

## Synthesis and characterization of a new ditopic bipyridine-terpyridine bridging ligand using a Suzuki cross-coupling reaction

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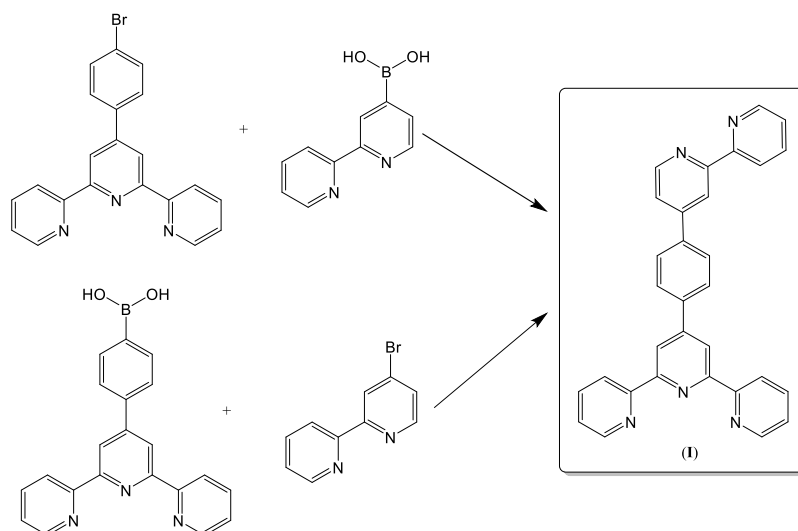
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### Abstract

Synthesis of a new bridging ligand 4'-{4-[(2,2'-bipyridin)-4-yl]-phenyl}-2,2':6'-2''-terpyridine (I) was reported. A Suzuki cross-coupling reaction was conducted for the preparation of such ligand in two different routes either between 4'-(4-bromophenyl)-2,2':6'-2''-terpyridine and 2,2'-bipyridyl-4-boronic acid or 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine and 4-bromo-2,2'-bipyridine.



**Keywords:** Synthesis, bipyridine, terpyridine, bridging ligand

## Introduction

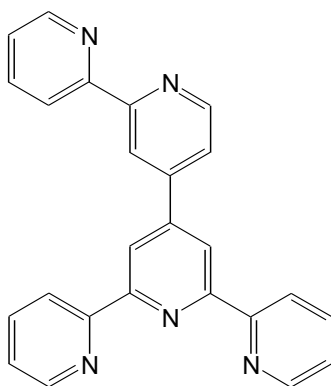
As part of our studies, we have been working on a research programme with the aim of synthesis of heterodinuclear complexes for the purpose of exploring the possibility of achieving light-induced ligand release.<sup>1,2</sup> In these studies, we are focussing on the preparation and use of ditopic bridging ligands where the two metal ion binding sites are differentiated either by the configuration of the binding sites or by the number of donor atoms in each site.

This binding site differentiation allows us to use the different coordination properties of the binding sites to prepare Ru(II)-Co(III) systems to ensure that the correct metal ion is incorporated at the correct binding site in the ligand, which provide a suitable environment during the reactions of complexes formation to decrease the number of isomers that might occur.

In this context, polypyridyl types of ligands have been selected as candidates. We were interested in the preparation of such bridging ligands in which the numbers of donor atoms in the two binding sites were different. This kind of approach has already been used and a number of heterodinuclear complexes have been developed using ligands with different binding sites. For example, Constable et al.<sup>3</sup> and Li et al.<sup>4</sup> in two different studies have prepared heteroditopic ligands involving a bipyridine bidentate metal ion binding site at one end and a tridentate terpyridine metal ion binding site at the other end. They investigated the electronic properties of heterodinuclear complexes prepared using such ligands. Das et al.<sup>5</sup> developed a polypyridyl-imidazole system where the number of the donor sites on the ligand as well as the types of the binding sites are differentiated for the purpose of multichannel anion and cation sensing studies. Although there are many reports on the synthesis of polypyridyl bridging ligands in the literature,<sup>6-20</sup> but polypyridyl bridging ligands with two binding sites where the number of donor atoms are different have been less studied.<sup>3,4,21-23</sup>

In our series of researches development of bridging ligands with bipyridine types at one end and terpyridine types of binding sites at the other end appealed.

