

# L-Glutamic acid and L-alanine derivatives as building blocks for the synthesis of a chiral monomer precursor of AABB-type polyamide

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**Dedicated to Prof. Roberto Rossi on his 60<sup>th</sup> birthday and Prof. Edmundo Rúveda on his 70<sup>th</sup> birthday**

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## Abstract

The chiral monomer *N*-(1'-amino-2'-(*S*)-propyl)-5-oxo-2-(*S*)-tetrahydrofurancarboxy-amide hydrochloride (**11**), a precursor of a AABB-type stereoregular polyamide, has been synthesized from pentachlorophenyl 5-oxo-2-(*S*)-tetrahydrofurancarboxylate (**2**) and 2-(*S*)-amino-1-propanol (**3**). Compounds **2** and **3** are derivatives of the natural amino acids L-glutamic acid and L-alanine, respectively. The regioselective attack of the amino group of **3** to the ester function of **2** led to *N*-(1'-hydroxy-2'-(*S*)-propyl)-5-oxo-tetrahydrofurancarboxyamide (**4**) in 80% yield. However, the tosylation of the primary hydroxyl group of **4**, and the subsequent substitution by azide to give **6**, took place with low yields. Therefore, an alternative route was conducted starting from **3**, which was selectively *N*-protected as the *tert*-butyloxycarbonyl derivative (*N*-Boc), *O*-tosylated and substituted by azide to afford 1-azido-2-(*S*)-*N*-(*tert*-butyloxycarbonyl)aminopropane (**9**) in 41% yield from **3**. The amino group of **9** was deprotected by acid hydrolysis and the resulting amine **10** was regioselectively condensed with **2** to give the azide derivative **6**. Hydrogenolysis of **6** afforded the desired monomer **11** in 69% yield from **2** and **10**.

**Keywords:** Chiral monomer, stereoregular polyamide, L-alanine, L-alaninol, L-glutamic acid

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## Introduction

Common polyamides are a source of environmental pollution as they are resistant to chemical and enzymatic degradation. The highly ordered structures of polyamides, due to strong intramolecular interactions caused by hydrogen bonding, are responsible for their low biodegradability. Such polyamides are based on petroleum, a non-renewable resource, which is

expected to become difficult to obtain in the near future. One strategy to solve the problems of fossil resources and environment relies upon the utilization of natural regrowing products for the chemical synthesis of polymers. In particular, carbohydrates and amino acids have shown to be highly convenient for the preparation of chiral, biodegradable polymers.<sup>1-3</sup>

The introduction of functionalities and stereocenters in a polymeric chain allows the control of the physical and mechanical properties of the polymer, which usually shows improved biocompatibility and biodegradability.<sup>1-4</sup> For example, the amide linkages of polyamides formed by sebacic acid and L-phenylalanine itself, or together with L-valine, were cleavable by chymotrypsin.<sup>5</sup> Also, copolyamides of caprolactam and L-phenylalanine were susceptible to biodegradation.<sup>6</sup> In our laboratory, we have employed common monosaccharides<sup>7-9</sup> and amino acids<sup>10-12</sup> for the synthesis of potentially biodegradable, stereoregular polyamides. In particular, the synthesis of stereoregular polyamides of AABB-type is difficult when the monomers derived from carbohydrates or amino acids possesses one or more stereocenters in their structures.<sup>1,12,13</sup> The requirement for the construction of a stereoregular polymer is the existence of a 2-fold axis of symmetry in the precursor monomer. Otherwise, regioisomerism occurs during the polycondensation leading to a non-stereoregular polyamide with the building blocks randomly oriented along the polymer chain. Therefore, stereocontrol in the polymerization is needed when non-symmetric monomers are employed.<sup>11,12,14</sup>

