg/mmol of starting material)] in THF (2.5 mL). $\text{Sm}(\text{O-}i\text{-Pr})_3$ (0.125 mL, 0.025 mmol, 0.2 M solution in THF) was added at 25 °C and stirred for 30 min. TBHP (0.060 mL, 0.30 mmol, 5 M solution in decane) was added and the stirring was continued for 10 min at the same temperature. **2a** (43.8 mg, 0.250 mmol) was added directly and the mixture was stirred at 25 °C. After stirring for 12 h at the same temperature, Me_3SiN_3 (0.066 mL, 0.500 mmol) was added and IR scan was started (the spectra were acquired 128 scans per spectrum at resolution 8, scan rate: every 2 min). The reaction mixture was stirred at the same temperature and IR scan was continued for 60 min.

3. Initial Rate Kinetic Study

3-1. Initial Rate Kinetic Studies with Anilides (*Scheme 3*)

(1) General Procedure for Catalytic Asymmetric Epoxidation of α,β -Unsaturated Anilides **6** (*Scheme 3*, Step A)

To a mixture of (*S*)-BINOL (14.3 mg, 0.050 mmol), triphenylarsine oxide (16.1 mg, 0.050 mmol) and MS 4A [500 mg (1000 mg/mmol of starting material)] in THF (5 mL) at 25 °C was added Sm(O-*i*-Pr)₃ (0.250 mL, 0.050 mmol, 0.2 M solution in THF). After stirring for 30 min, TBHP (0.12 mL, 0.60 mmol, 5 M solution in decane) was added and the stirring was continued for 10 min at the same temperature. **6c** (112mg, 0.500 mmol) was added directly and the mixture was stirred at 25 °C. Samples were taken at recorded times according to the following procedure: 0.2 mL of the reaction mixture was taken with a syringe and was immediately poured onto the mixture of 5% aqueous citric acid (1 mL) and EtOAc (1 mL). The resulting mixture was extracted with EtOAc. After evaporating the solvents, the crude residue was analyzed by ¹H NMR. Yield of **7c** was measured by comparison of integrated area of a proton at C-2 position of **6c** (6.58 ppm) and a proton at C-2 position of the **7c** (3.66 ppm).

(2) General Procedure for Catalytic Ring Opening of α,β -Epoxy Anilides **7** (*Scheme 3*, Step B)

To a stirred solution of **7c** (47.8 mg, 0.200 mmol) and Me₃SiN₃ (0.053 mL, 0.40 mmol) in THF (2 mL) at 25 °C was added Sm(O-*i*-Pr)₃ (0.100 mL, 0.0200 mmol, 0.2 M solution in THF). Samples were taken at recorded times according to the following procedure: 0.10 mL of the reaction mixture was taken with a syringe and was immediately poured onto the mixture of saturated aqueous NaHCO₃ (1 mL) and EtOAc (1 mL). The resulting mixture was extracted with EtOAc. After evaporating the solvents, the crude residue was analyzed by ¹H NMR. Total yield of **8c** and the corresponding trimethylsilyl ether (minor) was measured by comparison of integrated area of a proton at C-2 position of the **7c** (3.66 ppm) and a proton at C-2 position of the **8c** (5.20 ppm). (In the early stage of the reaction, **8c** was the major product.)

Figure S-3-1. Initial Rate Kinetics in Catalytic Asymmetric Epoxidation of Various α,β -Unsaturated Anilides **6** (Scheme 3, Step A)

Table S-3-1. Numerical Data for Plots in *Figure S1*

X = MeO	X = Me	X = H	X = F	X = CF ₃
time (sec) product (M)	time (sec) product (M)	time (sec) product (M)	time (sec) product (M)	time (sec) product (M)
1800 0.0016	3600 0.0023	7200 0.0072	3600 0.0015	7200 0.0058
3600 0.0035	7200 0.0044	10800 0.0093	7200 0.0035	10800 0.0066
5400 0.0044	10800 0.0066	14400 0.0108	14400 0.0062	18000 0.0089
7200 0.0063	14400 0.0077	18000 0.0117	18000 0.0068	20100 0.0093
9000 0.0078	18000 0.0092			
$y = 8.44\text{E-}07x + 1.60$ $R^2 = 9.91\text{E-}01$	$y = 4.75\text{E-}07x + 9.10\text{E-}04$ $R^2 = 9.83\text{E-}01$	$y = 4.17\text{E-}07x + 4.50\text{E-}03$ $R^2 = 9.69\text{E-}01$	$y = 3.69\text{E-}07x + 5.10\text{E-}04$ $R^2 = 9.73\text{E-}01$	$y = 2.83\text{E-}07x + 3.69\text{E-}03$ $R^2 = 9.95\text{E-}01$
Initial rate v (Ms ⁻¹): 8.44E-07	Initial rate v (Ms ⁻¹): 4.75E-07	Initial rate v (Ms ⁻¹): 4.17E-07	Initial rate v (Ms ⁻¹): 3.69E-07	Initial rate v (Ms ⁻¹): 2.83E-07

Additional Data

substrate	yield (%)	ee (%)
6a: X=MeO	37	95
6b: X=Me	28	92
6c: X=H	25	90
6d: X=F	25	91
6e: X= CF ₃	17	88

Figure S-3-2. Initial Rate Kinetics in Catalytic Ring Opening of Various α,β -Epoxy Anilides **7** (Scheme 3, Step B)

Table S-3-2. Numerical Data for Figure S2.

X = MeO		X = Me		X = H		X = F		X = CF ₃	
time (sec)	product (M)	time (sec)	product (M)	time (sec)	product (M)	time (sec)	product (M)	time (sec)	product (M)
600	0.0081	1200	0.0043	900	0.0021	1800	0.0039	1800	0.0048
1200	0.0175	1800	0.0064	1800	0.0061	3000	0.0062	3600	0.0075
1800	0.0278	2400	0.0102	2700	0.0089	4200	0.0083	5400	0.0104
2400	0.0405	3000	0.0125	3600	0.0129	5400	0.0112	7200	0.0116
3000	0.052			4500	0.0164	6000	0.0137		
$y = 1.85\text{E-}05x - 0.0041$ $R^2 = 0.9968$		$y = 4.73\text{E-}06x - 0.0016$ $R^2 = 0.9872$		$y = 3.93\text{E-}06x - 0.0013$ $R^2 = 0.9977$		$y = 2.24\text{E-}06x - 0.0005$ $R^2 = 0.9796$		$y = 1.29\text{E-}06x + 0.0027$ $R^2 = 0.9734$	
Initial rate v (Ms^{-1}): 1.85E-05		Initial rate v (Ms^{-1}): 4.73E-06		Initial rate v (Ms^{-1}): 3.93E-06		Initial rate v (Ms^{-1}): 2.24E-06		Initial rate v (Ms^{-1}): 1.29E-06	

Table S-3-3. Numerical Data for Hammett Plot of Step A and B in Scheme 3

X	σ_p	log v (Ms^{-1})	
		epoxidation (Step A)	epoxide opening (Step B)
MeO	-0.28	-6.07	-4.73
Me	-0.14	-6.32	-5.32
H	0	-6.38	-5.41
F	0.06	-6.43	-5.65
CF ₃	0.53	-6.55	-5.89

3-2. Initial Rate Kinetic Studies in the Epoxide Opening Reaction of α,β -Epoxy Amide **2I** (*Scheme 4*)

General Procedure for Kinetic Experiment in *Scheme 4*

To a stirred solution of **3I** (88.5 mg, 0.5 mmol) and $\text{Sm}(\text{O-}i\text{-Pr})_3$ (0.25 mL, 0.05 mmol, 0.2 M solution in THF) in THF (5.0 mL) at 25 °C was added Me_3SiN_3 (0.13 mL, 1.0 mmol). Samples were taken at recorded times according to the following procedure: 0.3 mL of the reaction mixture was taken with syringe and immediately poured onto the mixture of 10% aqueous citric acid (1 mL) and EtOAc (1 mL). The resulting mixture was extracted with EtOAc. After evaporating the solvents, the crude residue was analyzed by ^1H NMR. Total yield of **5I** was measured by comparison of integrated area of a proton at C2 position of the **3I** (3.85 ppm) and a proton at C2 position of the **5I** (4.99 ppm)

(1) Initial Rate Kinetics on the Concentration of Catalyst $[\text{Sm}(\text{O-}i\text{-Pr})_3]$

[cat] = 2.50×10^{-3} M		[cat] = 5.00×10^{-3} M		[cat] = 7.50×10^{-3} M		[cat] = 1.0×10^{-2} M	
Time (sec)	Yield (%)	Time (sec)	Yield (%)	Time (sec)	Yield (%)	Time (sec)	Yield (%)
600	2.5	600	5.0	300	3.6	300	2.7
900	3.6	900	6.2	600	5.7	600	6.5
1200	4.2	1200	8.6	900	9.7	900	9.9
1500	5.0	1500	10.6	1200	11.7	1200	12.7
				1500	14.2	1500	18.0

$$[\text{cat}] = 2.50 \times 10^{-3} \text{ (M)} \quad \left(\begin{array}{l} y = 2.7 \times 10^{-3}x + 0.98 \\ \text{Initial Rate: } 2.7 \times 10^{-6} \text{ (M/s)} \\ R = 0.9922 \end{array} \right)$$

$$[\text{cat}] = 5.00 \times 10^{-3} \text{ (M)} \quad \left(\begin{array}{l} y = 6.4 \times 10^{-3}x + 0.89 \\ \text{Initial Rate: } 6.4 \times 10^{-6} \text{ (M/s)} \\ R = 0.9829 \end{array} \right)$$

$$[\text{cat}] = 7.50 \times 10^{-3} \text{ (M)} \quad \left(\begin{array}{l} y = 9.1 \times 10^{-3}x + 0.75 \\ \text{Initial Rate: } 9.1 \times 10^{-6} \text{ (M/s)} \\ R = 0.9887 \end{array} \right)$$

$$[\text{cat}] = 1.0 \times 10^{-2} \text{ (M)} \quad \left(\begin{array}{l} y = 1.22 \times 10^{-2}x - 1.031 \\ \text{Initial Rate: } 1.22 \times 10^{-5} \text{ (M/s)} \\ R = 0.9903 \end{array} \right)$$

