Supporting Information

The Stereoselective Synthesis of Aziridine Analogues of Diaminopimelic Acid (DAP) and Their Interaction with DAP Epimerase.

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(1*S*,2*R*)-*N*-(2'-Chloroacetyl)bornane-10,2-sultam[1]

(1*S*,2*R*)-*N*-Bornane-10,2-sultam (7.0 g, 31 mmol) was dissolved in THF (100 mL) and cooled to –78 °C. *n*-BuLi (13.7 mL, 2.5 M in hexane, 34 mmol) was added dropwise. After 15 min, a solution of chloroacetyl chloride (3.9 g, 34 mmol) in THF (10 mL) was added. After a further 15 min, the reaction mixture was warmed to room temperature and quenched by the addition of a saturated solution of NH_4Cl (20 mL). The reaction mixture was concentrated and the resulting residue was dissolved in EtOAc (100 mL). The organic layer was washed with H_2O (2 x 75 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Recrystallisation from 10:1 Et_2O/CH_2Cl_2 gave the title compound (7.85 g, 84%) as a white crystalline solid. mp 123-125 °C (Et_2O/CH_2Cl_2); $[\alpha]_D$ –136.1 (*c* 0.8, $CHCl_3$); ν_{max}(Nujol Mull)/cm^{-1} 2925, 2854, 1702, 1460, 1334, 1215, 1133, 530; δ_H (300 MHz, $CDCl_3$) 0.96 and 1.14 (each 3H, 2 x s, 8-H_3 and 9-H_3), 1.39 (2H, m, 5-H_2), 1.82-1.98 (3H, m, 4-H and 6-H_2), 2.04-2.21 (2H, m, 3-H_2), 3.44 (1H, d, *J* = 14.0 Hz, 10-*H*H), 3.52 (1H, d, *J* = 14.0 Hz, 10-H*H*), 3.90 (1H, dd, *J* = 7.8 Hz, 4.7, 2-H), 4.48 (2H, m, 2'-H_2); δ_C (75.5 MHz, $CDCl_3$) 19.9, 20.8, 26.4, 32.8, 38.0, 42.4, 44.6, 47.9, 49.2, 52.7, 65.5, 164.7; *m/z* (ES) 292.1 (MNa^+). Found: C, 49.23; H, 6.27; N, 4.76. $C_{12}H_{18}NO_3ClS$ requires C, 49.23; H, 6.16; N, 4.80%.

(1*S*,2*R*)-*N*-(2'-Diethoxyphosphonoacetyl)bornane-10,2-sultam 7[1]

(1*S*,2*R*)-*N*-(2'-Chloroacetyl)bornane-10,2-sultam (0.755 g, 2.6 mmol) was suspended in triethyl phosphite (5 mL) and heated to 120 °C for 3 h. The reaction mixture was then cooled and concentrated *in vacuo*. The resulting residue was dissolved in EtOAc (100 mL), washed with H_2O (2 x 100 mL), dried ($MgSO_4$) and concentrated *in vacuo*.

Purification by flash column chromatography, elution with 8:2 EtOAc/hexane gave the title compound **7** (0.97 g, 95%) as a colourless oil. $[\alpha]_D$ –81.3 (*c* 0.4, $CHCl_3$); ν_{max}($CHCl_3$ cast)/cm^{-1} 2961, 1693, 1457, 1393, 1329, 1258, 1054, 1024, 536; δ_H (300 MHz, $CDCl_3$) 0.96 and 1.11 (each 3H, 2 x s, 8-H_3 and 9-H_3), 1.29-1.40 (8H, m, 2 x OCH_2CH_3 and 5-H_2), 1.82-1.96 (3H, m, 4-H and 6-H_2), 2.00-2.20 (2H, m, 3-H_2), 3.20 (1H, dd, *J* = 22.7 Hz, 15.5, 2'-*H*H), 3.42 (1H, d, *J* = 14.0 Hz, 10-*H*H), 3.51 (1H, d, *J* = 14.0 Hz, 10-H*H*), 3.53 (1H, dd, *J* = 22.7, 15.5 Hz, 2'-H*H*) 3.87 (1H, dd, *J* = 7.8, 4.7 Hz, 2-H), 4.09-4.22 (4H, m, 2 x OCH_2CH_3); δ_C (75.5 MHz, $CDCl_3$) 16.4 16.4, 19.9, 20.7, 26.5, 32.8, 35.0 (d, *J* = 135.8 Hz), 38.2, 44.6, 47.8, 48.3, 52.9, 62.5, 62.8, 65.3, 163.6; *m/z* (ES) 416.1 (MNa^+); Found: C, 48.60; H, 7.19; N, 3.49. $C_{16}H_{28}NO_6PS$ requires C, 48.85; H, 7.12; N, 3.56%.

