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## **PhD Thesis**

# ***Design, synthesis and structural analysis of some podands and polyheteroaromatic macrocyclic compounds***

**LAR CLAUDIA**

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# Introduction

Heterocyclic chemistry had a fast development due to its wide applications in supramolecular chemistry, and also because of its utility in material sciences.<sup>1</sup> Of these, a special importance gained the heterocycles containing nitrogen (and oxygen) atoms, an examples in this regard are terpyridine derivatives or oxazines,<sup>2</sup> compounds that open the perspective of synthesizing and studying new molecular assemblies. 2,2':6',2''-Terpyridines show a very rich coordination chemistry, mainly due to affinity for a wide variety of transitional metals cations but also of other metals.<sup>3</sup> Because of these properties, different metalo-supramolecular structures have been obtained with distinct photophysical, photochemical, electrochemical, catalytical and magnetical properties.<sup>1</sup> Also, the compounds where used in obtainment of nanostructures (ex. rotaxans, pseudorotaxans, molecular machines, etc).<sup>4</sup> Interesting properties present the heterocycles containing sulphur, especially thiophene whose contribution to semiconductor polymers is well-known.<sup>5</sup>

The results of research presented in thesis are divided in two main parts and include synthesis, structural analysis and properties of some new nitrogen and sulphur containing aromatic heterocycles. In the first part are presented the results obtained in synthesis and analysis of some new terpyridine derivatives. Are included the informations concerning new terpyridine substrates, precursors in the coronands and cryptands synthesis (is presented some literature data about the

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<sup>1</sup> (a) Cooke, M. W.; Hanan, G. S. *Chem. Soc. Rev.* **2007**, *36*, 1466; (b) Constable, E. C. *Chem. Soc. Rev.* **2007**, *36*, 246; (c) Kurth, D. G.; Higuchi, M. *Soft. Matter.* **2006**, *2*, 915; (d) Medlycott, E. A.; Hanan, G. S. *Chem. Soc. Rev.* **2005**, *34*, 133; (e) Andres, P. R.; Schubert, U. S. *Adv. Mater.* **2004**, *16*, 1043.

<sup>2</sup> (a) Nan, A.; David, L.; Tintas, M.; Lar, C.; Grosu, I. *Letters in Organic Chemistry*, acceptat spre publicare; (b) Star, A.; Goldberg, I.; Fuchs, B. *Angew. Chem. Int. Ed.* **2000**, *39*, 2685-2689; (c) Star, A.; Goldberg, I.; Fuchs, B. *J. Organomet. Chem.* **2001**, *630*, 67-77.

<sup>3</sup> (a) Schubert, U. S.; Eschbaumer, C. *Angew. Chem. Int. Ed.* **2002**, *41*, 2892-2926; (b) Kaes, C.; Katz, A.; Hosseini, M. V. *Chem. Rev.* **2000**, *100*, 3553-3590.

<sup>4</sup> Balzani, V.; Venturi, M.; Credi, A. *Molecular Devices and Machines*, Wiley-VCH: Weinheim, **2003**.

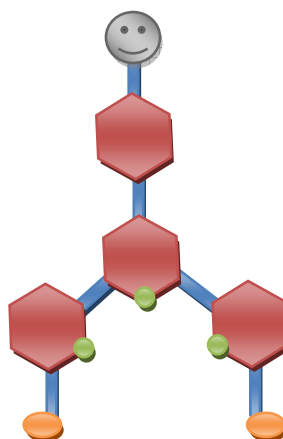
<sup>5</sup> (a) Shirakawa, H. *Angew. Chem. Int. Ed.* **2001**, *40*, 2574; (b) MacDiarmid, A. G. *Angew. Chem. Int. Ed.* **2001**, *40*, 2580; (c) Heeger, A. J. *Angew. Chem. Int. Ed.* **2001**, *40*, 2591; (d) Shi, L. H.; Garnier, F.; Roncali, J. *Synth. Met.* **1991**, *41-43*, 547.

study of the terpyridinic derivatives and also the original contributions brought by this thesis in the field of synthesis and structural analysis of these compounds). Are also discussed the attempts made in order to obtain new macrocycles with terpyridinic units, the syntheses methods and the structural analysis of the obtained compounds.

In the second part are presented the main results obtained in synthesis, structural analysis and properties of some bithiophene derivatives, precursors in the synthesis of supramolecular compounds. Also, the syntheses methods for two new macrocycles with a bithiophenic unit are presented.

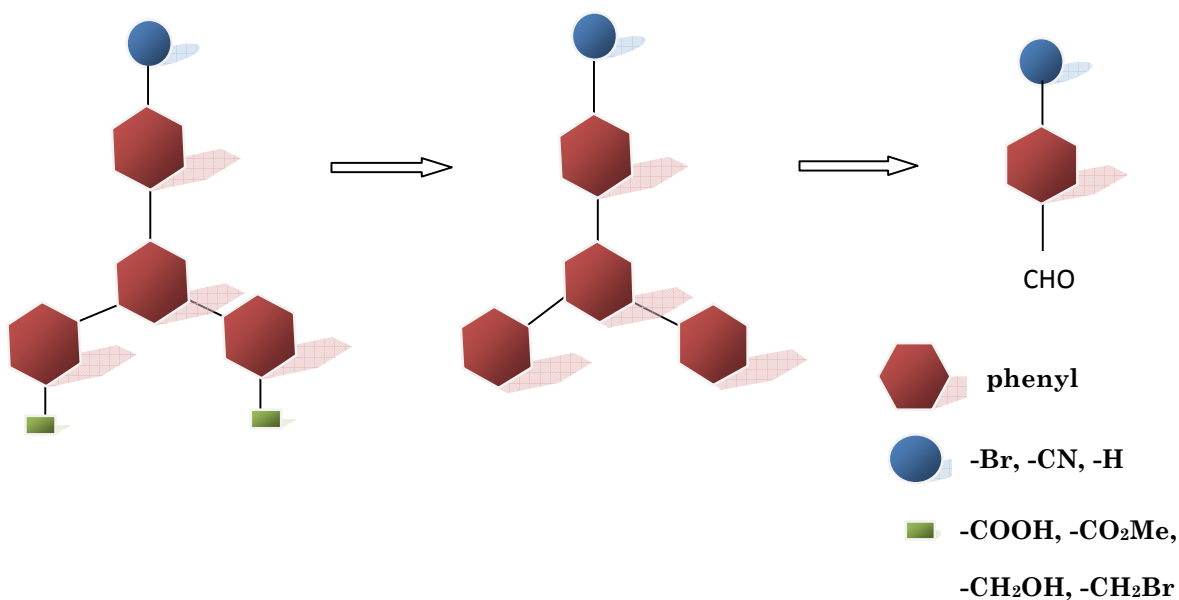
# PART I

## Design, synthesis and structural analysis of some podands and macrocyclic compounds with pyridine units



## I.2. Objectives

The objective of this part is the synthesis of compounds containing at least one terpyridine unit, precursors in the synthesis of macrocycles. The methods used to obtain macrocycles (coronands, cryptands, etc) starting from these podands are presented. These type of compounds shows coordinative properties, especially a high affinity for the transitional-metals cations and for cations of metals from the rare earth elements. Due to this properties, can be obtained various metallo-supramolecular structures which may present distinct photophysical, photochemical, electrochemical, catalytical and magnetical properties.<sup>1</sup> Moreover, the supramolecular structures have a well defined stereochemistry, which show a great importance, especially when the structure-property relationship is considered. In **Scheme 14** is shown the way of obtaining the target podands (intermediates in the macrocyclization reactions), proposed for characterisation and structural analysis.

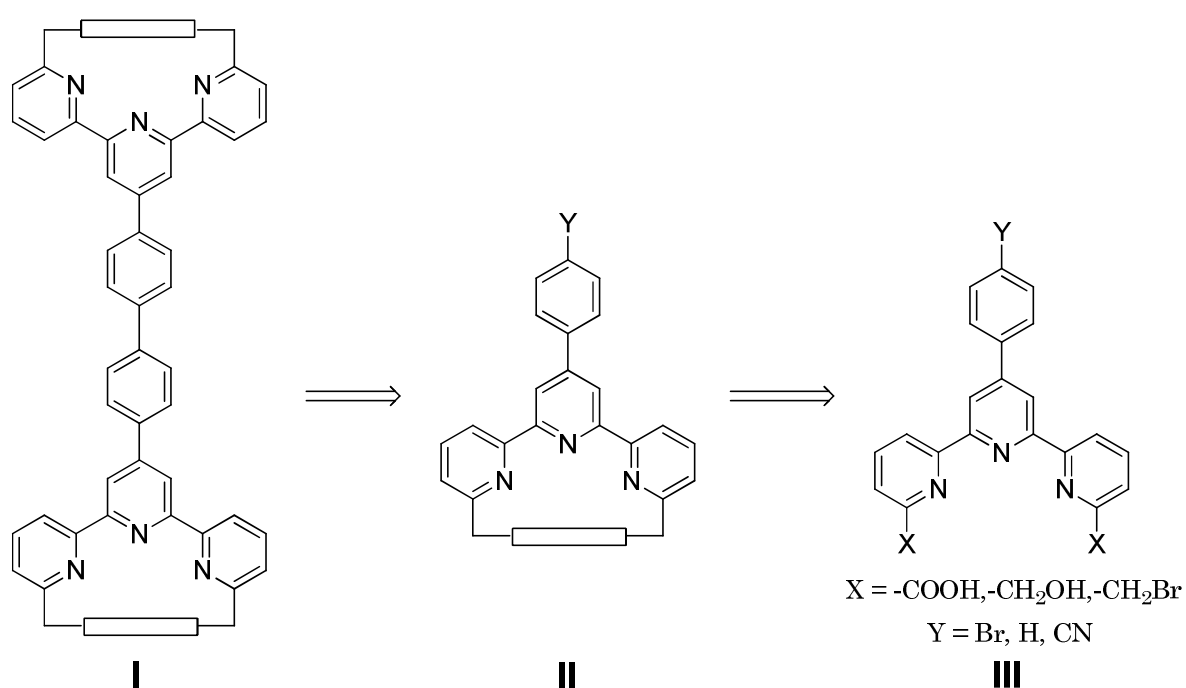


*Scheme 14*



### I.3. Results and discussions

It was proposed a plan that suppose obtainement of some monoterpyridinic structures functionalized with different groups (type **III**), step followed by macrocyclization process (type **II**)<sup>6,7</sup> and, at final step, will be used different coupling methods to obtain the desired structures of type **I**. The retrosynthetic scheme is presented below (*Scheme 19*).



