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DESIGN OF CHIRAL POLY(PYRROLES)

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Abstract. The synthesis of three 3-substituted and one N-substituted chiral pyrrole derivatives as well as their electropolymerization conditions are described. The new materials thus obtained possess recognition properties as enantioselective electrodes.

The development of potential applications for conducting polymers obtained by electrochemical polymerization of pyrrole derivatives as materials for modified electrodes requires the total control of the physical and chemical properties of such polymers. The control of the monomer structure together with optimized electropolymerization conditions may lead to materials with molecular definition in which the electronic properties inherent to the conjugated π-system are associated with the specific new properties due to functional groups like enantioselective molecular recognition[1-10].

In this paper, we describe the synthesis of the chiral pyrrole monomers **3**, **6**, **8** and **10** having (-)-ethyl L-lactate as the optically active moiety, and the enantioselective properties of the modified electrode surfaces obtained upon their electropolymerization. The steric and electronic effects of the chiral environment on the electropolymerization process

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are reduced by the introduction of a spacer unit between the pyrrole backbone and the (-)-ethyl L-lactate moiety. The general synthetic pathways developed in this paper are illustrated in figure 1.

Monomer **3** was synthesized in three steps. Preparation of **1** and **2** (step 1 and step 2) was done according to the literature[11]. The reaction of commercially available 2,5-dimethoxytetrahydrofuran with 1,2-ethanediamine in acetic acid/dioxan gives the amide **1** which is readily hydrolyzed under alkaline conditions to yield the amine **2**. Formation of **3** (yield 43%) was achieved by subsequent reaction of **2** with (-)-ethyl L-lactate.

For the synthesis of the monomers **6**, **8**, **10** we applied the method from Kakushima *et al.*[12], who published a high-yield and highly regioselective synthesis of 3-acylpyrroles in which 1-(tosyl)pyrrole (**4**) (readily obtained by reaction of potassium pyrrole with tosylchloride[13]) is used as a substrate in $AlCl_3$-catalyzed Friedel-Crafts acylation reactions. Acetylation of **4** with succinic anhydride (**a**) or 4-chlorobutyryl chloride (**b**) in the presence of $AlCl_3$ at 25°C in 1,2-dichloroethane solution gave essentially quantitative substitution at position 3, directed by the tosyl group in position 1. In analogy to the results of Kakushima *et al.*, in case of entry **a**, a 1:9 mixture of 2- and 3-isomers was isolated as a solid from which pure **5** was obtained by recrystallization. Starting from **5**, we synthesized the esters **6** and **8**. In the route described here for obtaining **8** it was found that the tosylate group was best removed before esterification occurs to avoid complications in the next step. A convenient synthesis of 3-acyl-1H-pyrroles is done by alkaline hydrolysis followed by acidification with conc. HCl[12] to afford acid **7** in 99% yield. Subsequent esterification of **5** and **7** were performed in dioxan with catalytic amounts of toluenesulfonic acid at a water separator. After purification by column chromatography on silica gel 18.4% of **6** and 18.7% of **8** were obtained.