Dimethyl (2*S*,5*E*)-*N,N*-Di-*tert*-Butoxycarbonyl-2-aminohept-5-ene-dioate[2]

Methyl (triphenylphosphoranylidene)acetate bromide (4.56 g, 11 mmol) was dissolved in H_2O (30 mL) and CH_2Cl_2 (30 mL) was added. A solution of NaOH (0.87 g, 22 mmol) in H_2O (10 mL) was added. After 20 min, the two layers were separated. The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. The resulting white solid was dissolved in THF (30 mL) and added to a solution of methyl (2*S*)-*N,N*-di-*tert*-butoxycarbonyl-2-amino-5-oxopentanoate **5**[2] (2.1 g, 6.1 mmol) in THF (50 ml). The solution was stirred at room temperature under argon for 2 days. The reaction mixture was then concentrated *in vacuo*. Purification by flash column chromatography, elution with 3:1 hexane/EtOAc gave the title compound (2.15 g, 88%) as a colourless oil. $[\alpha]_D$ –31.2 (*c* 1.3, $CHCl_3$); ν_{max}($CHCl_3$ cast)/cm^{-1} 2952, 1796, 1748, 1727, 1659, 1436, 1368, 1270, 1170, 1143,

1118, 854; δ_H ($CDCl_3$, 300 MHz) 1.48 (18H, s, 2 x O*t*-Bu), 2.05 (1H, m, 3-*H*H), 2.22-2.34 (3H, m, 3-H*H* and 4-H_2), 3.70 (6H, s, 2 x OMe), 4.85 (1H, dd, *J* = 8.5, 3.4 Hz, 2-H), 5.84 (1H, d, *J* = 15.9 Hz, 6-H), 6.94 (1H, dt, *J* = 15.9, 4.5 Hz, 5-H); δ_C (75.5 MHz, $CDCl_3$) 28.0, 28.5, 29.0, 51.4, 52.3, 57.6, 83.4, 121.7, 147.9, 152.1, 166.9, 171.0; *m/z* (ES) 424.2 (MNa^+); Found: C, 56.79; H, 7.78; N, 3.47. $C_{19}H_{31}NO_8$ requires C, 56.86; H, 7.73; N, 3.49%.

Dimethyl (2*S*,5*E*)-*N*-*tert*-Butoxycarbonyl-2-aminohept-5-ene-dioate 8[2]

Dimethyl (2*S*,5*E*)-*N*,*N*-di-*tert*-butoxycarbonyl-2-aminohept-5-ene-dioate[2] (0.27 g, 0.65 mmol) was dissolved in CH_2Cl_2 (10 mL). A solution of TFA (0.093 g, 0.81 mmol) in CH_2Cl_2 (2 mL) was added. After 3 h the reaction was concentrated *in vacuo*. Purification by flash column chromatography, elution with 7:3 hexane/EtOAc gave the title compound **8** (0.167 g, 88%) as a colourless oil. $[\alpha]_D$ +31.3 (*c* 0.4, $CHCl_3$); ν_{max}($CHCl_3$ cast)/cm^{-1} 2954, 1720, 1658, 1516, 1437, 1367, 1366, 1166, 1098, 1045, 780; δ_H (300 MHz, $CDCl_3$) 1.47 (9H, s, O*t*-Bu), 1.78 (1H, m, 3-*H*H), 1.98 (1H, m, 3-H*H*), 2.24 (2H, m, 4-H_2), 3.70 (3H, s, OMe), 3.72 (3H, s, OMe), 4.31 (1H, br q, *J* = 5.7 Hz, 2-H), 5.03 (1H, br d, *J* = 5.7 Hz, NH), 5.83 (1H, dt, *J* = 15.7, 1.7 Hz, 6-H), 6.90 (1H, dt, *J* = 15.7, 6.8 Hz, 5-H); δ_C (75.5 MHz, $CDCl_3$) 28.1, 28.3, 31.3, 51.5, 52.5, 53.0, 76.6, 122.0, 147.4, 155.3, 166.9, 172.8; MS (ES) 324.2 (MNa^+); Found: C, 55.51; H, 7.75; N, 4.65. $C_{14}H_{23}NO_6$ requires C, 55.81; H, 7.64; N, 4.65%.

(*R*)-2-(2-Phenyl-propionylamino)-benzoic acid methyl ester

A solution of (*R*)-2-phenyl propionic acid (1.0 g, 6.66 mmol) in thionyl chloride (25 mL) was heated to reflux for 2.5 h. The resulting mixture was then allowed to cool to room

temperature and the thionyl chloride was removed *in vacuo*. The residue was taken up into Et_2O (150 mL) and methyl anthranilate (1.9 mL, 14.7 mmol) was added dropwise with vigorous stirring. The resulting suspension was left to stand at room temperature for 48 h and then the precipitate was removed by filtration. Aqueous 2 M HCl (100 mL) was added, the organic layer separated and the aqueous layer was then extracted with EtOAc (× 3). The organic fractions were collected, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was recrystallised from EtOH to give the title compound (603 mg, 34%) as a white solid. mp 90 °C (EtOH); $[\alpha]_D$ + 111.1 (*c* 2.0, CH_2Cl_2); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3272, 1689, 1606, 1589, 1528, 1448, 1314, 1294, 1263, 1163, 1088, 756, 699; δ_H (500 MHz, $CDCl_3$) 1.61 (3H, d, *J* = 7.0 Hz, CHC*H*$_3$), 3.77 (1H, q, *J* = 7.0 Hz, C*H*CH$_3$), 3.85 (3H, s, CO_2CH_3), 7.00-7.04 (1H, m, ArC*H*), 7.23-7.27 (1H, m, PhC*H*), 7.32-7.35 (2H, m, PhC*H*), 7.40-7.42 (2H, m, PhC*H*), 7.46-7.50 (1H, m, ArC*H*), 7.94-7.96 (1H, m, ArC*H*), 8.69-8.71 (1H, m, ArC*H*); δ_C (125 MHz, $CDCl_3$) 18.4, 49.2, 52.3, 115.0, 120.2, 122.3, 127.2, 127.5, 128.7, 130.7, 134.4, 140.9, 141.5, 168.3, 173.0; *m/z* (ES) calcd. for $C_{17}H_{17}NO_3Na$ 306.1106 (M^+), found 306.1105; Found: C, 71.71; H, 6.01; N, 4.91. $C_{17}H_{17}NO_3$ requires C, 72.07; H, 6.05; N, 4.94%.

