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SYNTHESIS AND POLYMERIZATION OF 2-(3-PYRROLYL)ACETIC ACID DERIVATIVES FROM PYRROLE.

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Abstract. The synthesis of the 3-pyrrylacetic acid as well as the study of its esterification conditions are described. The new materials thus obtained are electropolymerized.

One of the main limitations to study and use organic conductive polymers are the difficulties encountered during the monomer synthesis. Among them, pyrrole derivatives present many potential advantages as it is possible to modulate the poly(pyrrole) properties by adjunction of functional group at the position 3 of the pyrrole backbone[1-3]. Therefore, the regioselective synthesis of pyrrole derivatives has been the subject of considerable interest in recent years. Unfortunately, pyrrole

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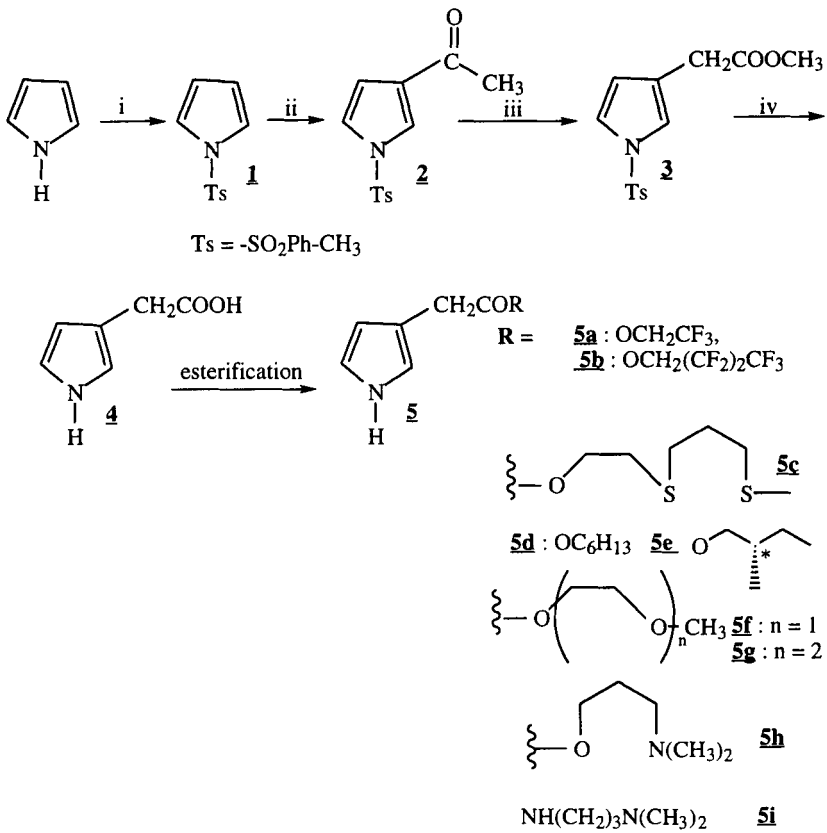
undergoes predominant kinetic electrophilic substitution[4] at the position 2 which is not suitable for polymerization.

In this paper, we describe the synthesis of various monomers derived from the 3-pyrrylacetic acid. This basic structure affords two main advantages : firstly, it possesses a spacer arm between the pyrrole backbone and the carboxylic function which allows a control of the electronic effects of the substituent on the properties of the polymer[5]. Secondly, it can provide access to a wide range of new compounds, by esterification for example. Optimization of the synthesis of this building block and the study of esterification with groups containing different functionalities (linear, branched or polyfluorinated oxyalkyl chains, thioethers, ...) are reported in this article as well as their electropolymerization abilities. The general synthetic pathway developed in this paper is illustrated in figure 1.

The key intermediate, the 2-(3-pyrrolyl)acetic acid **4**, was synthesized *via* the thallium transposition of the carbonyl compound **2** (Willgerodt-Kindler reaction) starting from the pyrrole moiety which first underwent Friedel-Crafts acylation at 3 position, oriented by substitution on the nitrogen atom with a tosyl group. For this tosylation, phase transfer catalysis[6] (NaOH in THF) has advantageously replaced the classical method which used potassium[7] but led to only 54% of the desired tosylated pyrrole **1**. With potassium t-butoxide in DMF instead of NaOH in THF, we isolated 85% of the pure product after recrystallisation in methanol. The 1-(phenylsulfonyl) pyrrole was acylated by $AlCl_3$ at the 3 position as demonstrated by Kakushima[8] *et al.* whereas the corresponding BF_3-OEt_2 catalyzed reactions led to 2-acylderivatives predominently. 90% of the pure product have thus been obtained.