Numerical Data

[cat] (M)	Initial Rate (M/s)	log [cat]	log [Initial Rate]
2.50×10^{-3}	2.7×10^{-6}	-2.602	-2.568
5.00×10^{-3}	6.4×10^{-6}	-2.301	-2.193
7.50×10^{-3}	9.1×10^{-6}	-2.124	-2.040
1.0×10^{-2}	1.22×10^{-5}	-2	-1.913

(2) Initial Rate Kinetics on the Concentration of Me_3SiN_3

[TMSN ₃] = 0.1 M		[TMSN ₃] = 0.125 M		[TMSN ₃] = 0.15 M		[TMSN ₃] = 0.175 M		[TMSN ₃] = 0.2 M	
Time (sec)	Yield (%)	Time (sec)	Yield (%)	Time (sec)	Yield (%)	Time (sec)	Yield (%)	Time (sec)	Yield (%)
300	2.5	300	2.8	300	3.0	300	2.4	300	2.2
600	5.9	600	5.5	600	6.5	600	5.8	600	6.1
900	9.1	900	8.9	900	10.6	900	7.5	900	9.7
1200	12.7	1200	12.4	1200	13.0	1200	11.6	1200	12.8
1500	15.6	1500	15.5	1500	15.4	1500	16.1	1500	16.0

[TMSN ₃] = 0.1 (M) Initial Rate: 1.1×10^{-5} (M/s)	$\left(\begin{array}{l} y = 1.1 \times 10^{-2}x - 0.768 \\ R = 0.9994 \end{array} \right)$
[TMSN ₃] = 0.125 (M) Initial Rate: 1.08×10^{-5} (M/s)	$\left(\begin{array}{l} y = 1.08 \times 10^{-2}x - 0.683 \\ R = 0.9981 \end{array} \right)$
[TMSN ₃] = 0.15 (M) Initial Rate: 1.04×10^{-5} (M/s)	$\left(\begin{array}{l} y = 1.04 \times 10^{-2}x + 0.276 \\ R = 0.987 \end{array} \right)$
[TMSN ₃] = 0.175 (M) Initial Rate: 1.1×10^{-5} (M/s)	$\left(\begin{array}{l} y = 1.1 \times 10^{-2}x - 1.233 \\ R = 0.9903 \end{array} \right)$
[TMSN ₃] = 0.2 (M) Initial Rate: 1.14×10^{-5} (M/s)	$\left(\begin{array}{l} y = 1.14 \times 10^{-2}x - 0.908 \\ R = 0.9981 \end{array} \right)$

Numerical Data

$[\text{Me}_3\text{SiN}_3]$ (M)	Initial Rate (M/s)	$\log [\text{Me}_3\text{SiN}_3]$	$\log [\text{Initial Rate}]$
0.1	1.1×10^{-5}	-1	-1.958
0.125	1.08×10^{-5}	-0.903	-1.966
0.15	1.04×10^{-5}	-0.823	-1.982
0.175	1.1×10^{-5}	-0.756	-1.958
0.2	1.14×10^{-5}	-0.698	-1.943

4. Synthesis of α,β -unsaturated amides.

α,β -Unsaturated amides (**2a–t**) and anilides (**6a–e**) were prepared from the corresponding carboxylic acid by standard methods (<Method 1>^{SI-1} (i) (COCl)₂, cat. DMF (ii) amine.; <Method 2>^{SI-2} EDCI, amine). **2a–f**, **2h**, **2i**, and **2k–t**, **6a–d** are known compounds.

(*E*)-*N,N*-dimethyl-3-(1-naphthyl)-2-propenamide (**2g**):

off-white solid; mp 58–59 °C; IR (KBr) ν 2926, 1645, 1410, 1137, 796 cm⁻¹; ¹H NMR (CDCl₃) δ 8.49 (d, J = 15.5 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 7.0 Hz, 1H), 7.57–7.46 (m, 3H), 6.95 (d, J = 15.5 Hz, 1H), 3.21 (s, 3H), 3.11 (s, 3H); ¹³C NMR (CDCl₃) δ 166.4, 139.5, 133.5, 133.0, 131.3, 129.6, 128.4, 126.5, 126.0, 125.3, 124.4, 123.7, 120.4, 37.3, 35.8; ESI-MS m/z 248 [M+Na⁺]; Anal. Calcd for C₁₅H₁₅NO: N 6.22, C 79.97, H 6.71; Found N 6.09, C 79.97, H 6.87.

(*E*)-3-(3-Furyl)-*N,N*-dimethyl-2-propenamide (**2j**):

white solid; mp 103 °C; IR (KBr) ν 3095, 2935, 1652, 1385 cm⁻¹; ¹H NMR (CDCl₃) δ 7.62 (s, 1H), 7.56 (d, J = 15.0 Hz, 1H), 7.42 (s, 1H), 6.61 (d, J = 15.0 Hz, 1H), 6.59 (s, 1H), 3.15 (s, 3H), 3.05 (s, 3H); ¹³C NMR (CDCl₃) δ 166.5, 144.0, 143.8, 132.3, 122.9, 116.8, 107.3, 37.2, 35.7; ESI-MS m/z 188 [M+Na⁺]; Anal. Calcd for C₉H₁₁NO₂: N 8.48, C 65.44, H 6.71; Found N 8.51, C 65.37, H 6.71.

(*E*)-3-Phenyl-*N*-(4-trifluoromethylphenyl)-2-propenamide (**6e**):

white solid; mp 187 °C; IR (KBr) ν 3326, 1660, 1623, 1529, 1325 cm⁻¹; ¹H NMR (CDCl₃) δ 7.79 (d, J = 15.6 Hz, 1H), 7.76 (d, J = 8.6 Hz, 2H), 7.61 (d, J = 8.6 Hz, 2H), 7.55 (m, 2H), 7.47 (br-s, 1H), 7.40 (m, 3H), 6.56 (d, J = 15.6 Hz, 1H); ¹³C NMR (DMSO-*d*₆) δ 164.1, 142.8, 141.1, 134.5, 129.9, 129.0, 127.8, 126.6 (d, J = 271 Hz) 126.1, 123.3 (ddd, J = 32, 32, 32 Hz), 121.7, 119.1; ESI-MS m/z 314 [M+Na⁺]; Anal. Calcd for C₁₆H₁₂F₃NO: N 4.81, C 65.98, H 4.15; Found N 4.73, C 65.97, H 4.37.

5. Synthesis of α,β -epoxy amides.

Chiral α,β -epoxy amide **3a**, **3l**, and **3o** (99% ee) were prepared from **2a**, **2l**, and **2o**, respectively by catalytic asymmetric epoxidation using Sm-(*S*)-BINOL-Ph₃As=O (1:1:1) complex **1**.^{9a} Racemic α,β -epoxy anilides **7a–e** were prepared from **6a–e** [*m*CPBA, KHCO₃, CH₂Cl₂, rt, (25~45% yield)]. Chiral **7a–e** were prepared by catalytic asymmetric epoxidation using Sm-(*S*)-BINOL-Ph₃As=O (1:1:1) complex **1** (see kinetic study section). **7c** is known compound.^{SI-3}

(2*R*,3*S*)-*N*-(4-Methoxyphenyl)-3-phenyl-oxiranecarboxamide (**7a**):

white solid; mp 162 °C; IR (KBr) ν 3279, 1669, 1509, 1233, 829 cm⁻¹; ¹H NMR (CDCl₃) δ 7.85 (br-s, 1H), 7.48 (d, *J* = 9.0 Hz, 2H), 7.38 (m, 3H), 7.31 (m, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 4.03 (d, *J* = 1.6 Hz, 1H), 3.81 (s, 3H), 3.65 (d, *J* = 1.6 Hz, 1H); ¹³C NMR (CDCl₃) δ 165.1, 156.7, 134.5, 129.7, 129.1, 128.7, 125.8, 121.4, 114.2, 59.3, 59.2, 55.4; ESI-MS *m/z* 292 [M+Na⁺]; Anal. Calcd for C₁₆H₁₅NO₃: N 5.20, C 71.36, H 5.61; Found N 5.11, C 71.33, H 5.67; [α]_D²⁴ -23.9 (*c* 1.55, CHCl₃) (95% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/1, flow 0.5 mL/min, detection at 254 nm) *t*_R 35.9 min (major) and 44.4 min (minor).

(2*R*,3*S*)-*N*-(4-Methylphenyl)-3-phenyl-oxiranecarboxamide (**7b**):

white solid; mp 168–170 °C; IR (KBr) ν 3334, 1671, 1551, 821 cm⁻¹; ¹H NMR (CDCl₃) δ 7.88 (br-s, 1H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.38 (m, 3H), 7.16 (d, *J* = 8.5 Hz, 2H), 4.03 (d, *J* = 2.0 Hz, 1H), 3.65 (d, *J* = 2.0 Hz, 1H), 2.33 (s, 3H); ¹³C NMR (CDCl₃) δ 165.1, 134.6, 134.5, 134.1, 129.6, 128.7, 125.8, 119.7, 59.3, 59.2, 20.9; ESI-MS *m/z* 276 [M+Na⁺]; HR-MS [FAB(+)] Calcd for C₁₆H₁₆NO₂⁺ [M+H⁺]: 297.1352; Found 297.1347; [α]_D²⁴ -39.8 (*c* 1.60, CHCl₃) (92% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/1, flow 0.5 mL/min, detection at 254 nm) *t*_R 18.6 min (minor) and 24.6 min (major).

(2*R*,3*S*)-*N*,3-Diphenyl-oxiranecarboxamide (**7c**):^{SI-3}

white solid; [α]_D²⁴ -34.1 (*c* 1.69, CHCl₃) (90% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/1, flow 0.5

mL/min, detection at 254 nm) t_R 15.9 min (minor) and 28.1 min (major).

