

Article

## Synthesis of the Novel 4,4'- and 6,6'- Dihydroxamic - 2,2'-Bipyridines and Improved Routes to 4,4'- and 6,6'- Substituted 2,2'-Bipyridines and Mono-N-Oxide-2,2'-Bipyridine

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Neste trabalho relatamos a preparação, por métodos mais eficientes e práticos, de derivados da 2,2'-bipiridina, que são importantes precursores para outros, tais como: 4,4'-dicarbóxi-2,2'-bipiridina (**I**), 6,6'-dicarbóxi-2,2'-bipiridina (**II**), 6,6'-dicarbotiamida - 2,2'-bipiridina (**III**), 4,4'-dinitro-N,N'-dióxido-2,2'-bipiridina (**IV**) e mono-N-óxido-2,2'-bipiridina (**VII**). A síntese dos ligantes inéditos 4,4'-diácido hidroxâmico-2,2'-bipiridina (**V**) e 6,6'-diácido hidroxâmico-2,2'-bipiridina (**VI**) é também relatada.

The preparation of key precursors for many 2,2'-bipyridine derivatives such as 4,4'-dicarboxy-2,2'-bipyridine (**I**), 6,6'-dicarboxy-2,2'-bipyridine- acid (**II**), 4,4'-dinitro-2,2'-bipyridine-N,N-dioxide (**III**), 6,6'-dicarbothioamide-2,2'-bipyridine (**IV**) and mono-N-oxide-2,2'-bipyridine (**VII**) through more efficient methods is described. The syntheses of the novel ligands 4,4'-dihydroxamic-2,2'-bipyridine (**V**) and 6,6'-dihydroxamic-2,2'-bipyridine (**VI**) are also reported.

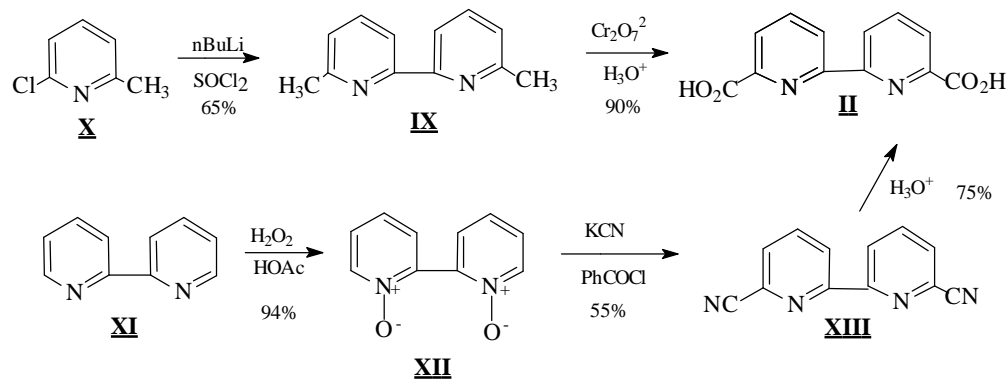
**Keywords:** 2,2'- bipyridine derivatives, improved syntheses, hydroxamic 2,2'-bipyridines

### Introduction

2,2'-Bipyridinyls continue to attract attention as important ligands of great interest for chelation of transition metals<sup>1</sup> due to their ability to form very stable complexes with many cations and to their remarkable anti-tumoral<sup>2-5</sup>, catalytic<sup>6</sup>, electrocatalytic<sup>7,8</sup> and photochemical<sup>9</sup> properties. Nevertheless, the methods available for the synthesis of new or even well-known symmetrical and unsymmetrical derivatives of 2,2'-bipyridines are usually not practical, and present low yields. 2,2'-Bipyridinyls can be prepared by three principal routes: *i*) from the cyclization of appropriately substituted precursors<sup>10a,b</sup>; *ii*) by coupling reactions of pyridines<sup>10c,11</sup>; *iii*) from the functionalization of the heteroaromatic ring of 2,2'-bipyridine through electrophilic and nucleophilic aromatic substitution reactions.

