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FULL PAPER

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$H_5BW_{12}O_{40}$ as a green and efficient homogeneous but recyclable catalyst in the synthesis of 4*H*-Pyrans *via* multicomponent reaction

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Keggin-type heteropolyacid, $H_5BW_{12}O_{40}$ (BWA) with a higher negative charge and stronger Brønsted acidity comparing to Si and P derivatives was used as an efficient, green, and reusable catalyst in a three-component reaction involving the cyclocondensation of various β-dicarbonyl compounds, differently substituted aromatic aldehydes and malononitrile in EtOH/H_2O for the facile, clean, and high yielding synthesis of 4*H*-pyrans. All reactions were completed in short times and the products were obtained in good to excellent yields. The reaction medium could be recycled and reused several times without any loss of efficiency.

KEYWORDS
$H_5BW_{12}O_{40}$, homogeneous catalysis, Keggin-type polyoxometalates, multicomponent reaction, one-pot synthesis

1 | INTRODUCTION

Nowadays, the design of active, selective, environmentally benign, and recyclable heterogeneous catalysts that have a major impact on industrial applications is a main purpose of the modern synthetic chemistry. Polyoxometalates (POMs) are composed of cations and polyanion clusters with unique properties that are the interesting field for researchers. These species have been known for almost two centuries and they have attracted much interest because of their applications in broad fields such as catalysis, sensing[1] magnetism,[2] medicine[3] and so on. In fact, POMs can be viewed as versatile catalysts because of their multiple active sites, including protons, oxygen atoms, and metals; i) protons can act as Brønsted acids to promote acid-catalyzed reactions. ii) Some oxygen atoms on the surface of POM anions with a high negative charge are basic enough to react with protons, even to abstract active protons from organic substrates. Accordingly, these surface oxygen atoms of POM catalysts can be the active sites in base-catalyzed reactions. iii) The metal ions on the skeleton of polyamines possess unoccupied orbitals that can accept electrons. In this way, polyamines can also act as Lewis acids.[4] Among the many types of POMs, Keggin-type structures are widely investigated for catalyzed reactions due to their suitable sizes, more stable

structures and low prices.[5] Keggin compounds as a common and important class of POMs have the general formula $H_nXM_{12}O_{40}$ where X is heteroatom (P, Si, As, Ge, B) and M is the addenda such as Mo or W.[6] Typically, they are water-soluble and form Keggin anions $[XM_{12}O_{40}]^{n-}$ and hydrated protons which are mobile in nature like H^+, H_3O^+, $H_5O_2^+$ and *etc*. ('Called as Heteropoly Acids (HPAs)'). It is well known that the anionic part of HPAs can stabilize the cationic organic intermediates[7] thereby promoting the catalytic reactions.

The $H_5BW_{12}O_{40}$ (BWA) Keggin-type structures carry higher negative charge comparing to $H_4SiW_{12}O_{40}$ (SiW) and $H_3PW_{12}O_{40}$ (PW) affording stronger Brønsted acid, however, this HPA is rarely explored as a catalyst in organic transformation in spite of its easy preparation methods. In order to see the role of the above three types of HPAs in the formation of new compounds we ran a Cambridge Structural Database (CSD) analysis (CSD, Version 5.38 updates May 2017). A survey revealed that number of the synthesized compounds of BWA is significantly less than SiWA and PWA ones (Figure 1).[8] Therefore, these advantages encouraged us to explore the critical role of BWA as a Brønsted acid catalyst which can be further expanded to the synthesis of the variety of organic compounds.

MCRs are considered as a striking and powerful protocol for the synthesis of a wide range of organic compounds in comparison with multi-step reactions due to the simultaneous generation of several new bonds in a one-pot fashion. The other apparent advantages are low number of reaction and purification steps, selectivity, being convergent, showing high atom economy, simplicity, and synthetic efficiency.[9] As a matter of fact, development of MCRs have resulted in novel and effective synthetic pathways to provide a plethora of small organic molecules in the field of modern organic, bio-organic, and medicinal chemistry.[10]

FIGURE 1 Distribution of the synthesized compounds for the three types of HPAs; $H_5BW_{12}O_{40}$ (BW), $H_3PW_{12}O_{40}$ (PW) and $H_4SiW_{12}O_{40}$ (SiW).

