Supporting Information

of

Optically Active *N*-Alkyl Aziridines via Stereospecific Reductive Cyclization of α-Mesylated Acetamides

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1. General Considerations.

All reactions were carried out under the designated conditions. Unless otherwise noted, commercialized reagents were used without further purifications. Toluene was purchased from Sigma-Aldrich Chemical Co. All other solvents were purified and dried according to standard methods prior to use.

¹H NMR, ¹⁹F NMR and ¹³C NMR data were recorded on a Bruker-Ultrashield PLUS400 NMR or a 500 NMR Agilent spectrometer with CDCl₃ as the solvent. ¹H chemical shifts were referenced to CDCl₃ at 7.26 ppm. ¹³C chemical shifts were referenced to CDCl₃ at 77.16 ppm and obtained with ¹H decoupling. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), sextet (sextet), septet (septet), multiplet (m), and broad (br). MS was measured on Agilent 7890A/5975C Series GC/MSD mass spectrometer. HPLC yield were determined on Agilent 1200 Infinity Series.

2. General procedures for substrates methanesulfonate

2.1 The synthesis of 1a-k and 1m



Procedure 1^[1]: To a stirred solution of acetic acid (1 equiv) in THF (140 mL) was added amine (1 equiv) via a syringe followed by N-hydroxysuccinimide (1.1 equiv).The mixture was cooled to 0 °C and N,N'-dicyclohexylcarbodiimide (1.1 equive) was added. After 15 min, the cooling bath was removed and the solution was stirred at r.t. overnight (20 h). The mixture was filtered through a sintered glass plate and the dicyclohexylurea cake washed with THF (2 × 10 mL). The solvent was removed under reduced pressure, and the residue was dissolved in EtOAc (300 mL). The organic layer was washed successively with sat. Na₂CO₃ (aq. 70 mL), H₂O (70 mL), 1 M HCl (aq. 70 mL), H₂O (70 mL), and brine (70 mL) and dried with MgSO₄. After filtration, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel eluting with hexane:EtOAc (8:2) to give the product α -hydroxyl amide as white solids.

Procedure 2^[2]: Compound α - hydroxyl amides (1.1 equiv) and NEt₃ (3 equiv) was dissolved in CH₂Cl₂, and MsCl (1.1 equiv) dissolved in CH₂Cl₂ was added under 0°C. The mixture was stirred at 0°C for 1 h, then stirred at r.t for 2 h. The reaction was quenched by addition of 1N HCl and the aqueous layer was washed with CH₂Cl₂ (20 mL × 3). The organic layer was concentrated under reduced pressure to give the product methanesulfonate as white solids.

2.1 The synthesis of 11 and 1n-o



Procedure 1^[3]: Aryl iodide (1 equiv) is charged to a suitable reactor, followed by copper (I) bromide (0.2 equiv) and dry THF. The batch is cooled to -15 to -12 °C. *i*-PrMgCl (2.0 M in THF, 1.1 equiv) is charged into the reactor at the rate which maintains the batch temp. < -10 °C. To another reactor charged with methyl chlorooxoacetate (1.1 equiv) and dry THF. The solution was cooled to -15 °C. The content of the 1st reactor (Grignard/cuprate) was charged into the 2nd reactor at the rate which maintains the batch temp. < -10 °C. The batch is agitated for 30 min. at -10 °C. Aqueous ammonium chloride solution (10%) is charged. The batch is agitated at 20 - 25 °C for 20 min. The aqueous layer is cut. The organic solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel eluting with hexane:EtOAc (50:1) to give the α-keto acetates as yellow oils.

Procedure 2: Acetate was charged into a suitable reactor. Sodium hydroxide solution (5%) was charged into the reactor. The mixture was stirred at r.t for 2 h. The PH was adjusted to 2-3 by addition of 1N HCl and the aqueous layer was washed with Et₂O (20 mL \times 3). The organic layer was concentrated under reduced pressure to give the product α -keto acetic acids without further purification.

Procedure 3^[4]: Acetic acid (1 equiv) was charged into a suitable reactor, followed by Et₃N (2 equiv) and CH₂Cl₂. The batch is cooled to 0 °C. Sulfurous dichloride (2 equiv) was charged into the reactor. After 20 min, phenylmethanamine (2 equiv) was charged. After 15 min, the cooling bath was removed and the solution was stirred at r.t. overnight. After this time, the reaction was quenched by addition of sodium carbonate solution and the aqueous layer was washed with CH₂Cl₂ (20 mL × 3). The organic layer was concentrated under reduced pressure and the crude product was purified by flash chromatography on silica gel to give the product α -keto amides as white solids.

Procedure 4^[5]: To a 4.0 mL vial was added the catalyst precursor [Ir(COD)Cl]₂ (3.4 mg, 5.0×10^{-3} mmol), f-amphox (5.8 mg, 10.5×10^{-3} mmol) and anhydrous *i*PrOH (1.0 mL) under argon atmosphere. The mixture was stirred for 1.0 h at 25°C giving orange red solution in the argon-filled glove box. The resulting solution (20 µL) and a solution of Cs₂CO₃ (200 µL, c=0.01mmol/mL) transferred by syringe into a 5.0 mL vial charged with α-keto amides (0.2 mmol) in 1.0 mL anhydrous *i*PrOH. The vials were transferred to an autoclave, which was then charged with 10 atm of H₂ and stirred at room temperature for 5 h-7 h. The hydrogen gas was released slowly in a well-ventilated hood and the solution was passed through a short column of silica gel to remove the metal complex to give the charil α- hydroxyl amides as white solids.

Procedure 5: α -keto amides (1 equiv) was charged into a suitable reactor, followed by CH₃OH. The batch is cooled to 0 °C NaBH₄ (3 equiv) is charged into the reactor. After 2 h, the organic layer was removed under reduced pressure and H₂O was added to the reactor. Then the aqueous layer was washed with EtOAc (20 mL × 3). The organic layer was concentrated under reduced pressure to give the racimic α - hydroxyl amides as white solids.

Procedure 6^[2]: Compound α - hydroxyl amides (1 equiv) and Et₃N (3 equiv) was dissolved in CH₂Cl₂, and MsCl (1.1 equiv) dissolved in CH₂Cl₂ was added under 0°C. The mixture was stirred at 0°C for 1 h then stirred at r.t for 2 h . The reaction was quenched by addition of 1N HCl and the aqueous layer was washed with CH₂Cl₂ (20 mL × 3). The organic layer was concentrated under reduced pressure to give the product methanesulfonate as white solids.

