

SUPPORTING INFORMATION

Quaternary Ammonium Bromide Functionalized-Polyethylene Glycol: A Highly Efficient and Recyclable Catalyst for Selective Synthesis of 5-Aryl-2-oxazolidinones from Carbon Dioxide and Aziridines Under Solvent-Free Conditions

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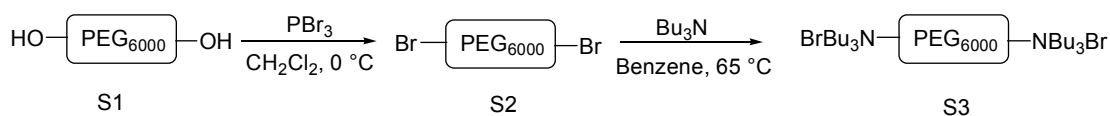
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General experimental methods: All reagents were obtained commercially without further purification. Benzene and diethyl ether were freshly distilled over sodium under nitrogen. Dichloromethane was distilled from calcium hydride. PEG sample was kept at 80 °C in vacuum for 2 h prior to use to remove trace of moisture. ^1H NMR spectra was recorded at Bruker 300 or Varian Mercury-Plus 400 spectrometer in CDCl_3 and TMS (0 ppm) was used as internal reference, ^{13}C NMR was recorded at 75 MHz or 100.6 MHz in CDCl_3 and CDCl_3 (77.0 ppm) was used as internal reference. LC-MS were performed on a Thermo Finnigan LCQ Advantage spectrometer in ESI model-I (ESI-MS) with spray voltage 4.8 KV and atmospheric pressure chemical ionization (APCI-MS). High-resolution mass spectrometry was conducted using an Ionspec 7.0T spectrometer by ESI-FTICR technique. GC-MS were measured on a Finnigan HP G1800A. GC analyses were performed on Shimadzu GC-2014, equipped with a capillary column (RTX-5, 30 m \times 0.25 μm) using a flame ionization detector. HPLC were performed on HP1100. Melting points were measured on an X4 apparatus and uncorrected.

(1) A synthetic procedure of $\text{PEG}_{6000}(\text{NBu}_3\text{Br})_2$ S3

$\text{PEG}_{6000}(\text{NBu}_3\text{Br})_2$ was synthesized as shown in Scheme S1 according to the reported procedures:¹

SCHEME S1



Synthesis of Br-PEG-Br S2

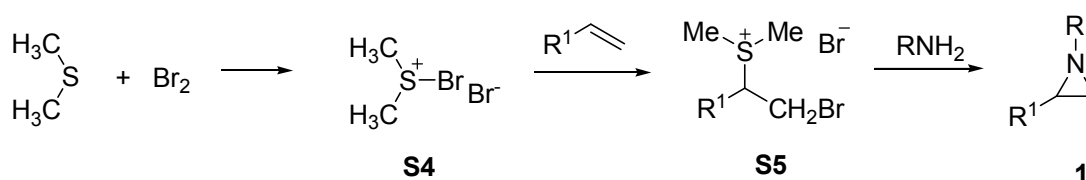
To a solution of polyethylene glycol (S1, 30 g, 5 mmol) in CH_2Cl_2 (50ml), freshly distilled tribromophosphine (0.48ml, 5 mmol) was added. The mixture was stirred for 24 h at room temperature. The solvent was evaporated in vacuum. The residue was dissolved in dichloromethane and precipitated in Et_2O . The product was obtained in 85 % yield.

Synthetic procedure of $\text{PEG}_{6000}(\text{NBu}_3\text{Br})_2$ S3

To a solution of polyethylene glycol dibromide (S2, 21.4 g, 3.5 mmol) in benzene (50ml), freshly distilled tri-n-butyl amine (12.6 ml, 15 equiv) was added. The mixture was stirred for 72 h at 65 °C. The solvent was evaporated in vacuo. The residue was dissolved in dichloromethane and precipitated in Et_2O . The product was obtained in 87 % yield.

(2) General procedure for the preparation of *N*-alkyl phenylaziridines (1a-1n).²

SCHEME S2



Bromodimethyl sulfonium Bromide S4

Dimethyl Sulfide (12.4 g, 0.2mol) and bromine (32.0g, 0.2mol) were separately dissolved in dry dichloromethane (40ml and 40ml respectively). The bromine solution was then added dropwise over 30min to ice-cooled solution of dimethyl sulfide. During the addition, light orange crystals of bromodimethyl sulfonium bromide began to separate. After the addition of bromine was completed, the crystals of **S4** were

collected by filtration and then washed with dry ether and dried under vacuum. Yield: 80%, Mp 80 °C (dec).

Styrene sulphonium bromide S5

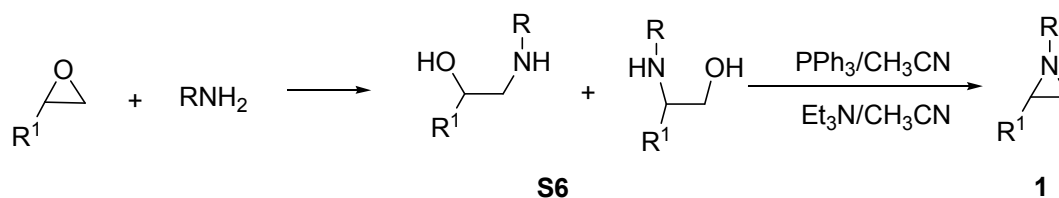
Olefin (160 mmol) was added dropwise to the 160 ml CH₃CN solution of compound S4 (35.56 g, 160 mmol) in ice-water bath. During the addition, the white solid began to separate. The solution was stirred for 10 min after the addition of olefin was completed. The crystals S5 was collected by filtration, dried under vacuum. Yield: 38.6 %.

