

Synthesis of 3,4-dihydropyrano[c]chromene derivatives using porous copper oxide as nanocatalyst and their electrochemical study

Aayushi Chanderiya¹, Atish Roy² and Ratnesh Das^{1,*}

Department Of Chemistry, Dr.Harisingh Gour Central University Sagar (M.P), 470003, India

Abstract: This research describes a multi-component condensation reaction of 3,4-dihydropyrano[c]chromene from aldehydes, Dicyanomethane, and 4-Hydroxy-2H-chromen-2-one in a solvent system having water and ethanol at ambient temperature. The ratio of water and ethanol was 1:1. Mild reaction temperatures, quick reaction durations, facile product isolation, use of less hazardous solvents, and excellent yields are all essential and valuable characteristics of this approach. In addition, nanoparticles showed perfect catalytic activity since they have more surface area. The electrochemical study of the synthesized product has been done by cyclic voltammetry.

Keywords: One-pot synthesis; Multi-component Synthesis; Nanocatalyst; Electrochemical study.

1. Introduction

Pharmacologically important chemicals are synthesized via multi-component reactions (MCRs). Therefore, it has become an essential topic of organic and medicinal chemistry research¹. 3,4-Dihydropyrano[c]chromenes and their analogs are precious molecules in various domains of chemical science, biological, biological, and medicine².

Dihydropyrano[c]chromenes and their analogs are important compounds because they have diversity in several biological features³, which are antihypertensive, anticoagulation⁴, anti-cancer⁵, and anti-anaphylactic action⁶.

One-pot methods for preparing 2-amino-4-aryl-5-oxo-4H,5H-pyrano[3,2-c] have recently been introduced. In addition, several studies are reported demonstrating the effectiveness of various catalysts in synthesizing chromene-3-carbonitrile from aromatic aldehyde, dicyanomethane, and 4-hydroxy-2H-chromen-2-one⁷.

Nanoscale materials are broadly applied in such syntheses. They have attracted a lot of recognition because of their numerous benefits, such as their insoluble nature across both organic and inorganic solvents. In the heterocyclic synthesis, the active methylene group of malononitrile performs an important and activating role⁸. Malononitrile is used in organic synthesis to convert various functional groups, including ketones, aldehydes, esters, oxides, and amines, to their respective carbanions. This

results in changes to the structure and spectrum characteristics of compound⁹. The catalyst and solvent characteristics are also important in determining the product and selectivity¹⁰. To date, a wide variety of different catalysts have efficaciously catalyzed the synthesis of 4, 5-dihydropyrano[3,2-c] chromenes derivatives, such as nano Zinc oxide¹¹, (NH₄)₂(HPO₄)¹², 1, 8-Diazabicyclo(5.4. 0)under-7-ene (DBU)¹³, TBAB(Tetrabutylammonium bromide)¹⁴, KAl(SO₄)₂·12H₂O¹⁵, TMGT¹⁶, Magnesium oxide¹⁷, Potassium carbonate¹⁸, pyridines¹⁹, [bmim]OH²⁰, morpholine²¹ Recently a reaction of 4,5-dihydropyrano[3,2-c]chromenes catalyzed by 4-dimethylaminopyridine²² was also reported, which was a one-pot, three-component reaction. These synthesized derivatives are also electroactive, and their electrochemical activity was studied by cyclic voltammetry. These cyclic voltammograms can also show the redox behavior of these compounds. Heterogeneous catalysis is used more frequently in organic reactions to perform synthetic transformations due to its importance from an environmental, economic, and practical standpoint²³. Several recently reported syntheses of 4,5-dihydropyrano[3,2-c]chromenes derivative and other biologically active compounds utilizing nanocatalysts. Some of those are a pot 3CR method for preparing biologically-active compound 2-amino-7,7-dimethyl-5-oxo-4-aryl-hexahydro by Fe₃O₄@SiO₂-creatine nanobiocatalyst was found to be cost-effective and recyclable²⁴. Recently, ZIF@ZnTiO₃ Nanocomposite was used as a reusable organocatalyst to produce Dihydropyrano [3, 2-c]

*Corresponding author: Ratnesh Das

Email address: ratneshdas1@gmail.com

DOI: <http://dx.doi.org/10.13171/mjc02211141647das>

Received August 10, 2022

Accepted September 2, 2022

Published November 14, 2022

chromenes and their derivatives. Good yields of pure products were seen with little reaction time²⁵. The ionic liquid can also develop derivatives of biscoumarin and dihydropyrano[3,2-c]chromene. Javad Safaei-Ghomi et al. designed and synthesized Dihydropyrano[3,2-c]chromene and Biscoumarin derivatives using ionic liquid immobilized on FeNi₃ nanocatalyst.²⁶

To produce tetrahydrobenzo[b]pyrans, nano-SiO₂ and 1,5-diazabicyclo[4.3.0]non-5-en was used in a one-pot three-component condensation, this process can be made with excellent yields and quickly²⁷. Recently 2-amino-5-oxo-4-phenyl-4, 5-dihydropyrano [3,2-c] chromene-3-carbonitrile derivatives were successfully synthesized. The reaction was catalyzed by an efficient heterogeneous catalyst DTP/SiO₂²⁸. Both 2-amino-4H-chromene derivatives and 3,4-dihydropyrano[c]chromenes could be effectively synthesized by utilizing the cutting-edge magnetic nanocatalyst Fe₃O₄@SiO₂-Sultone²⁹. Additionally, several reaction procedures have been used to synthesize tetrahydro-4H-chromenes using nanocatalysts including 4-Dialkylaminopyridine modified magnetic nanoparticles, silicon-supported magnetic nanocatalyst, nano-Fe₃O₄, nano-SiO₂, nano-BF₃, and nano-coconut shell-BF₃³⁰⁻³⁴. Our electrochemical investigation aims to shed light on the 3,4-dihydropyrano[c]chromene CV at carbon pest electrode redox behavior. 6-redox behavior previous research also demonstrated the CV method for 6-Bromo-3-[N-(3-chlorobenzylidene)-hydrazino]-chromene-2-one at a carbon pest electrode³⁵.