3. General procedures for reductive cyclization of α-mesylated acetamides

To a mixture of methanesulfonate (0.5 mmol, 1 equiv), $(9\text{-BBN})_2$ (1.0 mmol, 2 equiv) and Potassium phosphate (1 mmol, 2 equiv) was charged toluene (5 mL) under nitrogen. The resulting mixture was stirred at 60°C for 8 h. The reaction was cooled to room temperature. The crude product was purified by silica gel column chromatography to provide the products.

4. Mechanism study



Synthesis of **5**: To a solution of α -keto amide (**4**, 450 mg, 2.07 mmol, 1 equiv) in methanol (5 mL) at 0 °C was charged NaBD₄ (260mg, 6.22mmol, 3 equiv) and the mixture was stirred at rt for 2 h. The mixture was concentrated and to the residue was added water (5 mL) and EtOAc (10 mL). The EtOAc layer was separated and the aqueous layer was washed with EtOAc (10 mL \times 3). The combined EtOAc was concentrated to give the deuterium-labeled α -hydroxyl amide **5** as white solid (410 mg, 90% yield).

Synthesis of 1a': To a solution of deuterium-labeled α -hydroxyl amide (5, 300 mg, 1.36 mmol, 1 equiv) and Et₃N (0.57 mL, 4.09 mmol, 3 equiv) in CH₂Cl₂ at 0°C was charted MsCl (0.12 mL, 1.50 mmol, 1.1 equiv) in CH₂Cl₂. The mixture was stirred at 0°C for 1 h and then stirred at rt for 2h. The mixture was quenched by addition of 1 N HCl. The organic layer was separated and the aqueous layer was washed with CH_2Cl_2 (10 mL \times 3). The combined organic layer was concentrated to give the deuterium-labeled 1a' mesylate white soild (389 yield: 96%). as mg, 2-(cyclopentylamino)-2-oxo-1-phenylethyl-1-d methanesulfonate (1a'): Yield: 96%. ¹H NMR (500 MHz, CDCl₃) δ 7.40~7.45 (m, 5H), 6.44 (br, 1H), 4.19~4.26 (m, 1H), 2.83 (s, 3H) 1.96~2.03 (m, 2H), 1.66~1.73 (m, 2H), 1.57~1.64 (m, 2H), 1.39~1.48 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 166.2, 134.0, 129.9, 129.1, 127.8, 51.4, 39.4, 33.0, 32.9, 23.7. ESI-MS: m/z 321.10 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₄H₁₈DNNaO₄S]⁺: 321.0990; found: 321.0996.



1-cyclopentyl-2-phenylaziridine-2-*d* (**3a'**): Yield: 59%. ¹H NMR (500 MHz, CDCl₃) δ 7.32~7.37 (m, 5H), 6.07 (br, 1H), 4.14~4.17 (m, 2H), 1.92~1.95 (m, 2H), 1.56~1.64 (m, 2H), 1.26~1.37 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 139.7, 128.8, 128.5, 126.8, 51.2, 32.9, 23.6. ESI-MS: m/z 189.45 [M+H]⁺; HRMS (ESI) calculated for [M+Na, C₁₃H₁₇DN]⁺: 189.1497; found: 189.1499.

5. Analytical data of substrates.



(*R*)-N-benzyl-2-hydroxy-2-phenylacetamide: White solid, yield: 57%. ¹H NMR (500 MHz, CDCl₃) δ 7.26~7.43 (m, 8H), 7.18~7.20 (m, 2H), 6.42 (br, 1H), 5.10 (s, 1H), 4.42~4.51 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 172.0, 139.3, 137.7, 128.9, 128.8, 128.7, 127.6, 127.6, 126.9, 74.3, 43.6; EI-MS: *m/z* 241.0 [M]⁺; HRMS (EI) *m/z* calcd for C₁₅H₁₅NO₂ (M⁺): 241.1103, found: 241.1102. [α]_D²¹: -78.5° (c = 1.00, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 1.0 mL/min, 210 nm. *t*₁ = 6.90 min, *t*₂ = 10.16 min. T = 15.00 min.







(*R*)-2-(benzylamino)-2-oxo-1-phenylethyl methanesulfonate (1a): White solid, yield: 91% ¹H NMR (500 MHz, CDCl₃) δ 7.41~7.47 (m, 5H), 7.25~7.36 (m, 5H), 6.89 (br, 1H), 5.93 (s, 1H), 4.43~4.55 (m, 2H), 2.81 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.8, 137.3, 134.0, 130.0, 129.2, 128.8, 127.8, 127.8, 127.7, 81.5, 43.6, 39.3; ESI-MS: m/z 320.1 [M+H]⁺, 342.0 [M+Na]⁺; HRMS (ESI) calculated for [M+H, C₁₆H₁₇NO₄S]⁺: 320.0951; found: 320.0953. [α]_D²¹: -96.1° (c = 0.99, CHCl₃). 99% ee. Chiral HPLC conditions: OD-H, *i*-PrOH-hexane 40/60, flow rate 0.8 mL/min, 210 nm. *t*₁ = 9.28 min, *t*₂ = 13.82 min. T = 18.00 min.







(*R*)-*N*-(cyclohexylmethyl)-2-hydroxy-2-phenylacetamide: White solid, yield: 79%. ¹H NMR (500 MHz, CDCl₃) δ 7.32~7.41 (m, 5H), 6.12 (br, 1H), 5.01 (d, *J* = 3.4 Hz, 1H), 3.74 (br, 1H), 3.10 (t, *J* = 6.45 Hz, 2H), 1.58~1.70 (m, 5H), 1.38~1.44 (m, 1H), 1.06~1.23 (m, 3H), 0.81~0.89 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 172.1, 139.6, 128.9, 128.6, 126.8, 74.1, 45.8, 37.8, 30.6, 30.6, 26.3, 25.7; ESI-MS: m/z 248.05 [M+H]⁺, 270.15 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₅H₂₁NNaO₂]⁺: 270.1465; found: 270.1470. [α]_D²⁹: -58.0° (c = 0.525, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 6.32 min, *t*₂ = 8.61 min. T = 15.00 min.







(*R*)-2-((cyclohexylmethyl)amino)-2-oxo-1-phenylethyl methanesulfonate (1b): White solid, yield: 91% ¹H NMR (500 MHz, CDCl₃) δ 7.41~7.45 (m, 5H), 6.52 (br, 1H), 5.87 (s, 1H), 3.12~3.18 (m, 2H), 2.98 (s, 3H), 1.65~1.77 (m, 5H), 1.47~1.54 (m, 1H), 1.12~1.27 (m, 3H), 0.89~0.96 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 166.7, 134.1, 129.9, 129.1, 127.8, 81.7, 45.8, 39.4, 37.8, 30.7, 30.7, 26.3, 25.7, 25.7; ESI-MS: m/z 326.15 [M+H]⁺, 348.15 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₆H₂₃NNaO₄S]⁺: 348.1240; found: 348.1246. [α]_D²¹: -55.1° (c = 0.585, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 9.90min, *t*₂ = 13.47 min. T = 30.00 min.







