

# 12-Tungstoboric acid ( $H_5BW_{12}O_{40}$ ) as an efficient Lewis acid catalyst for the synthesis of chromenopyrimidine-2,5-diones and thioxochromenopyrimidin-5-ones: Joint experimental and computational study

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## ABSTRACT

$H_5BW_{12}O_{40}$  (BWA), Keggin-type heteropoly acid was employed as an effective, eco-friendly and reusable Lewis acid catalyst for the high yielding synthesis of chromenopyrimidine-2,5-diones and thioxochromenopyrimidin-5-ones via multicomponent reaction (MCR) of differently substituted benzaldehydes, urea/thiourea, and 4-hydroxycoumarin in refluxing water. The BWA catalyst could be recovered by a simple filtration and applied in three successive runs with no noticeable decrease in the yield. Interestingly, this catalyst structure pattern may act as useful model for the design and assembly of the functional molecule-based catalysts, especially in the field of molecular sieve materials. Moreover, thermochemical properties in the synthesis of title compounds were assessed using density functional theory (DFT) calculations.

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## 1. Introduction

The development of safe materials with catalytic potencies is an attractive and important issue in material chemistry as well as sustainable chemistry. In general, catalysts accelerate and improve the chemical reactions, thus most organic transformations, should be performed under catalysis. Catalysis is the process of enhancing the rate of a chemical reaction by using a substance as a catalyst. A catalyst is not exhaust in the catalyzed reaction and can continue to act, continually [1,2]. Green chemistry, so-called sustainable chemistry, is a domain in chemistry and especially in the chemical industry, focused on the designing of reactions and industrial processes that minimize or remove the utilization and creation of

hazardous materials [3].

Merits of green Chemistry are better human health cleaner air, less release of toxic chemicals to air, resulting less damage to lungs thus increased safety in the chemical industry; less use of toxic materials [4].

The catalytic behavior of heteropoly acids (HPAs) and polyoxometalates (POMs) compounds are notable both in activity and reusability. POMs or HPAs, as a family of POMs, are a class of transition-metal oxide clusters like Mo, W, V, Nb and Ta which possess a large range of structures in terms of size, shape, elemental composition with high negative charge, along with varied redox properties, have attracted much attention of synthetic organic chemists as catalysts of choice. The most unique features of POMs which make them suitable acting as catalyst are their ease of controlling acidity, reduction potential, solubility, super acidity, excellent structural stability undergoing multi-electron redox cycles, low toxicity and corrosion.

In the past decades, various HPAs and POMs have been employed as effective homogeneous and heterogeneous catalysts.

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In addition, HPAs are known as ideal catalysts as far as green chemistry concerns [5].

Among the numerous HPAs the Keggin type  $[H_nXM_{12}O_{40}]$  ( $X = B, P,$  or  $Si$ ;  $M = W$  and  $Mo$ ), have received much attention due to high acidity and the rich redox chemistry as their well-defined structures, high redox property and surface charge distribution [6–9]. Boron trifluoride is frequently employed as Lewis acid catalyst in several organic reactions [10].

Recently, we successfully examined the catalytic activity of Keggin-type  $H_5BW_{12}O_{40}$  (BWA), as a Lewis acid, as a heteropoly acid, having  $B^{3+}$  as the central heteroatom similar to boron tetrafluoride etherate as a homogeneous but recyclable catalyst in the synthesis of  $4H$ -pyrans via MCR [11].

Nowadays, exploring novel synthetic pathways using nontoxic solvent, reagents and catalysts has attracted much attention of synthetic organic chemists. Along with these considerations, implementation of the process *via* MCR in one pot fashion has stirred up the interest of synthetic organic chemists. The advantages of MCR in one-pot manner are performing the reaction without isolation of intermediate, diminishing of the reaction time and energy consumption [12–24]. Cascade MCRs are idyllic synthetic approaches, exhibiting a significant role in the formation of different heterocycles [25–30]. MCRs are widely studied computationally and experimentally, used for development of efficient chemical syntheses of compounds with the potent inhibitory activity [28,31–33]. In this line, tetrameric acid derivatives have been synthesized using MCRs and the assessment of their inhibitory behavior were performed *via* experimental methods in combination with DFT calculations on its tautomeric equilibrium forms [34].

