



Original Research Article

Synthesis of Dihydropyran Derivatives Using ZrCl₄@Arabic Gum Catalyst in Solvent-Free Conditions

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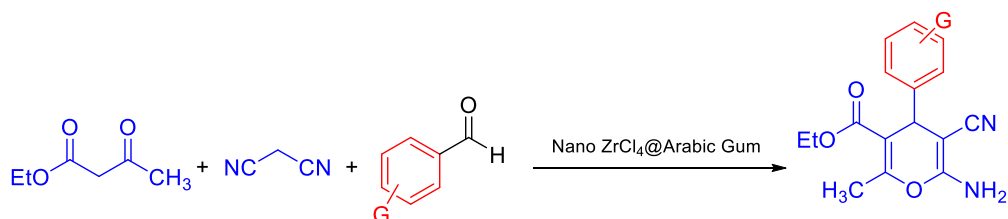
One-pot reaction

Green chemistry

ABSTRACT

In this article, a heterogeneous and recyclable Lewis acid, zirconium chloride immobilized on Arabic Gum (ZrCl₄@Arabic Gum) was used for the synthesis of Dihydropyran derivatives. Accordingly, Dihydropyran derivatives were synthesized with multicomponent reactions, without solvent, using different aldehydes in the presence of the mentioned catalyst at 50 °C. nano-ZrCl₄@Arabic Gum was used as a recyclable catalyst in organic synthesis. The advantages of this method compared to the previous works are high reaction efficiency, short time, simple operation, and catalyst recycling without significantly reducing the catalytic ability.

GRAPHICAL ABSTRACT



Introduction

Due to their pharmacological and biological effects, Dihydropyran have a special place in organic and medicinal chemistry [1]. Pharmacological investigation of the structure of these compounds shows a clear relationship between the spatial structure and their biological and medicinal properties. An important group of oxygenated heterocyclic is the unusual compounds of pyran rings, which are one of the

main components of natural products. Aberrant derivatives of pyran ring are used in the preparation of cosmetics and biodegradable chemicals due to their intrinsic activity and good intermediates [2]. In recent years, different catalysts have been used in different conditions for the synthesis of Dihydropyran derivatives [3-20]. Although the methods available in the sources each have advantages, but most of them have at least one drawback such as long time, difficulty of preparation, low area-selection, low

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efficiency of products. As a result, it is necessary to use a simple, efficient, and effective method for the synthesis of these compounds. Concerning the development of mild and easy methods for the synthesis of organic compounds in solvent-free environment and the use of recyclable and heterogeneous catalysts, nano- $ZrCl_4@Arabic$ Gum was used as a recyclable catalyst in organic syntheses, and in this project, the ability of this catalyst It has been reported in the production of Dihydropyran derivatives at 50 °C and solvent free. $ZrCl_4$ is considered as a solid Lewis acid and used as a good catalyst in many organic reactions. By placing $ZrCl_4$ particles on Arabic gum, it becomes $ZrCl_4@Arabic$ Gum nanoparticles, which are used as an activator and catalyst in chemical reactions [21].

In multicomponent reactions (MCRs) and convergence, three or more starting materials participate in the formation of a product so that essentially all or most of the atoms contribute to the preparation of the new product. Multicomponent reactions are widely used in the preparation of heterocycles [22-27].

Experimental

Chemicals and apparatus

The materials used in this study were obtained from reputable commercial companies. All synthesized materials were characterized by melting point and spectroscopic data. The melting points of the products were determined using the 9100 electrothermal device. IR spectrum was shown using Shimadzu 883 spectrometer (KBr pellets, Nujol Moles, 400-4000 cm^{-1}).

1H -NMR spectrum was recorded with a Bruker-Avance DRX 400 spectrometer and tetramethyl silane external standard. The morphology of the products was analyzed by scanning electron microscopy (SEM) and elemental analysis using energy dispersive X-ray spectroscopy (EDAX) using FESEM MIRA II model (TESCAN, Check

republic). Differential scanning calorimetry (DSC) and TG were performed on a TA device, model SDT Q600 V20.9 make 20 (USA), with a heating rate of 10 °C/min in air, from 25 to 400 °C.

Preparation of nano particles $ZrCl_4@arabic$ gum

To prepare the catalyst, 13.4 grams of zirconium tetrachloride was weighed, and then one gram of Arabic gum was added to it. In the next step, the required amount of dichloromethane solvent was added to the mixture and the mixed materials were mixed in a mortar for an hour. 10 mL of dichloromethane was used.

