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Synthesis of (*R*)-(−) and (*S*)-(+)-3-(1-pyrrolyl)propyl-*N*-(3,5-dinitrobenzoyl)-α-phenylglycinate and derivatives. A suitable chiral polymeric phase precursor

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Abstract

A synthetic route to obtain (*R*)-(−) (**1**), (*S*)-(+)-3-(1-pyrrolyl)propyl-*N*-(3,5-dinitrobenzoyl)-α-phenylglycinate (**2**) and derivatives is described. In a first step, pyrrole derivatives were prepared using the Clauson-Kaas method. The esterification, second step, was performed using basic conditions due to sensitivity of the pyrrole group toward acidic conditions. A tautomeric equilibrium involving the stereogenic center induces the product epimerization. The substitution of DMAP and Et_3N by a highly hindered base, proton-sponge®, furnished the final products without racemization. The ee of **1**, **2** and of the corresponding methyl esters (**3** and **4**) were determined by ^1H NMR analysis in the presence of optically active $Eu(tfc)_3$. Epimerization was not observed in the preparation of the carboxylate salts (**5**–**8**).

1. Introduction

The area of conducting polymers has developed rapidly over the last few years.[1] These polymers may be obtained by chemical or electrochemical oxidative polymerization of the corresponding monomers, such as pyrrole, thiophene, aniline and acetylene, among others.[1] Polymers containing every conceivable type of substituent have been prepared from these techniques by simple functionalization of the starting monomer.[2–4] The electropolymerization of pyrrole-bearing optically active groups, including glucose,[5] camphor,[6,7] amino acids,[8–10] cyclodextrin[11] and L-lactate,[12] have been used to modify electrode surfaces.

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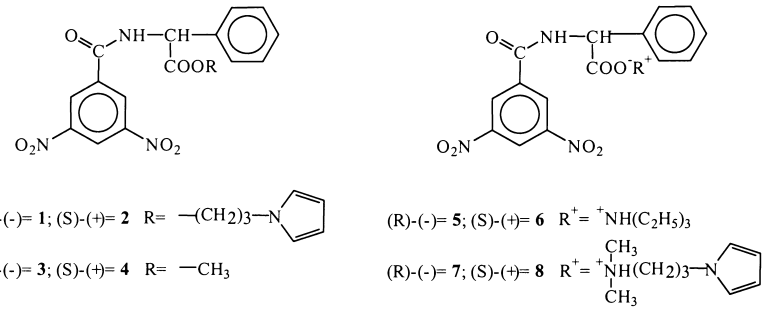
Polythiophene containing optically active substituents have also been described.[13,14] Thus, the polymerization of pyrrole-terminated chiral groups coupled to a π-acceptor or a π-donor functionality may lead to the preparation of optically active polymers applicable to enantioselective analysis, using Pirkle's methodology[15] for chiral recognition.[16] The present work describes a synthetic route to obtain **1** and **2** and derivatives **3** to **8**, with the aim of obtaining the corresponding polymeric films by chemical and electrochemical means.