2. Material and methods

- ▶ Chemicals from Sigma-Aldrich and Himedia were bought and utilized without additional purification. Then, the melting points were determined using an open capillary tube melting point device.
- ▶ A digital pH meter was used to measure the pH of the solution.
- ▶ All electrochemical assays were made on a Metrohm Autolab B.V. PGSTAT128N. software NOVA version 1.10.1.11. a 3-electrode system consisting of a modified carbon paste electrode as the working electrode, a Platinum wire as the auxiliary electrode, and the reference electrode Ag/AgCl electrode in KCl (3 M) solution.
- ▶ SEM analysis of synthesized nanomaterial was done by scanning an electron microscope FEI company model NOVA NANOSEM 450.
- ▶ XRD of synthesized nanomaterial was done by

powder –Ray diffractometer maker Bruker model D8 Advance.

- ▶ FTIR analysis of synthesized compounds was done by Bruker 37 tensor.
- ▶ NMR analysis of products was done by Bruker 500 MHz instrument.

2.1. Fabrication of carbon pest unmodified and modified electrode

An original carbon paste electrode (CPE) was formed by blending graphite powder with paraffin oil. The paste was 70% graphite powder and 30% paraffin oil, respectively. The mixture was homogenized for half an hour with a pestle and mortar before being left to rest for 24 hours for equal homogenization. After that, a plastic syringe was used to load the homogenized paste into the tip. To gain an electrical connection, a conductor was introduced from the backside of the syringe. The electrode's surface was then polished with light physical pressure against a smooth white paper until a shiny surface emerged. Our samples were used to modify electrodes afterward.

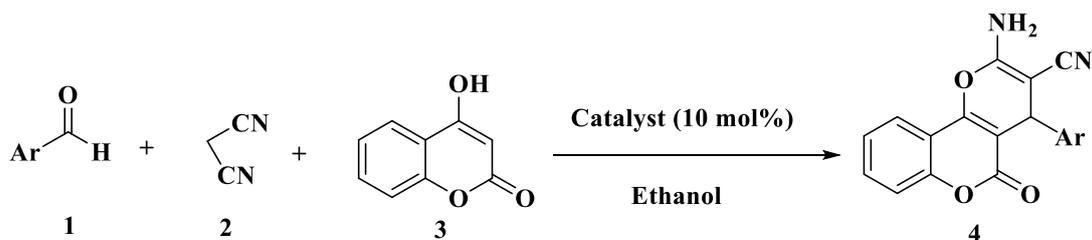
2.2. General analytical procedure

20 mL of 20mM phosphate buffer having pH 7.0, LiCl solution (supporting electrolyte), and stock solution (1mM K₃FeCN₆ solution in distilled water) were placed in a dry and sterilized voltammetric cell for the electrochemical measurement. This solution was purged with N₂ gas for 5 minutes while swirling the solution for electrochemical measurements. In a cathodic scan, the range of cyclic voltammograms was 1.5 to 1.5 V.

The modulation time was 10 ms, the step potential was 0.005 V, and all measurements were done at the scan rate of 0.5V s⁻¹.

3. Experimental section

In an experiment, aldehyde, Dicyanomethane, 4-Hydroxy-2H-chromen-2-one were taken in an equimolar amount, and porous CuO(Catalyst) (10 %) was mixed in a round bottom flask with ethanol: water solvent (10 mL) and agitated at reflux at 80°C. when all the reactants were consumed the reaction was stopped. With the help of TLC, the completion of the reaction was observed. The product was solid. It was refined by recrystallization from ethanol to get pure dihydropyrano[c] chromene. The reaction was completed, and all the spectral data of the compound was collected. After the complete synthesis of the desired compound, a series of different 3,4-dihydropyrano[c]chromene analogs were synthesized from various aromatic aldehydes, as shown in Table 1.

**Table 1.** Different derivatives of dihydropyrano[c]chromene.

| Entry | Aldehydes | Product | Yield % | Color | state |
|-------|-----------------------------------|---------|---------|----------------|-------|
| a | 5-chlorosalicylaldehyde | | 91 | Brown | solid |
| b | 5-Bromo-2-hydroxybenzaldehyde | | 82 | Dark yellow | solid |
| c | p nitro benzaldehyde | | 88 | Pale yellow | solid |
| d | 2,4 dichloro benzaldehyde | | 94 | white | solid |
| e | p-anisaldehyde | | 70 | Mustard yellow | solid |

3.1. Spectral data of compounds

(a) 2-Amino-4-(5-chloro-2-hydroxy-phenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile
Yield: 91%; m.p.: 115-116°C;
IR (KBr, ν , cm^{-1}) 3450 ($-\text{NH}_2$), 3284 ($-\text{OH}$), 2193 ($-\text{CN}$), 1708, 1665, 1367, 1102;

^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ_{H} (ppm): 4.9 (s, 1H, OH), 7.9 (m, 1H, NH_2), 6.5-7.5 (m, 7H, Ar-H), 4.4 (s, 1H, -CH);
 ^{13}C NMR ($\text{DMSO}-d_6$) 158.5, 152.7, 139.7, 133.5, 132.8, 129.2, 128.2, 123.0, 117.0, 113.2, 102.2, 56;
MS: (m/z) (%) 366.04 (100%), 368.04 (32.9%), 367.64 (21.4%), 369.04 (6.7%), 368.05 (2.1%).

