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Ultrasound-Assisted, $ZnCr_2O_4$ Nanocatalyzed Synthesis of Substituted Tetrahydroquinolines via Povarov Reaction

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Abstract: Eco-friendly, reusable $ZnCr_2O_4$ Nano catalyzed tetrahydroquinoline derivatives are prepared via Povarov reaction route from aromatic aldehydes, α-amino naphthalene, and 2,3-dihydrofuran under reflux/ultrasonic irradiation methods. This several affords several benefits like good to excellent yields, a higher percentage of atom economy. Substituted tetrahydroquinolines have been shown great biological potential.

Keywords: Povarov reaction; tetrahydroquinoline; $ZnCr_2O_4$; multi-component reaction.

1. Introduction

Recently, three-component reactions allow the construction of several new bonds in single pot reactions (MCRs) have uplifting importance in synthetic heterogenic chemistry, and their routes provide excellent benefits over conventional synthetic techniques [1] like saved reaction time, low energy consumption, high degree-atom economy, improved percentage of yield, easier progress of the reaction, less handling of hazardous substances are most importance [2]. Tetrahydroquinoline derivatives are one of the important classes of natural products, and they cover a broad area of biological fields such as cytotropic, psychotropic, anti-allergic, antipyretic, anti-inflammatory, antimicrobial, antibacterial, estrogenic, antimalarial, antitumoral, antiplatelet, and anticancer [3]. Povarov (Aza Diels-Alder) reaction is one of the powerful and efficient tools for the synthesis of substituted tetrahydroquinolines [4]. The imines formed from aldehydes and aromatic amines act as heterodienes, and they cyclize with various dienophiles in the presence of various Lewis's acid catalysts. The Lewis acid like $AlCl_3$ [5], $ZnCl_3$ [6], $BF_3.OEt_2$ [7], $TiCl_4$ [8], $InCl_3$ [9], $ZrCl_4$ [10], trifluoroacetic acid [11], *p*-TsOH [12], and HBH_3 [13], Lanthanide triflates [14], CAN [15], L-proline [16], protic acids [17], montmorillonite clay [18] and polymer-supported benzotriazole [19] has been used to catalysed in Povarov reactions. Besides, the Povarov (Aza-Diels-Alder) reactions have been reported to be carried under microwave irradiations and photochemical conditions as well as water media and ionic liquids [20]. Ultra-sonochemistry is the biggest application of ultrasound to chemical synthesis and its processes. Luche and Co-workers have described a number of schemes that

supplied the fundamental of ultra-sonochemistry [21]. Ultrasound technique can act for many organic syntheses due to Pressure inside the bubbles, cavitation collapse, and cavity induced at high temperature, and increases mass transfer [22]. This technique provides significant benefits compared to traditional techniques like short reaction time, low power consumption, a higher percentage of yields, mild reaction conditions, and easier handling [23].

Here, because of the above discussion and continuation of our previous work on thiazole and thiazolidinones of medicinal interest [24-35], we have reported on the three-component in one pot, recyclable $ZnCr_2O_4$ nano catalyzed Povarov (Aza-Diels-Alder) reaction for preparation of substituted tetrahydroquinolines under conventional/ ultrasonic irradiation techniques.

2. Materials and Methods

2.1. General characterization information.

All chemicals were used AR Grade. All chemicals were purchased from Avro Chemical Laboratory. The reaction was carried out in 5 L liquid holding capacity ultrasonic cleaner (230 V AC, 50 Hz power) at 70^{o}C temperature. The reactor was 100 ml Round Bottom flask. The water bath temperature is controlled by the addition or removal of water. Synthesized Tetrahydroquinoline derivatives were evaluated for spectroscopic characterization, such as FT-IR spectra were recorded on Bruker FT-IR spectrometer using KBr disc, the frequencies are reported in cm^{-1}. 1H NMR spectra were recorded a Bruker DRX-300 and Bruker 400MHz NMR spectrometer, 13C spectra were recorded on a Bruker DRX75 and 100 MHz NMR in $CDCL_3$/ DMSO-*d6*. Elemental analysis was performed using an Elementor Vario MICRO cube analyzer instrument. The Tetrahydroquinoline reaction was monitored by TLC technique (silica gel, 60F254 aluminum sheet as an absorbent). The melting point was measured on the Gallen Kamp melting point apparatus.