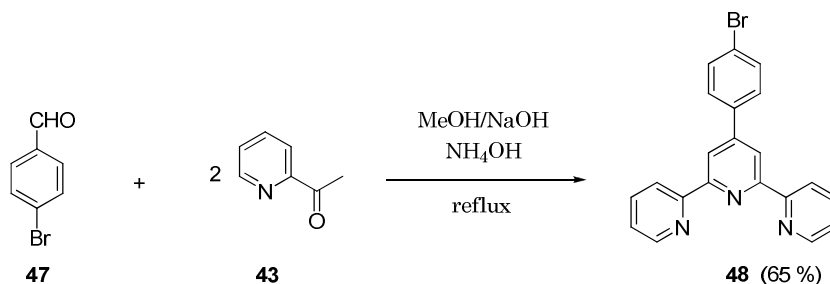
*Scheme 19*

<sup>6</sup> Grave, C.; Lentz, D.; Schafer, A.; Samori, P.; Rabe, J.; Franke, P.; Schluter, A. D. *J. Am. Chem. Soc.* **2003**, *125*, 6907-6918.

<sup>7</sup> Hamann, C.; Kern, J. M.; Sauvage, J. P. *Inorg. Chem.* **2003**, *42*, 1877-1883.

### I.3.1. Synthesis and structural analysis of podands with terpyridine unit

The starting materials used to obtain terpyridine compounds were benzaldehyde and 2-acetylpyridine derivatives. To obtain monoterpyridine **48**, was used 4-bromobenzaldehyde and 2-acetylpyridine.<sup>8</sup> The reaction took place in basic conditions, at reflux for two days (**Scheme 20**) when the desired compound yielded in 65 %.



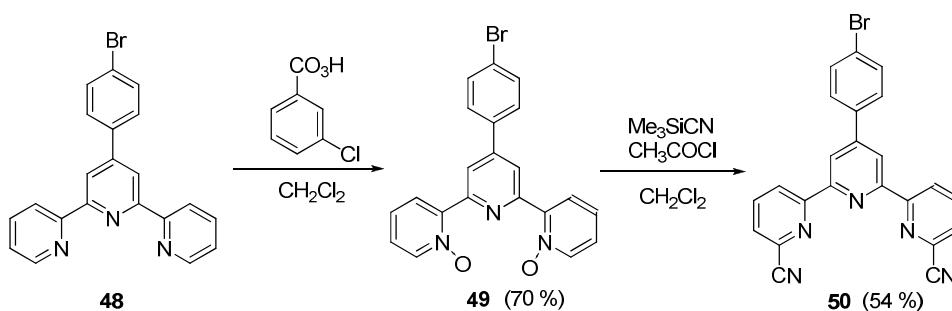
*Scheme 20*

This compound is known in literature data,<sup>8</sup> its structure was confirmed by spectroscopic and mass spectrometry data.

The compound **48** was used with success to obtain N,N-dioxide derivative **49** in presence of *m*-chloroperbenzoic acid, at room temperature and using DCM as solvent (**Scheme 21**). Derivative **49** is an important key intermediate for obtaining different terpyridine structures, because N-O group is an *orto*-directing group, which favours the new substituent to be located in *orto* position related to nitrogen atom. So, using a Reissert-Henze<sup>9</sup> type reaction, with trimethylsilylcyanide and acetyl chloride, from compound **49** was obtain 6,6''-dicyano monoterpyridine **50** (**Scheme 21**) in a good yield (50%). The structure of this compound was identified by NMR analysis (proton and carbon) and is identical with the literature data.<sup>8</sup>

<sup>8</sup> Han, F. S.; Higuchi, M.; Kurth, D. G. *Org. Lett.* **2007**, *9*, 559-562.

<sup>9</sup> Pauvert, M.; Collet, S. C.; Bertrand, M.; Guingant, A. Y.; Evain, M. *Tetrahedron Lett.* **2005**, *46*, 2983-2987.

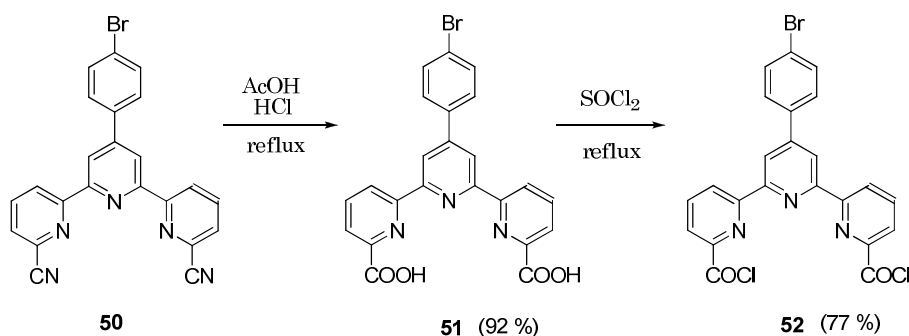


**Scheme 21**

The –CN group located on the pyridine structure, can be easily transformed in different other functional groups, allowing this compound to be considered a very important precursor to attain many functionalized terpyridine systems.

Thus, using derivative **50** as starting material was tried different methods to obtain some terpyridine derivatives<sup>10,11</sup> which can allow further (using different ligands) the synthesis of some new supramolecular assemblies (cryptands and/or coronands).

Firstly, was obtained 4'-(4-bromophenyl)-2,2':6',2''-terpyridin-6,6''-dicarboxylic acid **51** following a literature procedure.<sup>12,13</sup> This compound, further led to formation of diacid chloride **52** (**Scheme 22**).<sup>14</sup>



**Scheme 22**

<sup>10</sup> Cooper, M. E.; Sammes, P. G. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1695-1700.

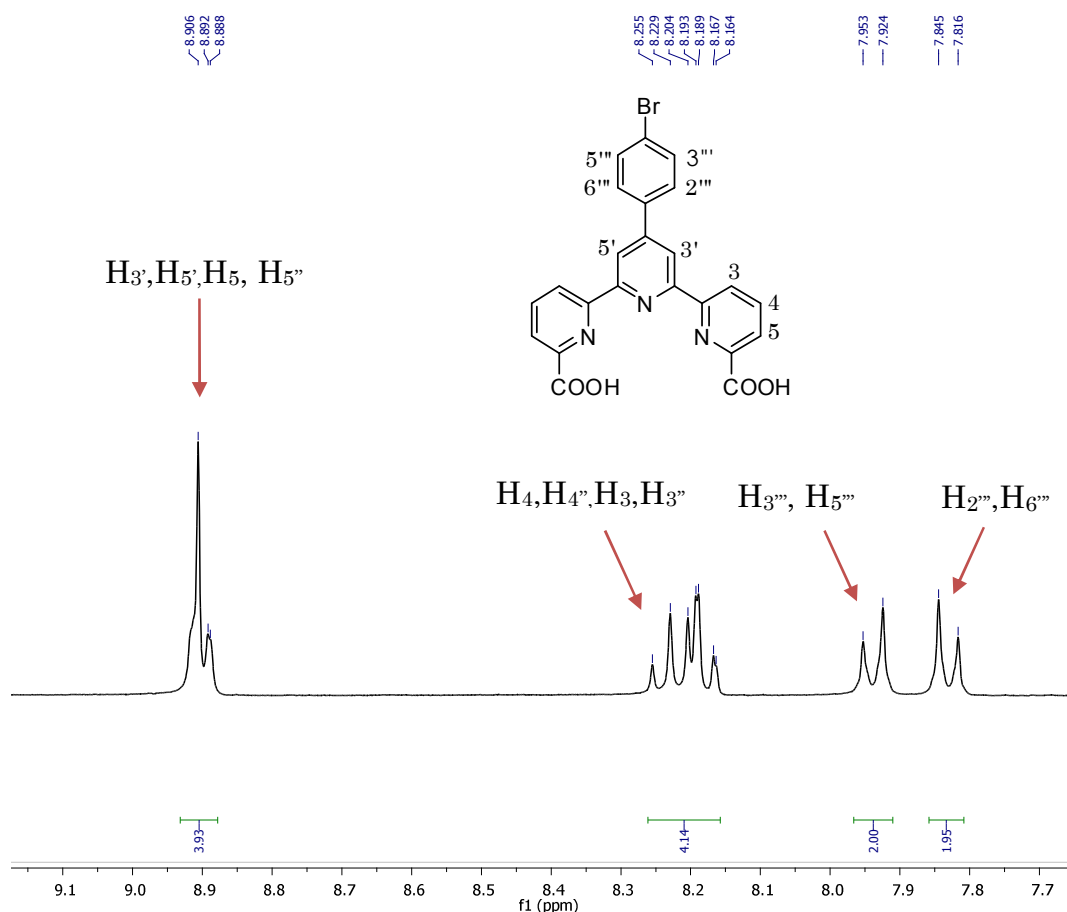
<sup>11</sup> Wessjohann, L. A.; Rivera, D. G.; Leon, F. *Org. Lett.* **2007**, 9, 4733-4736.

