Experimental: Synthesis of Starting Materials

5-(2′-Methoxyacetyl)-2,2,5-trimethyl-1,3-dioxane-4,6-dione 8a

To a stirred solution of methyl Meldrum's acid **7b** (0.66 g, 4.2 mmol) in dry DCM (25 mL), dry pyridine (0.74 mL, 9.2 mmol) was added under nitrogen atmosphere and stirred for 0.5 h. A solution of methoxyacetyl chloride (0.42 mL, 4.6 mmol) in dry DCM (3 mL) was added dropwise with stirring at 0 °C over 0.5 h. The reaction was stirred at 0 °C for a further 1 h and then for 6 h at rt. The contents were then poured into water (20 mL) and extracted with DCM. The organic layer was washed with water (3 x 20 mL) and sat. aq. $NaHCO_3$ (3 x 20 mL), dried over $MgSO_4$, filtered and the solvent removed *in vacuo*, affording the product **8a** (0.90 g, 94%) as a white crystalline solid without further purification; $R_f = 0.49$ (petrol (40-60):EtOAc 5:1); m.p. 95–96 °C; ν_{max} (film) 2989, 1725; δ_H (200 MHz; $CDCl_3$) 1.72 (3H, s, C(5)CH_3), 1.81 and 1.83 (6H, s, (CH_3)$_2$), 3.35 (3H, s, CH_2OCH_3), 4.07 (2H, s, CH_2OCH_3); δ_C (100 MHz, $CDCl_3$) 19.1 (C(5)CH_3), 28.6 (CH_3), 28.8 (CH_3), 59.0 (CH_2OCH_3), 69.5 (*C*(5)), 74.5 (CH_2OCH_3), 107.1 *C*(2)), 164.8 (*C*(3)), 164.8 (*C*(5)), 195.7 ($COCH_2OMe$); m/z (ESI$^+$) 253 ([M+Na]$^+$, 54%), 483 ([2M+Na]$^+$, 100%); HRMS (ESI$^+$) found 253.0684 for $C_{10}H_{14}NaO_6^+$ [M+Na]$^+$, requires 253.0683.

2,2,5-Trimethyl-5-(1′-oxo-3′–dimethyl-prop-2′-ene)-1,3-dioxane-4,6-dione 8b

To a solution of 2,2,5-trimethyl-1,3-dioxane-4,6-dione **7b** (1.0 g, 12.7 mmol) in dry DCM (15 mL), dry pyridine (2.0 g, 25.4 mmol) was added under nitrogen atmosphere. After stirring for 0.5 h, 3,3-dimethylacryloyl chloride (1.65 g, 14.0 mmol) in dry DCM (5 mL) was added dropwise at 0 °C over 0.5 h. The reaction mixture was stirred for a further 1 h at 0 °C and then at rt overnight. The contents were poured into water (30 mL) and the organic material was extracted with DCM (3 x 30 mL). The combined organic layers were then washed with water (3 x 20 mL) and sat. aq. $NaHCO_3$ (3 x 20 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo.* The crude product was purified by column chromatography on silica (petrol (40-60):EtOAc, 5:1) to give **8b** (1.34 g, 44%) as a white solid; m.p. 76–77 °C; $R_f = 0.29$ (petrol (40-60) : EtOAc 5:1); ν_{max} (film) 3003, 1732; δ_H (200 MHz; $CDCl_3$) 1.70 and 1.75 (6H, 2 x s, (CH_3)$_2$), 1.85 (3H, s, C(5)CH_3), 2.00 (3H, s, =C(CH_3)$_2$), 2.21 (3H, s, =C(CH_3)$_2$), 6.31 (1H, s, C(2′)*H*); δ_C (100 MHz, $CDCl_3$) 21.0 (=C(CH_3)), 27.9 (=C(CH_3)), 28.5 (CH_3), 29.3 (CH_3), 20.4 (C(5)CH_3), 64.5 (*C*(5)), 105.7 (*C*(2)), 117.4 (*C*(2′)), 165.1 (*C*(3′)), 166.0 (*C*(4)), 166.0 (*C*(6)), 187.3 (*C*(1′)); m/z (ESI$^+$) 263 ([M+Na]$^+$, 54%) 503 ([2M+Na]$^+$, 100%); HRMS (ESI)$^+$ found 263.0891 for $C_{12}H_6NaO_5^+$ [M+Na]$^+$, requires 263.0890.