The coupling methods give low yields and the cyclization methods generally require the preparation of complex precursors. In fact, the functionalization of 2,2'-bipyridine is the most used method to obtain substituted 2,2'-bipyridinyls but, in many cases, low yields are obtained. In this article we describe new, easier and more efficient methods to synthesize important precursors for substituted 2,2'-bipyridines, such as 6,6'-dicarboxy-2,2'-bipyridine acid (**I**), 4,4'-dicarboxy-2,2'-bipyridine- (**II**) and 4,4'-dinitro-2,2'-bipyridine-N,N'-dioxide (**III**). The 6,6'-dicarbothioamide-2,2'-bipyridine (**IV**), an important precursor for thiazolyl derivatives and a ligand for complexes with antitumoral activity<sup>2-5</sup>, was also prepared by an improved procedure.

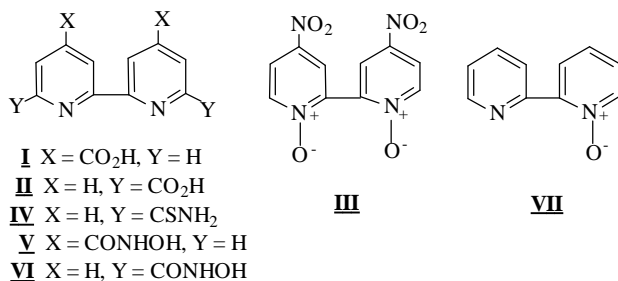
The synthesis of the novel ligands 4,4'-dihydroxamic-2,2'-bipyridine (**V**) and 6,6'-dihydroxamic-2,2'-bipyridine



**Scheme 2.** Synthetical routes to 6,6'-dicarboxy-2,2'-bipyridine (**II**).

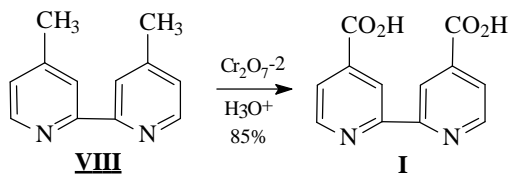
(**VI**) are also reported. These novel ligands are very interesting due to the possibility of coordination of both Fe(II) and Fe(III) to the same molecule.

An improved method is also reported to prepare mono- $\text{N}$ -oxide-2,2'-bipyridine (**VII**), the main precursor for the synthesis of unsymmetrical 2,2'-bipyridines.



## Results and Discussion

The 4,4'-dicarboxy-2,2'-bipyridine (**I**) and the 6,6'-derivative (**II**) are key intermediates to the synthesis of several carboxylic acid derivatives and other analogues. The preparation of 4,4'-dicarboxylic acid (**I**) (Scheme 1) has usually been carried out starting from the oxidation of the commercially available 4,4'-dimethyl-2,2'-bipyridine (**VIII**) with  $\text{KMnO}_4$ , but with low yield (< 40%)<sup>12</sup>. We obtained **I** from oxidation of **VIII** with dichromate acid solution in much higher yield (85%). The 6,6'-dicarboxy-2,2'-bipyridine (**II**) was prepared starting from 6,6'-dimethyl-2,2'-bipyridine (**IX**) (not available commercially), which could be synthesized from 6-chloro-2-picoline (**X**) by

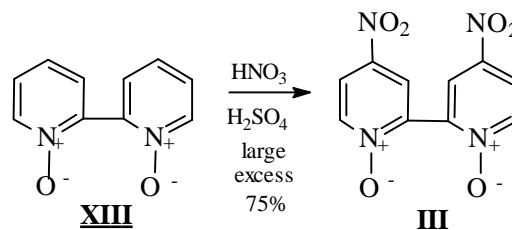


**Scheme 1.** Preparation of 4,4'-dicarboxy-2,2'-bipyridine (**I**).

Oae's method<sup>11</sup> (65% yield) followed by oxidation with dichromate acid solution, thus obtaining a much higher yield (90%) (yield = 50% from starting material **X**) (Scheme 2). (**II**) was also synthesized through a new route, starting from the 2,2'-bipyridine (**XI**) via 2,2'-bipyridine- $\text{N,N}'$ -dioxide (**XII**) and the 6,6'-dicyano-2,2'-bipyridine (**XIII**), a common precursor for many other derivatives<sup>13</sup> (Scheme 2).

