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Original Research Article

# Polyethylene glycol-bis (*N*-methylimidazolium) dihydroxide as an efficient and recyclable basic phase-transfer catalyst for the synthesis of 4*H*-pyran derivatives in aqueous media

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**ABSTRACT**

Polyethylene glycol-bis (*N*-methylimidazolium) dihydroxide, $[PEG(mim)_2][OH]_2$, was prepared from the reaction of polyethylene glycol-bis (*N*-methylimidazolium) dibromide and sodium hydroxide in aqueous media at ambient temperature. The obtained solid was used as a novel, green, recyclable and efficient basic phase-transfer catalyst in the synthesis of 2-amino-3-cyano-4*H*-pyrans *via* the one-pot three-component condensation reaction of aromatic aldehydes, malononitrile and 1,3-dicarbonyl compounds in water at room temperature. The reactions without any basic reactants and in the presence of trace amounts of the catalyst gave the corresponding products with high yields in short reaction times. The phase-transfer catalyst could be successfully reused without the significant decrease in its activity.



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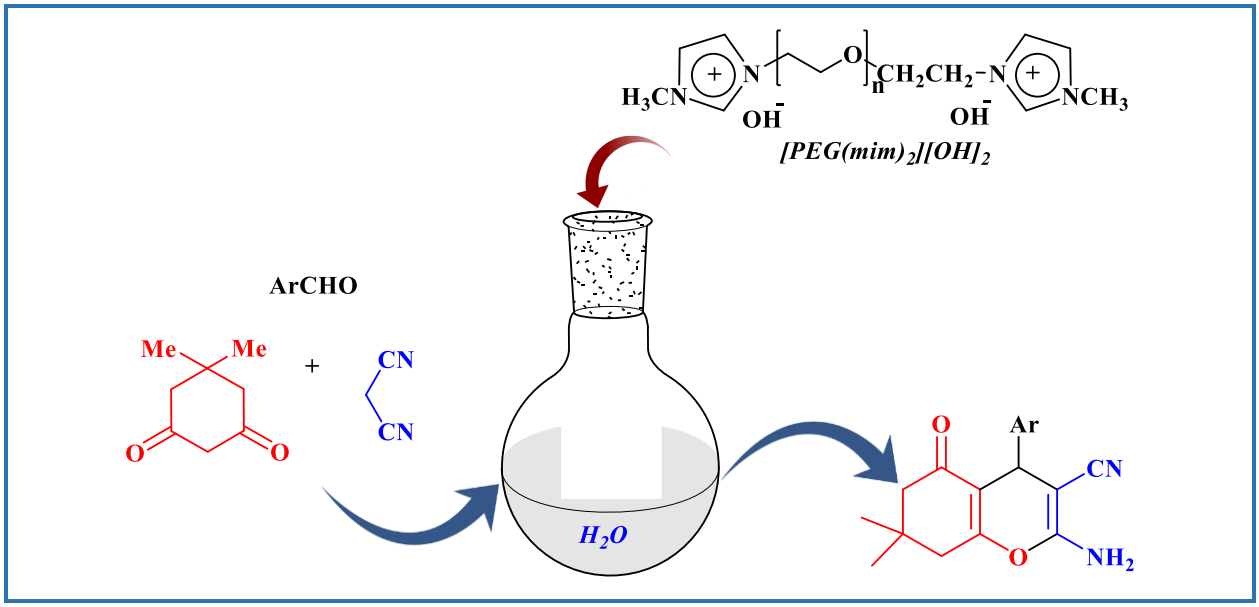
**Graphical Abstract**




## Introduction

The use of water as the solvent for organic reactions is one of the best solutions to the problem of flammability, volatility, toxicity, and disposal of organic solvents [1]. Since most of the organic reactants don't dissolve in water, the use of phase-transfer catalysts can overcome this problem. Both homogeneous and heterogeneous phase-transfer catalysts improve the intimate contact between inorganic reagents and organic substrates, but in most cases, the use of homogeneous PTCs increase the reactivity [2].