(b) 2-Amino-4-(5-Bromo-2-hydroxy-phenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile Yield: 82%; m.p.: 124-126°C;

IR (KBr, ν , cm^{-1}): 3426 (-NH₂), 3329 (-OH), 2193 (-CN), 1715, 1670, 1501, 1344, 1053, 826.

¹H NMR (500 MHz, DMSO-d₆) δ_{H} (ppm): 6.5-7.5 (m, 7H, Ar-H), 5.5 (s, 1H, OH), 7.9 (m, 1H, NH₂), 4.4 (s, 1H, -CH);

¹³C NMR (DMSO-d₆) 158.0, 152.0, 139.2, 133.0, 132.0, 129.3, 128.1, 123.01, 117.02, 113.21, 102.2, 56.00;

MS: (m/z) (%) 409.99 (100%), 411.99 (98.3%), 410.99 (21.4%), 412.99 (21.0%), 413.99 (2.9%), 412.00 (2.1%).

(c) 2-Amino-4-(4-nitro-phenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile

Yield: 88%; m.p.: 118- 119°C;

IR (KBr, ν , cm^{-1}): 3476(-NH₂), 3364, 2191 (-CN), 1714, 1668, 1500, 1342, 1051, 762;

¹H NMR (400 MHz, DMSO-d₆) δ_{H} (ppm): 7.00-8.00 (m, 8H, Ar-H), 8.19 (m, 1H, NH₂), 4.4 (s, 1H, -CH); ¹³C NMR (DMSO-d₆) 159.5, 122.6, 123.0, 123.7, 116, 127.8, 129.2, 133, 124.0, 129.19, 40.155, 102;

MS: (m/z) (%) 361.07 (100%), 362.07 (21.8%), 363.8 (2.1), 363.07 (1.3%).

(d) 2-Amino-4-(2,4-dichloro-phenyl)-5-oxo-4H,5H-pyrano[3,2-c] chromene-3-carbonitrile

Yield: 94%; m.p.: 148- 150°C;

IR (KBr, ν , cm^{-1}): 3827(-NH₂), 3746, 2166(-CN), 1709, 1677, 1524, 1375, 1049, 951, 700;

¹H NMR (500 MHz, DMSO-d₆) δ_{H} (ppm): 6.5-7.5 (m, 7H, Ar-H), 7.9 (m, 1H, NH₂), 4.4 (s, 1H, -CH); ¹³C NMR (DMSO-d₆) 133.9, 133.5, 132.8, 132.5, 158.5, 152.6, 129.19, 128.29, 125.17, 122.9, 119.14, 116.9, 113.13, 102.9, 113.13, 102.9, 39.3;

MS: (m/z) (%) 384.01 (100%), 386.00 (63.9%), 385.01 (20.8%), 387.01 (13.4%), 388.00 (10.3%), 386.01 (2.8%), 389.0 (2.2%), 388.01 (1.7%).

(e) 2-Amino-4-(4-methoxy-phenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile

Yield: 70%; m.p.: 132-134°C

IR (KBr, ν , cm^{-1}): 3438(-NH₂), 2194(-CN), 1711, 1699, 1372, 1055, 839, 752;

¹H NMR (500 MHz, DMSO-d₆) δ_{H} (ppm): 6.5-7.5 (m, 8H, Ar-H), 8.4 (m, 1H, NH₂), 4.4 (s, 1H, -CH); ¹³C NMR (DMSO-d₆) 164.8, 160.9, 133.8, 132.2, 129.1, 124.5, 124.3, 116.16, 115.6, 114.9, 114.2, 113.7, 104.5, 56.3, 40.6;

MS: (m/z) (%) 346.10 (100%), 347.10 (21.9%), 348.10 (3.3%).

3.2. Synthesis of catalyst

Porous CuO was synthesized using previously reported methods with some modifications³⁶. CuO nanoparticles were prepared by dispersing 1.0 g copper nitrate in 1.0 ml distilled water and 1.0 g Tween in 6.5 ml ultrapure water, then adding 2.0 g dextran (Mw = 2 106 M) to 3.0 ml distilled water at room temperature. The paste was formed by heating the gel for Half hour at 60°C on a magnetic stirrer until its color became light blue. The resultant gel was matured at room temperature for 3-4 days before being calcined at 500°C for 3 hours in a muffle furnace at 1°C/min, heating and cooling to room temperature.

3.3. SEM and EDX Images of the synthesized catalyst

The following figure shows the FESEM image of the synthesized porous CuO catalyst. The enlarged image of the catalyst specified that the morphology of the catalyst is porous pore size is shown in the figure. Elemental composition was determined by EDX Spectroscopy which was attached to an SEM instrument (Figures 1 and 2). This image indicates the presence of Cu And O elements.