5-(2-Methoxyacetyl)-2,2-dimethyl-1,3-dioxane-4,6-dione 8c[22]

To a solution of Meldrum's acid **7a** (0.50 g, 3.5 mmol) in dry DCM (10 mL) was added dry pyridine (0.56 mL, 6.9 mmol) under nitrogen atmosphere at -9 ^{o}C using an ice-methanol bath. The mixture was then left to stir for 20 min. A solution of methoxyacetyl chloride (0.35 mL, 3.8 mmol) in dry DCM (5 mL) was then added dropwise and the mixture was left to stir at -9 ^{o}C for 1 h and then at rt for a further 2 h. The mixture was then quenched with 1N hydrochloric acid (20 mL), the organic layer separated and the aqueous layer extracted with DCM (3 x 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and the solvent evaporated *in vacuo* to afford **8c** (0.67g, 89%) in a 1:4 keto:enol mixture as a dark orange oil without further purification; ν_{max} (film) 2943, 2360, 1737, 1670; keto δ_H (200 MHz; $CDCl_3$) 1.74 (6H, s, $C(CH_2)_3$), 3.51 (3H, s, OCH_3), 3.62 (1H, s, C(5)*H*), 5.25 (2H, s, CH_2OCH_3); δ_C (100 MHz; $CDCl_3$) 27.1 ($C(CH_3)_2$), 53.4 (CH_2OCH_3), 59.9 (*C*(5)), 72.1 (CH_2OCH_3), 105.9 ($C(CH_3)_2$), 194.1 (*C*(4)O); enol δ_H (200 MHz; $CDCl_3$) 1.74 (6H, s, $C(CH_2)_3$), 3.51 (3H, s, OCH_3), 4.85 (2H, s, CH_2OCH_3); δ_C (100 MHz; $CDCl_3$) 26.9 ($C(CH_3)_2$), 53.4 (CH_2OCH_3), 72.1 (CH_2OCH_3), 90.0 (*C*(5)), 105.9 ($C(CH_3)_2$), 194.1 (*C*(O)); m/z (ESI^-) 239 ($[M-H]^+$, 25%); HRMS (ESI^+) found 239.0526 for $C_9H_{12}NaO_6^+$ $[M+Na]^+$, requires 239.0528.

t-Butyl 4-methoxy-3-oxobutanoate 9a

To a solution of **8c** (2.0 g, 9.2 mmol) in toluene (10 mL) was added ^tBuOH (10 mL) under N_2, and the mixture refluxed for 2 h. The solvent was removed *in vacuo* to afford the crude product, which was purified by flash column chromatography on silica gel (petrol (40-60):EtOAc, 9:1) to give **9a** (1.38 g, 79%) as a pale yellow oil; $R_f = 0.51$ (petrol (40-60):EtOAc, 3:1); ν_{max} (film) 2981, 2936, 2827, 2360, 1722, 1655; δ_H (200 MHz; $CDCl_3$), 1.46 (9H, s, $C(CH_3)_3$), 3.41 (2H, s, $COCH_2CO$), 3.42 (3H, s, OCH_3), 4.08 (2H, s, CH_3OCH_2O); δ_C (100 MHz; $CDCl_3$), 27.9 ($C(CH_3)_3$). 47.2 ($COCH_2CO$), 59.3 (OCH_3), 77.3 (CH_3OCH_2CO) 82.1 ($C(CH_3)_3$), 166.1 ($COOC(CH_3)_3$)), 201.9 ($COCH_2OCH_3$); *m/z* (ESI^+) 211 ($[M+Na]^+$ 50%), 399 ($[2M+Na]^+$ 100%); HRMS (ESI^+) found 211.0941 for $C_9H_{16}NaO_4^+$ $[M+Na]^+$, requires 211.0941.