General method for the synthesis of Dihydropyran in the presence of $ZrCl_4@Arabic$ Gum Nano catalyst

In a test tube, ethyl acetoacetate (1 mmol, 0.13 mL), malononitrile (1 mmol, 0.055 mL), and derivatives of aromatic aldehydes (1 mmol) in the presence of nano catalyst $ZrCl_4 @Arabic$ Gum (0.01 g) under the conditions were stirred without solvent and at 50 °C. The progress of the reaction was monitored by TLC (n-hexane and ethyl acetate 6:2) every ten minutes, and the reaction was complete after half an hour. To isolate the catalyst, the reaction mixture was dissolved in dichloromethane and filtered, and the Dihydropyran product was obtained with high efficiency. The products were purified using hot ethanol, and after cooling, a precipitate was formed and the pure product was separated from ethanol. The synthesis of Dihydropyran derivatives using malononitrile and ethyl acetoacetate has been done for the first time.

Spectral data

6-Amino-5-cyano-2-methyl-4-(4-nitro-phenyl)-4H-pyran-3-carboxylic acid ethyl ester, Compound color cream with yield:%85, m.p:

180-183 °C, m.w: 331 mol/gr, IR(Group index): 3250 cm⁻¹ (NH₂), 2225 cm⁻¹ (CN), 1715 cm⁻¹ (C=O), 1450 cm⁻¹ (CH), and 1150 cm⁻¹ (C-O).

6-Amino-5-cyano-2-methyl-4-(3-nitro-phenyl)-4*H*-pyran-3-carboxylic acid ethyl ester, Compound color white with yield: %82, m.p: 182-183 °C, m.w: 331 mol/gr, IR (Group index): 3105 cm⁻¹ (NH₂), 2225 cm⁻¹(CN), 1705 cm⁻¹(C=O), 3400 cm⁻¹ (C₆H₆), 1523 cm⁻¹ (CH₂), and 11195 cm⁻¹ (C-O).

6-Amino-5-cyano-(4-hydroxy-3-methoxy-phenyl)-2-methyl-4*H*-pyran-3-carboxylic acid ethyl ester, Compound color cream with yield: %90, m.p: 195-196 °C, m.w: 332 mol/gr, IR(Group index): 3425 cm⁻¹ (CN), and 1735 cm⁻¹ (C=O).

6-Amino-5-cyano-4-(4-methoxy-phenyl)-2-methyl-4*H*-pyran-3-carboxylic acid ethyl ester, Compound color yellow with yield: %75, m.p: 142-144 °C, m.w: 314 mol/gr, IR (Group index): 3043 cm⁻¹ (NH₂), 2225 cm⁻¹(CN), 1697 cm⁻¹(C=O), 1496 cm⁻¹ (CH₂), and 1199 cm⁻¹ (C-O).

6-Amino-4-(4-bromo-phenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylic acid ethyl ester, Compound color cream with yield: %85, m.p: 145-147 °C, m.w: 365, IR (Group index): 3115 cm⁻¹ (NH₂), 2215 cm⁻¹(CN), 1715 cm⁻¹(C=O), 1460 cm⁻¹ (CH₂), and 1140 cm⁻¹ (C-O).

6-Amino-4-(3-chloro-phenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylic acid ethyl ester, Compound color cream with yield: %65, m.p: 110-112 °C, m.w: 320, IR (Group index): 3115 cm⁻¹ (NH₂), 2215 cm⁻¹(CN), 1720 cm⁻¹(C=O), 1480 cm⁻¹ (CH₂), and 1150 cm⁻¹ (C-O).

6-Amino-4-(4-chloro-phenyl)-5-cyano-2-methyl-4*H*-pyran-3-carboxylic acid ethyl ester, Compound color cream with yield: %65, m.p: 160-162 °C, m.w: 320, IR (Group index): 3115 cm⁻¹ (NH₂), 2215 cm⁻¹(CN), 1715 cm⁻¹(C=O), 1450 cm⁻¹ (CH₂), and 1150 cm⁻¹ (C-O).

6-Amino-5-cyano-4-(4-hydroxy-phenyl)-2-methyl-4*H*-pyran-3-carboxylic acid ethyl ester, Compound color cream with yield: %90, m.p: 170-172 °C, m.w: 302, IR (Group index): 3352

cm⁻¹ (NH₂), 3345 cm⁻¹ (OH) 2225 cm⁻¹(CN), 1612 cm⁻¹(C=O), 1442 cm⁻¹ (CH₂), and 1172 cm⁻¹ (C-O).