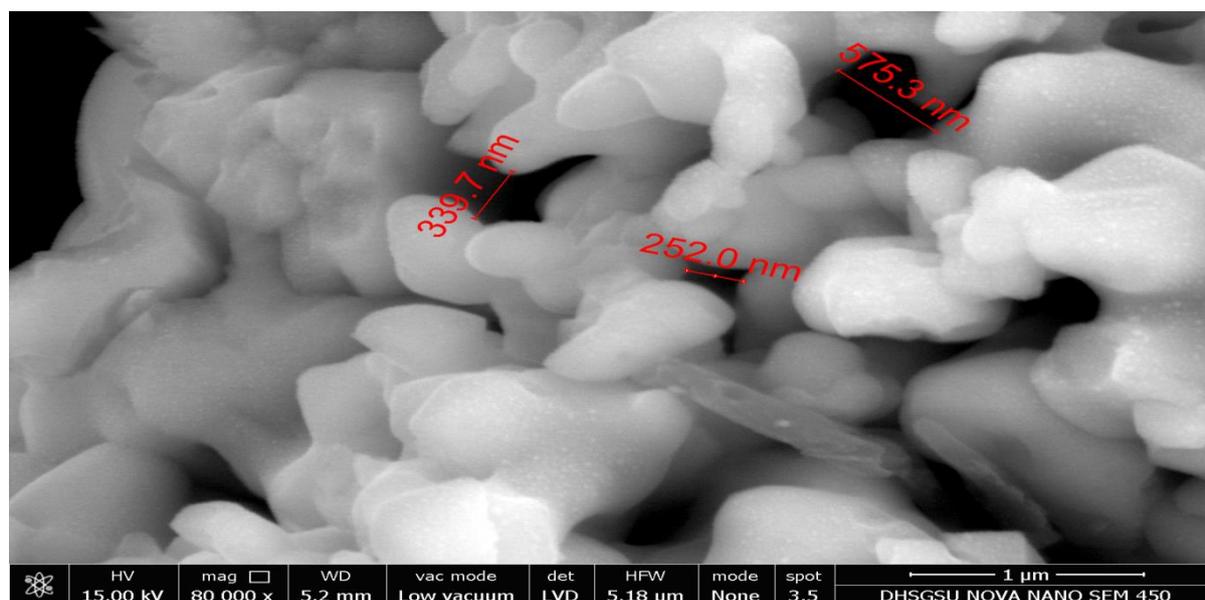


Figure 1. SEM Image o catalyst

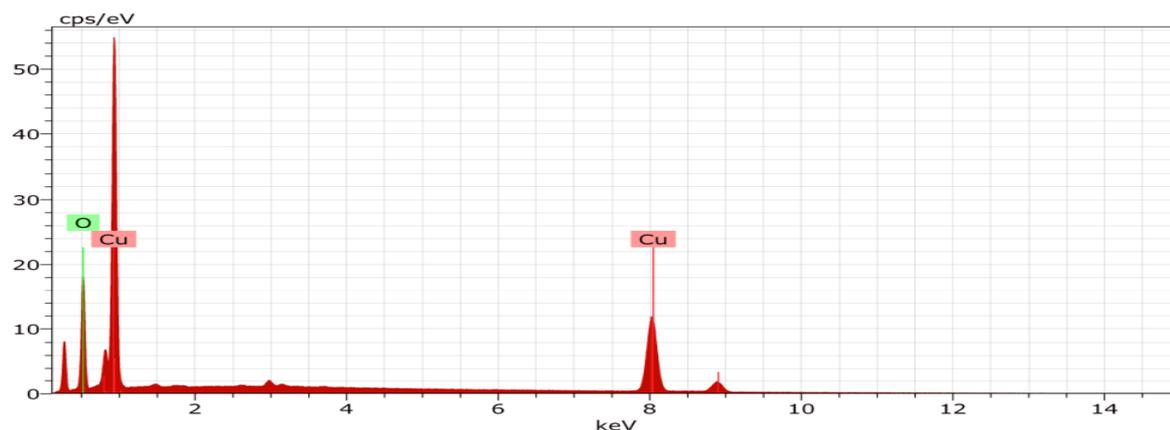


Figure 2. EDX Image of catalyst

3.4. XRD of catalyst

XRD Spectrum of the catalyst shows well-defined peaks with reflections at d spacing of 2.75, 2.52, 2.32, 1.86, 1.58, 1.50, 1.41, 1.40, 1.30, 1.26, and 1.16 Å

which correspond to lattice planes of a base-centered monoclinic unit cell (tenorite) crystal (110), (002), (200), (-202), (202), (-113), (022), (-311), (311), (004), and (312). (JCPDS No.04.783).