The 4,4'-dinitro-2,2'-bipyridine- $\text{N,N}'$ -dioxide (**III**) is another very important precursor to several bipyridine derivatives<sup>14,15</sup>. **III** is usually synthesized in low to moderate yields ( $\cong 45\%$ ), but the nitration of pyridine- $\text{N}$ -oxide<sup>16</sup> gives 80-90% yield. We noticed that in the nitration of pyridine- $\text{N}$ -oxide the sulfonitric solution was used in much greater excess (heteroaromatic/ $\text{HNO}_3$ / $\text{H}_2\text{SO}_4 = 1:35:10$  molar ratio) compared to the usually used for the 2,2'-bipyridyl nitration (heteroaromatic/ $\text{HNO}_3$ / $\text{H}_2\text{SO}_4 = 1:9:3.7$  molar ratio). In fact, we observed higher yields (75%) when we used a higher concentration of sulfonitric solution for the nitration of 2,2'-bipyridine- $\text{N,N}'$ -dioxide (**XIII**) (Scheme 3).

We have also been studying new derivatives of 6,6'-dicarboxy-2,2'-bipyridine (**IV**) which have shown anti-tumoral activity<sup>4,5</sup>, as well as their metal complexes (with Fe(II)). We are studying the complexation with other metals such as Fe(III), Ni(II), Ru(II), Pd(II) and Pt(II). It is noteworthy that in the last step of a previously reported synthesis<sup>3,4</sup> of **IV**, the conversion of the 6,6'-dicyano-2,2'-bipyridine (**XIII**) to the dithiocarbamide **IV** is very complicated (48 h, using liquid ammonia and gaseous  $\text{H}_2\text{S}$ ) and

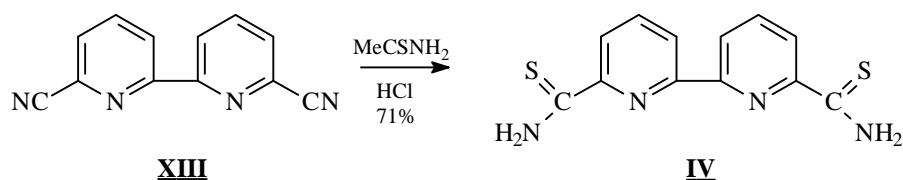


**Scheme 3.** Preparation of 4,4'-dinitro-2,2'-bipyridine- $\text{N,N}'$ -dioxide (**III**).

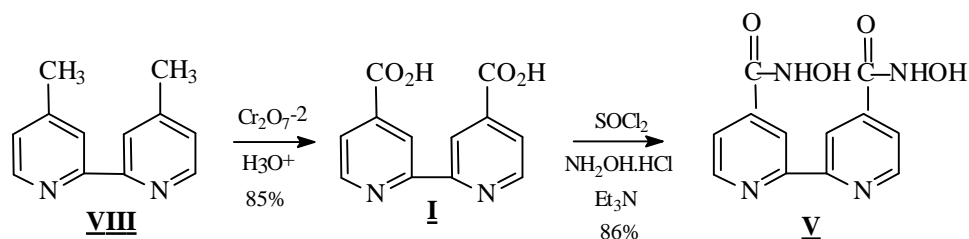
with only moderate yield (65% yield). We have devised a much easier and faster method<sup>17</sup> using thioacetamide with HCl on a steam bath for 30 min (71% yield) (Scheme 4).