Nitrogen containing heterocyclic compounds such as benzimidazoles, imidazoles, pyridines, quinolines, quinazolines, 2*H*- and 4*H*-pyrans, *etc*., are compounds that exhibit numerous biological and pharmaceutical activities [3–5]. Especially, among various 4*H*-pyran derivatives, 2-amino-3-cyano-4*H*-pyrans have potential applications in the treatment of rheumatoid, psoriasis, and cancer [6]. Also, these compounds have received considerable attention due to their various biological and pharmacological activities such as antitumoral [7], antimicrobial [8], hypotensive [9], antibacterial [10], antioxidant [11], antibiotical [12] and fungicidal [13]. Due to the important above-mentioned properties of 2-amino-3-cyano-4*H*-pyrans, remarkable attention has been focused on the development of environmentally friendly methodologies to the synthesis of 2-amino-3-cyano-4*H*-pyrans by three-component tandem reaction of aromatic/aliphatic aldehydes, malononitrile, and diverse enolizable C–H activated acidic compounds.

A literature survey shows that several modified methods have been reported using different homogeneous or heterogeneous catalysts such as KF-alumina [14], $Yb(PFO)_3$ [15], hexadecyldimethyl benzyl ammonium bromide (HDMBAB) [16], [2-aemim][$PF_6$] under microwave irradiation [17], TBAF [18], MgO [19], 2-hydroxyethylammonium formate [20], mesoporous silica nanoparticles [21], potassium phthalimide-*N*-oxyl (POPINO) [22], MNPs-Guanidine [23], $I_2$ under ultrasound irradiation [24], CsF [25], $C_4$(DABCO-$SO_3H)_2$.4Cl [26], [DiEG(mim)$_2$][OH]$_2$ [27], $FeTiO_3$ [28] and Cu(II)-schiff base/SBA-15 [29]. However, many proposed methods for the synthesis of these compounds suffer from disadvantages including relying on multi-step conditions, the use of toxic organic solvents or catalysts containing transition metals, harsh reaction conditions, need for an excessive amounts of the reagent, tedious work-up procedure, troublesome waste discarding, long reaction times, low yields of products and non-recyclability of the catalyst. Therefore, introducing simple, efficient and mild procedures with easily separable and reusable catalysts to overcome these problems is still in demand.

Based on our earlier success in the synthesis of novel catalysts [30–33], very recently we prepared polyethylene glycol-bis (*N*-methylimidazolium) dihydroxide, [PEG(mim)$_2$][OH]$_2$, as a novel basic phase-transfer catalysis and used it in the Knoevenagel condensation [34]. In this study, we investigated the catalytic activity of this catalyst in the synthesis of 2-amino-3-cyano-4*H*-pyrans *via* one-pot three-component reaction of aryl aldehydes, malononitrile and 1,3-dicarbonyl compounds including dimedone, 1,3-cyclohexanedione and ethyl acetoacetate under aqueous conditions at room temperature.

## Experimental

### *Materials and methods*

All materials and reagents were purchased from Fluka and Merck and used without further purification. Polyethylene glycol (400) was heated at 80 °C under vacuum for 30 min before use to remove traces of moisture. Products were characterized by comparing their physical data, IR, $^1$H NMR and $^{13}$C NMR spectra with the known samples. Melting points were obtained in open capillary tubes and were measured on an electrothermal 9200 apparatus. NMR spectra were recorded in $CDCl_3$ on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as the internal standard. IR spectra were recorded on a BOMEM MB-Series 1998 FT-IR spectrometer. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates.

### *Synthesis of polyethylene glycol dibromide, [PEG] $Br_2$*

Polyethylene glycol dibromide was prepared according to the reported method [35]. To a solution of polyethylene glycol-400 (20 g, 0.1 mol OH) and pyridine (7.9 g, 0.1 mol) in 500 mL of toluene, thionyl chloride (16 g, 0.14 mol) was slowly added with stirring over a period of half an hour. The mixture was then refluxed for about 6 h. After cooling and filtering off the pyridine hydrochloride, the solvent was removed in vacuo. The residue was dissolved in dichloromethane and treated with activated alumina. The process was repeated twice. The dichloromethane solution was filtered and evaporated to obtain polyethylene glycol dichloride. A mixture of polyethylene glycol dichloride (10 g, 0.015 mol) and sodium bromide (10.3 g, 0.1 mol) was heated in an oil bath at 120 °C overnight. After cooling, dichloromethane was added, the solution was filtered, and the solvent was removed in vacuo to obtain polyethylene glycol dibromide.

