Supporting Information

Catalytic Enantioselective Desymmetrization of *Meso*-*N*-Acylaziridines with TMSCN

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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, 126.65 MHz for ^{13}C NMR. Chemical shifts in CDCl_3 were reported in the scale relative to CHCl_3 (7.26 ppm) for ^1H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to CDCl_3 (77.0 ppm) as an internal reference. Chemical shifts in *d*-DMSO were reported in the scale relative to *d*-DMSO (2.49 ppm) for ^1H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to *d*-DMSO (39.5 ppm) as an internal reference. Chemical shifts in *d*-acetone were reported in the scale relative to *d*-acetone (2.04 ppm) for ^1H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to *d*-acetone (29.8 ppm) as an internal reference. Optical rotations were measured on a JASCO P-1010 polarimeter. ESI mass spectra were measured on Water-ZQ4000. FAB mass spectra were measured on JEOL S-SX102A. Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM). The enantiomeric excesses (ee's) were determined by HPLC. HPLC analysis was performed on JASCO HPLC systems containing of following: pump, PU-980; detector, UV-970, measured at 254 nm; column, Daicel Chiralpak AD-H, AS-H, or Daicel Chiralcel OD-H, OJ-H; mobile phase, 2-propanol/hexane; flow rate, 1.0 mL/min. In general, reactions were carried out in dry solvents under an argon atmosphere, unless noted otherwise. Dry solvents of tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purchased from Kanto Chemical. Co., Inc. $\text{Gd}(\text{O}^i\text{Pr})_3$ was purchased from Kojundo Chemical Laboratory Co., Ltd. (Fax: +81-492-84-1351, sales@kojundo.co.jp). Chiral ligand **1** was prepared by a reported method.¹ (This ligand is commercially available from Junsei Chemical. Co., Ltd. (Fax: +81-3-3270-5461)) Propionitrile was distilled from calcium hydride. Other reagents were purified by usual methods.

(A) Data of Substrates

7-(4-Nitrobenzoyl)-7-azabicyclo[4.1.0]heptane (3a): Known compound.²

6-(4-Nitrobenzoyl)-6-azabicyclo[3.1.0]hexane (3b): Known compound.²

3-Oxa-6-(4-nitrobenzoyl)-6-azabicyclo[3.1.0]hexane (3f): Known compound.³

***cis*-1-(4-Nitrobenzoyl)-2,3-dimethylaziridine (3h):** Known compound.⁴

***cis*-1-(4-Nitrobenzoyl)-2,3-diphenylaziridine (3i):** Known compound.²

¹ Kato, N.; Tomita, D.; Maki, K.; Kanai, M.; Shibasaki, M. *J. Org. Chem.* **2004**, *69*, 6128.

² Hayashi, M.; Ono, K.; Hoshimi, H.; Oguni, N. *Tetrahedron* **1996**, *52*, 7817.

³ Fanta, P. E.; Walsh, E. N. *J. Org. Chem.* **1966**, *31*, 59.

⁴ McManus, S. P.; Hearn, R. A. *J. Org. Chem.* **1976**, *41*, 1895.

8-(4-Nitrobenzoyl)-8-azabicyclo[5.1.0]octane (3c), **7-(4-nitrobenzoyl)-7-azabicyclo[4.1.0]hept-3-ene (3d)**, **N-(4-nitrobenzoyl)-2,3-iminotetralin (3e)** were prepared by the method similar to the reported one. (aziridination⁵ from the corresponding epoxide and acylation²).

3-Carbobenzyloxy-6-(4-nitrobenzoyl)-3,6-diazabicyclo[3.1.0]hexane (3g) was prepared via acylation² of 3-carbobenzyloxy-3,6-diazabicyclo[3.1.0]hexane.⁶

8-(4-Nitrobenzoyl)-8-azabicyclo[5.1.0]octane (3c): colorless solid; IR (KBr): 3110, 2998, 2918, 2846, 1673, 1521, 1340, 1296, 1093, 715 cm⁻¹; ¹H NMR (CDCl₃): δ = 8.30 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H), 2.83-2.71 (m, 2H), 2.16-1.93 (m, 4H), 1.79-1.52 (m, 5H), 1.38-1.21 (m, 1H); ¹³C NMR (CDCl₃): δ = 177.9, 150.0, 138.8, 130.0, 123.6, 42.4, 31.3, 28.9, 25.3; MS (ESI): *m/z* 283 [M+Na⁺]; Anal. calcd for C₁₄H₁₆N₂O₃: C, 64.60; H, 6.20; N, 10.76%. Found: C, 64.58; H, 6.22; N, 10.77%.