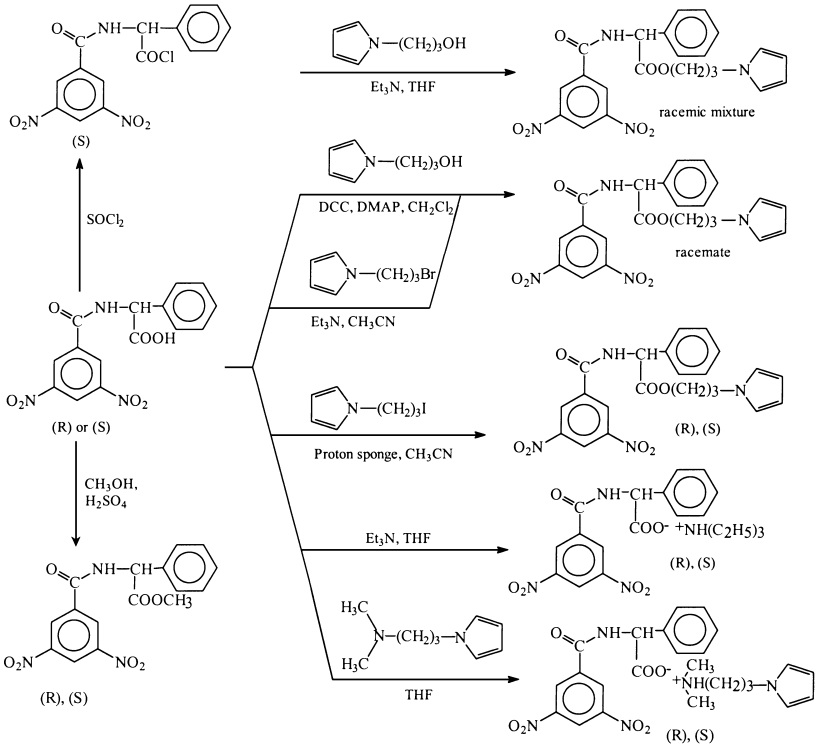


2. Results and discussion

The synthetic route to obtain **1** or **2** was divided into two steps: the first one involved preparation of pyrrole derivatives and the second the esterification step (Scheme 1). Pyrrole derivatives were prepared by condensation of primary amines with 2,5-dimethoxytetrahydrofuran, in glacial acetic acid, to give in one step *N*-substituted pyrroles. This method is applicable to a large variety of substituted aliphatic and aromatic amines. The reaction yields are dependent on the amine substituent and may vary from 40 to 90%.[17] The method, mainly developed by Clauson-Kaas and co-workers,[18] has the advantages of simplicity, mild conditions and good yields from readily available starting materials. In some cases, where acidic starting materials have been used, for instance, in the preparation of 1-(3-bromopropyl)-pyrrole, the medium turns very acid, and imposes the addition of sodium acetate and water, as buffering agent.[19] 1-(3-Hydroxypropyl)pyrrole was prepared in two ways: directly from aminopropanol and from β-alanine, in two steps. 1-(3-Iodopropyl)-pyrrole was prepared by nucleophilic substitution of the brominated precursor. The (*R*)-(−) (**9**), and (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-phenylglycine (**10**), are commercially available but were prepared as described by Pirkle.[20] Higher yields were obtained by increase of reaction time (10 days). Specific rotation values of the synthesized products give the same values (Table 1, entries 1 and 2) of commercial products (98% ee).

The esterification step should be carried out carefully in the case of pyrrole derivatives due to its sensitivity to oxidizing agents. Methyl esters **3** and **4** were easily prepared in acidic medium ($MeOH/H_2SO_4$) (entries 3 and 4). Compound **2** was obtained from (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-phenylglycinoyl chloride and 1-(3-hydroxypropyl)pyrrole reaction in low yield (entry 5), with specific rotation $[\alpha]_D^{20}$=+31, indicating partial epimerization. Some attempts were carried out using *N*,*N*′-dicyclohexylcarbodiimide (DCC). The esterification proceeds without the need of a preformed activated carboxylic acid derivative, at room temperature, under mild basic conditions. The reaction was carried out in dichloromethane, THF and toluene. Carboxylic acid intermediate from DCC was formed in all the tested solvents. Reactions performed in dichloromethane showed better results. Compound **2** was obtained with 37% yield and $[\alpha]_D^{20}$=0, indicating complete ester racemization (entry 6).

Nucleophilic substitution reaction of 1-(3-bromopropyl)pyrrole in the presence of the *N*-(3,5-dinitrobenzoyl)-α-phenylglycinate, generated by addition of triethylamine in acetonitrile, was successful. The



Scheme 1. Synthetic route to obtain dinitrobenzoyl-α-phenylglycine derivatives

Table 1
Product yields, ee and specific rotation values of performed reactions

Entry	Product	Yield (%)	*e.e.* (%)	$[\alpha]_D^{20}$
1	**9**	79	98	-102
2	**10**	82	98	+102
3	**3**	73	>98[a]	-101
4	**4**	69	>98[a]	+101
5	**2**	28	39	+31
6	**2**	36	0	0
7	**1**	60	0	0
8	**2**	63	0	0
9	**5**	86	98	-60
10	**6**	83	98	+60
11	**7**	71	98	-63
12	**8**	90	98	+63
13	**2**	58	97	+78
14	**1**	70	>98[a]	-80
15	**2**	73	>98[a]	+80

[a]- Products analyzed by ^{1}H-NMR, using $Eu(tfc)_3$ as shift reagent

desired ester was obtained in good yields, but in these reaction conditions, total racemization occurred as described above (entries 7 and 8). Reactions performed to obtain the triethylammonium carboxylate salts, **5** and **6**, showed no racemization in the same reaction conditions. These intermediate carboxylate salts are stable and were isolated and analyzed (entries 9 and 10). Other tertiary ammonium salts, the (*R*)-(−) (**7**) and (*S*)-(+)-3,3,3-dimethyl(1-pyrrolyl)propylammonium *N*-(3,5-dinitrobenzoyl)-α-phenylglycinate (**8**),

were prepared and analyzed (entries 11 and 12). Tautomeric equilibrium occurs only after ester formation, with the aid of reactional conditions like basicity, reaction time and temperature.

Epimerization may be avoided by use of a highly hindered base [1,8-bis(dimethylamino) naphthalene], proton-sponge®, a strong base with weak nucleophilic character, which was able to carry out proton abstraction selectively.[21] Nucleophilic substitution reaction of 1-(3-bromopropyl)pyrrole to obtain **2** (entry 13) gave low yields. Better results were obtained replacing bromine by iodine as a nucleofugal agent, and by filtration of the proton-sponge® hydroiodide salt formed during reaction. The enantiomers **1** and **2** were obtained with 70 and 73% yields, respectively (entries 14 and 15). Some studies involving proton-sponge® concentration variation were realized (0.5, 0.7 and 1.0 equiv.) and no change was observed in the specific rotation value ($[\alpha]_D^{20}$=80).

