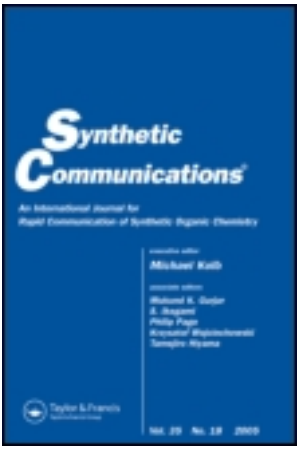

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SYNTHESIS OF A NEW CHIRAL AMINE:(S)-5,5-DIMETHYL-2-METHOXYMETHYL-PYRROLIDINE

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SYNTHESIS OF A NEW CHIRAL AMINE: (S)-5,5-DIMETHYL-2-METHOXYMETHYL-PYRROLIDINE

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ABSTRACT

The title compound, a potential 'quat' auxiliary,was prepared from (S)-glutamic acid derivatives like (S)-N-Benzyl-5-methoxymethyl-2-pyrrolidinone **1**. Other routes starting from (S)-pyroglutamic acid in an attempt to bypass N-Aryl compounds like **1** were also tested, but have not rendered the expected results yet.

Pyrrolidines, like SMP, have been early on a mainstay in the development of asymmetric synthesis.[1] In the twenty or more years since the SMP-derived hydrazine SAMP was first synthesized, it has shown its value as a chirality inducer in hydrazone-based synthetic methodology to form C-C bonds.[2,3] However, in the enantio-selective 'true' aldol condensation, results in stereoselectivity have not always matched those obtained in other reactions.[2b] A detailed picture of the conformation that the pyrrolidine ring of SAMP takes in while acting as auxiliary is available.[4] Taking this picture into account, it may be inferred that a more sterically congested ring would

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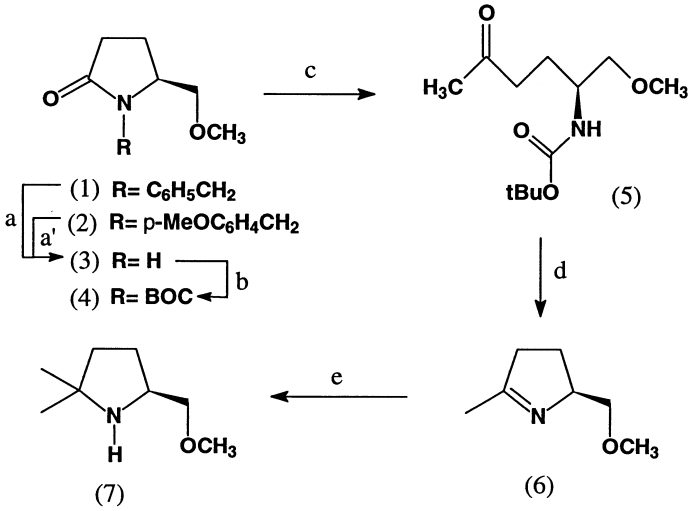
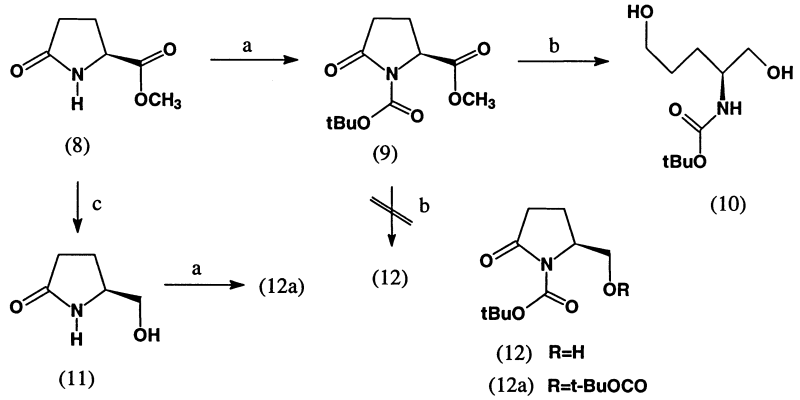
block even further one of the sides of the reacting aza-enolate, and could thereby enhance the inducing power of this hydrazine. To test this hypothesis, a modified hydrazine, itself easily obtainable from the corresponding amine **7**, could be used. The racemic amine has been synthesized already and **7** separated by resolution from its enantiomer.[5] Here we wish to outline our synthetic efforts towards the elusive amine **7** via a route involving the chiral imine **6**, a compound not previously known.