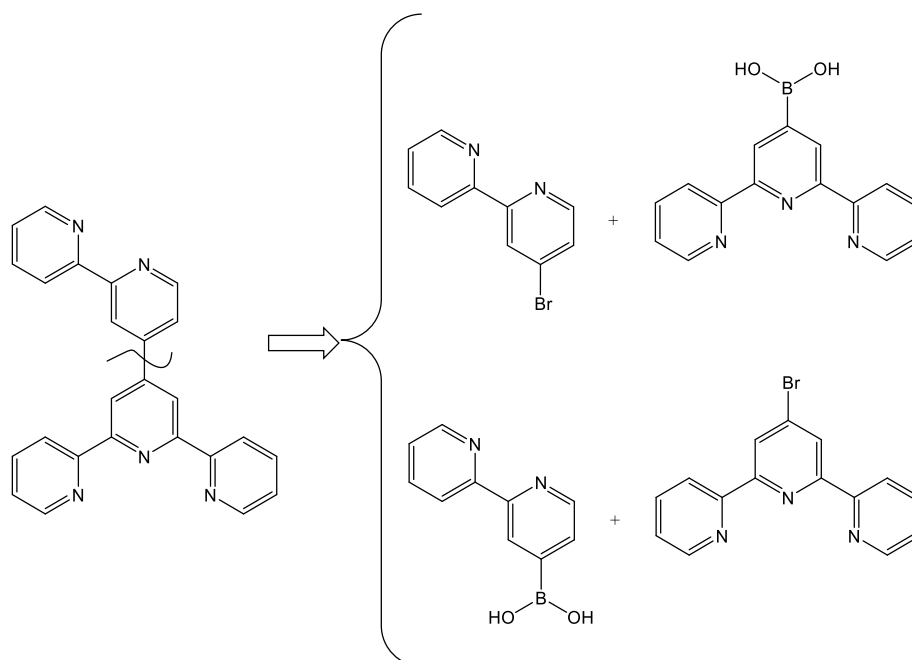
In our search for an appropriate polypyridyl bridging ligand, we found Constable et al's report on the synthesis of 4'-(2,2'-bipyridin-4-yl)-2,2':6'-2''-terpyridine (Figure 1)<sup>3</sup> which involved multi-step synthesis containing Kröhnke reaction, oxidation reaction using Bredereck's reagent and sodium periodate.



**Figure 1.** 4'-(2,2'-bipyridin-4-yl)-2,2':6'-2''-terpyridine ligand.<sup>3</sup>

Although the authors reported satisfactory synthesis of the ligand using the synthesis strategy they employed, we found that the oxidation step reaction either gave variable yields or in most cases convinced us to be a non-reproducible oxidation reaction. Additionally, we observed similar results when selenium dioxide was used.<sup>4</sup> In order to prepare the ligand 4'-(2,2'-bipyridin-4-yl)-2,2':6'-2''-terpyridine, we proposed the

disconnection approach synthesis towards the C-C bond formation between the two parts of the ligand, *i.e.* the bipyridyl and the terpyridyl domains which led us to propose a synthesis strategy involving a Suzuki cross-coupling reaction as shown in Figure 2.