2.2 General procedure for the synthesis substituted Tetrahydroquinoline (4a-j).

Aryl imine (1) (1.00 mmol), Aromatic aldehydes (2a-j) (1.00 mmol), freshly, pure 2,3-dihydrofuran (3) (3.00 mmol) were added successively to $ZnFe_2O_4$ (10 mol %) in dry PhMe (4.00 ml) at room temperature. The reaction was reflux at 110^{o}C for 5 hours under the nitrogen atmosphere. Completion of the reaction was monitored through TLC. The reaction mixture was diluted with water (10 ml) and extracted with ethyl acetate (2 x 10 ml). The combined organic phase was dried using Na_2SO_4, filtered, and concentrated in a vacuum. Resulted product of yield was purified by recrystallization of pure ethanol.

2.3. General procedure for the synthesis substituted Tetrahydroquinoline under ultrasonic irradiation method (4a-j).

For ultrasonication irradiation method, Aryl imine (1) (1.00 mmol), Aromatic aldehydes (2a-j) (1.00 mmol), freshly, pure 2,3-dihydrofuran (3) (3.00 mmol) were added successively to a solution of $ZnFe_2O_4$ (5 mol %) in dry PhMe (3.00 ml) at room temperature. The reaction was irradiated at 70^{o}C for 50 minutes under the nitrogen atmosphere. The reaction flask was placed at the center of the ultrasonic clear bath, and the surface of reactants was placed slightly lower than the level of the ultrasonic cleaner water bath. We have maintained the temperature of the water bath by the addition or removal of water. Completion of the

reaction was monitored through TLC. The reaction mixture was diluted with water (10 x 2 ml) and extracted with ethyl acetate (2 x 10 ml). The combined organic phase was dried using Na_2SO_4, filtered, and concentrated in a vacuum. Resulted product of yield was purified by recrystallization of pure ethanol.

2.3.1. 11-(phenyl)-2,3,3a,10,11,11a-hexahydrobenzo[h]furo[2,3-c]quinoline (4a).

Blackish grey crystal; M.P. 215-218 ^oC; FTIR (KBr cm^{-1}) 3357(-NH), 2922(-CH), 1578 (-C=C- aromatic), 1216 (ether); ^1H NMR (400 MHz, DMSO) δ 9.92 (s, 1H, D_2O exchangeable -NH), 8.32-7.47 (m, 6H,Ar),7.62-7.10 (m, 5H,Ar), 4.8 (t, 1H, -CH), 4.39 (d, 1H, -CH), 3.68-3.86 (m, 2H, $-CH_2$), 2.42 (m, 1H, $-CH_2$), 1.1-1.7 (m, 2H, $-CH_2$); ^{13}H NMR (100 MHz, DMSO) δ 191.98, 157.45, 153.97, 153.64, 127.92, 126.23, 125.36, 113.12, 112.20, 111.53, 110.14, 105.25, 92.23, 78.08, 76.11, 40.02, 38.13 ppm. Elemental Analysis: $C_{21}H_{19}NO$. C, 83.69, H,6.35, N, 4.65; Found C, 83.76, H, 6.41, N, 4.62.

2.3.2. 11-(2,5-dimethoxyphenyl)-2,3,3a,10,11,11a-hexahydrobenzo[h]furo[2,3-c]quinoline (4b).

White crystal; M.P. 220-222 ^oC: FTIR (KBr cm^{-1}) 3324(-NH), 2910(-CH), 1568 (-C=C-aromatic), 1210 (ether); ^1H NMR (400 MHz, DMSO) δ9.96 (s, 1H, D_2O exchangeable -NH), 8.32-7.45 (m, 6H,Ar), 6.9-7.10 (m, 2H,Ar), 6.75 (s, 1H, Ar),4.8 (t, 1H, -CH), 4.38 (d, 1H, -CH), 3.77-3.85 (m, 2H, $-CH_2$), 3.8-(s, 6H, $-CH_3$), 2.43 (m, 1H, -CH), 1.1-1.7(m, 2H, CH_2); ^{13}H NMR (100 MHz, DMSO) δ189.51, 156.24, 153.76, 151.34, 127.72, 125.26, 124.96, 112.90, 111.70, 111.34, 110.34, 104.37, 93.19, 78.0, 76.0, 56.10, 40.0, 38.0; Elemental Analysis : $C_{23}H_{23}NO_3$, C, 76.43, H, 6.41, N, 3.88; Found C, 73.43, H, 6.41, N, 3.88.