t-Butyl 4-methoxy-2-methyl-3-oxobutanoate 9b

To a solution of **9a** (1.0 g, 5.3 mmol) in THF (30 mL) at 0 ^{o}C was added ^tBuOK (0.78 g, 5.9 mmol). The mixture was warmed to rt and left to stir for 40 min. MeI (0.36 mL, 5.9 mmol) was added and the mixture left to stir for a further 5 h. The resulting mixture was partitioned between brine (50 mL) and diethyl ether (50 mL), and the aqueous layer extracted with diethyl ether (3 x 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent evaporated *in vacuo*, affording the crude product which was purified *via* column chromatography on silica gel (petrol (40-60):EtOAc, 3:1) giving **9b** as a colourless oil (0.97 g, 90%); $R_f = 0.42$ (petrol (40-60) : EtOAc, 3:1); ν_{max} (film) 2978, 2924, 2827, 1754, 1661; δ_H (400 MHz; $CDCl_3$) 1.26 (3H, d, J = 7.1 Hz, $COCH(C\mathit{H}_3)$), 1.42 (9H, s, $C(C\mathit{H}_3)_3$), 3.38 (3H, s, $C\mathit{H}_3OCH_2$), 3.53 (1H, q, J = 7.1 Hz, $C\mathit{H}(CH_3)$), 4.09 (2H, m, $CH_3OC\mathit{H}_2CO$); δ_C (100 MHz; $CDCl_3$) 12.1 ($CH(\mathit{C}H_3)$), 27.8 ($C(\mathit{C}H_3)_3$), 50.0 ($CO\mathit{C}H(CH_3)CO$), 59.2 ($\mathit{C}H_3OCH_2CO$), 76.8 ($CH_3O\mathit{C}H_2CO$), 81.7 ($\mathit{C}(CH_3)_3$), 169.3 ($\mathit{C}OOC(CH_3)_3$), 207.1 ($\mathit{C}OCH_2OCH_3$); *m/z* (ESI^+) 225 ($[M + Na]^+$, 78%), 427 ($[2M + Na]^+$, 100%); HRMS (ESI^+) found 225.1097 for $C_{10}H_{18}NaO_4^+$ $[M+Na]^+$, requires 225.1097.

4-Methoxy-3-oxobutanoic acid 10a

A solution of **9a** (0.20 g, 2.20 mmol) in TFA (6 mL) was stirred at rt for 24 h. The TFA was removed *in vacuo* by co-evaporation with toluene to afford **10a** (0.18 g, 89%) in a 4:1 keto:enol mixture. ν_{max} (film) 2942, 1724; δ_H (400 MHz; $CDCl_3$) keto 3.44 (3H, s, $OC\mathit{H}_3$), 3.58 (2H, s, $COC\mathit{H}_2CO$), 4.11 (2H, s, $C\mathit{H}_2OCH_3$), 9.11 (1H, br s, $O\mathit{H}$); enol 3.44 (3H, s, $OC\mathit{H}_3$), 4.01 (2H, s, $C\mathit{H}_2OCH_3$), 5.34 (1H, s, $C(OH)=C\mathit{H}$); δ_C (100 MHz; $CDCl_3$) keto 45.2 ($CO\mathit{C}H_2CO$), 59.3 ($\mathit{C}H_3O$), 78.1 ($CH_3O\mathit{C}H_2CO$), 172.1 ($\mathit{C}OOH$), 201.8 ($CH_3OCH_2\mathit{C}O$); enol 45.2 ($CO\mathit{C}H_2CO$), 59.3 ($\mathit{C}H_3O$), 76.7 ($CH_3O\mathit{C}H_2CO$), 87.8 ($\mathit{C}(OH)=CH$) 176.6 ($\mathit{C}OOH$); m/z (ESI^+) 155 ($[M+Na]^+$, 10%); HRMS ESI+ Found 155.0313 for $C_5H_8NaO_4^+$ $[M+Na]^+$, requires 155.0315.

4 –Benzyloxy-3-oxobutanoic acid 10b

Ethyl 4-(benzyloxy)-3-oxobutanoate **11a** (0.60 g, 2.01 mmol) was stirred with 1N NaOH (5.5 mL) and H_2O (8.5 mL) at rt. After 30 h, the resulting solution was washed with diethyl ether (5 × 10 mL). The aqueous layer was cooled in ice, acidified with 1N H_2SO_4 to pH 2 then saturated with NaCl and extracted with diethyl ether (5 × 10 mL). The combined ether extracts were washed with brine (30 mL), dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo* to give 4-benzyloxy-3-oxobutanoic acid **10b** (0.30 g, 72%) as yellow oil, in which keto tautomer was the major product;[26] δ_H(400 MHz; $CDCl_3$) 3.62 (2H, s, $C(2)\mathit{H}_2$), 4.16 (2H, s, $C(4)\mathit{H}_2$), 4.60 (2H, s, $C(6)\mathit{H}_2$), 7.30 – 7.37 (5H, m, $Ar\mathit{H}$), 8.3 (1H, br s, $O\mathit{H}$); δ_C (100 MHz; $CDCl_3$) 45.3 (C(2)), 66.5 (C(4)), 74.7 (C(6)), 127.8 (*para*-CH), 128.1, 128.2 (*ortho*- and *meta*-CH), 136.6 (*ipso*-CH), 172.0 (*C(1)*) and 202.0 (C(3)); *m/z* (ESI^+) 231 ($[M+Na]^+$, 100%); HRMS (ESI^+) $C_{17}H_{29}NNaO_6^+$ requires 366.1887, found 366.1884.

