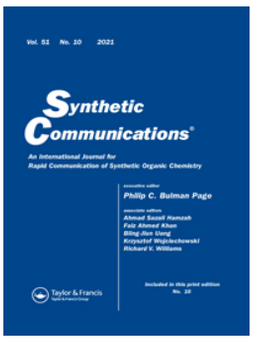

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# Terpyridinebenzaldehyde isomers: One-pot facile synthesis

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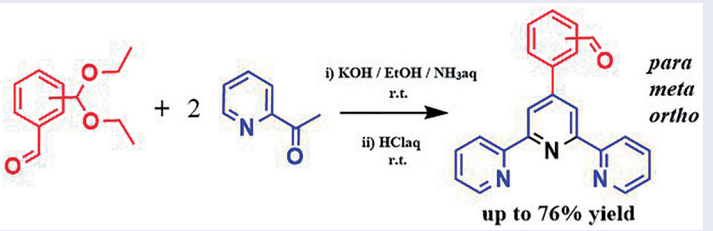
**ABSTRACT**

We have explored the use of (diethoxymethyl)benzaldehyde readily available as a starting material allowing us to end up with Terpyridinebenzaldehyde isomers. An environmentally friendly procedure was undertaken for the synthesis of a series of 4, 3 and 2-([2,2′:6′,2″-terpyridin]-4′-yl)benzaldehyde isomers (*para, meta* and *ortho* position). These compounds have been synthesized in one-pot conditions using ethanol and aqueous ammonia as solvents, at room temperature. This methodology offers substantial advantages with respect to its simplicity of operation, reaction time, satisfying yield of products and easy work-up procedure under mild reaction conditions. Apart from spectroscopic characterization, the structure of one of the Terpyridinebenzaldehyde derivative is confirmed by single-crystal X-ray diffraction.

**GRAPHICAL ABSTRACT**

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**KEYWORDS**
One-pot; terpyridine; (diethoxymethyl) benzaldehyde; terpyridinebenzaldehyde

## Introduction

Supramolecular chemistry, in particular the self-assembly of functional structures in metallosupramolecular architectures based on the use of transition metals and suitable ligands, has been a very active area of research in recent decades.[1–3] The use of functionalized "metallaligands" as "molecular bricks" is a simple way to form sophisticated molecular architectures, based on weak interactions such as hydrogen or covalent bonds like with imines. In this context, 2,2′;6′,2″-terpyridine and its functionalized derivatives have been widely used in the field of coordination and supramolecular chemistry to form "metallaligand".[4] Their remarkably high binding affinity toward most transition-metal ions and their chelation properties make terpyridine derivatives are highly attractive

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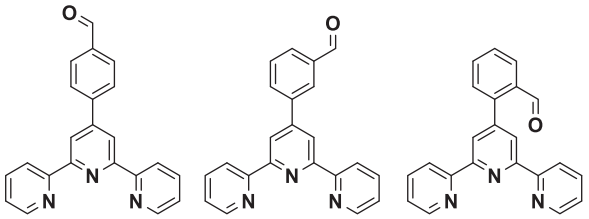



**Figure 1.** Terpyridinebenzaldehyde derivatives **L1**, **L2** and **L3**.

building blocks for the construction of complex metallosupramolecular systems.[5–10] Coordination complexes with functionalized terpyridines are used in catalysis,[11–13] photochemistry,[14–16] medical chemistry[17–19] and dye-sensitized solar cells.[20–24]

Along this line, it seems interesting to develop an easy synthesis for such terpyridine derivatives. Thus, we became interested in aldehydes because they are versatile reagents in organic synthesis and, especially aromatic aldehydes, have been extensively used as starting reagents for various imine reactions to synthesize supramolecular architectures.[25–28]

These efforts led to the development of a synthetic method for ligands of the terpyridine family, **L1**, **L2** and **L3**, bearing benzaldehyde derivative groups (Figure 1).