6-Amino-5-cyano-4-(4-methylamino-phenyl)-2-methyl-4*H*-pyran-3-carboxylic acid ethyl ester, Compound color cream with yield: %90, m.p: 150-152 °C, m.w: 315, IR (Group index): 3352 cm⁻¹ (NH₂), 3429 cm⁻¹ (OH) 2212 cm⁻¹(CN), 1635 cm⁻¹(C=O), 1448 cm⁻¹ (CH₂), and 1175 cm⁻¹ (C-O).

6-Amino-5-cyano-4-(3,4-dihydroxy-phenyl)-2-methyl-4*H*-pyran-3-carboxylic acid ethyl ester, Compound color cream with yield: %90, m.p: (120-127 °C), m.w: 318 mol/gr, IR (Group index): 3455cm⁻¹ (NH₂), 2220 cm⁻¹(CN), 1715 cm⁻¹(C=O), 1450 cm⁻¹ (CH₂), and 1150 cm⁻¹ (C-O).

6-Amino-5-cyano-4-(3-methoxy-phenyl)-2-methyl-4*H*-pyran-3-carboxylic acid ethyl ester, Compound color white with yield: %88, m.p: 96-98 °C, m.w: 314 mol/gr, IR (Group index): 3400 cm⁻¹ (NH₂), 2225 cm⁻¹(CN), 1715 cm⁻¹(C=O), 1450 cm⁻¹ (CH₂), and 1150 cm⁻¹ (C-O).

Results and discussion

Characterization by SEM-EDAX

SEM-EDX spectrum was taken for ZrCl₄@Arabic Gum nano catalyst to confirm its particle morphology, texture clarification and elemental analysis (Figure 1). Uneven distribution of particles (larger and smaller particles), healthy and porous surface with irregular arrangement of particles indicates the catalyst formation. The placement of smaller particles in a bed of larger particles is detected using the surface morphology of the composite.

The extreme peak of elemental Zr in the EDAX spectrum of ZrCl₄@Arabic gum was observed in the region of 2 kw and confirmed the presence of other elements such as carbon, oxygen and chloride (2.7 kw) of Arabic Gum coating.

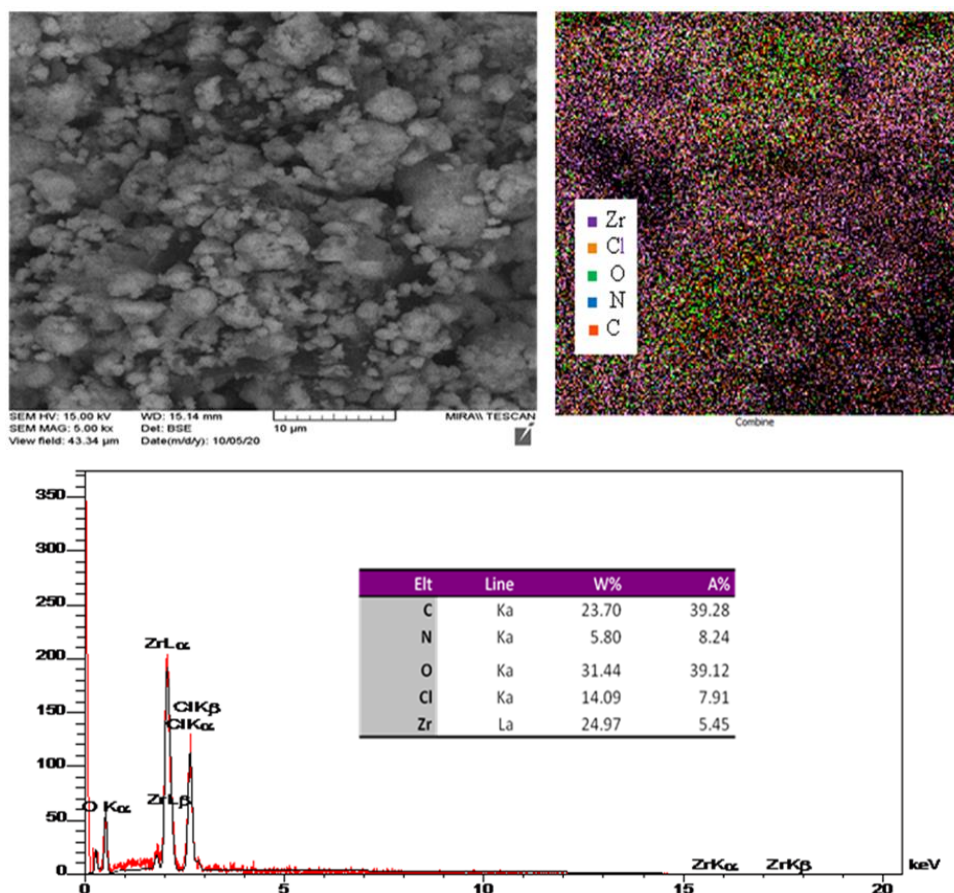


Figure 1. SEM-EDX analysis of the $ZrCl_4@Arabic\ Gum$.

