

## Synthesis, characterization and catalytic activity of coordination polymers derived from monohydroxybenzoic acids and divalent nickel ion

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### ABSTRACT

Three novel coordination polymers such as **2HBN**, **3HBN** and **4HBN**, respectively, were obtained from the reaction of nickel nitrate with the sodium salts of the 2-hydroxybenzoic acid, 3-hydroxybenzoic acid and 4-hydroxybenzoic acid. All of these polymers show solubility neither in water nor in the common organic solvents. Therefore they were characterized, in the solid state, by vibrational-, electronic-, electron spin resonance (ESR) spectra and thermogravimetric analysis. Infrared spectra of the polymers confirm the ligand coordination to the metal ions through carboxyl group. The absorption and ESR spectra of the polymers are typical of octahedral nickel(II) complexes. Thermal decomposition of **2HBN**, **3HBN** and **4HBN** seems like a multistep process, which starts with dehydration of adsorbed water followed by the release of coordination water and then fragments of the organic linkers leaving NiO as a final product above 480 °C. Coordination polymers have been of interest as materials for heterogeneous catalysis. Thus, **2HBN**, **3HBN** and **4HBN** were tested as catalytic systems against the decarboxylative cross coupling reaction of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids with dioxane. Indeed, expected oxyalkylated products were achieved when **3HBN** was used as a catalyst, whereas **2HBN** and **4HBN** not promoted the reaction. This may be associated to the enhanced electrophilicity of nickel(II) ion in **3HBN** when compared to that of **2HBN** and **4HBN**.

**Keywords:** carboxylates, coordination polymers, catalysis, cross-coupling, carbon-carbon bond formation.

### INTRODUCTION

The chemistry of metal carboxylates continues to be a frontier area of research in view of their fascinating architectures as well as their potential application as functional materials in many areas including catalysis, chiral recognition, gas separation, gas storage, ion-exchange, magnetism, molecular recognition and pharmaceuticals synthesis [1-6]. In addition, they have been used as model systems for the metalloactive sites in bioinorganic chemistry [7]. A large number of metal carboxylates have been synthesized and functional characters have been explored continuously by several researchers [8-12]. The structural diversity and the functional properties encountered in metal carboxylates are attributed to the nature and versatile ligational behavior of the organic linker/s [1-12]. For example, by introducing a nitro group on the carboxylate ligand, Li and coworkers [13] adjust a 2-fold interpenetrating 3-D framework of  $[\text{Zn}_2(\text{NO}_2\text{-ip})_2(\text{bimb})_{1.5}]_n(\text{H}_2\text{O})_n$  ( $\text{NO}_2\text{-ip}$  = 5-nitroisophthalate,  $\text{bimb}$  = 1,4-bis(imidazol-1'-yl)butane) to a porous 2-D layers structure  $[\text{Zn}(\text{MeO-ip})(\text{bmib})_{0.5}]_n(\text{H}_2\text{O})_{0.5n}$  ( $\text{MeO-ip}$  = 5-methoxyisophthalate,  $\text{bmib}$  = 1,4-bis(2-methylimidazol-1'-yl)butane), which represents a shape and size modulation of the layer apertures. However, the systematic studies on the effects of substituent group/s on the coordination



## RESULTS AND DISCUSSION

Complexes **2HBN**, **3HBN** and **4HBN** (Scheme 1), respectively, were prepared by the reaction of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with the sodium salts of 2-hydroxybenzoic acid, 3-hydroxybenzoic acid and 4-hydroxybenzoic acid in a molar ratio of 1:2 (M:L). They were found to be air and moisture stable, intensely colored (Figure 1) and decompose above 300 °C without melting. Moreover, these complexes (Scheme 1) were insoluble (0.01 g in 10 ml of solvent) in water and common organic solvents including acetone, dichloromethane, dimethylformamide, dimethyl sulfoxide, ethanol and toluene. A large number of strong dative- and hydrogen bonds sum up to a considerable amount of energy, as a result, complexes (Scheme 1) are likely to display a poor solubility in various medium. The high decomposition temperatures together with insolubility suggested that **2HBN**, **3HBN** and **4HBN** are polymeric in nature [5-10].