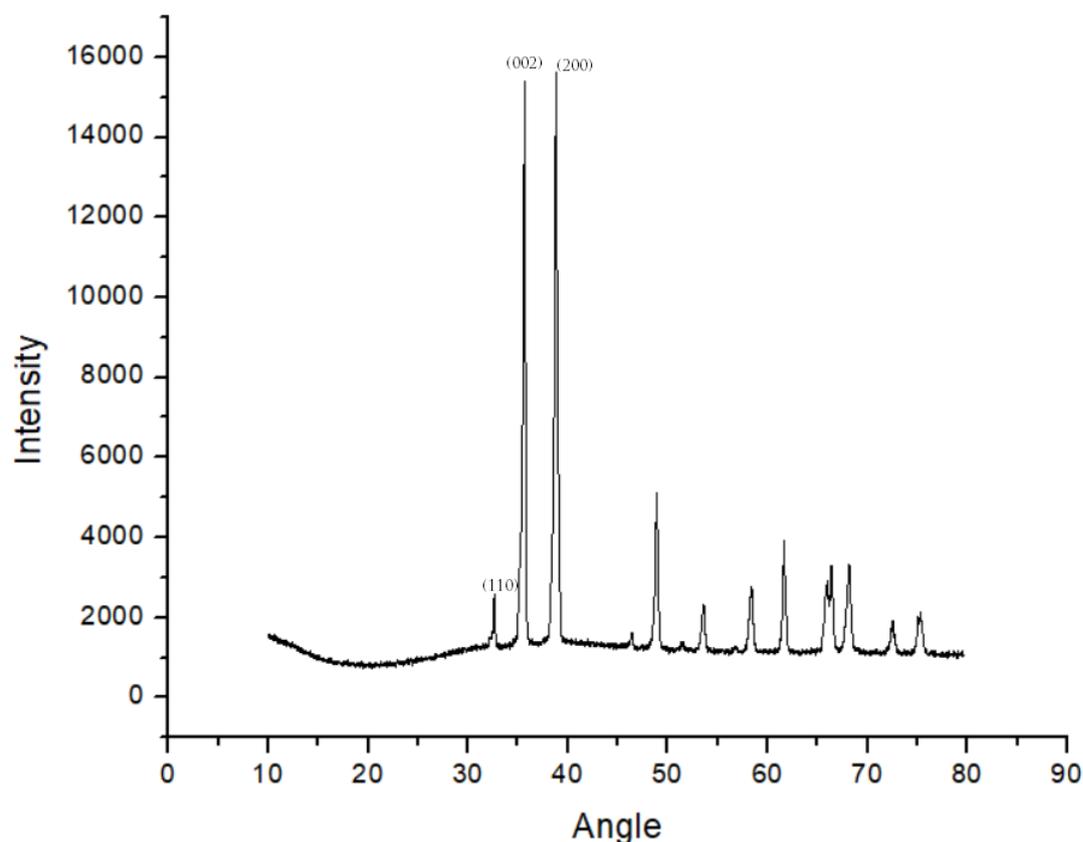


Figure 3. XRD of catalyst

4. Electrochemical study of synthesized derivatives

- ▶ 14.0 mL of 0.01 M stock solution (distilled water was used as solvent), 2.0 mL of 0.1 M LiCl solution 4.0 mL of 0.1 mol L⁻¹ phosphate buffer were mixed to make CV solutions. At room temperature, all electrochemical measurements were taken.
- ▶ On varied scan rates, the cyclic voltammogram of 3,4-Dihydropyrano[c]chromenes derivatives exhibits one electron reduction peak. By using cyclic voltammetric measurements for 0.001 M K₃Fe(CN)₆ probe in Potassium chloride electrolyte (0.1 M) at varied scan rates, the Peak

current for the irreversible system is given by Randle Sevcik equation.

- ▶ $I_p = 0.4463(F^3/RT)^{1/2} n^{3/2} A_0 D_0^{1/2} C_v^{1/2}$
- ▶ where I_p is peak current,
- ▶ n is the number of electrons transferred in the reaction
- ▶ A_0 is the area of the electrode (cm^2)

- ▶ v is the scan rate (VS^{-1})
- ▶ C is concentration of $\text{Fe}(\text{CN})_6^{3-/4-}$
- ▶ D_0 is the diffusion coefficient
- ▶ R and F are the molar gas and Faraday's constant, respectively.

