Supplementary Information

Asymmetric synthesis of β^2-amino acids: 2-substituted-3-aminopropanoic acids from *N*-acryloyl SuperQuat derivatives

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Experimental

General experimental

All reactions involving organometallic or other moisture sensitive reagents were carried out under a nitrogen or argon atmosphere using standard vacuum line techniques and glassware that was flame dried and cooled under nitrogen before use. The solvents were dried according to the procedure outlined by Grubbs and co-workers.[1] Water was purified by an Elix® UV-10 system. All other solvents were used as supplied (analytical or HPLC grade) without prior purification. Organic layers were dried over $MgSO_4$. Thin layer chromatography was performed on aluminium plates coated with 60 F_{254} silica. The plates were visualised using UV light (254 nm), iodine, 1% aq. $KMnO_4$ or 10% ethanolic phosphomolybdic acid. Flash column chromatography was performed on Kieselgel 60 silica.

Elemental analyses were recorded by the microanalysis service of the Inorganic Chemistry Laboratory, University of Oxford, UK. Melting points were recorded on a Gallenkamp Hot Stage apparatus and are uncorrected. Optical rotations were recorded on a Perkin–Elmer 241 polarimeter with a water-jacketed 10 cm cell. Specific rotations are reported in 10^{-1} deg cm^2 g^{-1} and concentrations in g/100 mL. IR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer as either a thin film on NaCl plates (film), a chloroform cell ($CHCl_3$) or a KBr disc (KBr), as stated. Selected characteristic peaks are reported in cm^{-1}. NMR spectra were recorded on Bruker Avance spectrometers in the deuterated solvent stated. The field was locked by external referencing to the relevant deuteron resonance. Low-resolution mass spectra were recorded on either

[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics* 1996, **15**, 1518–1520.

a VG MassLab 20–250 or a Micromass Platform 1 spectrometer. Accurate mass measurements were run on either a Bruker MicroTOF and were internally calibrated with polyanaline in positive and negative modes, or a Micromass GCT instrument fitted with a Scientific Glass Instruments BPX5 column (15 m × 0.25 mm) using amyl acetate as a lock mass.

General Procedure 1: Lithium Amide addition

n-BuLi (2.5 M, 1.6 eq) was added dropwise to a stirred solution of amine (1.6 – 2.0 eq) in THF (0.13 mL/mmol) at –78 ˚C. After stirring for 30 min at –78 ˚C, a solution of the acceptor (1.0 eq) in THF (0.08 mL/mmol) also at –78 ˚C was added dropwise *via* cannula. The resulting solution was stirred for between 10 min and 4 h before the addition of sat. aq. NH_4Cl solution. The product was extracted with ether (3 ×), the combined organic extracts were washed with aq. citric acid solution (10% w/v), sat. aq. $NaHCO_3$ solution and brine. The resultant organic solution was dried and concentrated *in vacuo*.

General Procedure 2: Tandem addition/alkylation

n-BuLi (2.5 M, 1.6 eq) was added dropwise to a stirred solution of amine (1.6 eq) in THF (0.5 mL/mmol) at –78 ˚C. After stirring for 30 min at –78 ˚C, a solution of the acceptor (1.0 eq) in THF (0.08 mL/mmol) also at –78 ˚C was added *via* cannula. The resulting solution was stirred for between 10 min and 4 h at –78 ˚C before the alkyl halide (1.6 eq) was added. The mixture was stirred at –78 ˚C for a further 2 h before allowing it to warm to rt over 16 h. The solvent was removed *in vacuo* and the resulting residue taken up in ether. The organic layer was washed with aq. citric acid solution (10% w/v) and sat. aq. $NaHCO_3$ solution, then dried and concentrated *in vacuo.*

General Procedure 3: Stepwise enolate alkylation

LiHMDS (1.1 eq, 1.0 M) was added dropwise to a solution of the (*β*-amino carbonyl)-oxazolidinone (1.0 eq) in THF (0.05 mL/mmol) at –78 ˚C. After 30 min, the alkyl halide (1.5 eq) was added and the resultant mixture stirred at –78 ˚C for a further 2 h before allowing it to warm to rt over 16h. The solvent was removed *in vacuo* and the residue taken up in ether. The organic layer was washed with sat. aq. NH_4Cl solution and brine then dried and concentrated *in vacuo*.

General Procedure 4: Tandem Enolate Trapping

n-BuLi (2.5 M, 1.6 eq) was added dropwise to a stirred solution of amine (1.6 eq) in THF (0.5 mL/mmol) at –78 ˚C. After stirring for 30 min at –78 ˚C a solution of the acceptor (1.0 eq), in THF (0.08 mL/mmol) at –78 ˚C, was added *via* cannula. The resulting solution was stirred between 2 h and 4 h at –78˚C before triethylsilyl chloride (1.6 eq) was added. The mixture was stirred at –78 ˚C for a further 30 min before being allowed to warm to rt. The solvent was then removed *in vacuo*.

General Procedure 5: Stepwise Enolate Trapping

LiHMDS (1.1 eq) was added dropwise to a solution of the *N*-*β*-amino oxazolidinone (1.0 eq) in THF (0.05 mL/mmol) at –78 ˚C. The resulting solution was stirred at –78 ˚C for 30 min. Triethylsilyl chloride (1.5 eq) was added in one portion and the mixture stirred at –78 ˚C for a further 30 min before being allowed to warm to rt. The solvent was then removed *in vacuo*.

General Procedure 6: Lithium Hydroxide Cleavage of Auxillary

LiOH (5.0 eq) in H_2O (3 mL/mmol) was added to a stirred solution of the acyl oxazolidinone (1.0 eq) in THF (30 mL/mmol) and the resulting solution was stirred at rt for 24 h. After which time the solution was acidified to pH 3 with sat. aq. $KHSO_4$ solution. The product was then extracted with EtOAc (3 ×), the combined organic extracts were dried and concentrated *in vacuo*.

General Procedure 7: Hydrogenolysis of Benzyl Protecting Groups

Pd (10% wt on C, 0.5g/g *β*-amino acid) was added to a degassed solution of the *β*-amino acid (1.0 eq) in MeOH (20 mL/g)/H_2O (2 mL/g)/AcOH (0.5 mL/g). The suspension was stirred under H_2 (1 atm) for 24 h before being filtered though Celite®. The Celite® pad was then further washed with MeOH and the filtrate was concentrated *in vacuo*.

General Procedure 8: Lithium Methoxide Cleavage of Auxiliary

n-BuLi (3.0 eq, 1.6 M) was added dropwise to MeOH (2 mL/mmol) at 0˚C. After 5 min a solution of the acyl oxazolidinone (1.0 eq) in MeOH (2 mL/mmol) was added dropwise. The resulting mixture was stirred at 0 ˚C for 30 min before being allowed to warm to rt then stirred for a further 15 h. The solvent was removed *in vacuo* and the residue partitioned between sat. aq. NH_4Cl solution and EtOAc. The aqueous layer

was extracted with EtOAc (2 ×). The combined organic extracts were washed with brine, dried and then concentrated *in vacuo*.

General Procedure 9: Ester Hydrolysis

To a stirred solution of the ester (1.0 eq) in THF (15 mL/mmol ester) was added lithium hydroxide (5.0 eq) in water (1.5 mL/mmol LiOH) and the mixture either stirred at rt or heated at reflux for 15 h. The crude reaction mixture was worked up as specified.

General Procedure 10: Alkylation of Ethyl Acetoacetate

To a suspension of potassium *tert*-butoxide (1.1 eq) in THF (2.5 mL/mmol base) was added ethyl acetoacetate (1.0 eq) and *tert*-butanol (0.1 eq) at 0°C. The resulting clear solution was stirred for 30 min and then alkyl halide (0.99 eq) was added. The solution was stirred at 70 °C for 12 h. The reaction was quenched with water (0.13 mL/mmol base), and then sat. aq. $NaHCO_3$ was added and the product extracted with ether (3 ×). The combined organic extracts were dried and the solvents removed *in vacuo* to yield the crude product.

General Procedure 11: Formation of 2-Alkylacrylate Esters

To a stirred solution of ethyl-2-alkyl-3-oxo-butyrate (1.0 eq) in THF (8 mL/mmol reactant) was added LiHMDS (1.0 M, 1.1 eq) at −78°C. The solution was stirred for 30 min then paraformaldehyde (xs) was added as a solid in one portion. The suspension was allowed to warm to rt and stirred for 6 h then filtered through Celite® to remove excess paraformaldehyde. The filtrate was concentrated *in vacuo* to yield the crude product.

General Procedure 12: Acylation of Oxazolidinone

Oxalyl chloride (1.86 eq) was added to a solution of the carboxylic acid (1.25 eq) in ether (10 mL/mmol acid). The solution was stirred for 1 h at rt. Et_3N (1.86 eq) was added dropwise and the solution stirred for a further 30 min. The supernatant was decanted and the solvent removed *in vacuo*. The crude acid chloride was taken up in THF (1 mL/mmol) and used without further purification.

To a stirred solution of the oxazolidinone (1.0 eq) in THF (3 mL/mmol) at –78 °C was added *n*-BuLi (2.5 M, 1.1 eq) dropwise. After stirring for 15 min, the acid chloride was added as the solution in THF followed by a THF wash (0.5 mL/mmol acid chloride). The solution was stirred at –78 °C for 30 min before warming to rt

over 2 h. The reaction was quenched by the addition of sat. aq. NH_4Cl and the product extracted with ethyl acetate (3 ×). The combined organic extracts were washed with brine, dried and the solvents removed *in vacuo*.

General Procedure 13: Tandem addition / 2,6-di-*tert*-butylphenol quench

n-BuLi (2.5 M, 1.6 eq) was added dropwise to a stirred solution of amine (1.6 eq) in THF (0.5 mL/mmol) at –78 ˚C. After stirring for 30 min at –78 ˚C, a solution of the acceptor (1.0 eq) in THF (0.08 mL/mmol) also at –78 ˚C was added *via* cannula. The resulting solution was stirred for 30 min at –78 ˚C and then a solution of 2,6-di-*tert*-butylphenol (3.0 eq) in THF (0.16 mL/mmol) was added dropwise *via* syringe. The mixture was stirred at –78 ˚C for a further 30 min before being allowed to warm to rt over 16 h. The solvent was removed *in vacuo* and the residue taken up in ether. The organic layer was washed with aq. citric acid solution (10% w/v) and sat. aq. $NaHCO_3$ solution, dried and concentrated *in vacuo.*

General Procedure 14: Tandem addition / 2-pyridone quench

To a stirred solution of amine (1.6 eq) in THF (0.5 mL/mmol) at –78 ˚C was added *n*-BuLi (2.5 M, 1.6 eq) dropwise. After stirring for 30 min at –78 ˚C a solution of the acceptor (1.0 eq) in THF (0.08 mL/mmol) also at –78 ˚C was added *via* cannula. The resulting solution was stirred for 30 min at –78 ˚C before a solution of 2-pyridone (3.0 eq) in THF (0.06 mL/mmol) was added dropwise *via* syringe. The mixture was stirred at –78 ˚C for a further 30 min before being allowed to warm to rt over 16 h. The solvent was removed *in vacuo* and the residue taken up in ether. The organic layer was washed with aq. citric acid solution (10% w/v) and sat. aq. $NaHCO_3$ solution, then dried and concentrated *in vacuo.*

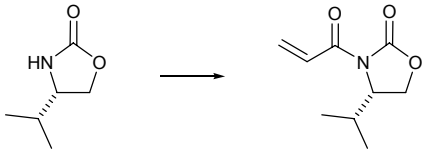
General Procedure 15: Lithium Hydroperoxide Cleavage of Auxillary

LiOH (6.0 eq) in H_2O (3 mL/mmol) and H_2O_2 (2 mL/mmol) was added to a stirred solution of the acyl oxazolidinone (1.0 eq) in THF (9 mL/mmol) at 0 °C. The resulting solution was allowed to warm to rt and stirred for 24 h before addition of Na_2SO_3 solution. The solution was acidified to pH 3 with sat. aq. $KHSO_4$ solution. The product was then extracted with EtOAc (3 ×), the combined organic extracts were dried and concentrated *in vacuo*.

General Procedure 16: Aldol reactions with 9-BBNOTf

To a stirred solution of *β*-amino-*N*-acyl oxazolidinone in DCM at 0°C was added 9-BBNOTf (0.5 M in hexanes, 1.2 eq) followed by Hünig's base (1.4 eq) after 10 mins. The resulting solution was stirred for a further 20 mins at 0°C before cooling to –78 °C followed by addition of an aldehyde (1.5 eq). The resulting solution was stirred for a further 30 mins at –78 °C before warming to 0 °C and stirring for a further 1 hr. The reaction was quenched with 1:1 (v/v) MeOH/H_2O_2(30% aq. solution), allowed to warm to rt and extracted with DCM (3 ×). The combined organic layers were washed with sat. aq. $NaHCO_3$, dried and concentrated *in vacuo* to yield a crude product.

(*S*)-4-*iso*-Propyl-3-acryloyl-oxazolidin-2-one 3

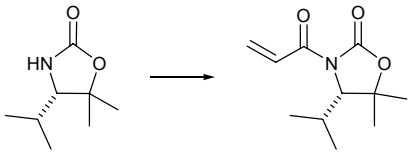


To a stirred solution of acrylic acid (0.75 mL, 10.9 mmol, 1.25 eq) in ethyl acetate (60 mL) at 0 °C was added Et_3N (1.51 mL, 10.9 mmol, 1.25 eq) followed by acryloyl chloride (0.88 mL, 10.9 mmol, 1.25 eq) over 2 min. The resulting solution was stirred at 0 °C for 40 min then at rt for 30 min. The suspension was filtered and the filtrate concentrated *in vacuo*. The residue was taken up in hexane (50 mL) and the resulting suspension filtered and the filtrate concentrated *in vacuo* again. The anhydride was dissolved in THF (1.5 mL) and used immediately.

To a suspension of oxazolidinone **1** (1.0 g, 8.69 mmol, 1.0 eq) and LiCl (0.46 g, 10.9 mmol, 1.25 eq) in THF (10 mL) was added Et_3N (1.50 mL, 10.9 mmol, 1.25 eq), the anhydride, followed by a THF wash (1.5 mL). The suspension was stirred at rt for 4 h before removal of the solvent *in vacuo*. The residue was taken up in ethyl acetate (100 mL) and washed with aq. HCl (1 M, 25 mL), dried and the solvent removed *in vacuo* to yield the crude product **3**. Purification was achieved by column chromatography (silica, 4:1 pentane:ether, v/v) to yield the pure product **3** as a white crystalline solid (1.03 g, 65%); mp 45–46°C (lit.[2] 44–45°C); $[\alpha]_D^{25}$ +116.4 (c 2.0, $CHCl_3$) {lit.[2] $[\alpha]_D$ +110 (c 1.0, $CHCl_3$)}; δ_H (400MHz, $CDCl_3$) 0.89 (3H, d, *J* 6.9, CH*Me*$_2$), 0.94 (3H, d, *J* 7.1, CH*Me*$_2$), 2.36–2.46 (1H, m, C*H*Me$_2$), 4.24 (1H, dd, J_{AB} 9.1, J_{AX} 3.2, CH_2), 4.31 (1H, dd, J_{BA} 9.1, J_{BX} 8.3, CH_2), 4.50 (1H, ddd, J_{XB} 8.3, J_{XA} 3.4, J_{XC} 3.4, NC*H*), 5.89 (1H, dd, $J_{A'X'}$ 10.5, $J_{A'B'}$ 1.9, CH=CH_2), 6.54 (1H, dd, $J_{B'X'}$ 17.0, $J_{B'A'}$ 1.8, CH=CH_2), 7.52 (1H, dd, $J_{X'B'}$ 17.0, $J_{X'A'}$ 10.4, C*H*=CH$_2$).

(*S*)-5,5-Dimethyl-4-*iso*-propyl-3-acryloyl-oxazolidin-2-one 4

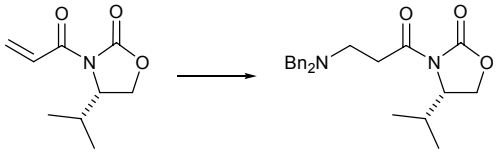
[2] D. A. Evans, S. J. Miller, T. Lectka, P. von Matt, *J. Am. Chem. Soc.*, 1999, **121**, 7559–7573.



To a stirred solution of acrylic acid (1.65 mL, 24 mmol, 1.25 eq) in ethyl acetate (120 mL) at 0 °C was added Et_3N (3.33 mL, 24 mmol, 1.25 eq) followed by acryloyl chloride (1.95 mL, 24 mmol, 1.25 eq) over 2 min. The resulting solution was stirred at 0 °C for 40 min then at rt for 30 min. The suspension was filtered and the filtrate concentrated *in vacuo*. The residue was taken up in hexane (100 mL) and the resulting suspension filtered and the filtrate concentrated *in vacuo* again. The anhydride was dissolved in THF (3 mL) and used immediately.

To a suspension of oxazolidinone **2** (3.0 g, 19.1 mmol, 1.0 eq) and LiCl (1.0 g, 24 mmol, 1.25 eq) in THF (18 mL) was added Et_3N (3.3 mL, 24 mmol, 1.25 eq), the anhydride, followed by a THF wash (3 mL). The suspension was stirred at rt for 4 h before removal of the solvent *in vacuo*. The residue was taken up in ethyl acetate (250 mL) and washed with aq. HCl (1M, 50 mL), dried and the solvent removed *in vacuo* to yield the crude product **4**. Purification was achieved by column chromatography (silica, 4:1 pentane:ether, v/v) to yield the pure product **4** as a white crystalline solid (2.9 g, 72%); mp 56–57°C (lit.[3] 56–57°C); $[\alpha]_D^{25}$ +55.3 (c 2.0, $CHCl_3$) {lit.[3] $[\alpha]_D^{20}$ +58.0 (c 1.0, $CHCl_3$); δ_H (400MHz, $CDCl_3$) 0.96 (3H, d, *J* 6.8, CH*Me*$_2$), 1.04 (3H, d, *J* 7.0, CH*Me*$_2$), 1.40 (3H, s, C*Me*$_2$), 1.52 (3H, s, C*Me*$_2$), 2.13–2.21 (1H, m, C*H*Me$_2$), 4.22 (1H, d, *J* 3.4, NC*H*), 5.90 (1H, dd, J_{AX} 10.5, J_{AB} 1.9, CH=CH_2), 6.54 (1H, dd, J_{BX} 17.0, J_{BA} 1.9, CH=CH_2), 7.56 (1H, dd, J_{XB} 17.0, J_{XA} 10.4, C*H*=CH_2).

(*S*)-4-*iso*-Propyl-3-[3'-(*N*,*N*-dibenzylamino)propanoyl]oxazolidin-2-one 6

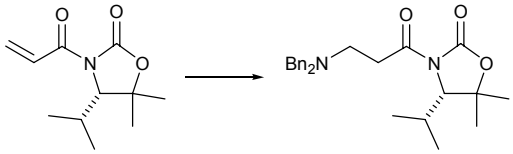


N-Acryloyl-oxazolidinone **3** (149 mg, 0.8 mmol, 1.0 eq) was reacted with dibenzylamine (0.23 mL, 1.7 mmol, 1.6 eq) and *n*-BuLi (0.48 mL, 1.7 mmol, 1.6 eq) according to **General Procedure 1**. Purification by column chromatography (silica, 9:1 pentane:ether, v/v) afforded **6** as a viscous, colourless oil (200mg, 66%); $[\alpha]_D^{25}$ +53.5 (c 0.4, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1773, 1700; δ_H (400MHz, $CDCl_3$) 0.83 (3H, d, *J* 7.0, CH*Me*$_2$), 0.91 (3H, d, *J* 6.8, CH*Me*$_2$), 2.31–2.40 (1H, m, C*H*Me$_2$), 2.82–2.98 (2H, m, CH_2NBn$_2$), 3.15–3.20 (2H, m, COCH_2), 3.60 (2H, d, *J* 13.5, NCH_2Ph), 3.69 (2H, d, *J* 13.5, NCH_2Ph), 4.14 (2H, d, *J* 5.6, OCH_2), 4.33–4.39 (1H, m, NC*H*), 7.19–7.40 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 14.6, 18.0, 28.3, 33.3, 48.9, 58.0,

[3] S. D. Bull, S. G. Davies, A. C. Garner, D. Kruchinin, M. S. Key, P. M. Roberts, E. D. Savory, A. D. Smith and J. E. Thomson, *Org. Biomol. Chem.*, 2006, **4**, 2945–2964.

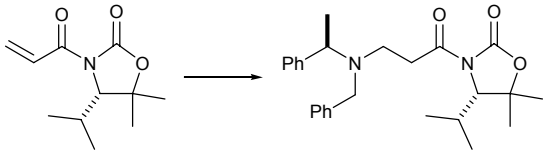
58.4, 63.2, 126.9, 128.2, 128.8, 139.4, 153.9, 172.0; *m/z* (ESI$^+$) 381 (MH$^+$, 100%); HRMS (ESI$^+$) 381.2184 ($C_{23}H_{29}N_2O_3$ requires 381.2178).

(*S*)-5,5-Dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)propanoyl]oxazolidin-2-one 7



N-Acryloyl-oxazolidin one **4** (296 mg, 1.40 mmol, 1.0 eq) was reacted with dibenzylamine (0.44 mL, 2.30 mmol, 1.6 eq) and *n*-BuLi (0.91 mL, 2.3 mmol, 1.6 eq) according to **General Procedure 1**. Purification by column chromatography (silica, 9:1 pentane: ether, v/v) afforded **7** as a viscous, colourless oil (525g, 92%); $[\alpha]_D^{25}$ +17.5 (c 1.6, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1772, 1700; δ_H (400MHz, $CDCl_3$) 0.96 (3H, d, *J* 6.8, CH*Me*$_2$), 1.04 (3H, d, *J* 7.0, CH*Me*$_2$), 1.37 (3H, s, C*Me*$_2$), 1.52 (3H, s, C*Me*$_2$), 2.11–2.19 (1H, m, C*H*Me$_2$), 2.93–3.00 (2H, m, C*H*$_2$NBn$_2$), 3.16–3.23 (1H, m, COC*H*$_2$), 3.28–3.35 (1H, m, COC*H*$_2$), 3.68 (4H, app s, N(C*H*$_2$Ph)$_2$), 4.16 (1H, d, *J* 3.2, NC*H*), 7.25–7.44 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 17.1, 21.4, 28.8, 29.5, 33.0, 49.0, 57.9, 66.2, 82.8, 126.9, 128.2, 128.9, 140.4, 153.6, 172.6; *m/z* (ESI$^+$) 409 (MH$^+$, 100%); HRMS (ESI$^+$) 409.2488 ($C_{25}H_{33}N_2O_3$ requires 409.2491).