Figure 1. The photographs of solids of **2HBN** (left), **3HBN** (middle) and **4HBN** (right) taken under ambient conditions

*Absorption spectral studies:* The electronic absorption spectra of solid samples of **2HBN**, **3HBN** and **4HBN** (Scheme 1) show three d→d transition bands (Figure 2 and Table 1), two of which have been assigned to the spin-allowed transitions, 367-387 nm [ $^3A_{2g} \rightarrow ^3T_{1g}(P)$ ,  $\nu_3$ ] and 656-674 nm ( $^3A_{2g} \rightarrow ^3T_{1g}$ ,  $\nu_2$ ), usually observed for octahedral Ni(II) complexes [28]. The third band located around 742-745 nm appearing as shoulder (Figure 2) of the  $\nu_2$  band has been assigned to a spin-forbidden transition from the  $^3A_{2g}$  state to the  $^1E_g$  level. The  $\nu_1$  ( $^3A_{2g} \rightarrow ^3T_{2g}$ ) band usually expected in the near infrared region (ca. 1000-1100 nm) could not be observed fully as the region is outside the spectral range of the instrument. Thus, with independent to the position of -OH substituent in respect to -COOH group, all ligands (Scheme 1) stabilize octahedral environment around Ni(II) ion as is observed when benzene dicarboxylic acid was used as a linker.

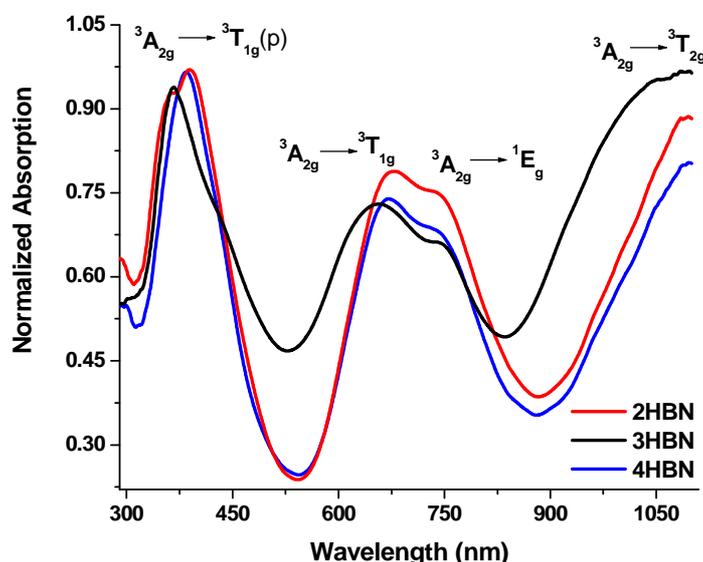


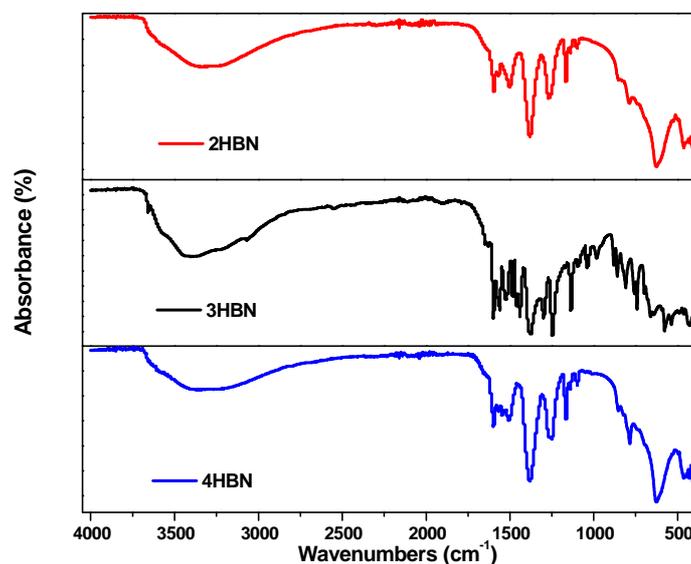
Figure 2. The absorption spectra of **2HBN** (red), **3HBN** (black) and **4HBN** (blue) measured at ambient conditions