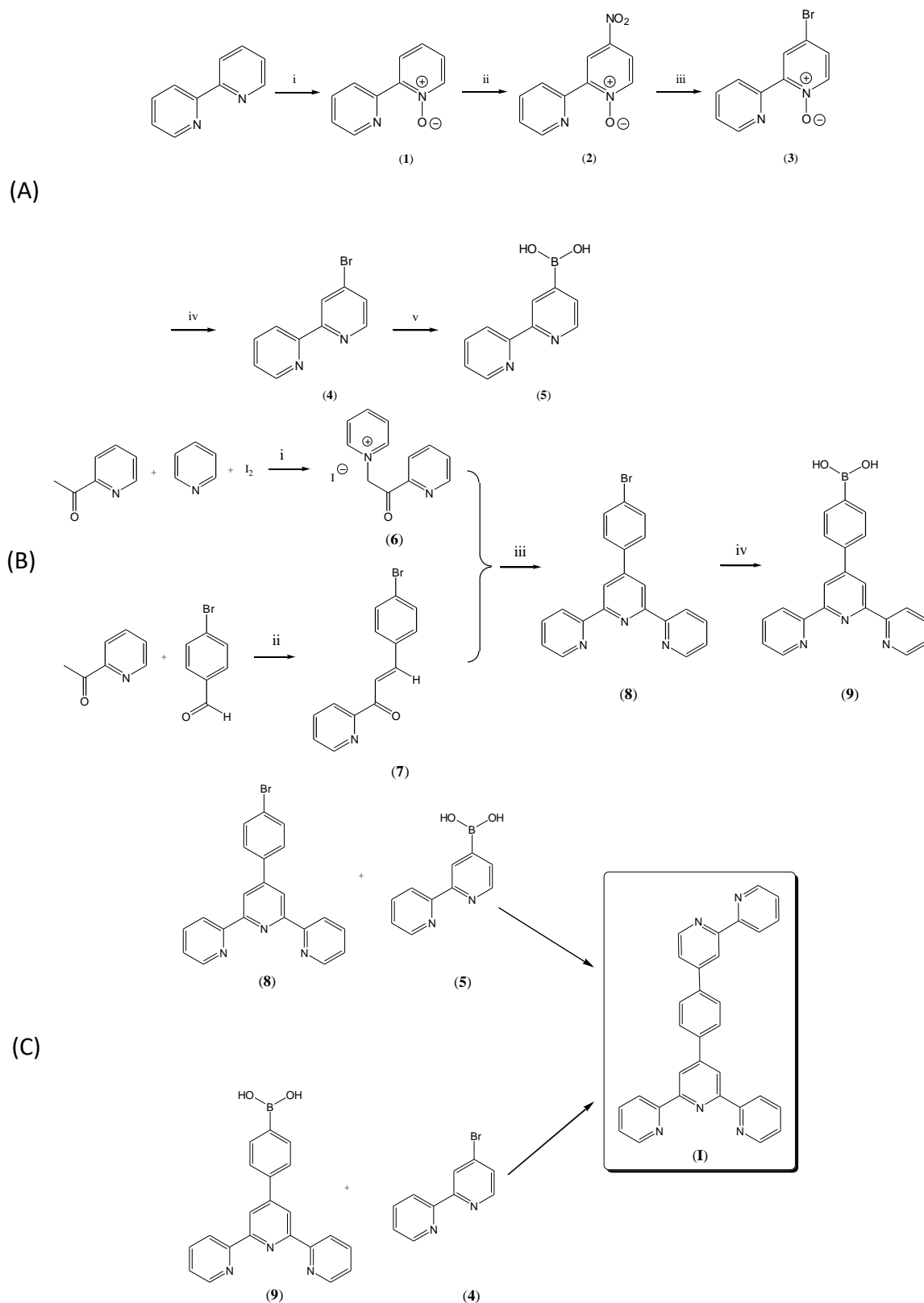
**Figure 2.** Proposed disconnection approach for the synthesis of 4'-(2,2'-bipyridin-4-yl)-2,2':6'-2''-terpyridine ligand.

For this purpose, two different routes were considered. Either the reaction of 4'-(bromo)-2,2':6'-2''-terpyridine and 2,2'-bipyridyl-4-boronic acid or the reaction of 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine and 4-bromo-2,2'-bipyridine led us for the preparation of the ditopic ligand. Since compound 4'-(4-bromophenyl)-2,2':6'-2''-terpyridine was available in our lab, we used such terpyridine material as an alternative bromo-terpyridine derivative for 4'-(bromo)-2,2':6'-2''-terpyridine towards the synthesis of the target ditopic ligand (**I**). This kind of approach has been used before, and a range of extended molecules have been prepared. For example, Schultz et al. have prepared a range of bis-, tris-, and tetrakis terpyridine types ligands that allowed them to prepare macromolecular complex isomers through self-assembly strategy.<sup>22</sup> S. Bonnet et al. have also prepared a terpyridyl derivative using a combination of Kröhnke reaction and a Suzuki cross-coupling reaction.<sup>24</sup> They preferred Kröhnke reaction for preparation of terpyridyl domain of the molecule, among other methods,<sup>25,26</sup> because of the simplicity, purification and straightforwardness of the method.<sup>24</sup>

Herein, we, using the strategy employed by S. Bonnet et al., report the synthesis and characterisation of new bridging ligand 4'-{4-[(2,2'-bipyridin)-4-yl]-phenyl}-2,2':6'-2''-terpyridine (**I**).

## Results and Discussion

Synthesis of ditopic ligand (**I**) is shown in Scheme 1. We employed a combination of Kröhnke reaction and a Suzuki cross-coupling reaction (Suzuki-Miyaura reaction) using tetrakis(triphenylphosphine)palladium catalyst in basic medium ( $\text{Na}_2\text{CO}_3$ , aq. 2M solution) to prepare the desired ligand.



**Scheme 1.** (A) (i) *m*-chloroperbenzoic acid,  $\text{CH}_3\text{Cl}$ , 0 °C then r.t., 18 h; (ii)  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , 105 °C, 5 h; (iii) acetyl bromide, HOAc, 60 °C, 2 h; (iv)  $\text{PBr}_3$ ,  $\text{CHCl}_3$ , 0 °C then reflux, under Ar; (v) triisopropyl borate, *n*-butyl lithium, THF, -78 °C, under Ar; (B) (i) 105-110 °C; (ii) aq. NaOH, MeOH, 30 min, rt; (iii)  $\text{NH}_4\text{OAc}$ , glacial acetic acid, reflux, 7 h, NaOH; (iv) triisopropyl borate, *n*-butyl lithium, THF, -78 °C, under Ar; (C)  $\text{Pd}(\text{PPh}_3)_4$ , aq.  $\text{Na}_2\text{CO}_3$ , under Ar, reflux, overnight.