*Synthesis of polyethylene glycol-bis (N-methylimidazolium) dibromide, [PEG(mim)$_2$] Br$_2$*

A mixture of polyethylene glycol dibromide (5 g, 0.01 mol) and *N*-methylimidazole (4.1 g, 0.05 mol) in acetonitrile (50 mL) was stirred at reflux for 48 h in a two-necked round bottom flask equipped with the water condenser. Then, the reaction mixture was cooled to room temperature. The solvent was evaporated under reduced pressure using a rotary evaporator. The reaction mixture was washed with ethyl acetate (3 × 10 mL) to remove unreacted starting materials and the resulting quaternized polyethylene glycol-bis (*N*-methylimidazolium) dibromide was obtained as a thick liquid [34].

*Synthesis of polyethylene glycol-bis (N-methylimidazolium) dihydroxide, [PEG(mim)$_2$][OH]$_2$*

A mixture of polyethylene glycol-bis (*N*-methylimidazolium) dibromide (1.2 g, 2.0 mmol) and sodium hydroxide (0.5 g, 12.5 mmol) in water (20 mL) was stirred at room temperature for 3 h. The solution was placed in air overnight to evaporate the water. Then, the formed white precipitate was washed with ethanol (3 × 10 mL) and ethyl acetate (10 mL) to give the quaternized polyethylene glycol-bis (*N*-methylimidazolium) dihydroxide in 92% yield [34].

*General procedure for the synthesis of 2-amino-3-cyano-4H-pyrans*

Polyethylene glycol-bis (*N*-methylimidazolium) dihydroxide (5.6 mg, 0.01 mmol) was added to a mixture of aromatic aldehydes (1 mmol), malononitrile (1 mmol) and 1,3-dicarbonyl compounds (1 mmol) in water (3 mL). The reaction mixture was stirred at ambient temperature for the appropriate time shown in Table 2. After completion of the reaction according to TLC analysis (*n*-hexane:ethyl acetate, 7:1), the mixture was filtered off and the filtrate was washed with cool ethanol to obtain the corresponding 4*H*-pyrans. The crude products were purified by recrystallization from ethanol.

*Selected spectroscopic data*

*2-amino-3-cyano-7,7-dimethyl-4-(4-methylphenyl)-5-oxo-4H-5,6,7,8-tetrahydrobenzopyran (**1c**)*

IR (KBr) ($\nu_{max}$/ $cm^{-1}$): 3425, 3329, 2956, 2191, 1674, 1637 and 1600. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 0.96 (s, 3H, $CH_3$), 1.04 (s, 3H, $CH_3$), 2.07 (d, 1H, $J$ = 16.0 Hz, CH-8), 2.23 (d, 1H, $J$ = 16.0 Hz, CH-8), 2.27 (s, 3H, $CH_3$), 3.37 (m, 2H, CH-6), 4.14 (s, 1H, CH-4), 6.98 (s, 2H, $NH_2$), 7.04 (d, 2H, $J$ = 8.0 Hz, ArH), 7.10 (d, 2H, $J$ = 8.0 Hz, ArH). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 20.5, 26.7, 28.3, 31.7, 35.1, 49.9, 58.4, 112.8, 119.7, 127.5, 128.8, 135.5, 141.7, 158.4, 162.2, 195.5.

*2-amino-3-cyano-7,7-dimethyl-4-(furan-2-yl)-5-oxo-4H-5,6,7,8-tetrahydrobenzopyran (**1l**)*

IR (KBr) ($\nu_{max}$/ $cm^{-1}$): 3396, 3332, 2970, 2195, 1683, 1660 and 1602. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 0.99 (s, 3H, $CH_3$), 1.05 (s, 3H, $CH_3$), 2.15 (d, 1H, $J$ = 16.0 Hz, CH-8), 2.27 (d, 1H, $J$ = 16.0 Hz, CH-8), 2.47-2.55 (m, 2H, CH-6), 4.33 (s, 1H, CH-4), 6.05 (m, 1H, ArH), 6.32 (m, 1H, ArH), 7.09 (s, 2H, $NH_2$), 7.48 (s, 1H, ArH). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 26.5, 28.4, 28.9, 31.7, 39.6, 49.8, 55.3, 105.0, 110.3, 110.4, 119.5, 141.7, 155.6, 159.2, 163.2, 195.3.