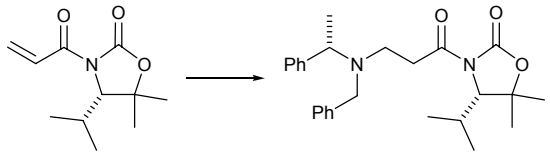
(4*S*,α*R*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]propanoyl}oxazolidin-2-one 9



N-Acryloyl-oxazolidinone **4** (296 mg, 1.40 mmol, 1.0 eq) was reacted with (*R*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (485 mg, 2.30 mmol, 1.6 eq) and *n*-BuLi (1.39 mL, 2.22 mmol, 1.6 eq) according to **General Procedure 1**. Purification by column chomatography (silica, 7:3 pentane:ether, v/v) yielded **9** (442 mg, 75%) as a white crystalline solid; mp 67–69 °C; $[\alpha]_D^{25}$ +26.9 (c 3.05, $CHCl_3$); ν_{max}/cm^{-1} (KBr) 1777, 1699; δ_H (400MHz, $CDCl_3$) 0.92 (3H, d, *J* 6.8, CH*Me*$_2$), 1.01 (3H, d, *J* 6.8, CH*Me*$_2$), 1.35 (3H, s, C*Me*$_2$), 1.45(3H, d, *J* 6.8, NCH*Me*), 1.50 (3H, s, C*Me*$_2$), 2.09–2.19 (1H, m, C*H*Me$_2$), 2.78–2.85 (1H, m, COCH$_2$C*H*$_2$), 3.03–3.12 (2H, m, COCH$_2$C*H*$_2$ and COC*H*$_2$), 3.13–3.20 (1H, m, COC*H*$_2$), 3.58 (1H, d, *J* 13.8, NC*H*$_2$Ph), 3.70 (1H, d, *J* 13.8, NC*H*$_2$Ph), 3.96 (1H, q, *J* 6.8, NC*H*Ph), 4.13 (1H, d, *J* 3.3, NC*H*^{i}Pr), 7.22–7.45 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 16.4, 17.1, 21.4, 28.8, 29.5, 33.5, 45.1, 54.5, 58.5, 66.2, 82.7, 126.7,

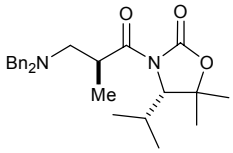
127.5, 127.8, 128.1, 128.5, 140.3, 143.5, 153.5, 172.7; *m/z* (ESI^+) 423 (MH^+, 100%); HRMS (ESI^+) 423.2658 ($C_{26}H_{35}N_2O_3$ requires 423.2648).

(4*S*,α*S*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]propanoyl}oxazolidin-2-one 10



N-Acryloyl-oxazolidinone **4** (296 mg, 1.40 mmol, 1.0 eq) was reacted with (*S*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (485 mg, 2.30 mmol, 1.6 eq) and *n*-BuLi (1.4 mL, 2.22 mmol, 1.6 eq) according to **General Procedure 1**. Purification by column chomatography (silica, 7:3 pentane:ether, v/v) furnished **10** (501 mg, 85%) as a yellow viscous oil; (Found C 75.8, H 8.5, N 6.6%. $C_{26}H_{34}N_2O_3$ requires C 73.9, H 8.1, N 6.6%); $[\alpha]_D^{25}$ +1.7 (c 2.9, $CHCl_3$); ν_{max}/cm^{-1} (film) 1772, 1700; δ_H (400MHz, $CDCl_3$) 0.91 (3H, d, *J* 6.8, CH*Me*$_2$), 0.99 (3H, d, *J* 6.8, CH*Me*$_2$), 1.33 (3H, s, C*Me*$_2$), 1.43 (3H, d, *J* 6.8, NCH*Me*), 1.49 (3H, s, C*Me*$_2$), 2.08–2.18 (1H, m, C*H*Me$_2$), 2.75–2.80 (1H, m, COCH$_2$C*H*$_2$), 2.89–3.12 (2H, m, COCH$_2$C*H*$_2$ and COC*H*$_2$), 3.21–3.27 (1H, m, COC*H*$_2$), 3.58 (1H, d, *J* 13.8, NC*H*$_2$Ph), 3.65 (1H, d, *J* 13.8, NC*H*$_2$Ph), 3.96 (1H, q, *J* 6.8, NC*H*Ph), 4.10 (1H, d, *J* 3.3, NC*H*^{i}Pr), 7.21–7.44 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 16.2, 17.0, 21.4, 28.8, 29.5, 33.5, 45.1, 54.4, 58.4, 66.2, 82.7, 126.7, 127.5, 127.8, 128.1, 128.6, 140.3, 143.5, 153.5, 172.7; *m/z* (ESI^+) 423 (MH^+, 100%); HRMS (ESI^+) 423.2653 ($C_{26}H_{35}N_2O_3$ requires 423.2648).

(2'*S*,4*S*)-5,5-Dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-methylpropanoyl]oxazolidin-2-one 11



Method A

N-Acryloyl-oxazolidinone **4** (1.48 g, 7.0 mmol, 1.0 eq) was reacted with dibenzylamine (2.18 mL, 11.5 mmol, 1.6 eq) and *n*-BuLi (4.34 mL, 11.5 mmol, 1.6 eq), followed by methyl iodide (0.65 mL, 10.5 mmol, 1.5 eq) according to **General Procedure 2**, to give **11** in 96% de. Purification by column chromatography (silica, 19:1 pentane:ether, v/v) afforded **11** (2.60 g, 88%) as a white crystalline solid (Found: C, 73.8; H, 7.8; N, 6.6%. $C_{26}H_{34}N_2O_3$ requires C, 73.9; H, 8.1; N, 6.6%); mp 82–83°C; $[\alpha]_D^{25}$ +12.0 (c 1.6, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1772, 1700; δ_H (400MHz, $CDCl_3$) 0.96 (3H, d, *J* 6.8, CH*Me*$_2$), 1.01 (3H, d, *J* 7.0, CH*Me*$_2$), 1.22 (3H, d, *J* 6.8, COCH*Me*), 1.43 (3H, s, C*Me*$_2$), 1.53 (3H, s, C*Me*$_2$), 2.10–2.20 (1H, m, C*H*Me$_2$),

2.50 (1H, dd, J_{AB} 12.7, J_{AX} 6.7, CH_2NBn$_2$), 2.90 (1H, dd, J_{BA} 12.7, J_{BX} 7.5, CH_2NBn$_2$), 3.52 (2H, d, J 13.7, NCH_2Ph), 3.68 (2H, d, J 13.8, NCH_2Ph), 4.19 (1H, d, J 3.4, NCH^iPr), 4.21–4.24 (1H, m, COCHMe), 7.21–7.39 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 16.5, 17.0, 21.4, 21.5, 28.7, 29.6, 36.3, 56.9, 58.3, 66.1, 82.5, 126.8, 128.1, 129.0, 139.1, 153.2, 176.8; *m/z* (ESI^+) 423 (MH^+, 100%); HRMS (ESI^+) 423.2652 ($C_{26}H_{35}N_2O_3$ requires 423.2648).

Method B

β-Amino-oxazolidinone **7** (100 mg, 0.24 mmol, 1.0 eq) was reacted with LiHMDS (0.30 mL, 0.2 mmol, 1.1 eq), followed by methyl iodide (23 μL, 0.37 mmol, 1.5 eq) according to **General Procedure 3**, to give **11** in 96% de. Purification by column chromatography (silica, 9:1 pentane:ether, v/v) afforded **11** (95 mg, 94%) with identical physical and spectroscopic properties to those described above.

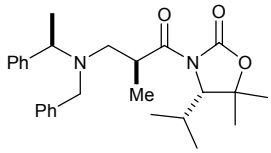
X-Ray crystal structure determination for 11

Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 190K. The structure was solved by direct methods, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[4]

X-ray crystal structure data for **11** [$C_{26}H_{34}N_2O_3$]: M = 422.57, monoclinic, space group P 2_1, a = 14.1180(3) Å, b = 6.1198(2) Å, c = 14.4072(4) Å, β = 108.4415(11)°, V = 1180.85(6) Å^3, Z = 4, μ = 0.077 mm^{-1}, colourless block, crystal dimensions = 0.2 × 0.2 × 0.2 mm^3. A total of 2840 unique reflections were measured for $5 < \theta < 27$ and 2657 reflections were used in the refinement. The final parameters were wR_2 = 0.0354 and R_1 = 0.0335 [$I>3\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 616167. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(4*S*,2'*S*,α*R*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-methyl propanoyl}oxazolidin-2-one 12

[4] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, C. K. Prout and D. J. Watkin, CRYSTALS, 2004, Issue 12, Chemical Crystallography Laboratory, University of Oxford, UK.



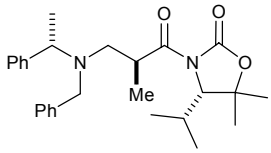
Method A

N-Acryloyl-oxazolidinone **4** (150 mg, 0.71 mmol, 1.0 eq) was reacted with (*R*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (240 mg, 1.14 mmol, 1.6 eq) and *n*-BuLi (0.46 mL, 1.14 mmol, 1.6 eq), followed by MeI (71 μL, 2.27 mmol, 1.6 eq) according to **General Procedure 2**, giving **12** in 93% de. Purification by column chomatography (silica, 9:1 pentane:ether, v/v) furnished **12** (235 mg, 76%) as a white crystalline solid; mp 125–127 ˚C; $[\alpha]_D^{25}$ +28.7 (c 1.05, $CHCl_3$); ν_{max}/cm^{-1} (KBr) 1752, 1702; δ_H (400MHz, $CDCl_3$) 0.94 (3H, d, *J* 6.8, CH*Me*$_2$), 1.01 (3H, d, *J* 6.8, CH*Me*$_2$), 1.10 (3H, d, *J* 6.8, COCH*Me*), 1.35 (3H, d, *J* 6.8, NCH*Me*), 1.45 (3H, s, C*Me*$_2$), 1.53 (3H, s, C*Me*$_2$), 2.11–2.18 (1H, m, C*H*Me$_2$), 2.25 (1H, dd, J_{AB} 12.9, J_{AX} 6.3, COCHC*H*$_2$), 3.09 (1H, dd, J_{BA} 12.9, J_{BX} 8.3, COCHC*H*$_2$), 3.58 (2H, AB q, *J*, 4.8, NC*H*$_2$Ph), 3.92 (1H, q, *J* 6.8, NC*H*Ph), 3.99–4.06 (1H, m, COC*H*Me), 4.22 (1H, d, *J* 3.3, NC*H*^{i}Pr), 7.21–7.34 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 14.0, 16.4, 17.0, 21.4, 28.7, 29.6, 37.0, 52.9, 54.9, 57.3, 66.1, 82.4, 126.7 127.8, 128.1, 128.2, 128.5, 140.2, 142.2, 153.5, 172.0; *m/z* (ESI^+) 437 (MH^+, 100%); HRMS (ESI^+) 437.2803 ($C_{27}H_{36}N_2O_3$ requires 437.2804).

Method B

β-Amino-oxazolidinone **9** (150 mg, 0.37 mmol, 1.0 eq) was reacted with LiHMDS (0.80 mL, 0.80 mmol, 1.1 eq), followed by MeI (35 μL, 0.55 mmol, 1.5 eq) according to **General Procedure 3**, giving **12** in 96% de. Purification by column chomatography (silica, 9:1 pentane:ether, v/v) furnished **12** (138 mg, 86%) as a white crystalline solid with identical physical and spectroscopic properties to those described above.

(4*S*,2'*S*,α*S*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-methyl-propanoyl}oxazolidin-2-one 13



Method A

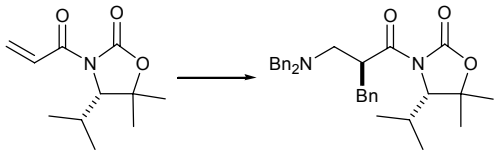
N-Acryloyl-oxazolidinone **4** (150 mg, 0.71 mmol, 1.0 eq) was reacted with (*R*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (240 mg, 1.14 mmol, 1.6 eq) and *n*-BuLi (0.46 mL, 1.14 mmol, 1.6 eq), followed by MeI (71 μL, 2.27 mmol, 1.6 eq) according to **General Procedure 2**, giving **13** in 95% de. Purification by

column chomatography (silica, 9:1 pentane:ether, v/v) furnished **13** (201 mg, 65%) as a yellow oil; $[\alpha]_D^{25}$ –12.3 (c 1.1, $CHCl_3$); ν_{max}/cm^{-1} (film) 1773, 1699; δ_H (400MHz, $CDCl_3$) 0.92 (3H, d, *J* 6.8, CH*Me*$_2$), 1.00 (3H, d, *J* 7.1, CH*Me*$_2$), 1.22 (3H,d, *J* 6.8, COCH*Me*), 1.39 (3H, s, C*Me*$_2$), 1.41 (3H, d, *J* 7.1, NCH*Me*), 1.51 (3H, s, C*Me*$_2$), 2.09–2.19 (1H, m, C*H*Me$_2$), 2.63 (1H, dd, J_{AB} 13.0, J_{AX} 7.3, COCHC*H*$_2$), 2.74 (1H, dd, J_{BA} 13.0, J_{BX} 6.8, COCHC*H*$_2$), 3.42 (1H, d, *J* 14.2, NC*H*$_2$Ph), 3.72 (1H, d, *J* 14.2, NC*H*$_2$Ph), 3.90 (1H, q, *J* 7.1, NC*H*Ph), 4.01–4.10 (1H, m, COC*H*Me), 4.12 (1H, d, *J* 3.3, NC*H*^{i}Pr), 7.22–7.42 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 16.6, 16.6, 16.9, 21.4, 21.4, 28.7, 29.6, 36.8, 52.9, 55.0, 58.1, 66.1, 82.4, 126.7, 127.9, 128.1, 128.3, 128.5, 128.9, 140.3, 142.0, 155.2, 176.9; *m/z* (ESI^+) 437 (MH^+, 100%); HRMS (ESI^+) 437.2809 ($C_{27}H_{36}N_2O_3$ requires 437.2804).

Method B

β-Amino-oxazolidinone **10** (100 mg, 0.23 mmol, 1.0 eq) was reacted with LiHMDS (0.26 mL, 1.0 M, 0.26 mmol, 1.1 eq), followed by MeI (25 μL, 0.36 mmol, 1.5 eq) according to **General Procedure 3**, giving **13** in 96% de. Purification by column chomatography (silica, 9:1 pentane:ether, v/v) yielded **13** (90 mg, 87%) as a yellow oil with identical physical and spectroscopic properties to those described above.

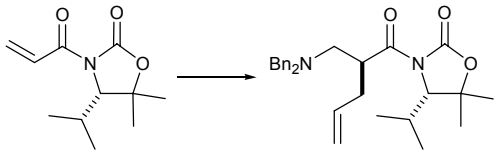
(2'*S*,4*S*)-5,5-Dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-benzyl-propanoyl]oxazolidin-2-one 14



N-Acryloyl-oxazolidinone **4** (333 mg, 1.58 mmol, 1.0 eq) was reacted with dibenzylamine (0.49 mL, 2.53 mmol, 1.6 eq) and *n*-BuLi (1.01 mL, 2.53 mmol, 1.6 eq), followed by benzylbromide (0.28 mL, 21.5 mmol, 1.5 eq) according to **General Procedure 2**, giving **14** in 97% de. Purification by column chromatography (silica, 9:1 pentane:ether, v/v) afforded **14** (670 mg, 85%) as a white crystalline solid (Found: C, 76.6; H, 7.7, N, 5.5%. $C_{32}H_{38}N_2O_3$ requires C, 77.1; H, 7.7; N, 5.6%); mp 75–76 °C; $[\alpha]_D^{25}$ +15.0 (c 1.8, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1772, 1709; δ_H (400MHz, $CDCl_3$) 0.62 (3H, d, *J* 7.2, CH*Me*$_2$), 0.76 (3H, d, *J* 7.1, CH*Me*$_2$), 1.43 (3H, s, C*Me*$_2$), 1.48 (3H, s, C*Me*$_2$), 1.93–2.01 (1H, m, C*H*Me$_2$), 2.56 (1H, dd, J_{AB} 12.6, J_{AX} 6.2, C*H*$_2$NBn$_2$), 2.83 (1H, dd, $J_{A'B'}$ 13.6, $J_{A'X'}$ 9.1, C*H*$_2$Ph), 2.91 (1H, dd, J_{BA} 12.6, J_{BX} 8.0, C*H*$_2$NBn$_2$), 3.00 (1H, dd, $J_{B'A'}$ 13.6, $J_{B'X'}$ 6.2, C*H*$_2$Ph), 3.65 (2H, d, *J* 13.7, NC*H*$_2$Ph), 3.79 (2H, d, *J* 13.6, NC*H*$_2$Ph), 4.13 (1H, d, *J* 2.8, NC*H*^{i}Pr), 4.74–4.85 (1H, m, COC*H*), 7.14–7.36 (15H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 16.3, 21.0,

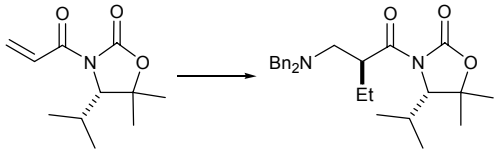
21.3, 28.8, 29.4, 37.1, 42.9, 56.0, 58.3, 66.4, 82.3, 126.2, 126.9, 128.1, 128.3, 129.1, 129.3, 138.8, 139.0, 153.4, 175.5; *m/z* (ESI^+) 499 (MH^+, 100%); HRMS (ESI^+) 499.2964 ($C_{32}H_{39}N_2O_3$ requires 499.2961).

(2'*S*,4*S*)-5,5-Dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-allyl-propanoyl]oxazolidin-2-one 15



N-Acryloyl-oxazolidinone **4** (333mg, 1.58mmol, 1.0eq) was reacted with dibenzylamine (0.486mL, 2.53mmol, 1.6eq) and *n*-BuLi (1.01mL, 2.5M, 2.53mmol, 1.6eq), followed by allylbromide (0.205mL, 21.5mmol, 1.5eq) according to **General Procedure 2**, giving **15** in 96% de. Purification by column chromatography (silica, 9:1 pentane:ether, v/v) afforded **15** (582mg, 82%) as a colourless, viscous oil; $[\alpha]_D^{25}$ +24.6 (c 1.6, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1769, 1697; δ_H (400MHz, $CDCl_3$) 0.96 (3H, d, *J* 6.8, CH*Me*$_2$), 1.01 (3H, d, *J* 7.0, CH*Me*$_2$), 1.44 (3H, s, C*Me*$_2$), 1.53 (3H, s, C*Me*$_2$), 2.10–2.21 (1H, m, C*H*Me$_2$), 2.31–2.39 (1H, m, C*H*$_2$CH=CH$_2$), 2.41–2.50 (1H, m, C*H*$_2$CH=CH$_2$), 2.56 (1H, dd, J_{AB} 12.7, J_{AX} 6.2, C*H*$_2$NBn$_2$), 2.87 (1H, dd, J_{BA} 12.7, J_{BX} 8.0, C*H*$_2$NBn$_2$), 3.59 (2H, d, *J* 7.5, NC*H*$_2$Ph), 3.63 (2H, d, *J* 7.7, NC*H*$_2$Ph), 4.21 (1H, d, *J* 2.8, NC*H*), 4.42–4.48 (1H, m, COC*H*), 5.00–5.11 (2H, m, CH=C*H*$_2$), 5.74–5.89 (1H, m, C*H*=CH$_2$), 7.15–7.37 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 16.9, 21.4, 21.4, 28.8, 29.6, 35.4, 41.0, 55.8, 58.3, 66.5, 82.5, 117.0, 126.9, 128.1, 129.1, 135.4, 138.9, 153.5, 175.5; *m/z* (ESI^+) 449 (100%); HRMS (ESI^+) 449.2801 ($C_{28}H_{36}N_2O_3$ requires 449.2804).

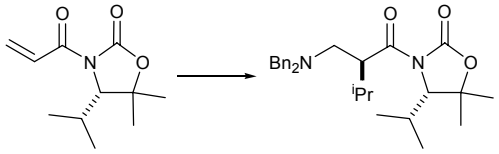
(2'*S*,4*S*)-5,5-Dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-ethyl-propanoyl]oxazolidin-2-one 16



N-Acryloyl-oxazolidinone **4** (333 mg, 1.58 mmol, 1.0 eq) was reacted with dibenzylamine (0.49 mL, 2.53 mmol, 1.6 eq) and *n*-BuLi (1.01 mL, 2.53 mmol, 1.6 eq), followed by ethyliodide (0.19 mL, 21.5 mmol, 1.5 eq) according to **General Procedure 2**, giving **16** in 96% de. Purification by column chromatography (silica, 9:1 pentane:ether, v/v) afforded **16** (429 mg, 62%) as a white crystalline solid (Found: C, 74.5; H, 8.1; N, 6.45%. $C_{27}H_{36}N_2O_3$ requires C, 74.3; H, 8.3, N, 6.4%); mp 78–79 °C; $[\alpha]_D^{25}$ +20.0 (c 2.3, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1770, 1695; δ_H (400MHz, $CDCl_3$) 0.93 (3H, t, *J* 7.5, CH$_2$*Me*), 0.99 (3H, d, *J* 6.8, CH*Me*$_2$), 1.05 (3H, d, *J* 7.1, CH*Me*$_2$), 1.45 (3H, s, C*Me*$_2$), 1.54 (3H, s, C*Me*$_2$), 1.61–1.72 (2H, m, C*H*$_2$Me), 2.14–2.23 (1H, m, C*H*Me$_2$), 2.55 (1H, dd, J_{AB} 12.7, J_{AX} 5.9, C*H*$_2$NBn$_2$), 2.89 (1H, dd, J_{BA} 12.7, J_{BX} 8.3, C*H*$_2$NBn$_2$),

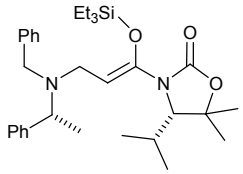
3.60 (4H, AB q, *J* 13.7, NC*H*$_2$Ph), 4.24 (1H, d, *J* 2.9, NC*H*^{i}Pr), 4.24–4.31 (1H, m, COC*H*), 7.21–7.38 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 11.5, 17.0, 21.4, 21.5, 24.3, 28.8, 29.6, 42.6, 55.8, 58.3, 66.4, 82.4, 126.9, 128.1, 129.1, 138.9, 153.5, 176.3; *m/z* (ESI^+) 437 (MH^+, 100%); HRMS (ESI^+) 437.2813 ($C_{27}H_{37}N_2O_3$ requires 437.2804).