7-(4-Nitrobenzoyl)-7-azabicyclo[4.1.0]hept-3-ene (3d): colorless solid; IR (KBr): 3114, 3034, 2913, 2834, 1666, 1521, 1349, 1301, 1104, 717 cm⁻¹; ¹H NMR (CDCl₃): δ = 8.29 (d, *J* = 9.0 Hz, 2H), 8.12 (d, *J* = 9.0 Hz, 2H), 5.57 (s, 2H), 2.96 (s, 2H), 2.67 (d, *J* = 18.5 Hz, 2H), 2.52 (d, *J* = 18.5 Hz, 2H); ¹³C NMR (CDCl₃): δ = 177.4, 150.1, 139.0, 130.0, 123.6, 122.2, 36.8, 23.9; MS (ESI): *m/z* 267 [M+Na⁺]; Anal. calcd for C₁₃H₁₂N₂O₃: C, 63.93; H, 4.95; N, 11.47%. Found: C, 63.93; H, 5.13; N, 11.44%.

N-(4-Nitrobenzoyl)-2,3-iminotetralin (3e): colorless solid; IR (KBr): 3113, 3009, 2908, 2832, 1665, 1518, 1418, 1337, 855, 717 cm⁻¹; ¹H NMR (CDCl₃): δ = 8.26 (d, *J* = 9.1 Hz, 2H), 7.98 (d, *J* = 9.1 Hz, 2H), 7.21 (dd, *J* = 3.4, 5.5 Hz, 2H), 7.10 (dd, *J* = 3.4, 5.5 Hz, 2H), 3.38 (d, *J* = 16.2 Hz, 2H), 3.29-3.17 (m, 4H); ¹³C NMR (CDCl₃): δ = 177.0, 150.1, 138.9, 131.9, 129.8, 129.2, 127.0, 123.5, 37.7, 29.4; MS (ESI): *m/z* 317 [M+Na⁺]; Anal. calcd for C₁₇H₁₄N₂O₃: C, 69.38; H, 4.79; N, 9.52%. Found: C, 69.40; H, 5.03; N, 9.45%.

3-Carbobenzyloxy-6-(4-nitrobenzoyl)-3,6-diazabicyclo[3.1.0]hexane (3g) colorless solid; IR (KBr): 3105, 3051, 2963, 2879, 1685, 1523, 1336, 1093, 843, 705 cm⁻¹; ¹H NMR (CDCl₃): δ = 8.22 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 8.7 Hz, 2H), 7.43-7.29 (m, 5H), 5.12 (d, *J* = 12.4 Hz, 1H), 5.05 (d, *J* = 12.4 Hz, 1H), 4.00 (dd, *J* = 12.5, 17.4 Hz, 2H), 3.51-3.33 (m, 4H); ¹³C NMR (CDCl₃): δ = 174.4, 154.7, 150.2, 138.2, 136.3, 129.6, 128.5, 128.2, 128.1, 123.7, 67.2, 46.2, 45.8, 41.3, 41.2; MS (ESI): *m/z* 390 [M+Na⁺]; Anal. calcd for C₁₉H₁₇N₃O₅: C, 62.12; H, 4.66; N, 11.44%. Found: C, 61.86; H, 4.84; N, 11.26%.

(B) General Procedure for Enantioselective Desymmetrization of *Meso*-N-(4-Nitrobenzoyl)aziridine with TMSCN

To a solution of ligand **1** (9.2 mg, 0.02 mmol) in THF (0.3 mL), Gd(O^{*i*}Pr)₃ (0.2 M in THF, 50 μ L, 0.01 mmol) was added at room temperature. The mixture was stirred at 45-60 °C for 1 h, and then the solvent was evaporated. After drying the resulting pre-catalyst under reduced pressure (< 5 mmHg) for 1 h,

⁵ Ittah, Y.; Sasson, Y.; Shahak, I.; Tsaroom, S.; Blum, J. *J. Org. Chem.* **1978**, *43*, 4271.

⁶ Oida, S.; Kuwano, H.; Ohashi, Y.; Ohki, E. *Chem. Pharm. Bull.* **1970**, *18*, 2478.

2,6-dimethylphenol (12.2 mg, 0.1 mmol), propionitrile (300 μ L), and trifluoroacetic acid (0.025 M in propionitrile, 200 μ L, 0.005 mmol) were added. After stirring for 30 min, **3a** (24.6 mg, 0.1 mmol) was added as a solid in one portion at room temperature, then cooled to 0 $^{\circ}$ C. After 10 min, TMSCN (40 μ L, 0.3 mmol) was added to start reaction. After 20 h, water was added followed by the addition of AcOEt. The organic layer was separated and the water layer was extracted with AcOEt twice and the combined organic layer was dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (hexane-AcOEt, 1:1) to afford the **4a** (25.9 mg) in 94% yield as colorless solid. The optical yield of the product was determined by HPLC analysis to be 87% ee. Enantiomerically pure **4a** (>99% ee) was obtained after recrystallization from 1-butanol (recrystallization yield; 79 %).