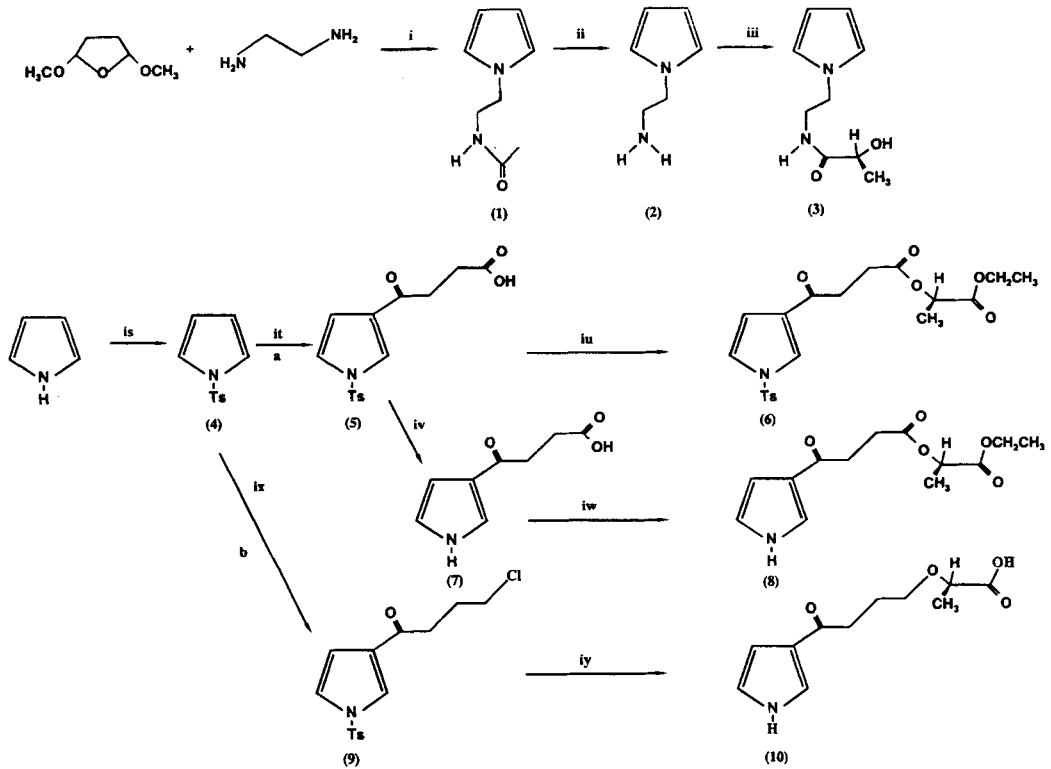

FIG 1: **General pathway for the synthesis of the chiral pyrrole derivatives 3,6,8,10**: **i:** CH_3COOH, dioxan; **ii:** KOH; **iii:** (-)-ethyl L-lactate, NH_4Cl; **is:** tBuOK, CH_3PhSO_2Cl, DMF; **it:** $AlCl_3$, 1,2-dichloroethane, **a:** succinic anhydride; **iu:** (-)-ethyl L-lactate, $CH_3C_6H_4SO_3H \cdot H_2O$, C_6H_6; **iv:** NaOH, dioxan; **iw:** (-)-ethyl L-lactate, $CH_3C_6H_4SO_3H \cdot H_2O$, dioxan; **ix:** $AlCl_3$, 1,2-dichloroethane, **b:** 4-chlorobutyrylchloride; **iy:** (-)-ethyl L-lactate, KOH, NaOH, DMSO.

In case of **9** the chiral unit is readily attached to the pendant alkyl chain via a Williamson synthesis using potassium hydroxide in dimethylsulfoxide to form an alkoxide followed by alkylation. This system was first successfully applied to the methylation of phenols and was later extended to the alkylation of indole and pyrroles[15,16]. It is interesting to note that the reported alkylating system of potassium carbonate in dimethylformamide failed to give ethers from alcohols at room temperature[16]. Simultaneously, deprotection occurs in the presence of 5 N NaOH. We isolated 18.2% of **10** after purification.

All monomers were tested in electropolymerization (Table). Except for monomer **6** and **10**, the monomers were electropolymerized potentiodynamically in a three compartment cell containing platinum working and counter electrodes (surface 1 cm^2) and a $Ag/AgNO_3$ reference system in acetonitrile (MeCN) with 0.1 M of various conducting agents. The modified electrodes are studied by cyclic voltammetry in the monomer free solution of the same concentration of conducting agent as above.

The table shows that the presence of substituents affects the polymerization reaction and also the reactivity properties of the film. As might be expected, the monomers **3**, **6**, **8** and **10** and the resulting polymers **poly-3** and **poly-8** exhibit a higher oxidation potential (E_{pa}) than pyrrole (E_{pa} = +0.42 V) and polypyrrole (PPy) (E_{pa} = -0.38 V) due to the sterical and electronical effects of the side chains[17, 18].

The failure to electropolymerize monomer **6** could be ascribed by the sterical effect of the tosyl group. The steric hindrance of this bulky group prevents the heterocycle from attaining a planar conformation.

In case of monomer **10** the carbonyl group in the α-position of the pyrrole nucleus exerts the decisive influence, because the alkyl spacer between the ether- or carbonyl group and the pyrrole unit will decrease the electrophilic effect of these groups.

Table. Cyclic voltammetric data for **3, 6, 8, 10**: monomer concentration 0.1 M in 0.1 M of the appropriate electrolyte salt-MeCN. Scan rate 10 mV s^{-1}. E_{pa}, E_{pc} / V vs. $Ag/AgNO_3$.