3. Enantiomeric excess analysis

Ee determination of compounds **1** to **8** was carried out by ^{1}H NMR spectroscopy in the presence of the shift reagent, [tris-(3-trifluoromethylhydroxymethylene)-(+)-camphorate]-europium(III), Eu(tfc)$_3$.[22,23] The splitting of resonance signals in the region δ=7.0 to 10.0, related to the aromatic protons, was observed in the racemate spectra (Fig. 1B and Fig. 2B) from compounds **1**, **2** and **3**, **4**. The spectra of the prepared racemate salts **5**, **6** and **7**, **8** do not show resonance lines splitting. Fig. 1 shows ^{1}H NMR spectra analysis for **1** and **2**; Fig. 1B shows the racemate spectrum in the presence of Eu(tfc)$_3$, where one can observe the splitting of three signals δ=7.35–7.46, 8.95 and 9.17 (from racemate spectrum Fig. 1A). The signal at δ=7.35–7.46 splits and shifts to δ=8.07 and 8.20, and corresponds to just two aromatic protons from the phenylglycine moiety. The signal at δ=8.95 splits and shifts to 9.67 and 9.73, and the signal at 9.17 just splits. The latter protons correspond to the dinitroaromatic ring. Spectra in Fig. 1C,D correspond to compounds **1** and **2** in the presence of Eu(tfc)$_3$ in different proportions. Signal shift is observed but not the splitting, showing a high optical purity of the products obtained after esterification step. The spectrum in Fig. 1E corresponds to the spectrum in Fig. 1D with the addition of a small amount of **1**. Fig. 2 shows the same analysis, described above, for enantiomers **3** and **4** with splitting of aromatic proton signals and of methyl proton signal.

The spectrum in Fig. 2E corresponds to the spectrum in Fig. 2C with the addition of a small amount of **4**. One can observe, moreover, that the proton signals from the dinitroaromatic ring have major downfield shifts in the case of (*R*)-enantiomers. On the other hand, phenylglycine aromatic and methyl protons suffered a downfield shift in the case of (*S*)-enantiomers. It was not possible to precisely determine the ee of the substances due to sensitivity of the technique but one can estimate that the tautomeric equilibrium was entirely avoided.

4. Conclusion

Compounds **1** to **8** were prepared in good yields and high ees. The esterification occurs without epimerization in acidic conditions. At the stage of carboxylate intermediaries, racemization is avoided, but, after ester formation, a tautomeric equilibrium mechanism can operate, leading to epimerization. The present study confirms that proton-sponge® may be applied to selective proton abstraction with different acidity degrees, which allows the esterification at basic conditions without modification of the chiral center.

