

Enhancement of nanoparticles of ZrO and Al₂O₃ by using new reagent 3-Nitro-2,1-(4-sulfophenyl)-3-methyi-5-pyrozolonazo phenol

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Abstract. The present work involves the prepare and characterization studying of 3-Nitro-2,1-(4-sulfophenyl)-3-methyi-5-pyrozolonazo phenol (3-NSPAP) as a new reagent is developed. The new 2-pyrazoline based ligand was identified by ¹³C NMR, NMR and FT-IR spectra. Enhancement of nanoparticles of Al₂O₃ and ZrO of the solutions of 3-Nitro-2,1-(4-sulfophenyl)-3-methyi-5-pyrozolonazo phenol (3-NSPAP) in aqueous solution was estimated against nanoparticles of Al₂O₃ and ZrO and the results measured by Atomic force microscope (AFM) showed that the metal complexes have greater activity in their spectrum.

1 Introduction

When microparticles turn into nanoparticles, their physical features can change in a number of ways. Increasing the surface-to-volume ratio and the size of the particles entering the system are the most important things in this field, where quantum effects are the most important [1,2].

The size of the particles decreases as the surface area-to-volume ratio increases. This means that the motion of the atoms on the surface is stronger than inside the particles. In our labs, Hussain and his colleagues have done important research on how to improve nanoparticles by using heterocyclicazo dyes [4-6]. Many people are interested in the chemistry of azo dyes and their metal complexes [7-11] because they are used in many different areas. In many different areas, such as optoelectronics and photonics [6], microtechnology and biomedical [12,13], and improved use of heterophenylazo dyes [14-18], azo compounds are the most commonly used type.

Figure out the tiny amounts of metal ions has been shown to be very important in studying the world and living things. Literature shows that pyrozolone derivatives are often used to find metal ions because they have sensitive colour, good stability, and very good chelatogenic properties [19-21]. We want to talk about the 3-NSPAP reagent, which is a selective reagent for improving nanoparticles of Al₂O₃ and ZrO.

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2 Materials and methods

Preparation of the reagent (3-NSPAP)

The chemical was made by mixing 2-amino-3-nitrophenol alcoholic solution with 1-(4-sulfophenyl)-3-methyl-5-pyrazolone. One gramme of 2-amino-3-nitrophenol was mixed with 15 mL of ethanol, 5 mL of distilled water, and concentrated hydrochloric acid to make a diazonium solution. Sodium nitrite solution was then added drop by drop at 0–5 °C. 1-methyl-5-pyrazolone that is 4-sulfophenyl 1.6510 g was mixed with 50 mL of ethanol, and 30 mL of 0.1 M was added at -5 °C. Everything was left to sit overnight. The solid part was filtered off, and ethanol was used to make it crystallise again [22].

Things used

A Test scan Shimadzu FT-IR 8000 series was used to record vibrational bands. The Angstrom improved atomic force microscope (AFM). Ultrasonic vibra cell VCX 130 PB–VCX 130 FSJ from Sonics. Our pH measurements were done with a Hanna HI9811-5 pH meter that had a glass-filled calomel mixed electrode. An electrothermal melting point device was used to find the melting points of both the ligand and the complex. We used an Alpha digital conductivity model -800 to measure the conductivity in a DMSO (10-3) solution.

Chemicals

Everything that was used was of scientific grade.

3-NSPAP stands for 3-Nitro-2,1-(4-sulfophenyl)-3-methyl-5-pyrazolonazo phenol. (1 mM) 250 ml of ethanol was mixed with 0.1048 g of solution.

How to improve the qualities of nano CoO and Zr2O3 (ligand exchange process on nanoparticles)

Nanoparticles of CoO and Zr2O3 were given a ligand exchange reaction to improve their qualities. This was done by mixing pure Ag nano crystals with ligands and stirring the mixture at room temperature. AFM was used to figure out the sizes of the CoO and Zr2O3 nanoparticles.

3 Results and Discussion

3.1. Improving the quality of zirconium oxide nanoparticles

This paper discusses methods to improve the properties of ZrO2 nanoparticles by reducing their size using the ligand exchange process [23]. The application of a ligand to the surface of nanoparticle composites inhibits agglomeration. The initial interaction between organic compounds and nanoparticles is physical, resulting in a natural tendency for these particles to aggregate over time. To improve the stability of nanoparticles, surface-bound ligands can be replaced by alternative ligands, potentially imparting new functions or characteristics [24]. This replacement results in stronger binding of the new ligands to the nanoparticles. The ligand exchange process involves mixing the nanoparticle substance with free ligands. In this study, purified ZrO2 nanocrystals were combined with ligands and stirred at room temperature. The structure and morphology were analyzed using AFM [25]. The results showed that the particles tended to form round aggregate shapes. The observed morphological changes can be explained by the removal of the original stearate ligands from 3-NSPAP, especially at reactive sites such as tips or corners, during the exchange process.