4-(*t*-Butoxy)-3-oxobutanoic acid 10c

Ethyl 4-(t-butoxy)-3-oxobutanoate **11b** (1.10 g, 5.44 mmol) was stirred with 1N NaOH (11 mL) and H_2O (17 mL) at rt. After 30 h, the resulting solution was washed with diethyl ether (5 × 20 mL). The aqueous layer was cooled in ice and acidified with 1N H_2SO_4 to pH 4, saturated with NaCl and extracted with diethyl ether (5 × 20 mL). The combined diethyl ether extracts were washed with brine (40 mL), dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo* to furnish 4-(t-butoxy)-3-oxobutanoic acid **10c** (0.59 g, 62%) as yellow oil, which keto tautomer was the major product: δ_H (400 MHz; $CDCl_3$) 1.19 (9H, s, $3 \times C\mathit{H}_3$), 3.58 (2H, s, $C(2)\mathit{H}_2$), 4.01 (2H, s, $C(4)\mathit{H}_2$) and 9.5 (1H, br s, O*H*); δ_C (100 MHz; $CDCl_3$) 27.2 ($3 \times \mathit{C}H_3$), 45.6 (C(2)), 67.8 (C(4)), 172.7 (*C(1)*) and 203.5 (C(3)); *m/z* (ESI^+) 197.08 ($[M+Na]^+$, 99%).

4-Methoxy-2-methyl-3-oxobutanoic acid 10d

To a solution of **9b** (0.2 g, 0.99 mmol) in DCM (1 mL) was added TFA (1 mL) at 0 ^{o}C. The reaction mixture was left to stir for 3 h at rt and the solvent removed *in vacuo*, affording the product **10d** (0.13 g, 91%) as an orange oil which was used without further purification; ν_{max} (film) 2929, 1732; δ_H (200 MHz; $CDCl_3$) 1.39 (3H, d, *J* = 7.3 Hz, $CH(C\mathit{H}_3)$), 3.44 (3H, s, $C\mathit{H}_3O$), 3.76 (1H, q, *J* = 7.3 Hz, $C\mathit{H}(CH_3)$), 4.18 (2H, s, $CH_3OC\mathit{H}_2CO$), 10.33 (1H, br s, COO*H*); δ_C (100 MHz; $CDCl_3$) 12.2 ($CH(\mathit{C}H_3)$), 48.6 ($\mathit{C}H(CH_3)$), 59.3 ($\mathit{C}H_3O$), 76.7 ($CH_3O\mathit{C}H_2CO$), 175.9 (*C*OOH), 204.0 ($CH_3OCH_2\mathit{C}O$); m/z $(ESI)^+$ 147 ($[M + H]^+$, 6%); HRMS (ESI^+) Found 169.0474 for $C_6H_{10}NaO_4^+$ $[M+Na]^+$, requires 169.0471.

4-(Benzyloxy)-2-methyl-3-oxobutanoic acid 10e

Benzyl 4-(benzyloxy)-2-methyl-3-oxobutanoate **11c** (0.51 g, 1.60 mmol) was stirred with 1N NaOH (5.5 mL) and H_2O (8.5 mL) at rt. After 30 h, the resulting solution was washed with diethyl ether (5 × 10 mL). The aqueous layer was cooled in ice and acidified with 1N H_2SO_4 to pH 5, saturated with NaCl and extracted with diethyl ether (5 × 10 mL). The combined ether extracts were washed with brine (20 mL), dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo* to furnish 4-(benzyloxy)-2-methyl-3oxobutanoic acid **10e** (0.15 g, 42%) as a low melting point solid: m.p. 28-29 °C; δ_H (400 MHz; $CDCl_3$) 1.38 (3H, d, *J* 7.2 Hz, $C(2)C\mathit{H}_3$), 3.80 (1H, q, *J* = 7.2, $C(2)\mathit{H}$), 4.21 (2H, s, $C(4)\mathit{H}_2$), 4.59 (2H, s, $C(6)\mathit{H}_2$), 7.33-7.38 (5H, m, Ar*H*), 12.24 (br, s, O*H*); δ_C (100 MHz; $CDCl_3$) 9.5 ($C(2)\mathit{C}H_3$), 48.70 (C(2)), 73.5 (C(6)), 74.2 (C(4)), 127.9 (*para*-*C*H), 128.5, 128.6 (*ortho*- and *meta*-*C*H), 136.8 (*ipso*-*C*H), 176.0 (*C(1)*) and 204.1 (C(3)); *m/z* (ESI$^-$) 221 ([M-H]$^-$, 57%); HRMS (ESI$^+$) $C_{12}H_{14}NNaO_4^+$ requires 245.0784, found 245.0787.

