Experimental

General. NMR spectra were recorded with a Gemini Varian spectrometer at 300 or 200 MHz (^{1}H NMR) and at 75 or 50 MHz (^{13}C NMR). - Chemical shifts are reported in δ values relative to the solvent peak of $CHCl_3$, set at 7.27 ppm. - Infrared spectra were recorded with an FT-IR NICOLET 205 spectrometer. - Melting points were determined in open capillaries and are uncorrected. - Flash chromatography was performed with Merck silica gel 60 (230-400 mesh). - THF was distilled from sodium benzophenone ketyl.

General Method for the Synthesis of *N*-Boc β-Amino Acids Methyl Esters *rac*-1a-c: $SOCl_2$ (10 mmol, 0.73 mL) was added to methanol (20 mL) at –10 °C and the mixture was stirred for 1 h. Then the solid β-amino acid (5 mmol) was added in one portion and the mixture was stirred overnight, while the temperature was reaching room temperature. The mixture was concentrated under reduced pressure and the β-amino acid methyl ester hydrochloride was dissolved in a mixture of water (10 mL) and *t*-butanol (15 mL). Sodium carbonate (15 mmol, 1.59 g) and Boc anhydride (7.5 mmol, 1.64 g) were added in one portion and the mixture was refluxed for 1.5 h. Then the mixture was cooled and ethyl acetate was added. The organic layer was separated, washed twice with water, dried over sodium sulphate and the solvent was removed under reduced pressure. The residue was directly utilized or purified by silica gel chromatography (cyclohexane/ethyl acetate 9:1 as eluant).

rac-**1a**: 80% yield. - IR (film): ν = 3357, 1813, 1717 cm^{-1}. - ^{1}H NMR ($CDCl_3$): δ = 1.22 (d, 3H, J = 6.7 Hz, CH_3CHN), 1.44 (s, 9H, *t*-Bu), 2.51 (d, 2H, J = 6.5 Hz, CH_2CO), 3.61 (s, 3H, OCH_3), 4.08 (m, 1H, CHN), 4.90 (bs, 1H, NH). - ^{13}C NMR ($CDCl_3$): δ = 20.3, 28.2, 40.6, 43.5, 51.3, 79.0, 154.9, 171.7.

rac-**1b**: 70% yield. - IR (film): ν = 3364, 1815, 1716 $cm^{-1.}$ - ^{1}H NMR ($CDCl_3$): δ = 0.91 (d, 6H, J = 6.9 Hz, $CH(CH_3)_2$), 1.44 (s, 9H, *t*-Bu), 1.70-1.88 (m, 1H, $CH(CH_3)_2$), 2.50 (d, J = 5.0 Hz, 2H, CH_2CO), 3.68 (s, 3H, OCH_3), 3.72-3.82 (m, 1H, CHN), 4.85 (d, 1H, J = 10.0 Hz, NH). - ^{13}C NMR ($CDCl_3$): δ = 18.5, 19.4, 28.5, 32.0, 37.3, 51.7, 53.2, 79.2, 155.6, 172.4.

rac-**1c**: 72% yield. - IR (film): ν = 3377, 1818, 1725 cm^{-1}. - ^{1}H NMR ($CDCl_3$): δ = 1.43 (s, 9H, $C(CH_3)_3$), 2.75-2.98 (m, 2H, CH_2CO), 3.62 (s, 3H, OCH_3), 5.05-5.22 (m, 1H, CHN), 5.45 (bs, 1H, NH), 7.22-7.40 (m, 5H, Ph). - ^{13}C NMR ($CDCl_3$): δ = 27.4, 28.3, 40.8, 51.7, 79.7, 126.1, 127.5, 128.6, 141.2, 155.0, 171.3.

General Method for the Synthesis of *N*-Boc 2-Carboxymethyl 3-Alkyl/Aryl Aziridines *trans-rac*-2 and *cis-rac*-3: LiHMDS (5.5 mmol, 1M sol. in THF, 5.5 mL) was added to a stirred solution of *N*-Boc β-amino acids methyl esters *rac*-**1a-c** (2.5 mmol) in dry THF (10 mL) under nitrogen atmosphere at –60 °C. The mixture was stirred 1 h at room temperature, then iodine was added (3 mmol, 0.76 g) in dry THF (10 mL). The mixture was stirred 30 min, then an aqueous saturated solution of ammonium chloride was added, THF was removed under reduced pressure and replaced with ethyl acetate. The organic layer was separated, washed twice with an aqueous saturated solution of sodium thiosulphate, twice with water, dried over sodium sulphate and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (cyclohexane/ethyl acetate 9:1 as eluant).

