3,3- and 4,4'-Dimethoxy-2,2'-bipyrroles and Aminopyrroles with high level electrons

Syntheses and Properties of new Poly-(2,2'-bipyrroles)

Dissertation
zur Erlangung des Doktorgrades (Dr. rer. nat.)
der Fakultät für Chemie und Pharmazie der Universität Regensburg

vorgelegt
von Sergiy Anikin
aus Odessa
2004

Promotionsgesuch eingereicht am:	24. Juni 2004
Promotionskolloquium voraussichtlich am:	12. Juli 2004
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Die vorliegende Arbeit entstand in der Zeit von Dezember 2000 bis Juni 2004 an der Fakultät für Chemie und Pharmazie der Universität Regensburg.

Sehr herzlich bedanken möchte ich mich bei meinem Doktorvater

Herrn Prof. Dr. Andreas Merz

für die interessante Themenstellung, sein ständiges Interesse am Fortgang dieser Arbeit, sowie die Ermöglichung zur Teilnahme an verschiedenen Tagungen und Konferenzen.

Herrn Prof. Dr. Oliver Reiser danke ich für die Bereitstellung seiner Laboratorien und dem angenehmen Betrieb an seinem Lehrstuhl.

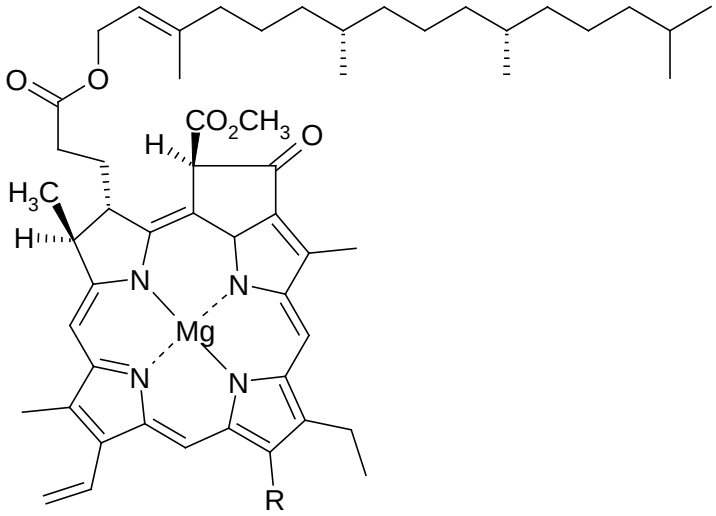
C O N T E N T S

Chapter 1

1.1 Pyrrole presence in the Nature

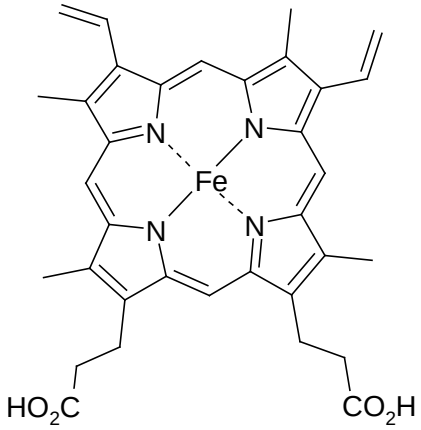
Pyrroles are widely distributed in the Nature. This five-membered heterocycle serves as a Nature building block in chlorophylls (**1**) and haem (**2**); nucleic acids, the bile pigments, the core of vitamin B_{12}, and many other biologically active compounds (also the derivatives of tetrapyrrole) [1]. The pyrrole ring occurs in a number of naturally occurring antibiotics (**3**), including the increasingly important netropsin (**4**). Furthermore, an indol fragment, where the pyrrole ring is fused with benzene is incorporated in the aminoacid triptophane, alkaloids (**6**) and in indigo (Figure 1.1).

It is also known that most of the naturally occurring organohalogen compounds are produced by marine organisms, bacteria, fungi and terrestrial plants, but very few of them were found in higher animals. Recently the presence of several halogenated bipyrroles was discovered [2] (**5**) in the eggs of Pacific and Atlantic Ocean seabirds (Figure 1.1).



1

Chlorophyll ***a*** and ***b***
R= CH_3, CHO



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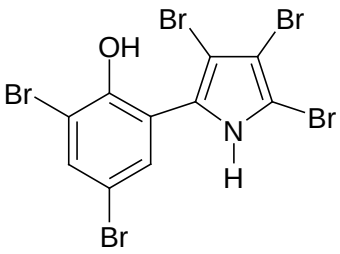
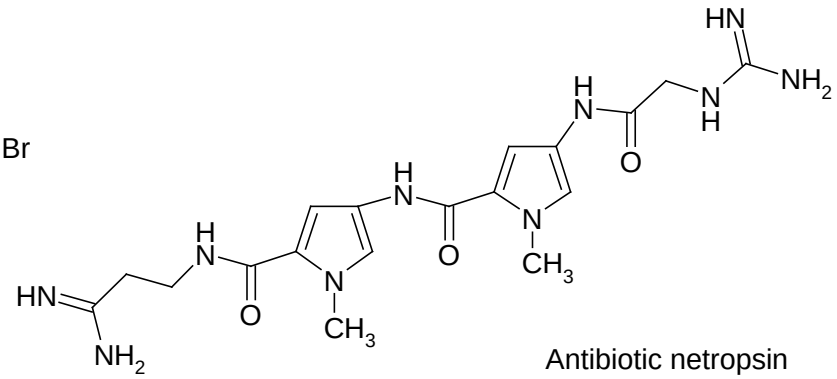
Haemoglobin



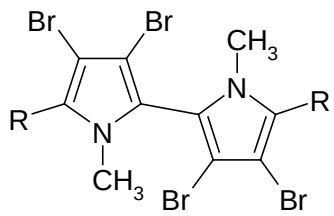
A natural antibiotic

3



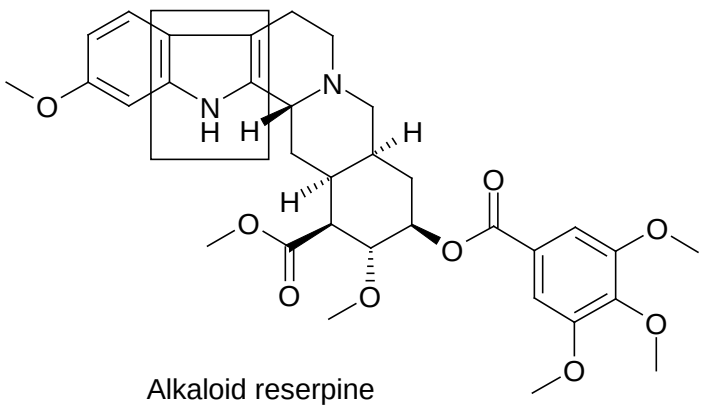
Antibiotic netropsin

4



R= Br, Cl

5



Alkaloid reserpine

6

Figure 1.1 Pyrrole ring in the natural compounds

1.2 Application of pyrroles

The derivatives of pyrrole have found a wide range of applications in the modern science and technology.

Thus, the Dervan group [3] has discovered that hairpin polyamides, containing imidazole and pyrroles, are capable of discriminating all four Watson-Crick base pairs in the DNA minor groove (Figure 1.2). The 3-hydroxypyrrole amino acid comes originally from Japanese chemist T. Momose [4]. This short synthesis gives hydroxypyrroles with good yields.

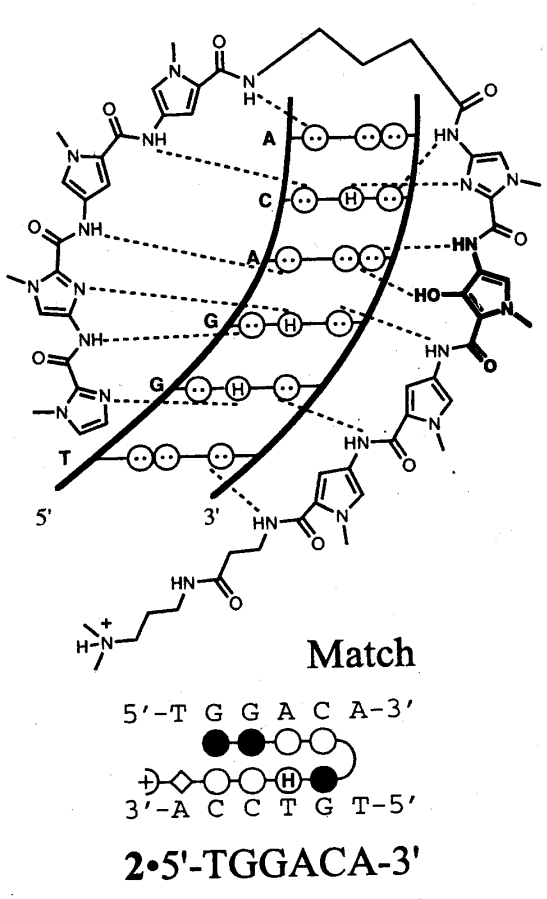


Figure 1.2 Matching of the hydroxypyrrole-pyrrole fragment to the base pair in DNA helix

Thus, H. Naarmann in BASF Co. has developed important continuous methods of the

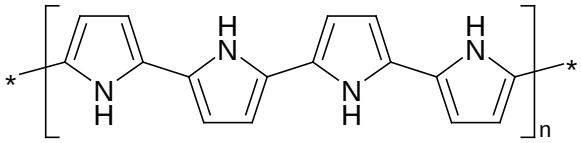


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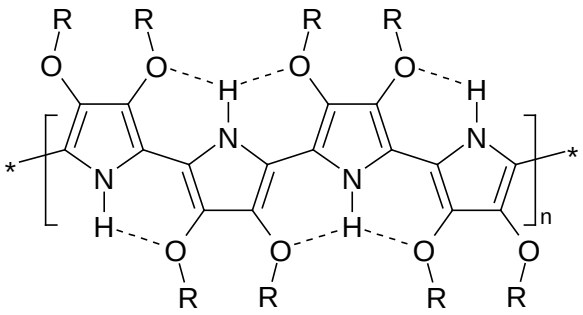
Figure 1.3 Naarmann's polypyrrole

polypyrrole (**7**) film formation [5, 6], practically without any lenght restrictions. He developed a batch process, using a rotating drum or moving belt as anode. Both methods are based on an electrochemical polymerisation from solution. In practice, a polymer film is being withdrawn directly from the electrolyte bath containing the pyrrole monomer and the electrolyte salt and than is wound up [7].

Polymers with different conductive properties can be obtained by using various substituted pyrrole monomers. The conductivity can be significantly improved when an electron realizing substituents are introduced into the pyrrole ring, e.g. by the electrochemical polymerisation of 3,4-alkoxypyrroles [8] was obtained poly-(3,4-dimethoxypyrrole) film (**8**) with conductivity better than for the unsubstituted polypyrroles.



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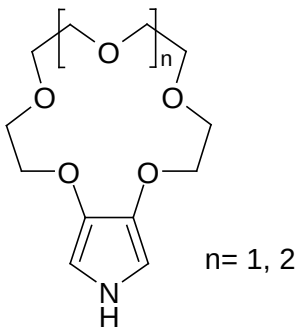


9, 10

Figure 1.4 The variety of pyrrole derivatives

Such pyrrole derivatives can be applied not only in the field of electrochemistry and polymers preparation. E. Dötterl [9] suggested an interesting method towards synthesis of pyrroles fused with a crownether ring (**9, 10**). Obviously, these compounds can be employed as phase transfer catalysts, since they have cavities for potassium and sodium cations. But, unfortunately, there is no much information on those materials available

today. In the scientific studies [9, 10], the first syntheses of symmetrical porphyrin cores were described, based on the “crown-pyrroles” (**9, 10**), which are expected to form the ion channels.

It was also found that such fused heterocycles can be electrochemically oxidised. Interestingly enough, only compound (**9**) was polymerised into the flat homogeneous polymer film [11].

1.3 Conducting polymers

Until about 30 years ago all carbon based polymers were commonly regarded as insulators. The idea that plastics could be made to conduct electricity would have been considered to be absurd. A rapid change of this perception started in 1967 year, when a postgraduate student of Hideki Shirakawa at the Tokyo Institute of Technology attempted to synthesise polyacetylene, and a silvery thin film was produced as a result of a mistake. When this film was investigated, it was found to be semiconducting, with a similar (10^{-3} Sm^{-1}) level of conductivity of the best conducting black powders; chemically obtained by Natta et al. in

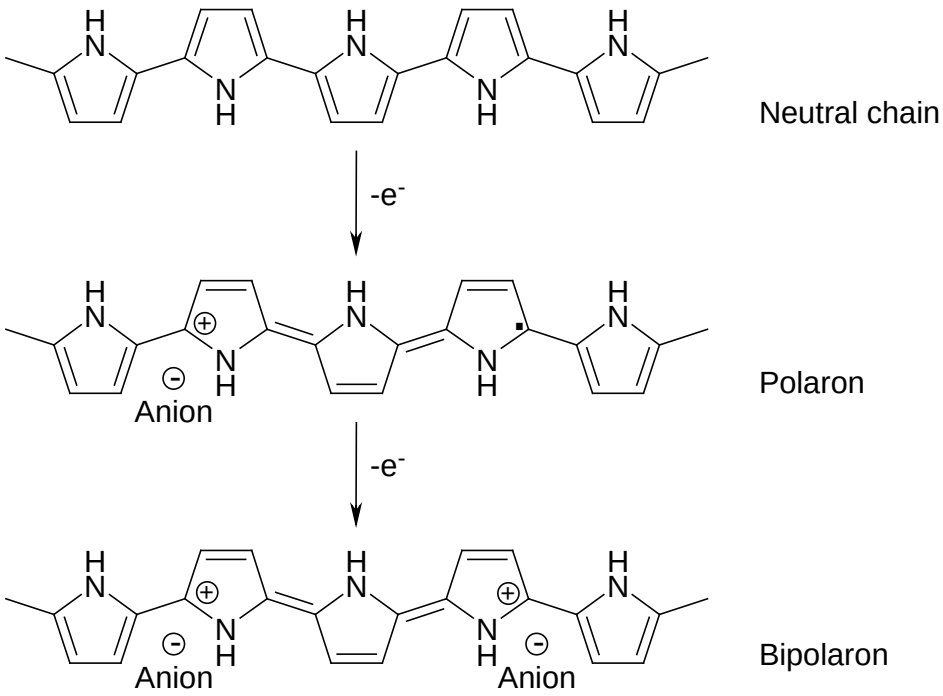


Figure 1.5 Polymer doping leads to conductivity

1958 [12]. Undoped, the polymer was silvery, insoluble and intractable, with a conductivity similar to that of semiconductors. But when it was weakly oxidised by compounds such as iodine it turned golden colour and its conductivity increased to about 10^4 $S \cdot cm^{-1}$.

In the 1980's polyheterocycles were first developed. Polyheterocycles were found to be much more air stable than polyacetylene, although their conductivities were not so high. By adding various side groups to the polymer backbone, derivatives that were soluble in various solvents were prepared. Other side groups affected properties such as their colour and their reactivity to oxidising and reducing agents [13-15].

Since then it has been found that about a dozen different polymers undergo this transition when doped with a weak oxidising or reducing agent. They are all various *p*-conjugated polymers. This early work has led to an understanding of the mechanisms of charge storage and charge transfer in these systems. All have a highly conjugated electronic state. This also causes the main problems with the use of these systems, that of processibility and stability. Most early conjugated polymers were unstable in air and were not capable of being processed. The most recent research in this has been the development of highly conducting polymers with good stability and acceptable processing attributes [16].

Since that time no other class of one-dimensional materials has trigged such large numbers of publication as conducting polymers. There are some reasons for the popularity of conducting polymers:

- conducting polymers are considered new materials with great potential for new applications;
- conducting polymers are derivatives of polymers, i.e., of compounds with extended systems of conjugated double bonds.

In recent years interest for the various pyrrole derivatives synthesis magnificently increased. It was induced not only because of its wide distribution in the natural materials, but by a high ability of the pyrrole ring to be easily polymerised forming film or powder possessing an electrical conductivity. Although there are different methods generally used to prepare polypyrrole: chemical polymerisation in solution [17, 18] and electrochemical polymerisation [19, 20]. The latter, gives thin and durable polymer film with good

conductivity [21, 22]. The formation of such polymeric films, based on pyrrole ring system, especially from the monomers having high electron density, show considerable promise in a conducting materials generation.

On the Figure 1.6 are shown some of the most important conducting polymers. Surely, the formation of a conducting organic films causes an intense interest in the synthesis and characterisation because of their electrical, electrochemical and optical properties [23, 24];

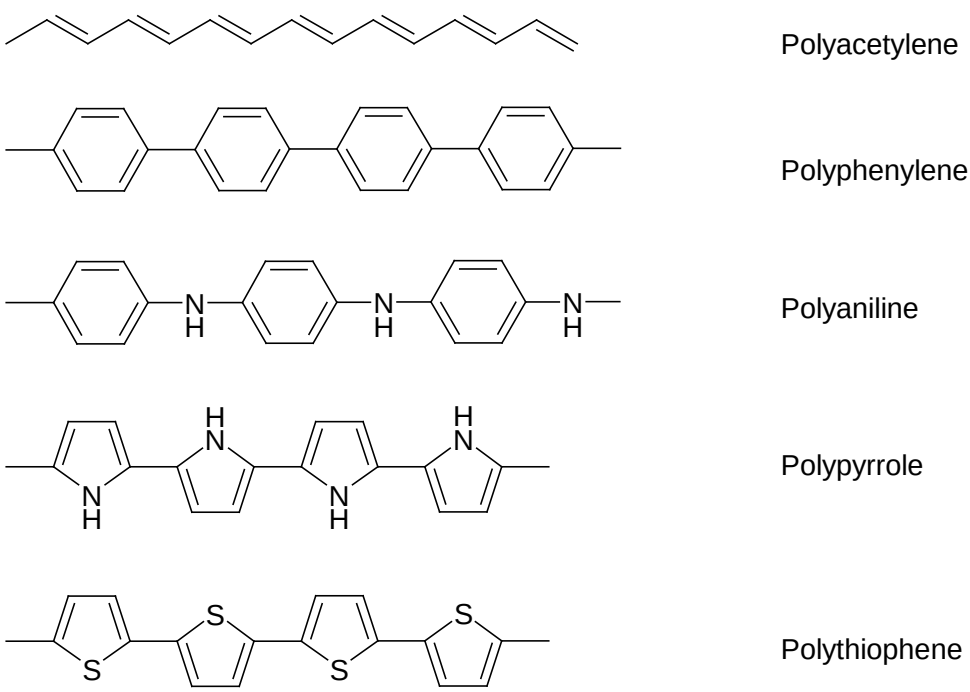


Figure 1.6 Ideal structures of the most important conducting polymers

and possible application to organic batteries [25, 26], sensors, various microelectronic devices, and even for the solar cells preparation [27].

The ability of pyrrole to form electrochemically nanosystems [28], is undoubtedly one of the most perspective field in the modern chemistry, stimulates an active exploration in this direction.

Among the classes of intrinsically conducting polymers, polypyrrole (PPy) is probably the one of the most frequently used in commercial applications [25, 26], mainly due to its relatively ease of synthesis, environmental stability and electrical conductivity [29].

1.4 Problem definition

A wide variety of the application fields for the conducting polymers formed from different pyrroles derivatives let us to expect some interesting chemical properties and electrochemical behaviour of alkoxy and amino pyrroles, we were interested in. So, our main goals were formulated in the following way:

- Synthesis of 3-alkoxypyrroles and their highly electronrich dimers, electrochemical characterisation of these compounds and their polymers.

- Synthesis of 3-methoxy-4-dimethylaminopyrrole followed by an electrochemical characterisation

- Synthesis of 3,4-didimethylaminopyrroles with an electrochemical description.

- Conductivity definition of obtained polymers.

- Possible application of the polymer film obtained by means of electrochemical methods.

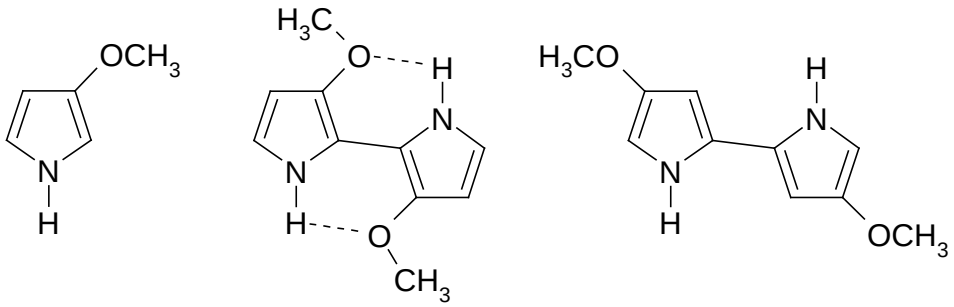
Chapter 2

Syntheses of Pyrroles and Bipyrroles

2.1 General preparation methods of pyrroles

There are many routes towards different pyrroles from aliphatic intermediates. The main stimulus of this research was a need in the intermediate pyrroles as for porphyrines and similar structures syntheses, which have biologic importance. The most important synthetic methods construct a substituted pyrrole core, where the substituents can be modified or eliminated later on.

On the first step of our investigation we were interested in the synthesis of 3-methoxypyrrole (**11**) and two isomers: 3,3'– (**12**) and 4,4'-dimethoxy-2,2'-bipyrroles (**13**) (Scheme 1), with further electrochemical characterisation of obtained products. All of these compounds have high electron density, and it was to be expected that such systems should be electrochemically active and form polymer film easily.



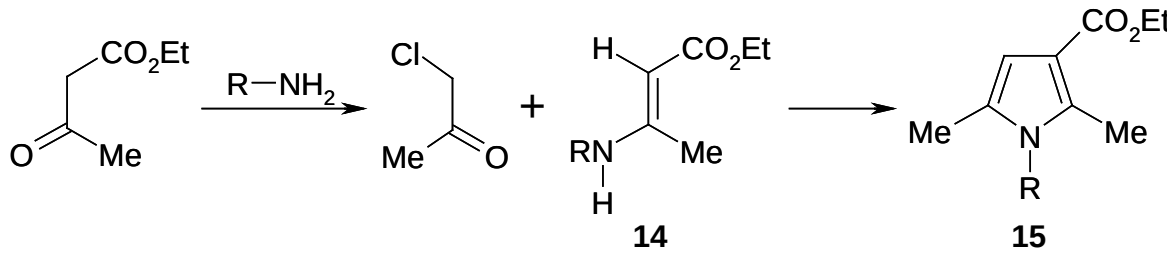
11 **12** **13**

Scheme 1

There are many routes towards pyrroles; the most relevant to our work will be considered later.

Hantzsch pyrrole synthesis

This method [30] is in the condensation of *a*-halogenketone with *b*-ketoester and ammonia

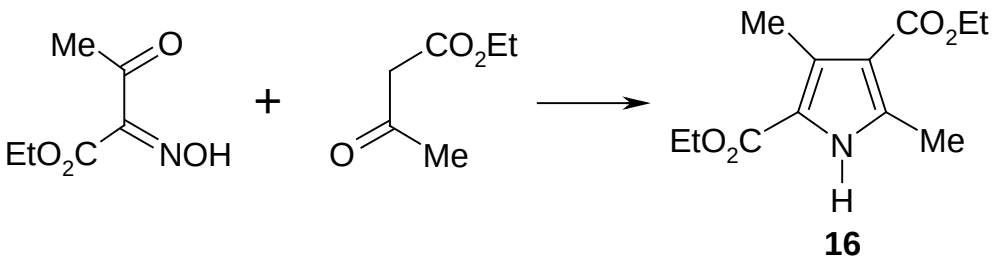


Scheme 2 Hantzsch synthesis

or an amine. The possible mechanism is depicted on the Scheme 2. An intermediate aminocrotonic ester (**14**) undergoes *b*-alkylation, as it usual with enamines. This method is useful for the 2,5-dialkyl- and 2,4,5-trialkylpyrrole-3-carboxylates synthesis [31].

Knorr pyrrole synthesis

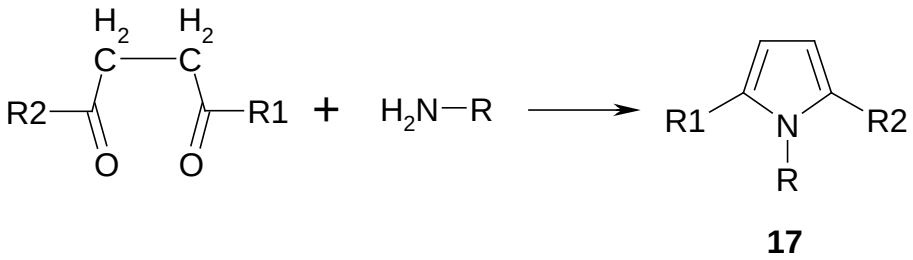
This reaction and its modification is the most important and widespread method of the pyrrole ring formation. Classical example of a such synthesis [32] is formation of the "Knorr's pyrrole" (**16**) with the reductive condensation of oxyiminoacetoacetate and acetoacetic ester with zinc in glacial acetic acid (Scheme 3):



Scheme 3 Knorr synthesis

Paal-Knorr pyrrole synthesis

This method [33] is in the condensation of 1,4-diketone with ammonia or primary amine and, as a rule, it gives pyrroles (**17**) with good yields (Scheme 4), many of such examples are considered in the review [34]. But this method is limited a little bit by accessibility of *g*-diketones.



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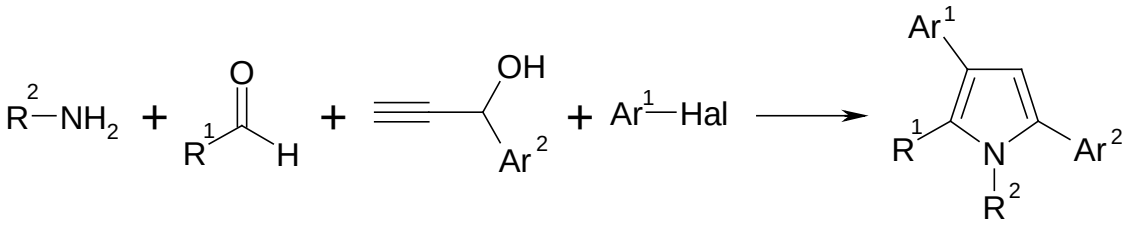
Scheme 4 Paal-Knorr synthesis

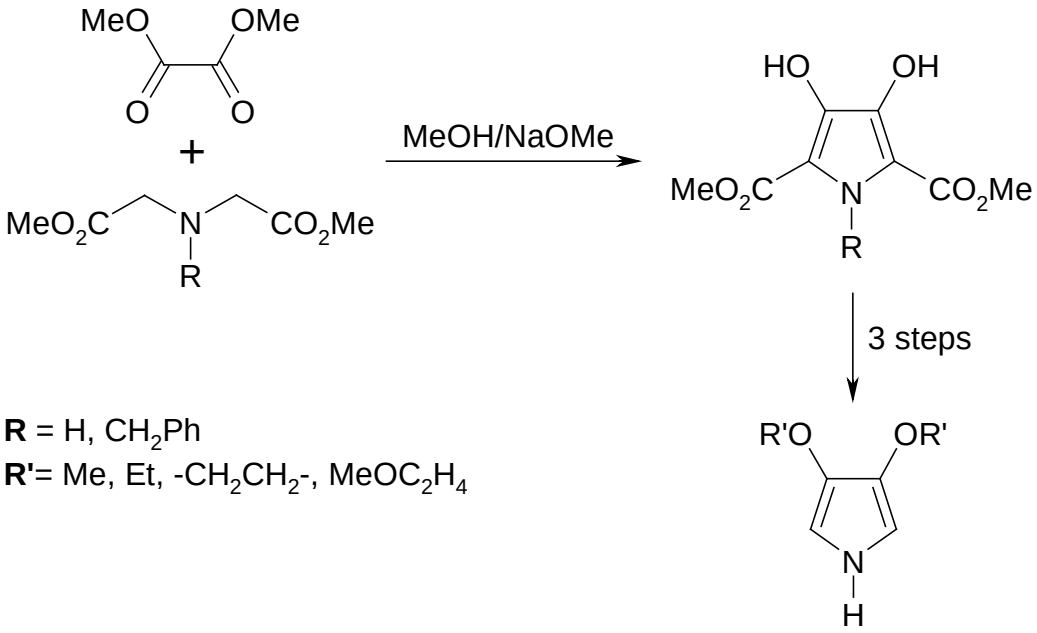
A recently reported [35] one-pot synthesis of 1,2,3,5-tetrasubstitued pyrroles is a three-step, four-component process. The last process occurs via a coupling-isomerisation-Stetter reaction-Paal-Knorr sequence (Scheme 5). The modification of the previous method allows to obtain pyrrole structures with required aryl substituents. There are only some limitations on the Ar-substituent type.



Scheme 5 Modification of the Paal-Knorr synthesis

Synthesis of 3,4-alkoxypyrroles

The next convenient method of alkoxy pyrroles formation was described by Merz et al. [36] 1990's. This method starts from a condensation of dimethyl N-benzylimino-diacetate and dimethyl oxalate to provide dimethyl 1-benzyl-3,4-dihydroxypyrrole-2,5-dicarboxylate, which gives after bis-*O*-alkylation the corresponding 3,4-diethers. A pyrrole N-benzyl cleavage followed by ester hydrolysis and decarboxylation leads to dialkoxypyrroles.

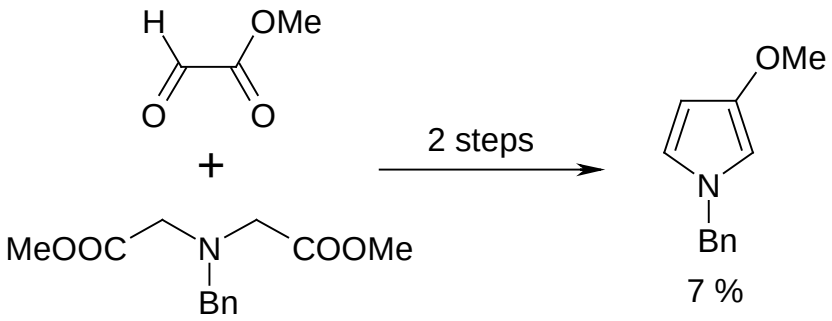


R = H, CH_2Ph
R'= Me, Et, $-CH_2CH_2-$, $MeOC_2H_4$

Scheme 6

Synthesis of 3-alkoxypyrroles

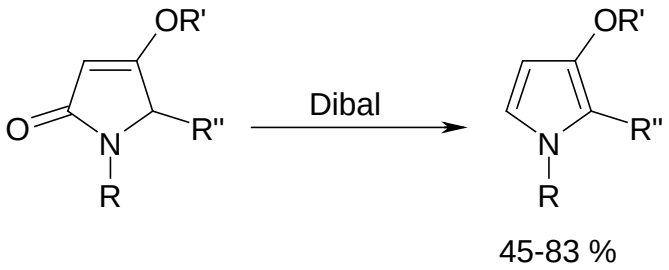
The method, described above, was slightly modified by Lieser [37]. It isa convenient route



Scheme 7 3-Alkoxypyrroles formaiton

towards 3-alkoxypyrroles. The starting materials alteration and three further steps lead to 3-methoxypyrrole, but one grave disadvantage was found – the yields were not higher than 7 %.

Another one possibility in 3-alkoxypyrrole synthesis was suggested by Kochhar and Pinnick [38]. Thus, this efficient method consists in the reduction of alkoxypyrrolinones



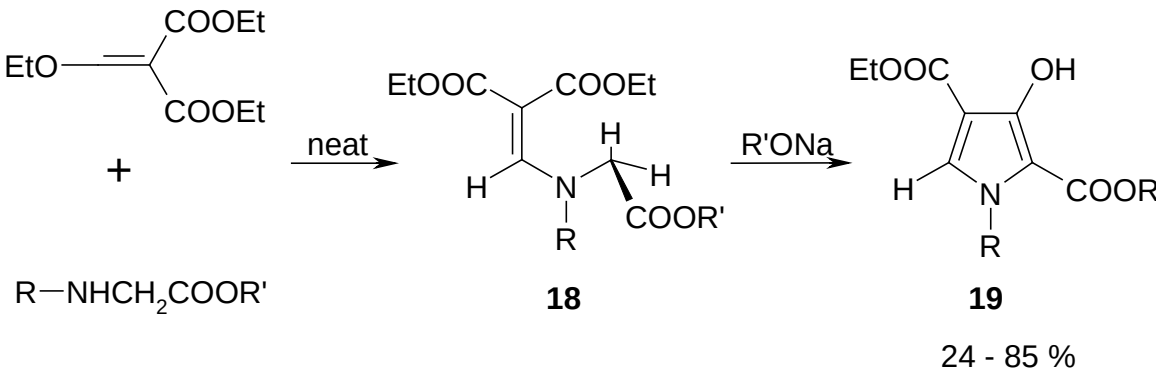
R = CH_3, C_2H_5, Bn
R' = CH_3, C_2H_5
R''= H, C_2H_5

Scheme 8 Alkoxypyrollinones reduction

with diisobutylaluminiumhydride (Scheme 8). A wide range of alkoxypyrroles can be prepared by this method, and the deficiencies of earlier preparation were avoided (limited substituted patterns, lengthy sequences, and the use of starting materials which are not readily available).

Momose route towards 3-hydroxypyrroles

In the group of Japan chemists was suggested a very good synthetic method [39] of 3-hydroxypyrrole-2,4-dicarboxylates (**19**) formation, which were obtained by Dieckmann condensation of compound (**18**) using alkoxide as condensing agent with pretty good yields (over 60 %), in a short sequence and from cheap starting reagents (Scheme 9).

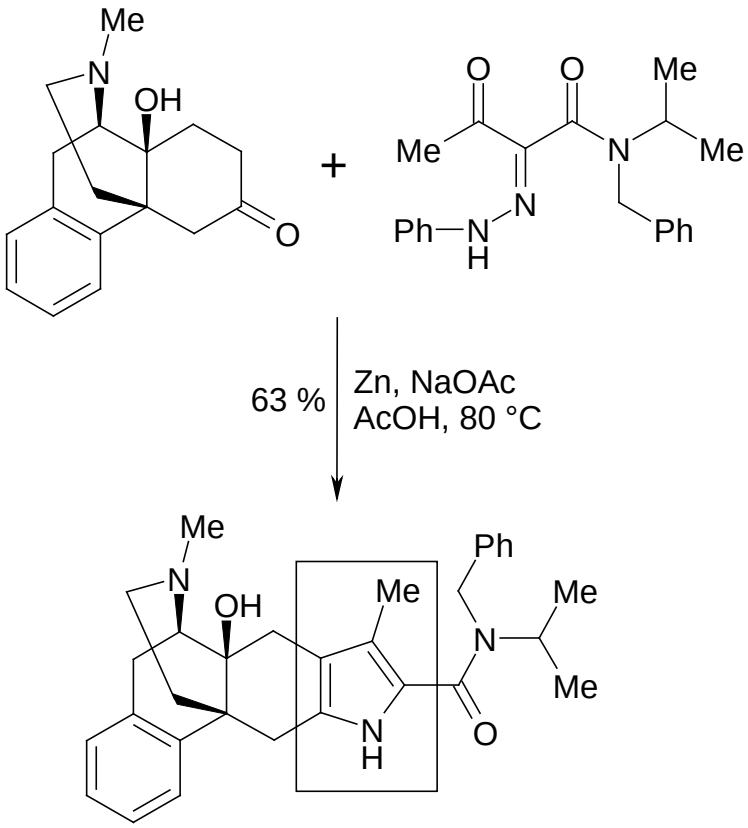


R = H, Me, **CH_2Ph**, Ph
R'= Et, *t*-Bu

Scheme 9 Momose pyrrole synthesis

Modified Knorr pyrrole synthesis

In the last years there is more and more of the heterocycles syntheses are dedicated to the nature compounds formation. Recently [40] the modification of the Knorr synthesis was



Scheme 10 A modified Knorr synthesis

described, which leads to *d*-opioid antagonist (Scheme 10). The modifications have practical benefit with respect to carrying out the reaction and isolating product.

2.2 Protecting at the pyrrole nitrogen

Due to the high reactivity of pyrroles, and especially alkoxy- or amino- derivatives, polymerisation or oxidation of the pyrrole ring may occur. The application of protection groups for the preparation of many electron-rich pyrroles, conjugated dimers and oligomers, helps to avoid this problem.

It is also helpful in the oxidative functionalisation at the *a*-position, e.g. with iodine or bromine, where instead of the electrophilic substitution of aromatic proton, radical cation or dication could be obtained. The last species undergo a variety of reactions, allowing many interesting derivatizations.

The same problem is in the case of coupling reactions, with many oxidising salts of the metals, e.g. copper (II) and nickel (II). In a such kind of reactions, an unprotected substrate always undergoes conversion into black residue – obviously pyrrole oxidation products.

Also, the protection of the N-hydrogen bond in the ring helps in reactions with organolithium reagents or with strong bases, where N-hydrogen is more reactive than one in *a*-position.

There are quite a wide set of protecting groups on the nitrogen atom and on the pyrrole ring positions [41]. For the first case the most useful ones are *tert*-butoxycarbonyl (*Boc*) group and the benzyl (*Bn*) group.

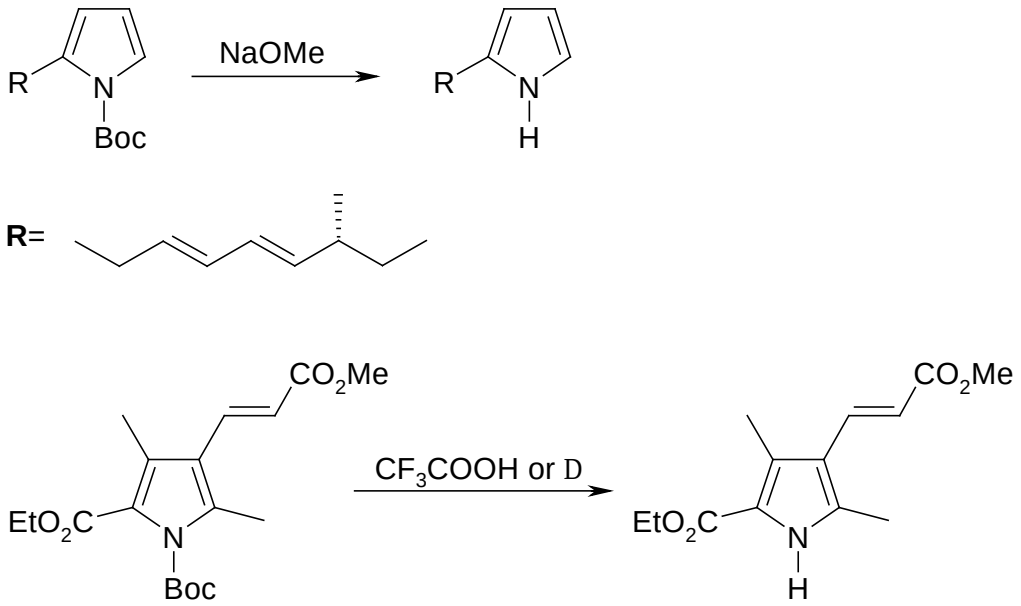
For the protection of the other pyrrole ring positions, the ethoxycarbonyl-group has been used. During the research was found out that two different (unsymmetrical) ester groups can be selectively converted to carboxylic acid, which can be selectively removed from the pyrrole ring.

Here are compared the main features of *Boc* or *Bn* protective groups, which application was generally acceptable for the “nitrogen” protection.

First of all, let us consider conditions of deprotection. Both groups can be cleaved by trifluoroacetic acid [42], usually this reaction proceeds with 80-90 % yields. But in our case with alkoxy-pyrroles, which easy undergo oxidation, this method was not applicable.

The next possibility of the *Boc* group removal is stirring of substrate with hydroxide or alkoholate at room temperature [43]. It is very mild method, also giving high yields; but we needed in our reaction sequences ester cleavage, proceeding in alkali media, what made this way of protection also not acceptable. One more opportunity to remove Boc group is

pyrolysis [42] in the protecting atmosphere at 180 °C. These conditions were not acceptable either, because we have used high temperatures for the Ullmann-coupling



Scheme 11 *Boc*-group removal

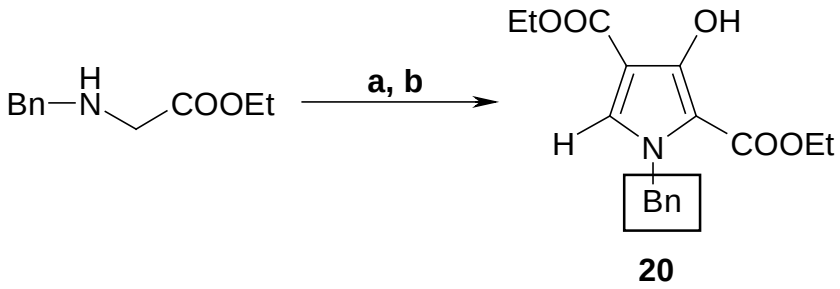
reactions (near 300 °C) and for decarboxylation (200 °C) (Scheme 11).

From the listed higher conditions of deprotection for the benzyl-group only the way with trifluoroacetic acid is the common one. Two other methods do not work with the Bn group, so it can be used for all conversions we used. For the removal of this group exists very good method using the solution of sodium in liquid ammonia – it proceeds in mild conditions and normally gives yields near 90-95 %.

And at last it can be adduced that the Bn-group is not conjugated with the pyrrole ring, and it shows no or only a little mesomeric influence on the pyrrole *p*-system, so only steric factor could be taken in consideration.

It would be also preferable to have the protected pyrrole at an earlier stage – what becomes possible using Bn-group, which helps to the pyrrole-derivatives to “survive” such quite vigorous conditions of the intermediate steps like pH value about 2-3 and heating. It was possible already on the first stage to produce N-benzylated aminoacid ester and using the Momose method [39] of heterocycle formation, pyrrole ring can be N-protected

immediately after the heterocycle formation (Scheme 12) and protective group can be maintained till the end of our sequence:



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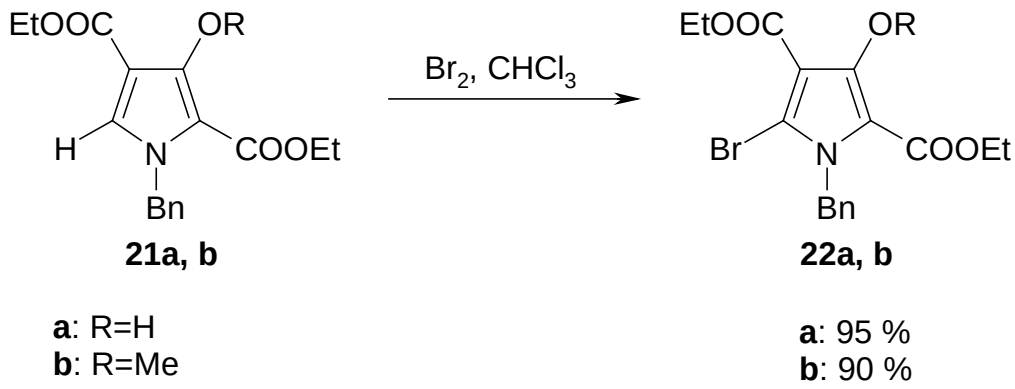
a: diethyl ethoxymethylenemalonate;
b: NaOEt/EtOH

Scheme 12 *Bn*-group introduction

2.3 Preparation of the pyrrole for carbon-carbon coupling reactions

For the further ring coupling we have chosen Ullmann-coupling [44] and oxidative dimerisation of the *a*-lithiated alkoxypyrroles with $NiCl_2$ assistance [45]. Both methods can be used in the synthesis of inner- and outer-alkoxy bipyrroles respectively. Precursors for these methods can be obtained in good yields (over 60 %) and in relatively mild conditions, which were necessary for unprotected pyrrole.