(2*R*,3*S*)-3-Phenyl-*N*-(4-fluorophenyl)oxiranecarboxamide (7d):

white solid; mp 143–145 °C; IR (KBr) ν 3328, 1671, 1560, 1509, 839 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.92 (br-s, 1H), 7.55 (dd, $J=8.9$, 4.6 Hz, 2H), 7.39 (m, 3H), 7.31 (m, 2H), 7.05 (dd, $J=8.9$, 8.7 Hz, 2H), 4.04 (d, $J=1.8$ Hz, 1H), 3.66 (d, $J=1.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 165.2, 160.0 (d, $J=244$ Hz), 134.3, 132.7, 129.2, 128.7, 125.8, 121.5 (d, $J=7.2$ Hz), 115.8 (d, $J=23$ Hz), 59.3, 59.1; ESI-MS m/z 280 $[\text{M}+\text{Na}^+]$; Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{FNO}_2$: N 5.44, C 70.03, H 4.70; Found N 5.19, C 69.87, H 5.00; $[\alpha]_D^{24}$ -26.9 (c 1.04, CHCl_3) (91% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/1, flow 0.5 mL/min, detection at 254 nm) t_R 16.1 min (minor) and 26.8 min (major).

(2*R*,3*S*)-3-Phenyl-*N*-(4-trifluoromethylphenyl)oxiranecarboxamide (7e):

white solid; mp 166–169 °C; IR (KBr) ν 3314, 1685, 1542, 1331, 1115 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.08 (br-s, 1H), 7.72 (d, $J=8.3$ Hz, 2H), 7.62 (d, $J=8.3$ Hz, 2H), 7.40 (m, 3H), 7.31 (m, 2H), 4.06 (d, $J=1.9$ Hz, 1H), 3.69 (d, $J=1.9$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 165.6, 139.7, 134.1, 129.3, 128.7, 126.9 (d, $J=33$ Hz), 126.4, 125.8, 123.9 (d, $J=271$ Hz), 119.4, 59.3, 59.1; ESI-MS m/z 330 $[\text{M}+\text{Na}^+]$; Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{F}_3\text{NO}_2$: N 4.56, C 62.54, H 3.94; Found N 4.29, C 62.76, H 4.22; $[\alpha]_D^{25}$ -35.5 (c 1.24, CHCl_3) (88% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/1, flow 0.5 mL/min, detection at 254 nm) t_R 9.9 min (minor) and 13.3 min (major).

6. Synthesis of *anti*- β -azido- α -hydroxyamides

Procedure for Catalytic Regioselective Epoxide Opening of **3a** with Me_3SiN_3 (Table 1, entry 3)

To a stirred solution of **3a** (95.6 mg, 0.5 mmol) and $\text{Sm}(\text{O}-i\text{-Pr})_3$ (0.005 mL, 0.001 mmol, 0.2 M solution in THF) in THF (0.1 mL) at room temperature was added Me_3SiN_3 (0.132 mL, 1.00 mmol). After the consumption of the starting material (2 h), the reaction was cooled with ice bath and 1N HCl aq.–MeOH (1:1) was added. The mixture was allowed to warm to room

temperature and stirred until desilylation was completed (1 h). The resulting mixture was diluted with ethyl acetate, and then poured into saturated aqueous NaHCO₃. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, and then dried over Na₂SO₄. After concentration under reduced pressure, the resulting residue was purified by flash column chromatography (SiO₂, hexane/ethyl acetate =4/1 to 2/1) to give **4a** (113 mg, 97%).

General Procedure for One-Pot Sequential Catalytic Asymmetric Epoxidation-Regioselective Epoxide Opening Process with Me₃SiN₃ Using Sm-(*S*)-BINOL-Ph₃As=O Complex 1. (Table 2, 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 [500 mg (1000 mg/mmol of starting material)] in THF (2.5 mL) at room temperature was added Sm(O-*i*-Pr)₃ (0.125 mL, 0.025 mmol, 0.2 M solution in THF). After stirring for 30 min, TBHP (0.12 mL, 0.60 mmol, 5 M solution in decane) was added and the stirring was continued for 10 min at the same temperature. **2a** (87.6 mg, 0.500 mmol) was added directly and the mixture was stirred at room temperature. After a consumption of the starting material (12 h), Me₃SiN₃ (0.13 mL, 1.0 mmol) was added and the reaction mixture was stirred at room temperature. After a consumption of the corresponding α,β-epoxy amide (1 h), the reaction was cooled with ice bath and 1N HCl aq.-MeOH (1:1) was added. The mixture was allowed to warm to room temperature and stirred until desilylation was completed (1~3 h). The mixture was filtered through a celite pad and diluted with ethyl acetate, then poured into saturated aqueous NaHCO₃. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with 10% aqueous Na₂S₂O₃ and brine, then dried over Na₂SO₄. After concentration under reduced pressure, the resulting residue was purified by flash column chromatography (SiO₂, hexane/ethyl acetate =4/1 to 2/1) to give **4a** (116 mg, 99%, 99% ee).

(2*R*,3*R*)-3-Azido-2-hydroxy-*N,N*-dimethyl-3-phenylpropanamide (4a**):**

off-white solid; mp 73 °C; IR (KBr) ν 3185, 2127, 1629, 1290, 1102, 698 cm⁻¹; ¹H NMR (CDCl₃) δ 7.42-7.35 (m, 5H), 4.66-4.59 (m, 2H), 3.60 (d, *J* = 8.5 Hz, 1H), 3.02 (s, 3H), 2.92 (s, 3H); ¹³C NMR (CDCl₃) δ

171.2, 135.7, 128.9, 128.8, 127.8, 70.2, 68.7, 36.9, 36.1; ESI-MS *m/z* 257 [M+Na⁺]; Anal. Calcd

for C₁₁H₁₄N₄O₂: N 23.92, C 56.40, H 6.02; Found N 23.74, C 56.52, H 6.10; [α]_D²⁵ -130 (*c* 1.03, CHCl₃) (99% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/4, flow 0.5 mL/min, detection at 254 nm) *t*_R 19.4 min (minor) and 22.4 min (major).

4-[(2*R*,3*R*)-3-Azido-2-hydroxy-1-oxo-3-phenylpropyl]morpholine (4b):

pale yellow solid; mp 88 °C; IR (KBr) ν 3197, 2968, 2845, 2106, 1617, 1260, 1115, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 7.44-7.35 (m, 5H), 4.64 (d, *J* = 7.0 Hz, 1H), 4.56 (dd, *J* = 7.6, 7.0 Hz, 1H), 3.73-3.53 (m, 7H), 3.37 (m, 2H); ¹³C NMR (CDCl₃) δ 170.0, 135.6, 129.0, 128.9, 127.7, 69.8, 68.7, 66.5, 66.3, 46.0, 43.0; ESI-MS *m/z* 299 [M+Na⁺]; Anal. Calcd for C₁₃H₁₆N₄O₃: N 20.28, C 56.51, H 5.84; Found N 20.00, C 56.76, H 5.98; [α]_D²⁵ -116 (*c* 1.10, CHCl₃) (99% ee); The enantiomeric excess was determined after conversion to the corresponding *N*-Boc amine **S1** [cat. Pd-C, Boc₂O, H₂ (1 atm), EtOAc, rt].

4-[(2*R*,3*R*)-3-(*tert*-butoxycarbonylamino)-2-hydroxy-1-oxo-3-phenylpropyl]morpholine (S1):

white foam; IR (KBr) ν 3393, 2976, 2859, 1708, 1647, 1497 cm⁻¹; ¹H NMR (CDCl₃) δ 7.44-7.20 (m, 5H), 5.79 (d, *J* = 8.3 Hz, 1H), 4.88 (d, *J* = 8.3 Hz, 1H), 4.78 (d, *J* = 7.9 Hz, 1H), 3.74-3.45 (m, 9H), 1.44 (s, 9H); ¹³C NMR (CDCl₃) δ 169.6, 155.3, 136.0, 128.4, 128.2, 127.1, 69.9, 66.5, 66.3, 56.9, 45.5, 42.6, 28.3; ESI-MS *m/z* 373 [M+Na⁺]; HR-MS [FAB(+)] Calcd for C₁₈H₂₇N₂O₅⁺ [M+H⁺]: 351.1920; Found 351.1924; [α]_D²⁶ +7.4 (*c* 1.29, CHCl₃) (99% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/4, flow 0.5 mL/min, detection at 254 nm) *t*_R 23.7 min (minor) and 28.2 min (major).

(2*R*,3*R*)-3-Azido-2-hydroxy-3-(4-methoxyphenyl)-*N,N*-dimethylpropanamide (4c):

pale yellow solid; mp 74 °C; IR (KBr) ν 3435, 2100, 1639, 1509, 1251, 1068 cm⁻¹; ¹H NMR (CDCl₃) δ 7.27 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.60-4.56 (m, 2H), 3.82 (s, 3H), 3.53 (d, *J* = 7.7 Hz, 1H), 3.02 (s, 3H), 3.00 (s, 3H); ¹³C NMR (CDCl₃) δ 171.3, 159.9, 129.0, 127.5, 114.1, 70.1, 68.0, 55.2, 36.8, 36.0; ESI-MS *m/z* 287 [M+Na⁺]; HR-MS [FAB(+)] Calcd for

$C_{12}H_{17}N_4O_3^+$ $[M+H]^+$: 265.1301; Found 265.1310. $[\alpha]_D^{25}$ -146 (c 1.17, $CHCl_3$) (>99% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/4, flow 0.5 mL/min, detection at 254 nm) t_R 29.5 min (minor) and 35.1 min (major).

4-[(2*R*,3*R*)-3-Azido-2-hydroxy-3-(4-methoxyphenyl)-1-oxopropyl]morpholine (4d):

off-white solid; mp 107 °C; IR (KBr) ν 3200, 3020, 2964, 2104, 1603, 1250, 1116, 1032 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.29 (d, J = 9.0 Hz, 2H), 6.94 (d, J = 9.0 Hz, 2H), 4.59-4.51 (m, 2H), 3.82 (s, 3H), 3.73-3.54 (m, 6H), 3.53 (d, J = 8.5 Hz, 1H), 3.41 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 170.1, 160.0, 129.0, 127.3, 114.2, 69.7, 68.2, 66.5, 66.4, 55.2, 46.0, 42.9; ESI-MS m/z 329 $[M+Na]^+$; Anal. Calcd for $C_{14}H_{18}N_4O_4$: N 18.29, C 54.89, H 5.92; Found N 18.22, C 54.99, H 5.97; $[\alpha]_D^{25}$ -124 (c 1.34, $CHCl_3$) (99% ee); The enantiomeric excess was determined after conversion to the corresponding *N*-Boc amine **16d**.