4-(*t*-Butoxy)-2-methyl-3-oxobutanoic acid 10f

Ethyl 4-(*t*-butoxy)-2-methyl-3-oxobutanoate **11d** (0.73 g, 3.4 mmol) was stirred with 1N NaOH (5.5 mL) and H_2O (8.5 mL) at rt. After 30 h, the resulting solution was washed with diethyl ether (5 × 15 mL). The aqueous layer was cooled in ice and acidified with 1N H_2SO_4 to pH 4, saturated with NaCl and extracted with diethyl ether (5 × 15 mL). The combined ether extracts were washed with brine (35 mL), dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo* to give 4-(*t*-butoxy)-2-methyl-3-oxobutanoic acid **10f** (0.34 g, 54%) which was used without further purification; δ_H (400 MHz; $CDCl_3$) 1.20 (9H, s, C(C*H*$_3$)$_3$), 1.35 (3H, d, *J* = 7.2, C*H*$_3$), 3.80 (1H, q, *J* = 7.2, C(2)*H*), 4.07 (2H, s, C(4)*H*$_2$) and 9.75 (br, s, O*H*); δ_C (100 MHz; $CDCl_3$) 12.6 (*C*H$_3$), 27.5 (3 × *C*H$_3$), 49.4 (C(2)), 67.8 (C(4)), 176.8 (*C(1)*) and 206.1 (C(3)); *m/z* (ESI$^+$) 211 ([M+Na]$^+$, 70%); HRMS (ESI$^+$) $C_9H_{16}NaO_4^+$ requires 211.0941, found 211.0941.

Benzyl 4-(benzyloxy)-3-oxobutanoate 11a

To a stirred suspension of NaH (2.19 g, 91.1 mmol) in dry THF (20 mL) at 10 °C was added anhydrous benzyl alcohol (20 mL), dropwise over 10 min, followed by a solution of ethyl 4-chloroacetoacetate (3.0 g, 18.2 mmol) in dry benzyl alcohol (10 mL). After stirring overnight at rt, the mixture was acidified with glacial AcOH (5 mL) under ice cooling. Water (30 mL) was added and the reaction mixture was extracted with diethyl ether (5 × 15 mL). The combined organic layers were washed with sat. $NaHCO_3$ (30 mL), dried over $MgSO_4$, filtered and concentrated. The crude product was purified by fractional distillation (11 mbar, 150 °C) to remove benzyl alcohol and to give benzyl 4-(benzyloxy)-3-oxobutanoate **11a** (4.09 g, 75%) as a yellow liquid with keto tautomer being the major product: R$_f$ 0.36 (5:1 petrol:EtOAc); $\boldsymbol{\nu}_{\mathbf{max}}$ (film)/cm^{-1} 2925, 1726,1456, 1319, 741, 699, 405; δ_H (400 MHz; $CDCl_3$) 3.61 (2H, s, C(2)*H*$_2$), 4.13 (2H, s, C(4)*H*$_2$), 4.55 (2H, s, OC*H*$_2$Ph), 5.17 (2H, s, COOC*H*$_2$Ph), 7.33-7.37 (5H, m, Ar*H*); δ_C (100 MHz; $CDCl_3$) 46.0 (C(2)), 67.2 (COO*C*H$_2$Ph), 73.5 (C(6)), 74.8 (C(4)), 127.7 (*para*-*C*H), 128.5, 128.6 (*ortho*- and *meta*-*C*H), 136.8 (*ipso*-*C*H), 166.9 (*C(1)*) and 201.6 (C(3)); *m/z* (ESI$^+$) 619 ([2M+Na]$^+$, 100%); HRMS (ESI$^+$) $C_{18}H_{18}NaO_4^+$ requires 321.1097, found 321.1095.