Synthesis of aziridine 1a-1n

To a stirred solution of styrene sulphonium bromide S5 (10 mmol) in 20 ml of water at r.t., a solution of amine (20-50 mmol) in water was added dropwise and the resulting mixture was stirred overnight. The mixture was poured into 20 ml of saturated brine, extracted with diethyl ether (3×20 ml), dried with MgSO₄ and the solvent evaporated under reduced pressure. Pure product was obtained by distillation under reduced pressure (85-100 % yield).

(3) General procedure for the preparation of aziridines (1o, 1p).³

SCHEME S3



Synthesis of amino alcohol S6

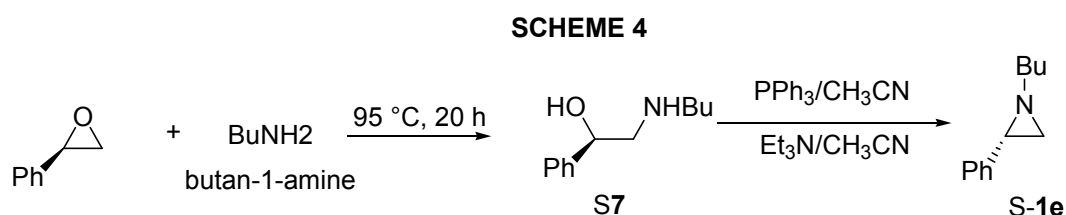
LiBr (87 mg, 5mol %) was added to a magnetically stirred mixture of oxirane (20

mmol) and amine (20 mmol) at room temperature under nitrogen. After completion of the reaction, the reaction mixture was diluted with water (10 ml) and extracted with Et₂O (2×30 ml). The combined ethereal extracts were dried (MgSO₄) and concentrated under vacuum to afford amino alcohol **S6** (yield: 90%).

Synthesis of aziridine **1o**, **1p**

An ice-cold solution of bromine (1.60 g, 10 mmol) in 6 ml of CH₃CN was added dropwise to an ice-cold solution of 2.63 g (10 mmol) of triphenylphosphine in 15 ml of CH₃CN. To the mixture was slowly added the amino alcohol **S6** (10 mmol), followed by drop by drop addition of 3.03 g (30 mmol) of triethylamine in 6 ml of acetonitrile at 0 °C. The mixture was then stirred at room temperature for 30 min. Triethylamine hydrobromide was filtered off and the solution was concentrated by rotary evaporation. The residue was treated with hexane (2×20 ml), concentrated to 10 ml, and filtered to remove triphenylphosphine oxide, then the solution was evaporated to give the aziridine **1**. (65-78 % yield).

(4) Synthesis of (*S*)-1-butyl-2-phenylaziridine (*S*)-**1e**.⁴



Conversion of (*R*)-2-phenyloxirane to (*R*)-2-(butylamino)-1-phenylethanol **S7**

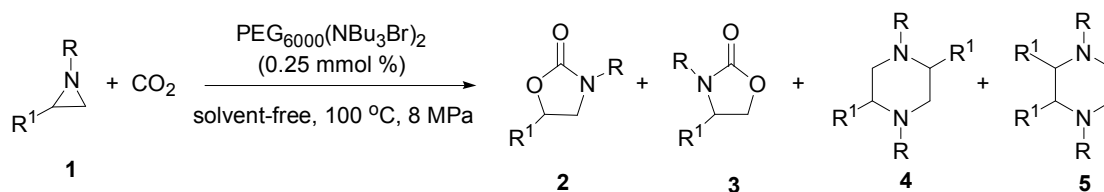
A mixture of (*R*)-phenyloxirane (1.80 g, 15 mmol) and butan-1-amine (4.39 g, 60 mmol) was stirred in autoclave for 20 h at 95 °C. After evaporation of excess

butan-1-amine, the residue was purified by column chromatography on silica gel. (*R*)-2-(butylamino)-1-phenylethanol **S7** was obtained with 75 % yield.

Conversion of (*R*)-2-(butylamino)-1-phenylethanol **S7** to (*S*)-1-butyl-2-phenylaziridine (**S**)-1e

To an ice-cold solution of 1.29 g (4.9 mmol) of triphenylphosphine in 8 ml of acetonitrile was added, drop by drop, an ice-cold solution of 0.26 ml (4.9 mmol) of bromine in 3 ml of acetonitrile. To the resulting solution was slowly added 0.95 g (4.9 mmol) of (*R*)-2-(butylamino)-1-phenylethanol, followed by drop-by-drop addition of 1.49 g (15 mmol) of distilled triethylamine in 3 ml of acetonitrile (all done at 0 °C). The reaction mixture was then stirred at ambient temperature for 30 min. Triethylamine hydrobromide was filtered off and the solution was concentrated by rotary evaporation. The residue was treated with hexane (5×10 ml), concentrated to 10 ml, and filtered to remove triphenylphosphine oxide, then the solution was evaporated and the residue was purified by column chromatography on silica gel. (*S*)-1-butyl-2-phenylaziridine (**S**)-1e was obtained with 55 % yield.