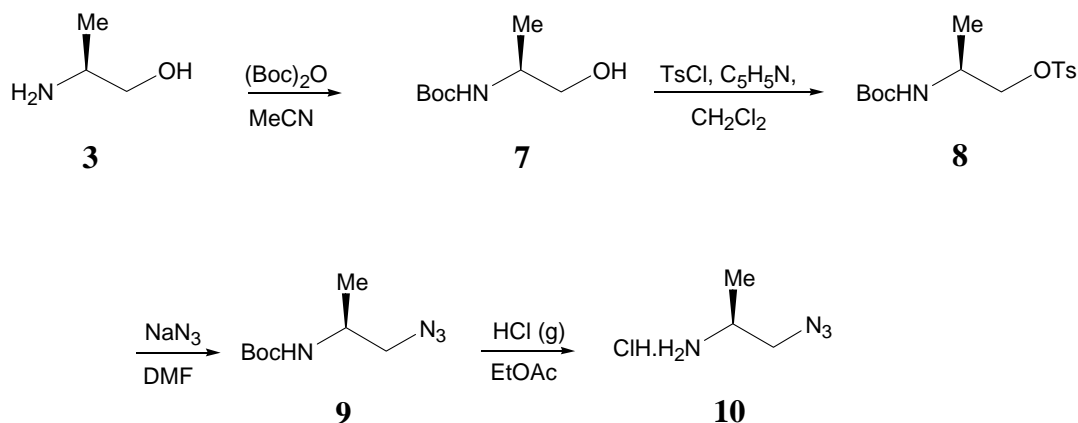
In the present work we wish to report the synthesis of a monomer precursor of a non-peptidic stereoregular AABB-type polyamide. For the preparation of such a monomer we employed a diacid derived from L-glutamic acid and a diamine derived from L-alanine. The resulting polyamide will possess in both, the diamine and diacid units, a stereocenter having the *S*-configuration. It has been reported<sup>1-3</sup> that analogous materials could be employed as chiral matrices in asymmetric synthesis.

## Results and Discussion

The diacid derivative **2** was prepared by deamination of L-glutamic acid (**1**) with nitrous acid<sup>15</sup> followed by activation of the carboxylic acid function with pentachlorophenol.<sup>11</sup> Compound **2** reacted with L-alaninol (2-(*S*)-amino-1-propanol, **3**), the commercially available product of reduction of L-alanine (Scheme 1). The reaction was highly chemo- and regio-selective to give the single regioisomer **4** from the four theoretically possible. Compound **4** was obtained crystalline from the reaction mixture in 80% yield. The high selectivity for the addition through the amino group of **3** should be expected as the amine function is a better nucleophile than the alcohol. The higher reactivity of the pentachlorophenyl ester of **2** with respect to the lactone group may be attributed to the fact that the pentachlorophenolate is a weaker base (a better leaving group) than the alkoxide, and also because the ester group possesses a hydroxy substituent on the  $\alpha$ -carbon, which increases the rate of aminolysis.<sup>16</sup> The structure of **4** was confirmed by NMR spectroscopy. Thus, the <sup>13</sup>C NMR spectrum of **4** showed the signals for the

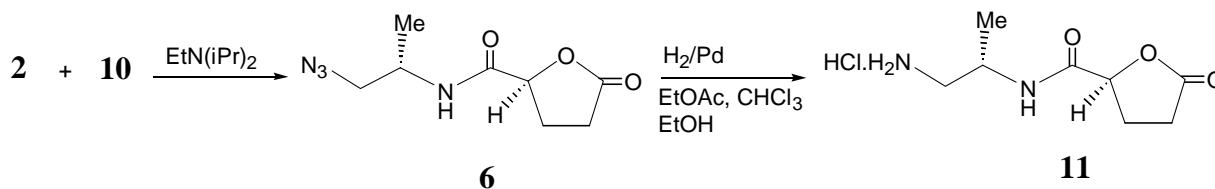


(Scheme 3). The hydrogenolysis of the azide function of **6** with 10% Pd/C in hydrochloric acid solution or in hydrogen chloride in methanol led to a low yield of the amine hydrochloride **11**, because the lactone ring underwent partial opening by hydrolysis or alcoholysis.



### Scheme 2

However, the hydrogenolysis of the azide group of **6** could be conducted without affecting the lactone by using the same catalyst and a 10:1:2 mixture of EtOAc-EtOH-CHCl<sub>3</sub> as solvent. In this way, hydrogen chloride was smoothly generated by hydrogenation of chloroform to give the hydrochloride of the amino group formed in the same reaction.<sup>18</sup> The hydrochloride derivative **11** was thus obtained as a crystalline product in 86% yield. As described for **4**, compound **11** exhibited in its <sup>13</sup>C NMR spectrum the resonances due to the amide and lactone carbonyl carbons. The low field signals for C-2 (76.9 ppm) and for H-2 (4.89 ppm), in the respective <sup>13</sup>C and <sup>1</sup>H NMR spectra of **11** indicated the presence of the lactone ring. Furthermore, the amino acid **11** gave a satisfactory elemental analysis. The polymerization of **11** under various reaction conditions is being studied.