2.3.3. 11-(4-cynophenyl)-2,3,3a,10,11,11a-hexahydrobenzo[h]furo[2,3-c]quinoline (4c).

Yellow crystal; M.P. 250-253 ^oC: FTIR (KBr cm^{-1}) 3324(-NH), 3372(-NH), 2965(-CH), 2183(-CN), 1559 (-C=C- aromatic), 1215 (ether); ^1H NMR (400 MHz, DMSO) δ 10.14 (s, 1H, D_2O exchangeable -NH), 8.33- 7.45(m, 6H,Ar), 7.64 (d, 2H, Ar), 7.34 (d,2H, Ar), 4.82 (t, 1H, CH), 4.37 (d, 1H, CH), 3.77-3.85 (m, 2H, CH_2), 2.43 (m, 1H, CH), 1.1-1.7(m, 2H, CH_2); ^{13}H NMR (100 MHz, DMSO) 188.51, 156.14, 153.71, 150.92, 127.69, 125.36, 125.05, 112.84, 111.66, 118.0, 111.3, 110.41, 104.39, 93.19, 78.0, 76.0, 40.0, 38.9; Elemental Analysis : $C_{22}H_{18}N_2O$, C, 80.56, H, 5.56, N, 8.58, Found C, 80.56, H, 5.56, N, 8.58.

2.3.4. 11-(3-methoxy-4-hydroxyphenyl)-2,3,3a,10,11,11a-hexahydrobenzo[h]furo[2,3-c]quinoline (4d).

Brown crystal; M.P. 210-212 ^oC: FTIR (KBr cm^{-1}) 3377(-OH), 3338(-NH), 2940(-CH), 1556 (-C=C-aromatic), 1213(ether); ^1H NMR (400 MHz, DMSO) δ 9.95 (s, 1H, D_2O exchangeable -NH), 8.32-7.44 (m, 6H,Ar),7.12-6.92 (d, 2H,Ar), 7.02 (s, 1H, Ar, 4.9 (s, 1H,-OH), 4.8 (t, 1H, -CH), 4.39 (d, 1H, -CH), 3.67-3.88 (m, 2H, $-CH_2$), 3.8 (s, 3H, $-CH_3$), 2.43 (m, 1H, $-CH_2$), 1.1-1.8 (m, 2H, $-CH_2$); ^{13}H NMR (100 MHz, DMSO) 192.60, 157, 153.98, 152.44, 128.02, 126.26, 125.16, 113.10, 112.20, 111.53, 110.14, 105.01, 93.20, 78.0, 76.0, 56.11, 40.10, 38.5; Elemental Analysis : $C_{22}H_{21}NO_3$, C,76.06, H, 6.09, N, 4.03; Found C, 76.06, H, 6.09, N, 4.03.

2.3.5. 11-(3-bromophenyl)-2,3,3a,10,11,11a-hexahydrobenzo[h]furo[2,3-c]quinoline (4e).

Brownish crystal; M.P. 195-197°C: FTIR (KBr cm^{-1}) 3372(-NH), 2930(-CH), 1581(-C=C-aromatic), 1237 (ether); ^{1}H NMR (400 MHz, DMSO) δ 9.93 (s, 1H, D_2O exchangeable -NH), 8.33-7.47 (m, 6H,Ar),7.46 (s, 1H,Ar), 7.52-7.26(m, 3H, Ar), 4.8 (t, 1H, -CH), 4.39 (d, 1H, -CH), 3.67-3.88 (m, 1H, -CH), 2.44 (m, 2H, $-CH_2$), 1.1-1.79 (m, 2H, $-CH_2$); ^{13}H NMR (100 MHz, DMSO) 192.63, 148.25, 154.18, 152.10, 127.87, 126.12, 124.96, 114.00, 112.21, 111.62, 110.04, 105.11, 93.31, 78.12, 76.06, 40.25, 38.07; Elemental Analysis : $C_{21}H_{18}BrNO$ C, 66.33, H, 4.77, N, 3.68, Founded: C, 66.36, H, 4.79, N, 3.63.