*2-amino-3-cyano-4-phenyl-5-oxo-4H-5,6,7,8-tetrahydrobenzopyran (**2a**)*

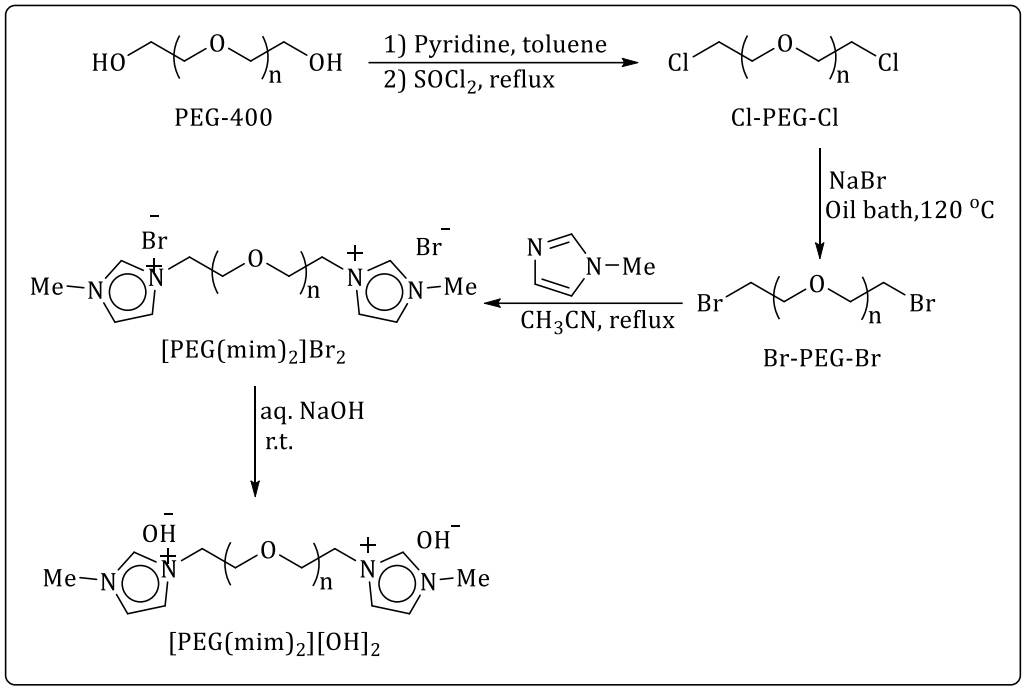
IR (KBr) ($\nu_{max}$/ $cm^{-1}$): 3394, 3325, 3209, 2962, 2885, 2198, 1678 and 1600. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 1.95-2.00 (m, 2H, $CH_2$-6), 2.25-2.35 (m, 2H, $CH_2$-8), 2.61-2.64 (m, 2H, $CH_2$-7), 4.20 (s, 1H, CH-4), 7.0 (s, 2H, $NH_2$), 7.16-7.20 (m, 3H, ArH), 7.27-7.31 (m, 2H, ArH). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 19.7, 26.4, 35.4, 36.2, 58.1, 113.7, 119.7, 126.4, 127.0, 128.3, 144.7, 158.4, 164.4, 195.8.

## Results and Discussion

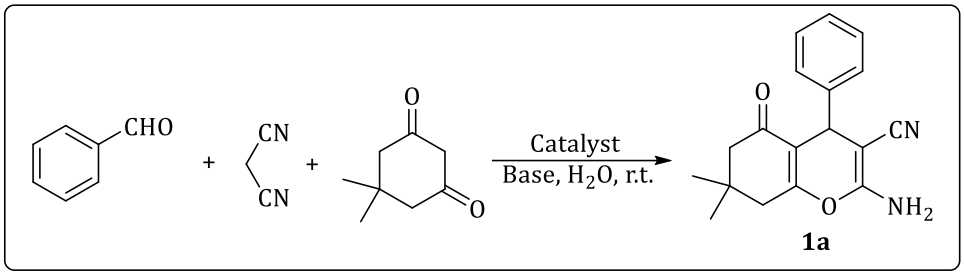
Polyethylene glycol-bis (*N*-methylimidazolium) dihydroxide was synthesized as shown in Scheme 1. Polyethylene glycol dichloride and dibromide were prepared according to the literature method [35]. Then, polyethylene glycol dibromide was treated with two equivalent of *N*-methylimidazole in acetonitrile under reflux conditions to afford the dicationic PTC with bromide anion. Ultimately, the stirring of the PTC in aqueous NaOH at room temperature led to the formation of polyethylene glycol-bis (*N*-methylimidazolium) dihydroxide, $[PEG(mim)_2][OH]_2$, as a white solid with basic characteristic [34].