(*R*)-*N*-cyclopentyl-2-hydroxy-2-phenylacetamide: White solid, yield: 70% ¹H NMR (500 MHz, CDCl₃) δ 7.31~7.39 (m, 5H), 6.11 (br, 1H), 4.97 (d, *J* = 3.60 Hz, 1H), 4.14~4.21 (m, 1H), 3.76 (d, *J* = 3.65 Hz, 1H), 1.91~1.99 (m, 2H), 1.55~1.64 (m, 4H), 1.29~1.61 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 171.58, 139.62, 128.83, 128.57, 126.82, 74.08, 51.28, 32.97, 32.95, 23.65; ESI-MS: m/z 220.00 [M+H]⁺, 242.00 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₃H₁₇NNaO₂]⁺: 242.1151; found: 242.1152. [α]_D²⁹: -40.9° (c = 0.385, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 5.96 min, *t*₂ = 8.56 min. T = 15.00 min.







(*R*)-2-(cyclopentylamino)-2-oxo-1-phenylethyl methanesulfonate(1c): White solid, yield: 93% ¹H NMR (500 MHz, CDCl₃) δ 7.40~7.45 (m, 5H), 6.46 (br, 1H), 5.84 (s, 1H), 4.19~4.26 (m, 1H), 2.83 (s, 3H), 1.94~2.04 (m, 2H), 1.68~1.73 (m, 2H), 1.59~1.64 (m, 2H), 1.39~1.47 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 166.22, 134.10, 129.88, 129.11, 127.81, 81.58, 51.43, 39.35, 32.95, 32.85, 23.73; ESI-MS: m/z 298.05 [M+H]⁺, 320.05 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₄H₁₉NNaO₄S]⁺: 320.0927; found: 320.0933. [α]_D²⁸: -58.2° (c = 0.265, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 9.46 min, *t*₂ = 16.39 min, T = 30.00 min.







(*R*)-*N*-cyclohexyl-2-hydroxy-2-phenylacetamide: White solid, yield: 70% ¹H NMR (500 MHz, CDCl₃) δ 7.29~7.35 (m, 5H), 6.22 (br, 1H), 4.93 (d, *J* = 4.25 Hz, 1H), 4.07 (br, 1H), 3.70~3.74 (m, 1H), 1.81~1.84 (m, 2H), 1.56~1.68 (m, 3H), 1.26~1.36 (m, 2H), 1.04~1.18 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.28, 139.77, 128.71, 128.43, 126.80, 74.03, 48.28, 32.87, 32.78, 25.41, 24.70, 24.66; ESI-MS: m/z 234.00 [M+H]⁺, 256.00 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₄H₁₉NNaO₂]⁺: 256.1308; found: 256.1313. [α]_D²⁹: -49.94° (c = 0.495, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 6.15 min, *t*₂ = 10.50 min. T = 18.00 min.







(*R*)-2-(cyclohexylamino)-2-oxo-1-phenylethyl methanesulfonate(1d): White solid, yield: 91% ¹H NMR (500 MHz, CDCl₃) δ 7.41~7.46 (m, 5H), 6.32 (br, 1H), 5.84 (s, 1H), 3.78~3.85 (m, 1H), 2.83 (s, 3H), 1.90~1.96 (m, 3H), 1.70~1.75 (m, 3H), 1.60~1.65 (m, 1H), 1.30~1.42 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.70, 134.14, 129.90, 129.12, 127.83, 81.64, 48.59, 39.38, 32.89, 32.75, 25.38, 24.74, 24.71; ESI-MS: m/z 312.05 [M+H]⁺, 334.10 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₅H₂₁NNaO₄S]⁺: 334.1083; found: 334.1087. [α]D²⁹: -64.3° (c = 0.445, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 210 nm. *t*₁ = 9.64 min, *t*₂ = 16.16 min. T = 30.00min.







(*R*)-*N*-cycloheptyl-2-hydroxy-2-phenylacetamide: White solid, yield: 75%. ¹H NMR (500 MHz, CDCl₃) δ 7.30~7.38 (m, 5H), 6.19 (br, 1H), 4.94 (d, J = 3.55 Hz, 1H), 3.87~3.95 (m, 2H), 1.80~1.87 (m, 2H), 1.51~1.59 (m, 4H), 1.33~1.47 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 170.9, 139.7, 128.8, 128.5, 126.8, 74.0, 50.6, 34.9, 34.8, 27.8, 24.0, 23.9; ESI-MS: 270.40 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₅H₂₁NNaO₂]⁺: 270.1465; found: 270.1469. [α]_D²⁹: -39.2° (c = 0.58, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. $t_1 = 6.28$ min, $t_2 = 9.98$ min. T = 15.00 min.







(*R*)-2-(cycloheptylamino)-2-oxo-1-phenylethyl methanesulfonate(1e): White solid, yield: 91% ¹H NMR (500 MHz, CDCl₃) δ 7.39~7.45 (m, 5H), 6.42 (br, 1H), 5.83 (s, 1H), 3.96~3.99 (m, 1H), 2.84 (s, 3H), 1.89~1.97 (m, 2H), 1.57~1.66 (m, 4H), 1.45~1.52 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 165.4, 134.2, 129.9, 129.1, 127.8, 81.6, 50.8, 39.4, 34.9, 34.8, 27.8, 27.8, 24.1, 24.0; ESI-MS: m/z 348.40 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₆H₂₃NNaO₄S]⁺: 348.1240; found: 348.1245. [α]_D²⁸: -44.7° (c = 0.545, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 9.60 min, *t*₂ = 15.08 min. T = 25.00 min.





(*R*)-*N*-butyl-2-hydroxy-2-phenylacetamide: White solid, yield: 81% ¹H NMR (500 MHz, CDCl₃) δ 7.32~7.38 (m, 5H), 6.12 (br, 1H), 4.99 (s, 1H), 3.76 (br, 1H), 3.20~3.28 (m, 2H), 1.41~1.48 (m, 2H), 1.24~1.32 (m, 2H), 0.89 (t, *J* = 3.75 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.01, 139.57, 128.85, 128.61, 126.83, 74.12, 39.35, 31.48, 19.91, 13.65; ESI-MS: m/z 299.95 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₂H₁₇NNaO₂]⁺: 230.1151; found: 230.1152. [α]_D²⁹: -64.19° (c = 1.215, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 5.68 min, *t*₂ = 7.15 min. T = 18.00 min.