(1S,2S)-1-Cyano-2-[N-(4-nitrobenzoyl)amino]cyclohexane (4a): colorless solid; IR (KBr): 3334, 3113, 2950, 2865, 2244, 1647, 1521, 1344, 877, 725 cm^{-1} ; ^1H NMR (*d*-DMSO): δ = 8.92 (d, *J* = 8.5 Hz, 1H), 8.35 (d, *J* = 9.0 Hz, 2H), 8.06 (d, *J* = 9.0 Hz, 2H), 4.12-3.97 (m, 1H), 2.86-2.75 (m, 1H), 2.17-2.06 (m, 1H), 1.91-1.81 (m, 1H), 1.77-1.55 (m, 3H), 1.44-1.27 (m, 2H), 1.25-1.12 (m, 1H); ^{13}C NMR (*d*-DMSO): δ = 164.0, 149.1, 139.8, 128.7, 123.7, 121.3, 49.7, 33.8, 31.7, 28.8, 23.9, 23.8; MS (ESI): *m/z* 296 [$\text{M}+\text{Na}^+$]; Anal. calcd for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_3$: C, 61.53; H, 5.53; N, 15.38%. Found: C, 61.13; H, 5.61; N, 15.21%; $[\alpha]_D^{22} +72.5$ (*c* = 0.350, Acetone) (>99% ee); HPLC (Chiralpak AD-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm.): t_R 18.4 min (minor) and 20.9 min (major).

(1S,2S)-1-Cyano-2-[N-(4-nitrobenzoyl)amino]cyclopentane (4b): (20 mol % catalyst and 5 mol % TFA were used.) colorless solid; IR (KBr): 3354, 3091, 2961, 2944, 2240, 1655, 1519, 1345, 872, 720 cm^{-1} ; ^1H NMR (CDCl_3): δ = 8.24 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 6.9 Hz, 1H), 4.58-4.52 (m, 1H), 3.03-2.98 (m, 1H), 2.34-2.16 (m, 2H), 2.06-1.952 (m, 1H), 1.947-1.83 (m, 2H), 1.82-1.66 (m, 1H); ^{13}C NMR (CDCl_3): δ = 165.6, 149.6, 139.3, 128.3, 123.8, 121.5, 56.3, 34.6, 31.4, 29.4, 22.9; MS (ESI): *m/z* 282 [$\text{M}+\text{Na}^+$]; HRMS (FAB): *m/z* calcd for $\text{C}_{13}\text{H}_{14}\text{N}_3\text{O}_3$ [$\text{M}+\text{H}^+$]: 260.1035. Found: 260.1042; $[\alpha]_D^{25} +99.4$ (*c* = 0.960, Acetone) (93% ee); HPLC (Chiralpak AS-H, 2-propanol/hexane 1/4, flow 1.0 mL/min, detection at 254 nm.): t_R 35.2 min (major) and 52.5 min (minor).

trans-1-Cyano-2-[N-(4-nitrobenzoyl)amino]cycloheptane (4c): (10 mol % catalyst and 2.5 mol % TFA were used.) colorless solid; IR (KBr): 3317, 2936, 2863, 2239, 1645, 1538, 1344, 1313, 876, 726 cm^{-1} ; ^1H NMR (CDCl_3): δ = 8.23 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H), 6.70 (d, *J* = 6.5 Hz, 1H), 4.39-4.26 (m, 1H), 3.13-3.03 (m, 1H), 2.14-1.99 (m, 2H), 1.98-1.48 (m, 8H); ^{13}C NMR (CDCl_3): δ = 165.1, 149.5, 139.7, 128.3, 123.7, 121.5, 53.1, 36.5, 33.4, 28.3, 27.0, 25.2, 23.7; MS (ESI): *m/z* 310 [$\text{M}+\text{Na}^+$]; HRMS (FAB): *m/z* calcd for $\text{C}_{15}\text{H}_{18}\text{N}_3\text{O}_3$ [$\text{M}+\text{H}^+$]: 288.1348. Found: 288.1359; $[\alpha]_D^{25} +63.3$ (*c* = 0.765, Acetone) (>99% ee); HPLC (Chiralpak AD-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm.): t_R 29.8 min (minor) and 34.1 min (major). Enantiomerically pure **4c** (>99% ee) was obtained after recrystallization from 2-propanol (recrystallization yield; 58 %).