To evaluate the catalytic activity of $[PEG(mim)_2][OH]_2$ as an effective basic phase-transfer catalyst, initially, the three-component reaction of benzaldehyde, malononitrile, and dimedone was tested to determine the catalyst efficiency and to survey the optimized reaction conditions (Scheme 2 and Table 1). After several experiments, it was found that a mixture of benzaldehyde, malononitrile and dimedone in the presence of trace amounts of $[PEG(mim)_2][OH]_2$ (1 mol%, 5.6 mmol) in water at

ambient temperature afforded 2-amino-3-cyano-7,7-dimethyl-4-phenyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzopyran **1a** with excellent yield in short reaction time (Table 1, entry 7).




**Scheme 1.** Preparation of $[PEG(mim)_2][OH]_2$




**Scheme 2.** Synthesis of **1a** under aqueous conditions

The reaction in the presence of NaOH and $K_2CO_3$ (10 mol%) without PTC did not complete even in longer time and gave the corresponding product in 35% and 30% yields, respectively (Table 1, entries 1 and 2). The reaction in the presence of $K_2CO_3$ (10 mol%) and PEG-400, $[PEG(mim)_2]Cl_2$ or $[PEG(mim)_2]Br_2$ (each, 10 mol%) gave the corresponding product in higher yields at the same reaction times, but the reactions did not yet complete (Table 1, entries 3-5). Although, this condensation was performed in the presence of $K_2CO_3$ (10 mol%) and $[PEG(mim)_2][OH]_2$ (1 mol%) in less time (Table 1, entry 6), but the best conditions was the use of $[PEG(mim)_2][OH]_2$ (1 mol%) in the absence of base.

**Table 1.** Optimization of the reaction conditions for the synthesis of tetrahydrobenzopyran **1a**[a]

| Entry | Catalyst (mol%) | Base (mol%) | Time (min) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | - | NaOH (10) | 90 | 35 |
| 2 | - | $K_2CO_3$ (10) | 90 | 30 |
| 3 | PEG-400 (10) | $K_2CO_3$ (10) | 90 | 65 |
| 4 | $[PEG(mim)_2]Cl_2$ (10) | $K_2CO_3$ (10) | 90 | 75 |
| 5 | $[PEG(mim)_2]Br_2$ (10) | $K_2CO_3$ (10) | 90 | 80 |
| 6 | $[PEG(mim)_2][OH]_2$ (1) | $K_2CO_3$ (10) | 18 | 94 |
| 7 | $[PEG(mim)_2][OH]_2$ (1) | - | 20 | 95 |

[a] Reaction conditions: benzaldehyde (1 mmol), malononitrile (1 mmol), dimedone (1 mmol), required amounts of the catalysts and bases, water (3 mL), r.t.

[b] Isolated yield

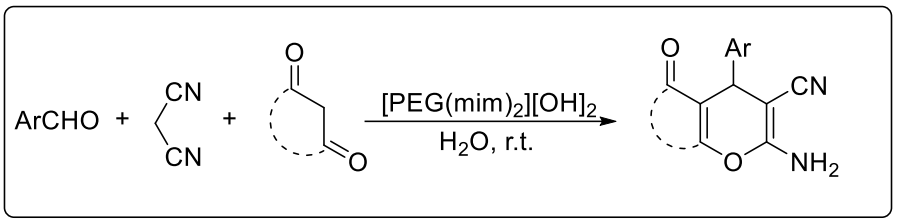
Subsequently, the generality and synthetic scope of this three-component protocol for the synthesis of a series of 2-amino-3-cyano-4*H*-pyrans were demonstrated by the reaction of various aryl aldehydes with malononitrile and 1,3-dicarbonyl compounds including dimedone, 1,3-cyclohexanedione and ethyl acetoacetate under optimal conditions (Scheme 3 and Table 2). As shown in Table 2, yields of products are good to excellent for aromatic aldehydes bearing both electron-donating and electron-withdrawing groups.