(2*R*,3*R*)-3-Azido-2-hydroxy-*N,N*-dimethyl-3-(4-methylphenyl)propanamide (4e):

pale yellow solid; mp 76 °C; IR (KBr) ν 3245, 2101, 1621, 1075 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.26-7.21 (m, 4H), 4.64-4.59 (m, 2H), 3.65 (d, J = 8.5 Hz, 1H), 3.02 (s, 3H), 2.95 (s, 3H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.2, 138.6, 129.4, 132.5, 129.4, 127.6, 70.0, 68.3, 36.8, 36.0, 21.1; ESI-MS m/z 271 $[M+Na]^+$; Anal. Calcd for $C_{12}H_{16}N_4O_2$: N 22.57, C 58.05, H 6.50; Found N 22.42, C 58.27, H 6.56; $[\alpha]_D^{25}$ -155 (c 1.17, $CHCl_3$) (99% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/4, flow 0.5 mL/min, detection at 254 nm) t_R 19.1 min (minor) and 21.6 min (major).

(2*R*,3*R*)-3-Azido-3-(4-fluorophenyl)-2-hydroxy-*N,N*-dimethylpropanamide (4f):

off-white solid; mp 80 °C; IR (KBr) ν 3185, 2127, 1628, 1509, 1237, 830 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.34 (dd, J = 8.6, 8.4 Hz, 2H), 7.09 (dd, J = 8.6, 5.5 Hz, 2H), 4.62-4.54 (m, 2H), 3.57 (d, J = 8.6 Hz, 1H), 3.03 (s, 3H), 3.00 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.2, 162.8 (d, J = 247 Hz), 131.5, 129.5 (d, J = 8.3 Hz), 115.7 (d, J = 22 Hz), 70.0, 67.7, 36.9, 36.1; ESI-MS m/z 275 $[M+Na]^+$; Anal.

Calcd for $C_{11}H_{13}FN_4O_2$: N 22.21, C 52.38, H 5.19; Found N 22.05, C 52.49, H 5.27; $[\alpha]_D^{26} -119$ (c 1.19, $CHCl_3$) (>99% ee); HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm) t_R 12.6 min (major) and 17.7 min (minor).

(2*R*,3*R*)-3-Azido-2-hydroxy-*N,N*-dimethyl-3-(1-naphthyl)propanamide (4g):

pale yellow oil; IR (neat) ν 3379, 3049, 2936, 2104, 1644, 1256, 1078, 781 cm^{-1} ; 1H NMR ($CDCl_3$) δ 8.13 (d, J = 8.15 Hz, 1H), 7.91-7.86 (m, 2H), 7.61-7.49 (m, 4H), 5.56 (d, J = 5.5 Hz, 1H), 4.90 (dd, J = 8.5, 7.3 Hz, 1H), 2.94 (s, 3H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.9, 133.7, 131.2, 131.0, 129.4, 129.2, 126.8, 125.9, 125.7, 125.2, 122.2, 69.7, 66.0, 36.5, 35.9; ESI-MS m/z 307 $[M+Na^+]$; HR-MS [FAB(+)] Calcd for $C_{15}H_{17}N_4O_2^+ [M+H^+]$: 285.1352; Found 285.1338; $[\alpha]_D^{25} -55.3$ (c 1.45, $CHCl_3$) (98% ee); HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 1/9, flow 0.5 mL/min, detection at 254 nm) t_R 27.7 min (major) and 44.5 min (minor).

(2*R*,3*R*)-3-Azido-2-hydroxy-*N,N*-dimethyl-3-(2-naphthyl)propanamide (4h):

white solid; mp 141 $^{\circ}C$; IR (KBr) ν 3336, 2102, 1624, 1263, 752 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.90-7.82 (m, 4H), 7.53-7.46 (m, 3H), 4.82 (d, J = 7.0 Hz, 1H), 4.70 (dd, J = 7.8, 7.0 Hz, 1H), 3.67 (m, 1H), 3.03 (s, 3H), 2.94 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.2, 133.3, 133.0, 128.7, 128.0, 127.7, 127.5, 126.5, 126.5, 124.6, 69.9, 68.9, 37.0, 36.1; ESI-MS m/z 307 $[M+Na^+]$; Anal. Calcd for $C_{15}H_{16}N_4O_2$: N 19.71, C 63.37, H 5.67; Found N 19.67, C 63.54, H 5.77; $[\alpha]_D^{26} -150$ (c 1.13, $CHCl_3$) (>99% ee); HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 1/4, flow 0.5 mL/min, detection at 254 nm) t_R 35.5 min (major) and 59.8 min (minor).

(2*R*,3*R*)-3-Azido-3-(2-furyl)-2-hydroxy-*N,N*-dimethylpropanamide (4i):

pale yellow oil; IR (neat) ν 3398, 2936, 2106, 1644, 1255 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.45 (s, 1H), 6.47 (s, 1H), 6.40 (s, 1H), 4.80 (dd, J = 8.6, 7.0 Hz, 1H), 4.60 (d, J = 7.0 Hz, 1H), 3.73 (d, J = 8.6 Hz, 1H), 3.03 (s, 3H), 3.02 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.8, 148.4, 143.2, 110.6, 110.2, 68.4, 61.5, 36.9, 36.1; ESI-MS m/z 247 $[M+Na^+]$; HR-MS [FAB(+)] Calcd for $C_9H_{13}N_4O_3^+ [M+H^+]$: 225.0988;

Found 225.0980. $[\alpha]_D^{24}$ -140 (*c* 1.68, CHCl₃) (>99% ee); HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm) *t_R* 13.3 min (major) and 17.4 min (minor).

(2*R*,3*R*)-3-Azido-3-(3-furyl)-2-hydroxy-*N,N*-dimethylpropanamide (4j):

brown solid; mp 75–76 °C; IR (KBr) ν 3174, 2950, 2128, 1624, 1275

cm⁻¹; ¹H NMR (CDCl₃) δ 7.52 (s, 1H), 7.46 (s, 1H), 6.48 (s, 1H), 4.62–4.51 (m, 2H), 3.71 (d, *J* = 8.0 Hz, 1H), 3.06 (s, 3H), 3.02 (s, 3H);

¹³C NMR (CDCl₃) δ 170.9, 143.7, 141.1, 119.7, 109.2, 70.0, 60.0, 36.9, 36.2; ESI-MS *m/z* 247 [M+Na⁺]; Anal. Calcd for C₉H₁₂N₄O₃: N 24.99, C 48.21, H 5.39; Found N 24.93, C 48.48, H 5.47; $[\alpha]_D^{25}$ -53.6 (*c* 1.03, CHCl₃) (>99% ee); HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm) *t_R* 15.6 min (major) and 17.6 min (minor).

(*E*)-(2*R*,3*R*)-3-Azido-2-hydroxy-*N,N*-dimethyl-5-phenyl-4-pentenamide (4k):

pale yellow solid; mp 101–102 °C; IR (KBr) ν 3398, 2941, 2104,

1638, 1081 cm⁻¹; ¹H NMR (CDCl₃) δ 7.43–7.26 (m, 5H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.26 (dd, *J* = 15.9, 8.3 Hz, 1H), 4.54 (dd, *J* = 8.3,

5.8 Hz, 1H), 4.11 (dd, *J* = 8.3, 5.8 Hz, 1H), 3.80 (d, *J* = 8.3 Hz, 1H), 3.09 (s, 3H), 3.03 (s, 3H); ¹³C NMR (CDCl₃) δ 170.9, 135.7, 135.5, 128.5, 128.3, 126.7, 121.8, 69.8, 66.1, 36.8, 36.1; ESI-MS *m/z* 283 [M+Na⁺]; HR-MS [FAB(+)] Calcd for C₁₃H₁₇N₄O₂⁺ [M+H⁺]: 261.1352; Found 261.1361. $[\alpha]_D^{25}$ +19.0 (*c* 1.17, CHCl₃) (>99% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm) *t_R* 20.3 min (minor) and 22.5 min (major).

(2*R*,3*R*)-3-Azido-2-hydroxy-*N*-methyl-3-phenylpropanamide (4l):

pale yellow solid; mp 70–71 °C; IR (KBr) ν 3420, 3254, 2100, 1650, 1541, 1112, 712 cm⁻¹; ¹H NMR (CDCl₃) δ 7.40–7.35 (m, 5H), 6.10 (br-s,

1H), 5.06 (d, *J* = 4.5 Hz, 1H), 4.39 (dd, *J* = 4.5, 4.5 Hz, 1H), 3.00 (d, *J* = 4.5 Hz, 1H), 2.70 (d, *J* = 5.0 Hz, 3H); ¹³C NMR (CDCl₃) δ 170.4, 134.2, 128.7, 128.4, 128.0, 74.0, 67.1, 25.7; ESI-MS *m/z* 243 [M+Na⁺]; Anal. Calcd for C₁₀H₁₂N₄O₂: N 25.44, C 54.54, H 5.49; Found N 25.27, C

54.72, H 5.49; $[\alpha]_D^{24} -90.7$ (c 0.820, CHCl_3) (99% ee); HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm) t_R 8.2 min (major) and 10.8 min (minor).