(5) General Procedure for Carboxylation of Aziridine with CO₂



A 25 mL autoclave reactor was charged with catalyst PEG₆₀₀₀(NBu₃Br)₂ (32.4 mg, 0.005 mmol) and aziridine (2 mmol). CO₂ was introduced into the autoclave and then the mixture was stirred at 100 °C for 5 min to allow equilibration. Finally, the

pressure was adjusted to 8 MPa and the mixture was stirred continuously. When the reaction finished, the reactor was cooled in ice-water and CO₂ was ejected slowly. An aliquot of sample was taken from the resultant mixture and dissolved in CH₂Cl₂ for GC analysis. The residue was purified by column chromatography on silica gel (200-300 mesh, eluting with 8:1 to 1:1 petroleum ether/ ethyl acetate) to afford the product. The products were further identified by NMR and MS which are consistent with those reported in the literature and in good agreement with the assigned structures.

(6) Characterization of aziridine 1a-1q and (S)-1e.

1-Ethyl-2-phenylaziridine 1a. ¹H NMR (400 MHz, CDCl₃) δ 1.17 (t, ³J=9.6 Hz, 3H), 1.65 (d, ³J=8.8 Hz, 1H), 1.89 (d, ³J=4.4 Hz, 1H), 2.30 (q, ³J=4.0 Hz, ³J=4.4 Hz, 1H), 2.44 (q, ³J=9.6 Hz, 2H), 7.18-7.31 (m, 5H); ESI-MS calcd for C₁₀H₁₃N 147.10, found 148.31 (M + H)⁺.

1-Methyl-2-phenylaziridine 1b. ¹H NMR (400 MHz, CDCl₃) δ 1.62 (d, ³J=6.4 Hz, 1H), 1.90 (d, ³J=3.2 Hz, 1H), 2.26 (q, ³J=3.2 Hz, 1H), 2.48 (s, 3H), 7.19-7.30 (m, 5H).

2-Phenylaziridine 1c. ¹H NMR (400 MHz, CDCl₃) δ 0.81 (s, 1H), 1.79 (d, ³J=3.2 Hz, 1H), 2.20 (d, ³J=6.0 Hz, 1H), 3.01 (q, ³J=3.6 Hz, ³J=2.4 Hz, 1H), 7.21-7.32 (m, 5H); ESI-MS calcd for C₈H₉N 119.07, found 120.26 (M + H)⁺.

2-Phenyl-1-propylaziridine 1d. ¹H NMR (400 MHz, CDCl₃) δ 0.95 (t, ³J=10.0 Hz, 3H), 1.60-1.67 (m, 3H), 1.89 (d, ³J=4.0 Hz, 1H), 2.24-2.33 (m, 2H), 2.43-2.51 (m,

1H), 7.18-7.31 (m, 5H); ESI-MS calcd for C₁₁H₁₅N 161.12, found 162.28 (M + H)⁺.

1-Butyl-2-phenylaziridine 1e. ¹H NMR (300 MHz, CDCl₃) δ 0.91 (t, ³J= 7.2 Hz, 3H), 1.33-1.45 (m, 2H), 1.55-1.67 (m, 3H), 1.88 (d, ³J=3.3 Hz, 1H), 2.27-2.36 (m, 2H), 2.45-2.54 (m, 1H), 7.17-7.31 (m, 5H); ESI-MS calcd for C₁₂H₁₇N 175.14, found 176.38 (M + H)⁺.

(S)-1-Butyl-2-phenylaziridine (S)-1e. [α]_D²⁰: + 142.5 (c 1.0, CHCl₃), ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, ³J= 7.2 Hz, 3H), 1.34-1.45 (m, 2H), 1.56-1.67 (m, 3H), 1.88 (d, ³J=3.3 Hz, 1H), 2.27-2.36 (m, 2H), 2.45-2.54 (m, 1H), 7.17-7.31 (m, 5H); ESI-MS calcd for C₁₂H₁₇N 175.14, found 176.38 (M + H)⁺.

1-Benzyl-2-phenylaziridine 1f. ¹H NMR (300 MHz, CDCl₃) δ 1.84 (d, ³J=6.3 Hz, 1H), 1.98 (d, ³J=3.3 Hz, 1H), 2.50 (q, ³J= 3.3 Hz, 1H), 3.65 (ABq, J_{AB}=13.8 Hz, Δv_{AB}=18.8 Hz, 2H), 7.18-7.38 (m, 10H).

1-Tert-butyl-2-phenylaziridine 1g. ¹H NMR (300 MHz, CDCl₃) δ 1.05 (s, 9H), 1.64 (dd, ²J= 3.0 Hz, ³J=0.9 Hz, 1H), 1.89 (dd, ²J=6.3 Hz, ³J=0.6 Hz, 1H), 2.62 (q, ³J=3.0 Hz, 1H), 7.16-7.33 (m, 5H); ESI-MS calcd for C₁₂H₁₇N 175.14, found 176.19 (M + H)⁺.

1-Isopropyl-2-phenylaziridine 1h. ¹H NMR (300 MHz, CDCl₃) δ 1.17 (d, ³J=0.9 Hz, 3H), 1.19 (d, ³J=0.9 Hz, 3H), 1.57-1.66 (m, 2H), 1.89 (d, ³J=3.3 Hz, 1H), 2.34 (q, ³J=3.3 Hz, 1H), 7.17-7.31 (m, 5H); ESI-MS calcd for C₁₁H₁₅N 161.12, found 162.32 (M + H)⁺.