trans-4-Cyano-5-[N-(4-nitrobenzoyl)amino]cyclohexene (4d): colorless solid; IR (KBr): 3324, 2942, 2853, 2244, 1644, 1541, 1344, 1322, 846, 663 cm^{-1} ; ^1H NMR (*d*-Acetone): δ = 8.42-8.25 (m, 3H), 8.12 (d, J = 9.0 Hz, 2H), 5.77-5.63 (m, 2H), 4.50-4.37 (m, 1H), 3.29-3.18 (m, 1H), 2.69-2.58 (m, 1H), 2.57-2.44 (m, 2H), 2.37-2.23 (m, 1H); ^{13}C NMR (*d*-Acetone): δ = 165.7, 150.5, 141.1, 129.5, 126.0, 124.6, 124.3, 121.2, 47.7, 31.4, 31.0, 29.2; MS (ESI): m/z 294 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calcd for $\text{C}_{14}\text{H}_{14}\text{N}_3\text{O}_3$ [$\text{M}+\text{H}^+$]: 272.1035. Found: 272.1034; $[\alpha]_{\text{D}}^{23} +118.1$ (c = 0.850, Acetone) (82% ee); HPLC (Chiralpak AD-H, 2-propanol/hexane 1/4, flow 1.0 mL/min, detection at 254 nm.): t_{R} 10.0 min (minor) and 11.8 min (major). Enantiomerically pure **4d** (>99% ee) was obtained after recrystallization from 2-propanol (recrystallization yield; 66 %).

trans-2-Cyano-3-[N-(4-nitrobenzoyl)amino]tetralin (4e) colorless solid; IR (KBr): 3315, 3073, 3022, 2931, 2849, 2244, 1642, 1539, 1349, 749 cm^{-1} ; ^1H NMR (*d*-Acetone): δ = 8.51 (d, J = 7.5 Hz, 1H), 8.32 (d, J = 8.0 Hz, 2H), 8.14 (d, J = 8.0 Hz, 2H), 7.20-7.11 (m, 4H), 4.70-4.60 (m, 1H), 3.52-3.45 (m, 1H), 3.39-3.19 (m, 3H), 3.08-3.00 (m, 1H); ^{13}C NMR (*d*-Acetone): δ = 165.9, 150.5, 141.1, 134.2, 133.1, 129.9, 129.5, 129.4, 127.5, 127.3, 124.4, 121.1, 48.4, 34.6, 32.3, 32.0; MS (ESI): m/z 344 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calcd for $\text{C}_{18}\text{H}_{16}\text{N}_3\text{O}_3$ [$\text{M}+\text{H}^+$]: 322.1192. Found: 322.1179; $[\alpha]_{\text{D}}^{27} +67.0$ (c = 0.552, Acetone) (83% ee); HPLC (Chiralpak AD-H, 2-propanol/hexane 1/4, flow 1.0 mL/min, detection at 254 nm.): t_{R} 22.2 min (minor) and 24.9 min (major).

trans-3-Cyano-4-[N-(4-nitrobenzoyl)amino]tetrahydrofuran (4f): (20 mol % catalyst and 5 mol % TFA were used.) colorless solid; IR (KBr): 3357, 3104, 3073, 2871, 2250, 1656, 1522, 1348, 1099, 719 cm^{-1} ; ^1H NMR (*d*-Acetone): δ = 8.49 (brs, 1H), 8.32 (d, J = 8.4 Hz, 2H), 8.14 (d, J = 8.4 Hz, 2H), 4.92-4.83 (m, 1H), 4.25-4.17 (m, 2H), 3.99 (dd, J = 5.2, 9.4 Hz, 1H), 3.89 (dd, J = 4.5, 9.4 Hz, 1H), 3.50-3.41 (m, 1H); ^{13}C NMR (*d*-Acetone): δ = 166.1, 150.6, 140.4, 129.6, 124.3, 120.6, 72.5, 70.8, 56.6, 36.8; MS (ESI): m/z 284 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calcd for $\text{C}_{12}\text{H}_{12}\text{N}_3\text{O}_4$ [$\text{M}+\text{H}^+$]: 262.0828. Found: 262.0818; $[\alpha]_{\text{D}}^{24} +109.0$ (c = 1.155, Acetone) (88% ee); HPLC (Chiralpak AD-H, 2-propanol/hexane 1/9, flow 1.2 mL/min, detection at 254 nm.): t_{R} 33.9 min (major) and 46.2 min (minor).