For the Ullmann-coupling bromine derivatives of 3-alkoxypyrrole-2,4-dicarboxylates were used. Thus, the halogen atom can be easily introduced into the *a*-position using electrophilic substitution in the aromatic ring with electrophilic species Br^+ (Br_2) and I^+ (ICl). As an aromatic substrate for the S_E-reaction can be used 3-hydroxypyrrole (**21a**) or 3-methoxypyrrole (**21b**) derivatives. However, the best results were obtained using (Scheme 13) diethyl 1-benzyl-3-hydroxypyrrole-2,4-dicarboxylate (**21a**) and bromine [46].



21a, b **22a, b**

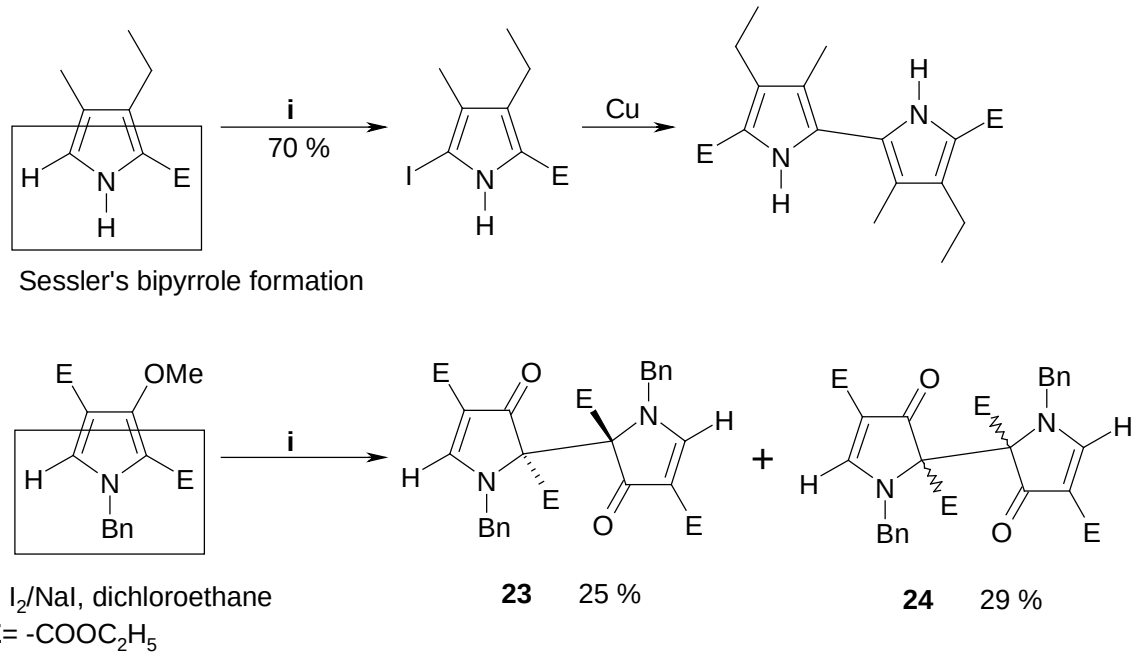
a: R=H
b: R=Me

a: 95 %
b: 90 %

Scheme 13 Halogen introducing

2.3.1 Side reaction

It is known from the literature that in the Ullmann reaction better yields could be obtained with iodo-derivatives application [47] – therefore we decided to dimerise our substrate



Scheme 14 Sessler's coupling method and its applying on our substrate

introducing iodine in the *a*-position of pyrrole in the same way as it was described by Sessler et al. [48] (Scheme 14), as we had a similar aromatic structure. Yet, the obtained results are quite unexpected..

Dimerisation does indeed occur, however at the *2*-position, and with formation of a 2,2'-bipyrrolidone as the crystalline *racemic* (±-**23**) and the achiral resinous *meso*-form (**24**).

The assignment of the stereochemistry has been confirmed by an X-ray structure presented on the Figure 2.1.

The ^{1}H NMR spectra of (**23**) and (**24**) display manifold diastereotropic $-CH_2-$ groups of the ethyl esters and benzyl groups. Both ethyl $-CH_2-$ groups in (**23**) show a 4 x 2 x 2 line signal, whereas only the inner groups split into a 4 x 2 signal in (**24**).

Being based on the NMR ^{1}H and ^{13}C correlation (Figure 2.2) can be defined at which carbon atom in (**23**) is either one or another hydrogen is located, on the shown spectra one can see ^{1}J coupling constants.

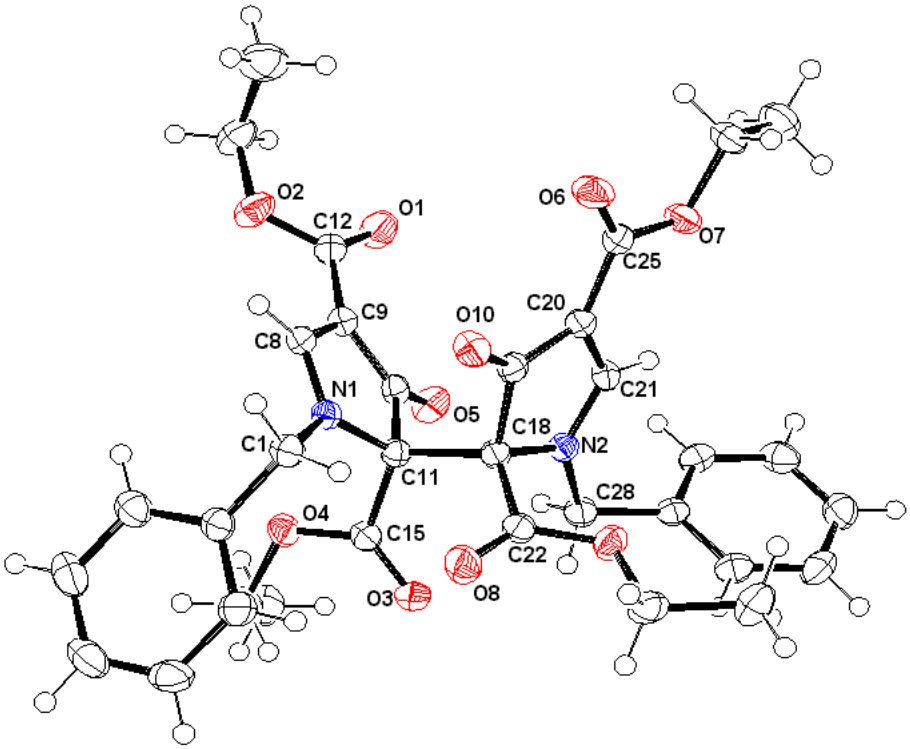


Figure 2.1 X-Ray structure of (**23**)

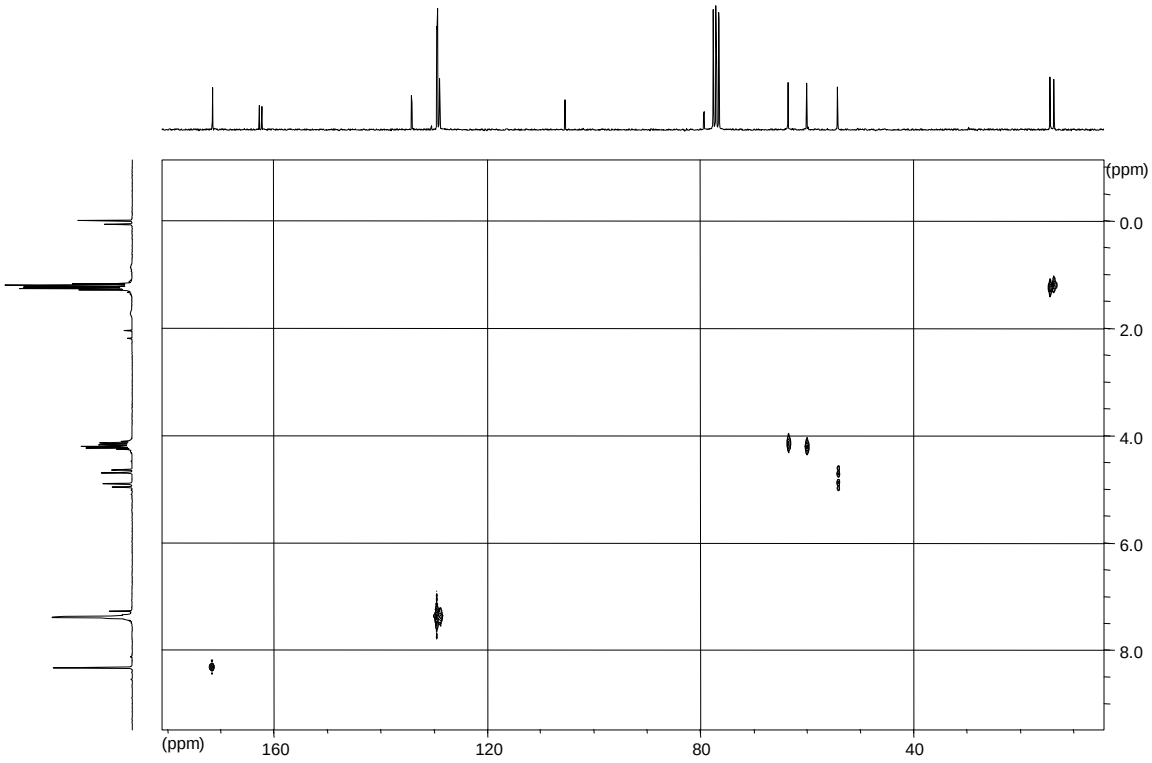
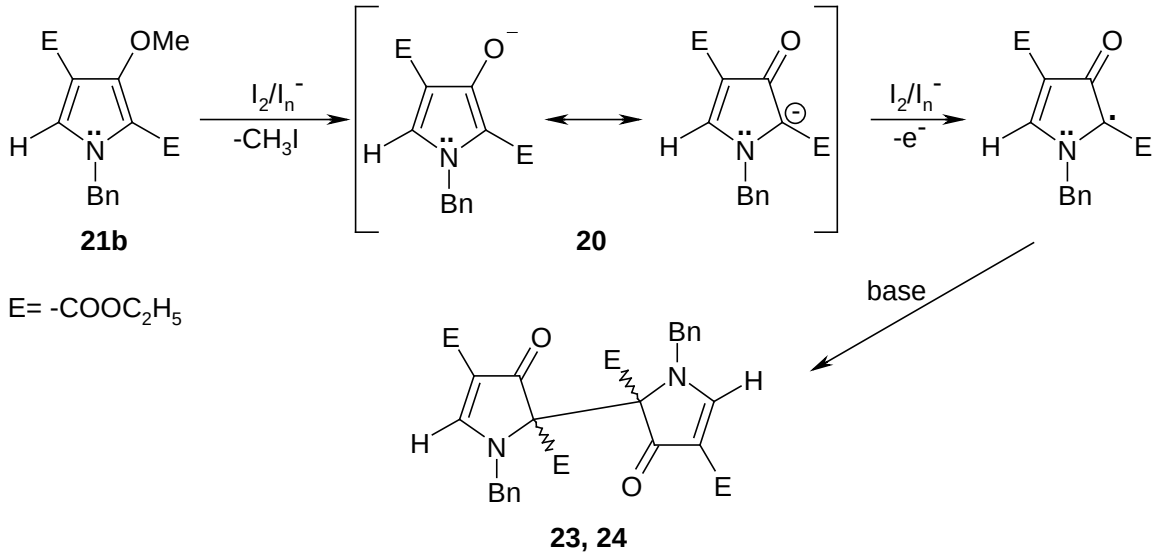
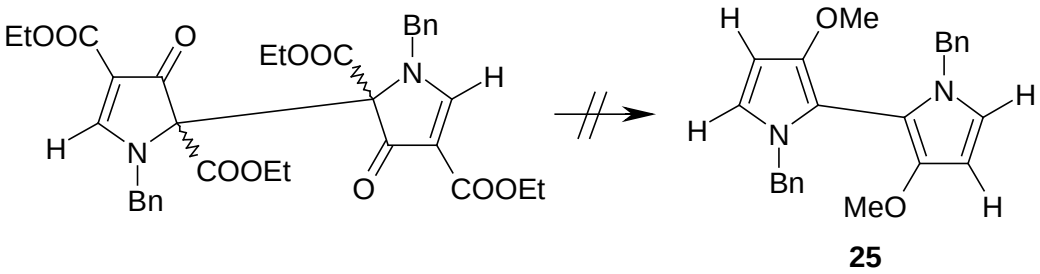


Figure 2.2 Correlation of ^{1}H (Y axis) and ^{13}C (X axis) spectra of (**23**)



Scheme 15 Possible explanation of dimerisation

Surprisingly, the demethylation at the methoxy group occurs faster than the direct oxidation. The slightly alkaline aqueous phase ($NaHCO_3$ in water) together with the organic solvent 1,2-dichloroethane seem to be a mild phase-transfer medium that favours the Finkelstein type S_N2 reaction of the iodide or polyiodide ion to give iodomethane and the mesomeric anion of (**20**) (Scheme 15). Oxidation of $\mathbf{20}^-$ by the I_2/I_n^- system can give rise to the resonance-stabilised neutral radical $\mathbf{20}^{\cdot}$, which then dimerises to (**23**) and (**24**). A possible route from (**23**) and/or (**24**) to bipyrrole **25** by ester hydrolysis, decarboxylation, and *re*-methylation could not be realized, however.



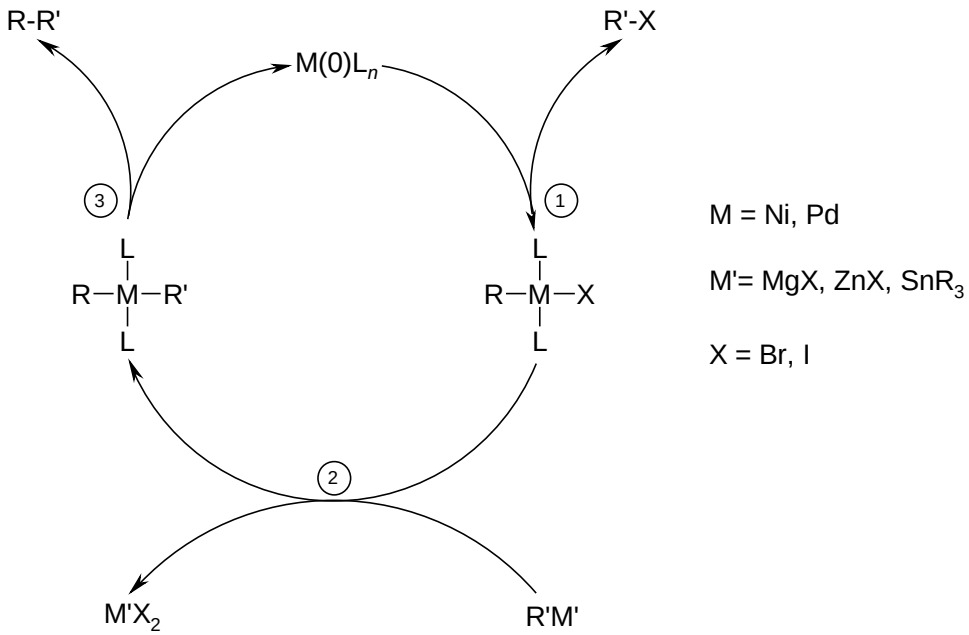
Scheme 16 Not realized route

2.4 Pyrrole Coupling Reactions

Coupling reactions can be divided into two general groups: with formation of symmetrical or unsymmetrical molecules.
As in the field of our interest we have only symmetrical bipyrroles, so we can take in the consideration some general methods which could be applied for pyrroles coupling.

2.4.1 Cross-Coupling Reactions

As for the preparation of pyrrole dimers and oligomers so for the different aromatic compounds in the literature can be found quite a large sets of cross-coupling reactions, which can be more or less preferable in one or another situation. C. Rehm has investigated and applied (mostly in the field of thiophenes) [49] in her work a large amount of reactions mostly for five-membered heterocycles.



Scheme 17 General cross-coupling cycle

Cross-coupling has found a limited application in organic synthesis for two reasons: firstly, because of the concurrent elimination and exchange which leads to decrease in selectivity; and, secondly, on account of the inertness of organic halides possessing a halogen on an sp^2 atom.

For nickel- and palladium catalysed cross-coupling of organometallic compounds with organic halides it is generally accepted that the mechanism of the reaction involves an initial *oxidative addition* (step 1) of R'X to the zero-valent metal complex M(0), followed by transmetallation with formation of a complex RMR'L_2 (step 2), having two *s*-bonded organic residues; and *reductive elimination* (step 3) of R–R' completes the cycle with regeneration of M(0) (Scheme 17).

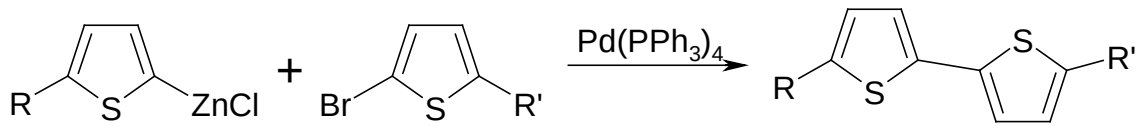
However, the Scheme 17 reflects only the most characteristic features of catalytic cross-coupling [50, 51].

So, in every case for the unsymmetrical coupling it should be two different participants. One of the species must have carbon-halogen and another one polarised metal-carbon bond.

Thus, there are some of the mostly used coupling methods.

2.4.2 Negishi – Coupling

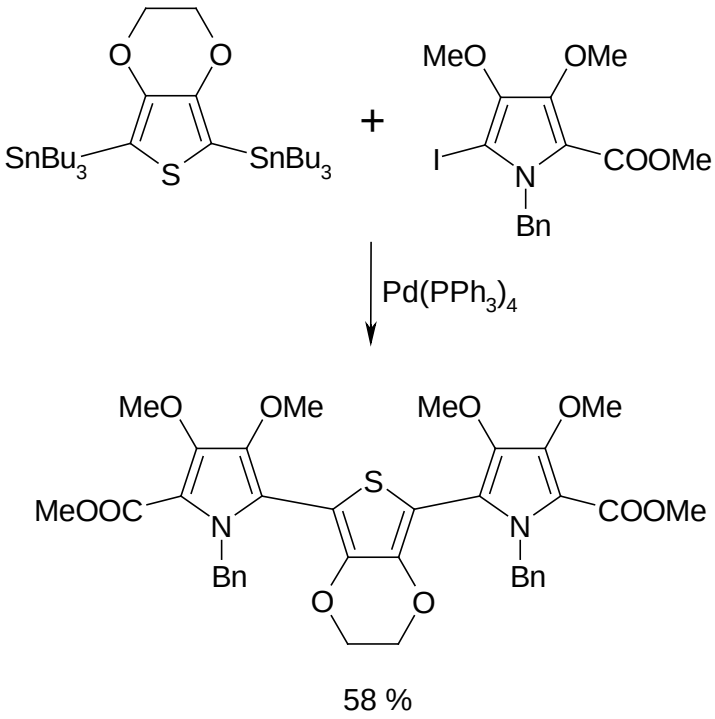
For the synthesis of unsymmetrical biaryls exists highly chemo- and regioselective method of catalytic coupling of organozinc compound with organic halide in the presence of Ni or Pd catalyst, provided by Negishi [52]. This method was well adapted for the syntheses of bi- and oligothiophenes by C. Rehm [49].



Scheme 18 Negishi coupling

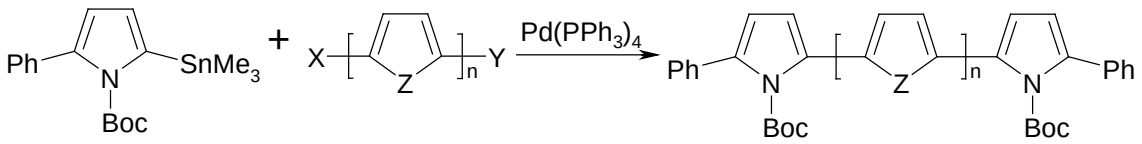
2.4.3 Stille – Coupling

The next method for the selective formation of bi- or oligo- pyrroles, thiophenes or mixed species is when metallorganic component is organotin (-$SnAlkyl_3$) derivative.
This method of coupling can be applied for thiophene-pyrrole oligomers (Scheme 19) and unsymmetrical bipyrroles synthesis [53].



Scheme 19 Mixed oligomer formation

Van Haare et al. [54] have synthesised phenyl end-capped *a*-oligoheteroaromatic compounds consisting of pyrrole and thiophene units via Stille coupling reactions. In this group target bi- and oligomers were obtained with quite good yields for the cross-coupling reactions (Scheme 20).



X=Ph, **Y**= Br, **Z**= N-Boc, n=1
X=**Y**= Cl, **Z**= N-Boc, n=1
X=**Y**= Br, **Z**= N-Boc, n=2

n=0 54 %
Z= N-Boc, n=1 43 %
Z= N-Boc, n=2 39 %

Scheme 20

2.4.4 The Ullmann – Coupling

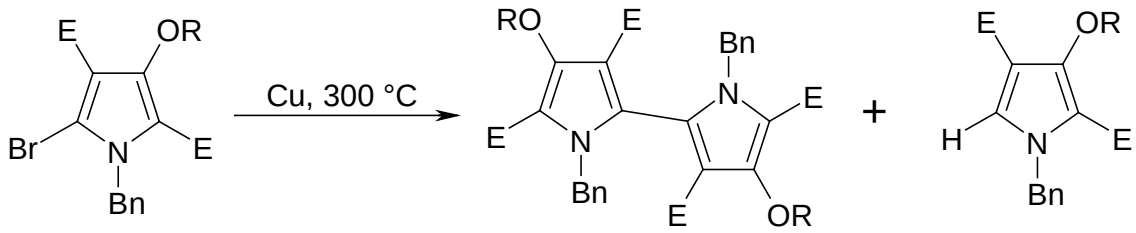
Despite of such big amount of coupling methods for thiophenes and aryls there is a small set of reactions, which could be applied to pyrroles. One of the most convenient and acceptable methods for the symmetrical bipyrroles formation is Ullmann coupling. The Ullmann synthesis of biaryl compounds involves the reactions where, two molecules of aryl halide are condensed in the presence of finely divided copper to form a new aryl-aryl bond with the elimination of copper halide. The reaction can be used for the preparation of symmetrical and unsymmetrical heterocyclic biaryls [55]. Obviously, the best leaving group is iodide, and the reaction is most often done on aryl iodides [56], but bromides, chlorides, and even thiocyanates have been used.

Though it is widely used method, the mechanism is still not known with certainty. It seems likely that it is basically a two-step process [44, 57, 58]:

$$ArI + Cu \longrightarrow ArCu \qquad \text{step 1}$$

$$ArCu + ArI \longrightarrow ArAr \qquad \text{step 2}$$

From the research of Kronberger [53] it was known that 2-iodopyrroles are not easy obtainable and not very stable. Possibly because deiodination and oligomerisation result in black powder formation. Although using 2-bromopyrroles only debromination was observed (section 2.5.2). So it was decided to use bromopyrrole derivatives for the formation of 4,4'-alkoxy-2,2'-bipyrroles (Scheme 21):



26 **27** **21**

R= CH_3, C_4H_9
E= $-COOC_2H_5$

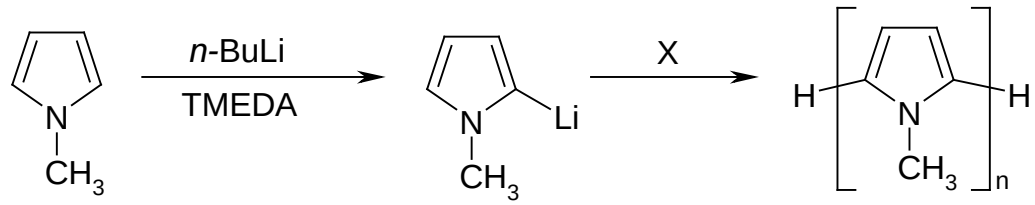
60 % less than 10 %

Scheme 21 "Outer" alkoxy-bipyrroles formation

It is well known, that alkoxypyrroles without any substituents in the ring, along with the essential direction, where the product are formed, also could be easily oxidised, oligomerised or polymerised especially at high temperature. So we have used in the Ullmann-coupling reaction compounds with no hydrogens in the pyrrole ring.
As a side reaction debromination of the pyrrole (**26**) has been observed, with formation of compound (**21**), with yields less than 10 % and formation of the black tar – obviously the mixture of oxidised, oligomerised and polymerised species of (**21**), (**26**) and (**27**). Anyway, our target alkoxybipyrroles (**26**) was obtained in quite good yields of 45 to 60 percent.

2.4.5 Kauffmann-Coupling

The next method of the oxidative coupling of the lithiated aromatic compounds with copper(II), cobalt(II) or nickel(II) halides was suggested by Kauffmann. This method has found a good application in the filed of five-membered heterocycles: furanes [59], thiophenes [60] and pyrroles [45], and means the formation of symmetrical dimers and oligomers. In this method the pyrrole ring was metallated [61, 62] in the *a*-position with butyllithium, followed by metal (II) chloride oxidation with a dimer formation (Scheme 22):



28

X= $CuCl_2$ (50 %), $CoCl_2$ (50 %), $NiCl_2$ (80 %) n= 2,3,4,5,6

Scheme 22 Oxidative dimerisation by Kauffmann

Application of the nickel (II) chloride gives yields of pyrrole dimer (n=2) up to 80 %, while as sub products can be isolated higher homologues of (**28**) with n=3,4,5,6. However, in case of 1-benzyl-3-methoxypyrrole we have not found any subproducts (section **2.5.3**, Scheme 33). Described in the literature [62] low yields of (**28** n=2) can be explained by

unfavourable treatment, since dimer (**28**) is unstable and must be purified by lower temperature and avoiding bright light. The formation of the sub products can be explained by an inessential bislithiation of the N-methylpyrrole.

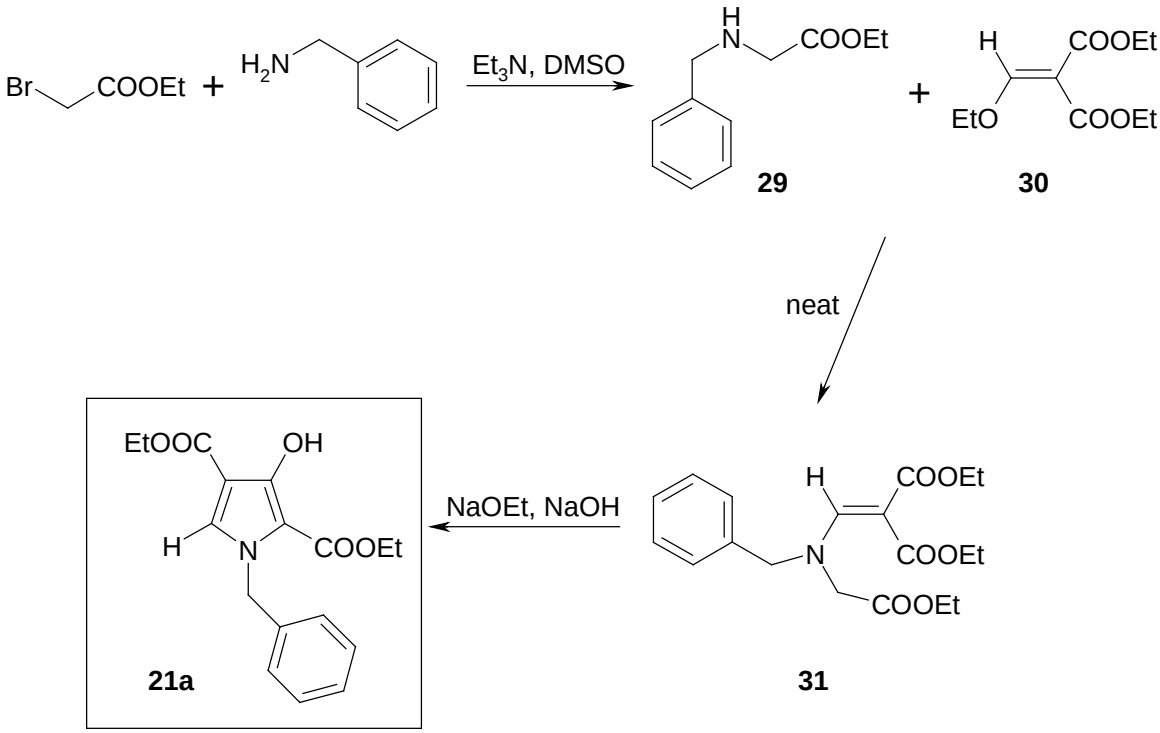
2.5 Synthesis of 3-alkoxypyrroles, 3,3'-dimethoxy-2,2'-bipyrrole and 4,4'-dialkoxy-2,2'-bipyrroles

We have chosen as our strategy – 3-alkoxypyrrole derivatives synthesis followed by coupling of the obtained species.

Necessary for the 3-alkoxypyrroles formation 3-hydroxypyrroles were synthesised by the Momose methods [39, 46].

2.5.1 Synthesis of 3-alkoxypyrroles

Required N-benzylglycinate (**29**) for the condensation with diethyl ethoxymethylenemalonate (Scheme 23) was prepared using procedure of nucleophilic substitution described by Lorthiois [63] on a 100 g scale with good yields - about 60 %. Condensation of glycinate (**29**) and (**30**) proceeds with quantitative yields forming (**31**),



Scheme 23

which following by the Dieckmann cyclisation gives diethyl 1-benzyl-3-hydroxypyrrole-2,4-dicarboxylate (**21a**).

Since it was shown [64, 65], that monohydroxypyrrole derivatives can tautomerizes it was interesting to find an answer on this question concerning our 3-hydroxypyrrole (**21a**). Investigation of crystals (**21a**) by means of X-Ray analysis was determined that this compound exists as a “hydroxy” form, the spectrum is shown on the Figure 2.3. The

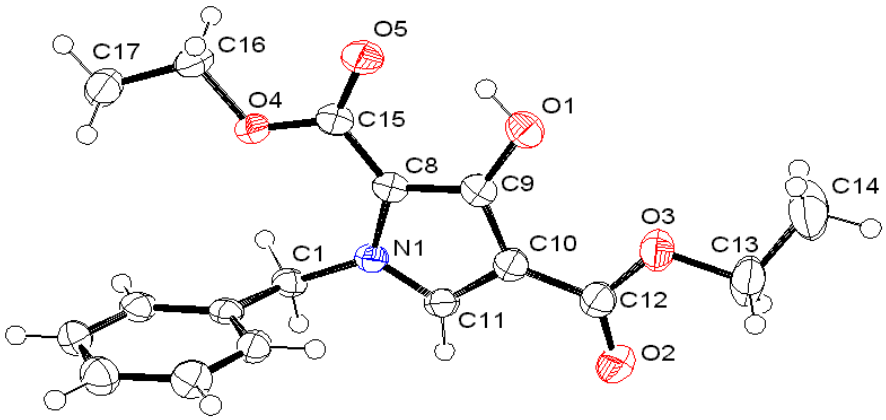
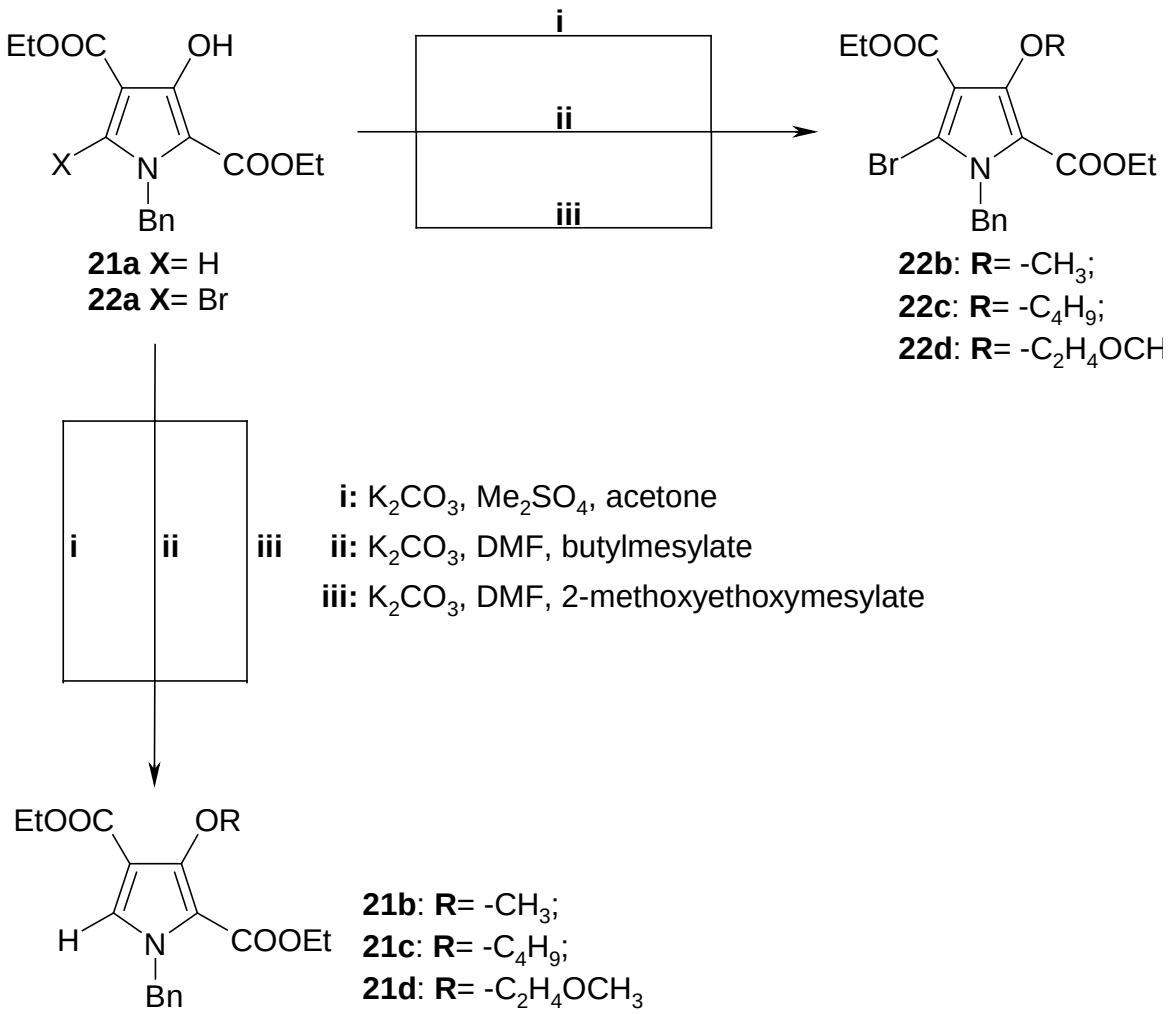


Figure 2.3 X-Ray structure of (**21a**)

description of the X-Ray spectrum is given in **Appendix A.**

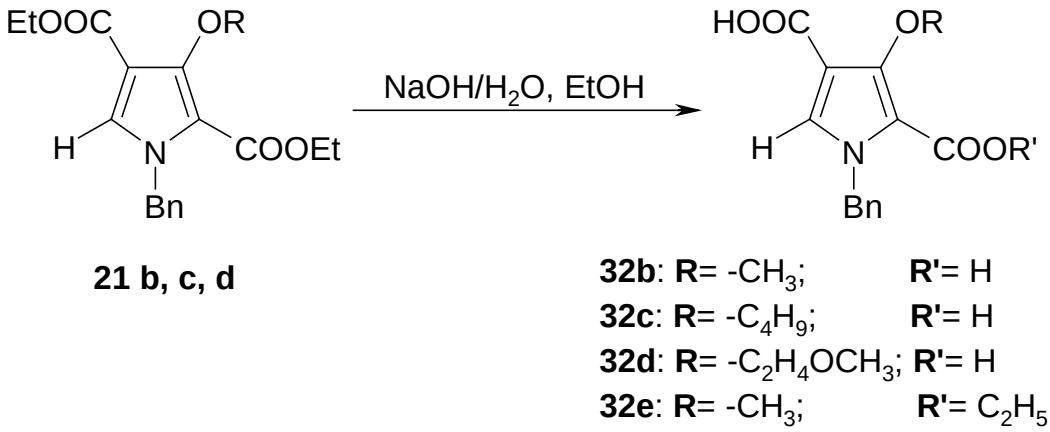
For the 3-alkoxypyrroles synthesis alkylation of a phenol-type hydroxy-group with dimethyl sulphate or alkyl mesylates was applied, where methylsulfonate and methylsulphate are good leaving groups. The yields are close to 90 %.



Scheme 24 Alkoxy derivatives formation

In that way obtained 4-alkoxy-2-bromo derivatives (**22b-d**) were used for the next syntheses of 4,4'-alkoxy-2,2'-bipyrroles (section **2.5.2**, Scheme 28).

1-Benzyl-3-alkoxypyrrole-2,4-dicarboxylates (**21b-d**) were modified through the short chain of reactions into 3-alkoxy derivatives (**34b-d**) shown below. On the first stage, ester groups were saponificated in usual alkaline conditions (Scheme 25). It was found that

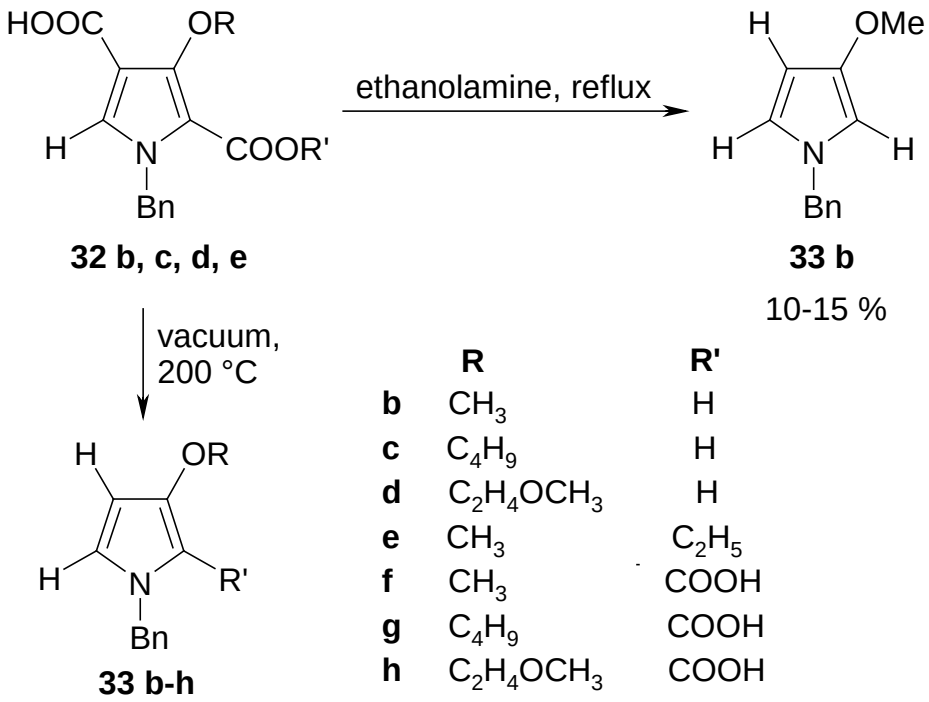


Scheme 25 Ester saponification

using the protection atmosphere (nitrogen, argon) on this step, lead to higher yields and purer products. Obviously, the hydrolysis of ethylester groups proceeds in two steps. On the first step the ester group in the *b*-position was cleaved, and on the second stage the *a*-carboxylate group reacted. So, it is possible to hydrolyse ester groups partially, obtaining *b*-carboxylic acid, as it was observed for (**32e**).

It is possible to decarboxylate pyrrolecarboxylic acids (**32b-d**) in solution or suspension by refluxing them in toluene, ethyleneglycol or ethanolamine [66]. By using this method decarboxylation occurs in the relatively mild conditions and quickly – at boiling point and normal pressure, so, good yields ought to be expected.

However, in the case of 3-methoxy derivatives the yields less than 15 % (Scheme 26) were



Scheme 26 Thermic decarboxylation

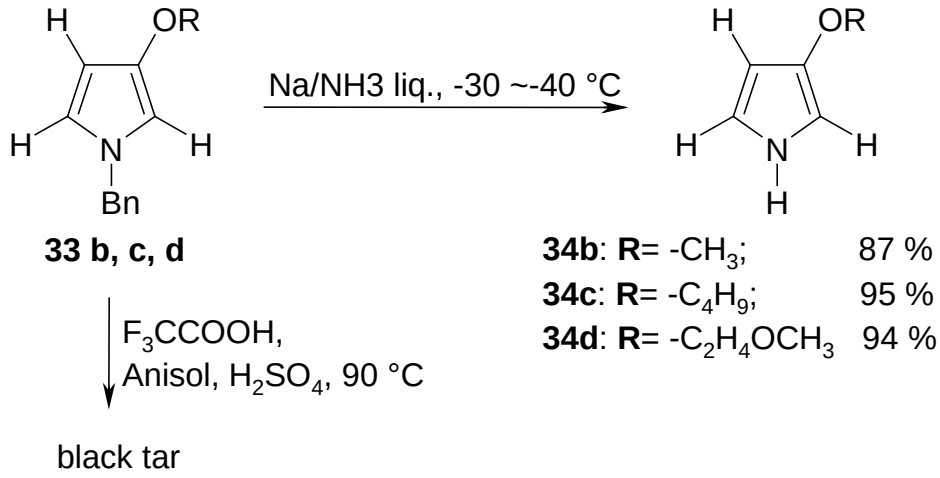
observed On some occasions the reaction mixture got dark very quickly, or the reaction did not proceed at low temperatures. Possible reason could be in lowering by the solvent of activation barrier for the polymerisation or oligomerisation process.

Interestingly, during decarboxylation without any solvent and under reduced pressure (100-150 mBar), a liberation of $CO_2$was observed already at 200 °C (Scheme 26) giving N-protected alkoxypyrroles (**33b-d**) with almost quantitative yields.

As it takes place in the saponification, pyrolisis proceeds in two steps. At first, carboxylic group in the *b*-position (**33f-h**) is removed, and secondly the carboxylic group in the *a*-position (**33b-d**) reacts.