(1*R*,2*R*)-2-Azido-*N*-benzyl-1-hydroxycyclopentanecarboxamide (4m):

pale yellow oil; IR (neat) ν 3346, 2924, 2102, 1650, 1530, 1260 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.32-7.21 (m, 5H), 6.85 (br-s, 1H), 4.50 (dd, $J = 14.5, 5.5$ Hz, 1H), 4.44 (dd, $J = 14.5, 5.5$ Hz, 1H), 3.78 (t, $J = 5.0$ Hz, 1H), 3.69 (br-s, 1H), 2.25-2.09 (m, 2H), 1.97-1.75 (m, 6H); ^{13}C NMR (CDCl_3) δ 172.8, 137.6, 128.7, 127.6, 82.7, 70.3, 44.0, 36.4, 29.7, 20.5; ESI-MS m/z 283 $[\text{M}+\text{Na}^+]$; HR-MS $[\text{FAB}(+)]$ Calcd for $\text{C}_{13}\text{H}_{17}\text{N}_4\text{O}_2^+ [\text{M}+\text{H}^+]$: 261.1352; Found 261.1344; $[\alpha]_D^{24} -57.4$ (c 1.17, CHCl_3) (96% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm) t_R 15.7 min (major) and 31.0 min (minor).

(1*R*,2*R*)-2-Azido-*N*-benzyl-1-hydroxycyclohexanecarboxamide (4n):

off-white solid; mp 96–98 °C; IR (KBr) ν 3388, 2929, 2095, 1649, 1527, 727 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.36-7.20 (m, 5H), 6.91 (br-s, 1H), 4.52 (dd, $J = 15.0, 6.0$ Hz, 1H), 4.46 (dd, $J = 15.0, 6.0$ Hz, 1H), 3.63 (br-s, 1H), 3.54 (t, $J = 5.0$ Hz, 1H), 2.10 (m, 2H), 1.86 (m, 1H), 1.72-1.65 (m, 3H), 1.53-1.46 (m, 2H); ^{13}C NMR (CDCl_3) δ 173.8, 137.7, 128.7, 127.5, 127.5, 73.9, 43.7, 33.3, 29.6, 26.2, 21.0; ESI-MS m/z 297 $[\text{M}+\text{Na}^+]$; HR-MS $[\text{FAB}(+)]$ Calcd for $\text{C}_{14}\text{H}_{19}\text{N}_4\text{O}_2^+ [\text{M}+\text{H}^+]$: 275.1508; Found 275.1503. $[\alpha]_D^{24} -48.0$ (c 1.03, CHCl_3) (99% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm) t_R 16.1 min (major) and 19.7 min (minor).

(2*R*,3*R*)-3-Azido-2-hydroxy-*N,N*-dimethyl-5-phenylpentanamide (4o):

colorless oil; IR (neat) ν 3391, 2929, 2105, 1644, 1254, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.31-7.17 (m, 5H), 4.51 (dd, $J = 7.9, 4.9$ Hz, 1H), 3.74 (d, $J = 7.9$ Hz, 1H), 3.14 (m, 1H), 2.96 (s, 3H), 2.89 (m, 1H), 2.85 (s, 3H), 2.65 (m, 1H), 2.00 (m, 1H), 1.85 (m, 1H); ^{13}C NMR (CDCl_3) δ 171.2, 140.6, 128.4, 128.4, 126.1, 70.5, 62.1, 36.5, 36.0, 31.7, 29.8; ESI-MS m/z 285 $[\text{M}+\text{Na}^+]$; HR-MS

[FAB(+)] Calcd for $C_{13}H_{19}N_4O_2^+$ $[M+H]^+$: 263.1508; Found 263.1505; $[\alpha]_D^{24} +55.6$ (*c* 2.35, $CHCl_3$) (98% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm) t_R 10.9 min (minor) and 14.3 min (major).

4-[(2*R*,3*R*)-3-Azido-2-hydroxy-1-oxo-5-phenylpentyl]morpholine (4p):

off-white solid; mp 62-63 °C; IR (KBr) ν 3267, 2911, 2849, 2099, 1624, 1264, 1113 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.32-7.18 (m, 5H), 4.46 (dd, $J = 7.9, 4.9$ Hz, 1H), 3.71-3.49 (m, 6H), 3.25 (m, 3H), 3.03 (m, 1H), 2.89 (m, 1H), 2.66 (m, 1H), 2.04 (m, 1H), 1.83 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 170.0, 140.5, 128.6, 128.5, 126.3, 70.4, 66.4, 66.0, 62.0, 45.6, 43.0, 31.5, 29.7; ESI-MS m/z 327 $[M+Na]^+$; HR-MS [FAB(+)] Calcd for $C_{15}H_{21}N_4O_3^+$ $[M+H]^+$: 305.1614; Found 305.1608; $[\alpha]_D^{24} +25.6$ (*c* 1.03, $CHCl_3$) (98% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm) t_R 22.6 min (minor) and 37.2 min (major).

(2*R*,3*R*)-3-Azido-2-hydroxy-*N,N*-dimethylhexanamide (4q):

colorless oil; IR (neat) ν 3389, 2960, 2108, 1644, 1258, 1086 cm^{-1} ; 1H NMR ($CDCl_3$) δ 4.47 (dd, $J = 8.0, 5.8$ Hz, 1H), 3.70 (d, $J = 8.0$ Hz, 1H), 3.22 (m, 1H), 3.04 (s, 3H), 3.02 (s, 3H), 1.67-1.36 (m, 4H), 0.92 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 171.7, 70.3, 63.8, 36.7, 36.1, 30.6, 19.1, 13.7; ESI-MS m/z 223 $[M+Na]^+$; HR-MS [FAB(+)] Calcd for $C_8H_{17}N_4O_2^+$ $[M+H]^+$: 201.1352; Found 201.1355; $[\alpha]_D^{24} +13.1$ (*c* 1.39, $CHCl_3$) (98% ee); The enantiomeric excess was determined after conversion to the corresponding benzoate **S2**. HPLC conditions for **S2** (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 2/98, flow 1.0 mL/min, detection at 254 nm) t_R 10.0 min (major) and 12.1 min (minor).

(2*R*,3*R*)-3-Azido-3-cyclohexyl-2-hydroxy-*N,N*-dimethylpropanamide (4r):

white solid; mp 107-108 °C; IR (KBr) ν 3159, 2926, 2852, 2097, 1619, 1259, 1072 cm^{-1} ; 1H NMR ($CDCl_3$) δ 4.39 (dd, $J = 9.2, 9.2$ Hz, 1H), 3.48 (d, $J = 9.2$ Hz, 1H), 3.26 (dd, $J = 9.2, 2.8$ Hz, 1H), 3.08 (s, 3H), 3.05 (s, 3H), 1.95 (m, 1H), 1.78-1.62 (m, 5H), 1.35-1.13 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 173.1,

71.6, 66.4, 38.6, 37.0, 36.2, 30.9, 26.3, 26.2, 25.9; ESI-MS m/z 263 $[M+Na^+]$; HR-MS [FAB(+)] Calcd for $C_{11}H_{21}N_4O_2^+ [M+H^+]$: 241.1665; Found 241.1672; $[\alpha]_D^{25}$ -16.0 (c 1.08, $CHCl_3$) (99% ee); The enantiomeric excess was determined after conversion to the corresponding benzoate **S3**. HPLC conditions for **S3** (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 2/98, flow 0.5 mL/min, detection at 254 nm) t_R 17.3 min (major) and 19.4 min (minor).

β -Azido- α -hydroxyanilides **8a-e** were prepared from racemic α,β -epoxy anilides **7a-e**.

(2*R,3*R**)-3-Azido-2-hydroxy-*N*-(4-methoxyphenyl)-3-phenylpropanamide (8a):**

white solid; mp 110–111 °C; IR (KBr) ν 3352, 2099, 1646, 1546, 1509, 1102, 832 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.88 (s, 1H), 7.40–7.33 (m, 5H), 7.18 (d, J = 8.9 Hz, 2H) 6.79 (d, J = 8.9 Hz, 2H) 5.17 (d, J = 3.7 Hz, 1H) 4.54 (dd, J = 3.8, 3.7 Hz, 1H), 3.82 (br-s, 1H), 3.75 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 167.8, 156.8, 134.0, 129.3, 128.8, 128.5, 128.0, 122.1, 114.0, 74.2, 67.2, 55.3; ESI-MS m/z 335 $[M+Na^+]$; HR-MS [FAB(+)] Calcd for $C_{16}H_{17}N_4O_3^+ [M+H^+]$: 313.1302; Found 313.1308.

(2*R,3*R**)-3-Azido-2-hydroxy-*N*-(4-methylphenyl)-3-phenylpropanamide (8b):**

white solid; mp 131–132 °C; IR (KBr) ν 3345, 2098, 1647, 1542, 1103 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.84 (s, 1H), 7.39–7.35 (m, 5H), 7.18 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.3 Hz, 2H), 5.18 (d, J = 3.7 Hz, 1H), 4.54 (s, 1H), 3.55 (s, 1H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 167.6, 134.6, 134.0, 133.8, 129.4, 128.9, 128.6, 128.0, 120.2, 74.3, 67.3, 20.8; ESI-MS m/z 319 $[M+Na^+]$; HR-MS [FAB(+)] Calcd for $C_{16}H_{17}N_4O_2^+ [M+H^+]$: 297.1352; Found 297.1360.

(2*R,3*R**)-3-Azido-2-hydroxy-3-*N*-phenylpropanamide (8c):**

white solid; mp 94–96 °C; IR (KBr) ν 3347, 2097, 1649, 1544, 1102, 693 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.94 (s, 1H), 7.40–7.25 (m, 9H), 7.10 (m, 1H), 5.18 (d, J = 4.0 Hz, 1H), 4.56 (s, 1H), 3.70 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 167.8, 136.3, 133.9, 128.9, 128.6, 128.0, 124.9, 120.2, 74.3, 67.2; ESI-MS m/z 305 $[M+Na^+]$; Anal. Calcd for $C_{15}H_{14}N_4O_2$: N 19.85, C 63.82, H 5.00; Found N

19.55, C 63.84, H 5.17.