(2'*S*,4*S*)-5,5-Dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-*iso*-propyl-propanoyl]oxazolidin-2-one 17



N-Acryloyl-oxazolidinone **4** (333 mg, 1.58 mmol, 1.0 eq) was reacted with dibenzylamine (0.486 mL, 2.53 mmol, 1.6 eq) and *n*-BuLi (1.01 mL, 2.53 mmol, 1.6 eq), followed by 2-iodopropane (0.237 mL, 21.5 mmol, 1.5 eq) according to **General Procedure 2**, giving **17** in 96% de. Purification by column chromatography (silica, 9:1 pentane:ether, v/v) afforded **17** as a colourless, viscous oil (57 mg, 8%); $[\alpha]_D^{25}$ +12.0 (c 0.1, $CHCl_3$); δ_H (400MHz, $CDCl_3$) 0.89 (3H, d, *J* 6.1, COCHCH*Me*$_2$), 0.91 (3H, d, *J* 6.3, COCHCH*Me*$_2$), 1.05 (3H, d, *J* 6.8, CH*Me*$_2$), 1.12 (3H, d, *J* 7.1, CH*Me*$_2$), 1.38 (3H, s, C*Me*$_2$), 1.54 (3H, s, C*Me*$_2$), 1.81 (1H, m, COCHC*H*Me$_2$), 2.22 (1H, m, C*H*Me$_2$), 2.56 (1H, dd, J_{AB} 12.7, J_{AX} 3.8, CH_2NBn$_2$), 3.04 (1H, dd, J_{BA} 12.7, J_{BX} 10.4, CH_2NBn$_2$), 3.46 (2H, d, *J* 13.7, NCH_2Ph), 3.66 (2H, d, *J* 13.6, NCH_2Ph), 4.24 (1H, d, *J* 2.7, NC*H*), 4.32 (1H, m, COC*H*), 7.25 (10H, m, *Ph*).

(4*S*,*αR*)-5,5-Dimethyl-4-*iso*-propyl-3-{1'-triethylsilyloxy-3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]prop-1'-enyl}oxazolidin-2-one 18



Method A

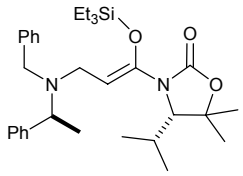
N-Acryloyl-oxazolidinone **4** (80 mg, 0.38 mmol, 1.0 eq) was reacted with (*R*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (130 mg, 0.61 mmol, 1.6 eq) and *n*-BuLi (0.24 mL, 0.61 mmol, 1.6 eq), followed by triethylsilyl chloride (64 μL, 0.61 mmol, 1.6 eq) according to **General Procedure 4** furnishing **18** and starting material **4** in a 4:1 ratio; ν_{max}/cm^{-1} (film) 1756; δ_H (400MHz, $CDCl_3$) 0.60 (6H, q, *J* 7.9, Si(CH_2Me)$_3$), 0.91 (9H, t, *J* 7.9, Si(CH$_2$*Me*)$_3$), 1.04 (3H, d, *J* 6.8, CH*Me*$_2$), 1.06 (3H, d, *J* 7.3, CH*Me*$_2$), 1.41 (3H, d, *J* 6.8, NCH*Me*), 1.44 (6H, s, C*Me*$_2$), 1.98–2.06 (1H, m, C*H*Me$_2$), 3.10 (1H, dd, J_{AB} 14.4, J_{AX} 8.8

COCHCH_2), 3.31 (1H, dd, J_{BA} 14.4, J_{BX} 4.6 COCHCH_2), 3.36 (1H, d, *J* 14.1 NCH_2Ph), 3.56 (1H, d, *J* 2.5, NC*H*^{i}Pr), 3.62 (1H, d, *J* 14.1 NCH_2Ph), 3.87 (1H, q, *J* 6.8, NC*H*Me), 5.17 (1H, dd, J_{XA} 8.8, J_{XB} 4.6 C=C*H*), 7.18–7.45 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 5.0, 6.8, 16.6, 18.3, 20.7, 22.2, 29.6, 29.7, 45.1, 54.1, 58.5, 67.9, 80.5, 103.6, 126.7, 126.5 126.5, 127.7, 128.0, 128.5, 140.0, 140.7, 143.3, 154.9; *m/z* (ESI$^+$) 537 (MH$^+$, 70%); HRMS (ESI$^+$) 537.3512 ($C_{32}H_{48}N_2O_3Si$ requires 537.3511).

Method B

(4*S*,α*R*)-**9** (80 mg, 0.19 mmol, 1.0 eq) was reacted with LiHMDS (0.21 mL, 0.21 mmol, 1.1 eq), followed by triethylsilyl chloride (48 μL, 0.29 mmol, 1.5 eq) according to **General Procedure 5** to yield **18** and recovered starting material **9** in a 5:1 ratio with identical spectroscopic properties as those described above.

(4*S*,α*S*)-5,5-Dimethyl-4-*iso*-propyl-3-{1'-triethylsilyloxy-3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]prop-1'-enyl}-oxazolidin-2-one 19



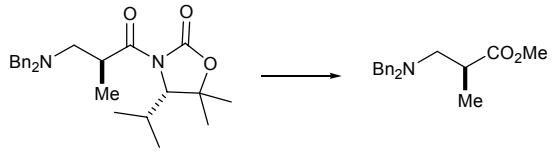
Method A

N-Acryloyl-oxazolidinone **4** (80 mg, 0.38 mmol, 1.0 eq) was reacted with (*S*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (130 mg, 0.61 mmol, 1.6 eq) and *n*-BuLi (0.24 mL, 0.61 mmol, 1.6 eq), followed by triethylsilyl chloride (64 μL, 0.61 mmol, 1.6 eq) according to **General Procedure 4** to give **19** and returned starting material **4** in a 2:1 ratio; ν_{max}/cm^{-1} (film) 1759; δ_H (400MHz, $CDCl_3$) 0.60 (6H, q, *J* 8.1, Si(CH_2Me)$_3$), 0.96 (9H, t, *J* 8.1, Si(CH$_2$*Me*)$_3$), 1.04 (3H, d, *J* 6.8, CH*Me*$_2$), 1.05 (3H, d, *J* 7.3, CH*Me*$_2$), 1.37 (3H, d, *J* 6.8, NCH*Me*), 1.44 (6H, s, C*Me*$_2$), 1.97–2.05 (1H, m, C*H*Me$_2$), 3.08 (1H, dd, J_{AB} 14.4, J_{AX} 4.5 CCHCH_2), 3.34 (1H, dd, J_{BA} 14.4, J_{BX} 9.1, CCHCH_2), 3.47 (1H, d, *J* 13.9, NCH_2Ph), 3.57 (1H, d, *J* 2.3, NC*H*^{i}Pr), 3.62 (1H, d, *J* 13.9 NCH_2Ph), 3.92 (1H, q, *J* 6.8, NC*H*Me), 5.17 (1H, dd, J_{XA} 9.1, J_{XB} 4.5, C=C*H*), 7.18–7.43 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 5.1, 6.6, 16.1, 16.5, 20.7, 22.2, 29.7, 29.7, 44.7, 53.7, 57.5, 67.9, 80.5, 103.8, 126.6, 126.7 127.7, 127.8, 128.0, 128.5, 140.5, 141.0 143.2, 154.9; *m/z* (ESI$^+$) 537 (MH$^+$, 30%); HRMS (ESI$^+$) 537.3513 ($C_{32}H_{48}N_2O_3Si$ requires 537.3511).

Method B

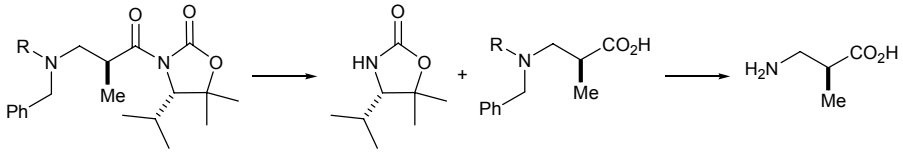
(4*S*,α*S*)-**10** (80 mg, 0.19 mmol, 1.0 eq) was reacted with LiHMDS (0.21 mL, 0.21 mmol, 1.1 eq), followed by triethylsilyl chloride (48 μL, 0.29 mmol, 1.5 eq) according to **General Procedure 5** to yield **19** and returned starting material **10** in a 3:1 ratio with identical spectroscopic properties as those described above.

Methyl (*S*)-3-(*N*,*N*-dibenzylamino)-2-methyl propanoate 28



3'-Amino-2'-methyl-oxazolidinone **11** (200 mg, 0.47 mmol, 1.0 eq) was reacted with *n*-BuLi (890 μL, 1.6 M, 1.42 mmol, 3.0 eq) according to **General Procedure 8**. Purification by column chromatography (silica, 49:1 to 19:1 pentane:ether, v/v) afforded (*S*)-**28** as a colourless oil (137 mg, 98%); $[\alpha]_D^{25}$ +9.9 (c 0.5, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1728; δ_H (400MHz, $CDCl_3$) 1.13 (3H, d, *J* 6.2, CH*Me*), 2.44 (1H, dd, J_{AB} 16.1, J_{AX} 10.1, CCHCH_2), 2.75–2.82 (2H, m, CC*H*CH_2, CCHCH_2), 3.50 (2H, d, *J* 13.4, NCH_2Ph), 3.64 (2H, d, *J* 13.4, NCH_2Ph), 3.66 (3H, s, O*Me*), 7.22–7.42 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 15.3, 38.6, 51.4, 57.4, 58.4, 126.9, 128.1, 128.9, 139.2, 176.2; *m/z* (ESI^+) 298 (MH^+, 100%); HRMS (ESI^+) 298.1803 ($C_{19}H_{24}NO_2$ requires 298.1807).

(*S*)-3-Amino-2-methyl propanoic acid 25



Method A:

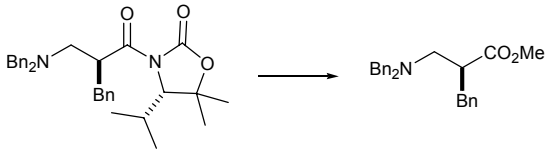
3'-Amino-2'-methyl-oxazolidinone **11** (1.20 g, 2.84 mmol, 1.0 eq) was reacted with LiOH (596 mg, 14.2 mmol, 5.0 eq) according to **General Procedure 6**. The crude mixture of products was treated with Pd (400mg, 10% wt on C) under H_2 (1atm) according to **General Procedure 7**. The solvent was removed *in vacuo* and the residue co-evaporated with aq. HCl (2 M). Purification by ion exchange chromatography (Dowex 50W-X8, 1M aq. NH_4OH eluent) yielded the free amino acid (*S*)-**25** as a white crystalline solid (246 mg, 84%); mp 175–177°C {lit.[5] 179–181°C}; $[\alpha]_D^{25}$ +17.0 (c 1.0, H_2O) {lit.[5] $[\alpha]_D^{25}$ +14.2 (c 1.0, H_2O)}; δ_H (200MHz, $CDCl_3$) 1.05 (3H, d, *J* 7.3, CH*Me*), 2.44–2.51 (1H, m, CC*H*CH_2), 2.84 (1H, dd, J_{AB} 12.8, J_{AX} 7.3, CCHCH_2), 2.97 (1H, dd, J_{BA} 12.8, J_{BX} 8.3, CCHCH_2).

[5] Y. Jin, D.H. Kim, *Synlett* 1998, **11**, 1189–1190.

Method B:

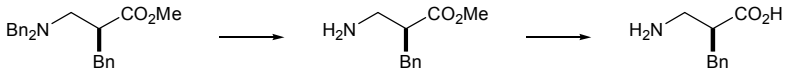
β-Amino ester **28** (100 mg, 0.34 mmol, 1.0 eq) was treated with Pd (50 mg, 10% wt on C) under H_2 (1 atm) according to **General Procedure 7**. The crude product was treated with LiOH (71 mg, 1.70 mmol, 5.0 eq) according to **General Procedure 9**. The solvents were removed *in vacuo* and the residue co-evaporated with aq. HCl (2 M). Purification by ion exchange chromatography yielded the free amino acid (*S*)-**25** as a white crystalline solid (33 mg, 95%) with identical spectroscopic properties to those described above.

Methyl (*S*)-3-(*N*,*N*-dibenzylamino)-2-benzyl-propanoate 29



3'-Amino-2'-benzyl-oxazolidinone **14** (200 mg, 0.40 mmol, 1.0 eq) was treated with *n*-BuLi (750 μL, 1.20 mmol, 3.0 eq) according to **General Procedure 8**. Purification by column chromatography (silica, 49:1 to 19:1 pentane:ether, v/v) afforded (*S*)-**29** as a colourless oil (148 mg, 99%); $[\alpha]_D^{25}$ +22.7 (c 1.1, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1731; δ_H (400MHz, $CDCl_3$) 2.57 (1H, dd, J_{AB} 12.6, J_{AX} 5.8, CCHCH_2N), 2.81 (2H, d, *J* 7.4, CHCH_2Ph), 2.88 (1H, dd, J_{BA} 12.6, J_{BX} 9.1, CCHCH_2N), 3.00–3.07 (1H, m, CC*H*CH_2), 3.48 (2H, d, *J* 13.5, NCH_2Ph), 3.60 (3H, s, O*Me*), 3.71 (2H, d, *J* 13.5, NCH_2Ph), 7.11–7.39 (15H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 36.5, 46.9, 51.4, 55.9, 58.5, 126.3, 127.0, 128.2, 128.4, 128.7, 129.0, 139.1, 139.2, 174.9; *m/z* (ESI^+) 374 (MH^+, 100%); HRMS (ESI^+) 374.2101 ($C_{25}H_{28}NO_2$ requires 374.2120).

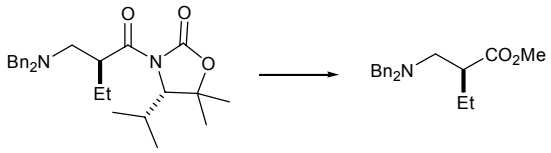
(*S*)-3-Amino-2-benzyl propanoic acid 31



β-Amino ester **29** (373 mg, 1.00 mmol, 1.0 eq) was treated with Pd (200mg, 10% wt on C) under H_2 (1atm) according to **General Procedure 7**. The crude product was treated with LiOH (210 mg, 5.00 mmol, 5.0 eq) according to **General Procedure 9**. The solvents were removed *in vacuo* and the residue co-evaporated with aq. HCl (2 M). Purification by ion exchange chromatography (Dowex 50W-X8, 1M aq. NH_4OH eluent) yielded the free amino acid (*S*)-**31** as a white crystalline solid (160 mg, 89%); mp 212–213°C {lit.[6] 224–225°C}; $[\alpha]_D^{25}$ –13.1 (c 0.3, H_2O) {lit.[6] for (*R*)-**31** $[\alpha]_D^{25}$ +17.8 (c 1.0, H_2O)}; δ_H (400MHz, D_2O) 2.85 (1H, dd, J_{AB} 12.5, J_{AX} 6.0, CCHCH_2N), 2.95 (1H, dd, J_{BA} 12.5, J_{BX} 9.0, CCHCH_2N), 3.00–3.13 (3H, m, CCHCH_2Ph and CC*H*CH_2), 7.17–7.42 (5H, m, *Ph*).

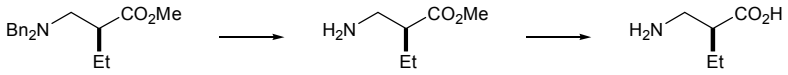
[6] Y. Jin, D.H. Kim, *Synlett* 1998, **11**, 1189–1190.

Methyl (*S*)-3-(*N*,*N*-dibenzylamino)-2-ethyl-propanoate 30



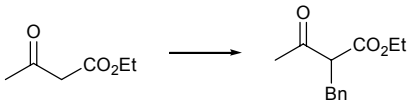
3'-Amino-2'-ethyl-oxazolidinone **16** (200 mg, 0.46 mmol, 1.0 eq) was treated with *n*-BuLi (860 μL, 1.37 mmol, 1.6 M, 3.0 eq) according to **General Procedure 8**. Purification by column chromatography (silica, 49:1 to 19:1 pentane:ether, v/v) afforded (*S*)-**30** as a colourless oil (137 mg, 96%); $[\alpha]_D^{25}$ +31.2 (c 0.9, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1728; δ_H (400MHz, $CDCl_3$) 0.85 (3H, t, *J* 7.5, $CHCH_2$*Me*), 1.48–1.56 (2H, m, $CHCH_2Me$), 1.97 (1H, dd, J_{AB} 12.4, J_{AX} 5.5, $CHCH_2N$), 2.63–2.70 (1H, m, C*H*), 2.79 (1H, dd, J_{BA} 12.4, J_{BX} 9.3, C(3)H_2), 3.44 (2H, d, *J* 13.6, NCH_2Ph), 3.67 (3H, s, O*Me*), 3.70 (2H, d, *J* 13.6, NCH_2Ph), 7.22–7.38 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 11.8, 23.5, 46.5, 51.3, 56.0, 58.4, 126.9, 128.1, 128.9, 139.2, 175.6; *m/z* (ESI^+) 312 (MH^+, 100%); HRMS (ESI^+) 312.1960 ($C_{20}H_{26}NO_2$ requires 312.1964).

(*S*)-3-Amino-2-ethyl propanoic acid 32



β-Amino ester **30** (357 mg, 1.15 mmol, 1.0 eq) was treated with Pd (200mg, 10% wt on C) under H_2 (1atm) according to **General Procedure 7**. The crude product was treated with LiOH (241 mg, 5.75 mmol, 5.0 eq) according to **General Procedure 9**. The solvents were removed *in vacuo* and the residue co-evaporated with aq. HCl (2 M). Purification by ion exchange chromatography (Dowex 50W-X8, 1M aq. NH_4OH eluent) yielded the free amino acid (*S*)-**32** as a white crystalline solid (125 mg, 93%); mp 220–221°C {lit.[7] 206–207°C}; $[\alpha]_D^{25}$ –6.8 (c 0.4, H_2O) {lit.[7] for (*R*)-**32** $[\alpha]_D^{25}$ +4.5 (c 1.0, H_2O)}; δ_H (400MHz, D_2O) 0.78 (3H, t, *J* 7.4, CH_2*Me*), 1.44–1.51 (2H, m, CH_2Me), 2.31–2.39 (1H, m, C(2)*H*), 2.91 (1H, dd, J_{AB} 12.9, J_{AX} 5.1, C(3)H_2), 3.00 (1H, dd, J_{BA} 12.9, J_{BX} 8.6, C(3)H_2).

Ethyl 2-benzyl-3-oxo-butyrate 33

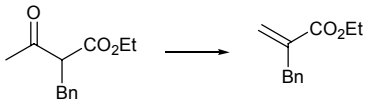


Potassium *tert*-butoxide (4.31 g, 38.4 mmol, 1.1 eq) was treated with ethyl acetoacetate (4.77 mL, 37.7 mmol, 1.0 eq) and *tert*-butanol (335 μL, 3.5 mmol, 0.1 eq) followed by benzylbromide (4.45 mL, 37.4

[7] E. Juaristi, M. Balderas, H. López-Ruiz, V. M. Jiménez-Pérez, M. L. Kaiser-Carril and Y. Ramírez-Quirós, *Tetrahedron: Asymmetry*, 1999, **10**, 3493–3505.

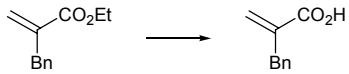
mmol, 0.99 eq) according to **General Procedure 10**. Purification by column chromatography (silica, 19:1 pentane: ether, v/v) afforded **33** as a colourless oil (7.25 g, 88%); δ_H (200MHz, $CDCl_3$) 1.18 (3H, t, *J* 7.2, CH_2*Me*), 2.17 (3H, s, CO*Me*), 3.14 (2H, d, *J* 7.2, CH_2Ph), 3.76 (1H, t, *J* 7.6, C*H*CH_2Ph), 4.13 (2H, q, *J* 7.2, CH_2Me), 7.08–7.29 (5H, m, *Ph*).

Ethyl 2-benzyl acrylate 36



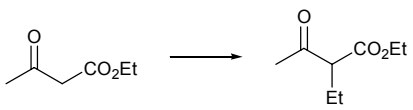
Ethyl 2-benzyl-3-oxo-butyrate **33** (3.0 g, 14 mmol, 1.0 eq) was treated with LiHMDS (15 mL, 1.0 M, 15 mmol, 1.1 eq) followed by paraformaldehyde (2.5 g, xs) according to **General Procedure 11**. Purification by column chromatography (silica, 49:1 pentane: ether, v/v) afforded **36** as a colourless oil (2.1 g, 80%); δ_H (200MHz, $CDCl_3$) 1.25 (3H, t, *J* 7.2, OCH_2*Me*), 3.62 (2H, app s, CH_2Ph), 4.17 (2H, q, *J* 7.1, OCH_2Me), 5.42–5.46 (1H, m, C=CH_2), 6.21–6.25 (1H, m, C=CH_2), 7.13–7.32 (5H, m, *Ph*).

2-Benzyl acrylic acid 39



Ethyl 2-benzyl acrylate **36** (2.5 g, 13 mmol, 1.0 eq) was treated with LiOH (2.8 g, 66 mmol, 5.0 eq) according to **General Procedure 9**. Upon cooling, the mixture was acidified to pH 2 and the product extracted with ether (3 × 100 mL). The combined organic extracts were dried and the solvents removed *in vacuo* to afford **39** as a white crystalline solid which was used without further purification (2.1 g, quant.); mp 61–63°C (lit.[8] 66–68°C); δ_H (200MHz, $CDCl_3$) 3.63 (2H, app s, CH_2Ph), 5.56–5.60 (1H, m, C=CH_2), 6.37–6.41 (1H, m, C=CH_2), 7.14–7.39 (5H, m, *Ph*).