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According to Figure 1, the EDAX spectrum is free of impurities, which confirms the purity of $ZrCl_4@Arabic\ Gum$. Furthermore, the following peaks of conium-chloride-carbon are shown in the weight ratio of 25:14:23.7, respectively.

TG and DSC analysis

Figure 2 depicts the combination of DSC curve and TG curve for 5.6760 mg $ZrCl_4@Arabic\ Gum$. Impurities and moisture can be seen up to 150 °C with a 25% mass reduction. This degradation continues with a gentler slope up to 400 °C with a 50% decrease in total mass, which can be attributed to the loss of water and the decomposition of the carboxylic functional groups of the Arabica Gum. At high temperature, the DSC thermogram of $ZrCl_4@Arabic\ Gum$ shows two exothermic events, melting of

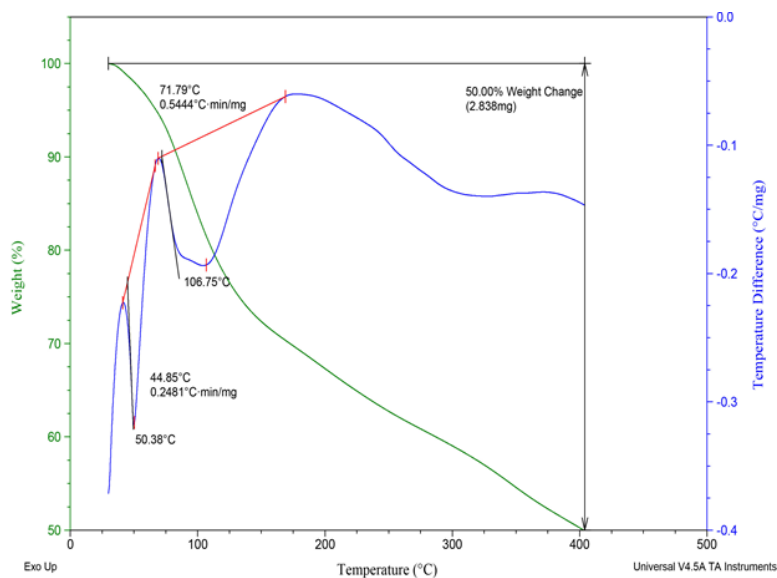


Figure 2. TG and DSC analysis by $ZrCl_4@Arabic\ Gum$.

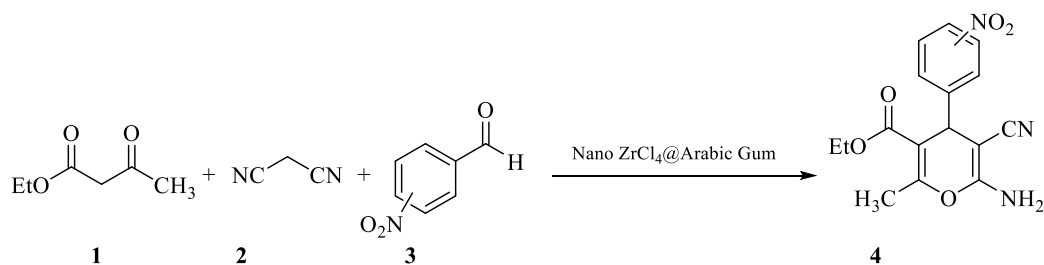
crystallites during heating, around 50 °C and 100 °C, reflecting water- and heat-induced disordering of the crystals due to the $ZrCl_4$ presence.

Preparation of dihydropyran in the presence of $ZrCl_4@arabic\ gum$ nano catalyst

In this study, the synthesis of Dihydropyran was investigated in the presence of $ZrCl_4@Arabic\ Gum$ nano catalyst. To optimize the reaction, 4-nitrobenzaldehyde (1 mmol), ethyl acetoacetate and malononitrile (1 mmol) were used. The reaction was carried out under different

conditions of raw materials in the presence of $ZrCl_4@Arabic\ gum$. The best solution was given in the conditions without solvent in a paraffin bath, temperature 50 degrees Celsius and molar ratio of, ethyl acetoacetate (1), malononitrile (2), and 4-nitrobenzaldehyde (3) 1:1:1 and the amount of 0.01 g of catalyst (Scheme 1 and Table 1).