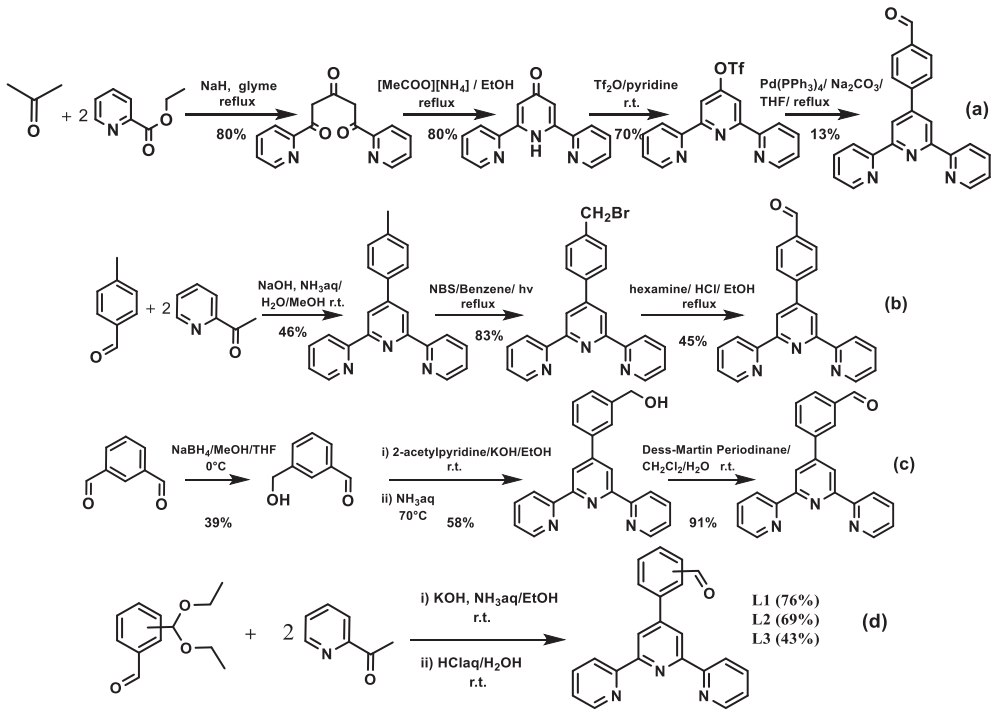
In the literature, two types of synthetic strategies have been reported for the synthesis of 4-([2,2′: 6′,2″-terpyridin]-4′-yl)benzaldehyde **L1** and one for 3-([2,2′:6′,2″-terpyridin]-4′-yl)benzaldehyde **L2**. First, **L1** has been prepared in four steps (Scheme 1(a)).[29] The last step reaction of this pathway is based on the palladium-catalysed cross-coupling of 4′-triflate-terpyridine with 4-formylphenylboronic acids, with an overall yield of 6%.

The second synthetic approach for **L1**[30] (Scheme 1(b)) is based, in the first step, on the preparation of 4′-tolyl-2,2′:6′,2"-terpyridine followed by bromination and finally oxidation, with an overall yield of 17% yield. Concerning **L2**, one synthetic strategy has been recently described.[31] This product was synthesized in three steps from isophalaldehyde with an overall yield of almost 20% (Scheme 1(c)).

Nevertheless, there are certain limitations to these three methods: too long synthesis time, the use of expensive reagents and toxic solvents. In addition to all these drawbacks, the overall yield of these three methods is low: 6%, 17% and 20%, respectively.

The development of an efficient and general approach for obtaining 4-([2,2′:6′,2″-terpyridin]-4′-yl)benzaldehyde **L1** or terpyridinebenzaldehyde isomers, 3-([2,2′:6′,2″-terpyridin]-4′-yl)benzaldehyde **L2** and the positional isomer 2-([2,2′:6′,2″-terpyridin]-4′-yl)benzaldehyde **L3**, under metal-free conditions using a one-pot synthesis, is of overriding value and challenging. Therefore, an efficient protocol should be using straightforward and readily available starting components, which appears really appealing.

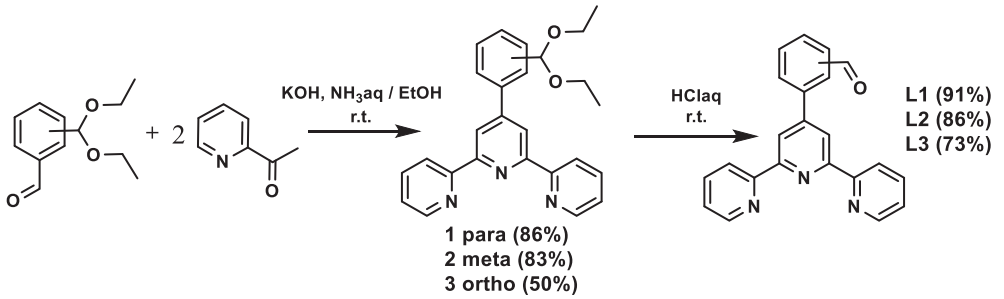
Herein, we report an efficient and easy method to obtain terpyridinePh-CHO(-CHO in *para*, *meta* or *ortho* position (**L1, L2** or **L3**)). Indeed, these compounds have been synthesized in one-pot reactions under metal-free conditions using ethanol and water as solvents. This procedure features short reaction times, easy work-up, and good yields. Most of the used starting materials are commercially available and non-expensive.