Ethyl 2-ethyl-3-oxo-butyrate 34

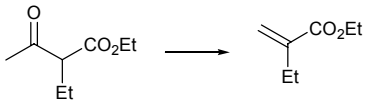


Potassium *tert*-butoxide (8.8 g, 77 mmol, 1.1 eq) was treated with ethyl acetoacetate (9.6 mL, 75 mmol, 1.0 eq) and *tert*-butanol (670 μL, 7.0 mmol, 0.1 eq) followed by ethyliodide (6.0 mL, 75 mmol, 0.99 eq) according to **General Procedure 10**. Purification by column chromatography (silica, 19:1 pentane: ether, v/v) afforded **34** as a colourless oil (8.8 g, 74%); δ_H (200MHz, $CDCl_3$) 0.89 (3H, t, *J* 7.5, $CHCH_2$*Me*), 1.24

[8] S. Serota, J. R. Simon, E.B. Murray and W. M. Linfield, *J. Org. Chem.* 1981, **46**, 4147–4151.

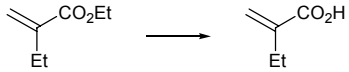
(3H, t, *J* 7.2, OCH_2Me), 1.76–1.90 (2H, m, $CHCH_2Me$), 2.19 (3H, s, $COMe$), 3.30 (1H, t, *J* 7.4, $CHCH_2Me$), 4.16 (2H, q, *J* 7.2, OCH_2Me).

Ethyl 2-ethyl acrylate 37



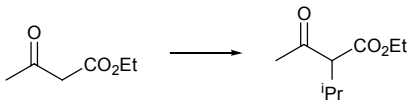
Ethyl 2-ethyl-3-oxo-butyrate **34** (5.0 g, 32 mmol, 1.0 eq) was treated with LiHMDS (35 mL, 1.0 M, 35 mmol, 1.1 eq) followed by paraformaldehyde (2.5 g, xs) according to **General Procedure 11**. Purification by column chromatography (silica, 49:1 pentane: ether, v/v) afforded **37** as a colourless oil (3.5 g, 85%); δ_H (400MHz, $CDCl_3$) 1.05 (3H, t, *J* 7.4, CH_2Me), 1.28 (3H, t, *J* 7.2, OCH_2Me), 2.27–2.34 (2H, m, CH_2Me), 4.16 (2H, q, *J* 7.1, OCH_2Me), 5.47–5.51 (1H, m, $C=CH_2$), 6.06–6.10 (1H, m, $C=CH_2$).

2-Ethyl acrylic acid 40



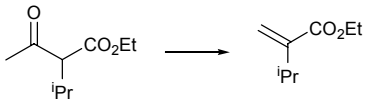
Ethyl 2-ethyl acrylate **37** (2.6 g, 20 mmol, 1.0 eq) was treated with LiOH (5.4 g, 101 mmol, 5.0 eq) according to **General Procedure 9**. Upon cooling, the mixture was acidified to pH 2 and the product extracted with ether (3 × 50 mL). The combined organic extracts were dried and the solvents removed *in vacuo* to yield **40** as a colourless oil which was used without further purification (1.98 g, 99%); δ_H (200MHz, $CDCl_3$) 1.05 (3H, t, *J* 7.4, CH_2Me), 2.28 (2H, app q, *J* 7.4, CH_2Me), 5.57 (1H, app d, *J* 1.4, $C=CH_2$), 6.20 (1H, app d, *J* 0.8, $C=CH_2$).

Ethyl 2-*iso*-propyl-3-oxo-butyrate 35



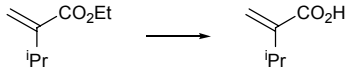
Potassium *tert*-butoxide (8.8 g, 77 mmol, 1.1 eq) was treated with ethyl acetoacetate (9.6 mL, 75 mmol, 1.0 eq) and *tert*-butanol (670 µL, 7.0 mmol, 0.1 eq) followed by 2-iodopropane (7.48 mL, 75 mmol, 0.99 eq) according to **General Procedure 10**. Purification by column chromatography (silica, 19:1 pentane: ether, v/v) afforded **35** as a colourless oil (8.0 g, 62%); δ_H (200MHz, $CDCl_3$) 0.90 (3H, d, *J* 6.7, $CHMe_2$), 0.95 (3H, d, *J* 6.7, $CHMe_2$), 1.24 (3H, t, *J* 7.1, CH_2Me), 2.20 (3H, s, $COMe$), 2.35–2.44 (1H, m, $CHMe_2$), 3.15 (1H, d, *J* 9.5, $CHCHMe_2$), 4.16 (2H, q, *J* 7.1, CH_2Me).

Ethyl 2-*iso*-propyl acrylate 38



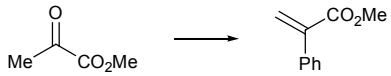
Ethyl 2-*iso*-propyl-3-oxo-butyrate **35** (3.0 g, 17 mmol, 1.0 eq) was treated with LiHMDS (19 mL, 1.0M, 19 mmol, 1.1 eq) followed by paraformaldehyde (2.5 g, xs) according to **General Procedure 11**. Purification by column chromatography (silica, 49:1 pentane: ether, v/v) afforded **38** as a colourless oil (1.98 g, 82%); δ_H (200MHz, $CDCl_3$) 1.05 (6H, d, *J* 6.8, CH*Me*$_2$), 1.24 (3H, t, *J* 7.0, CH_2*Me*), 2.76–2.82 (1H, m, C*H*Me$_2$), 4.18 (2H, q, *J* 7.1, C*H*$_2$Me), 5.47 (1H, app s, C=C*H*$_2$), 6.08 (1H, app s, C=C*H*$_2$).

2-*iso*-Propyl acrylic acid 41



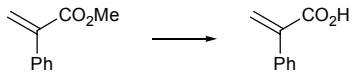
Ethyl 2-*iso*-propyl acrylate **38** (1.0 g, 7.0 mmol, 1.0 eq) was treated with lithium hydroxide (1.5 g, 35.2 mmol, 5.0 eq) according to **General Procedure 9**. Upon cooling, the mixture was acidified to pH 2 and the product extracted with ether (3 × 50 mL). The combined organic extracts were dried and the solvents removed *in vacuo* to yield **41** as a colourless oil which was used without further purification (0.8 g, 99%); δ_H (200MHz, $CDCl_3$) 1.09 (6H, d, *J* 6.8, CH*Me*$_2$), 2.75–2.83 (1H, sep, *J* 6.8, C*H*Me$_2$), 5.63 (1H, d, *J* 0.9, C=C*H*$_2$), 6.28 (1H, d, *J* 0.9, C=C*H*$_2$).

Methyl 2-phenyl acrylate 43



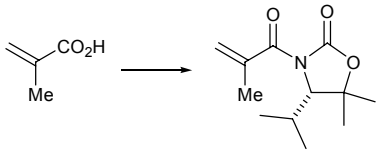
To a stirred solution of methyl pyruvate (4.42 mL, 49 mmol, 1.0 eq) in THF (200 mL) was added phenyl magnesium bromide (49.5 mL, 1.0 M in THF, 49 mmol, 1.01 eq) dropwise with cooling to 0 °C. After addition was complete, the mixture was heated to 60 °C for 30 min, cooled, and quenched by the addition of water (10 mL). The resulting precipitate was dissolved with aq. HCl (1 M, 2 × 50 mL). The mixture was extracted with ethyl acetate (3 × 100 mL) and the combined organic layers washed with brine (2 × 50 mL), dried and the solvents removed *in vacuo*. The crude α-hydroxy ester **42** was dissolved in toluene (500 mL) and pTSA (1.0 g, 5.0 mmol, 0.1 eq) was added. The resulting mixture was refluxed under Dean and Stark conditions for 4 h. Upon cooling the reaction mixture was washed with sat. aq. $NaHCO_3$ (50 mL), brine (50 mL), dried and the solvent removed *in vacuo*. Purification by bulb-to-bulb distillation (bp 160–165°C/2mmHg) afforded **43** as a pale yellow oil (5.6 g, 70%); δ_H (400MHz, $CDCl_3$) 3.84 (3H, s, O*Me*), 5.92 (1H, d, *J* 1.2, C=C*H*$_2$), 6.39 (1H, d, *J* 1.2, C=C*H*$_2$), 7.32–7.44 (5H, m, *Ph*).

2-Phenylacrylic acid 44



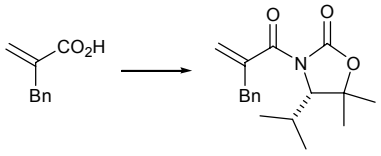
Methyl 2-phenylacrylate **43** (4.5 g, 28 mmol, 1.0 eq) was treated with LiOH (3.5 g, 83 mmol, 3.0 eq) according to **General Procedure 9**. Upon acidification to pH 2 with sat. aq. $KHSO_4$, the product was extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were dried and the solvents removed *in vacuo* to afford **44** as a white crystalline solid (4.0 g, 97%); mp 100–102°C (lit.[9] mp 107–108°C); δ_H (200MHz, $CDCl_3$) 6.04 (1H, d, *J* 1.1, C=C*H*$_2$), 6.57 (1H, d, *J* 1.1, C=C*H*$_2$), 7.31–7.51 (5H, m, *Ph*).

(*S*)-5,5-Dimethyl-4-*iso*-propyl-3-(2'-methylacryloyl)oxazolidin-2-one 45



To a stirred solution of oxazolidinone **2** (3.0 g, 19.1 mmol, 1.0 eq) in THF (60 mL) at –78 °C was added *n*-BuLi (7.7 mL, 2.5 M, 19.3 mmol, 1.01 eq) dropwise. The solution was stirred at –78 °C for 15 min before methacryloyl chloride (2.1 mL, 21.0 mmol, 1.1 eq) was added. The resulting solution was stirred at –78 °C for 30 min then at 0 °C for a further 15 min before quenching with sat. aq. NH_4Cl (5 mL). Upon warming to rt, the product was extracted with ether (3 × 30 mL). The combined organic extracts were washed with brine (30 mL), dried and the solvents removed *in vacuo*. Purification by column chromatography (silica, 7:3 pentane:ether, v/v) afforded **45** as a white crystalline solid (3.4 g, 79%); mp 56–57°C; $[\alpha]_D^{25}$ +44.5 (c 2.2, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1782, 1685, 1639; δ_H (400MHz, $CDCl_3$) 0.97 (3H, d, *J* 11.8, CH*Me*$_2$), 1.02 (3H, d, *J* 13.5, CH*Me*$_2$), 1.40 (3H, s, C*Me*$_2$), 1.51 (3H, s, C*Me*$_2$), 2.05 (3H, dd, J_{XA} 1.5, J_{XB} 1.2, H_2C=C*Me*), 2.10–2.21 (1H, m, C*H*Me$_2$), 4.18 (1H, d, *J* 3.4, NC*H*^{i}Pr), 5.39–5.41 (2H, m, *H*$_2$C=C); δ_C (100MHz, $CDCl_3$) 17.0, 19.4, 21.4, 21.4, 29.0, 29.5, 66.1, 82.9, 120.0, 140.0, 152.7, 171.7; *m/z* (ESI^+) 248 (MNa^+, 100%); HRMS (ESI^+) 226.1448 ($C_{12}H_{20}NO_3$ requires 226.1443).

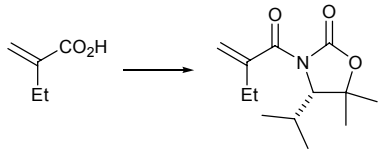
(*S*)-5,5-Dimethyl-4-*iso*-propyl-3-(2'-benzylacryloyl)oxazolidin-2-one 46



[9] C. A. Kerr, *J. Chem. Soc.* 1927, 1943–1948.

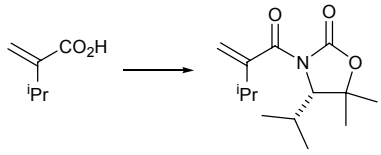
2-Benzylacrylic acid **39** (1.00 g, 6.2 mmol, 1.25 eq) was reacted with oxalyl chloride (810 μL, 9.3 mmol, 1.86 eq) and Et_3N (1.29 mL, 9.3 mmol, 1.86 eq), followed by oxazolidinone **2** (780 mg, 4.9 mmol, 1.0 eq) and *n*-BuLi (2.17 mL, 2.5 M, 5.4 mmol, 1.1 eq) according to **General Procedure 12**. Purification by column chromatography (silica, 4:1 pentane:ether, v/v) afforded **46** as a white crystalline solid (1.27 g, 85%); mp 54–55°C; $[\alpha]_D^{25}$ +16.0 (c 1.5, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1780, 1684, 1636; δ_H (400MHz, $CDCl_3$) 0.91 (3H, d, *J* 7.1, CH*Me*$_2$), 0.92 (3H, d, *J* 6.6, CH*Me*$_2$), 1.26 (3H, s, C*Me*$_2$), 1.49 (3H, s, C*Me*$_2$), 2.10 (1H, m, C*H*Me$_2$), 3.79 (2H, s, C*H*$_2$Ph), 4.15 (1H, d, *J* 3.3, NC*H*^{i}Pr), 5.34 (1H, app s, C=C*H*$_2$), 5.51 (1H, app s, C=C*H*$_2$), 7.19–7.32 (5H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 16.8, 21.3, 21.4, 28.8, 29.5, 39.6, 66.0, 82.7, 120.4, 126.6, 137.3, 143.4, 152.6, 170.8; *m/z* (CI^+) 302 (MH^+, 100%); HRMS (CI^+) 302.1738 ($C_{18}H_{24}NO_3$ requires 302.1756).

(*S*)-5,5-Dimethyl-4-*iso*-propyl-3-(2'-ethylacryloyl)oxazolidin-2-one 47



2-Ethylacrylic acid **40** (2.02 g, 20.2 mmol, 1.25 eq) was reacted with oxalyl chloride (2.64 mL, 30.3 mmol, 1.86 eq), and Et_3N (4.22 mL, 30.3 mmol, 1.86 eq), followed by oxazolidinone **2** (2.54 g, 16.2 mmol, 1.0 eq) and *n*-BuLi (7.13 mL, 2.5 M, 17.8 mmol, 1.1 eq) according to **General Procedure 12**. Purification by column chromatography (silica, 7:3 pentane:ether, v/v) afforded **47** as a colourless, viscous oil (3.30 g, 68%); $[\alpha]_D^{25}$ +33.3 (c 2.7, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1780, 1684, 1636; δ_H (400MHz, $CDCl_3$) 1.01 (3H, d, *J* 6.8, CH*Me*$_2$), 1.05 (3H, d, *J* 7.0, CH*Me*$_2$), 1.13 (3H, t, *J* 7.5, CH$_2$*Me*), 1.42 (3H, s, C*Me*$_2$), 1.53 (3H, s, C*Me*$_2$), 2.12–2.22 (1H, m, C*H*Me$_2$), 2.34–2.51 (2H, m, C*H*$_2$Me), 4.22 (1H, d, *J* 3.3, NC*H*^{i}Pr), 5.35–5.39 (2H, m, C=C*H*$_2$); δ_C (100MHz, $CDCl_3$) 11.9, 17.0, 21.5, 21.5, 26.2, 29.0, 29.6, 66.1, 82.8, 116.8, 146.0, 153.2, 171.2; *m/z* (CI^+) 240 (MH^+, 100%); HRMS (CI^+) 240.1601 (MH^+ $C_{13}H_{22}NO_3$ requires 240.1600).

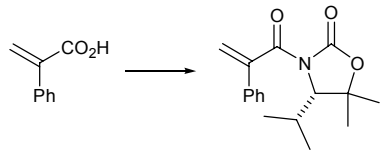
(*S*)-5,5-Dimethyl-4-*iso*-propyl-3-(2'-*iso*-propylacryloyl)oxazolidin-2-one 48



2-*iso*-Propylacrylic acid **41** (200 mg, 1.8 mmol, 1.25 eq) was reacted with oxalyl chloride (230 μL, 2.6 mmol, 1.86 eq), and Et_3N (370 μL, 2.6 mmol, 1.86 eq), followed by oxazolidinone **2** (220 mg, 1.4 mmol, 1.0 eq) and *n*-BuLi (620 μL, 2.5 M, 1.5 mmol, 1.1 eq) according to **General Procedure 12**. Purification by column chromatography (silica, 4:1 pentane:ether, v/v) afforded **48** as a colourless, viscous oil (210 mg,

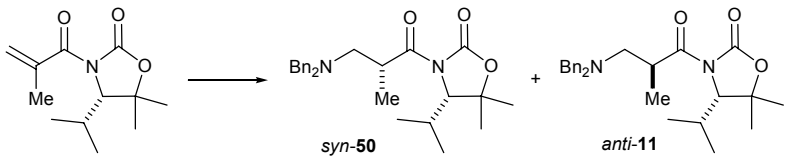
58%); $[\alpha]_D^{25}$ +29.0 (c 1.2, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1782, 1685, 1636; δ_H (400MHz, $CDCl_3$) 1.01 (3H, d, *J* 6.8, CH*Me*$_2$), 1.06 (3H, d, *J* 7.0, CH*Me*$_2$), 1.11 (3H, d, *J* 6.9, COCCH*Me*$_2$), 1.18 (3H, d, *J* 6.8, COCCH*Me*$_2$), 1.41 (3H, s, C*Me*$_2$), 1.53 (3H, s, C*Me*$_2$), 2.15–2.22 (1H, m, C*H*Me$_2$), 2.71–2.82 (1H, m, COCC*H*Me$_2$), 4.23 (1H, d, *J* 3.2, NC*H*^{i}Pr), 5.28 (1H, d, *J* 1.2, C=C*H*$_2$), 5.35 (1H, d, *J* 1.2, C=C*H*$_2$); δ_C (100MHz, $CDCl_3$) 17.0, 20.4, 21.4, 21.4, 21.5, 29.0, 29.6, 31.2, 66.0, 82.6, 114.8, 138.9, 150.3, 171.8; *m/z* (CI^+) 254 (MH^+, 17%), 158 (100); HRMS (CI^+) 254.1750 ($C_{14}H_{24}NO_3$ requires 254.1756).

(*S*)-5,5-Dimethyl-4-*iso*-propyl-3-(2'-phenylacryloyl)oxazolidin-2-one 49



2-Phenylacrylic acid **44** (2.00 g, 20.2 mmol, 1.25 eq) was reacted with oxalyl chloride (1.76 mL, 30.3 mmol, 1.86 eq), and Et_3N (4.22 mL, 30.3 mmol, 1.86 eq), followed by oxazolidinone **2** (1.69 g, 16.2 mmol, 1.0 eq) and *n*-BuLi (4.75 mL, 2.5 M, 17.8 mmol, 1.1 eq) according to **General Procedure 12**. Purification by column chromatography (silica, 7:3 pentane:ether, v/v) afforded **49** as a white crystalline solid (4.24 g, 91%); mp 73–74°C; $[\alpha]_D^{25}$ +70.8 (c 0.6, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1785, 1687, 1641; δ_H (400MHz, $CDCl_3$) 0.88 (3H, d, *J* 10.0, CH*Me*$_2$), 1.02 (3H, d, *J* 9.9, CH*Me*$_2$), 1.39 (3H, s, C*Me*$_2$), 1.51 (3H, s, C*Me*$_2$), 2.18–2.28 (1H, m, C*H*Me$_2$), 4.26 (1H, d, *J* 3.2, NC*H*^{i}Pr), 5.48 (1H, app s, C=C*H*$_2$), 5.79 (1H, app s, C=C*H*$_2$), 7.31–7.44 (5H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 17.0, 21.5, 21.6, 29.0, 29.7, 66.5, 83.0, 116.5, 126.2, 128.5, 128.6, 135.7, 144.7, 152.1, 169.9; *m/z* (ESI^+) 310 (MNa^+, 100%), 289 (MH^+, 5); HRMS (ESI^+) 288.1596 ($C_{17}H_{22}NO_3$ requires 288.1600).

(2'*R*,4*S*)-5,5-Dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-methyl-propanoyl]oxazolidin-2-one 50 and (2'*S*,4*S*)-5,5-dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-methyl-propanoyl] oxazolidin-2-one 11



Method A

N-Acryloyl-oxazolidinone **45** (200 mg, 0.89 mmol, 1.0 eq) was reacted with dibenzylamine (0.342 mL, 1.78 mmol, 2.0 eq) and *n*-BuLi (0.712 mL, 1.78 mmol, 2.0 eq) according to **General Procedure 1** to give a non-separable mixture of diastereoisomers **50** and **11** in a ratio of 66:34. Column chromatography (silica, 9:1

pentane:ether, v/v) afforded the 66:34 mixture of diastereoisomers **50** and **11** as a colourless, viscous oil (360 mg, 96%).

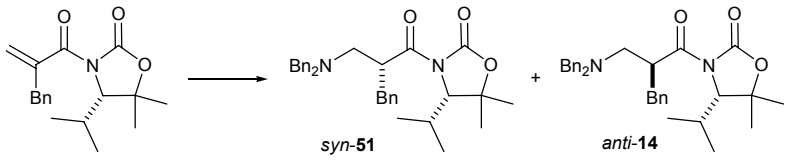
Method B

N-Acryloyl-oxazolidinone **45** (200 mg, 0.89 mmol, 1.0 eq) was reacted with dibenzylamine (0.34 mL, 1.78 mmol, 2.0 eq) and *n*-BuLi (0.71 mL, 1.78 mmol, 2.0 eq), followed by 2,6-di-*tert*-butylphenol (551 mg, 2.67 mmol, 3.0 eq) according to **General Procedure 13** to give a mixture of diastereoisomers **50** and **11** in a ratio of 92:8. Column chromatography (silica, 49:1 to 9:1 pentane:ether, v/v) followed by recrystallisation from pentane/ether afforded **50** as a white crystalline solid (342 mg, 91%); mp 74–75°C; $[\alpha]_D^{25}$ +53.7 (c 1.3, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1769, 1697; δ_H (400MHz, $CDCl_3$) 1.00 (3H, d, *J* 6.9, CH*Me*$_2$), 1.07 (3H, d, *J* 7.0, CH*Me*$_2$), 1.17 (3H, d, *J* 6.8, COCH*Me*), 1.36 (3H, s, C*Me*$_2$), 1.54 (3H, s, C*Me*$_2$), 2.12–2.21 (1H, m, C*H*Me$_2$), 2.48 (1H, dd, J_{AB} 12.4, J_{AX} 7.8, C*H*$_2$NBn$_2$), 2.95 (1H, dd, J_{BA} 12.4, J_{BX} 6.7, C*H*$_2$NBn$_2$), 3.54 (2H, d, *J* 13.8, NC*H*$_2$Ph), 3.77 (2H, d, *J* 13.8, NC*H*$_2$Ph), 4.19 (1H, d, *J* 3.4, NC*H*^{i}Pr), 4.22–4.30 (1H, m, COC*H*), 7.16–7.41 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 15.6, 17.1, 21.3, 21.5, 28.8, 29.5, 36.1, 57.1, 58.3, 66.3, 82.6, 126.9, 128.1, 129.0, 139.2, 153.4, 176.5; *m/z* (ESI^+) 423 (MH^+, 100%); HRMS (ESI^+) 423.2658 ($C_{26}H_{35}N_2O_3$ requires 423.2658).