The use of safe and inexpensive solvents along with heterogeneous and recyclable catalysts is the most serious concerns in green chemistry.[9] Thus, aqua mediated reactions are one of desirable and attractive selection in organic synthesis because of keeping the environment clean and safe. For these reasons water as the most abundant and non-toxic molecule in nature and being virtually free of cost is an ideal solvent in chemical reactions.[11]

Pyrans are significant moieties in several naturally occurring compounds[12] as well as photochromic materials.[13] Compounds containing a pyran unit exhibit several biological properties and play vital roles in biological processes.[13] In addition, 4*H*-pyrans are beneficial intermediates for the synthesis of wide verity of heterocyclic systems, such as pyranopyridine derivatives,[14] pyrano[2] pyrimidines[15] and pyridine-2-ones.[16] Thus, preparation of this heterocyclic core has extended high reputation in heterocyclic chemistry. Several strategies have been reported for the synthesis of pyrans, mostly *via* a three-component reaction involving the cyclocondesation of various β-dicarbonyl compounds, differently substituted aromatic aldehydes and alkylmalonates.[17] This MCR have been catalyzed with a wide range of catalytic systems such as MgO,[18] (*S*)-proline,[19] SiO_2 nanoparticles,[20] hexadecyltrimethyl ammonium bromide (HMTAB),[21] rare earth perfluorooctanoate (RE $(PFO)_3$),[22] silica bonded *n*-propyl-4-aza-1-azonia bicycle [2,2,2] octane chloride (SB-DABCO),[23] amino functionalized ionic liquids,[17,24] magnetic iron oxide supported phenylsulfonic acid (Fe_3O_4@Ph-SO_3H),[25] nano-SiO_2,[26] HPA-dendrimer-functionalized magnetic nanoparticles (Fe_3O_4@D-NH_2-HPA),[27] a mixed-ligand Cu (II) Schiff base complex,[28] amine-functionalized hyper-crosslinked polyphenanthrene as a metal-free catalyst,[29] bis (4-pyridylamino) triazine stabilized on silica-coated nano-Fe_3O_4 particles,[30] polypyrrole/Fe_3O_4/CNT,[31] polystyrene-supported DABCO ionic liquid ([*P*-DABCO]Cl),[32] 12-molybdophosphoric acid encapsulated in the nanocavities of modified dealuminated zeolite Y (MDAZY),[33] and magnetically nanomaterial consisting of dihydrogen phosphate ions supported on silica-coated magnetite nanoparticle (magnetite-dihydrogen phosphate)[34] which each of them has its merits and shortcomings. Therefore, development of an efficient, MCR with chemoselective as well as being performed under heterogeneous catalysis and green conditions for the synthesis of 4*H*-pyrans is still in much demand.

We are interested in heterocyclic chemistry[35] and especially in the synthesis of heterocyclic systems *via* MCR[36] being performed under heterogeneous catalysis in water.[37] We have recently reported the synthesis of pyran derivatives by using heteropolyacids as support in water[38] and electrosynthesis.[39] From the last decade till date our research group has manipulated different heteropolyacids

as efficient catalysts in the art of organic synthesis which have been cited in two comprehensive reviews.[40]

A literature survey showed that the one-pot three-component synthesis of 4*H*-pyrans can be catalyzed in the presence of acidic as well as basic catalysts. Thus, based on the above facts and as a part of our research program to develop selective, efficient and green methods in organic synthesis, herein we wish to reveal for the first time the application of a newly reported heteropolyacid (BWA) acting as an efficient, green, and homogeneous but reusable catalyst for the diversity-oriented synthesis of 4*H*-pyrans *via* a one-pot three-component cyclocondensation reaction between aldehydes **1**, malononitrile **2** and carbonyl compounds **3** possessing a reactive α-methylene group in the presence of BWA in refluxing EtOH/H_2O (Scheme 1).

2 | EXPERIMENTAL

2.1 | Materials

All chemicals employed for the investigating of the catalytic activity of the BWA as catalyst were purchased from Merck Company and used as received. Heteropolyacid, $H_5BW_{12}O_{40}$ (BWA) was prepared in accordance with procedure reported in 2015.[41] Melting points were measured by an electrothermal 9200 apparatus. IR spectra were recorded on the FT-IR Tensor 27 Spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 MHz Spectrometer in $CDCl_3$ as a solvent. All products were known and identified by comparison of their physical (melting points) and spectral (FTIR spectra) with those of authentic samples which were found being identical. For more certainty ^{1}H-NMR of spectra of two products (**4b** and **4d**) were also recorded which are given in supplementary section along with their FTIR spectra. *Synthesis of 4H-pyrans: General Procedure.*

A mixture of an appropriate aldehyde (1 mmol), malononitrile (1 mmol) and dimedone, 4-hydroxycoumarin or 3-methyl-4*H*-pyrazole-5(4*H*)-one (1 mmol) in the presence of catalytic amount of ($H_5BW_{12}O_{40}$) (10 mol %) was refluxed in a mixture of EtOH/H_2O (1:1) (5 ml) for the indicated reaction time. The progress of the reaction was monitored by TLC (7:3 *n*-hexance/ethylacetate). Upon completion of the reaction (indicated by TLC), the mixture was filtered off under vacuum. The filtrate was cooled to room temperature and the precipitated solid as the reaction product was isolated by filtration. The crude products were purified by recrystallization from a mixture of EtOH/H_2O to give the corresponding desired products. These products were identified by comparison of their melting points along with their FTIR spectra and in two cases (**4b** and **4d**) ^{1}H-NMR.