<sup>12</sup> Coates, J.; Sammes, P. G.; West, R. M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1275-1282.

<sup>13</sup> Adolfsson, H.; Warnmark, K.; Moberg, C. *J. Org. Chem.* **1994**, 59, 2004-2009.

<sup>14</sup> Petitjean, A.; Khoury, R. G.; Kyritsakas, N.; Lehn, J.-M. *J. Am. Chem. Soc.* **2004**, 126, 6637-6647.

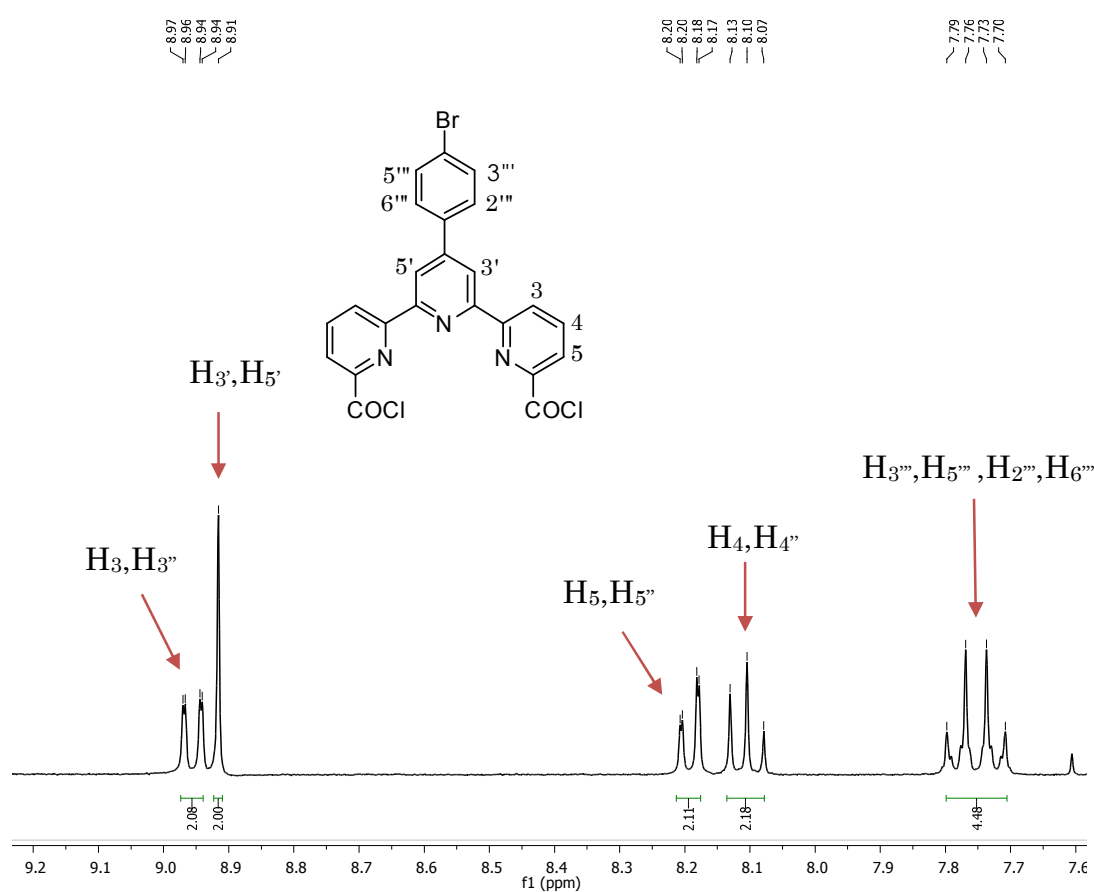
To our knowledge, compounds **51** and **52** have not being reported in literature till now. Here, they are presented and fully analysed for the first time. The structure of derivative **51** was resolved based on proton (**Figure 13**) and carbon NMR analysis and confirmed by mass spectrometry.



**Figure 13.**  $^1\text{H}$  NMR fragment spectrum of compound **51** (300 MHz, DMSO  $d_6$ )

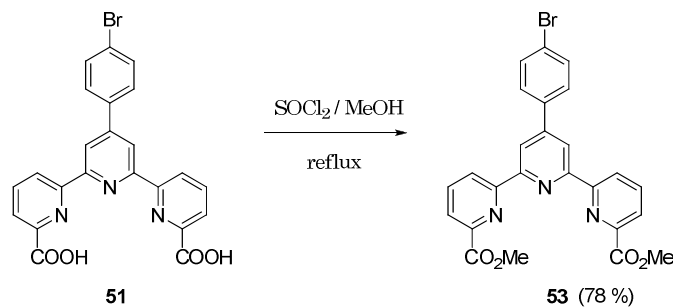
In  $^1\text{H}$  NMR spectrum (**Figure 13**), the  $\text{H}_{3'}$  and  $\text{H}_{5'}$  protons give a singlet at  $\delta = 8.89$  ppm; this signal is overlapped with signal gave by the  $\text{H}_5$ ,  $\text{H}_{5''}$  protons. Superimposed signals appear also in the case of  $\text{H}_4$ ,  $\text{H}_{4''}$  and  $\text{H}_3$ ,  $\text{H}_{3''}$  protons in region 8.16-8.25 ppm.

Diacide chloride **52** was obtained from diacid **51** in reaction with thionyl chloride (SOCl<sub>2</sub>), at reflux for two hours, the yield of this derivative being very good (77%). The structure of this compound was investigated by NMR spectroscopy (<sup>1</sup>H and <sup>13</sup>C) and mass spectrometry. The <sup>1</sup>H NMR spectrum of compound **52** (**Figure 16**) shows a doublet for H<sub>3</sub> and H<sub>3'</sub> protons at δ = 8.95 ppm. At δ = 8.91 ppm was identified the signal for H<sub>3'</sub> and H<sub>5'</sub>, while the most shielded protons are those on phenyl nuclei. Complete analysis for this compound was possible using also 2D-analysis (COSY).



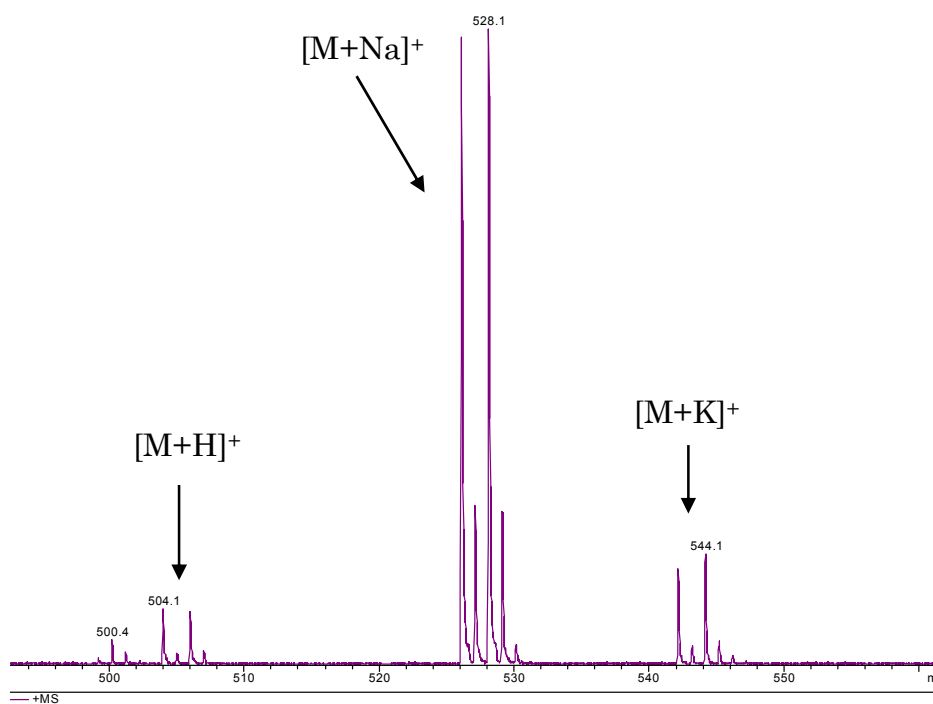
**Figure 16.** <sup>1</sup>H NMR fragment spectrum of compound **52** (300 MHz, CDCl<sub>3</sub>)

Diester **53** (*Scheme 23*)<sup>15</sup> was obtained using dicarboxylic acid **51** as starting material. Also, this compound is for the first time presented here, its structure being identified and confirmed by NMR spectroscopy and mass spectrometry.