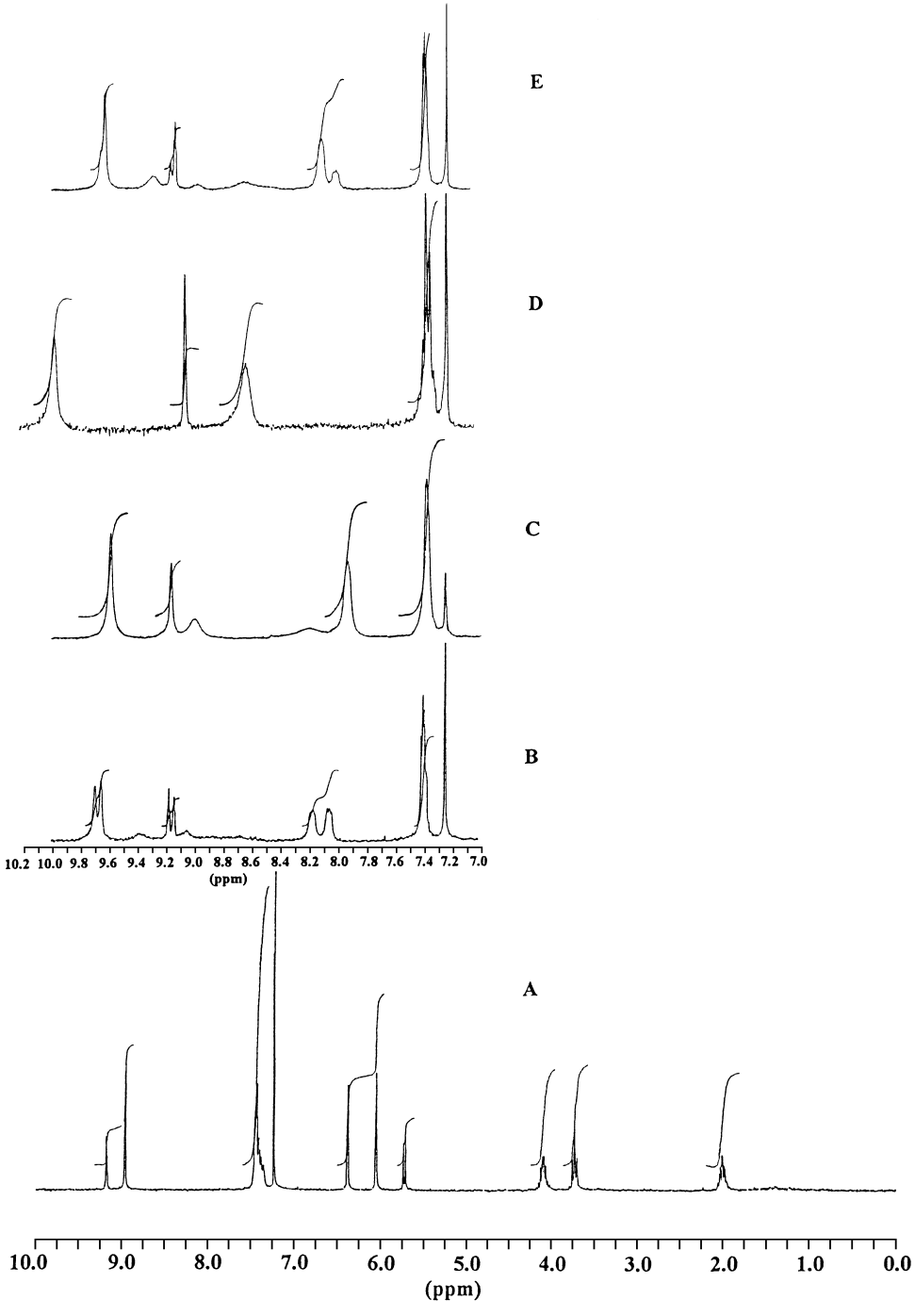


Figure 1. ^{1}H NMR spectra ($CDCl_3$, 250 MHz) of compounds **1**, **2** and respective racemates. Ee determination in the presence of optically active $Eu(tfc)_3$. (A) Racemate; (B) racemate with $Eu(tfc)_3$ addition; (C) **1** and $Eu(tfc)_3$; (D) **2** and $Eu(tfc)_3$; (E) D with addition of a small amount of **1**