1-Isobutyl-2-phenylaziridine 1i. ¹H NMR (300 MHz, CDCl₃) δ 0.95 (d, ³J=6.6 Hz,

3H), 0.98 (d, $^3J=6.6$ Hz, 3H), 1.65 (d, $^3J=6.3$ Hz, 1H), 1.85-1.94 (m, 2H), 2.08 (dd, $^3J=6.3$ Hz, $^2J=11.4$ Hz, 1H), 2.28 (q, $^3J=3.3$ Hz, 1H), 2.44 (dd, $^3J=7.2$ Hz, $^2J=11.4$ Hz, 1H), 7.17-7.31 (m, 5H); ESI-MS calcd for C₁₂H₁₇N 175.14, found 176.36(M + H)⁺.

1-Isopentyl-2-phenylaziridine 1j. ¹H NMR (300 MHz, CDCl₃) δ 0.88 (s, 3H), 0.91 (s, 3H), 1.47-1.57 (m, 2H), 1.60-1.71 (m, 2H), 1.87 (d, $^3J=3.3$ Hz, 1H), 2.27-2.38 (m, 2H), 2.44-2.53 (m, 1H), 7.18-7.31 (m, 5H) ; ESI-MS calcd for C₁₃H₁₉N 189.15, found 190.31(M + H)⁺.

1-Cyclopropyl-2-phenylaziridine 1k. ¹H NMR (300 MHz, CDCl₃) δ 0.41-0.50 (m, 2H), 0.55-0.67 (m, 2H), 1.60-1.67 (m, 1H), 1.86-1.88 (m, 2H), 2.57 (dd, $^3J=3.6$ Hz, $^3J=3.0$ Hz, 1H), 7.17-7.30 (m, 5H); ESI-MS calcd for C₁₁H₁₃N 159.10, found 160.32(M + H)⁺.

1-Cyclohexyl-2-phenylaziridine 1l. ¹H NMR (300 MHz, CDCl₃) δ 1.19-1.87 (m, 13H), 2.34 (dd, $^3J=3.3$ Hz, $^3J=3.0$ Hz, 1H), 7.17-7.27 (m, 5H); ESI-MS calcd for C₁₄H₁₉N 201.15, found 202.37(M + H)⁺.

1-Cyclohexyl-2-p-tolylaziridine 1m. ¹H NMR (300 MHz, CDCl₃) δ 1.19-1.85 (m, 13 H), 2.29-2.32 (m, 4H), 7.07-7.16 (m, 4H).

2-(4-Chlorophenyl)-1-cyclohexylaziridine 1n. ¹H NMR (300 MHz, CDCl₃) δ 1.16-1.82 (m, 13 H), 2.31 (dd, $^3J=3.3$ Hz, $^3J=3.0$ Hz, 1H), 7.17-7.26 (m, 4H).

1-Benzyl-2-(phoxymethyl)aziridine 1o. ¹H NMR (300 MHz, CDCl₃) δ 1.58 (d, $^3J=6.6$ Hz, 1H), 1.86 (d, $^3J=3.3$ Hz, 1H), 1.99-2.04 (m, 1H), 3.51(ABq, $J_{AB}=13.5$ Hz, $\Delta\nu_{AB}=15.7$ Hz, 2H) (m, 2H), 3.95 (d, $^3J=5.4$ Hz, 2H), 6.87-6.95 (m, 3H), 7.23-7.39

(m, 7H). ^{13}C NMR (75 MHz, CDCl_3) δ 31.9, 37.8, 64.2, 70.1, 114.6, 120.7, 127.0, 127.9, 128.3, 129.3, 138.3, 158.6; ESI-MS calcd for $\text{C}_{16}\text{H}_{17}\text{NO}$ 239.13, found 240.20 ($\text{M} + \text{H}$) $^+$.

1, 2-Diphenylaziridine 1p. GC-MS calcd for $\text{C}_{14}\text{H}_{13}\text{N}$ 195.10, found m/z 194.

(7) Characterization of oxazolidinone.

3-Methyl-5-phenyloxazolidin-2-one 2b. White crystals. Mp 50-52 $^{\circ}\text{C}$ (lit.^{5a} mp 53 $^{\circ}\text{C}$). ^1H NMR (300 MHz, CDCl_3) δ 2.89 (s, 3H), 3.42 (t, $^3J=8.4$ Hz, 1H), 3.90 (t, $^3J=8.4$ Hz, 1H), 5.45 (t, $^3J=8.0$ Hz, 1H), 7.33-7.38 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 30.7, 54.0, 73.0, 125.3, 128.5, 128.6, 138.4, 157.9; ESI-MS calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_2$ 177.08, found 178.21 ($\text{M} + \text{H}$) $^+$, 200.25 ($\text{M} + \text{Na}$) $^+$, 377.00 ($2\text{M} + \text{Na}$) $^+$.