*Scheme 23*

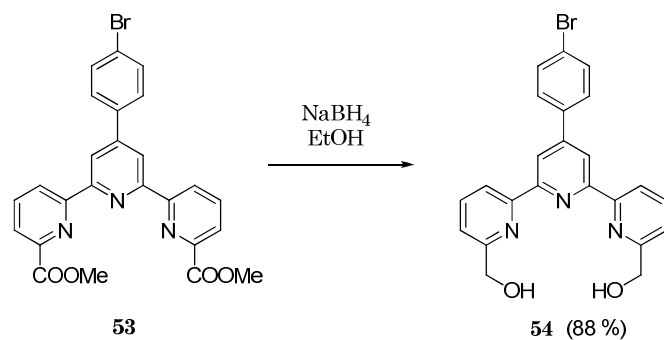
In the mass spectrum of diester **53** (*Figure 20*) can be observed molecular peak corresponding to  $[M+H]^+$  at  $m/z = 504.1$  and  $506.1$  respectively; to  $[M+Na]^+$  at  $m/z = 526.1$ ,  $528.1$  and also  $[M+K]^+$  at  $m/z = 542.1$  and  $544.1$  respectively.



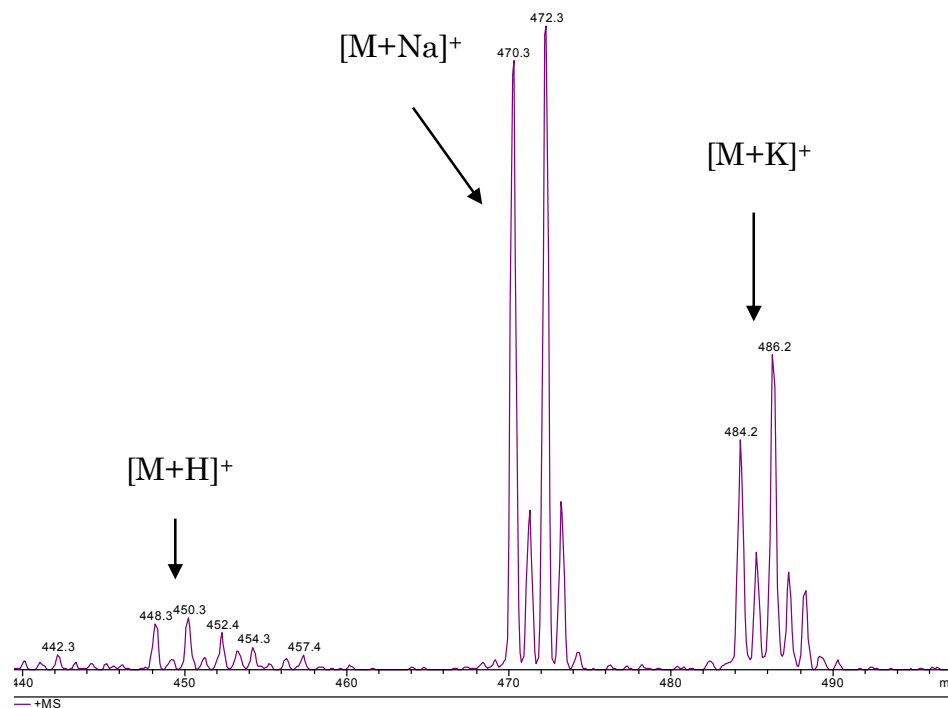
*Figure 20.* Mass spectrum (MALDI+/DCTB) fragment of **53**

<sup>15</sup> Galaup, C.; Couchet, J.-M.; Bedel, S.; Tisnes, P.; Picard, C. *J. Org. Chem.* **2005**, *70*, 2274-2284.

The compound **53** was reduced to its alcohol **54** using NaBH<sub>4</sub>, in anhydrous ethanol (**Scheme 24**), following a procedure described in literature.<sup>15</sup> The obtained compound was identified and analyzed by NMR spectroscopy (<sup>1</sup>H NMR (**Figure 21**) and APT) but also by mass spectrometry.

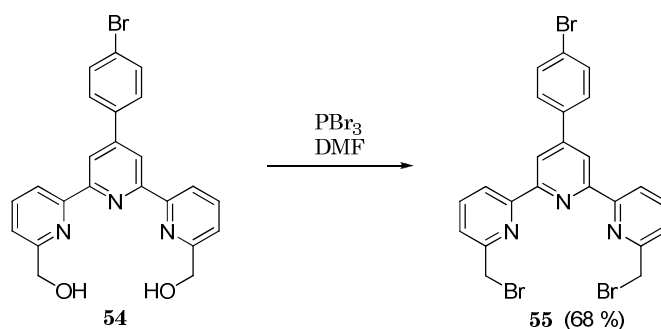


The molecular ion peak  $[M+H]^+$  of **54** (**Figure 22**) can be observed in mass spectrum at  $m/z = 448.3$  and  $450.3$  respectively;  $[M+Na]^+$  at  $m/z = 470.3$  and  $472.3$  but also  $[M+K]^+$  at  $m/z = 486.3$  and  $488.3$ .



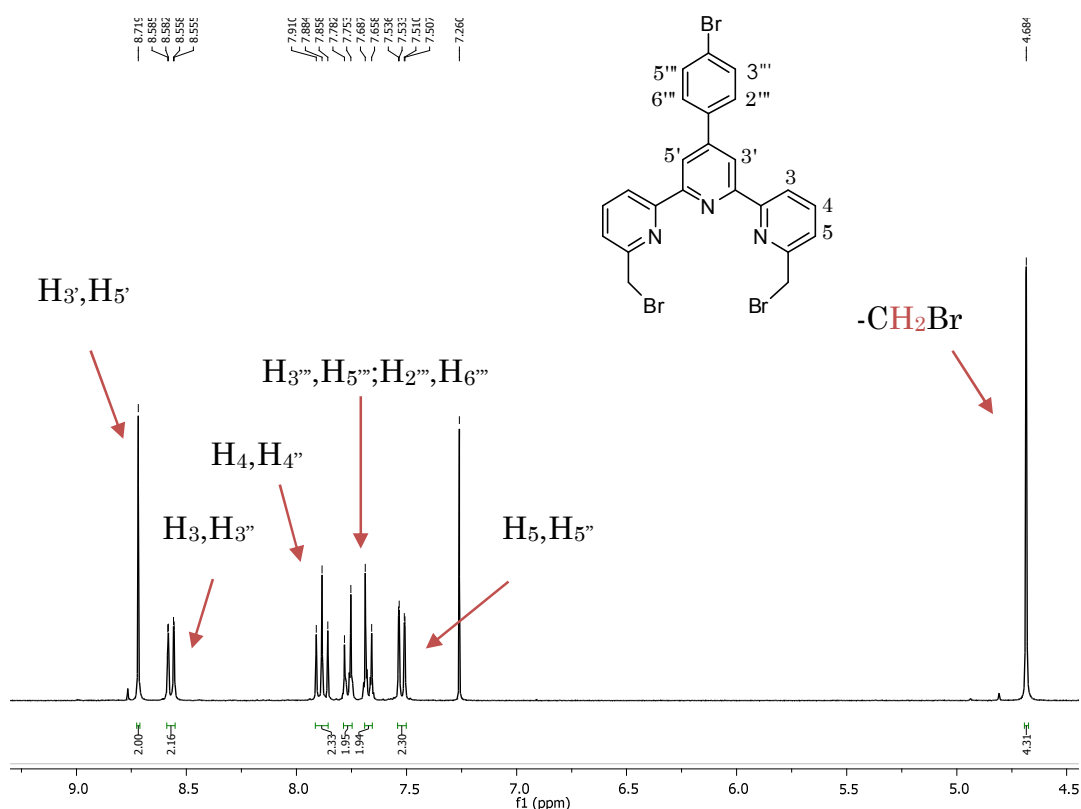
**Figure 22.** Mass spectrum (MALDI+/DCTB) fragment for compound **54**

Starting from alcohol **54**, was obtained derivative **55**,<sup>15</sup> in good yields (**Scheme 25**); its structure was identified by NMR spectroscopy (**Figure 23**) and mass spectrometry.



**Scheme 25**

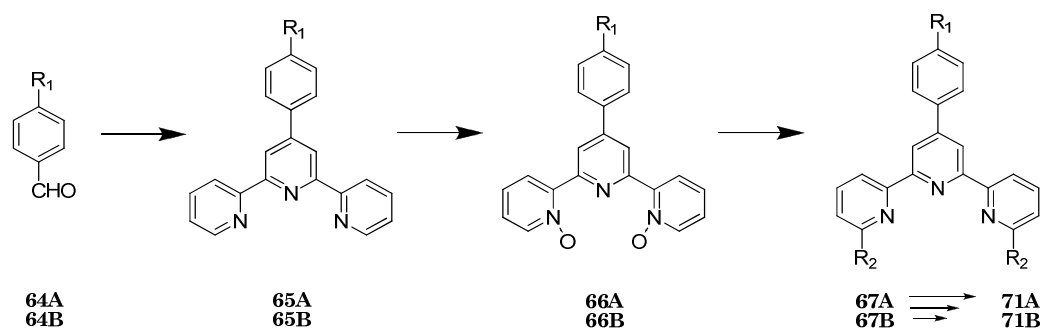




**Figure 23.**  $^1\text{H}$  NMR fragment spectrum of compound **55** (300 MHz,  $\text{CDCl}_3$ )

In  $^1\text{H}$  NMR spectrum of **55** was observed a singlet at 8.71 ppm corresponding to  $\text{H}_{3',5'}$ ; phenyl protons give AB system at 7.75 ppm; also  $\text{H}_{3,3''}$  give a doublet 8.57 ppm, at 7.88 ppm appear one triplet for  $\text{H}_{4,4''}$  and one doublet at 7.52 ppm for  $\text{H}_{5,5''}$ . Methylene protons ( $-\text{CH}_2\text{-Br}$ ) gave a singlet at 4.68 ppm.