**Scheme 1.** Conventional Methods: (a) and (b) reported for the preparation of 4-([2,2′:6′, 2″-terpyridin]-4′-yl)benzaldehyde; (c) for the preparation of 3-([2,2′:6′,2″ -terpyridin]-4′-yl)benzaldehyde; (d) the one-pot strategy developed herein (this work).

## Results and discussion

The first known synthesis for terpyridine derivatives is the one reported by Kröhnke et al. in 1976,[32] followed by other methods such as the use of the Stille coupling, for example.[33] But, the recently reported synthetic methods[34–36] marked a significant improvement. Indeed, the functionalized terpyridines were easily obtained *via* a condensation sequence of aldol and Michael addition, involving the use of solid NaOH, followed by treatment with ammonium acetate or aqueous ammonia in a one-pot reaction, with high yield. Our strategy for obtaining **L1, L2** or **L3** is based on the adaptation of an already reported method of this synthesis, that leads to terpyridinebenzaldehyde isomers. The electrophilic nature of the carbonyl group of these compounds is a dominant feature of its possible extensive chemistry. Here, in order to synthesize these compounds, we need a starting material containing two carbonyl groups. It is therefore necessary to protect one carbonyl that we would like to find at the end of synthesis, from a nucleophilic attack. The use of readily available (diethoxymethyl) benzaldehyde seems perfectly suitable since one carbonyl will undergo a nucleophilic attack to synthesize the terpyridine moiety while the other carbonyl is protected against this attack.[37] This proposed strategy allows generation of the carbonyl at the end of the reaction and therefore to have access to benzaldehyde moiety. A mild and easy regeneration of the carbonyl compounds from their resulting 1,1-diacetals has been carried out. Indeed,




**Scheme 2.** Two steps synthetic pathway for the obtention of **L1, L2** and **L3.**

these acetals easily undergo deacetalization to yield terpyridinebenzaldehyde isomers, under acidic conditions at room temperature.

The proposed synthetic pathways, for the synthesis of **L1**, **L2** and **L3,** considering this strategy, are presented in Scheme 1(d) and Scheme 2. The required starting compounds, 3 and 4-(diethoxymethyl)benzaldehyde isomers, are commercially available. The 2-(diethoxymethyl)benzaldehyde is easily prepared by lithiation of commercially available 2-bromo-(diethoxymethyl)benzene with *n*-BuLi at −70 °C and subsequent treatment with DMF, as described in the literature.[38,39]

For the synthesis of **L1**, **L2** and **L3**, we adopted two strategies: the first one (Scheme 2) is based on separating the diacetalterpyridine derivatives as intermediate products before reaching the targeted products. The second strategy (Scheme 1(d)) is under one-pot conditions.

The two-step synthesis (Scheme 2 see ESI for experimental details) of the terpyridine-benzaldehyde isomers begins by mixing 2-acetylpyridine and different (diethoxymethyl)-benzaldehyde precursors in ethanol in 2:1 molar ratio in the presence of KOH pellets and $NH_3$ aqueous solution. The reaction is completed by stirring the mixture at room temperature overnight. After reducing the volume, the mixture is extracted with ethyl acetate and purified by short column chromatography affording the desired (diethoxy-methyl)benzaldehyde derivatives **1, 2** and **3** in 86%, 83% and 50% respectively. In the second step, a dilute HCl solution is added to deprotect the aldehyde; neutralizing the medium allows to obtain the desired aldehyde products **L1**, **L2** and **L3** in 91%, 86% and 73% yield, respectively.

The one-pot approach (Scheme 1(d)) is based on the use of the reactivity profile in the basic medium of protected benzaldehydes, in order to achieve the targeted products. (Diethoxymethyl)benzaldehyde (*para*, *meta* or *ortho*) is added to 2-acetylpyridine in ethanol in 2:1 molar ratio (see ESI for experimental details), in the presence of KOH pellets and $NH_3$ aqueous solution. To the mixture, a dilute HCl solution is added, neutralizing the medium and allowing us to obtain the desired aldehyde products **L1**, **L2** and **L3** in 76%, 69% and 43% yield, respectively. The yield of the two synthesis methods are slightly similar (see Table 1).