Scheme 1. Reagents: (a) 4 eq. Li (NH_3-THF-H_2O); (a′) CAN (CH_3CN-H_2O); (b) $(BOC)_2O$ DMAP (CH_3CN); (c) CH_3MgBr (THF/Et_2O); (d) CF_3COOH (CH_2Cl_2); (e) CH_3MgBr-$CeCl_3$ (THF/Et_2O).

Initially, our plan called for the introduction of alkyl groups at the carbonyl position of pyrrolidinone **1**, available from previous work.[6] Yet, the N-benzyl group did not activate the carbonyl moiety in the desired mode. Thus it had to be changed for another group. Although the debenzylation to produce derivative **3** did not take place under catalytic hydrogenation conditions like those usually employed for pyrrolidines, it could be achieved with Li in liquid ammonia.[7,8] Key compound **4** did react in the Grignard addition to produce the ring-opened derivative **5** as shown in Scheme 1, in agreement with other findings.[9–12] No N-BOC splitting was detected in this reaction. This is in contrast to those cases where the addition has been done on similar molecules carrying the N-Cbz group, whose carbonyl moiety did react sometimes to give this kind of scission.[13] In fact, the Grignard addition in the presence of th BOC group is of such a

selective nature, that even a relatively unhindered ester moiety in pyroglutamates remains unaffected.[14] Removal of the N-protecting group in methylketone **5** with excess trifluoroacetic acid in CH_2Cl_2 gave pyrroline **6** in 14% overall yield from (S)-glutamic acid.[15] Introduction of the second methyl group (step e) required the addition of an organometallic reagent to the C = N bond. Reviews about such reactions published during the course of this work, confirmed that additions to ketimines are not commonly successful due to side-reactions.[16,17] Nevertheless, we decided to try the organometallic reagents considered most suitable according to literature precedents, including the organocopper and the Grignard reagent, both in the presence of a Lewis acid, as well as the Cerium compound. We could obtain compound **7** in small amount (up to 15% yield) with the Cerium transmetallated Grignard reagent.[18] Unfortunately, this was not invariably the case and imine **6** could always be recovered to some extent.



Scheme 2. Reagents: (a) $(BOC)_2O$ DMAP (CH_3CN); (b) 1) $NaBH_4$ (DME-MeOH); 2) AcOH (H_2O); (c) 1) $LiBH_4$ (THF); 2) AcOH (H_2O).

While trying to scale up the procedure, we found that the removal of the benzylic group in **1** (step (a); Scheme 1) was not easily manageable due to the large amount of ammonia required.[19] As the preparation of compound **1** itself involved several steps, we sought a shorter way that would allow bypassing this pyrrolidinone to arrive at key intermediate **4** starting from (S)-pyroglutamic acid.[20] Its esterification to **8** and N-protection afforded compound **9** (see Scheme 2). Our previous experience with N-benzylpyroglutamates suggested that we could carry out the reduction of the ester moiety in derivative **9** in a selective manner, but this time over-reduction to **10** took place.[6] Then we tried to obtain **12** reversing the order

of the protection-reduction protocol, that is, via (S)-pyroglutaminol **11**.[21] In this case, however, we observed lack of selectivity during the N-protection step, which yielded in fair amount compound **12a** instead. We did consider the selective hydrolysis of the carbonate in compound **12a**, but judged it impractical since it meant another step in the process and anyway, pursuing the synthesis along this path would be wasteful of valuable BOC_2O. Compound **12**, precursor to intermediate **4**, remained thus rather intangible by any of these routes. Hence, we had to turn back to the original plan in order to obtain key derivative **4**. This time we prepared pyrrolidinone **2**, using anisaldehyde instead of benzaldehyde and performed an oxidative removal of the protecting group.[22] This change allowed a slight increase in the yield of **3**, so that pyrroline **6** could be obtained in 38% yield from compound **2** (17% overall). But more importantly, we were able to carry out the synthesis at a larger scale.