trans-1-Carbobenzyloxy-3-cyano-4-[N-(4-nitrobenzoyl)amino]pyrrolidine (4g) (20 mol % catalyst and 5 mol % TFA were used.) colorless solid; IR (KBr): 3323, 3078, 2941, 2254, 1705, 1649, 1526, 1418, 1124, 697 cm^{-1} ; ^1H NMR (*d*-Acetone): δ = 8.58 (brs, 1H), 8.32 (d, J = 8.7 Hz, 2H), 8.13 (d, J = 8.7 Hz, 2H), 7.46-7.28 (m, 5H), 5.13 (s, 2H), 5.03-4.91 (m, 1H), 4.05-3.89 (m, 2H), 3.85-3.700 (m, 1H), 3.695-3.53 (m, 2H); ^{13}C NMR (*d*-Acetone): δ = 166.2, 154.8/154.7(rotamer), 150.7, 140.4, 137.9, 129.7, 129.3, 128.8, 128.7, 124.3, 119.6, 67.4, 54.4/53.5(rotamer), 50.1/49.9(rotamer), 48.4/48.0(rotamer), 34.8/33.9(rotamer); MS (ESI): m/z 417 [$\text{M}+\text{Na}^+$]; HRMS (FAB): m/z calcd for $\text{C}_{20}\text{H}_{19}\text{N}_4\text{O}_5$ [$\text{M}+\text{H}^+$]: 395.1355. Found: 395.1344; $[\alpha]_{\text{D}}^{24} +4.5$ (c = 0.354, Acetone) (84% ee); HPLC (Chiralpak AD-H, 2-propanol/hexane 1/4, flow 1.0 mL/min, detection at 254 nm.): t_{R} 26.5 min (major) and 31.3 min (minor).

(2S,3S)-2-Cyano-3-[N-(4-nitrobenzoyl)amino]butane (4h): colorless solid; IR (KBr): 3404, 3287, 2983, 2241, 1649, 1543, 1524, 1339, 844, 718 cm^{-1} ; ^1H NMR (CDCl_3): δ = 8.28 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 8.8 Hz, 2H), 6.46 (d, J = 9.0 Hz, 1H), 4.57-4.42 (m, 1H), 3.04-2.90 (m, 1H), 1.44 (d, J = 7.0 Hz, 3H), 1.38 (d, J = 7.0 Hz, 3H); ^{13}C NMR (CDCl_3): δ = 165.5, 149.7, 139.3, 128.3, 123.8, 120.5, 47.2, 32.8, 19.3, 15.1; MS (ESI): m/z 270 $[\text{M}+\text{Na}^+]$; HRMS (FAB): m/z calcd for $\text{C}_{12}\text{H}_{14}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}^+]$: 248.1035. Found: 248.1035; $[\alpha]^{25}_{\text{D}} +6.8$ (c = 1.00, Acetone) (85% ee); HPLC (Chiralpak AD-H, 2-propanol/hexane 1/9, flow 1.0 mL/min, detection at 254 nm.): t_{R} 14.9 min (minor) and 19.0 min (major).

anti-1-Cyano-2-[N-(4-nitrobenzoyl)amino]-1,2-diphenylethane (anti-4i): colorless solid; IR (KBr): 3321, 2934, 2240, 1654, 1603, 1542, 1520, 1348, 1077, 705 cm^{-1} ; ^1H NMR (CDCl_3): δ = 8.28 (d, J = 8.8 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H), 7.43-7.32 (m, 6H), 7.31-7.21 (m, 4H), 6.75 (d, J = 8.5 Hz, 1H), 5.72 (dd, J = 5.0, 8.5 Hz, 1H), 4.54 (d, J = 5.0 Hz, 1H); ^{13}C NMR (CDCl_3): δ = 165.0, 149.8, 139.2, 136.6, 131.6, 129.09, 129.06, 129.02, 128.97, 128.24, 128.21, 126.8, 124.0, 118.3, 56.8, 44.2; MS (ESI): m/z 394 $[\text{M}+\text{Na}^+]$; HRMS (FAB): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}^+]$: 372.1348. Found: 372.1353; $[\alpha]^{24}_{\text{D}} -2.3$ (c = 0.530, CHCl_3) (89% ee); HPLC (Chiralpak AD-H, 2-propanol/hexane 1/4, flow 1.0 mL/min, detection at 254 nm.): t_{R} 24.0 min (minor) and 37.7 min (major).