Selected spectral data

1. 2-Amino-4-(4-chlorophnyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**4a**):[21]

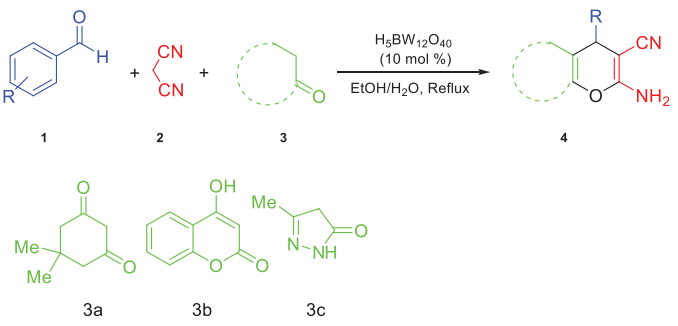
FT-IR (KBr): υ_{max} = 3367, 3191, 2969, 2194, 1687, 1658, 1606, 1510, 1490 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.1 (3H, s, CH_3), 1.1 (3H, s, CH_3), 2.2 (2H, s, CH_2), 2.5 (2H, s, CH_2), 4.5 (1H, s, CH), 6.3 (2H, s, NH_2), 7.4 (2H, d, *J* = 8.0, ArH), 8.0 (2H, d, *J* = 8.0, ArH) ppm; ^{13}C-NMR (DMSO-d_6): δ = 27.5 (Me), 29.0 (Me), 32.5 (C-7), 35.8 (C-4), 40.4 (C-8), 50.6 (C-6), 58.5 (C-3), 113.0 (C-4a), 120.2 (CN), 129.0, 130.0, 131.8, 144.4, (C-Ar), 159.2 (C-2), 163.2 (C-8a), 196.3 (C-5) ppm.

2. 2-Amino-4-(3-nitrophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**4b**):[21]

FT-IR (KBr): υ_{max} = 3400, 3300, 3195, 2200, 695,1600 cm^{-1}, ^{1}H-NMR ($CDCl_3$, 400 MHz): δ_H = 1.01 (s, 3H, Me), 1.1 (s, 3H, Me), 2.3 (s, 2H, 8-H), 2.5 (m, 2H, 6-H), 4.2 (s, 1H, 4-H), 5.0 (s, 2H, NH_2), 7.4–8.0 (m, 4H, ArH) ppm.

3. 2-Amino-4-(4-metoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**4c**):[21]

FT-IR (KBr) υ_{max} = 3377, 3186, 2963, 2194, 1680, 1658, 1606, 1510, 1463 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz); δ = 1.0 (3H, s, CH_3), 1.2 (3H, s, CH_3), 2.2



SCHEME 1 Synthesis of 4*H*-pyran derivatives **4** *via* one-pot and multicomponent reaction

(2H, s, CH_2), 2.4 (2H, s, CH_2), 3.8 (3H, s, OCH_3), 4.4 (1H, s, CH), 4.5 (2H, br s, NH_2), 6.8 (2H, d, J = 6.8, ArH), 7.1 (2H, d, J = 6.8, ArH) ppm; ^{13}C-NMR (DMSO-d_6): δ = 27.5 (Me), 29.1 (Me), 32.5 (C-7), 35.4 (C-4), 40.4 (C-8), 50.7 (C-6), 55.7 (OMe), 59.3 (C-3), 113.7 (C-4a), 120.4 (CN), 114.4, 129.0, 137.5, 158.6 (C-Ar), 159.1 (C-2), 162.8 (C-8a), 196.3 (C-5) ppm.

4. 2-Amino-4-(phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**4d**):[21]

FT-IR (KBr): υ_{max} = 3390, 3290, 2935, 2200, 1685, 1600 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 1.0 (s, 3H, Me), 1.0 (s, 3H, Me), 2.1 (d, 1H, J = 16.0 Hz, 8-H), 2.2 (d, 1H, J = 16.0 Hz, 8-H), 2.4–2.5 (m, 2H, 6-H), 4.3 (s, 1H, 4-H), 6.1 (s, 2H, NH2), 7.1–7.3 (m, 5H, ArH) ppm.

5. 2-Amino-4-(4-methylphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (**4e**):[21]

FT-IR (KBr) υ_{max} = 3425, 3330, 3266, 3221, 2191, 1675, 1638, 1602, 1367 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 500 MHz): δ =1.8–1.9 (1H, m), 1.9–2.0 (1H, m), 2.2–2.3 (5H, m), 2.6 (2H, m), 4.1 (1H, s), 6.9 (2H, s), 7.0 (2H, d, J = 8.0 Hz), 7.0 (2H, d, J = 8.0 Hz,) ppm; ^{13}C-NMR ($DMSOd_6$, 125 MHz): δ = 20.6, 21.4, 27.3, 35.9, 37.2, 59.2, 114.8, 120.6, 127.9, 129.7, 136.4, 142.7, 159.3, 165.1, 196.6 ppm.