In conclusion, this is the first synthesis of amine **7** by means of a nonracemic pathway. This route allows the creation of pyrrolidines with a chiral quaternary center vicinal to nitrogen. We continue exploring ways to shorten the synthetic sequence to **7** in order to obtain it in larger quantities and be able to test it routinely as a chiral 'quat' auxiliary.[23]

EXPERIMENTAL

Commercial THF was distilled under an inert atmosphere from sodium benzophenone ketyl prior to use. Other reagents and solvents were purchased and used without further purification unless stated otherwise. Work up as usual means separating the organic phase, drying over Na_2SO_4 and concentrating on a rotary evaporator. Melting points were taken on a Fisher-Johns apparatus and are uncorrected.

^{1}H-NMR and ^{13}C-NMR data were recorded on a Varian Gemini 200 (200 MHz) and Varian Unity Plus (300 MHz) and are given as δ ppm displacements from TMS as internal standard; coupling constants (**J**) are expressed in Hertz. IR spectra were obtained on a Nicolet 55-XFT and a Perkin Elmer 283B. Low (EI+ mode) and HRMS were determined on JEOL instruments, JMS-AX505HA (EI+ mode) and JMS-SX102A (FAB+ mode). Optical rotations were taken at r.t. on a Jasco DIP-60 polarimeter. Analytical TLC was done on Macherey-Nagel aluminum foils coated with F_{254} silica gel cut in 7×2–3 cm pieces and viewed with UV light and/or ethanolic 10% phosphomolybdic acid solution. Column chromatography was carried out using 70–230 mesh silica gel from Merck.

(S)-1-(4′-Methoxybenzyl)-5-methoxymethyl-pyrrolidin-2-one. **2**. This compound, a yellow oil, was obtained according to the published procedure

for the preparation of **1**, using 4-methoxy-benzaldehyde instead.[6] Overall yield: 45% (5 steps from (S)-glutamic acid). $[\alpha]_D = +81.9^\circ$ (c = 1.00; $CHCl_3$); lit.[24] $[\alpha]_D = +85.5^\circ$ (c = 1.2 $CHCl_3$). **IR** (film, cm^{-1}): 2930, 1686, 1612, 1513, 1246, 1119. **^{1}H-NMR** ($CDCl_3$): 7.19 (AA′BB′, 2H, J = 7.6), 6.84 (AA′BB′, 2H, **J** = 7.6), 4.85 (d, H_A, J = 14.8), 4.11 (d, H_B, J = 14.8), 3.78 (s, 3H), 3.64–3.53 (m, 1H), 3.42–3.28 (m, 2H), 3.26 (s, 3H), 2.61–2.45 (ddd, 1H, J = 16.8, 9.6, 3.1), 2.44–2.25 (ddd, 1H, J = 16.8, 9.6, 3.1), 2.13–1.97 (m, 1H), 1.89–1.72 (m, 1H). **^{13}C-NMR** ($CDCl_3$): 175.2, 158.8, 129.2, 128.5, 113.7, 73.6, 58.9, 56.6, 55.1, 44.1, 30.1, 21.5. **MS** m/z (%): 249 (**M^+**, 35), 204 (40), 121 (100), 91 (6), 78 (9), 55 (5). **EI-HRMS** calcd for $C_{14}H_{19}NO_3$ (M^+) 249.1365, found 249.1363.