Electro-lyte	3 mono-mer	3 polymer		6 mono-mer	8 mono-mer	8 polymer		10 mono-mer
	E_{pa}	E_{pa}	E_{pc}	E_{pa}	E_{pa}	E_{pa}	E_{pc}	E_{pa}
$LiClO_4$	+ 1.15	+ 0.20	+ 0.15	+ 1.8	+ 1.09	+ 0.54	+ 0.47	+ 1.45
Et_4NClO_4	+ 1.25	+ 0.21	+ 0.15		+ 1.09	+ 0.52	+ 0.47	
Bu_4NClO_4	+ 1.23	+ 0.15	+ 0.10		+ 1.09	+ 0.53	+ 0.47	
Et_4NBF_4	+ 1.16	+ 0.25	+ 0.26		+ 1.14	+ 0.59	+ 0.50	
Me_4NPF_6	+ 1.0	+ 0.22	+ 0.15		+ 1.16	+ 0.55	+ 0.48	

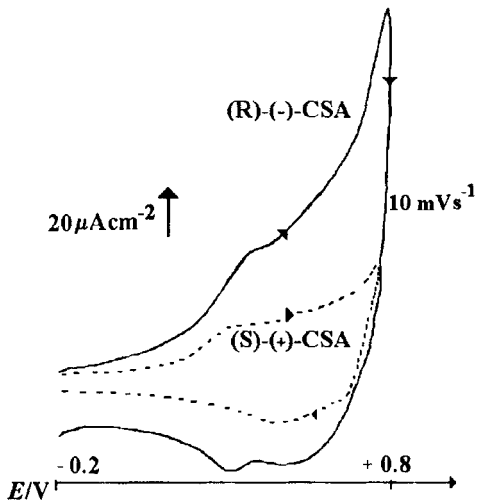

FIG 2: Enantioselective properties of **poly-8** in MeCN containing (R)-(-)-CSA or (S)-(+)-CSA (0.1 M) as doping agent. Scan rate: 10 mV s^{-1}.

Poly-3 and **poly-8** exhibit high electrochemical stability under redox cycling and several tens of voltammetric cycles have been performed without any loss of electroactivity. Compared with PPy, an enhanced redox reversibility of the electrochemical redox switching was obtained ($\Delta Ep \approx 50$-70 mV, see Table; PPY: $\Delta Ep \approx 330$ mV). They also show a long-term and potential stability.

In order to verify the enantioselectivity of **poly-3** and **poly-8**, we compared the cyclic voltammograms recorded in MeCN using optically active anions, *eg* (S)-(+)-10- and (R)-(-)-10-camphorsulfonic acid (CSA). As shown in figure 2 for **poly-8**, higher current densities in the presence of the (R)-(-)-isomer were observed. This is also valid for **poly-3**.

This observed difference in oxidation could be caused by stereoselective recognition of the optically active counter anions, which have to penetrate in a chiral environment[19]. But the results should not be overinterpreted, because the observed differences in oxidation rate were very low (10-70 μA).

More meaningful are the film forming abilities of monomer **3** and **8** in a chiral environment. While electropolymerization can be easily achieved in MeCN containing (S)-(+)-CSA (0.1 M) and Bu_4NClO_4 (0.05 M), the polymerization is completely inhibited using (R)-(-)-CSA. This observation suggests, that the requirement for using these electrodes in the enantioselective syntheses is fulfilled[20].

EXPERIMENTAL

Solvents, common reagents and catalysts were obtained commercially and used as received. ^1H NMR spectra were recorded on a Bruker AM 300 MHz instrument, using $CDCl_3$ and Me_2SO-d_6 as solvent and tetramethylsilane (TMS) as internal standard. FT-IR

spectra were obtained on a Bio-Rad FTS-7. Optical rotations were measured with a Perkin-Elmer polarimeter M343. TLC was performed on aluminium foil precoated with silica gel (Merck 60 F_{254}). Melting points were determined with a Gallenkamp apparatus and are uncorrected. Elemental analyses were performed with a Carlo Erba model 1104.

The electrochemical experiments were carried out using a potentiostat (BANK POS 73) coupled with a Wenking model VS672 voltage scan function generator (BANK) and a x,y-recorder PM 8132 (Philips). The film preparations as well as the electrochemical investigations were performed in a three compartment cell containing platinum working and counter electrodes and a $Ag/AgNO_3$ reference system. All solutions were degassed by purging with nitrogen prior to polymerization.