(2*R,3*R**)-3-Azido-*N*-(4-fluorophenyl)-2-hydroxy-3-phenylpropanamide (8d):**

white solid; mp 107–108 °C; IR (KBr) ν 3291, 2106, 1637, 1509, 1119 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.91 (s, 1H), 7.38–7.35 (m, 5H), 7.24 (dd, J = 8.3, 4.9 Hz, 2H), 6.95 (dd, J = 8.3, 8.3 Hz, 2H), 5.17 (d, J = 3.1 Hz, 1H), 4.56 (s, 1H), 3.63 (s, 1H); ^{13}C NMR (CDCl_3) δ 167.8, 160.0 (d, J = 244 Hz), 133.8, 132.3, 128.9, 128.6, 128.0, 122.1 (d, 8.3 Hz), 115.6 (d, J = 23 Hz), 74.3, 67.2; ESI-MS m/z 323 [$\text{M}+\text{Na}^+$]; Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{FN}_4\text{O}_2$: N 18.66, C 60.00, H 4.36; Found N 18.41, C 60.08, H 4.58.

(2*R,3*R**)-3-Azido-2-hydroxy-3-phenyl-*N*-(4-trifluoromethylphenyl)propanamide (8e):**

white solid; mp 95–96 °C; IR (KBr) ν 3293, 2106, 1671, 1335, 1109 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.00 (s, 1H), 7.52 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.38–7.35 (m, 5H), 5.21 (d, J = 3.4 Hz, 1H), 4.60 (s, 1H), 3.24 (s, 1H); ^{13}C NMR (CDCl_3) δ 168.0, 139.4, 133.6, 129.1, 128.7, 128.0, 126.6 (d, J = 32 Hz), 126.2, 123.9 (d, J = 272 Hz), 119.6, 74.4, 67.2; ESI-MS m/z 373 [$\text{M}+\text{Na}^+$]; HR-MS [FAB(+)] Calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N}_4\text{O}_2$ [$\text{M}+\text{H}^+$]: 351.1069; Found 351.1052.

7. Synthesis of β -phenylthio- α -hydroxyamides

General Procedure for One-Pot Sequential Catalytic Asymmetric Epoxidation-Regioselective Epoxide Opening Process with PhSSiMe_3 Using Sm-(*S*)-BINOL- $\text{Ph}_3\text{As}=\text{O}$ Complex **1** (Table 5, 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 (1000 mg/mmol of starting material)] in THF (2.5 mL) at room temperature was added $\text{Sm}(\text{O}-i\text{-Pr})_3$ (0.125 mL, 0.025 mmol, 0.2 M solution in THF). After stirring for 30 min, TBHP (0.060 mL, 0.30 mmol, 5 M solution in decane) was added and the stirring was continued for 10 min at the same temperature. **2a** (43.8 mg, 0.250 mmol) was added directly and the mixture was stirred at room temperature. After a consumption of the starting material (11 h), PhSSiMe_3 (0.095 mL, 0.50 mmol) was added and the reaction mixture was

stirred at room temperature. After a consumption of the corresponding α,β -epoxy amide (1 h), the reaction was cooled with ice bath and 1N HCl aq.–MeOH (1:1) was added. The mixture was allowed to warm to room temperature and stirred until desilylation was completed (1~3 h). The mixture was filtered through a celite pad and diluted with Et₂O, then poured into saturated aqueous NaHCO₃. The aqueous layer was extracted with Et₂O and the combined organic layers were washed with brine, and then dried over Na₂SO₄. After concentration under reduced pressure, the resulting residue was purified by flash column chromatography (SiO₂, hexane/ethyl acetate =8/1 to 2/1) to give **9a** (64.7 mg, 86%, 99% ee).

General Procedure for One-Pot Sequential Catalytic Asymmetric Epoxidation-Regioselective Epoxide Opening Process with PhSH Using Sm-(*S*)-BINOL-Ph₃As=O Complex (Table 5, entry 2)

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 (1000 mg/mmol of starting material)] in THF (2.5 mL) at room temperature was added Sm(O-*i*-Pr)₃ (0.125 mL, 0.025 mmol, 0.2 M solution in THF). After stirring for 30 min, TBHP (0.060 mL, 0.30 mmol, 5 M solution in decane) was added and the stirring was continued for 10 min at the same temperature. **2a** (43.8 mg, 0.250 mmol) was added directly and the mixture was stirred at room temperature. After a consumption of the starting material (11 h), PhSH (0.077 mL, 0.75 mmol) was added and the reaction mixture was stirred at room temperature. After a consumption of the corresponding α,β -epoxy amide (1 h), The mixture was filtered through a celite pad and diluted with Et₂O, then poured into 5% aqueous citric acid. The aqueous layer was extracted with Et₂O and the combined organic layers were washed with brine, and then dried over Na₂SO₄. After concentration under reduced pressure, the resulting residue was purified by flash column chromatography (SiO₂, hexane/ethyl acetate =8/1 to 2/1) to give **9a** (70.0 mg, 93%, 99% ee).

(2*S*,3*R*)-2-Hydroxy-*N,N*-dimethyl-3-phenyl-3-phenylthiopropionamide (9a**):**

off-white solid; mp 110–111 °C; IR (KBr) ν 3159, 1623, 1074 cm⁻¹; ¹H

NMR (CDCl₃) δ 7.37-7.18 (m, 10H), 4.80 (dd, *J* = 8.5, 4.6 Hz, 1H), 4.39 (d, *J* = 4.6 Hz, 1H), 3.64 (d, *J* = 8.5 Hz, 1H), 2.89 (s, 3H), 2.86 (s,

3H); ¹³C NMR (CDCl₃) δ 137.1, 134.8, 132.0, 128.9, 128.7, 128.2, 127.9, 127.3, 70.0, 57.2,

36.5, 35.8; ESI-MS m/z 324 $[M+Na]^+$; HR-MS [FAB(+)] Calcd for $C_{17}H_{20}NO_3S^+$ $[M+H]^+$: 302.1215; Found 302.1203; $[\alpha]_D^{24}$ -162 (c 0.500, $CHCl_3$) (99% ee); HPLC (DAICEL CHIRALCEL OJ-H, 2-propanol/hexane 1/4, flow 1.0 mL/min, detection at 254 nm) t_R 11.5 min (major) and 19.2 min (minor).

4-[(2*S*,3*R*)-2-hydroxy-1-oxo-3-phenyl-3-phenylthiopropyl]morpholine (9b):

white foam; IR (KBr) ν 3245, 2988, 2862, 1611, 1116, 747 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.38-7.22 (m, 10H), 4.77 (dd, J = 8.9, 4.6 Hz, 1H), 4.33 (d, J = 4.6 Hz, 1H), 3.62-3.23 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 170.0, 136.7, 134.6, 132.1, 129.0, 128.7, 128.4, 128.1, 127.5, 69.7, 66.5, 66.1, 57.6, 45.5, 42.7; ESI-MS m/z 366 $[M+Na]^+$; HR-MS [FAB(+)] Calcd for $C_{19}H_{22}NO_3S^+$ $[M+H]^+$: 344.1320; Found 344.1321; $[\alpha]_D^{25}$ -169 (c 0.970, $CHCl_3$) (99% ee); HPLC (DAICEL CHIRALCEL OJ-H, 2-propanol/hexane 1/4, flow 1.0 mL/min, detection at 254 nm) t_R 25.4 min (major) and 36.8 min (minor).

(2*S*,3*R*)-2-Hydroxy-*N,N*-dimethyl-3-(4-methoxyphenyl)-3-phenylthiopropylamide (9c):

white solid; mp 140 $^{\circ}C$; IR (KBr) ν 3200, 2935, 1625, 1509, 1249 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.38 (d, J = 8.6 Hz, 2H), 7.27-7.21 (m, 5H), 6.82 (d, J = 8.6 Hz, 2H), 4.77 (dd, J = 8.6, 4.6 Hz, 1H), 4.37 (d, J = 4.6 Hz, 1H), 3.78 (s, 3H), 3.69 (d, J = 8.6 Hz, 1H), 2.89 (s, 3H), 2.86 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 171.2, 159.1, 134.8, 132.0, 129.7, 128.8, 128.8, 127.3, 113.6, 69.9, 56.4, 55.1, 36.5, 35.8; ESI-MS m/z 354 $[M+Na]^+$; HR-MS [FAB(+)] Calcd for $C_{18}H_{22}NO_3S^+$ $[M+H]^+$: 332.1320; Found 332.1326; $[\alpha]_D^{25}$ -219 (c 1.10, $CHCl_3$) (>99% ee); HPLC (DAICEL CHIRALCEL OJ-H, 2-propanol/hexane 1/4, flow 1.0 mL/min, detection at 254 nm) t_R 17.7 min (major) and 37.7 min (minor).

(2*S*,3*R*)-2-Hydroxy-*N*-methyl-3-phenyl-3-phenylthiopropylamide (9l):

off-white solid; mp 129-131 $^{\circ}C$; IR (KBr) ν 3417, 3253, 1648, 1541, 1106 cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.49 (d, J = 7.0 Hz, 2H), 7.38 (d, J = 6.4 Hz, 2H), 7.33-7.27 (m, 6H), 6.26 (br-s, 1H), 4.90 (d, J = 3.1 Hz, 1H), 4.32 (br-s, 1H), 3.18 (d, J = 3.1 Hz, 1H), 2.54 (d, J = 4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 170.6, 135.8, 133.0, 132.2, 129.3, 128.9, 128.2, 128.0, 127.9, 72.7, 56.3, 25.4; ESI-MS m/z 301

[M+Na⁺]; HR-MS [FAB(+)] Calcd for C₁₆H₁₈NO₂S⁺ [M+H⁺]: 288.1058; Found 288.1063; [α]_D²⁵ –89.0 (*c* 0.740, CHCl₃) (99% ee); HPLC (DAICEL CHIRALCEL OJ-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm) *t*_R 6.0 min (minor) and 7.2 min (major).

