Supporting Information

Experimental Section

General methods. Melting points were measured and are uncorrected. Spectral measurements were recorded on a mass spectrometer (MS) and $^1$H and $^{13}$C NMR in chloroform-$d$ (CDCl$_3$). TLC was carried out on a Merck silica gel 60 F$_{254}$ using the same solvent systems as those used in column chromatography. The spots were visualized under UV light (254 nm) or by iodine indication. Column chromatography was performed. Elemental analyses were performed on an MT-5 elemental analyzer. Infrared spectra were recorded using a diffuse reflectance accessory with KBr or NaCl.

General procedure for oxazolidinone. Primary amine (1 mmol ratio) was added to methanol (5 mL) containing an excess amount of halomethyloxirane (5 or 10 mmol ratio), K$_2$CO$_3$ (5 or 10 mmol ratio) and TEA (5 or 10 mmol ratio) under reflux overnight. After the solution was cooled to room temperature, the reaction mixture was filtered for removing the solidified, unreacted carbonate salts. Then, the organic layer was evaporated and the residue was solved in AcOEt. The organic layer was washed with NaCl aq dried using Na$_2$SO$_4$. The solvent was evaporated in vacuo. The residue was isolated by silica-gel column chromatography with chloroform/methanol (10:1).

N-allyl-5-hydroxymethyloxazolidin-2-one (3a). To a stirred suspension solution of bromomethyloxirane 2a (1.00 mL, 12 mmol) and Ag$_2$CO$_3$ (1.66 g, 6 mmol) in methanol (24 mL) was added allylamine (890 µL, 12 mmol). The reaction mixture was stirred overnight under dark and then filtered on Celite for removing the solid. The organic layer was evaporated, and the residue was purified by silica gel column chromatography (chloroform/methanol 5:1) to obtain 3a (1.05 g, 50% unoptimized yield): mp 59-60 °C (crystallized from ethyl acetate); IR (KBr) 3180-3700, 1732 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 3.43 (1H, dd, $J = 9.0, 7.0$ Hz), 3.53 (1H, dd, $J = 9.0$ Hz), 3.63 (1H, dd, $J = 12.0, 4.0$ Hz), 3.83 (1H, ddd, $J = 16.0, 6.0, 1.5$ Hz), 3.85 (1H, dd, $J = 16.0, 6.0, 2.0$ Hz), 3.87 (1H, ddd, $J = 12.0, 3.0$ Hz), 4.60 (1H, m, $J = 7.0, 9.0, 4.0, 3.0$ Hz), 5.23 (1H, ddd, $J = 3.0, 10.0, 1.5$ Hz), 5.25 (1H, ddd, $J = 3.0, 2.0$ Hz), 5.75 (1H, m, $J = 10.0, 17.0, 6.0$ Hz); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 45.3, 46.7, 62.8, 73.6, 118.5, 131.7, 157.8; MS (El) m/z 157 (M$^+$. Anal. Calcd for C$_7$H$_{11}$NO$_3$: C, 53.50; H, 7.01; N, 8.92, Fond: C, 53.28; H, 6.91; N, 8.91.

Conversion of N-Benzyl-5-hydroxyoxazinan-2-one (4b) to N-Benzyl-5-hydroxymethyloxazolidin-2-one (3b). A methanol solution (1 mL) containing 4b (20.0 mg, 0.097 mmol) and DBU (72 µL, 0.483 mmol) was stirred under reflux for 5.5 h. The reaction mixture was evaporated in vacuo, and the residue was purified by column chromatography on silica gel using
chloroform/methanol (10:1) to obtain product 3b (19.2 mg, 96%). IR (film) 3180-3680, 1729 cm⁻¹; ¹H NMR: (600 MHz, CDCl₃) δ 3.33 (1H, dd), 3.44 (1H, dd), 3.61 (1H, dd), 3.84 (1H, dd), 4.37, 4.48 (d, 1H), 4.58 (1H, m), 7.25-7.38 (5H, m); MS (EI) m/z 207 (M)⁺.

3-O-(4-Methoxyphenyl)-2-hydroxypropanol (6). Anhydrous DMF (20 mL) containing 2,3-epoxypropyl 4-methoxyphenyl ether 5 (10.0 g, 55 mmol), TEA (80 mL, 576 mmol), and K₂CO₃ (77 g, 555 mmol) were mixed and stirred at 80 °C overnight. The reaction mixture was filtered to remove the K₂CO₃. The residue was evaporated, and the brown liquid obtained was purified by silica gel column chromatography with chloroform/ethyl acetate (5:1) to give the pure product 6 (4.7 g, 43%) as a pale yellow solid: mp 80–81 °C (crystallized from ethyl acetate/hexane); IR (KBr) 3110-3540, 1241, 1037 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 2.25 (1H, broad), 2.78 (1H, broad), 3.74 (1H, dd, J = 12.0, 6.0 Hz), 3.77 (3H, s), 3.83 (1H, dd, J = 12.0, 3.0 Hz), 3.98 (1H, dd, J = 9.0, 5.0 Hz), 4.01 (1H, dd, J = 9.0, 4.0 Hz), 4.08 (1H, m), 6.82-6.86 (4H, m); ¹³C NMR (150 MHz, CDCl₃) δ 55.7, 63.7, 70.4, 114.7, 115.5, 152.5, 154.2; MS (EI) m/z 198 (M)⁺. Anal. Calcd for C₁₀H₁₄NO₄: C, 60.60; H, 7.12. Found: C, 60.52; H, 7.08.

(R)-N-Benzyl-5-hydroxymethylazolidin-2-one (8). Yield 80% as a pale white solid; mp: 75-76 °C; [α]D₂¹ = -53.0°(c 0.213, MeOH); IR (film) 3160-3600, 1729 cm⁻¹; ¹H NMR: (600 MHz, CDCl₃) δ 3.13 (1H, dd, J = 7.0, 9.0 Hz), 3.42 (1H, dd, J = 8.0, 9.0 Hz), 3.60 (1H, d, J = 13.0, 4.0 Hz), 3.83 (1H, d, J = 13.0, 3.0 Hz), 4.35, 4.46 (1H, d, J = 15.0 Hz), 4.56 (1H, m, J = 8.0, 7.0, 4.0, 3.0 Hz), 7.23-7.35 (5H, m); ¹³C NMR (150 MHz, CDCl₃) δ 45.2, 48.3, 63.2, 73.4, 127.9, 128.1, 135.6, 157.9; MS (FAB) m/z : 208 (M+H)⁺, 415 (2M + H)⁺. Anal. Calcd for C₁₁H₁₄NO₄: C, 63.8; H, 6.32; N, 6.76. Found: C, 63.5; H, 6.29; N, 6.95.