The 4,4'-dihydroxamic-2,2'-bipyridine (**V**) and 6,6'-dihydroxamic-2,2'-bipyridine (**VI**) were prepared starting from their carboxylic acid analogues, **I** and **II** prepared as mentioned before, going through the diacyl dichloride (formed with  $\text{SOCl}_2$ ) and followed by direct reaction with hydroxylamine hydrochloride in the presence of dried triethylamine<sup>18</sup> (Schemes 5 and 6). The IR spectrum shows the characteristic bands of the hydroxamic group ( $\text{C}=\text{ON}-\text{HOH}$ ) and the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra showed the occurrence of (E-Z) isomerism in accordance with the studies of Brown and co-workers<sup>19</sup>.

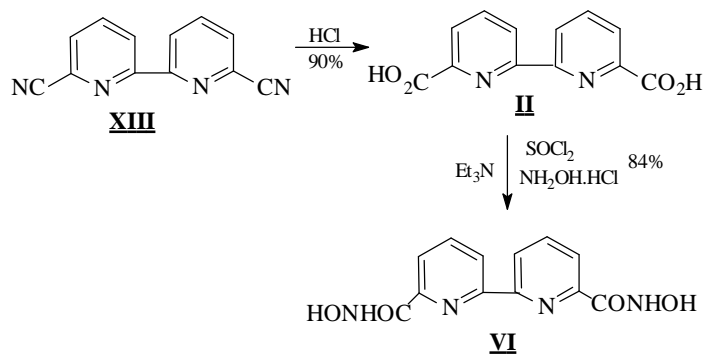
The mono-N-oxide-2,2'-bipyridine (**VII**) is the main precursor for the synthesis of unsymmetrical mono-substituted 2,2'-bipyridines due to the higher reactivity of the mono-N-oxide ring. The synthesis of unsymmetrical bipyridines has received attention, even recently<sup>20</sup>, due to their potential as precursors of unsymmetrical heterocycles. Nevertheless, the mono-N-oxide **VII** is usually made using peracetic acid prepared *in situ* (3 h, 49% yield)<sup>5</sup>, or by using *meta*-chloro perbenzoic acid (MCPBA) (15h, 79%)<sup>21</sup>. We prepared the mono-N-oxide **VII** in 80% yield using a new, and more selective oxidant named magnesium monoperoxyphthalate (MMPP) (**XIV**), in glacial acetic acid for 6 h at 85 °C (Scheme 7). Oxidations with MMPP



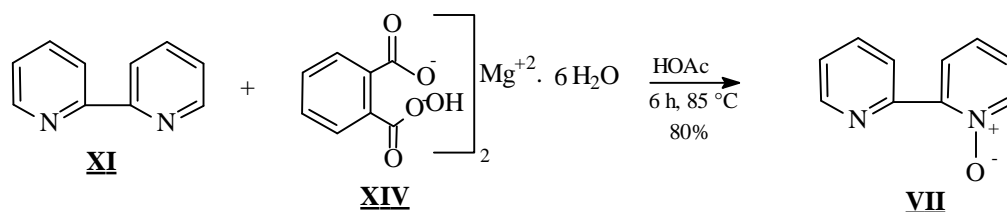
**Scheme 4.** Preparation of 6,6'-dicarbothioamide-2,2'-bipyridine (**IV**).



**Scheme 5.** Preparation of 4,4'-dihydroxamic-2,2'-bipyridine (**V**).



**Scheme 6.** Preparation of 6,6'-dihydroxamic-2,2'-bipyridine (**VI**).



**Scheme 7.** Preparation of mono-N-oxide-2,2'-bipyridine (**VII**).

afford N-oxides, sulfoxides and epoxides in good yields using mild conditions.

## Experimental

Melting points were determined on a Mettler apparatus and were uncorrected.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on an AC-80 (80 MHz) Bruker instrument. FT-IR spectra were recorded on a Mattson instrument model Galaxy 3000. The microanalysis were performed on a Perkin-Elmer 240B elemental analyser.