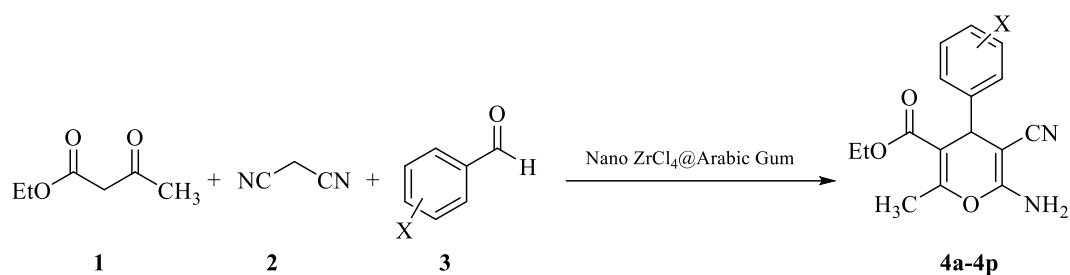
After optimizing the reaction conditions, the synthesis of Dihydropyran derivatives (1) was performed with ethyl acetoacetate (1), malononitrile (2) and different aldehydes (3) to prepare Dihydropyrans at a temperature of 50 °C and without solvent (Scheme 2 and Table 2).



Scheme 1. The $ZrCl_4@Arabic\ Gum$ catalyst for the dihydropyran synthesis.

Table 1. Comparison of the results obtained from the reaction 4-nitrobenzaldehyde, ethyl acetoacetate, and malononitrile and 0.01 g ZrCl₄@Arabic Gum catalyst in various situations

Entry	Catalyst (g)	Solvent	Conditions	Time (min)	Yield (%)
1	ZrCl ₄ @Arabic Gum (0.01)	Chloroform	Rt	60	-
2	ZrCl ₄ @Arabic Gum (0.01)	Ethanol	Rt	60	5
3	ZrCl ₄ @Arabic Gum (0.01)	Chloroform	Reflux	30	10
4	ZrCl ₄ @Arabic Gum (0.01)	Ethanol	Reflux	30	70
5	ZrCl ₄ @Arabic Gum (0.01)	Chloroform	60 °C	60	30
6	ZrCl ₄ @Arabic Gum (0.01)	Ethanol	60 °C	60	50
7	ZrCl ₄ @Arabic Gum (0.01)	Solvent-free	25 °C	50	60
8	ZrCl ₄ @Arabic Gum (0.01)	Solvent-free	50 °C	95	92
9	ZrCl ₄ @Arabic Gum (0.02)	Solvent-free	50 °C	95	98

**Scheme 2.** Preparation of dihydropyran derivatives using three-component reaction.**Table 2.** The Dihydropyran synthesis using ZrCl₄@Arabic Gum as catalyst

Entry	R	Composition	Product	M.P. (°C)
1	4-NO ₂ Ph	4a		180-183
2	2-NO ₂ Ph	4b		190-192
3	3-NO ₂ Ph	4c		182-183
4	4-OH-3-OCH ₃ Ph	4d		150-152

Table 2. Continued...

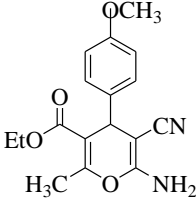
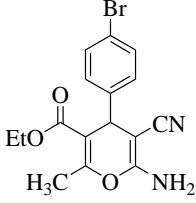
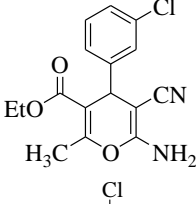
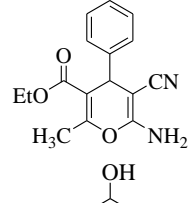
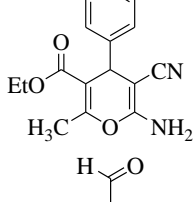
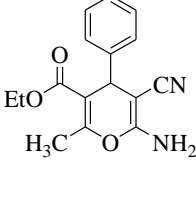
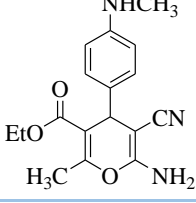
Entry	R	Composition	Product	M.P. (°C)
5	4-OCH ₃ Ph	4e		142-144
6	4-BrPh	4f		145-147
7	3-ClPh	4g		110-112
8	4-ClPh	4h		160-162
9	4-OHPh	4i		170-172
10	4-CHOPh	4j		100-102
11	4-NHCH ₃ Ph	4k		150-152

Table 2. Continued...

