Supplementary Material (ESI) for Organic and Biomolecular Chemistry

Supplementary Information

SuperQuat 5,5-Dimethyl-4-*iso*-propyl-oxazolidin-2-one as a Mimic of Evans 4-*tert*-Butyl oxazolidin-2-one

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General Procedure 1': *N*-Acylation of oxazolidin-2-ones[1]

To a stirred solution of oxazolidin-2-one (1.0 eq) in THF at –78°C, BuLi (1.01 eq) was added over 10 min. The corresponding acid chloride (1.1 eq) (or mixed anhydride made *in situ via* mixing the corresponding acid with pivaloyl chloride) was added and stirred for a further 30 min at –78°C. The reaction mixture was allowed to warm to rt over 30 min and quenched with NH_4Cl (sat, aq) and the organic material extracted with EtOAc. The combined organic layers were washed sequentially with $NaHCO_3$ (sat, aq) and brine then dried and concentrated *in vacuo* to afford the crude product. Purification *via* either recrystallisation or column chromatography on silica gave the required product.

General Procedure 2': Preparation of Esters

To a stirred solution of racemic secondary alcohol (1.0 eq), NEt_3 (1.1 eq) and DMAP (0.1 eq) in THF or DCM at rt, the corresponding acid chloride (1.0 eq) was added dropwise. The reaction mixture was heated to reflux overnight and then allowed to cool to rt and quenched with NH_4Cl (sat, aq). The organic material was extracted with DCM and the combined organic layers were dried and concentrated *in vacuo* to afford the crude product. Purification *via* column chromatography on silica furnished the required product.

General Procedure 3': Diels-Alder cycloadditions of α,β-unsaturated *N*-acyl oxazolidin-2-ones

To a stirred solution of oxazolidin-2-one (1.0 eq) and isoprene (1.0 mL/0.3 mmol of oxazolidin-2-one) in DCM at –78°C, Et_2AlCl (1.4 eq) was added *via* syringe. The reaction mixture was allowed to warm up to −30°C, stirred for 3 hr and quenched with HCl (1M, aq). The organic material was extracted with DCM and the combined organic layers were dried and concentrated *in vacuo* to afford the crude reaction product. Purification *via* column chromatography on silica furnished the required product.

General Procedure 4': *exo*-Cyclic *N*-acyl cleavageError! Bookmark not defined.

To a stirred solution of *N*-acyl oxazolidin-2-one (1.0 eq) in THF/H_2O (3.6:1.0) at 0°C H_2O_2 (8.0 eq) was added followed by LiOH (2.0 eq). The reaction mixture was allowed to warm up to rt and stirred for a further 15 hr before being cooled to 0°C after which it was treated with a solution of Na_2SO_3 (8.9 eq) in H_2O followed by $NaHCO_3$ (0.5M, aq) The THF was evaporated *in vacuo* and the aqueous layer was diluted with H_2O, organic material extracted with DCM and the combined organic layers dried and concentrated *in vacuo* to afford the crude oxazolidin-2-one. The remaining aqueous layer was then acidified to pH 1-2 with HCl (1M, aq) and extracted with EtOAc. The combined organic layers were dried. Evaporation of the solvent *in vacuo* gave the crude reaction product which was purified *via* column chromatography to afford the required acid product.

General Procedure 5': Preparation of Acid Chlorides[2]

To a stirred solution of acid (1.0 eq) and DMF (0.13 eq) in DCM at 0°C, oxalyl chloride (1.4 eq) was added dropwise. The reaction mixture was then allowed to warm up to rt slowly and stirred for 18 hr. Evaporation of the solvent and excess oxalyl chloride *in* vacuo gave the crude product which was used immediately without any further purification.

General Procedure 6': Palladium Catalysed Acetalisation of α,β-Unsaturated Compounds[3]

To a stirred slurry of α,β-unsaturated amide or ester (1.0 eq), $PdCl_2$ (0.1 eq) and CuCl (1.0 eq) in DME under an oxygen atmosphere, the corresponding alcohol was added *via* syringe. The reaction mixture was stirred at an indicated temperature for a given time and was filtered through Florisil®, eluting with Et_2O. Evaporation of the solvent *in vacuo* gave the crude product. Purification *via* column chromatography on silica gave the

required product.

(4*S*,2´*R*)-4-*iso*-Propyl-3-(2'-phenylpropionyl)oxazolidin-2-one 17 and (4*S*,2´S)-4-*iso*-propyl-3-(2'-phenylpropionyl)oxazolidin-2-one 18

Following general procedure 1', (*S*)-4-*iso*-propyl-oxazolidin-2-one (300 mg, 2.33 mmol), BuLi (1.02 mL, 2.5M in hexanes, 2.56 mmol) and (*RS*)-2-phenylpropionyl chloride (510 mg, 3.02 mmol) gave the crude reaction mixture of **17** and **18** in 57:43 ratio (14% de) as a yellow oil. Purification *via* column chromatography (EtOAc/hexanes 1:15) gave (4*S*,2´*S*)-**17** and (4*S*,2'*R*)-**18** as yellow oils with spectroscopic properties consistent with the literature.[4]

(4*S*,2'*R*)-4-*tert*-Butyl-3-(2'-phenylpropionyl)oxazolidin-2-one 19 and (4*S*,2'S)-4-*tert*-butyl-3-(2'-phenylpropionyl)oxazolidin-2-one 20

Following general procedure 1', (*S*)-4-*tert*-butyl-oxazolidin-2-one (100 mg, 0.70 mmol), BuLi (0.48 mL, 1.6M in hexanes, 0.77 mmol) and (*RS*)-2-phenylpropionyl chloride (150 mg, 0.91 mmol) gave the crude mixture of products **19** and **20** in 59:41 ratio (18% de) as a yellow oil. Purification *via* column chromatography (EtOAc/hexanes 1:13) gave (4*S*,2´*S*)-**19** and (4*S*,2´*R*)-**20** as yellow oils with spectroscopic properties consistent with the literature.[5]

(4*S*,2´*S*)-4-*iso*-Propyl-3-(2'-phenylpropionyl)-5,5-dimethyl-oxazolidin-2-one 21 and (4*S*,2´*R*)-4-*iso*-propyl-3-(2'-phenylpropionyl)-5,5-dimethyl-oxazolidin-2-one 22

Following general procedure 1', SuperQuat **13** (300 mg, 1.91 mmol), BuLi (0.84 mL, 2.5M in hexanes, 2.10 mmol) and (*RS*)-2-phenylpropionyl chloride (417 mg, 2.48 mmol) gave the crude reaction mixture in the ratio 55:45 (10% de) as a white solid. Purification *via* column chromatography (EtOAc/hexanes 1:15) gave (4*S*,2´*S*)-**21** (287 mg, 52%) and (4*S*,2´*R*)-**22** (228 mg, 41%) as white crystalline solids.

Data for (4*S*,2´*S*)-**21**: (Found: C, 70.5; H, 8.0; N, 4.9. $C_{17}H_{23}NO_3$ requires C, 70.6; H, 8.0; N, 4.8%); mp 107-108°C; $[\alpha]_D^{22}$ +103.0 (c 1.0 in $CHCl_3$); ν_{max} (film) 1763 ($C{=}O_{exo}$), 1691 ($C{=}O_{endo}$); δ_H (400 MHz, $CDCl_3$) 0.99 (3H, d, *J* 6.6, $CH(CH_3)_2$), 0.99 (3H, s, $C(CH_3)_2$), 1.08 (3H, d, *J* 6.8, $CH(CH_3)_2$), 1.44 (3H, s, $C(CH_3)_2$), 1.53 (3H, d, *J* 7.0, $CHCH_3$), 2.15 (1H, septd, *J* 6.9 and 3.3, $CH(CH_3)_2$), 4.02 (1H, d, *J* 3.4, CHN),

5.15 (1H, q, *J* 7.0, C*H*CH_3), 7.21-7.35 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 17.1, 19.4, 21.3, 21.5, 28.2, 29.5, 43.1, 67.2, 82.8, 127.2, 128.0, 128.5, 140.4, 153.3, 175.0; *m*/*z* ($APCI^+$) 290 (8%, MH^+), 158 (100).

Data for (4*S*,2′*R*)-**22**: (Found: C, 70.4; H, 8.1; N, 4.8. $C_{17}H_{23}NO_3$ requires C, 70.6; H, 8.0; N, 4.8%); mp 116-118°C; $[\alpha]_D^{22}$ −34.2 (c 1.0 in $CHCl_3$); ν_{max} (KBr) 1788 (C=O_{exo}), 1694 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.56 (3H, d, *J* 6.9, CH(CH_3)$_2$), 0.78 (3H, d, *J* 7.0, CH(CH_3)$_2$), 1.40 (3H, s, C(CH_3)$_2$), 1.45 (3H, s, C(CH_3)$_2$), 1.50 (3H, d, *J* 7.1, CHCH_3), 1.98 (1H, septd, *J* 6.9 and 2.6, C*H*$(CH_3)_2$), 4.23 (1H, d, *J* 3.0, C*H*N), 5.20 (1H, q, *J* 7.0, C*H*CH_3), 7.22-7.47 (5H, m, *Ph*); δ_C (50 MHz, $CDCl_3$) 16.1, 18.5, 21.2, 21.3, 28.9, 29.7, 43.0, 65.8, 82.4, 127.1, 128.3, 128.4, 140.5, 153.0, 175.2; *m*/*z* ($APCI^+$) 290 (63%, MH^+), 158 (100).

(*RS*)-1-Phenyl-ethan-1-yl benzoate 26

Following general procedure 2', (*RS*)-1-phenyl ethanol (0.43 mL, 3.52 mmol), NEt_3 (0.54 mL, 3.88 mmol), DMAP (43 mg, 0.35 mmol) and phenylacetyl chloride (540 mg, 3.52 mmol) in THF (14.0 mL) furnished the crude reaction mixture. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:8) gave **26** as a clear colourless oil (741 mg, 88%) with spectroscopic properties consistent with the literature.[6]

(*RS*)-1-Phenyl-propan-1-yl benzoate 30

Following the general procedure 2', (*RS*)-1-phenyl propan-1-ol **27** (0.49 mL, 3.52 mmol), NEt_3 (0.54 mL, 3.88 mmol), DMAP (43 mg, 0.35 mmol) and phenylacetyl chloride (540 mg, 3.52 mmol) in THF (14.0 mL) furnished the crude reaction mixture. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:8), gave **30** as a clear colourless oil (721 mg, 84%) with spectroscopic properties consistent with the literature.[7]

(*RS*)-2-Methyl-1-phenyl-propan-1-yl benzoate 31

Following general procedure 2', (*RS*)-2-methyl-1-phenyl-propan-l-ol **28** (0.49 mL, 3.52 mmol), NEt_3 (0.54 mL, 3.88 mmol), DMAP (43 mg, 0.35 mmol) and phenylacetyl chloride (540 mg, 3.52 mmol) in THF (14.0 mL) furnished the crude reaction mixture. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:8) gave **31** as a clear colourless oil (565 mg, 64%) with spectroscopic properties consistent with the literature.[8]

(*RS*)-1,2,3,4-Tetrahydro-naphth-1-yl benzoate 32

Following the general procedure 2', (*RS*)-1,2,3,4-tetrahydro-naphth-1-ol **29** (0.61 mL, 3.50 mmol), NEt_3 (0.54 mL, 3.88 mmol), DMAP (43 mg, 0.35 mmol) and phenylacetyl chloride (540 mg, 3.52 mmol) in THF (14.0 mL) furnished the crude reaction mixture. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:8) gave **32** as a clear colourless oil (431 mg, 43%), with spectroscopic properties consistent with the literature.[9]

(*RS*)-1-Phenylethan-1-yl 4'-methoxybenzoate 35

Following the general procedure 2', (*RS*)-1-phenyl ethanol **33** (0.43 mL, 3.52 mmol), NEt_3 (0.54 mL, 3.88 mmol), DMAP (43 mg, 0.35 mmol) and *p*-anisoyl chloride (600 mg, 3.52 mmol) in THF (14.0 mL) furnished the crude reaction mixture. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:8) gave **35** as a clear colourless oil (793 mg, 88%), with spectroscopic properties consistent with the literature.[10]

(*RS*)-1-Phenylpropan-1-yl 4'-methoxybenzoate 36

Following the general procedure 2', (*RS*)-1-phenyl-propan-1-ol **27** (0.48 mL, 3.52 mmol), NEt_3 (0.54 mL, 3.88 mmol), DMAP (43 mg, 0.35 mmol) and *p*-anisoyl chloride (600 mg, 3.52 mmol) in THF (14.0 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:8) gave **36** as a clear colourless oil (859 mg, 90%); ν_{max} (film) 1716 (C=O); δ_H (500 MHz, $CDCl_3$) 0.96-0.99 (3H, m, CH_2CH_3), 1.90-2.11 (2H, m, CH_2CH_3), 3.87 (3H, s, OCH_3), 5.91 (1H, t, *J* 6.8, $CHCH_2$), 6.93-6.95 (2H, m, C(3')*H* and C(5')*H*), 7.27-7.43 (5H, m, *Ph*), 8.05-8.08 (2H, m, C(2')*H* and C(6')*H*); δ_C (125 MHz, $CDCl_3$) 10.4, 30.0, 55.9, 77.4, 114.0, 123.5, 126.9, 128.2, 128.8, 132.1, 141.3, 163.8, 166.1; *m*/*z* (CI^+) 288 (100%, $[M+NH_4]^+$), 271 (16); (Found: MNH_4^+ 288.160. $C_{17}H_{22}NO_3$ requires 288.1594).

(*RS*)-2-Methyl-1-phenylpropan-1-yl 4'-methoxybenzoate 37

Following the general procedure 2', (*RS*)-2-methyl-1-phenyl-propan-1-ol **28** (0.55 mL, 3.52 mmol), NEt_3

(0.54 mL, 3.88 mmol), DMAP (43 mg, 0.35 mmol) and *p*-anisoyl chloride (600 mg, 3.52 mmol) in THF (14.0 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:8) gave **37** as a clear colourless oil (855 mg, 88%); ν_{max} (film) 1713 (C=O); δ_H (500 MHz, $CDCl_3$) 0.91 (3H, d, *J* 6.8, CH(C*H*$_3$)$_2$), 1.05 (3H, d, *J* 6.7, CH(C*H*$_3$)$_2$), 2.23-2.27 (1H, m, C*H*(CH$_3$)$_2$), 3.87 (3H, s, OC*H*$_3$), 5.72 (1H, d, *J* 7.1, C*H*CH(CH$_3$)$_2$), 6.93-6.95 (2H, m, C(3')*H* and C(5')*H*), 7.27-7.39 (5H, m, *Ph*), 8.05-8.07 (2H, m, C(2')*H* and C(6')*H*); δ_C (125 MHz, $CDCl_3$) 18.3, 18.7, 33.8, 55.3, 80.9, 113.5, 122.9, 126.8, 127.5, 128.0, 131.5, 139.8, 163.2, 165.4; *m*/*z* (CI^+) 302 (62%, $[M+NH_4]^+$), 285 (14); (Found: MNH_4^+ 302.1756. $C_{18}H_{24}NO_3$ requires 302.1751).