(*R*)-2-(butylamino)-2-oxo-1-phenylethyl methanesulfonate(1f): White solid, yield: 91% ¹H NMR (500 MHz, CDCl₃) δ 7.41~7.46 (m, 5H), 6.49 (br, 1H), 5.86 (s, 1H), 3.30~3.35 (m, 2H), 2.84 (s, 3H), 1.51~1.56 (m, 2H), 1.31~1.39 (m, 2H), 0.93 (t, *J* = 7.35Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.62, 134.09, 129.92, 129.13, 127.80, 81.67, 39.41, 39.37, 31.42, 19.96, 13.67; ESI-MS: m/z 286.05 [M+H]⁺, 308.05 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₃H₁₉NNaO₄S]⁺: 308.0927; found: 308.0929. [α]_D²⁷: -68.30° (c = 0.455, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 8.60 min, *t*₂ = 13.00 min. T = 18.00 min.





(*R*)-2-hydroxy-*N*-pentyl-2-phenylacetamide: White solid, yield: 82% ¹H NMR (500 MHz, CDCl₃) δ 7.31~7.39 (m, 5H), 6.22 (br, 1H), 4.97 (d, *J* = 3.4Hz, 1H), 3.90 (br, 1H), 3.20~3.24 (m, 2H), 1.42~1.48 (m, 2H), 1.19~1.30 (m, 4H), 0.86 (t, *J* = 7.05 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.08, 139.63, 128.79, 128.53, 126.80, 74.08, 39.55, 29.09, 28.87, 22.25, 13.93; ESI-MS: m/z 222.05 [M+H]⁺, 244.10 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₃H₁₉NNaO₂]⁺: 244.1308; found: 244.1313. [α]_D²⁸: -50.49° (c = 2.63, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 5.62 min, *t*₂ = 7.13 min. T = 18.00 min.





(*R*)-2-oxo-2-(pentylamino)-1-phenylethyl methanesulfonate(1g): White solid, yield: 94% ¹H NMR (400 MHz, CDCl₃) δ 7.39~7.45 (m, 5H), 6.50 (br, 1H), 5.85 (s, 1H), 3.26~3.33 (m, 2H), 2.83 (s, 3H), 1.49~1.57 (m, 2H), 1.26~1.35 (m, 4H), 0.88 (t, J = SI-18

8.55Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.7, 134.1, 129.9, 129.1, 127.8, 81.7, 39.7, 39.4, 29.1, 28.9, 22.3, 13.9 ; ESI-MS: m/z 300.10 [M+H]⁺, 322.15 [M+Na]⁺; HRMS (ESI) calculated for [M+H, C₁₄H₂₁NNaO₄S]⁺: 322.1083; found: 322.1087. [α]_D²⁸: -52.4° (c = 0.575, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. t_1 = 8.30 min, t_2 = 12.76 min. T = 15.00 min.





(*R*)-*N*-dodecyl-2-hydroxy-2-phenylacetamide: White solid, yield: 72% ¹H NMR (500 MHz, CDCl₃) δ 7.32~7.38 (m, 5H), 6.22 (br, 1H), 4.97 (s, 1H), 3.94 (br, 1H), 3.21~3.24 (m, 2H), 1.40~1.49 (m, 2H), 1.23~1.32 (m, 18H), 0.89 (t, *J* = 6.80 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.10, 139.65, 128.77, 128.52, 126.81, 74.09, 39.59, 29.63, 29.61, 29.54, 29.49, 29.42, 29.34, 29.19, 26.73, 22.68, 14.11; ESI-MS: m/z 320.3 [M+H]⁺, 342.3 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₂₀H₃₃NNaO₂]⁺: 342.2404; found: 324.2411. [α]_D²⁹: -24.37° (c = 0.12, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 4.59 min, *t*₂ = 5.44 min. T = 15.00 min.





(*R*)-2-(dodecylamino)-2-oxo-1-phenylethyl methanesulfonate(1h): White solid, yield: 91% ¹H NMR (500 MHz, CDCl₃) δ 7.41~7.46 (m, 5H), 6.47 (br, 1H), 5.86 (s, 1H), 3.28~3.34 (m, 2H), 2.84 (s, 3H), 1.26~1.29 (m, 20H),0.89 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.59, 134.10, 129.91, 129.13, 127.79, 81.68, 39.71, 39.38, 31.90, 29.63, 29.61, 29.54, 29.49, 29.38, 29.33, 29.19, 26.77, 22.68, 14.11; ESI-MS: m/z 398.30 [M+H]⁺, 420.30 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₂₁H₃₅NNaO₄S]⁺: 420.2179; found: 420.2183. [α]_D²⁸: -47.72° (c = 0.245, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 210 nm. *t*₁ = 6.27 min, *t*₂ = 9.31 min. T = 18.00 min.





(*R*)-2-hydroxy-*N*-isobutyl-2-phenylacetamide: White solid, yield: 72% ¹H NMR (500 MHz, CDCl₃) δ 7.31~7.40 (m, 5H), 6.23 (br, 1H), 4.99 (d, *J* = 3.5 Hz, 1H), 3.89 (d, *J* = 3.55 Hz, 1H), 3.02~3.11 (m, 2H), 1.68~1.75 (m, 1H), 0.84 (d, *J* = 5.2 Hz, 3H), 0.83 (d, *J* = 5.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.18, 139.65, 128.82, 128.58, 126.79, 74.13, 46.80, 28.46, 19.91, 19.88; ESI-MS: m/z 208.40 [M+H]⁺, 230.40 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₂H₁₇NNaO₂]⁺: 230.1151; found: 230.1156. [α]_D²⁹: -53.68° (c = 0.94, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 5.60 min, *t*₂ = 7.21 min. T = 15.00 min.





(*R*)-2-(isobutylamino)-2-oxo-1-phenylethyl methanesulfonate(1i): White solid, yield: 91% ¹H NMR (500 MHz, CDCl₃) δ 7.41~7.47 (m, 5H), 6.52 (br, 1H), 5.88 (s, 1H), 3.14~3.17 (m, 2H), 2.86 (s, 3H), 1.78~1.87 (m, 1H), 0.93 (d, *J* = 3.80 Hz, 3H), 0.92 (d, *J* = 3.80 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.73, 134.11, 129.91, 129.14, 127.74, 81.69, 46.87, 39.37, 28.46, 20.00, 19.96; ESI-MS: m/z 286.15 [M+H]⁺, 308.10 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₃H₁₉NNaO₄S]⁺: 308.0927; found: 308.0931. [α]_D²⁹: -57.68° (c = 0.575, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 8.37 min, *t*₂ = 13.02 min. T = 18.00 min.