4.1. Cyclic voltammogram of synthesized compounds

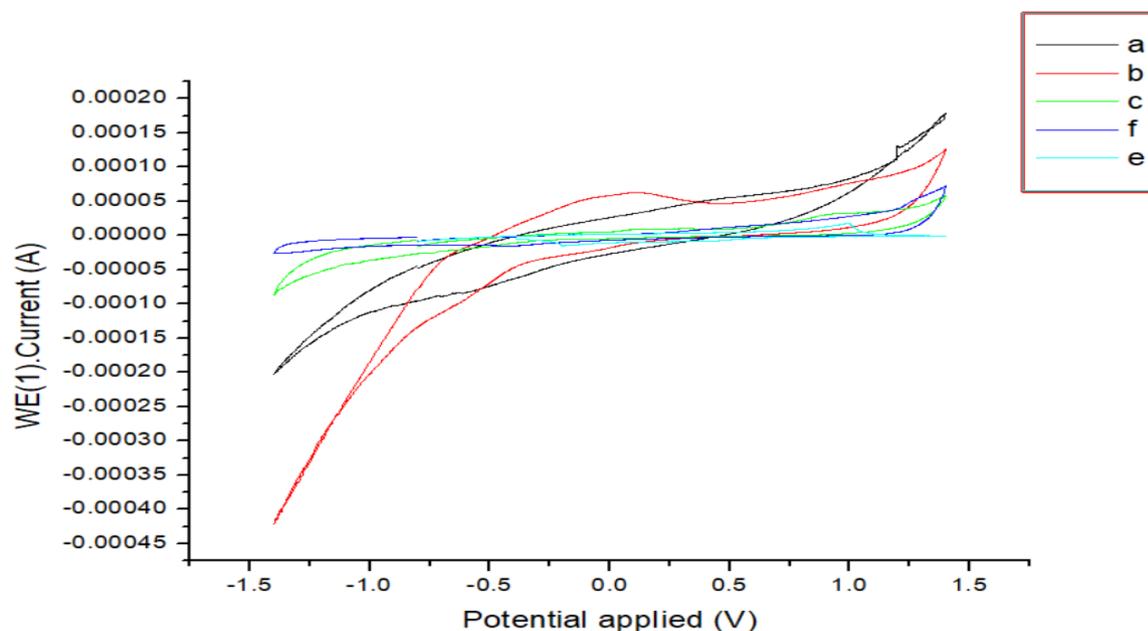


Figure 4. Cyclic voltammogram of synthesized compounds

4.2. Results and Discussion

This paper proposes an effective, environmentally friendly, and versatile technique for preparing 3,4-dihydropyrano[c]chromene analogs in an ethanol and water system. First, cyclic voltammetry was used to investigate their electrochemical state. The 3 component reaction of an aromatic aldehyde (1), Dicyanomethane (2), and 4-Hydroxy-2H-chromen-2-one (3) in the existence of a catalyst yielded 3,4-dihydropyrano[c]chromene. The reaction

was done in water at a low temperature to produce high yields of products (Table 1). Then, using various aromatic aldehydes with different groups of 4-hydroxycoumarin and Dicyanomethane in ethanol, several diverse substituted 3,4-dihydropyrano [c]chromene analogs were produced. The anodic half cycle and cathodic half cycle show one peak, as in Table 2 and Figure 4. The reduction and oxidation peak current and potential of synthesized products are shown in Table 2.

Table 2. Reduction and oxidation peak current and potential of synthesized products.

| Entry | | $E_a(\text{V})$ | $I_a(10^{-5}\text{A})$ | E_c | $I_c(10^{-5}\text{A})$ |
|----------|--|-----------------|------------------------|-----------|------------------------|
| a | | 0.4228 | 5.6 | -5.026 | -7.41 |
| b | | -0.009 | 5.8 | -0.389979 | -4.44 |
| c | | 0.065 | 3.09 | -0.814667 | -2.69 |
| d | | 0.747 | 2.2 | -0.209198 | -1.03 |
| e | | 0.562286 | .513 | -0.30926 | 0.652 |

Compounds have strong oxidation and potential reduction peaks and are electrochemically active, acting as good oxidizing and reducing agents. Several compounds displayed modest oxidation and potential reduction values.

Whereas in the spectra of bare GCE, these redox peaks were not seen. It was clear that all compounds underwent a single, irreversible one-electron oxidation process, adhering to the well-known EC-mechanism pattern at a potential almost identical to

that of the primary aromatic amine (-NH₂initial)'s oxidation wave ³⁷. They underwent one electron loss during oxidation to produce the radical-cation, which underwent one proton loss to produce the corresponding (-NH) radical. A dimerization reaction takes place on the generated radical ³⁸ to produce the (E-E) form of the bis-compound.

The reaction was also done without a catalyst, but the formation of products was time-consuming Table 3 compares the product formation time with and without a catalyst. As a result, this method could be classified as green chemistry. These synthesized derivatives are also electroactive.

Table 3. Comparison between the time of product formation with and without catalyst.

| Entry | product | Time with catalyst(min) | Time without |
|-------|--|-------------------------|--------------|
| a | 2-Amino-4-(5-chloro-2-hydroxy-phenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile | 10 | 90 |
| b | 2-Amino-4-(5-Bromo-2-hydroxy-phenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile | 15 | 85 |
| c | 2-Amino-4-(4-nitro-phenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile | 10 | 75 |
| d | 2-Amino-4-(2,4-dichloro-phenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile | 20 | 95 |
| e | 2-Amino-4-(4-methoxy-phenyl)-5-oxo-4H,5H-pyrano[3,2-c]chromene-3-carbonitrile | 40 | 90 |

5. Conclusion

To summarize, our research has shown a straightforward, quick, effective, and environmentally friendly methodology for preparing dihydropyrano[c]chromene derivatives catalyzed by nanoparticles because finding an easy, affordable, curable, and practicable catalyst for preparing organic molecules is critical. The reaction conditions are mild, and the reaction provides high product yields. There is no harmful organic solvent used in this process. As the catalyst was synthesized at a low cost and is recoverable, it can be used in the reaction several times.

Acknowledgments

The authors thank Dr. Harisingh Gour Central University Sagar (M.P) India and our university's Sophisticated Instrumentation Centre (SIC) for providing essential laboratory resources. Prof. Dr. Ratnesh Das provided additional direction and support to the Author.

Reference

- Balme G., Bossharth E., Monteiro N., Pd-Assisted Multicomponent Synthesis of Heterocycles, *Eur. J. Org. Chem.*, **2003**, 21,4101-4111
- Geen G R, Evans J M and Vong A K, In *Comprehensive heterocyclic chemistry II*; **1996**, 469.
- Kanakaraju S, Sagar Vijay Kumar P, Prasanna B, Chandramouli GVP, Design, Synthesis, and In Vitro Antimicrobial Evaluation of Fused Pyrano[3,2- e]tetrazolo[1,5- c]pyrimidines and Diazepines . *ISRN Org Chem.* **2013**, 1-9.