(2*S*,3*R*)-2-Hydroxy-*N*-methyl-5-phenyl-3-phenylthiopentanamide (9s):

white solid; mp 140-141 °C; IR (KBr) ν 3376, 3267, 3028, 2950, 1649, 1535 cm⁻¹; ¹H NMR (CDCl₃) δ 7.35-7.12 (m, 10H), 6.63 (br-s, 1H), 4.02 (br-s, 1H), 3.68 (dt, *J* = 10, 3.1 Hz, 1H), 3.02 (d, *J* = 2.5 Hz, 1H), 2.92 (m, 1H), 2.72 (d, *J* = 4.9 Hz, 3H), 2.66 (m, 1H), 1.82 (m, 1H), 1.68 (m, 1H); ¹³C NMR (CDCl₃) δ 171.1, 141.2, 133.0, 131.8, 129.3, 128.4, 128.4, 127.5, 126.0, 72.2, 52.8, 33.7, 29.8, 25.6; ESI-MS *m/z* 338 [M+Na⁺]; HR-MS [FAB(+)] Calcd for C₁₈H₂₂NO₂S⁺ [M+H⁺]: 316.1371; Found 316.1371; [α]_D²⁵ +8.57 (*c* 1.05, CHCl₃) (99% ee); HPLC (DAICEL CHIRALCEL OJ-H, 2-propanol/hexane 1/9, flow 0.5 mL/min, detection at 254 nm) *t*_R 27.8 min (minor) and 33.6 min (major).

(2*S*,3*R*)-3-Cyclohexyl-2-hydroxy-*N*-methyl-3-phenylthiopropenamide (9t):

white solid; mp 179-180 °C; IR (KBr) ν 3347, 2918, 2854, 1633, 1541, 1054 cm⁻¹; ¹H NMR (CDCl₃) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.30-7.21 (m, 3H), 6.71 (br-s, 1H), 4.12 (dd, *J* = 4.0, 3.5 Hz, 1H), 3.53 (dd, *J* = 4.3, 4.0 Hz, 1H), 3.21 (d, *J* = 3.5 Hz, 1H), 2.80 (d, *J* = 5.2 Hz, 3H), 2.00 (m, 1H), 1.84-1.53 (m, 5H), 1.30-1.12 (m, 5H); ¹³C NMR (CDCl₃) δ 172.0, 134.1, 131.4, 129.2, 127.2, 72.7, 59.4, 38.7, 32.0, 29.8, 26.4, 26.3, 26.0, 25.8; ESI-MS *m/z* 316 [M+Na⁺]; HR-MS [FAB(+)] Calcd for C₁₆H₂₄NO₂S⁺ [M+H⁺]: 294.1528; Found 294.1520; [α]_D²⁴ +18.6 (*c* 0.480, CHCl₃) (99% ee); HPLC (DAICEL CHIRALCEL OJ-H, 2-propanol/hexane 2/98, flow 1.0 mL/min, detection at 254 nm) *t*_R 26.7 min (major) and 34.8 min (minor).

8. Synthesis of β -cyano- α -trimethylsilyloxyamide.

Procedure for Catalytic Regioselective Ring Opening of α,β -Epoxy Amides **3o** with Me₃SiCN (Table 6, entry 4).

To a stirred solution of **3o** (109 mg, 0.5 mmol) and Sm(O-*i*-Pr)₃ (0.025 mL, 0.05 mmol, 0.2 M solution in THF) in THF (5.0 mL) at room temperature was added Me₃SiCN (0.199 mL, 1.50

mmol). Then reaction mixture was warmed to 50 °C. After the consumption of the starting material (36 h), the reaction mixture was diluted with ethyl acetate, and then poured into saturated aqueous NaHCO₃. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, and then dried over Na₂SO₄. After concentration under reduced pressure, the resulting residue was purified by flash column chromatography (SiO₂, hexane/ethyl acetate =4/1) to give **10o** (113 mg, 71%).

(2*R*,3*S*)-3-Cyano-*N,N*-dimethyl-3-phenyl-2-[(trimethylsilyl)oxy]propanamide (10a):

white solid; mp 56–57 °C; IR (KBr) ν 2247, 1649, 1110 cm⁻¹; ¹H NMR

(CDCl₃) δ 7.31–7.36 (m, 5H), 4.76 (d, J = 6.8 Hz, 1H), 4.22 (d, J = 6.3

Hz, 1H), 2.90 (s, 3H), 2.77 (s, 3H); ¹³C NMR (CDCl₃) δ 169.1, 132.0,

128.9, 128.6, 118.5, 74.0, 42.4, 36.6, 36.5, -0.5; HR-MS [FAB(+)]

Calcd for C₁₅H₂₃N₂O₂Si⁺ [M+H⁺]: 291.1529; Found 291.1530; [α]_D²³ +3.45 (c 0.51, CHCl₃) (99% ee).

(2*R*,3*S*)-3-Cyano-*N*-methyl-3-phenyl-2-[(trimethylsilyl)oxy]propanamide (10l):

white solid; mp 89–90 °C; IR (neat) ν 3267, 2246, 1651, 1114 cm⁻¹; ¹H

NMR (CDCl₃) δ 7.23–7.38 (m, 5H), 6.03 (br-s, 1H), 4.61 (d, J = 2.3 Hz,

1H), 4.42 (d, J = 2.3 Hz, 1H), 2.57 (d, J = 5.1 Hz, 3H), 0.24 (s, 9H); ¹³C

NMR (CDCl₃) δ 169.7, 130.3, 129.0, 128.5, 128.3, 119.5, 74.3, 41.8,

25.6, -0.1; ESI-MS m/z 298 [M+Na⁺]; HR-MS [FAB(+)] Calcd for C₁₄H₂₁N₂O₂Si⁺ [M+H⁺]: 277.1372; Found 277.1364; [α]_D²³ +62.7 (c 0.91, CHCl₃) (99% ee).

(2*R*,3*S*)-Cyano-*N,N*-dimethyl-5-phenyl-2-[(trimethylsilyl)oxy]pentanamide (10o):

white solid; mp 68–68.5 °C; IR (KBr) ν 2241, 1658, 1115, 845

cm⁻¹; ¹H NMR (CDCl₃) δ 7.26–7.29 (m, 2H), 7.17–7.21 (m, 3H),

4.57 (1H, d, J = 6.85 Hz), 2.90–2.96 (m, 5H), 2.67–2.73 (m, 1H),

1.93–2.05 (m, 2H); ¹³C NMR (CDCl₃) δ 169.1, 139.9, 128.5,

128.3, 126.3, 119.3, 70.7, 37.1, 36.2, 35.7, 32.8, 29.4, -0.14; HR-MS [FAB(+)] Calcd for C₁₇H₂₇N₂O₂Si⁺ [M+H⁺]: 319.1842; Found 319.1838; [α]_D²⁴ +62.1 (c 0.46, CHCl₃) (99% ee).

9. Enantioselective Synthesis of Taxol Side Chain 11

Ent-4a was prepared from **2a** using 5 mol % of Sm-(*R*)-BINOL-Ph₃As=O complex according to general procedure for the one-pot sequential catalytic asymmetric epoxidation-regioselective epoxide opening process with Me₃SiN₃ (99% yield, 99% ee).

(2*S*,3*S*)-3-Azido-2-benzoyloxy-*N,N*-dimethyl-3-phenylpropanamide (**13**):

To a stirred solution of *ent-4a* (234 mg, 1.00 mmol) in CH₂Cl₂ at 4 °C was added triethylamine (0.174 mL, 1.25 mmol), DMAP (12.0 mg, 0.100 mmol) and benzoyl chloride (0.140 mL, 1.20 mmol). After stirring for 2 h, the reaction mixture was quenched with saturated aqueous NaHCO₃. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, and then dried over Na₂SO₄. After filtration and concentration under reduced pressure, the resulting residue was purified by flash column chromatography (SiO₂, hexane/ethyl acetate = 10/1 to 5/1) to give **13** (331 mg, 98%). white solid; mp 98–100 °C; IR (KBr) ν 2105, 1727, 1653, 1271, 1109, 709 cm⁻¹; ¹H NMR (CDCl₃) δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.52–7.30 (m, 8H), 5.61 (d, *J* = 9.0 Hz, 1H), 5.20 (d, *J* = 9.0 Hz, 1H), 3.25 (s, 3H), 3.08 (s, 3H); ¹³C NMR (CDCl₃) δ 166.6, 164.3, 134.6, 132.4, 128.7, 128.0, 127.8, 127.6, 127.3, 126.8, 69.8, 65.1, 36.3, 35.3; ESI-MS *m/z* 361 [M+Na⁺]; Anal. Calcd for C₁₈H₁₈N₄O₃: N 16.56, C 63.89, H 5.36; Found N 16.49, C 64.01, H 5.48; [α]_D²⁶ +90.7 (*c* 1.44, CHCl₃) (99% ee)

(2*S*,3*S*)-3-Benzoylamino-2-hydroxy-*N,N*-dimethyl-3-phenylpropanamide (**14**):

A mixture of **13** (331 mg, 0.979 mmol) and Pd-C (10%, 10 mg, 0.0195 mmol) in ethyl acetate (4 mL) was stirred under hydrogen atmosphere (1 atm) at room temperature. After stirring for 135 h at the same temperature, the reaction mixture was filtered through a Celite pad and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (SiO₂, hexane/ethyl acetate = 1/1) to give **14** (294 mg 96%).

white foam; IR (KBr) ν 3349, 2935, 1646, 1520, 1076, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 7.86 (m,

2H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.52-7.43 (m, 3H), 7.35-7.26 (m, 5H), 5.50 (dd, $J = 8.0, 3.0$, Hz, 1H), 4.87 (d, $J = 3.0$ Hz, 1H), 3.94 (br-s, 1H), 2.96 (s, 3H), 2.92 (s, 3H); ^{13}C NMR (CDCl_3) δ 170.7, 166.9, 136.3, 133.9, 131.6, 128.5, 128.5, 128.2, 127.0, 127.0, 69.9, 55.9, 36.5, 35.7; ESI-MS m/z 335 $[\text{M}+\text{Na}^+]$; HR-MS $[\text{FAB}(+)]$ Calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_3^+$ $[\text{M}+\text{H}^+]$: 313.1552; Found 315.1559. $[\alpha]_{\text{D}}^{26} -41.7$ (c 1.20, CHCl_3) (99% ee)

(4*S*,5*R*)-2,4-Diphenyl-4,5-dihydro-5-oxazolecarboxylic acid (15**):** ^{30d}, SI-4

To a stirred solution of **14** (150 mg, 0.480 mmol) in CHCl_3 at 4 °C was added SOCl_2 (0.35 mL, 4.80 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was quenched with saturated aqueous NaHCO_3 and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, and then dried over Na_2SO_4 . Filtration and concentration under reduced pressure gave the crude 4,5-dihydrooxazolecarboxamide. The crude residue was dissolved in ethanol (4 mL) and 1 N NaOH (0.75 mL), and then heated to 60 °C. After stirring for 15 h at the same temperature, the reaction mixture was cooled to room temperature and poured into water. After extraction with ether, the aqueous layer was acidified with 1 N HCl , and then extracted with ether. The organic layer was washed with brine, and then dried over Na_2SO_4 . Filtration and concentration under reduced pressure gave **15** (89 mg, 70% in 2 steps), which was pure enough to be used for the next step without further purification.

white solid; The spectral data were in agreement with literature value.^{SI-4}

$[\alpha]_{\text{D}}^{25} -9.38$ (c 0.640, 0.05 N NaOH aq.) (99% ee) [lit. ^{SI-4} $[\alpha]_{\text{D}} -9.97$ (c 1.01, 0.05 N NaOH aq.)]