**Table 1. Electronic and Infrared spectral data of 2HBN, 3HBN and 4HBN**

compound	<sup>a</sup> Absorption wavelength/nm (cm <sup>-1</sup> )	<sup>b</sup> Peak assignment	<sup>c</sup> Infrared wavenumber (cm <sup>-1</sup> )	<sup>b,d</sup> Peak assignment
2HBN	387 (25840)	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (P)	2900-3650 (b)	V <sub>(H2O)/V<sub>(OH)/V<sub>(Ar-H)</sub></sub></sub>
	674 (14837)	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub>	1596	V <sub>(CO)</sub>
	745 (s, 13423)	<sup>3</sup> A <sub>2g</sub> → <sup>1</sup> E <sub>g</sub>	1573	V <sub>asy(COO)</sub>
	NA <sup>e</sup>	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g</sub>	1511	V <sub>sy(COO)</sub>
3HBN	367 (27248)	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (P)	2800-3700 (b)	V <sub>(H2O)/V<sub>(OH)/V<sub>(Ar-H)</sub></sub> V<sub>(CO)</sub></sub>
	656 (15244)	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub>	1598	V <sub>asy(COO)</sub>
	744 (s, 13441)	<sup>3</sup> A <sub>2g</sub> → <sup>1</sup> E <sub>g</sub>	1561	V <sub>sy(COO)</sub>
	NA <sup>e</sup>	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g</sub>	1524	V <sub>sy(COO)</sub>
4HBN	382 (26178)	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> (P)	2750-3800 (b)	V <sub>(H2O)/V<sub>(OH)/V<sub>(Ar-H)</sub></sub></sub>
	670 (14925)	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub>	1597	V <sub>(CO)</sub>
	742 (s, 13477)	<sup>3</sup> A <sub>2g</sub> → <sup>1</sup> E <sub>g</sub>	1567	V <sub>asy(COO)</sub>
	NA <sup>e</sup>	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g</sub>	1519	V <sub>sy(COO)</sub>

<sup>a</sup> absorption spectra of solids of 2HBN, 3HBN and 4HBN measured at ambient conditions; <sup>b</sup> Ref 28; <sup>c</sup> infrared spectra were recorded using KBr; <sup>d</sup> Ref [29]; <sup>e</sup> Could not be observed as the region is outside the spectral range of the instrument; s, shoulder; b, broad; sy, symmetry; asy, antisymmetric.

*Infrared spectral studies:* In order to study the bonding mode of the ligands (monohydroxybenzoic acids, Scheme 1) with the Ni(II) ion, the infrared (IR) spectra of the free ligands and the prepared polymers (Scheme 1) have been compared and the results are reported in Table 1. The IR spectra of the free ligands exhibited broad bands at 3255-3390 cm<sup>-1</sup> were assigned to the stretching vibration of ν<sub>(OH)</sub> of carboxyl group. This band has disappeared in the spectra (Figure 3) of 2HBN, 3HBN and 4HBN indicating its involvement in the coordination with Ni(II) ion. Moreover, the characteristic bands in the ligands spectra at 1590-1598 cm<sup>-1</sup> and 1540-1560 cm<sup>-1</sup> were assigned to the antisymmetric and symmetric stretching of ν<sub>(COO)</sub> were also shifted to lower frequency by ~30 cm<sup>-1</sup> (Figure 3 and Table 1), which are indicative of the involvement of the carboxylate oxygen in the coordination with metal ion [29]. Besides, in comparison with spectra of ligands, the great changes in intensity as well as in position of signals were observed in the spectra of polymers (Scheme 1) suggesting the complexation of monohydroxybenzoic acids with Ni(II) ion. Horrifically, the existence of water of hydration/crystallization and water of coordination in the spectra (Figure 3) of all polymers (Scheme 1) render difficulties to get the conclusion from phenolic -OH group, which would be overlapped by those of the water molecules.