(S)-5-Methoxymethyl-pyrrolidin-2-one **3** by reductive cleavage.[8] In a 500 ml three-necked round bottom flask compound **1**[6] (4.5 g; 20.54 mmol) was dissolved in 55 ml THF and 4.5 ml water. The flask, fitted with a glass stopper and a dry ice filled cold finger connected to a dry ice cooled trap, was placed in a dry ice/acetone bath. Liquid ammonia (~220 ml), collected from a cylinder in a dry ice cooled trap, was distilled into the flask connecting the trap to the reaction flask by means of a rubber hose and a glass fitting and gently warming it with a water/methanol bath. Stirring was started next and Lithium (2.76 g; ~4 eq.) cut into small pieces, washed in hexane and immersed briefly in methanol to turn it shiny, was added as quickly as possible. The reaction mixture turned blue and the next piece was not added until the color had disappeared; pieces were added until the color did not vanish immediately. Cooling bath and cold finger were removed next and the mixture left overnight in a hood for ammonia to evaporate. Solvents were then removed in vacuo, the solid residue suspended in THF, filtered and the solution worked up as usual. Yield: 2.2 g (84.6%) of a light yellow oil used without further purification. $[\delta]_D = +61.44^\circ$ (c = 1.04; $CHCl_3$).

By oxidative cleavage:[22]. To compound **2** (5.5 g; 22 mmol) dissolved in 20 ml CH_3CN in a 250 ml round bottom flask were added, ammonium cerium (IV) nitrate (CAN) (48.5 g; 4 eq.), 0.4 ml water and another 20 ml CH_3CN (to keep a 1:100 water/CH_3CN ratio). The mixture was stirred 2 h, then 60 ml CH_2Cl_2 were added and stirring was continued a further 30 min. Solids were next filtered off and the reaction mixture was concentrated in vacuo at r.t. The residue was taken up in 100 ml ethyl ether and solid $NaHCO_3$ was added until the brown precipitate turned deep yellow. After separation of the solids the mixture was worked up as usual. The residue was purified by silica gel column chromatography; elution: hexane/ethyl acetate 9:1. Yield: 2.8 g (97.9%) of a colorless oil.

$[\alpha]_D = +60.5^\circ$ (c = 1.0; $CHCl_3$). **IR** (film, cm^{-1}): 3269, 1691, 1267, 1124. **^{1}H-NMR** ($CDCl_3$): 7.01 (br, s, 1H), 3.88–3.80 (m, 1H), 3.41 (dd, H_A,

J = 9.6, 4.2), 3.37 (s, 3H), 3.29 (dd, H_B, J = 9.6, 7.2), 2.35 (ddd, 1H, J = 7.2, 3.3, 0.3), 2.32 (ddd, 1H, J = 7.2, 4.5 0.3), 2.27–2.13 (m, 1H). **^{13}C-NMR** ($CDCl_3$): 178.3, 76.0, 58.8, 53.6, 29.54, 22.9. **MS** m/z (%): 129 (M^+, 15), 84 (100), 56 (24), 41 (46). **EI-HRMS** calcd for $C_6H_{12}NO_2$ $(M+1)^+$ 130.0868, found 130.0866.

Introduction of the amino protecting group (General procedure). The substrate was dissolved in CH_3CN. Next, DMAP (0.1 eq.) was added, followed by solid BOC_2O (1.2 eq), added in small portions. The mixture in the flask, stoppered with a glass valve that allowed the relief of pressure buildup (CO_2 generation), monitored by TLC, was stirred 24 h; upon reaction completion it was concentrated in vacuo at r.t. The residue was dissolved in ether and worked up as described elswhere.[25]

(S)-1-(tert-Butoxycarbonyl)-5-methoxymethyl-pyrrolidin-2-one **4** Prepared as described above dissolving compound **3** (6.11 g; 47.36 mmol) in 50 ml CH_3CN, adding DMAP (0.584 g) and BOC_2O (12.44 g). Yield: 813 g (75%) of a yellow oil. $[\alpha]_D = -75.31^\circ$ (c = 1.04; $CHCl_3$); lit.[26] $[\alpha]_D = -58.8^\circ$ (c = 1.0; $CHCl_3$).

IR (film, cm^{-1}): 2981, 1787, 1710, 1313, 1154, 1023. **^{1}H-NMR** ($CDCl_3$): 4.28–4.22 (m, 1H), 3.58 (dd, 1H, J = 9.6, 4.8), 3.51 (dd, 1H, J = 9.6, 3.0), 3.35 (s, 3H), 2.69 (ddd, 1H, J = 1.77, 10.2, 1.2), 2.37 (ddd, 1H, J = 17.7, 10.2, 2.7), 2.18–2.05 (m, 1H), 2.04–1.93 (m, 1H), 1.54 (s, 9H). **^{13}C-NMR** ($CDCl_3$): 174.6, 149.8, 82.6, 73.3, 59.1, 57.1, 31.8, 27.9, 21.1. **MS** m/z (%): 230 (M+1, 10), 184 (21), 156 (32), 130 (44), 84 (100), 57 (93).