Ethyl 4-(*t*-butoxy)-3-oxobutanoate 11b

To a stirred suspension of NaH (1.35 g, 33.7 mmol) and KO^{t}Bu (3.78 g, 33.7 mmol) in THF (70 mL) was added ethyl 4-chloro-3-oxobutanoate (5.00 g, 30.4 mmol); the temperature was not allowed to rise above 40 °C. The reaction mixture was stirred at rt and monitored by mass spectrometry. After 20 h, the brownish suspension was acidified by pouring into a mixture of ice (20 mL) and conc. HCl (10 mL). The product was extracted with diethyl ether (4 × 20 mL). The combined diethyl ether extracts were washed with brine (20 mL), dried over $MgSO_4$, filtered and concentrated to give a dark brown oil (4.70 g). Purification by Kugelrohr distillation gave ethyl 4-(t-butoxy)-3-oxobutanoate **11b** (1.92 g, 31%) as a yellow liquid with the keto tautomer being the major product: R_f 0.60 (3:1 petrol:EtOAc); ν_{max} (film)/cm^{-1} 2981, 1731, 1369, 1195, 1031, 859, 410; δ_H (400 MHz; $CDCl_3$) 1.15 (9H, s, C(C*H*3)3), 1.22 (3H, t, *J* = 7.1 Hz, OCH_2CH_3), 3.48 (2H, s, C(2)H_2), 3.96 (2H, s, C(4)H_2) and 4.11 (2H, q, *J* = 7.1 Hz, OCH_2CH_3); δ_C (100 MHz; $CDCl_3$) 27.1 (3 × CH_3), 29.6 (OCH_2CH_3), 46.1 (C(2)), 61.2 (OCH_2CH_3), 67.2 (C(4)), 166.5 (C(1)) and 203.6 (C(3)); *m/z* (ESI$^+$) 225 ([M+Na]$^+$, 60%); HRMS (ESI$^+$) $C_{10}H_{18}NaO_4^+$ requires 225.1103, found 225.1097.

Benzyl 4-(benzyloxy)-2-methyl-3-oxobutanoate 11c

To a stirred solution of benzyl 4-(benzyloxy)-3-oxobutanoate **11a** (1.5 g, 5.0 mmol) in THF (25 mL) at 0 °C was added, portionwise, KO^{t}Bu (0.68 g, 6.1 mmol). The mixture was allowed to warm to rt and stirred for 40 min before a solution of MeI (0.79 g, 5.5 mmol) in THF (5 mL) was added dropwise over 10 min. After stirring for a further 5 h the mixture was partitioned between diethyl ether (30 mL) and water (30 mL). The aqueous layer was extracted with diethyl ether (3 × 15 mL) and the combined organic extracts were washed with brine (40 mL), dried over $MgSO_4$, filtered and concentrated. Purification by column chromatography (20:1 petrol:EtOAc) gave ester **11c** (1.1 g, 67%) as a pale yellow liquid: R_f 0.33 (20:1 petrol :EtOAc); ν_{max} (film)/cm^{-1} 3065, 3033, 2988, 2942, 2880, 1723, 1498, 1379, 1320, 1191, 1029; δ_H (400 MHz; $CDCl_3$) 1.38 (3H, d, *J* = 7.2 Hz, CH_3), 3.80 (1H, q, *J* = 7.2 Hz, C(2)*H*), 4.15 (2H, s, C(4)H_2), 4.49 (2H, s, CH_2OCH_2Ph), 5.12 (2H, s, $COOCH_2Ph$) and 7.31-7.36 (5H, m, Ar*H*); δ_C (100 MHz; $CDCl_3$) 12.2 (CH_3), 49.1 (C(2)), 67.0 (OCH_2Ph), 73.4 (C(6)), 74.3 (C(4)), 127.8 (*para*-CH), 128.0, 128.3 (*ortho*- and *meta*-CH), 136.9 (*ipso*-CH), 170.0 (C(1)) and 204.2 (C(3)); *m/z* (ESI$^+$) 647 ([2M+Na]$^+$, 100%); HRMS (ESI)$^+$ $C_{19}H_{20}NaO_4^+$ requires 335.1254, found 335.1252.

Ethyl 4-(*t*-butoxy)-2-methyl-3-oxobutanoate 11d

To a stirred solution of ethyl 4-(*t*-butoxy)-3-oxobutanoate **11b** (1.00 g, 4.94 mmol) in THF (20 mL) at 0 °C was added, portionwise, KO^{t}Bu (0.67 g, 6.0 mmol). The mixture was allowed to warm to rt and stirred for 40 min before a solution of MeI (0.77 g, 5.44 mmol) in THF (5 mL) was added dropwise over 10 min. After stirring for a further 5 h, the mixture was partitioned between diethyl ether (30 mL) and water (30 mL). The aqueous layer was extracted with diethyl ether (4 × 20 mL) and the combined organic extracts were washed with brine (50 mL), dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo*. Purification by column chromatography (20:1 petrol:EtOAc) gave ethyl-4-(*t*-butoxy)-2-methyl-3-oxobutanoate **11d** (0.73 g, 68%) as a colourless liquid: R_f 0.23 (20:1 petrol:EtOAc); ν_{max} (film)/cm^{-1} 2979, 1722, 1456, 1367, 1320, 1107, 1025, 886; δ_H (400 MHz; $CDCl_3$) 1.16 (9H, s, $C(CH_3)_3$), 1.22 (3H, t, J = 7.1 Hz, OCH_2CH_3), 1.29 (3H, d, J = 7.2 Hz, CH_3), 3.72 (1H, q, J = 7.2 Hz, C(2)*H*), 3.98 (1H, d, J = 16.6 Hz, C(4)*H*) and 4.02 (1H, d, J = 16.6 Hz, C(4)*H*) and 4.12 (2H, q, J = 7.1 Hz, OCH_2CH_3); δ_C (100 MHz; $CDCl_3$) 12.1 (CH_3), 14.0 (OCH_2CH_3), 27.1 (CH_3), 49.1 (C(2)), 61.0 (OCH_2CH_3), 67.3 (C(4)), 170.7 (C(1)) and 206.0 (C(3)); *m/z* (ESI^+) 239 ($[M+Na]^+$, 100%); HRMS (ESI^+) $C_{11}H_{20}NaO_4^+$ requires 239.1254, found 239.1253.