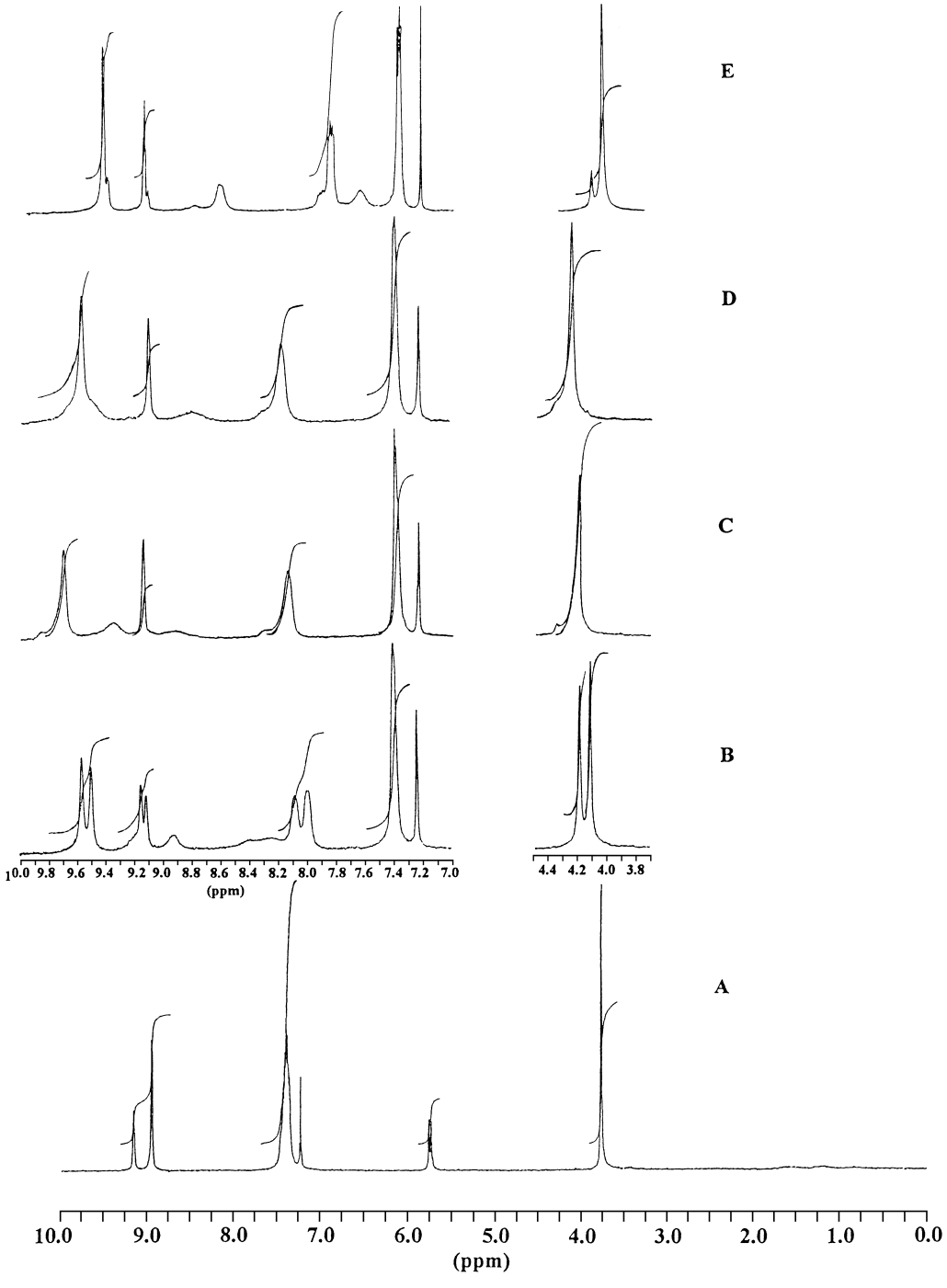


Figure 2. ^{1}H NMR spectra ($CDCl_3$, 250 MHz) of compounds **3**, **4** and respective racemate. Ee determination in the presence of optically active $Eu(tfc)_3$. (A) Racemate; (B) racemate with $Eu(tfc)_3$ addition; (C) **3** and $Eu(tfc)_3$; (D) **4** and $Eu(tfc)_3$; (E) C with addition of a small amount of **4**

5. Experimental

5.1. General

All melting points were determined with a MicroQuímica MQAPF 301 melting point apparatus and were uncorrected. Infrared (IR) spectra were recorded on a Perkin–Elmer FTIR 1600 spectrometer. ^{1}H NMR spectra were measured with Varian EC-360 (60 MHz) and Bruker (250 and 400 MHz) spectrometers. The chemical shifts are expressed in ppm, using tetramethylsilane (δ=0) and/or residual chloroform (δ=7.24) as internal standards. Mass spectra were taken with a Fisons-VG Autospec mass spectrometer. Optical rotation measurements were performed on a Perkin–Elmer digital polarimeter with 1 dm optical way cell (*c* 1, THF).

5.2. 3-(1-Pyrrolyl)propanoic acid

This compound (62%) was prepared from β-alanine (5.0 g, 56.1 mmol) and 2,5-dimethoxytetrahydrofuran (2.5 mL, 19.3 mmol) in glacial acetic acid (7.5 mL), using the method described by Clauson-Kaas.[17,18] Mp 54–56°C; IR (KBr) 3200–2700, 1708, 1429, 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.9 (s, 1H), 6.60 (t, *J*=2.1 Hz, 2H), 6.10 (t, *J*=2.1 Hz, 2H), 4.09 (t, *J*=6.8 Hz, 2H), 2.71 (t, *J*=6.8 Hz, 2H).

5.3. 1-(3-Hydroxypropyl)pyrrole

This compound was obtained (96%) from reduction of 3-(1-pyrrolyl)propanoic acid (1.33 g, 9.6 mmol) by $LiAlH_4$ (0.73 g, 19.1 mmol) in THF (20 mL). Another procedure,[24] using 3-amino-1-propanol and 2,5-dimethoxytetrahydrofuran as starting materials, gave 46% yield. IR (KBr) 3400–3300, 1450, 1055, 730 cm^{-1}; ^{1}H NMR (400 MHz, d_6 acetone) δ 6.68 (t, *J*=2.1 Hz, 2H), 5.99 (t, *J*=2.1 Hz, 2H), 4.00 (t, *J*=6.9 Hz, 2H), 3.51 (t, *J*=6.1 Hz, 2H), 1.91 (m, *J*=6.5 Hz, 2H); MS *m/z* (relative intensity) 125 (M^+, 60), 80 (100).

5.4. 1-(3-Bromopropyl)pyrrole[25]

This compound (0.96 g, 44%) was prepared from 3-bromopropylamine hydrobromide (2.53g, 11.5 mmol), 2,5-dimethoxytetrahydrofuran (1.5 mL, 11.5 mmol) and sodium acetate (2.0 g, 24.4 mmol) in acetic acid:distilled water 1:1 (10 mL). IR (KBr) 3100, 1442, 1242, 728, 562 cm^{-1}; ^{1}H NMR (60 MHz, d_4 methanol) δ 6.7 (t, *J*=2.0 Hz, 2H), 6.0 (t, *J*=2.0 Hz, 2H), 3.9 (t, *J*=6.0 Hz, 2H), 3.2 (t, *J*=6.0 Hz, 2H), 2.1 (m, *J*=6.0 Hz, 2H); MS *m/z* (relative intensity) 188 (M^+, 57), 80 (100).