(*RS*)-1,2,3,4-Tetrahydro-naphth-1-yl 4'-methoxybenzoate 38

Following the general procedure 2', (*RS*)-1,2,3,4-tetrahydro-naphth-1-ol **29** (521 mg, 3.52 mmol), NEt_3 (0.54 mL, 3.88 mmol), DMAP (43 mg, 0.35 mmol) and *p*-anisoyl chloride (600 mg, 3.52 mmol) in THF (14.0 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:8) gave **38** as a clear colourless oil (752 mg, 76%); ν_{max} (film) 1707 (C=O); δ_H (500 MHz, $CDCl_3$) 1.87-1.92 (1H, m, C(3)*H*$_2$), 2.04-2.14 (3H, m, C(2)*H*$_2$ and C(3)*H*$_2$), 2.79-2.85 (1H, m, C(4)*H*$_2$), 2.91-2.96 (1H, m, C(4)*H*$_2$), 3.86 (OC*H*$_3$), 6.23-6.25 (1H, m, C(1)*H*), 6.90-6.92 (2H, m, C(3')*H* and C(5')*H*), 7.16-7.38 (4H, m, C(5)*H*, C(6)*H*, C(7)*H* and C(8)*H*), 8.01-8.03 (2H, m, C(2')*H* and C(6')*H*); δ_C (125 MHz, $CDCl_3$) 19.0, 29.0, 29.2, 55.3, 70.2, 113.4, 123.0, 125.9, 127.8, 128.9, 129.4, 131.6, 134.8, 137.9, 163.2, 165.9; *m*/*z* (CI^+) 300 (47%, $[M+NH_4]^+$); (Found: MNH_4^+ 300.1600. $C_{18}H_{22}NO_3$ requires 300.1588).

(*RS*)-4,6-Dimethylcyclohex-3-ene-1-carbonyl chloride

Following the general procedure 1', unsubstituted oxazolidin-2-one (2.50 g, 28.7 mmol), BuLi (11.5 mL, 2.5M in hexane, 28.8 mmol), and *trans*-crotonyl chloride (3.04 mL, 31.6 mmol) in THF (100 mL) gave the crude product as a yellow solid. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:10) gave 3-(but-2'-enoyl)-oxazolidin-2-one as a white solid (4.23 g, 95%) with spectroscopic properties consistent with the literature.[11]

Following the general procedure 3', 3-(but-2'-enoyl)-oxazolidin-2-one (1.97 g, 12.7 mmol), Et_2AlCl (9.87 mL, 1.8M in toluene, 17.8 mmol) and isoprene (42.3 mL) in DCM (42.3 mL) gave the crude product as a yellow solid. Purification *via* column chromatography on silica (EtOAc/pentane 1:6) gave 3-[(4',6'-dimethylcyclohex-3'-ene-1'-yl)carbonyl]-oxazolidin-2-one as a pale yellow solid (2.44 g, 86%); mp 44-52°C; ν_{max} (KBr) 1779 (C=O_{exo}), 1697 (C=O_{endo}); δ_H (500 MHz, $CDCl_3$) 0.96 (3H, d, *J* 6.3, C(2')HCH_3), 1.66 (3H, s, H(5')C=C(4')CH_3), 1.75-1.80 (1H, m, C(3')H_2), 2.00-2.09 (2H, m, C(2')*H* and C(3')H_2), 2.14-2.20 (1H, m, C(6')H_2), 2.26-2.30 (1H, m, C(6')H_2), 3.63-3.68 (1H, m, C(1')*H*), 4.04-4.08 (2H, m, NCH_2), 4.39-4.43 (2H, m, OCH_2) 5.36-5.37 (1H, m, *H*(5')C=C(4')CH_3); δ_C (125 MHz, $CDCl_3$) 19.4, 23.1, 29.2, 31.0, 38.0, 42.6, 43.8, 61.6, 118.6, 133.6, 153.1, 176.9; *m*/*z* (GC ToF MS^+) 224 (100%, $[M+H]^+$); (Found: $[M+H]^+$ 224.1287. $C_{12}H_{18}NO_3$ requires 224.1287).

Following the general procedure 4', 3-[(4',6'-dimethylcyclohex-3'-ene-1'-yl)carbonyl]-oxazolidin-2-one (1.00 g, 4.48 mmol), LiOH (215 mg, 8.96 mmol), H_2O_2 (3.17 mL, 35% w/w, 35.9 mmol) in THF (67.3 mL) and H_2O (18.8 mL) gave the crude product as a yellow solid. Purification *via* column chromatography on silica (EtOAc/pentane 1:6) gave the racemic *trans*-(4',6'-dimethylcyclohex-3'-ene-1'-yl)-carboxylic acid as a pale yellow solid (452 mg, 65%) with spectroscopic properties consistent with the literature.[12]

Following the general procedure 5', (4',6'-dimethylcyclohex-3'-ene-1'-yl)-carboxylic acid (252 mg, 1.64 mmol), DMF (0.02 mL, 0.16 mmol) and oxalyl chloride (0.21 mL, 2.46 mmol) in DCM (15.0 mL) gave the crude (4',6'-dimethylcyclohex-3'-ene-1'-yl)carbonyl chloride as a yellow residue. This crude product was used immediately without any further purification**.**

(4*S*,1'*S*,6'*S*)-3-[(4',6'-Dimethylcyclohex-3'-ene-1'-yl)carbonyl]-4-*iso*-propyl-oxazolidin-2-one 42 and (4*S*,1'*R*,6'*R*)-3-[(4',6'-dimethylcyclohex-3'-ene-1'-yl)carbonyl]-4-*iso*-propyl-oxazolidin-2-one

Following the general procedure 1', (*S*)-4-*iso*-propyl-oxazolidin-2-one (211 mg, 1.64 mmol), BuLi (0.66 mL, 2.5M in hexane, 1.65 mmol), and (4',6'-dimethylcyclohex-3'-ene-1'-yl)carbonyl chloride (281 mg, 1.64 mmol) in THF (15.0 mL) gave the crude product as a brown oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:22) furnished (4*S*,1'*S*,6'*S*)-**42** as a yellow solid (125 mg, 29%) and (4*S*,1'*R*,6'*R*) as a white solid (48 mg, 11%).

Data for (4*S*,1'*S*,6'*S*)-**42**: mp 64-65°C; $[\alpha]_D^{23}$ +171.7 (*c* 0.5 in $CHCl_3$); ν_{max} (KBr) 1762 (C=O*exo*), 1699 (C=O*endo*); δ_H (400 MHz, $CDCl_3$) 0.85-0.96 (9H, m, CH(C*H*$_3$)$_2$ and C(2')HC*H*$_3$), 1.64 (3H, s, H(5')C=C(4')C*H*$_3$), 1.70-1.78 (1H, m, C(3')*H*$_2$), 1.99-2.15 (3H, m, C(2')*H*, C(3')*H*$_2$ and C(6')*H*$_2$), 2.31-2.39 (1H, m, C(6')*H*$_2$), 3.59-3.66 (1H, m, C(1')*H*), 4.18-4.30 (2H, m, OC*H*$_2$), 4.46-4.51 (1H, m, NC*H*), 5.36 (1H, br s, *H*(5')C=C(4')CH$_3$); δ_C (100 MHz, $CDCl_3$) 14.6, 17.9, 19.6, 23.2, 28.4, 29.9, 30.4, 38.1, 44.3, 58.4, 63.1, 118.6, 133.6, 153.7, 176.5; *m*/*z* (ESI^+) 288 (100%, $[M+Na]^+$); (Found: $[M+H]^+$ 266.1759. $C_{15}H_{24}NO_3Na$ requires 266.1756).

Data for (4*S*,1'*R*,6'*R*)-diastereomer: (Found: C, 67.9; H, 8.6; N, 5.1. $C_{15}H_{23}NO_3$ requires C, 67.9; H, 8.7; N, 5.2%); mp 44.5-46.5°C; $[\alpha]_D^{23}$ −6.4 (*c* 1.0 in $CHCl_3$); ν_{max} (KBr) 1780 (C=O*exo*), 1697 (C=O*endo*); δ_H (400 MHz, $CDCl_3$) 0.89 (3H, d, *J* 6.9, CH(C*H*$_3$)$_2$), 0.92 (3H, d, *J* 6.8, CH(C*H*$_3$)$_2$), 0.97 (3H, d, *J* 6.5, C(2')HC*H*$_3$), 1.65 (3H, s, H(5')C=C(4')C*H*$_3$), 1.74-1.82 (1H, m, C(3')*H*$_2$), 1.98-2.25 (3H, m, C(2')*H*, C(3')*H*$_2$ and C(6')*H*$_2$), 2.36-2.45 (1H, m, C(6')*H*$_2$), 3.67-3.73 (1H, m, C(1')*H*), 4.18-4.28 (2H, m, OC*H*$_2$), 4.47-4.51 (1H, m, NC*H*), 5.36 (1H, br s, *H*(5')C=C(4')CH$_3$); δ_C (100 MHz, $CDCl_3$) 14.4, 18.0, 19.4, 23.3, 28.3, 29.1, 31.5, 38.0, 43.9, 58.6, 62.8, 118.8, 133.3, 153.8, 177.0; *m*/*z* (ESI^+) 288 (50%, MNa^+); (Found: MH^+ 266.1749. $C_{15}H_{24}NO_3$ requires 266.1756).

GC gave resolution of both diastereoisomers: BPX5 Column, 160°C 10 min, 4°C/min, 220°C 20min, (4*S*,1'*S*,6'*S*)-**42** t_R = 28.8 min and (4*S*,1'*R*,6'*R*)-diastereomer t_R = 30.0 min.

(4*S*,1'*S*,6'*S*)-3-[4',6'-Dimethyl-cyclohex-3'-ene-1'-yl)-carbonyl]-4-*tert*-butyl-oxazolidin-2-one 43 and (4*S*,1'*R*,6'*R*)-3-[4',6'-dimethyl-cyclohex-3'-ene-1'-yl)-carbonyl]-4-*tert*-butyl-oxazolidin-2-one

Following the general procedure 1', (*S*)-4-*tert*-butyl-oxazolidin-2-one (234 mg, 1.64 mmol), BuLi (0.66 mL, 2.5M in hexane, 1.65 mmol), and (4',6'-dimethylcyclohex-3'-ene-1'-yl)carbonyl chloride (281 mg, 1.64 mmol) in THF (15.0 mL) gave the crude product as a brown oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:22) gave (4*S*,1'*S*,6'*S*)-**43** as a yellow solid (173 mg, 38%) and (4*S*,1'*R*,6'*R*)-diastereomer as a white solid (59 mg, 13%).

Data for (4*S*,1'*S*,6'*S*)-**43**: mp 47-49°C; $[\alpha]_D^{23}$ +147.5 (*c* 1.0 in $CHCl_3$); ν_{max} (KBr) 1780 (C=O*exo*), 1702 (C=O*endo*); δ_H (400 MHz, $CDCl_3$) 0.92 (9H, s, C(C*H*$_3$)$_3$), 0.93 (3H, d, *J* 6.4, C(2')HC*H*$_3$), 1.65 (3H, s, H(5')C=C(4')C*H*$_3$), 1.71-1.78 (1H, m, C(3')*H*$_2$), 2.00-2.19 (3H, m, C(2')*H*, C(3')*H*$_2$ and C(6')*H*$_2$), 2.34-2.39

(1H, m, C(6')H_2), 3.62-3.69 (1H, m, C(1')*H*), 4.23 (1H, dd, *J* 9.2, 7.5, OCH_2), 4.28 (1H, dd, *J* 9.2, 1.5, OCH_2), 4.51 (1H, dd, *J* 7.4, 1.6, NC*H*), 5.38 (1H, br s, *H*(5')C=C(4')CH_3); δ_C (100 MHz, $CDCl_3$) 19.5, 23.2, 25.6, 30.3, 30.4, 35.8, 38.1, 44.3, 60.7, 65.1, 118.6, 133.7), 154.3, 176.4; *m*/*z* (ESI^+) 302 (23%, $[M+Na]^+$); (Found: $[M+H]^+$ 280.1909. $C_{16}H_{26}NO_3$ requires 280.1913).

Data for (4*S*,1'*R*,6'*R*)-diastereomer: mp 93.5-95°C; $[\alpha]_D^{23}$ −29.0 (*c* 0.5 in $CHCl_3$); ν_{max} (KBr) 1778 (C=O_{exo}), 1697 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.96 (9H, s, C(CH_3)$_3$, 1.04 (3H, d, *J* 6.4, C(2')HCH_3), 1.66 (3H, s, H(5')C=C(4')CH_3), 1.76-1.83 (1H, m, C(3')H_2), 2.01-2.22 (4H, m, C(2')*H*, C(3')H_2 and C(6')H_2), 3.64-3.70 (1H, m, C(1')*H*), 4.21 (1H, dd, *J* 9.2, 7.5, OCH_2), 4.28 (1H, dd, *J* 9.2, 1.4, OCH_2), 4.49 (1H, dd, *J* 7.5, 1.5, NC*H*), 5.35 (1H, br s, *H*(5')C=C(4')CH_3); δ_C (100 MHz, $CDCl_3$) 19.7, 23.3, 25.8, 29.2, 31.0, 35.7, 38.0, 44.0, 61.3, 65.0, 118.6, 133.4, 154.5, 176.7; *m*/*z* (ESI^+) 302 (78%, $[M+Na]^+$); (Found: $[M+H]^+$ 280.1916. $C_{16}H_{26}NO_3$ requires 280.1913).

GC gave resolution of both diastereoisomers: BPX5 Column, 160°C 10 min, 4°C/min, 220°C 20min, (4*S*,1'*S*,6'*S*)-**43** t_R = 30.2 min and (4*S*,1'*R*,6'*R*)-diastereomer t_R = 31.5 min.

(4*S*,1'*S*,6'*S*)-3-[(4',6'-Dimethylcyclohex-3'-ene-1'-yl)carbonyl]-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one 44 and (4*S*,1'*R*,6'*R*)-3-[4',6'-dimethylcyclohex-3'-ene-1'-yl)carbonyl]-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one 45

Following the general procedure 1', 4-(*S*)-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (257 mg, 1.64 mmol), BuLi (0.66 mL, 2.5M in hexane, 1.65 mmol), and (4',6'-dimethylcyclohex-3'-ene-1'-yl)carbonyl chloride (281 mg, 1.64 mmol) in THF (15.0 mL) gave the crude product as a brown oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:22) gave (4*S*,1'*S*,6'*S*)-**44** as a yellow solid (134 mg, 26%) and (4*S*,1'*R*,6'*R*)-**45** as a white solid (55 mg, 10%).

Data for (4*S*,1'*S*,6'*S*)-**44**: mp 65-67°C; $[\alpha]_D^{23}$ +117.8 (*c* 1.0 in $CHCl_3$); ν_{max} (KBr) 1772 (C=O_{exo}), 1698 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.93-0.95 (6H, m, CH(CH_3)$_2$ and C(2')HCH_3), 1.01 (3H, d, *J* 7.0, CH(CH_3)$_2$), 1.38 (3H, s, C(CH_3)$_2$), 1.51 (3H, s, C(CH_3)$_2$), 1.65 (3H, s, H(5')C=C(4')CH_3), 1.71-1.78 (1H, m, C(3')H_2), 1.99-2.21 (4H, m, C*H*(CH_3)$_2$, C(2')*H*, C(3')H_2 and C(6')H_2), 2.39-2.43 (1H, m, C(6')H_2), 3.63-3.70 (1H, m, C(1')*H*), 4.22 (1H, d, *J* 3.3, NC*H*), 5.39 (1H, br s, *H*(5')C=C(4')CH_3); δ_C (100 MHz, $CDCl_3$) 17.0, 19.6, 21.3, 21.6, 23.2, 28.6, 30.0, 30.2, 30.5, 38.0, 44.4, 66.1, 82.4, 118.8, 133.6, 153.3, 177.2; *m*/*z*

(ESI$^+$) 352 (100%, [M+MeCN+NH$_4$]$^+$), 316 (55, [M+Na]$^+$); (Found: [M+H]$^+$ 294.2070. $C_{17}H_{28}NO_3$ requires 294.2069).