(*R*)-3-Amino-2-(1-phenyl-ethyl)-3*H*-quinazolin-4-one 21

A solution of $NH_2NH_2.H_2O$ (0.9 mL, 19.6 mmol) and (*R*)-2-(2-phenyl-propionylamino)-benzoic acid methyl ester (527 mg, 1.86 mmol) in absolute EtOH (1 mL) were placed in a sealed tube and heated at 140 °C for 16 h. The mixture was allowed to cool to room temperature and was then concentrated *in vacuo*. The residue was taken up into H_2O and then extracted with Et_2O (× 3). The organic fractions were collected, dried ($MgSO_4$) and

concentrated *in vacuo*. Purification by flash column chromatography elution with 7:3 hexane/EtOAc gave the title compound **21** (424 mg, 86%) as a pale yellow solid. mp (hexane/EtOAc) 93-94 °C; $[\alpha]_D$ – 48.8 (c 2.0, CH_2Cl_2); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3311, 3206, 1675, 1611, 1591, 1567, 1472, 772, 696; δ_H (500 MHz, $CDCl_3$) 1.69 (3H, d, *J* = 7.0 Hz, $CHCH_3$), 4.70 (2H, bs, NNH_2), 4.83 (1H, q, *J* = 7.0 Hz, $CHCH_3$), 7.18-7.21 (1H, m, PhCH), 7.24-7.32 (4H, m, PhCH), 7.42-7.46 (1H, m, ArCH), 7.72-7.80 (2H, m, ArCH), 8.20-8.22 (1H, m, ArCH); δ_C (125 MHz, $CDCl_3$) 20.9, 42.9, 120.0, 126.4, 126.9, 127.7, 128.8, 134.0, 142.5, 146.7, 158.0, 161.4; *m/z* (ES) calcd. for $C_{16}H_{16}N_3O$ 266.1293 (M^+), found 266.1296; Found: C, 71.96; H, 5.53; N, 15.71; $C_{17}H_{17}NO_3$ requires C, 72.43; H, 5.70; N, 15.84%.

(*R*)-2-(2-Benzyloxyethoxy)propionoic acid[3]

2-Benzyloxyethanol (4.8 mL, 33.8 mmol) was added dropwise to a suspension of NaH (1.80 g, 75 mmol) in DMF (60 mL) at 0 °C. After stirring for 15 min (*S*)-(-)-2-bromopropionic acid (98% ee, 1.4 mL, 15.5 mmol) was added dropwise to the solution and the mixture was stirred at 0 °C for 4 h and then allowed to warm to room temperature and stirred for a further 16 h. The mixture was concentrated *in vacuo* and the residue was taken up into H_2O and washed with Et_2O (× 2). The aqueous layer was then acidified using 1N HCl and extracted with Et_2O (× 3). The organic fractions were dried ($MgSO_4$) and concentrated *in vacuo* to give the title compound as a light yellow oil (6% DMF remained as determined by ^1H NMR). $[\alpha]_D$ + 9.7 (*c* 5.4, CH_2Cl_2); $\nu_{max}(CH_2Cl_2$ cast)/cm^{-1} 2936, 2870, 1749, 1453, 1206, 1124, 739, 698; δ_H (500 MHz, $CDCl_3$) 1.46 (3H, d, *J* = 7.0 Hz, C*H*$_3$CH), 3.64-3.68 (2H, m, OCH$_2$C*H*$_2$OBn), 3.72-3.74 (2H, m, OC*H*$_2$CH$_2$OBn), 4.09

(1H, q, *J* = 7.0 Hz, C*H*O), 4.59 (2H, s, PhCH_2), 7.26-7.35 (5H, m, Ph); δ_C (125 MHz, $CDCl_3$) 18.4, 69.1, 69.7, 73.3, 75.2, 127.8, 128.4, 137.6, 177.0; *m/z* (EI) calcd. for $C_{12}H_{16}O_4$ 224.1049 (M^+), found 224.1052.

(*R*)-2-(2-Benzyloxyethoxy)propionoic acid methyl ester

A mixture of (*R*)-2-(2-benzyloxyethoxy)propionoic acid (37 mg, 0.17 mmol) and polymer bound PTSA (30-60 mesh, 2.0-3.5 mmol g^{-1}, 37 mg) in anhydrous MeOH (1 mL) was shaken at room temperature for 16 h under an argon atmosphere. The resin was removed by filtration and washed with MeOH. The resulting solution was concentrated *in vacuo* to give the title compound (39 mg, Quant.) as a colourless oil. Optical purity (94% ee) was determined by ^{1}H NMR (500 MHz) titration studies with Eu(hfc)$_3$.[4] $[\alpha]_D$ – 32.5 (*c* 1.2, CH_2Cl_2); ν_{max}(CH_2Cl_2 cast)/cm^{-1} 1751, 1207, 1152, 1118, 738, 698; δ_H (500 MHz, $CDCl_3$) 1.43 (3H, d, *J* = 7.0 Hz, CH_3CH), 3.60-3.67 (3H, m, OC*H*HCH_2OBn), 3.73 (3H, s, OCH_3), 3.78-3.80 (1H, m, OCH*H*CH_2OBn), 4.08 (1H, q, *J* = 7.0 Hz, C*H*O), 4.57 (2H, s, PhCH_2), 7.27-7.35 (5H, m, Ph); δ_C (125 MHz, $CDCl_3$) 18.7, 51.8, 69.5, 69.6, 73.2, 75.4, 127.6, 127.7, 128.3, 138.2, 173.7; *m/z* (EI) calcd. for $C_{13}H_{18}O_4$ 238.1205 (M^+), found 238.1205.