Method C

N-Acryloyl-oxazolidinone **45** (150 mg, 0.67 mmol, 1.0 eq) was reacted with dibenzylamine (0.26 mL, 1.34 mmol, 2.0 eq) and *n*-BuLi (0.84 mL, 1.34 mmol, 2.0 eq) according to **General Procedure 14**, to give a mixture of diastereoisomers **50** and **11** in a ratio of 98:2. Purification by column chomatography (silica, 9:1 pentane:ether, v/v) furnished **50** (245 mg, 87%) with identical physical and spectroscopic properties as those described previously.

(2'*R*,4*S*)-5,5-dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-benzyl-propanoyl] oxazolidin-2-one 51 and (2'*S*,4*S*)-5,5-Dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-benzyl-propanoyl]oxazolidin-2-one 14



syn-**51** + *anti*-**14**

Method A

N-Acryloyl-oxazolidinone **46** (200 mg, 0.67 mmol, 1.0 eq) was reacted with dibenzylamine (0.26 mL, 1.34 mmol, 2.0 eq) and *n*-BuLi (0.84 mL, 1.6 M, 1.34 mmol, 2.0 eq) according to **General Procedure 1** to give a non-separable mixture of diastereoisomers **51** and **14** in a ratio of 20:80. Column chromatography (silica, 9:1 pentane:ether, v/v) afforded the mixture of diastereoisomers **51** and **14** as a colourless, viscous oil (274 mg, 82%).

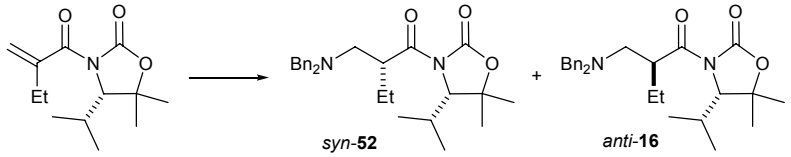
Method B

N-Acryloyl-oxazolidinone **46** (133 mg, 0.44 mmol, 1.0 eq) was reacted with dibenzylamine (0.17 mL, 0.88 mmol, 2.0 eq) and *n*-BuLi (0.35 mL, 0.88 mmol, 2.0 eq), followed by 2,6-di-*tert*-butylphenol (274 mg, 1.33 mmol, 3.0 eq) according to **General Procedure 13** to give a non-seperable mixture of diastereoisomers **51** and **14** in a ratio of 79:21. Column chromatography (silica, 49:1 to 9:1 pentane:ether, v/v) afforded the mixture of diastereoisomers **51** and **14** as a colourless, viscous oil (173 mg, 79%).

Method C

N-Acryloyl-oxazolidinone **46** (100 mg, 0.34 mmol, 1.0 eq) was reacted with dibenzylamine (0.13 mL, 0.68 mmol, 2.0 eq) and *n*-BuLi (0.27 mL, 0.68 mmol, 2.0 eq), followed by 2-pyridone (97 mg, 1.02 mmol, 3.0 eq) according to **General Procedure 14** to give a non-seperable mixture of diastereoisomers **51** and **14** in a ratio of 90:10. Column chromatography (silica, 49:1 to 9:1 pentane:ether, v/v) afforded the mixture of diastereoisomers **51** and **14** as a colourless, viscous oil (144 mg, 85%). Data for (2'*R*,4*S*)-*syn* diastereoisomer **51**: $[\alpha]_D^{21}$ +26.1 (c 1.0, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1770, 1696; δ_H (400MHz, $CDCl_3$) 0.72 (3H, s, C*Me*$_2$), 0.99 (3H, d, *J* 6.8, CH*Me*$_2$), 1.05 (3H, d, *J* 6.7, CH*Me*$_2$), 1.41 (3H, s, C*Me*$_2$), 2.07–2.15 (1H, m, C*H*Me$_2$), 2.65 (1H, dd, $J_{A'B'}$ 12.4, $J_{A'X'}$ 7.2, C*H*$_2$Ph), 2.69 (1H, dd, J_{AB} 13.2, J_{AX} 10.4, C*H*$_2$NBn$_2$), 2.97 (1H, dd, $J_{B'A'}$ 12.4, $J_{B'X'}$ 6.8, C*H*$_2$Ph), 3.08 (1H, dd, J_{BA} 13.2, J_{BX} 4.6, C*H*$_2$NBn$_2$), 3.66 (2H, d, *J* 14.2, N(C*H*$_2$Ph)$_2$), 3.79 (2H, d, *J* 14.2, N(C*H*$_2$Ph)$_2$), 3.93 (1H, d, *J* 3.2, NC*H*^{i}Pr), 4.79–4.84 (1H, m, COC*H*), 7.29 (15H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 17.1, 21.3, 21.3, 27.6, 29.4, 37.1, 43.0, 56.5, 58.3, 66.5, 82.4, 126.2, 126.8, 128.1, 128.2, 128.4, 129.1, 139.0, 139.3, 153.3, 175.1; *m/z* (ESI^+) 499 (MH^+, 66%), 210 (100); HRMS (ESI^+) 499.2951 ($C_{32}H_{39}N_2O_3$ requires 499.2955).

(2'*R*,4*S*)-5,5-Dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino-2'-ethyl-propanoyl]oxazolidin-2-one 52 and (2'*S*,4*S*)-5,5-dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-ethyl-propanoyl]oxazolidin-2-one 16



Method A

N-Acryloyl-oxazolidinone **47** (100 mg, 0.42 mmol, 1.0 eq) was reacted with dibenzylamine (0.16 mL, 0.83 mmol, 2.0 eq) and *n*-BuLi (0.52 mL, 1.6 M, 0.83 mmol, 2.0 eq) according to **General Procedure 1** to give an inseparable mixture of returned starting material **47** and diastereoisomers **52** and **16** in a ratio of 17:72:11 respectively. Column chromatography (silica, 9:1, pentane:ether, v/v) afforded the mixture of diastereoisomers **52** and **16** as a colourless, viscous oil (126 mg, 69%).

Method B

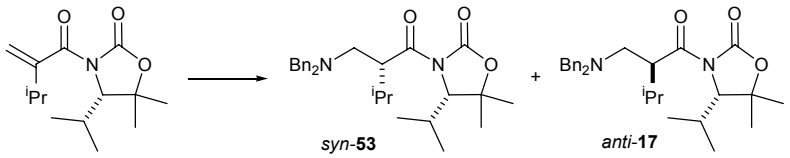
N-Acryloyl-oxazolidinone **47** (105 mg, 0.44 mmol, 1.0 eq) was reacted with dibenzylamine (0.169 mL, 0.88 mmol, 2.0 eq) and *n*-BuLi (0.352 mL, 0.88 mmol, 2.0 eq), followed by 2,6-di-*tert*-butylphenol (274 mg, 1.33 mmol, 3.0 eq) according to **General Procedure 13** to give a non-seperable mixture of diastereoisomers **52** and **16** in a ratio of 92:8. Column chromatography (silica, 49:1 to 9:1 pentane:ether, v/v) afforded the mixture of diastereoisomers **52** and **16** as a colourless, viscous oil (115 mg, 60%).

Method C

N-Acryloyl-oxazolidinone **47** (41 mg, 0.17 mmol, 1.0 eq) was reacted with dibenzylamine (35 μL, 0.28 mmol, 1.6 eq) and *n*-BuLi (0.11 mL, 0.28 mmol, 1.6 eq) according to **General Procedure 14**, giving a mixture of diastereoisomers **52** and **16** in a ratio of 97:3. Purification by column chomatography (silica, 9:1 pentane:ether, v/v) furnished **52** as a colourless oil (56 mg, 79%); $[\alpha]_D^{25}$ +12.5 (c 1.0, $CHCl_3$); ν_{max}/cm^{-1} (film) 1773, 1698; δ_H (400MHz, $CDCl_3$) 0.84 (3H, t, *J* 7.6, CH_2Me), 1.02 (3H, d, *J* 6.8, $CHMe_2$), 1.08 (3H, d, *J* 7.1, $CHMe_2$), 1.38 (3H, s, CMe_2), 1.53 (3H, s, CMe_2), 1.52–1.70 (2H, m, CH_2Me) 2.13–2.21 (1H, m, $CHMe_2$), 2.53 (1H, dd, J_{AB} 12.4, J_{AX} 6.6, $COCHCH_2N$), 2.91 (1H, dd, J_{BA} 12.4, J_{BX} 7.3, $COCHCH_2N$), 3.61 (2H, d, *J* 13.6, NCH_2Ph), 3.69 (2H, d, *J* 14.0, NCH_2Ph), 4.19 (1H, d, *J* 3.4, NCH^iPr), 4.28–4.34 (1H, m, $COCHCH_2$), 7.18–7.38 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 11.7, 17.1, 21.4, 24.0, 28.8, 29.6, 42.5, 56.1, 58.2, 66.5, 82.4, 126.8 127.9, 128.1, 129.2, 138.9, 139.0, 153.5, 176.1; *m/z* (ESI^+) 437 (MH^+, 100%); HRMS (ESI^+) 437.2800 ($C_{27}H_{37}N_2O_3$ requires 437.2804).

(2'*R*,4*S*)-5,5-Dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-*iso*-propyl-propanoyl]oxazolidin-2-one 53 and (2'*S*,4*S*)-5,5-dimethyl-4-*iso*-propyl-3-[3' (*N*,*N*-dibenzylamino)-2'-*iso*-propyl-propanoyl]

oxazolidin-2-one 17



Method A

N-Acryloyl-oxazolidinone **48** (113 mg, 0.45 mmol, 1.0 eq) was reacted with dibenzylamine (0.17 mL, 0.89 mmol, 2.0 eq) and *n*-BuLi (0.36 mL, 0.89 mmol, 2.0 eq) according to **General Procedure 1** to give an inseparable mixture of returned starting material **48** and diastereoisomers **53** and **17** in a ratio of 20:74:6 respectively. Column chromatography (silica, 9:1, pentane:ether, v/v) afforded the mixture of diastereoisomers **53** and **17**. Recrystallisation from pentane/ether gave **53** as a white crystalline solid (130 mg, 65%); mp 70–71°C; $[\alpha]_D^{25}$ –11.9 (c 0.1, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1768, 1702; δ_H (400MHz, $CDCl_3$) 0.89 (3H, d, *J* 6.8, COCHCH*Me*$_2$), 0.91 (3H, d, *J* 6.7, COCHCH*Me*$_2$), 1.05 (3H, d, *J* 6.9, CH*Me*$_2$), 1.13 (3H, d, *J* 7.1, CH*Me*$_2$), 1.39 (3H, s, C*Me*$_2$), 1.54 (3H, s, C*Me*$_2$), 1.77–1.83 (1H, m, COCHC*H*Me$_2$), 2.17–2.26 (1H, m, C*H*Me$_2$), 2.56 (1H, dd, J_{AB} 12.6, J_{AX} 3.8, C*H*$_2$NBn$_2$), 3.05 (1H, dd, J_{BA} 12.6, J_{BX} 10.0, C*H*$_2$NBn$_2$), 3.50 (2H, d, *J* 13.7, NC*H*$_2$Ph), 3.76 (2H, d, *J* 13.7, NC*H*$_2$Ph), 4.22(1H, d, *J* 2.9, NC*H*^{i}Pr), 4.36–4.44 (1H, m, COC*H*), 7.20–7.35 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 17.3, 19.9, 20.4, 21.0, 21.6, 29.0, 29.7, 30.5, 46.0, 54.2, 58.0, 66.7, 82.0, 126.8, 128.0, 129.3, 138.7, 153.7, 175.8; *m/z* (ESI^+) 451 (MH^+, 100%); HRMS (ESI^+) 451.2966 ($C_{28}H_{39}N_2O_3$ requires 451.2961).

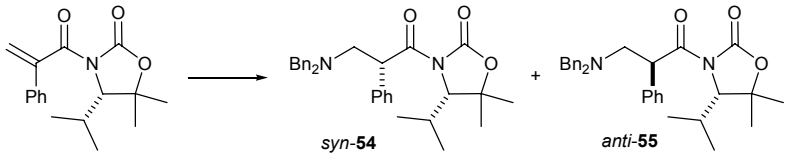
Method B

N-Acryloyl-oxazolidinone **48** (111 mg, 0.44 mmol, 1.0 eq) was reacted with dibenzylamine (0.17 mL, 0.88 mmol, 2.0 eq) and *n*-BuLi (0.35 mL, 0.88 mmol, 2.0 eq), followed by 2,6-di-*tert*-butylphenol (274 mg, 1.33 mmol, 3.0 eq) according to **General Procedure 13** to give a mixture of diastereoisomers **53** and **17** in a ratio of 82:18. Column chromatography (silica, 49:1 to 9:1 pentane:ether, v/v) afforded the mixture of diastereoisomers **53** and **17** as a colourless, viscous oil (119mg, 60%).

Method C

N-Acryloyl-oxazolidinone **48** (50 mg, 0.20 mmol, 1.0 eq) was reacted with dibenzylamine (61 µL, 0.31 mmol, 1.6 eq) and *n*-BuLi (0.12 mL, 0.31 mmol, 1.6 eq) according to **General Procedure 14**, giving a mixture of diastereoisomers **53** and **17** in a ratio of 95:5. Purification by column chomatography (silica, 9:1 pentane:ether, v/v) furnished **53** (70mg, 78%) with identical physical and spectroscopic properties to those described above.

(2'*R*,4*S*)-5,5-Dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-phenyl-propanoyl]oxazolidin-2-one 54 and (2'*S*,4*S*)-5,5-dimethyl-4-*iso*-propyl-3-[3'-(*N*,*N*-dibenzylamino)-2'-phenyl-propanoyl] oxazolidin-2-one 55



Method A

N-Acryloyl-oxazolidinone **49** (200 mg, 0.89 mmol, 1.0 eq) was reacted with dibenzylamine (0.34 mL, 1.78 mmol, 2.0 eq) and *n*-BuLi (0.71 mL, 1.78 mmol, 2.0 eq) according to **General Procedure 1** to give a non-separable mixture of diastereoisomers **54** and **55** in a ratio of 62:38. Column chromatography (silica, 49:1 to 9:1 pentane:ether, v/v) afforded the mixture of diastereoisomers **54** and **55** as a colourless viscous oil (293 mg, 68%).

Method B

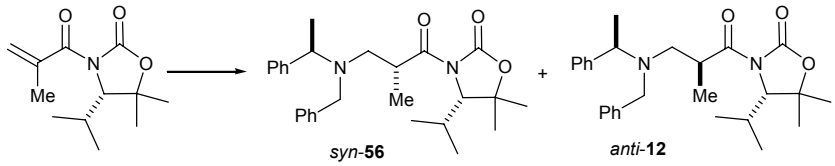
N-Acryloyl-oxazolidinone **49** (200 mg, 0.89 mmol, 1.0 eq) was reacted with dibenzylamine (0.34 mL, 1.78 mmol, 2.0 eq) and *n*-BuLi (0.71 mL, 1.78 mmol, 2.0 eq) followed by 2,6-di-*tert*-butylphenol (548 mg, 2.67 mmol, 3.0 eq) according to **General Procedure 13** to give a non-separable mixture of diastereoisomers **54** and **55** in a ratio of 40:60. Column chromatography (silica, 49:1 to 9:1 pentane:ether, v/v) afforded the mixture of diastereoisomers **54** and **55** as a colourless viscous oil (267 mg, 62%) each with identical spectroscopic properties as described previously.

Method C

N-Acryloyl-oxazolidinone **49** (50 mg, 0.18 mmol, 1.0 eq) was reacted with dibenzylamine (55 µL, 0.28 mmol, 1.6 eq) and *n*-BuLi (0.11 mL, 0.28 mmol, 1.6 eq) according to **General Procedure 14**. Column chomatography (silica, 9:1 pentane:ether, v/v) furnished an inseparable mixture of diastereoisomers **54** and **55** (65 mg, 75%) in a ratio of 12:88 as a colourless viscous oil; Data for mixture; $[\alpha]_D^{25}$ +4.5 (c 1.1, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1771, 1699; δ_H (400MHz, $CDCl_3$) major diastereoisomer **55**; 0.92 (3H, s, CMe_2), 1.04 (3H, d, *J* 6.3, CHMe_2), 1.12 (3H, d, *J* 6.6, CHMe_2), 1.44 (3H, s, CMe_2), 2.11–2.22 (1H, m, C*H*Me$_2$), 2.82 (1H, dd, J_{AB} 12.8, J_{AX} 6.1 COCHCH_2), 3.36 (1H, dd, J_{BA} 12.8, J_{BX} 7.6, COCHCH_2), 3.68 (4H, app s, NCH_2Ph), 4.03 (1H, d, *J* 2.8, NC*H*^{i}Pr), 5.50–5.56 (1H, m, COC*H*CH$_2$), 7.14–7.40 (15H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 17.1, 21.3, 21.5, 28.2, 29.5, 46.9, 57.1, 58.2, 67.1, 82.7, 126.8, 126.8, 127.3, 127.8, 128.4,

128.7, 128.1, 128.9, 128.9, 137.3, 139.0, 139.0, 153.5, 173.3; *m/z* (ESI^+) 485 (MH^+, 100%); HRMS (ESI^+) 485.2809 ($C_{31}H_{37}N_2O_3$ requires 485.2804).

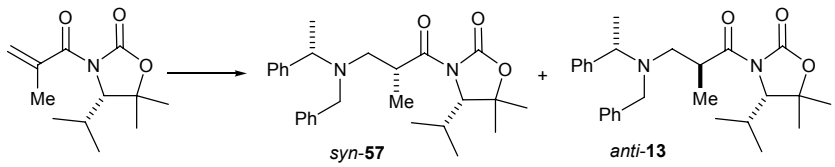
(4*S*,2'*R*,α*R*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-methyl-propanoyl}oxazolidin-2-one 56 and (4*S*,2'*S*,α*R*)-5,5-dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-methyl-propanoyl}oxazolidin-2-one 12



syn-**56** *anti*-**12**

N-Acryloyl-oxazolidinone **45** (150 mg, 0.67 mmol, 1.0 eq) was reacted with (*R*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (283 mg, 1.34 mmol, 2.0 eq) and *n*-BuLi (0.84 mL, 1.34 mmol, 1.6 eq) according to **General Procedure 14**, giving a mixture of diastereoisomers **56** and **12** in a ratio of 98:2. Purification by column chomatography (silica, 9:1 pentane/ether, v/v) furnished **56** (240 mg, 82%) as a colourless oil; $[\alpha]_D^{25}$ +51.4 (c 1.5, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1769, 1698; δ_H (400MHz, $CDCl_3$) 0.95 (3H, d, *J* 6.8, CH*Me*$_2$), 1.02 (3H, d, *J* 6.8, CH*Me*$_2$), 1.17 (3H, d, *J* 6.8, COCH*Me*), 1.35 (3H, s, C*Me*$_2$), 1.43 (3H, d, *J* 6.8, NCH*Me*), 1.50 (3H, s, C*Me*$_2$), 2.08–2.17 (1H, m, C*H*Me$_2$), 2.60 (1H, dd, J_{AB} 12.6, J_{AX} 8.3 COCHC*H*$_2$), 2.77 (1H, dd, J_{BA} 12.6, J_{BX} 6.1, COCHC*H*$_2$), 3.43 (1H, d, *J* 14.4, NC*H*$_2$Ph), 3.82 (1H, d, *J* 14.4, NC*H*$_2$Ph), 3.98 (1H, q, *J* 7.1, NC*H*Ph), 4.06–4.16 (1H, m, COC*H*Me), 4.14 (1H, d, *J* 3.3, NC*H*^{i}Pr), 7.19–7.40 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 15.5, 16.7, 17.0, 21.3, 21.3, 28.8, 29.5, 36.6, 53.1, 54.6, 57.8, 66.3, 82.5, 126.6 127.8, 128.1, 128.2, 128.7, 128.9, 140.3, 141.6, 153.5, 176.7; *m/z* (ESI^+) 437 (MH^+, 100%); HRMS (ESI^+) 437.2814 ($C_{27}H_{36}N_2O_3$ requires 437.2804).