### 4,4'-Dicarboxy-2,2'-bipyridine (I)

To a solution of 3.14 g (9.7 mmol) of  $\text{Na}_2\text{Cr}_2\text{O}_7$  in 10.6 mL of concentrated sulfuric acid, was slowly added, under magnetic stirring, 0.80 g (4.3 mmol) of 4,4'-dimethyl-2,2'-bipyridine (VII). The resultant orange slurry became dark green after a while and reaction was complete after 30 min. The reaction mixture was then poured into 100 mL of cold water forming a light yellow precipitate. After filtration and drying, the solid was dissolved in an alkaline 10% NaOH aqueous solution followed by slow acidification (pH = 2) with 10% aqueous HCl solution. This recrystallization afforded the desired compound free of Cr(+3) ions. After a second filtration compound I was dried under vacuum ( $\text{P}_2\text{O}_5$  as drying agent) to provide a white solid (0.90 g, 85%) with m.p. > 300 °C. All spectroscopic and physical data were in full agreement with those obtained for a commercial sample.

### 6,6'-Dicarboxy-2,2'-bipyridine(II)

The N,N'-dioxide (XII) and 6,6'-dicyano-(XIII) derivatives<sup>13</sup> were prepared as indicated in the cited reference. The 6,6'-dicarboxy-2,2'-bipyridine (II) was prepared by the acid hydrolysis of the 6,6'-dicyano-(XIII) derivative<sup>21</sup> (yield 90%), or by the same oxidation method (yield: 90%) described above as applied to the 6,6'-dimethyl-derivative (IX), prepared by Oae's coupling methodology<sup>12</sup>. All spectroscopic and physical data (m.p. > 300 °C) were compatible both with the expected product and the literature data<sup>22</sup>.

IR(KBr,  $\text{cm}^{-1}$ ): 3300-3000 ( $\nu_{\text{O-H}}$ ), 1700 ( $\nu_{\text{C=O}}$ ); Anal. Calcd. for  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4$  C 59.02; H 3.28; N 11.48; Found: C 59.06; H 3.30; N 11.44.

### 4,4'-Dinitro-2,2'-bipyridine-N,N'-dioxide (III)

To 2,2'-bipyridine-N,N'-dioxide (XII) (5 g, 27 mmol), cooled in an ice-water bath, was slowly added a mixture of oleum-sulphuric acid (1:2 v/v, 25 mL) and fuming nitric acid (20 mL). The mixture was heated to 100 °C for 6 h with the reflux condenser fitted with a calcium chloride drying tube. After cooling, the mixture was cautiously poured onto ice (100 g) and after filtration and drying 5.7 g (75%) of a yellow solid was obtained (m.p. = 272-

274 °C). (Lit<sup>23</sup> = 272-275 °C); IR (KBr,  $\text{cm}^{-1}$ ): 1550, 1350 ( $\nu_{\text{NO}_2}$ ); 1250 ( $\nu_{\text{N-O}}$ ); Anal. Calcd. for  $\text{C}_{10}\text{H}_6\text{N}_4\text{O}_6$  C 43.15; H 2.15; N 20.15; Found: C 43.26; H 2.20; N 20.22.