(*R*)-2-[2-(2-Benzyloxy-ethoxy)-propionylamino]-benzoic acid methyl ester[3]

Thionyl chloride (6.0 mL, 82 mmol) was added to a crude mixture of (*R*)-2-(2-benzyloxyethoxy)propionoic acid in CH_2Cl_2 (60 mL). This was then heated at 40 °C for 90 min. The mixture was then concentrated *in vacuo*, the residue was taken up into Et_2O (400 mL) and the solution was cooled to 0 °C. Methyl anthranilate (4.4 mL, 34.0 mmol)

was added dropwise with vigorous stirring and the resulting suspension was allowed to warm to room temperature and stirred for 16 h. The solid precipitate was removed by filtration and the filtrate was washed with sat. $NaHCO_3$ and then 1N HCl. The organic layer was then dried ($MgSO_4$) and concentrated *in vacuo*. Purification by flash chromatography, elution with 3:1 hexane/EtOAc gave the title compound (3.5 g, 63%) as a yellow oil. Optical purity (93% ee) was determined by chiral HPLC using a chiracel OJ column, IPA/hexane 1:9, 50 μL injection volume of 1 mg mL^{-1} solution, flow rate 1 ml min^{-1}, t_R 20.8 min, (*R*)-isomer; t_R 22.8 min, (*S*)-isomer. $[\alpha]_D$ + 33.0 (*c* 2.2, CH_2Cl_2); $\nu_{max}(CH_2Cl_2$ cast)/cm^{-1} 1693, 1584, 1519, 1450, 1266, 1089; δ_H (500 MHz, $CDCl_3$) 1.51 (3H, d, *J* = 6.5 Hz, C*H*$_3$CH), 3.76-3.84 (4H, m, OC*H*$_2$C*H*$_2$O), 3.87 (3H, s, OC*H*$_3$), 4.09 (1H, q, *J* = 6.5 Hz, C*H*O), 4.60 (2H, q, *J* = 12.0 Hz, PhC*H*$_2$), 7.09-7.12 (1H, m, ArC*H*), 7.24-7.35 (5H, m, Ph), 7.53-7.57 (1H, m, ArC*H*), 8.03-8.05 (1H, m, ArC*H*), 8.77-8.79 (1H, m, ArC*H*); δ_C (125 MHz, $CDCl_3$) 18.8, 52.2, 69.5, 70.0, 73.4, 18.1, 115.8, 120.4, 122.7, 127.5, 127.6, 128.3, 130.9, 134.4, 138.2, 140.8, 168.0, 170.8, 172.8; *m/z* (ES) calcd. for $C_{20}H_{23}NO_5Na$ 380.1468 (M^+), found 380.1469.

(*R*)-3-Amino-2-[1-(2-hydroxy-ethoxy)-ethyl]-3*H*-quinazolin-4-one 22[3]

A suspension of 10% Pd/C (250 mg), and (*R*)-2-[2-(2-benzyloxy-ethoxy)-propionylamino]-benzoic acid methyl ester (1.33 g, 3.7 mmol) in MeOH (50 mL) was stirred vigorously under an atmosphere of hydrogen for 16 h at room temperature. A second portion of 10% Pd/C (250 mg) was added to the suspension and stirred vigorously under an atmosphere of hydrogen for a further 3 h. The reaction mixture was then filtered and the filtrate was concentrated *in vacuo*. The residue was taken up into absolute EtOH

(10 mL) and transferred to a sealed tube. $NH_2NH_2.H_2O$ (1 mL) was added and the reaction mixture was heated at 140 °C for 2 h. The mixture was allowed to cool to room temperature and then concentrated *in vacuo*. Purification by flash chromatography, elution with EtOAc gave the title compound **22** (645 mg, 69 %) as a white solid. $[\alpha]_D$ + 59.1 (*c* 2.0, CH_2Cl_2); $\nu_{max}(CH_2Cl_2$ cast)/cm^{-1} 3314, 1674, 1598, 1474, 1249, 1061, 773; δ_H (500 MHz, $CDCl_3$) 1.67 (3H, d, *J* = 6.5 Hz, C*H*$_3$CH), 3.58-3.62 (1H, m, OCH*H*CH_2O), 3.69-3.72 (1H, m, OCH_2CH*H*O), 3.84-3.90 (2H, m, OCH*H*CH*H*O), 5.10 (1H, q, *J* = 6.5 Hz, C*H*O), 5.15 (2H, bs, N*H*$_2$), 7.49-7.52 (1H, m, ArC*H*), 7.73-7.79 (2H, m, ArC*H*), 8.26-8.28 (1H, m, ArC*H*); δ_C (125 MHz, $CDCl_3$) 18.4, 61.7, 71.2, 74.4, 120.1, 126.4, 127.0, 127.4, 134.4, 146.2, 156.4, 161.2; *m/z* (ES) calcd. for $C_{12}H_{16}N_3O_3$ 250.1186 (M^+), found 250.1187; Found C, 57.44; H, 6.11; N, 17.02; $C_{12}H_{16}N_3O_3$ requires C, 57.82; H, 6.07; N, 16.86%.