Data for (4*S*,1'*R*,6'*R*)-**45**: mp 107.5-109°C; $[\alpha]_D^{23}$ −42.4 (*c* 0.5 in $CHCl_3$); ν_{max} (KBr) 1770 (C=O$_{exo}$), 1700 (C=O$_{endo}$); δ_H (400 MHz, $CDCl_3$) 0.98 (3H, d, *J* 6.8, CH(C*H*$_3$)$_2$), 1.03 (3H, d, *J* 6.4, C(2')HC*H*$_3$), 1.06 (3H, d, *J* 7.0, CH(C*H*$_3$)$_2$), 1.36 (3H, s, C(C*H*$_3$)$_2$), 1.51 (3H, s, C(C*H*$_3$)$_2$), 1.63 (3H, s, H(5')C=C(4')C*H*$_3$), 1.76-1.83 (1H, m, C(3')*H*$_2$), 2.01-2.23 (5H, m, C*H*(CH$_3$)$_2$, C(2')*H*, C(3')*H*$_2$ and C(6')*H*$_2$), 3.70-3.76 (1H, m, C(1')*H*), 4.20 (1H, d, *J* 3.0, NC*H*), 5.35 (1H, br s, *H*(5')C=C(4')CH$_3$); δ_C (100 MHz, $CDCl_3$) 17.0, 19.7, 21.3, 21.6, 23.3, 28.7, 29.4, 29.5, 30.9, 38.0, 44.0, 66.4, 82.4, 118.6, 133.6, 153.5, 177.3; *m*/*z* (ESI$^+$) 352 (100%, [M+MeCN+NH$_4$]$^+$), 316 (30, [M+Na]$^+$); (Found: [M+Na]$^+$ 316.1887. $C_{17}H_{27}NO_3Na$ requires 316.1889).

GC gave resolution of both diastereoisomers: BPX5 Column, 140°C 10 min, 4°C/min, 220°C 20min, (4*S*,1'*S*,6'*S*)-**44** t_R = 35.6 min and (4*S*,1'*R*,6'*R*)-**45** t_R = 36.2 min.

(*RS*)-(4-Methylcyclohex-3-ene-1-yl)carbonyl chloride

To a stirred solution of acrylic acid (17.2 mL, 0.25mol) and NEt_3 (35.0 mL, 0.25mol) in EtOAc(1.25L) at 0°C, acrolyl chloride (20.2 mL, 0.25mol) was added over 2 min and stirred for a further 40 min. The reaction mixture was allowed to warm up to room temperature, stirred for 30 min and then filtered. Evaporation of the solvent *in vacuo* gave a cloudy oil. The crude reaction mixture was dissolved in hexanes and the resulting suspension was filtered and concentrated *in vacuo* to furnish a colourless oil which was dissolved in THF (20 mL) and used immediately. To a stirred suspension of oxazolidin-2-one (17.4 g, 0.20mol) and LiCl (10.6 g, 0.25mol) in THF (80 mL) at room temperature, NEt_3 (35.0 mL, 0.25mol) was added followed by the acryloyl anhydride. The reaction mixture was then stirred for 4 hr. Evaporation of the solvent *in vacuo* gave white paste which was dissolved in HCl (1M, aq). The organic material was extracted with DCM and the combined organic layers were washed sequentially with $NaHCO_3$ (sat, aq) and brine and dried. Evaporation of the solvent *in vacuo* gave the crude product as a pale yellow oil, which after purification *via* column chromatography on silica (EtOAc/hexanes 1:3) gave the 3-(oxazolidin-2-one)- acryloamide as a white solid (20.9 g, 74%) with spectroscopic properties consistent with the literature.[13]

Following the general procedure 3', 3-(oxazolidin-2-one)-acryloamide (3.00 g, 21.3mol), Et_2AlCl (16.6 mL, 1.8M in toluene, 29.8mol) and isoprene (70.9 mL) in DCM (70.9 mL) gave the crude product as a yellow

solid. Purification *via* column chromatography on silica (EtOAc/pentane 1:6) gave the 3-[(4'-methylcyclohex-3'-ene-1'-yl)carbonyl]-oxazolidin-2-one as a slightly yellow solid (3.31 g, 74%) with spectroscopic properties consistent with the literature.[14]

Following the general procedure 4', 3-[(4'-methylcyclohex-3'-ene-1'-yl)carbonyl]-oxazolidin-2-one (2.50 g, 12.0 mmol), LiOH (573 mg, 23.9 mmol), H_2O_2 (8.46 mL, 35% w/w, 95.7 mmol) in THF (179 mL) and H_2O (50.2 mL) gave the crude product as a yellow solid. Purification *via* column chromatography on silica (EtOAc/pentane 1:6) gave the (4'-methylcyclohex-3'-ene-1'-yl)-carboxylic acid as a slightly yellow solid (1.05 g, 62%) with spectroscopic properties consistent with the literature.[15]

Following the general procedure 5', (4'-methylcyclohex-3'-ene-1'-yl)-carboxylic acid (500 mg, 3.57 mmol), DMF (0.04 mL, 0.46 mmol) and oxalyl chloride (0.37 mL, 4.29 mmol) in DCM (33.0 mL) gave the crude product as a yellow residue. This crude acid chloride was used immediately without any further purification.

(4*S*,1'*S*)-3-[(4'-Methylcyclohex-3-ene-1'-yl)carbonyl]-4-*iso*-propyl-oxazolidin-2-one 49 and (4*S*,1'*R*)-3-[(4'-methylcyclohex-3-ene-1'-yl)carbonyl]-4-*iso*-propyl-oxazolidin-2-one

Following the general procedure 1', (*S*)-4-*iso*-propyl-oxazolidin-2-one (74 mg, 0.57 mmol), BuLi (0.23 mL, 2.5M in hexane, 0.58 mmol), and (4'-methylcyclohex-3'-ene-1'-yl)carbonyl chloride (90 mg, 0.57 mmol) in THF (5.24 mL) gave the crude product as a brown oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:22) furnished an inseparable mixture of diastereoisomers (4*S*,1'*S*)-**49** and (4*S*,1'*R*)-diastereomer as a yellow oil (116 mg, 81%) with spectroscopic properties for (4*S*,1'*S*)-**49** consistent with the literature;[16] ν_{max} (KBr) 1780 (C=O_{exo}), 1699 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.87-0.93 (12H, m, CH(CH_3)$_2$), 1.67 (6H, br s, H(5')C=C(4')CH_3), 1.69-1.78 (2H, m, C(2')H_2), 1.88-2.20 (10H, m, C(2')H_2, C(3')*H*, C*H*(CH$_3$)$_2$, C(3')H_2 and C(6')H_2), 2.26-2.39 (2H, m, C(6')H_2), 3.66-3.73 (2H, m, C(1')*H*), 4.19-4.30 (4H, m, NC*H* and OCH_2), 4.45-4.48 (2H, m, OCH_2), 5.40 (2H, br s, *H*(5')C=C(4')CH$_3$); δ_C (100 MHz, $CDCl_3$) 14.6, 14.7, 17.9, 17.9, 23.4, 25.3, 26.7, 26.8, 28.2, 28.4, 29.4, 29.6, 38.4, 38.5, 58.4, 63.2, 119.0, 119.2, 133.8, 133.9, 153.7, 175.6, 176.6; *m*/*z* (ESI$^+$) 274 (100%, [M+Na]$^+$); (Found: [M+H]$^+$ 252.1592. $C_{14}H_{22}NO_3$ requires 252.1600).

Chiral GC gave resolution of both diastereoisomers: CYDEX-β Column, 40°C 10 min, 4°C/min, 140°C 240 min, (4*S*,1'*S*)-**49** t_R = 205.2 min and (4*S*,1'*R*)-diastereomer t_R = 209.5 min.

(4*S*,1'*S*)-3-[(4'-Methylcyclohex-3-ene-1'-yl)carbonyl]-4-*tert*-butyl-oxazolidin-2-one 50 and (4*S*,1'*R*)-3-[(4'-methylcyclohex-3-ene-1'-yl)carbonyl]-4-*tert*-butyl-oxazolidin-2-one

Following the general procedure 1', (*S*)-4-*tert*-butyl-oxazolidin-2-one (82 mg, 0.57 mmol), BuLi (0.23 mL, 2.5M in hexane, 0.58 mmol), and (4'-methylcyclohex-3'-ene-1'-yl)carbonyl chloride (90 mg, 0.57 mmol) in THF (5.24 mL) gave the crude product as a brown oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:22) furnished an inseparable mixture of diastereoisomers (4*S*,1'*S*)-**50** and (4*S*,1'*R*)-diastereomer as a yellow oil (121 mg, 80%); ν_{max} (KBr) 1778 (C=O_{exo}), 1703 (C=O_{endo}); δ_H (500 MHz, $CDCl_3$) 0.91 (9H, s, C(CH_3)$_3$), 0.92 (9H, s, C(CH_3)$_3$), 1.66 (6H, br s, H(5')C=C(4')CH_3), 1.61-1.78 (2H, m, C(2')H_2), 1.84-1.90 (1H, m, C(2')H_2), 1.96-2.22 (1H, br s, C(2')H_2), 2.00 (1H, br s, C(3')H_2), 2.09-2.23 (7H, m, CH(CH$_3$)$_2$, C(3')H_2 and C(6')H_2), 2.28-2.31 (1H, m, C(6')H_2), 2.34-2.40 (1H, m, C(6')H_2), 3.70-3.73 (2H, m, C(1')H), 4.18-4.19 (2H, m, NCH), 5.41 (2H, br s, H(5')C=C(4')CH$_3$); δ_C (125 MHz, $CDCl_3$) 23.4, 28.8, 25.6, 25.6, 26.1, 27.5, 29.0, 29.3, 35.8, 38.6, 38.6, 60.6, 60.6, 65.1, 65.2, 119.0, 119.2, 133.5, 134.0, 154.2, 154.2, 176.5, 176.6; *m*/*z* (ESI$^+$) 288 (100%, [M+Na]$^+$), 266 (49, [M+H]$^+$); (Found: [M+H]$^+$ 266.1755. $C_{15}H_{24}NO_3$ requires 266.1756).

Chiral GC gave resolution of both diastereoisomers: CYDEX-β Column, 40°C 10 min, 4°C/min, 140°C 280 min, (4*S*,1'*S*)-**50** t_R = 249.2 min and (4*S*,1'*R*)-diastereomer t_R = 257.1 min.

(4*S*,1'*S*)-3-[(4'-Methylcyclohex-3-ene-1'-yl)carbonyl]-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one 51 and (4*S*,1'*R*)-3-[(4'-Methylcyclohex-3-ene-1'-yl)carbonyl]-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one

Following the general procedure 1', 4-(*S*)-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (561 mg, 3.57 mmol), BuLi (1.44 mL, 2.5M in hexane, 3.61 mmol), and (4'-methylcyclohex-3'-ene-1'-yl)carbonyl chloride (564 mg, 3.57 mmol) in THF (32.8 mL) gave the crude product as a brown oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:22) furnished an inseparable mixture of diastereoisomers (4*S*,1'*S*)-**51** and (4*S*,1'*R*)-diastereomer as a yellow solid (840 mg, 84%); mp 38-42°C; ν_{max} (KBr) 1773 (C=O_{exo}), 1700 (C=O_{endo}); δ_H (500 MHz, $CDCl_3$) 0.94-0.97 (6H, m, CH(CH_3)$_2$), 1.01 (3H, d, *J* 6.9, CH(CH_3)$_{2(\mathbf{51})}$), 1.02 (3H, d, *J* 6.9, CH(CH_3)$_2$), 1.38 (3H, s, C(CH_3)$_2$), 1.39 (3H, s, C(CH_3)$_{2(\mathbf{51})}$), 1.51 (6H, s, C(CH_3)$_2$), 1.67 (6H, s, H(5')C=C(4')CH_3), 1.68-1.76 (2H, m, C(2')H_2), 1.87-1.88 (1H, m, C(2')H_2), 1.96

(1H, br s, C(2')H_2), 2.00 (1H, br s, C(3')H_2), 2.09-2.23 (7H, m, CH(CH_3)$_2$, C(3')H_2 and C(6')H_2), 2.28-2.31 (1H, m, C(6')H_2), 2.34-2.40 (1H, m, C(6')H_2), 3.70-3.73 (2H, m, C(1')H), 4.18-4.19 (2H, m, NCH), 5.41 (2H, br s, H(5')C=C(4')CH_3); δ_C (125 MHz, $CDCl_3$) 16.8, 16.9, 21.2, 21.3, 21.4, 23.3, 25.2, 25.5, 26.8, 26.9, 28.7, 28.7, 29.3, 29.5, 29.5, 29.6, 38.4, 66.0, 82.5, 119.0, 133.5, 133.7, 153.1, 176.9; *m/z* (ESI^+) 338 (100%, $[M+MeCN+NH_4]^+$), 302 (98, $[M+Na]^+$), 280 (90, $[M+H]^+$); (Found: $[M+H]^+$ 280.1914. $C_{16}H_{26}NO_3$ requires 280.1913).

Chiral GC gave resolution of both diastereoisomers: CYDEX-β Column, 40°C 10 min, 4°C/min, 140°C 280 min, (4*S*,1'*S*)-**51** t_R = 246.2 min and (4*S*,1'*R*)-diastereomer t_R = 254.1 min.

Racemic compounds *endo*-3-methylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride and *exo*-3-methylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

Following a literature procedure,[17] a mixture of *trans*-crotonic acid (12.1 g, 14.1 mmol) and freshly distilled cyclopentadiene (176 g, 2.60mol) was stirred at 50°C for 48 hr. The reaction was allowed to cool to room temperature and was partitioned between Et_2O and $NaHCO_3$ (sat, aq), the organic layer discarded and the aqueous layer was acidified with HCl (1M, aq) to pH 1. The organic material was extracted from the aqueous layer with Et_2O, and the combined organic layers were dried and concentrated *in vacuo* to afford the crude reaction product as a yellow solid. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:10) gave an inseparable 1.3:1.0 (*endo*:*exo*) mixture of Diels-Alder products as a white solid (10.7 g, 50%) with spectroscopic properties consistent with the literature.[18]

The *endo:exo* mixture was separated *via* formation of racemic 6-hydroxy-5-iodo-3-methylbicyclo[2.2.1]heptane-2-carboxylic acid lactone made from the *endo* product;

To a stirred solution of *endo*- and *exo*-3-methylbicyclo[2.2.1]hept-5-ene-2-carboxylic acids (3.00 g, 19.7 mmol) in 2:1 (v/v) $NaHCO_3$ (5%, aq)/THF (103 mL) potassium iodide (11.3 g, 69.0 mmol) was added followed by iodine (17.5 g, 69.0 mmol). After 8 hr the reaction mixture was partitioned between Et_2O and $NaHCO_3$ (sat, aq) organic material was re-extracted from the aqueous layer with Et_2O and the combined organic layers washed with $Na_2S_2O_3$ (sat, aq) and dried. (Aqueous layer contains *exo*-product). Evaporation of the solvent *in vacuo* gave the crude reaction product as a light brown oil, which after purification *via*

column chromatography on silica (EtOAc/30-40 petroleum ether 1:10) gave the lactone as a brown oil (2.58 g, 47%) with spectroscopic properties consistent with the literature.[19]

The aqueous layer was acidified to pH 1 with HCl (1M, aq) and the organic material was extracted with Et_2O. The combined organic layers were washed with $Na_2S_2O_3$ (sat, aq) and dried. Evaporation of the solvent *in vacuo* gave the crude reaction product as a light brown solid. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:10) gave the *exo*-3-methylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid as a pale yellow solid (664 mg, 22%) with spectroscopic properties consistent with the literature.[20]

6-Hydroxy-5-iodo-3-methylbicyclo[2.2.1]heptane-2-carboxylic acid lactone (8.00 g, 28.8 mmol) was dissolved in acetic acid (222 mL) and activated zinc metal (8.43 g, 0.13mol) was added. After 30 min, the reaction mixture was partitioned between H_2O and EtOAc, the aqueous layer acidified to pH 1 with HCl (1M, aq) and the organic material extracted with EtOAc. The combined organic layers were dried. Evaporation of the solvent *in vacuo* gave the crude reaction product. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:10) gave the *endo*-3-methylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid as a pale yellow solid (3.82 g, 87%) with spectroscopic properties consistent with the literature.[21]

endo-3-Methylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride[22]

To a stirred solution of 3-methylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid (500 mg, 3.29 mmol) and pyridine (1 drop) in benzene (8.97 mL) at room temperature, oxalyl chloride (0.52 mL, 5.98 mmol) was added dropwise and stirred for 15 hr. Evaporation of the solvent and excess oxalyl chloride *in vacuo* gave the crude product as a yellow residue. The crude product was used immediately without any further purification.

exo-3-Methylbicyclo[2.2.1]heptene-2-carbonyl chloride

Following the general procedure 5', *exo*-3-methylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid (500 mg, 3.29 mmol) and thionyl chloride (0.07 mL, 4.61 mmol) furnished the crude reaction product as a pale yellow oil. The crude product was used immediately without any further purification.