**Figure 3. Infrared spectra of solids of 2HBN (top), 3HBN (middle) and 4HBN (bottom) measured at ambient conditions**

*Powder X-ray diffraction studies:* The X-ray powder diffraction patterns (PXRD) were recorded to check the homogeneity and crystalline nature of the polymers (Scheme 1) and results are shown in Figure 4. Notice that

the both **2HBN** and **4HBN** exhibited approximately similar profiles with defined sharp peaks in the  $2\theta$  region of 10–50° suggesting their anisotropic behaviors with the same morphology.<sup>30</sup> While the PXRD of **3HBN** showed broad weak peaks indicating its amorphous nature [30]. In general, highly porous coordination polymers exhibit packing difficulties, leading to an amorphous nature [24,25]. The crystallization was found to occur only in the presence of suitable guest molecules that may be included in the lattice.

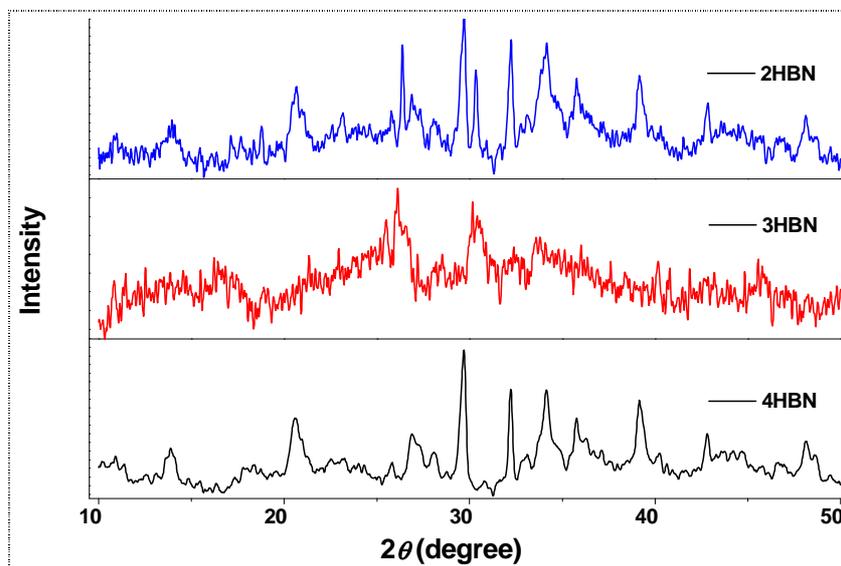


Figure 4. The X-ray powder diffraction patterns of solids of **2HBN** (top), **3HBN** (middle) and **4HBN** (bottom) measured at ambient conditions