The next step towards 3-alkoxy substituted pyrroles was the removal of the benzyl-protecting group. There were two alternative routs: stirring in trifluoroacetic acid at 90 °C or using the solution of sodium in liquid ammonia [36]. Both methods are suitable, and give yields up to 90 %, but the first one needs quite aggressive conditions – what were not acceptable for 3-alkoxypyrroles (**34b-d**), as they don't have substituents in *a*-positions and

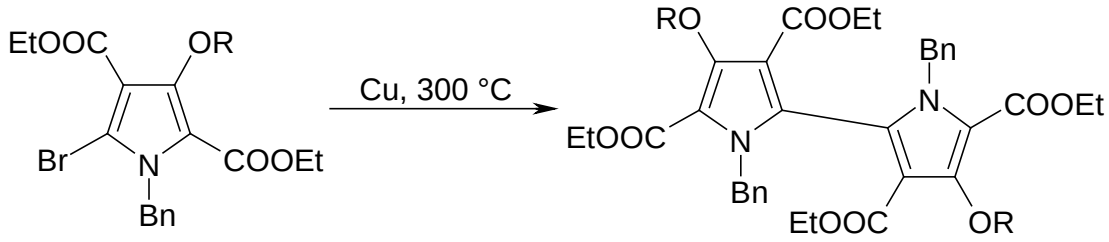
could be oxidised very easily. In contrast, the second method is very mild, proceeds at low temperature and gives better yields (Scheme 27).



Scheme 27 Pyrrole ring deprotection

2.5.2 4,4’-Dialkoxy-2,2’-bipyrroles

For the 4,4’-dialkoxy-2,2’-bipyrroles Ullmann-coupling method was applied (Section **2.4.2**). The coupling proceeds upon heating under argon (Scheme 28).



22b: **R**= -CH_3; **35b:** 60 %
22c: **R**= -C_4H_9; DMF traces **35c:** 62 %

Scheme 28 Ullmann coupling

The structure of (**35b**) was determined by X-ray spectroscopy (Figure 2.4). All data are given in **Appendix A**.

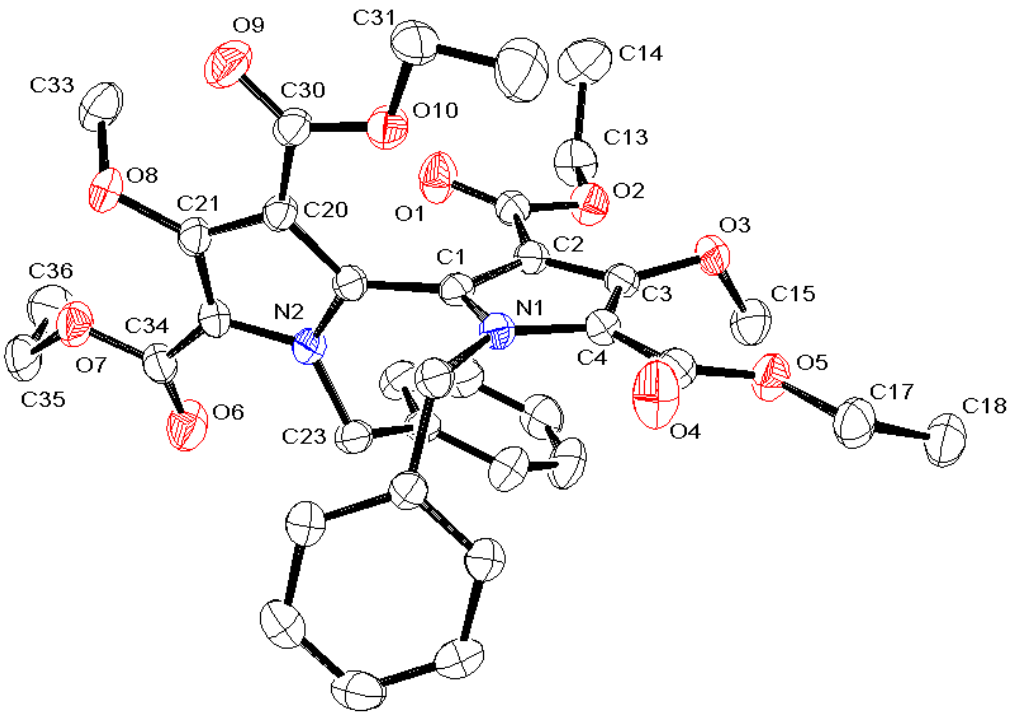
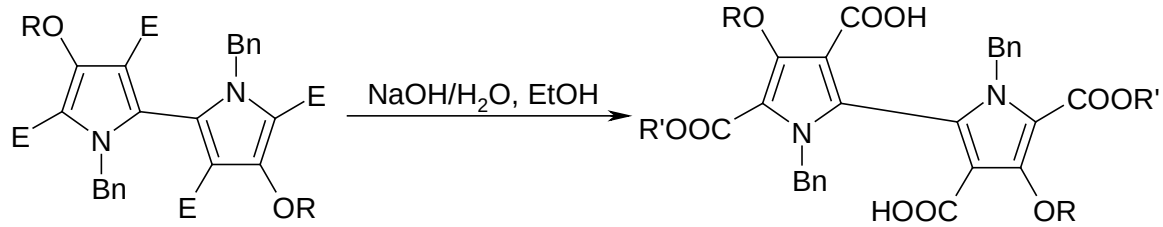


Figure 2.4 Structure of (**35b**): prisms

Synthesis of the target pyrroles follows the route, similar to one leading to 3-alkoxypyrroles: saponification, decarboxylation and Bn-group cleavage. Interestingly, that as it was in the case with pyrrole (**21b**) chemoselective saponification takes place. First of all the hydrolysis of 3,3'-ester groups proceeds (Scheme 29) giving 90 % yield of semiester (**36b,d**).



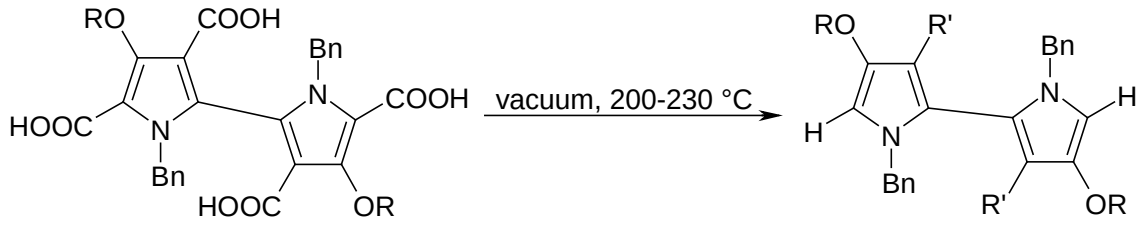
35 b,c

E= -$COOC_2H_5$

36b: **R**= -CH_3; **R'**= H
36c: **R**= -C_4H_9; **R'**= H
36d: **R**= -CH_3; **R'**= -C_2H_5

Scheme 29 Ester groups cleavage

After complete hydrolysis of compounds (**35b,c**) into corresponding tetracarboxylic acids (**36b,c**) the later were fully decarboxylated by heating (Scheme 30). Remarkably, that only dimethoxybipyrrole (**36b**) can be decarboxylated with heating to 230 ºC without any



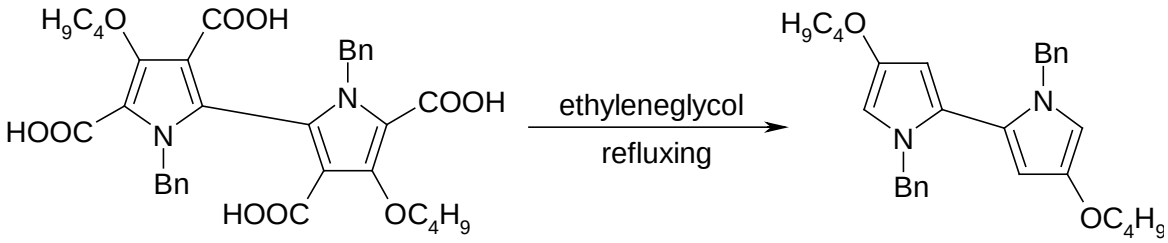
36 b,d

37b: **R**= -CH_3; **R'**= H
37d: **R**= -CH_3; **R'**= COOH

Scheme 30 Thermic decarboxylation

solvent. Contrary to (**32**) and (**36b**), dibutoxybipyrrole derivative (**36c**), due to its higher reactivity, gave only about 10 % yields in pyrolysis without solvent and the rest of material

was obtained as a black residue. But using the method of refluxing in ethyleneglycol (Scheme 31) pyrrole (**37c**) was obtained with 80-90 % yield

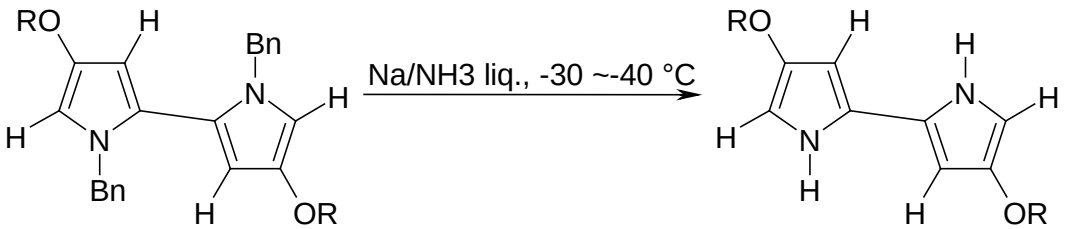


36c **37c**

Scheme 31 Ester groups cleavage

However, it is also possible to pyrolise carboxylic acid (**36b-d**) with carboxylic groups in 5- and 5'- positions only (Scheme 31) in a similar manner as it can be realized for monopyrroles (Scheme 26).

The step of pyrrole ring deprotection was carried out with sodium in liquid ammonia in a similar way to 3-alkoxypyrroles. 4,4'-Alkoxy-2,2-bipyrroles (**38b-d**) are very sensitive to oxygen or any oxidative media and transform rapidly into black substances.



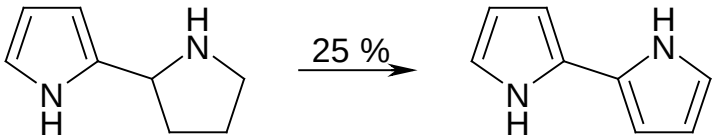
37b,c

38b: **R**= -CH_3;
38c: **R**= -C_4H_9

Scheme 32 Pyrrole ring deprotection

2.5.3 3,3'-Dimethoxy-2,2'-bipyrrole

Efficient methods for the 2,2'-bipyrrole synthesis can be found in the literature. Thus, for prodigiosin synthesis Rapoport has reported [62, 63] bipyrroles system synthesis by the catalytic dehydrogenation of 2,2'-pyrrolidinylpyrroles (Scheme 33), obtained by the



Scheme 33

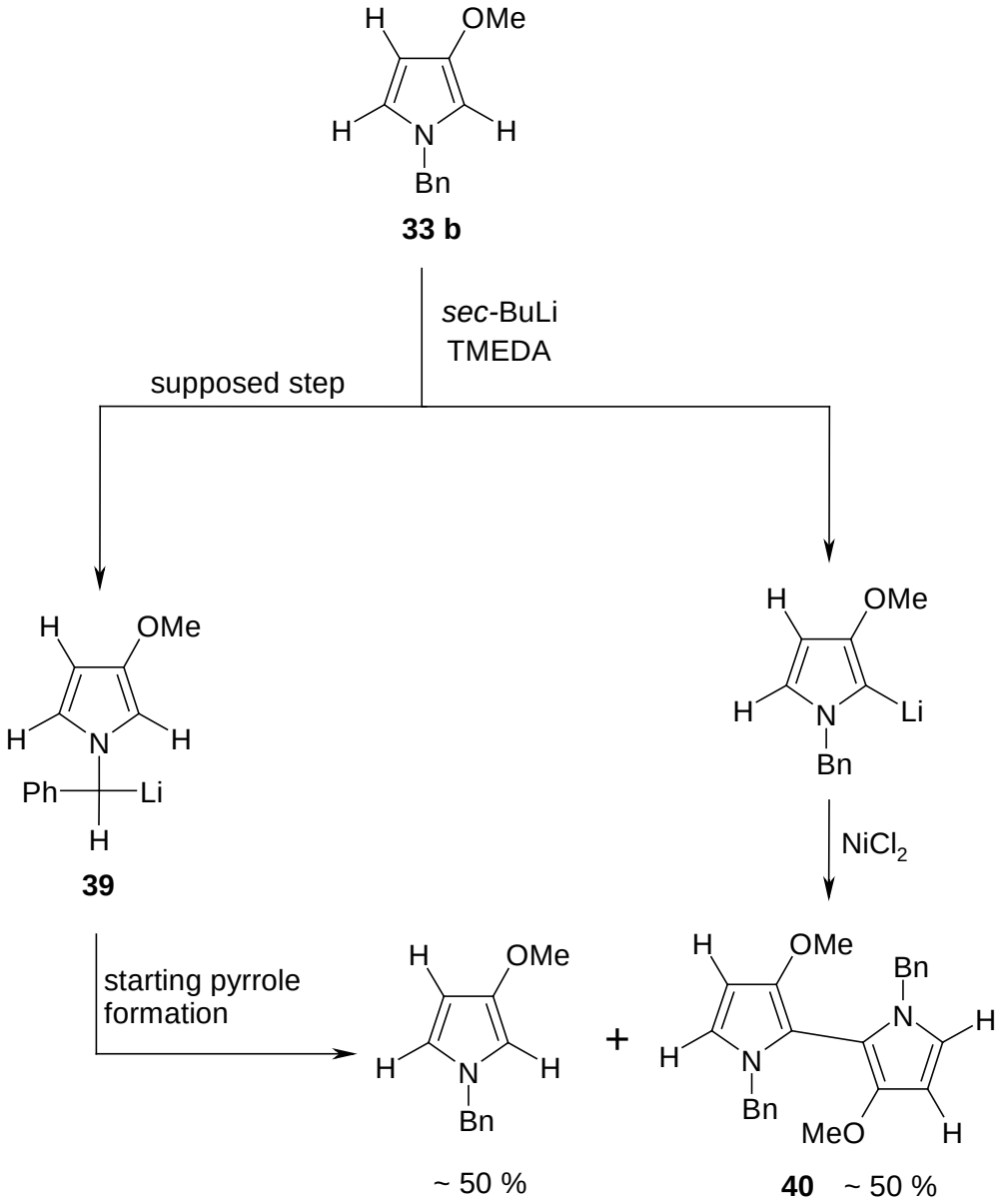
However, we were interested only in such routes, where at the first stage pyrrole derivative is lithiated at the *a*-position.

Therefore the synthesis of 3,3'-dimethoxy-2,2'-bipyrrole was carried out by a method of oxidative dimerisation of pyrrollithium derivatives developed by Kauffmann [45].

Interestingly, that the highest yield was obtained only with N,N,N',N'-tetramethylethylenediamine (TMEDA) as an additive, and no bislithiation occurred. In the case when the reaction was carried out without TMEDA, it almost quantitatively yielded the starting material. The explanation can be found in the suggestion that the molecule of TMEDA is coordinated with 2-lithiumpyrrole and forms stable complex, which can be crystallised [69] at lower temperature.

We have not found any sub-products in the reaction with 1-benzyl-3-methoxypyrrole (**33b**), as it was in the case of N-methylpyrrole [45], though only ca. 50 % of starting compound was dimerised and the rest (ca. 50 %) left unchanged and could be distilled and reused. Our suggestion was that the lithiation occurs not only in the *a*-position but also in the methylene group of benzyl substituent. We attempted to prove this suggestion by adding to the organolithium intermediate deuterated protic solvents (D_2O or CD_3OD), but no hydrogen-deuterium substitution was observed.

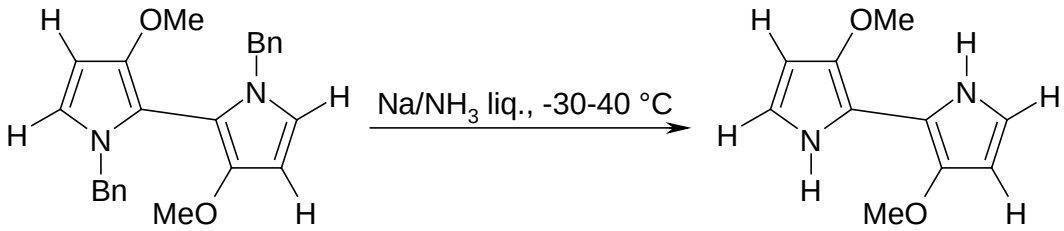
However, this sub-lithiated molecule does not react anyhow and further, by working out, starting pyrrole could be isolated (Scheme 34). Here, it should be noted, that application of



Scheme 34 "Inner" methoxybipyrrole formation

sec-butyllithium instead of *n*-butyllithium raises yields of bipyrrole (**40**) from 25-30 % to 50-55 %.

Deprotection of the bipyrrole (**40**) can be realized through the analogous operation in liquid ammonia-sodium solution as it was described before. With 1-benzyl-3,3'-dimethoxy-2,2'-bipyrrole this reaction yields 70 % (Scheme 35) of pyrrole (**41**) that is extremely sensitive to air and turns to black substance within minutes. Being on the earlier oxidation stages, e.g. in solution, violet colour can be observed. However, in dark place in freezer and under argon it can be stored for months.



40 **41** 70 %

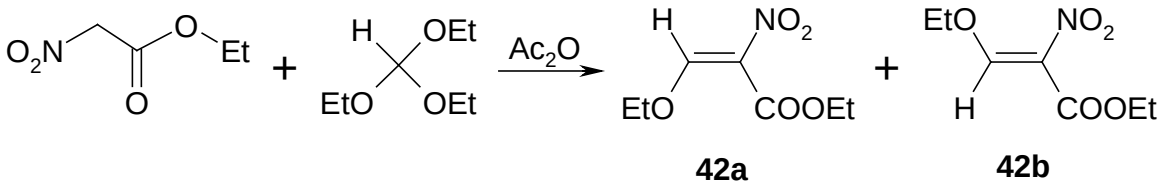
Scheme 35 Pyrrole ring deprotection

2.6 Syntheses of 3-methoxy-4-aminopyrroles

The group of Bonaccina [70] suggested an interesting synthetic rout towards 1-alkyl-3-methoxy-4-nitropyrroles, which can be further reduced to 4-aminopyrroles. In the synthesis 3,4-dinitropyrroles have been used as starting compounds which were synthesised as described in the paper [71, 72]. We also used this method in the current work for 3,4-diaminopyrroles synthesis (section **2.7**).

Method of pyrrole ring construction developed by Japanese chemists has found a good application in the field of 3-alkoxypyrroles syntheses. Our attempt to modify this method for 4-nitro-3-methoxypyrroles preparation was found the reflection in the literature suggested by Phillion [73].

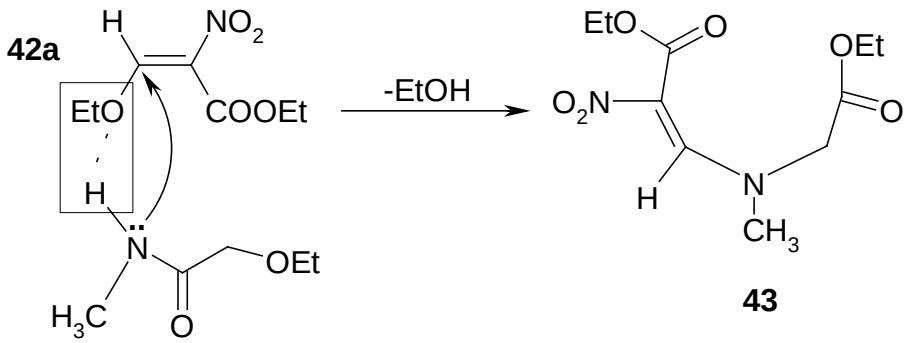
As the first step it was necessary to obtain ethyl 2-nitro-3-ethoxyacrylate. An aldol-type



42a **42b**

Scheme 36

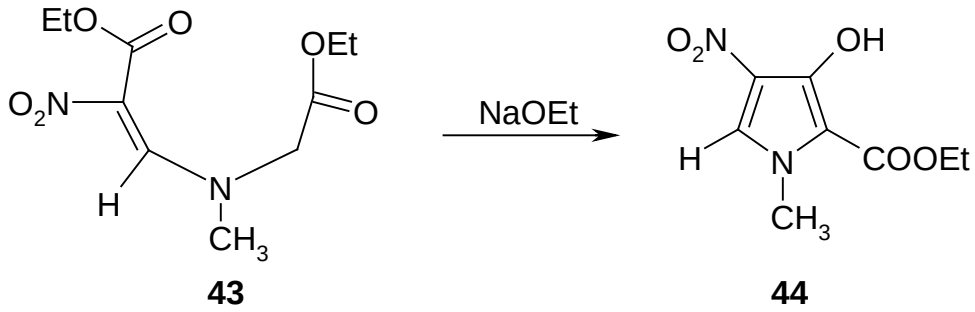
condensation of ethyl nitroacetate with ethylorthoformate gave product (**42**). Obviously, it consists of *Z*- and *E*-isomers. The next condensation of (**42a**) with ethyl sarcosinate gives the precursor (**43**) for the following Dieckmann cyclisation (Schemes 37, 38).



43

Scheme 37

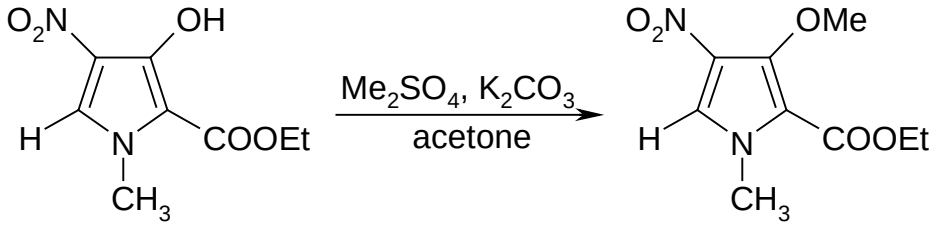
Similar to Momose' pyrroles [39, 46] this compound could be converted into ethyl 1-methyl-4-nitro-3-hydroxypyrrole-2-carboxylate using sodium ethanolate (Scheme 38).



43 **44**

Scheme 38 Nitro-pyrrole ring formation

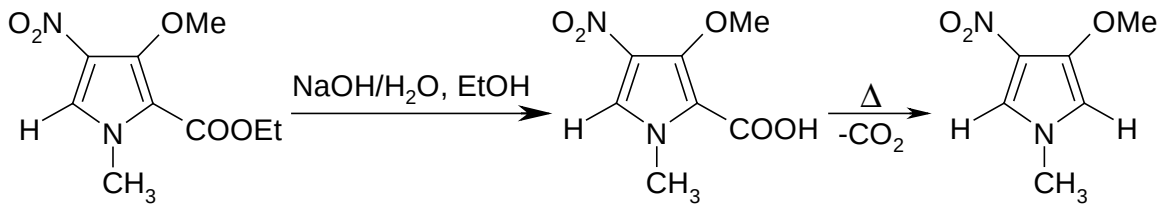
Again, the nucleophilic substitution with dimethylsulfate and potassium pyrrolate (Scheme 39). was applied for the hydroxy group methylation



44 **45**

Scheme 39 Methylation of hydroxy group

For 2-ethoxycarbonyl-group removal we used the same steps as in the monopyrrole case: ester cleavage and pyrolisys of pyrrolecarboxylic acid (**46**). As it turned out 1-methyl-4-nitro-3-methoxypyrrole (**47**), contrary to 1-benzyl-3-alkoxypyrroles (**35 b-d**), was enough

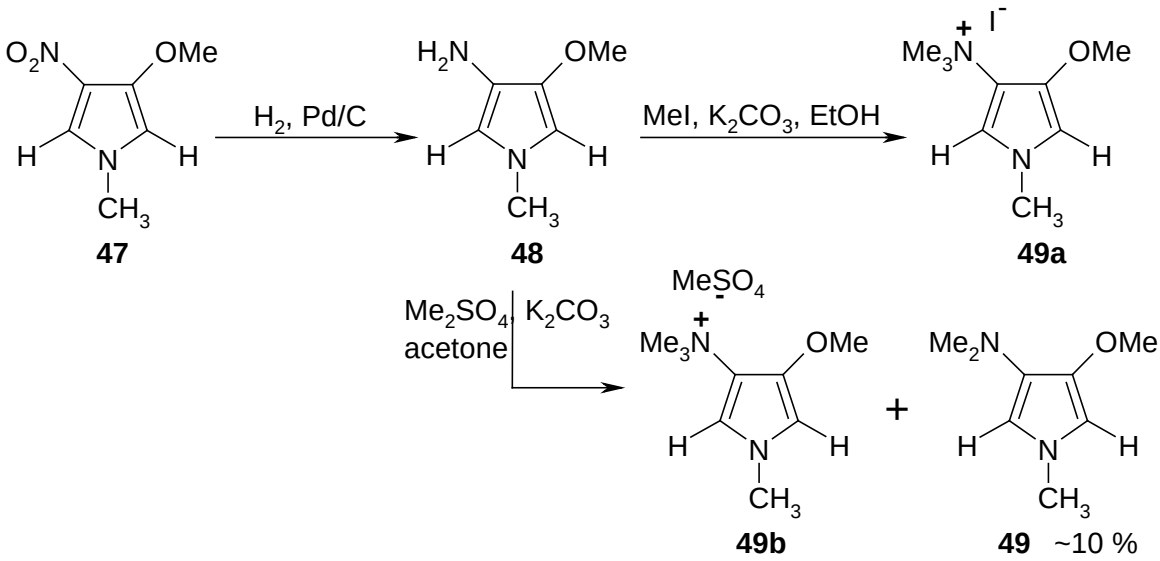


45 **46** **47**

Scheme 40 Ethoxycarbonyl group removal

stable, and there were no changes found in the reaction mixture left staying on the air at room temperature after 3-4 months.

Conversion of a nitro-group to dimethylamino group could be realized through the intermediate aminopyrrole (**48**), obtained by a catalytic reduction with hydrogen, followed by dimethylation of aminogroup by methyliodide. However, it is difficult to carry this reaction out selectively. Thus, application of methyliodide [74] as a methylation agent

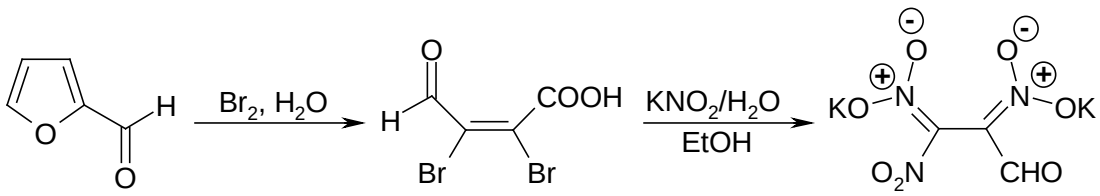


Scheme 41 Attempt of aminopyrrole dimethylation

leads to ammonium salt (**49a**) formation. By an attempt to methylate the amino group with dimethyl sulphate [75] was obtained the mixture of tri- (**49b**) and dimethylated (**49**) aminopyrroles. But isolation of obtained compound (**49**) was not successful, because of its high reactivity. Conducting the chromatography under argon did not prevent that compound from being oxidised into dark residue.

2.7 Synthesis of 3,4-diaminopyrroles

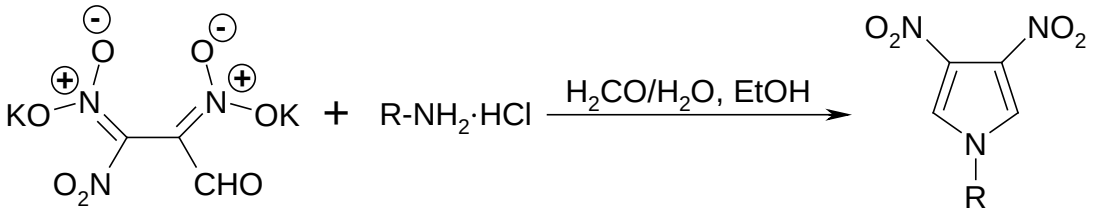
This new method of a pyrrole ring formation was discovered by Russian chemists in the middle of last century [71, 72]. In this method, starting from furfural (**50**), through the step of a dipotassium salt (**52**) formation (Scheme 42) and reaction with amines containing



50 **51** **52**

Scheme 42

various functional groups, it is possible to obtain N-substituted-3,4-dinitropyrroles (**53**) in short sequences (Scheme 43). Formaldehyde can be replaced in the reaction by its



52 **53 a, b**

R= -CH_3, -CH_2Ph

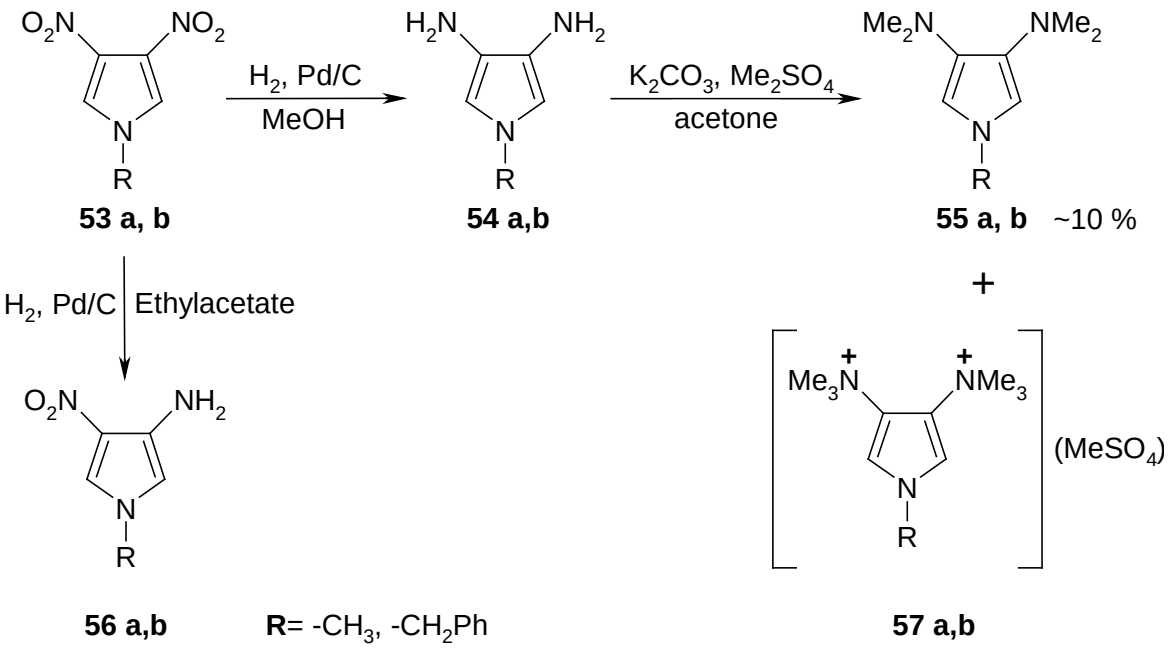
Scheme 43 Nitropyrroles formation

homologs – acetaldehyde and propionaldehyde. In this case the products are 1,2-dimethyl- and 1,2-diethyl- 3,4-dinitropyrroles.

To make N-substituted-3,4-aminopyrroles (**54**), the reaction of a catalytic hydrogenation of nitrogroup in the solution on a palladium catalyst was applied. The result of reduction depends on the nature of the solvent used. If the reaction was carried out in the methanol solution the dinitro- compounds can be converted into 3,4-diaminopyrroles (**55**).

But in the case of ethylacetate, it was found out, that it is possible to reduce only one nitrogroup selectively yielding 3-amino-4-nitropyrroles (**56**) with yields about 90 %.
For the *a*-hydrogen atoms of (**56a**) location determination NMR spectroscopy was applied. On the Figure 2.5 are displayed HMBC and HMQC correlations. Based upon such spectra correlation between hydrogen and carbon atoms can be determined. On the HMBC (up) one can determine $^{1,2,3}J$ coupling constants, while on the HMQC(down) only ^{1}J coupling constants to be seen.

Next, we attempted to carry out selective methylation of aminogroups in compounds (**54**) with dimethyl sulphate. Similarly as it was in the case of 3-amino-4-methoxypyrrole, this method leads mainly to quaternary ammonium salt – bis-trimethylammonium salt (**57**).
In the obtained mixture of aminopyrrole derivatives was discovered about 10 % of target



Scheme 44 3,4-Dinitro- to 3,4-diaminopyrroles conversion

didimethylamino pyrroles (**55**). It is sufficient amount, but due to high instability and oxidation ability of these compounds we failed to isolate them with appreciable for the further investigation yields.

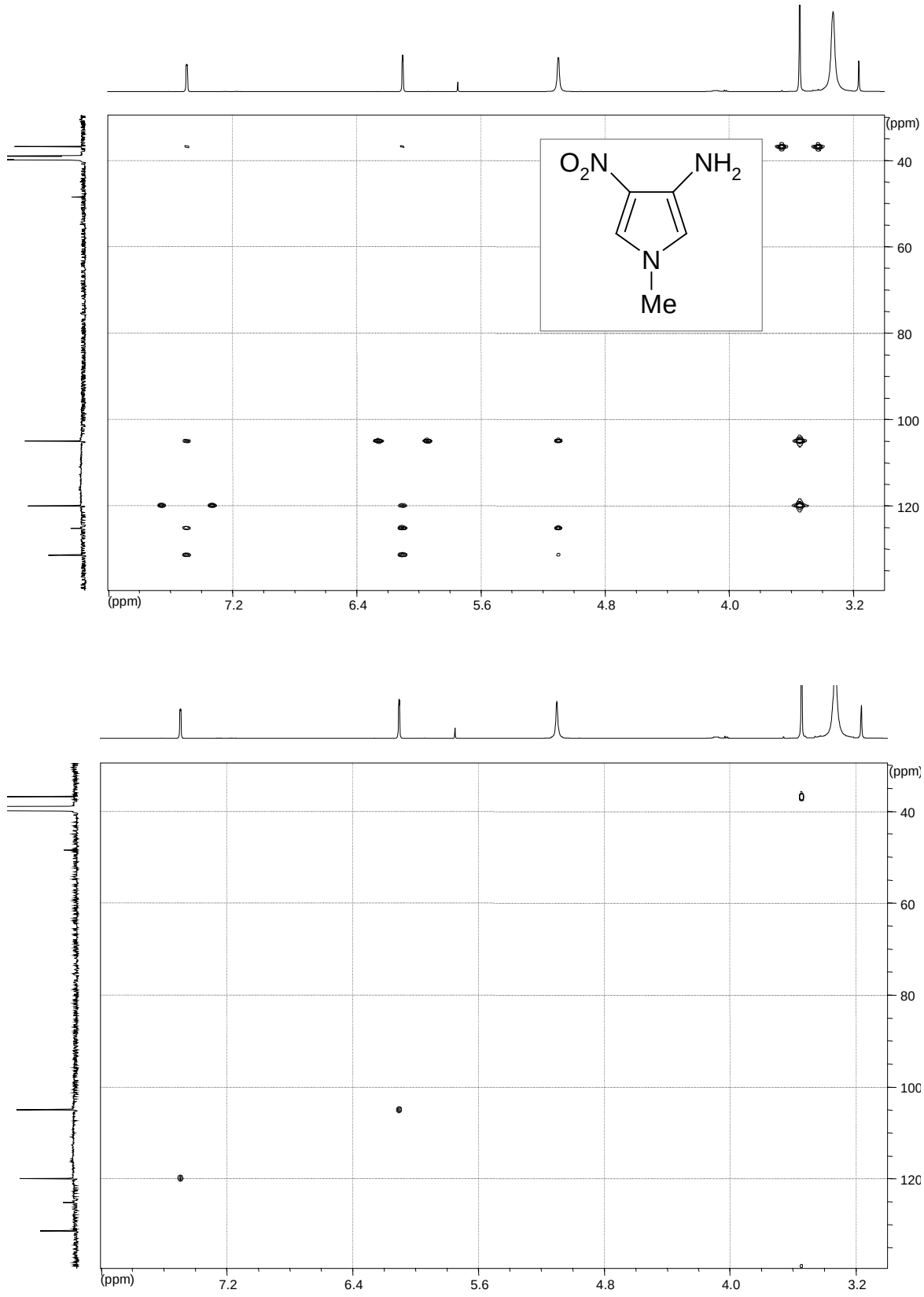


Figure 2.5 HMBC (up) and HMQC (down) correlations for (**56a**)

Chapter 3

3.1 A short introduction into the Cyclic Voltammetry technique

Cyclic voltammetry is a dynamic electrochemical method for measuring redox events. It can be used to study the electrochemical behaviour of species diffusing to an electrode surface, interfacial phenomena at an electrode surface, and bulk properties of materials in or on electrodes [76]. Anyway, this method became one of the most important and informative one for the electroactive compounds characterisation, and it was defined by Heinze as the “spectroscopy” for the electrochemist already twenty years ago [77].
Cyclic voltammetry (CV) has been in the forefront of the study of electron transfer and its consequences. With the cyclic voltammetry one can simultaneously activate molecules by electron transfer and probe subsequent chemical reactions. The cyclic voltammetry curve thus provides information about electron transfer kinetics and thermodynamics as well as the consequences of electron transfer.

Using the electrochemical technique it is also possible to realize polymerisation with formation of thin films. Although, there is possible to polymerise species else chemically and by “chemical vapour deposition” (CVD), such advantages as a simple control of the polymerisation process, polymer film thickness and film structure makes these electrochemical methods very attractive. The fact that electrochemically obtained polymers are doped with electrolyte anions makes this way still more preferable. By the electrochemical polymerisation is possible to control polymerisation using different techniques: potentiodynamically (CV), potentiostatically or galvanostatically, what leads to the products with different structure and properties. During the first method of polymerisation occurs potential sweeping from any starting value through some positive potential and backward. Indeed these potential values, type of the electrolyte, scanning speed and other parameters playing very important role on the morphology and properties of the growing polymer film [78, 79].

On the contrary polymerisation under potentiostatical control realizes by holding some fixed potential measuring the quantity of the flowing current.

Using galvanostatical technique, fixed value of current is applied, what can be useful in some cases.

However, usually by potential scanning were obtained polymers with better conductivity and a smoother surface than using other electropolymerisation methods.

3.2 Polymerisation mechanism

Several possibilities have been considered for the carbon-carbon bond formation, i.e. coupling between two cation radicals (CR-CR) [80] or two neutral radicals (R-R) [81, 82] and also the reaction between the cation radical and the starting monomer (CR-M). The R-R mechanism differs from the other two mechanisms in the order of the different reaction steps, i.e., deprotonation is prior to the carbon-carbon bond formation. It was found [83] that in the case of substituted pyrroles, the first step involves formation of the cation radical of pyrrole, followed by coupling between two cation radicals and then deprotonation, whereas coupling between the radical cation and starting molecule is unimportant.

Thus, during the anodic oxidation of 4,4'-alkoxy-2,2'-bipyrrole derivatives one can observe some important steps. In the beginning, the formation of the radical-cation occurs, with an electron removal from the *a*-position. Mesomeric structures stabilizing this

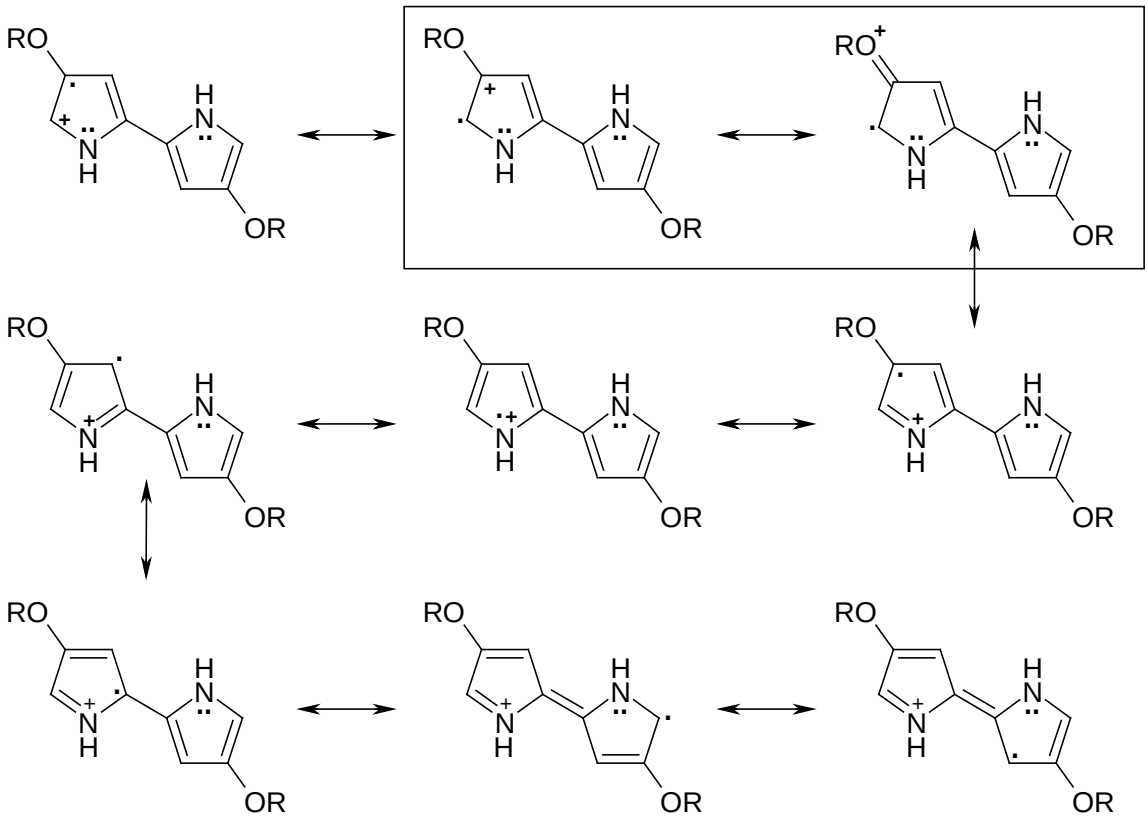


Figure 3.1 Mesomerie in the radical cation of 4,4'-alkoxy-2,2'-bipyrroles

radical-cation can be seen on the Figure 3.1. The structures, where unpaired electron located in the *a*-position and positive charge in 4-position are relative stable. Early was shown, that structures with positive charge located in the 4-position and unpaired electron in 2-position are the most stable [84]. Thus, such species can recombine with formation of positively charged dimer. Subsequent cleavage of two protons leads to the thermodynamically stable neutral product. This step is a slow process [85] and in some cases can be catalysed, for example by means of small amount of water. For some compounds the addition of 1 % of water can even induce the process of polymerisation or fully suppress it.