(4*S*,1'*R*,2'*R*,*3'S*,4'*S*)-3-[(3'-Methylbicyclo[2.2.1]hept-5'-ene-2'-yl)carbonyl]-4-*iso*-propyl-oxazolidin-2-one (*endo* I)-55 and (4*S*,1'*S*,2'*S*,*3'R*,4'*R*)-3'-[(3'-methylbicyclo[2.2.1]hept-5-ene-2'-yl)carbonyl]-4-*iso*-propyl-oxazolidin-2-one

(*endo* II)

Following the general procedure 1', (*S*)-4-*iso*-propyl-oxazolidin-2-one (424 mg, 3.29 mmol), BuLi (1.33 mL, 2.5M in hexane, 3.32 mmol), and *endo*-3-methylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (559 mg, 3.29 mmol) in THF (30.0 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:18) gave an inseparable mixture of (*endo* I)-**55** and (*endo* II) as a clear colourless oil (464 mg, 54%) with spectroscopic properties consistent with the literature.[23]

(4*S*,1'*S*,2'*R*,*3'S*,4'*R*)-3-[(3'-Methylbicyclo[2.2.1]hept-5-ene-2'-yl)carbonyl]-4-*iso*-propyl-oxazolidin-2-one (*exo* I) and (4*S*,1'*R*,2'*S*,*3'R*,4'*S*)-3-[(3'-methylbicyclo[2.2.1]hept-5-ene-2'-yl)carbonyl]-4-*iso*-propyl-oxazolidin-2-one (*exo* II)

Following the general procedure 1', (*S*)-4-*iso*-propyl-oxazolidin-2-one (424 mg, 3.29 mmol), BuLi (1.33 mL, 2.5M in hexane, 3.32 mmol), and *exo*-3-methylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (559 mg, 3.29 mmol) in THF (30.0 mL) gave the crude product as a brown oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:18) furnished an inseparable mixture of (*exo* I) and (*exo* II) as a yellow solid (513 mg, 59%) with spectroscopic properties consistent with the literature.[24]

(4*S*,1'*R*,2'*R*,*3'S*,4'*S*)-3-[(3'-Methylbicyclo[2.2.1]hept-5-ene-2'-yl)carbonyl]-4-*tert*-butyl-oxazolidin-2-one (*endo* I)-56 and (4*S*,1'*S*,2'*S*,*3'R*,4'*R*)-3-[(3'-methylbicyclo[2.2.1]hept-5-ene-2'-yl)carbonyl]-4-*tert*-butyl-oxazolidin-2-one (*endo* II)

Following the general procedure 1', (*S*)-4-*tert*-butyl-oxazolidin-2-one (470 mg, 3.29 mmol), BuLi (1.33 mL, 2.5M in hexane, 3.32 mmol), and *endo*-3-methylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (559 mg, 3.29 mmol) in THF (30.0 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:18) furnished an inseparable mixture of (*endo* I)-**56**

and (*endo* II) as a white solid (668 mg, 73%); mp 78-110°C; ν_{max} (KBr) 1779 (C=O_{exo}), 1703 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.90 (9H, s, C(CH_3)$_3$), 0.91 (9H, s, C(CH_3)$_3$), 1.11 (3H, d, *J* 7.0, CHC$H_{3(\mathbf{56})}$), 1.17 (3H, d, *J* 7.1, CHCH_{3B}), 1.44-1.50 (2H, m, C(7')H_2), 1.68 (1H, d, *J* 8.7, C(7')H_2), 1.73 (1H, d, *J* 8.6, C(7')H_2), 1.97-2.13 (2H, m, C(3')*H*), 2.52 (2H, br s, C(4')*H*), 3.16 (1H, br s, C(1')$H_{(endo\ II)}$), 3.42 (1H, br s, C(1')$H_{(\mathbf{56})}$), 3.53 (1H, dd, *J* 4.5, 3.4, C(2')$H_{(\mathbf{56})}$), 3.65 (1H, dd, *J* 4.7, 3.3, C(2')$H_{(endo\ II)}$), 4.20-4.29 (4H, m, OCH_2), 4.39-4.44 (2H, m, **N**CH), 5.80-5.84 (2H, m, C(6')*H*), 6.35 (1H, dd, *J* 5.5, 3.2, C(5')*H*), 6.39 (1H, dd, *J* 5.5, 3.2, C(5')*H*); δ_C (100 MHz, $CDCl_3$) 20.4, 20.5, 25.6, 25.7, 35.6, 35.7, 35.8, 39.0, 47.0, 47.2, 47.4, 48.3, 49.3, 49.6, 51.0, 51.7, 60.9, 61.2, 64.9, 65.2, 131.0, 131.3, 139.1, 139.8, 154.6, 174.1, 174.7; *m*/*z* (ESI^+) 336 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+H]^+$ 278.1750. $C_{16}H_{24}NO_3$ requires 278.1756).

(4*S*,1'*S*,2'*R*,*3'S*,4'*R*)-3-[(3'-Methylbicyclo[2.2.1]hept-5-ene-2'-yl)carbonyl]-4-*tert*-butyl-oxazolidin-2-one (*exo* I) and (4*S*,1'*R*,2'*S*,*3'R*,4'*S*)-3-[(3'-methylbicyclo[2.2.1]hept-5-ene-2'-yl)carbonyl]-4-*tert*-butyl-oxazolidin-2-one (*exo* II)

Following the general procedure 1', (*S*)-4-*tert*-butyl-oxazolidin-2-one (470 mg, 3.29 mmol), BuLi (1.33 mL, 2.5M in hexane, 3.32 mmol), and *exo*-3-methylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (559 mg, 3.29 mmol) in THF (30.0 mL) furnished the crude product as a brown oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:18) gave an inseparable mixture of (*exo* I) and (*exo* II) as a pale yellow solid (302 mg, 33%); mp 76-88°C; ν_{max} (KBr) 1780 (C=O_{exo}), 1690 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.82 (3H, d, *J* 6.8, CHC$H_{3(exo\ I)}$), 0.91-0.93 (21H, m, C(CH_3)$_3$ and CHCH_3), 1.38 (2H, d, *J* 8.4, C(7')H_2), 1.57 (1H, d, *J* 8.4, C(7')H_2), 1.72 (1H, d, *J* 8.5, C(7')H_2), 2.53-2.60 (1H, m, C(2')$H_{(exo\ II)}$), 2.75 (2H, br s, C(1')*H*), 2.76-2.79 (1H, m, C(2')$H_{(exo\ I)}$), 2.81 (1H, br s, C(4')*H*), 2.84 (1H, d, *J* 4.7, C(3')$H_{(exo\text{-}I)}$), 2.97-2.99 (2H, m, C(4')$H_{(exo\ II)}$ and C(3')$H_{(exo\ II)}$), 4.21-4.29 (4H, m, OCH_2), 4.46-4.50 (2H, m, NC*H*), 6.13-6.16 (2H, m, C(6')*H*), 6.28 (1H, dd, *J* 5.6, 3.2, C(5')*H*), 6.36 (1H, dd, *J* 5.6, 3.2, C(5')*H*); δ_C (100 MHz, $CDCl_3$) 18.7, 18.8, 25.5, 25.6, 35.8, 35.9, 36.0, 39.4, 46.6, 46.9, 47.5, 47.6, 48.8, 50.2, 50.3, 51.8, 60.9, 64.9, 65.1, 135.3, 135.5, 136.8, 137.1, 154.4, 154.5, 174.8, 176.1; *m*/*z* (ESI^+) 336 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+H]^+$ 278.1759. $C_{16}H_{24}NO_3$ requires 278.1756).

(4*S*,1'*R*,2'*R*,*3'S*,4'*S*)-3-[(3'-Methylbicyclo[2.2.1]hept-5-ene-2'-yl)carbonyl]-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (*endo* I)-57 and (4*S*,1'*S*,2'*S*,*3'R*,4'*R*)-3-[(3'-methylbicyclo[2.2.1]hept-5-ene-2'-yl)carbonyl]-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (*endo* II)

Following the general procedure 1', 4-(*S*)-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (516 mg, 3.29 mmol), BuLi (1.33 mL, 2.5M in hexane, 3.32 mmol), and *endo*-3-methylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (559 mg, 3.29 mmol) in THF (30.0 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:18) gave an inseparable mixture of (*endo* I)-**57** and (*endo* II) as a white amorphous solid (758 mg, 79%); mp 88-130°C; ν_{max} (KBr) 1786 (C=O_{exo}), 1693 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.93 (3H, d, *J* 6.9, CH(CH_3)$_2$), 0.95-0.98 (6H, m, CH(CH_3)$_2$), 0.99 (3H, d, *J* 7.0, CH(CH_3)$_2$), 1.11 (3H, d, *J* 6.9, CHCH_3), 1.16 (3H, d, *J* 7.1, CHCH_3), 1.37 (6H, s, C(CH_3)$_2$), 1.43-1.47 (2H, m, C(7')H_2), 1.50 (6H, s, C(CH_3)$_2$), 1.69-1.74 (2H, m, C(7')H_2), 2.05-2.17 (4H, m, CH(CH_3)$_2$ and C(3')*H*), 2.53 (2H, br s, C(4')*H*), 2.52 (1H, br s, C(1')$H_{(57)}$), 3.17 (1H, br s, C(1')$H_{(endo\ II)}$), 3.53 (1H, dd, *J* 4.4, 3.5, C(2')$H_{(endo\ II)}$), 3.67 (1H, dd, *J* 4.4, 3.4, C(2')$H_{(57)}$), 4.04 (1H, d, *J* 3.4, NC*H*), 4.16 (1H, d, *J* 2.9, NC*H*), 5.77 (1H, dd, *J* 5.6, 2.8, C(6')$H_{(57)}$), 5.81 (1H, dd, *J* 5.7, 2.7, C(6')$H_{(endo\ II)}$) 6.35-6.40 (2H, m, C(5')$H_{(57)}$ and C(5')$H_{(endo\ II)}$); δ_C (100 MHz, $CDCl_3$) 16.9, 17.1, 20.4 20.5, 21.3, 21.4, 21.5, 28.7, 28.9, 29.4, 29.7, 29.8, 35.7, 36.9, 47.1, 47.2, 47.3, 48.2, 49.4, 49.5, 51.0, 51.9, 66.1, 67.0, 82.4, 130.8, 131.0, 139.6, 139.8, 153.4, 153.7, 174.6, 174.7; *m*/*z* (ESI$^+$) 350 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+H]^+$ 292.1908. $C_{17}H_{26}NO_3$ requires 292.1913).

(4*S*,1'*S*,2'*R*,*3'S*,4'*R*)-3-[(3'-Methylbicyclo[2.2.1]hept-5-ene-2'-yl)carbonyl]-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (*exo* I) and (4*S*,1'*R*,2'*S*,*3'R*,4'*S*)-3-[(3'-methylbicyclo[2.2.1]hept-5-ene-2'-yl)carbonyl]-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (*exo* II)

Following the general procedure 1', 4-(*S*)-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (516 mg, 3.29 mmol), BuLi (1.33 mL, 2.5M in hexane, 3.32 mmol), and *exo*-3-methylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (559 mg, 3.29 mmol) in THF (30.0 mL) furnished the crude product as a brown oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:18) gave an inseparable mixture of (*exo* I) and (*exo* II) as a slightly oily yellow solid (668 mg, 70%); mp 58-66°C; ν_{max} (KBr) 1773 (C=O_{exo}), 1696 (C=O_{endo});

δ_H (400 MHz, $CDCl_3$) 0.84 (3H, d, *J* 6.6, CH(CH_3)$_2$), 0.91-1.03 (15H, m, CH(CH_3)$_2$ and CHCH_3), 1.35-1.43 (2H, m, C(7')H_2), 1.39 (3H, s, C(CH_3)$_2$), 1.40 (3H, s, C(CH_3)$_2$), 1.51 (6H, s, C(CH_3)$_2$), 1.63 (1H, d, *J* 8.5, C(7')H_2), 1.72 (1H, d, *J* 8.4, C(7')H_2), 2.09-2.20 (3H, m, C*H*(CH_3)$_2$ and C(2')*H*), 2.58-2.66 (1H, m, C(2')*H*), 2.74 (2H, br s, C(1')*H*), 2.79 (1H, br s, C(4')$H_{(exo\ II)}$), 2.85-2.86 (1H, m, C(3')$H_{(exo\ I)}$), 3.00 (1H, br s, C(4')$H_{(exo\ I)}$), 3.04 (1H, dd, *J* 5.0, 1.1, C(3')$H_{(exo\ II)}$), 4.18 (1H, d, *J* 3.3, NC*H*), 4.19 (1H, d, *J* 3.4, NC*H*), 6.14-6.17 (2H, m, C(6')*H*), 6.30 (1H, dd, *J* 5.6, 3.2, C(5')$H_{(exo\ II)}$), 6.37 (1H, dd, *J* 5.5, 3.1, C(5')$H_{(exo\ I)}$); δ_C (100 MHz, $CDCl_3$) 17.0, 17.1, 18.8, 18.9, 21.4, 21.5, 21.6, 28.8, 29.0, 29.4, 29.5, 29.7, 36.6, 38.7, 46.5, 46.9, 47.5, 47.6, 49.2, 50.1, 50.3, 51.4, 66.3, 66.4, 82.3, 82.5, 135.4, 135.5, 136.9, 137.0, 153.4, 153.5, 175.6, 176.4; *m/z* (ESI$^+$) 350 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+H]^+$ 292.1907. $C_{17}H_{26}NO_3$ requires 292.1913).