(*R*)-Myrtenal derivative of (*R*)-3-Amino-2-[1-(2-hydroxy-ethoxy)-ethyl]-3*H*-quinazolin-4-one 22[3]

Acetic acid (0.5 mL) was added to a solution of **22** (100 mg, 0.40 mmol) and (1*R*)-(-)-myrtenal (70 mg, 0.47 mmol) in absolute EtOH (10 mL). The mixture was then heated at 70 °C for 16 h. The solution was concentrated *in vacuo* and the crude mixture was subjected to ^{1}H NMR (500 MHz, $CDCl_3$) to determine the de (89%) by comparison with the myrtenal derivatives of both **23** and a 1:1 mixture of **22**:**23** (*vide infra*). Purification by flash column chromatography elution with 9:1 hexane/EtOAc gave the title compound (143 mg, 93%) as a colourless oil.

(*S*)-3-Amino-2-[1-(2-hydroxy-ethoxy)-ethyl]-3*H*-quinazolin-4-one 23

Preparation of the title compound and optical purity determinations were performed in an identical manner to that described for the (*R*) enantiomer described above. Spectral data of title compound was found to be identical to **22**. $[\alpha]_D$ – 61.8 (*c* 2.9, CH_2Cl_2), 89% ee (*c.f.* (*R*)-myrtenal derivative).

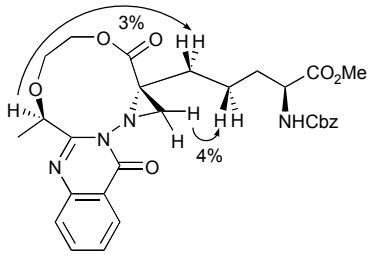
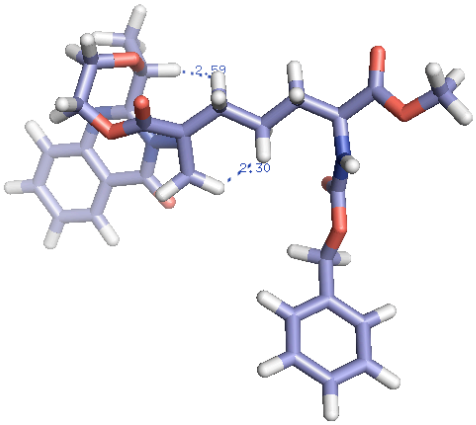
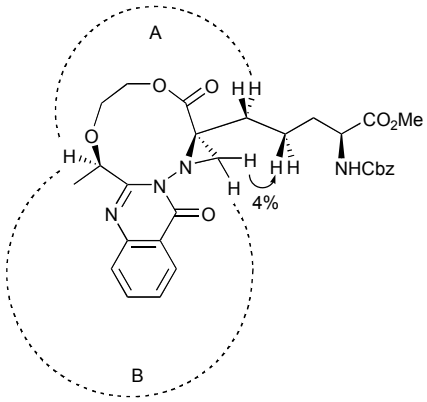
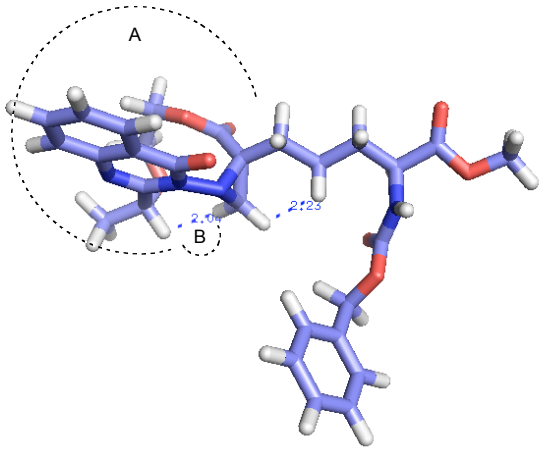
(2*S*)-2-Benzyloxycarbonylamino-6-methyl-heptanedioic acid dimethyl ester

Dry magnesium turnings (25 mg, 1.0 mmol) were added to a solution of ester **16** (128 mg, 0.40 mmol) in anhydrous MeOH (5 mL) under an atmosphere of argon. The mixture was then sonicated at room temperature for 15 min (gas evolution was observed). The mixture was then stirred for 16 h and concentrated *in vacuo*. The residue was taken up into 1N HCl and washed with CH_2Cl_2 (× 3). The aqueous layer was then basified with sat $NaHCO_3$ and then further extracted with CH_2Cl_2 (× 3). The organic fractions were collected, dried ($MgSO_4$) and concentrated *in vacuo* to give a mixture of the title compound (as inseparable diastereomers) and starting material (98 mg). Repeating the reaction on this material did not lead to an increase in conversion (90% determined by ^{1}H NMR). ν_{max}(CH_2Cl_2 cast)/cm^{-1} 3349, 2951, 1731, 1526, 1455, 1436, 1346, 1210, 1171, 1058; $\delta_{\square}$ (500 MHz, $CDCl_3$) 1.13 (3H, d, *J* = 7.5 Hz, C*H*$_3$CH), 1.29-1.44 (2H, m, 4-C*H*$_2$), 1.58 (1H, m, 5-C*H*H), 1.65-1.67 (2H, m, 3 & 5-H$_2$), 1.82-1.86 (1H, m, 3-C*H*$_2$), 2.40-2.44 (1H, m, C*H*CH$_3$), 3.66 (3H, s, CO$_2$C*H*$_3$), 3.75 (3H, s, CO$_2$C*H*$_3$), 4.38 (1H, m, C*H*N), 5.11 (2H, s, PhC*H*$_2$), 5.24 (1H, d, *J* = 8.5 Hz, N*H*), 7.31-7.38 (5H, m, Ph); δ_C (125 MHz, $CDCl_3$) 17.0, 22.9, 32.5, 33.1, 51.2, 52.3, 53.7, 67.0, 125.3, 128.1, 128.2, 128.6, 136.2, 155.8, 172.8, 176.8; *m/z* (ES) calcd. for $C_{18}H_{26}NO_9$ 352.1755 (M^+), found 352.1751.