For the 4,4'-alkoxy-2,2'-bipyrroles the mechanism of electro-polymerisation includes the formation of the neutral oligomer or polymer chain. By further anodic oxidation it can be obtained polymers with the larger degree of polymerisation or neutral form of the polymer can be doped with an electrolyte anion. As it was shown with analogous

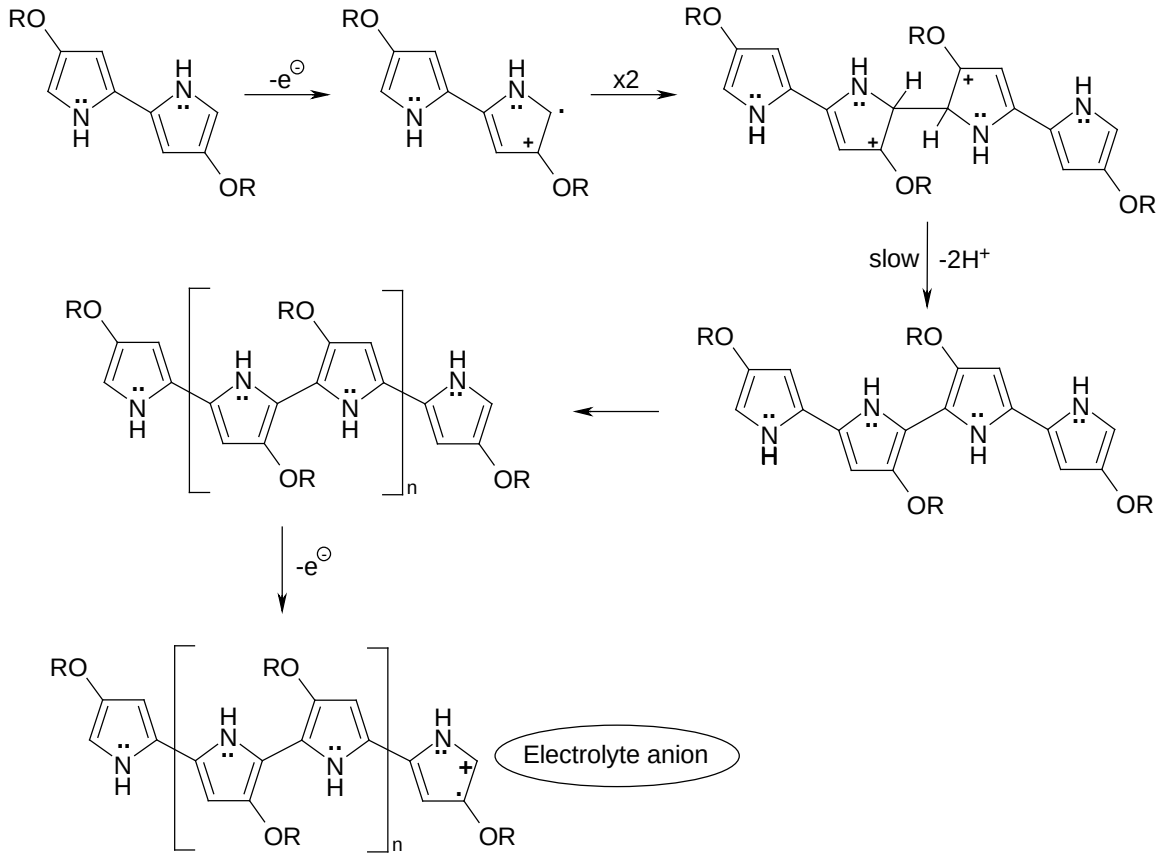


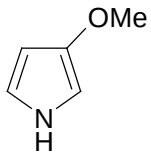
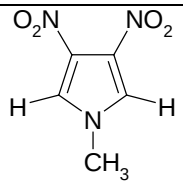
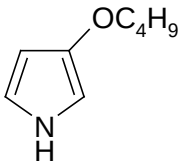
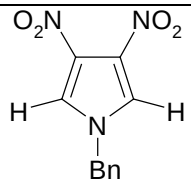
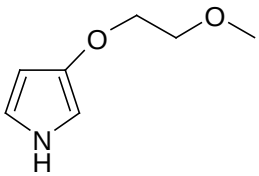
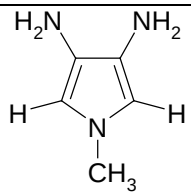
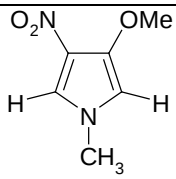
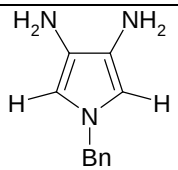
Figure 3.2 Radical-radical mechanism for the polymerisation of alkoxybipyrrole

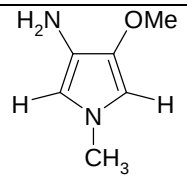
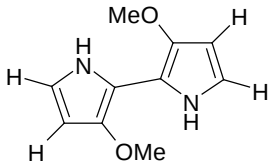
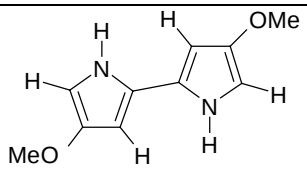
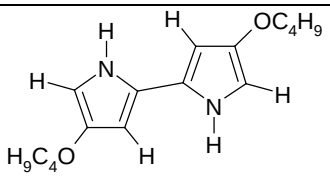
4,4’-dimethoxy-2,2-bithiophene [86] and unsubstituted pyrrole [85, 87, 88] two radical-cations generated by anodic oxidation undergo fast coupling and lead to the products with high degree of polymerisation, because the reactive 2-positions of the dimer and the respective oligomers are not inaccessible and therefore available for the further polymerisation process.

3.3 Electrochemical characterisation of 3- and 3,4-alkoxy substituted pyrroles

Pyrrole derivatives are able to form conducting polymer films under electrochemical treatment. Compounds with higher electron density should give materials with better conductivity. Thus, we aimed to compare electrochemical behaviour of mono- and bipyrroles with alkoxy-, and amino- substituents in the ring.

Compounds, which have been electrochemically tested and their characteristic oxidation and reduction peak potentials represented in the following chart:

Monomer	Polymerpeaks position [V]	Monomer	Polymerpeaks position [V]
 (**34b**)	E_{Ox}= 0.841 V Polymerisation is not observed	 (**53a**)	Polymerisation is not observed
 (**34c**)	E_{Ox}= -0.266 V E_{Ox}= 0.953 V E_{Red}= 0.029 V E_{Red}= -0.362 V	 (**53b**)	Polymerisation is not observed
 (**34d**)	E_{Ox}= -0.186 V E_{Ox}= 0.098 V E_{Red}= 0.070 V E_{Red}= -0.173 V	 (**54a**)	E_{Ox}= -0.401 V E_{Red}= -1.503 V Polymerisation is not observed
 (**47**)	E_{Ox}= 1.443 V E_{Red}= -1.611 V E_{Ox} = -1.383 V Polymerisation is not observed	 (**54b**)	E_{Ox}= -1.374 V E_{Ox}= -0.531 V E_{Red}= -1.608 V Polymerisation is not observed

 (**48**)	E_{Ox}= -0.100 V E_{Red}= -1.527 V	 (**41**)	E_{Ox}= 0.096 V Polymerisation is not observed
 (**38b**)	E_{Ox}= 0.350 V E_{Red}= -0.560 V	 (**38c**)	E_{Ox}= -0.244 V E_{Red}= -0.379 V

From this chart can be seen, almost in the way it was expected, that only some alkoxymonopyrroles and 4,4'-dialkoxy-2,2'-bipyrroles are active in electropolymerisation. An interesting fact was observed, that despite the higher activity of 3,3'-dimethoxy-2,2'-bipyrrole (**41**) in chemical oxidation comparatively to the 4,4'-dimethoxy isomer, the first one is completely indifferent in electropolymerisation, although the pyrrole (**38b**) polymerises rapidly with formation of conducting polymer.

The effect of water on the electropolymerization of pyrrole in acetonitrile has long been known [89-91]. As has been shown in numerous publications, the addition of 1 wt % water to a solution of pyrrole in acetonitrile causes increasing the polymerisation rate, improves film adherence and morphology, and enhances the conductivity of the resulting polymer. Why? It is quite difficult to answer on this question unambiguously. Initially, it was suggested that water might reduce solubility of oligomers and leads to a faster deposition of species on the electrode. Later was proposed that water, owing to its higher dielectric constant, reduces the Coulombic repulsion between the radical cations [92] and thus, facilitates the radical-radical coupling. Obviously, this opinion cannot offer a convincing explanation for other monomer-solvent systems.

Thus, it is also accepted that in the cases pyrrole-acetonitrile the presence of water [93] accelerates the slow step of proton elimination (Figure 3.2). But in cases for 3-alkoxypyrroles and 3,4-dialkoxypyrroles [94] it was shown that in the presence of small amount of water the polymer formation was hindered. The possible explanation can be

seen on the Figure 3.3, where molecule of H_2O can enter into the nucleophilic substitution reaction with dealkoxylation of the corresponding pyrrole.

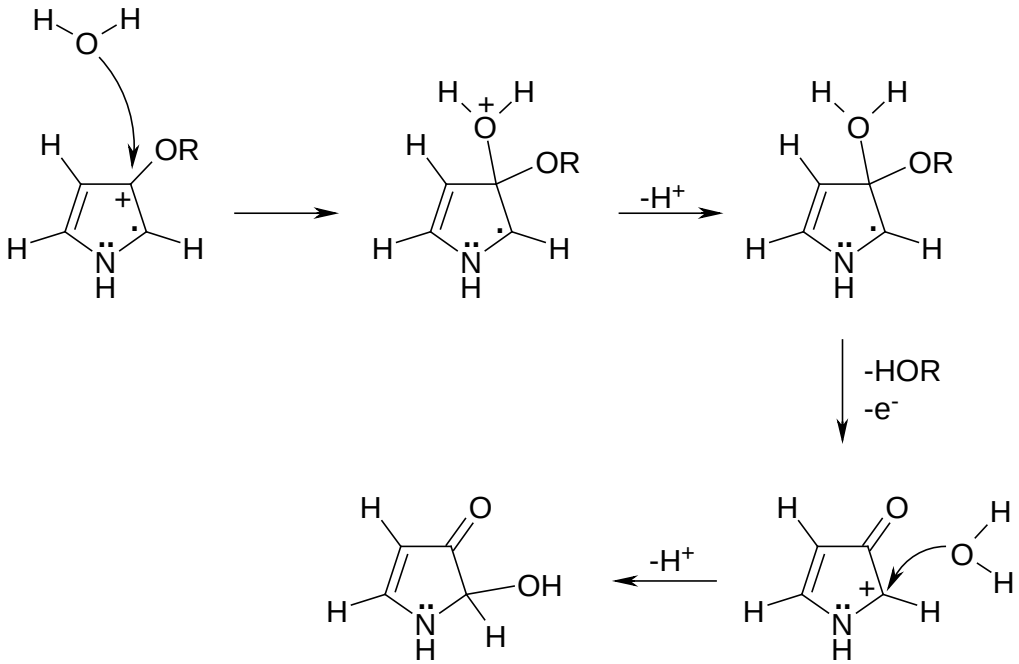


Figure 3.3 Nucleophile attack of radical-cation with water

By potentiodynamic polymerisation oxidation potential of polymer located distinctly far from the oxidation potential of monomer and shifted to the negative field. The value of the oxidation peak of the polymer is usually between –0.2 V and 0.0 V. Thus the difference between monomer- and polymer oxidation peak is approximately 1 V. .

In the most cases by CV curves can be polymerisation proved. Though not every compound forms good film, which is suitable for the further investigation. But the formation of oligomers or unstable polymer can be sometimes observed by means of CV.

For the formation of a polymer with appropriate properties the position of substituents in the pyrrole ring plays a large role. Thus, N-substituted pyrroles can be hardly polymerised and conductivity of obtained polymer films is usually small. For instance, by R. Schwarz [95] in case of N-methyl-3,4-dimethoxypyrrole was discovered that no polymer film on the electrode was generated. Furthermore, only brown colouring of the cell-solution was observed, and from such solutions some oligomer mixture can be isolated. On the other side, N-unsubstituted pyrrole derivatives polymerizing under potential cycling. Hence, by S. Graf [94] from 3,4-dimethoxypyrrole a polypyrrole film with good conductivity and mechanical properties was obtained.

But, there is, of course not only the problem in N-substituents. Usually pyrrole monomers polymerising giving conducting polymers in the *a*-position, so it can be expected that pyrroles bearing in *b*-positions electron donating substituents, like alkoxy- or aminogroups, will be more active in anodic polymerisation process with formation of conducting film.

Thus, by multisweep experiment of 3-methoxypyrrole (**34b**) there was no polymerisation observed [96]. The oxidation peak of the first wave can be observed at +0.85 V (**Appendix B**), as an chemically irreversible process. With every cycle a slow current decrease to be seen, what can be interpreted as the formation of oligomers. The latter ones are not depositing on the electrode surface and slight colour changes can be registered, proving that generated oligomers goes into the solution from the electrode surface.

This behaviour of (**34b**) was expected in analogy with 3-methoxythiophene. It was observed [97] that the latter compound forms radical cation not followed by polymerisation.

3-Butoxypyrrole (**33c**) has a similar to 3-methoxypyrrole structure and it was quite

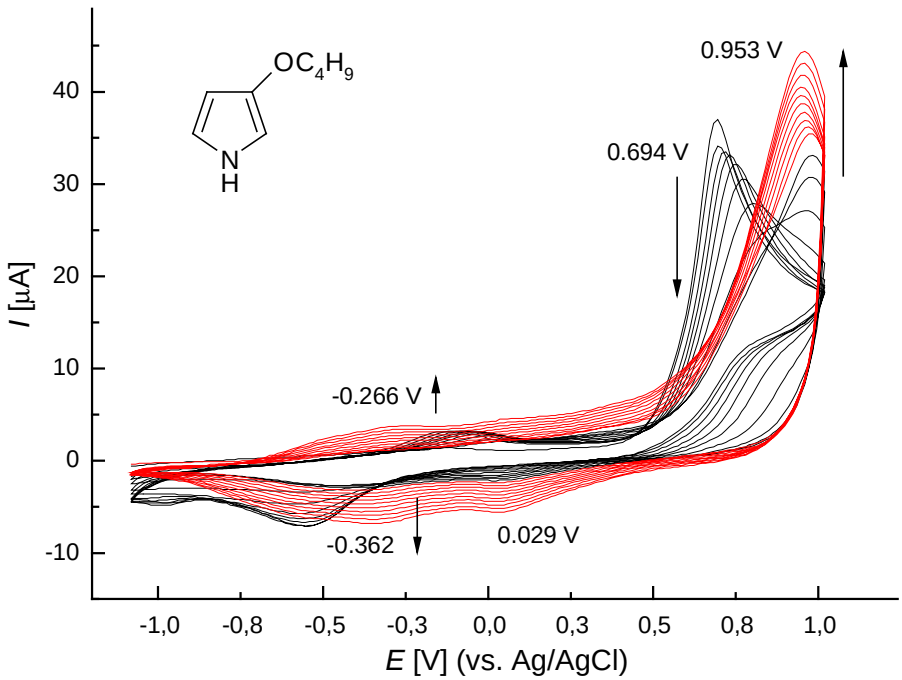


Figure 3.4 Multisweep polymerization of **33c** (c = $1.8 \cdot 10^{-3}$ M) in Bu_4NBF_4 (0.1 M) acetonitrile

unexpected, that some polymerisation-like process proceeds by an anodic oxidation. The first wave has an oxidation maximum at +0.69 V. Starting the experiment, by potential

sweeping can be observed the current falling during ca. 7-8 cycles, followed by formation of a new growing oxidation peak at +0.95 V. With this starts also a slow growth of a polymer oxidation and reduction peaks at –0.27 V and 0.03 V and –0.36 V correspondingly. However, the polymerisation stops after 30 cycles what can be explained by partially conjugated polymer formation with a low conductivity.

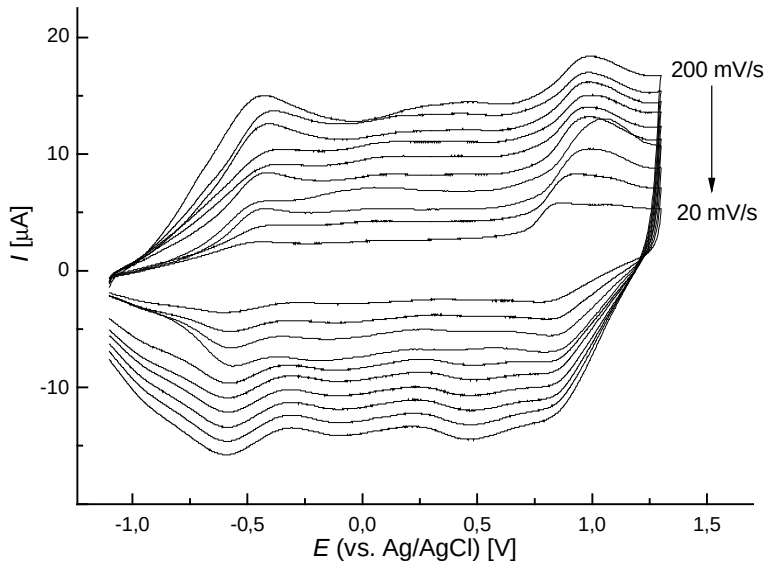


Figure 3.5 Cyclovoltammetric characterisation of butoxypolypyrrole with scan rates from 20 to 200 mV/s

The corresponding polymer film of (**33c**) was characterised by means of cyclic voltammetry in the monomer free solution. Employing this method, the working electrode is previously covered by a polymer film in the cell with monomer. Thus, obtained butoxypolypyrrole, as a dark film on the Pt-electrode, is not stable and during multisweep potential scanning destruction can be seen. However, at the potential cycling with scan rates increase (from 20 to 200 mV/s) the growth of the correspondent peak current was observed. Thus, there were registered two peaks by an anodic oxidation at –0.43 V and 0.99 V, followed by reverse scan with three reduction peaks at potentials of 0.46 V, -0.10 V and –0.58 V (Figure 3.5).

The electropolymerisation experiments that were carried out with

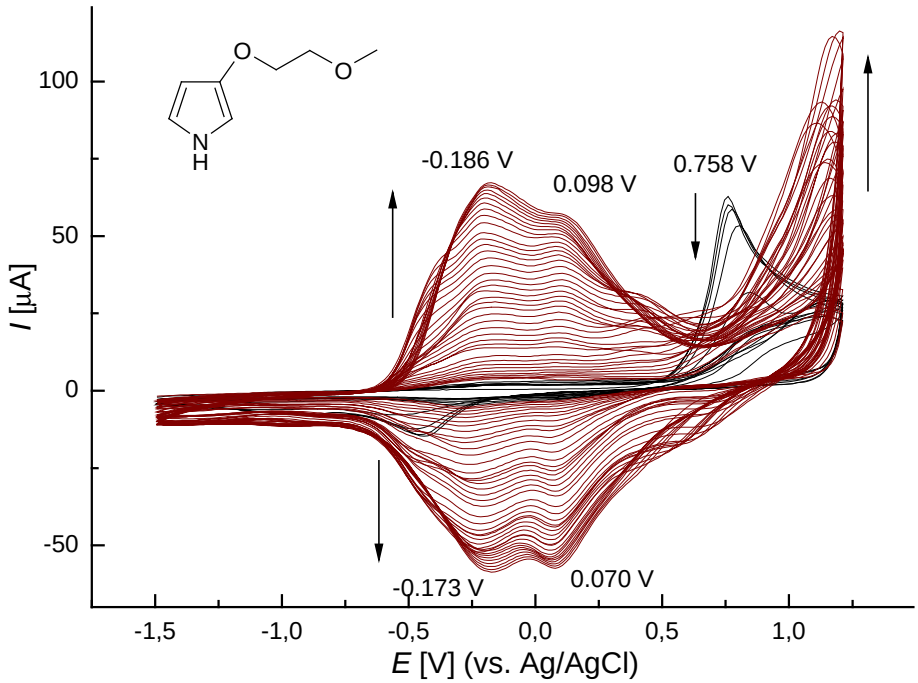


Figure 3.6 Multisweep polymerisation of **33d** (c = $1.77 \cdot 10^{-3}$ M) in Bu_4NBF_4 (0.1 M) acetonitrile

3-(2-methoxyethoxy)pyrrole (**33d**) show partly the similar to (**33c**) behaviour. Again, in the beginning of the process was observed the falling of the first oxidation waves peaks (5 cycles), followed by shifting of this maximum from 0.76 V to more positive potentials (ca. 300 mV) and with relative intensive growth of the polymer peaks (Figure 3.6). The polymer film formation was observed with quite stable speed and can be characterised by two oxidation maximums at potentials of –0.19 V and 0.098 V, and two reduction peaks by the reverse scanning at 0.07 V and –0.17 V.

In contrast to (**33c**), characterisation of the corresponding polymer film of (**33d**) shows the pretty stable polymer (Figure 3.7) generation. The film was also characterised by means of solid-state voltammetry in a monomer free cell. Scan rates were varied from 100 to 200 mV/s, showing proportional growth of the corresponding peaks. The positions of the

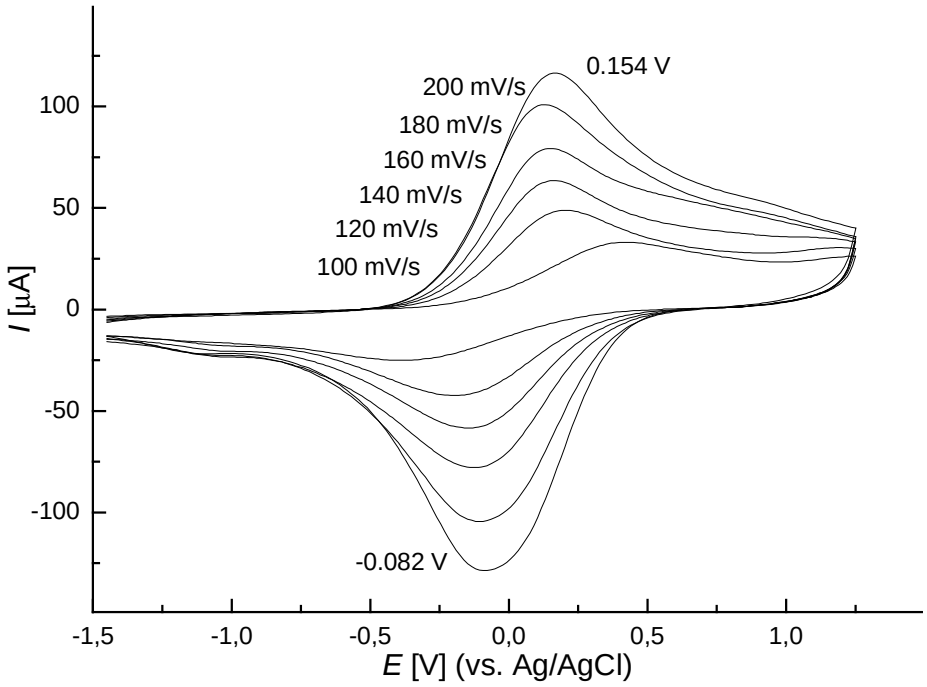


Figure 3.7 Cyclovoltammetric characterisation of poly(**33d**) with 100-200 mV/s scan rates range

maximal oxidation and reduction peaks are at +0.15 V and –0.08 V respectively. However, similar to the case of butoxypolypyrrole by multisweep experiment (50-10 cycles) a constant decreasing of the peaks value was observed.

The addition of 1 % water suppressed the polymer formation in both cases, and almost no current falling can be later observed. Possible explanation of this fact can be in the nucleophilic attack of water (Figure 3.3) molecule at the positive positions of radical-cation, what leads to the neutralising of the active charged species.

The electropolymerisation experiments of 3,3'-dimethoxy-2,2'-bipyrrole which were carried out in acetonitrile in the presence of 1 % of water give results in good agreement with the expectations. Figure 3.8 shows a voltammetric multisweep experiment with (**41**).

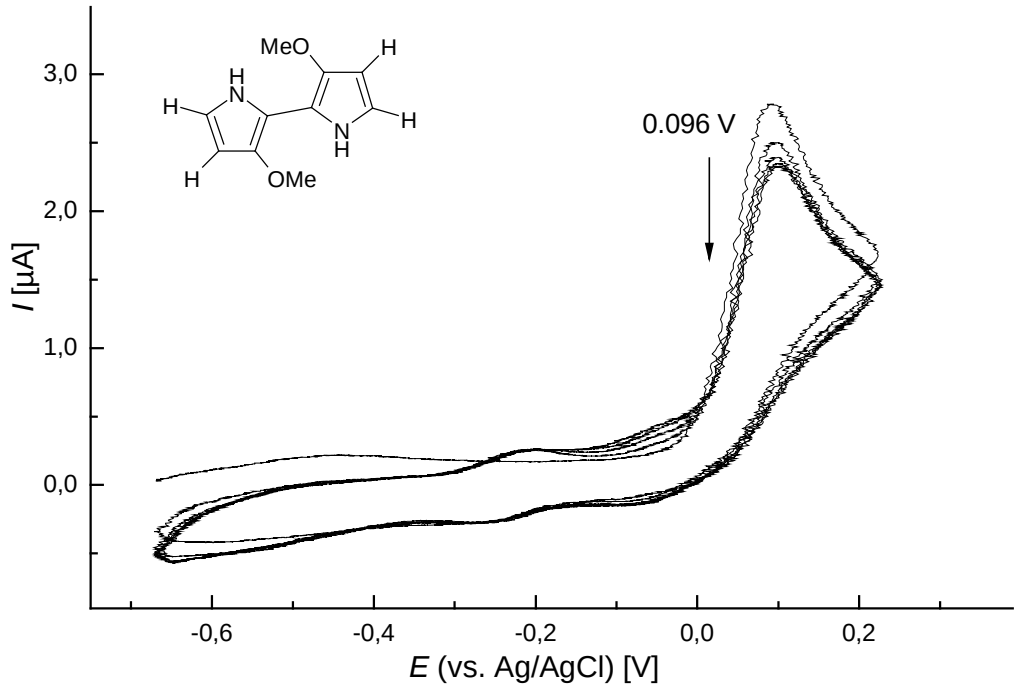


Figure 3.8 Multisweep voltammogram of **41** ($c = 8 \cdot 10^{-4}$ M) in Bu_4NPF_6 (0.1 M) acetonitrile + 1 % water

Surprisingly this bipyrrole did not polymerise electrochemically, though it was extremely sensitive to air, forming black flakes of polymer within minutes. Anyway, the oxidation of bipyrrole (**41**) occurs at the remarkable low potential of +0.09 V vs. Ag/AgCl, as an chemically irreversible process. During the anodic oxidation slightly crimson colouring can be observed, the same as by oxidation on the air (on early stages). However, no generation or deposition of an extended oligomer or polymer is observed during potentiodynamic cycling, only two small redox waves at potentials of –0.25 V and –0.0 V can be seen. Evidently (**41**), in accordance with the findings obtained for 3,3'-dimethoxybithiophene [86, 97, 98], forms a *s*-dimer that slowly eliminates proton to give a neutral tetramer (Figure 3.2). This can be charged up to a dication without further follow-up reactions. The coupling tendency of the tetrameric species is low due to the fact that the spin density at the outer *a*-positions is low.

By contrast, pyrrole (**38b**) polymerises rapidly in acetonitrile in the presence of 1 wt % of water. It is oxidised at a peak potential of E_P=+0.35 V, and shows a following broad cathodic wave in the reverse scan. In a multisweep experiment, fast growth of a conducting polymer film can be observed (Figure 3.9). The current peak in the cyclic voltammogram

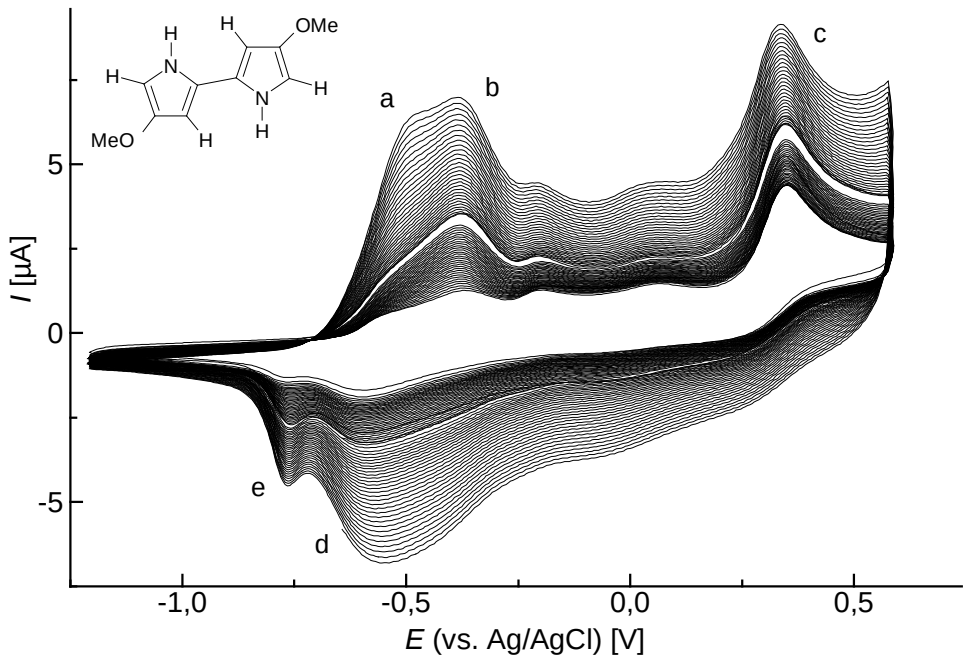


Figure 3.9 Multisweep polymerisation of **38b** (c = $10 \cdot 10^{-3}$ M) in Bu_4NPF_6 (0.1 M) acetonitrile + 1 % water

increases with each scan. The reason for the fast polymerisation process lies in the reactivity of the radical cation **(38b)**$^{\bullet+}$, which has its highest spin density at the nonblocked *a*-positions; this favors a fast coupling reaction and evidently also facilitates proton elimination. The further products of the coupling steps again have substituents in the "outer" *b*-positions of the growing oligomer; these make it very reactive.

The corresponding polymer film of (**38b**) was characterized by using solid state voltammery (Figure 3.10). The oxidation potential of the main wave lies at –0.51 V and a second wave appears at –0.35 V. In contrast to Figure 3.8, the first oxidation wave is higher than the second one. As in the case of the unsubstituted polypyrrole [85, 87, 88], we

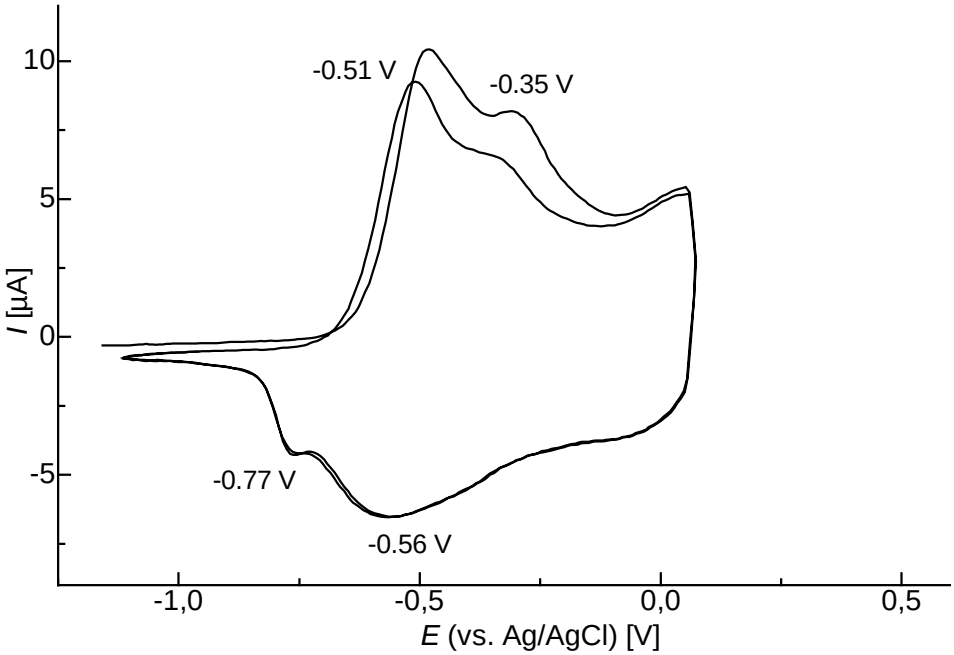


Figure 3.10 Voltammogram of a PPy generated during the potentiocycling of (**38b**) in the abscence of monomer

assume that two structurally different polypyrrole systems are generated during the electrochemical oxidation. As usual in conducting polymers, the reduction peak is more negative (peak at -0.56 V). A second reduction wave, at –0.77 V vs. Ag/AgCl, however, is the lowest potential ever observed for the discharging of a p-doped polymer. The strong hysteresis between oxidation and reduction gives evidence that during charging a thermodynamically stabilized network with *s*-interchain bonds is formed. The *s*-bond generation produces a significant stabilization of the charged polymer and, in addition, results in localized charges.

On the contrary to the (**38b**) 4,4'-dibutoxy-2,2'-bipyrrole (**38c**) undergoes anodic potentiocycling polymerisation very easy without presence of water. The fast growth of the polymer peaks starts from the first cycle and the current peak in the cyclic voltammogram increases with every scan (Figure 3.11). The last oxidation peaks lie at potentials of –0.24 V and 0.31 V, followed by a broad cathodic peak at –0.38 V in the reverse scan. Similar to

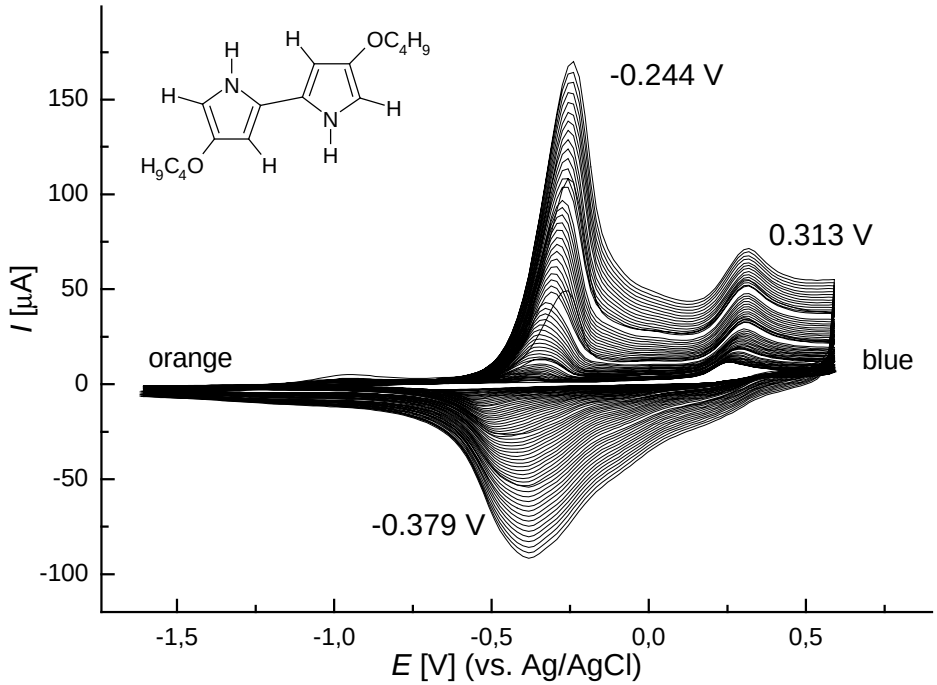


Figure 3.11 Potentiodynamic polymerization of **38c** (c = $3 \cdot 10^{-3}$ M) in Bu_4NBF_4 (0.1 M) acetonitrile

(**38b**), the explanation of the fast polymerisation process is connected with the reactivity of the radical cation **38c**$^{\bullet+}$, which has its higher spin density at the free *a*- positions, what favors a fast coupling reaction with proton elimination. The following coupled species again have substituents in the *b*-positions what facilitate the next polymerisation steps.

On the electrode the process of polymerisation, by scanning the potential, was observed the electrochromic effect of the polymer film. Being oxidised the film changes the colour from orange-red to dark-blue and by reverse scan back from dark-blue to orange-red. In a short time this effect should be characterised by means of spectroelectrochemical method.

Formed corresponding polymer film of (**38c**) was also characterised using cyclic voltammetry (Figure 3.12). On the obtained voltammogram can be discerned two different states of the polymer film. The first oxidation wave lies at -0.596 V and the second potential appears at 0.154 V. Similar to (**38b**), the reduction peak is more negative and lies at –0.188 V. The second reduction wave is located at the potential of –0.88 V.

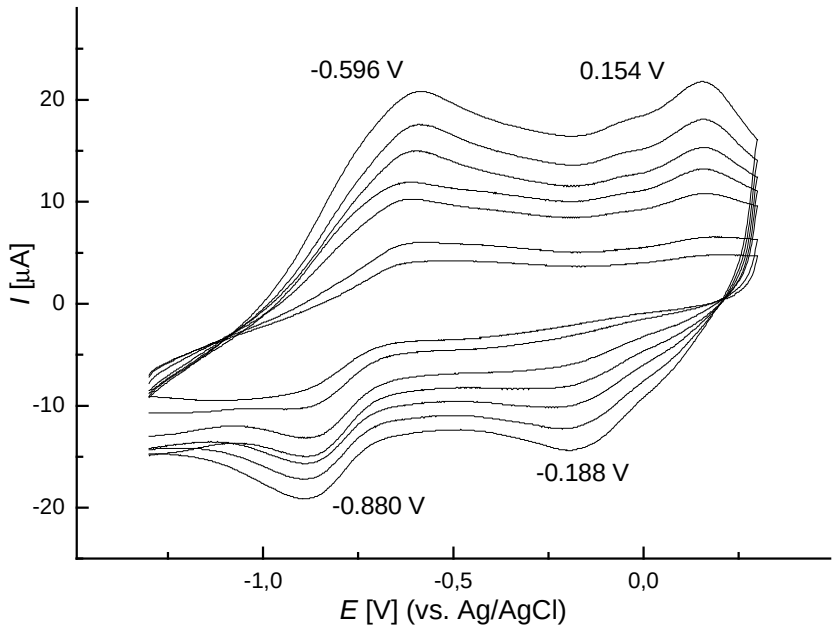


Figure 3.12 Poly(**38c**) film characterization

Aminopyrroles derivatives, as it was displayed in the Chart 3.1 are not disposed towards electro polymerisation, though being exposed to air colourless compounds become brown quickly.

Thus, by the cyclovoltammetric experiment of 1-methyl-3-amino-4-methoxypyrrole (**48**) only one oxidation peak at –0.100 V vs Fc^+/Fc is to be observed.

1-Methyl-3,4-diaminopyrrole (**54a**) and 1-benzyl-3,4-diaminopyrrole (**53b**) also are not active in the electropolymerisation process. However, oxidation peaks lie at low oxidation potential of –0.401 V for (**54a**) and –1.374 V (**54b**) vs Fc^+/Fc.

All cyclovoltammetric curves with peak potentials of the non-polymerisable pyrrole derivatives can be found in the **Appendix B**.

3.4 Polymer films conductivity

Firstly obtained in the end of 1970 polymer films where mainly good insulators [99]. Later, it was discovered that polymers, e.g. polyacetylene, which has an intrinsic conductivity much lower than 10^{-5} (Scm^{-1}), could be made highly conducting, ~10^{3} (Scm^{-1}), by exposing it to oxidizing or reducing agents [100]. This process is often referred to as "doping" by analogy with the doping of inorganic semiconductors.

Often solids are classified by their conductivity at room temperature: for typical conductors the conductivity is greater than several thousands Scm^{-1}, for typical insulators it is less than some 10^{-12} Scm^{-1}, and for semiconductors it is in between. Polymer conductivity values extend over the whole region from insulating, such as diamond, to highly conducting, such as copper.

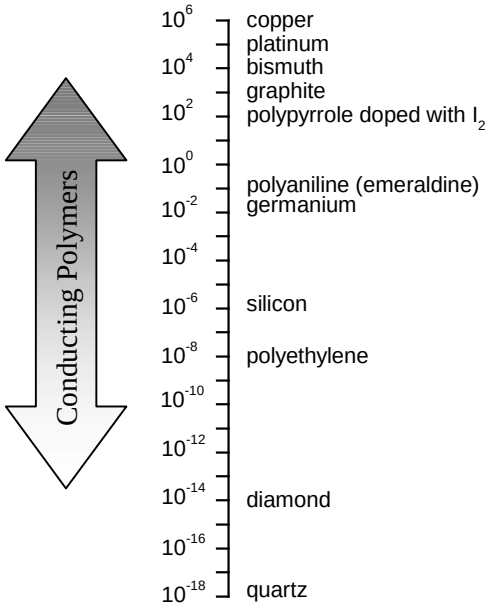


Figure 3.13 Comparison of the room-temperature conductivity values of conducting polymers with conductivities of other materials

3.4.1 Conductivity measurements

For the measurement of conductivity there were two general methods available – film resistance measurements and the four-points (four-lead) principle. In many cases it is easy, but in many others there will be difficulties. The major problems are:

- The conductivity, which can vary over a large range, either from sample to sample or within a sample if the temperature, the pressure, or the doping level is changed.
- Effects of contacts on the measurement.
- Homogeneity and anisotropy of the sample.

For a sample with very low resistance, an ohmmeter would just determine the resistance of the leads. With samples of very low conductivity, only leakage currents through the cable insulation would be measured, rather than currents through the sample. To avoid lead and contact resistance for low resistance samples, the "four-lead method" is favourable, where current leads are separated from voltage leads. Four thin gold wires are glued to the sample with silver paste. The current I is applied through the outer leads and the voltage V is picked up at inner leads (voltage probes).

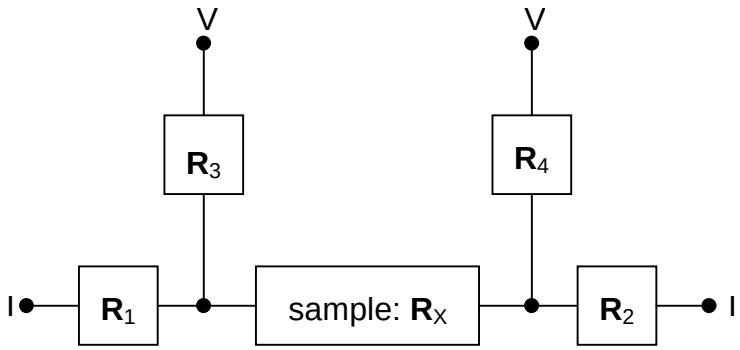


Figure 3.14 Equivalent circuit for four-lead method

The current I passes through the sample and creates a voltage drop $R_X I$. The equivalent resistors R_1 and R_2 represent the resistance of the leads and the contact resistance from lead to sample (Figure 3.14), respectively (which can be much higher than any other resistance in the circuit). There are voltage drops $R_1 I$ and $R_2 I$; the current source "sees" the sum $R_1 I + R_X I + R_2 I$. The voltmeter, however, measures the voltage drops $R_3 I' + R_X(I + I') + R_4 I'$, where I' is the current in the voltmeter circuit and $I' << I$, so that it actually determines R_X even if R_3, $R_4 = R_X$.