### Scheme 3

In summary, the synthesis of **11** was successfully accomplished starting from readily accessible derivatives of L-glutamic acid and L-alanine. The carboxylic acid of **11** is activated for the homopolycondensation, as lactones readily undergo aminolysis reactions. The polymerization of **11** will yield a stereoregular AABB-type polyamide having S-configuration

for both stereocenters of the repeating unit.

## Experimental Section

**General Procedures.** Solvents were dried and purified by appropriate standard procedures. Melting points were determined with a Fisher-Johns apparatus and are uncorrected. Analytical thin layer chromatography (TLC) was performed on 0.2 mm silica gel 60 F<sub>254</sub> (Merck) aluminum supported plates. Detection was effected by exposure to UV light or charring with 5% H<sub>2</sub>SO<sub>4</sub> (v/v) in EtOH containing 0.5% *p*-anisaldehyde. Column chromatography was performed with silica gel 60 (230-400 mesh, Merck). Optical rotations were measured with a Perkin-Elmer 343 digital polarimeter at 25 °C. Nuclear magnetic resonance (NMR) were recorded on a Bruker AC 200 spectrometer at 200 MHz (<sup>1</sup>H) and 50.3 MHz (<sup>13</sup>C) in CDCl<sub>3</sub> solutions (unless otherwise indicated) with TMS as an internal standard.

***N*-(1'-Hydroxy-2'-(*S*)-propyl)-5-oxo-2-(*S*)-tetrahydrofurancarboxamide (4).** A solution of pentachlorophenyl 5-oxo-2-(*S*)-tetrahydrofurancarboxylate<sup>11</sup> (**2**, 1.00 g, 2.64 mmol) in dry DMF (10 mL) and *N,N*-diisopropylethylamine (0.4 mL) was cooled to 0 °C, and a solution of 2-(*S*)-amino-1-propanol (L-alaninol, **3**, 0.20 g, 2.66 mmol) in DMF (10 mL) was added dropwise. The mixture was stirred at room temperature for 16 h and concentrated in vacuum; the residue crystallized from 1:1 EtOAc-hexane. Recrystallization from the same solvent gave chromatographically pure (*R<sub>f</sub>* 0.30, EtOAc) crystals of **4** (0.39 g, 80%); mp 100-102 °C; [ $\alpha$ ]<sub>D</sub> -42 (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR  $\delta$  6.75 (bs, 1H, NH), 4.86 (dd, 1H, *J* = 4.5, 7.5 Hz, H-2), 4.05 (m, 1H, H-2'), 3.65 (dd, 1H, *J* = 4.0, 11.2 Hz, H-1'a), 3.51 (dd, 1H, *J* = 5.9, 11.2 Hz, H-1'b), 3.17 (bs, 1H, OH), 2.66-2.32 (m, 4H, H-3a, 3b, 4a, 4b), 1.15 (d, 3H, *J* = 6.7 Hz, H-3'); <sup>13</sup>C NMR  $\delta$  176.1, 169.6 (C-5, 6), 77.5 (C-2), 65.8 (C-1'), 47.4 (C-2'), 27.6, 25.7 (C-3, 4), 16.7 (C-3'). Anal. Calcd for C<sub>8</sub>H<sub>13</sub>NO<sub>4</sub>: C, 51.33; H, 7.00; N, 7.48. Found: C, 51.62; H, 6.83; N, 7.56.