Racemic compounds *endo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride and *exo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride

Following a literature procedure,[25] a reaction mixture of *trans*-cinammic acid (20.0 g, 0.14mol) and freshly distilled cyclopentadiene (300 g, 4.55mol) was stirred at 50°C for 48 hr after which it was allowed to cool to room temperature and partitioned between Et_2O and $NaHCO_3$ (sat, aq). The organic layer was discarded and the aqueous layer was acidified with HCl (1M, aq) to pH 1, partitioned between Et_2O and H_2O and the combined organic layers dried and concentrated *in vacuo* to afford the crude reaction product as a yellow solid. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:10) gave an inseparable 1.0:1.4 (*endo*:*exo*) mixture 3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid as a pale yellow solid (16.1 g, 56%) with spectroscopic properties consistent with the literature.[26]

The *endo:exo* mixture was separated *via* formation of racemic 6-hydroxy-5-iodo-3-phenylbicyclo[2.2.1]heptane-2-carboxylic acid lactone made from the *endo* product

To a stirred solution of *endo*- and *exo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylic acids (15.0 g, 0.07mol) in 2:1 (v/v) $NaHCO_3$ (5%, aq)/THF (369 mL) potassium iodide (40.4 g, 0.24mol) was added followed by iodine (61.8 g, 0.24 mmol). After 8 hr the reaction mixture was partitioned between Et_2O and $NaHCO_3$ (sat, aq), the organic material extracted from the aqueous layer with Et_2O, combined organic layers washed with $Na_2S_2O_3$ (sat, aq) and dried. (Aqueous layer contains the *exo*-product). Evaporation of the

solvent *in vacuo* gave the crude reaction product as a light brown oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:10) gave the racemic 6-hydroxy-5-iodo-3-phenylbicyclo[2.2.1]heptane-2-carboxylic acid lactone as a light brown solid (9.91 g, 42%) with spectroscopic properties consistent with the literature.[27]

The aqueous layer was acidified to pH1 with HCl (1M, aq) and the organic material was extracted with Et_2O. The combined organic layers were washed with $Na_2S_2O_3$ (sat, aq) and dried. Evaporation of the solvent *in vacuo* gave the crude reaction product as a light brown solid. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:10) gave the *exo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid as a pale yellow solid (5.95 g, 40%) with spectroscopic properties consistent with the literature.[28]

To a solution of 6-hydroxy-5-iodo-3-phenylbicyclo[2.2.1]heptane-2-carboxylic acid lactone (9.80 g, 28.8 mmol) dissolved in acetic acid (222 mL), activated zinc metal (8.43 g, 0.13mol) was added. After 30 min, the reaction mixture was partitioned between H_2O and EtOAc and the aqueous layer acidified to pH 1 with HCl (1M, aq) and the organic material was extracted with EtOAc. The combined organic layers were dried and concentrated *in vacuo* to furnish the crude reaction product. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:10) gave the *endo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid as a pale yellow solid (4.01 g, 65%) with spectroscopic properties consistent with the literature.[29]

Following the general procedure 5', *endo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid (500 mg, 2.34 mmol) pyridine (1 drop) in benzene (6.37 mL) and oxalyl chloride (0.37 mL, 4.21 mmol) gave the *endo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride as a yellow residue. The crude product was used immediately without any further purification.

Following the general procedure 5', *exo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carboxylic acid (500 mg, 3.29 mmol) and thionyl chloride (0.06 mL, 4.61 mmol) in benzene (7 mL) furnished the *exo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride as a pale yellow oil. The crude product was used immediately without any further purification.

(4*S*,1'*R*,2'*R*,*3'S*,4'*S*)-3-[(3'-Phenylbicyclo[2.2.1]hept-5'-ene-2'-yl)-carbonyl]-4-*iso*-propyl-oxazolidin-2-one (*endo* I)-58 and (4*S*,1'*S*,2'*S*,*3'R*,4'*R*)-3-[(3'-phenylbicyclo[2.2.1]hept-5'-ene-2'-yl)-carbonyl]-4-*iso*-

propyl-oxazolidin-2-one

(*endo* II)

Following the general procedure 1', (*S*)-4-*iso*-propyl-oxazolidin-2-one (301 mg, 2.34 mmol), BuLi (1.47 mL, 1.6M in hexane, 2.36 mmol), and *endo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (542 mg, 2.34 mmol) in THF (21.0 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:18) gave (*endo* I)-**58** (330 mg, 44%) as a white solid and (*endo* II) (295 mg, 39%) as a colourless oil with spectroscopic properties consistent with the literature.[30]

(4*S*,1'*S*,2'*R*,*3'S*,4'*R*)-3-[(3'-Phenylbicyclo[2.2.1]hept-5'-ene-2'-yl)carbonyl]-4-*iso*-propyl-oxazolidin-2-one (*exo* I) and (4*S*,1'*R*,2'*S*,*3'R*,4'*S*)-3-[(3'-phenylbicyclo[2.2.1]hept-5'-ene-2'-yl)carbonyl]-4-*iso*-propyl-oxazolidin-2-one

(*exo* II)

Following the general procedure 1', (*S*)-4-*iso*-propyl-oxazolidin-2-one (301 mg, 2.34 mmol), BuLi (1.47 mL, 1.6M in hexane, 2.36 mmol), and *exo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (542 mg, 2.34 mmol) in THF (21.0 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:18) gave (*exo* I) (212 mg, 28%) as a colourless oil and (*exo* II) (101 mg, 13%) as a white solid with spectroscopic properties consistent with the literature.[31]

(4*S*,1'*R*,2'*R*,*3'S*,4'*S*)-3-[(3'-Phenylbicyclo[2.2.1]hept-5'-ene-2'-yl)carbonyl]-4-*tert*-butyl-oxazolidin-2-one (*endo* I)-59 and (4*S*,1'*S*,2'*S*,*3'R*,4'*R*)-3-[(3'-phenylbicyclo[2.2.1]hept-5'-ene-2'-yl)carbonyl]-4-*tert*-butyl-oxazolidin-2-one

(*endo* II)

Following the general procedure 1', (*S*)-4-*tert*-butyl-oxazolidin-2-one (334 mg, 2.34 mmol), BuLi (1.47 mL, 1.6M in hexane, 2.36 mmol), and *endo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (542 mg, 2.34 mmol) in THF (21.0 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:18) gave (*endo* I)-**59** as a pale yellow oil and (*endo* II) as a white solid; (*endo* I)-**59** (366 mg, 46%); $[\alpha]_D^{23}$ +172.0 (*c* 1.0 in $CHCl_3$); ν_{max} (film) 1779 ($C{=}O_{exo}$),

1702 (C=O*endo*); δ_H (400 MHz, $CDCl_3$) 0.95 (9H, s, C(C*H*$_3$)$_3$), 1.63 (1H, dd, *J* 8.7, 1.3, C(7')*H*$_2$), 2.02 (1H, d, *J* 8.6, C(7')*H*$_2$), 2.98 (1H, br s, C(1')*H*), 3.35-3.36 (1H, m, C(2')*H*), 3.64 (1H, br s, C(4')*H*), 4.19-4.23 (2H, m, OC*H*$_2$ and C(3')*H*), 4.28 (1H, dd, *J* 9.2, 1.3, OC*H*$_2$), 4.45 (1H, dd, *J* 7.6, 1.3, NC*H*), 5.97 (1H, dd, *J* 5.6, 2.7, C(5')*H*), 6.56 (1H, dd, *J* 5.4, 3.2, C(6')*H*), 7.18-7.32 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 25.7, 35.7, 46.4, 48.2, 48.4, 49.7, 50.7, 61.0, 65.2, 126.1, 127.6, 128.5, 132.3, 140.3, 143.9, 154.5, 173.6; *m*/*z* (ESI^+) 398 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+H]^+$ 340.1906. $C_{21}H_{26}NO_3$ requires 340.1913).

(*endo* II) (309 mg, 39%); mp 78-80°C; $[\alpha]_D^{25}$ −123.8 (*c* 1.0 in $CHCl_3$); ν_{max} (KBr) 1777 (C=O*exo*), 1702 (C=O*endo*); δ_H (400 MHz, $CDCl_3$) 0.90 (9H, s, C(C*H*$_3$)$_3$), 1.60 (1H, dd, *J* 8.7, 1.6, C(7')*H*$_2$), 1.95 (1H, d, *J* 8.6, C(7')*H*$_2$), 3.06 (1H, br s, C(1')*H*), 3.31-3.32 (1H, m, C(2')*H*), 3.36 (1H, br s, C(4')*H*), 4.22-4.30 (3H, m, OC*H*$_2$ and C(3')*H*), 4.42-4.44 (1H, m, NC*H*), 5.94 (1H, dd, *J* 5.6, 2.8, C(5')*H*), 6.54 (1H, dd, *J* 5.5, 3.2, C(6')*H*), 7.19-7.34 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 25.8, 35.8, 47.2, 48.4, 48.5, 49.5, 50.3, 61.5, 65.1, 126.1, 127.4, 128.5, 132.2, 139.9, 143.8, 154.5, 174.1; *m*/*z* (ESI^+) 398 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+H]^+$ 340.1913. $C_{21}H_{26}NO_3$ requires 340.1913).

(4*S*,1'*S*,2'*R*,*3'S*,4'*R*)-3-[(3'-Phenylbicyclo[2.2.1]hept-5'-ene-2'-yl)carbonyl]-4-*tert*-butyl-oxazolidin-2-one (*exo* I) and (4*S*,1'*R*,2'*S*,*3'R*,4'*S*)-3-[(3'-phenylbicyclo[2.2.1]hept-5'-ene-2'-yl)carbonyl]-4-*tert*-butyl-oxazolidin-2-one (*exo* II)

Following the general procedure 1', (*S*)-4-*tert*-butyl-oxazolidin-2-one (334 mg, 2.34 mmol), BuLi (1.47 mL, 1.6M in hexane, 2.36 mmol), and *exo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (542 mg, 2.34 mmol) in THF (21.0 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:18) gave (*exo* I) and (*exo* II) as white solids; (*exo* I) (271 mg, 34%); mp 102-103.5°C; $[\alpha]_D^{25}$ +227.4 (*c* 1.0 in $CHCl_3$); ν_{max} (KBr) 1779 (C=O*exo*), 1698 (C=O*endo*); δ_H (400 MHz, $CDCl_3$) 0.98 (9H, s, C(C*H*$_3$)$_3$), 1.52 (1H, dd, *J* 8.5, 1.4, C(7')*H*$_2$), 1.78 (1H, d, *J* 8.5, C(7')*H*$_2$), 3.13 (1H, br s, C(1')*H*), 3.22 (1H, br s, C(4')*H*), 3.71 (1H, d, *J* 4.9, C(3')*H*), 4.10 (1H, dd, *J* 5.1, 3.7, C(2')*H*), 4.21 (1H, dd, *J* 9.2, 7.6, OC*H*$_2$), 4.29 (1H, dd, *J* 9.3, 1.4, OC*H*$_2$), 4.48 (1H, dd, *J* 7.5, 1.4, NC*H*), 6.07 (1H, dd, *J* 5.6, 2.9, C(6')*H*), 6.54 (1H, dd, *J* 5.5, 3.2, *C*(5')*H*), 7.16-7.27 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 25.7, 35.9, 46.1, 46.8, 49.3, 50.7, 51.2, 61.0, 65.2, 126.1, 128.0, 128.1, 135.9, 137.1, 143.1, 154.4,

174.0; *m*/*z* (ESI^+) 398 (57%, $[M+MeCN+NH_4]^+$); (Found: $[M+H]^+$ 340.1909. $C_{21}H_{26}NO_3$ requires 340.1913.).

(*exo* II) (73 mg, 9%); mp 148-150°C; $[\alpha]_D^{23}$ −164.0 (*c* 0.5 in $CHCl_3$); ν_{max} (KBr) 1778 ($C=O_{exo}$), 1708 ($C=O_{endo}$); δ_H (400 MHz, $CDCl_3$) 0.89 (9H, s, $C(CH_3)_3$), 1.49 (1H, dd, *J* 8.5, 1.5, C(7')H_2), 1.90 (1H, d, J 8.6, C(7')H_2), 2.98 (1H, br s, C(1')*H*), 3.18 (1H, br s, C(4')*H*), 3.84 (1H, dd, *J* 5.4, 1.1, C(3')*H*), 3.98 (1H, dd, *J* 5.3, 3.6, C(2')*H*), 4.27-4.29 (2H, m, OCH_2), 4.51 (1H, dd, *J* 6.4, 3.0, NC*H*), 6.07 (1H, dd, *J* 5.6, 2.9, C(6')*H*), 6.43 (1H, dd, *J* 5.6, 3.2, C(5')*H*), 7.16-7.27 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 25.7, 35.8, 46.7, 48.6, 48.7, 49.8, 49.9, 61.2, 64.9, 126.1, 127.9, 128.0, 135.9, 137.1, 142.9, 154.5, 175.2; *m*/*z* (ESI^+) 398 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+H]^+$ 340.1901. $C_{21}H_{26}NO_3$ requires 340.1913).

(4*S*,1'*R*,2'*R*,3'*S*,4'*S*)-3-[(3'-Phenylbicyclo[2.2.1]hept-5'-ene-2'-yl)carbonyl]-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (*endo* I)-60 and (4*S*,1'*S*,2'*S*,3'*R*,4'*R*)-3-[(3'-phenylbicyclo[2.2.1]hept-5'-ene-2'-yl)carbonyl]-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (*endo* II)

Following the general procedure 1', 4-(*S*)-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (367 mg, 2.34 mmol), BuLi (1.47 mL, 1.6M in hexane, 2.36 mmol), and *endo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (542 mg, 2.34 mmol) in THF (21.0 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:30) gave (*endo* I)-**60** as a yellow oil and (*endo* II) as a yellow solid; (*endo* I)-**60** (114 mg, 14%); $[\alpha]_D^{25}$ +150.0 (*c* 1.0 in $CHCl_3$); ν_{max} (film) 1772 ($C=O_{exo}$), 1698 ($C=O_{endo}$); δ_H (400 MHz, $CDCl_3$) 1.00 (3H, d, *J* 6.9, $CH(CH_3)_2$), 1.02 (3H, d, *J* 7.1, $CH(CH_3)_2$), 1.35 (3H, s, $C(CH_3)_2$), 1.51 (3H, s, $C(CH_3)_2$), 1.61-1.63 (1H, m, C(7')H_2), 1.99 (1H, d, *J* 8.6, C(7')H_2), 2.14 (1H, septd, *J* 6.9, 4.0, $CH(CH_3)_2$), 3.01 (1H, br s, C(1')*H*), 3.39 (1H, dd, *J* 5.2 and 1.4, C(2')*H*), 3.64 (1H, br s, C(4')*H*), 4.19-4.21 (2H, m, NC*H* and C(3')*H*), 5.97 (1H, dd, *J* 5.7, 2.8, C(5')*H*), 6.56 (1H, dd, *J* 5.6, 3.2, C(6')*H*), 7.17-7.32 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 16.9, 21.4, 21.6, 28.9, 29.7, 46.3, 48.2, 48.3, 49.6, 50.9, 66.2, 82.6, 126.1, 127.6, 128.5, 132.3, 140.3, 144.0, 153.3, 174.2; *m*/*z* (ESI^+) 412 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+H]^+$ 354.2057. $C_{22}H_{28}NO_3$ requires 354.2069).