$4$ -Hydroxycoumarins are biologically important compounds as well as being useful intermediates in the total synthesis of natural products as well as, complex molecules exhibiting diverse biological potencies. They are also present in the structural cores of several naturally occurring compounds [35–39]. Their derivatives have demonstrated a wide range of biological and pharmacological properties [40–42].

We are interested in heterocyclic chemistry [43–49] and especially in the catalyzed-synthesis of heterocyclic compounds through MCR [50–54] being performed under green conditions [43,53,54]. From the last decade our research group has influenced in the applications of different heteropoly acids and POMs as efficient homogeneous and heterogeneous catalysts in the art of organic synthesis, which have been appeared in our comprehensive reviews [14,55–57].

Noticeably, we have reported the effective and green synthesis of pyrans by using heteropoly acids as support in water [58] and through electrosynthesis [59]. In continuation of our interest in the applications of heteropoly acids as catalyst, we encountered to two reports, claiming that by an increase in the number of protons in Keggin heteropolyanions their acidic strength decrease, determined by absorption calorimetry of ammonia. For example the

order of acidity of HPAs with different numbers of protons are found being as follows,  $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_6P_2W_{21}O_{71}(H_2O)_3 > H_6P_2W_{18}O_{62}$  [60,61], thus we assume that,  $H_5BW_{12}O_{40}$ , with low proton numbers acts in our reactions as a powerful Lewis acid catalyst. Thus, the synthesis of chromenopyrimidine-2,5-diones and thioxochromenopyrimidin-5-ones *via* MCR involving aldehydes, 4-hydroxycoumarin and urea/thiourea in water in one pot fashion is catalyzed by Lewis acidic character of  $H_5BW_{12}O_{40}$ , (Scheme 1).

Moreover, in continuation of our previous computational studies on the catalyzed click and coupling reactions [62–65], we explored the thermochemical aspects in the synthesis of chromenopyrimidine-2,5-diones and thioxochromenopyrimidin-5-ones considering the solvent effects *via* computational chemistry methods.

## 2. Experimental section

### 2.1. Materials and methods

All chemicals used for the studying of the catalytic activity of the BWA as catalyst were provided from Merck Company and utilized as received. HPA,  $H_5BW_{12}O_{40}$  (BWA) was synthesized according to method reported, previously [64]. All products were known and identified by comparison of their melting points and FT-IR spectra with those of authentic samples, which were found being identical. Melting points were measured by an electro thermal 9200 apparatus. FTIR spectra were recorded using Bruker Tensor.

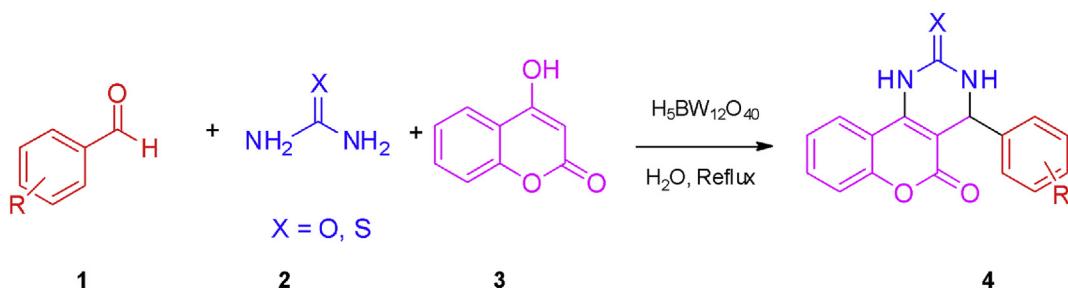
### 2.2. Synthesis of chromenopyrimidine-2,5-dione and thioxochromenopyrimidin-5-one derivatives: general procedure

A mixture of an appropriate aldehyde (1 mmol), urea or thiourea (1 mmol) and 4-hydroxycoumarin (1 mmol) in the presence of catalytic amount of ( $H_5BW_{12}O_{40}$ ) (5 mg) were refluxed in water (5 ml) for the indicated reaction times. The progress of the reaction was monitored by TLC (7:3 *n*-hexane/ethylacetate). Upon completion of the reaction (indicated by TLC), the mixture was filtered off. The filtrate was cooled to room temperature and the precipitated solid was isolated by filtration. The crude products were purified by recrystallization from a mixture of EtOH/H<sub>2</sub>O.