The key materials of bromo- and boric acid derivatives **4**, **5**, **8** and **9** were prepared as shown in Scheme 1. The 2,2'-bipyridine-4-boronic acid (**5**) ligand was prepared in a five-steps reaction starting with 2,2'-bipyridine and the 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine (**9**) ligand was synthesized in a four-steps reaction involving a Kröhnke reaction to prepare 1-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide (**6**), 4-bromo-2'-azachalcone (**7**), and 4'-(4-bromophenyl)-2,2':6',2''-terpyridine (**8**). All compounds (**1**),<sup>27</sup> (**2**),<sup>27</sup> (**3**),<sup>28</sup> (**4**),<sup>28</sup> (**5**),<sup>29</sup> (**6**),<sup>30</sup> (**7**),<sup>31</sup> (**8**),<sup>31</sup> and (**9**)<sup>22,29</sup>, were characterized using conventional methods such as NMR and mass spectrometry. All data were consistent with the literature values (see Supplementary Material).

C-C bond formation using Suzuki-Miyaura reaction which was employed by S. Bonnet et al.,<sup>24</sup> was adopted for the preparation of ligand (**I**). For this purpose, two different routes were considered (Scheme 1(C)). The coupling reaction of 4'-(4-bromophenyl)-2,2':6',2''-terpyridine (**8**)<sup>31</sup> and 1.5 equivalent of 2,2'-bipyridine-4-boronic acid (**5**)<sup>29</sup> or the coupling reaction of 4-bromo-2,2'-bipyridine (**4**)<sup>28</sup> and 1.5 equivalent of 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine (**9**)<sup>22,29</sup> yielded in the formation of the desired ligand (**I**) in relatively high yield. The product which was obtained was then analyzed by NMR (Figure 3 and 4), MS (Figure 5) and elemental analysis techniques. COSY and HMQC experiments allowed the assignment of the spectra of the ligand. As it is shown in Figure 3, <sup>1</sup>H NMR spectrum indicated 2 characteristic singlets assigned to single protons associated with the pyridine rings of bipyridyl and terpyridyl domains which are bound to the phenyl ring in the middle of the ligand (**I**) appearing at  $\delta$  8.65 and 8.60, respectively. The signals associated with the protons of the phenyl group appeared as iso(AB) spin system with the chemical shift at  $\delta$  7.68-7.53 (7.68 (2 H, d,  $J_{AB} = 8$  Hz, H<sub>phenyl</sub>), 7.54 (2 H, d,  $J_{AB} = 8$  Hz, H<sub>phenyl</sub>)) which show that the phenyl group is symmetrical in the NMR time scale. Table 1 show the comparison study of the <sup>1</sup>H NMR data of the ligand (**I**) and the bridging ligands which were reported by Constable et al.<sup>3</sup> and Li et al.<sup>4</sup>

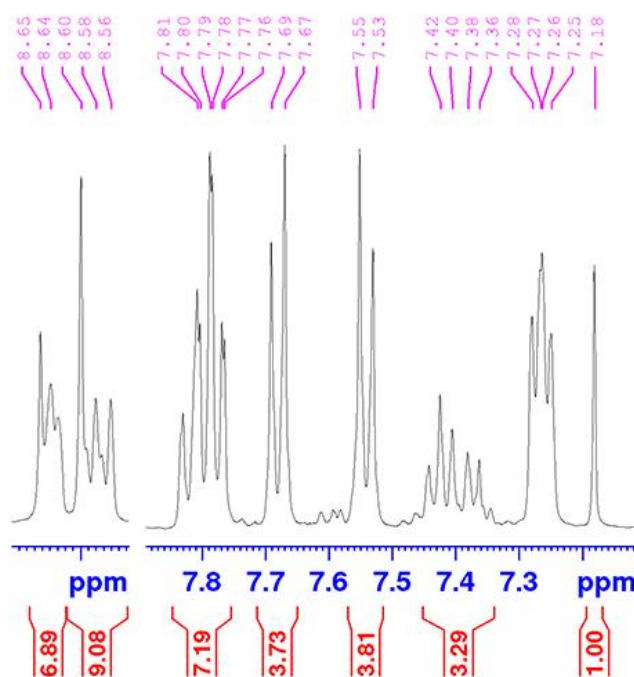


Figure 3. <sup>1</sup>H NMR spectrum of ligand (**I**) in CDCl<sub>3</sub>.