AFM measurements showed that the average size of ZrO₂ nanoparticles decreased from 89.03 nm to 78.54 nm after ligand replacement. These results are presented in Table 1 and illustrated in Figures 1 and 2.

Table 1. Shows the diameters of ZrO₂ before and after ligand of 3-NSPAP exchange

Status	Grain size (G.S.)	Roughness average (Ron.)	Root mean square (R.M.S)
Before	89.41 nm	0.469 nm	0.555 nm
After	78.54 nm	0.418 nm	0.507 nm

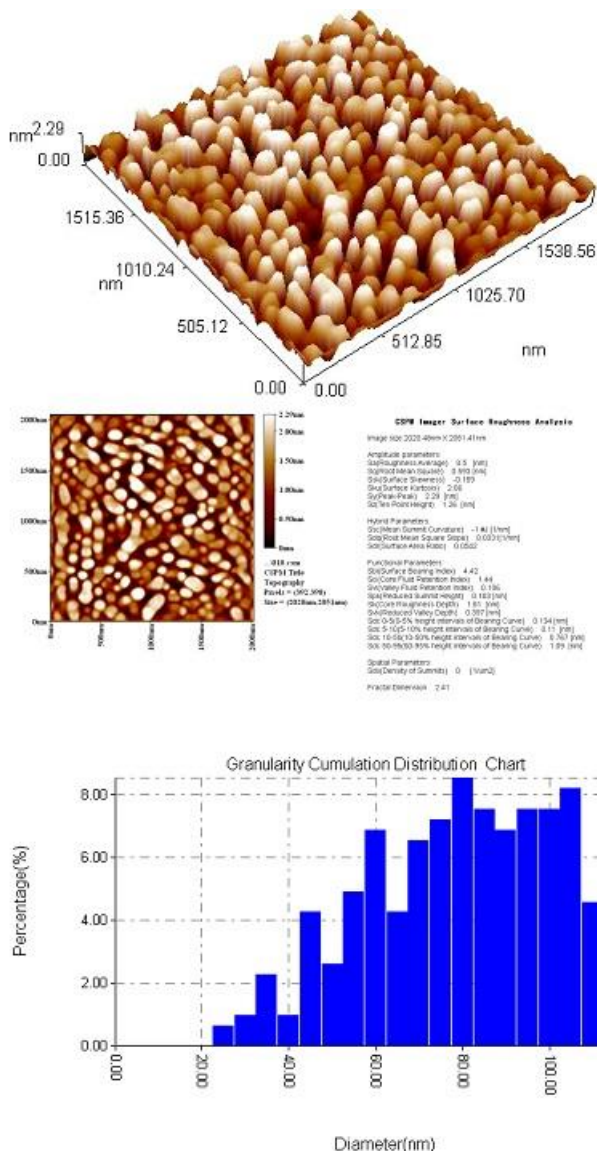


Fig. 1. The average diameters determined by the AFM for ZrO₂ (89.41) nm before 3-NSPAP ligand exchange.