- Rajput S.S. Synthesis and Characterization of Bis-heterocyclic Derivatives of 1-(3-chlorophenyl) - Pyrrolidine-2,5-Dione. *International Journal of advances in Pharmacy, Biology and Chemistry*, **2012**, 1(2), 242-246.
- Ameta KL, Rathore NS, Kumar B. Synthesis of some novel chalcones and their facile one-pot conversion to 2-aminobenzene-1, 3-dicarbonitriles using malononitrile. *Analele Univ Bucuresti Chim.* **2011**, 20(1), 15-24.
- a) Niknam K, Piran A., Silica-Grafted Ionic Liquids as Recyclable Catalysts for the Synthesis of 3,4-Dihydropyrano[c]chromenes and Pyrano[2,3-c]pyrazoles, *Green Sustain Chem.* **2013**, 03(02), 1-8.
- b) Zheng J, Li Y. One-pot synthesis of tetrahydrobenzo [b] pyran and dihydropyrano [c] chromene derivatives in aqueous media by using trisodium citrate as a green catalyst., *Arch Appl Sci Res.* ,**2011**, 3(2), 381-388.
- c) L Bonsignore, G Loy, D Secci, A Calignano, Synthesis and pharmacological activity of 2-oxo-(2H) 1-benzopyran-3-carboxamide derivatives, *Eur. J. Med. Chem.* , **1992**.
- Jitender M. Khurana Sanjay Kumar, Tetrabutylammonium bromide (TBAB): a neutral and efficient catalyst for the synthesis of biscoumarin and 3,4-dihydropyrano[c]chromene derivatives in water and solvent-free conditions, *Catalysis Communications*, **2009**.
- S.Makarem A.A.Mohammadi A.R.Fakhari, A multi-component electro-organic synthesis of 2-amino-4H-chromenes, *Tetrahedron Lett.*, **2008**, 49, 7194-7196
- Dove MT, Farrelly G, Rae AIM, Wright L. The re-entrant phase transitions in malononitrile:

- Specific heat capacity measurements. *J Phys C Solid State Phys.* **1983**, 16(6).
10. Fringuelli F, Piermatti O, Pizzo F, Chimica D, Perugia U, Elce V. One-Pot Synthesis of 7-Hydroxy-3-carboxycoumarin in Water, *W. J Chem Educ.*, **2008**, 1(6), 6-8.
 11. Paul S., Bhattacharyya P., Asish R.Das. One-pot synthesis of dihydropyrano[2,3-*c*]chromenes via a three-component coupling of aromatic aldehydes, malonitrile, and 3-hydroxycoumarin catalyzed by nano-structured ZnO in water: a green protocol, *Tetrahedron Lett.*, **2011**, 52,4 636-4641 page
 12. Abdol mohammadi S., Balalaie S. Novel and efficient catalysts for the one-pot synthesis of 3,4-dihydropyrano[*c*]chromene derivatives in aqueous media, *Tetrahedron Lett*, **2007**, 48, 299-3303
 13. Jitender M., Khurana Bhaskara, Nand Pooja Saluja. DBU: a highly efficient catalyst for one-pot synthesis of substituted 3,4-dihydropyrano[3,2-*c*]chromenes, dihydropyrano[4,3-*b*]pyranes, 2-amino-4*H*-benzo[*h*]chromenes and 2-amino-4*H* benzo[*g*]chromenes in aqueous medium, *tetrahedron*, **2010**, 66, 5637-5641
 14. Jitender M. Khurana S.K. Tetrabutylammonium bromide (TBAB): a neutral and efficient catalyst for the synthesis of biscoumarin and 3,4-dihydropyrano[*c*]chromene derivatives in water and solvent-free conditions, *Tetrahedron Lett*, **2009**, 50(28), 4125-4127
 15. Ali Reza Karimi, Fahime Sedaghatpour, Novel Mono- and Bis(spiro-2-amino-4*H*-pyrans): Alum-Catalyzed Reaction of 4-Hydroxycoumarin and Malonitrile with Isatins, Quinones, or Ninhydrin, *Synthesis*, **2010**, 10, 1731-1735
 16. Shaabani A, Samadi S, Badri Z, Rahmati A. Ionic liquid promoted efficient and rapid one-pot synthesis of pyran annulated heterocyclic systems. *Catal Letters*. 2005, 104(1-2), 39-43.
 17. Seifi M, Sheibani H. High surface area MgO as a highly effective heterogeneous base catalyst for three-component synthesis of tetrahydrobenzopyran and 3,4-dihydropyrano[*c*]chromene derivatives in aqueous media. *Catal Letters*. **2008**, 126(3-4), 275-279.
 18. M. Kidwai and S. Saxena, Convenient Preparation of Pyrano Benzopyranes in Aqueous Media, *Synthetic Communications*, 2007, 18, 2737-2742.
 19. R M Shaker: Synthesis and reactions of some new 4*H*-pyrano[3,2-*c*]benzopyran-5-one derivatives and their potential biological activities, **1996**, 51(3), 148-51.
 20. Kai Gong, Hua-Lan Wang, Jun Luo, Zu-Liang Liu, One-pot synthesis of polyfunctionalized pyrans catalyzed by a basic ionic liquid in aqueous media. *J. Heterocycl. Chem.* **2009**, 46, 1145-1150
 21. Majid M. Heravi, Masoumeh Zakeri, Narges Mohammadi. Morpholine Catalyzed One-pot Multicomponent Synthesis of Compounds Containing Chromene Core in Water, *Chin. J. Chem.* **2011**, 29, 1163-1166
 22. Robabeh Baharfar, Sakineh A and Narges S. Green Synthesis of 2-Amino-3-Cyano-4*H*-Chromenes in Water Using Nano Silica-Bonded Nano Catalyst. *J Chil Chem Soc.* **2015**, 60(2) 2900-2904.
 23. Adrienn, H., Zoltán, H., Ilona, V.: Convenient one-pot heterogeneous catalytic method for the preparation of 3,4-Dihydropyrimidin-2(1*H*)-ones. *Synth. Commun.* **2006**, 36(1), 129-136.
 24. Reza Eivazzadeh-Keihan, Shahrzad Bahrami, Mostafa Ghafari Gorab, Zahra Sadat & Ali Maleki Functionalization of magnetic nanoparticles by creatine as a novel and efficient catalyst for the green synthesis of 2-amino-4*H*-chromene derivatives, *Scientific Reports*. **2022**, 12, 10664.
 25. Taybeh Farahmand, Saeedeh Hashemian, and Ali Shibani, ZIF@ZnTiO₃ Nanocomposite as Reusable Organocatalyst for the Synthesis of 3, 4-dihydropyrano[*c*]chromene Derivatives, *current Organocatalysis*, **2019**, 6, 248-256.
 26. Javad Safaei-Ghomi, Fahime Eshteghal, and Hossein Shahbazi-Alavi, An Efficient Synthesis of Dihydropyrano[3,4-*c*]chromene and Biscoumarin Derivatives Catalyzed by Ionic Liquid Immobilized on FeNi₃ Nanocatalyst, *polycyclic aromatic compounds*, **2017**, 40, 13-20.
 27. Maryam Mehravar, Bi Bi Fatemeh Mirjalili, Elaheh Babaei, Abdolhamid Bamoniri, Nano-SiO₂/DBN: An efficacious and reusable catalyst for one-pot synthesis of tetrahydrobenzo[*b*]pyran derivatives, *Research Square*, **2021**, 15;34
 28. R.D. Kamble, M.V. Gaikwad, M.R. Tapare, S.V. Hese, S.N. Kadam, A.N. Ambhore, B.S. Dawane. DTP/SiO₂: An Efficient and Reusable Heterogeneous Catalyst for synthesis of Dihydropyrano[3,2-*c*]Chromene-3-Carbonitrile Derivatives. *J. Appl. Organomet. Chem.*, **2021**, 1(1), 22-28.
 29. Monireh Pourghasemi Lati, Farhad Shirini, Mokhtar Alinia-Asli, and Mohammad Ali Rezvani, Fe₃O₄@SiO₂-Sultone: A Novel and Recyclable Magnetic Nanocatalyst for the Efficient Synthesis of 3,4 Dihydropyrano[*c*]Chromenes and 2-Amino-4*H*-Chromene Derivatives, *Nanosci. Nanotechnol.* **2020**, 20, 973-982.
 30. Ali maleki, Sepide Azadegan. Preparation and characterization of silica-supported magnetic nanocatalyst and application in the synthesis of 2-amino-4*H*-chromene-3-carbonitrile derivatives. *Inorganic and nano metal chemistry.*, **2017**, 47, 917-924
 31. Bagher Amirheidari, Mohammad Seifi, Mehdi Abaszadeh. Evaluation of magnetically recyclable nano-Fe₃O₄ as a green catalyst for the synthesis of mono- and bistetrahydro-4*H*-chromene and mono and bis 1,4-dihydropyridine derivatives. *Res*