6. 2-Amino-4-(4-chlorophenyl)-5-oxo-4,5-dihydropyrano-[3,2-*c*]chromene-3-carbonitrile (**4f**):[42]

FT-IR (KBr) υ_{max} = 3404, 2924, 2255, 2184, 2128, 1704, 1668, 1378, 1026, 1001, 763 cm^{-1};^{1}H NMR (300 MHz, DMSO-d_6); δ = 7.9 (1H, d, J = 7.5 Hz), 7.7 (1H, t, J = 7.5 Hz), 7.4–7.5 (3H, m), 7.3–7.4 (4H, d, J = 8.4 Hz, 19.5 Hz), 4.5 (1H, s) ppm; ^{13}C-NMR (75 MHz, DMSO-d_6) δ = 160.0, 158.4, 154.0, 152.6, 142.8, 133.5, 132.2, 130.1, 128.9, 125.1, 123.0, 119.5, 117.0, 113.4, 103.9, 58.0, 36.8 ppm.

7. 2-Amino-4-(4-methoxyphenyl)-5-oxo-4,5-dihydropyrano-[3,2-*c*]chromene-3-carbonitrile (**4g**):[42]

FT-IR (KBr) υ_{max} = 3364, 3313, 3177, 2920, 2850, 2189, 1710, 1668, 1371, 1051, 766 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) δ = 7.9 (1H, d, J = 7.8 Hz), 7.7 (1H, t, J = 7.5 Hz), 7.4–7.5 (3H, m), 7.2–7.3 (1H, t, J = 8.4 Hz), 6.8 (1H, s), 6.8 (2H, s), 4.4 (1H, s), 3.7 (3H, s) ppm; ^{13}C-NMR (75 MHz, DMSO-d_6) δ = 159.5, 159.2, 157.9, 153.4, 152.1, 144.8, 132.9, 129.6, 124.6, 122.4, 119.7,119.1, 116.5, 113.8, 112.9, 111.9, 103.8, 57.8, 54.9, 36.8 ppm.

8. 2-Amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-*c*]-chromene-3-carbonitrile (**4h**):[42]

FT-IR (KBr) υ_{max} = 3350, 3320, 2921, 2852, 2195, 1700, 1669, 1603, 1373, 1044, 759 cm^{-1}; ^{1}H-NMR (300 MHz, DMSO-d_6) δ = 7.9 (1H, d, J = 7.8 Hz), 7.7 (1H, t, J = 6.9 Hz), 7.4–7.5 (3H, m), 7.2–7.3 (5H, m), 4.5 (1H, s) ppm; ^{13}C-NMR (75 MHz, DMSO-d_6) δ = 159.5, 157.9, 153.4, 152.1, 143.3, 132.9, 128.5, 127.6, 127.1, 124.6, 122.4, 119.2, 116.5, 112.9, 104.0, 57.9, 36.9 ppm.

9. 2-Amino-4-(3-nitrophenyl)-5-oxo-4,5-dihydropyrano-[3,2-*c*]chromene-3-carbonitrile (**4i**):[42]

FT-IR (KBr) υ_{max} = 3398, 3323, 3190, 3087, 2194, 1712, 1674, 1603, 1532, 1379, 1212, 1063 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6) δ = 4.7 (1H, s, CH), 7.2–7.9 (10H, m, Ar–H and NH_2) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 38.0 (C–H), 59.8 (=C–CN), 102.7, 112.8 (C=C), 116.4 (C–H Ar), 119.8 (C ≡ N), 122.1, 124.3, 123.5, 125.5, 130.0, 133.0, 134.6 (C–H Ar), 145.4 (C=C), 148.7 (=C–NO_2), 152.2 (=C–NH_2), 153.7, 159.1 (=C–O), 159.5 (O=C–O) ppm;

10. 6-Amino-3-methyl-4-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (**4k**):[43]

^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ = H 1.8 (3H, s, CH_3), 4.6 (1H, s), 6.9 (2H, br, s, NH_2), 7.1 (2H, d, J = 7.3 Hz), 7.2 (1H, m), 7.3–7.3 (2H, m), 12.1 (1H, s, NH) ppm; ^{13}C-NMR (100 MHz; $CDCl_3$): δ = 9.7, 36.2, 57.2, 97.6, 120.8, 126.7, 127.5, 128.4, 135.6, 144.4, 154.8, 160.9 ppm.

11. 6-Amino-4-(4-chlorophenyl)-3-methyl-2,4dihydropyrano[2.3-*c*]pyrazol-5-carbonitrile (**4l**):[43]

FT-IR (KBr) υ_{max} = 3483, 3357, 3221, 2210, 1634, 1600 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6) δ = 1.9 (3H, s, CH_3), 4.6 (1H, s, CH), 7.0 (2H, s, NH_2), 7.3 (2H, d, J = 8.4 Hz, ArH), 8.1 (2H, d, J = 8.4 Hz, ArH), 11.9 (1H, s, NH) ppm.