rac-trans-**2a**: IR (film): ν = 1759, 1719 cm^{-1}. - ^{1}H NMR ($CDCl_3$): δ = 1.36 (d, 3H, *J* =5.4 Hz, CHNCH_3), 1.52 (s, 9H, $C(CH_3)_3$), 2.80 (d, 1H, *J* = 2.7 Hz, CHNCO), 2.83 (dq, *J* = 2.7, 5.4 Hz, C*H*NCH_3), 3.76 (s, 3H, OCH_3). - ^{13}C NMR ($CDCl_3$): δ = 16.3, 27.9, 39.6, 41.3, 52.4, 81.7, 158.0, 168.8.

rac-cis-**3a**: IR (film): ν = 1759, 1719 cm^{-1}. - ^{1}H NMR ($CDCl_3$): δ = 1.37 (d, 3H, *J* =5.7 Hz, CHNCH_3), 1.52 (s, 9H, $C(CH_3)_3$), 2.73 (dq, *J* = 5.7, 6.6 Hz, C*H*NCH_3), 3.10 (d, 1H, *J* = 6.6 Hz, CHNCO), 3.78 (s, 3H, OCH_3). - ^{13}C NMR ($CDCl_3$): δ = 13.0, 27.8, 38.8, 39.8, 52.4, 81.7, 158.0, 168.8.

rac-trans-**2b**: IR (film): ν = 1752, 1719 cm^{-1}. - ^{1}H NMR ($CDCl_3$): δ = 0.97 (d, 3H, *J* = 6.9 Hz, CH_3CHCH_3), 1.03 (d, 3H, *J* = 6.9 Hz, CH_3CHCH_3), 1.45 (s, 9H, $C(CH_3)_3$), 1.45-1.58 (m, 1H, CH_3C*H*CH_3), 2.62 (dd, 1H, *J* = 2.7, 6.9 Hz, CHC*H*N), 2.85 (d, 1H, *J* = 2.7 Hz, CHNCO), 3.75 (s, 3H, OCH_3). - ^{13}C NMR ($CDCl_3$): δ = 18.7, 20.2, 27.6, 39.6, 49.5, 51.9, 81.4, 158.5, 168.4.

rac-cis-**3b**: IR (film): ν = 1752, 1719 cm^{-1}. - ^{1}H NMR ($CDCl_3$): δ = 0.87 (d, 3H, *J* = 6.6 Hz, CH_3CHCH_3), 1.15 (d, 3H, *J* = 6.6 Hz, CH_3CHCH_3), 1.45 (s, 9H, $C(CH_3)_3$), 1.45-1.58 (m, 1H, CH_3C*H*CH_3), 2.31 (dd, 1H, *J* = 6.6, 9.6 Hz, CHC*H*N), 2.85 (d, 1H, *J* = 9.6 Hz, CHNCO), 3.77 (s, 3H, OCH_3). - ^{13}C NMR ($CDCl_3$): δ = 18.7, 19.0, 27.6, 39.1, 49.5, 51.9, 81.0, 158.5, 168.4.

rac-trans-**2c**: IR (film): ν = 1751, 1736 cm^{-1}. - ^{1}H NMR ($CDCl_3$): δ = 1.48 (s, 9H, $C(CH_3)_3$), 3.11 (d, *J* = 2.3 Hz, C*H*NPh), 3.81 (s, 3H, OCH_3), 3.83 (d, 3H, *J* = 2.3 Hz, CHNCO), 7.20-7.42 (m, 5H, Ph). - ^{13}C NMR ($CDCl_3$): δ = 28.5, 44.3, 45.5, 53.1, 82.4, 126.4, 128.3, 128.5, 135.7, 161.0, 168.4.

rac-cis-**3c**: IR (film): ν = 1751, 1736 cm^{-1}. - ^{1}H NMR ($CDCl_3$): δ = 1.42 (s, 9H, $C(CH_3)_3$), 3.43 (d, *J* = 6.9 Hz, C*H*NPh), 3.51 (s, 3H, OCH_3), 3.85 (d, 3H, *J* = 6.9 Hz, CHNCO), 7.20-7.42 (m, 5H, Ph). - ^{13}C NMR ($CDCl_3$): δ = 28.5, 43.1, 45.0, 52.6, 82.6, 127.0, 128.6, 129.0, 133.5, 161.0, 167.0.

General Method for the Synthesis of 4-Carboxymethyl 5-Alkyl/Aryl Oxazolidin-2-ones *trans*-4 and *cis*-5:

Method A: To a stirred solution of *N*-Boc aziridine (1 mmol) in dry methylene chloride (10 mL) was added $BF_3.Et_2O$ or $BF_3.2H_2O$ (the amount is described in Table 2). The mixture was stirred the required time under nitrogen at room temperature (see Table 2), then an aqueous saturated solution of Na_2CO_3 was added, the organic layer was dried over sodium sulphate and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (cyclohexane/ethyl acetate 9:1 as eluant).