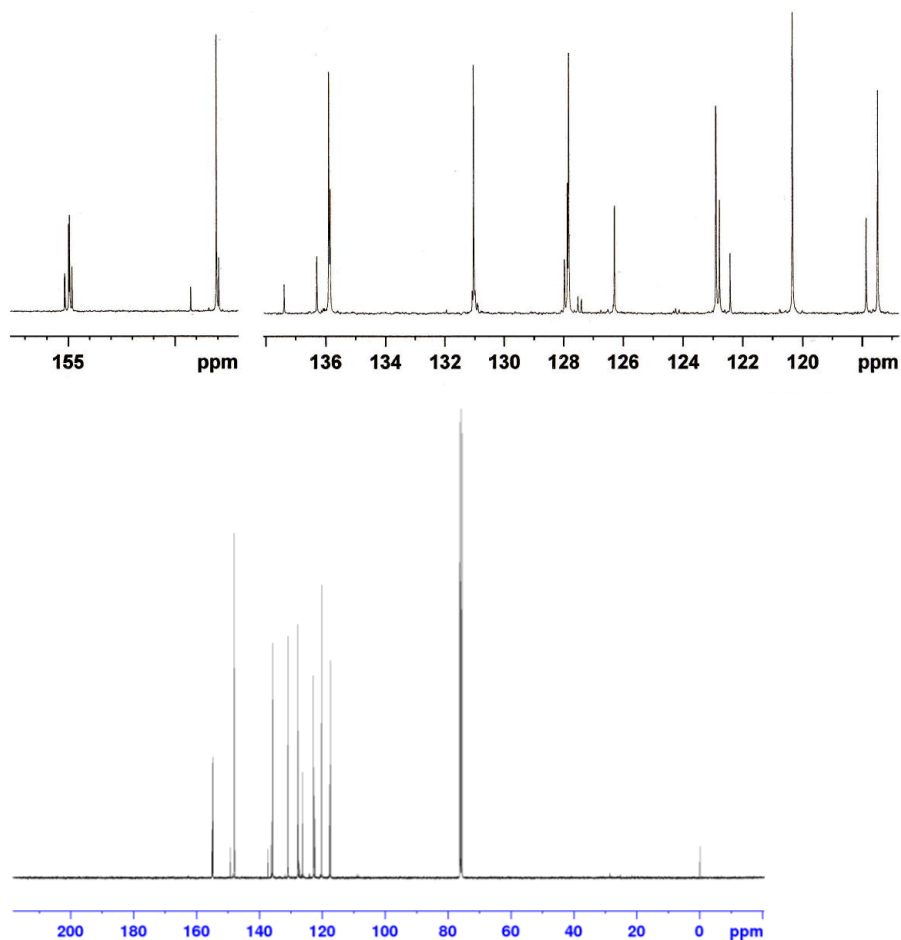
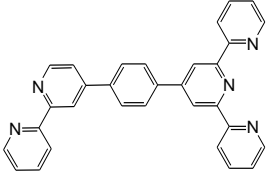


Figure 4.  $^{13}\text{C}$  NMR of ligand (I) in  $\text{CDCl}_3$ .

Table 1.  $^1\text{H}$  NMR spectral comparison of the ligand (I) with the literature values of analogs