Also, were obtained two series of terpyridine podands (precursors in macrocyclization reactions); general scheme is presented below (**Scheme 32**) and reaction conditions are gathered in **Table 1**.



**Scheme 32**

**Tabel 1.** General reaction conditions for terpyridine derivatives **65-71**

Compound	<b>65</b> A(R <sub>1</sub> =H) B(R <sub>1</sub> =CN)	<b>66</b> A(R <sub>1</sub> =H) B(R <sub>1</sub> =CN)	<b>67</b> A(R <sub>1</sub> =H R <sub>2</sub> =CN) B(R <sub>1</sub> ,R <sub>2</sub> =CN)	<b>68</b> A(R <sub>1</sub> =H R <sub>2</sub> =CO <sub>2</sub> H) B(R <sub>1</sub> ,R <sub>2</sub> =CO <sub>2</sub> H)	<b>69</b> A(R <sub>1</sub> =H R <sub>2</sub> =CO <sub>2</sub> Me) B(R <sub>1</sub> ,R <sub>2</sub> =CO <sub>2</sub> Me)	<b>70</b> A(R <sub>1</sub> =H R <sub>2</sub> =CH <sub>2</sub> OH) -	<b>71</b> A(R <sub>1</sub> =H R <sub>2</sub> =CH <sub>2</sub> Br) -
Reaction conditions	NaOH NH <sub>4</sub> OH MeOH reflux	<i>m</i> -CPBA DCM r.t.	Me <sub>3</sub> SiCN CH <sub>3</sub> COCl DCM r.t.	AcOH HCl reflux	SOCl <sub>2</sub> MeOH reflux	NaBH <sub>4</sub> EtOHanh	PBr <sub>3</sub> DMFanh
Yield (%)	<b>65A</b> (49%) <b>65B</b> (92%)	<b>66A</b> (74%) <b>66B</b> (77%)	<b>67A</b> (37 %) <b>67B</b> (73 %)	<b>68A</b> (66 %) <b>68B</b> (88 %)	<b>69A</b> (72 %) <b>69B</b> (83 %)	79 %	84 %
Literature data	8	8	8	12	15	15	15

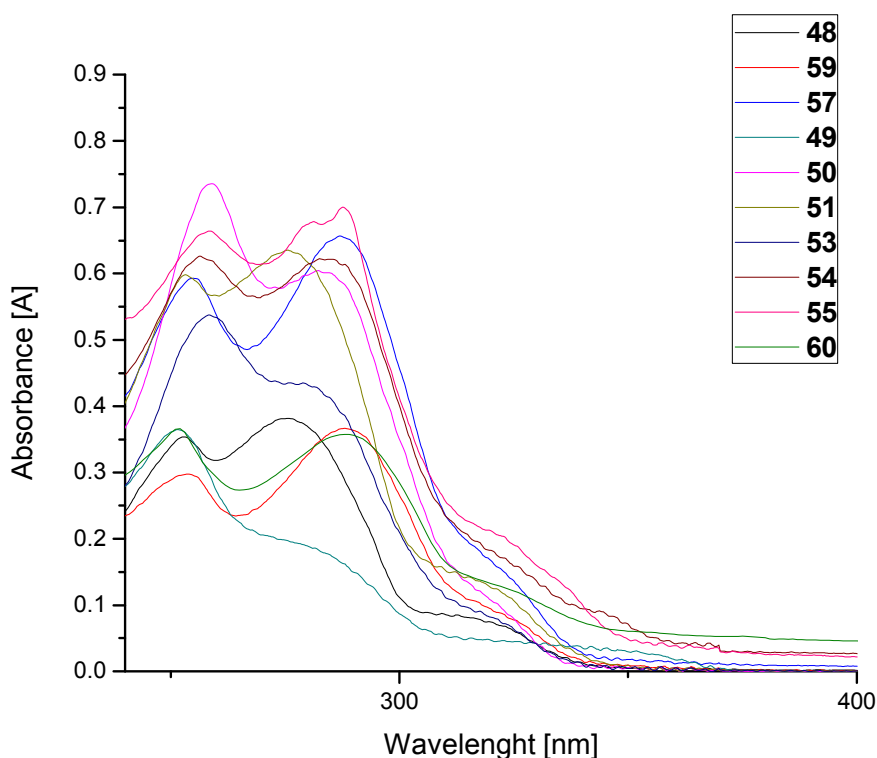
Most of these compounds are new, their structure being resolved by NMR spectroscopy and mass spectrometry. Their general data are presented in experimental part.

### I.3.2. Photochemical properties

#### 3.2.1. UV-Vis studies

For derivatives **48-60** were inregistered UV-Vis spectra using CH<sub>3</sub>CN as solvent (**Figure 31**) keeping the same concentrations for all samples (5x10<sup>-6</sup>M). The

maxima absorbtion ( $\lambda_{\text{abs.}}$ ) of the terpyridine system is not influenced by the presence of different type of substituent, no matter that the substituent is an electrono-withdrawing (-CN,-COOH) or electronodonating group (-OMe).



**Figure 31.** UV-Vis spectra of terpyridine derivatives in  $\text{CH}_3\text{CN}$  ( $5 \times 10^{-6} \text{ M}$ )

Molar absorbtivity instead ( $\log \epsilon$  in **Tabel 2**) is corelated with substituent's nature. The presence of  $-\text{CN}$  group (electronowithdrawing) located on pyridine nuclei led to a slight growth of molar absorbtivity if compared with mother terpyridine **48** (with no substituent on pyridine structure). As can be deduced from **Tabel 2**, the nature of substituents located on terpyridine unit led to a slight growth of absorbance if compared with the unsubstituted derivative.

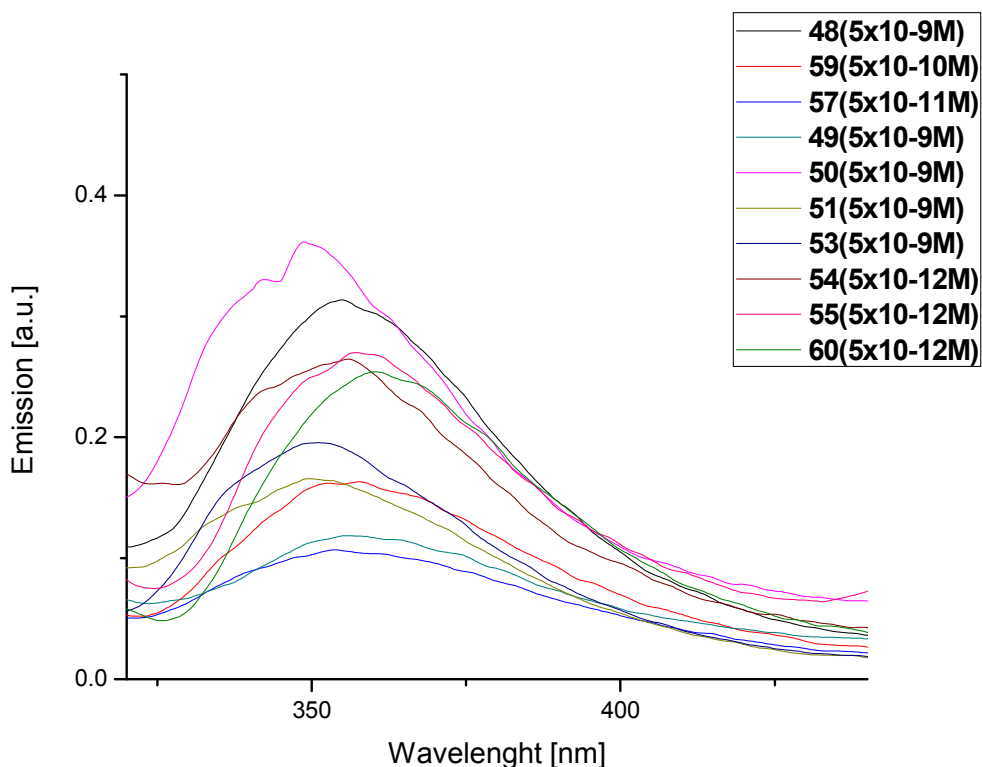
**Tabel 2.** Absorbance properties of terpyridine derivatives ( $5 \times 10^{-6} \text{M}$ ,  $\text{CH}_3\text{CN}$ )

Compound	$\lambda_{\text{abs}}(\text{nm})$ ( $\log 10 \epsilon$ )
<b>48</b>	253 (4.84), 275 (4.88)
<b>49</b>	251 (4.86), 280 (4.57)
<b>50</b>	258 (5.17), 282 (5.08)
<b>51</b>	253 (5.07), 275 (5.14)
<b>53</b>	258 (5.02), 281 (4.93)
<b>54</b>	256 (5.09), 284 (5.09)
<b>55</b>	258 (5.12), 288 (5.14)
<b>57</b>	255 (5.07), 287 (5.11)
<b>59</b>	254 (4.77), 289 (4.86)
<b>60</b>	252 (4.84), 288 (4.85)

In the same conditions were recorded absorbance spectra for the same compounds using DMSO as solvent. As before, the electronwithdrawing/electronodonating influences of substituents have little contribution to the absorbance maxima peaks, which are located to a lower wavelength region (278-293 nm).

### 3.2.2. Fluorescence studies

Also were investigated fluorescence properties for derivatives **48-60**; the solvent used was  $\text{CH}_3\text{CN}$ . The aim of this study was to determinate the influences of the substituents located either on pyridine or phenyl rings. In **Figure 33** was noticed that electronodonating groups located on phenyl ring bring a high influence to emission intensity than electronodonating groups located on pyridine.