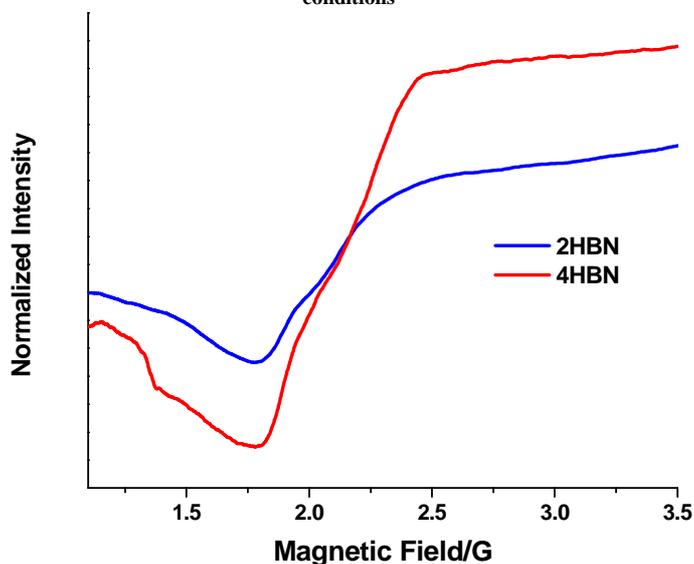


Figure 5. The electron spin resonance spectra of solids of **2HBN** (blue) and **4HBN** (red) measured at ambient conditions

*Electron spin resonance studies:* The Ni(II) ion, a non-Krammer's ion, electron spin resonance (ESR) spectra is observable generally at low temperatures [31]. However, there are few reports in the literature about the ESR study of  $d^8$  ion at room temperature [32]. We have made some attempts to get electronic and bonding features of polymers (Scheme 1) through ESR analysis at room temperature. Notice that the ESR spectra of **2HBN** and **4HBN** show an isotropic pattern ( $g = 2.1564 \pm 0.0002$  for **2HBN** and  $2.1352 \pm 0.0002$  for **4HBN**) with intense broad signals having no hyperfine splitting, cf. Figure 5. The absence of any hyperfine splitting can be attributed to the dipolar line broadening/dipolar exchange as well as unresolved weak hyperfine coupling, which predominantly have been

noticed in polymeric materials [1-3]. The isotropic 'g' values determined from **2HBN** and **4HBN** can be assigned to an octahedral geometry (around metal ion) as they are in good agreement with the 'g' values reported for other high spin octahedral Ni(II) complexes [28] and the results of absorption measurements, cf. Figure 2. In general, Ni(II) ion favors octahedral coordination geometry over tetrahedral and square planar geometries due to large octahedral site stabilization energy and large crystal field stabilization energy [33]. Thus, **2HBN**, **3HBN** and **4HBN** are polymeric in nature and possess Ni(II) ion in an octahedral geometry.

*Thermogravimetric studies:* Thermal analysis is useful in determining the water content in the coordination polymers and their thermal stability under controlled conditions. The thermal behavior of **2HBN**, **3HBN** and **4HBN** were investigated using thermogravimetric analysis (TGA) at a heating rate of 10 °C/min over the temperature range of 25-1000 °C, cf. Figure 6. The analysis of TGA curves indicates that all polymers (Scheme 1) decompose in the multistage. The initial step of degradation within 40-125 °C corresponds to the removal of lattice water that equally detected in IR measurements (Figure 3) as well. The second step decomposition in TG curves (Figure 6) shows the slow rate of mass losses among 130-270 °C owing to the loss of coordinated water. The mass loss of 19-23% and 13-17%, respectively, at third- (270-410 °C) and fourth steps (420-470 °C) associated to the loss of ligands. The weight losses of ligands occur in the temperature range 270-410 °C and 420-470 °C, respectively, are attributed to the decarboxylation as well as the combustion processes [20]. A stable residue obtained after 485 °C, from all polymers, is corresponds to the metal oxide that normally detected from coordination complexes [1-3].