Method B: To a stirred solution of *N*-Boc aziridine (1 mmol) in dry methylene chloride (10 mL) was added $Cu(OTf)_2$ or $Sn(OTf)_2$ or $Zn(OTf)_2$ (0.1 mmol). The mixture was stirred the required time under nitrogen at room temperature (see Table 3), then an aqueous saturated solution of Na_2CO_3 was added, the organic layer was dried over sodium sulphate and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (cyclohexane/ethyl acetate 8:2 to pure ethyl acetate as eluant).

Rac-***trans*-4a**: IR (film): ν = 3315, 1758 cm^{-1}. - ^1H NMR ($CDCl_3$): δ = 1.55 (d, 3H, *J* = 6.3 Hz, $CHOCH_3$), 3.79 (s, 3H, OCH_3), 4.01 (d, 1H, *J* = 5.5 Hz, CHN), 4.72 (dq, 1H, *J* = 5.5, 6.3 Hz, CHO), 6.48 (bs, 1H, NH). - ^{13}C NMR ($CDCl_3$): δ = 21.5, 53.5, 60.9, 76.2, 159.0, 170.7.

Rac-***cis*-5a**: IR (film): ν = 3315, 1758 cm^{-1}. - ^1H NMR ($CDCl_3$): δ = 1.36 (d, 3H, *J* = 6.4 Hz, $CHOCH_3$), 3.78 (s, 3H, OCH_3), 4.43 (d, 1H, *J* = 5.5 Hz, CHN), 4.93 (dq, 1H, *J* = 5.5, 6.3 Hz, CHO), 6.40 (bs, 1H, NH). - ^{13}C NMR ($CDCl_3$): δ = 16.7, 53.0, 59.0, 74.9, 159.0, 170.2.

Rac-***trans*-4b**: IR (film): ν = 3324, 1746 cm^{-1}. - ^1H NMR ($CDCl_3$): δ = 0.93 (d, 6H, *J* = 6.7 Hz, CH_3CHCH_3), 1.82-1.99 (m, 1H, CH_3CHCH_3), 3.72 (s, 3H, OCH_3), 4.04 (d, 1H, *J* = 4.7 Hz, CHN), 4.30 (dd, 1H, *J* = 4.7, 6.1 Hz, CHO), 6.90 (bs, 1H, NH). - ^{13}C NMR ($CDCl_3$): δ = 17.0, 17.6, 32.9, 53.4, 56.9, 84.0, 159.4, 171.6.

Rac-***cis*-5b**: IR (film): ν = 3324, 1746 cm^{-1}. - ^1H NMR ($CDCl_3$): δ = 0.93 (d, 6H, *J* = 6.7 Hz, CH_3CHCH_3), 1.82-1.99 (m, 1H, CH_3CHCH_3), 3.72 (s, 3H, OCH_3), 4.28-4.40 (m, 2H, CHN + CHO), 5.90 (bs, 1H, NH). - ^{13}C NMR ($CDCl_3$): δ = 18.9, 19.2, 30.2, 53.2, 57.9, 84.4, 159.4, 171.6.

Rac-***trans*-4c**: IR (film): ν = 3288, 1772, 1718 cm^{-1}. - ^1H NMR ($CDCl_3$): δ = 3.86 (s, 3H, OCH_3), 4.29 (d, 1H, *J* = 4.8 Hz, CHN), 5.65 (d, 1H, *J* = 4.8 Hz, CHO), 6.18 (bs, 1H, NH), 7.25-7.45 (m, 5H, Ph). - ^{13}C NMR ($CDCl_3$): δ = 53.3, 53.6, 61.5, 79.6, 125.5, 129.1, 129.3, 138.2, 158.4, 170.3.

Rac-***cis*-5c**: IR (film): ν = 3288, 1772, 1718 cm^{-1}. - ^1H NMR ($CDCl_3$): δ = 3.22 (s, 3H, OCH_3), 4.66 (d, 1H, *J* = 9.0 Hz, CHN), 5.61 (bs, 1H, NH), 5.83 (d, 1H, *J* = 49.0 Hz, CHO), 7.25-7.45 (m, 5H, Ph).

Hydrolysis of *trans* 4-Carboxymethyl 5-Phenyl Oxazolidin-2-one *rac*-4c

A solution of oxazolidin-2-one *rac*-**4c** (0.68 mmol, 150 mg) and LiOH (3.4 mmol, 82 mg) in water (5 mL) was stirred at room temperature for 2 h, then 2 M HCl was added till pH = 1. The mixture was concentrated under reduced pressure and water (2 mL) was added. The mixture was adsorbed on cation exchange resin, then the resin was washed with water until the washing came out neutral, then with 1M aqueous NH_4OH to recover the *rac*-*threo*-phenylserine in 90% yield. M.p. = 189-191 °C. - ^1H NMR (D_2O) δ = 3.86 (d, 1H, *J* = 4.2 Hz, CHN), 5.25 (d, 1H, *J* = 4.2 Hz, CHO), 7.42 (m, 5H, Ph).