1-(2-acetylaminoethyl)-pyrrole (1)

A mixture of 43 g 2,5-dimethoxytetrahydrofuran (340 mmol), 18 g 1,2-ethanediamine (300 mmol), acetic acid (300 ml), and dioxan (400 ml) is heated under reflux for 4 h, and then stirred at room temperature overnight. The volatiles are removed at reduced pressure, the residue is dissolved in $CHCl_3$ (150 ml) and washed with 10% sodium hydrogen carbonate solution (50 ml) and water (50 ml). The organic phase is dried with $MgSO_4$, filtered, and evaporated to give **1** (34 g, 75% based on 1,2-ethanediamine). Recrystallization was carried out from ethylacetate/ether. m. p.: 58-60°C. ^1H NMR (300 MHz, $CDCl_3$) δ: 6.65 (t, 2H, Hpyr), 6.27 (t, 2H, Hpyr), 4.2 (m, 2H, CH_2N), 3.55 (m, 2H, CH_2NH), 1.95 (s, 3H, CH_3). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 170.29 (C=O), 120.63 (2·Cpyr), 108.75 (2·Cpyr), 48.81 (CH_2), 40.99 (CH_2), 23.172 (CH_3). IR (KBr) 3287 (NH); 3100, 1537 (aromat); 2975, 2950 and 2838 (alkyl CH_2 and CH_3); 1650 (C=O) cm^{-1}.

1-(2-aminoethyl)-pyrrole (2)[11]

A suspension of **1** (5.3 g, 34.8 mmols) in 10% aqueous potassium hydroxide (100 ml) is heated under reflux for 2 h, cooled, and extracted with $CHCl_3$ (2·100 ml). The combined extracts are washed with 10% HCl (100 ml), the aqueous layer is separated, rendered basic with 50% aqueous NaOH, and extracted with $CHCl_3$ (2·80 ml). Evaporation of the solvent gives almost pure **2** (2.5 g, 65%), b. p.: 47°C / 2 torr. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.66 (t, 2H, Hpyr), 6.17 (t, 2H, Hpyr), 3.90 (m, 2H, CH_2N), 3.05 (m, 2H, CH_2NH_2), 1.04 (s, 2H, NH_2) ^{13}C NMR (300 MHz, $CDCl_3$) δ: 120.58 (2·Cpyr), 106.26 (2·Cpyr), 52.74 (CH_2), 43.29 (CH_2). IR (KBr) 3350, 3300 (NH_2); 3050, 1500 (aromat); 1280 (NH) cm^{-1}.

(S)-2-hydroxy-N-(2-pyrrole-1-yl-ethyl)-propionamide (3)

A mixture of **2** (22 g, 200 mmols), 25 ml of (-)-ethyl L-lactate (300 mmols) and a small quantity of NH_4Cl was refluxed for 1 h, during which time the ethanol produced was distilled off. The cooled mixture was taken up in $CHCl_3$ and washed with water. After evaporation of $CHCl_3$, and of non reacted (-)-ethyl L-lactate and purification by column chromatography on silica gel (eluent: ethylacetate) 15.7 g (43%) of **3** was obtained as a yellow oil. $[\alpha]_D^{21} = -9.6°$ ($CHCl_3$, c 0.986). IR (KBr) 3400 (NH, OH); 2950, 2900 and 2880 (alkyl CH_2 and CH_3); 1750 (C=O); 1660 (aromat); 1540 (NH)cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 6.65 (t, 2H, Hpyr), 6.2 (t, 2H, Hpyr), 4.2 (q, 1H, CH), 4.05 (m, 2H, CH_2N), 3.6 (m, 2H, CH_2NH), 1.4 (d, 3H, CH_3). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 174.89 (C=O), 120.68 (2·Cpyr), 108.71 (2·Cpyr), 68.317 (C), 48.66 (CH_2), 40.48 (CH_2), 21.14 (CH_3). Analytically calculated for $C_9H_{14}O_2N_2$: C, 59.322; H, 7.743; N, 3.32. Found: C, 58.534; H, 7.564; N, 15.053.