(S)-5-tert-Butoxycarbonylamino-6-methoxy-hexan-2-one **5** In a dry 100 ml round bottom flask provided with stirring bar, septum and under Argon atmosphere, pyrrolidone **4** (8 g; 34.93 mmol) was dissolved in 15 ml anhydrous THF. The flask was cooled in a dry ice/acetone bath kept at -60° to -40°C and under stirring, an ethereal solution of 3M methyl magnesium bromide (20 ml; 1.7 eq.) was added dropwise via syringe. The bath was next removed and the resulting milky, slightly yellow mixture was stirred 1 h at r.t., cooled to -20°C and quenched with 30 ml of a NH_4Cl saturated aqueous solution. After phase separation, the aqueous was extracted with ethyl ether (3×30 ml), the extracts combined with the organic phase and worked up as usual. The product was crystallized from an ethyl ether-hexane mixture. Yield: 6.5 g (75.8%) of a slightly yellow crystalline compound; m.p. 42°C. $[\alpha]_D = -13.5^\circ$ (c = 1.0; $CHCl_3$). **IR** (film, cm^{-1}): 2976, 1714, 1525, 1455, 1366, 1171. **^{1}H-NMR** ($CDCl_3$): 4.75 (br. s. 1H), 3.7–3.66 (m, 1H), 3.36–3.33 (m, 2H), 3.33 (s, 3H), 2.52 (dt, 2H, J = 7.3, 2.1), 2.14 (s, 3H), 1.86–1.71 (m, 2H), 1.44 (s, 9H). **^{13}C-NMR** ($CDCl_3$): 208.2, 155.6, 79.1, 74.7, 58.9, 49.7, 40.3, 29.8, 28.3, 26.2. **MS** m/z (%): 245 (M^+, 23), 190 (49), 172 (21), 144 (71), 128 (34), 100 (95), 83 (44),

57 (100). **EI-HRMS** calcd for $C_{12}H_{24}NO_4$ $(M+1)^+$ 246.1705, found 246.1699.

(S)-5-Methoxymethyl-2-methyl-Δ^1-pyrroline **6**. In a 250 ml round bottom flask, trifluoroacetic acid (17.3 ml; 10 eq.) was added dropwise by means of an addition funnel to compound **5** (5.5 g; 22.44 mmol) dissolved in 100 ml CH_2Cl_2. The reaction was stirred 5 h at r.t. and then quenched by careful addition of 30 ml of $NaHCO_3$ saturated aqueous solution. The aqueous phase was extracted with CH_2Cl_2 (2×10 ml), the extracts were mixed with the organic phase and worked up as usual to give a brown liquid purified by distillation. Yield: 1.93 g (67.71%) of a colorless volatile oil that was kept away from light in the refrigerator under Argon atmosphere; b.p. (Kugelrohr) 50°C (0.1 mmHg). $[\alpha]_D = +131.36^\circ$ (c = 1.02; $CHCl_3$). **IR** (film, cm^{-1}): 2923, 1650, 1197, 1124. **^{1}H-NMR** ($CDCl_3$): 4.17–4.11 (m, 1H), 3.53 (dd, 1H, J = 9.0, 5.1), 3.44 (dd, 1H, J = 9.0, 6.0), 3.38 (s, 3H), 2.61–2.42 (m, 2H), 2.04 (d, 3H, J = 3), 2.07–1.95 (m, 1H), 1.75–1.6 (m, 1H). **^{13}C-NMR** ($CDCl_3$): 175.6, 75.8, 72.1, 59.0, 38.8, 25.7, 19.6 **MS** m/z (%): 128 (M+1, 98), 97 (36), 82 (100), 55 (26). **FAB-HRMS** calcd for $C_7H_{14}NO$ $(M+1)^+$ 128.1075, found 128.1078.