5-Phenyloxazolidin-2-one 2c. White crystals. Mp 85-86 $^{\circ}\text{C}$ (lit.^{5b} mp 88-90 $^{\circ}\text{C}$). ^1H NMR (300 MHz, CDCl_3) δ 3.55 (t, $^3J=8.4$ Hz, 1H), 3.99 (t, $^3J=8.4$ Hz, 1H), 5.62 (t, $^3J=8.4$ Hz, 1H), 6.08 (brs, 1H), 7.35-7.43 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 48.2, 77.8, 125.6, 128.9, 138.4, 160.1; ESI-MS calcd for $\text{C}_9\text{H}_9\text{NO}_2$ 163.06, found m/z 164.18 ($\text{M} + \text{H}$) $^+$, 186.28 ($\text{M} + \text{Na}$) $^+$, 349.03 ($2\text{M} + \text{Na}$) $^+$.

5-Phenyl-3-propyloxazolidin-2-one 2d. Colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ 0.91 (t, $^3J=7.2$ Hz, 3H), 1.52-1.61 (m, 2H), 3.18-3.31 (m, 2H) 3.40 (t, $^3J=8.0$ Hz, 1H), 3.90 (t, $^3J=8.8$ Hz, 1H), 5.46 (t, $^3J=8.0$ Hz, 1H), 7.31-7.37 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 10.7, 20.3, 45.5, 51.8, 74.0, 125.2, 128.4, 128.5, 138.7, 157.6; ESI-MS calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_2$ 205.11, found 206.30 ($\text{M} + \text{H}$) $^+$, 228.30 ($\text{M} + \text{Na}$) $^+$, 433.04 ($2\text{M} + \text{Na}$) $^+$.

3-Butyl-5-phenyloxazolidin-2-one 2e. Colorless liquid. ^1H NMR (300 MHz, CDCl_3)

δ 0.94 (t, $^3J=7.2$ Hz, 3H), 1.31-1.40 (m, 2H), 1.51-1.58 (m, 2H), 3.23-3.38 (m, 2H)

3.43 (t, $^3J=8.0$ Hz, 1H), 3.92 (t, $^3J=8.8$ Hz, 1H), 5.49 (t, $^3J=8.0$ Hz, 1H), 7.28-7.42 (m,

5H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.4, 19.5, 29.1, 43.6, 51.8, 74.1, 125.2, 128.4,

128.5, 138.7, 157.7; ESI-MS calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ 219.13, found 220.34 ($\text{M} + \text{H}$) $^+$,

259.48 ($\text{M} + \text{K}$) $^+$, 461.05 ($2\text{M} + \text{Na}$) $^+$.

(S)-3-Butyl-5-phenyloxazolidin-2-one (S)-2e. Colorless liquid. $[\alpha]_{\text{D}}^{20}$: + 13.6 (c 1.5,

CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 0.94 (t, $^3J=7.2$ Hz, 3H), 1.31-1.40 (m, 2H),

1.51-1.58 (m, 2H), 3.23-3.38 (m, 2H) 3.43 (dd, $^2J=8.8$ Hz, $^3J=7.6$ Hz, 1H), 3.92 (t,

$^3J=8.8$ Hz, 1H), 5.49 (t, $^3J=8.0$ Hz, 1H), 7.35-7.43 (m, 5H); ESI-MS calcd for

$\text{C}_{13}\text{H}_{17}\text{NO}_2$ 219.13, found 220.34 ($\text{M} + \text{H}$) $^+$, 259.48 ($\text{M} + \text{K}$) $^+$, 461.05 ($2\text{M} + \text{Na}$) $^+$.

HRMS: calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 220.1332, found 220.1335.

(S)-3-Butyl-5-phenyloxazolidin-2-one (S)-3e. Colorless liquid. $[\alpha]_{\text{D}}^{20}$: + 31.1 (c 0.8,

CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, $^3J=7.2$ Hz, 3H), 1.23-1.27 (m, 2H),

1.37-1.45 (m, 2H), 2.70-2.77 (m, 1H), 3.42-3.49 (m, 1H), 4.11 (dd, $^2J=8.4$ Hz, $^3J=6.8$

Hz, 1H) 4.61 (t, $^3J=8.8$ Hz, 1H), 4.78 (dd, $^2J=8.8$ Hz, $^3J=6.8$ Hz, 1H), 7.28-7.43 (m,

5H); ESI-MS calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ 219.13, found 220.33 ($\text{M} + \text{H}$) $^+$, 439.07($2\text{M} + \text{H}$) $^+$.

HRMS: calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 220.1332, found 220.1335.

3-Benzyl-5-phenyloxazolidin-2-one 2f. White crystals. Mp 60-64 $^{\circ}\text{C}$ (lit.^{5c} mp

63.5-65 $^{\circ}\text{C}$). ^1H NMR (300 MHz, CDCl_3) δ 3.28 (t, $^3J=8.4$ Hz, 1H), 3.75 (t, $^3J=8.7$ Hz,

1H), 4.45 (ABq, $J_{\text{AB}}=15.0$ Hz, $\Delta\nu_{\text{AB}}=36.0$ Hz, 2H), 5.43 (t, $^3J=8.1$ Hz, 1H), 7.27-7.35

(m, 10H); ^{13}C NMR (75 MHz, CDCl_3) δ 48.1, 51.3, 74.3, 125.3, 127.8, 127.9, 128.6, 128.7, 135.5, 138.5, 157.8; ESI-MS calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_2$ 253.11, found 276.44($\text{M} + \text{Na}$) $^+$, 781.66 ($3\text{M} + \text{Na}$) $^+$.