(*R*)-2-hydroxy-*N*-(pentan-3-yl)-2-phenylacetamide: White solid, yield: 66% ¹H NMR (500 MHz, CDCl₃) δ 7.31~7.40 (m, 5H), 5.81 (br, 1H), 4.99 (s, 1H), 3.92 (br, 1H), 3.73~3.75 (m, 1H), 1.46~1.56 (m, 2H), 1.23~1.40 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H), 0.75 (t, *J* = 7.45 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.19, 139.83, 128.81, 128.56, 126.81, 74.10, 52.39, 27.48, 27.33, 10.21, 9.94; ESI-MS: m/z 222.40 [M+H]⁺, 244.35 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₃H₁₉NNaO₂]⁺: 244.1308; found: 244.1314. [α]_D²⁹: -49.59° (c = 1.215, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 5.23 min, *t*₂ = 6.84 min. T = 15.00 min.





(*R*)-2-oxo-2-(pentan-3-ylamino)-1-phenylethyl methanesulfonate(1j): White solid, yield: 91% ¹H NMR (500 MHz, CDCl₃) δ 7.41~7.47 (m, 5H), 6.14 (d, *J* = 7.75 Hz, 1H), 5.88 (s, 1H), 2.86 (s, 3H), 1.56~1.64 (m, 2H), 1.40~1.47 (m, 2H), 0.93 (td, *J* = 7.45 Hz, 8.50 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 166.45, 134.23, 129.88, 129.13, 127.72, 81.74, 52.57, 39.35, 27.40, 27.37, 10.27, 10.13; ESI-MS: m/z 300.10 [M+H]⁺, 322.15 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₄H₂₁NNaO₄S]⁺: 322.1083; found: 322.1088. [α]_D²⁸: -53.78° (c = 0.515, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 230 nm. *t*₁ = 7.79 min, *t*₂ = 14.40 min. T = 18.00 min.





(*S*)-N-benzyl-2-(2-chlorophenyl)-2-hydroxyacetamide: White solid, yield: 75% ¹H NMR (500 MHz, CDCl₃) δ 7.42~7.44 (m, 1H), 7.36~7.37 (m, 1H), 7.23~7.32 (m, 5H), 7.18~7.19 (m, 2H), 6.74 (br, 1H), 5.51 (d, *J* = 4.4 Hz, 1H), 4.38~4.50 (m, 2H), 4.31 (d, *J* = 4.4 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 171.6, 137.5, 137.3, 132.8, 129.8, 129.7, 128.7, 128.6, 127.6, 127.5, 127.5, 70.4, 43.7; ESI-MS: m/z 276.0 [M+H]⁺, 298.0 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₅H₁₄ClNO₂Na]⁺: 298.0605; found: 298.0607. [α]_D²¹: 95.9° (c = 1.12, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 210 nm. *t*₁ = 9.55 min, *t*₂ = 11.12 min. T = 15.00 min.





(*S*)-2-(benzylamino)-1-(2-chlorophenyl)-2-oxoethyl methanesulfonate (1k): White solid, yield: 90% ¹H NMR (500 MHz, CDCl₃) δ 7.45~7.50 (m, 2H), 7.29~7.40 (m, 7H), 6.75 (br, 1H), 6.33 (s, 1H), 4.46~4.62 (m, 2H), 2.94 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.1, 137.1, 133.9, 132.0, 131.3, 130.4, 130.3, 128.8, 127.8, 127.6, 78.4, 43.8, 39.2; ESI-MS: m/z 354.1 [M+H]⁺, 376.1 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₆H₁₆ClNO₄NaS]⁺: 376.0381; found: 376.0383. [α]_D²¹: 68.2° (c = 1.02, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 40/60, flow rate 0.8 mL/min, 210 nm. t_1 = 9.31 min, t_2 = 10.77 min. T = 15.00 min.





(*S*)-N-benzyl-2-(3-chlorophenyl)-2-hydroxyacetamide: White solid, yield: 99% ¹H NMR (500 MHz, CDCl₃) δ 7.41 (s, 1H), 7.26~7.34 (m, 6H), 7.17~7.20(m, 2H), 6.79 (br, 1H), 5.01 (s, 1H), 4.40 (d, *J* = 5.4 Hz, 2H), 4.02 (s, 1H) . ¹³C NMR (125 MHz, CDCl₃) δ 171.5, 141.4, 137.5, 134.6, 130.0, 128.8, 128.7, 127.7, 127.6, 126.8, 124.9, 73.5, 43.5; ESI-MS: m/z 276.0 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₅H₁₅O₂NCl]⁺: 276.0786; found: 276.0783. [α]_D²⁸: 50.6° (c = 0.53, CHCl₃). 91% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8mL/min, 210 nm. *t*₁ = 5.72 min, *t*₂ = 7.96 min. T = 15.00 min.





(*S*)-2-(benzylamino)-1-(3-chlorophenyl)-2-oxoethyl methanesulfonate (11): White solid, yield: 88% ¹H NMR (500 MHz, CDCl₃) δ 7.46 (s, 1H), 7.30~7.41 (m,6H), 7.25~7.28 (m, 2H), 6.82 (br, 1H), 5.89 (s, 1H), 4.45~4.56 (m, 2H), 2.90 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.2, 137.2, 135.9, 135.1, 130.4, 130.1, 128.9, 127.8, 127.7, 127.7, 125.9, 80.2, 43.7, 39.4; ESI-MS: m/z 354.1 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₆H₁₇ClNO₄NaS]⁺: 354.0561; found: 354.0558. [α]_D²⁷: 86.5° (c = 0.28, CHCl₃). 90% ee. Chiral HPLC conditions: OD-H, *i*-PrOH-hexane 40/60, flow rate 0.8 mL/min, 210 nm. t_1 = 8.42 min, t_2 = 11.81 min. T = 16.00 min.





(*R*)-N-benzyl-2-(4-chlorophenyl)-2-hydroxyacetamide: White solid, yield: 77% ¹H NMR (500 MHz, CDCl₃) δ 7.28~7.33 (m, 7H), 7.17~7.19 (m, 2H), 6.69 (br, 1H), 5.02 (s, 1H), 4.36~4.44 (m, 2H), 3.81 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 171.7, 137.9, 137.5, 134.5, 128.9, 128.8, 128.1, 127.7, 127.6, 73.5, 43.5; ESI-MS: m/z 276.0 [M+H]⁺, 398.0 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₅H₁₄ClNO₂Na]⁺: 298.0605; found: 298.0608. [α]_D²²: -76.7° (c = 1.00, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 210 nm. t_1 = 7.80 min, t_2 =13.31 min. T = 20.00 min.