(2*S*)-2-Amino-6-methyl-heptanedioic acid 18[5]

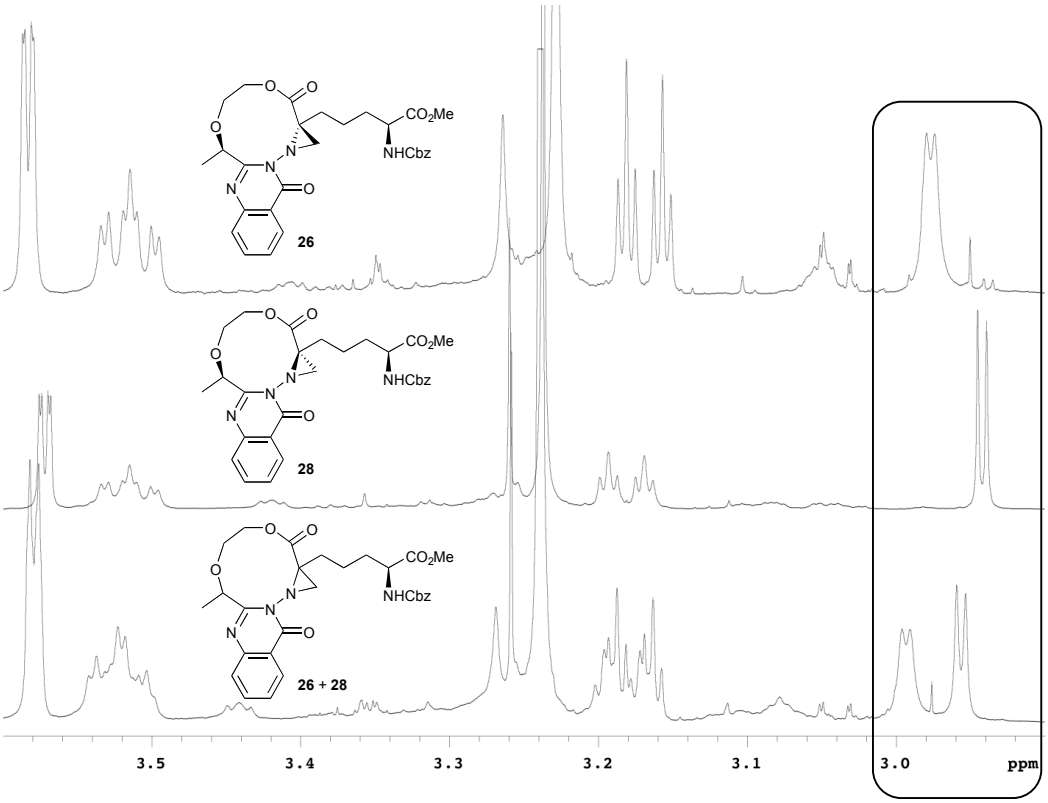
A solution of $LiOH.H_2O$ (29 mg, 69 mmol) in H_2O (0.3 mL) was added to a solution of (2*S*)-2-benzyloxycarbonylamino-6-methyl-heptanedioic acid dimethyl ester (60 mg, 0.17 mmol) in MeOH (1 mL) at room temperature and the mixture was stirred for 16 h. The mixture was concentrated *in vacuo*. A glass coated stirrer bar was introduced and the residue was cooled to –78 °C. Anhydrous NH_3 (5 mL) was distilled into the flask at –78 °C and then lithium was added portionwise until the reaction mixture maintained a blue colour. The reaction mixture was stirred for 15 mins and then quenched with EtOH. The mixture was returned to room temperature and the NH_3 was allowed to evaporate. Purification by preparative TLC (Uniplate™ Silica gel HLF plates with organic binder – solvent system 5% NH_4OH in MeOH, product removed from silica using 20% NH_4OH in MeOH) gave the title compound (18 mg, 58%) as an inseparable pair of diastereomers after lyophilisation. ν_{max}(microscope)/cm^{-1} 3050, 2940, 1693, 1583, 1513, 1441, 1408; δ (300 MHz, D_2O) 1.10 (3H, d, *J* = 11.5 Hz, C*H*$_3$), 1.32-1.51 (3H, m, C*H*H, C*H*$_2$), 1.58-1.65 (1H, m, CH*H*), 1.81-1.92 (2H, m, C*H*$_2$), 2.38-2.46 (1H, m, C*H*CH_3), 3.73 (1H, t, *J* = 6.5 Hz, C*H*N), δ_C (100 MHz, D_2O) 17.8 & 17.9, 23.2 & 23.3, 31.2 & 31.2, 33.9, 41.6 & 41.7, 55.5 & 55.6, 175.7, 185.1; *m/z* (ES) calcd. for $C_8H_{14}NO_4$ 188.0917 (M^+), found 188.0918.

Assignment of stereochemistry for aziridine 26 based on molecular models and nOe measurements (^{1}H NMR 600 MHz, C_6D_6).

Possible reaction products and observed nOe interactions.	Minimised structure and predicted diagnostic nOe interactions (distance in Å)
 Predicted nOe's observed. Structure assigned as product **26**	
 Predicted nOe interaction B not observed.	 Observed nOe interaction A not possible for this isomer.