(S)-5,5-Dimethyl-2-methoxymethyl-pyrrolidine **7**. Finely ground $CeCl_3 \times 7H_2O$ (4.55 g; 12.21 mmol) was dried under high vacuum in a 100 ml round bottom flask placed in an oil bath at 135–140°C for at least 2 h. The hot flask was then purged with Argon until cool, capped with a septum and put in an ice bath to add 50 ml of anhydrous THF via syringe. The mixture was stirred for another 2 h at r.t., the flask cooled again to 0°C and an ethereal solution of 2 M methyl magnesium bromide (6 ml; 12 mmol) was added dropwise via syringe. After $1\frac{1}{2}$ h stirring at 0°C, cooling to −78°C, adding vial syring pyrroline **6** (0.19 g; 1.49 mmol) dissolved in a little THF, the mixture was monitored by TLC and stirred another 3 h at −25° to 0°C. Since TLC did not show further change, the reaction was quenched with 10 ml of a NH_4Cl saturated aqueous solution, phases were separated, the aqueous extracted with ethyl ether (2×10 ml), the extracts and organic phase combined and worked up as usual. The residue was purified by silica gel column chromatography; elution: CH_2Cl_2/CH_3OH 95:5. Yield: 10 mg (15%). $[\alpha]_D = +0.66^\circ$ (c = 0.3; $CHCl_3$). **IR** (film, cm^{-1}): 3412, 2928, 1633, 1380. **^{1}H-NMR** ($CDCl_3$): 8.01 (br. s, 1H), 4.18–4.09 (m, 1H), 3.73 (d, 2H, J = 45), 3.44 (s, 3H) 2.19–1.99 (m, 2H), 1.94–1.88 (m, 2H), 1.64 (s, 3H), 1.63 (s, 3H). **^{13}C-NMR** ($CDCl_3$): 70.2, 65.8, 59.1, 58.5, 38.4, 25.9, 25.8, 25.6. **MS** m/z (%): 144 (M^+,7), 129 (10), 98 (62), 83 (100), 45 (42). Anal. calcd for $C_8H_{17}NO$ C, 67.09 H, 11.96 N, 9.78. Found: C, 66.95 H, 11.90 N, 9.67%.

Methyl (S)-pyroglutamate **8**. To (S)-pyroglutamic acid (64.5 g; 500 mmol) dissolved in 500 ml absolute methanol in a 1 l round bottom flask, $SOCl_2$ (54 ml; 739.22 mmol) was slowly added at 0°C. The mixture

was next refluxed for 30 min, then concentrated in vacuo at r.t., trapping acid fumes with solid KOH. The residue was taken up in 500 ml CH_2Cl_2 and neutralized with Et_3N. The precipitate was filtered and washed with Et_2O. The combined organic phases were evaporated, the residue redissolved in ether for additional salt precipitation, filtered if necessary and worked up as usual. Yield: 71g (99.3%) of a light yellow oil whose physical data were in accordance with those reported.[27,28]

(S)-1-tert-Butoxycarbonyl-5-methoxycarbonyl-pyrrolidin-2-one **9**. Prepared as indicated in the general procedure above, dissolving methyl (S)-pyroglutamate **8** (70 g; 489.5 mmol) in 200 ml CH_3CN, adding DMAP (6 g) and BOC_2O (100 g). The crystalline compound obtained was recrystallized from ethyl ether/CH_2Cl_2. Yield: 81.74 g (68.7%); m.p. 83–84°C. $[\alpha]_D = -32.4^\circ$ (c = 1.01; $CHCl_3$); lit.[28] m.p. 72.5–73.5°C (hexane/ethyl acetate). $[\alpha]_D = -30.4^\circ$ (c = 1.0; $CHCl_3$). **IR** (film, cm^{-1}): 2980, 1794, 1750, 1716, 1371, 1312, 1154. **^{1}H-NMR** ($CDCl_3$): 4.62 (dd, 1H, J = 9.6, 3.0), 3.78 (s, 3H), 2.69–2.57 (dt, 1H, J = 17.4, 9.9), 2.54–2.38 (ddd, 1H, J = 17.4, 9.9, 4.2), 2.4–2.26 (dddd, 1H, J = 12.9, 9.9, 4.2, 0.9), 2.085–1.98 (dddd, 1H, J = 12.9, 6.6, 3.0, 0.9), 1.49 (s, 9H). **^{13}C-NMR** ($CDCl_3$): 173.1, 171.7, 149.2, 83.48, 58.7, 52.4, 31.1, 27.79, 21.39. **MS** m/z (%): 243 (M^+, 1), 228 (4), 184 (23), 170 (12), 144 (28), 84 (100) 57 (96), 41 (27).