In addition to their spectroscopic data (see ESI for characterization details), the structure of **L3** has been confirmed by single crystal X-ray diffraction studies in the solid state (Figure 2). Single crystals suitable for X-ray diffraction analysis have been obtained

**Table 1.** Comparison of the results of both synthetic methods.

| | L1 | L2 | L3 |
|---|---|---|---|
| Isolated yield (%) : two step synthesis method | 78%, | 71% | 36% |
| Isolated yield (%) : one-pot synthesis method | 76%, | 69% | 43% |

**Figure 2.** Single crystal X-ray structure of **L3**. Hydrogen atoms are omitted for the sake of clarity.

for **L3**, so far by slow evaporation of a $CHCl_3$/EtOH solution at room temperature (see the ESI for crystallographic data, CCDC 2018232 (**L3**)). The compound crystallizes in the monoclinic space group, *P* $2_1/n$. The C=C, C–C, C–N, C=N and C=O distances are within the expected range for this type of covalent bonds ($d = 1.208 - 1.493$ Å). The three pyridine groups are almost coplanar. The benzaldehyde group is not coplanar with the central pyridine, but tilted by –46.87°.

## Conclusions

The use of (diethoxymethyl)benzaldehyde as a readily available starting material allowed us to obtain three terpyridinebenzaldehyde isomer derivatives. This methodology offers substantial advantages with respect to its simplicity of operation, availability of starting materials, reaction times, yield of products and easy work-up procedure under mild reaction conditions. These significant features are expected to contribute to the development of a green strategy for the synthesis of new terpyridinebenzaldehyde derivatives and subsequently to novel metallosupramolecular architectures.

## Experimental section

### *General method for the synthesis of the terpyridinebenzaldehyde isomer L1*

To a solution of 2-acetylpyridine (1.16 g, 9.5 mmol), potassium hydroxide (0.54 g, 9.6 mmol) and the corresponding (diethoxymethyl)benzaldehyde in 10 mL of absolute ethanol (1 g, 4.8 mmol), were added 12 mL of 32% aqueous ammonia solution. The mixture was stirred overnight at room temperature. The reaction volume was reduced by half, then 15 ml of a 15% aqueous HCl solution were added. After 3 h at room temperature, the solution was neutralized by a 10% aqueous $K_2CO_3$ solution. The mixture was extracted with dichloromethane ($3 \times 30$ mL). The combined organic layer was dried with $Na_2SO_4$, filtered and the solvent was removed under reduced pressure. The aldehyde phenyl-Terpyridne derivatives **L1** was obtained as a white solid by washing the

crude product with methanol in 76% yield. If necessary, the crude product was purified by a short column chromatography ($Al_2O_3$, eluant, ethyl acetate/cyclohexane 1:1). Note, to make a pure product, it's necessary to wash with MeOH.

**Compound L1:** white solid, 1.2 g, 76% yield, m.p. = 195 °C.

**$^1$H-NMR ($CDCl_3$, 300 MHz):** $\delta$ (ppm) = 7.37 (ddd, $j_1$=1.5 Hz, $j_2$=5Hz, $j_3$=7.5 Hz, 2 H), 7.89 (td, $j$ = 7.5 Hz, 1 H), 8.04 (m, 4H), 8.68 (d, $j_1$=8.1 Hz, 2H), 8.74 (m, 2 H), 8.77 (s, 2 H), 10.10 (s, 1 H).

**$^{13}$C-NMR ($CDCl_3$, 75 MHz):** $\delta$ (ppm) = 191.9, 156.0, 155.7, 149.0, 148.9, 144.4, 137.1, 136.4, 130.3, 128.1, 124.1, 121.5, 119.1

**Elemental analysis** (%) for $C_{22}H_{15}N_3O$, calculated: C, 78.32; H, 4.48; N, 12.46; found: C, 78.36; H, 4.54; N, 12.40.

Full experiment details, characterization data ($^1$H NMR, $^{13}$C NMR spectra and elemental analysis) and copies of $^1$H NMR and $^{13}$C NMR spectra are included in the Supplementary material. CIF data of compound (**L3**) is deposited in Cambridge Crystallographic Data CentreCenter (CCDC) and its CCDC number: 2018232. The data is available free of charge at http://www.ccdc.cam.ac.uk.

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