The transposition of the 1-tosyl-3-acetylpyrrole **2** into the corresponding methylacetate **3** known as the Willgerodt-Kindler reaction was performed in acidic conditions using thallium (III) nitrate[9]. The previously described conditions (Table



i)tBuOK, DMF, TsCl; ii) $AlCl_3$, $(CH_3CO)_2O$, CH_2Cl_2; iii) $Tl(NO_3)_3$, CH_3OH, K-10; iv) NaOH, MeOH, HCl; esterification : see below.

Figure 1: general pathway for the synthesis of various 2-(3-pyrrolyl)acetic acid derivatives.

1, entry 2) led to 55% of the desired product **3** together with products **6** and **7** (Figure 2).

The main problem was the separation of the different products. This operation considerably reduced the final yields (90% measured by gas

Table 1 : Influence of the experimental conditions on the transposition using thallium (III) nitrate.

Entry	T(°C)	$Tl(NO_3)_3$ / **2**	Acid	Yield (% GC)	Isolated Yield (%) product **3**	Reaction Time (hours)
1	20	1.5	$HClO_4$	90	-	12
2	20	1.13	$HClO_4$	90	55	12
3	reflux	1.13	$HClO_4$	80	-	12
4	20	1.13	$HClO_4$	90	-	3
5	20	1.13	H_2SO_4	93	59	3
6	20	1.13	$CH(OCH_3)_3$	93	-	18
7	20	1.13	K-10 clay	90	90	12

Conditions : [**2**] = 0.1M.

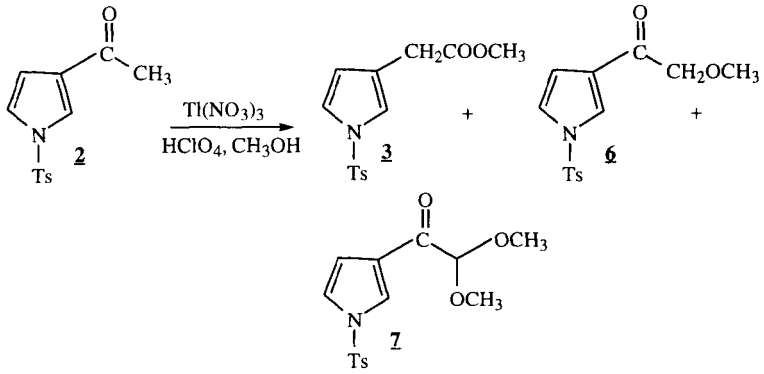


Figure 2 : different products from the Willgerodt-Kindler reaction transposition of **2**.

chromatography and only 50-55% of isolated product after chromatography on silica). Moreover, the solution of perchloric acid in methanol was potentially dangerous and therefore, we have optimized other conditions (Table 1).

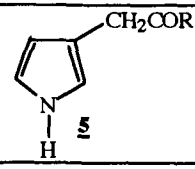
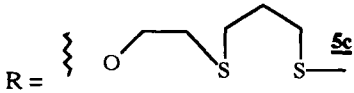
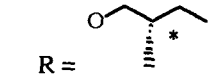
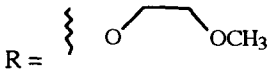
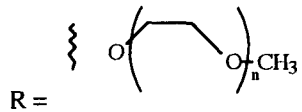
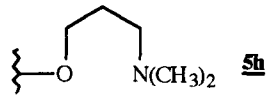
Because of the instability of thallium nitrate, an increase of the temperature was not favorable to the reaction (Table 1, entry 3). Moreover, an excess of thallium did not change the final yield (Table 1, entries 1, 2). For safty reasons, we have replaced perchloric acid by sulfuric acid which increased the kinetic of the reaction without modification of the synthesized final products (Table 1, entries 2 and 9). Other oxidants could replace the thallium nitrate, like I_2 or its derivatives (ICl, ICl_3, ...)[10]. Nevertheless, by-products were always obtained in large proportions. The transposition could also take place electrochemically, using I_2 or MeI in catalytic amount[11] without formation of secondary products, but the main disadvantage of this method was the difficulty to scale it up. To increase the thallium activity, thallium nitrate has been supported on K-10 clay[12-14]. We have used this method for our pyrrole substrate, the K-10 clay being acidic enough to avoid the use of an other acid. Thus 90% of the desired product was isolated without formation of by-products. The use of thallium (III) nitrate supported on Montmorillonite has been already described for transposition purpose on α-methylpyrroles[14] bearing an electronwithdrawing group on the α' position and led to the corresponding α-formylpyrroles in good yields. In our case, the transposition took place without further oxidation. Product **3** was deprotected using NaOH in methanol[8] solution and then acidified with HCl 35% to obtain the acid **4** in 80% yield. The pH value must be kept above 3.4 to avoid spontaneous polymerization of the pyrrole ring.