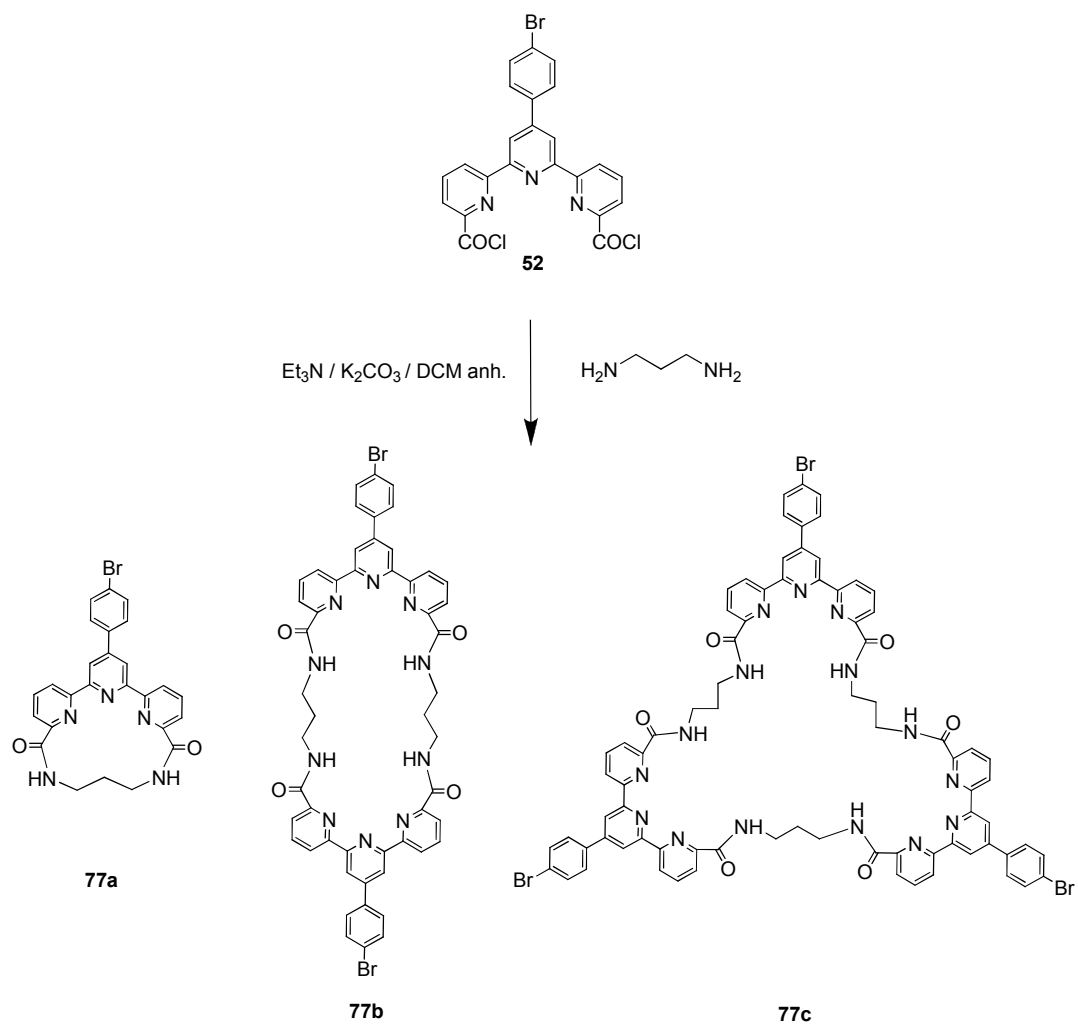
**Figure 33.** Emission spectra of terpyridine derivatives in CH<sub>3</sub>CN (298 K)

These podands are starting materials for supramolecular assemblies such as rotaxans, coronands, cryptands, paraquats, etc.

Starting from diacid chloride **52** with diamine derivatives, were tried some macrocyclization reactions.

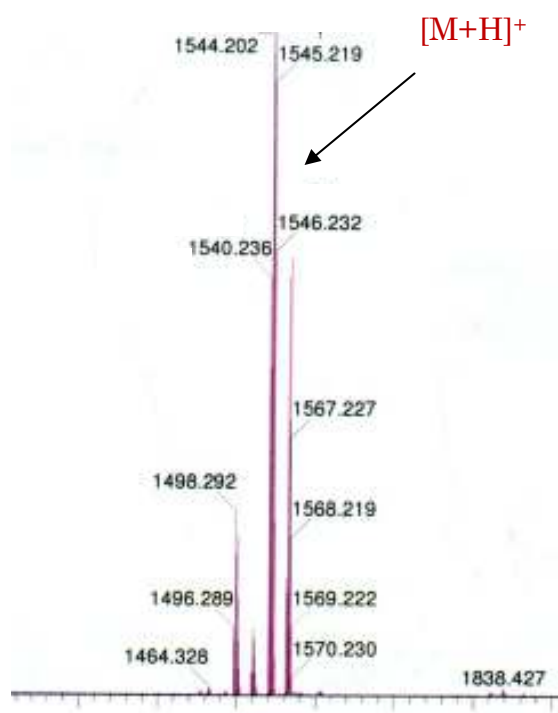
The reaction between **52** and 1,3-diaminopropane was carried out in ultradiluted conditions, in presence of Et<sub>3</sub>N and anhydrous dichloromethane as solvent.<sup>16</sup> Using mass spectrometry (MALDI-TOF), were identified the monomer **77a**, the dimer **77b** but also the trimer derivative **77c** (*Scheme 37*).

<sup>16</sup> Ahmed, H. M. E.; Ashraf, A. A. *Tetrahedron* **2000**, *56*, 885-895.



***Scheme 37***

Taking the compound **77c** as example, in mass spectrum (MALDI-TOF) were observed the molecular ion peak for  $[\text{M}+\text{H}]^+$  at  $m/z = 1540.2, 1542.2, 1544.2$  and  $1546.2$  (**Figure 37**).



**Figure 37.** Mass spectrum (MALDI-TOF) fragment of compound **77c**

A new way to achieve macrocycles which present a terpyridine unit is the synthesis of paraquats. These compounds are used in the synthesis of rotaxans and catenands, structures which can form inclusion complexes with aromatic molecules.<sup>17,18,19,20</sup>

The synthesis of **55** with 4,4'-bipyridine (**Scheme 41**)<sup>21</sup> led to formation of derivative **81** and not the desired macrocycle, the <sup>1</sup>H NMR and <sup>31</sup>P NMR being in concordance with this conclusion.

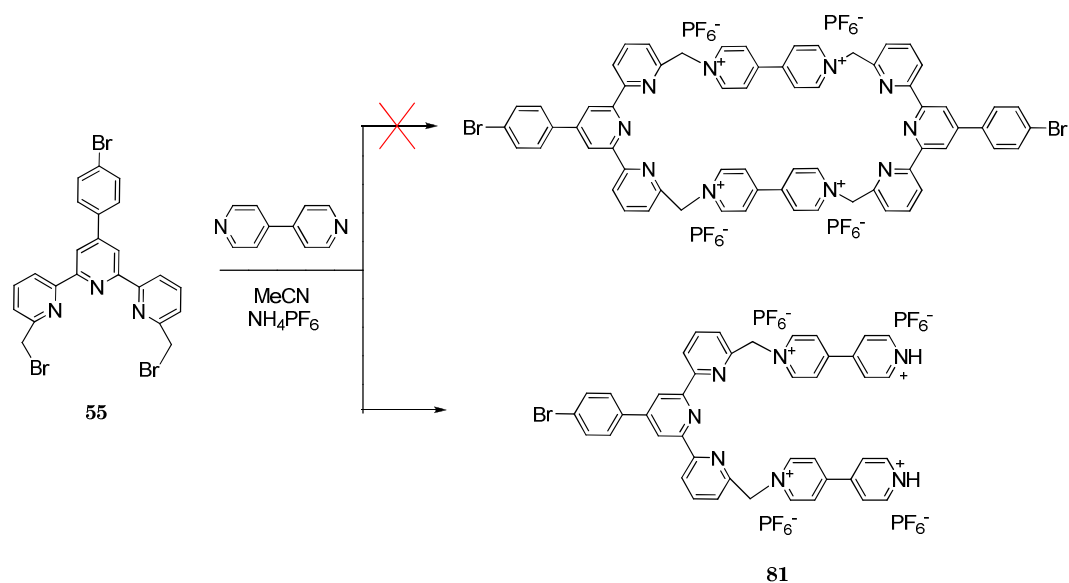
<sup>17</sup> (a) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725-2828; (b) Asakawa, M.; Ashton, P. R.; Boyd, S. E.; Brown, C. L.; Menzer, S.; Pasini, D.; Stoddart, J. F.; Tolley, M. S.; White, A. J. P.; Williams, D. J.; Wyatt, P. G. *Chem. Eur. J.* **1997**, *3*, 463-481.

<sup>18</sup> Amabilino, D. B.; Ashton, P. R.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1998**, *4*, 460-468.

<sup>19</sup> Houk, K. N.; Menzer, S.; Newton, S. P.; Raymo, F. M.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 1479-1487.