3-Tert-butyl-5-phenyloxazolidin-2-one 2g. Colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ 1.41 (s, 9H), 3.45 (t, $^3J=8.4$ Hz, 1H), 3.95 (t, $^3J=8.7$ Hz, 1H), 5.36 (t, $^3J=8.1$ Hz, 1H), 7.32-7.41 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 27.3, 50.9, 53.5, 73.4, 125.4, 128.5, 128.7, 138.9, 156.6; ESI-MS calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ 219.13, found 242.46 ($\text{M} + \text{Na}$) $^+$, 259.30 ($\text{M} + \text{K}$) $^+$.

3-Isopropyl-5-phenyloxazolidin-2-one 2h. Colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ 1.16 (d, $^3J=6.8$ Hz, 3H), 1.22 (d, $^3J=6.8$ Hz, 3H), 3.37 (t, $^3J=8.0$ Hz, 1H), 3.87 (t, $^3J=8.8$ Hz, 1H), 4.13-4.23 (m, 1H), 5.48 (t, $^3J=8.0$ Hz, 1H), 7.34-7.42 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 19.1, 19.6, 44.5, 47.0, 74.2, 125.1, 128.3, 128.5, 138.7, 156.7; ESI-MS calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_2$ 205.11, found 206.29 ($\text{M} + \text{H}$) $^+$, 433.08 ($2\text{M} + \text{Na}$) $^+$.

3-Isobutyl-5-phenyloxazolidin-2-one 2i. White crystals. Mp 38-42 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ 0.91 (d, $^3J=4.8$ Hz, 3H), 0.93 (d, $^3J=4.8$ Hz, 3H), 1.81-1.95 (m, 1H), 3.02-3.16 (m, 2H), 3.42 (dd, $^2J=8.7$ Hz, $^3J=7.5$ Hz, 1H), 3.91 (t, $^3J=8.7$ Hz, 1H), 5.48 (t, $^3J=8.4$ Hz, 1H), 7.32-7.41 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 19.7, 19.8, 26.7, 51.6, 52.6, 74.1, 125.3, 128.5, 128.7, 138.8, 158.0; ESI-MS calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ 219.13, found 461.22 ($2\text{M} + \text{Na}$) $^+$, 679.70 ($3\text{M} + \text{Na}$) $^+$. HRMS: calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 220.1332, found 220.1339.

3-Isopentyl-5-phenyloxazolidin-2-one 2j. Colorless liquid. ^1H NMR (300 MHz, CDCl_3) δ 0.92 (d, $^3J=3.3$ Hz, 3H), 0.94 (d, $^3J=3.3$ Hz, 3H), 1.43 (q, $^3J=7.5$ Hz, 2H), 1.54-1.65 (m, 1H), 3.22-3.36 (m, 2H), 3.41(t, $^3J=7.8$ Hz, 1H), 3.91 (t, $^3J=8.7$ Hz, 1H), 5.46 (t, $^3J=8.1$ Hz, 1H), 7.33-7.39 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 22.2, 22.3, 25.6, 35.9, 42.4, 52.0, 74.2, 125.3, 128.6, 128.7, 138.8, 157.7; ESI-MS calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$ 233.14, found 489.17 $(2\text{M}+\text{Na})^+$, 721.97 $(3\text{M}+\text{Na})^+$. HRMS: calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_2$ $(\text{M} + \text{H})^+$ 234.1489, found 234.1489.

3-Cyclopropyl-5-phenyloxazolidin-2-one 2k. White crystals. Mp 52-55 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ 0.75 (s, 4H), 2.55-2.59 (m, 1H), 3.43 (t, $^3J=8.1$ Hz, 1H), 3.88 (t, $^3J=8.7$ Hz, 1H), 5.42 (t, $^3J=8.1$ Hz, 1H), 7.28-7.37 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 5.4, 5.8, 25.7, 53.3, 74.3, 125.4, 128.6, 128.7, 138.5, 157.9; ESI-MS calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$ 203.09, found 429.27 $(2\text{M} + \text{Na})^+$, 631.80 $(3\text{M} + \text{Na})^+$.

3-Cyclohexyl-5-phenyloxazolidin-2-one 2l. White crystals. Mp 92-93 $^\circ\text{C}$ (lit.^{5d} 97.3-98 $^\circ\text{C}$). ^1H NMR (300 MHz, CDCl_3) δ 1.0-1.8 (m, 10H), 3.38 (t, $^3J=8.4$ Hz, 1H), 3.70-3.73 (m, 1H), 3.88 (t, $^3J=8.7$ Hz, 1H), 5.45 (t, $^3J=8.4$ Hz, 1H), 7.35-7.38 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3) δ 25.1, 25.2, 29.9, 30.3, 48.1, 52.4, 74.4, 125.3, 128.5, 128.7, 138.9, 157.0; ESI-MS calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2$ 245.14, found 246.27 $(\text{M} + \text{H})^+$, 757.70 $(3\text{M} + \text{Na})^+$.