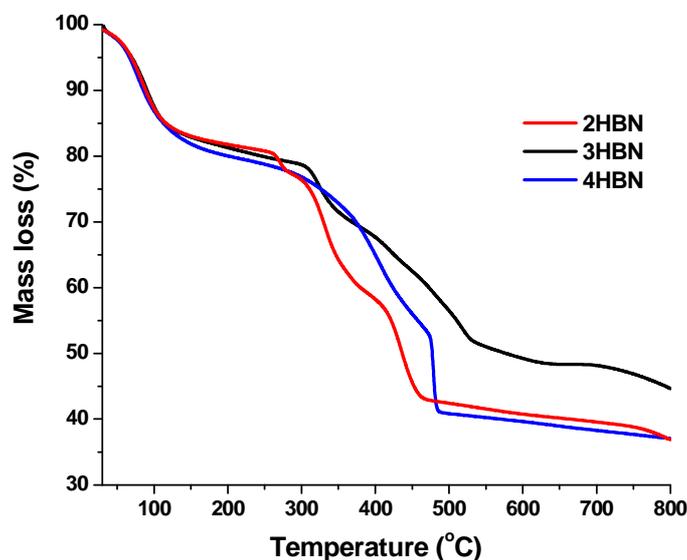


Figure 6. Thermogravimetric profiles of solids of **2HBN** (red), **3HBN** (black) and **4HBN** (blue) measured at a heating rate of 10 °C/min

*Catalytic activity of coordination polymers:* In recent years researchers have become increasingly interested in using coordination polymers as heterogeneous catalysts due to their ordered network structure with uniform channels penetrating through the entire structure [1-6]. Furthermore, metal ions of coordination polymers exposed at the surface of the channels catalyze the reaction within the coordination network as well as on its outer surface giving it an extremely large reactive surface area resulting in faster reaction rates. Therefore, we decided to explore the catalytic activity of novel coordination polymers **2HBN**, **3HBN** and **4HBN** shown in Scheme 1. To probe the catalytic activity of these polymers, we have chosen decarboxylative C–C bond forming reaction [34]. For this, cinnamic acid (Scheme 2), a representative substrate, was allowed to react with 1,3-dioxane in the presence of the catalyst (**2HBN** or **3HBN** or **4HBN**). Results from these catalytic reactions are collected in Table 2. Notice that the **3HBN** yielded the oxyalkylated product (Scheme 2 and Figure 7) in good yield. Whereas, **2HBN** and **4HBN** were not suitable for this transformation as the reaction was sluggish (Table 2). Facile catalytic activity of **3HBN** points the importance of position of substituent in the ligand. Since electron donating tendency of 3-hydroxybenzoic acid to Ni(II) ion is significantly lower than the 2- and 4-hydroxybenzoic acids. As a result, Ni(II) ion is more electrophilic in **3HBN** leading to faster reaction rates. Viz., Ni(II) center readily interacts with carboxylate of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acid and activate the substrates, which then reacts with the dioxane leading to the expected product, cf. Scheme 2.

Scheme 2. 2HBN/3HBN/4HBN mediated synthesis of 2-(1,3-dioxan-2-yl)-1-phenylethanone from cinnamic acid

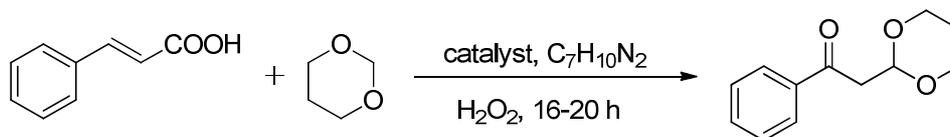


Table 2. The effect of catalysts on the decarboxylative C–C bond forming reactions of cinnamic acid and dioxane

entry	catalyst	time (h)	<sup>a</sup> product yield (%) <sup>a</sup>
1	<b>2HBN</b>	>48	<1
2	<b>3HBN</b>	16-20	82
3	<b>4HBN</b>	>48	<5

All reactions were run with cinnamic acid (2.0 mmol), catalyst (30 mg), H<sub>2</sub>O<sub>2</sub> (6 mmol), base (C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>, 20 mol %) in dioxane (5.0 mL). <sup>a</sup> Isolated yield.