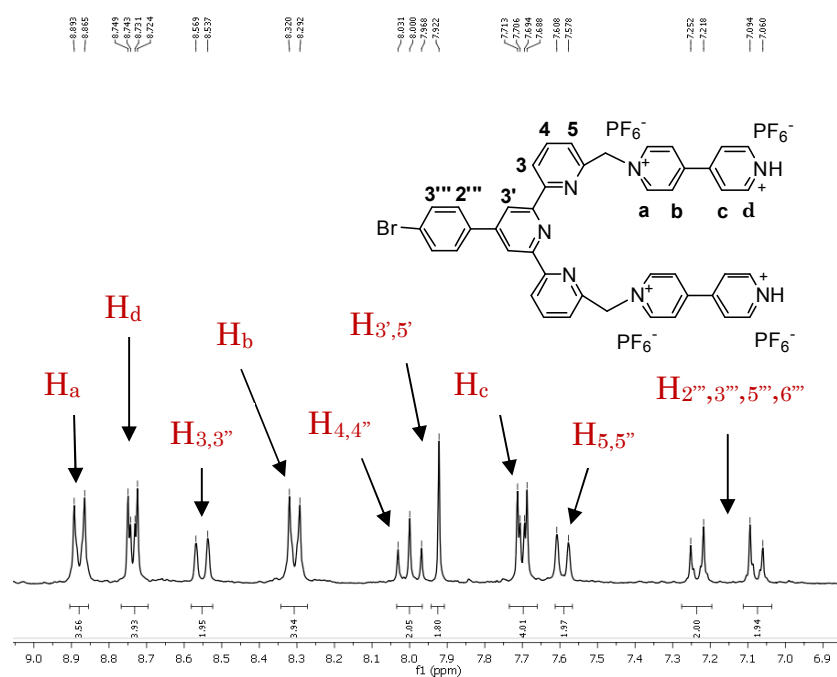
<sup>20</sup> Ghosh, K.; Sarkar, A. R. *Tetrahedron Lett.* **2009**, *50*, 85-88.

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**Scheme 41**

In  $^1\text{H}$  NMR spectrum (**Figure 42**) were identified the corresponding signals for terpyridine and bipyridine units. The most deshielded signals belong to pyridine protons, followed by signals for terpyridine protons.



**Figure 42.**  $^1\text{H}$  NMR fragment spectrum for compound **81** (400 MHz,  $\text{DMSO } d_6$ )



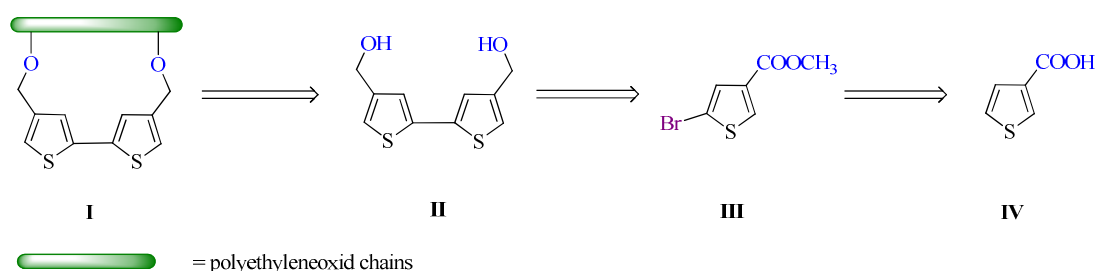
## **PART II**

# **Synthesis and Structural Analysis of Some New Macrocycles with Bithiophene Units**

## II.2. Objectives

The main target of this thesis was the synthesis of some macrocyclic compounds possessing one bithiophene unit and which contains in  $\beta$  position  $-\text{CH}_2\text{O}$  units; these units are *spacers* between bithiophene unit and the ligand. For macrocyclization reactions were used tosylated polyethyleneglycol chains with different length, which are later attached to the spacers. It will be studied their supramolecular properties and also their abilities to complex cations. Due to this properties, can be obtained metallo-supramolecular structures with interesting photochemical, electrochemical catalitical and magnetical properties. More than that, the supramolecular structures would have a well-defined stereochemistry which can have a major importance when structure-property relationship is taken into consideration.

The synthetic pathway of the targeted macrocyclic derivatives is presented below in *Scheme* .

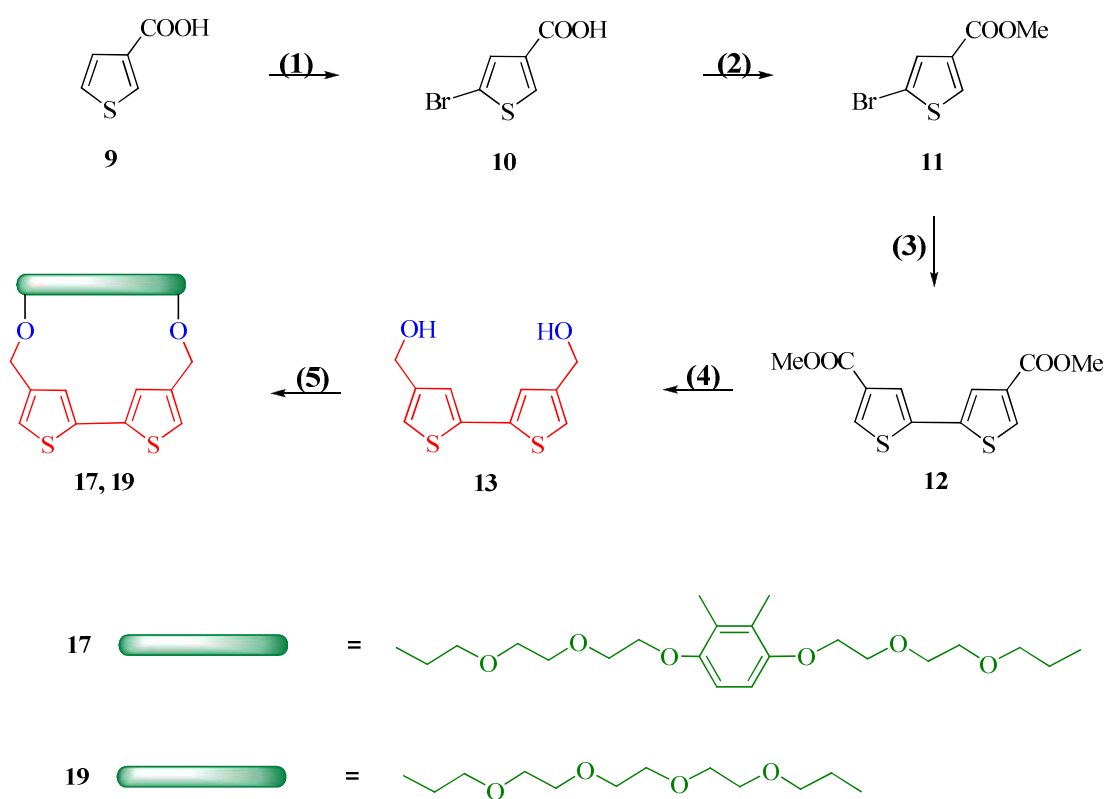


*Scheme 4*

The bromination of thiophene acid **IV**, followed by esterification reaction led to derivative **III**. This compound, by homocoupling reaction ensue by reduction, forms the alcohol **II**. The diol in reaction with different ditosylated polyethyleneglycol chains, in presence of a base led to the target macrocycles **I**.

## II.3. Results and discussions

The path followed to obtain the target macrocycles is shortly presented in **Scheme 5**. The procedure suppose the synthesis of compounds **17** and **19** in five steps; the intermediates **9-13** were obtained using procedures from literature data,<sup>22</sup> while for the two macrocycles (**17** and **19**) were used modified procedures from literature.<sup>23</sup>

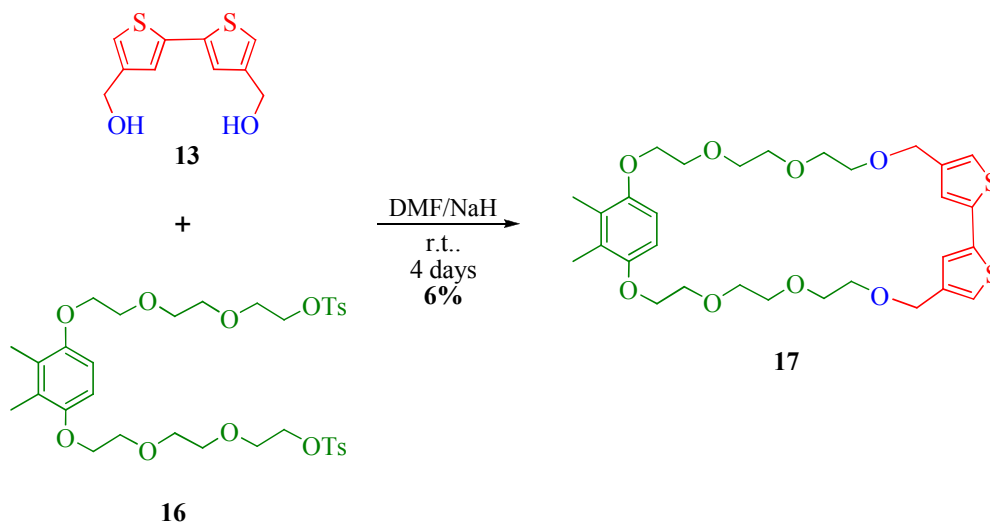


**Scheme 5**

<sup>22</sup> (a) Pomerantz, M.; Chang, Y.; Kasim, R. K.; Elsenbaumer, R. L. *J. Mater. Chem.* **1999**, 2155; (b) Satonaka, H. *Bull. Chem. Soc. Jpn.* **1983**, 56, 3337; (c) Taylor, E. C.; Vogel, D. E. *J. Org. Chem.* **1985**, 50, 1002; (d) Fanta, P. E. *Chem. Rev.* **1964**, 64, 613; (e) Fanta, P. E. *Synthesis* **1974**, 9; (f) Masui, K.; Ikegami, H.; Mori, A. *J. Am. Chem. Soc.* **2004**, 126, 5074.