Entry	R	Composition	Product	M.P. (°C)
12	3,4-OHPH	4l		125-127
13	3-ClPh	4m		112-115
14	4-COOHPh	4n		103-105
15	3-OCH3Ph	4o		96-98
16	4-COCH3Ph	4p		102-104

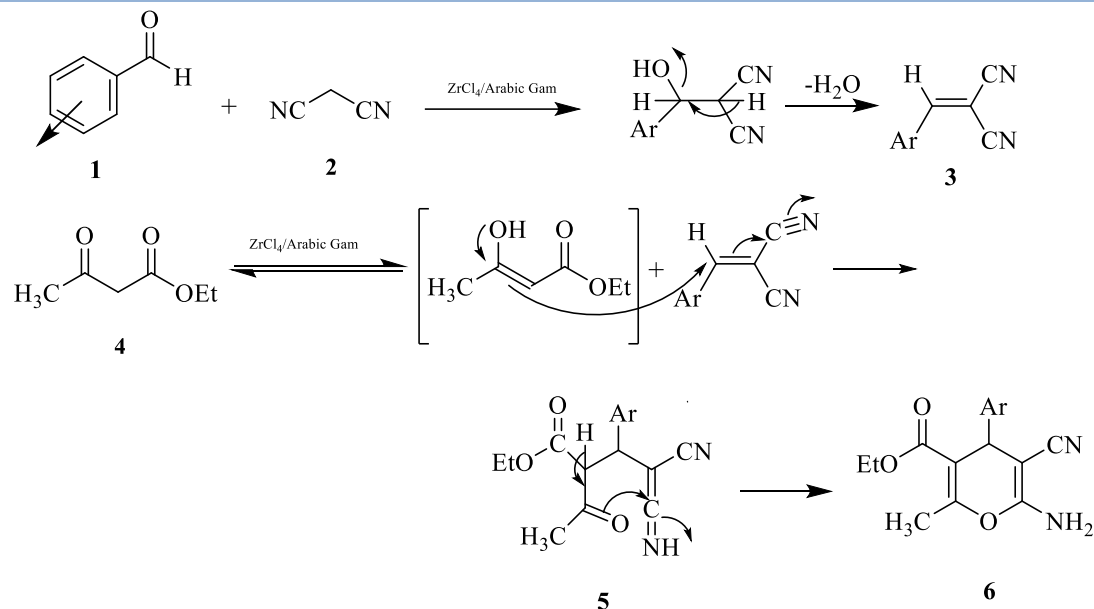
After each reaction, dichloromethane was added to the reaction mixture, and then the product was filtered, the catalyst was separated, and finally it was washed with CH_2Cl_2 and reused. Thereafter, the recovered catalyst was used in the same reaction. The results show that the activity of the catalyst has not changed much compared to the original catalyst (Table 3, entry 2). This experiment was repeated several times, and at each stage the activity of the catalyst decreased to a small amount compared to the original catalyst, which can be caused by deactivation of very few active sites of the catalyst.

In this reaction, a sequential mechanism is carried out, which was determined by examining the reaction by TLC that at the beginning of this reaction, a Knoevenagel reaction was performed, then a Michael addition, and at the last stage, the main product is formed by an intramolecular attack.

The reaction mechanism starts through cyano arylidene (3) as the result of the condensation of aryl aldehyde (1) and malononitrile (2), and simultaneously combines with (4) to form the intermediate (5). After cyclization, it produces compound (6), which can be mentioned that the water removal in the initial stage plays an essential role in the cyclization process.

Table 3. Investigation of the activity of recycled catalyst in the model reaction

Entry	Improved catalyst	Time/minute	Efficiency (%)
1	The first stage	30	85
2	The second stage	30	79
3	The third stage	30	77

**Scheme 3.** Reaction mechanism of dihydropyran synthesis using ethyl acetoacetate, malononitrile, and aryl aldehydes.

Conclusion

In this study, ZrCl₄@Arabic Gum Nano catalyst was used as a very efficient, useful, and recyclable catalyst for the synthesis of dihydropyran derivatives. In this reaction, dihydropyran derivatives were synthesized through the multi-component reaction of ethyl acetoacetate, malononitrile and different aryl aldehydes and the aforementioned catalyst in solvent-free conditions and at 50 °C. The results of the reaction showed that this reaction was carried out at a high speed, at a low temperature and without the use of harmful organic solvents. One of the advantages of this catalyst is its easy application, cheapness, and availability, and this feature has made it an attractive catalyst for the dihydropyran synthesis.