Kingston et al. reported that taxol can be prepared in good yield from 7-(triethylsilyl)baccatin III by esterification with **15** followed by hydrolysis of the resulting oxazoline ester.^{30d}

(2*R*,3*S*)-Methyl 3-benzoylamino-2-hydroxy-3-phenylpropanoate (11**):** ^{SI-5}

To a stirred solution of **15** (11.6 mg, 0.0434 mmol) in Et_2O (0.4 mL) and MeOH (0.1 mL) at room temperature was added (trimethylsilyl)diazomethane (0.030 mL, 0.060 mmol, 2.0 M solution in hexanes). After stirring for 30 min, the mixture was concentrated to

give crude methyl ester. The residue was dissolved in MeOH (0.3 mL) and 1 N HCl (0.1 mL), and then heated to refluxed temperature. After 2 h, the mixture was cooled to room temperature and poured into saturated aqueous NaHCO₃. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, and then dried over Na₂SO₄. After filtration and concentration under reduced pressure, the resulting residue was purified by flash column chromatography (SiO₂, hexane/ethyl acetate = 5/1) to give **11** (11.0 mg, 89% in 2 steps). white solid; IR (KBr) ν 3424, 2924, 1734, 1630, 1422, 1112 cm⁻¹; ¹H NMR (CD₃OD) δ 7.82 (d, J = 8.3 Hz, 2H), 7.56-7.26 (m, 8H), 5.58 (d, J = 3.7 Hz, 1H), 4.59 (d, J = 3.7 Hz, 1H), 3.67 (s, 3H); ¹³C NMR (CD₃OD) δ 174.3, 170.0, 140.3, 135.5, 132.9, 129.6, 129.5, 128.6, 128.4, 128.2, 74.9, 57.6, 52.7; ESI-MS m/z 322 [M+Na⁺]; HR-MS [FAB(+)] Calcd for C₁₇H₁₈NO₄⁺ [M+H⁺]: 300.1236; Found 300.1224; [α]_D²³ -34.0 (c 0.30, CH₃OH) (99% ee) [lit.^{SI-5a} [α]_D -48 (c 0.92, CH₃OH)]

10. Enantioselective Total Synthesis of (-)-Cytosazone (12)

4-[(2*R*,3*R*)-3-(*tert*-butoxycarbonylamino)-2-hydroxy-3-(4-methoxyphenyl)-1-oxopropyl]-morpholine (**16d**):

A mixture of **4d** (390 mg, 1.27 mmol), Boc₂O (0.350 mL, 1.53 mmol) and Pd-C (10 %, 13.5 mg, 0.0127 mmol) in ethyl acetate (12 mL) was stirred under hydrogen atmosphere (1 atm) at room temperature. After stirring for 15 h, the reaction mixture was filtered through a Celite pad and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (SiO₂, hexane/ethyl acetate = 3/1 to 1/1) to give **16d** (479 mg, 99%).

white foam; IR (KBr) ν 3393, 2975, 2859, 1706, 1648, 1511, 1247 cm⁻¹; ¹H NMR (CDCl₃) δ 7.13 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 5.61 (d, J = 8.0 Hz, 1H), 4.80 (d, J = 8.0 Hz, 1H), 4.76 (d, J = 6.5 Hz, 1H), 3.75 (s, 3H), 3.67-3.41 (m, 9H), 1.43 (s, 9H); ¹³C NMR (CDCl₃) δ 169.7, 159.3, 155.3, 128.3, 127.9, 113.8, 79.9, 70.1, 66.6, 66.5, 56.2, 55.1, 45.5, 42.7, 28.3; ESI-MS m/z 403 [M+Na⁺]; HR-MS [FAB(+)] Calcd for C₁₉H₂₉N₂O₆⁺ [M+H⁺]: 381.2026; Found 381.2017; [α]_D²⁶ +11.1 (c 1.98, CHCl₃) (99% ee); HPLC (DAICEL CHIRALPAK AS-H, 2-propanol/hexane 1/4, flow 0.5 mL/min, detection at 254 nm) t_R 35.0 min (minor) and 39.0 min (major).

16c was prepared from **4c** by the same procedure for the synthesis of **16d**.

(2*R*,3*R*)-3-(*tert*-butoxycarbonylamino)-2-hydroxy-*N,N*-dimethyl-3-(4-methoxyphenyl)-propanamide (16c):

white foam; IR (KBr) ν 3394, 2978, 2935, 1698, 1645, 1499, 1238, 1164 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.07 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 5.75 (d, J = 8.3 Hz, 1H), 4.90 (m, 1H), 4.73 (m, 1H), 3.75 (s, 3H), 3.73 (d, J = 8.3 Hz, 1H), 3.01 (s, 3H), 2.87 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (CDCl_3) δ 170.7, 159.2, 155.3, 128.6, 128.1, 113.7, 79.6, 70.3, 55.9, 55.0, 36.5, 35.7, 28.3; ESI-MS m/z 361 [$\text{M}+\text{Na}^+$]; HR-MS [FAB(+)] Calcd for $\text{C}_{17}\text{H}_{27}\text{N}_2\text{O}_5$ [$\text{M}+\text{H}^+$]: 339.1920; Found 339.1908; $[\alpha]_{\text{D}}^{25}$ -7.81 (c 1.45, CHCl_3) (99% ee).

(-)-Cytosazone (12):

[1] Stepwise Procedure

To a stirred suspension of LiAlH_4 (75.9 mg, 2.00 mmol) in THF (4 mL) at -40°C was slowly added THF solution (1 mL) of **16d** (190 mg, 0.500 mmol). The reaction mixture was gradually warmed up to 0°C over the period of 3 h. The reaction was quenched with water, and the aqueous layer was extracted with ether. The combined organic layers were washed with brine, and then dried over Na_2SO_4 . Filtration and concentration under reduced pressure gave crude aldehyde, which was used for the next step without further purification. To a stirred solution of the crude aldehyde in THF (2 mL) and MeOH (2 mL) at 4°C was added NaBH_4 (28.3 mg, 0.75 mmol). After stirring for 30 min at room temperature, the reaction was quenched with water. The aqueous layer was extracted with ethyl acetate, and the combined organic layers were washed with brine, and then dried over Na_2SO_4 . Filtration and concentration under reduced pressure gave crude diol, which was used for the next step without further purification. To a stirred solution of the crude diol in THF (10 mL) at room temperature was added NaH (40 mg, 1.00 mmol, 60% in mineral oil). After stirring for 12 h, the reaction was quenched with saturated aqueous NH_4Cl . 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 filtration and concentration under reduced pressure, the resulting residue was purified by flash column chromatography (SiO_2 , hexane/ethyl acetate = 2/1 to 1/1) to give (-)-cytosazone (**12**) (64.7 mg,

58% in 3 steps).

white crystalline solid; mp 120–121 °C (lit.³¹ 118–120 °C); IR (KBr) ν 3466, 3373, 2960, 1757, 1615, 1514, 1254 cm^{-1} ; ^1H NMR ($\text{DMSO-}d_6$) δ 8.03 (s, 1H), 7.14 (d, J = 8.3 Hz, 2H), 6.92 (d, J = 8.3 Hz, 2H), 4.89 (d, J = 8.3 Hz, 1H), 4.80 (t, J = 5.2 Hz, 1H), 4.68 (m, 1H), 3.74 (s, 3H), 2.96 (m, 2H); ^{13}C NMR (acetone- d_6) δ 160.6, 159.5, 130.2, 129.0, 114.5, 81.4, 62.5, 57.8, 55.5; ESI-MS m/z 246 $[\text{M}+\text{Na}^+]$; HR-MS [FAB(+)] Calcd for $\text{C}_{11}\text{H}_{14}\text{NO}_4$ $[\text{M}+\text{H}^+]$: 224.0923; Found 224.0931; $[\alpha]_D^{22}$ –69.3 (c 1.18, CH_3OH) (99% ee) [lit.³¹ $[\alpha]_D^{23}$ –69.7 (c 0.5, CH_3OH)]

[2] One-Pot Procedure

To a suspension of $\text{BH}_3\cdot\text{NH}_3$ (90%, 24 mg, 0.70 mmol) in THF (0.7 mL) at 0 °C was added $n\text{-BuLi}$ (0.44 mL, 0.69 mmol, 1.58 M in hexane). The resulting solution was stirred at 0 °C for 5 min, at room temperature for 5 min, then was cooled to 0 °C. A solution of **16c** (36.8 mg, 0.108 mmol) in THF (0.2 mL) was slowly added to the solution and the reaction mixture was warmed to room temperature. After stirring for 16 h, the reaction was quenched with 5% aqueous citric acid. The aqueous layer was extracted with Et_2O and the combined organic layers were washed with brine, and then dried over Na_2SO_4 . After concentration under reduced pressure, the resulting residue was purified by flash column chromatography (SiO_2 , hexane/ethyl acetate = 2/1 to 1/1) to give (–)-**cytoxazone** (6.2 mg, 39%).

(–)-**Cyttoxazone (12)** was also synthesized from **16d** by the same procedure (40% yield).

References for the Supporting Information

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