(*endo* II) (72 mg, 9%); mp 128-130.5°C; $[\alpha]_D^{23}$ −101.6 (*c* 0.5 in $CHCl_3$); ν_{max} (KBr) 1767 ($C=O_{exo}$), 1697 ($C=O_{endo}$); δ_H (400 MHz, $CDCl_3$) 0.91 (3H, d, *J* 6.8, $CH(CH_3)_2$), 1.02 (3H, d, *J* 7.0, $CH(CH_3)_2$), 1.42 (3H, s, $C(CH_3)_2$), 1.52 (3H, s, $C(CH_3)_2$), 1.57-1.60 (1H, m, C(7')H_2), 1.94 (1H, d, *J* 8.7, C(7')H_2), 2.14 (1H, septd, *J*

7.0, 3.6, C*H*(CH_3)$_2$), 3.06 (1H, br s, C(1')*H*), 3.36-3.40 (2H, m, C(2')*H* and C(4')*H*), 4.10 (1H, d, *J* 3.4, NC*H*), 4.32-4.35 (1H, m, C(3')*H*), 5.90 (1H, dd, *J* 5.7, 2.8, C(5')*H*), 6.54 (1H, dd, *J* 5.6, 3.3, C(6')*H*), 7.18-7.37 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 17.1, 21.3, 21.5, 28.8, 29.4, 46.9, 47.2, 48.2, 49.3, 50.2, 67.2, 82.6, 126.0, 127.5, 128.5, 131.9, 140.2, 143.9, 153.6, 174.3; *m*/*z* (ESI^+) 412 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+H]^+$ 354.2061. $C_{22}H_{28}NO_3$ requires 354.2069).

(4*S*,1'*S*,2'*R*,*3'S*,4'*R*)-3-[(3'-Phenylbicyclo[2.2.1]hept-5'-ene-2'-yl)carbonyl]-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (*exo* I) and (4*S*,1'*R*,2'*S*,*3'R*,4'*S*)-3-[(3'-phenylbicyclo[2.2.1]hept-5'-ene-2'-yl)carbonyl]-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (*exo* II)

Following the general procedure 1', 4-(*S*)-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (367 mg, 2.34 mmol), BuLi (1.47 mL, 1.6M in hexane, 2.36 mmol), and *exo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbonyl chloride (542 mg, 2.34 mmol) in THF (21.0 mL) furnished the crude product as a brown oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:30) gave (*exo* I) as a colourless oil and (*exo* II) as pink needles; (*exo* I) (129 mg, 16%); $[\alpha]_D^{23}$ +189.0 (*c* 1.0 in $CHCl_3$); ν_{max} (film) 1776 (C=O$_{exo}$), 1695 (C=O$_{endo}$); δ_H (400 MHz, $CDCl_3$) 1.02 (3H, d, *J* 6.8, CH(C*H*$_3$)$_2$), 1.06 (3H, d, *J* 7.0, CH(C*H*$_3$)$_2$), 1.35 (3H, s, C(C*H*$_3$)$_2$), 1.52 (3H, s, C(C*H*$_3$)$_2$), 1.50-1.52 (1H, m, C(7')*H*$_2$), 1.81 (1H, d, *J* 8.5, C(7')*H*$_2$), 2.19 (1H, septd, *J* 7.0, 3.6, C*H*(CH$_3$)$_2$), 3.14 (1H, br s, C(4')*H*), 3.23 (1H, br s, C(1')*H*), 3.72 (1H, d, *J* 5.2, C(3')*H*), 4.10-4.12 (1H, m, C(2')*H*), 4.21 (1H, d, *J* 3.2, NC*H*), 6.05 (1H, dd, *J* 5.6, 2.8, C(6')*H*), 6.53 (1H, dd, *J* 5.5, 3.2, C(5')*H*), 7.15-7.27 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 17.1, 21.4, 21.7, 28.8, 29.7, 46.4, 46.6, 49.2, 50.6, 51.0, 66.4, 82.6, 126.1, 128.0, 128.1, 135.9, 137.1, 143.2, 153.3, 174.7; *m*/*z* (ESI^+) 412 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+H]^+$ 354.2064. $C_{22}H_{28}NO_3$ requires 354.2069).

(*exo* II) (98 mg, 12%); mp 147-149°C; $[\alpha]_D^{23}$ −155.2 (*c* 1.0 in $CHCl_3$); ν_{max} (KBr) 1763 (C=O$_{exo}$), 1693 (C=O$_{endo}$); δ_H (400 MHz, $CDCl_3$) 0.89 (3H, d, *J* 6.8, CH(C*H*$_3$)$_2$), 1.00 (3H, d, *J* 7.0, CH(C*H*$_3$)$_2$), 1.44 (3H, s, C(C*H*$_3$)$_2$), 1.49 (1H, dd, *J* 8.6, 1.5, C(7')*H*$_2$), 1.52 (3H, s, C(C*H*$_3$)$_2$), 1.88 (1H, d, *J* 8.5, C(7')*H*$_2$), 2.14 (1H, septd, *J* 6.9, 3.5, C*H*(CH$_3$)$_2$), 2.96 (1H, br s, C(4')*H*), 3.18 (1H, br s, C(1')*H*), 3.92 (1H, dd, *J* 5.4, 1.1, C(3')*H*), 4.04-4.06 (1H, m, C(2')*H*), 4.21 (1H, d, *J* 3.5, NC*H*), 6.05 (1H, dd, *J* 5.6, 2.9, C(6')*H*), 6.43 (1H, dd, *J* 5.6, 3.2, C(5')*H*), 7.15-7.27 (5H, m, *Ph*); δ_C (100 MHz, $CDCl_3$) 17.1, 21.4, 21.6, 29.1, 29.5, 46.7, 47.7,

48.7, 49.8, 50.1, 66.7, 82.4, 126.0, 127.9, 128.0, 135.8, 137.0, 143.1, 153.5, 175.3; *m*/*z* (ESI^+) 412 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+H]^+$ 354.2066. $C_{22}H_{28}NO_3$ requires 354.2069).

(*RS*)-3,3-dimethoxy-2-methyl-propanoyl chloride

Following general procedure 6', methyl methacrylate (3.50 g, 35.0 mmol), $PdCl_2$ (621 mg, 3.50 mmol), CuCl (3.46 g, 35.0 mmol) and MeOH (14.2 mL, 0.35mol) in DME (56.1 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:20) gave the methyl 3,3-dimethoxy-2-methyl-propionate as a pale yellow oil (1.76 g, 31%) with spectroscopic properties consistent with the literature.[32]

To a stirred solution of NaOH (546 mg, 13.6 mmol) in H_2O (3.00 mL), methyl 3,3-dimethoxy-2-methyl-propionate (1.00 g, 6.17 mmol) was added and the reaction mixture was stirred at 50°C overnight, after which it was allowed to cool to room temperature and acidified to pH2-3 with HCl (2M, aq). The organic material was extracted with Et_2O and the combined organic layers were dried over Na_2SO_4. Evaporation of the solvent *in vacuo* gave (*RS*)-3,3-dimethoxy-2-methyl-propionic acid as a yellow oil (897 mg, 98%) with spectroscopic properties consistent with the literature.[33]

Following general procedure 5', 3,3-dimethoxy-2-methyl-propionic acid (145 mg, 0.98 mmol), DMF (9μL, 0.01 mmol), and oxalyl chloride (0.17 mL, 1.96 mmol) in DCM (1.00 mL) furnished the crude (*RS*)-3,3-dimethoxy-2-methyl-propanoyl chloride as a mixture of yellow oil and solid. The crude product was used immediately without any further purification.

(4*S*,2'*S*)-3-(3',3'-Dimethoxy-2'-methyl-acryloyl)-4-*iso*-propyl-oxazolidin-2-one 64 and (4*S*,2'*R*)-3-(3',3'-dimethoxy-2'-methyl-acryloyl)-4-*iso*-propyl-oxazolidin-2-one

Following the general procedure 1', (*S*)-4-*iso*-propyl-oxazolidin-2-one (82 mg, 0.64 mmol), BuLi (0.26 mL, 2.5M in hexane, 0.64 mmol), (*RS*)-3,3-dimethoxy-2-methyl-propanoyl chloride (113 mg, 0.76 mmol), pivaloyl chloride (0.09 mL, 0.76 mmol) and NEt_3 (0.21 mL, 1.53 mmol) in THF (4.00 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) gave the mixture of **64** and the (4*S*,2'*R*)-diastereomer as a yellow oil (134 mg, 81%) with spectroscopic properties consistent with the literature[34]

(4*S*,2'*S*)-3-(3',3'-Dimethoxy-2'-methyl-acryloyl)-4-*tert*-butyl-oxazolidin-2-one 65 and (4*S*,2'*R*)-3-(3',3'-dimethoxy-2'-methyl-acryloyl)-4-*tert*-butyl-oxazolidin-2-one

Following the general procedure 1', (*S*)-4-*tert*-butyl-oxazolidin-2-one (91 mg, 0.64 mmol), BuLi (0.26 mL, 2.5M in hexane, 0.64 mmol), (*RS*)-3,3-dimethoxy-2-methyl-propanoyl chloride (113 mg, 0.76 mmol), pivaloyl chloride (0.09 mL, 0.76 mmol) and NEt_3 (0.21 mL, 1.53 mmol) in THF (4.00 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) gave the mixture of **65** and the (4*S*,2'*R*)-diastereomer as a yellow oil (135 mg, 78%); ν_{max} (film) 1780 (C=O_{exo}), 1705 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.93 (9H, s, C(CH_3)$_{3(2'R)}$), 0.94 (9H, s, CH(CH_3)$_{3(2'S)}$), 1.15 (3H, d, *J* 6.9, CHC$H_{3(2'R)}$), 1.25 (3H, d, *J* 7.0, CHC$H_{3(2'S)}$), 3.32 (3H, s, OC$H_{3(2'S)}$), 3.35 (3H, s, OC$H_{3(2'S)}$), 3.36 (3H, s, OC$H_{3(2'R)}$), 3.37 (3H, s, OC$H_{3(2'R)}$), 4.20-4.39 (6H, m, C*H*CH_3 and OCH_2), 4.44 (1H, dd, *J* 7.3, 1.4, NC$H_{(2'S)}$), 4.50 (1H, dd, *J* 7.6, 1.8, NC$H_{(2'R)}$), 4.57 (1H, d, *J* 8.3, C*H*(OCH_3)$_{2(2'S)}$), 4.62 (1H, d, *J* 7.5, C*H*(OCH_3)$_{2(2'R)}$); δ_C (100 MHz, $CDCl_3$) 12.2, 14.0, 25.4, 25.6, 35.7, 35.9, 39.4, 40.3, 51.2, 52.2, 54.9, 55.6, 60.6, 61.1, 64.9, 65.2, 105.2, 105.7, 154.3, 154.4, 174.2; *m*/*z* (ESI^+) 296 (60%, $[M+Na]^+$); (Found: $[M+H]^+$ 274.1652. $C_{13}H_{23}NO_5$ requires 274.1654).

(4*S*,2'*S*)-3-(3',3'-Dimethoxy-2'-methyl-acryloyl)-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one 66 and (4*S*,2'*R*)-3-(3',3'-dimethoxy-2'-methyl-acryloyl)-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one

Following general procedure 1, 4-(*S*)-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (100 mg, 0.64 mmol), BuLi (0.26 mL, 2.5M in hexane, 0.64 mmol), (*RS*)-3,3-dimethoxy-2-methyl-propanoyl chloride (113 mg, 0.76 mmol), pivaloyl chloride (0.09 mL, 0.76 mmol) and NEt_3 (0.21 mL, 1.53 mmol) in THF (4.00 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) gave the mixture of **66** and the (4*S*,2'*R*)-diastereomer as an amorphous yellow oily solid (156 mg, 85%); m.p. 36-40°C; ν_{max} (KBr) 1764 (C=O_{exo}), 1692 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.94 (3H, d, *J* 6.8, CH(CH_3)$_{2(2'S)}$), 0.97 (3H, d, *J* 6.9, CH(CH_3)$_{2(2'R)}$), 1.00-1.03 (6H, m, CH(CH_3)$_2$), 1.16 (3H, d, *J* 6.9, CHC$H_{3(2'R)}$), 1.23 (3H, d, *J* 6.8, CHC$H_{3(2'S)}$), 1.37 (3H, s, C(CH_3)$_{2(2'R)}$), 1.40 (3H, s, C(CH_3)$_{2(2'S)}$), 1.51 (6H, s, C(CH_3)$_2$), 2.09-2.17 (2H, m, C*H*(CH_3)$_2$), 3.31 (6H, s, OC$H_{3(2'S)}$), 3.36 (3H, s, OC$H_{3(2'R)}$), 3.38 (3H, s, OC$H_{3(2'R)}$), 4.14 (1H, d, *J* 3.4, NC$H_{(2'S)}$), 4.23 (1H, d, *J* 2.9, NC$H_{(2'R)}$), 4.36-4.43 (2H, m, C*H*CH_3), 4.53 (1H,

d, *J* 8.4, C*H*(OCH_3)$_{2(2'S)}$), 4.64 (1H, d, *J* 7.6, C*H*(OCH_3)$_{2(2'R)}$); δ_C (100 MHz, $CDCl_3$) 12.5, 13.6, 16.5, 17.0, 21.2, 21.3, 21.5, 28.3, 28.8, 29.5, 29.8, 39.3, 40.2, 50.9, 52.1, 54.9, 55.3, 65.9, 66.5, 82.4, 82.8, 105.6, 105.7, 153.3, 153.6, 174.7, 174.8; *m*/*z* (ESI^+) 346 (100%, $(M+MeCN+NH_4)^+$); (Found: $[M+H]^+$ 288.1812. $C_{14}H_{26}NO_5$ requires 288.1811).

(*RS*)-3,3-Diethoxy-2-methyl-propionic acid

Following general procedure 1', oxazolidin-2-one (7.00 g, 80.5 mmol), BuLi (35.4 mL, 2.5M in hexane, 88.5mol), and methacryloyl chloride (9.03 mL, 92.5 mmol) in THF (117 mL) furnished, after purification *via* column chromatography on silica (EtOAC/30-40 petroleum ether 1:7) 3-(2'-methyl-acryloyl)-oxazolidin-2-one as white solid (6.817 g, 55%) with spectroscopic properties consistent with the literature.[35]

Following general procedure 6', 3-(2'-methyl-acryloyl)-oxazolidin-2-one (4.00 g, 0.03mol), $PdCl_2$ (458 mg, 2.58 mmol), CuCl (2.56 g, 0.03mol) and EtOH (10.5 mL, 0.26mol) in DME (56.1 mL) gave, after purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:3) the (*RS*)-3-(3',3'-diethoxy-2'-methyl-acryloyl)-oxazolidin-2-one as a pale yellow oil (4.15 g, 59%); ν_{max} (film) 1779 (C=O$_{exo}$), 1700 (C=O$_{endo}$); δ_H (400 MHz, $CDCl_3$) 1.12-1.22 (9H, m, CHC*H*$_3$ and OCH_2CH_3), 3.45-3.69 (4H, m, OCH_2CH_3), 4.01-4.06 (2H, m, NCH_2), 4.19-4.26 (1H, m, C*H*CH_3), 4.35-4.44 (2H, m, OCH_2), 4.71 (1H, d, *J* 8.0, C*H*(OCH_2CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 13.1, 15.1, 15.3, 40.9, 42.7, 60.4, 61.8, 63.5, 103.7, 153.2, 174.4; *m*/*z* (ESI^+) 309 (42%, $[M+MeCN+Na]^+$), 268 (27, $[M+Na]^+$); (Found $[M+Na]^+$ 268.1169. $C_{11}H_{19}NO_5Na$ requires 268.1161).