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References

- [1] G. Pund, S. Dhumal, M. Hebade, M. Farooqui, B. Dobhal, Meglumine catalysed green synthesis of Ethyl-6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate derivatives, *Journal of Applied Organometallic Chemistry*, **2022**, 2 15-23. [[CrossRef](#)], [[Publisher](#)]
- [2] Z.A.K. Al-Messri, Synthesis, characterization, and effectiveness of pyranopyrimidine

- derivatives as multi-function additive for lubricating oils, *Chemical Methodologies*, **2023**, *7*, 581-593. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [3] T. Yao, J.E. She, T. Li, X. Qin, Highly regio- and diastereoselective synthesis of 6, 7-dihydro-4H-furo [3, 4-c] pyran derivatives through Pd-catalyzed formal (3+3) allylic cycloaddition of 2-butene-1, 4-diols with 2-(1-alkynyl)-2-alken-1-ones, *Organic Letters*, **2024**, *26*, 2018-2022. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [4] A. Brodzka, F. Borys, D. Koszelewski, R. Ostaszewski, Studies on the synthesis of endocyclic enol lactones via a RCM of selected vinyl esters, *The Journal of Organic Chemistry*, **2018**, *83*, 8655-8661. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [5] S.R. Yetra, T. Kaicharla, S.S. Kunte, R.G. Gonnade, A.T. Biju, Asymmetric N-heterocyclic carbene (NHC)-catalyzed annulation of modified enals with enolizable aldehydes, *Organic Letters*, **2013**, *15*, 5202-5205. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [6] S. Chen, L. Hao, Y. Zhang, B. Tiwari, Y.R. Chi, Asymmetric access to the smallest enolate intermediate via organocatalytic activation of acetic ester, *Organic Letters*, **2013**, *15*, 5822-5825. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [7] M.A. Ameen, S.M. Motamed, F.F. Abdel-latif, Highly efficient one-pot synthesis of dihydropyran heterocycles, *Chinese Chemical Letters*, **2014**, *25*, 212-214. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [8] A. Kulesza, F.H. Ebetino, R.K. Mishra, D. Cross-Doersen, A.W. Mazur, Synthesis of 2, 4, 5-trisubstituted tetrahydropyrans as peptidomimetic scaffolds for melanocortin receptor ligands, *Organic Letters*, **2003**, *5*, 1163-1166. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [9] B. Baghernejad, M. Fiuzat, Application of ninhydrin as an efficient and novel catalyst for the preparation of 2-amino-4H-pyran derivatives, *Journal of Applied Organometallic Chemistry*, **2021**, *1*, 17-21. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [10] A. Sánchez, F. Hernández, P.C. Cruz, Y. Alcaraz, J. Tamariz, F. Delgado, M.A. Vázquez, Infrared irradiation-assisted multicomponent synthesis of 2-amino-3-cyano-4H-pyran derivatives, *Journal of the Mexican Chemical Society*, **2012**, *56*, 121-127. [[Google Scholar](#)], [[Publisher](#)]
- [11] J. Li, C.W. Lv, X.J. Li, D. Qu, Z. Hou, M. Jia, X.X. Luo, X. Li, M.K. Li, Synthesis of biscoumarin and dihydropyran derivatives and evaluation of their antibacterial activity, *Molecules*, **2015**, *20*, 17469-17482. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [12] B. Baghernejad, M. Alikhani, Nano-cerium oxide/aluminum oxide as an efficient catalyst for the synthesis of xanthene derivatives as potential antiviral and anti-inflammatory agents, *Journal of Applied Organometallic Chemistry*, **2020**, *2*, 140-147. [[Crossref](#)], [[Publisher](#)]
- [13] N.S. Babu, N. Pasha, K.V. Rao, P.S. Prasad, N. Lingaiah, A heterogeneous strong basic Mg/La mixed oxide catalyst for efficient synthesis of polyfunctionalized pyrans, *Tetrahedron Letters*, **2008**, *49*, 2730-2733. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [14] M. Saeedi, M.M. Heravi, Y.S. Beheshtiha, H.A. Oskooie, One-pot three-component synthesis of the spiroacenaphthylene derivatives, *Tetrahedron*, **2010**, *66*, 5345-5348. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [15] A. Davoodnia, S. Allameh, S. Fazli, N. Tavakoli-Hoseini, One-pot synthesis of 2-amino-3-cyano-4-arylsubstituted tetrahydrobenzo [b] pyrans catalysed by silica gel-supported polyphosphoric acid (PPA-SiO₂) as an efficient and reusable catalyst, *Chemical Papers*, **2011**, *65*, 714-720. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [16] R. Peña, S. Jiménez-Alonso, G. Feresin, A. Tapia, S. Méndez-Alvarez, F. Machín, Á.G. Ravelo, A. Estévez-Braun, Multicomponent