(S)-2-tert-Butoxycarbonylamino-1,5-dihydroxypentane **10**. In a 1l round bottom flask pyroglutamate **9** (81.77 g; 336 mmol) was dissolved in 350 ml DME and 17.5 ml methanol. Stirring was started, the flask cooled in an ice bath and $NaBH_4$ (25.42 g, 2 eq.) was added. The mixture was then stirred at r.t. for $1\frac{1}{2}$ days and adjusted to pH = 6 by the addition of aqueous 20% AcOH. The aqueous phase was extracted with CH_2Cl_2 (2×100 ml). The combined organic phases were worked up as usual and the residue crystallized in an ethyl acetate/hexane mixture. Yield: 50 g (73.9%) of crystalline white solid; m.p. = 55°C. $[\alpha]_D = -48.2^\circ$ (c = 0.99; $CHCl_3$). **IR** (film, cm^{-1}): 3349, 2985, 1682, 1533, 1170. **^{1}H-NMR** ($CDCl_3$): 5.1 (br, s, 1H), 3.65–3.62 (m, 2H), 3.6 (m, 2H), 3.58 (m, 1H), 1.66–1.56 (m, 4H), 1.43 (s, 9H). **^{13}C-NMR** ($CDCl_3$): 156.5, 79.52, 64.94, 62.11, 52.27, 28.68, 28.37, 27.91, **MS** m/z (%): 188 (M^+, 6), 146 (15), 132 (94), 88 (32), 71 (35), 57 (100), 41 (21), Anal. calcd for $C_{10}H_{21}NO_4$ C, 54.77 H, 9.65 N, 6.39. Found: C, 54.69 H, 9.71 N, 6.29%.

(S)-1-tert-Butoxycarbonyl-5-tert-butoxycarbonyloxymethyl-pyrrolidin-2-one **12a**. Prepared as indicated in the general procedure above, dissolving pyroglutaminol **11** (4.88 g; 42.43 mmol) in 20 ml CH_3CN and 40 ml CH_2Cl_2, adding DMAP (0.518 g) and BOC_2O (18.52 g; 2 eq.). In this case however, the first eq. Of BOC_2O was added and the reaction monitored by TLC, but since starting material did not disappear completely, the rest was added in portions. After work up, the product was purified by

recrystallization from ether/hexane. Yield: 8.2 g (61.3%) of a white solid; m.p. 52°C. $[\alpha]_D = -59.14°$ (c = 1.0; $CHCl_3$). **IR** (film, cm^{-1}): 2980, 1790, 1784, 1716, 1285. **^{1}H-NMR** ($CDCl_3$): 4.41–4.33 (m, 2H), 4.17–4.11 (m, 1H), 2.68 (ddd, 1H, J = 17.7, 11.1, 9.6), 4.42 (ddd, 1H, J = 17.7, 9.6, 2.4), 2.24–2.07 (m, 1H), 2.03–1.94 (m, 1H), 1.54 (s, 9H), 1.47 (s, 9H). **^{13}C-NMR** ($CDCl_3$): 173.8, 153.1, 149.2, 83.2, 82.5, 66.6, 56.2, 31.5, 27.8, 27.6, 20.8. **MS** m/z (%): 316 (M+1, 2), 204 (7), 160 (17), 142 (20), 97 (57), 84 (100), 57 (93). **FAB-HRMS** calcd for $C_{15}H_{26}NO_6$ $(M+1)^+$ 316.1760, found 316.1755.

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