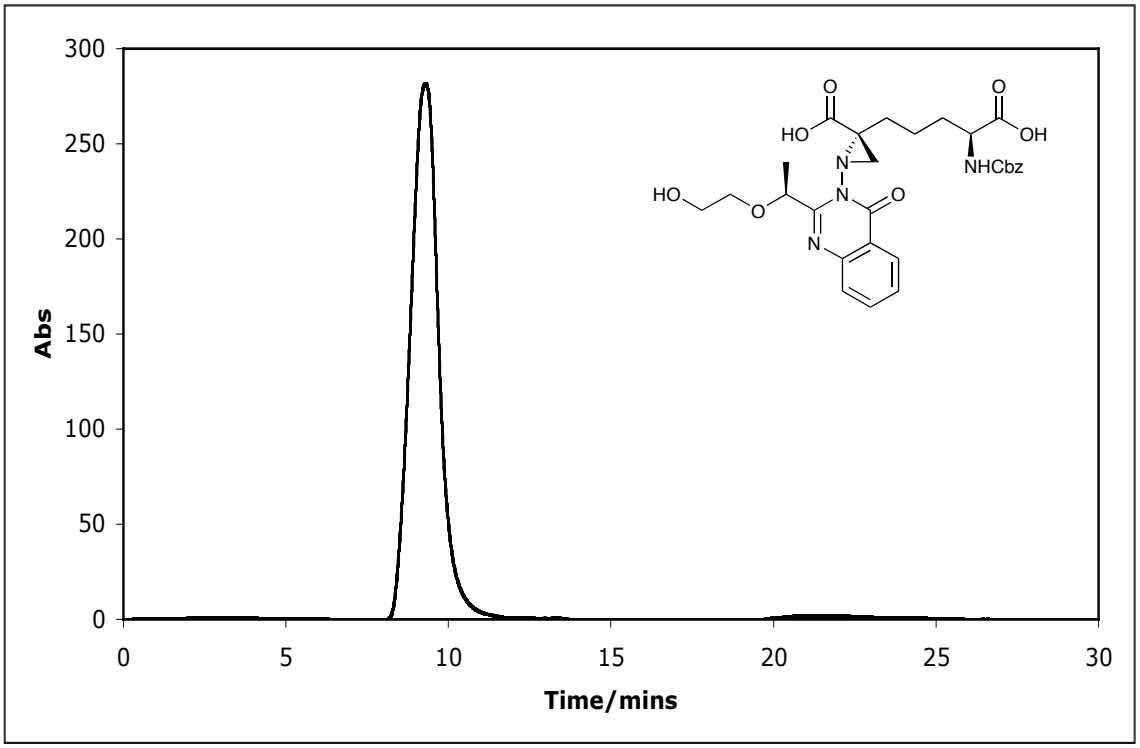
Measurement of the dr for the aziridination reactions 25 → 26, and 27 → 28.

^{1}H NMR (600 MHz, C_6D_6) of crude aziridination reactions. Signals in box correspond to the diagnostic aziridine methylene CH signals. Top, dr = 98:2; Middle, dr = >99:1; Bottom, 1:1 mixture of **26** and **28**.



RP-HPLC for azi-DAP 14 precursor.

Gracevydac reverse phase polymer column (259VHP810), elution with 9:1 *i*-PrOH/50 mM NH_4OH, detection at 220 nm, 450 μL injection volume of 2 mg mL^{-1} solution, flow rate 1 mL min^{-1}.



MS/MS Analysis of Trypsin Digest of DAP Epimerase Inhibited with Azi-DAP 14.

Sequence coverage (40%). Black: undetected residues. Red: sequence coverage. Boxed: Fragment containing Cys-73.

1	MQFSK	**MHGLG**	**NDFVV**	**VDGVT**	**QNVFF**
26	**TPETI**	**RR**LAN	R**HCGI**	**GFDQL**	**LIVEA**
51	**PYDPE**	**LDFHY**	**RI**	**FNA**	**DGSEV**	**SQCGN**
76	**GAR**	CF	ARFVT	LKGLT	NK**KDI**	**SVSTQ**
101	**K**GNMV	LTVKD	MNQIR	**VNMGE**	**PIWEP**
126	**AKIPF**	**TANKF**	**EK**NYI	LRTDI	QTVLC
151	GAVSM	GNPHC	VVQVD	DIQTA	NVEQL
176	GPLLE	SHERF	PER**VN**	**AGFMQ**	**IINKE**
201	**HIK**LR	VYERG	AGETQ	ACGSG	ACAAV
226	AVGIM	QGLLN	NNVQV	DLPGG	SLMIE
251	WNGVG	HPLYM	TGEAT	HIYDG	FITL

MS/MS Analysis of Trypsin Digest of DAP Epimerase Inhibited with Azi-DAP 29.

Sequence coverage (32%).

1	MQFSK	**MHGLG**	**NDFVV**	**VDGVT**	**QNVFF**
26	**TPETI**	**RR**LAN	RHCGI	GFDQL	LIVEA
51	PYDPE	LDFHY	RI	**FNA**	**DGSEV**	**SQCGN**
76	**GAR**	CF	ARFVT	LKGLT	NK**KDI**	**SVSTQ**
101	**K**GNMV	LTVKD	MNQIR	**VNMGE**	**PIWEP**
126	**AKIPF**	**TANKF**	**EK**NYI	LRTDI	QTVLC
151	GAVSM	GNPHC	VVQVD	DIQTA	NVEQL
176	GPLLE	SHERF	PER**VN**	**AGFMQ**	**IINKE**
201	**HIK**LR	VYERG	AGETQ	ACGSG	ACAAV
226	AVGIM	QGLLN	NNVQV	DLPGG	SLMIE
251	WNGVG	HPLYM	TGEAT	HIYDG	FITL

MS/MS Analysis of CNBr/Trypsin Digest of DAP Epimerase.