12. 6-Amino-4-(4-methylpheny)-3-methyl-2,4dihydropyrano[2.3-*c*]pyrazol-5-carbonitrile (**4n**):[43]

FT-IR (KBr) υ_{max} = 3406, 3315, 3188, 2191, 1646, 1600 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6) δ = 1.8 (3H, s, CH_3), 3.9 (3H, s, CH_3), 4.6 (1H, s, CH), 6.9 (2H, s, NH_2), 7.4 (2H, d, J = 8.4 Hz, ArH), 8.1 (2H, d, J = 8.4 Hz, ArH), 11.9 (1H, s, NH) ppm.

13. 6-Amino-4-(4-metoxyphenyl)-3-methyl-2,4dihydropyrano[2.3-*c*]pyrazol-5-carbonitrile (**4o**):[43]

FT-IR (KBr) υ_{max} = 3483, 3249, 3122, 2190, 1643, 1600 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6) δ = 1.9 (3H, s, CH_3), 3.8 (3H, s, CH_3), 4.6 (1H, s, CH), 6.9 (2H, s, NH_2), 7.4 (2H, d, *J* = 8.4 Hz, ArH), 8.1 (2H, d, *J* = 8.4 Hz, ArH), 11.9 (1H, s, NH) ppm.

2.2 | Results and discussion

In general, the difference between homogeneous and heterogeneous catalysis needs further refinement. Homogeneous catalysis is a reaction or process, where the catalyst is the same phase as the reactants. Thus in homogeneous catalysis two or three-phases can be present (for example two-phase catalysis or liquid–gas reactions) but the reaction should take place in the phase where the catalyst is present (the reactants need to dissolve into the catalysts phase). In case of heterogeneous catalysts, which typically a solid, the reactants are in another phase, usually liquids, liquids-gases or gases. Thus, one can conclude that homogeneous catalysis should be more efficient whereas the separation of heterogeneous catalyst is generally much easier (simple filtration, or just passing the reactants through a solid bed) and more importantly the heterogeneous can be reused after separation.[44]

We have already found out that HPAs have both advantages in addition of being green and acting efficiently in water as the greenest solvent and since organic compounds are rarely soluble in water due to their inherent lipophilicity.[40a, 45] In the last decade, we established HPAs as efficient heterogeneous[46] and homogeneous catalysts,[47] which were both were easily separated from the reaction mixture. In both cases, they could be effectively reused for several times without loss of their catalytic activities.

We have also observed and reported that Keggin-type heteropolyacids show high catalytic activities for many organic transformations. It has been shown that the catalytic activities of the heteropolyacids were much higher than those of traditional acid catalysts such as sulfuric acid and *p*-toluensulfonic acid.[48] On the basis of comparative measurements of electrical conductivity, acidity, and softness of anion for the solutions of acid catalysts, the effectiveness acid catalysis by heteropolyacid was proposed to be due to the specific properties of the heteropoly anion, which can be characterized by very weak basicity and great softness, along with the large size of the polyhedral structure.

In continuation of our interest in the catalytic synthesis of heterocyclic compounds *via* MCR under eco-friendly conditions and our special interest using HPAs as efficient and green catalysts,[49] we synthesized a newly reported HPA, $H_5BW_{12}O_{40}$ (BWA). This HPA was also developed as an electrolyte for solid super capacitors[8] but its catalytic activity in organic transformations has not been investigated, thus for the first time we examined it as an efficient catalyst in a typical organic transformation. Its structure was well characterized by using FTIR and XRD, which were compared to those of the known silicotungstic acid $H_4SiW_{12}O_{40}$, (SiWA) HPA.

Boron trifluoride is most typically used as Lewis acid catalyst in several organic reactions.[50] Examples include: as initiator in polymerisation reactions of unsaturated compounds, such as polyethers[51] and some other polymerization, isomerization, acylation,[52] alkylation, esterification, dehydration, condensation, Mukaiyama aldol addition and *etc*.[53] $H_5BW_{12}O_{40}$ (BWA), a heteropolyacid having B^{3+} as the central heteroatom attracted our attention and we thought it is worthwhile to examine its catalytic activity as a stronger Lewis acid than boron tetrafluoride etherate in the synthesis of a heterocyclic system *via* MCR.

Initially, the necessity of the presence of the catalyst was studied. For this purpose, the reaction of benzaldehyde, malononitrile and dimedone was selected as the model reaction and performed it in water as solvent but in the absence of the any catalyst. In the absence of catalyst the reaction proceeded sluggishly and only trace amount of the desired product was obtained. Then, we prepared $H_5BW_{12}O_{40}$ (BWA) according to the procedure already reported.[41] The aforementioned reaction was conducted in the presence of catalytic amount of $H_5BW_{12}O_{40}$ (BWA). The progress of reaction was monitored by TLC (7:3 *n*-hexance/ethylacetate). This monitoring showed the smooth and clean conversion of starting materials along with the generation of the expected product. To find the optimal reaction conditions, the influence of solvent, quantities of catalyst loading and temperature were examined in a model reaction involving benzaldehyde, dimedone and malononitrile. The results are shown in Table 1. The effects of various solvents, polar and non-polar were examined in this reaction. Initially, to find the best solvent, the model reaction was conducted in solvent-free conditions. Then, water as the greenest solvent was used which gave the desired compound **4a** in 75% yield (Table 1, entry 1). In addition, we examined other solvents such as EtOH, DMF, CH_3CN and CH_2Cl_2. As illustrated in Table 1, when the above-mentioned reaction was performed in DMF, gave the expected product **4a** in only 50% yield (Table 1, entry 3). In CH_2Cl_2 product **4a** was obtained in 60% yield (Table 1, entry 2). EtOH and CH_3CN provided the corresponding products in, 78 and 85% yield respectively (Table 1, entries 4 and 5).