***N*-(1'-Azido-2'-(*S*)-propyl)-5-oxo-2-(*S*)-tetrahydrofurancarboxamide (6).** To a solution of **4** (0.40 g, 2.14 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and pyridine (0.5 mL, 6.42 mmol), cooled to 0 °C, was added tosyl chloride (0.84 g, 4.28 mmol) in small portions. The mixture was stirred at room temperature for 20 h, and then diluted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The solution was washed with saturated aqueous K<sub>2</sub>CO<sub>3</sub>, then with water, and dried (MgSO<sub>4</sub>). Concentration of the organic extract led to **5** (0.22 g, 34%) as a chromatographically homogeneous syrup (*R<sub>f</sub>* 0.55, EtOAc); <sup>1</sup>H NMR  $\delta$  7.74, 7.30 (2 d, 4H, *J* = 8.2 Hz, H-aromatic), 5.23 (bd, 1H, *J* = 8.1 Hz, NH), 4.90 (dd, 1H, *J* = 4.3, 6.9 Hz, H-2), 4.12 (dd, 1H, *J* = 6.5, 11.3 Hz, H-1a), 4.05 (d, 1H, *J* = 4.8, 11.3 Hz, H-1b), 3.65 (m, 1H, H-2'), 2.70-2.34 (m, 4H, H-3a, 3b, 4a, 4b), 2.41 (s, 3H, ArCH<sub>3</sub>), 1.01 (d, 3H, *J* = 6.7 Hz, H-3'); <sup>13</sup>C NMR  $\delta$  176.2, 169.8 (C-5, 6), 143.6, 137.8, 129.8, 126.9 (C-aromatic), 77.6 (C-2), 67.9 (C-1'), 48.6 (C-2'), 26.7, 25.7 (C-3.4), 21.5 (ArCH<sub>3</sub>), 17.7 (C-3').

Crude compound **5** (0.31 g, 1.02 mmol) was dissolved in dry DMF (10 mL) and sodium azide (0.18 g, 2.76 mmol) was added. The mixture was stirred at 60 °C for 2 h, then filtered, and the

filtrate concentrated. The syrup, which showed several spots on TLC (EtOAc), was subjected to column chromatography with mixtures of increasing polarity of hexane-EtOAc (from 2:1 to 1:4). The colorless syrup that had  $R_f$  0.50 was identified as **6** (0.04 g, 21%);  $[\alpha]_D$  -38 (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR  $\delta$  6.45 (bs, 1H, *NH*), 4.79 (t, 1H,  $J = 7.6$  Hz, H-2), 4.11 (m, 1H, H-2'), 3.40 (dd, 1H,  $J = 4.9, 12.3$  Hz, H-1'a), 3.31 (dd, 1H,  $J = 5.1, 12.3$  Hz, H-1'b), 2.63-2.23 (m, 4H, H-3a, 3b, 4a, 4b), 1.16 (d, 3H,  $J = 6.8$  Hz, H-3'); <sup>13</sup>C NMR  $\delta$  175.6, 168.8 (C-5, 6), 77.3 (C-2), 55.2 (C-1'), 44.9 (C-2'), 27.6, 25.6 (C-3, 4), 17.8 (C-3'). Anal. Calcd for C<sub>8</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>: C, 45.28; H, 5.70; N, 26.40. Found: C, 44.73; H, 5.45; N, 26.55.

Alternatively, compound **6** was prepared by condensation of **2** with the L-alaninol derivative **10**. A solution of **2** (1.19 g, 3.15 mmol) in dry DMF (17 mL) and *N,N*-diisopropylethylamine (1.12 mL) was cooled to 0 °C and a solution of **10** (0.43 g, 3.15 mmol) in dry DMF (17 mL) was added dropwise. The mixture was stirred at room temperature for 16 h and then the solvent was evaporated under reduced pressure. The residue was purified by column chromatography using mixtures of increasing polarity of hexane-EtOAc (from 9:1 to 1:4). Fractions containing the product having  $R_f$  0.50 (EtOAc) were concentrated to give **6** (0.53 g, 80%). Compound **6** exhibited the same physical and spectral properties as the product described above.