(4*S*,2'*R*,α*S*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-methyl-propanoyl}oxazolidin-2-one 57 and (4*S*,2'*S*,α*S*)-5,5-dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-methyl-propanoyl}oxazolidin-2-one 13

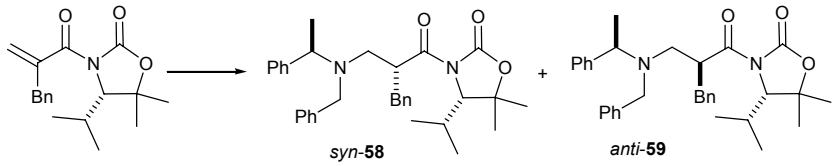


syn-**57** *anti*-**13**

N-Acryloyl-oxazolidinone **45** (150 mg, 0.67 mmol, 1.0 eq) was reacted with (*S*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (283 mg, 1.34 mmol, 2.0 eq) and *n*-BuLi (0.84 mL, 1.34 mmol, 2.0 eq) according to **General Procedure 14**, giving a mixture of diastereoisomers **57** and **13** in a ratio of 84:16. Column chomatography (silica, 9:1 pentane:ether, v/v) furnished an inseparable mixture of **57** and **13** (349 mg, 90%)

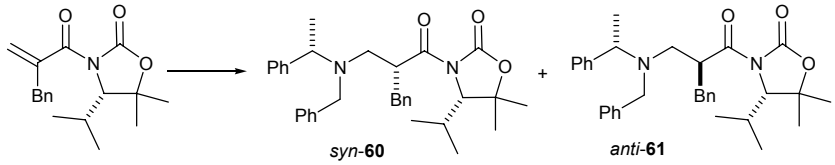
as a yellow oil. $[\alpha]_D^{25}$ +12.9 (c 0.7, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1770, 1694; Data for the major diastereoisomer **57**; δ_H (400MHz, $CDCl_3$) 1.02 (3H, d, *J* 6.1, CH*Me*$_2$), 1.04 (3H, d, *J* 7.2, CH*Me*$_2$), 1.07 (3H, d, *J* 5.8, COCH*Me*), 1.36 (3H, s, C*Me*$_2$), 1.41 (3H, d, *J* 6.8, NCH*Me*), 1.52 (3H, s, C*Me*$_2$), 2.12–2.22 (1H, m, C*H*Me$_2$), 2.24 (1H, dd, J_{AB} 12.6, J_{AX} 7.5 COCHC*H*$_2$), 3.11 (1H, dd, J_{BA} 12.6, J_{BX} 6.5, COCHC*H*$_2$), 3.63 (2H, d, *J* 2.4, NC*H*$_2$Ph), 4.02 (1H, q, *J* 7.1, NC*H*Ph), 4.06–4.15 (1H, m, COC*H*Me), 4.17 (1H, d, *J* 2.8, NC*H*^{i}Pr), 7.18–7.40 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 13.3, 15.4, 17.1, 21.4, 21.5, 28.7, 29.5, 36.6, 52.6, 54.5, 56.6, 66.3, 82.5, 126.7 127.8, 128.1, 128.3, 128.6, 128.9, 140.3, 142.4, 153.4, 176.8; *m/z* (ESI^+) 437 (MH^+, 100%); HRMS (ESI^+) 437.2802 ($C_{27}H_{36}N_2O_3$ requires 437.2804).

(4*S*,2'*R*,α*R*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-benzyl-propanoyl}oxazolidin-2-one 58 and (4*S*,2'*S*,α*R*)-5,5-dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-benzyl-propanoyl}oxazolidin-2-one 59



N-Acryloyl-oxazolidinone **46** (100 mg, 0.34 mmol, 1.0 eq) was reacted with (*R*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (144 mg, 0.68 mmol, 2.0 eq) and *n*-BuLi (0.27 mL, 0.68 mmol, 2.0 eq) according to **General Procedure 14**, giving a mixture of diastereoisomers **58** and **59** in a ratio of 86:14. Column chromatography (silica, 9:1 pentane:ether, v/v) afforded an inseparable mixture of **58** and **59** (150 mg, 86%), as a colourless, viscous oil. Data for major diastereoisomer **58**: $[\alpha]_D^{21}$ +72.2 (c 1.0, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1769, 1695; δ_H (400MHz, $CDCl_3$) 0.75 (3H, s, C*Me*$_2$), 0.98 (3H, d, *J* 6.8, CH*Me*$_2$), 1.06 (3H, d, *J* 7.1, CH*Me*$_2$), 1.44 (3H, s, C*Me*$_2$), 1.54 (3H, d, *J* 6.8, NCH*Me*), 2.08–2.17 (1H, m, C*H*Me$_2$), 2.77 (1H, dd, J_{AB} 13.4, J_{AX} 10.9, COCHC*H*$_2$), 2.81–2.88 (2H, m, COCHC*H*$_2$Ph), 3.24 (1H, dd, J_{BA} 13.4, J_{BX} 4.6, COCHC*H*$_2$), 3.58 (1H, d, *J* 14.2, C*H*$_2$Ph), 3.95 (1H, d, *J* 3.3, NC*H*^{i}Pr), 3.96 (1H, d, *J* 14.2, C*H*$_2$Ph), 4.13 (1H, q, *J* 6.8, NC*H*Me), 4.66–4.77 (1H, m, COC*H*CH$_2$), 7.14–7.48 (15H, m, *Ph*); δ_C 17.0, 17.1, 21.2, 21.3, 27.7, 29.4, 37.0, 43.7, 52.7, 54.7, 58.1, 66.4, 82.5, 126.2, 126.7, 126.8, 128.0, 128.2, 128.3, 128.4, 128.9, 129.3, 139.7, 140.3, 141.6, 153.3, 175.3;. *m/z* (ESI^+) 513 (MH^+, 6%), 409 (100); HRMS (ESI^+) 513.3112 ($C_{33}H_{41}N_2O_3$ requires 513.3122).

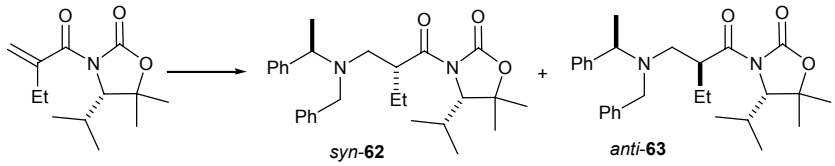
(4*S*,2'*R*,α*S*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-benzyl-propanoyl}oxazolidin-2-one 60 and (4*S*,2'*S*,α*S*)-5,5-dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-benzyl-propanoyl}oxazolidin-2-one 61



syn-**60** *anti*-**61**

N-Acryloyl-oxazolidinone **46** (100 mg, 0.34 mmol, 1.0 eq) was reacted with (*S*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (144 mg, 0.68 mmol, 2.0 eq) and *n*-BuLi (0.272 mL, 0.68 mmol, 2.0 eq) according to **General Procedure 14**, giving a mixture of diastereoisomers **60** and **61** in a ratio of 92:8. Column chromatography (silica, 9:1 pentane:ether, v/v) afforded an inseparable mixture of **60** and **61** in a ratio of 92:8 (155 mg, 89%), as a colourless, viscous oil. Data for **60**: $[\alpha]_D^{21}$ +5.1 (c 1.2, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1768, 1697; δ_H (400MHz, $CDCl_3$) 0.71 (3H, s, C*Me*$_2$), 1.00 (3H, d, *J* 6.8, CH*Me*$_2$), 1.07 (3H, d, *J* 7.1, CH*Me*$_2$), 1.41 (3H, s, C*Me*$_2$), 1.45 (3H, d, *J* 6.8, NCH*Me*), 2.07–2.17 (1H, m, C*H*Me$_2$), 2.46 (1H, dd, J_{AB} 12.6, J_{AX} 7.6, COCHC*H*$_2$), 2.54 (1H, dd, $J_{A'B'}$ 13.5, $J_{A'X'}$ 10.7, COCHC*H*$_2$Ph), 2.99 (1H, dd, $J_{B'A'}$ 13.5, $J_{B'X'}$ 4.7, COCHC*H*$_2$Ph), 3.10 (1H, dd, J_{BA} 12.6, J_{BX} 6.4, COCHC*H*$_2$), 3.66 (1H, d, *J* 14.2, C*H*$_2$Ph), 3.80 (1H, d, *J* 14.2, C*H*$_2$Ph), 3.93 (1H, d, *J* 3.0, NC*H*^{i}Pr), 4.14 (1H, q, *J* 6.8, NC*H*Me), 4.67–4.77 (1H, m, COC*H*CH$_2$), 7.09–7.44 (15H, m, *Ph*); δ_C 13.8, 17.2, 21.3, 27.7, 29.4, 36.9, 43.5, 52.3, 54.7, 56.7, 66.6, 82.5, 126.2, 126.8, 126.8, 128.0, 128.2, 128.3, 128.4, 129.0, 129.1, 139.6, 140.1, 142.1, 153.4, 175.4;. *m/z* (ESI^+) 513 (MH^+, 7%), 409 (100); HRMS (ESI^+) 513.3113 ($C_{32}H_{39}N_2O_3$ requires 513.3112).

(4*S*,2'*R*,α*R*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-ethyl-propanoyl}oxazolidin-2-one 62 and (4*S*,2'*S*,α*R*)-5,5-dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-ethyl-propanoyl}oxazolidin-2-one 63

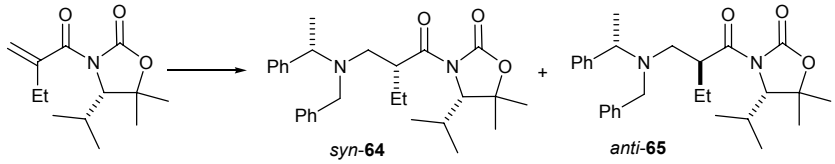


syn-**62** *anti*-**63**

N-Acryloyl-oxazolidinone **47** (30 mg, 0.13 mmol, 1.0 eq) was reacted with (*R*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (45 μL, 0.28 mmol, 1.6 eq) and *n*-BuLi (0.11 mL, 0.28 mmol, 1.6 eq) according to **General Procedure 14**, giving a mixture of diastereoisomers **62** and **63** in a ratio of 98:2. Purification by column chomatography (silica, 9:1 pentane:ether, v/v) furnished **62** (50 mg, 88%) as a colourless oil; $[\alpha]_D^{25}$ +75.2 (c 1.3, $CHCl_3$); ν_{max}/cm^{-1} (film) 1772, 1698; δ_H (400MHz, $CDCl_3$) 0.84 (3H, t, *J* 7.3, CH_2*Me*), 0.95 (3H, d, *J* 6.8, CH*Me*$_2$), 1.02 (3H, d, *J* 7.1, CH*Me*$_2$), 1.35 (3H, s, C*Me*$_2$), 1.41 (3H, d, *J* 7.1, NCH*Me*), 1.51

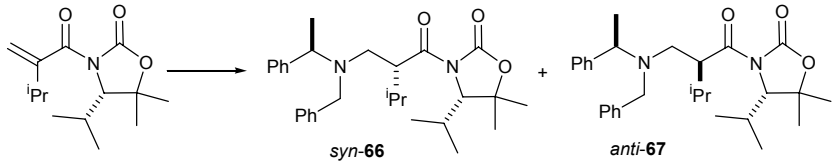
(3H, s, C*Me*$_2$), 1.51–1.81 (2H, m, C*H*$_2$Me), 2.08–2.20 (1H, m, C*H*Me$_2$), 2.64 (1H, dd, J_{AB} 12.6, J_{AX} 7.6 COCHC*H*$_2$N), 2.73 (1H, dd, J_{BA} 12.6, J_{BX} 6.3, COCHC*H*$_2$N), 3.45 (1H, d, *J* 14.4, NC*H*$_2$Ph), 3.80 (1H, d, *J* 14.4, NC*H*$_2$Ph), 4.02 (1H, q, *J* 7.1, NC*H*Ph), 4.10–4.21 (1H, m, COC*H*CH$_2$N), 4.16 (1H, d, *J* 2.8, NC*H*^{i}Pr), 7.19–7.40 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 11.8, 16.4, 17.1, 21.2, 21.4, 28.8, 29.5, 43.1, 52.0, 54.4, 57.7, 66.4, 66.4, 82.3, 126.6 126.7, 127.8, 128.1, 128.3, 128.8, 140.2, 141.7, 153.4, 176.1;. *m/z* (ESI$^+$) 451 (MH$^+$, 100%); HRMS (ESI$^+$) 451.2968 ($C_{28}H_{39}N_2O_3$ requires 451.2961).

(4*S*,2'*R*,α*S*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-ethyl-propanoyl}oxazolidin-2-one 64 and (4*S*,2'*S*,α*S*)-5,5-dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-ethyl-propanoyl}oxazolidin-2-one 65



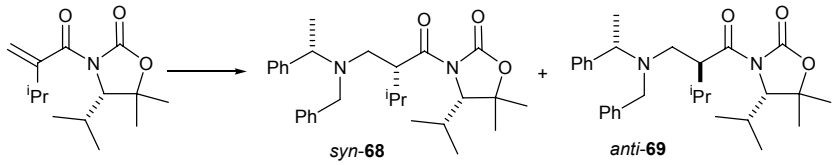
N-Acryloyl-oxazolidinone **47** (30 mg, 0.13 mmol, 1.0 eq) was reacted with (*S*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (45 μL, 0.28 mmol, 1.6 eq) and *n*-BuLi (0.11 mL, 0.28 mmol, 1.6 eq) according to **General Procedure 14**, giving a mixture of diastereoisomers **64** and **65** in a ratio of 89:11. Purification by column chomatography (silica, 9:1 pentane:ether, v/v) furnished **64** (47 mg, 81%) as a colourless viscous oil; $[\alpha]_D^{25}$ –7.2 (c 0.9, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1775, 1698; δ_H (400MHz, $CDCl_3$) 0.79 (3H, t, *J* 7.6, CH$_2$*Me*), 1.03 (3H, d, *J* 6.8, CH*Me*$_2$), 1.15 (3H, d, *J* 6.8, CH*Me*$_2$), 1.38 (3H, s, C*Me*$_2$), 1.40 (3H, d, *J* 7.1, NCH*Me*), 1.40–1.60 (2H, m, C*H*$_2$Me), 1.52 (3H, s, C*Me*$_2$), 2.16–2.25 (1H, m, C*H*Me$_2$), 2.26 (1H, dd, J_{AB} 12.6, J_{AX} 6.6, COCHC*H*$_2$N), 3.08 (1H, dd, J_{BA} 12.6, J_{BX} 7.3, COCHC*H*$_2$N), 3.52 (1H, d, *J* 14.0, NC*H*$_2$Ph), 3.70 (1H, d, *J* 14.0, NC*H*$_2$Ph), 4.02 (1H, q, *J* 6.8, NC*H*Ph), 4.18–4.29 (1H, m, COC*H*CH$_2$), 4.20 (1H, d, *J* 2.8, NC*H*^{i}Pr), 7.20–7.39 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 11.6, 14.3, 17.1, 21.4, 23.7, 28.8, 29.6, 43.0, 51.5, 54.4, 56.6, 66.5, 66.5, 82.3, 126.7, 127.8, 128.1, 128.3, 128.8, 140.1, 142.0, 153.5, 176.2; *m/z* (ESI$^+$) 451 (MH$^+$, 100%); HRMS (ESI$^+$) 451.2951 ($C_{28}H_{39}N_2O_3$ requires 451.2961).

(4*S*,2'*R*,α*R*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-*iso*-propyl-propanoyl}oxazolidin-2-one 66 and (4*S*,2'*S*,α*R*)-5,5-dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-*iso*-propyl-propanoyl}oxazolidin-2-one 67



N-Acryloyl-oxazolidinone **48** (50 mg, 0.20 mmol, 1.0 eq) was reacted with (*R*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (45 μL, 0.31 mmol, 1.6 eq) and *n*-BuLi (0.13 mL, 0.28 mmol, 2.0 eq) according to **General Procedure 14**, giving a mixture of diastereoisomers **66** and **67** in a ratio of 92:8. Purification by column chomatography (silica, 9:1 pentane:ether, v/v) furnished **66** (80 mg, 87%) as a colourless oil; $[\alpha]_D^{25}$ +39.3 (c 0.9, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1771, 1700; δ_H (400MHz, $CDCl_3$) 0.91 (3H, *J* 6.8, COCHCH*Me*$_2$), 0.93 (3H, d, *J* 6.8, COCHCH*Me*$_2$), 1.02 (3H, d, *J* 6.8, NCHCH*Me*$_2$), 1.08 (3H, d, *J* 7.1, NCHCH*Me*$_2$), 1.35 (3H, s, C*Me*$_2$), 1.40 (3H, d, *J* 7.0, NCH*Me*), 1.51 (3H, s, C*Me*$_2$), 1.77–1.86 (1H, m, COCHC*H*Me$_2$), 2.10–2.19 (1H, m, NCHC*H*Me$_2$), 2.66 (1H, dd, J_{AB} 12.9, J_{AX} 6.2, COCHC*H*$_2$), 3.04 (1H, dd, J_{BA} 12.9, J_{BX} 9.9, COCHC*H*$_2$), 3.62 (2H, app s, NC*H*$_2$Ph), 4.06 (1H, q, *J* 7.0, NC*H*Me), 4.12 (1H, d, *J* 3.4, NC*H*^{i}Pr), 4.26–4.34 (1H, m, COC*H*CH$_2$) 7.18–7.36 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 14.3, 17.3, 19.9, 20.3, 20.3, 21.6, 21.7, 29.5, 46.3, 49.7, 49.7, 54.2, 57.4, 66.6, 82.0, 126.6 126.7, 127.8, 128.0, 128.2, 129.1, 139.8, 142.8, 153.7, 175.4; *m/z* (ESI^+) 465 (MH^+, 100%); HRMS (ESI^+) 465.3108 ($C_{29}H_{41}N_2O_3$ requires 465.3117).

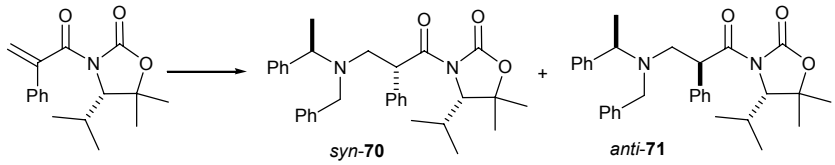
(4*S*,2'*R*,α*S*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-*iso*-propyl-propanoyl}oxazolidin-2-one 68 and (4*S*,2'*S*,α*S*)-5,5-dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-*iso*-propyl-propanoyl}oxazolidin-2-one 69



syn-**68** *anti*-**69**

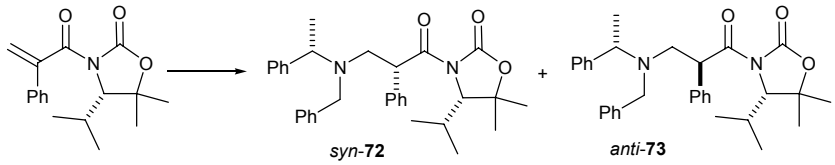
N-Acryloyl-oxazolidinone **48** (50 mg, 0.20 mmol, 1.0 eq) was reacted with (*S*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (45 μL, 0.31 mmol, 1.6 eq) and *n*-BuLi (0.13 mL, 0.28 mmol, 1.6 eq) according to **General Procedure 14**, giving a mixture of diastereoisomers **68** and **69** in a ratio of 97:3. Purification by column chomatography (silica, 9:1 pentane:ether, v/v) furnished **68** (79 mg, 85%) as a colourless, viscous oil; $[\alpha]_D^{25}$ –45.3 (c 1.9, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1772, 1698; δ_H (400MHz, $CDCl_3$) 0.85 (3H, *J* 6.8, COCHCH*Me*$_2$), 0.87 (3H, d, *J* 6.8, COCHCH*Me*$_2$), 1.07 (3H, d, *J* 6.8, NCHCH*Me*$_2$), 1.16 (3H, d, *J* 7.1, NCHCH*Me*$_2$), 1.39 (3H, s, C*Me*$_2$), 1.42 (3H, d, *J* 6.3, NCH*Me*), 1.55 (3H, s, C*Me*$_2$), 1.70–1.81 (1H, m, COCHC*H*Me$_2$), 2.18–2.29 (2H, m, NCHC*H*Me$_2$ and COCHC*H*$_2$), 3.20 (1H, dd, J_{BA} 13.8, J_{BX} 8.9, COCHC*H*$_2$), 3.29 (1H, d, *J* 13.6, NC*H*$_2$Ph), 3.85 (1H, d, *J* 13.6, NC*H*$_2$Ph), 3.98 (1H, q, *J* 6.3, NC*H*Me), 4.23 (1H, d, *J* 4.1, NC*H*^{i}Pr), 4.29–4.37 (1H, m, COC*H*CH$_2$) 7.18–7.39 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 17.1, 17.3, 19.9, 20.4, 21.1, 21.4, 21.6, 29.7, 30.4, 46.6, 49.8, 54.6, 57.0, 66.7, 82.0, 126.7 126.8, 127.8, 128.0, 128.5, 129.0, 139.9, 141.0, 153.7, 175.9; *m/z* (ESI^+) 465 (MH^+, 100%); HRMS (ESI^+) 465.3104 ($C_{29}H_{41}N_2O_3$ requires 465.3117).

(4*S*,2'*R*,α*R*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-phenyl-propanoyl}oxazolidin-2-one 70 and (4*S*,2'*S*,α*R*)-5,5-dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-phenyl-propanoyl}oxazolidin-2-one 71



N-Acryloyl-oxazolidinone **49** (50 mg, 0.17 mmol, 1.0 eq) was reacted with (*R*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (60 μL, 0.28 mmol, 1.6 eq) and *n*-BuLi (0.11 mL, 0.28 mmol, 1.6 eq) according to **General Procedure 14** furnished a mixture of diastereoisomers **71** and **70** in the ratio 93:7. Column chomatography (silica, 9:1 pentane:ether, v/v) furnished the mixture of diastereoisomers **71** and **70** (57 mg, 68%) in a ratio of 98:2 as a colourless viscous oil; data for **71**: $[\alpha]_D^{25}$ +59.2 (c 0.3, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1772, 1698; δ_H (400MHz, $CDCl_3$) 0.88 (3H, s, C*Me*$_2$), 1.00 (3H, d, *J* 6.5, CH*Me*$_2$), 1.07 (3H, d, *J* 7.1, CH*Me*$_2$), 1.32 (3H, d, *J* 6.8, NCH*Me*) 1.42 (3H, s, C*Me*$_2$), 2.08–2.17 (1H, m, C*H*Me$_2$), 2.90 (1H, dd, J_{AB} 13.1, J_{AX} 6.3, COCHC*H*$_2$), 3.30 (1H, dd, J_{BA} 13.1, J_{BX} 8.1, COCHC*H*$_2$), 3.55 (1H, d, *J* 13.9, C*H*$_2$Ph), 3.72 (1H, d, *J* 13.9 C*H*$_2$Ph), 3.97 (1H, d, *J* 3.3, NC*H*^{i}Pr), 4.00 (1H, q, *J* 6.8, NC*H*Me), 5.31–5.38 (1H, m, COC*H*CH$_2$), 7.16–7.35 (15H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 15.4, 17.1, 21.2, 21.2, 28.2, 29.4, 47.8, 53.9, 54.7, 58.1, 67.0, 82.6, 126.7, 127.3, 127.9, 128.0, 128.1, 128.4, 128.7, 128.8, 128.9, 137.6, 140.1, 142.6, 153.5, 173.3;. *m/z* (ESI^+) 499 (MH^+, 100%); HRMS (ESI^+) 499.2959 ($C_{32}H_{39}N_2O_3$ requires 499.2961).