2.3.6. -(4-methoxyphenyl)-2,3,3a,10,11,11a-hexahydrobenzo[h]furo[2,3-c]quinoline (4f).

Whitish Grey crystals; M.P. 216-218°C: FTIR (KBr cm^{-1}) 3377(-NH), 2931(-CH), 1562 (-C=C- aromatic), 1234 (ether); ^{1}H NMR (400 MHz, DMSO) δ 9.94 (s, 1H, D_2O exchangeable –NH), 8.31-7.43 (m, 6H,Ar),7.23 (d, 2H,Ar), 7.04 (d, 2H, Ar), 4.81 (t, 1H, -CH), 4.40 (d, 1H, -CH), 3.67-3.86 (m, 2H, $-CH_2$), 3.82 (s, 3H, $-CH_3$), 2.44 (m, 1H, $-CH_2$), 1.13-1.80 (m, 2H, $-CH_2$); ^{13}H NMR (100 MHz, DMSO) 189.63, 157.25, 154.15, 152.54, 128.22, 126.46, 125.12, 113.08, 112.15, 111.51, 111.01, 105.31, 92.96, 78.0.1, 76.22, 56.21, 40.30, 38.06; Elemental Analysis : $C_{22}H_{21}NO_2$, C, 77.73, H, 6.39, N, 4.23, Founded: C, 77.68, H, 6.42, N, 4.19.

2.3.7. 11-(4-chlorophenyl)-2,3,3a,10,11,11a-hexahydrobenzo[h]furo[2,3-c]quinoline (4g).

White crystals; M.P. 222-223°C: FTIR (KBr cm^{-1}) 3382(-NH), 2917(-CH), 1563(-C=C-aromatic), 1209 (ether); ^{1}H NMR (400 MHz, DMSO) δ 9.96 (s, 1H, D_2O exchangeable -NH), 8.31-7.45 (m, 6H,Ar),7.66 (d, 2H,Ar), 7.52 (d, 2H, Ar), 4.80 (t, 1H, -CH), 4.41 (d, 1H, -CH), 3.67-3.85 (m, 2H, $-CH_2$), 2.44 (m, 1H, $-CH_2$), 1.13-1.78 (m, 2H, $-CH_2$); ^{13}H NMR (100 MHz, DMSO) 186.41, 148.60, 148.40, 148.11, 139.99, 136.80, 131.14, 129.79, 131.72, 127.02, 126.81, 126.44, 126.57, 123.97, 123.91, 113.30, 93.00, 79.12, 78.00, 40.12, 38.20.; Elemental Analysis : $C_{21}H_{18}ClNO$, C, 77.11, H, 5.40, N, 4.17, Founded: C, 77.03, H, 5.37, N, 4.23.

2.3.8. 11-(2,4-dichlorophenyl)-2,3,3a,10,11,11a-hexahydrobenzo[h]furo[2,3-c]quinoline (4h).

White crystals; M.P. 226-228°C: FTIR (KBr cm^{-1}) 3384(-NH), 2932(-CH), 1545 (-C=C-aromatic), 1218 (ether); ^{1}H NMR (400 MHz, DMSO) δ 9.98 (s, 1H, D_2O exchangeable -NH), 8.32-7.47 (m, 6H,Ar),7.78 (s, 1H,Ar), 7.46 (d, 1H, Ar), 7.11 (d, 1H, Ar), 4.82 (t, 1H, -CH), 4.40 (d, 1H, -CH), 3.67-3.86(m, 2H, $-CH_2$), 2.45 (m, 1H, $-CH_2$), 1.14-1.79 (m, 2H, $-CH_2$)**;** ^{13}H NMR (100 MHz, DMSO) 190.61, 156.00, 153.88, 12.44, 127.92, 126.16, 125.10, 113.13, 112.21, 121.93, 110.09, 105.11, 93.19, 78.05, 76.11, 40.22, 38.12; Elemental Analysis : $C_{21}H_{17}Cl_2NO$, C, 68.12, H, 4.63, N, 3.78, Founded: C, 68.21, H, 4.66, N, 3.71.