- synthesis of antibacterial dihydropyridin and dihydropyran embelin derivatives, *The Journal of Organic Chemistry*, **2013**, *78*, 7977-7985. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [17] E. Sheikhhosseini, D. Ghazanfari, V. Nezamabadi, A new method for synthesis of tetrahydrobenzo [b] pyrans and dihydropyrano [c] chromenes using p-dodecylbenzenesulfonic acid as catalyst in water, *Iranian Journal of Catalysis*, **2013**, *3*, 197-201. [[Google Scholar](#)], [[Publisher](#)]
- [18] R. Kamble, M. Gaikwad, M. Tapare, S. Hese, S. Kadam, A. Ambhore, B. Dawane, DTP/SiO₂: An efficient and reusable heterogeneous catalyst for synthesis of dihydropyrano[3,2-c]chromene-3-carbonitrile derivatives, *Journal of Applied Organometallic Chemistry*, **2021**, *1*, 22-28. [[CrossRef](#)], [[Publisher](#)]
- [19] R. Ranjbar-Karimi, S. Hashemi-Uderji, M. Mousavi, Selectfluor promoted environmental-friendly synthesis of 2H-chromen-2-ones derivatives under various reaction conditions, *Journal of the Iranian Chemical Society*, **2011**, *8*, 193-197. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [20] T. Aoyama, T. Suzuki, T. Nagaoka, T. Takido, M. Kodomari, Silica-gel supported sulfamic acid (SA/SiO₂) as an efficient and reusable catalyst for conversion of ketones into oxathioacetals and dithioacetals, *Synthetic Communications*, **2013**, *43*, 553-566. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [21] F. Hakimi, B. Mousavian, F. Banifateme, E. Golrasan, ZrCl₄@Arabic Gum: An effective and environmentally friendly catalyst for the preparation of 14-aryl-14H-dibenzo[a,j]xanthene derivatives at ambient temperature without solvent, *Asian Journal of Green Chemistry*, **2021**, *5*, 378-386. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [22] O. Soleimani, A. Hosseinian, Direct synthesis of xanthenes from benzyl alcohols using choline peroxydisulfate ionic liquid as a reagent under otherwise solvent-free conditions, *Journal of Chemical Research*, **2018**, *42*, 337-340. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [23] M. Shiri, M.M. Heravi, H. Hamidi, M.A. Zolfigol, Z. Tanbakouchian, A. Nejatinezhad-Arani, N.A. Koorbanally, Transition metal-free synthesis of quinolino [2', 3': 3, 4] pyrazolo [5, 1-b] quinazolin-8 (6H)-ones via cascade dehydrogenation and intramolecular N-arylation, *Journal of the Iranian Chemical Society*, **2016**, *13*, 2239-2246. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [24] B.B.F. Mirjalili, A. Bamoniri, A. Akbari, BF₃·SiO₂: an efficient alternative for the synthesis of 14-aryl or alkyl-14H-dibenzo [a, j] xanthenes, *Tetrahedron Letters*, **2008**, *49*, 6454-6456. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [25] F. Hakimi, M. Fallah-Mehrjardi, E. Golrasan, Yttrium aluminum garnet (YAG: Al₅Y₃O₁₂) as an efficient catalyst for the synthesis of benzimidazole and benzoxazole derivatives, *Chemical Methodologies*, **2020**, *4*, 234-244. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [26] F. Hakimi, M. Dehghan Niri, S. H. Banitaba, E. Golrasan, A facile synthesis of benzimidazole derivatives over zinc sulfide nanoparticles as heterogeneous catalyst, *Asian Journal of Green Chemistry*, **2020**, *4*, 239. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]
- [27] F. Hakimi, F.S. Oreyzi, F. Banifateme, E. Golrasan, A new application of nickel nanoparticles as a heterogeneous catalyst for synthesis of 1-amidoalkyl-2-naphthols according to green chemistry principles, *Asian Journal of Green Chemistry*, **2020**, *4*, 134-141. [[CrossRef](#)], [[Google Scholar](#)], [[Publisher](#)]

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