TABLE 1 Optimization of reaction conditions for the synthesis of 4*H*-pyrans

Entry	Solvent	Temperature	Time (min)	Catalyst amount (mol%)	Yield (%)
1	H2O	Reflux	120	10	75
2	CH_2Cl_2	Reflux	180	10	60
3	DMF	Reflux	180	10	50
4	EtOH	Reflux	90	10	85
5	CH_3CN	Reflux	90	10	78
6	EtOH/H_2O	Room	420	10	50
7	EtOH/H_2O	Reflux	420	-	trace
8	EtOH/H_2O	Reflux	60	5	85
9	EtOH/H_2O	Reflux	60	10	98
10	EtOH/H_2O	Reflux	60	15	98

Extraordinarily, the best results (98% yields) was reached when the model reaction was conducted in EtOH/H_2O (1:1) at reflux condition (Table 1, entry 9). Since, polar protic solvents such as EtOH/H_2O, raised the yields substantially. This might be due to the more solubility of starting materials in polar solvents. Thus, EtOH/H_2O (1:1) was selected as the solvent of choice.

In the following, in order to find the influence of temperature, the model reaction was conducted in the presence of $H_5BW_{12}O_{40}$ (BWA) in EtOH/H_2O at ambient temperature that gave only 50% yield (Table 1, entry 6). This model reaction under reflux condition in EtOH/H_2O led to the desired products in highest yield (98% yield) (Table 1, entry 9).

Finally, to find the effect of the catalyst amount, the model reaction was conducted without any catalyst which failed (Table 1, entry 7), while in the presence of 5 mol%, BWA the desired product was isolated in 85% which indicated the important role of our catalyst in the reaction progress (Table 1, entry 8). As expected, the yield was increased from 85% to 98% with raising BWA amount from 5 mol% to 10 mol% (Table 1, entry 9). The improvement of the yield by increasing the BWA quantity can be attributed to the increase in the number of active sites as well as the amended and enhanced the contact and collision opportunity between the BWA surface with the molecules of the starting materials. Worthy to mention that further increase in the BWA amount from 10 mol% to 15 mol% resulted in no change in yield % (Table 1, entry 10). Thus, 10 mol% of catalyst was chosen as the optimized catalyst loading (Table 1, entry 9). The best result was obtained when the reaction was conducted in the presence of 10 mol% catalyst in EtOH/H_2O under reflux condition, which corresponding 4*H*-pyran **4a** was generated in 98% yield after 60 minutes (Table 1, entry 9).

With these results in hand, we then investigated the substrate scopes and limitations of the synthesis of 4*H*-pyrans in the presence of 10 mol% BWA as catalyst under reflux condition in EtOH/H_2O and the results are listed in Table 2. The generality of the current method was investigated in the reaction of differently substituted aldehydes, containing either electron donating or electron-withdrawing functional groups in the *ortho*, *meta*, and *para* positions with malononitrile and either dimedone or 4-hydroxycoumarin or 3-methyl-4*H*-pyrazole-5(4*H*)-one under already secured optimal reaction condition (Scheme 1). The corresponding 4*H*-pyran derivatives were obtained in good to excellent yields in relatively short times without formation of any by-products. The results are summarized in Table 2. As can be realized, in all cases the desired products successfully produced with in satisfactory yields.

As illustrated, aldehydes bearing electron-donating groups (such as 4-MeO-benzaldehyde and 4-Me-benzaldehyde) as well as electron-withdrawing groups (such as 3-NO_2-benzaldehyde and 4-Cl-benzaldehyde) were used as substrate. The reaction of benzaldehyde, malononitrile and dimedone **3a** provided the desired product **4d** after 50 min in 98% yield (Table 2, entry 4). Aldehydes containing electron-donating groups containing 4-OMe, 4-Me provided the desired products **4c** and **4e** in 90 and 88% yield respectively (Table 2, entries 3 and 5). Also, aldehydes containing electron-withdrawing groups including 4-Cl and 3-NO_2 gave the corresponding products **4a** and **4b** in 92 and 85% yields respectively (Table 2, entries 1 and 2).

In the following, as we mentioned above, for library validation, we examined 4-hydroxycoumarin and 3-methyl-4*H*-pyrazole-5(4*H*)-one instead of dimedone, which gave the corresponding products in good to excellent yields.