2.3.9. 11-(4-nitrophenyl)-2,3,3a,10,11,11a-hexahydrobenzo[h]furo[2,3-c]quinoline (4i).

Yellow crystals; M.P. 232-233°C: FTIR (KBr cm^{-1}) 3300(-NH), 2921(-CH), 1550 (-C=C-aromatic), 1217 (ether); ^{1}H NMR (400 MHz, DMSO) δ 10.00 (s, 1H, D_2O exchangeable -NH), 8.77-7.10 (m, 6H,Ar),8.11 (d, 2H,Ar), 7.61 (d, 2H, Ar), 4.80 (t, 1H, -CH), 4.37 (d, 1H, -CH), 3.68-3.33 (m, 2H, $-CH_2$), 2.44 (m, 1H, $-CH_2$), 1.1-1.45 (m, 2H, $-CH_2$)**;** ^{13}H NMR (100 MHz, DMSO) 187.51, 158.69, 149.30, 147.51, 141.90, 133.90, 130.04, 128.89, 127.92, 126.96, 126.80, 126.34, 126.25, 124.17, 123.81, 113.20, 93.00, 79.10, 78.00, 40.02, 38.23; Elemental Analysis : $C_{21}H_{18}N_2O_3$, C, 72.82, H, 5.24, N, 8.09, Founded: C, 72.86, H, 5.30, N, 8.06.

2.3.10. 11-(4-fluorophenyl)-2,3,3a,10,11,11a-hexahydrobenzo[h]furo[2,3-c]quinoline (4j).

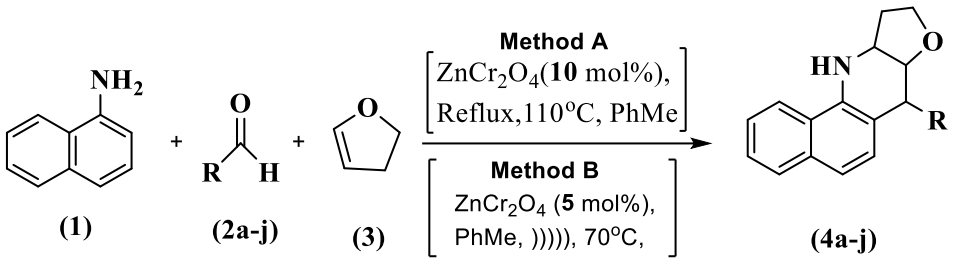
Pale Yellow crystals; M.P. 211-213^{o}C: FTIR (KBr cm^{-1}) 3321(-NH), 2920(-CH), 1536(-C=C-aromatic), 1205 (ether); ^{1}H NMR (400 MHz, DMSO) δ 9.94 (s, 1H, D_2O exchangeable -NH), 8.31-7.44 (m, 6H,Ar),7.32 (d, 2H,Ar), 7.21 (d, 2H, Ar), 4.80 (t, 1H, -CH), 4.39 (d, 1H, -CH), 3.66-3.80 (m, 2H, -CH_2), 2.43 (m, 1H, -CH_2), 1.13-1.70 (m, 2H, -CH_2)**;** ^{13}H NMR (100 MHz, DMSO) 179.21, 152.49, 148.30, 147.33, 141.84, 133.72, 131.14, 127.89, 127.88, 127.16, 126.65, 126.96, 125.83, 124.10, 123.41, 113.90, 92.90, 78.93, 78.00, 40.00, 38.13; Elemental Analysis : $C_{21}H_{18}N_2O_3$, C, 78.98, H, 5.68, N, 4.39, Founded: C, 78.99, H, 5.71, N, 4.20.

3. Results and Discussion

Although cyclopentadiene has been extensively used in three-component one-pot Povarov (Aza-Diels-Alder) reaction, there are few examples of tetrahydroquinolines synthesized using the Povarov reaction of 2,3 dihydrofuran.