## 3. Results and discussion

### 3.1. Catalytic activity

In order to determine the catalytic activity of  $H_5BW_{12}O_{40}$  for the synthesis of chromenopyrimidine-2,5-diones and thioxochromenopyrimidin-5-ones, the reaction of benzaldehyde, 4-hydroxycoumarin and urea was selected as a model reaction. At first, we have investigated product formation in the absence of the



**Scheme 1.** Synthesis of (denoted as O-product) and thioxochromenopyrimidin-5-ones (denoted as S-product) **4** *via* MCR in the presence of  $H_5BW_{12}O_{40}$  in water.



activity  $H_5BW_{12}O_{40}$  was compared with those previously employed and reported. The outcome showed, our selected catalyst can catalyze the reaction effectively. In addition, it gives the corresponding products in short reaction times. As far as the principles of green chemistry concern, the reusability of the catalyst along with water as the solvent render this catalyst environmentally benign. Noticeably, the purpose of this work is introducing the catalyst with potential applications for improving the synthesis of chromenopyrimidine-2,5-dione and thioxochromenopyrimidin-5-one derivatives.

#### 4. Computational study

From the computational chemistry viewpoint, we have focused on the comparative assessment of thermophysical aspects in the synthesis of chromenopyrimidine-2,5-diones and thioxochromenopyrimidin-5-ones using density functional theory methods [76,77]. In this respect, we modeled the reaction of benzaldehyde, 4-hydroxycoumarin and urea/thiourea for the production of chromenopyrimidine-2,5-diones/thioxochromenopyrimidin-5-ones and then calculated the reaction thermodynamical properties change in the gas and solution phases. It should be mentioned that in our previously published papers, we have investigated computationally the thermodynamical properties of coupling and multicomponent click reactions using quantum chemistry approaches [60–62,78].

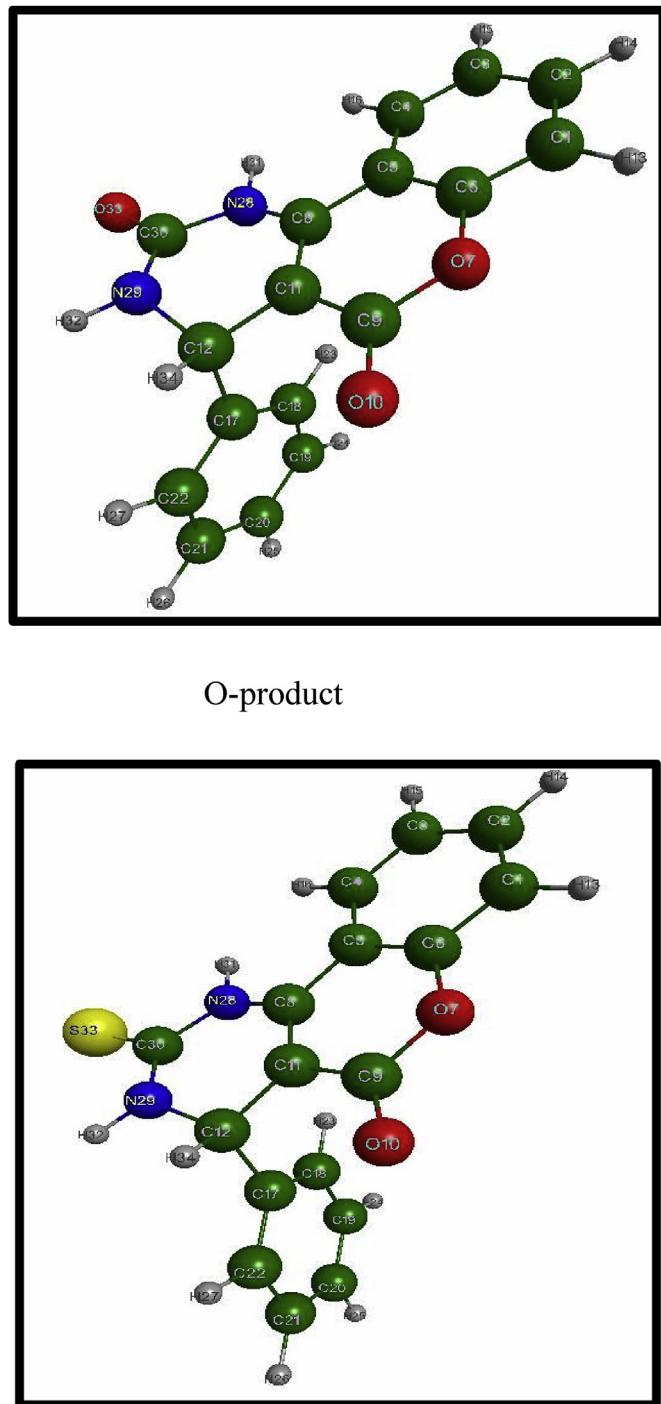
At the first step, the optimized structures of all reagents and products were obtained *via* geometry optimization procedure at M08-HX/6-31G\* level of theory [79] with no symmetry restrictions. Furthermore, we used the harmonic frequency analysis to confirm that the optimized geometries located to the true minima. More precisely speaking, theoretical calculation of frequencies is derived from the Hessian matrix straightforwardly after geometry optimization procedure to confirm the energy minimized structures, corresponded to no imaginary frequencies.