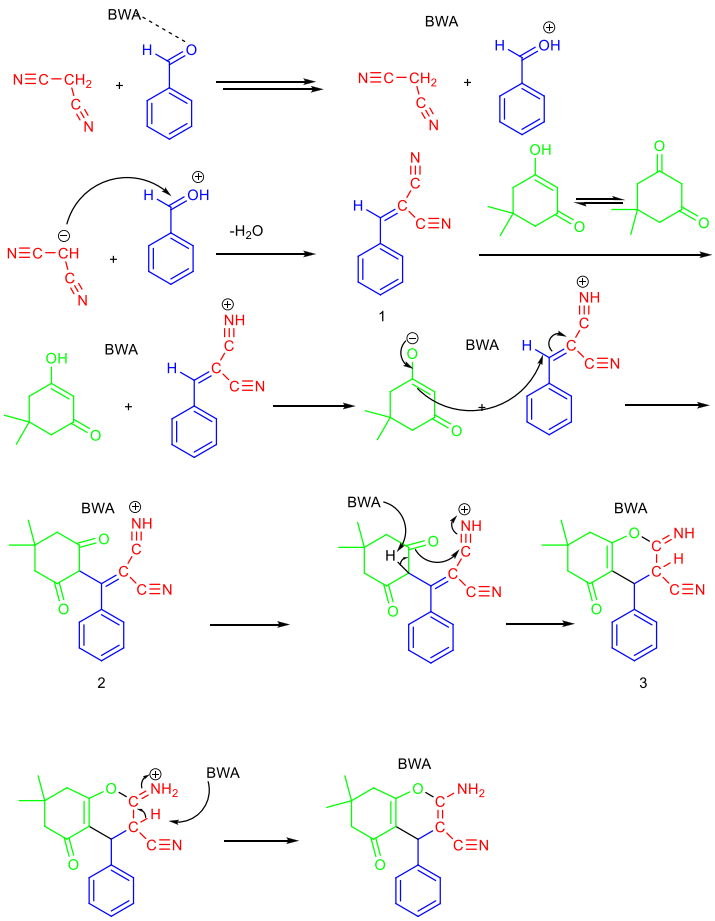
2.3 | Reaction Mechanism

In a proposed mechanism (Scheme 2), firstly, malononitrile reacts with carbonyl group of aldehyde, which already is activated by the BWA and affords intermediate **1** after removing one molecule of H_2O. Dimedone converts to enole form after tautomerisation and attacks to cyanoolefin compound **1** as Michael acceptor to produce **2**. Finally, cyclocondensation of **2** gives **3** which is converted to the desired product.

To display the merits of this catalyst, its catalytic activity for the development of the model compound (benzaldehyde, malononitrile and dimedone) was compared with those surveyed previously (Table 3). As shown in Table 3, the catalytic activity of BWA was compared

TABLE 2 Synthesis of 4*H*-pyrans in the presence of $H_5BW_{12}O_{40}$ in EtOH/H_2O under reflux condition

Entry	Product 4	Carbonyl compound 3	R^1	Yield (%)	Time (min)	mp (°C) Found	mp (°C) Lit
1	4a	3a	4-Cl	92	75	206	203–205[58]
2	4b	3a	3-NO_2	85	300	212	209–211[58]
3	4c	3a	4- OCH_3	90	255	198	201–202[43]
4	4d	3a	H	98	60	221–223	224–225[59]
5	4e	3a	4-CH_3	88	90	212–213	215–216[21]
6	4f	3b	4-Cl	98	270	230–232	233–234[60]
7	4g	3b	4-OCH_3	85	270	222	220–222[61]
8	4g	3b	H	98	210	257–258	258–260[59]
9	4i	3b	3-NO_3	90	195	253–255	256–257[61]
10	4j	3b	4-OH	85	225	264–268	266–268[42]
11	4k	3c	H	94	120	244–246	244–246[62]
12	4l	3c	4-Cl	90	90	232	234–236[62]
13	4m	3c	4-OH	92	190	224	223–224[62]
14	4n	3c	4-CH_3	77	90	213	215–217[63]
15	4o	3c	4- OCH_3	90	120	212	212–213[64]



SCHEME 2 Suggested mechanism for the synthesis of 4*H*-pyran derivatives

TABLE 3 The comparison of the catalytic activity of $H_5BW_{12}O_{40}$ with formerly reported catalysts