3-Cyclohexyl-5-p-tolyloxazolidin-2-one 2m. White crystals. Mp 89-91 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ 1.03-1.86 (m, 10H), 2.36 (s, 3H), 3.38 (t, $^3J=8.0$ Hz, 1H), 3.71-3.75 (m, 1H), 3.85 (t, $^3J=8.7$ Hz, 1H), 5.43 (t, $^3J=8.0$ Hz, 1H), 7.17-7.26 (m,

4H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.1, 25.2, 25.3, 25.4, 30.1, 30.5, 48.3, 52.5, 74.5, 125.5, 129.5, 136.0, 138.6, 157.3; ESI-MS calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_2$ 259.16, found 260.02 ($\text{M} + \text{H}$) $^+$, 799.55 ($3\text{M} + \text{Na}$) $^+$. HRMS: calcd for $\text{C}_{16}\text{H}_{21}\text{NO}_2$ ($\text{M} + \text{H}$) $^+$ 260.1645, found 260.1652.

5-(4-Chlorophenyl)-3-cyclohexyloxazolidin-2-one 2n. White crystals. Mp 94-96 °C. ^1H NMR (300 MHz, CDCl_3) δ 1.05- 1.83 (m, 10H), 3.34 (t, $^3J=8.0$ Hz, 1H), 3.69-3.76 (m, 1H), 3.89 (t, $^3J=8.7$ Hz, 1H), 5.44 (t, $^3J=8.0$ Hz, 1H), 7.27-7.38 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 25.2, 25.3, 30.0, 30.4, 48.2, 52.6, 73.8, 126.8, 129.0, 134.5, 137.6, 156.8; APCI-MS calcd for $\text{C}_{15}\text{H}_{18}\text{ClNO}_2$ 279.10, found 839.62 ($3\text{M}+\text{H}$) $^+$, 859.60 ($3\text{M}+\text{Na}$) $^+$. HRMS: calcd for $\text{C}_{15}\text{H}_{18}\text{ClNO}_2$ ($\text{M} + \text{H}$) $^+$ 280.1099, found 280.1101.

3-Benzyl-5-(phenoxymethyl)oxazolidin-2-one 2o. White crystals. Mp 62-65 °C. ^1H NMR (300 MHz, CDCl_3) δ 3.42 (dd, $^2J=8.7$ Hz, $^3J=6.0$ Hz, 1H), 3.56 (t, $^3J=9.0$ Hz, 1H), 4.08 (m, 2H), 4.45 (ABq, $J_{AB}=15.0\text{Hz}$, $\Delta\nu_{AB}=17.2$ Hz, 2H), 4.76-4.84 (m, 1H), 6.84 (d, $^3J=8.1$ Hz, 2H), 6.96 (t, $^3J=7.2$ Hz, 1H), 7.24-7.37 (m, 7H); ^{13}C NMR (75 MHz, CDCl_3) δ 45.9, 48.2, 68.0, 70.8, 114.5, 121.5, 127.9, 128.0, 128.8, 129.5, 135.6, 157.6, 158.0; ESI-MS calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$, 283.12, found 871.56 ($3\text{M} + \text{Na}$) $^+$. HRMS: calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$ ($\text{M} + \text{H}$) $^+$ 284.1281, found 284.1278.

3-Benzyl-4-(phenoxymethyl)oxazolidin-2-one 3o. Yellow crystals. Mp 73-79 °C. ^1H NMR (300 MHz, CDCl_3) δ 3.92-4.03 (m, 3H), 4.18-4.29 (m, 2H), 4.37 (t, $^3J=8.7$ Hz, 1H), 4.80 (d, $^2J=15.0$ Hz, 1H), 6.80-6.83 (m, 2H), 6.95-6.99 (m, 1H), 7.24-7.32 (m,

7H); ^{13}C NMR (75 MHz, CDCl_3) δ 46.6, 53.6, 64.6, 66.8, 114.3, 121.5, 127.8, 128.0, 128.7, 129.4, 135.8, 157.8, 158.3; ESI-MS calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$, 283.12, found 589.12 ($2\text{M} + \text{Na}$) $^+$. HRMS: calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_3$ ($\text{M} + \text{H}$) $^+$ 284.1281, found 284.1278.

(8) Characterization of Piperazines 4a and 5a.