Usually by this method *two*-points and *four*-points values were measured independently. By Hao et al. was suggested the principle of simultaneous *two*- and *four*-point measurement [101] with modified electrode and measurement technique. Typical electrode geometry for resistance measurements by *two*-point techniques is the interdigitated structure (Figure 3.15). This provides an effective using of area of an electrode support in

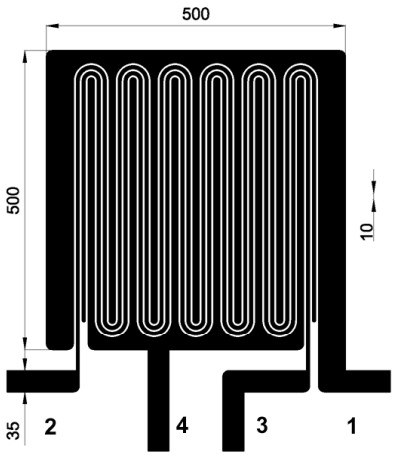


Figure 3.15 Working part of the electrode for resistance measurement (all dimensions in μm)

terms of increasing of polymer/electrode interface and decreasing of absolute values of polymer conductance. More detailed technical description of the setup and electrode surface reported in works [102, 103].

Thus modificated method was more preferable for us since the area of electrode is about 0.4 mm^2 and for the polymerisation is not necessary big amount of the electroactive compound. But as the main advantage can be marked the possibility of the resistance measurement in different media.

The main problem, which can prevent the usage of this technique, that the growth of polymer film should be lateral, and so far that the film must cover all four measuring electrodes. Other way there is no overlapping by film of all electrodes and no reliable measurement is possible.

By the potentiocyclic polymerisation on the micro-electrode, with geometry described before, was obtained polymer film of 4,4'-dimethoxy-2,2'-bipyrrole. Although conditions

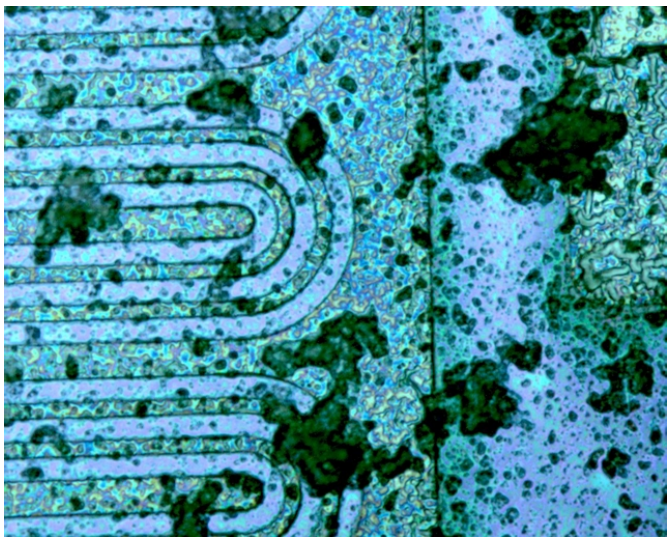


Figure 3.16 Electrode surface with polymer in optical microscope (magnification x1000)

of the polymerisation were almost similar the shape of the cyclovoltammetric curve was different. The possible explanation in this difference can be in the specific size and geometry of the electrode.

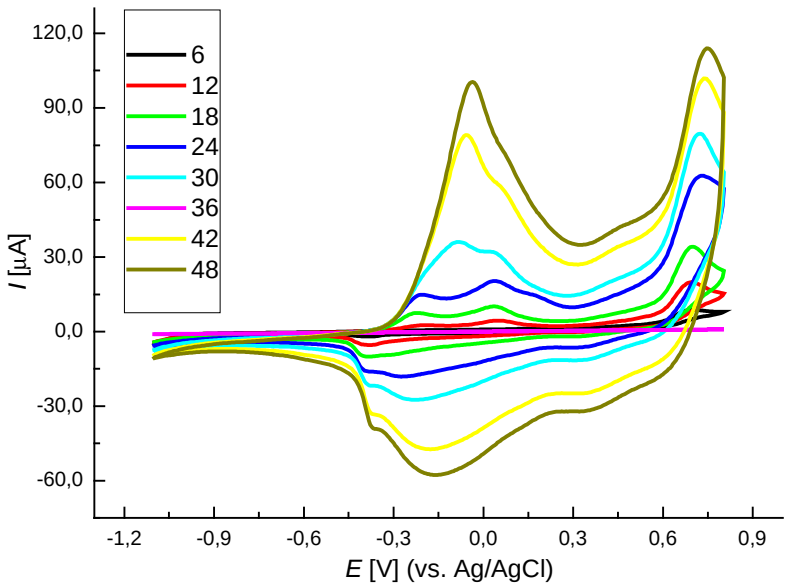


Figure 3.17 Shape of the CV on the Pt-"micro" electrode, conditions of the experiment the same as with usual Pt-disc electrode, digits on the graph are scan numbers

However, obtained film has shown stability in the air (toward oxygen), contrary to the monomer. Subsequent investigation of the polymer properties was carried out in such order:

- resistance in argon;
- resistance in air;
- resistance over water surface;
- resistance over 0.1 M HCl aqueous solution;
- resistance over $NH_{3(conc.)}$ aqueous solution.

A measurement of these dependences was accomplished with simultaneous *two*- and *four*-point resistance real-time tracking. Acquired data are represented on the Figure 3.18.

Measuring the resistance of obtained polymer was occasionally discovered it's good response to the different analytes – such as water, oxygen, HCl.

On the left represented curve (Figure 3.18), it can be seen the dependence of the resistance of the sample as a function of time. Thus, in argon atmosphere (section **a**) was only little

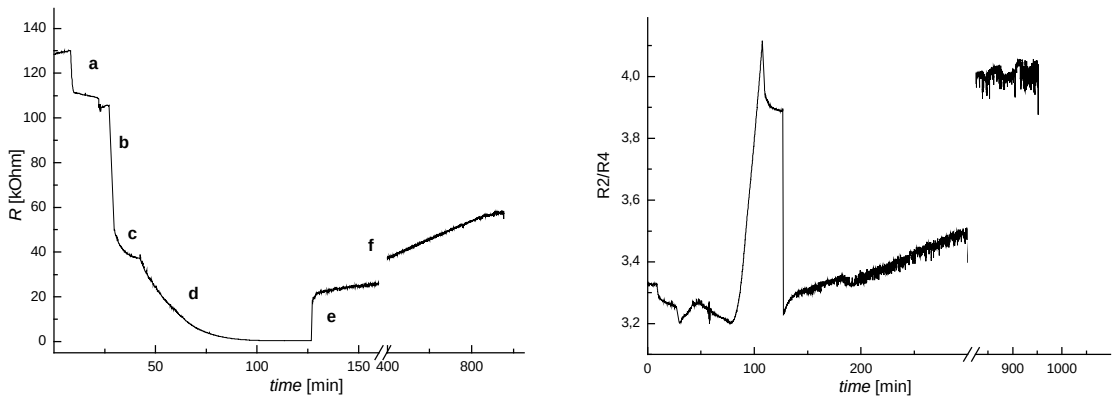


Figure 3.18 The *four*-point resistance and R2/R4 ratio measurement of the polymer film **38b**

decrease of *R* observed, whereas being placed in the air more than 50 % decrease was registered during a short time (section **b**). The sample when placed over the water surface shows a gentle slope of the curve (section **c**). It can be explained by that fact that the

difference between water concentration in air and near the water surface is not considerable.

Resistance measuring near the 0.1 M HCl aqueous solution displays further *R* falling till the value about 400 Ohm within 2 hours (curve section **d**). After replacement of the HCl solution back to argon, in order to check the reversibility of the process, rash resistance increase was seen (section **e**) followed by a gentle slope, which was not changed even by usage of ammonia solution (section **f**).

Analyte	Curve fragment	Time, [min]	Resistance, [kOhm]
Argon	a	0-27	128-105
Air	b	27-30	105-50
Water	c	30-42	50-37
HCl	d	42-126	37-0.4
Argon	e	126-127	0.4-18
NH_3	f	127-952	18-404

The right picture on the Figure 3.18 shows the R2/R4 ratio, which meaning can be defined as a resistance of the Metal-Polymer contact. Thus tracking this parameter can show if there is exfoliation of the film takes place. Using such electrodes, R2/R4 ratio minimal value is about 3. So, by polymerisation we have obtained the film with a good adhesion, seems to be affected during the interaction with HCl vapours, but it is shown to be reversible.

pH dependencies of polypyrrole resistance

Obtained preliminary results (shown on the Figure 3.18) were confirmed by measuring of the pH dependence – resistance on pH-value. These properties were tested on gold and platinum interdigitated electrodes (IDT4), which were electrochemically coated by polydimethoxybipyrrole (**38b**). For this experiment polymer-modified electrode was submerged into the aqueous media with simultaneous measuring of the resistance (R2, R4, ratio R2/R4) values.

During polymerisation on the IDT4 it was found out that formation of two different polymer films is possible. The difference can be good seen on the multisweep experiment figures (Figure 3.19) – various shapes of the CV curves.

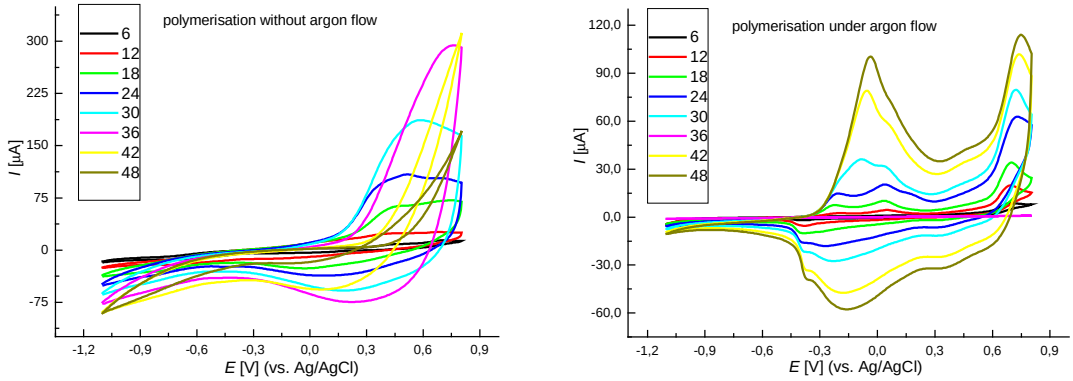


Figure 3.19 Two different poly(**38b**) films formation. On the graphs are shown every 6^{th} cycle

Thus, as it was expected polymer obtained under argon is better conductive comparatively to the one obtained without protecting atmosphere. Anyway, there was measured a response of both kinds of films in the media with various pH value.

Changes of the resistance, measured by two- and four-point techniques, are shown in Figure 3.20. On the Graph **a** presented alteration of resistance from pH during time. Here can be seen a considerable difference between R of both polymers. Resistance of the film obtained without argon is much higher than for the film of another type of polymer. Obviously, conjugation of the polymer chain, deposited without protecting gas, is somehow disrupted by small amount of oxygen (from air), what leads to the conductivity decrease. On the Graph **b** represented average readings of the R2 and R4 values. On the Graph **c** are shown the same data, but for a better appearance it is represented as a logarithmic dependence. Interestingly that ratio R2/R4 (**d**) of film, obtained without argon changes very little contrary to the second one, were remarkable decrease of ratio to be observed. It shows the fall of resistance of contact metal-polymer, what can be explained by a chemical influence on the polymer.

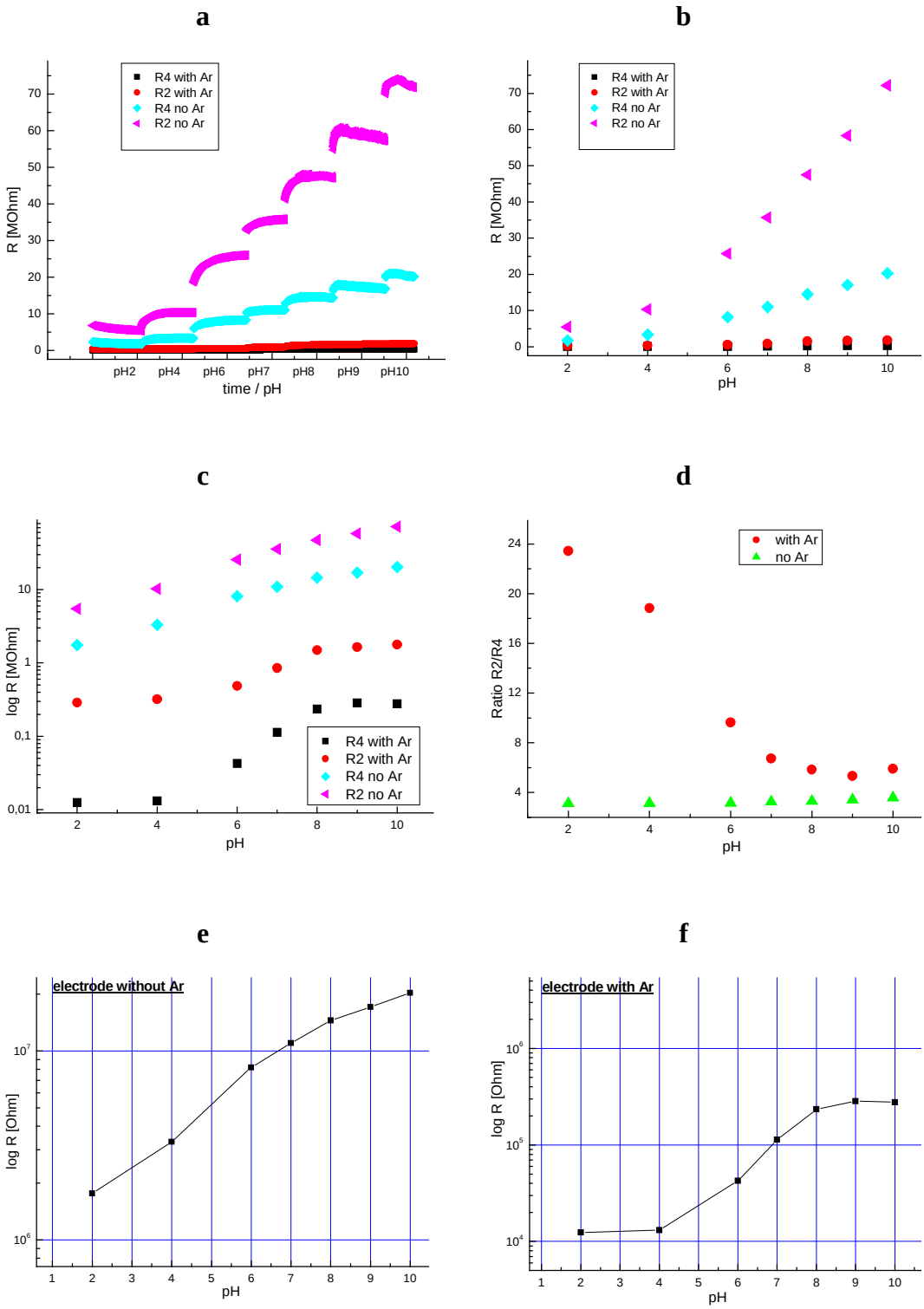
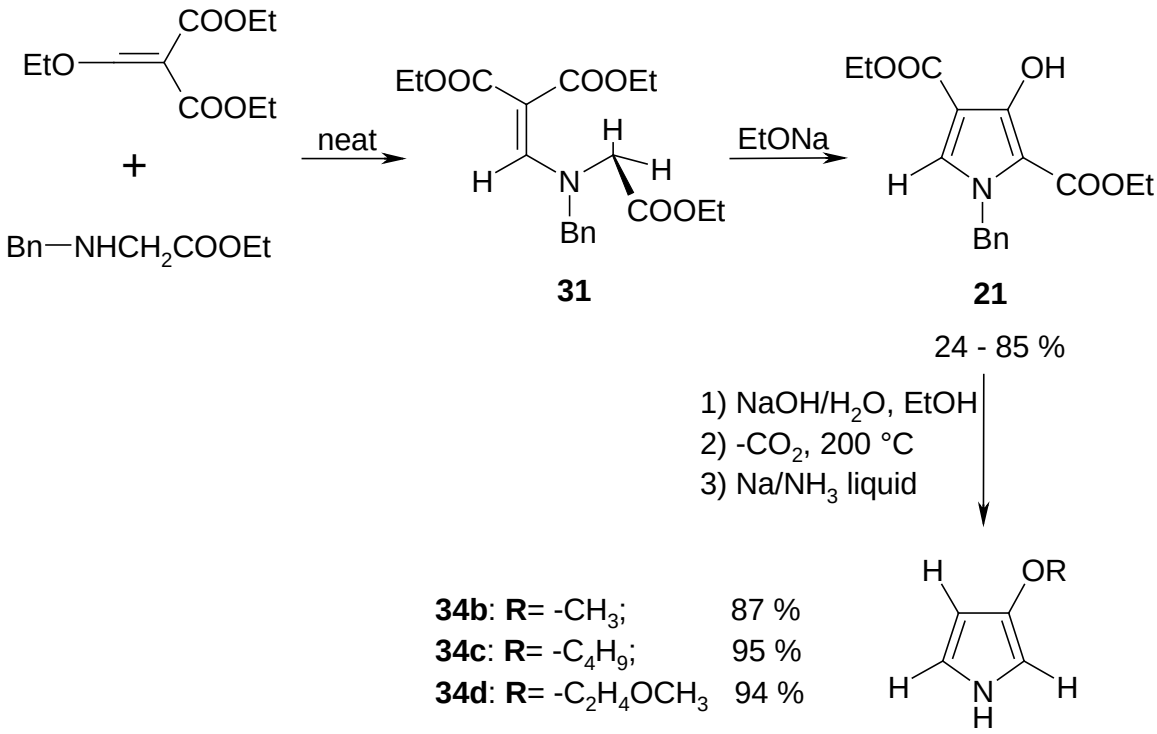


Figure 3.20 Response of electropolymerised poly(**38b**) on Pt electrodes to different pH value of the aqueous media.

Summary

In the present work we have shown short efficient pathways toward alkoxypyrroles, alkoxybipyrroles and aminopyrroles.

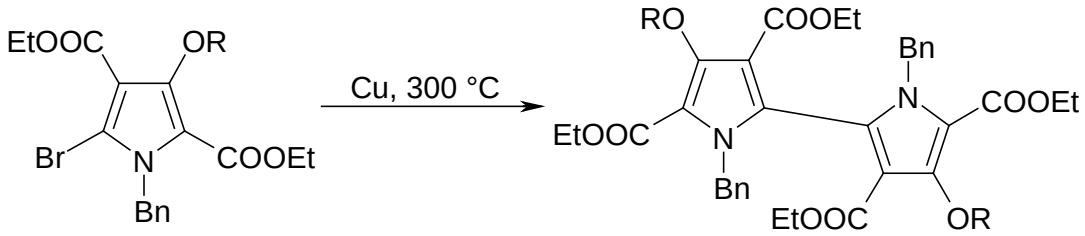
Syntheses of the alkoxypyrroles (**34**) proceed in a short synthetic sequence. Starting from the available glycinate and diethyl malonate derivative was obtained precursor (**31**) for the



34b: **R**= -CH_3; 87 %
34c: **R**= -C_4H_9; 95 %
34d: **R**= -$C_2H_4OCH_3$ 94 %

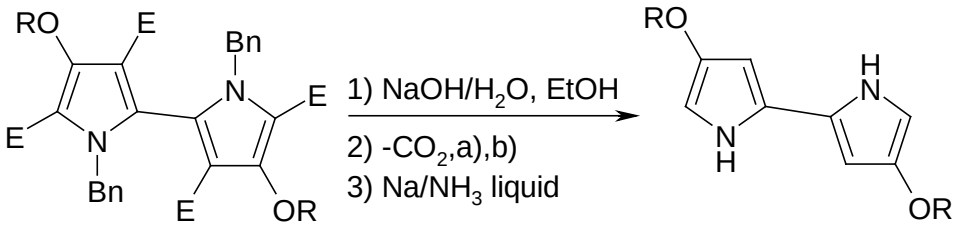
pyrrole ring formation. Dieckmann cyclisation proceeds with good yields giving diethyl 1-benzyl-3-hydroxypyrrole-2,4-dicarboxylate (**21a**). Further conversions of the pyrrole ring lead to 3-alkoxypyrroles (**34**) yielding ca. 90 % of target compounds.

In electrochemical experiments polymerisation activity increases in the sequence **34b, 34c, 34d.** 3-Butoxy and 3-(2-methoxyethoxy)pyrroles polymerise with formation of the polymer films.



22b: **R**= -CH_3;
22c: **R**= -C_4H_9; DMF trace

35b: 60 %
35c: 62 %



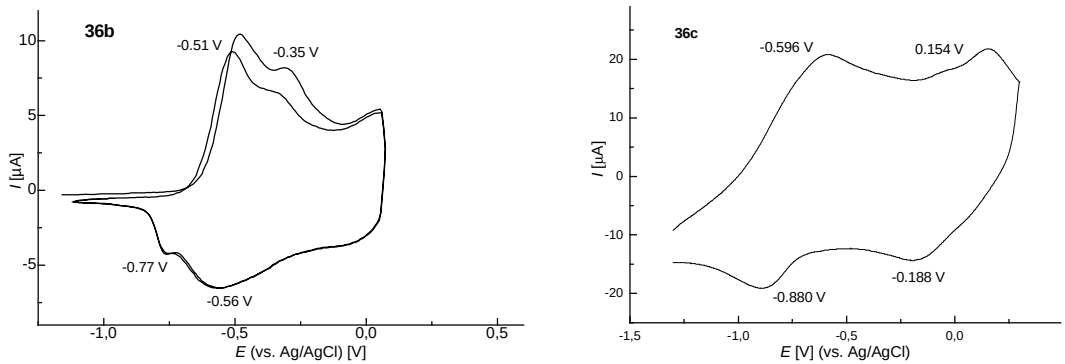
35 b,c

36b: **R**= -CH_3
36c: **R**= -C_4H_9

E= -$COOC_2H_5$

a) 200 °C; b) ethylene glycol, reflux

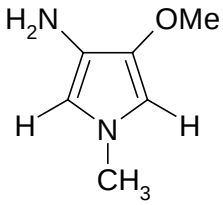
Starting from alkoxypyrrole derivatives **(22b-c)** new 3,3'- and 4.4'-dialkoxy-2,2'-bi-pyrroles were obtained. Obtained alkoxybipyrroles are active in electrochemical experiments and show rush polymerisation at potential sweeping. Characteristic curves for



polymethoxy- (left) and polybutoxypyrroles (right) proving the formation of conducting polypyrrolefilms. Mentioned polymers possessing conductivity and electrodes modified with such films displayed sensitivity to the oxygen, HCl and different pH values in

aqueous media. Furthermore, for the polybutoxypyrrole was observed an electrochromic effect.

In this work was shown that not every high electronrich pyrrole monomer leads to anodic polymerisation. Amino pyrroles (**47, 53a**) and (**53b**) can be only irreversible oxidized on



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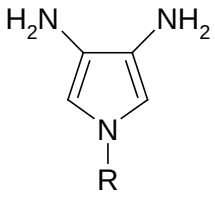
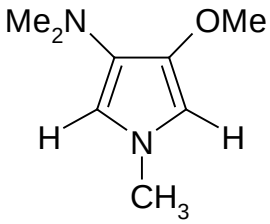


53a: R=-CH_3
53b: R=-CH_2Ph

anode without any polymer deposition. However, oxidation potentials shown by these pyrroles are the lowest from the set of compounds investigated in this work.

Our goal to synthesise pyrroles with even higher electron density (**48** and **54a,b**) in the ring was unfortunately not successful, due to a high oxidating ability of these compounds and complexity in selective methylation of amino groups.



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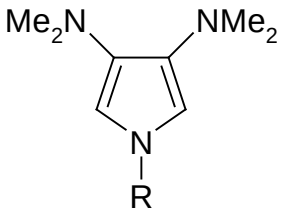


54a: R=-CH_3
54b: R=-CH_2Ph

All obtained substances were characterized and identified with analytical and spectroscopic methods.

Chapter 5

Experimental part

5.1 Analytical and spectral measurements

5.1.1 Analytical measurements

IR spectroscopy:

IR spectra were recorded at Bio-rad Excalibur Series FT-IR.

UV/Vis spectroscopy:

UV/Vis spectra were recorded at HitachiU2000, registration with Spectracalc Arithmetic A2, 12, (1988).

NMR spectroscopy:

NMR spectra were recorded at Bruker AC250 (250 MHz), Bruker AVANCE 300 (300 MHz), Bruker ARX400 (400 MHz) and Bruker AVANCE 600 (600 MHz) instruments.

Mass spectrometry:

Mass spectra were measured at a Finnigan Mat 95 or Varian Mat 311 A.

Elemental analysis:

Elemental analysis (CHN) was carried out at an Elementar vario EL III device.

X-Ray analysis:

X-Ray spectra were measured at Rentgencrystaldiffractiometer Stoe Imaging Plate Diffraction System (IPDS) (Stoe & Cie GmbH, Darmstadt).

Melting points:

Melting points were measured at Büchi 510 Modell, Reichert Thermovar–microscope with the heating table and polarisation-filter. All melting points are uncorrected.

5.1.2 Electrochemical measurements

Cells: The electrochemical measurements were carried out in specially constructed cells containing an internal drying column with highly activated alumina. The working electrode was a Pt disk sealed in soft glass (1.0 mm diameter). All electropolymerisation experiments were carried out at 100 mV/s scan rate.

A typical cell design for a cyclic voltammetry experiment is shown in the Figure 5.1. The simplest approach is merely to have the three electrodes immersed in the solution in close proximity.

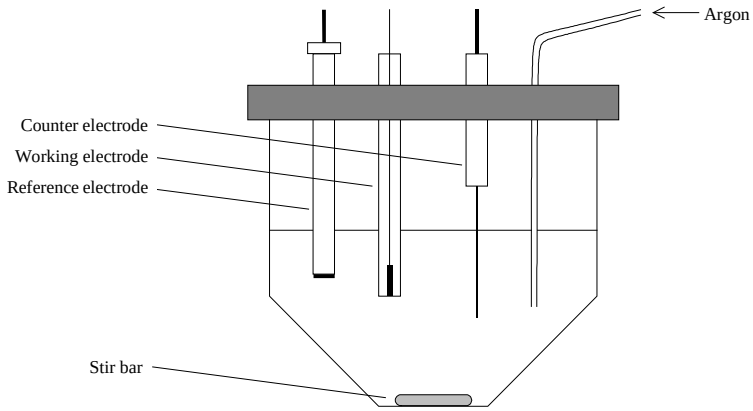


Figure 5.1 Typical electrochemical cell

Equipment:

All experiments were controlled by a Jaissle Potentiostat-Galvanostat IMP 88 or IMP 88 PC. The potential scans were performed with an EG&G PARC Model 175 Universal Programmer scan generator and the cyclovoltammetric response was recorded with an IMK PSO 8100 transient system and EG&G Model 283. The measured potentials refer to the Ag/AgCl-electrode and were determined by an internal calibration with the cobaltocinium/cobaltocene or ferrocinium/ferrocene redox pair.

Solvents:

Acetonitrile (AN) (Merck, Uvasol or HPLC quality) was refluxed with NaH for 10 min, distilled and filtered through a cooled (-40 ºC) chromatographic column with acidic Al_2O_3. To the eluent was added CaH_2 and the solvent was immediately distilled in a nitrogen atmosphere and stored in the dark under argon.
Dimethyl sulfoxide was obtained from the Fluka Co.

Supporting electrolyte:

Tetrabutylammonium tetrafluoroborate and tetrabutylammonium hexafluorophosphate (electrochemical grade) were obtained from Fluka Co. and dried in high vacuum before using.

5.2 Chemicals, equipment and technique

Chemicals were obtained from the Aldrich, Fluka, Lancaster or Merck companies and used without purification.
Solvents were purified and dehydrated by using standard methods [104] – followed by distillation under protecting atmosphere of nitrogen or argon.

Protecting atmosphere:

Most of the syntheses were carried out under protecting of nitrogen or argon atmosphere. Protecting gases were passed for the oxygen removal through the BTS-catalyst (from the BASF AG Co.) heated to 140-160 °C. Water traces were removed by filled with Sicapent (from the Merck Co.) U-tube.
Solvents for NMR spectra of the oxygen-sensitive compounds were frozen with liquid nitrogen, degassed in *vacuo* and saturated with argon.

All Ullmann-coupling reactions were carried out in the apparatus shown on the Figure 5.1. Where rotating round bottom flask was continuously flushed with inert-gas and heated with a heat-gun to about 300 ºC.

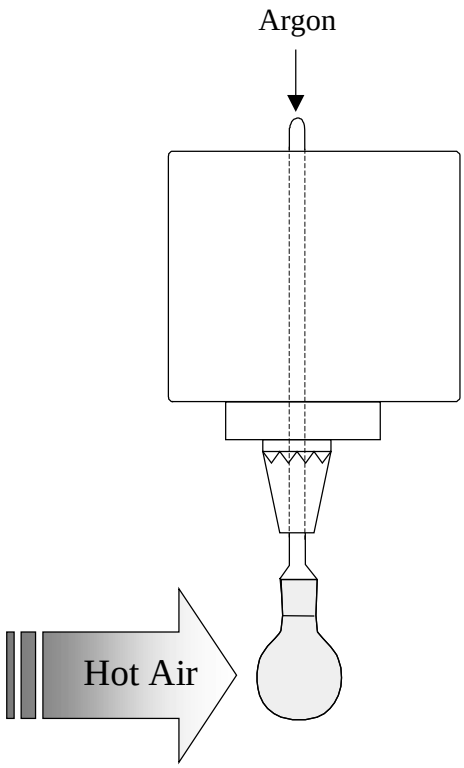


Figure 5.1 Setup for the Ullmann coupling

5.3 Synthesis and properties of alkoxypyrroles

5.3.1 Pyrrole ring formation

5.3.1.1 Ethyl N-benzylglycine ester

To a solution of benzyl amine (50 g, 0.47 mol) and triethylamine (47.2 g, 0.47 mol) in dry DMSO (300 ml) was slowly (ca. 1 h) added ethylbromoacetate (71.5 g, 0.47 mol). After being stirred for 1 h at room temperature, the reaction mixture was treated with a solution of NH_4Cl(10 %)/NH_4OH(10 %) 2:1. The aqueous phase was extracted with ether. Extract was washed with brine, dried over Na_2SO_4 and concentrated. The crude material (67 g of light-yellow oil) was distilled at 0.07 mBar, 85-92 °C to give **5.3.1.1**.

Yield: 50g, 55 %, colourless oil.

IR(film): $\tilde{n}$ = 3339, 3063, 2982, 2907, 1738, 1454, 1190, 1142, 1028, 738, 699 cm^{-1}.

^{1}H-NMR (250 MHz; $CDCl_3$): δ = 1.28 (t, J = 7.13 Hz, 3H, C$\underline{H}_3$), 1.89 (s, 1H), 3.41 (s, 2H), 3.81 (s, 2H), 4.19 (q, J = 7.13 Hz, 2H, C$\underline{H}_2$CH$_3$), 7.34-7.26 (m, 5H, Ph) ppm;

^{13}C-NMR (63 MHz; $CDCl_3$): δ = 50.0, 51.9, 53.4, 127.3, 128.4, 128.6, 139.6, 173.0 ppm;

5.3.1.2 Ethyl N-benzyl-N-[2,2-bis(ethoxycarbonyl)vinyl]glycinate

A mixture of **5.3.1.1** (46.1 g, 220 mmol) and diethyl ethoxymethylenemalonate (46.6 g, 220 mmol) was heated at 120 °C with stirring overnight to give **5.3.1.2** as a pale yellow oil. Formed ethanol was removed from the reaction mixture *in vacuo*.

Yield: quantitative; pale yellow oil.

IR(film/CCl_4): $\tilde{n}$ = 1760, 1708, 1695, 1606 cm^{-1}.

^{1}H-NMR (250 MHz; $CDCl_3$): δ = 1.26 (m, 9H), 3.87 (s, 2H), 4.17 (m, 6H), 4.54 (s, 2H), 7.2-7.4 (m,5H, Ph), 7.63 (s, 1H,HC=C) ppm;

MS (70 eV, EI): m/z (%) = 363 (6.2, M^+), 91 (100, $C_7H_7^+$);

elemental analysis calcd. (%) for $C_{19}H_{25}NO_6$ (363.41): C 62.80, H 6.93, N 3.85; found: C 62.73, H 6.86, N 4.15.

5.3.1.3 n-Butylmethanesulfonate

To a mixture of n-butyl alcohol (11.12 g, 115 mmol) and triethylamine (24.29 g, 240 mmol) in dichloromethane (100 mL) cooled with ice/NaCl-mixture (-10 °C) was added a solution of methanesulfonyl chloride (20.62 g, 180 mmol) in abs. dichloromethane (75 mL) such way, that the inner temperature does not exceed 0 °C. After the cool-bath removal the mixture was stirred for 1h, poured into the ice-water (200 ml) and extracted with dichloromethane. Organic phase was washed with cooled 50 mL 2M HCl, 50 mL H_2O, 50 mL satd. $NaHCO_3$ and dried over sodium sulphate. After solvent evaporation the rest (28.6 g) was distilled in vacuum (0.067 mBar, 41-43 °C) to give title compound.

Yield: 20.41 g, 90 %; colourless liquid.

IR (film): $\tilde{n}$ = 3026, 2962, 2875, 1466, 1354, 1174 cm^{-1};

^{1}H-NMR (300 MHz; $CDCl_3$): δ = 0.96 (t, J = 7.27 Hz, 3H, CH_2CH_3), 1.45 (sext, J = 7.46 Hz, 2H, CH_2CH_3), 1.74 (pent, J = 7.14 Hz, 2H, $OCH_2CH_2CH_2$), 3.01 (s, 3H, S-CH_3), 4.24 (t, J = 6.59 Hz, 2H, OCH_2) ppm;

^{13}C-NMR (75 MHz; $CDCl_3$): δ = 13.49, 18.69, 31.08, 37.36, 69.92 ppm;

MS (CI): m/z (%) = 170 (100) [M+NH_4^+];

5.3.1.4 2-Methoxyethylmethanesulfonate

To a mixture of 2-methoxyethanol (15.2 g, 200 mmol) and abs. triethylamine (32.4 g, 320 mmol) in abs. dichloromethane (150 mL), cooled with ice/NaCl-mixture (-10 °C), was dropped a solution of methanesulfonyl chloride (25.2 g, 220 mmol) in abs. dichloromethane (75 mL) such way, that the inner temperature does not exceed 0 °C. After stirring of the mixture at 0 °C for 1h, it was poured into ice-water (200 ml) and extracted with dichloromethane. Organic phase was washed with cooled 2M HCl (75 mL), 5 % $NaHCO_3$ (75 mL), H_2O (75 mL) and dried over sodium sulphate. After solvent evaporation the rest (42 g) was distilled in vacuum (0.013 mBar, 69-71 °C) to give colourless oil.

Yield: 28.1 g, 90 %; colourless oil.

IR (film): $\tilde{n}$ = 3020-2800, 1350, 1160, 1120 cm^{-1}.

^{1}H-NMR (300 MHz; $CDCl_3$): δ = 3.07 (s, 3H, $OC\underline{H}_3$), 3.41 (s, 3H, $SO_3C\underline{H}_3$), 3.63-3.72(m, 2H, $CH_2C\underline{H}_2OCH_3$), 4.32-4.42 (m, 2H, $CH_2C\underline{H}_2SO_3$) ppm;

^{13}C-NMR (75 MHz; $CDCl_3$): δ = 37.66, 59.07, 68.96, 70.28 ppm;

5.3.1.5 Benzylmethanesulfonate

To a solution prepared from benzyl alcohol (10 g, 93 mmol) and dichloromethane (80 mL) cooled to –30 °C was added methanesulfonyl chloride (12.72 g, 111 mmol) followed by drop wise addition of triethylamine (18.7 g, 185 mmol) such way, that the inner temperature does not exceed -10 °C. After addition of Et_3N the mixture was stirred for 30 min at 0 °C. Then the reaction mixture was poured into ice-water (100 ml) and extracted with dichloromethane. Organic phase was washed with H_2O, cold 2M HCl and dried over sodium sulphate. After solvent evaporation was obtained pale oil.

Yield: 16 g, 93 %; pale oil.

IR (film): $\tilde{n}$ = 3010, 1490, 1350, 1170 cm^{-1}.

^{1}H-NMR (300 MHz; $CDCl_3$): δ = 2.91 (s, 3H, CH_3), 5.25 (s, 2H, CH_2Ph), 7.29-7.51 (m, 5H, C_6H_5) ppm;

^{13}C-NMR (75 MHz; $CDCl_3$): δ = 38.42, 71.59, 128.95, 129.47, 133.36 ppm;

MS (70 eV, EI): m/z (%) = 186 (18) [$M^{+\cdot}$], 107 (68) [$\Delta CH_3SO_2^+$], 91 (100) [$C_7H_7^+$];

5.3.1.6 Diethyl 1-benzyl-3-hydroxypyrrole-2,4-dicarboxylate (21a)

To a solution of **5.3.1.2** (101 g, 280 mmol) in abs. EtOH (600 mL) was added a sodium ethoxide solution prepared from sodium (9.6 g, 420 mmol) and abs. ethanol (250 mL). The mixture was refluxed for 1.5 h, poured into the ice-water (750 ml), acidified with 20 % H_2SO_4, and extracted with toluene. The extract was washed with satd. $NHCO_3$, brine and dried over Na_2SO_4. The solvent was evaporated, and the residue (75 g) was recrystallised from MeOH to give **21a** as light-yellow crystals**.**

Yield: 72 g, 82 %; m.p. 60-61 °C, light-yellow crystals.

IR (KBr): $\tilde{n}$ = 3414, 2986-2890, 1705, 1686, 1648, 1580, 1495, 1439, 1262, 1093, 779, 736 cm^{-1}.

^{1}H-NMR (300 MHz; $CDCl_3$): δ = 1.27 (t, J = 7.14 Hz, 3H, $CH_2C\underline{H}_3$), 1.35 (t, J = 7.14 Hz, 3H, $C\underline{H}_3$), 4.29 (q, J = 7.14 Hz, 2H, $C\underline{H}_2CH_3$), 4.32 (q, J = 7.14 Hz, 2H, $C\underline{H}_2CH_3$), 5.39 (s, 2H, $C\underline{H}_2Ph$), 7.02-7.42 (m, 6H, Ph, H5-pyrrole), 8.90 (s, 1H, OH) ppm;

^{13}C-NMR (75 MHz; $CDCl_3$): δ = 14.35, 14.45, 53.54, 60.25, 60.37, 103.03, 107.07, 126.83, 127.93, 128.81, 129.83, 136.72, 154.54, 161.80, 164.37 ppm;

MS (70 eV, EI): m/z (%) = 317 (18.2) [M^+], 91 (100) [$C_7H_7^+$];

elemental analysis calcd. (%) for $C_{17}H_{19}NO_5$ (317.34): C 64.34, H 6.03, N 4.41; found: C 64.18, H 6.05, N 4.55.

5.3.1.7 Diethyl 1-benzyl-3-methoxypyrrole-2,4-dicarboxylate (21b)

To a stirred solution of **5.3.1.6** (30 g, 95 mmol) in abs. acetone (300 ml) under N_2 was added K_2CO_3 (33 g, 240 mmol) and dimethyl sulfate (9 ml, 95 mmol), and the reaction mixture was refluxed overnight. Then it was cooled to the room temperature and precipitate was filtered. After the solvent removal and double recrystallisation from ethanol white crystals of the title compound were obtained.

Yield: 26.6 g, 85 %; mp 69-71 °C, white crystals.

IR (KBr): $\tilde{n}$ = 2981-2870, 1698, 1551, 1449, 1388, 1295, 1247,1202, 1085, 1028,998, 787, 699 cm^{-1}.

^{1}H-NMR (250 MHz; $CDCl_3$): δ = 1.31 (t, J = 7.13 Hz, 3H, $CH_2C\underline{H}_3$), 1.34 (t, J = 7.13 Hz, 3H, $CH_2C\underline{H}_3$), 3.91 (s, 3H, OCH_3), 4.27 (q, J = 7.13 Hz, 2H, $C\underline{H}_2CH_3$), 4.29 (q, J = 7.13 Hz, 2H, $C\underline{H}_2CH_3$), 5.46 (s, 2H, $C\underline{H}_2$Ph), 7.07-7.38 (m, 6H, Ph, H5-pyrrole) ppm;

^{13}C-NMR (63 MHz; $CDCl_3$): δ = 14.24, 14.39, 53.45, 59.94, 60.18, 62.83, 108.47, 114.30, 127.13, 127.87, 128.78, 130.27, 136.86, 153.36, 160.56, 162.82 ppm;

MS (70 eV, EI): m/z (%) = 331 (37, M^+), 91 (100, $C_7H_7^+$);

elemental analysis calcd. (%) for $C_{18}H_{21}NO_5$ (331.4): C 65.24, H 6.39, N 4.23; found: C 65.25, H 6.33, N 4.23.

5.3.1.8 Diethyl 1-benzyl-3-butoxypyrrole-2,4-dicarboxylate (21c)

In the heat-dried three-necked flask under nitrogen atmosphere to *n*-butylmesylate (8.2 g, 53.87 mmol) with stirring were added the solution, prepared under nitrogen from **5.3.1.4**

(11.5 g, 35.9 mmol) and dry dimethylformamide (300 mL), and potassium carbonate (23.5 g, 170 mmol). Some minutes later the mixture became thick and some time later again fluid. After being stirred at 130 °C for 2h (TLC controlled) the cooled reaction mixture was poured into H_2O (200 mL) and 2M HCl (100 mL) and extracted with diethyl ether. The extract was washed with $NaHCO_3$, brine and dried over sodium sulphate. After solvent evaporation and drying in high vacuum light-yellow thick oil was obtained.

Yield: 12.47 g, 93 %; light-yellow oil.

IR (KBr): $\tilde{n}$ = 2951, 1697, 1550, 1444, 1385, 1292, 1246, 1080, 775 cm^{-1}.

^{1}H-NMR (250 MHz; $CDCl_3$): δ = 0.97 (t, *J* = 7.33 Hz, 3H, $O(CH_2)_3C\underline{H}_3$), 1.25-1.39 (m, *J* = 7.13, 6H, 2 x $OCH_2C\underline{H}_3$), 1.51 (sext, *J* = 7.45 Hz, 2H, $CH_2C\underline{H}_2CH_3$), 1.79 (pent, *J* = 7.13 Hz, 2H, $OCH_2C\underline{H}_2CH_2$), 4.05 (t, *J* = 6.54 Hz, 2H, $OC\underline{H}_2CH_2$), 4.25 (q, *J* = 7.13 Hz, 2H, $OC\underline{H}_2CH_3$), 4.28 (q, *J* = 7.13 Hz, 2H, $OC\underline{H}_2CH_3$), 5.46 (s, 2H, $C\underline{H}_2$Ph), 7.06-7.37 (m, 6H, Ph, H5-pyrrole) ppm;

^{13}C-NMR (63 MHz; $CDCl_3$): δ = 14.03, 14.28, 14.40, 19.19, 32.23, 53.47, 59.87, 60.08, 75.78, 108.49, 114.29, 126.99, 127.77, 128.72, 130.60, 136.97, 152.38, 162.89 ppm;

MS (70 eV, EI): m/z (%) = 373 (8) [$M^{+\cdot}$], 328 (2) [$\Delta\cdot$OEt], 271 (38) [$\Delta\cdot OC_4H_9$], 91 (100) [$C_7H_7^+$];

elemental analysis calcd. (%) for $C_{21}H_{27}NO_5$ (373.45): C 65.24, H 6.39, N 4.23; found: C 65.25, H 6.33, N 4.23.