1-(tosyl)pyrrole (4)

Compound **4** was prepared according to the literature[13]. 8.4 g pyrrole (125 mmol) was added at 0°C to a solution of 16.3 g potassium t-butoxide (145 mmol) in 80 ml of N,N-dimethylformamide (DMF). After 1 h stirring at room temperature, the reaction mixture was cooled at 0°C and 33.4 g tosyl chloride (175 mmol) in 120 ml DMF was added. The mixture was stirred overnight at room temperature. After evaporation of DMF, the black coloured residue was taken up in $CHCl_3$, washed several times with water and dried over Na_2SO_4. After recrystallization from heptane, 23.5 g (85%) of the desired product **4** was obtained, m. p.: 98-100°C. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.75 (d, 2H, Haro), 7.28 (m, 2H, Haro), 7.15 (m, 2H, Hpyr), 6.29 (m, 2H, Hpyr), 2.4 (s, 3H, CH_3). ^{13}C NMR (300 MHz, $CDCl_3$) δ: 144.9 (CSO_2), 135.9 (CCH_3), 129.93 (2·$CHCSO_2$), 126.81 (2·$CHCCH_3$), 120.71 (2·CHN), 113.47 (2·CHCHN), 21.59 (CH_3).

4-[1-(tosyl)-3-pyrrolyl]-4-oxobutyric acid (5)

To a suspension of 29.33 g anhydrous $AlCl_3$ (220 mmol) in 400 ml of 1,2-dichloroethane was added at 25°C 11 g succinic anhydride (**a**) (110 mmol), and the mixture was stirred at 25°C for 30 min, during which time the solids dissolved. A solution of 20.7 g of **4** (100 mmol) in 50 ml of 1,2-dichloroethane was added, and the mixture was stirred at 25°C for 90 min. The reaction was quenched with ice and water (500 ml) and the product extracted with dichloromethane. The organic layer was washed with water, dried over Na_2SO_4 and concentrated to give a 1:9 mixture of the 2-isomer and **5** as a colourless solid (29.8 g, 97%). Crystallization from dichloromethane gave pure **5**: 15.81g (51%), m. p.: 125-127°C. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.1-7.4 (m, 6H, Haro), 7.18 (dd, 1H, Hpyr), 6.72 (dd, 1H, Hpyr), 3.10 (t, 2H, CH_2), 2.73 (t, 2H, CH_2).

4-[1-(tosyl)-3-pyrrolyl]-4-oxobutyric acid-2-(S)-(-)-propionic acid ethylester (6)

5 g of **5** (15.5 mmols), 3.21 g (-)-ethyl L-lactate (27.2 mmols), and 0.1 g toluenesulfonic acid monohydrate (0.52 mmols) in 100 ml benzol was refluxed for 48 h at a water separator monitoring the reaction by TLC (eluent: hexane-ethylacetate 1:1). The mixture was then washed with water, aqueous $NaHCO_3$ solution, and water. Evaporation of benzol yielded an oil which was chromatographed on silica gel using hexane-ethylacetate (1:3) afterwards using hexane-ethylacetate (1:1) as eluent. Compound **6** was obtained as a yellow oil in 18.4% (2.5 g). $[\alpha]_D^{21} = -16°$ ($CHCl_3$, c 1). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.75 (m, 3H, Hpyr, Haro), 7.35 (d, 2H, Haro), 7.13 (dd, 1H, Hpyr), 6.7 (d, 1H, Hpyr), 5.0 (q, 1H, CH) 4.25-4.1 (m, 2H, CH_2), 3.2-3.0 (m, 2H, CH_2), 2.8 (m, 2H, CH_2), 2.4 (s, 3H, CH_3), 1.47 (d, 3H, CH_3), 1.3-1.25 (m, 3H, CH_3). Analytically calculated for $C_{20}H_{23}O_7NS$: C, 57.99; H, 5.50; N, 3.32; S, 7.60. Found: C, 57.00; H, 5.50; N, 3.30; S, 7.52.

4-(3-pyrrolyl)-4-oxobutyric acid (7)

A solution of **5** (10 g, 31.1 mmol) in 130 ml of dioxan was refluxed with 130 ml of 5 N NaOH for 12 h. The organic layer was collected and acidified with conc. HCl until the pH value reached 3. After evaporation of dioxan, the residue was taken up in H_2O. **7** was obtained by filtering with suction and subsequent washings with water as light pink crystals: 3.3 g (63.4%), m. p.: 170°C. ^1H NMR (300 MHz, Me_2SO-d_6) δ: 12.0-10.3 (br, 2H, NH, CO_2H), 7.63 (m, 1H, Hpyr), 6.87 (m, 1H, Hpyr), 6.50 (m, 1H, Hpyr), 3.0 (t, 2H, CH_2), 2.53 (t, 2H, CH_2).