Entry	Catalyst	Time	Catalyst Amount	Temperature	Solvent	Yield (%)	Ref.
1	POPINO (Potassium phthalimide-N-oxyl)	15 min	5 mmol%	reflux	H_2O	95	[54]
2	nano ZnO	180 min	10 mmol%	r.t.	EtOH/H_2O	86	[55]
3	(*S*)-proline	120 min	5 mmol%	reflux	EtOH/H_2O	82	[19]
4	Silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2] octane chloride (SB-DABCO)	35 min	6 mmol%	reflux	EtOH/H_2O	96	[23]
5	nano-TiO_2/ $H_{14}[NaP_5W_{30}O_{110}]$	20 min	25 mg	ultrasound	EtOH	93–95	[65]
6	LiBr	15 min	10 mmol%	reflux	H_2O	95	[66]
7	Fe_3O_4@SiO_2-Imid-PMA^n PMA^n: nano $H_3PMo_{12}O_{40}$	20 min	15 mg	reflux	H_2O	94	[56]
8	Na_2SeO_4	60 min	10 mg	reflux	EtOH/H_2O	97	[57]
9	Hexadecyltrimethyl ammonium bromide (HTMAB)	180 min	10 mmol%	reflux	H_2O	91	[21]
10	RE $(PFO)_3$	300 min	5 mmol%	90 °C	EtOH	90	[22]
11	Magnetic Fe_3O_4 /phenylsulfonic acid	25 min	0.2 mol%	50 °C	H_2O	95	[25]
12	Nano-SiO_2	8 min	20 mol%	70 °C	H_2O	94	[26]
13	HPA-den drimer functionalized ma gnetic nanop article (Fe_3O_4@ D-NH_2-HPA)	5 min	0.02 g	reflux	EtOH	92	[27]
14	Mixed-ligand Cu (II) Schiff base complex (Cu (L)(Py))	15 min	20 mg	50 °C	EtOH	95	[28]
15	Amine-functionalized hyper-crosslinked polyphenanthrene	1 min	10 mg	Room temperature	Neat	92	[29]
16	Polypyrrole/Fe_3O_4/CNT	15 min	0.032 g	90 °C	Solvent-free	95	[31]
17	Polystyrene-supported DABCO ionic liquid	60 min	10 mol%	Room temperature	H_2O	92	[32]
18	12-molybdophos phoric acid encapsulated in the nanocavities of modified dealuminated zeolite Y	15 min	140 mg	80 °C	EtOH	89	[33]
19	Magnetite-dihydrogen phosphate	15 min	0.03 g	60 °C	Solvent-free	88	[34]

with diverse catalysts such as POPINO (Potassium phthalimide-N-oxyl),[54] nano ZnO,[55] (*S*)-proline,[19] Fe_3O_4@SiO_2-Imid-PMA^n,[56] (PMA^n: nano $H_3PMo_{12}O_{40}$) Na_2SeO_4,[57] which have been previously employed as catalysts in the aforementioned reaction. The findings demonstrated that comparing to other catalysts; our planned catalyst can mediate the reaction in an appropriate amount. Furthermore, it supplies the corresponding products in short reaction time. From the green chemistry point of view, the reusability of the catalyst and using EtOH/H_2O as the reaction media render this catalyst green and eco-friendly. Notably, the purpose of this work, which is presenting a catalyst with potential usage for improving organic reactions and synthesis of 4*H*-pyrans is just particular as a model organic transformation.

2.4 | Catalyst reusability

Finally, as shown in Figure 2, we investigated the reusability of the catalyst. The catalyst was soluble in EtOH/H_2O and could be removed easily by evaporation of the solvent. After evaporating of solvent, the catalyst was washed with diethyl ether, dried at 130 °C for 1 h, and re-used in another reaction. The recycled catalyst was used for three consecutive reactions without observation of appreciable loss in its catalytic activities.

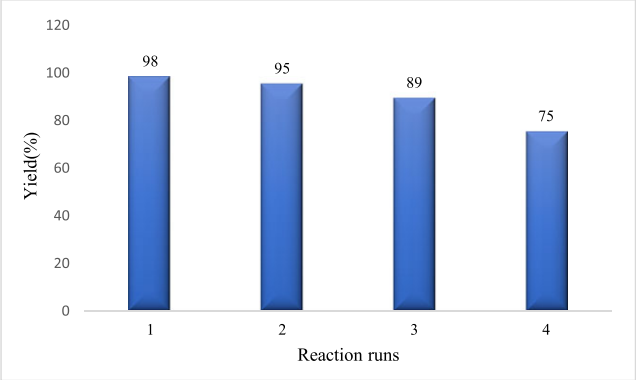


FIGURE 2 Recyclability of catalyst for the synthesis 4*H*-pyrans

3 | CONCLUSION

In this work, we introduce the first example of catalytic activity of the heteropoly acid, $H_5BW_{12}O_{40}$ as an efficient, green, reusable and homogeneous catalyst for a one-pot three-component synthesis of 4*H*-pyran derivatives in EtOH/H_2O under reflux condition which are biologically and pharmacologically active compounds. This method not only offers substantial improvements in the reaction rates and yields, but also avoids the use of hazardous catalysts or solvents. In general, the presented methodology has many advantages that make it useful and attractive, such as efficiency, generality, high yield, short reaction time, clean reaction profile, ease of product isolation, simplicity, a potential for recycling of the reaction medium and finally, agreement with green chemistry protocols.

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