(*R*)-2-(benzylamino)-1-(4-chlorophenyl)-2-oxoethyl methanesulfonate (1m): White solid, yield: 87% ¹H NMR (500 MHz, CDCl₃) δ 7.26~7.43 (m, 9H), 6.76 (br, 1H), 5.91 (s, 1H), 4.45~4.58 (m, 2H), 2.88 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.3, 137.1, 136.1, 132.5, 129.4, 129.1, 128.9, 127.9, 127.8, 80.4, 43.7, 39.4; ESI-MS: m/z 354.1 [M+H]⁺, 376.1 [M+Na]⁺; HRMS (ESI) calculated for [M+Na, C₁₆H₁₆ClNO₄NaS]⁺: 376.0381; found: 376.0383. [α]_D²²: -107.0° (c = 1.10, CHCl₃). 99% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 40/60, flow rate 0.8 mL/min, 210 nm. *t*₁ = 9.46 min, *t*₂ = 12.89 min. T = 16.00 min.





(*S*)-N-benzyl-2-(4-bromophenyl)-2-hydroxyacetamide: White solid, yield: 99% ¹H NMR (500 MHz, CDCl₃) δ 7.49~7.52 (m, 2H), 7.28~7.34 (m, 5H), 7.19~7.20 (m, 2H), 6.54 (br, 1H), 5.05 (s, 1H), 4.40~4.48 (m, 2H), 3.60 (br, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 171.4, 138.3, 137.5, 132.0, 128.8, 128.4, 127.7, 127.6, 122.7, 73.6, 43.6; ESI-MS: m/z 321.0 [M+H]⁺, 344.0 [M+Na]⁺; HRMS (ESI) calculated for [M+H, C₁₅H₁₅O₂NBr]⁺: 320.0281; found: 320.0278. [α]_D²⁸: 70.2° (c = 0.55, CHCl₃). 94% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 210 nm. $t_1 = 6.56$ min, $t_2 = 11.76$ min. T = 16.00 min.





(*S*)-2-(benzylamino)-1-(4-bromophenyl)-2-oxoethyl methanesulfonate (1n): White solid, yield: 82% ¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 8.5 H_Z, 2H), 7.29~7.37(m, 5H), 7.24~7.27 (m, 2H), 6.84 (br, 1H), 5.89 (s, 1H), 4.42~4.56 (m, 2H), 2.87 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.3, 137.1, 133.0, 132.3, 129.3, 128.9, 127.8, 127.7, 124.3, 80.4, 43.7, 39.4; ESI-MS: m/z 338.1 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₆H₁₇O₄NBrS]⁺: 398.0056; found: 398.0051. [α]_D²⁷: 123.1° (c = 0.19, CHCl₃). 94% ee. Chiral HPLC conditions: OD-H, *i*-PrOH-hexane 40/60, flow rate 0.8 mL/min, 210 nm. *t*₁ = 9.29 min, *t*₂ = 14.00 min. T = 16.00 min.





(*S*)-*N*-benzyl-2-(2-bromophenyl)-2-hydroxyacetamide: White solid, yield: 99% ¹H NMR (500 MHz, CDCl₃) δ 7.57 (dd, J = 8.0 Hz, 1.1 Hz, 1H), 7.47 (dd, J = 7.8 Hz, 1.7Hz, 1H), 7.36 (td, J = 7.6 Hz, 1.1Hz, 1H), 7.27~7.34 (m, 3H), 7.17~7.23 (m, 3H), 6.53 (br, 1H), 5.56 (s, 1H), 4.41~4.56 (m, 2H), 4.11 (br s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 171.5, 138.9, 137.4, 133.0, 130.1, 128.7, 128.3, 127.6, 127.4, 122.8, 72.3, 43.8; ESI-MS: m/z 320.1 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₅H₁₅O₂NBr]⁺: 320.0281; found: 320.0281. [α]p²⁸: 94.2° (c = 0.61, CHCl₃). 97% ee. Chiral HPLC conditions: AD-H, *i*-PrOH-hexane 20/80, flow rate 0.8 mL/min, 210 nm. *t*₁ = 8.12 min, *t*₂ = 9.00 min. T = 16.00 min.





(*S*)-2-(benzylamino)-1-(2-bromophenyl)-2-oxoethyl methanesulfonate (1o): White solid, yield: 68% ¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, J = 8.0 Hz, 2H), 7.47~7.48 (m, 1H), 7.26~7.43 (m, 7H), 6.74 (br, 1H), 6.34 (s, 1H), 4.45~4.61 (m, 2H), 2.97 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.1, 137.1, 133.7, 133.6, 131.4, 130.3, 128.8, 128.3, 127.8, 123.7, 80.2, 43.8, 39.3. ESI-MS: m/z 398.0 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₆H₁₇O₄NBrS]⁺: 398.0056; found: 398.0055. [α]_D²⁸: 45.9° (c = 1.50, CHCl₃). 97% ee. Chiral HPLC conditions: OD-H, *i*-PrOH-hexane 40/60, flow rate 0.8 mL/min, 230 nm. *t*₁ = 8.33 min, *t*₂ = 9.14 min. T = 16.00 min.



6. Analytical data of aziridines products



(*S*)-1-benzyl-2-phenylaziridine (3a): yellow oil, 62% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.38 (d, J = 7.48Hz, 2H), 7.27~7.34 (m, 6H), 7.21~7.25 (m, 2H), 3.60~3.72 (m, 2H), 2.52 (dd, J = 3.36 Hz, 6.50 Hz, 1H), 2.00 (d, J = 3.30 Hz, 1H), 1.86 (d, J = 6.80 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 140.1, 139.1, 128.3, 127.8, 126.9, 126.2, 64.7, 41.5, 37.9; ESI-MS: m/z 210.25 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₅H₁₆N]⁺: 210.1277; found: 210.1279. [α]_D²⁷: 13.8° (c = 0.275, EtOH). 97% ee. Chiral



HPLC conditions: IC-H, *i*-PrOH-hexane-Et₂NH 5/95/0.1, flow rate 0.5 mL/min, 250 nm.