Comparison of the catalytic strength of $[PEG(mim)_2][OH]_2$ in the three-component condensation of benzaldehyde, malononitrile and dimedone to produce the corresponding 4*H*-pyran **1a** with some of the methods reported in the literature is presented in Tables 3. The results showed that our procedure provided high yields of products in short reaction times under mild and green conditions.

Finally, the recyclability and reusability of the catalyst were studied for the synthesis of compound **1a**. After the reaction completion, the reaction mixture was filtered and the precipitate was washed with ethanol. The catalyst was recycled by evaporating the aqueous ethanolic phase in the air and washing with ethyl acetate. After being air dried, the recycled catalyst could be reused as such in subsequent experiments (Up to five cycles) under similar reaction conditions. The yields of the product remained comparable in all experiments (95, 93, 92, 90, and 88 in cycles 1-5, respectively), indicating that the catalyst can be recycled at least five times with no considerable loss in its activity.

## Conclusion

In conclusion, the present study describes the preparation of a novel basic phase-transfer catalyst by the reaction of polyethylene glycol-bis (*N*-methylimidazolium) dibromide and sodium hydroxide




**Scheme 3.** Synthesis of 4*H*-pyrans in the presence of $[PEG(mim)_2][OH]_2$ in water

**Table 2.** Synthesis of 2-amino-3-cyano-4*H*-pyrans catalyzed by $[PEG(mim)_2][OH]_2$ in water[a]

| Entry | Ar | 1,3-Dicarbonyl | Time (min) | Product | Yield (%)[b] | Mp (°C) | |
|---|---|---|---|---|---|---|---|
| | | | | | | Found | Reported [ref] |
| 1 | $C_6H_5$ | Dimedone | 20 | **1a** | 95 | 229-231 | 231-232 [26] |
| 2 | 4-$MeOC_6H_4$ | Dimedone | 40 | **1b** | 91 | 192-193 | 197-199 [36] |
| 3 | 4-$MeC_6H_4$ | Dimedone | 50 | **1c** | 92 | 215-216 | 219-221 [23] |
| 4 | 2-$ClC_6H_4$ | Dimedone | 25 | **1d** | 93 | 204-206 | 208-210 [37] |
| 5 | 3-$ClC_6H_4$ | Dimedone | 20 | **1e** | 91 | 226-228 | 226-227 [37] |
| 6 | 4-$ClC_6H_4$ | Dimedone | 40 | **1f** | 89 | 214-215 | 217-219 [37] |
| 7 | 4-$BrC_6H_4$ | Dimedone | 20 | **1g** | 89 | 202-204 | 201-203 [37] |
| 8 | 4-$HOC_6H_4$ | Dimedone | 20 | **1h** | 90 | 225-237 | 226-228 [23] |
| 9 | 4-$Me_2NC_6H_4$ | Dimedone | 50 | **1i** | 88 | 209-211 | 210-212 [23] |
| 10 | 3-$O_2NC_6H_4$ | Dimedone | 20 | **1j** | 82 | 211-212 | 210-212 [26] |
| 11 | 2,5-$(MeO)_2C_6H_3$ | Dimedone | 25 | **1k** | 83 | 171-173 | - |
| 12 | 2-Furyl | Dimedone | 20 | **1l** | 93 | 219-221 | 220-222 [23] |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 13 | $C_6H_5$ | 1,3-Cyclohexanedione | 40 | **2a** | 94 | 237-240 | 238-240 [26] |
| 14 | 4-$MeOC_6H_4$ | 1,3-Cyclohexanedione | 45 | **2b** | 92 | 195-197 | 192-193 [26] |
| 15 | 4-$MeC_6H_4$ | 1,3-Cyclohexanedione | 55 | **2c** | 93 | 160-162 | - |
| 16 | 2-$ClC_6H_4$ | 1,3-Cyclohexanedione | 30 | **2d** | 91 | 206-208 | - |
| 17 | 3-$ClC_6H_4$ | 1,3-Cyclohexanedione | 20 | **2e** | 90 | 160-162 | - |
| 18 | 4-$ClC_6H_4$ | 1,3-Cyclohexanedione | 20 | **2f** | 88 | 224-227 | 224-226 [26] |
| 19 | 4-$BrC_6H_4$ | 1,3-Cyclohexanedione | 40 | **2g** | 87 | 236-237 | 238-240 [36] |
| 20 | 4-$HOC_6H_4$ | 1,3-Cyclohexanedione | 25 | **2h** | 89 | 261-263 | - |
| 21 | 4-$Me_2NC_6H_4$ | 1,3-Cyclohexanedione | 20 | **2i** | 88 | 179-180 | - |
| 22 | 3-$O_2NC_6H_4$ | 1,3-Cyclohexanedione | 20 | **2j** | 89 | 225-227 | 229-230 [36] |
| 23 | 2,5-$(MeO)_2C_6H_3$ | 1,3-Cyclohexanedione | 25 | **2k** | 90 | 220-222 | - |
| 24 | 2-Furyl | 1,3-Cyclohexanedione | 20 | **2l** | 88 | 195-196 | - |
| 25 | $C_6H_5$ | Ethyl acetoacetate | 40 | **3a** | 93 | 181-183 | 195-196 [38] |
| 26 | 2-$ClC_6H_4$ | Ethyl acetoacetate | 50 | **3b** | 87 | 178-180 | - |
| 27 | 4-$ClC_6H_4$ | Ethyl acetoacetate | 35 | **3c** | 87 | 170-172 | 172-174 [38] |
| 28 | 4-$BrC_6H_4$ | Ethyl acetoacetate | 35 | **3d** | 86 | 157-159 | - |
| 29 | 3-$O_2NC_6H_4$ | Ethyl acetoacetate | 30 | **3e** | 92 | 182-183 | 182-183 [38] |
| 30 | 2-Furyl | Ethyl acetoacetate | 55 | **3f** | 90 | 190-192 | - |