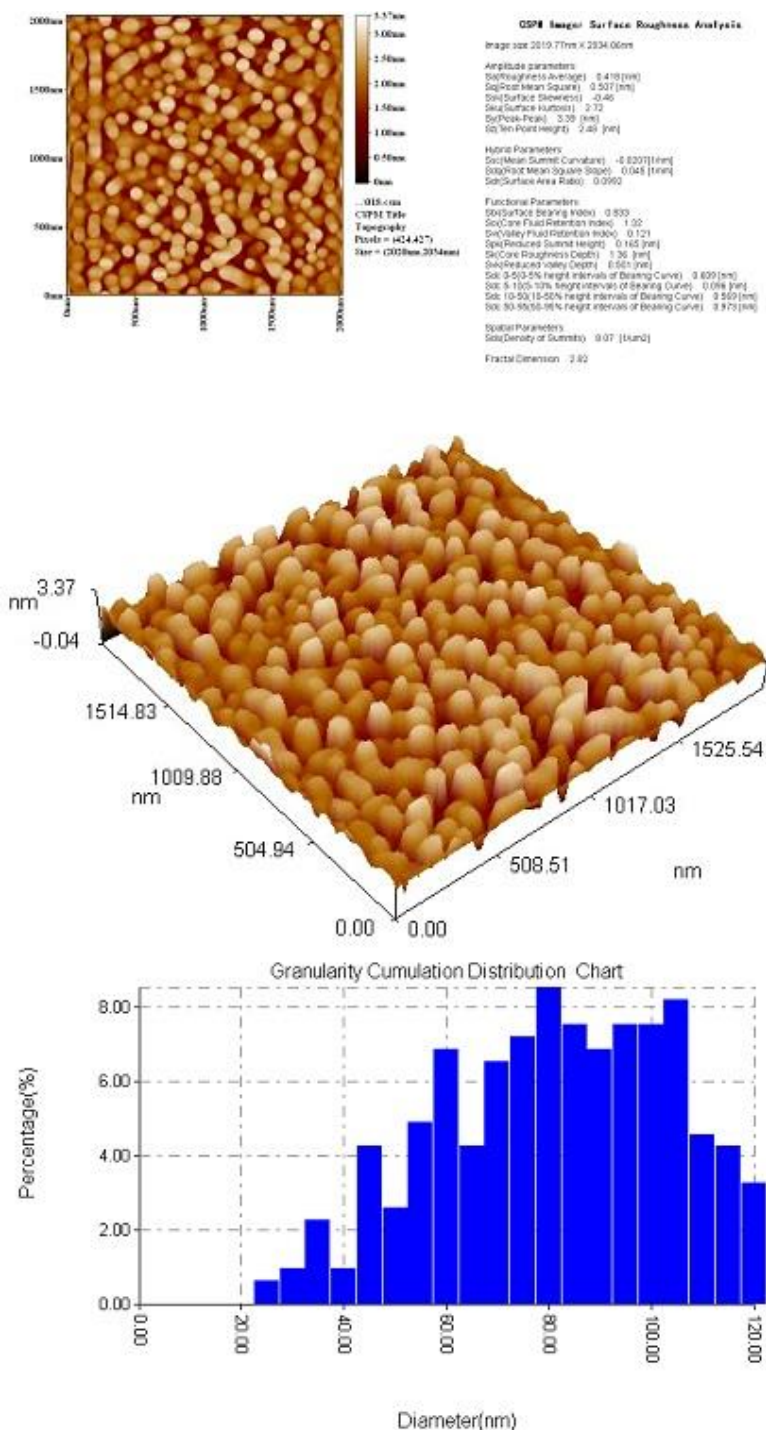


Fig. 2. The average diameters determined by the AFM for ZrO₂ (78.54) nm after 3-NSPAP ligand exchange.

3.2 Making the qualities of aluminium oxide nanoparticles better

Ligands typically form a protective layer on the surface of nanoparticles, preventing aggregation of nanoparticle cores. However, interactions between the artificial nanoparticle surface and stabilizing ligands, such as electron-donating ligands like thiols, amines, or phosphines, are dynamic and involve continuous binding and unbinding processes. This dynamic behavior can lead to particle aggregation over time [26]. To improve nanoparticle stability, surface-bound ligands can be replaced by other ligands that impart new properties or functionalities [27]. This process enhances the bond between ligand molecules and the artificial nanoparticle surface [28]. The ligand exchange reaction is a well-established method for altering ligands bound to nanoparticles. It involves the introduction of free ligands into a mixture with nanoparticles, facilitating the replacement of existing ligands with new ones. This approach offers a simple and adaptable means to alter the composition of the ligand shell of a nanoparticle. Furthermore, the ligand shell is exposed to external solvents and reagents, affecting nanoparticle properties such as solubility and chemical and physical characteristics. By changing the attached ligands, nanoparticles can be tailored for use as biosensors, catalysts, or optoelectronic devices. Furthermore, changes in the ligand structure can affect particle size [29,30]. In this study, pure alumina particles were combined with ligands and subjected to shaking at room temperature for 24 hours [31]. The shape change may be partly due to the fact that surface alumina that was bound to the original ligands was removed at highly reactive points, such as the tips or corners of the nanopyramids, during the ligand exchange process. It has been shown that azoligenes or short chain alcohols on the surface of colloidal nanocrystals remove atoms from the surface of these nanocrystals. On the other hand, AFM results of Al₂O₃ nanocrystals show that the average sizes of nanoalumina were 92.55 nm before ligand exchange and 89.03 nm after, as shown in Table 2. Fig. 3.4.