- Chem Intermed, **2016**, 42, 3413–3423.
32. Ebrahim Mollashahi, Mohammad Nikraftar. Nano-SiO₂ catalyzed three-component preparations of pyrano[2,3-d]pyrimidines, 4H-chromenes, and dihydropyrano[3,2-c]chromenes. Journal of Saudi Chemical Society, 2018, 22, 42–48.
 33. Amin Mohammadzadeh, Ahmad Poursattar Marjani and Asghar Zamani. A Novel Biopolymer-based Nanomagnetic Catalyst for the Synthesis of 4H-pyran and Tetrahydro-4H-chromene Derivatives. S. Afr. J. Chem., **2020**, 73, 55–63.
 34. Hamid Reza Molaei, Bahareh Sadeghi. Microwave Assisted Multi-component Synthesis of 4Hchromene Derivatives by Nano-coconut Shell-BF₃ as a New Heterogeneous Catalyst.
 35. Journal of Applied Chemical Research, **2019**, 13, 85-96.
 36. R. Das, S. Saxena, A. Saxena, Electrochemical study of 6-bromo-3-[N-(3-chloro-benzylidene)-hydrazino]-chromene-2-one by cyclic voltammetry, its DNA interaction study using UV- visible spectroscopy, J. Adv. Electrochem, **2015**, 1(1) 16–18.
 37. G.A. Khan et al., Porous CuO catalysed green synthesis of some novel 3-alkylated indoles as potent antitubercular agents, Journal of Saudi Chemical Society, 2016. 22,6-15
 38. Janz, G.J.; Tomkins, R.P.T. Nonaqueous electrolytes hand book, chapter VI, organic electrolyte. Academic press, Inc. **1973**, 2, 352.
 39. A.A. El Maghraby Electrochemical Study of Some Substituted Chromene Derivatives in Nonaqueous Media at Pt, Au and Glassy Carbon Electrodes., The Open Electrochemistry Journal, **2009**, 1, 8-14.