5.5. 1-(3-Iodopropyl)pyrrole

1-(3-Bromopropyl)pyrrole (0.52 g, 2.84 mmol) and NaI (0.47 g, 3.12 mmol) were added to 3 mL of acetone under stirring. The reaction mixture was refluxed during 3 h. NaBr formed during reaction was filtered and washed with ethyl ether. The resulting solution was evaporated and, after addition of ethyl ether, the white solid was filtered again. After evaporation, a colorless liquid was obtained with 96% yield. IR (KBr) 3100, 1442, 1216, 726, 564, 511 cm^{-1}; ^{1}H NMR (60 MHz, d_4 methanol) δ 6.8 (t, *J*=2.0 Hz, 2H), 6.0 (t, *J*=2.0 Hz, 2H), 3.9 (t, *J*=6.0 Hz, 2H), 3.1 (t, *J*=6.0 Hz, 2H), 2.1 (m, *J*=6.0 Hz, 2H).

5.6. 1-(3-Dimethylaminopropyl)pyrrole

This product was prepared using the same procedure described for 1-(3-bromopropyl)pyrrole and it was a gift from LEOPR–CNRS.

5.7. (R)-(−)-N-(3,5-Dinitrobenzoyl)-α-phenylglycine (**9**) (Table 1, entry 1)

This product was prepared by a method described by Pirkle et al.[20] with slight modification. After 10 days (instead of 7 days as described), the title compound was obtained with 79% yield (lit. 54%), mp 213–215°C (lit. 216–217°C); $[\alpha]_D^{20}$=−102. IR (KBr): 3369, 3200–2700, 1704, 1648, 1539, 1470, 1346, 1217, 1077, 858, 723 cm^{-1}; ^1H NMR (400 MHz, d_6 acetone) δ 9.14 (s, 1H), 9.08 (d, *J*=1.8 Hz, 2H), 8.99 (d, *J*=6.8 Hz, 1H), 7.58–7.37 (m, 5H), 5.81 (t, *J*=6.8 Hz, 2H); MS *m/z* (relative intensity) 345 (M^+, 2), 300 (64), 195 (100), 149 (25).

5.8. (S)-(+)-N-(3,5-Dinitrobenzoyl)-α-phenylglycine (**10**) (Table 1, entry 2)

This compound was prepared in the same manner as above with 82% yield. Mp=218–220°C (lit. 218–220°C); $[\alpha]_D^{20}$=+102.

5.9. (R)-(−)-Methyl N-(3,5-dinitrobenzoyl)-α-phenylglycinate (**3**) (Table 1, entry 3)

A solution of (*R*)-(−)-*N*-(3,5-dinitrobenzoyl)-α-phenylglycine (0.42 g, 1.22 mmol) in methanol (20 mL) was treated with five drops of H_2SO_4. The mixture was refluxed for 4 h, neutralized with a solution of 5% $NaHCO_3$, and extracted with CH_2Cl_2. The organic solution was dried with sodium sulfate and the solvent removed under vacuum. The crude product was chromatographed on silica (eluent: CH_2Cl_2) to give 1.12 g (73%) of the title compound as a white solid. Mp 176–178°C; $[\alpha]_D^{20}$=−101. IR (KBr): 3346, 1738, 1684, 1536, 1437, 1348, 1194, 1083, 924, 729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.97 (d, *J*=1.8 Hz, 2H), 7.55 (d, *J*=6.8 Hz, 1H), 7.44–7.35 (m, 5H), 5.78 (t, *J*=6.8 Hz, 2H), 3.81 (s, 3H); MS *m/z* (relative intensity) 359 (M^+, 2), 300 (100), 195 (95), 149 (47). Anal. calcd for $C_{16}H_{13}N_3O_7$: C, 53.49; H, 3.65; N, 11.70. Found: C, 54.27; H, 3.59; N, 11.76.

5.10. (S)-(+)-Methyl-N-(3,5-dinitrobenzoyl)-α-phenylglycinate (**4**) (Table 1, entry 4)

This compound was prepared in the same manner described above, from (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-phenylglycine with 1.05 g yield (69%). Mp 178–180°C; $[\alpha]_D^{20}$=+101.