Table 2. The diameters of Al₂O₃ before and after ligand of 3-NSPAP exchange

Status	Grain size (G.S.)	Roughness average (Ron.)	Root mean square (R.M.S)
Before	92.55 nm	0.506 nm	0.609 nm
After	89.03 nm	0.500 nm	0.593 nm

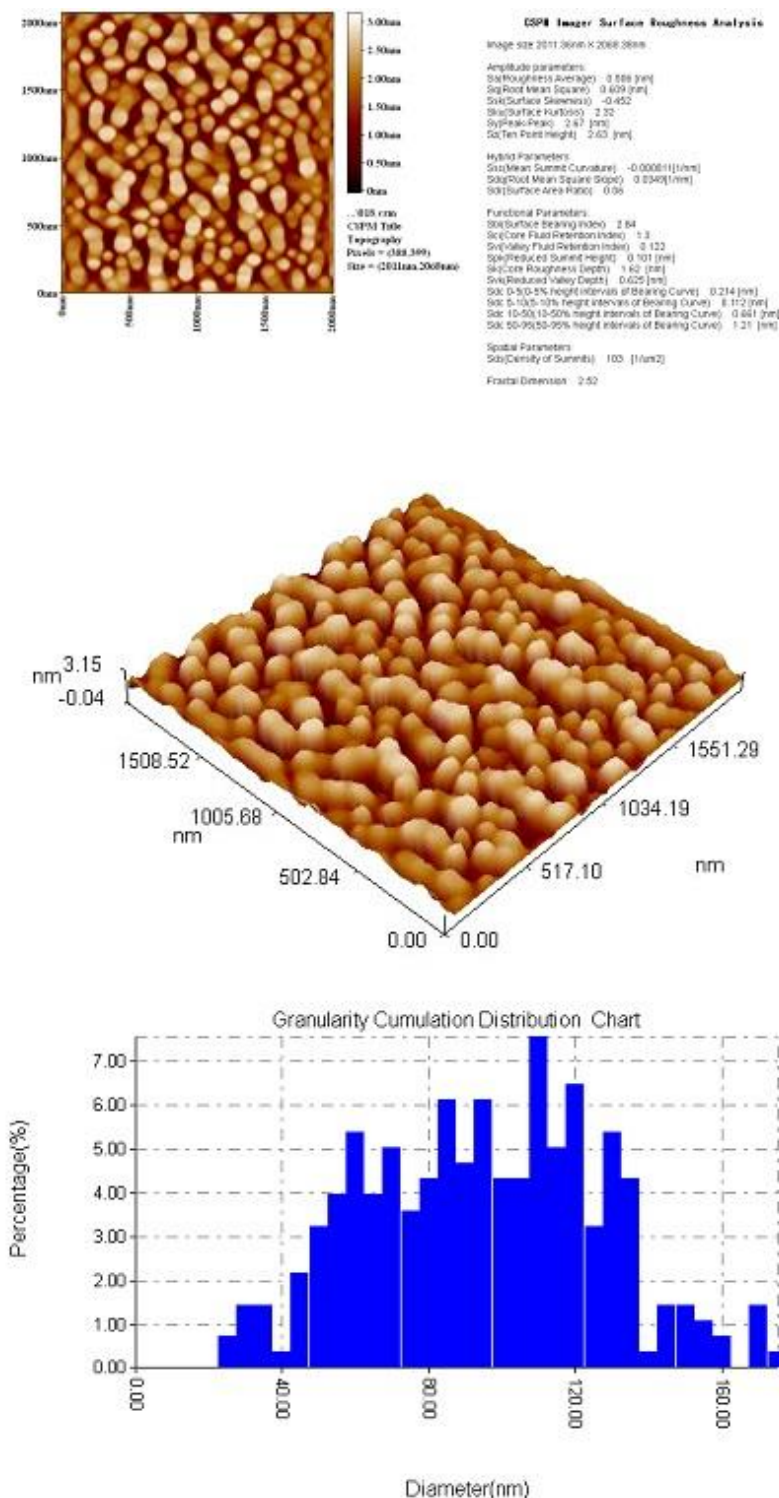


Fig.3. The average diameters determined by the AFM for Al₂O₃ (92.55) nm before 3-NSPAP exchange