(2*R*,5*R*)-Methyl 2-(*t*-butyl)-1-(4-methoxy-3-oxobutanoyl)oxazolidine-5-carboxylate 13a

To a stirred solution of oxazolidine **12**[29] (1.29 g, 6.9 mmol) in DCM (25 mL) was added EDAC.HCl (1.33 g, 6.9 mmol) and DMAP (0.058 g, 0.47 mmol). The mixture was cooled to 0 °C for 15 min and a solution of acid **10a** (0.91 g, 6.9 mmol) in DCM (15 mL) was added dropwise. The mixture was stirred at 0 °C for a further 15 min, then at rt for 3 h. The reaction mixture was then washed with sat. aq. NaH_2PO_4 (3 x 50 mL) and the aqueous layer extracted with DCM (3 x 50 mL). The combined organic extracts were washed with brine (50 mL), dried over $MgSO_4$, filtered and the solvent evaporated *in vacuo*, affording the crude product which was purified by flash column chromatography on silica gel (petrol (40-60):EtOAc, 3:1) to give **13a** as a 1:1 keto:enol mixture as a colourless oil (0.667 g, 32%); R_f = 0.29 (petrol (40-60):EtOAc, 3:1); ν_{max} (film) 2959 1745 1667; $[\alpha]_D^{20}$ = + 15.1 (c = 0.24 in EtOH); keto δ_H (400 MHz; $CDCl_3$) 0.90 (9H, s, $C(CH_3)_3$), 3.42 (3H, s, CH_3OCH_2), 3.71 (2H, s, $COCH_2CO$), 3.70-3.90 (1H, m, C(4)*H*), 3.80 (3H, s, CO_2CH_3), 4.05 (1H, m, C(4)*H*), 4.12 (2H, s, CH_3OCH_2CO), 4.53 (1H, m, C(5)*H*), 5.30 (1H, s, $CH(CH_3)_3$); δ_C (100 MHz; $CDCl_3$) 25.6 ($CH(CH_3)_3$), 47.4 ($COCH_2CO$), 52.7 (CO_2CH_3), 59.4 (CH_3OCH_2), 67.8 (C(4)), 67.9 (C(5)), 77.3 (CH_3OCH_2CO), 96.6 (C(2)), 168.1 (C(8)), 174.9 (CO_2Me); enol δ_H (400 MHz; $CDCl_3$) 0.94 (9H, s, $C(CH_3)_3$), 3.42 (3H, s, CH_3OCH_2CO), 3.75 (1H, m, C(4)*H*), 3.80 (3H, s, CO_2CH_3), 3.99 (2H, s, CH_3OCH_2CO), 4.05 (1H, m, C(4)*H*), 4.53 (1H, m, C(5)*H*), 5.42 (1H, s, $CH(CH_3)_3$), 7.36 (1H, s, $CH{=}C(OH)$), 14.03 (1H, s, C(O*H*)); δ_C (100 MHz; $CDCl_3$); 25.8 ($CH(CH_3)_3$), 52.7 (CO_2CH_3), 59.4 (CH_3OCH_2), 67.8 (*C*(4)), 67.9 (C(5)), 71.5 (CH_3OCH_2CO), 87.3 (C(2)), 168.1 (C(8)), 174.9 (CO_2Me); *m/z* (ESI^+) 324 ($[M+Na]^+$, 54%), 625 ($[2M+Na]^+$, 100%); HRMS (ESI^+) found 324.1417 for $C_{14}H_{23}NaO_6^+$ $[M+Na]^+$, requires 324.1418.