syn-1-Cyano-2-[N-(4-nitrobenzoyl)amino]-1,2-diphenylethane (syn-4i): colorless solid; IR (KBr): 3304, 3064, 2915, 2245, 1649, 1601, 1542, 1526, 1345, 701 cm^{-1} ; ^1H NMR (CDCl_3): δ = 8.34 (d, J = 8.8 Hz, 2H), 7.98 (d, J = 8.8 Hz, 2H), 7.39-7.08 (m, 10H), 6.86 (d, J = 6.8 Hz, 1H), 5.40 (dd, J = 5.5, 6.8 Hz, 1H), 4.95 (d, J = 5.5 Hz, 1H); ^{13}C NMR (CDCl_3): δ = 165.5, 150.0, 139.1, 134.7, 131.4, 129.3, 128.94, 128.89, 128.6, 128.3, 128.1, 127.5, 124.1, 118.6, 58.1, 43.3; MS (ESI): m/z 394 $[\text{M}+\text{Na}^+]$; HRMS (FAB): m/z calcd for $\text{C}_{22}\text{H}_{18}\text{N}_3\text{O}_3$ $[\text{M}+\text{H}^+]$: 372.1348. Found: 372.1353; $[\alpha]^{23}_{\text{D}} -55.8$ (c = 0.120, CHCl_3) (89% ee); HPLC (Chiralpak AD-H, 2-propanol/hexane 1/4, flow 1.0 mL/min, detection at 254 nm.): t_{R} 19.6 min (major) and 25.6 min (minor).

The relative configuration of **4i** was temporarily determined. The **syn-4i** was perhaps generated via epimerization of the α -position of cyanide of **anti-4i**.

(C) Transformation into β -Amino Acid

(1S,2S)-2-Amino-cyclohexanecarboxylic acid

Amido nitrile **4a** (>99% ee; recrystallized from 1-butanol) (201.0 mg, 0.735 mmol) was treated with 12 M HCl (20 mL) at 90 °C for 5 days. The mixture was concentrated under reduced pressure and the residue was dissolved in 1 M HCl. The solution was washed with CH_2Cl_2 three times and the aqueous phase was

concentrated. The residue was purified through ion exchange chromatography [Dowex 50Wx8-100 (acidic) (10 g)] to afford (1*S*,2*S*)-2-amino-cyclohexanecarboxylic acid⁷ (97.1 mg) as a white solid in 92% yield. The absolute configuration was determined to be 1*S*,2*S* based on the comparison of the optical rotation with the reported value.⁷ [α]_D²³ +78.8 (*c* = 0.246, MeOH). [lit. [α]_D²⁰ +63.0 (*c* = 0.25, MeOH) for 1*S*,2*S* enantiomer.]

(1*S*,2*S*)-2-Amino-cyclopentanecarboxylic acid

Amido nitrile **4b** (93% ee) (17.6 mg, 0.068 mmol) was treated with 12 M HCl (2 mL) at 90 °C for 3 days. The mixture was concentrated under reduced pressure and the residue was dissolved in 1 M HCl. The solution was washed with CH₂Cl₂ three times and the aqueous phase was concentrated. The residue was purified through ion exchange chromatography [Dowex 50Wx8-100 (acidic) (2.2 g)] to afford (1*S*,2*S*)-2-amino-cyclopentanecarboxylic acid⁸ as a white solid in quantitative yield. The absolute configuration was determined to be 1*S*,2*S* based on the comparison of the optical rotation with the reported value.⁸ [α]_D²⁴ +49.9 (*c* = 0.225, H₂O). [lit. [α]_D²⁰ +51.8 (*c* = 1.0, H₂O) for 1*S*,2*S* enantiomer.]

(2*S*,3*S*)-3-Amino-2-methyl butyric acid

To a solution of amido nitrile **4h** (80% ee) (14.6 mg, 0.059 mmol) in MeOH/H₂O (2 mL), H₂O₂ (1 mL) and saturated aq. Na₂CO₃ (1 mL) were added and the mixture was stirred at room temperature for 3 h. Na₂S₂O₆ and CH₂Cl₂ were added and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ twice and the combined organic layer was dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was treated with 6 M HCl (2 mL) at 90 °C. After 62 h, the mixture was diluted with water and washed with CH₂Cl₂ twice. The aqueous phase was concentrated and the residue was purified through ion exchange chromatography [Dowex 50Wx8-100 (acidic) (2.2 g)] to afford (2*S*,3*S*)-3-amino-2-methyl butyric acid⁹ (6.1 mg) as a white solid in 88% yield. The absolute configuration was determined to be 2*S*,3*S* based on the comparison of the optical rotation with the reported value.⁹ [α]_D²³ +6.5 (*c* = 0.270, H₂O). [lit. [α]_D²⁵ -8.0 (*c* = 1, H₂O) for 2*R*,3*R* enantiomer with 96% ee.]