Sequence coverage (31%). Boxed: Fragment containing Cys-217.

1	MQFSK	MHGLG	NDFVV	VDGVT	QNVFF
26	TPETI	RRLAN	RHCGI	GFDQL	LIVEA
51	PYDPE	LDFHY	RIFNA	DGSEV	SQCGN
76	GARCF	ARFVT	LKGLT	NKK**DI**	**SVSTQ**
101	**KGNM**V	LTVKD	MNQIR	V**NMGE**	**PIWEP**
126	**AK**IPF	TANKF	EKNYI	LRTDI	QTVLC
151	GAVSM	GNPHC	VVQVD	DIQTA	NVEQL
176	GPLLE	SHERF	PERVN	AGFMQ	IINKE
201	HIKLR	VYER**G**	**AGETQ**	**ACGSG**	**ACAAV**
226	**AVGIM**	**QGLLN**	**NNVQV**	**DLPGG**	**SLMIE**
251	**WNGVG**	**HPLYM**	TGEAT	HIYDG	FITL

MS/MS data for trypsin digest fragments containing labeled and unlabeled Cys-73.[a]

IFNADGSEVSQCGNGAR 1723.8 Ion score 125				IFNADGSEVSQC(**14**)GNGAR 1925.9 Ion score 116		
#b	*b*	*y*	*Seq.*	*b*	*y*	*#y*
1	114.1		I	114.1		17
2	261.2	1611.7	F	261.2	1813.8	16
3	375.2	1464.6	N	375.2	1666.7	15
4	446.2	1350.6	A	446.2	1552.7	14
5	561.3	1279.5	D	561.3	1481.6	13
6	618.3	1164.5	G	618.3	1366.6	12
7	705.3	1107.5	S	705.3	1309.6	11
8	834.4	1020.5	E	834.4	1222.6	10
9	933.4	891.4	V	933.4	1093.5	9
10	1020.5	792.3	S	1020.5	994.4	8
11	1148.5	705.3	Q	1148.5	907.4	7
12	1251.5	577.3	C	1453.6	779.4	6
13	1308.6	474.2	G	1510.7	474.2	5
14	1422.6	417.2	N	1624.7	417.2	4
15	1479.6	303.2	G	1681.7	303.2	3
16	1550.7	246.2	A	1752.8	246.2	2
17		175.1	R		175.1	1

[a]Red: Matches observed.

MS/MS for trypsin/thermolysin digest fragments: labeled and unlabeled Cys-73.[a]

IFNADGSEVSQC[a]GNGAR 1780.8 Ion score 59				IFNADGSEVSQC(**29**)GNGARC[a] 1925.9 Ion score 117		
#b	*b*	*y*	*Seq.*	*b*	*y*	*#y*
1	114.1		I	114.1		18
2	261.2	1668.7	F	261.2	1974.8	17
3	375.2	1521.6	N	375.2	1827.7	16
4	446.2	1407.6	A	446.2	1713.7	15
5	561.3	1336.6	D	561.3	1642.6	14
6	618.3	1221.5	G	618.3	1527.6	13
7	705.3	1164.5	S	705.3	1470.6	12
8	834.4	1077.5	E	834.4	1383.6	11
9	933.4	948.4	V	933.4	1254.5	10
10	1020.5	849.4	S	1020.5	1155.5	9
11	1148.5	762.3	Q	1148.5	1068.4	8
12	1308.6	634.3	C	1453.6	940.4	7
13	1365.6	474.2	G	1510.7	635.3	6
14	1479.6	417.2	N	1625.7	578.2	5
15	1536.6	303.2	G	1682.7	463.2	4
16	1607.7	246.2	A	1753.7	406.2	3
17		175.1	R	1909.8	335.2	2
18			(C)		179.1	1

[a]Free cysteines capped with carbamidomethyl groups after inhibition, prior to digestion

MS/MS for trypsin/thermolysin digest fragments: labeled and unlabeled Cys-217.[a]

VYERGAGETQAC[a]GSGAC[a] 1771.7 Ion score 92				VYERGAGETQAC(**29**)GSGAC[a] 1916.8 Ion score 71		
#b	*b*	*y*	*Seq.*	*b*	*y*	*#y*
1	100.1		V	100.1		17
2	263.1	1673.7	Y	263.1	1818.7	16
3	392.2	1510.6	E	392.2	1655.7	15
4	548.3	1381.6	R	548.3	1526.6	14
5	605.3	1225.5	G	605.3	1370.5	13
6	676.3	1168.4	A	676.3	1313.5	12
7	733.4	1097.4	G	733.4	1242.5	11
8	862.4	1040.4	E	862.4	1185.5	10
9	963.5	911.3	T	963.5	1056.4	9
10	1091.5	810.3	Q	1091.5	955.4	8
11	1162.6	682.2	A	1162.6	827.3	7
12	1322.6	611.2	C	1467.7	756.3	6
13	1379.6	451.2	G	1524.7	451.2	5
14	1466.6	394.1	S	1611.7	394.1	4
15	1523.7	307.1	G	1668.7	307.1	3
16	1594.7	250.1	A	1739.8	250.1	2
17		179.1	C		179.1	1

[a]Free cysteines capped with carbamidomethyl groups after inhibition, prior to digestion

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