5.3.1.9 Diethyl 1-benzyl-3-(2-methoxyethoxy)pyrrole-2,4-dicarboxylate (21d)

In the dry three-necked flask with nitrogen flushing to 2-methoxyethylmethanesulfonate (10 g, 65 mmol) with a mechanical stirring were added a solution, prepared under nitrogen from **5.3.1.6** (20.58 g, 65 mmol) and dry dimethylformamide (350 mL), and potassium carbonate (22.4 g, 162 mmol). Some minutes later the mixture became thick and some time

later again fluid. After being stirred at 130 °C for 3 h (TLC controlled) the cooled (under nitrogen flow) reaction mixture was poured into H_2O (500 mL) and extracted with dichloromethane. The extract was washed with brine and dried over sodium sulphate. After solvent evaporation and drying in high vacuum brown thick oil was obtained. The crude material was used unpurified for the further saponification.

Yield: 24 g, 98 %; brown thick oil.

IR (film): $\tilde{n}$ = 2981, 2934, 2904, 1698, 1551, 1443, 1388, 1356, 1296, 1250, 1201, 1129, 1085, 1031, 785 cm^{-1}.

^{1}H-NMR (300 MHz; $CDCl_3$): δ = 1.32 (t, J = 7.14 Hz, 3H, $CH_2C\underline{H}_3$), 1.34 (t, J = 7.14 Hz, 3H, $CH_2C\underline{H}_3$), 3.43 (s, 3H, OCH_3), 3.76 (t, J = 4.94 Hz, 2H, $C\underline{H}_2CH_2$), 4.22 (t, J = 4.94 Hz, 2H, $CH_2C\underline{H}_2$), 4.26 (q, J = 7.14 Hz, 2H, $C\underline{H}_2CH_3$), 4.28 (q, J = 7.14 Hz, 2H, $C\underline{H}_2CH_3$), 5.46 (s, 2H, $C\underline{H}_2$Ph), 7.05-7.39 (m, 6H, C_6H_5, H5-pyrrole) ppm;

^{13}C-NMR (75 MHz; $CDCl_3$): δ = 14.25, 14.41, 53.49, 59.04, 59.98, 60.26, 71.83, 74.37, 108.47, 114.42, 127.03, 127.83, 128.76, 130.37, 136.87, 151.96, 160.59, 162.80 ppm;

MS (70 eV, EI): m/z (%) = 375 (6) [$M^{+\cdot}$], 271 (27) [Δ[$\cdot$OEt+$\cdot CH_2CH_2OCH_3$], 91 (100) [$C_7H_7^+$];

elemental analysis calcd. (%) for $C_{20}H_{25}NO_6$ (375.43): C 63.99, H 6.71, N 3.73; found: C 64.07, H 6.64, N 3.81.

5.3.1.10 Diethyl 1-benzyl-3-benzyloxypyrrole-2,4-dicarboxylate

In the heat-dried three-necked flask under nitrogen atmosphere to benzyl mesylate (6g, 32 mmol) with stirring were added the solution, prepared under nitrogen from **5.3.1.6** (10.23 g, 32 mmol) and dry dimethylformamide (175 mL), and potassium carbonate (11.13 g, 81 mmol). Some minutes later the mixture became thick and some time later again fluid. After being stirred at 130 °C for 3h the cooled under nitrogen flow reaction mixture was poured

into H_2O (500 mL) and extracted with dichloromethane. The extract was washed with brine and dried over sodium sulphate. After solvent evaporation and drying in high vacuum light-yellow thick oil was obtained, which crystallises in freezer. Recrystallisation from ethanol gave white crystals.

Yield: 12.47 g, 95 %; mp 53-54 °C, white crystals.

IR (KBr): $\tilde{n}$ = 3032, 2981, 2935, 2906, 1719, 1693, 1547, 1441, 1395, 1373, 1295, 1247, 1201, 1075, 1028, 981, 780, 742, 717, 698 cm^{-1}.

^{1}H-NMR (300 MHz; $CDCl_3$): δ = 1.20 (t, J = 7.14 Hz, 3H, $CH_2C\underline{H}_3$), 1.29 (t, J = 7.14 Hz, 3H, $CH_2C\underline{H}_3$), 4.20 (q, J = 7.14 Hz, 2H, $C\underline{H}_2CH_3$), 4.28 (q, J = 7.14 Hz, 2H, $C\underline{H}_2CH_3$), 5.12 (s, 2H, $C\underline{H}_2$Ph), 5.47 (s, 2H, $C\underline{H}_2$Ph), 7.00-7.60 (m, 11, 2x Ph, H5-pyrrole) ppm;

^{13}C-NMR (75 MHz; $CDCl_3$): δ = 14.27, 14.45, 53.52, 60.01, 60.23, 108.70, 114.73, 127.01, 127.83, 127.89, 128.23, 128.36, 128.78, 130.59, 136.93, 137.40, 151.47, 160.59, 162.88 ppm;

MS (70 eV, EI): m/z (%): 407 (4) [$M^{+\cdot}$], 361 (3) [ΔEtOH], 316 (4) [$\Delta\cdot C_7H_7$], 91 (100) [$C_7H_7^+$];

elemental analysis calcd. (%) for $C_{24}H_{25}NO_5$ (407.47): C 70.75, H 6.18, N 3.44; found: C 70.87, H 5.82, N 3.28.

5.3.2 Syntheses of precursors for ring coupling

5.3.2.1 Diethyl 1-benzyl-2-bromo-4-hydroxypyrrole-3,5-dicarboxylate (22a)

To a solution of **5.3.1.6** (10 g, 30 mmol) in abs. chloroform (100 mL) in the round bottom flask, covered with aluminium foil, was added drop wise during 30 min a solution of bromine (7.6 g, 50 mmol) in abs. chloroform (20 mL). The reaction mixture was stirred one hour at room temperature. Then, the mixture was washed with a mixture of

10% $Na_2S_2O_3$ and satd. $NaHCO_3$ solution (1:1) and dried over Na_2SO_4. After removal of the solvent, the residue was recrystallised from methanol to give **12.**

Yield: 11.8 g, 95%; m.p. 87.5-88 °C from MeOH.

IR (KBr): $\tilde{n}$ = 3294, 2984, 1698, 1493, 1205, 1096 cm^{-1};

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.13 Hz, 3H, C<u>H</u>$_3$), 1.40 (t, *J* = 7.13 Hz, 3H, C<u>H</u>$_3$), 4.27 (q, *J* = 7.13 Hz, 2H, C<u>H</u>$_2$CH$_3$), 4.39 (q, *J* = 7.13 Hz, 2H, C<u>H</u>$_2$CH$_3$), 5.68 (s, 2H, C<u>H</u>$_2$Ph), 6.95-7.38 (m, 6H, C_6H_5, H5-pyrrole), 9.37 (s, 1H, OH) ppm;

^{13}C-NMR (63 MHz, $CDCl_3$): δ = 14.30, 50.60, 60.57, 60.84, 103.31, 108.52, 115.15, 126.17, 127.50, 128.66, 130.27, 136.46, 154.63, 160.87, 164.32 ppm;

MS (70 eV, EI): *m/z* (%): 395 (18) [M^+], 351 (25) [M^+-EtOH], 91 (100) [$C_7H_7^+$];

elemental analysis calcd. (%) for $C_{17}H_{18}BrNO_5$ (396.24): C 51.53, H 4.58, N 3.53; found: C 51.48, H 4.48, N 4.47.

5.3.2.2 Diethyl 1-benzyl-2-bromo-4-methoxypyrrole-3,5-dicarboxylate (22b)

Here are possible two reaction ways:

Path A:

To a stirred solution of **5.3.2.1** (4 g, 10 mmol) in dry acetone (60 mL) under N_2 was added K_2CO_3 (3.5 g, 25 mmol) and dimethyl sulphate (1.27 g, 10 mmol), and the reaction mixture was refluxed overnight. Then it was cooled to the room temperature and precipitate was filtered. After the solvent removal and crystallisation from methanol white crystals of the title compound were obtained. Yield: 3.9 g, 95 %; m.p. 49-50 °C, white crystals.

Path B:

To a solution of **5.3.1.7** (0.15 g, 0.45 mmol) in abs. chloroform (10 mL) in the round bottom flask, covered with aluminium foil, with the dropping funnel was added during 30 min a solution of bromine (0.109 g, 0.68 mmol) in abs. chloroform (10 mL). The reaction mixture was stirred one hour at room temperature. Then, the mixture was washed with a mixture of 10% $Na_2S_2O_3$ and satd. $NaHCO_3$ solution (1:1), brine and dried over Na_2SO_4. After removal of the solvent the target compound was obtained**.**

Yield: 0.163 g, 90 %, m.p. 49-51 °C, white crystals.

IR (KBr): $\tilde{n}$ = 2981, 1706, 1542, 1493, 1416, 1288, 1242, 1095, 1029, 696 cm^{-1};

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.13 Hz, 3H, $CH_2C\underline{H}_3$), 1.39 (t, *J* = 7.13 Hz, 3H, $CH_2C\underline{H}_3$), 3.89 (s, 3H, OCH_3), 4.26 (q, *J* = 7.13 Hz, 2H, $C\underline{H}_2CH_3$), 4.36 (q, *J* = 7.13 Hz, 2H, $C\underline{H}_2CH_3$), 5.74 (s, 2H, $C\underline{H}_2Ph$), 6.94-7.37 (m, 5H, C_6H_5) ppm;

^{13}C-NMR (63 MHz, $CDCl_3$): δ = 14.17, 14.29, 50.54, 60.44, 60.52, 63.20, 109.39, 115.06, 115.89, 126.31, 127.43, 128.63, 136.59, 153.33, 159.81, 162.12 ppm;

MS (CI): *m/z* (%): 410 (100) [MH^+], 330 (54) [MH^+-HBr];

elemental analysis calcd. (%) for $C_{18}H_{20}BrNO_5$ (410.27): C 52.7, H 4.91, N 3.41; found: C 52.43, H 4.78, N 3.35.

5.3.2.3 Diethyl 1-benzyl-2-bromo-4-butoxypyrrole-3,5-dicarboxylate (22c)

In the heat-dried three-necked flask under nitrogen atmosphere to butylmesylate **5.3.1.1** (11.85 g, 77.87 mmol) with stirring were added a solution, prepared under nitrogen from **5.3.2.1** (20.64 g, 51.91 mmol) and dry dimethylformamide (300 mL), and potassium carbonate (23.5 g, 170 mmol). Some minutes later the mixture became thick and some time later again fluid. After being stirred at 130 °C for 2h (TLC controlled) the cooled under nitrogen flow reaction mixture was poured into H_2O (200 mL) and 2M HCl (100 mL) and

extracted with diethyl ether. The extract was washed with $NaHCO_3$, brine and dried over sodium sulphate. After solvent evaporation and drying in high vacuum light-yellow thick oil was obtained.

Yield: 20.45 g, 87 %; light-yellow oil.

IR (KBr): $\tilde{n}$ = 2955, 1704, 1539, 1429, 1285, 1241, 1197, 1095, 1027, 697 cm^{-1};

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.33 Hz, 3H, $O(CH_2)_2C\underline{H}_3$), 1.29 (t, J = 7.13 Hz, 3H, $OCH_2C\underline{H}_3$), 1.38 (t, J = 7.13 Hz, 3H, $OCH_2C\underline{H}_3$), 1.39-1.54 (m, 2H, $CH_2C\underline{H}_2CH_3$), 1.79 (pent, J = 7.13 Hz, 2H, $C\underline{H}_2CH_2CH_3$), 4.01 (t, J = 6.74 Hz, 2H, $OC\underline{H}_2CH_2CH_2CH_3$), 4.25 (q, J = 7.13 Hz, 2H, $OC\underline{H}_2CH_3$), 4.35 (q, J = 7.13 Hz, 2H, $OC\underline{H}_2CH_3$), 5.75 (s, 2H, $C\underline{H}_2Ph$), 6.95-7.35 (m, 5H, C_6H_5) ppm;

^{13}C-NMR (63 MHz, $CDCl_3$): δ = 14.04, 14.23, 14.32, 19.17, 32.13, 50.54, 60.37, 60.44, 76.24, 109.39, 115.26, 115.87, 126.20, 127.35, 128.58, 136.65, 152.27, 159.89, 162.19 ppm;

MS (70 eV, EI): *m/z* (%): 451 (2) [$M^{+\cdot}$], 349 (6) [$\Delta \cdot C_4H_9$], 91 (100) [$C_7H_7^+$];

elemental analysis calcd. (%) for $C_{21}H_{26}BrNO_5$ (452.35): C 55.76, H 5.79, N 3.10; found: C 55.76, H 5.59, N 3.16.

5.3.2.4 *Racemic*- and *meso*-Tetraethyl-1,1'-dibenzyl-3,3'-dioxo-1,1',3,3'-tetrahydro-[2,2'] bipyrrole-2,2',4,4'-tetracarboxylates (23) and (24)

A solution of $NaHCO_3$ (2.63 g, 30 mmol) in H_2O (10 mL) was heated to 50 °C and 1,2-dichloroethane (115 mL) added, followed by **5.3.1.7** (3 g, 9.1 mmol). A mixture of I_2 (2.6 g, 10 mmol) and NaI (3.2 g, 20 mmol) in water (10 mL) was added within 5 min and the resulting mixture was heated for one hour. Some undissolved I_2 was washed into the mixture with H_2O during the reaction. The mixture was transferred to a separating funnel, the organic layer was separated, and the aqueous phase washed with $CHCl_3$ (3 x 30 mL).

The combined organic layers were washed with 5 % solution of $Na_2S_2O_3$ (3 x 30 mL), 5 % solution of $NaHCO_3$ (3 x 30 mL), brine (3 x 30 mL), and then dried over Na_2SO_4. During the stripping off of the solvent, **23** was precipitated, and **24** left in the solution.

5.3.2.4.1 ±-23

White crystals (0.7 g, 25 %), m.p. 198-199 °C.

IR (KBr): $\tilde{n}$ = 3448, 3039, 2989, 2902, 1745, 1565, 1375, 1340, 1222, 1176, 1083, 1018, 966, 771, 703 cm^{-1};

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.11 Hz, 6H, 2 x $CH_2C\underline{H}_3$, 3,3´), 1.34 (t, *J* = 7.15 Hz, 6H, 2 x $CH_2C\underline{H}_3$, 4,4), 4.10 (qdd, *J* = 7.32, *J* = 3,52, 4H, $C\underline{H}_2CH_3$), 4.31 (qdd, *J* = 7.16, 3.57, 2H, 2 x $C\underline{H}_2CH_3$), 4.99, 5.12 (AB, *J* = 14.02 Hz, 4H, 2 x $C\underline{H}_2Ph$), 7.35-7.56 (m, 10H, 2 x C_6H_5), 8.12 (s, 2H, 2 x H-pyrrole) ppm;

^{13}C-NMR (63 MHz, $CDCl_3$): δ = 14.08, 14.34, 56.22, 59.78, 63.65, 80.06, 101.98, 129.01, 129.31, 130.49, 133.81, 161.75, 164.24, 169.72, 184.78 ppm;

MS (CI): *m/z* (%): 318 (68) [$(M/2+1)H^+$], 335 (100) [$(M/2+1)+NH_4^+$], 633 (3) [MH^+], 650 (8) [$M+NH_4^+$];

elemental analysis calcd. (%) for $C_{34}H_{36}N_2O_{10}$ (632.67): C 64.55, H 5.74, N 4.43; found: C 64.21, H 5.60, N 4.36.

5.3.2.4.2 *rac*-24

(0.82 g, 29 %) yellow thick oil;

IR (KBr): $\tilde{n}$ = 3454, 2982, 1733, 1689, 1569, 1373, 1238, 1020, 769, 702 cm^{-1};

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.21 (t, *J* = 7.11 Hz, 6H, 2 x $CH_2C\underline{H}_3$), 1.26 (t, *J* = 7.05 Hz, 6H, 2 x $CH_2C\underline{H}_3$), 4.15 (q x d, *J* = 7.12 Hz, 2H, 2 x $HC\underline{H}CH_3$), 4.16 (q, *J* = 7.16 Hz, 2H, 2 x $\underline{H}CHCH_3$), 4.22 (q, *J* = 7.11 Hz, 4H, 4 x $C\underline{H}_2CH_3$), 4.93, 4.70 (AB, *J* = 14.55 Hz, 4H, 2 x $C\underline{H}_2Ph$), 7.32-7.46 (m, 10H, 2 x C_6H_5), 8.33 (s, 2H, 2 x H-pyrrole) ppm;

^{13}C-NMR (63 MHz, $CDCl_3$): δ = 13.72, 14.48, 54.31, 60.04, 63.53, 79.32, 105.37, 128.86, 129.27, 129.38, 134.11, 162.20, 162.74, 171.47, 187.99 ppm;

MS (FI): *m/z* (%): 316 (7) [$M/2^+$], 632 (100) [M^+];

elemental analysis calcd. (%) for $C_{34}H_{36}N_2O_{10}$ (632.67): C 64.55, H 5.74, N 4.43; found: C 64.47, H 5.66, N 4.24.

5.3.3 Bipyrrole skeleton synthesis

5.3.3.1 1,1'-Dibenzyl-3,3'-dimethoxy-2,2'-bipyrrole (40)

A solution of **5.3.5.2** (1 g, 5.3 mmol) in dry THF/diethyl ether (1:1, 15 mL) with TMEDA (0.4 mL, 2.8 mmol) was cooled to –70 °C with stirring and under argon *sec*-Butyllithium in cyclohexane/hexane (92/8, 0.34 g, 5.3 mmol) was added. The mixture was allowed to warm to the room temperature during 2.5 h. The mixture was cooled again to -40 °C and dry $NiCl_2$ was added (0.83 g, 6.4 mmol). With vigorous stirring the mixture was allowed to warm up to 0 °C (3.5 h). MeOH (10 mL) and water (20-30 mL) were added with stirring. Finally all solvents were removed in *vacuo*, and the dark oily residue was distilled at 80-85 °C (0.013 mBar). The distillate was starting material **33b** (ca. 50 %), the dark residue was recrystallised from ethyl acetate to give colourless crystals (0.38 g, 40 %), m.p. 69-71 °C.

IR (KBr): $\tilde{n}$ = 3463, 3062-2831, 1606, 1550, 1479, 1452, 1411, 1330, 1091, 997, 711, 628 cm^{-1};

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 3.68 (s, 6H, 2 x OC<u>H</u>$_3$), 4.59 (AB, 4H, 2 x C<u>H</u>$_2$Ph), 5.94 (d, *J* = 3.17 Hz, 2H, 2 x H-pyrrole), 6.45 (d, *J* = 3.17 Hz, 2H, 2 x H-pyrrole), 6.86-7.27 (m, 10H, 2 x C_6H_5) ppm;

^{13}C-NMR (63 MHz, $CDCl_3$): δ = 50.91, 58.00, 95.24, 106.82, 118.73, 127.19, 127.83, 128.32, 138.27, 147.39 ppm;

HRMS (70eV, PI-EI) calcd. for $C_{24}H_{24}N_2O_2$: 372.1838; found *m/z*: 372.1836.

5.3.3.2 Tetraethyl 1,1'-dibenzyl-4,4'-dimethoxy-2,2'-bipyrrole-3,3',5,5'-tetra-carboxylate (35b)

A mixture of **5.3.2.2** (4 g, 9.8 mmol) and copper powder (15.6 g, 240 mmol) was heated at 300 °C for 30 min in an open rotating flask (see figure) with argon flushing. After cooling, the content was taken up with ethyl acetate, the solvent was evaporated, and the brown-black residue was recrystallised from methanol to give light-yellow crystals.

Yield: 3.80 g, 60 %; m.p. 90-91 °C.

IR (KBr): $\tilde{n}$ = 2981-2821, 1714, 1492, 1413, 1286, 1241, 1193, 1083, 1025, 194, 711 cm^{-1};

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.12 Hz, 6H, 2 x $CH_2C\underline{H}_3$), 1.33 (t, *J* = 7.12 Hz, 6H, 2 x $CH_2C\underline{H}_3$), 3.79 (q, *J* = 7.12 Hz, 2H, 2 x $H_3CHC\underline{H}CO$), 3.83 (q, *J* = 7.12 Hz, 2H, 2 x $H_3CHC\underline{H}CO$), 3.95 (s, 6H, 2 x OC<u>H</u>$_3$), 3.98 (q, *J* = 7.15 Hz, 2H, 2 x $H_3CHC\underline{H}CO$), 4.02 (q, *J* = 7.15 Hz, 2H, 2 x $H_3CHC\underline{H}CO$), 4.30 (q, *J* = 7.09, 4H, 2 x $H_3CC\underline{H}_2CO$), 4.88 (d, *J* = 2.43, 4H, 2 x C<u>H</u>$_2$Ph), 6.81-7.19 (m, 10H, 2 x C_6H_5) ppm;

^{13}C-NMR (63 MHz, $CDCl_3$): δ = 13.91, 14.21, 49.89, 59.63, 60.53, 63.08, 110.58, 115.30, 127.10, 127.48, 128.31, 129.48,136.52, 153.10, 160.41, 161.69 ppm;

MS (FD): *m/z* (%): 660 (100) [M^+];

elemental analysis calcd. (%) for $C_{36}H_{40}N_2O_{10}$ (660.73): C 65.44, H 6.10, N 4.24; found: C 65.28, H 6.09, N 4.19.

5.3.3.3 Tetraethyl 1,1'-dibenzyl-4,4'-dibutoxy-2,2'-bipyrrole-3,3',5,5'-tetracarboxylate (35c)

A mixture of **5.3.2.3** (3 g, 6.6 mmol) and copper powder (11.85 g, 77.87 mmol) was heated with DMF traces at 300 °C for 30 min in an open rotating flask (see Figure) with argon flushing. After cooling, the content was washed with ethyl acetate. The solvent was evaporated in *vacuo*. The dark-brown residue (1.75 g, 71 %) was dissolved in diethyl ether and mixed with some SiO_2. After silica filtration and solvent evaporation were obtained light-yellow thick oil.

Yield: 1.5 g, 62 %; light-yellow thick oil.

IR (film): $\tilde{n}$ = 2959-2873, 1701, 1535, 1490-1431, 1288, 1242, 1194, 1135, 1085, 1028, 697 cm^{-1};

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.33 Hz, 6H, 2 x $OCH_2C\underline{H}_3$), 1.02 (t, *J* = 7.13 Hz, 6H, 2 x $OCH_2C\underline{H}_3$), 1.32 (t, *J* = 7.13 Hz, 6H, 2 x $O(CH_2)_3C\underline{H}_3$), 1.52 (sext, *J* = 7.45 Hz, 4H, 2 x $OCH_2CH_2C\underline{H}_2CH_3$), 1.83 (pent, *J* = 7.13 Hz, 4H, 2 x $OCH_2C\underline{H}_2CH_2CH_3$), 3.84 (q, *J* = 7.13 Hz, 2H, $OC\underline{H}_2CH_3$), 3.96 (q, *J* = 7.13 Hz, 2H, $OC\underline{H}_2CH_3$), 4.07 (t, *J* = 6.74 Hz, 2H, $OC\underline{H}_2CH_2CH_2CH_3$), 4.08 (t, *J* = 6.74 Hz, 2H, $OC\underline{H}_2CH_2CH_2CH_3$), 4.29 (q, *J* = 7.13 Hz, 4H, 2 x $OC\underline{H}_2CH_3$), 4.85 (d, *J* = 3.17, 4H, 2 x $C\underline{H}_2Ph$), 6.69-7.40 (m, 10H, 2 x $C_6\underline{H}_5$) ppm;

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.99, 14.10, 14.30, 19.22, 32.25, 49.84, 59.59, 60.44, 76.02, 110.52, 115.27, 127.01, 127.38, 128.27, 129.78, 136.61, 152.12, 160.52, 161.77 ppm;

MS (ESI): *m/z* (%): 762 (18) [$M+NH_4^+$], 745 (100) [MH^+];

elemental analysis calcd. (%) for $C_{48}H_{48}N_2O_{10}$ (812.93): C 70.92, H 5.95, N 3.45; found: C 70.98, H 6.05, N 3.50.

5.3.4 Pyrrole- and bipyrrole- carboxylic acids

5.3.4.1 1-Benzyl-3-hydroxypyrrole-2-ethoxycarbonyl-4-carboxylic acid (32e)

To a solution prepared from **5.3.1.6** (5 g, 16 mmol) and ethanol (50 mL) was added a solution of NaOH (3.8 g, 95 mmol) in H_2O (50 mL) and the mixture was refluxed for 3 h. Ethanol was removed in *vacuo* and the rest was acidified with H_2SO_4 (10 %) to pH~2-3. The pyrrole-acid was extracted with ether. After the solvent evaporation was obtained the crude material (7.5 g). Recrystallisation from ethanol (8 mL) gave light-brown crystals.

Yield: 10.5 g, 92 %; m.p. 142-143 °C, light-brown crystals.

^{1}H-NMR (300 MHz, DMSO-d6): δ = 1.15 (t, J = 7.00 Hz, 3H, $CH_2C\underline{H}_3$), 4.14 (q, J = 7.00 Hz, 2H, $\underline{C}H_2CH_3$), 3.95 (s, 6H, 2 x $OC\underline{H}_3$), 5.43 (s, 2H, $C\underline{H}_2Ph$), 6.89-7.46 (m, 5H, C_6H_5), 7.70 (s, 1H, H5-pyrrole) ppm;

^{13}C-NMR (75 MHz, DMSO-d6): δ = 14.11, 52.19, 59.29, 102.51, 106.18, 126.41, 127.27, 128.39, 130.91, 137.92, 153.32, 160.44, 165.53 ppm;

MS (70 eV, EI): m/z (%) = 289 (6) [$M^{+\cdot}$], 271 (18) [$(M-H_2O)^{+\cdot}$], 91 (100) [$C_7H_7^+$];

elemental analysis calcd. (%) for $C_{15}H_{15}NO_5$ (289.29): C 62.28, H 5.23, N 4.84; found: C 62.06, H 5.02, N 4.76.

5.3.4.2 1-Benzyl-3-methoxypyrrole-2,4-dicarboxylic acid (32b)

To a solution prepared from **5.3.1.6** (19 g, 57 mmol) and ethanol (300 mL) was added a solution of NaOH (13.8 g, 344 mmol) in H_2O (300 mL) and the mixture was refluxed for

12 h. Ethanol was removed in *vacuo* and the rest was acidified with H_2SO_4 (10 %) to pH~2-3 under cooling. The acid **5.3.4.2** was extracted with ether. Solvent evaporation and recrystallisation from ethanol gave almost colourless crystals.

Yield: 10.5 g, 92 %; m.p. 142-143 °C, almost colourless crystals.

IR (KBr): $\tilde{n}$ = 3434, 3032-2880, 2615, 1663, 1547, 1461, 1280, 1073, 1001, 924 cm^{-1};

^{1}H-NMR (400 MHz, DMSO-d6): δ = 3.75 (s, 1H, OC$\underline{H}_3$), 5.48 (s, 2H, C$\underline{H}_2$Ph), 7.07-7.37 (m, 5H, C_6H_5), 7.65 (s, 1H, H-pyrrole), 12.17 (s, 2H, 2 x COOH) ppm;

^{13}C-NMR (100 MHz, DMSO-d6): δ = 52.05, 62.09, 107.72, 113.65, 126.79, 127.38, 128.49, 131.07, 138.10, 152.65, 161.09, 163.43 ppm;

MS (70 eV, PI-EIMS): *m/z* (%): 275 (12) [$M^{+\cdot}$], 231 (19) [$(M\text{-}CO_2)^{+\cdot}$], 91 (100) [$C_7H_7^+$];

elemental analysis calcd. (%) for $C_{14}H_{13}NO_5$ (275.2): C 61.09, H 4.76, N 5.09; found C 60.98, H 4.65, N 4.01.

5.3.4.3 1-Benzyl-3-butoxypyrrole-2,4-dicarboxylic acid (32c)

To a solution prepared from **5.3.1.8** (12.47 g, 33 mmol) and ethanol (150 mL) was added a solution of NaOH (8.7 g, 218 mmol) in H_2O (150 mL) and the mixture was refluxed under nitrogen for 48 h. Ethanol was removed in *vacuo* and the rest was acidified under cooling with H_2SO_4 (10 %) to pH~2-3. The acid **5.3.4.3** was extracted with ether. Solvent evaporation and recrystallisation from methanol gave white crystals.

Yield: 9 g, 85 %; m.p. 134-135 °C, white crystals.

IR (KBr): $\tilde{n}$ = 3425, 2958, 2869, 1703, 1659, 1549, 1461, 1381, 1277, 1086, 919, 723, 527 cm^{-1};

^{1}H-NMR (300 MHz, DMSO-d6): δ = 0.88 (t, J = 7.41 Hz, 3H, O(CH$_2$)$_2$C<u>H</u>$_3$), 1.39 (sext, 2H, OCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$), 1.62 (pent, J = 7.07 Hz, 2H, OCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$), 3.96 (t, J = 6.45 Hz, 2H, OC<u>H</u>$_2$CH$_2$CH$_2$CH$_3$), 5.48 (s, 2H, C<u>H</u>$_2$Ph), 7.00-7.47 (m,

5H, C$_6$H$_5$), 7.66 (s, 1H, H5-pyrrole), 12.21 (s, 2H, 2x COOH) ppm;
^{13}C-NMR (75 MHz, DMSO-d6): δ = 13.66, 18.41, 31.43, 51.98, 74.37, 107.77, 113.69, 126.64, 127.26, 128.39, 131.14, 138.09, 151.60, 161.10, 163.40 ppm;

MS (ESI): *m/z* (%): 316 (100) [(M-H$^+$)$^-$], 318 (31) [MH$^+$], 335 (100) [M+NH$_4^+$], 633 (60) [(2M-H$^+$)$^-$];

elemental analysis calcd. (%) for C$_{17}$H$_{19}$NO$_5$ (317.34): C 64.34, H 6.03, N 4.41; found C 64.30, H 5.77, N 4.28.

5.3.4.4 1-Benzyl-3-(2-methoxyethoxy)pyrrole-2,4-dicarboxylic acid (32d)

To a solution prepared from **5.3.1.9** (10 g, 27 mmol) and ethanol (80 mL) was added a solution of NaOH (6.4 g, 160 mmol) in H$_2$O (80 mL) and the mixture was refluxed under nitrogen for 3 h. Ethanol was removed in *vacuo* and the rest was acidified under cooling with H$_2$SO$_4$ (10 %) to pH~2-3. The acid **5.3.4.4** was extracted with diethyl ether. Solvent evaporation gave white crystals.

Yield: 6.1 g, 72 %; m.p. 139-141 °C (melts with decarboxylation), white crystals.

IR (KBr): $\tilde{n}$ = 3437, 2932, 2893, 2619, 2561, 1701, 1662, 1548, 1464, 1409, 1279, 1126, 1089, 1029, 922, 734 cm^{-1}.

^{1}H-NMR (300 MHz; DMSO-d6): δ = 3.25 (s, 3H, OCH$_3$), 3.59 (t, J = 5.08 Hz, 2H, C<u>H</u>$_2$CH$_2$), 4.11 (t, J = 5.08 Hz, 2H, CH$_2$C<u>H</u>$_2$), 5.49 (s, 2H, C<u>H</u>$_2$Ph), 7.00-7.43 (m, 5H, C$_6$H$_5$), 7.69 (s, 1H, H5-pyrrole), 12.24 (s, 2H, 2x COOH) ppm;

^{13}C-NMR (75 MHz; $CDCl_3$): δ = 51.96, 57.80, 70.86, 73.52, 107.58, 113.58, 126.63, 127.28, 128.40, 131.16, 138.04, 151.28, 160.90, 163.36 ppm;

MS (70 eV, EI): m/z (%) = 319 (4) [$M^{+\cdot}$], 91 (100) [$C_7H_7^+$], 59 (35) [$\Delta \cdot C_2H_4OCH_3$];

elemental analysis calcd. (%) for $C_{16}H_{17}NO_6$ (319.32): C 60.18, H 5.37, N 4.39; found: C 60.21, H 5.42, N 4.37.

5.3.4.5 1,1'-Dibenzyl-4,4'-dimethoxy-2,2'-bipyrrole-3,3',5,5'-tetracarboxylic acid (36b)

Compound **5.3.3.2** (19 g, 29 mmol) was dissolved in ethanol (500 mL) and a solution of NaOH (23 g, 580 mmol) in water (500 mL) was added. The mixture was refluxed overnight. Most of ethanol was stripped off, and the aqueous solution was brought to pH~2-3 with 10% H_2SO_4. The white precipitate was extracted with diethyl ether continuous overnight (figure). Evaporation of the solvent gave title compound.

Yield: 14.5 g, 98 %, m.p. 110-112°C, white crystals.

IR (KBr): $\tilde{n}$ = 3446, 2940, 2550, 1681, 1494, 1278, 1143, 1079, 993, 898, 750, 698 cm^{-1};

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 6H, 2 x OC<u>H</u>$_3$), 4.84 (d, 4H, 2 x C<u>H</u>$_2$Ph), 6.79-7.17 (m, 10H, 2 x C_6H_5), 12.25 (s, 4H, 4 x OH) ppm;

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 49.26, 62.45, 110.13, 114.97, 126.53, 126.97, 128.06, 129.37, 136.98, 152.19, 160.98, 162.78 ppm;

MS (ESI): *m/z* (%): 547 (100) [M-H^+];

elemental analysis calcd. (%) for $C_{28}H_{24}N_2O_{10}$ (548.51): C 61.31, H 4.41, N 5.11; found: C 61.48, H 4.69, N 5.21.

5.3.4.6 1,1'-Dibenzyl-4,4'-dibutoxy-2,2'-bipyrrole-3,3',5,5'-tetracarboxylic acid (36c)

To a solution prepared from **5.3.3.3** (1.53 g, 2.05 mmol) and ethanol (15 mL) was added a solution of NaOH (1.64 g, 41 mmol) in H_2O (15 mL) and the mixture was refluxed under nitrogen for 24 h. Ethanol was removed in *vacuo* and the rest was acidified with H_2SO_4 (10 %) to pH~2-3. The acid **5.3.4.6** was extracted with ether (figure). Solvent evaporation gave orange crystals.

Yield: 1.24 g, 96 %; m.p. 90-100 °C, melting with decarboxylation, orange crystals.

IR (KBr): $\tilde{n}$ = 3418, 3032, 2961-2874, 1677, 1493, 1454, 1283, 1145, 1082, 956, 749, 699 cm^{-1};

^{1}H-NMR (250 MHz, DMSO-d6): δ = 0.89 (t, J = 7.33 Hz, 6H, 2 x $O(CH_2)_3C\underline{H}_3$), 1.40 (sext, J = 7.45 Hz, 4H, 2 x $OCH_2CH_2C\underline{H}_2CH_3$), 1.64 (pent, J = 7.03 Hz, 4H, 2 x $OCH_2C\underline{H}_2CH_2CH_3$), 3.95 (t, J = 6.54 Hz, 2H, $OC\underline{H}_2CH_2CH_2CH_3$), 3.97 (t, J = 6.54 Hz, 2H, $OC\underline{H}_2CH_2CH_2CH_3$), 4.83 (s, 4H, 2 x $C\underline{H}_2Ph$), 6.74-7.39 (m, 10H, 2 x $C_6\underline{H}_5$), 12.21 (s, br, 4H, COO$\underline{H}$) ppm;

^{13}C-NMR (63 MHz, $CDCl_3$): δ = 13.77, 18.51, 31.51, 49.19, 74.68, 110.20, 115.04,

126.45, 126.90, 127.98, 129.48, 137.02, 151.07, 161.02, 162.85 ppm;

MS (ESI): *m/z* (%): 632 (37) [M], 631 (100) [M-H^+];

elemental analysis calcd. (%) for $C_{34}H_{36}N_2O_{10}$ (632.67): C 64.55, H 5.74, N 4.43; found: C 65.34, H 6.01, N 4.52.

5.3.5 Thermic decarboxylation

5.3.5.1 1-Benzyl-3-methoxypyrrole (33b)

5.3.4.2 (5 g, 18 mmol) was decarboxylated during 1 h in a round bottom flask at 150 mBar and 220-230 °C using the heat gun (see Figure 5.2). The pressure was lowered to 2 mbar and pyrrole **33b** was distilled (bp. 160-170 °C). Obtained compound is colourless, air sensitive oil to be stored under argon.

Yield: 3.4 g, 95%; colourless oil;

IR (film): $\tilde{n}$ = 2933, 1564, 1339, 1043, 736 cm^{-1};

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 3.69 (s, 1H, OC$\underline{H}_3$), 4.95 (s, 1H, C$\underline{H}_2$Ph), 5.86 (d, *J* = 2.77 Hz, 1H, H4-pyrrole), 6.23 (s, 1H, H2-pyrrole), 6.48 (d, *J* = 2.77 Hz, 1H, H5-pyrrole), 7.08-7.37 (m, 5H, C_6H_5) ppm;

^{13}C-NMR (63 MHz, $CDCl_3$): δ = 53.90, 57.89, 97.29, 103.11, 119.30, 127.03, 127.65, 128.69, 138.17, 149.34 ppm;

MS (70 eV, EI): *m/z* (%): 187 (45) [M^+], 172 (9) [M^+-CH_3], 91 (100) [$C_7H_7^+$];

elemental analysis calcd. (%) for $C_{12}H_{13}NO$ (187.2): C 76.98, H 7.00, N 7.48; found: C 76.28, H 6.93, N 7.53.

5.3.5.2 1-Benzyl-3-butoxypyrrole (33c)

5.3.4.3 (2 g, 6.3 mmol) was decarboxylated during 1 h in a 10 mL round bottom flask at 150 mBar and 150-200 °C using the heat gun (see figure). The pressure was lowered and title pyrrole was distilled (0.013 mbar, 112-125 °C). Obtained compound is colourless, air sensitive oil, to be stored under argon.

Yield: 1.37 g, 95%; colourless oil;

IR (film): $\tilde{n}$ = 2959, 2933, 2870, 1717, 1560, 1503, 1455, 1335, 1173, 1072, 1029, 733, 698 cm^{-1};

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, J = 7.41 Hz, 3H, $O(CH_2)_3C\underline{H}_3$), 1.44 (sext, J = 7.57, 2H, $CH_2C\underline{H}_2CH_3$), 1.71 (pent, J = 7.14 Hz, 2H, $OCH_2C\underline{H}_2CH_2$), 3.80 (t, J = 6.59 Hz, 2H, $OC\underline{H}_2CH_2$), 4.94 (s, 2H, $C\underline{H}_2Ph$), 5.82-5.90 (m, 1H, H-pyrrole), 6.18-6.28 (m, 1H, H-pyrrole), 6.43-6.52 (m, 1H, H-pyrrole), 7.06-7.41 (m, 6H, Ph) ppm;

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.96, 19.30, 31.61, 53.84, 70.37, 97.55, 103.48, 119.20, 126.97, 127.62, 128.69, 138.22, 148.23 ppm;

MS (70 eV, EI): *m/z* (%): 229 (22) [$M^{+\cdot}$], 173 (25) [ΔC_4H_8], 91 (100) [$C_7H_7^+$];

HRMS (70eV, PI-EI) calcd. for $C_{15}H_{19}NO$: 229.1467; found *m/z*: 229.1471.

5.3.5.3 1-Benzyl-3-(2-methoxyethoxy)pyrrole (33d)

5.3.4.4 (3 g, 9.4 mmol) was decarboxylated during 1 h in a 10 mL round bottom flask at 150 mBar and 150-220 °C using the heat gun (see figure). The pressure was lowered and decarboxylated pyrrole was distilled (0.013 mbar, 125-135 °C). Obtained compound is colourless, air sensitive oil to be stored under argon.

Yield: 1.92 g, 88%; colourless oil;

IR (film): $\tilde{n}$ = 3030, 2980, 2923, 2877, 1818, 1559, 1505, 1454, 1332, 1199, 1176, 1128, 1076, 1030, 991, 899, 853 cm^{-1};

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.42 (s, 3H, $OC\underline{H}_3$), 3.63-3.71 (m, 2H, $OC\underline{H}_2CH_2O$), 3.94-4.00 (m, 2H, $OCH_2C\underline{H}_2O$), 4.94 (s, 2H, $C\underline{H}_2Ph$), 5.87-5.92 (m, 1H, H-pyrrole), 6.22-6.27 (m, 1H, H-pyrrole), 6.45-6.49 (m, 1H, H-pyrrole), 7.06-7.37 (m, 5H, Ph) ppm;

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 53.83, 59.17, 69.77, 71.28, 97.74, 103.79, 119.21, 126.92, 127.62, 128.69, 138.19, 147.85 ppm;

MS (70 eV, EI): *m/z* (%): 231 (19) [$M^{+\cdot}$], 173 (29) [$\Delta H_2C{=}CHOCH_3$], 91 (100) [$C_7H_7^+$];

HRMS (70eV, PI-EI) calcd. for $C_{14}H_{17}NO_2$: 231.1259; found *m/z*: 231.1258.

5.3.5.4 1,1'-Dibenzyl-4,4'-dimethoxy-2,2'-bipyrrole (37b)

Tetracarboxylic acid **5.3.4.6** (5 g, 9.1 mmol) was decarboxylated without solvent (200-230 °C, 150 mBar) in a similar manner to **5.3.5.1**. The dark residue was recrystallised from absolute ethyl acetate under argon to give colourless crystals of **37b.**

Yield: 2.34 g (70 %), m.p. 135-137 °C, colourless crystals.

IR (KBr): $\tilde{n}$ = 3440, 3066-2825, 1565, 1405, 1326, 1132, 1035, 771, 698, 630 cm^{-1};

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.37 (s, 6H, 2 x O$C\underline{H}_3$), 4.58 (s, 4H, 2 x $C\underline{H}_2$Ph), 6.08 (AB, 4H, $\underline{H}$-pyrrole), 6.77-7.05 (m, 10H, 2 x C_6H_5) ppm;

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 50.49, 57.20, 100.50, 104.14, 122.99, 126.98, 127.29, 128.63, 139.41, 149.33 ppm;

HRMS (70eV, PI-EI) calcd. for $C_{24}H_{24}N_2O_2$: 372.1838; found *m/z*: 372.1835.