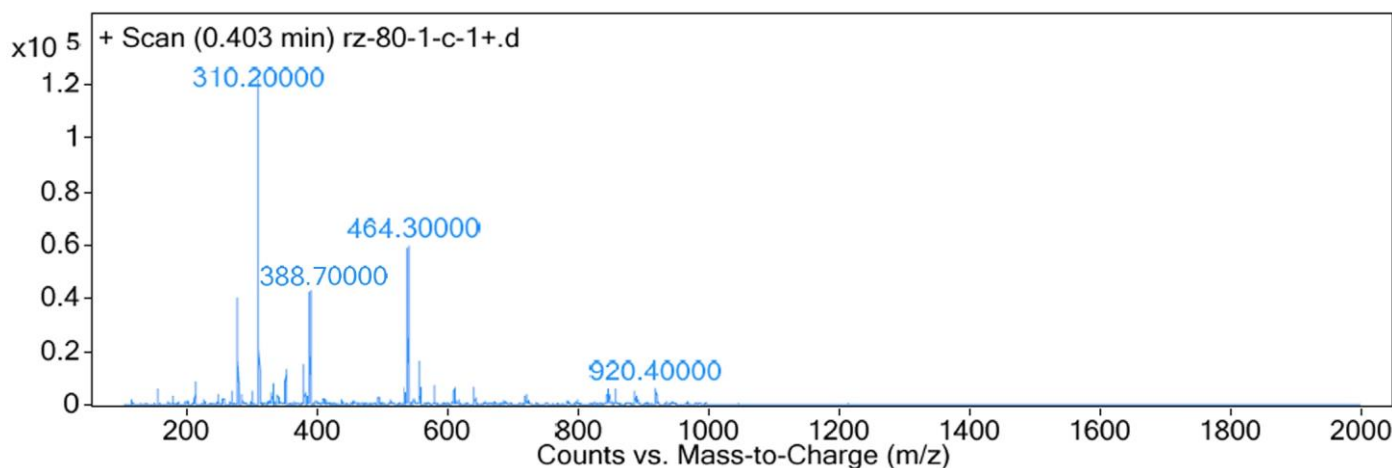
Compound	$^1\text{H}$ NMR spectral data
	(250 MHz, $\text{CDCl}_3$ ) $\delta$ 8.93 (1H, d, $J$ 2.0 Hz, F3), 8.88 (2 H, s, G3), 8.84 (1H, dd, $J$ 2.0, 5.0 Hz, F6), 8.75 (3H, m, H6, E6), 8.70 (2 H, d, $J$ 7.7 Hz, H3), 8.49 (1H, d, $J$ 7.7 Hz, E3), 7.91 (2H, dt, $J$ 1.7, 7.7 Hz, H4), 7.88 (1H, m, E4), 7.83 (1H, m, F5), 7.38 (3H, m, H5, E5). <sup>3</sup>
	(400 MHz, $\text{CDCl}_3$ ) $\delta$ 8.90 (d, 1H, $J$ = 1.0 Hz), 8.86 (s, 2H), 8.82 (d, 1H, $J$ = 5.1 Hz), 8.74 (d, 2H, $J$ = 4.0 Hz), 8.68 (d, 2H, $J$ = 7.9 Hz), 8.60 (d, 1H, $J$ = 4.9 Hz), 8.31 (s, 1H), 7.89 (td, 2H, $J$ = 7.8, 1.7 Hz), 7.80 (dd, 1H, $J$ = 5.0, 1.0 Hz), 7.37 (td, 2H, $J$ = 4.9, 1.8 Hz), 7.18 (d, 1H, $J$ = 4.8 Hz), 2.48 (s, 3H). <sup>4</sup>
	(250 MHz, $\text{CDCl}_3$ ) $\delta$ 8.85 (s, H3'), 8.78 (d, H6), 8.72 (d, H3), 8.10 (s, H <sub>aromatic</sub> ), 7.93 (dd, H4) and 7.40 (dd, H5); $J(\text{H5H6}) = 4.2$ , $J(\text{H3H4}) = 8.0$ Hz. <sup>32</sup>

Table 1. Continued

Compound	<sup>1</sup> H NMR spectral data
 ligand (I)	(400 MHz; CDCl <sub>3</sub> ) δ 8.65 (1H, s), 8.64 (2 H, d, <i>J</i> = 4 Hz), 8.60 (2 H, s), 8.58 (3 H, dd, <i>J</i> = 8 Hz), 7.81 (2 H, d, <i>J</i> = 4 Hz), 7.79 (2 H, ddd, <i>J</i> = 4 Hz, <i>J</i> = 8 Hz), 7.68 (2 H, d, <i>J</i> <sub>AB</sub> = 8 Hz, H <sub>phenyl</sub> ), 7.54 (2 H, d, <i>J</i> <sub>AB</sub> = 8 Hz, H <sub>phenyl</sub> ), 7.41 (1 H, d, <i>J</i> = 8 Hz), 7.38 (1 H, dd, <i>J</i> = 8 Hz), 7.27 (3 H, ddd, <i>J</i> = 4 Hz, <i>J</i> = 8 Hz). (this study)

As it is shown in Table 1, in all compounds, the pyridine rings in the terpyridyl domains exhibit symmetrical pattern in the NMR time scale and additionally, in all spectra significant overlapping of signals were observed which were arising from the protons associated with the bipyridyl rings. <sup>13</sup>C NMR spectrum of the ligand (I) (Figure 4) exhibits seven characteristics peaks corresponding to the C atoms bound to H atoms belong to the phenyl ring and the pyridine rings of the terpyridyl site which supports the structure of the ligand (I).