⁷ Cannizzaro, C. E.; Ashley, J. A.; Janda, K. D.; Houk, K. N. *J. Am. Chem. Soc.* **2003**, *125*, 2489.

⁸ Yamazaki, T.; Zhu, Y. -F.; Probstl, A.; Chadha, R. K.; Goodman, M. *J. Org. Chem.* **1991**, *56*, 6644.

⁹ Sibi, M. P.; Prabakaran, N.; Ghorpade, S. G.; Jasperse, C. P. *J. Am. Chem. Soc.* **2003**, *125*, 11796.

(D) Various Reaction Conditions

Table S1. Screening of Various Metals

entry	metal	time (h)	yield ^a	ee (%) ^b
1	La	24	49	-6
2	Sm	5	93	74
3	Eu	8	94	76
4	Gd	3	>99	80
5	Yb	5	86	52

^a Isolated yield. ^b Determined by chiral HPLC.

Table S2. Screening of Benzoyl Derivatives

entry	Ar	time (h)	yield (%) ^a	ee (%) ^b
1	Ph	13	96	79
2	<i>o</i> -NO ₂ -Ph	4	98	72
3	<i>m</i> -NO ₂ -Ph	4	97	74
4	<i>p</i> -NO ₂ -Ph	3	>99	80
5	3,5-(NO ₂) ₂ -Ph	69	25	93
6	3,5-(CF ₃) ₂ -Ph	4	99	48

^a Isolated yield. ^b Determined by chiral HPLC.

Table S3. Screening of Various Acids

entry	additive	amount (mol%)	time (h)	yield (%) ^a	ee (%) ^b
1	-	-	3	>99	80
2	TsOH	5	18	>99	78
3	TfOH	5	17	>99	74
4	TSMOTf	5	14	96	71
5	BzOH	5	14	96	78
6	AcOH	5	5	>99	80
7	TCA ^c	5	5	>99	83
8	TFA ^d	5	2	>99	83
9	TFA	10	26	67	83
10	TFA	50	26	0 ^e	
11 ^f	TFA	5	3	96	83

^a Isolated yield. ^b Determined by chiral HPLC. ^c TCA = trichloroacetic acid.

^d TFA = trifluoroacetic acid. ^e Desired product was not obtained.

^f In the absence of 2,6-dimethylphenol.

(E) ESI-MS Data of the Catalyst

(F) ^1H NMR Data of the Products

C:\My Documents\PGousei\MITA Tsuyoshi\Aziridine-Paper\FM-6-aziridine-N-COC6H4NO2-1H-DMSO-2.als

1H Line

DFILE C:\My Documents\PGousei\MIT
COMNT 1H Line
DATIM Sat Jul 2 16:22:06 2005
OBNUC 1H
EXMOD non

499.10 MHz

120.00 KHz

8108.5 Hz

32768

10000.0 Hz

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

CTEMP

PW1

PD

ACQTM

SCANS

POINT

FREQU

64

3.277 sec

3.723 sec

5.8 us

24.3 C

2.49 ppm

0.12 Hz

21

RGAIN

SLVNT DMSO

EXREF

BF

IRNUC 1H

C:\My Documents\PGousei\MITA Tsuyoshi\Aziridine-Paper\FM-5-aziridine-N-COC6H4NO2-1H.als
 FM-5-N-COC6H4NO2-CN

DFILE C:\My Documents\PGousei\MITA
 COMNT FM-5-N-COC6H4NO2-CN
 DATIM 15-01-2005 22:37:55
 OBNJC 1H
 EXMOD single_pulse.ex2
 OBFRQ 495.13 MHz
 OBSET 4.38 KHz
 OBFIN 9.6 Hz
 POINT 13107
 FREQU 7429.3 Hz
 SCANS 16
 ACQTM 1.764 sec
 PD 5.000 sec
 PW1 5.6 us
 IRNJC 1H
 CTEMP 17.3 c
 SLVNT CDCL3
 EXREF 7.26 ppm
 BF 0.12 Hz
 RGAIN 48

C:\My Documents\PGousei\MITA Tsuyoshi\Aziridine-Paper\FM-7-aziridine-N-COC6H4NO2-1H-2.als
1H Line

DFILE C:\My Documents\PGousei\MIT
CONVT 1H Line
DATIM Sat Jul 2 16:42:56 2005
OBNUC 1H
EXMOD non
OBFRQ 499.10 MHz
OBSET 120.00 KHz
OBFIN 8108.5 Hz
POINT 32768
FREQU 10000.0 Hz
SCANS 64
ACQTM 3.277 sec
PD 3.723 sec
PWL 5.8 us
IRNUC 1H
CTEMP 24.3 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 19