Following general procedure 4', (*RS*)-3-(3',3'-diethoxy-2'-methyl-acryloyl)-oxazolidin-2-one (1.97 mg, 8.06 mmol), LiOH (677 mg, 16.1 mmol), H_2O_2 (6.45 mL, 30% w/w, 64.5 mmol) in THF (120 mL) and H_2O (33.9 mL) furnished, after purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) (*RS*)-3,3-diethoxy-2-methyl-propionic acid as a colourless oil (1.23 mg, 87%); ν_{max} (film) 1714 (C=O); δ_H (400 MHz, $CDCl_3$) 1.18-1.23 (9H, m, CHC*H*$_3$ and OCH_2CH_3), 2.75-2.82 (1H, m, C*H*CH_3), 3.46-3.77 (4H, m, OCH_2CH_3), 4.65 (1H, d, *J* 7.1, C*H*(OCH_2CH_3)$_2$); δ_C (100 MHz, $CDCl_3$) 12.4, 15.1, 15.2, 44.0, 62.2, 63.3, 103.3, 178.9; *m*/*z* (ESI^-) 175 (100%, $[M]^-$); (Found $[M]^-$ 175.0970. $C_8H_{15}O_4$ requires 175.0970).

(*RS*)-3,3-Di-*n*-propoxy-2-methyl-propionic acid

Following the general procedure 6', 3-(2'-methyl-acryloyl)-oxazolidin-2-one (4.00 g, 0.03 mol), $PdCl_2$ (458 mg, 2.58 mmol), CuCl (2.56 g, 0.03 mol) and *n*-PrOH (10.5 mL, 0.26 mol) in DME (56.1 mL) after purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:3) furnished (*RS*)-3-(3',3'-dipropoxy-2'-methyl-acryloyl)-oxazolidin-2-one as a pale yellow oil (4.23 mg, 60%); ν_{max} (film) 1779 (C=O_{exo}), 1699 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.87 (3H, t, *J* 7.4, $OCH_2CH_2CH_3$), 0.93 (3H, t, *J* 7.4, $OCH_2CH_2CH_3$), 1.20 (3H, d, *J* 6.9, $CHCH_3$), 1.48-1.60 (4H, m, $OCH_2CH_2CH_3$), 3.32-3.63 (4H, m, $OCH_2CH_2CH_3$), 3.95-4.06 (2H, m, *J* 14.7, NCH_2), 4.23-4.30 (1H, m, $CHCH_3$), 4.34-4.44 (2H, m, OCH_2), 4.69 (1H, d, *J* 8.0, $CH(OCH_2CH_2CH_3)_2$); δ_C (100 MHz, $CDCl_3$) 10.5, 10.7, 13.1, 22.8, 23.1, 40.7, 42.7, 61.8, 66.3, 69.6, 103.9, 153.2, 174.5; *m*/*z* (ESI^+) 296 (22%, $[M+Na]^+$); (Found $[M+Na]^+$ 296.1480. $C_{11}H_{19}NO_5Na$ requires 296.1474).

Following the general procedure 4', (*RS*)-3-(3',3'-dipropoxy-2'-methyl-acryloyl)-oxazolidin-2-one (2.20 g, 8.06 mmol), LiOH (677 mg, 16.1 mmol), H_2O_2 (6.45 mL, 30% w/w, 64.5 mmol) in THF (120 mL) and H_2O (33.9 mL) furnished, after purification *via* flash column chromatography on silica (EtOAC/30-40 petroleum ether 1:7) (*RS*)-3,3-dipropoxy-2-methyl-propionic acid as a yellow oil (941 mg, 57%); ν_{max} (film) 1713 (C=O); δ_H (400 MHz, $CDCl_3$) 0.89-0.97 (6H, m, $OCH_2CH_2CH_3$), 1.22 (3H, d, *J* 7.1, $CHCH_3$), 1.56-1.63 (4H, m, $OCH_2CH_2CH_3$), 2.77-2.84 (1H, m, $CHCH_3$), 3.40-3.49 (2H, m, $OCH_2CH_2CH_3$), 3.55-3.68 (2H, m, $OCH_2CH_2CH_3$), 4.64 (1H, d, *J* 7.1, $CH(OCH_2CH_2CH_3)_2$); δ_C (100 MHz, $CDCl_3$) 10.5, 10.6, 12.4, 22.9, 23.0, 43.9, 68.3, 69.6, 103.6, 178.8; *m*/*z* (ESI^-) 203 (100%, $[M]^-$); (Found $[M]^-$ 203.1280. $C_8H_{15}O_4$ requires 203.1283).

3,3-Di-*iso*-propoxy-2-methyl-propionic acid

Following the general procedure 6', 3-(2'-methyl-acryloyl)-oxazolidin-2-one (4.00 g, 0.03mol), $PdCl_2$ (458 mg, 2.58 mmol), CuCl (2.56 g, 0.03mol) and *i*-PrOH (10.5 mL, 0.258mol) in DME (56.1 mL) furnished, after purification *via* column chromatography on silica (Et_2O/30-40 petroleum ether 1:3) (*RS*)-3-(3',3'-di-*iso*-propoxy-2'-methyl-acryloyl)-oxazolidin-2-one as a pale yellow oil (3.29 g, 47%); ν_{max} (film) 1778 (C=O_{exo}), 1703 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 1.09 (3H, d, *J* 6.1, $OCH(CH_3)_2$), 1.14 (3H, d, *J* 6.0, $OCH(CH_3)_2$), 1.15 (3H, d, *J* 6.3, $OCH(CH_3)_2$), 1.19-1.22 (6H, m, $OCH(CH_3)_2$ and $CHCH_3$), 3.83-4.19 (6H, m, $OCH(CH_3)_2$, OCH_2 and NCH_2), 4.34-4.49 (1H, m, $CHCH_3$), 4.81 (1H, d, *J* 7.2, $CH(OCH(CH_3)_2)_2$); δ_C

(100 MHz, $CDCl_3$) 12.6, 22.0, 22.8, 23.3, 23.5, 42.3, 42.7, 61.8, 67.9, 68.9, 100.7, 153.2, 174.3; *m*/*z* (ESI^+) 332 (100%, $[M+MeCN+NH_4]^+$), 296 (93, $[M+Na]^+$); (Found $[M+Na]^+$ 296.1469. $C_{13}H_{23}NO_5Na$ requires 296.1472).

Following general procedure 4', (*RS*)-3-(3',3'-di-*iso*-propoxy-2'-methyl-acryloyl)-oxazolidin-2-one (2.00 g, 7.33 mmol), LiOH (615 mg, 14.7 mmol), H_2O_2 (5.86 mL, 30% w/w, 58.6 mmol) in THF (110 mL) and H_2O (30.8 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography (EtOAc/pentane 1:7) gave 3,3-di-*iso*-propoxy-2-methyl-propionic acid as a pale yellow oil (993 mg, 66%); ν_{max} (film) 1716 (C=O); δ_H (400 MHz, $CDCl_3$) 1.17-1.24 (15H, m, $CH(CH_3)_2$ and $CHCH_3$), 2.64-2.71 (1H, m, $CHCH_3$), 3.84-3.94 (2H, m, $CH(CH_3)_2$), 4.78 (1H, d, *J* 6.0, $CH(OCH(CH_3)_2)_2$); δ_C (100 MHz, $CDCl_3$) 12.0, 22.2, 22.3, 23.2, 23.3, 45.5, 68.9, 69.0, 100.6, 178.0; *m*/*z* (ESI^-) 203 (100%, $[M]^-$); (Found $[M]^-$ 203.1288. $C_{10}H_{19}O_4$ requires 203.1283).

(4*S*,2'*S*)-3-(3',3'-Diethoxy-2'-methyl-acryloyl)-4-*iso*-propyl-oxazolidin-2-one 68 and (4*S*,2'*R*)-3-(3',3'-diethoxy-2'-methyl-acryloyl)-4-*iso*-propyl-oxazolidin-2-one

Following the general procedure 1', (*S*)-4-*iso*-propyl-oxazolidin-2-one (82 mg, 0.64 mmol), BuLi (0.26 mL, 2.5M in hexane, 0.64 mmol), (*RS*)-3,3-diethoxy-2-methyl-propionic acid (135 mg, 0.76 mmol), pivaloyl chloride (0.09 mL, 0.76 mmol) and NEt_3 (0.21 mL, 1.53 mmol) in THF (4.00 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) gave an inseparable mixture of **68** and the (4*S*,2'*R*)-diastereomer as a yellow oil (164 mg, 92%); ν_{max} (film) 1781 ($C=O_{exo}$), 1700 ($C=O_{endo}$); δ_H (400 MHz, $CDCl_3$) 0.91-0.97 (12H, m, $CH(CH_3)_2$), 1.16-1.27 (18H, m, OCH_2CH_3 and $CHCH_3$), 2.34-2.42 (2H, m, $CH(CH_3)_2$), 3.49-3.77 (8H, m, OCH_2CH_3), 4.21-4.37 (6H, m, NCH and OCH_2), 4.41-4.47 (1H, m, $CHCH_{3(2'S)}$), 4.50-4.54 (1H, m, $CHCH_{3(2'R)}$), 4.72 (1H, d, *J* 7.9, $CH(OCH_2CH_3)_{2(2'S)}$), 4.78 (1H, d, *J* 8.1, $CH(OCH_2CH_3)_{2(2'R)}$); δ_C (100 MHz, $CDCl_3$) 13.2, 14.0, 15.1, 15.3, 15.5, 15.6, 15.7, 15.7, 18.3, 18.4, 28.7, 29.2, 41.3, 41.5, 58.6, 59.1, 60.5, 60.9, 63.4, 63.6, 63.8, 64.0, 104.1, 104.4, 154.2, 154.2, 174.8, 174.9; *m*/*z* (ESI^+) 310 (100%, $[M+Na]^+$); (Found: $[M+Na]^+$ 310.1631. $C_{14}H_{25}NO_5Na$ requires 310.1630).

(4*S*,2'*S*)-3-(3',3'-Dipropoxy-(2'*R*)-methyl-acryloyl)-4-*iso*-propyl-oxazolidin-2-one 69 and (4*S*,2'*R*)-3-

(3',3'-dipropoxy-(2'*R*)-methyl-acryloyl)-4-*iso*-propyl-oxazolidin-2-one

Following the general procedure 1', (*S*)-4-*iso*-propyl-oxazolidin-2-one (82 mg, 0.64 mmol), BuLi (0.26 mL, 2.5M in hexane, 0.64 mmol), (*RS*)-3,3-dipropoxy-2-methyl-propionic acid (156 mg, 0.76 mmol), pivaloyl chloride (0.09 mL, 0.76 mmol) and NEt_3 (0.21 mL, 1.53 mmol) in THF (4.00 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) gave an inseparable mixture of **69** and (4*S*,2'*R*)-diastereomer as a yellow oil (198 mg, 99%); ν_{max} (film) 1782 (C=O_{exo}), 1699 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.83-0.96 (24H, m, $CH(CH_3)_2$ and $OCH_2CH_2CH_3$), 1.20 (3H, d, *J* 6.9, $CHCH_{3(2'S)}$), 1.22 (3H, d, *J* 6.9, $CHCH_{3(2'R)}$), 1.48-1.64 (8H, m, $OCH_2CH_2CH_3$), 2.25-2.40 (2H, m, $CH(CH_3)_2$), 3.34-3.63 (8H, m, $OCH_2CH_2CH_3$), 4.16-4.54 (8H, m, NC*H*, C*H*CH_3, and OCH_2), 4.67 (1H, d, *J* 8.2, $CH(OCH_2CH_2CH_3)_{2(2'S)}$), 4.75 (1H, d, *J* 7.9, $CH(OCH_2CH_2CH_3)_{2(2'R)}$); δ_C (100 MHz, $CDCl_3$) 10.5, 10.6, 10.7, 10.8, 12.9, 13.6, 14.6, 14.8, 17.9, 18.0, 22.1, 22.9, 28.2, 28.8, 40.6, 41.0, 58.2, 58.7, 62.9, 63.3, 65.8, 66.4, 69.4, 69.7, 103.8, 103.9, 153.7, 153.8, 174.3, 174.3; *m*/*z* (ESI^+) 338 (100%, $[M+Na]^+$); (Found: $[M+Na]^+$ 338.1951. $C_{16}H_{29}NO_5Na$ requires 338.1951).

(4*S*,2'*S*)-3-(3',3'-Di-*iso*-propoxy-2'-methyl-acryloyl)-4-*iso*-propyl-oxazolidin-2-one 70 and (4*S*,2'*R*)-3-(3',3'-di-*iso*-propoxy-2'-methyl-acryloyl)-4-*iso*-propyl-oxazolidin-2-one

Following the general procedure 1', (*S*)-4-*iso*-propyl-oxazolidin-2-one (82 mg, 0.64 mmol), BuLi (0.26 mL, 2.5M in hexane, 0.64 mmol), 3,3-di-*iso*-propoxy-2-methyl-propionic acid (156 mg, 0.76 mmol), pivaloyl chloride (0.09 mL, 0.76 mmol) and NEt_3 (0.21 mL, 1.53 mmol) in THF (4.00 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) gave the an inseparable mixture of **70** and (4*S*,2'*R*)-diastereomer as a yellow oil (140 mg, 70%); ν_{max} (film) 1781 (C=O_{exo}), 1703 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.86-0.97 (12H, m, $CH(CH_3)_2$), 1.05-1.28 (30H, m, $OCH(CH_3)_2$ and $CHCH_3$), 2.30-2.39 (2H, m, $CH(CH_3)_2$), 3.83-4.02 (4H, m, $OCH(CH_3)_2$), 4.16-4.27 (6H, m, NC*H* and OCH_2), 4.36-4.40 (1H, m, $CHCH_{3(2'S)}$), 4.44-4.48 (1H, m, $CHCH_{3(2'R)}$), 4.76 (1H, d, *J* 7.7, $CH(OCH(CH_3)_2)_{2(2'S)}$), 4.88 (1H, d, *J* 7.7, $CH(OCH(CH_3)_2)_{2(2'R)}$); δ_C (100 MHz, $CDCl_3$) 10.6, 12.7, 13.4, 14.6, 14.7, 17.9, 18.0, 21.5, 21.8, 23.0, 23.2, 23.6, 25.3, 25.3, 28.0, 28.8, 42.0, 42.3, 58.2, 58.6, 62.8, 64.3, 63.7, 67.6, 68.1, 68.7, 100.5, 100.9, 153.8, 153.9, 174.2, 174.2; *m*/*z* (ESI^+) 374 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+NH_4]^+$ 333.2384. $C_{16}H_{33}N_2O_5Na$ requires 333.2389).