(2*R*, 5*S*)-Methyl 1'-(4'-(benzyloxy)-3'-oxobutanoyl)-2-(*t*-butyl)-5-carboxylate oxazolidine 13b

To a stirred solution of oxazolidine **12**^{29} (0.38 g, 2.0 mmol), DMAP (0.022 g, 0.18 mmol), EDAC (0.46 g, 2.41 mmol) in DCM (7 mL) at 0 °C was added a solution of 4- benzyloxy-3-oxobutanoic acid **10b** (0.50 g, 2.40 mmol) in DCM (3 mL). The reaction mixture was stirred at 0 °C for 15 min and then at rt for 5 h. The crude reaction mixture was partitioned between DCM (40 mL) and aq. NH_4Cl (40 mL) and the organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo* to give a brown oil (0.70 g). Purification by column chromatography (3:1 petrol:EtOAc) gave *cis*-oxazolidine (0.35 g, 39%) as a pale yellow thick oil: R_f 0.33 (3:1 petrol: EtOAc); ν_{max} (film)/cm^{-1} 3424, 2921, 1744, 1639, 1366, 1210, 1102; keto δ_H (400 MHz; $CDCl_3$) 0.89 (9H, s, C(C*H*$_3$)$_3$), 3.67-3.76 (5H, m, C(2)'*H*$_2$ and COOC*H*$_3$), 4.09 (2H, s, C(4)'*H*$_2$), 4.58 (2H, s, C(6)'*H*$_2$), 3.85-4.55 (3H, m, C(4)*HH* and C(5)*H*), 5.30 (1H, s, C(2)*H*), 7.27-7.35 (5H, m, Ar*H*); δ_C (100 MHz; $CDCl_3$) 25.8 C(*C*H$_3$)$_3$), 37.4 (*C*(CH$_3$)$_3$), 47.5 (C(2)'), 52.6 (COO*C*H$_3$), 59.6 (C(5)), 67.8 (C(4)), 73.1 (C(6)'), 73.6 (C(4)'), 96.6 (C(2)), 127.6 (*para*-CH), 128.5, 128.6 (*ortho*- and *meta*-*C*H), 136.9 (*ipso*-*C*H), 168.2, 175.1 and 203.0 (3 × *C*=O); *m/z* (ESI$^+$) 777 ([2M+Na]$^+$, 100%); HRMS (ESI$^+$) $C_{20}H_{27}NNaO_6^+$ requires 400.1731, found 400.1730.

(2*R*, 5*S*)-Methyl-1'-(4'-(*t*-butoxy)-3'-oxobutanoyl)-2-(*t*-butyl)-5-carboxylate oxazolidine 13c

To a stirred solution of oxazolidine **12**^{29} (0.53 g, 2.80 mmol), DMAP (0.030 g, 0.25 mmol), EDAC (0.65 g, 3.4 mmol) in DCM (7 mL) at 0 °C was added a solution of 4-(*t*-butoxy)-3-oxobutanoic acid **10c** (0.59 g, 3.36 mmol) in DCM (3 mL). The reaction mixture was stirred at 0 °C for 15 min and then at rt for 5 h. The crude reaction mixture was partitioned between DCM (40 mL) and aq. NH_4Cl (40 mL) and the organic layer was dried over $MgSO_4$, filtered and concentrated to give brown oil (1.12 g). Purification by column chromatography (3:1 petrol:EtOAc) gave *cis*-oxazolidine as a mixture of keto and enol tautomers, (0.47 g, 41%) as a pale yellow thick oil: R_f 0.31 (3:1 petrol: EtOAc); ν_{max} (film)/cm^{-1} 3467, 2975, 1747, 1642, 1463, 1367, 1193, 1104, 1030; keto δ_H (400 MHz; $CDCl_3$) 0.88 (9H, s, C(C*H*$_3$)$_3$), 1.20 (9H, s, OC(C*H*$_3$)$_3$), 3.72 (2H, s, C(2)'*H*$_2$), 3.77 (3H, s, COOC*H*$_3$), 3.95 (2H, s, C(4)'*H*$_2$), 4.04 and 4.53 (2H, 2 x m, C(4)*HH*), 4.66 (1H, m, C(5)*H*), 5.30 (1H, s, C(2)*H*); δ_C (100 MHz; $CDCl_3$) 25.8 (C(*C*H$_3$)$_3$), 27.3 (C(*C*H$_3$)$_3$), 47.5 (C(2)'), 52.6 (COO*C*H$_3$), 59.5 (C(5)), 61.5 (C(4)'), 68.1 (C(4)), 96.6 (C(2)), 168.5, 177.0 and 204.4 (3 × *C*=O); *m/z* (ESI$^+$) 709 ([2M+Na]$^+$, 100%); HRMS (ESI$^+$) $C_{17}H_{29}NNaO_6^+$ requires 366.1887, found 366.1887.