5.3.5.5 1,1'-Dibenzyl-4,4'-dibutoxy-2,2'-bipyrrole (37c)

Tetracarboxylic acid **5.3.4.7** (0.78 g, 1.23 mmol) was dissolved in ethylene glycol (5 mL) under argon atmosphere and refluxed during 2.5 h. To the cooled reaction mixture (10 mL) water was added and the product was extracted with dichloromethane. Obtained dark-green solution was filtered through the silica to give almost colourless liquid. During evaporation of the solvent colourless crystals of the title compound were obtained.

Yield: 0.37 g (65 %), colourless crystals.

IR (KBr): $\tilde{n}$ = 3440, 3066-2825, 1565, 1405, 1326, 1132, 1035, 771, 698, 630 cm^{-1};

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.41 Hz, 6H, 2 x $O(CH_2)_3C\underline{H}_3$), 1.42 (sext, *J* = 7.14, 4H, 2 x $CH_2C\underline{H}_2CH_3$), 1.69 (pent, *J* = 7.27 Hz, 4H, 2 x $OCH_2C\underline{H}_2CH_2$), 3.77 (t, *J* = 6.59 Hz, 4H, 2 x $OC\underline{H}_2CH_2$), 4.79 (s, 4H, 2 x $C\underline{H}_2Ph$), 5.83 (d, *J* = 2.20 Hz, 2H, 2 x H-pyrrole), 6.23 (d, *J* = 2.20 Hz, 2H, 2 x H-pyrrole), 6.86-7.47 (m, 10H, 2 x Ph) ppm;

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.92, 19.26, 50.38, 70.23, 100.14, 104.40, 122.42, 126.82, 127.21, 128.49, 138.78, 147.37 ppm;

MS (70 eV, PI-EI): *m/z* (%): 456 (74) [$M^{+\cdot}$], 365 (45) [$\Delta^{\cdot}C_7H_7$], 91 (100) [$C_7H_7^{+}$];

5.3.6 Pyrrole ring deprotection

5.3.6.1 3-Methoxypyrrole (34b)

Compound **6** (0.25 g 11 mmol) was treated with Na/liquid NH_3 in the same way as described for **1** and **2**. Vacuum distillation of the crude material gave a colourless oil at ***RT,*** under argon, which crystallises in the freezer

Yield: 0.084 g (87 %), colourless oil.

IR (film): $\tilde{n}$ = 3402, 3000-2900, 2829, 1571 cm^{-1};

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 3.78 (s, 3H, $OC\underline{H}_3$), 5.99 (d, 1H, H4-pyrrole), 6.37 (s, 1H, H2-pyrrole), 6.59 (d, 1H, H5-pyrrole), 7.86 (s, 1H, NH) ppm;

^{13}C-NMR (63 MHz, $CDCl_3$): δ = 58, 97, 99, 117, 149 ppm;

MS (70 eV, EI): *m/z* (%): 97 (75) [M^+], 82 (100) [M^+-CH_3];

elemental analysis calcd. (%) for C_5H_7NO (97.12): C 61.84, H 7.26, N 14.42; found: C 61.51, H 7.28, N 14.57.

5.3.6.2 3-Butoxypyrrole (34c)

Compound **5.3.5.3** (0.3 g, 1.3 mmol) was treated with Na/NH_3 liquid (0.121 g, 5.2 mmol / ca. 10 mL) as described for **5.3.6.1**. Almost colourless oil was distilled at the "Kugelrohrdestillator" (0.067 Torr, heating t = 100-150 °C). Obtained colourless oil crystallised in the fridge.

Yield: 0.173 g (95 %), m.p. 35-36 °C, colourless crystals.

IR (KBr): $\tilde{n}$ = 3343, 2960, 2934, 2874, 1572, 1498, 1475, 1464, 1385, 1282, 1078, 1064, 1032, 1008, 973, 906, 880, 736 cm^{-1};

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.41 Hz, 3H, $O(CH_2)_3C\underline{H}_3$), 1.47 (sext, *J* = 7.46, 2H, $CH_2C\underline{H}_2CH_3$), 1.73 (pent, *J* = 7.14 Hz, 2H, $OCH_2C\underline{H}_2CH_2$), 3.85 (t, *J* = 6.59 Hz, 2H, $OC\underline{H}_2CH_2$), 5.89-5.97 (m, 1H, H-pyrrole), 6.29-6.38 (m, 1H, H-pyrrole), 6.52-6.61 (m, 1H, H-pyrrole), 7.65 (s, br, 1H, NH) ppm;

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.93, 19.29, 31.60, 70.47, 98.21, 99.88, 116.30, 148.20 ppm;

MS (70 eV, PI-EI): *m/z* (%): 139 (37) [$M^{+\cdot}$], 91 (11) [$C_7H_7^+$], 83 (100) [ΔC_4H_8];

HRMS (70eV, PI-EI) calcd. for $C_8H_{13}NO$: 139.0997; found *m/z*: 139.0994.

5.3.6.3 3-(2-Methoxyethoxy)pyrrole (34d)

Compound **5.3.5.4** (0.3 g, 1.29 mmol) was treated with Na/NH_3 liquid (0.119 g, 5.19 mmol / ca. 10 mL) as described for **5.3.6.1**. Evaporation of the solvent gave pale oil. Which after distillation in vacuum gave colourless liquid.

Yield: 0.172 g (94 %); colourless oil.

IR (film): $\tilde{n}$ = 3381, 2982-2821, 1567, 1495, 1454, 1282, 1128, 1082, 1029, 978, 878, 852, 745 cm^{-1};

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.44 (s, 3H, $OC\underline{H}_3$), 3.64-3.78 (m, 2H, $OC\underline{H}_2CH_2O$), 3.95-4.09 (m, 2H, $OCH_2C\underline{H}_2O$), 5.91-6.01 (m, 1H, H-pyrrole), 6.30-6.42 (m, 1H, H-pyrrole), 6.51-6.63 (m, 1H, H-pyrrole), 7.71 (s, br, 1H, NH) ppm;

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 59.16, 69.92, 71.29, 98.24, 100.34, 116.32, 147.77 ppm;
MS (70 eV, EI): *m/z* (%): 141 (31) [$M^{+\cdot}$], 83 (100) [$\Delta H_2C{=}CHOCH_3$];

HRMS (70eV, PI-EI) calcd. for $C_7H_{11}NO_2$: 141.0790; found *m/z*: 141.0793.

5.3.6.5 3,3'-Dimethoxy-2,2'-bipyrrole (41)

By using syringe techniques and strict argon protection, sodium (50 mg, 2.2 mmol) was dissolved in liquid ammonia (5-10 mL) at -60 to -70 °C. Compound **7** (0.1 g, 0.27 mmol) was dissolved in THF (2 mL) and added drop wise to the blue solution. After 2 h, the mixture was allowed to warm to ambient temperature, and a solution of $NaHCO_3$ (0.18 g, 2.2 mmol) in argon-saturated water (3 mL) was added carefully. When the excess sodium was completely dissolved, toluene (2 mL) was added, and the contents were stirred for 10 min. The toluene phase was removed by syringe under argon, and the extraction was repeated with toluene (2 mL). The total toluene solution was placed in a freezer at ≥ -20 °C, and **41** was obtained as colourless crystals. The crystal suspension is recommended for storage.

Yield: 36mg (70 %), m.p. 173-175 °C, colourless crystals;

UV/Vis (CH_3CN): λ_{max} = 286 nm, ε = 17210;

IR (KBr): $\tilde{\nu}$ = 3354, 2964, 1540, 1262, 1103, 1069, 1036, 803, 695 cm^{-1};

^{1}H-NMR (250 MHz, C_6D_6): δ = 3.44 (s, 6H, 2 x OC<u>H</u>$_3$), 5.93 (t, J = 3.07 Hz, 2H, 2 x H4-pyrrole), 6.16 (t, J = 3.07 Hz, 2H, 2 x H5-pyrrole), 8.49 (s, 2H, 2 x N<u>H</u>) ppm;

^{13}C-NMR (63 MHz, C_6D_6): δ = 58.19, 96.30, 113.35, 142.23 ppm;

HRMS (70eV, PI-EI) calcd. for $C_{10}H_{12}N_2O_2$: 192.0899; found *m/z*: 192.0896.

5.3.6.6 4,4'-Dimethoxy-2,2'-bipyrrole (38b)

Compound **5.3.6.6** was prepared from **5.3.5.4** in exactly the manner as described for **5.3.6.5**. Again, the product **5.3.6.6,** crystallised from the toluene solution at low temperature, was put in the freezer under argon. The crystal suspension is recommended for storage.

Yield: 32 mg (70 %); m.p. (black melt) ca. 130-140 °C, colourless crystals.

UV/Vis (CH_3CN): λ_{max} = 286 nm, ε = 11937;

IR (KBr): $\tilde{\nu}$ = 3354, 2964, 1540, 1262, 1103, 1069, 1036, 803, 695 cm^{-1};

^{1}H-NMR (250 MHz, C_6D_6): δ = 3.51 (s, 6H, 2 OC<u>H</u>$_3$), 5.87 (s, 4H, 4 x H-pyrrole), 6.48 (s, br, 2H, 2 N<u>H</u>) ppm;

^{1}H-NMR (250 MHz, CD_2Cl_2): δ = 3.70 (s, 6H, 2 OC<u>H</u>$_3$), 5.90 (t, J = Hz, 4H, 4 x H-pyrrole), 6.48 (s, 2H, 2 x N<u>H</u>) ppm;

^{13}C-NMR (63 MHz, C_6D_6): δ = 57.51, 93.69, 98.99 ppm;

In both solvents, the fourth quaternary-carbon signal (C2,2') was too weak to be observed in NMR spectra.

MS-CI: *m/z* (%) = 193 (100) [MH^+], 373 (100) [MH^+];

HRMS (70eV, PI-EI) calcd. for $C_{10}H_{12}N_2O_2$: 192.0899; found *m/z*: 192.0896.

5.3.6.7 4,4'-Dibutoxy-2,2'-bipyrrole (38c)

Compound **38c** was prepared from solution of **5.3.5.5** (0.182 g, 0.399 mmol) in THF (6 mL) and sodium (0.073 mg, 3.19 mmol) in exactly the manner as described for **5.3.6.5**. Again, the product **38c,** crystallised from the toluene solution at low temperature, was put in the freezer under argon. The crystal suspension is recommended for storage.

Yield: 76 mg (70 %); was not possible to measure m.p., after 100 °C crystals turned to black, with heating to 200 °C no melting was observed, colourless crystals.

IR (KBr): $\tilde{n}$ = 3354, 2964, 1540, 1262, 1103, 1069, 1036, 803, 695 cm^{-1};

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.41 Hz, 6H, 2 x $C\underline{H}_3$), 1.47 (sext, *J* = 7.63 Hz, 4H, 2 x $OCH_2CH_2C\underline{H}_2CH_3$), 1.73 (pent, *J* = 7.27 Hz, 4H, 2 x $OCH_2C\underline{H}_2CH_2CH_3$), 3.86 (t, *J* = 6.45 Hz, 4H, $OC\underline{H}_2CH_2CH_2CH_3$), 5.86-5.96 (m, 2H, 2 x H-pyrrole), 6.23-6.36 (m, 2H, 2 x H-pyrrole), 7.55 (s, br, 2H, NH) ppm;

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 13.91, 19.27, 31.53, 70.41, 93.82, 99.51, 148.85 ppm;
The fourth quaternary-carbon signal (C2,2') was too weak to be observed in NMR spectra.

MS (FD): *m/z* (%): 276 (100) [M^+];

HRMS (70eV, PI-EI) calcd. for $C_{16}H_{24}N_2O_2$: 276.3764; found *m/z*: 276.3768.

5.4 Syntheses and properties of aminopyrroles

5.4.1 Nitropyrrole ring formation

5.4.1.1 Isonitrosoacetoacetic ester

To the solution of fresh distilled acetoacetic ethyl ester (109 g, 0.84 mol) in glacial acetic acid (130.8 g), in the two-necked round bottom flask with thermometer under cooling was dropped saturated solution of $NaNO_2$ (63.64 g, 0.92 mol) in water so, that the temperature in the flask doesn't exceed 10 °C. After addition of the $NaNO_2$ solution the reaction mixture was poured into ice-water (550 mL) and left overnight. Then the mixture was extracted with diethyl ether and the organic phase was dried over sodium sulphate. Solvent evaporation gave the crude material (140 g), which can be directly used for the next step.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 1.35 (t, J = 7.13, 3H, CH_2-C<u>H</u>$_3$), 2.41 (s, 1H, O=C-C<u>H</u>$_3$), 4.38 (q, J = 7.13, 2H, C<u>H</u>$_2$-CH_3), 10.03 (s, br, 1H, OH) ppm;

5.4.1.2 Ethyl nitroacetate

To isonitrosoacetoacetic ester **5.4.1.1** (76 g) in the Erlenmeyer flask under intensive stirring and cooling with ice was slowly added the mixture of the saturated solution prepared from $Na_2Cr_2O_7$ (57 g, 190 mmol) in water and diluted H_2SO_4 (122 mL, 1:1). Then the reaction mixture was stirred for 5 minutes until the colour become green, and extracted with ether. The organic phase was dried over Na_2SO_4 and the solvent was evaporated. The rest (52.6 g) was distilled in vacuum (0.05 Torr, 40-48 °C) to give slightly yellow oil.

Yield: 24.3 g, (47 %), slightly-yellow oil.

IR (film): $\tilde{n}$ = 3036, 2986, 2945, 1754, 1566, 1471, 1460, 1372, 1337, 1265, 1221, 1097, 1025, 860, 768, 689 cm^{-1};

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.33 (s, CH_3), 4.32 (s, O-C<u>H</u>$_2$), 5.20 (N-C<u>H</u>$_2$) ppm;

^{13}C-NMR (23 MHz, $CDCl_3$): δ = 13.92, 63.30, 76.53, 162.20 ppm;

MS (75 eV, EI): *m/z* (%): 88 (100), 87 (43), 74 (14), 59 (43); 45 (27), 44 (11), 43 (21), 42 (38), 31 (11), 30 (20), 29 (58), 28 (16), 27 (20);

elemental analysis calcd. (%) for $C_4H_7NO_4$ (133.10): C 36.10, H 5.30, N 10.52; found: C 36.05, H 5.32, N 10.58.

5.4.1.3 2,3-Dibromfumaraldehydic acid (51) []

In the round bottom flask with a stirrer, dropping funnel and backflow condenser was prepared suspension from furfural (10 g, 104 mmol) and water (90 mL). To the suspension was added bromine (25 ml, 488 mmol) with vigorous stirring thus, so during first 30 seconds was dropped ~12.5 mL of bromine, and then every minute ~2.5 mL. In the beginning mixture vigorously was boiled and keep boiling further by bromine dropping. Some amount of bromine was flown out through the condenser. After addition of all Br_2 amount mixture was heated. After 5 min the condenser and the dropping funnel were took out and the thermometer was plugged in the flask, the second neck was left open till the end of bromine traces evaporation. During this procedure the temperature in the flask should not be higher than 122 °C. Almost colourless solution was poured into the glass and cooled down on the ice bath. Precipitated crystals were filtered out and washed with 1 % sodium disulphite solution, water and dried in the air. Obtained acid (17.9 g, 65%) is white crystals.

Yield: 17.9 g (65 %), m.p. 120-121 °C, white crystals.

5.4.1.4 *a,b,b*-Trinitropropionic aldehyde dipotassium salt (52) []

To the solution of 2,3-dibromfumaraldehydic acid (17.9 g, 65 mmol) in ethanol (35 mL) was added concentrated solution of KNO_2 (22.4 g, 263 mmol) in water (6.8 mL). The mixture warmed up and the liberation of gas can be observed. From time to time the reaction mixture was cooled with water thus, that temperature in the flask was 30-35 °C.

After 30 min stirring, the mixture was cooled down and precipitated orange salt (32.9 g) was separated. Obtained product was used for the next syntheses without purification. For the safety work (the salt explodes by hitting) the wet salt can be dissolved in water and small amount of ammonia (product is not stable in neutral and especially in acid media) and so used for further steps. Necessarily the salt can be precipitated with ethanol from water.

5.4.1.5 Ethyl ethoxymethylenenitroacetate (42)

A mixture of **5.4.1.2** (10 g, 75 mmol), triethyl orthoformate (22.3 g, 150 mmol) and acetic anhydride (21.5 g, 200 mmol) were heated for 1 h at 120 °C and for a next 1 h at 130 °C in a distillation apparatus. The reaction mixture was finally heated at 140 °C and the colourless distillate (ca. 30 mL, 77-84 °C) was collected. The excess of triethyl orthoformate and acetic anhydride was removed under reduced pressure (0.05 Torr, 92-106 °C) to give the yellow liquid (15 g, 98%), which contains *Z*- and *E*- products in ratio 73:27 respectively.

Z-isomer:
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7.2 Hz, 3H, CH_2-C<u>H</u>$_3$), 1.43 (t, *J* = 7.2, 3H, CH_2-C<u>H</u>$_3$), 4.30 (q, *J* = 7.2 Hz, 2H, C<u>H</u>$_2$-CH_3), 4.31 (q, *J* = 7.2 Hz, 2H, C<u>H</u>$_2$-CH_3), 7.52 (s, 1H, CH) ppm;

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.05, 15.11, 61.88, 73.93, 127.01, 155.94, 159.81 ppm;
MS (70 eV, EI): *m/z* (%): 190 (5) [M+1], 189 (49) [M^+], 172 (36), 144 (60), 116 (55), 115 (100), 99 (61), 88 (63), 87 (54), 86 (70), 71 (85), 70 (56);

E-isomer:
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 7.2 Hz, 3H, CH_2-C<u>H</u>$_3$), 1.46 (t, *J* = 7.2, 3H, CH_2-C<u>H</u>$_3$), 4.35 (q, *J* = 7.2 Hz, 2H, C<u>H</u>$_2$-CH_3), 4.36 (q, *J* = 7.2 Hz, 2H, C<u>H</u>$_2$-CH_3), 8.22 (s, 1H, CH) ppm;

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 13.92, 15.15, 61.97, 74.60, 129.35, 159.06, 162.86 ppm;

MS (70 eV, EI): *m/z* (%): 190 (5) [M+1], 189 (37) [M^+], 144 (96), 116 (65), 115 (100), 99 (56), 88 (62), 86 (77), 71 (93);

5.4.1.6 Sarcosine ethyl ester

Sarcosine ethyl ester was prepared by passing, dried with KOH, ammonia through a suspension of sarcosine ethyl ester hydrochloride (18.7 g, 122 mmol) and diethyl ether (100 mL) cooled to -10-20 °C, under intensive stirring during 1.5-2 h. After getting the mixture to the room temperature the precipitate was filtered out and evaporating of ether gave colourless liquid with a typical smell of amine.

Yield: 14 g (quantitative), colourless oil;

IR (film): $\tilde{n}$ = 3351, 2980, 2939, 2911, 2798, 1740, 1372, 1203, 1175, 1125, 1030 cm^{-1};
^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.28 (t, *J* = 7.14 Hz, 3H, CH_2-C<u>H</u>$_3$), 2.44 (s, 3H, N-C<u>H</u>$_3$), 3.36 (s, 2H, N-C<u>H</u>$_2$-C=O), 4.19 (q, *J* = 7.14, 2H, C<u>H</u>$_2$-CH_3) ppm;

5.4.1.7 Ethyl-1-[(2-(nitro-2-ethoxycarbonyl)vinyl)]sarcosinate (43)

Sarcosine ethyl ester (14.3 g, 120 mmol) was added to **5.4.1.5** (22.95 g, 120 mmol) at room temperature without solvent under vigorous stirring, an exothermic reaction occurred, and a dark orange-brown mixture was obtained. The reaction mixture was stirred at room temperature for 2 h. Compound **43** was used for the next step without any treatment. Obviously, both *Z*-, *E*- isomers were obtained, but at the next stage only *E*-isomer forms corresponding pyrrole.

MS (70 eV, EI): *m/z* (%): 261 (1) [M^++1], 260 (12) [M^+], 187 (37), 159 (100), 113 (41), 85 (72), 42 (70).

5.4.1.8 Ethyl 1-methyl-4-nitro-3-hydroxypyrrole-2-carboxylate (44)

To a solution of crude **5.4.1.7** (69.8 g) in absolute ethanol (100 mL) was added a solution of sodium ethoxide prepared from sodium (8.65 g, 380 mmol) and absolute ethanol (220 mL), and the reaction mixture was refluxed under nitrogen atmosphere for 2 h to afford a thick dark-brown solution. Ethanol was removed in *vacuo* to give a dark-brown residue. The rest was dissolved in water (300 mL) and acidified with 20 % H_2SO_4 to give a brown precipitate. Then the mixture was extracted with CH_2Cl_2, washed with brine and dried over sodium sulphate. Solvent evaporation gave dark solid (39 g), which was dissolved in CH_2Cl_2 and passed through the column with Silica gel (ca. 200 g). Removal of the solvent gave the dark solid (15.4 g). Which after recrystallisation from ethanol afforded light-yellow crystals.

Yield: 14 g (25%), m.p. 128-130 °C, light-yellow crystals.

IR (KBr): $\tilde{n}$ = cm^{-1};

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.41 (t, *J* = 7.2 Hz, 3H, CH_2-C<u>H</u>$_3$), 3.88 (s, 3H, N-CH_3), 4.41 (q, *J* = 7.2 Hz, 2H, C<u>H</u>$_2$-CH_3), 7.40 (s, 1H, H5-pyrrole), 8.85 (s, 1H, OH) ppm;

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.35, 38.77, 61.06, 107.45, 123.44, 125.24, 147.42, 161.52 ppm;

MS (70 eV, EI): *m/z* (%): 215 (3) [M+1], 214 (30) [M^+], 168 (100), 152 (26), 140 (14), 94 (8), 53 (19), 42 (11);

elemental analysis calcd. (%) for $C_8H_{10}N_2O_5$ (214.18): C 44.86, H 4.70, N 13.07; found: C 44.97, H 4.76, N 12.97.

5.4.1.9 Ethyl 1-methyl-4-nitro-3-methoxypyrrole-2-carboxylate (45)

To a solution of **5.4.1.8** (5 g, 23 mmol) in dry acetone (150 mL) under nitrogen was added potassium carbonate (8.2 g, 58 mmol), as the salt was added the colour of the solution was changed to orange, and dimethyl sulphate (3 g, 25 mmol), and the reaction mixture was refluxed overnight. When the reaction was over, potassium carbonate was filtered out (as an orange precipitate) and the acetone was evaporated on the rotary evaporator to give an almost white crystalline solid. By washing with aqueous ammonia (20 mL) was destroyed the rest of the dimethyl sulphate. Water (60 mL) was added and the mixture was extracted with ether. The organic phase was dried with sodium sulphate and the solvent evaporation and recrystallisation from ethyl acetate gave colourless needles.

Yield: 3 g (57 %), m.p. 138-140 °C, colourless needles;

IR (KBr): $\tilde{n}$ = 3138, 2995, 2947, 1690, 1560, 1517, 1498, 1447, 1376, 1333, 1288, 1176, 1103, 1068, 1016, 987, 896, 844, cm^{-1};

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.40 (t, *J* = 7.2 Hz, 3H, CH_2-C<u>H</u>$_3$), 3.91 (d, *J* = 0.58 Hz, 3H, N-CH_3), 3.95 (s, 3H, O-CH_3), 4.36 (q, *J* = 7.2 Hz, 2H, C<u>H</u>$_2$-CH_3), 7.48 (q, *J* = 0.58 Hz, 1H, H5-pyrrole) ppm;

FID file obtained from the NMR-device was mathematically processed in WINNMR program with “Windows Function” (Lorenz-Gauss multiplication, LB=-0.550 Hz, GB=41.000 %), “Zero Filling”=512k and Fourier Transformation;

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 14.22, 38.92, 60.67, 63.02, 114.73, 125.76, 127.79, 146.18, 160.09 ppm;

MS (70 eV, EI): *m/z* (%): 229 (3) [M+1], 228 (30) [M^+], 152 (100), 53 (31);

elemental analysis calcd. (%) for $C_9H_{12}N_2O_5$ (228.20): C 47.37, H 5.29, N 12.27; found: C 47.44, H 5.36, N 12.28.

5.4.1.10 1-Methyl-4-nitro-3-methoxypyrrole-2-carboxylic acid (46)

A solution prepared from NaOH (0.5 g, 12 mmol) and water (10 mL) was added to a solution of **5.4.1.9** (0.94 g, 4.1 mmol) and ethanol (15 mL) and the mixture was refluxed for 1 h. Ethanol was removed *in vacuo* and the rest was acidified with H_2SO_4 (10 %) to pH≈2-3 under cooling. The acid **46** was extracted with diethyl ether overnight. After removal of the solvent were obtained slightly-brown crystals (0.8 g, 95 %), m.p. ~180 °C. At this temperature together with melting starts decarboxylation.

Yield: 0.8 g (95 %), m.p. ~180 °C (melts with destruction), slightly-brown crystals;

IR (film): $\tilde{n}$ = 3440, 3136, 3027, 2951, 2890, 2638, 1669, 1558, 1523, 1499, 1445, 1412, 1368, 1336, 1302, 1179, 1161, 1103, 1070, 986, 887, 835, 784, 759, 718 cm^{-1};

^{1}H-NMR (300 MHz, DMSO-d6): δ = 3.43 (s, br, CO<u>OH</u>), 3.81 (s, 3H, NCH_3), 3.83 (s, 3H, OCH_3), 8.09 (s, 1H, H5-pyrrole) ppm;

^{13}C-NMR (75 MHz, DMSO-d6): δ = 38.22, 62.31, 114.56, 126.42, 126.97, 145.09, 160.53 ppm;

MS (70 eV, PI-EIMS): *m/z* (%): 200 (48) [$M^{+\cdot}$],·183 (9) [Δ·OH], 167 (16), 152 (86), 142 (50), 67 (12), 53 (40), 49 (13), 44 (53), 42 (100);

elemental analysis calcd. (%) for $C_7H_8N_2O_5$ (200.15): C 42.01, H 4.03, N 14.00; found: C 41.98, H 4.04, N 14.06.

5.4.1.11 1-Methyl-4-nitro-3-methoxypyrrole (47)

Acid **5.4.1.10** (0.8 g, 3.9 mmol) in the round bottom flask was decarboxylated under vacuum (100-180 mbar) and heating (150-200 °C) during 1 h. Dark solid obtained after heating was partially dissolved in CH_2Cl_2 and passed through the column with 12 g Silica gel. Evaporation of the solvent gave canary crystals.

Yield: 0.57 g (95 %), m.p. 92-93 °C, canary crystals;

IR (film): $\tilde{n}$ = 3142, 3130, 2965, 2941, 2839, 1580, 1531, 1460, 1426, 1393, 1335, 1232, 1196, 1172, 1128, 1089, 1012, 845, 802, 758, 721, 623, 598, 586 cm^{-1};

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.64 (d, J = 0.55 Hz, 3H, N-CH_3), 3.82 (s, 3H, O-CH_3), 6.11 (d, J = 2.85 Hz, 1H, H2-pyrrole), 7.32 (d, J = 0.55 Hz, 1H, H5-pyrrole) ppm;

FID file obtained from the NMR-device was mathematically processed in WINNMR program with "Windows Function" (Lorenz-Gauss multiplication, LB = -0.800 Hz, GB = 60.000 %), "Zero Filling"=512k and Fourier Transformation;

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 37.87, 58.61, 104.11, 121.52, 143.49 ppm;

MS (CI, NH_3): *m/z* (%): 191 (7), 174 (100) [$M+NH_4^+$], 157 (12) [MH^+];

elemental analysis calcd. (%) for $C_6H_8N_2O_3$ (156.14): C 46.15, H 5.16, N 17.94; found: C 46.52, H 5.30, N 18.51.

5.4.1.12 1-Methyl-3,4-dinitropyrrole (53a)

To the fresh prepared solution of trinitropropionic aldehyde dipotassium salt (32.9 g) - amount obtained from 17.9 g 2,3-dibromfumaraldehydic acid, in water (100 mL) with some drops of NH_4OH under stirring was added methylamine hydrochloride (9.8 g, 145 mmol) and in 1-2 minutes 12 mL 35% formaldehyde solution. The reaction mixture warms up and foams and it was stirred overnight. Precipitate was separated and after drying at 100-110 °C brown crystals were obtained.

Yield: 3.8 g (35 % - calculated through 2,3-dibromfumaraldehydic acid), m.p. 162-166 °C, brown fine crystals;

IR (KBr): $\tilde{n}$ = 3125, 1539, 1526, 1485, 1466, 1447, 1385, 1325, 1308, 1130, 1105, 1072, 874, 858, 806, 750, 650, 608, 469 cm^{-1};

^{1}H-NMR (300 MHz, DMSO-d6): δ = 3.74 (s, 3H, CH_3), 8.11 (s, 2H, H2,H5-pyrrole) ppm;

^{13}C-NMR (75 MHz, DMSO-d6): δ = 37.47, 126.32, 128.45 ppm;

MS (70 eV, EI): *m/z* (%): 171 (88) [$M^{+\cdot}$], 141 (26) [ΔNO], 125 (4) [ΔNO_2], 67 (16), 42 (100), 28 (73);

elemental analysis calcd. (%) for $C_5H_5N_3O_4$ (171.11): C 35.10, H 2.95, N 24.56; found: C 34.69, H 2.99, N 24.04.

5.4.1.13 1-Benzyl-3,4-dinitropyrrole (53b)

To the solution of trinitropropionic aldehyde dipotassium salt (30 g) – amount obtained from 16.9 g 2,3-dibromfumaraldehydic acid in water (100 mL) with some drops of NH_4OH was added 5.5 mL of 35% formaldehyde solution and benzylamine hydrochloride (5.1 g, 36 mmol). The mixture was shaken vigorously and then allowed to stand for 3-4 hours. The reaction started after 10-15 minutes after the mixing of the reactants with heat evolution and some liberation of gas. The precipitated fine crystals together with resinous products was separated, washed with water and dried in the air. After recrystallisation from methanol slightly yellow crystals (3.1 g, 20 % – calculated over 2,3-dibromfumaraldehydic acid) were obtained, m.p. 107-108 °C.

IR (KBr): $\tilde{n}$ = 3125, 3115, 1545, 1531, 1456, 1449, 1439, 1391, 1356, 1342, 1300, 1206, 1167, 1121, 858, 804, 783, 748, 718, 635, 501 cm^{-1};

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.09 (s, 2H, C$\underline{H}_2$-Ph), 7.21-7.53 (m, 5H, C_6H_5), 7.43 (s, 2H, H2,H5-pyrrole) ppm;

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 55.45, 123.07, 128.29, 129.66, 129.70, 132.86 ppm;

MS (70 eV, EI): *m/z* (%): 247 (16) [$M^{+\cdot}$], 91 (100) [$C_7H_7^+$];

elemental analysis calcd. (%) for $C_{11}H_9N_3O_4$ (247.21): C 53.54, H 3.67, N 17.00; found: C 53.43, H 3.73, N 17.13.

5.4.2 Nitro compounds reduction

5.4.2.1 1-Methyl-3-amino-4-methoxypyrrole (48)

To a solution prepared from **5.4.1.11** (0.1 g, 0.64 mmol) and saturated with argon methanol (7 mL) was added Pd/C 10 % (20 mg), and the mixture was stirred at room temperature under hydrogen for 1 h. Then the solution was filtered under argon through the layer of celite and the solvent was evaporated in vacuum. The oily slightly-green residue, was dried in *vacuo* and directly used for the next step or electrochemical experiments. Compound **48** is quite sensitive to oxygen. Within minutes was taken from light-green to brown colour.

Yield: 70 mg (85%), slightly-green oil;

IR (film): $\tilde{n}$ = 3397, 3327, 2933, 1645, 1585, 1556, 1454, 1386, 1209, 1165, 1109, 1031, 746 cm^{-1};

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 2.87 (s, br, 2H, NH_2), 3.46 (s, 3H, N-CH_3), 3.70 (s, 3H, O-CH_3), 6.01 (d, *J* = 2.74 Hz, 1H, *a*H-pyrrole), 6.06 (d, *J* = 2.74 Hz, 1H, *a*H-pyrrole) ppm;

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 36.53, 58.34, 102.74, 108.86, 119.27, 140.62 ppm;

MS (70 eV, PI-EI): *m/z* (%): 235 (15), 126 (100) [$M^{+\cdot}$], 111 (99) [$\Delta\cdot CH_3$], 84 (19), 49 (26), 42 (52);

HRMS (70 eV, PI-EI) calcd. for $C_6H_{10}N_2O$: 126.0793; found *m/z*: 126.0793.

5.4.2.2 1-Methyl-3-amino-4-nitropyrrole (56a)

To a solution prepared from 1-methyl-3,4-dinitropyrrole (0.05 g, 0.29 mmol) and absolute ethyl acetate (10 mL) was added Pd/C 10 % (15 mg) and the mixture was stirred at room temperature under hydrogen during 48 hours. Then the reaction mixture was filtered under argon through the layer of celite. Obtained light-orange solution after solvent evaporation gave dark-red crystals.

Yield: 0.081 g (98 %); dark-red crystals.

IR (KBr): $\tilde{n}$ = 3442, 3346, 3138, 1605, 1572, 1529, 1479, 1454, 1437, 1402, 1346, 1332, 1238, 1178, 1131, 1086, 1006, 806, 758, 705, 618, 599 cm^{-1};

^{1}H-NMR (300 MHz, DMSO-d6): δ = 3.55 (s, 3H, N-CH_3), 5.10 (s, 2H, NH_2), 6.10 (d, *J* = 2.83, 1H, H2-pyrrole), 7.49 (d, *J* = 2.83, 1H, H5-pyrrole) ppm;

^{13}C-NMR (75 MHz, DMSO-d6): δ = 36.92, 104.96, 119.94, 125.13, 131.23 ppm;

MS (70 eV, PI-EI): *m/z* (%):141 (100) [$M^{+\cdot}$], 107 (27), 54 (18), 42 (24);

HRMS (70eV, PI-EI) calcd. for $C_5H_7N_3O_2$: 141.0540; found *m/z*: 141.0538.

5.4.2.3 1-Benzyl-3-amino-4-nitropyrrole (56b)

To a solution prepared from 1-benzyl-3,4-dinitropyrrole (0.1 g, 0.41 mmol) and dry ethyl acetate (10 mL) was added Pd/C 10 % (10 mg) and the mixture was stirred at room temperature under hydrogen overnight. Then the reaction mixture was filtered under argon through the layer of celite. Obtained light-orange solution after solvent evaporation gave dark-red crystals.

Yield: 0.087 g (99 %); dark-red crystals.

^{1}H-NMR (300 MHz, DMSO-d6): δ = 4.32 (s, br, 2H, NH_2), 4.92 (s, 2H, CH_2), 6.06 (d, *J* = 2.74, 1H, H2-pyrrole), 7.13-7.24 (m, 2H, Ph), 7.30 (d, *J* = 2.74, 1H, H5-pyrrole), 7.33-7.44 (m, 3H, Ph) ppm;

^{13}C-NMR (75 MHz, DMSO-d6): δ = 55.45, 105.95, 120.93, 124.15, 130.35, 127.27, 128.64, 128.50, 133.85 ppm;

MS (CI, NH_3): *m/z* (%): 218 (100) [MH^+];

HRMS (70eV, PI-EI) calcd. for $C_{11}H_{11}N_3O_2$: 217.1535; found *m/z*: 217.1538.

5.4.2.4 1-Methyl-3,4-diaminopyrrole (54a)

To a solution prepared from 1-methyl-3,4-dinitropyrrole (0.15 g, 0.88 mmol) and absolute methanol (50 mL) was added Pd/C 10 % (20 mg) and the mixture was stirred at room temperature under hydrogen for 14 days. During this time was used 830 mL of hydrogen. Then the reaction mixture was filtered under argon through the layer of celite. Obtained solution was almost colourless but due to extreme sensitivity of diamine to air the solution became dark quickly. After solvent removal in vacuum, brown-red oil was obtained.

Yield: 0.095 g (99 %); dark thick oil.

^{1}H-NMR (300 MHz, DMSO-d6): δ = 3.17 (s, 4H, 2 x NH_2), 3.29 (s, 3H, NCH_3), 5.85 (s, 2H, 2 x *a*H-pyrrole) ppm;

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 34.63, 98.76, 121.23 ppm;

MS (CI, NH_3): *m/z* (%): 112 (100) [MH^+];

HRMS (70eV, PI-EI) calcd. for $C_5H_9N_3$: 111.0447; found *m/z*: 111.0449.

5.4.2.5 1-Benzyl-3,4-diaminopyrrole (54b)

To a solution prepared from 1-benzyl-3,4-dinitropyrrole (0.1 g, 0.405 mmol) and absolute methanol (40 mL) was added Pd/C 10 % (20 mg) and the mixture was stirred at room temperature under hydrogen for 14 days. During this time was used 410 mL of hydrogen. The reaction mixture was treated in the same way as for **5.4.2.4**. Solvent evaporation gave brown-red oil.

Yield: 0.074 g, 98%; brown-red thick oil.

^{1}H-NMR (300 MHz, DMSO-d6): δ = 3.17 (s, 4H, 2 x NH_2), 4.72 (s, 2H, PhC$\underline{H}_2$), 5.96 (s, 2H, 2 x *a*H-pyrrole), 6.95-7.49 (m, 5H, C_6H_5) ppm;

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 52.11, 106.06, 123.63, 126.76, 126.79, 128.08 ppm;

MS (CI, NH_3): *m/z* (%): 188 (100) [MH^+];

HRMS (70eV, PI-EI) calcd. for $C_{11}H_{13}N_3$: 187.1405; found *m/z*: 187.1408.

5.4.3 Amino derivatives methylation

5.4.3.1 1-Methyl-3-dimethylamino-4-methoxypyrrole (49)

In dry acetone (5 mL) under argon was dissolved **5.4.2.1** (100 mg, 0.79 mmol), followed by potassium carbonate (329 mg, 2.38 mmol) addition. Then was added solution prepared from dimethyl sulphate (90 mg, 0.71 mmol) and acetone (2 mL). The reaction mixture was refluxed overnight. Potassium carbonate was filtered out under argon and after solvent evaporation was obtained brown residue. This mixture contains ca. 10 % of (**49**) and the rest is trimethylammonium salt (**49b**).

All given analysis data are for trimethylammonium salt **49b.**

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.54 (s, 3H, N-CH_3), 3.58 (s, 9H, N(CH_3)$_3$), 3.62 (s, 3H, CH_3SO_4), 3.69 (s, 3H, OCH_3), 6.16 (d, *J* = 2.74 Hz, 1H, H5-pyrrole), 7.03 (d, *J* = 2.74 Hz, 1H, H2-pyrrole) ppm;

^{13}C-NMR (100 MHz, $CDCl_3$): δ = 37.29, 54.25, 56.63, 58.38, 104.70, 113.14, 119.69, 139.46 ppm;

MS (70 eV, PI-EI): *m/z* (%):154 (100) [$M^{+\cdot}$], 139 (32) [$\Delta\cdot CH_3$], 110 (25) [$\Delta\cdot N(Me)_2$];

HRMS (70eV, PI-EI) calcd. for $C_8H_{14}N_2O$: 154.1106; found *m/z*: 154.1107.

Appendix A

X-Ray structures description

Data processing and graphical presentation of the obtained roentgen spectra were performed by means of the program ORTEP-3 for Windows [105].