In the present study, we reported mild and efficient conditions for the synthesis of tetrahydroquinolines derivatives (Scheme 1, Table 1) through Povarov ((Aza-Diels-Alder) reaction using $ZnCr_2O_4$ nanocatalyst with good to excellent yields. This reaction was first explored by stirring a reaction mixture of 1-amino naphthylamine (1), benzaldehyde (2a), and 2,3 dihydrofuran (3) with $ZnCr_2O_4$ nanocatalyst 10 mol % at room temperature in ethanol solvent for 20 hours (table 1). Then the same reaction was carried out in refluxing with ethanol solvent for 6 hours but again, the tetrahydroquinolines product was not observed at room temperature. After we changed solvent like toluene. The tetrahydroquinolines product was not observed at room temperature. Once again, the same reaction mixture was refluxed, but that time provided 110^{o}C temperature for 20 hours. tetrahydroquinolines, 60 % product, was observed due to the significant effect of temperature (Table 1).

Finally, all the above experiments were performed under ultrasonic irradiation in order to observe the effect of the ultrasonic irradiations. The reaction mixture of 1-amino naphthylamine (1), benzaldehyde (2a), and 2,3 dihydrofuran (3) with $ZnCr_2O_4$ 10 mol % at room temperature in PhMe solvent for 5 hours did not give THQs product (Table 1). Then, we changed the reaction temperature from room temperature to 70^{o}C gave the THQs 75 % product; the reaction was completed in 50 minutes (Table 1). In the present study, we sequenced observed the effect of the amount of $ZnCr_2O_4$ nanocatalyst on the reaction; then, we performed the same experiments using the varied amount of catalyst as shown in Table 1. If the amount of $ZnCr_2O_4$ decreased to 15 %, 10 %, and 5%, the yield of the THQs increased to 75 %, 76 %, and 78 %, respectively. From the optimal above, it has been shown that 1-amino naphthylamine (1), benzaldehyde (2a), and 2,3 dihydrofuran (3) with $ZnCr_2O_4$ 5 mol % at 70^{o}C in toluene under the ultrasonic irradiation presented an efficient protocol in terms of and shorter reaction time and excellent yield. By using these optimal reaction conditions, we have then examined various functional group-containing aromatic aldehydes in conventional and ultrasonic irradiated catalytic Povarov reactions. Various N-arylimines cyclized smoothly with 2,3 dihydrofuran (3) under conventional and ultrasonic techniques to afford the corresponding tetrahydroquinolines. Comparatively, in every case, ultrasonic irradiation improved the percentage of yields, and reactions were completed within 50 minutes. (Table 2). The effect of ultrasound was equally effective on both electron-deficient and electron-rich aromatic aldehydes.



Scheme 1. One-pot Povarov (Aza-Diels-Alder) reaction of amine (1), aromatic aldehydes (2a-j), and 2,3 dihydrofuran (3) with $ZnCr_2O_4$ catalyst. Method A: 10 mol % $ZnCr_2O_4$ catalyst reflux in PhMe at 110°C for 5 hours. Method B: 5 mol % $ZnCr_2O_4$ catalyst, ultrasound irradiated in PhMe at 70°C for 50 minutes.

Table 1. Screening for Direct Povarov reaction with 2,3 dihydrofuran (3).

Entry	Tech.	Solvent	Catalyst	Temp. (°C)	Time	Yields (%)
1	Stirring	Ethanol	$ZnCr_2O_4$ (10 mol %)	r.t.	20 hrs	-
2	Refluxing	Ethanol	$ZnCr_2O_4$ (10 mol %)	85	6 hrs	-
3	Stirring	PhMe	$ZnCr_2O_4$ (10 mol %)	r.t.	20 hrs	-
4	Refluxing	PhMe	$ZnCr_2O_4$ (10 mol %)	110	6 hrs	60
5	Ultrasound	PhMe	$ZnCr_2O_4$ (10 mol %)	r.t.	5 hrs	-
6	Ultrasound	PhMe	$ZnCr_2O_4$15 mol %)	70	50 mins	75
7	Ultrasound	PhMe	$ZnCr_2O_4$ (10 mol %)	70	50 mins	76
8	Ultrasound	PhMe	$ZnCr_2O_4$ (5 mol %)	70	50 mins	78

Reaction condition: naphthylamine (1) (1 mmol), aromatic aldehydes (2a-j) (1 mmol), 2,3 dihydrofuran (3) (3 mmol) dry toluene (4 ml).