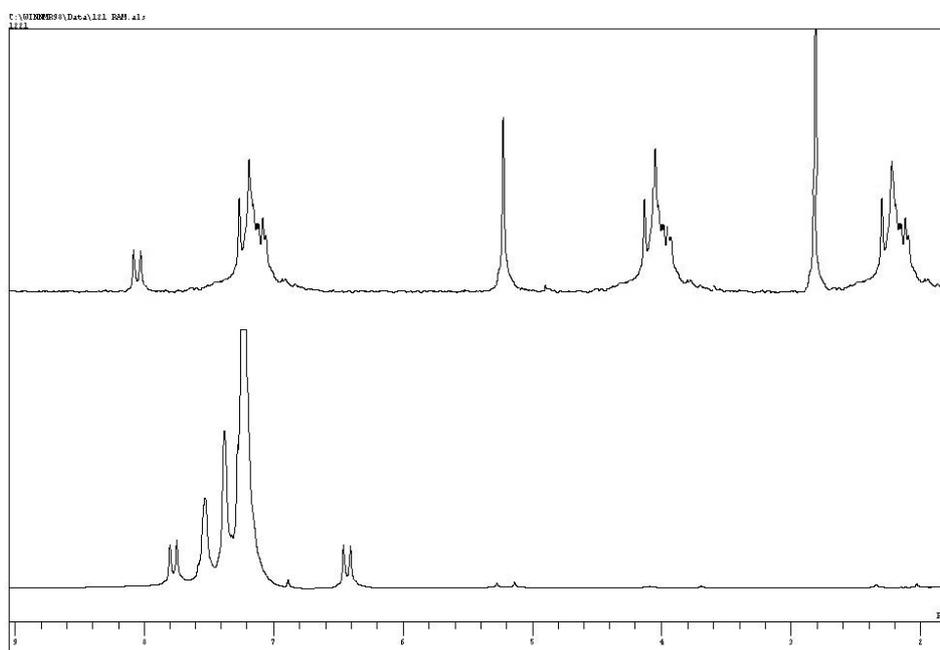


Figure 7. The <sup>1</sup>H NMR (300 MHz) spectroscopic monitoring of conversion of cinnamic acid (bottom) into 2-(1,3-dioxan-2-yl)-1-phenylethanone (top) in CDCl<sub>3</sub>

Encouraged by the positive results observed from the cross-coupling reaction of cinnamic acid and dioxane, it was extended to 4-methoxy- and 4-bromocinnamic acids to explore the scope of the catalytic activity of **3HBN**. Indeed, the reactions proceed smoothly yielding the expected 2-(1,3-dioxan-2-yl)-1-arylethanones in high yields under the same experimental conditions (Scheme 2 and Table 2). Nevertheless, no reaction occurs without the catalyst (i.e., **3HBN**). It is worthy to mention that the 2-(1,3-dioxan-2-yl)-1-arylethanones are key derivatives in the synthesis of fine chemicals and pharmaceuticals [35].

## CONCLUSION

In this study, we have synthesized and characterized three novel coordination polymers of Ni(II) ion with monohydroxybenzoic acid ligands. A structure for these compounds has been explored on the basis of spectroscopic and thermal analysis data. Interestingly, one of the polymer (**3HBN**) derived from the reaction of Ni(NO<sub>3</sub>)<sub>2</sub> and 3-hydroxybenzoate shows remarkable catalytic activity towards decarboxylative cross coupling reaction of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids with dioxane. Detailed analysis shows that the position of substituent group in the ligand is important for the remarkable catalytic activity of **3HBN**. Since OH group substituted *ortho*- and *para*- to

COOH is the culprit that decreases the electrophilicity of Ni(II) ion in cases of **2HBN** and **4HBN**. As a result, metal ions in these polymers have less capability to activate the substrate through coordination. We believe that the present study on systematic investigation of substituent effects on structure and functions of coordination polymers may enable researchers to recognize the importance of position of peripheral substitution/s on functional characters of metal organic frame works.

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