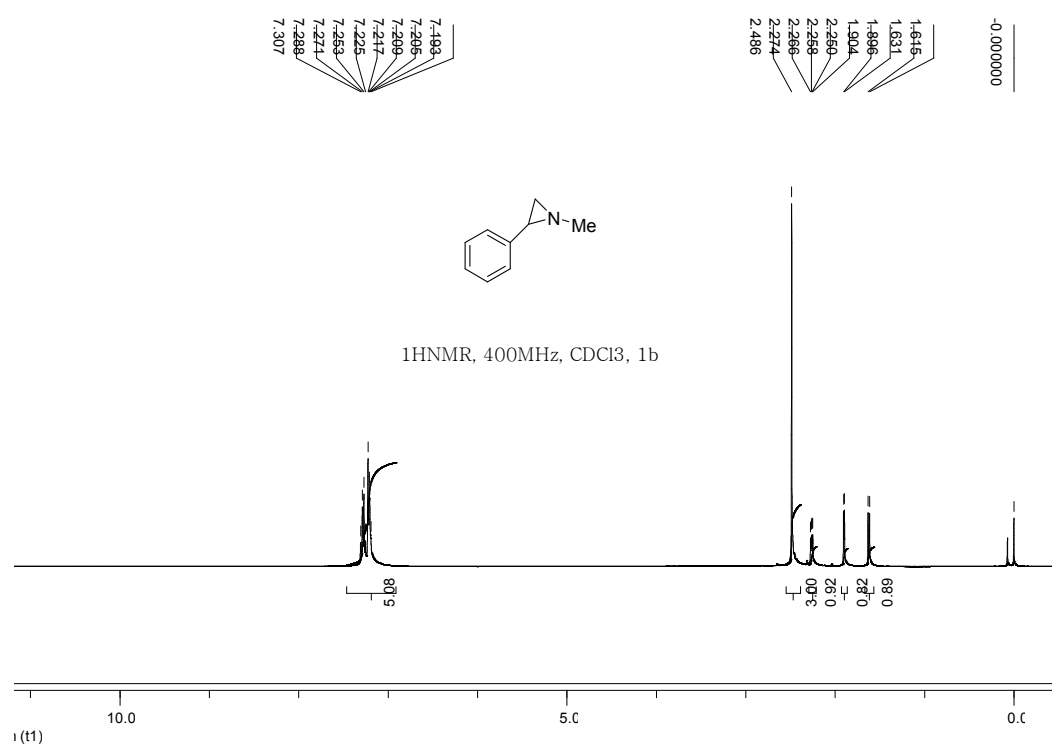
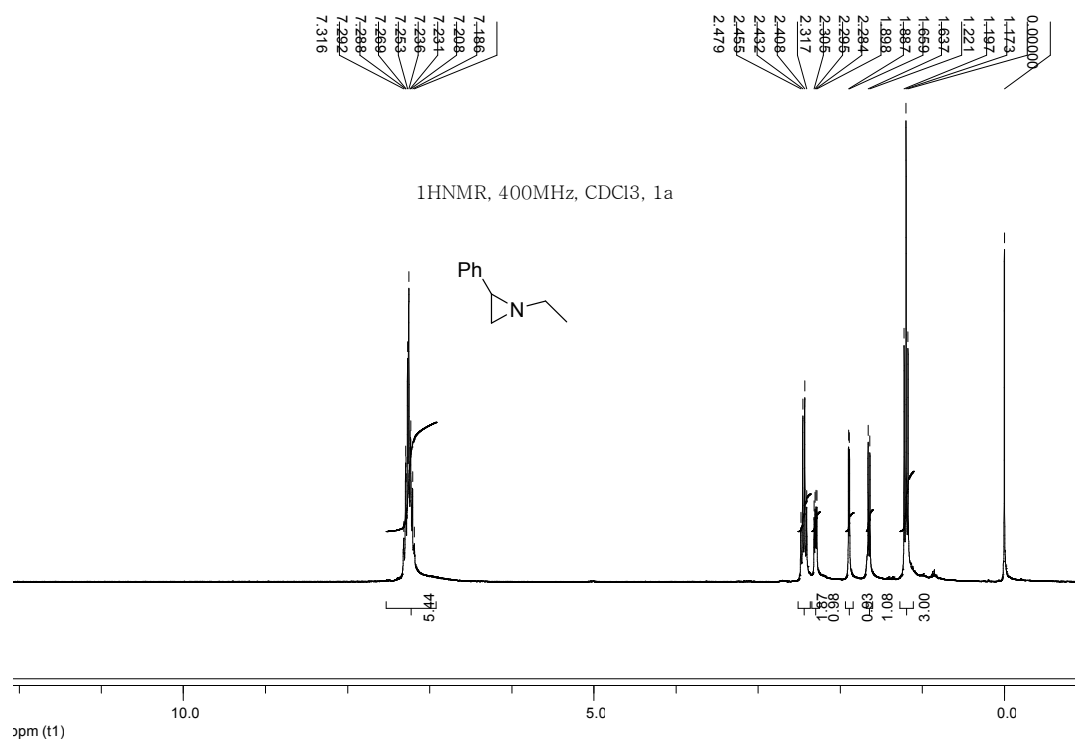
1, 4-Diethyl-2, 5-diphenylpiperazine 4a. White crystals. Mp 116-119 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 0.91 (t, $^3J=7.2$ Hz, 6H), 1.99-2.05 (m, 2H), 2.30 (t, $^3J=10.8$ Hz, 2H), 2.54-2.62 (m, 2H), 3.08 (dd, $^2J=11.6$ Hz, $^3J=2.4$ Hz, 2H), 3.45 (dd, $^3J=2.0$ Hz, $^2J=12.0$ Hz, 2H), 7.29-7.43 (m, 10H). LC-MS, calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2$ 294.21, found 295.35 ($\text{M} + \text{H}$) $^+$. HRMS: calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2$ ($\text{M} + \text{H}$) $^+$ 295.2169, found 295.2164.

1, 4-Diethyl-2, 3-diphenyl-piperazine 5a. Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 1.01 (t, $^3J=7.2$ Hz, 6H), 2.17-2.26 (m, 2H), 2.33-2.26 (m, 2H), 2.65-2.69 (m, 2H), 2.95-2.99 (q, $^3J=6.0$ Hz, 2H), 3.73 (s, 2H), 7.27-7.38 (m, 6H), 7.69-7.71 (d, $^3J=7.2$ Hz, 4H). LC-MS, calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2$ 294.21, found 295.31($\text{M}+\text{H}$) $^+$. HRMS: calcd for $\text{C}_{20}\text{H}_{26}\text{N}_2$ ($\text{M} + \text{H}$) $^+$ 295.2169, found 295.2167.

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The charts of ^1H NMR of aziridines



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