4-(3-pyrrolyl)-4-oxobutyric acid-2-(S)-(-)-propionic acid ethylester (8)

A solution of 5 g of 7 (29 mmols), 24.7 g of (-)-ethyl L-lactate (200 mmol) and 0.1 g

toluenesulfonic acid monohydrate (0.52 mmols) in 100 ml dioxan was refluxed for 24 h at a water separator. The progress of the reaction was monitored by TLC (eluent: hexane-ethylacetate 1:3). The residue remaining after concentration at reduced pressure was taken up in $CHCl_3$, washed with water and dried over Na_2SO_4. Evaporation of $CHCl_3$ yielded an oil which was chromatographed on a column of silica gel, eluting with hexane-ethylacetate (1:3), to afford **8** as white crystals, 1.6 g (18.7%), m. p.: 87-89°C. $[\alpha]_D^{21}$ = -22° ($CHCl_3$, c 0.937). ^1H NMR ($CDCl_3$) δ: 9.2 (br, 1H, NH), 7.4 (m, 1H, Hpyr), 6.7 (m, 1H, Hpyr), 6.6 (m, 1H, Hpyr), 5.0 (dd, 1H, CH), 4.2 (m, 2H, CH_2), 3.2-3.1 (m, 2H, CH_2), 2.8-2.6 (m, 2H, CH_2), 1.42 (d, 3H, CH_3), 1.2 (m, 3H, CH_3). Analytically calculated for $C_{13}H_{17}NO_5$: C, 58.27; H, 6.36; N, 5.48. Found: C, 59.2; H, 6.46; N, 5.40.

1-[(1-tosyl)-3-pyrrolyl]-4-chloro-1-butanone (9)

Compound **9** was prepared according to a procedure already described[12]. To a suspension of 12.8 g anhydrous $AlCl_3$ (96 mmol) in 190 ml 1,2-dichloroethane at 25°C was added dropwise 10.8 ml 4-chlorobutyrylchloride (**b**) (96 mmol). The resulting solution was stirred at 25°C for 10 min, a solution of **4** (10 g, 48 mmol) in 50 ml of 1,2-dichloroethane was added, and the mixture was stirred at 25°C for 20 min. The reaction was quenched with 0.5 N HCl, and the product was extracted into dichloromethane. The extracts were washed with brine, 0.1 N NaOH, and brine, dried over Na_2SO_4, and concentrated under reduced pressure. After purification by column chromatography on silica gel (eluent: ethylacetate-hexane 3:10) 13 g (83%) of **9** was obtained as white chrystals. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.1-7.4 (m, 6H, Hpyr, Haro), 7.18 (1H, Hpyr), 3.70 (t, 2H, CH_2), 2.95 (t, 2H, CH_2), 2.4 (s, 3H, CH_3), 2.20 (dd, 2H, CH_2).

4-(3-pyrrolyl)-4-oxo-butoxyl-2-(S)-(-)-propionic acid (10)

A mixture of 12.5 g (-)-ethyl L-lactate (153 mmols), 14.5 g potassium hydroxide (260 mmols), and 55 ml DMSO was stirred vigorously for 1 h with a rise in temperature of 10°C. 5 g of **9** (15.3 mmols) in 55 ml DMSO was added dropwise and the resulting reaction mixture was then refluxed for 24 h to ensure complete reaction. After addition of 5 N NaOH, the reaction mixture was refluxed for further 12 h. The organic layer was separated and acidified with conc. HCl until the pH value reached 5-6. After concentration at reduced pressure, the residue was taken up in ether, washed with water, dried over Na_2SO_4 and purified on a column of silica gel using hexane-ethylacetate (1:1) as eluent, 1.2 g (27.5%). $[\alpha]_D^{21}$ = -18.5° ($CHCl_3$, c 1). ^1H NMR ($CDCl_3$) δ: 7.7 (m, 1H, Hpyr), 6.9 (m, 1H, Hpyr), 6.4 (m, 1H, Hpyr), 4.0 (dd, 1H, CH), 3.3 (s, 1H, OH), 2.45 (m, 2H, 2H), 1.4 (t, 2H, CH_2), 0.8 (m, 5H, CH_3, CH_2). Analytically calculated for $C_{11}H_{15}NO_4$: C, 58.6; H, 6.66; N, 6.22; S, 10.28. Found: C, 59.2, H, 6.46; N, 6.20; S, 10.00.

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