5.11. (±)-3-(1-Pyrrolyl)propyl-N-(3,5-dinitrobenzoyl)-α-phenylglycinate

(a) 1-(3-Hydroxypropyl)pyrrole (0.07 g, 0.56 mmol), (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-phenylglycine (0.19 g, 0.56 mmol) and DMAP (0.06 g, 0.56 mmol) were added to CH_2Cl_2 under N_2. The mixture was cooled with ice-salt bath (−2 to 0°C). Then a solution of DCC (0.13 g, 0.62 mmol) in CH_2Cl_2 (1 mL) was added drop by drop, during 1 h. After this, the ice bath was removed and the reaction mixture stirred for 24 h at room temperature. Dicyclohexylurea precipitated and was removed by filtration. The filtrate was concentrated with a rotary evaporator under vacuum and the crude product was purified using silica gel column chromatography, eluted with CH_2Cl_2. The solvent was evaporated yielding a yellow oil. The

product was crystallized in $CHCl_3$ followed by addition of ethyl ether giving 0.10 g (36%) of yellow needle crystals. Mp 137–140°C; $[\alpha]_D^{20}=0$ (Table 1, entry 6).

(b) (*R*)-(−)-*N*-(3,5-Dinitrobenzoyl)-α-phenylglycine (0.18 g, 0.53 mmol), 1-(3-bromopropyl)pyrrole (0.10 g, 0.53 mmol) and Et_3N (2.3 mL) were added to acetonitrile (5 mL). The reaction was refluxed for 7 h under stirring. The mixture was concentrated under vacuum and the product was purified and crystallized as described above, giving 0.14 g (60%) of the title product. Mp 135–139°C; $[\alpha]_D^{20}=0$ (Table 1, entry 7).

(c) The same procedure described above was realized, using (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-phenylglycine as starting material, giving 0.15 g (63%) of the title product. Mp 137–140°C; $[\alpha]_D^{20}=0$ (Table 1, entry 8).

*5.12. (*R*)-(−) or (*S*)-(+)-3-(1-Pyrrolyl)propyl-*N*-(3,5-dinitrobenzoyl)-α-phenylglycinate*

(a) A solution of (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-phenylglycinoyl chloride (0.50 g, 1.37 mmol) in 3 mL of anhydrous THF was added under N_2 to a mixture of 1-(3-hydroxypropyl)pyrrole (0.17 g, 1.37 mmol), Et_3N (0,15 mL, 1.1 mmol) in 2 mL of dry THF. The reaction mixture was allowed to stir for 24 h at room temperature after which time the solvent was eliminated under vacuum. The crude product was chromatographed on silica (eluent: CH_2Cl_2) to give a yellow residue which was crystallized in a $CHCl_3$/ether mixture to give 0.17 g (28%) of the title product enantiomeric mixture. Mp 137–140°C; $[\alpha]_D^{20}=+31$ (Table 1, entry 5).

(b) To a solution of (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-phenylglycine (0.15 g, 0.41 mmol) in 2 mL of acetonitrile, 1-(3-bromopropyl)pyrrole (0.078 g, 0.41 mmol) and proton-sponge® (0.06 g, 0.29 mmol) were added and the mixture was allowed to stir at 50°C for 24 h. The precipitate was removed by filtration and washed with $CHCl_3$. The filtrate was evaporated and the crude product crystallized in a $CHCl_3$/ether mixture to give **2** in 58% yield; mp 142–143°C; $[\alpha]_D^{20}=+78$ (Table 1, entry 13).

(c) To a solution of (*R*)-(−)-*N*-(3,5-dinitrobenzoyl)-α-phenylglycine (0.10 g, 0.29 mmol) in 2 mL of acetonitrile, 1-(3-iodopropyl)pyrrole (0.09 g, 0.40 mmol) and proton-sponge® (0.06 g, 0.29 mmol) were added and the mixture was allowed to stir at 50°C for 1.5 h. The white precipitate was removed by filtration. Acetonitrile (2 mL) was added to the crude product, stirred and the precipitate removed again by filtration. The filtration step was repeated until no more precipitate was formed. After crystallization in $CHCl_3$/ether mixture, 0.09 g (70%) of **1** was obtained. Mp 140–141°C; $[\alpha]_D^{20}=-80$. IR (KBr): 3346, 1738, 1684, 1536, 1437, 1348, 1194, 1083, 924, 729 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 9.17 (t, *J*=2.4 Hz, 1H), 8.95 (d, *J*=2.4 Hz, 2H), 7.46–7.35 (m, 6H), 6.39 (t, *J*=2.4 Hz, 2H), 6.07 (t, *J*=2.4 Hz, 2H) 5.74 (t, *J*=6.35 Hz, 2H), 4.17–4.06 (m, 2H), 3.75 (t, *J*=6.35 Hz, 2H), 2.07–2.00 (m, *J*=5.55, 2 H); MS *m/z* (relative intensity) 452 (M^+, 11), 300 (35), 195 (40), 149 (100) (Table 1, entry 14). Anal. calcd for $C_{22}H_{20}N_4O_7$: C, 58.41; H, 4.46; N, 12.38. Found: C, 60.12; H, 4.44; N, 12.46.