(*S*)-1-(cyclohexylmethyl)-2-phenylaziridine (3b): yellow oil, 54% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.20~7.31 (m, 5H), 2.45 (dd, *J* = 7.00 Hz, 11.65 Hz, 1H), 2.28 (dd, *J* = 3.05 Hz, 6.15 Hz, 1H), 2.11 (dd, *J* = 6.40 Hz, 11.65 Hz, 1H), 1.60~1.91 (m, 8H), 1.11~1.28 (m, 3H), 0.93~1.03 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 140.6, 128.2, 126.7, 126.1, 68.7, 41.5, 38.8, 38.0, 31.7, 31.6, 26.6, 26.1, 26.1; ESI-MS: m/z 216.05 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₅H₂₂N]⁺: 216.1747; found: 216.1751. [α]_D²⁸: 93.6° (c = 0.605, EtOH). 99% ee. Chiral HPLC conditions: OD-H, *i*-PrOH-hexane-Et₂NH 2/98/0.1, flow rate 0.5 mL/min, 260 nm.






(*S*)-1-cyclopentyl-2-phenylaziridine (3c): yellow oil, 71% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.19~7.31 (m, 5H), 2.39 (dd, J = 3.30 Hz, 6.50 Hz, 1H), 2.06~2.11 (m, 1H), 1.77~1.88 (m, 3H), 1.67~1.76 (m, 5H), 1.51~1.60 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 140.7, 128.2, 126.6, 126.4, 72.4, 40.9, 36.9, 32.9, 32.2, 24.4, 24.3; ESI-MS: m/z 188.30 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₃H₁₈N]⁺: 188.1434; found: 188.1435. [α]_D²⁷: -92.4° (c = 0.87, EtOH). 97% ee. Chiral HPLC conditions: OD-H, *i*-PrOH-hexane-Et₂NH 5/95/0.1, flow rate 0.5 mL/min, 254 nm.







(*S*)-1-cyclohexyl-2-phenylaziridine (3d): yellow oil, 56% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.19~7.31 (m, 5H), 2.36 (dd, *J* = 3.30 Hz, 6.50 Hz, 1H), 1.87~1.90 (m, 3H), 1.77~1.83 (m, 2H), 1.68 (d, *J* = 6.60 Hz, 1H), 1.41~1.48 (m, 2H), 1.17~1.33 (m, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 140.7, 128.2, 126.7, 126.5, 69.7, 40.1, 35.9, 33.0, 32.3, 26.2, 24.9, 24.9; ESI-MS: m/z 202.10 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₄H₂₀N]⁺: 202.1590; found: 202.1592. [α]_D²⁸: 82.3° (c = 0.31, EtOH). 90% ee. Chiral HPLC conditions: OD-H, *i*-PrOH-hexane-Et₂NH 5/95/0.1, flow rate 0.5 mL/min, 254 nm.







(*S*)-1-cycloheptyl-2-phenylaziridine (3e): yellow oil, 74% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.19~7.31 (m, 5H), 2.37(dd, J = 3.30 Hz, 6.55 Hz, 1H), 1.89~1.94 (m, 3H), 1.64~1.81 (m, 5H), 1.52~1.61 (m, 4H), 1.44~1.51 (m, 1H), 1.35~1.43 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 140.7, 128.2, 126.7, 126.4, 72.5, 41.1, 36.8, 34.8, 34.0, 28.2, 28.1, 24.6, 24.6; ESI-MS: m/z 216.45 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₅H₂₂N]⁺: 216.1747; found: 216.1751. [α]_D²⁷: 86.7° (c = 0.705, EtOH). 93% ee. Chiral HPLC conditions: IC-H, *i*-PrOH-hexane-Et₂NH 2/98/0.1, flow rate 0.5 mL/min, 260nm.







(*S*)-1-butyl-2-phenylaziridine (3f): yellow oil, 60% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.21~7.31 (m, 5H), 2.48~2.54 (m, 1H), 2.29~2.36 (m, 2H), 1.90 (d, *J* = 2.90 Hz, 1H), 1.66 (d, *J* = 6.45 Hz, 1H), 1.58~1.64 (m, 2H), 1.36~1.44 (m, 2H), 0.93 (t, *J* = 7.40 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 140.5, 128.2, 126.7, 126.2, 61.6, 41.3, 37.7, 32.0, 20.6, 14.1; ESI-MS: m/z 176.00 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₂H₁₈N]⁺: 176.1434; found: 176.1429. [α]_D²⁷: 15.3° (c = 0.12, EtOH). 97% ee. Chiral HPLC conditions: OD-H, *i*-PrOH-hexane-Et₂NH 5/95/0.1, flow rate 0.5 mL/min, 254nm.







(*S*)-1-pentyl-2-phenylaziridine (3g): yellow oil, 63% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.20~7.32 (m, 5H), 2.46~2.51 (m, 1H), 2.33~2.37 (m, 1H), 2.30 (dd, *J* = 3.60 Hz, 6.75 Hz, 1H), 1.90 (d, *J* = 3.30 Hz, 1H), 1.60~1.67 (m, 3H), 1.30~1.40 (m, 4H), 0.93 (t, *J* = 7.00 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 140.5, 128.2, 126.7, 126.2, 61.9, 41.3, 37.8, 29.6, 29.5, 22.7, 14.0; ESI-MS: m/z 190.05 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₃H₂₀N]⁺: 190.1590; found: 190.1595. [α]_D²⁷: 76.3° (c = 0.355, EtOH). 96% ee. Chiral HPLC conditions: OD-H, *i*-PrOH-hexane-Et₂NH 2/98/0.1, flow rate 0.5 mL/min, 260nm.







(*S*)-1-dodecyl-2-phenylaziridine (3h): yellow oil, 52% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.20~7.31 (m, 5H), 2.43~2.51 (m, 1H), 2.28~2.36 (m, 2H), 1.89 (d, *J* = 3.25 Hz, 1H), 1.66 (d, *J* = 6.50 Hz, 1H), 1.53~1.64 (m, 2H), 1.26~1.38 (m, 18H), 0.89 (t, *J* = 6.60 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 140.5, 128.2, 126.7, 126.2, 61.9 41.9, 41.3, 37.8, 31.9, 29.8, 29.7, 29.6, 29.6, 29.6, 29.3, 27.4, 22.7, 14.1; ESI-MS: m/z 288.65 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₂₀H₃₄N]⁺: 288.2686; found: 288.2692. [α]_D²⁸: 62.8° (c = 1.785, EtOH). 99% ee. Chiral HPLC conditions: OD-H, *i*-PrOH-hexane-Et₂NH 4/96/0.1, flow rate 0.5 mL/min, 250 nm.