### 6,6'-Dicarbothioamide-2,2'-bipyridine (IV)

A solution of 1.00 g (4.86 mmol) of 6,6'-dicyano-2,2'-bipyridine (XIII) and 1.46 g (19.4 mmol) of thioacetamide in 10 mL of dimethylformamide, under magnetic stirring, was saturated with dried HCl and heated for 30 min using a steam bath. After cooling the solution was evaporated to half of its initial volume. Upon addition of 100mL of anhydrous ethanol precipitation of a very intense yellow solid occurs. After filtration and drying under vacuum 1.1 g (82%) of a yellow solid was obtained, m.p.: 247 - 254 °C; (Lit<sup>13</sup> = 247-257 °C); IR (KBr,  $\text{cm}^{-1}$ ): 2249 ( $\nu_{\text{CN}}$ );  $^1\text{H}$ -NMR ( $\delta$ , DMF): 10.45-10.29 (2H, br s,  $\text{NH}_2$ ), 9.10 (2H, dd, J = 7.8 Hz, 1Hz); 8.75 (2H, dd, J = 7.9 Hz, 1 Hz) and 8.22 (2H, dd, J = 7.9 Hz, 7.9 Hz);  $^{13}\text{C}$ -NMR ( $\delta$ , DMF): 195.79; 153.53; 152.17; 138.94; 125.90; 124.59; Anal. Calcd. for  $\text{C}_{12}\text{H}_{10}\text{N}_4\text{S}_2$  C 52.55; H 3.65; N 20.44; Found: C 52.34; H 3.67; N 20.27.

### 4,4'-Dihydroxamic-2,2'-bipyridine (V)

a) Preparation of 2,2'-bipyridine-4,4'-dicarboxylic acid dichloride: To 0.86 g (3.5 mmol) of 4,4'-dicarboxy-2,2'-bipyridine (I) was added 9.0 mL (124 mmol) of thionyl chloride ( $\text{SOCl}_2$ ), under magnetic stirring. The mixture was heated for 3 h under reflux. After cooling the solution was evaporated in the presence of anhydrous benzene (30 mL) for total elimination of  $\text{SOCl}_2$  and the crude dichloride was directly submitted to the following reaction:

b) A solution of 0.58 g (8.4 mmol) of hydroxylamine hydrochloride and 2.3 mL of triethylamine (16.8 mmol) in 7.0 mL of chloroform was added to a 25 mL round bottom flask equipped with a magnetic stirrer, dropping funnel and reflux condenser containing the crude acid dichloride in 7 mL of dry chloroform. The mixture was stirred for 48 h at room temperature and after filtration and drying 0.82 g (86%) of a light brown solid was obtained with m.p. = 202-204 °C.

IR (KBr,  $\text{cm}^{-1}$ ): 3300-2700 ( $\nu_{\text{NH}}$  e  $\nu_{\text{OH}}$ ); 1680, 1640 ( $\nu_{\text{C=O}}$ ); 1580, 1450 ( $\nu_{\text{CN}}$  e  $\delta_{\text{NH}}$ ); 1120 ( $\delta_{\text{OH}}$ );  $^1\text{H}$ -NMR ( $\delta$ ,  $\text{DMSO-d}_6$ ): 8.84-8.78 (2H<sub>6,d</sub>), 8.73 (2H<sub>5,s</sub>), 7.78 (2H, m, 2H<sub>3</sub>);  $^{13}\text{C}$ -NMR ( $\delta$ ,  $\text{DMSO-d}_6$ ): 161.97 (C<sub>7</sub>); 155.45(C<sub>2</sub>); 150.07(C<sub>6</sub>); 141.49(C<sub>4-</sub>(E)); 125.44(C<sub>4-</sub>(Z)), 123.94 (C<sub>5-</sub>(E)), 121.48 (C<sub>5-</sub>(Z)), 120.42 (C<sub>3-</sub>(E)), 118.03 (C<sub>3-</sub>(Z)); Anal. Calcd. for  $\text{C}_{12}\text{H}_{10}\text{N}_4\text{S}_2$  C 52.55; H 3.48; N 20.44; Found: C 52.36; H 3.40; N 20.32.

### 6,6'-Dihydroxamic-2,2'-bipyridine (VI)

a) Preparation of 2,2'-bipyridine-6,6'-dicarboxylic acid dichloride: Following the same procedure described before 0.43 g (1.8 mmol) of 4,4'-dicarboxy-2,2'-bipyridine (I) and

5.0 mL (69 mmol) of thionyl chloride (SOCl<sub>2</sub>) were combined. The crude dichloride was directly submitted to the following reaction:

b) 0.54 g (8.1 mmol) of hydroxylamine hydrochloride and 2.2 mL of triethylamine (16.2 mmol) in 7.0 mL chloroform were put to react as described before. 0.40 g (84%) of a white solid was obtained with m.p. > 300 °C.