(d) The same procedure described above was realized, using (*S*)-(+)-*N*-(3,5-dinitrobenzoyl)-α-phenylglycine as starting material, giving 0.10 g, 73% yield of **2**; mp 142–143°C; $[\alpha]_D^{20}=+80$ (Table 1, entry 15).

*5.13. (*R*)-(−)-Triethylammonium N-(3,5-dinitrobenzoyl)-α-phenylglycinate (**5**) (Table 1, entry 9)*

(*R*)-(−)-*N*-(3,5-Dinitrobenzoyl)-α-phenylglycine (0.70 g, 2.0 mmol) and Et_3N (0.28 mL, 2.0 mmol) were added to dry THF. The reaction mixture was stirred at ambient temperature during 24 h. A sodium bicarbonate solution (5%) was added to the solution and extracted with CH_2Cl_2 (3×10 mL), and the organic solution dried with anhydrous sodium sulfate. The solvent was removed under vacuum, the crude

product solubilized in THF and precipitated by addition of ethyl ether. A colorless solid (0.78 g, 86%) was obtained. Mp 137–139°C; $[\alpha]_D^{20}$+60. IR (KBr): 3356, 1667, 1610, 1543, 1455, 1352, 1180, 1071, 830, 728 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 9.12 (t, *J*=1.6 Hz, 1H), 9.03 (d, *J*=1.6 Hz, 2H), 8.35 (d, *J*=4.9, 1H) 7.52 (d, *J*=7.4 Hz, 2H), 7.33–7.21 (m, *J*=7.2 Hz, 3H), 5.42 (d, *J*=5.6 Hz, 1H), 3.10 (q, *J*=7.0 Hz, 6H), 1.21 (t, *J*=6.8 Hz, 9H); MS *m/z* (relative intensity) 327 ($M^+-C_6H_{15}N$, 3), 300 (32), 195 (63), 149 (26), 86 (100). Anal. calcd for $C_{21}H_{26}N_4O_7$: C, 56.50; H, 5.87; N, 12.55. Found: C, 56.57; H, 5.74; N, 12.76.

*5.14. (S)-(+)-Triethylammonium N-(3,5-dinitrobenzoyl)-α-phenylglycinate (**6**) (Table 1, entry 10)*

This compound was prepared in the same manner as above with 0.72 g (83%); mp 140–141°C; $[\alpha]_D^{20}$=−60.

*5.15. (R)-(−)-3,3,3-Dimethyl(1-pyrrolyl)propylammonium N-(3,5-dinitrobenzoyl)-α-phenylglycinate (**7**) (Table 1, entry 11)*

(*R*)-(−)-*N*-(3,5-Dinitrobenzoyl)-α-phenylglycine (0.100 g, 0.29 mmol), 1-(3-dimethylaminopropyl)-pyrrole (0.048 g, 0.32 mmol), were added to 10 mL of dry THF, at 0°C. The reaction mixture was stirred for 2 or 3 min. The solvent was removed under vacuum; the crude product was solubilized in $CHCl_3$ under ice bath, and precipitated by addition of cold ethyl ether. A yellow solid (0.10 g, 71%) was obtained. Mp 68–70°C; $[\alpha]_D^{20}$=−63. IR (KBr): 3494, 1628, 1549, 1457, 1344, 1161, 1078, 920, 722 cm^{-1}; ^1H NMR (250 MHz, d_6 acetone) δ 9.11 (d, *J*=2.4 Hz, 1H), 9.04 (d, *J*=2.4 Hz, 2H), 8.25 (d, *J*=5.5, 1H), 7.48 (d, *J*=6.3 Hz, 2H), 7.34–7.24 (m, 3H), 6.54 (t, *J*=2.4 Hz, 2H), 6.11 (t, *J*=2.4 Hz, 2H), 5.53 (d, *J*=6.3 Hz, 1H), 3.89 (t, *J*=6.3 Hz, 2H), 2.73 (t, *J*=7.9 Hz, 2H), 2.61 (s, 6H), 2.06 (m, *J*=7.9 Hz, 2H); MS *m/z* (relative intensity) 327 ($M^+-C_9H_{16}N_2$, 9), 300 (15), 195 (29), 149 (12), 152 (25), 58 (100). Anal. calcd for $C_{24}H_{26}N_5O_7$: C, 58.06; H, 5.28; N, 14.11. Found: C, 57.50; H, 5.22; N, 13.93.

*5.16. (S)-(+)-3,3,3-Dimethyl(1-pyrrolyl)propylammonium N-(3,5-dinitrobenzoyl)-α-phenylglycinate (**8**) (Table 1, entry 12)*

This compound was prepared in the same manner as above with 0.13 g yield (90%). Mp 70–72°C; $[\alpha]_D^{20}$=+63.

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