Starting from this key intermediate **4**, we synthesized the different esters **5**. Even if we can find numerous efficient methods for esterification in the literature,

only few of them allow to work at room temperature and without using a large excess of alcohol, which is, for practical and economical reasons, the main limitation of the development of the corresponding monomer. Among them, dicyclohexylcarbodiimide is often used[15] in the presence of a base (most of the time triethylamine) for the peptide synthesis. The reaction proceeded with good yield, but elimination of the dicyclohexylurea generated during the synthesis considerably reduced the final isolated yield. Therefore, Weinshenker and Shen[16] supported this carbodiimide on an unsoluble polymer which led to an easier separation. An other method to avoid these problems of separation was the use of carbodiimide giving rise to soluble urea derivative. Nevertheless, this product remains expensive and was only used when none of the other reagents worked. So, first of all, for each monomer, we tried the less expensive and also the simplest method for esterification which used trimethylchlorosilane[20]. When it did not work, we tried phenyldichlorophosphate[18] or boron trifluoride-etherate[19] reagents and finally dicyclohexylcarbodiimide, in its soluble form when this one was too difficult to be eliminated (Table 2).

Water-soluble carbodiimide derivative (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride named DEC in Table 2) was thus used to synthesize esters **5a**, **5b** and **5c** in respectively 35%, 41% and 30% isolated yields. In the case of esters **5f** and **5g**, neither phenyldichlorophosphate[18] nor boron trifluoride-etherate[19] reagents allowed the formation of the desired esters. Finally, using trimethylchlorosilane[20], 75% of ester **5f** and 65% of ester **5g** were obtained. Following the same method, esters **5d** and **5e** were isolated. It has been impossible to obtain products **5h** and **5i**, whatever the esterification method we tried. We also tried to synthesize the acid chloride using triphenylphosphine in CCl_4[21] or alkylchloroformate with triethylamine[22], but it was not successful. This was

Table 2 : different methods of esterification depending on the nature of the alcohol.

Entry	Ester  **5**	METHOD	YIELD (%)
1	R = OCH_2CF_3 **5a**	Soluble DEC	35
2	R = $OCH_2(CF_2)_2CF_3$ **5b**		41
3	R =  **5c**		30
4	R = OC_6H_{13} **5d**	Me_3SiCl	60
5	R =  **5e**		60
6	R =  **5f**		75
7	R =  n=2 **5g**		65
8	 **5h**	All the described methods	0
9	$NH(CH_2)_3N(CH_3)_2$ **5i**		0

Conditions : for esterification conditions see experimental part.

Table 3. Some characteristics of the polymers obtained by electropolymerization.

Entry	Polymer	Epa (V/SCE)	Conductivity ($S.cm^{-1}$)
1	poly(**5a**)	0.27	10^{-1}
2	poly(**5b**)	0.26	10^{-1}
3	poly(**5c**)	-*	-
4	poly(**5d**)	0.14	2
5	poly(**5e**)	0.14	11
6	poly(**5f**)	0.11	2
7	poly(**5g**)	0.11	5

*Do not polymerize; Electropolymerization conditions : synthesis : propylene carbonate-$LiClO_4$ 0.1M; [monomer] = 0.1M; Analysis : acetonitrile-$LiClO_4$ 0.1M (50mV/s); current density : 100mC cm^{-2}.

probably due to the nucleophilic properties of the amine function which induced side reactions with the different reagents present in the reaction solution.

All the previous monomers were tested in electropolymerization (Table 3). Except monomer **5c**, all the products electropolymerized under galvanostatic conditions in propylene carbonate using $LiClO_4$ as electrolyte. The polymers were obtained as deposit films on platinum electrode (surface 0.7 cm^2) and studied by cyclic voltammetry in acetonitrile with 0.1M $LiClO_4$. The conductivities were measured by the four-probe method[23] on films of 7μm thickness, corresponding to a deposition charge of 2 Ccm^{-2} using an ITO glass electrode of 2cm^2. In the same conditions, the poly(pyrrole) exhibited a conductivity of 10 $S.cm^{-1}$ and an oxidation

potential of 0V/SCE. Thus, it could be assumed that the carboxylic ester function had only little effect on both oxidation potential and conductivity in the case of polymers with an alkyl (linear or branched) or oxyalkyl ester chain (Table 3, entries 4-7). Only strong electronwithdrawing substituents (perfluoroalkyl chains) induced an important decrease of conductivity and an increase of the oxidation potential (Table 3, entries 1and 2).