Product could also be identified from its MS by the facile loss of a pyridine ring from the parent ion. The parent ion mass/charge ratio signal of the product in LC-MS determination was 464.3000 ([M + H]<sup>+</sup>), while the mass/charge ratio signal of 388.7000 can be assigned as ([M – C<sub>5</sub>H<sub>4</sub>N + H]<sup>+</sup>) (Figure 5) which was in consistent with the results reported previously for the ligand synthesized by Constable et al.<sup>3</sup>



**Figure 5.** LC-MS of the ligand (I) in CDCl<sub>3</sub> showed a pick at *m/z* 464.3 ([M+H]<sup>+</sup>) and a peak at *m/z* 388.7 ([M – C<sub>5</sub>H<sub>4</sub>N + H]<sup>+</sup>).

Overall, since the two synthetic methods of the target ligand (I) are different in their last steps of the reactions, considering the yields of the bromo and boronic acid derivatives (*i.e.* 61%, 73%, 79%, and 73% for compounds (4), (5), (8), and (9), respectively, see Experimental Section), compound (4) is the one which can form the smallest amount of the product considered and can be counted as a limiting compound for the synthesis in both routes and using compound (4) directly can influence the overall yield of the product. In this prospect, based on the yields obtained, the route two (*i.e.* the one involving the reaction of 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine (9) and 4-bromo-2,2'-bipyridine (4)) is preferred.

## Conclusions

A new aromatic ditopic bipy-terpy bridging ligand 4'-{4-[(2,2'-bipyridin)-4-yl]-phenyl}-2,2':6'-2''-terpyridine (**1**) was synthesized in two different routes starting with either 4'-(4-bromophenyl)-2,2':6'-2''-terpyridine and 2,2'-bipyridyl-4-boronic acid or [4-(2,2':6',2''-Terpyridin-4'-yl)phenyl]boronic acid and 4-bromo-2,2'-bipyridine. A combination of Kröhnke reaction and a Suzuki cross-coupling reaction was employed for the preparation of the ligand (**1**). The method that we approached, despite of its multistep reactions strategy, in compare with the methods which introduced earlier in the literature, proved its reproducibility of the product in efficient yield. The products which were obtained in two different routes were characterized using the conventional methods and based on the yield and the data which were obtained, we concluded that both products were identical.

## Experimental Section

**General.** Reagent grade commercial compounds were used as starting materials, and their purity was checked by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The 400 MHz  $^1\text{H}$  NMR and 100 MHz  $^{13}\text{C}$  NMR spectra were acquired on a Bruker-400 spectrometer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts are reported relative to tetramethylsilane. Infrared spectra (400-4000  $\text{cm}^{-1}$ ) were obtained using a Shimadzu 8201PC Series FTIR interfaced with an Intel 486 PC operating Shimadzu HyperIR software. Spectra were obtained using diffuse reflectance method in solid KBr. An agilent LC/MS-6410 Triple Quadruple mass spectrometer interfaced with electrospray ionization (ESI) ion source was used at Shahid Beheshti University of Medical Sciences and microanalyses were performed at the same university.

The materials 2,2'-bipyridine-*N*-oxide (**1**),<sup>27</sup> 4-nitro-2,2'-bipyridine-*N*-oxide (**2**),<sup>27</sup> 4-bromo-2,2'-bipyridine-*N*-oxide (**3**),<sup>28</sup> 4-bromo-2,2'-bipyridine (**4**),<sup>28</sup> 2,2'-bipyridine-4-boronic acid (**5**),<sup>29</sup> 1-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide (**6**),<sup>30</sup> 4-bromo-2'-azachalcone (**7**),<sup>31</sup> 4'-(4-bromophenyl)-2,2':6',2''-terpyridine (**8**),<sup>31</sup> 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine (**9**),<sup>22,29</sup> and palladium tetrakis(triphenylphosphine)<sup>33</sup> were synthesized by published methods. The analyses data were consistent to those reported in the literature as shown in the supplementary material.

### Syntheses:

**2,2'-bipyridine-*N*-oxide (1).**<sup>27</sup> Yield 85%, mp 59-60 °C (lit. mp 60 °C,<sup>27</sup> 59 °C<sup>34</sup>)

**4-nitro-2,2'-bipyridine-*N*-oxide (2).**<sup>27</sup> Yield 67%, mp 183-184 °C (lit. mp 181 °C)<sup>34</sup>

**4-bromo-2,2'-bipyridine-*N*-oxide (3).**<sup>28</sup> Yield 86%, mp 66-67 °C (lit. mp 65.8-66.2 °C)<sup>28</sup>

**4-bromo-2,2'-bipyridine (4).**<sup>28</sup> Yield 61%, mp 53 °C (lit. mp = 52.9-53.6 °C)<sup>28</sup>

**2,2'-bipyridine-4-boronic acid (5).**<sup>29</sup> Yield 73%, mp > 300 °C (lit. mp > 250 °C)<sup>28</sup>

**1-[2-oxo-2-(2-pyridyl)ethyl]pyridinium iodide (6).**<sup>30</sup> Yield 78%. Yellow-green solid.

**4-bromo-2'-azachalcone (7).**<sup>31</sup> 4-bromobenzaldehyde (3.7 g) was used as starting material according to the already published method.<sup>31</sup> The light yellow solid which was collected was used to prepare compound (**8**) without further purification, therefore the yield and melting point were not determined.