**2-(S)-(N-tert-Butyloxycarbonyl)alaninol (7)**. To a solution of L-alaninol (1.00 g, 13.33 mmol) in dry acetonitrile (40 mL) was added di-*tert*-butyldicarbonate (3.00 g, 13.77 mmol) and triethylamine (1.86 mL, 12.91 mmol). The mixture was stirred at room temperature for 24 h, and concentrated. The residue was dried in vacuum to afford **7** (2.25 g, 97%) as a colorless syrup that crystallized on standing; mp 59-60 °C;  $[\alpha]_D$  -10 (*c* 1.0; CHCl<sub>3</sub>); <sup>1</sup>H NMR  $\delta$  4.85 (bs, 1H, *NH*), 3.68 (m, 1H, H-2), 3.56 (dd, 1H,  $J = 4.0, 10.9$  Hz, H-1), 3.43 (dd, 1H,  $J = 5.8, 10.9$  Hz, H-1'), 2.55 (bs, 1H, OH), 1.40 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>), 1.10 (d, 3H,  $J = 6.6$  Hz, H-3); <sup>13</sup>C NMR  $\delta$  156.4 (NCO<sub>2</sub>), 79.8 (Me<sub>3</sub>CO), 67.1 (C-1), 48.6 (C-2), 28.3 ((CH<sub>3</sub>)<sub>3</sub>CO), 17.3 (C-3). Anal. Calcd for C<sub>8</sub>H<sub>17</sub>NO<sub>3</sub>: C, 54.84; H, 9.78. Found: C, 54.64; H 9.65.

**2-(S)-(N-tert-Butyloxycarbonyl)amino-1-O-p-tosylsulfonyloxypropane (8)**. A solution of **7** (2.00 g, 11.43 mmol) in anhydrous chloroform (10 mL) and pyridine (2.70 mL, 33.38 mmol) was externally cooled with an ice-water bath, and tosyl chloride (3.18 g, 16.71 mmol) was slowly added. The mixture was stirred at room temperature for 10 h, diluted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and washed with 5% aqueous HCl, water, and saturated aqueous NaHCO<sub>3</sub>. The organic solution was dried (MgSO<sub>4</sub>) and concentrated to afford **8** (2.63 g, 70%) as a homogeneous syrup ( $R_f$  0.60, 2:1 toluene-EtOAc). The product was pure enough for the next step; <sup>1</sup>H NMR  $\delta$  7.80, 7.33 (2 d, 4H,  $J = 8.3$  Hz, H-aromatic), 4.62 (bs, 1H, *NH*), 4.07-3.88 (m, 3H, H-1, 1', 2), 2.45 (s, 3, ArCH<sub>3</sub>), 1.15 (d, 3H, H-3); <sup>13</sup>C NMR  $\delta$  154.9 (NCO<sub>2</sub>), 144.9, 132.7, 129.8, 128.0 (C-aromatic), 79.6 (Me<sub>3</sub>CO), 72.5 (C-1), 45.3 (C-2), 28.3 ((CH<sub>3</sub>)<sub>3</sub>C), 21.6 (ArCH<sub>3</sub>), 17.2 (C-3).

An analytical sample of **8** was obtained by filtration through a short column of silicagel, which was eluted first with toluene to remove some *p*-tolylsulfonyl chloride remaining. The column was eluted with toluene-AcOEt (from 10:1 to 1:1). Evaporation of the fractions containing the product of  $R_f$  0.60 (2:1 toluene-EtOAc) afforded solid **8**, which recrystallized from EtOAc-hexane gave mp 64-67 °C;  $[\alpha]_D$  -14 (*c* 1.0, CHCl<sub>3</sub>); and the same spectral data as described

above. Anal. Calcd for  $C_{15}H_{23}NO_5S \cdot 0.5 H_2O$ : C, 53.21; H, 7.15; N, 4.14. Found: C, 53.54; H, 6.82; N, 4.50.