In continuation, the vibrational frequency calculations were performed to obtain enthalpy and Gibbs free energy values. It is important to mention that in thermal corrections calculation, the pressure and temperature were set as 1 atm and 25 °C, respectively.

All DFT computations have been performed using GAMESS suite of programs [80]. We have illustrated M08-HX/6-31G\* optimized structures of chromenopyrimidine-2,5-diones and thioxochromenopyrimidin-5-ones that were produced in the presence of urea or thiourea (hereafter denoted as O-product and S-product, respectively) (Fig. 1).

In order to assess the planarity of O-product and S-product, we analyzed some important selected dihedral angles and reported their corresponded calculated values together with some other geometrical data in Table 4. As it can be concluded from the reported results of Tables 4 and 3, 4-dihydro-1*H*-chromeno[4,3-*d*] pyrimidine-2,5-dione and thioxo-3,4-dihydro-chromo[4,3-*d*] pyrimidin-5(2*H*)-one parts are nearly planar in O-product and S-product, respectively, while the phenyl group of benzaldehyde is not located in the same plane with chromeno pyrimidine-2,5-dione and thioxo-chromo pyrimidine-5(2*H*)-one.

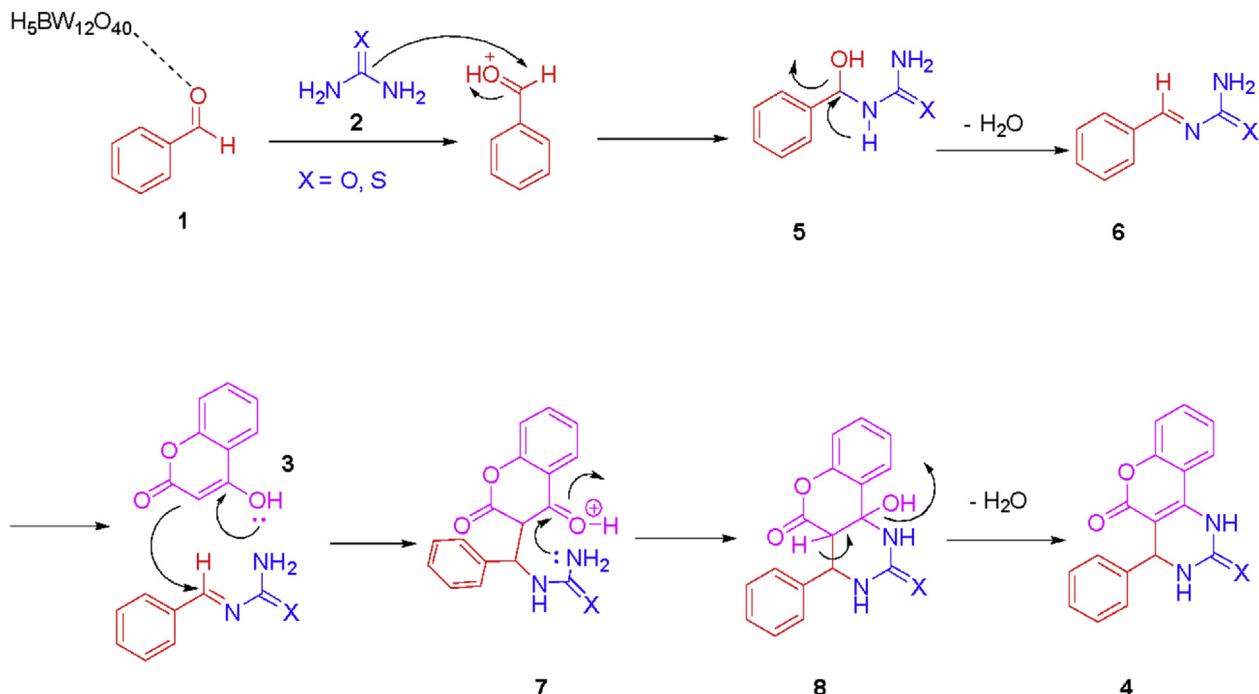
In continuation, the calculated hessian frequencies were employed to make a comparative assessment with the corresponded observed FT-IR values. In this line, the calculated stretching frequencies for C=O (in amide group), C=O (in ester group) and C=N bonds in chromenopyrimidine-2,5-diones were obtained about 1900 cm<sup>-1</sup>, 1890 cm<sup>-1</sup> and 1100 cm<sup>-1</sup>, respectively and C=S, C=N and C=O bonds (in ester group) in thioxochromenopyrimidin-5-ones were obtained about 1200 cm<sup>-1</sup>, 1600 cm<sup>-1</sup> and 1400 cm<sup>-1</sup>, respectively that is in reliable agreement with the FT-IR spectroscopic data.