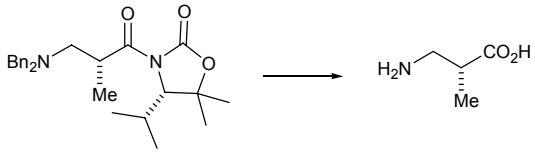
(4*S*,2'*R*,α*S*)-5,5-Dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-phenyl-propanoyl}oxazolidin-2-one 72 and (4*S*,2'*S*,α*S*)-5,5-dimethyl-4-*iso*-propyl-3-{3'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]-2'-phenyl-propanoyl}oxazolidin-2-one 73



N-Acryloyl-oxazolidinone **49** (50 mg, 0.17 mmol, 1.0 eq) was reacted with (*S*)-*N*-benzyl-(*N*-α-methylbenzyl)amine (60 μL, 0.28 mmol, 1.6 eq) and *n*-BuLi (0.11 mL, 0.28 mmol, 2.0 eq) according to **General Procedure 14** furnished a mixture of diastereoisomers **73** and **72** in the ratio 66:34. Column chomatography (silica, 9:1 pentane:ether, v/v) furnished the mixture of diastereoisomers **73** and **72** (57 mg, 68%) in a ratio of 97:3 as a colourless viscous oil; $[\alpha]_D^{22}$ + 8.6 (c 1.0, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1773, 1696; δ_H (400MHz, $CDCl_3$) 0.92 (3H, s, C*Me*$_2$), 1.04 (3H, d, *J* 6.8, CH*Me*$_2$), 1.16 (3H, d, *J* 7.1, CH*Me*$_2$),

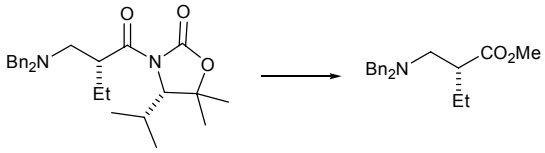
1.43 (3H, s, C*Me*$_2$), 1.44 (3H, d, *J* 6.3, NCH*Me*), 2.09–2.18 (1H, m, C*H*Me$_2$), 2.60 (1H, dd, J_{AB} 13.1, J_{AX} 5.8, COCHC*H*$_2$), 3.50 (1H, dd, J_{BA} 13.1, J_{BX} 7.1, COCHC*H*$_2$), 3.53 (1H, d, *J* 13.9, C*H*$_2$Ph), 3.72 (1H, d, *J* 13.9, C*H*$_2$Ph), 3.99 (1H, q, *J* 6.8, NC*H*Me), 4.04 (1H, d, *J* 3.3, NC*H*^{i}Pr), 5.32–5.39 (1H, m, COC*H*CH$_2$), 7.10–7.30 (15H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 14.4, 17.1, 21.3, 21.3, 28.2, 29.5, 47.9, 53.2, 54.7, 57.4, 67.1, 82.6, 126.6, 126.7, 127.9, 128.0, 128.1, 128.4, 128.7, 128.8, 128.9, 137.3, 140.0, 142.1, 153.5, 173.3;. *m/z* (ESI^+) 499 (MH^+, 100%); HRMS (ESI^+) 499.2954 ($C_{32}H_{39}N_2O_3$ requires 499.2961).

(*R*)-3-Amino-2-methyl propanoic acid 25



3'-Amino-2'-methyl-oxazolidinone **50** (1.20 g, 2.84 mmol, 1.0 eq) was reacted with LiOH (596 mg, 14.2 mmol, 5.0 eq) according to **General Procedure 6**. The crude mixture of products was treated with Pd (400 mg, 10% wt on C) under H_2 (1 atm) according to **General Procedure 7**. The solvent was removed *in vacuo*, the residue co-evaporated with aq. HCl (2 M). Purification by ion exchange chromatography (Dowex 50W-X8, 1M aq. NH_4OH eluent) yielded the free amino acid (*R*)-**25** as a white crystalline solid (260 mg, 89%); mp 175–177°C {lit.[10] 179–181°C}; $[\alpha]_D^{25}$ –12.4 (c 1.0, H_2O) {lit.[10] for (*S*)-**25** $[\alpha]_D^{25}$ +14.2 (c 1.0, H_2O)}; δ_H (200MHz, D_2O) 1.05 (3H, d, *J* 7.3, CCH*Me*), 2.44–2.51 (1H, m, CC*H*CH$_2$), 2.84 (1H, dd, J_{AB} 12.8, J_{AX} 7.3, CCHC*H*$_2$), 2.97 (1H, dd, J_{BA} 12.8, J_{BX} 8.3, CCHC*H*$_2$).

Methyl (*R*)-3-(*N*,*N*-dibenzylamino)-2-ethyl propanate 30

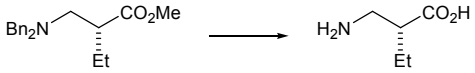


3'-Amino-2'-ethyl-oxazolidinone **52** (741 mg, 1.70 mmol, 1.0 eq) was treated with *n*-BuLi (3.19 mL, 5.10 mmol, 3.0 eq) according to **General Procedure 8**. Purification by column chomatography (silica, 9:1 pentane:ether, v/v) furnished (*R*)-**30** as a colourless oil (444 mg, 85%); $[\alpha]_D^{22}$ –32.7 (c 1.0, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1730; δ_H (400MHz, $CDCl_3$) 0.85 (3H, t, *J* 7.3, CH$_2$*Me*), 1.46–1.54 (2H, m, C*H*$_2$Me), 2.47 (1H, dd, J_{AB} 12.8, J_{AX} 5.5, COCHC*H*$_2$N), 2.60–2.69 (1H, m, COC*H*), 2.77 (1H, dd, J_{AB} 12.8, J_{BX} 8.8, COCHC*H*$_2$N), 3.42 (2H, d, *J* 13.4, NC*H*$_2$Ph), 3.67 (3H, s, O*Me*), 3.70 (2H, d, *J* 13.4, NC*H*$_2$Ph), 7.18–7.35 (10H, m, *Ph*); δ_C

[10] Y. Jin, D.H. Kim, *Synlett* 1998, **11**, 1189–1190.

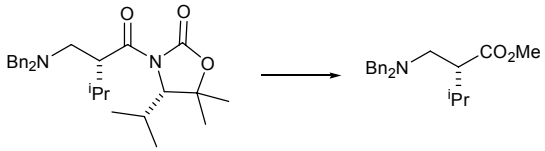
(100MHz, $CDCl_3$) 11.8, 23.5, 46.5, 51.3, 55.9, 58.4, 126.9, 128.1, 128.1, 128.9, 128.9, 139.2, 175.6; *m/z* (ESI^+) 312 (MH^+, 100%); HRMS (ESI^+) 312.1966 ($C_{20}H_{26}NO_2$ requires 312.1964).

(*R*)-3-Amino-2-ethyl-propanoic acid 32



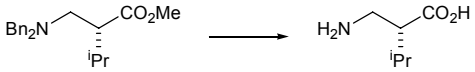
β-Amino ester **30** (444 mg, 1.43 mmol, 1.0 eq) was treated with Pd (400 mg, 10% wt on C) under H_2 (1 atm) according to **General Procedure 7**. The crude product was then treated with LiOH (290 mg, 8.0 mmol, 5.0 eq) according to **General Procedure 9**. The solvents were removed *in vacuo* and the residue was co-evaporated with aq. HCl (2 M). Purification by ion exchange chomatography (Dowex 50W-X8, 1 M aq. NH_4OH eluent) furnished the free amino acid (*R*)-**32** as a white crystalline solid (123 mg, 82%); mp 210–212˚C {lit.[11] 206–207˚C}; $[\alpha]_D^{22}$ –7.4 (c 1.0, H_2O) {lit.[11] $[\alpha]_D^{22}$ –4.5 (c 1.0, H_2O)}; δ_H (400MHz, D_2O) 0.76 (3H, t, *J* 7.2, CH_2*Me*), 1.43–1.50 (2H, m, C*H*$_2$Me), 2.32–2.39 (1H, m, C*H*CH_2), 2.92 (1H, dd, J_{AX} 13.7, J_{AB} 6.9, COCHC*H*$_2$), 2.97 (1H, dd, J_{BX} 12.8, J_{BA} 6.9, COCHC*H*$_2$).

Methyl (*R*)-3-dibenzylamine-2-*iso*-propyl-propanate 78



3'-Amino-2'-*iso*-propyl-oxazolidinone **53** (711 mg, 1.58 mmol, 1.0 eq) was treated with *n*-BuLi (2.97 mL, 4.74 mmol, 3.0 eq) according to **General Procedure 8**. Purification by column chomatography (silica, 9:1 pentane:ether, v/v) furnished (*R*)-**78** as a colourless oil (401 mg, 78%); $[\alpha]_D^{22}$ –28.1 (c 1.7, $CHCl_3$); ν_{max}/cm^{-1} ($CHCl_3$) 1730; δ_H (400MHz, $CDCl_3$) 0.81 (3H, d, *J* 6.3, CH*Me*$_2$), 0.88 (3H, d, *J* 6.8, CH*Me*$_2$), 1.71–1.82 (1H, m, C*H*Me$_2$), 2.41–2.56 (2H, m, COC*H* and COCHC*H*$_2$N), 2.77 (1H, dd, J_{BA} 12.4, J_{BX} 8.8, COCHC*H*$_2$N), 3.32 (2H, d, *J* 13.4, NC*H*$_2$Ph), 3.65 (3H, s, O*Me*), 3.74 (2H, d, *J* 13.4, NC*H*$_2$Ph), 7.19–7.34 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 20.5, 20.8, 29.2, 41.9, 51.1, 54.4, 58.4, 126.9, 128.1, 128.1, 129.0, 139.2, 175.1; *m/z* (ESI^+) 326 (MH^+, 100%); HRMS (ESI^+) 326.2126 ($C_{21}H_{28}NO_2$ requires 326.2126).

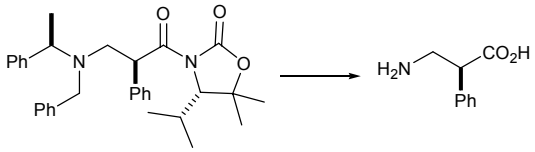
(*R*)-3-Amino-2-*iso*-propyl propanoic acid 79



[11] Y. Jin, D.H. Kim, *Synlett* 1998, **11**, 1189–1190.

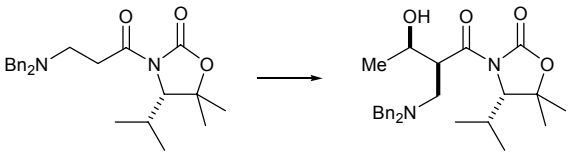
β-Amino ester **78** (401 mg, 1.23 mmol, 1.0 eq) was treated with Pd (400 mg, 10% wt on C) under H_2 (1 atm) according to **General Procedure 7**. The crude product was then treated with LiOH (230 mg, 5.5 mmol, 5.0 eq) according to **General Procedure 9**. The solvents were removed *in vacuo* and the residue was co-evaporated with aq. HCl (2 M). Purification by ion exchange chomatography (Dowex 50W-X8, 1 M aq. NH_4OH eluent) furnished the free amino acid (*R*)-**79** as a white crystalline solid (81 mg, 93%); mp 212–214˚C {lit.[11] 220–221˚C}; $[\alpha]_D^{25}$ −13.1 (c 1.01, H_2O) {lit.[11] $[\alpha]_D^{25}$ −11.4 (c 1.0, H_2O)}; δ_H (200MHz, D_2O) 0.76 (3H, d, *J* 7.2, CH*Me*$_2$), 0.82 (3H, d, *J* 7.2, CH*Me*$_2$), 1.72–1.93 (1H, m, C*H*Me$_2$), 2.12–2.28 (1H, m, COC*H*), 2.92 (1H, dd, J_{AB} 13.7, J_{AX} 5.0, COCHC*H*$_2$), 2.97(1H, dd, J_{BA} 13.7, J_{BX} 8.8, COCHC*H*$_2$).

(*S*)-3-Amino-2-phenyl-propanoic acid (*S*)-81



3'-Amino-2'-phenyl-oxazolidinone **71** (688 mg, 1.38 mmol, 1.0 eq) was treated with LiOH (340 mg, 7.8 mmol, 6.0 eq) and hydrogen peroxide (2.8 mL, 2.8 mmol, 2.0 eq) according to **General Procedure 15** to furnish a mixture of the acid (*S*)-**80** and chiral auxiliary **2**. This mixture was subsequently treated with Pd (800 mg, 10% wt on C) under H_2 (1 atm) according to **General Procedure 7**. The residue was co-evaporated with aq. HCl (2 M) then purified by ion exchange chomatography (Dowex 50W-X8, 1 M aq. NH_4OH eluent) to furnish the free amino acid (*S*)-**81** as a white crystalline solid (195 mg, 95%); mp 230–232˚C {lit.[12] 224–225˚C}; $[\alpha]_D^{25}$ +93.0 (c 1.0, H_2O) {lit.[12] $[\alpha]_D^{25}$ +95.0 (c 1.0, H_2O)}; δ_H (200MHz, D_2O) 3.19 (1H, dd, J_{AB} 12.8, J_{AX} 7.3, COCHC*H*$_2$), 2.97 (1H, dd, J_{BA} 12.8, J_{BX} 7.8, COCHC*H*$_2$), 3.62–3.72 (1H, m, COC*H*), 7.14–7.39 (5H, m, *Ph*).

(4*S*,2'*S*,3'*R*)-5,5-Dimethyl-4-*iso*-propyl-3-{[2'-(*N*,*N*-dibenzylamino)methyl]-3'-hydroxybutanoyl} oxazolidin-2-one 83

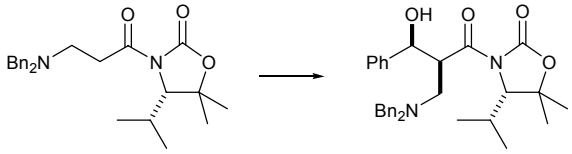


3'-Amino-oxazolidinone **7** (100 mg, 0.24 mmol, 1.0 eq), 9-BBNOTf (0.58 mL, 0.29 mmol, 1.2 eq), Hünig's base (0.06 mL, 0.34 mmol, 1.4 eq) and acetaldehyde (0.02 mL, 0.36 mmol, 1.5 eq, distilled from $CaCl_2$) were reacted according to **General Procedure 16**. Purification by column chromatography (silica, 9:1

[12] J. A. Garbarino and O. Nunez, *J. Chem. Soc., Perkin Trans. 1*, 1981, 906–908.

petrol:ether v/v) gave **83** as a viscous pale yellow oil (72 mg, 65%); $[\alpha]_D^{22}$ + 119.4 (*c* 0.5, $CHCl_3$); ν_{max}/cm^{-1} (film) 3425, 1771, 1693; δ_H (400MHz, $CDCl_3$) 0.96 (3H, d, *J* 6.8, CH*Me*$_2$), 1.00 (3H, d, *J* 7.2, CH*Me*$_2$), 1.12 (3H, d, *J* 5.8, C(OH)*Me*), 1.39 (3H, s, C*Me*$_2$), 1.52 (3H, s, C*Me*$_2$), 2.04–2.22 (1H, m, C*H*Me$_2$), 2.72–2.78 (1H, m, C*H*$_2$NBn$_2$), 3.02–3.07 (1H, m, C*H*$_2$NBn$_2$), 3.26 (2H, d, *J* 13.3, N(C*H*$_2$Ph)$_2$), 3.89–4.03 (1H, m, C*H*OH), 4.06–4.22 (3H, m, N(C*H*$_2$Ph)$_2$, NC*H*^{i}Pr), 4.28–4.49 (1H, m, COC*H*), 6.35 (1H, br s, O*H*), 7.17–7.45 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 17.1, 20.9, 21.3, 21.6, 28.6, 29.4, 46.7, 56.2, 58.4, 67.6, 70.9, 82.9, 127.5, 128.2, 129.3, 137.2, 153.5, 172.9; *m/z* (ESI^+) 453 (MH^+, 100%); HRMS (ESI^+) 453.2746 ($C_{27}H_{37}N_2O_4$ requires 453.2753).

(4*S*,2'*S*,3'*S*)-5,5-Dimethyl-4-*iso*-propyl-3-{[2'-(*N*,*N*-dibenzylamino)methyl]-3'-hydroxy-3'-phenylpropanoyl}oxazolidin-2-one 84



3'-Amino-oxazolidinone **7** (100 mg, 0.24 mmol, 1.0 eq), 9-BBNOTf (0.58 mL, 0.29 mmol, 1.2 eq), Hünig's base (0.06 mL, 0.34 mmol, 1.4 eq) and benzaldehyde (0.04 mL, 0.36 mmol, 1.5 eq, distilled from CaH_2) were reacted according to **General Procedure 16**. Purification by column chromatography (silica, 9:1 petrol:ether v/v) gave **84** as a pale yellow crystalline solid (44 mg, 36%); mp 112–114°C; $[\alpha]_D^{22}$ +88.2 (*c* 1.0, $CHCl_3$); ν_{max}/cm^{-1} (KBr) 3414, 1786, 1655; δ_H (400MHz, $CDCl_3$) 0.53 (3H, s, C*Me*$_2$), 0.88 (3H, d, *J* 6.8, CH*Me*$_2$), 0.93 (3H, d, *J* 6.8, CH*Me*$_2$), 1.35 (3H, s, C*Me*$_2$), 1.97–2.07 (1H, m, C*H*Me$_2$), 2.77–2.85 (1H, m, CHC*H*$_2$N), 3.26–3.32 (1H, m, CHC*H*$_2$N), 3.35 (2H, d, *J* 13.3, N(C*H*$_2$Ph)$_2$), 3.70 (1H, d, *J* 3.41, NC*H*^{i}Pr), 4.26 (2H, d, *J* 13.3, N(C*H*$_2$Ph)$_2$), 4.80 (1H, d, *J* 9.2, C*H*OH), 4.87–4.96 (1H, m, COC*H*), 7.10–7.52 (15H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 17.0, 21.2, 21.4, 27.2, 29.2, 46.8, 56.4, 58.4, 66.1, 78.5, 82.8, 127.5, 127.9, 127.6, 128.3, 128.7, 129.5, 136.9, 141.7, 153.2, 171.7); *m/z* (ESI^+) 515 (MH^+, 100%); HRMS (ESI^+) 515.2914 ($C_{32}H_{39}N_2O_4$ requires 515.2910).

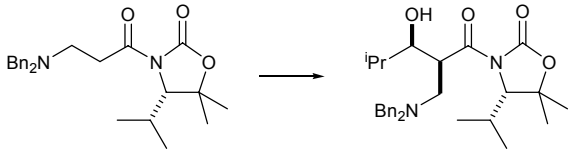
X-Ray crystal structure determination for 84

Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-*K*α radiation using standard procedures at 190K. The structure was solved by direct methods, all non-hydrogen

atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[13]

X-ray crystal structure data for **84** [$C_{32}H_{38}N_2O_4$]: M = 514.66, orthorhombic, space group P 2_1 2_1 2_1, a = 8.6876(2) Å, b = 14.8422(3) Å, c = 22.3552(4) Å, V = 2882.5(1) Å^3, Z = 4, μ = 0.078 mm^{-1}, colourless block, crystal dimensions = 0.1 × 0.1 × 0.1 mm^3. A total of 3676 unique reflections were measured for $5 < \theta < 27$ and 2810 reflections were used in the refinement. The final parameters were wR_2 = 0.0433 and R_1 = 0.0375 [$I>3\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 616168. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(4*S*,2'*S*,3'*R*)-5,5-Dimethyl-4-*iso*-propyl-3-{[2'-(*N*,*N*-dibenzylamino)methyl]-3'-hydroxy-4'-methylpentanoyl}oxazolidin-2-one 85



3'-Amino-oxazolidinone **7** (100 mg, 0.24 mmol, 1.0 eq), 9-BBNOTf (0.58 mL, 0.29 mmol, 1.2 eq), Hünig's base (0.06 mL, 0.34 mmol, 1.4 eq) and *iso*-butyraldehyde (0.03 mL, 0.36 mmol, 1.5 eq, distilled from $CaCl_2$) were reacted according to **General Procedure 16**. Purification by column chromatography (silica, 9:1 petrol:ether v/v) afforded **85** as a colourless crystalline solid (74 mg, 64%); mp. 44–46°C; $[\alpha]_D^{22}$ +107.6 (*c* 2.0, $CHCl_3$); ν_{max}/cm^{-1} (KBr) 3429, 1774, 1649; δ_H (400MHz, $CDCl_3$) 0.90–1.01 (12H, m, CH*Me*$_2$, C(OH)CH*Me*$_2$), 1.38 (3H, s, C*Me*$_2$), 1.53 (3H, s, C*Me*$_2$), 1.57–1.61 (1H, m, C(OH)C*H*Me$_2$), 2.12–2.19 (1H, m, C*H*Me$_2$), 2.77 (1H, dd, J_{AB} 12.1, J_{AX} 3.0, CHC*H*$_2$N), 3.09 (1H, dd, J_{BA} 12.1, J_{BX} 10.9, CHC*H*$_2$N), 3.25 (2H, d, *J* 13.4, N(C*H*$_2$Ph)$_2$), 3.81–3.83 (2H, m, C*H*OH, O*H*), 4.10–4.15 (3H, m, N(C*H*$_2$Ph)$_2$, NC*H*^{i}Pr), 4.51 (1H, m, COC*H*), 7.27–7.36 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 15.2, 17.1, 20.0, 21.4, 21.5, 28.6, 29.5, 31.1, 42.9, 56.7, 58.2, 66.5, 78.5, 82.9, 127.4, 128.6, 129.4, 137.1, 153.3, 173.2; *m/z* (ESI$^+$) 481 (MH$^+$, 100%); HRMS (ESI$^+$) 481.3059 ($C_{29}H_{41}N_2O_4$ requires 481.3066).

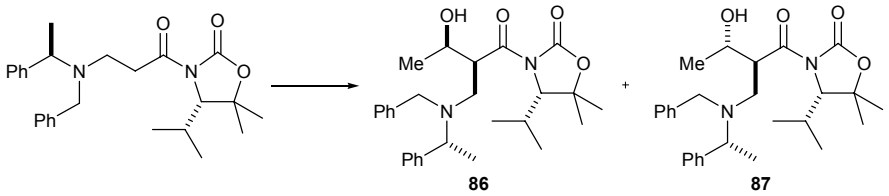
X-Ray crystal structure determination for 85

[13] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, C. K. Prout and D. J. Watkin, CRYSTALS, 2004, Issue 12, Chemical Crystallography Laboratory, University of Oxford, UK.