The fail of electropolymerization of **5c** could be ascribed to the oxidation of the thioether function or/and to the poisoning of the electrodes by this function. Nevertheless, the pyrrylacetic moiety appeared to be a convenient basic structure to functionalize poly(pyrrole) in view of controling the overall properties of this type of materials.

EXPERIMENTAL SECTION

Solvents and common reagents were obtained commercially and used as received. IR spectra were recorded as KBr pellets in the case of solids or as liquid films between NaCl salt disks in the case of oils using a Nicolet 205 spectrometer. NMR spectra were determined on a Varian Anaspect 360 (60MHz) or a Bruker AC-200 (200 MHz and ^{13}C spectra). ^{1}H NMR were recorded with Me_3SiCl as the internal reference, the chemical shifts of the ^{13}C spectra were given in ppm related to the resonance of $CDCl_3$ (77.0 ppm). Column chromatography was conducted on Merck silica gel 60. Melting points were determined on a Wagner & Munz melting point apparatus and are uncorrected. Capillary gas chromatography spectra were recorded on a Shimadzu GC 14A, equiped with J&W capillary columns. Electrosynthesis and cyclic voltammetry experiments were performed using a Tacussel PJT24-1 potentiostat/galvanostat, a Tacussel PIL101T generator and a

Tacussel IG6-N coulometer equipped with a BBC SE 790 recorder. All electrochemical experiments were performed in an undivided three-electrode cell containing a Pt working electrode, a Pt counter electrode and a saturated calomel electrode (SCE) as a reference. All the solutions were degassed by argon bubbling prior to electropolymerizaton.

1-tosylpyrrole **1**.

8.4g (125 mmol) of pyrrole were added at 0°C to a solution of 16.3g (145 mmol) of potassium t-butoxide in 80 ml of N,N-dimethylformamide (DMF). After 1h stirring, at room temperature, the reaction mixture was cooled at 0°C and 33.4g (175 mmol) of tosylchloride in 120 ml DMF were added. After one night at room temperature under stirring, the solution was poured into water, extracted 3 times with ethylacetate (AcOEt) and dried over $MgSO_4$. Recrystallisation in heptane afforded 85% of the pure desired product **1**.

mp[7] : 98-100°C

1-tosyl-3-acetylpyrrole **2**.

62g (607 mmol) of acetic anhydride were added at 0°C to a solution of 180g (1.35 mol) of aluminum chloride in 800 ml CH_2Cl_2. After 30 min of stirring at room temperature, the reaction mixture was cooled at 0°C and then 50g (226 mmol) of product **1** in 200 ml CH_2Cl_2 were added. After 1 night of stirring under argon, the solution was poured into cold water and extracted with CH_2Cl_2. Recristallisation in heptane afforded 90% of the pure desired product **2**.

^1H NMR (60 MHz, $CDCl_3$) δ: 7.8-7.2 (m, 6H, 4Haro + 2Hpyr), 6.7 (d, 1H, Hpyr), 3.7 (s, 3H, $COCH_3$), 2.4 (s, 3H, CH_3).

m.p. : 88-90°C.

methyl 2-(1-tosyl-3-pyrrolyl)acetate **3**.

- Thallium trinitrate on K-10.

150 ml of trimethylorthoformate and 120 ml of MeOH were added in one time to 60g (135 mmol) of $Tl(NO_3)_3.3H_2O$. After 5 min of stirring, 135g of K-10 montmorillonite were added. After 15 min of stirring, the solvent was distillated.

methyl 2-(1-tosyl-3-pyrrolyl)acetate **3**.

135 mmol of Tl(III) prepared according to the above procedure were added to 30g (114 mmol) of product **2** in 1 l MeOH. After one night stirring at room temperature, the solution was filtered off. The solid was washed with CH_2Cl_2/MeOH 9/1. The organic phase was then washed with water, dried over $MgSO_4$ and after evaporation of the solvent, 90% of the pure product were obtained.