(*S*)-1-isobutyl-2-phenylaziridine(3i): yellow oil, 51% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.21~7.32 (m, 5H), 2.46 (dd, *J* = 7.10 Hz, 11.55 Hz, 1H), 2.29 (dd, *J* = 3.25 Hz, 6.45 Hz, 1H), 2.08 (dd, *J* = 6.50 Hz, 11.55 Hz, 1H), 1.86~1.97 (m, 2H), 1.67 (d, *J* = 6.45 Hz, 1H), 1.00 (d, *J* = 6.70 Hz, 3H), 0.96 (d, *J* = 6.70 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 140.6, 128.2, 126.7, 126.1, 69.7, 41.5, 37.8, 29.3, 21.0, 20.9; ESI-MS: m/z 176.45 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₂H₁₈N]⁺: 176.1434; found: 176.1439. [α]_D²⁸: 83.0° (c = 0.547, EtOH). 99% ee. Chiral HPLC conditions: OD-H, *i*-PrOH-hexane-Et₂NH 4/96/0.1, flow rate 0.5 mL/min, 254 nm.







(*S*)-1-(pentan-3-yl)-2-phenylaziridine(3j): yellow oil, 54% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.20~7.32 (m, 5H), 2.36 (dd, *J* = 3.35 Hz, 6.55 Hz, 1H), 1.91 (d, *J* = 3.25 Hz, 1H), 1.71 (d, *J* = 6.55 Hz, 1H), 1.54~1.67 (m, 4H), 1.32~1.37 (m, 1H), 0.99 (t, *J* = 7.50 Hz, 3H), 0.92 (t, *J* = 7.50 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 140.7, 128.2, 126.6, 126.4, 72.7, 40.5, 36.7, 26.8, 26.5, 10.7, 10.2; ESI-MS: m/z 190.40 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₃H₂₀N]⁺: 190.1590; found: 190.1592. [α]_D²⁸: 62.4° (c = 0.227, EtOH). 95% ee. Chiral HPLC conditions: OD-H, *i*-PrOH-hexane-Et₂NH 4/96/0.1, flow rate 0.5 mL/min, 250 nm.







(*R*)-1-benzyl-2-(2-chlorophenyl)aziridine(3k): yellow oil, 51% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.28~7.40 (m, 7H), 7.13~7.22 (m, 2H), 3.63~3.75 (m, 2H), 2.89 (dd, *J* = 3.35 Hz, 6.55 Hz, 1H), 1.91~1.94 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 139.0, 137.6, 133.8, 128.9, 128.4, 128.0, 127.8, 127.5, 127.1, 126.8, 64.6, 39.0, 37.3; ESI-MS: m/z 244.20 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₅H₁₅NCl]⁺: 244.0888; found: 244.0889. [α]_D²⁸: -49.9° (c = 0.545, EtOH). 99% ee. Chiral HPLC conditions: IC-H, *i*-PrOH-hexane-Et₂NH 5/95/0.1, flow rate 0.8 mL/min, 230 nm.







(*R*)-1-benzyl-2-(3-chlorophenyl)aziridine(3l): yellow oil, 59% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.27~7.40 (m, 6H), 7.15~7.23 (m, 3H), 3.60~3.70 (m, 2H), 2.48 (dd, *J* = 3.30 Hz, 6.50 Hz, 1H), 1.96 (d, *J* = 3.30 Hz, 1H), 1.87 (d, *J* = 6.40 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 142.4, 138.8, 134.3, 129.5, 128.4, 127.8, 127.1, 127.0, 126.3, 124.5, 64.6, 40.8, 38.2; ESI-MS: m/z 243.90 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₅H₁₅NCl]⁺: 244.0888; found: 244.0886. [α]_D²⁸: -86.1° (c = 0.135, EtOH). 89% ee Chiral HPLC conditions: IC-H, *i*-PrOH-hexane-Et₂NH 5/95/0.1, flow rate 0.8 mL/min, 250 nm. t_1 = 5.00 min, t_2 =5.36min.





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(*S*)-1-benzyl-2-(4-chlorophenyl)aziridine (3m): yellow oil, 42% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.29~7.36 (m, 6H), 7.17~7.24 (m, 3H), 3.55~3.72 (m, 2H), 2.47 (dd, *J* = 4.10 Hz, 8.00 Hz, 1H), 1.94 (d, *J* = 3.30 Hz, 1H), 1.86 (d, *J* = 6.50 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.9, 138.7, 132.6, 128.4, 128.4, 127.8, 127.6, 127.1, 64.6, 40.8, 38.1. ESI-MS: m/z 243.90 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₅H₁₅NCl]⁺: 244.0888; found: 244.0886. 99% ee. [α]_D²⁷: 41.5° (c = 0.28, EtOH). Chiral HPLC conditions: IC-H, *i*-PrOH-hexane-Et₂NH 5/95/0.1, flow rate 0.8 mL/min, 230 nm.





(*R*)-1-benzyl-2-(4-bromophenyl)aziridine (3n): yellow oil, 64% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.30~7.37 (m, 4H), 7.19~7.27 (m, 5H), 3.56~3.73 (m, 2H), 2.48 (dd, *J* = 3.30 Hz, 6.50 Hz, 1H), 1.95 (d, *J* = 3.30 Hz, 1H), 1.87 (d, *J* = 6.50 Hz, 1H); δ 138.9, 138.7, 132.5, 128.4, 128.4, 127.8, 127.6, 127.0, 64.6, 40.8, 38.1; ESI-MS: m/z 287.95 [M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₅H₁₅NBr]⁺: 288.0382; found: 288.0382. [α]_D²⁸: -75.0° (c = 0.59, EtOH). 93% ee. Chiral HPLC conditions: IC-H, *i*-PrOH-hexane-Et₂NH 5/95/0.1, flow rate 0.8 mL/min, 230 nm.



(*R*)-1-benzyl-2-(2-bromophenyl)aziridine(3o): yellow oil, 43% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.51 (dd, J = 0.95 Hz, 7.95 Hz, 1H),7.28~7.42 (m, 6H), 7.22~7.26 (m, 1H), 7.09 (td, J = 1.75 Hz, 7.75 Hz, 1H), 3.63~3.76 (m, 2H), 2.84 (dd, J = 3.35 Hz, 6.55 Hz, 1H), 1.93 (d, J = 6.55 Hz, 1H), 1.90 (d, J = 3.30 Hz, 1H); ESI-MS: m/z 287.95[M+H]⁺; HRMS (ESI) calculated for [M+H, C₁₅H₁₅NBr]⁺: 288.0382; found: 288.0385. [α]_D²⁸: -12.8° (c = 0.355, EtOH). 93% ee. Chiral HPLC conditions: IC-H, *i*-PrOH-hexane-Et₂NH 5/95/0.1, flow rate 0.8 mL/min, 230 nm.



7. References

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8. NMR spectra






























































