**4'-(4-bromophenyl)-2,2':6',2''-terpyridine (8).**<sup>31</sup> Yield 79%. M.p. 161-162 °C (lit. m.p 158-160 °C)<sup>31</sup>

**4'-(4-boronatophenyl)-2,2':6',2''-terpyridine (9).**<sup>22,29</sup> Yield 73%. M.p. > 300 °C (lit. m.p > 300 °C)<sup>29</sup>

**palladium tetrakis(triphenylphosphine).**<sup>33</sup> Yield 98%.



**Synthesis of ligand (I). Method 1.** In a dry degassed three-necked 250 mL round-bottom flask under argon gas was dissolved 0.388 g (1 mmol) 4'-(4-bromophenyl)-2,2':6',2''-terpyridine (**8**)<sup>31</sup> in 30 mL toluene. To the solution under Schlenk condition was added 0.087 g palladium tetrakis(triphenylphosphine)<sup>33</sup> and 10 mL amount of 2 molar degassed aqueous solution Na<sub>2</sub>CO<sub>3</sub> by cannula. To the mixture was then added 0.30 g (1.5 mmol) 2,2'-bipyridine-4-boronic acid (**5**)<sup>29</sup> dissolved in mixture of dry and degassed toluene (25 mL) and EtOH (10 mL). The mixture was allowed to stir at rt while degassing for 15 min. The mixture was refluxed under argon flow overnight during which a brown solution was obtained. The reaction mixture was cooled until a brown precipitate was formed. The solvent was evaporated on vacuum, and then water was added and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The collected organic extracts were collected, washed with water, then the solution was taken to dryness under vacuum and the residue was purified by column chromatography (alumina, eluting with toluene/diethyl amine, 95:5). The major orange-yellow band was collected and evaporated to dryness *in vacuo* to afford the product as a yellow solid (**I**) (88%).

**Method 2.** Similar procedure was adopted as explained in method 1; however, mixture of 0.235 g (1 mmol) 4-bromo-2,2'-bipyridine (**4**)<sup>28</sup> and 0.530 g (1.5 mmol) 4'-(4-boronatophenyl)-2,2':6',2''-terpyridine (**9**)<sup>22,29</sup> were used instead of (**8**)<sup>31</sup> and (**5**)<sup>29</sup> as starting materials. The product was collected as a yellow solid (**I**). (yield: 89%). Mp > 300 °C. <sup>1</sup>H NMR (400 MHz; solvent CDCl<sub>3</sub>) δ 8.65 (1H, s), 8.64 (2 H, d, *J* 4 Hz), 8.60 (2 H, s), 8.58 (3 H, dd, *J* 8 Hz), 7.81 (2 H, d, *J* 4 Hz), 7.79 (2 H, ddd, *J* 4 Hz, *J* 8 Hz), 7.68 (2 H, d, *J*<sub>AB</sub> 8 Hz, H<sub>phenyl</sub>), 7.54 (2 H, d, *J*<sub>AB</sub> 8 Hz, H<sub>phenyl</sub>), 7.41 (1 H, d, *J* 8 Hz), 7.38 (1 H, dd, *J* 8 Hz), 7.27 (3 H, ddd, *J* 4 Hz, *J* 8 Hz). <sup>13</sup>C NMR (100 MHz; solvent CDCl<sub>3</sub>) δ 155.1, 155.0 (2 C), 154.9 (2 C), 154.8, 149.3, 158.0 (2 C), 147.9, 137.4, 136.3, 135.9 (2 C), 135.8, 131.0 (2 C), 127.96, 127.86, 127.8 (2 C), 126.3, 122.9, 122.8, 122.4, 120.3, 117.9, 117.5 (2 C). MS: *m/z* 464.3000 ([M + H]<sup>+</sup>), 388.7000 ([M – C<sub>5</sub>H<sub>4</sub>N + H]<sup>+</sup>). Anal. Calc. for C<sub>31</sub>H<sub>21</sub>N<sub>5</sub> (463.53): C 80.32, H 4.57, N 15.11%; found: C 80.67, H 4.63, N 14.93%.

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## Supplementary Material

NMR spectra and mass spectra of the compounds (**1**)-(9) and (**I**) are available in the online edition of the text.

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