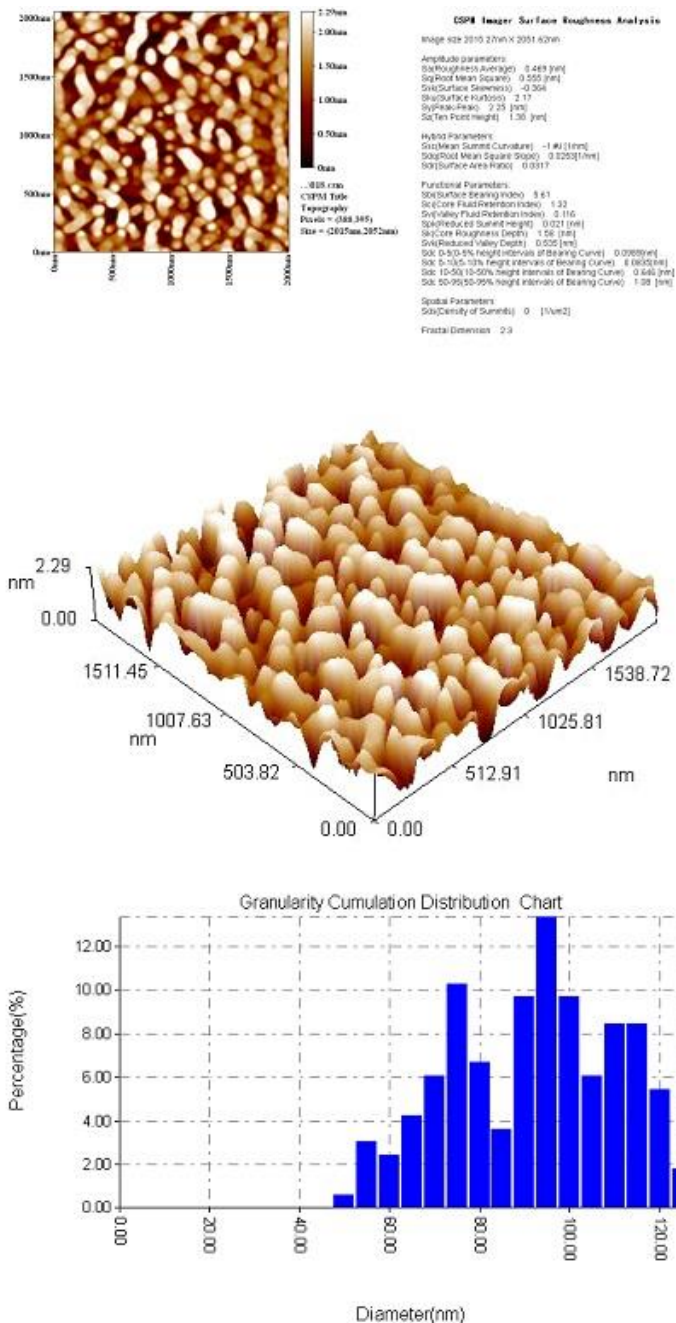


Fig.4. The average diameters determined by the AFM for Al₂O₃ (89.03) nm after 3-NSPAP exchange

3.3 The creation and study of 3-NSPAP

The creation and study of 3-NSPAP (3-Nitro-2,1-(4-sulfophenyl)-3-methyl-5-pyrazolonazo phenol) were revealed by electronic absorption, FT-IR, and 1H-13CNMR spectral data in an earlier work [22].

Spectra of FTIR

The FT-IR measurements of the chemical 3-NSPAP and its complex are shown in Table 3 along with a guess of what they are related to. When the spectrum of the complex is compared to the spectrum of the chemical, significant bands are seen that can help in finding donor sites. You can see that the free ligand has a broad band around 3380.27 cm⁻¹ in the infrared spectrum. This is probably due to the O-H atoms stretching and vibrating at a lower frequency. When the complex is formed, the carbonyl group of the ligand $\nu(\text{C}=\text{O})$ moves from 1634.69 (s) cm⁻¹ to a lower frequency range cm⁻¹. Likewise, the frequency that corresponded to $\nu(\text{N}=\text{N})$ at 1499.04 moved between 1432.48 and 1496.41 cm⁻¹ [32, 33]. Figure 5.