IR (KBr, cm<sup>-1</sup>): 3300-2900 (ν<sub>NH</sub> e ν<sub>OH</sub>); 1690, 1650 (ν<sub>C=O</sub>); 1550,1450 (ν<sub>CN</sub> e δ<sub>NH</sub>); 1120 (δ<sub>OH</sub>); <sup>1</sup>H-NMR (δ, DMSO-d<sub>6</sub>): 11.69 (2H, s, OH), 9.21 (2H, s, H<sub>5</sub>), 9.08 (4H, d, H<sub>3</sub>), 8.12 (2H, br, NH) and 8.05 (2H, d, H<sub>4</sub>); <sup>13</sup>C-NMR (δ, DMSO-d<sub>6</sub>): 165.86 (C<sub>7</sub>); 160.97 (C<sub>2</sub>); 153.53 (C<sub>6</sub> - (E)); 149.39 (C<sub>6</sub> - (Z)); 138.90 (C<sub>5</sub> - (E)); 137.58 (C<sub>6</sub> - (Z)), 125.40 (C<sub>3</sub> - (E)); 124.06 (C<sub>3</sub> - (Z)), 122.24 (C<sub>4</sub>); Anal. Calcd. for C<sub>12</sub>H<sub>10</sub>N<sub>4</sub>S<sub>2</sub>C 52.55; H 3.68; N 20.43; Found: C 52.51; H 3.25; N 20.3.

### Mono-N-oxide-2,2'-bipyridine (VII)

To a solution of 1.0 g (6.4 mmol) of 2,2'-bipyridine (XI) in 10 mL of glacial acetic acid, in a round bottom flask equipped with magnetic stirrer and reflux condenser, was slowly added 0.80 g (1.6 mmol) of magnesium monophtalate (MMPP). After 6 h of heating at 80 °C, the solution was cooled and evaporated in a desiccator, with sodium hydroxide, under vacuum. Then the mixture was dissolved in chloroform (20 mL) and washed with a 5% sodium bicarbonate aqueous solution. The organic phase was then dried with anhydrous magnesium sulfate, filtered and evaporated to afford 0.88 g (80%) of a gray solid, m.p. = 56-58 °C (Lit<sup>4</sup> m.p. = 57-58 °C); IR (KBr, cm<sup>-1</sup>): 1250(ν<sub>N-O</sub>); Anal. Calcd. for C<sub>10</sub> H<sub>8</sub> N<sub>2</sub>O C 69.77; H 4.65; N 16.28; Found: C 69.81; H 4.70; N 16.32.

### Conclusions

The desired substituted 2,2'-bipyridines [4,4'-dicarboxy-2,2'-bipyridine (I), 6,6'-dicarboxy-2,2'-bipyridine (II), 4,4'-dinitro-2,2'-bipyridine-N,N-dioxide (III) and 6,6'-dicarbothioamide-2,2'-bipyridine (IV)] and also mono-N-oxide-2,2'-bipyridine (VII), were prepared by improved methods. The novel 4,4'-dihydroxamic- 2,2'-bipyridine (V) and 6,6'-dihydroxamic-2,2'-bipyridine (VI) synthesized revealed themselves as excellent ligands for Fe(II) and Fe(III). Therefore, it should be relevant to investigate the utilization of V and VI as siderophores for treatment of both iron overload and deficiency conditions<sup>24</sup>. Finally, with these improved methods we could synthesize novel, 2,2'-bipyridine derivatives and their corresponding complexes (such as rhodium, cobalt, etc) which are currently being studied. These results will be reported in due course.

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