**1-Azido-2-(S)-(N-tert-butyloxycarbonyl)aminopropane (9).** To a solution of crude **8** (2.50 g, 7.60 mmol) in dry DMF (20 mL) was added sodium azide (1.48 g, 22.8 mmol) and the mixture was heated to 70 °C for 5 h, with stirring. The resulting suspension was left to reach room temperature and filtered. The solid was washed with  $CH_2Cl_2$  and the filtrate was concentrated and extracted with  $CH_2Cl_2$ . The organic extracts and washing liquids were pooled together and the solvent evaporated to afford a syrup that was subjected to column chromatography (hexane-EtOAc from 99:1 to 95:5). The fractions of the column that contained the product having  $R_f$  0.60 (3:1 hexane-EtOAc) were concentrated to give oily **9** (0.70 g, 60%);  $[\alpha]_D -27$  (*c* 1.0,  $CHCl_3$ );  $^1H$  NMR  $\delta$  4.56 (bs, 1H, NH), 3.82 (m, 1H, H-2), 3.41 (dd, 1H,  $J = 4.9, 12.1$  Hz, H-1), 3.31 (dd, 1H,  $J = 4.7, 12.1$  Hz, H-1'), 1.45 (s, 9H,  $((CH_3)_3C)$ ), 1.18 (d, 3H,  $J = 6$  Hz, H-3);  $^{13}C$  NMR  $\delta$  155.1 ( $NCO_2$ ), 79.7 ( $Me_3CO$ ), 56.1 (C-1), 46.3 (C-2), 28.4 ( $((CH_3)_3CO)$ ), 17.2 (C-3). Anal. Calcd for  $C_8H_{16}N_4O_2$ : C, 47.99; H, 8.05, N, 27.98. Found: C, 47.57; H, 8.50; N, 28.10.

**2-(S)-Amino-1-azidopropane (10).** To a solution of **9** (0.70 g, 3.50 mmol) in dry EtOAc (7.0 mL) was added a saturated solution of hydrogen chloride in EtOAc (7.0 mL). The mixture was stirred at room temperature for 5 h and then concentrated. The residue was dissolved in MeOH (1 mL), the solution was diluted with  $CH_2Cl_2$  (5 mL) and, upon slowly addition of ethyl ether, white crystals of **10** (0.43 g, 90%) were obtained; mp 45-47 °C;  $[\alpha]_D +18$  (*c* 1.0, DMSO);  $^1H$  NMR (DMSO- $d_6$ , 200 MHz)  $\delta$  8.43 (bs, 3H,  $NH_3^+$ ), 3.66 (dd, 1H,  $J = 5.4, 12.8$  Hz, H-1), 3.56 (dd, 1H,  $J = 6.1, 12.8$  Hz, H-1'), 3.32 (m, 1H, H-2), 1.21 (d, 3H,  $J = 6.6$  Hz, H-3);  $^{13}C$  NMR (DMSO- $d_6$ , 50.3 MHz)  $\delta$  53.3 (C-1), 46.3 (C-2), 16.0 (C-3). Anal. Calcd for  $C_3H_9N_4Cl$ : C, 26.36; H, 6.64; N, 41.03. Found: C, 26.72; H, 7.01; N, 41.36.

**N-(1'-Amino-2'(S)-propyl)-5-oxo-2-(S)-tetrahydrofurancarboxamide hydrochloride (11).** Compound **6** (0.50 g, 2.36 mmol) dissolved in 10:1:2 EtOAc-EtOH- $CHCl_3$  (15 mL) was hydrogenated in the presence of 10% Pd/C (70 mg) at room temperature and under pressure (45 psi). After 4 h the mixture was filtered and the catalyst was washed with methanol. The filtrate and the washing liquids were pooled and concentrated to give a syrup that was dissolved in anhydrous methanol. Dropwise addition of dry ethyl ether afforded crystalline **11** (0.45 g, 86%); mp 169-171 °C,  $[\alpha]_D +40$  (*c* 1.0, DMSO);  $^1H$  NMR (DMSO- $d_6$ , 200 MHz)  $\delta$  8.43 (d, 1H,  $J = 8.0$  Hz, CONH), 8.19 (bs, 3H,  $NH_3^+$ ), 4.89 (dd, 1H,  $J = 5.5, 7.7$  Hz, H-2), 4.06 (m, 1H,  $J = 6.7$  Hz, H-2'), 2.86 (d, 2H,  $J = 6.7$  Hz, H-1'), 2.55-2.15 (m, 4H, H-3a, 3b, 4a, 4b), 1.13 (d, 3H,  $J = 6.7$  Hz, H-3');  $^{13}C$  NMR (DMSO- $d_6$ , 50.3 MHz)  $\delta$  176.9, 169.3 (C-5, 6), 76.9 (C-2), 42.8 (C-1', 2'), 27.1, 25.3 (C-3, 4), 17.8 (C-3'). Anal. Calcd for  $C_8H_{14}N_2O_3Cl$ : C, 43.15; H, 6.79; N, 12.58. Found: C, 43.11; H, 6.82; N, 12.45.

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