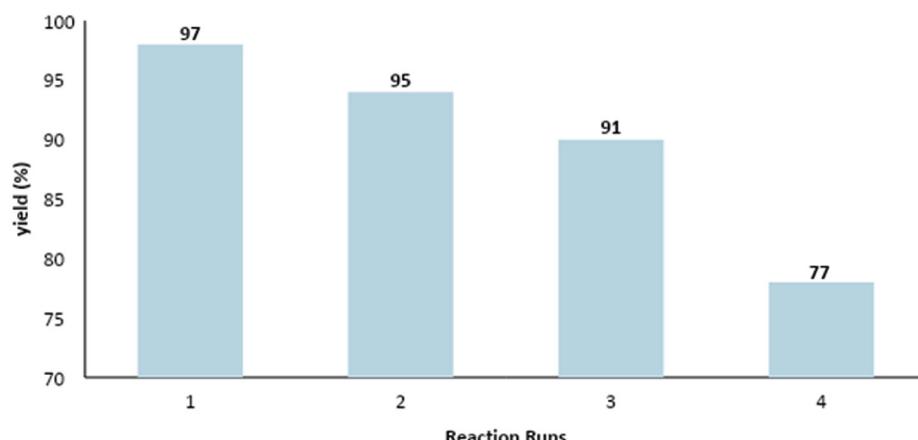
**Fig. 1.** Optimized structures of O-product and S-product, calculated at M08-HX/6-31G\* level of theory.

We have reported the reaction thermochemical data including electronic energy (with and without zero-point energy corrections), enthalpy and Gibbs free energy for the synthesis of O-product and S-product in the gas and water solution phases calculated at M08-HX/6-31G\* level of theory in Table 5. It should be mentioned that in the case of solvation effect, we applied the polarized continuum model (PCM) computations which takes into





**Scheme 2.** A plausible mechanistic pathway for the synthesis of derivatives 4.



**Fig. 2.** Recyclability of catalyst for the synthesis chromenopyrimidine-2,5-dione.

transformations. Furthermore, the computational assessment on thermochemical features in the synthesis of chromenopyrimidine-2,5-diones and thioxochromenopyrimidin-5-ones demonstrated the more thermodynamical favor in generation of O-product. More importantly, the use of combination of B atom with Keggin-type polyoxometalates should attract the attention of synthetic organic chemists as an effective, safe, green and recoverable catalyst in the other Lewis acid-catalyzed organic transformations.

#### Author contribution section

Equal Contribution

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molstruc.2019.127598>.

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