Table 3. The most important spectral data for reagent

Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{H})$ arom.	$\nu(\text{N}=\text{N})$	$\nu(\text{C}=\text{O})$
3-NSPAP	3380.27	1616	Merged	1499.04	1634.69

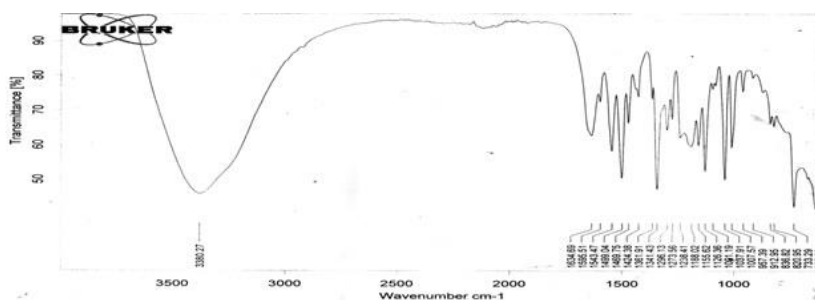


Fig.5. FT-IR spectrum of 3-NSPAP azo reagent

3.4 ¹H-NMR and ¹³C-NMR Studies

The ¹H-NMR and ¹³C-NMR spectra of the prepared azo compound were mixed with ligand in DMSO solutions and tetramethylsilane was used as a reference. The results show the following signals. On the ¹H NMR spectrum for (L), there is a multiplet at $\epsilon(7-7.8)$ ppm (m,H Ar) that the phenyl group causes. There is also a multiplet at $\epsilon(11.7)$ ppm (s,H), at $\epsilon(2.260)$ ppm for C-CH₃, at $\epsilon(1.5)$ ppm for the S-OH group, and at $\epsilon(13.3)$ and $\mu(6.4)$. There are five signs that can be seen in the ¹³CNMR spectrum of 3-NSPAP: 157.23 ppm for C=O; 149.02 ppm for C-NO₂; 146.19 and 145.60 ppm for N-C and S-C, respectively [34]. In Table 4-5 and Fig. 6-7, you can see the ¹H NMR and ¹³C-NMR spectra of the Cs(I) complex.

Table 4. The ¹H NMR values of the reagent 3-NSPAP and its complex with Cs(I)

Compound	C-CH ₃	H aromatic	N-H	O-H
3-NSPAP	2.260	7 - 7.8	1.5	6.4

Table 5. The ^{13}C -NMR data of the reagent 3-NSPAP and its complex with Cs(I)

Compound	C-CH3	C-NO	N-C, S-C	Aromatic	C=O
3-NSPAP	11.98	149.02	146.19, 145.60	130-100	157.23

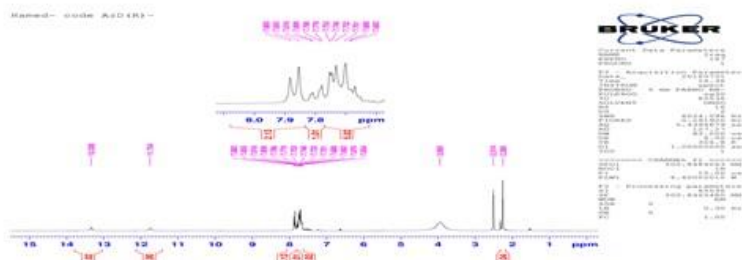


Fig. 6. The ^1H NMR spectrum of 3-NSPAP reagent compound

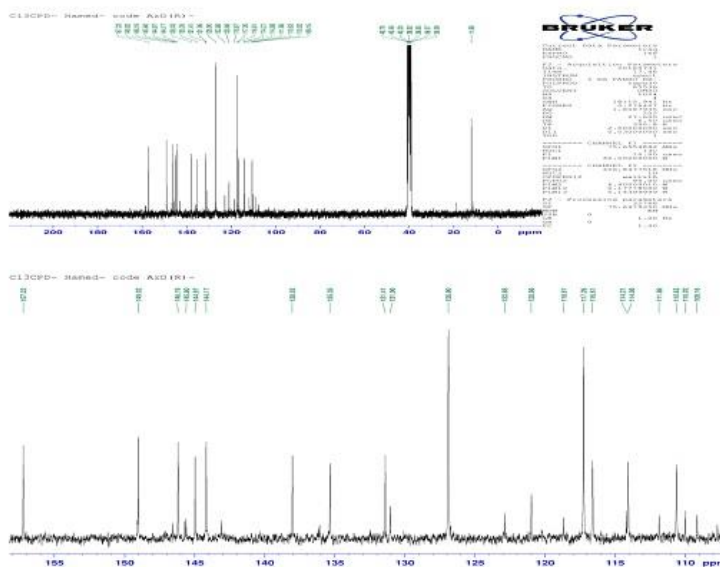


Fig. 7. The ^{13}C NMR spectrum of 3-NSPAP reagent compound.

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