[a] Reaction conditions: aryl aldehyde (1 mmol), malononitrile (1 mmol), 1,3-dicarbonyl (1 mmol), PTC (1 mol%), water (3 mL), r.t.

[b] Isolated yield

in aqueous media at ambient temperature. Then, the catalytic activity of this green, recoverable and efficient catalyst was investigated in the one-pot three-component synthesis of 2-amino-3-cyano-4*H*-pyrans under aqueous media at room temperature. This novel catalytic method offers several

advantages including environmental friendliness, high yield, short reaction time, the use of mild reaction conditions, involving a simple work-up procedure, ease of separation, and recyclability of the catalyst. Thus, we think that this procedure can be considered as a new and suitable addition to the present methodologies in this area.

**Table 3.** Comparison of synthesis of tetrahydrobenzopyran **1a** with different methods

| Entry | Base or/and catalyst | Solvent | Condition | Time (min) | Yield (%) | Ref. |
|---|---|---|---|---|---|---|
| 1 | $Yb(PFO)_3$ | EtOH | 60 °C | 300 | 90 | [15] |
| 2 | TBAF | $H_2O$ | reflux | 30 | 97 | [18] |
| 3 | MgO | EtOH, $H_2O$ | reflux | 30 | 92 | [19] |
| 4 | $[H_3N^+CH_2CH_2OH][HCO_2^-]$ | Neat | r.t. | 5 | 70 | [20] |
| 5 | MSNs | EtOH | 60 °C | 15 | 94 | [22] |
| 6 | MNPs-Guanidine | PEG, $H_2O$ | r.t. | 15 | 95 | [24] |
| 7 | $K_2CO_3$, $[DiEG(mim)_2][OH]_2$ | $H_2O$ | r.t. | 20 | 92 | [27] |
| 8 | $SiO_2$ NPs | EtOH | r.t. | 25 | 94 | [39] |
| 9 | $Cs_2CO_3$ | EtOH | Visible light | 60 | 85 | [40] |
| 10 | $[PEG(mim)_2][OH]_2$ | $H_2O$ | r.t. | 20 | 95 | -[a] |

[a] Present work

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**Disclosure Statement**

No potential conflict of interest was reported by the authors.

**Orcid**

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