^1H NMR (60 MHz, $CDCl_3$) δ : 7.8 (d, 2H, Haro), 7.3 (m, 4H, 2Haro + 2Hpyr), 6.3 (m, 1H, Hpyr), 3.7 (s, 3H, $COCH_3$), 3.5 (s, 2H, CH_2CO), 2.4 (s, 3H, CH_3).

2-(3-pyrryl)acetic acid **4**.

310 ml of NaOH 5N (1.55 mol) were added dropwise to a solution of 32g (106 mmol) of product **3** in 310 ml of MeOH. After 1 night refluxing and evaporation of the solvent, water was added. This aqueous phase was washed with Et_2O, then acidified with HCl until the pH reached 3.5. After saturation with NaCl, the aqueous phase was extracted with AcOEt. The organic phase was then dried over $MgSO_4$. After evaporation of the solvent, the product was washed with heptane . Yield 80%.

^1H NMR (60 MHz, DMSO-d_6) δ : 12-10 (s, 1H, COOH), 6.6 (m, 2H, H_2 H_5), 6 (m, 1H, H4), 3.3 (s, 2H, CH_2COOH).

Esterification

General procedure with water-soluble diimide as reagent.

24 mmol of alcohol and 1.9g (10 mmol) of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride were added to 1g (8 mmol) of **4** and 1 ml of triethylamine in 20 ml CH_3CN and stirred at room temperature for 1 day. After evaporation of the organic solvent and extraction with CH_2Cl_2, the product was purified by chromatography over SiO_2 (CH_2Cl_2).

5a : yield = 35%; ^1H NMR (200 MHz, $CDCl_3$) δ : 6.6 (m, 2H, H_2 H_5), 6.1 (m, 1H, H_4), 4.4 (q, 2H, J_{HF} = 8.5 Hz, CH_2CF_3), 3.6 (s, 2H, CH_2CO); ^{13}C NMR (50 MHz, $CDCl_3$) δ : 171.3 (CO), 123.1 (q, CF_3, J_{CF} = 277 Hz), 118.4 (C2), 116.9 (C5), 114.3 (C3), 109 (C4), 60.5 (q, OCH_2, J_{CF} = 37 Hz), 32.3 ($\underline{CH_2}CO$); ^{19}F NMR (188 MHz, $CDCl_3$) δ : -74.2 (t, 3F, J_{FH} = 8 Hz). IR (cm^{-1}) : 3406, 2974, 1757, 1285, 1169. HRms: calculated : 207.0507; found : 207.0506.

5b : yield = 41%; ^1H NMR (200 MHz, $CDCl_3$) δ : 6.7 (m, 2H, H_2 H_5), 6.1 (m, 1H, H_4), 4.6 (tt, 2H, J_{HF} = 13.6 Hz, J_{HF} = 1.3 Hz, CH_2CF_2), 3.6 (s, 2H, CH_2CO); ^{13}C NMR (50 MHz, $CDCl_3$) δ : 171.3 (CO), 120.8 (qt, J_{CF} = 286 Hz, J_{CF} = 32 Hz, CF_3), 118.4 (C2), 116.9 (C5), 115.1 (tt, J_{CF} = 285 Hz, J_{CF} = 31 Hz, CF_2), 114.3 (C3), 109.2 (m, CF_2), 109 (C4), 60 (t, OCH_2, J_{CF} = 28 Hz), 32.4 ($\underline{CH_2}CO$); ^{19}F NMR (188 MHz, $CDCl_3$) δ : -81.4 (t, 3F, J_{FH} = 9 Hz), -120.9 (m, 2F), -128.1 (m, 2F). IR (cm^{-1}): 3407, 2970, 1757, 1349, 1296, 1128. HRms: calculated : 307.0443; found : 307.0440

5c : synthesis of the alcohol : 5.16g (129 mmol) of NaOH were dissolved in 60 ml EtOH. Then, 13 ml (129 mmol) of dithiol were added. After 1 h stirring at room temperature, 4.8 ml (129 mmol) of CH_3I in 10 ml EtOH were added dropwise. After 6 h stirring, 7.74g (193 mmol) of NaOH in 50 ml EtOH were added. 15 min later, 13 ml (193 mmol) of 1-chloroethanol were added. The reaction mixture was

stirred at room temperature for 2 days, then refluxed for 1 day. The solution was extracted with Et_2O, the organic phase thus obtained washed with water, and after with $NaHCO_3$ (10% in water). Purification SiO_2 (heptane-ACOEt / 1-1). Yield 50%. ^1H NMR (200 MHz, $CDCl_3$) δ : 4.2 (t, 2H, OCH_2), 2.6 (m, 6H, CH_2S), 2.1 (s, 3H, SCH_3), 1.8 (m, 2H, CH_2).