(4*S*,2'*S*)-3-(3',3'-Diethoxy-2'-methyl-acryloyl)-4-*tert*-butyl-oxazolidin-2-one 71 and (4*S*,2'*R*)-3-(3',3'-diethoxy-2'-methyl-acryloyl)-4-*tert*-butyl-oxazolidin-2-one

Following the general procedure 1', (*S*)-4-*tert*-butyl-oxazolidin-2-one (91 mg, 0.64 mmol), BuLi (0.26 mL, 2.5M in hexane, 0.64 mmol), (*RS*)-3,3-diethoxy-2-methyl-propionic acid (135 mg, 0.76 mmol), pivaloyl chloride (0.09 mL, 0.76 mmol) and NEt_3 (0.21 mL, 1.53 mmol) in THF (4.00 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) gave an inseparable mixture of **71** and the (4*S*,2'*R*)-diastereomer as a yellow oil (168 mg, 88%); ν_{max} (film) 1781 (C=O_{exo}), 1704 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.93 (9H, s, C(CH_3)$_{3(2'R)}$), 0.94 (9H, s, C(CH_3)$_{3(2'S)}$), 1.11-1.25 (18H, m, CHCH_3 and OCH_2CH_3), 3.42-3.74 (8H, m, OCH_2CH_3), 4.17-4.34 (6H, $CHCH_3$ and OCH_2), 4.41 (1H, dd, *J* 7.3, 1.5, $NCH_{(2'S)}$), 4.47 (1H, dd, *J* 7.5, 1.7, $NCH_{(2'R)}$), 4.63 (1H, d, *J* 8.4, $CH(OCH_2CH_3)_{2(2'S)}$), 4.78 (1H, d, *J* 7.3, $CH(OCH_2CH_3)_{2(2'R)}$); δ_C (100 MHz, $CDCl_3$) 12.4, 13.9, 15.0, 15.1, 15.2, 15.3, 25.5, 25.6, 35.6, 35.9, 40.4, 41.2, 59.7, 60.6, 60.6, 61.2, 62.7, 63.6, 64.9, 65.1, 103.6, 103.9, 154.3, 154.5, 174.3, 173.4; *m*/*z* (ESI^+) 324 (100%, $[M+Na]^+$); (Found: $[M+Na]^+$ 324.1791. $C_{15}H_{27}NO_5Na$ requires 324.1787).

(4*S*,2'*S*)-3-(3',3'-Dipropoxy-2'-methyl-acryloyl)-4-*tert*-butyl-oxazolidin-2-one 72 and (4*S*,2'*R*)-3-(3',3'-dipropoxy-2'-methyl-acryloyl)-4-*tert*-butyl-oxazolidin-2-one

Following the general procedure 1', (*S*)-4-*tert*-butyl-oxazolidin-2-one (91 mg, 0.64 mmol), BuLi (0.26 mL, 2.5M in hexane, 0.64 mmol), (*RS*)-3,3-dipropoxy-2-methyl-propionic acid (156 mg, 0.76 mmol), pivaloyl chloride (0.09 mL, 0.76 mmol) and NEt_3 (0.21 mL, 1.53 mmol) in THF (4.00 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) gave an inseparable mixture of **72** and the (4*S*,2'*R*)-diastereomer as a yellow oil (187 mg, 89%); ν_{max} (film) 1782 (C=O_{exo}), 1705 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.85-0.96 (12H, m, $OCH_2CH_2CH_3$), 0.93 (9H, s, C(CH_3)$_{3(2'R)}$), 0.94 (9H, s, C(CH_3)$_{3(2'S)}$), 1.16 (3H, d, *J* 6.9, $CHCH_{3(2'R)}$), 1.24 (3H, d, *J* 6.8, $CHCH_{3(2'S)}$), 1.47-1.65 (8H, m, $OCH_2CH_2CH_3$), 3.31-3.62 (8H, m, $OCH_2CH_2CH_3$), 4.11-4.39 (6H, $CHCH_3$ and OCH_2), 4.42 (1H, dd, *J* 7.5, 1.4, $NCH_{(2'S)}$), 4.47 (1H, dd, *J* 7.6, 1.9, $NCH_{(2'R)}$), 4.63 (1H, d, *J* 8.1, $CH(OCH_2CH_2CH_3)_{2(2'S)}$), 4.78 (1H, d, *J* 7.5, $CH(OCH_2CH_2CH_3)_{2(2'R)}$); δ_C (100 MHz, $CDCl_3$) 10.5, 10.6,

10.7, 10.8, 12.6, 13.9, 22.9, 23.0, 23.1, 25.5, 25.6, 35.7, 35.8, 40.1, 41.0, 60.6, 61.1, 64.9, 65.1, 65.5, 66.6, 68.8, 69.7, 103.6, 104.0, 154.3, 154.5, 174.3, 174.3; *m*/*z* (ESI^+) 352 (61%, $[M+Na]^+$); (Found: $[M+Na]^+$ 352.2107. $C_{17}H_{31}NO_5Na$ requires 352.2100).

(4*S*,2'*S*)-3-(3',3'-Di-*iso*-propoxy-2'-methyl-acryloyl)-4-*tert*-butyl-oxazolidin-2-one 73 and (4*S*,2'*R*)-3-(3',3'-di-*iso*-propoxy-2'-methyl-acryloyl)-4-*tert*-butyl-oxazolidin-2-one

Following the general procedure 1', (*S*)-4-*tert*-butyl-oxazolidin-2-one (91 mg, 0.64 mmol), BuLi (0.26 mL, 2.5M in hexane, 0.64 mmol), 3,3-di-*iso*-propoxy-2-methyl-propionic acid (156 mg, 0.76 mmol), pivaloyl chloride (0.09 mL, 0.76 mmol) and NEt_3 (0.21 mL, 1.53 mmol) in THF (4.00 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) gave an inseparable mixture of **73** and the (4*S*,2'*R*)-diastereomer as a yellow oil (159 mg, 76%); ν_{max} (film) 1780 ($C{=}O_{exo}$), 1705 ($C{=}O_{endo}$); δ_H (400 MHz, $CDCl_3$) 0.93 (9H, s, $C(CH_3)_{3(2'S)}$), 0.95 (9H, s, $C(CH_3)_{3(2'R)}$), 1.03 (3H, d, *J* 6.1, $CH(CH_3)_{2(2'S)}$), 1.12-1.21 (24H, m, $CH(CH_3)_2$ and $CHCH_3$), 1.25 (3H, d, *J* 6.9, $CHCH_{3(2'S)}$), 3.84-3.90 (1H, m, $CH(CH_3)_{2(2'S)}$), 3.94-4.32 (9H, m, $CH(CH_3)_2$, $CHCH_3$, and OCH_2), 4.39-4.41 (1H, m, $NCH_{(2'S)}$), 4.45-4.48 (1H, m, $NCH_{(2'R)}$), 4.71 (1H, d, *J* 8.0, $CH((OCH(CH_3)_2)_{2(2'S)}$), 5.02 (1H, d, *J* 6.4, $CH((OCH(CH_3)_2)_{2(2'R)}$); δ_C (100 MHz, $CDCl_3$) 12.1, 14.0, 21.6, 21.7, 22.4, 23.1, 23.3, 23.4, 23.5, 23.7, 25.3, 25.6, 35.6, 35.8, 41.4, 42.8, 60.8, 61.6, 65.0, 65.6, 67.3, 68.4, 67.5, 67.8, 99.3, 101.2, 154.5, 154.6, 173.9, 174.3; *m*/*z* (ESI^+) 388 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+NH_4]^+$ 347.2536. $C_{17}H_{35}N_2O_5$ requires 347.2546).

(4*S*,2'*S*)-3-(3',3'-Diethoxy-2'-methyl-acryloyl)-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one 74 and (4*S*,2'*R*)-3-(3',3'-diethoxy-2'-methyl-acryloyl)-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one

Following general procedure 1, 4-(*S*)-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (100 mg, 0.64 mmol), BuLi (0.26 mL, 2.5M in hexane, 0.64 mmol), (*RS*)-3,3-diethoxy-2-methyl-propionic acid (135 mg, 0.76 mmol), pivaloyl chloride (0.09 mL, 0.76 mmol) and NEt_3 (0.21 mL, 1.53 mmol) in THF (4.00 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) gave an inseparable mixture of **74** and the (4*S*,2'*R*)-diastereomer as a yellow oil (195 mg, 97%); ν_{max} (film) 1776 ($C{=}O_{exo}$), 1700 ($C{=}O_{endo}$); δ_H (400 MHz, $CDCl_3$) 0.91 (3H, d, *J* 6.8, $CH(CH_3)_2$), 0.94 (3H,

d, *J* 6.8, CH(CH_3)$_2$), 0.99 (3H, d, *J* 6.8, CH(CH_3)$_2$), 1.08 (3H, t, *J* 7.2, OCH$_2$C$H_{3(2'R)}$), 1.12-1.19 (15H, m, CH(CH_3)$_2$, OCH$_2$CH_3, OCH$_2$CH_3 and CHCH_3), 1.21 (3H, d, *J* 6.9, CHC$H_{3(2'S)}$), 1.33 (3H, s, C(CH_3)$_{2(2'R)}$), 1.37 (3H, s, C(CH_3)$_{2(2'S)}$), 1.48 (6H, s, C(CH_3)$_2$), 2.06-2.14 (2H, m, C*H*(CH$_3$)$_2$), 3.40-3.72 (8H, m, OCH_2CH$_3$), 4.10 (1H, d, *J* 3.6, NC$H_{(2'S)}$), 4.19 (1H, d, *J* 2.9, NC$H_{(2'R)}$), 4.27-4.34 (2H, m, C*H*CH$_3$), 4.64 (1H, d, *J* 8.3, C*H*(OCH$_2$CH$_3$)$_{2(2'S)}$), 4.77 (1H, d, *J* 7.6, C*H*(OCH$_2$CH$_3$)$_{2(2'R)}$); δ_C (100 MHz, CDCl$_3$) 12.7, 14.0, 15.1, 15.2, 15.3, 16.6, 16.9, 21.2, 21.3, 21.4, 21.5, 28.3, 28.8, 29.4, 29.7, 40.3, 41.0, 59.6, 60.4, 62.8, 63.3, 65.8, 66.4, 82.3, 82.7, 103.6, 103.9, 153.2, 153.4, 174.8, 174.9; *m*/*z* (ESI$^+$) 374 (100%, [M+MeCN+NH$_4$]$^+$); (Found: [M+Na]$^+$ 338.1954. $C_{16}H_{29}NO_5Na$ requires 338.1943).

(4*S*,2'*S*)-3-(3',3'-Dipropoxy-(2'*R*)-methyl-acryloyl)-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one 75 and (4*S*,2'*R*)-3-(3',3'-dipropoxy-(2'*R*)-methyl-acryloyl)-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one

Following general procedure 1, 4-(*S*)-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (100 mg, 0.64 mmol), BuLi (0.26 mL, 2.5M in hexane, 0.64 mmol), (*RS*)-3,3-dipropoxy-2-methyl-propionic acid (156 mg, 0.76 mmol), pivaloyl chloride (0.09 mL, 0.76 mmol) and NEt$_3$ (0.21 mL, 1.53 mmol) in THF (4.00 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) gave an inseparable mixture of **75** and the (4*S*,2'*R*)-diastereomer as a yellow oil (215 g, 98%); ν_{max} (film) 1778 (C=O$_{exo}$), 1700 (C=O$_{endo}$); δ_H (400 MHz, CDCl$_3$) 0.81-1.01 (24H, m, CH(CH_3)$_2$ and OCH$_2$CH$_2$CH_3), 1.15 (3H, d, *J* 6.8, CHC$H_{3(2'R)}$), 1.22 (3H, d, *J* 6.9, CHC$H_{3(2'S)}$), 1.34 (3H, s, C(CH_3)$_{2(2'R)}$), 1.37 (3H, s, C(CH_3)$_{2(2'S)}$), 1.45-1.60 (8H, m, OCH$_2$CH_2CH$_3$), 1.48 (6H, s, C(CH_3)$_2$), 2.06-2.15 (2H, m, C*H*(CH$_3$)$_2$), 3.32-3.59 (8H, m, OCH_2CH$_2$CH$_3$), 4.11 (1H, d, *J* 3.4, NC$H_{(2'S)}$), 4.18 (1H, d, *J* 2.8, NC$H_{(2'R)}$), 4.24-4.34 (2H, m, C*H*CH$_3$), 4.68 (1H, d, *J* 8.4, C*H*(OCH$_2$CH$_2$CH$_3$)$_{2(2'S)}$), 4.79 (1H, d, *J* 7.6, C*H*(OCH$_2$CH$_2$CH$_3$)$_{2(2'R)}$); δ_C (100 MHz, CDCl$_3$) 10.5, 10.6, 10.7, 10.8, 12.9, 14.0, 16.7, 17.0, 21.2, 21.3, 21.4, 21.5, 22.8, 22.9, 23.0, 23.1, 28.4, 28.8, 29.5, 29.7, 40.3, 40.9, 65.6, 65.8, 66.3, 66.4, 68.9, 69.6, 82.4, 82.7, 103.5, 103.9, 153.2, 153.4, 174.8, 174.9; *m*/*z* (ESI$^+$) 402 (100%, [M+MeCN+NH$_4$]$^+$); (Found: [M+NH$_4$]$^+$ 361.2696. $C_{18}H_{37}N_2O_5$ requires 361.2702).

(4*S*,2'*S*)-3-(3',3'-Di-*iso*-propoxy-2'-methyl-acryloyl)-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one 76 and (4*S*,2'*R*)-3-(3',3'-di-*iso*-propoxy-2'-methyl-acryloyl)-4-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one

Following general procedure 1, 4-(*S*)-*iso*-propyl-5,5-dimethyl-oxazolidin-2-one (100 mg, 0.64 mmol), BuLi (0.26 mL, 2.5M in hexane, 0.64 mmol), 3,3-di-*iso*-propoxy-2-methyl-propionic acid (156 mg, 0.76 mmol), pivaloyl chloride (0.09 mL, 0.76 mmol) and NEt_3 (0.21 mL, 1.53 mmol) in THF (4.00 mL) furnished the crude product as a yellow oil. Purification *via* column chromatography on silica (EtOAc/30-40 petroleum ether 1:7) gave the mixture of **76** and the (4*S*,2'*R*)-diastereomer as a yellow oil (163 mg, 75%); ν_{max} (film) 1778 (C=O_{exo}), 1699 (C=O_{endo}); δ_H (400 MHz, $CDCl_3$) 0.93 (3H, d, *J* 6.8, CH(CH_3)$_{2(2'S)}$), 0.97 (3H, d, *J* 6.8, CH(CH_3)$_{2(2'R)}$), 1.00-1.04 (12H, m, CH(CH_3)$_2$ and OCH(CH_3)$_2$), 1.10 (3H, d, *J* 6.5, OCH(CH_3)$_2$), 1.13-1.17 (12H, m, OCH(CH_3)$_2$), 1.19 (6H, d, *J* 6.4, OCH(CH_3)$_2$ and CHCH_3), 1.24 (3H, d, *J* 6.9, CHCH_3), 1.34 (3H, s, C(CH_3)$_{2(2'R)}$), 1.40 (3H, s, C(CH_3)$_{2(2'S)}$), 1.49 (6H, s, C(CH_3)$_2$), 2.08-2.16 (2H, m, C*H*(CH$_3$)$_2$), 3.85-4.03 (4H, m, OC*H*(CH$_3$)$_2$), 4.11 (1H, d, *J* 3.6, NC$H_{(2'S)}$), 4.18 (1H, d, *J* 2.8, NC$H_{(2'R)}$), 4.15-4.30 (2H, m, C*H*CH$_3$), 4.78 (1H, d, *J* 8.0, C*H*(OCH(CH_3)$_2$)$_{2(2'S)}$), 4.98 (1H, d, *J* 6.9, C*H*(OCH(CH_3)$_2$)$_{2(2'R)}$); δ_C (100 MHz, $CDCl_3$) 12.7, 14.3, 16.9, 17.0, 21.3, 21.4, 21.5, 21.8, 22.8, 23.2, 23.3, 23.4, 23.6, 23.7, 28.5, 28.9, 29.5, 29.7, 41.7, 42.4, 66.0, 66.3, 67.5, 67.6, 68.2, 82.2, 82.6, 99.8, 101.1, 153.4, 153.4, 174.5, 174.9; *m*/*z* (ESI$^+$) 402 (100%, $[M+MeCN+NH_4]^+$); (Found: $[M+NH_4]^+$ 361.2709. $C_{18}H_{37}N_2O_5$ requires 361.2702).

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