Diethyl 1-benzyl-3-hydroxy-2,4-dicarboxylate 21a

Bond lengths [Å]

C1-N1	1.460	C6-C7	1.384	C11-N1	1.337	C16-C17	1.498
C1-C2	1.517	C7-C6	1.384	C11-C10	1.391	C17-C16	1.498
C2-C3	1.388	C7-C2	1.390	C12-O2	1.205	N1-C11	1.337
C2-C7	1.390	C8-C9	1.388	C12-O3	1.339	N1-C8	1.394
C2-C1	1.517	C8-N1	1.394	C12-C10	1.460	N1-C1	1.460
C3-C4	1.383	C8-C15	1.434	C13-O3	1.450	O1-C9	1.346
C3-C2	1.388	C9-O1	1.346	C13-C14	1.493	O2-C12	1.205
C4-C3	1.383	C9-C8	1.388	C14-C13	1.493	O3-C12	1.339
C4-C5	1.384	C9-C10	1.407	C15-O5	1.222	O3-C13	1.450
C5-C6	1.383	C10-C11	1.391	C15-O4	1.335	O4-C15	1.335
C5-C4	1.384	C10-C9	1.407	C15-C8	1.434	O4-C16	1.452
C6-C5	1.383	C10-C12	1.460	C16-O4	1.452	O5-C15	1.222

Bond angles (degrees)

N1-C1-C2	112.77	N1-C8-C15	129.26	O3-C13-C14	107.52
C3-C2-C7	118.86	O1-C9-C8	125.13	O5-C15-O4	123.16
C3-C2-C1	121.50	O1-C9-C10	126.85	O5-C15-C8	121.19
C7-C2-C1	119.59	C8-C9-C10	108.02	O4-C15-C8	115.65
C4-C3-C2	120.35	C11-C10-C9	106.09	O4-C16-C17	108.10
C3-C4-C5	120.42	C11-C10-C12	122.64	C11-N1-C8	108.85
C6-C5-C4	119.63	C9-C10-C12	131.27	C11-N1-C1	123.82
C5-C6-C7	119.97	N1-C11-C10	109.92	C8-N1-C1	127.18
C6-C7-C2	120.73	O2-C12-O3	123.81	C12-O3-C13	115.67
C9-C8-N1	107.12	O2-C12-C10	124.50	C15-O4-C16	115.72
C9-C8-C15	123.62	O3-C12-C10	111.68		

Torsion angles (degrees)

C12-O3-C13-C14	166.10	C3-C4-C5-C6	-1.30
C13-O3-C12-O2	-0.50	C4-C5-C6-C7	0.80
C13-O3-C12-C10	179.27	C5-C6-C7-C2	0.70
C16-O4-C15-O5	-3.16	N1-C8-C15-O5	-177.80
C16-O4-C15-C8	176.27	C15-C8-C9-O1	-1.20
C15-O4-C16-C17	-171.59	C9-C8-C15-O4	-178.03
C11-N1-C1-C2	100.61	N1-C8-C9-C10	-1.11
C1-N1-C8-C9	176.62	C9-C8-C15-O5	1.40
C8-N1-C1-C2	-74.41	C15-C8-C9-C10	179.53
C11-N1-C8-C15	-179.71	N1-C8-C15-O4	2.80
C1-N1-C11-C10	-176.28	N1-C8-C9-O1	178.15
C11-N1-C8-C9	0.98	O1-C9-C10-C11	-178.41
C1-N1-C8-C15	-4.10	O1-C9-C10-C12	0.90
C8-N1-C11-C10	-0.47	C8-C9-C10-C11	0.83
N1-C1-C2-C3	-27.70	C8-C9-C10-C12	-179.85
N1-C1-C2-C7	154.60	C9-C10-C12-O3	-0.40
C1-C2-C3-C4	-176.33	C11-C10-C12-O3	178.83
C3-C2-C7-C6	-1.80	C11-C10-C12-O2	-1.40
C7-C2-C3-C4	1.40	C12-C10-C11-N1	-179.62
C1-C2-C7-C6	175.92	C9-C10-C12-O2	179.39
C2-C3-C4-C5	0.20	C9-C10-C11-N1	-0.23

Tetraethyl 1,1'-dibenzyl-4,4'-dimethoxy-2,2'-bipyrrole-3,3',5,5'-tetracarboxylate (35b)

Bond lengths [Å]

C1-N1	1.358	C19-C20	1.387	H7a-C7	0.930
C1-C2	1.395	C19-C1	1.476	H8a-C8	0.930
C1-C19	1.476	C20-C19	1.387	H9a-C9	0.930
C2-C1	1.395	C20-C21	1.412	H10a-C10	0.930
C2-C3	1.413	C20-C30	1.474	H11a-C11	0.930
C2-C12	1.478	C21-O8	1.362	H13a-C13	0.970
C3-O3	1.368	C21-C22	1.386	H13b-C13	0.970
C3-C4	1.391	C21-C20	1.412	H14a-C14	0.960
C3-C2	1.413	C22-C21	1.386	H14b-C14	0.960
C4-C3	1.391	C22-N2	1.394	H14c-C14	0.960
C4-N1	1.394	C22-C34	1.469	H15a-C15	0.960
C4-C16	1.467	C23-H23a	0.970	H15b-C15	0.960
C5-H5b	0.970	C23-H23b	0.970	H15c-C15	0.960
C5-H5a	0.970	C23-N2	1.478	H17a-C17	0.970
C5-N1	1.480	C23-C24	1.512	H17b-C17	0.970
C5-C6	1.516	C24-C25	1.385	H18a-C18	0.960
C6-C7	1.389	C24-C29	1.389	H18b-C18	0.960
C6-C11	1.390	C24-C23	1.512	H18c-C18	0.960
C6-C5	1.516	C25-H25a	0.930	H23a-C23	0.970
C7-H7a	0.930	C25-C24	1.385	H23b-C23	0.970
C7-C6	1.389	C25-C26	1.387	H25a-C25	0.930
C7-C8	1.390	C26-H26a	0.930	H26a-C26	0.930
C8-H8a	0.930	C26-C27	1.372	H27a-C27	0.930
C8-C9	1.369	C26-C25	1.387	H28a-C28	0.930
C8-C7	1.390	C27-H27a	0.930	H29a-C29	0.930
C9-H9a	0.930	C27-C26	1.372	H31a-C31	0.970
C9-C8	1.369	C27-C28	1.379	H31b-C31	0.970
C9-C10	1.381	C28-H28a	0.930	H32a-C32	0.960
C10-H10a	0.930	C28-C27	1.379	H32b-C32	0.960
C10-C9	1.381	C28-C29	1.385	H32c-C32	0.960
C10-C11	1.386	C29-H29a	0.930	H33a-C33	0.960
C11-H11a	0.930	C29-C28	1.385	H33b-C33	0.960
C11-C10	1.386	C29-C24	1.389	H33c-C33	0.960
C11-C6	1.390	C30-O9	1.205	H35a-C35	0.970
C12-O1	1.203	C30-O10	1.339	H35b-C35	0.970
C12-O2	1.347	C30-C20	1.474	H36a-C36	0.960
C12-C2	1.478	C31-H31a	0.970	H36b-C36	0.960
C13-H13a	0.970	C31-H31b	0.970	H36c-C36	0.960
C13-H13b	0.970	C31-O10	1.452	N1-C1	1.358
C13-O2	1.457	C31-C32	1.486	N1-C4	1.394
C13-C14	1.497	C32-H32b	0.960	N1-C5	1.480
C14-H14a	0.960	C32-H32a	0.960	N2-C19	1.362
C14-H14b	0.960	C32-H32c	0.960	N2-C22	1.394
C14-H14c	0.960	C32-C31	1.486	N2-C23	1.478
C14-C13	1.497	C33-H33c	0.960	O1-C12	1.203
C15-H15a	0.960	C33-H33a	0.960	O2-C12	1.347
C15-H15b	0.960	C33-H33b	0.960	O2-C13	1.457
C15-H15c	0.960	C33-O8	1.433	O3-C3	1.368
C15-O3	1.434	C34-O6	1.207	O3-C15	1.434

C16-O4	1.212	C34-O7	1.342	O4-C16	1.212
C16-O5	1.336	C34-C22	1.469	O5-C16	1.336
C16-C4	1.467	C35-H35a	0.970	O5-C17	1.456
C17-H17a	0.970	C35-H35b	0.970	O6-C34	1.207
C17-H17b	0.970	C35-O7	1.456	O7-C34	1.342
C17-O5	1.456	C35-C36	1.501	O7-C35	1.456
C17-C18	1.499	C36-H36a	0.960	O8-C21	1.362
C18-H18a	0.960	C36-H36b	0.960	O8-C33	1.433
C18-H18b	0.960	C36-H36c	0.960	O9-C30	1.205
C18-H18c	0.960	C36-C35	1.501	O10-C30	1.339
C18-C17	1.499	H5a-C5	0.970	O10-C31	1.452
C19-N2	1.362	H5b-C5	0.970		

Bond angles (degrees)

N1-C1-C2	109.09	H15a-C15-H15c	109.47	C27-C28-C29	120.62
N1-C1-C19	123.65	H15a-C15-O3	109.47	H29a-C29-C28	119.87
C2-C1-C19	127.26	H15b-C15-H15c	109.46	H29a-C29-C24	119.88
C1-C2-C3	106.49	H15b-C15-O3	109.48	C28-C29-C24	120.25
C1-C2-C12	123.16	H15c-C15-O3	109.48	O9-C30-O10	123.92
C3-C2-C12	130.30	O4-C16-O5	123.01	O9-C30-C20	125.21
O3-C3-C4	125.24	O4-C16-C4	125.52	O10-C30-C20	110.86
O3-C3-C2	126.36	O5-C16-C4	111.45	H31a-C31-H31b	108.68
C4-C3-C2	108.12	H17a-C17-H17b	108.52	H31a-C31-O10	110.49
C3-C4-N1	107.18	H17a-C17-O5	110.25	H31a-C31-C32	110.49
C3-C4-C16	129.55	H17a-C17-C18	110.24	H31b-C31-O10	110.50
N1-C4-C16	123.25	H17b-C17-O5	110.25	H31b-C31-C32	110.50
H5b-C5-H5a	107.84	H17b-C17-C18	110.24	O10-C31-C32	106.17
H5b-C5-N1	109.11	O5-C17-C18	107.34	H32b-C32-H32a	109.48
H5b-C5-C6	109.12	H18a-C18-H18b	109.46	H32b-C32-H32c	109.47
H5a-C5-N1	109.12	H18a-C18-H18c	109.47	H32b-C32-C31	109.47
H5a-C5-C6	109.12	H18a-C18-C17	109.47	H32a-C32-H32c	109.46
N1-C5-C6	112.43	H18b-C18-H18c	109.47	H32a-C32-C31	109.47
C7-C6-C11	118.46	H18b-C18-C17	109.48	H32c-C32-C31	109.47
C7-C6-C5	120.14	H18c-C18-C17	109.47	H33c-C33-H33a	109.48
C11-C6-C5	121.39	N2-C19-C20	108.96	H33c-C33-H33b	109.47
H7a-C7-C6	119.99	N2-C19-C1	120.32	H33c-C33-O8	109.47
H7a-C7-C8	119.99	C20-C19-C1	130.45	H33a-C33-H33b	109.47
C6-C7-C8	120.02	C19-C20-C21	106.83	H33a-C33-O8	109.47
H8a-C8-C9	119.41	C19-C20-C30	126.59	H33b-C33-O8	109.47
H8a-C8-C7	119.42	C21-C20-C30	126.57	O6-C34-O7	123.17
C9-C8-C7	121.17	O8-C21-C22	125.28	O6-C34-C22	125.11
H9a-C9-C8	120.36	O8-C21-C20	126.60	O7-C34-C22	111.71
H9a-C9-C10	120.36	C22-C21-C20	108.03	H35a-C35-H35b	108.05
C8-C9-C10	119.29	C21-C22-N2	107.30	H35a-C35-O7	109.47
H10a-C10-C9	119.91	C21-C22-C34	130.80	H35a-C35-C36	109.47
H10a-C10-C11	119.92	N2-C22-C34	121.60	H35b-C35-O7	109.46
C9-C10-C11	120.17	H23a-C23-H23b	107.50	H35b-C35-C36	109.46
H11a-C11-C10	119.56	H23a-C23-N2	108.48	O7-C35-C36	110.88
H11a-C11-C6	119.56	H23a-C23-C24	108.49	H36a-C36-H36b	109.47
C10-C11-C6	120.88	H23b-C23-N2	108.48	H36a-C36-H36c	109.47

O1-C12-O2	123.89	H23b-C23-C24	108.48	H36a-C36-C35	109.47
O1-C12-C2	124.17	N2-C23-C24	115.16	H36b-C36-H36c	109.47
O2-C12-C2	111.94	C25-C24-C29	118.60	H36b-C36-C35	109.47
H13a-C13-H13b	107.99	C25-C24-C23	118.96	H36c-C36-C35	109.47
H13a-C13-O2	109.36	C29-C24-C23	122.37	C1-N1-C4	109.09
H13a-C13-C14	109.36	H25a-C25-C24	119.60	C1-N1-C5	123.09
H13b-C13-O2	109.37	H25a-C25-C26	119.62	C4-N1-C5	127.75
H13b-C13-C14	109.37	C24-C25-C26	120.79	C19-N2-C22	108.87
O2-C13-C14	111.32	H26a-C26-C27	119.86	C19-N2-C23	123.38
H14a-C14-H14b	109.48	H26a-C26-C25	119.85	C22-N2-C23	126.77
H14a-C14-H14c	109.47	C27-C26-C25	120.29	C12-O2-C13	115.90
H14a-C14-C13	109.46	H27a-C27-C26	120.28	C3-O3-C15	114.68
H14b-C14-H14c	109.48	H27a-C27-C28	120.28	C16-O5-C17	116.31
H14b-C14-C13	109.47	C26-C27-C28	119.44	C34-O7-C35	115.62
H14c-C14-C13	109.47	H28a-C28-C27	119.68	C21-O8-C33	114.94
H15a-C15-H15b	109.47	H28a-C28-C29	119.70	C30-O10-C31	117.34

Torsion angles (degrees)

C(13)-O(2)-C(12)-O(1)	-1.60	C(1)-C(2)-C(12)-O(1)	12.50
C(13)-O(2)-C(12)-C(2)	178.15	C(1)-C(2)-C(12)-O(2)	-167.23
C(12)-O(2)-C(13)-C(14)	85.01	O(3)-C(3)-C(4)-N(1)	173.71
C(15)-O(3)-C(3)-C(2)	-88.07	O(3)-C(3)-C(4)-C(16)	-5.20
C(15)-O(3)-C(3)-C(4)	98.73	C(2)-C(3)-C(4)-N(1)	-0.53
C(17)-O(5)-C(16)-O(4)	1.20	C(2)-C(3)-C(4)-C(16)	-179.46
C(17)-O(5)-C(16)-C(4)	-177.56	C(3)-C(4)-C(16)-O(4)	165.52
C(16)-O(5)-C(17)-C(18)	171.14	N(1)-C(4)-C(16)-O(5)	165.47
C(35)-O(7)-C(34)-O(6)	-4.30	C(3)-C(4)-C(16)-O(5)	-15.80
C(35)-O(7)-C(34)-C(22)	174.40	N(1)-C(4)-C(16)-O(4)	-13.30
C(34)-O(7)-C(35)-C(36)	-84.50	N(1)-C(5)-C(6)-C(11)	51.40
C(33)-O(8)-C(21)-C(20)	83.50	N(1)-C(5)-C(6)-C(7)	-127.62
C(33)-O(8)-C(21)-C(22)	-100.55	C(5)-C(6)-C(7)-C(8)	179.18
C(31)-O(10)-C(30)-O(9)	0.30	C(11)-C(6)-C(7)-C(8)	0.10
C(31)-O(10)-C(30)-C(20)	-179.14	C(5)-C(6)-C(11)-C(10)	-178.42
C(30)-O(10)-C(31)-C(32)	170.56	C(7)-C(6)-C(11)-C(10)	0.60
C(1)-N(1)-C(4)-C(3)	1.26	C(6)-C(7)-C(8)-C(9)	-0.70
C(1)-N(1)-C(4)-C(16)	-179.73	C(7)-C(8)-C(9)-C(10)	0.50
C(4)-N(1)-C(1)-C(2)	-1.51	C(8)-C(9)-C(10)-C(11)	0.20
C(4)-N(1)-C(1)-C(19)	178.58	C(9)-C(10)-C(11)-C(6)	-0.80
C(5)-N(1)-C(1)-C(2)	-178.78	N(2)-C(19)-C(20)-C(21)	-0.92
C(5)-N(1)-C(1)-C(19)	1.30	N(2)-C(19)-C(20)-C(30)	177.91
C(1)-N(1)-C(5)-C(6)	85.82	C(1)-C(19)-C(20)-C(30)	-8.30
C(5)-N(1)-C(4)-C(3)	178.37	C(1)-C(19)-C(20)-C(21)	172.89
C(5)-N(1)-C(4)-C(16)	-2.60	C(30)-C(20)-C(21)-O(8)	-2.30
C(4)-N(1)-C(5)-C(6)	-90.92	C(19)-C(20)-C(21)-C(22)	0.03
C(23)-N(2)-C(19)-C(1)	17.60	C(19)-C(20)-C(21)-O(8)	176.54
C(22)-N(2)-C(19)-C(1)	-173.07	C(19)-C(20)-C(30)-O(10)	-0.60
C(22)-N(2)-C(19)-C(20)	1.47	C(30)-C(20)-C(21)-C(22)	-178.81
C(22)-N(2)-C(23)-C(24)	107.61	C(19)-C(20)-C(30)-O(9)	-179.98
C(23)-N(2)-C(19)-C(20)	-167.88	C(21)-C(20)-C(30)-O(9)	-1.40

C(19)-N(2)-C(22)-C(21)	-1.44	C(21)-C(20)-C(30)-O(10)	178.03
C(19)-N(2)-C(22)-C(34)	172.81	O(8)-C(21)-C(22)-C(34)	10.70
C(23)-N(2)-C(22)-C(21)	167.46	O(8)-C(21)-C(22)-N(2)	-175.72
C(23)-N(2)-C(22)-C(34)	-18.30	C(20)-C(21)-C(22)-C(34)	-172.68
C(19)-N(2)-C(23)-C(24)	-84.99	C(20)-C(21)-C(22)-N(2)	0.86
N(1)-C(1)-C(2)-C(3)	1.15	N(2)-C(22)-C(34)-O(6)	0.80
C(2)-C(1)-C(19)-N(2)	77.89	C(21)-C(22)-C(34)-O(7)	-5.10
C(2)-C(1)-C(19)-C(20)	-95.30	N(2)-C(22)-C(34)-O(7)	-177.82
C(19)-C(1)-C(2)-C(12)	3.30	C(21)-C(22)-C(34)-O(6)	173.59
N(1)-C(1)-C(2)-C(12)	-176.64	N(2)-C(23)-C(24)-C(25)	131.84
C(19)-C(1)-C(2)-C(3)	-178.95	N(2)-C(23)-C(24)-C(29)	-51.00
N(1)-C(1)-C(19)-N(2)	-102.21	C(23)-C(24)-C(25)-C(26)	177.41
N(1)-C(1)-C(19)-C(20)	84.60	C(29)-C(24)-C(25)-C(26)	0.20
C(1)-C(2)-C(3)-O(3)	-174.52	C(23)-C(24)-C(29)-C(28)	-177.93
C(3)-C(2)-C(12)-O(1)	-164.73	C(25)-C(24)-C(29)-C(28)	-0.80
C(3)-C(2)-C(12)-O(2)	15.60	C(24)-C(25)-C(26)-C(27)	0.60
C(1)-C(2)-C(3)-C(4)	-0.36	C(25)-C(26)-C(27)-C(28)	-0.70
C(12)-C(2)-C(3)-O(3)	3.10	C(26)-C(27)-C(28)-C(29)	0.10
C(12)-C(2)-C(3)-C(4)	177.21	C(27)-C(28)-C(29)-C(24)	0.70

Tetraethyl-1,1'-dibenzyl-3,3'-dioxo-1,1',3,3'-tetrahydro-[2,2'] bipyrrole-2,2',4,4'-tetra-carboxylate (23)

Bond lengths [Å]

O1-C12	1.203	C1-H1a	0.970	C18-C22	1.534
O2-C12	1.350	C1-N1	1.481	C18-C11	1.580
O2-C13	1.460	C1-C2	1.521	C18-C19	1.597
O3-C15	1.203	C2-C3	1.390	C19-O10	1.215
O4-C15	1.324	C2-C7	1.393	C19-C20	1.435
O4-C16	1.463	C2-C1	1.521	C19-C18	1.597
O5-C10	1.215	C3-H3a	0.929	C20-C21	1.380
O6-C25	1.212	C3-C2	1.390	C20-C19	1.435
O7-C25	1.340	C3-C4	1.392	C20-C25	1.461
O7-C26	1.455	C4-H4a	0.930	C21-H21a	0.930
O8-C22	1.195	C4-C5	1.387	C21-N2	1.325
O9-C22	1.333	C4-C3	1.392	C21-C20	1.380
O9-C23	1.464	C5-H5a	0.930	C22-O8	1.195
O10-C19	1.215	C5-C6	1.376	C22-O9	1.333
N1-C8	1.331	C5-C4	1.387	C22-C18	1.534
N1-C11	1.472	C6-H6a	0.930	C23-H23b	0.970
N1-C1	1.481	C6-C5	1.376	C23-H23a	0.970
N2-C21	1.325	C6-C7	1.397	C23-O9	1.464
N2-C18	1.472	C7-H7a	0.930	C23-C24	1.501
N2-C28	1.488	C7-C2	1.393	C24-H24a	0.960
H1a-C1	0.970	C7-C6	1.397	C24-H24b	0.960
H1b-C1	0.969	C8-H8a	0.931	C24-H24c	0.960
H3a-C3	0.929	C8-N1	1.331	C24-C23	1.501
H4a-C4	0.930	C8-C9	1.378	C25-O6	1.212
H5a-C5	0.930	C9-C8	1.378	C25-O7	1.340
H6a-C6	0.930	C9-C10	1.433	C25-C20	1.461
H7a-C7	0.930	C9-C12	1.468	C26-H26b	0.970
H8a-C8	0.931	C10-O5	1.215	C26-H26a	0.970
H13a-C13	0.970	C10-C9	1.433	C26-O7	1.455
H13b-C13	0.970	C10-C11	1.599	C26-C27	1.498
H14a-C14	0.960	C11-N1	1.472	C27-H27a	0.960
H14b-C14	0.960	C11-C15	1.531	C27-H27c	0.960
H14c-C14	0.959	C11-C18	1.580	C27-H27b	0.961
H16a-C16	0.970	C11-C10	1.599	C27-C26	1.498
H16b-C16	0.970	C12-O1	1.203	C28-H28b	0.969
H17a-C17	0.961	C12-O2	1.350	C28-H28a	0.970
H17b-C17	0.960	C12-C9	1.468	C28-N2	1.488
H17c-C17	0.961	C13-H13b	0.970	C28-C29	1.512
H21a-C21	0.930	C13-H13a	0.970	C29-C34	1.390
H23a-C23	0.970	C13-O2	1.460	C29-C30	1.394
H23b-C23	0.970	C13-C14	1.496	C29-C28	1.512
H24a-C24	0.960	C14-H14c	0.959	C30-H30a	0.931
H24b-C24	0.960	C14-H14a	0.960	C30-C31	1.389
H24c-C24	0.960	C14-H14b	0.960	C30-C29	1.394
H26a-C26	0.970	C14-C13	1.496	C31-H31a	0.929
H26b-C26	0.970	C15-O3	1.203	C31-C32	1.383
H27a-C27	0.960	C15-O4	1.324	C31-C30	1.389

H27b-C27	0.961	C15-C11	1.531	C32-H32a	0.930
H27c-C27	0.960	C16-H16a	0.970	C32-C33	1.381
H28a-C28	0.970	C16-H16b	0.970	C32-C31	1.383
H28b-C28	0.969	C16-O4	1.463	C33-H33a	0.929
H30a-C30	0.931	C16-C17	1.491	C33-C32	1.381
H31a-C31	0.929	C17-H17b	0.960	C33-C34	1.386
H32a-C32	0.930	C17-H17c	0.961	C34-H34a	0.930
H33a-C33	0.929	C17-H17a	0.961	C34-C33	1.386
H34a-C34	0.930	C17-C16	1.491	C34-C29	1.390
C1-H1b	0.969	C18-N2	1.472		

Bond angles (degrees)

C12-O2-C13	117.06	O1-C12-C9	124.70	H23a-C23-O9	110.35
C15-O4-C16	117.08	O2-C12-C9	111.15	H23a-C23-C24	110.32
C25-O7-C26	116.25	H13b-C13-H13a	108.18	O9-C23-C24	106.87
C22-O9-C23	116.59	H13b-C13-O2	109.67	H24a-C24-H24b	109.54
C8-N1-C11	110.18	H13b-C13-C14	109.68	H24a-C24-H24c	109.38
C8-N1-C1	122.63	H13a-C13-O2	109.68	H24a-C24-C23	109.48
C11-N1-C1	127.17	H13a-C13-C14	109.69	H24b-C24-H24c	109.49
C21-N2-C18	110.00	O2-C13-C14	109.92	H24b-C24-C23	109.44
C21-N2-C28	125.75	H14c-C14-H14a	109.44	H24c-C24-C23	109.50
C18-N2-C28	124.24	H14c-C14-H14b	109.54	O6-C25-O7	123.68
H1b-C1-H1a	107.56	H14c-C14-C13	109.49	O6-C25-C20	124.51
H1b-C1-N1	108.66	H14a-C14-H14b	109.40	O7-C25-C20	111.81
H1b-C1-C2	108.67	H14a-C14-C13	109.52	H26b-C26-H26a	108.62
H1a-C1-N1	108.68	H14b-C14-C13	109.44	H26b-C26-O7	110.29
H1a-C1-C2	108.65	O3-C15-O4	126.13	H26b-C26-C27	110.22
N1-C1-C2	114.42	O3-C15-C11	124.37	H26a-C26-O7	110.27
C3-C2-C7	119.16	O4-C15-C11	109.43	H26a-C26-C27	110.23
C3-C2-C1	120.67	H16a-C16-H16b	108.10	O7-C26-C27	107.21
C7-C2-C1	120.09	H16a-C16-O4	109.55	H27a-C27-H27c	109.43
H3a-C3-C2	119.66	H16a-C16-C17	109.60	H27a-C27-H27b	109.46
H3a-C3-C4	119.66	H16b-C16-O4	109.55	H27a-C27-C26	109.43
C2-C3-C4	120.68	H16b-C16-C17	109.55	H27c-C27-H27b	109.49
H4a-C4-C5	120.18	O4-C16-C17	110.45	H27c-C27-C26	109.49
H4a-C4-C3	120.25	H17b-C17-H17c	109.51	H27b-C27-C26	109.51
C5-C4-C3	119.57	H17b-C17-H17a	109.45	H28b-C28-H28a	107.74
H5a-C5-C6	119.79	H17b-C17-C16	109.50	H28b-C28-N2	108.94
H5a-C5-C4	119.84	H17c-C17-H17a	109.47	H28b-C28-C29	109.00
C6-C5-C4	120.37	H17c-C17-C16	109.45	H28a-C28-N2	108.93
H6a-C6-C5	119.96	H17a-C17-C16	109.46	H28a-C28-C29	108.99
H6a-C6-C7	119.88	N2-C18-C22	110.96	N2-C28-C29	113.10
C5-C6-C7	120.17	N2-C18-C11	113.18	C34-C29-C30	118.77
H7a-C7-C2	120.02	N2-C18-C19	101.86	C34-C29-C28	120.26
H7a-C7-C6	119.94	C22-C18-C11	115.24	C30-C29-C28	120.96
C2-C7-C6	120.05	C22-C18-C19	106.28	H30a-C30-C31	119.83
H8a-C8-N1	122.82	C11-C18-C19	108.14	H30a-C30-C29	119.90
H8a-C8-C9	122.87	O10-C19-C20	132.20	C31-C30-C29	120.26
N1-C8-C9	114.32	O10-C19-C18	122.67	H31a-C31-C32	119.91
C8-C9-C10	108.05	C20-C19-C18	105.12	H31a-C31-C30	119.83

C8-C9-C12	127.92	C21-C20-C19	108.04	C32-C31-C30	120.26
C10-C9-C12	123.85	C21-C20-C25	127.20	H32a-C32-C33	120.16
O5-C10-C9	131.88	C19-C20-C25	124.64	H32a-C32-C31	120.06
O5-C10-C11	122.92	H21a-C21-N2	122.62	C33-C32-C31	119.79
C9-C10-C11	105.15	H21a-C21-C20	122.64	H33a-C33-C32	119.91
N1-C11-C15	111.96	N2-C21-C20	114.74	H33a-C33-C34	119.96
N1-C11-C18	114.48	O8-C22-O9	125.05	C32-C33-C34	120.13
N1-C11-C10	101.38	O8-C22-C18	124.77	H34a-C34-C33	119.63
C15-C11-C18	113.17	O9-C22-C18	109.96	H34a-C34-C29	119.66
C15-C11-C10	107.58	H23b-C23-H23a	108.59	C33-C34-C29	120.70
C18-C11-C10	107.22	H23b-C23-O9	110.32		
O1-C12-O2	124.12	H23b-C23-C24	110.39		

Torsion angles (degrees)

C(12)-O(2)-C(13)-C(14)	-96.33	O(5)-C(10)-C(11)-C(15)	-50.59
C(13)-O(2)-C(12)-C(9)	177.57	C(9)-C(10)-C(11)-N(1)	9.41
C(13)-O(2)-C(12)-O(1)	-4.70	O(5)-C(10)-C(11)-N(1)	-168.23
C(15)-O(4)-C(16)-C(17)	-90.65	C(9)-C(10)-C(11)-C(18)	-110.92
C(16)-O(4)-C(15)-C(11)	-178.53	C(9)-C(10)-C(11)-C(15)	127.05
C(16)-O(4)-C(15)-O(3)	4.30	C(18)-C(11)-C(15)-O(4)	178.02
C(26)-O(7)-C(25)-O(6)	2.70	N(1)-C(11)-C(18)-C(22)	81.75
C(25)-O(7)-C(26)-C(27)	-167.92	C(18)-C(11)-C(15)-O(3)	-4.73
C(26)-O(7)-C(25)-C(20)	-176.53	C(10)-C(11)-C(15)-O(4)	-63.72
C(22)-O(9)-C(23)-C(24)	-172.46	N(1)-C(11)-C(15)-O(4)	46.83
C(23)-O(9)-C(22)-O(8)	-2.50	C(10)-C(11)-C(18)-N(2)	-37.44
C(23)-O(9)-C(22)-C(18)	172.37	N(1)-C(11)-C(18)-N(2)	-149.04
C(1)-N(1)-C(8)-C(9)	-179.20	N(1)-C(11)-C(18)-C(19)	-36.98
C(8)-N(1)-C(11)-C(10)	-7.23	C(10)-C(11)-C(15)-O(3)	113.53
C(1)-N(1)-C(11)-C(18)	-70.46	C(10)-C(11)-C(18)-C(22)	-166.65
C(8)-N(1)-C(11)-C(15)	-121.65	C(15)-C(11)-C(18)-C(22)	-48.18
C(8)-N(1)-C(11)-C(18)	107.83	C(15)-C(11)-C(18)-N(2)	81.03
C(1)-N(1)-C(11)-C(10)	174.48	C(15)-C(11)-C(18)-C(19)	-166.91
C(8)-N(1)-C(1)-C(2)	106.41	N(1)-C(11)-C(15)-O(3)	-135.92
C(11)-N(1)-C(8)-C(9)	2.42	C(10)-C(11)-C(18)-C(19)	74.62
C(1)-N(1)-C(11)-C(15)	60.06	C(22)-C(18)-C(19)-O(10)	-58.10
C(11)-N(1)-C(1)-C(2)	-75.49	N(2)-C(18)-C(22)-O(8)	-158.70
C(28)-N(2)-C(18)-C(22)	62.24	C(19)-C(18)-C(22)-O(8)	91.35
C(21)-N(2)-C(18)-C(11)	111.95	C(11)-C(18)-C(22)-O(9)	156.68
C(28)-N(2)-C(18)-C(19)	175.03	N(2)-C(18)-C(19)-O(10)	-174.34
C(21)-N(2)-C(18)-C(19)	-3.90	N(2)-C(18)-C(19)-C(20)	4.80
C(21)-N(2)-C(28)-C(29)	28.75	C(11)-C(18)-C(22)-O(8)	-28.40
C(21)-N(2)-C(18)-C(22)	-116.69	C(11)-C(18)-C(19)-C(20)	-114.68
C(18)-N(2)-C(21)-C(20)	1.60	C(22)-C(18)-C(19)-C(20)	121.04
C(18)-N(2)-C(28)-C(29)	-150.01	C(19)-C(18)-C(22)-O(9)	-83.56
C(28)-N(2)-C(21)-C(20)	-177.31	C(11)-C(18)-C(19)-O(10)	66.18
C(28)-N(2)-C(18)-C(11)	-69.12	N(2)-C(18)-C(22)-O(9)	26.39

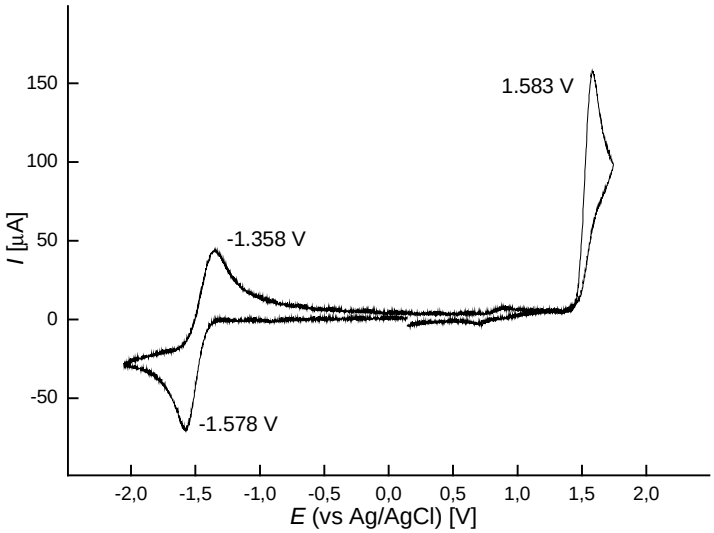
N(1)-C(1)-C(2)-C(7)	116.85	O(10)-C(19)-C(20)-C(25)	-1.60
N(1)-C(1)-C(2)-C(3)	-66.45	C(18)-C(19)-C(20)-C(25)	179.42
C(3)-C(2)-C(7)-C(6)	0.10	O(10)-C(19)-C(20)-C(21)	174.88
C(1)-C(2)-C(3)-C(4)	-177.29	C(18)-C(19)-C(20)-C(21)	-4.14
C(7)-C(2)-C(3)-C(4)	-0.60	C(19)-C(20)-C(25)-O(7)	175.23
C(1)-C(2)-C(7)-C(6)	176.89	C(19)-C(20)-C(25)-O(6)	-4.00
C(2)-C(3)-C(4)-C(5)	0.50	C(19)-C(20)-C(21)-N(2)	1.86
C(3)-C(4)-C(5)-C(6)	-0.10	C(25)-C(20)-C(21)-N(2)	178.18
C(4)-C(5)-C(6)-C(7)	-0.40	C(21)-C(20)-C(25)-O(6)	-179.77
C(5)-C(6)-C(7)-C(2)	0.30	C(21)-C(20)-C(25)-O(7)	-0.50
N(1)-C(8)-C(9)-C(12)	179.60	N(2)-C(28)-C(29)-C(30)	-80.56
N(1)-C(8)-C(9)-C(10)	4.36	N(2)-C(28)-C(29)-C(34)	100.65
C(8)-C(9)-C(12)-O(2)	-19.0	C(30)-C(29)-C(34)-C(33)	1.60
C(8)-C(9)-C(12)-O(1)	163.31	C(28)-C(29)-C(30)-C(31)	178.19
C(10)-C(9)-C(12)-O(1)	-22.10	C(28)-C(29)-C(34)-C(33)	-179.61
C(12)-C(9)-C(10)-O(5)	-6.70	C(34)-C(29)-C(30)-C(31)	-3.00
C(10)-C(9)-C(12)-O(2)	155.60	C(29)-C(30)-C(31)-C(32)	1.70
C(12)-C(9)-C(10)-C(11)	176.00	C(30)-C(31)-C(32)-C(33)	1.00
C(8)-C(9)-C(10)-O(5)	168.81	C(31)-C(32)-C(33)-C(34)	-2.50
C(8)-C(9)-C(10)-C(11)	-8.53	C(32)-C(33)-C(34)-C(29)	1.20
O(5)-C(10)-C(11)-C(18)	71.44		

Appendix B

Cyclovoltammetric curves of the non-polymerizing compounds were obtained at the potential scan rate 100 mV/s.

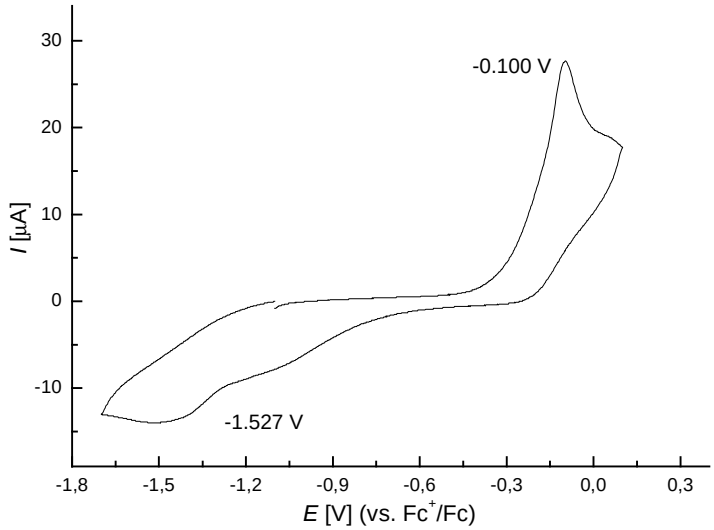
1-Methyl-4-nitro-3-methoxypyrrole (47),

c = $2.1 \cdot 10^{-3}$ M in Bu_4NBF_4 (0.1 M) acetonitrile



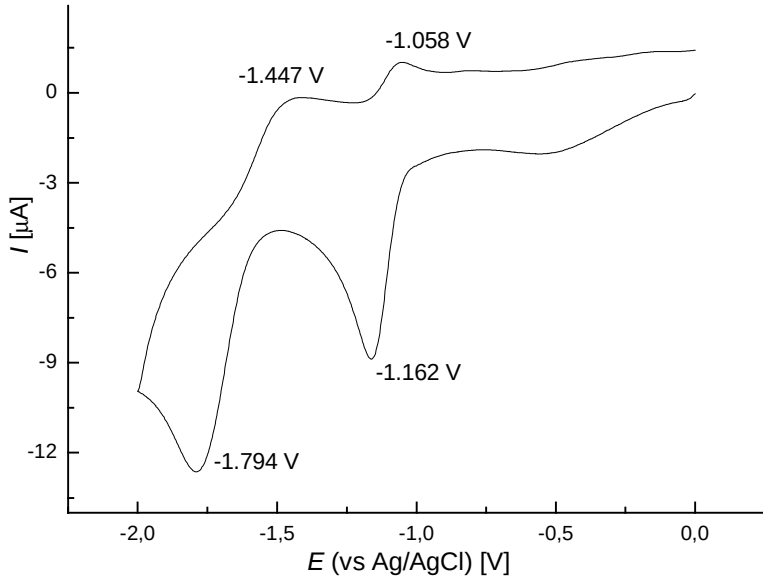
1-Methyl-3-amino-4-methoxypyrrole (48)

c = $1.9 \cdot 10^{-3}$ M in Bu_4NBF_4 (0.1 M) acetonitrile



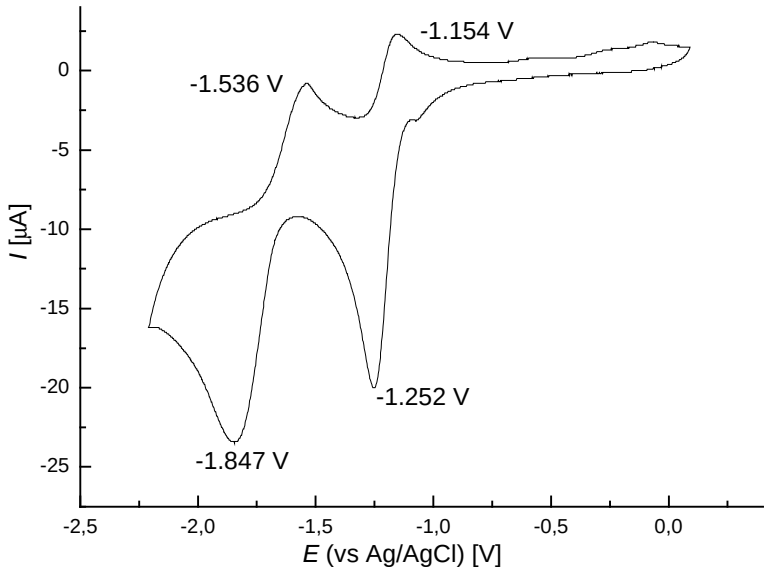
1-Methyl-3,4-dinitropyrrole (53a)

c = $1.46 \cdot 10^{-3}$ M in Bu_4NBF_4 (0.1 M) acetonitrile



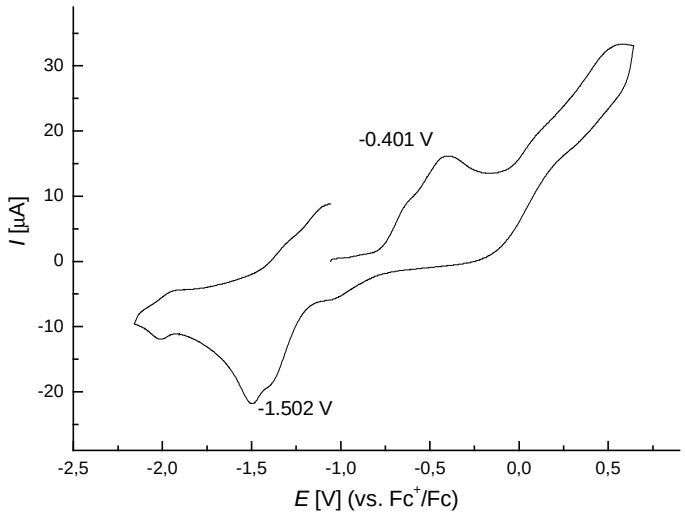
1-Benzyl-3,4-dinitropyrrole (53b)

c = $2.2 \cdot 10^{-3}$ M in Bu_4NBF_4 (0.1 M) acetonitrile



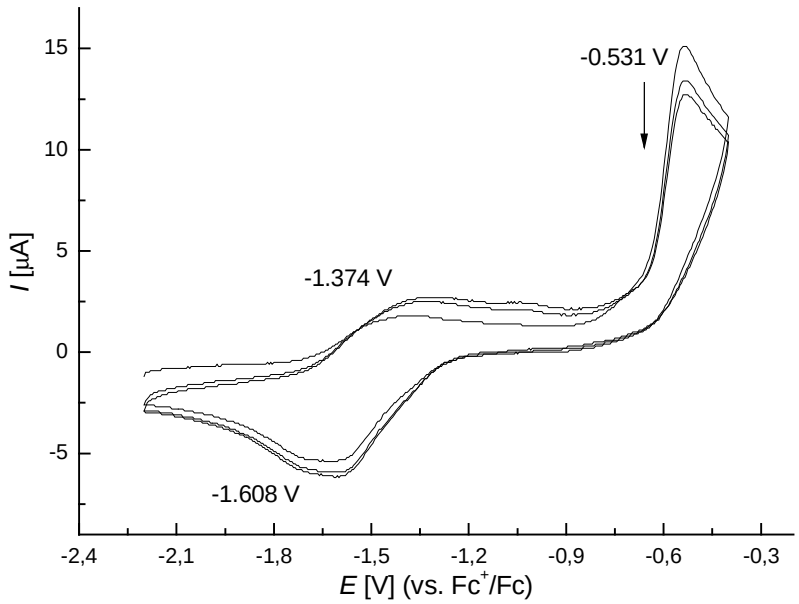
1-Methyl-3,4-diaminopyrrole (54a)

c = $3.5 \cdot 10^{-3}$ M in Bu_4NBF_4 (0.1 M) DMSO



1-Benzyl-3,4-diaminopyrrole (54b)

c = $2.3 \cdot 10^{-3}$ M in Bu_4NBF_4 (0.1 M) DMSO



Appendix C

Some parts of the work were published and presented as posters.

Merz A., Anikin S., Lieser B., Heinze J., and John H.
3,3'- and 4,4'-dimethoxy-2,2'-bipyrroles: highly electron-rich model compounds for polypyrrole formation
Chem. Eur. J. **2003**, *9*(2), 449-455.

S. Anikin and A. Merz
Synthesis and electrochemical properties of highly electron rich compounds:
3,3´- and 4,4´-dimethoxy-2,2´-bipyrroles 3- and 3,4- aminopyrroles
Poster at the 19th International Congress of Heterocyclic Chemistry, Colorado State University, Colorado, USA, August10-15 2003

S. Anikin, G. Broncova, V. Mirsky, O. Wolfbeis, Kral, A. Merz
Electrochemical properties of alkoxybipyrroles
Advanced Materials, in preparation

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Acknowledgements

I am grateful to everyone who helped me and gave me support throughout my work:

- My parents and my brother for encouraging and supporting me, always when I needed them

- Prof. Dr. J. Daub and his group for providing me with the possibility to use the electrochemical laboratory, Gilbert Nöll and Christian Trieflinger for their friendly help with measuring technique

- Prof. Dr. Reiser for his laboratory and his group, especially Brigitte Paulus, Klaus Döring, Georg Adolin and Dr. Peter Kreitmeier for their great support in solving of technical problems

- Dr. Mirsky, V.Kulikov, G. Broncova for analytical measurements of polymer properties and their friendly atmosphere

- Dr. T. Burgrmeister, F. Kastner, A. Schramm, G. Stühler for the NMR measurements and discussion of the spectra

- Dr. K. Mayer, J. Kiermaier and W. Söllner for the measuring and discussion of the MS-spectra

- H. Schüller for the elemental analysis realization

- Dr. Manfred Zabel, Sabine Stempfhuber for the X-ray spectra measuring

- Victor Prutyanov for the language corrections

- Deutsche Forschungsgemeinschaft for the financial support

- To everybody who is not listed here and contributed by their a piece to this work