C:\My Documents\PGousei\MITA Tsuyoshi\Aziridine-Paper\FM-6en-adiridine-N-COC6H4NO2-1H-Acetone.als
1H Line

C:\My Documents\PGousei\MIT
COMET 1H Line
DATIM Mon May 9 10:57:48 2005
OBNUC 1H
EXMOD non
OBFRQ 499.10 MHz
OBSET 120.00 KHz
OBFIN 8250.0 Hz
POINT 32768
FREQU 9980.0 Hz
SCANS 16
ACQTM 3.283 sec
PD 3.717 sec
PW1 5.8 us
IRNUC 1H
CTEMP 22.1 c
SLVNT ACETN
EXREF 2.04 ppm
BF 0.12 Hz
RGAIN 21

C:\My Documents\PGousei\MITA Tsuyoshi\Aziridine-Paper\FM-6naptha-aziridine-N-COC6H4NO2-1H-Acetone-3.als
1H Line

DFILE C:\My Documents\PGousei\MIT
COMNT 1H Line
DATIM Tue Jun 7 00:15:15 2005
OBNUC 1H
EXMOD non
OBFRQ 499.10 MHz
OBSET 120.00 KHz
OBFIN 8250.0 Hz
POINT 32768
FREQU 9980.0 Hz
SCANS 16
ACQTM 3.283 sec
PD 3.717 sec
PWL 5.8 us
IRNUC 1H
CTEMP 23.0 c
SLVNT ACETN
EXREF 2.04 ppm
BF 0.12 Hz
RGAIN 20

C:\My Documents\PGousei\MITA Tsuyoshi\Aziridine-Paper\PM-5THF-aziridine-N-COC6H4NO2-1H.als
5THF

DFILE C:\My Documents\PGousei\MIT
COMNT 5THF
DATIM 01-06-2005 21:03:08
OBNJC 1H
EXMOD single_pulse.ex2
OBFRQ 495.13 MHz
OBSET 4.38 KHz
OBFIN 9.6 Hz
POINT 13107
FREQU 7429.3 Hz
SCANS 16
ACQTM 1.764 sec
PD 5.000 sec
PW1 5.6 us
IRNUC 1H
CTEMP 20.2 c
SLVNT ACETN
EXREF 2.04 ppm
BF 0.12 Hz
RGAIN 54

C:\My Documents\PGousei\MITA Tsuyoshi\Aziridine-Paper\FM-5NZ-aziridine-N-COC6H4NO2-1H-Acetone.als
FM-ZN5

C:\My Documents\PGousei\MIT
FM-ZN5
09-07-2005 22:51:52
1H
single_pulse.ex2
495.13 MHz
4.38 KHz
9.6 Hz
10485
5943.4 Hz
16
1.764 sec
5.000 sec
6.2 us
22.6 c
2.04 ppm
0.12 Hz
50
RGAIN

C:\My Documents\PGousei\MITA Tsuyoshi\Aziridine-Paper\FM-diMe-aziridine-N-COC6H4NO2-1H.als
1H Line

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRO
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\My Documents\PGousei\MIT
1H Line
Mon Feb 28 21:43:50 2005
1H
non
500.00 MHz
160.00 KHz
2160.0 Hz
32768
10000.0 Hz
16
3.277 sec
3.723 sec
6.0 us
1H
20.9 c
CDCL3
7.26 ppm
0.12 Hz
16

C:\My Documents\PGousei\MITA Tsuyoshi\Aziridine-Paper\FM-diPh-trans-aziridine-N-COC6H4NO2-1H-2.als
1H Line

DFILE C:\My Documents\PGousei\MIT
COMNT 1H Line
DATIM Tue May 10 10:47:00 2005
OBNUC 1H
EXMOD non
OBFRQ 499.10 MHz
OBSET 120.00 KHz
OBFIN 8250.0 Hz
POINT 32768
FREQU 9980.0 Hz
SCANS 16
ACQTM 3.283 sec
PD 3.717 sec
PW1 5.8 us
IRNUC 1H
CTEMP 21.9 c
SLVNT CDCL3
EXREF 7.26 ppm
BF 0.12 Hz
RGAIN 23

C:\My Documents\PGousei\MITA Tsuyoshi\Aziridine-Paper\FM-diPh-cis-aziridine-N-COC6H4NO2-1H.als
1H Line

DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFRO
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

C:\My Documents\PGousei\MIT
1H Line
Tue May 10 10:30:01 2005
1H
non
499.10 MHz
120.00 KHz
8250.0 Hz
32768
9980.0 Hz
16
3.283 sec
3.717 sec
5.8 us
1H
22.0 c
CDCL3
7.26 ppm
0.12 Hz
25