<sup>23</sup> (a) Pomerantz, M.; Chang, Y.; Kasim, R. K.; Elsenbaumer, R. L. *Synth. Met.* **1999**, 101, 162; (b) Amarasekara, A. S.; Pomerantz, M. *Synthesis* **2003**, 14, 2255.

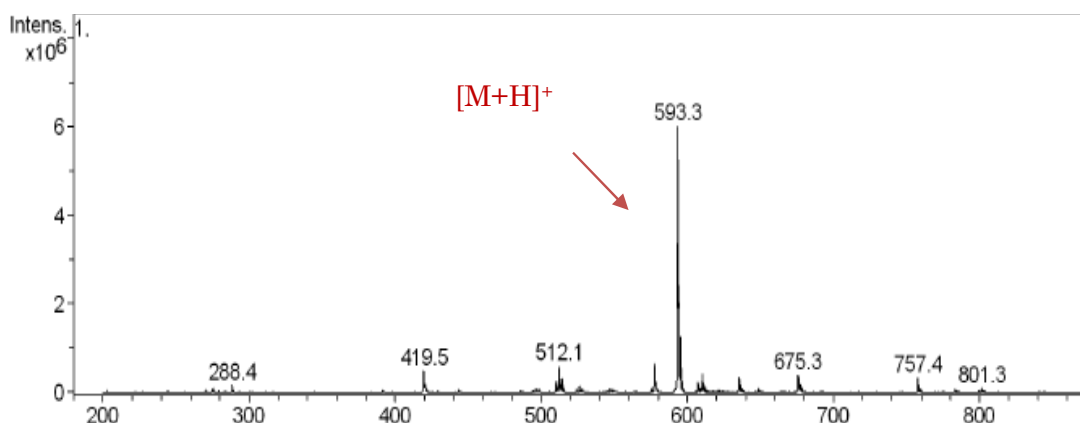
The compound **16** was used as bonding chain in macrocyclization reaction with alcohol **13**. This reaction occurs in anhydrous and degassed DMF, in presence of NaH as a base, which favorise the nucleophilic attack of tosylated derivatives (**Scheme 11**). The ditosylated compound **16** is added dropwise at room temperature for one day, after that the reaction is left three days at room temperature.



**Scheme 11**

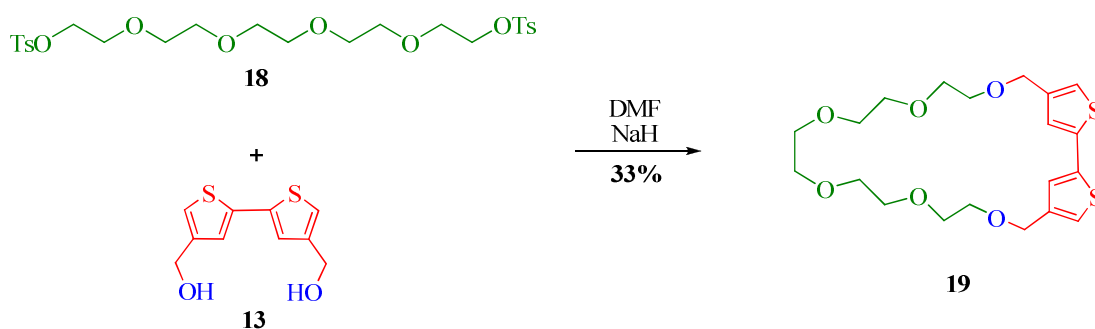
The structure of compound **17** was identified by NMR spectroscopy and mass spectrometry.

In the mass spectrum (APCI+) of **17** (**Figure 8**) was observed the molecular ion peak  $[M+H]^+$  at  $m/z = 593.3$ .



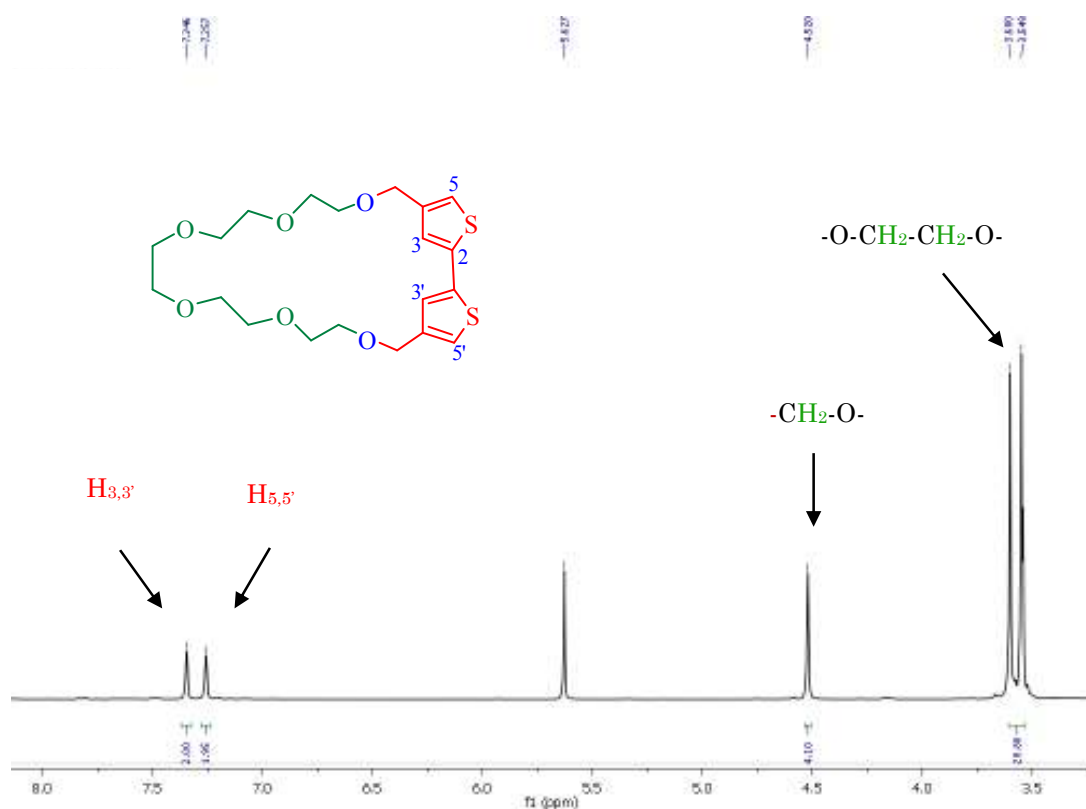
**Figure 8.** Fragment of APCI+ spectrum of derivative **17**

Following the same protocol as before, from alcohol **13**, in reaction with ditosylated pentaethyleneglycol **18**, was obtained macrocycle **19**, in good yields (**Scheme 13**).



**Scheme 12**

The structure of derivative **19** was identified by NMR spectroscopy and mass spectrometry. In the aromatic region of  $^1\text{H}$  spectrum (**Figure 9**) were identified two singlets for  $\text{H}_{3,3'}$  (7.34 ppm) and  $\text{H}_{5,5'}$  (7.25 ppm). In aliphatic area, at  $\delta = 4.52$  ppm appears the singlet corresponding for  $-\text{CH}_2\text{O}-$ , and in 3.54-3.60 ppm region are assigned the signals corresponding to polyethyleneglycol protons.



**Figure 9.**  $^1\text{H}$  NMR fragment spectrum of compound **19**  
(300 MHz, acetone  $d_6$ )

The compounds **17** and **19** will further be tested in view of their complexation properties when added different cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Ba}^{2+}$ ); also will be used cyclic voltammetry, UV-Vis and Fluorescence spectroscopy to investigate the possible modifications in their aspects when complexation occurs.

## GENERAL CONCLUSIONS

In this thesis are presented the results obtained in synthesis and characterization of some new heterocyclic derivatives with terpyridine and thiophene units.

In the first part are described the methods of synthesis and structural analysis of 19 new podands with a terpyridinic unit; their structure was determined by NMR spectroscopy and mass spectrometry. Were also studied the photochemical properties by UV-Vis and fluorescence showing the differences in wavelength movement and the intensity of absorption / emission depending on the nature of solvent but also, depending on the substituents attached to the terpyridine structure.

The terpyridinic podands were used as precursors in the synthesis of new supramolecular structures; were synthesised three new macrocycles (monomer, dimer and trimer) by the reaction of acid dichloride **52** and 1,3-diaminopropane; from the reaction of terminal alchine **79** and the azide **78** (*click reaction*) the complex **80** was obtained and after synthesis of paraquat has been identified a new terpyridinic derivative **81**. These compounds were identified and analyzed by NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$ ) and confirmed by mass spectrometry (ESI, APCI or MALDI).

In the second part are presented the results obtained in synthesis and characterisation of some new macrocycles with a bithiophene unit. Thus, we succeeded to obtain, in good yields, two new macrocycles (**17** and **19**), containing as “spacer” the  $-\text{CH}_2\text{O}-$  group between the bithiophene unit and the polyethyleneglicolic chain.

The structure of these compounds was determined by nuclear magnetic resonance (NMR) and by mass spectrometry.

These compounds will be subjected to complexation reactions with various cations and neutral molecules in order to study their properties and possible applications in different fields: nanotechnology, medicine, etc.

**Keywords:** heteroarene, terpyridine, bithiophene, podands, macrocycles, absorbtion, fluorescence