Esterification : product **5c** : Yield : 20%. ^1H NMR (200 MHz, $CDCl_3$) δ : 8.5 (NH), 6.7 (m, 2H, H_2 H_5), 6.3 (m, 1H, H_4), 4.3 (t, 2H, OCH_2), 3.5 (s, 2H, CH_2-CO), 2.6 (m, 6H, CH_2S), 2.1 (s, 3H, CH_3-S), 1.8 (m, 2H, CH_2).

General procedure with trimethylsilylchloride reagent.

To a solution of 1g (8 mmol) of **4** in 20 ml tetrahydrofurane (THF) were added sequentially 24 mmol of alcohol and 0.5 ml (4 mmol) of trimethylsilylchloride. After 5 h stirring at room temperature, the solvent was evaporated. The residue was extracted with CH_2Cl_2 and this organic phase was washed with water and then dried over $MgSO_4$. Purification over SiO_2 (Et_2O).

5d : yield = 60%; ^1H NMR (200 MHz, $CDCl_3$) δ : 8.55 (NH), 6.7 (m, 2H, H_2 H_5), 6.1 (m, 1H, H_4), 4.1 (t, 2H, J = 6.7 Hz, OCH_2R), 3.5 (s, 2H, CH_2CO), 1.3-1.6 (m, 8H, CH_2), 0.9 (t, 3H, J = 6.5 Hz, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ : 173.1 (CO), 118.1 (C2), 116.6 (C5), 115.2 (C3), 108.8 (C4), 64.8 (OCH_2), 32.8, 31.4, 28.5, 25.4, 22.5 (CH_2), 14 (CH_3); IR (cm^{-1}): 3397, 2956, 2871, 1730, 1071; HRms: calculated : 209.1415; found : 209.1410.

5e : yield = 60%; ^1H NMR (200 MHz, $CDCl_3$) δ : 8.6 (NH), 6.7 (m, 2H, H_2 H_5), 6.3 (m, 1H, H_4), 3.9 (m, 2H, OCH_2), 3.5 (s, 2H, CH_2CO), 1.1-1.7 (m, 3H), 0.9 (d, 2H, J = 6.8 Hz, CH_3), 0.85 (t, 3H, J = 6.8 Hz, CH_3).^{13}C NMR (50 MHz, $CDCl_3$) δ : 173 (CO), 118.2 (C2), 116.7 (C5), 115.1 (C3), 108.8 (C4), 69.3 (OCH_2), 34.1 (CH), 33.1 and 26 (CH_2), 16.3 and 11.2 (CH_3); IR (cm^{-1}): 3397,

2964, 2878, 1729, 1072; HRms: calculated : 195.1259; found : 195.1260; $[\alpha]_D^{25}$ = +2.78 (C= 0.94, $CHCl_3$).

5f : yield = 75%; ^1H NMR (200 MHz, $CDCl_3$) δ : 8.4 (NH), 6.7 (m, 2H, H_2 H_5), 6.3 (m, 1H, H_4), 4.3 (m, 2H, $COO\underline{CH_2}$), 3.6 (m, 4H, CH_2CO + CH_2O), 3.4 (s, 3H, CH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ : 172.8 (CO), 118.1 (C2), 116.7 (C5), 115.1 (C3), 109 (C4), 70.4 ($COO\underline{CH_2}$), 63.6 (OCH_2), 58.9 (OCH_3), 32.8 ($\underline{CH_2}CO$). IR (cm^{-1}) : 3392, 2932, 1734, 1163, 1099. HRms: calculated : 183.0895; found : 183.0890.

5g : yield = 65%; ^1H NMR (200 MHz, $CDCl_3$) δ : 9 (NH), 6.7 (m, 2H, H_2 H_5), 6.3 (m, 1H, H_4), 4.3 (m, 2H, $COOCH_2$), 3.6 (m, 8H, CH_2CO + CH_2O), 3.4 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ : 173.1 (CO), 118.1 (C2), 116.8 (C5), 115 (C3), 108.7 (C4), 72.5, 71.8, 70.1, 61.4 (OCH_2), 58.8 (OCH_3), 32.9 ($\underline{CH_2}CO$); IR (cm^{-1}): 3370, 2883, 1735, 1137, 1071. HRms: calculated : 227.1157; found : 227.1160.

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