Table 2. Direct Povarov reaction with 2,3 dihydrofuran.

Entry	R	Comp.	Yield (%) (Method A)	Yield (%) (Method B)
1.	Phenyl	**4a**	60	80
2.	2,5-Dimethoxyphenyl	**4b**	63	79
3.	4-Cynophenyl	**4c**	61	78
4.	3-Methoxy,4-Hydroxyphenyl	**4d**	65	81
5.	3-Bromophenyl	**4e**	58	78
6.	4-Methoxyphenyl	**4f**	55	77
7.	4-chlorophenyl	**4g**	59	80
8.	2,4-Dichlrophenyl	**4h**	54	78
9.	4-Nitrophenyl	**4i**	53	76
10.	4-Flurophenyl	**4j**	55	77

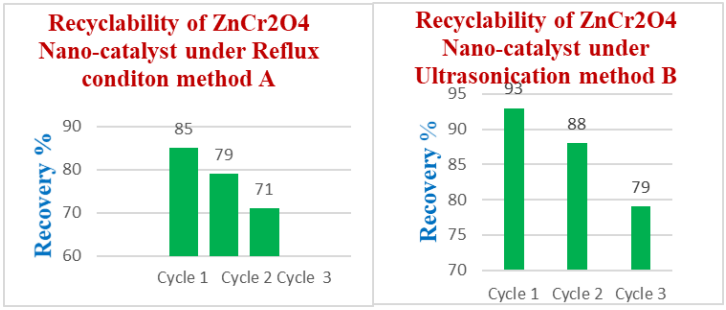


Figure 1. Recyclability of $ZnCr_2O_4$ nanocatalyst.

Reaction condition: Method A: 1 naphthylamine (1) (1 mmol), aromatic aldehydes(2a-j) (1 mmol), 2,3 dihydrofuran (3) (3 mmol), $ZnCr_2O_4$ (10 mol %), dry toluene (4 ml), reflux at 110°C. Method B: 1-naphthylamine (1) (1 mmol), aromatic aldehydes(2a-j) (1 mmol), 2,3 dihydrofuran (3) (3 mmol), $ZnCr_2O_4$ (5 mol %), dry toluene (4 ml) ultrasonic irradiation at 70°C.

Recyclability of $ZnFe_2O_4$: Recyclability of $ZnCr_2O_4$ nanocatalyst was studied for the model reaction. Isolation of $ZnCr_2O_4$ nanocatalyst was carried out through centrifuging reaction mass after diluting ethyl acetate solvent. Consequently, $ZnCr_2O_4$ nanocatalyst proved

its ability to re-use two-three times with the corresponding yield and no change in yield purity. The reusability of the $ZnCr_2O_4$ nano- catalyst for three cycles is shown in Figure 1.

Ultrasound-assisted recyclable $ZnCr_2O_4$ nano catalytic amount is higher than that of the refluxing method due to the ultrasonic effect. The synthesized products were identified by FT-IR, ^{1}H NMR, ^{13}C NMR, and mass spectroscopic data.

4. Conclusions

We conclude that we have developed an efficient and easy method for the synthesis of substituted tetrahydroquinolines (4a-j) through multi-component one-pot Povarov (Aza-Diels-Alder) reaction of 1-naphthylamine (1), aromatic aldehydes (2a-j), 2,3 dihydrofuran (3), using commercially available $ZnCr_2O_4$ as a nanocatalyst. One of the important benefits we are mentioned here, $ZnCr_2O_4$ nanocatalyst was recyclable and reusable. Recyclable catalytic amount $ZnCr_2O_4$ nanoparticles were slightly higher in the Ultrasonic method than that of a conventional method. Hence, we suggest that the ultrasonic method for organic synthesis purposes.

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Conflicts of Interest

The authors declare no conflict of interest.

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