Data were collected using an Enraf-Nonius κ-CCD diffractometer with graphite monochromated Mo-$K\alpha$ radiation using standard procedures at 190K. The structure was solved by direct methods, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at idealised positions. The structure was refined using CRYSTALS.[14]

X-ray crystal structure data for **85** [$C_{29}H_{40}N_2O_4$]: M = 480.65, orthorhombic, space group P 2_1 2_1 2_1, a = 11.5661(2) Å, b = 12.0490(2) Å, c = 20.5677(4) Å, V = 2866.31(9) Å^3, Z = 4, μ = 0.074 mm^{-1}, colourless plate, crystal dimensions = 0.2 × 0.1 × 0.1 mm^3. A total of 3648 unique reflections were measured for $5 < \theta < 27$ and 2582 reflections were used in the refinement. The final parameters were wR_2 = 0.0502 and R_1 = 0.0426 [$I>2\sigma(I)$]. Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 616169. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

(4*S*,2'*S*,3'*R*,α*R*)-5,5-Dimethyl-4-*iso*-propyl-3-({2'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]methyl}-3'-hydroxybutanoyl)oxazolidin-2-one 86 and (4*S*,2'*S*,3'*S*,α*R*)-5,5-dimethyl-4-*iso*-propyl-3-({2'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]methyl}-3'-hydroxybutanoyl)oxazolidin-2-one 87

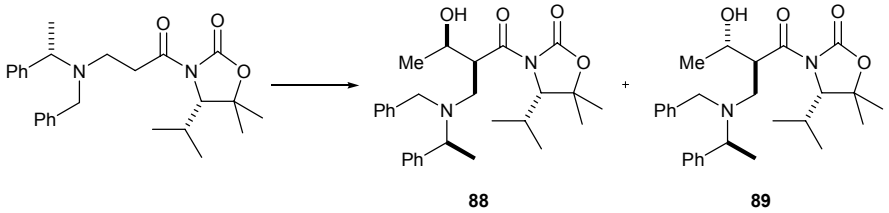


3'-Amino-oxazolidinone **9** (236 mg, 0.56 mmol, 1.0 eq), 9-BBNOTf (0.5 M in hexanes, 1.34 mL, 0.23 mmol, 1.2 eq), Hünigs base (0.14 mL, 0.27 mmol, 1.4 eq) and acetaldehyde (0.05 mL, 0.84 mmol, 1.5 eq, distilled from $CaCl_2$) were reacted according to **General Procedure 16**. Purification by column chromatography (silica, 9:1 petrol:ether, v/v) gave an inseparable 92:8 mixture of diastereoisomers **86** and **87** (178 mg, 68%) as a colourless oil. Data for major diastereoisomer **86**; ν_{max}/cm^{-1} (film) 3443, 1771, 1693; δ_H (400MHz, $CDCl_3$) 0.88 (3H, d, J 6.8, CHMe_2), 0.95 (3H, d, J 6.8, CHMe_2), 1.14 (3H, d, J 6.1, CHMe), 1.38 (3H, s, CMe_2), 1.50 (3H, s, CMe_2), 1.59 (3H, d, J 7.1, NCHMe), 2.07–2.14 (1H, m, CHMe$_2$), 2.53 (1H, dd, J_{AB} 12.8, J_{AX} 2.9, CHCH_2N), 3.01 (1H, d, J 13.6, NCH_2Ph), 3.09–3.15 (1H, m, CHCH_2N), 4.02–4.09 (1H, m, CHOH), 4.12–4.16 (2H, m, NCH^{i}Pr and NCHMe), 4.20 (1H, d, J 13.9, NCH_2Ph), 4.37–4.43 (1H, m, COCH), 7.27–7.39 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 16.9, 18.7, 21.1, 21.3, 21.6, 28.6, 29.5, 49.7, 52.8,

[14] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, C. K. Prout and D. J. Watkin, CRYSTALS, 2004, Issue 12, Chemical Crystallography Laboratory, University of Oxford, UK.

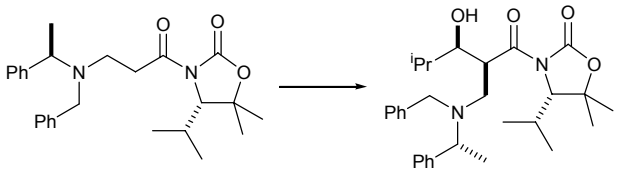
54.4, 57.3, 66.3, 71.1, 88.9, 127.4, 127.6, 128.1, 128.7, 128.9, 129.2, 137.8, 138.0, 153.4, 173.2; *m/z* (ESI^+) 467 (MH^+, 100%); HRMS (ESI^+) 467.2907 ($C_{28}H_{39}N_2O_4$ requires 467.2910).

(4*S*,2'*S*,3'*R*,α*S*)-5,5-dimethyl-4-*iso*-propyl-3-({[2'-(*N*-benzyl-*N*-(α-methylbenzyl)amino]methyl}-3'-hydroxybutanoyl)oxazolidin-2-one 88 and (4*S*,2'*S*,3'*S*,α*S*)-5,5-dimethyl-4-*iso*-propyl-3-({[2'-(*N*-benzyl-*N*-(α-methylbenzyl)amino]methyl}-3'-hydroxybutanoyl)oxazolidin-2-one 89



3'-Amino-oxazolidinone **10** (93 mg, 0.22 mmol, 1.0 eq), 9-BBNOTf (0.5 M in hexanes, 0.52 mL, 0.26 mmol, 1.2 eq), Hünig's base (0.05 mL, 0.31 mmol, 1.4 eq) and acetaldehyde (0.02 mL, 0.33 mmol, 1.5 eq, distilled from $CaCl_2$) were reacted according to **General Procedure 16**. Purification by column chromatography (silica, 9:1 petrol:ether, v/v) gave an inseparable 94:6 mixture of diastereoisomers **88** and **89** as a yellow oil (89 mg, 86%). Data for major diastereoisomer **88**; ν_{max}/cm^{-1} (film) 3426, 1772, 1694; δ_H (400MHz, $CDCl_3$) 0.98 (3H, d, *J* 6.8, CH*Me*$_2$), 1.02–1.05 (6H, m, CH*Me*$_2$ and CH*Me*), 1.38–1.40 (6H, m, C*Me*$_2$ and NCH*Me*Ph), 1.52 (3H, s, C*Me*$_2$), 2.13–2.20 (1H, m, C*H*Me$_2$), 2.88–2.95 (2H, m, CHC*H*$_2$N), 3.45 (1H, d, *J* 13.4, NC*H*$_2$Ph), 3.67–3.75 (1H, m, C*H*OH), 4.07 (1H, d, *J* 13.4, NC*H*$_2$Ph), 4.12 (1H, d, *J* 3.3, NC*H*^{i}Pr), 4.12–4.18 (1H, q, *J* 6.8, NC*H*MePh), 4.29–4.34 (1H, m, COC*H*), 7.25–7.37 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 9.9, 17.2, 20.8, 21.4, 21.6, 28.6, 29.5, 46.9, 51.4, 54.4, 56.0, 66.5, 70.7, 82.9, 127.3, 127.4, 128.3, 128.3, 128.6, 129.3, 138.1, 141.7, 153.5, 173.3; *m/z* (ESI^+) 467 (MH^+, 100%); HRMS (ESI^+) 467.2907 ($C_{28}H_{39}N_20_4$ requires 467.2910).

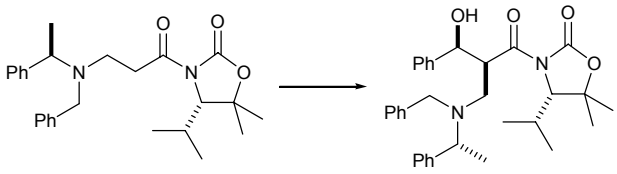
(4*S*,2'*S*,3'*R*,α*R*)-5,5-Dimethyl-4-*iso*-propyl-3-(2'-{[*N*-benzyl-*N*-(α-methylbenzyl)amino]methyl}-3'-hydroxy-4'-methylpentanoyl)oxazolidin-2-one 90



3'-Amino-oxazolidinone **9** (100 mg, 0.24 mmol, 1.0 eq), 9-BBNOTf (0.5 M in hexanes, 0.57 mL, 0.28 mmol, 1.2 eq), Hünig's base (0.06 mL, 0.33 mmol, 1.4 eq) and *iso*-butyraldehyde (0.03 mL, 0.35 mmol, 1.5 eq, distilled from CaH_2) were reacted according to **General Procedure 16**. Purification by column chromatography (silica, 4:1 petrol:ether, v/v) gave **90** as a colourless oil (49 mg, 42%); $[\alpha]_D^{23}$ +402.0 (*c* 0.5,

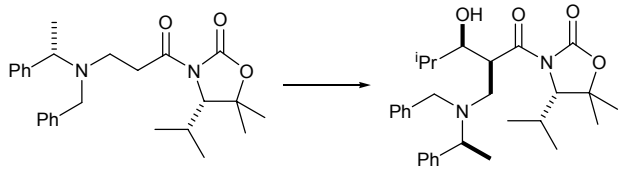
$CHCl_3$); ν_{max}/cm^{-1} (film) 3426, 1771, 1692; δ_H (400MHz, $CDCl_3$) 0.87 (3H, d, *J* 6.8, CH*Me*$_2$), 0.90 (3H, d, *J* 7.1, C(OH)CH*Me*$_2$), 0.96 (3H, d, *J* 6.8, CH*Me*$_2$), 1.01 (3H, d, *J* 6.8, C(OH)CH*Me*$_2$), 1.37 (3H, s, C*Me*$_2$), 1.51 (3H, s, C*Me*$_2$), 1.58 (3H, d, *J* 7.1, NCH*Me*), 1.58–1.63 (1H, m, C(OH)C*H*Me$_2$), 2.08–2.16 (1H, m, C*H*Me$_2$), 2.51 (1H, dd, J_{AB} 12.6, J_{AX} 2.8, CHC*H*$_2$N), 3.04 (1H, d, *J* 13.9, NC*H*$_2$Ph), 3.17–3.22 (1H, m, CHC*H*$_2$N), 3.95 (1H, dd, *J* 1.8, 9.1, C*H*OH), 4.09 (1H, q, *J* 7.1, NC*H*MePh), 4.11 (1H, d, *J* 3.3, NC*H*^{i}Pr), 4.23 (1H, d, *J* 13.9, NC*H*$_2$Ph), 4.43–4.49 (1H, m, COC*H*), 7.27–7.38 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 15.1, 16.9, 18.6, 20.1, 21.4, 21.5, 28.6, 29.5, 31.3, 42.8, 53.0, 54.5, 57.2, 66.4, 78.6, 82.9, 127.3, 127.6, 128.0, 128.6, 129.0, 129.2, 137.7, 138.1, 153.2, 173.4; *m/z* (ESI$^+$) 495 (MH$^+$, 100%); HRMS (ESI$^+$) 495.3221 ($C_{30}H_{43}N_2O_4$ requires 495.3223).

(4*S*,2'*S*,3'*S*,α*R*)-5,5-Dimethyl-4-*iso*-propyl-3-({2'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]methyl}-3'-hydroxy-3'-phenyl propanoyl)oxazolidin-2-one 91



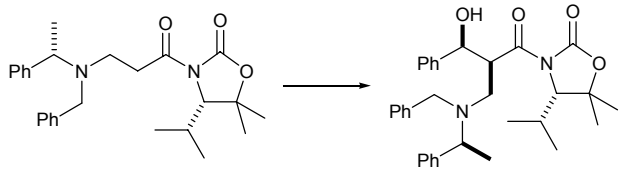
3'-Amino-oxazolidinone **9** (100 mg, 0.24 mmol, 1.0 eq), 9-BBNOTf (0.5 M in hexanes, 0.57 mL, 0.28 mmol, 1.2 eq), Hünig's base (0.06 mL, 0.33 mmol, 1.4 eq) and benzaldehyde (0.04 mL, 0.35 mmol, 1.5 eq, distilled from CaH_2) were reacted according to **General Procedure 16**. Purification by column chromatography (silica, 4:1 petrol:ether, v/v) gave **91** as a colourless, viscous oil (65 mg, 52%); $[\alpha]_D^{23}$ +462.4 (*c* 0.5, $CHCl_3$); ν_{max}/cm^{-1} (film) 3427, 1769, 1692; δ_H (400MHz, $CDCl_3$) 0.51 (3H, s, C*Me*$_2$), 0.83 (3H, d, *J* 6.8, CH*Me*$_2$), 0.89 (3H, d, *J* 6.8, CH*Me*$_2$), 1.34 (3H, s, C*Me*$_2$), 1.70 (3H, d, *J* 7.0, NCH*Me*), 1.96–2.03 (1H, m, C*H*Me$_2$), 2.61 (1H, dd, J_{AB} 12.8, J_{AX} 1.9, CHC*H*$_2$N), 3.05 (1H, d, *J* 13.6, NC*H*$_2$Ph), 3.34 (1H, app. t, *J* 11.9, CHC*H*$_2$N), 3.70 (1H, d, *J* 3.3, NC*H*^{i}Pr), 4.22–4.32 (2H, m, NC*H*Me and NC*H*$_2$Ph), 4.84 (1H, d, *J* 9.1, C*H*OH), 4.88–4.93 (1H, m, COC*H*), 7.16–7.44 (15H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 17.3, 19.4, 21.6, 21.8, 27.7, 29.6, 47.0, 53.4, 54.9, 58.0, 66.5, 79.0, 83.1, 127.9, 128.1, 128.3, 128.0, 128.6, 128.7, 129.1, 129.4, 129.7, 138.1, 138.2, 142.1, 153.6, 172.4; *m/z* (ESI$^+$) 529 (MH$^+$, 100%); HRMS (ESI$^+$) 529.3065 ($C_{33}H_{41}N_2O_4$ requires 529.3066).

(4*S*,2'*S*,3'*R*,α*S*)-5,5-dimethyl-4-*iso*-propyl-3-{2'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]methyl)-3'-hydroxy-4'-methylpentanoyl}oxazolidin-2-one 92



3'-Amino-oxazolidinone **10** (100 mg, 0.24 mmol, 1.0 eq), 9-BBNOTf (0.5 M in hexanes, 0.57 mL, 0.28 mmol, 1.2 eq), Hünig's base (0.06 mL, 0.33 mmol, 1.4 eq) and *iso*-butyraldehyde (0.03 mL, 0.35 mmol, 1.5 eq, distilled from CaH_2) were reacted according to **General Procedure 16**. Purification by column chromatography (silica, 4:1 petrol:ether, v/v) gave **92** as a colourless oil (33 mg, 28%); $[\alpha]_D^{23}$ +70.8 (*c* 1.0, $CHCl_3$); ν_{max}/cm^{-1} (film) 3441, 1771, 1683; δ_H (400MHz, $CDCl_3$) 0.88 (3H, d, *J* 6.8, C(OH)CH*Me*$_2$), 0.90 (3H, d, *J* 7.1, C(OH)CH*Me*$_2$), 0.99 (3H, d, *J* 6.8, CH*Me*$_2$), 1.04 (3H, d, *J* 6.8, CH*Me*$_2$), 1.37 (3H, s, C*Me*$_2$), 1.39 (3H, d, *J* 7.1, NCH*Me*), 1.49–1.53 (1H, m, C(OH)C*H*Me$_2$), 1.53 (3H, s, C*Me*$_2$), 2.14–2.22 (1H, m, C*H*Me$_2$), 2.91–2.98 (2H, m, CHC*H*$_2$N), 3.45 (1H, d, *J* 13.4, NC*H*$_2$Ph), 3.52 (1H, dd, *J* 2.5, 8.6, C*H*OH), 4.05 (1H, d, *J* 13.4, NC*H*$_2$Ph), 4.11 (1H, d, *J* 3.0, NC*H*^{i}Pr), 4.18 (1H, q, *J* 6.8, NC*H*Me), 4.43–4.49 (1H, m, COC*H*), 5.90 (1H, br s, CHO*H*), 7.26–7.36 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 10.7, 15.8, 17.5, 20.3, 21.8, 21.9, 29.0, 29.9, 31.4, 43.4, 52.0, 54.8, 56.6, 67.0, 78.8, 83.3, 127.6, 127.7, 128.7, 128.7, 128.9, 129.8, 138.5, 141.9, 153.7, 174.1; *m/z* (ESI$^+$) 495 (MH$^+$, 100%); HRMS (ESI$^+$) 495.3218 ($C_{30}H_{43}N_2O_4$ requires 495.3223).

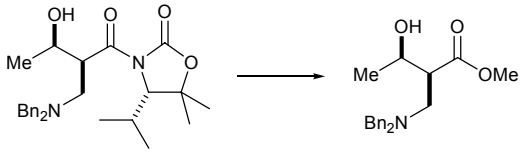
(4*S*,2'*S*,3'*S*,α*S*)-5,5-Dimethyl-4-*iso*-propyl-3-({2'-[*N*-benzyl-*N*-(α-methylbenzyl)amino]methyl}-3'-hydroxy-3'-phenyl-propanoyl)oxazolidin-2one 93



3'-Amino-oxazolidinone **10** (100 mg, 0.24 mmol, 1.0 eq), 9-BBNOTf (0.5 M in hexanes, 0.57 mL, 0.28 mmol, 1.2 eq), Hünig's base (0.06 mL, 0.33 mmol, 1.4 eq) and benzaldehyde (0.04 mL, 0.35 mmol, 1.5 eq, distilled from CaH_2) were reacted according to **General Procedure 16** gave a mixture of diastereoisomers in a ratio of 77:23, with **93** as the major product. Purification by column chromatography (silica, 9:1 petrol:ether, v/v) gave **93** as a yellow oil (86 mg, 68%, 80% de); ν_{max}/cm^{-1} (film) 3427, 1771, 1692; δ_H (400MHz, $CDCl_3$) 0.52 (3H, s, C*Me*$_2$), 0.90 (3H, d, *J* 6.8, CH*Me*$_2$), 0.96 (3H, d, *J* 6.8, CH*Me*$_2$), 1.35 (3H, s, C*Me*$_2$), 1.45 (3H, d, *J* 6.8, CH*Me*), 1.99–2.06 (1H, m, C*H*Me$_2$), 2.95 (1H, dd, J_{AB} 12.6, J_{AX} 2.5, CHC*H*$_2$N), 3.22–3.26 (1H, m, CHC*H*$_2$N), 3.51 (1H, d, *J* 12.6, NC*H*$_2$Ph), 3.68 (1H, d, *J* 3.3, NC*H*^{i}Pr), 4.22–4.30 (2H, m,

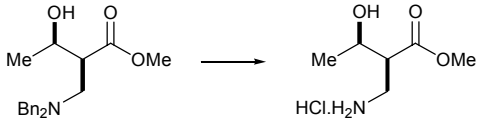
NC*H*$_2$Ph and NC*H*Me), 4.51 (1H, d, *J* 9.1, C*H*OH), 4.78–4.84 (1H, m, COC*H*), 7.14–7.42 (15H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 9.7, 17.1, 21.3, 21.4, 27.3, 29.2, 47.0, 51.8, 54.6, 56.1, 66.3, 78.3, 82.9, 127.4, 127.6, 127.8, 127.5, 128.2, 128.4, 128.5, 128.7, 129.5, 137.8, 141.5, 141.8, 153.3, 172.1; *m/z* (ESI^+) 529 (MH^+, 100%); HRMS (ESI^+) 529.3062 ($C_{33}H_{41}N_2O_4$ requires 529.3066).

Methyl (2*S*,3*R*)-2-(*N*,*N*-dibenzylamino)methyl-3-hydroxybutanoate 94



Aldol adduct **83** (147 mg, 0.32 mmol, 1.0 eq), *n*-BuLi (2.5 M, 0.13 mL, 0.32 mmol, 1.0 eq) were reacted according to **General Procedure 8**. Purification by column chromatography (silica, 4:1 petrol:ether, v/v) gave **94** as a colourless oil (103 mg, 97%); $[\alpha]_D^{22}$ +80.0 (*c* 0.4, $CHCl_3$); ν_{max}/cm^{-1} (film) 3443, 1643; δ_H (400MHz, $CDCl_3$) 1.14 (3H, d, *J* 6.1, CH*Me*), 2.71 (1H, dd, J_{AB} 12.5, J_{AX} 4.2, CHC*H*$_2$N), 2.76–2.82 (1H, m, COC*H*), 3.05 (1H, dd, J_{BA} 11.9, J_{BX} 10.9, CHC*H*$_2$N), 3.31 (2H, d, *J* 13.1, N(C*H*$_2$Ph)$_2$), 3.66 (3H, s, O*Me*), 3.79–3.86 (1H, m, C*H*OH), 3.91 (2H, d, *J* 13.1, N(C*H*$_2$Ph)$_2$), 7.27–7.38 (10H, m, *Ph*); δ_C (100MHz, $CDCl_3$) 21.7, 50.4, 52.1, 55.8, 59.0, 70.8, 127.9, 129.0, 129.7, 137.7, 173.3; *m/z* (ESI^+) 328 (MH^+, 100%); HRMS (ESI^+) 328.1912 ($C_{20}H_{26}NO_3$ requires 328.1913.

Methyl (2*S*,3*R*)-2-aminomethyl-3-hydroxybutanoate hydrochloride 95



β-Amino ester **94** (50 mg, 0.15 mmol, 1.0 eq) was treated with Pd (10% wt on C, 25mg) under H_2 (1atm) according to **General Procedure 7**. HCl (2M in ether, 0.09mL, 0.18mmol, 1.2eq) was added to the filtrate and the solvents removed *in vacuo*. Trituration with ether furnished **95** (28 mg, quant.) as a colourless, viscous oil; $[\alpha]_D^{23}$ –6.7 (*c* 0.85, MeOH) {lit.[15] $[\alpha]_D^{30}$ –7.0 (*c* 0.85, MeOH)}; δ_H (400MHz, $CDCl_3$) 1.28 (3H, d, *J* 6.3, CH*Me*), 2.73–2.77 (1H, m, COC*H*), 3.28–3.33 (2H, m, CHC*H*$_2$NH$_2$), 3.78 (3H, s, O*Me*), 4.19–4.25 (1H, m, C*H*OH).

[15] H. Ohtake, Y. Imada and S. I. Murahashi, *J. Org. Chem.*, 1999, **64**, 3790–3791.