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# Recent advances in polyoxometalates acid-catalyzed organic reactions

Yu-Feng Liu[a], Chang-Wen Hu[b,*], Guo-Ping Yang[a,*]

[a] Jiangxi Province Key Laboratory of Synthetic Chemistry, Jiangxi Key Laboratory for Mass Spectrometry and Instrumentation, East China University of Technology, Nanchang 330013, China
[b] Key Laboratory of Cluster Science of Ministry of Education, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China

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ABSTRACT

Polyoxometalates (POMs) have conducive properties such as controlled Brønsted and Lewis acidity, high thermal stability, nontoxic nature, tunable solubility, and less corrosiveness. POMs have been extensively applied in catalytic organic reactions and have an exciting prospect for industrial applications. This review summarized recent progress in the application of POMs as acid catalysts for various organic reactions including C–C bond formation, C–N bond formation, C–O bond formation, heterocyclic synthesis reactions, cyanosilylation and hydrolysis reactions. Various POMs catalysts including heteropoly acids (HPAs) and cationic functionalized HPAs with Brønsted acidity, HPAs supported on non-precious metal support with Brønsted acidity (or both Brønsted and Lewis acidity), transition metal substituted POMs with Lewis acidity were applied in above reactions. This review attempts to provide up-to-date information about POMs acid-catalyzed organic reactions and propose future prospects.



## 1. Introduction

POMs are a class of discrete anionic metal-oxygen clusters with various dynamic molecular structures and extensively alterable physical and chemical properties, which are widely applied in materials science, biology, electrochemistry, and catalysis [1–17]. Particularly, they have attracted more and more interest in acid-catalyzed reactions due to their adjustable acidity, thermal stability, as well as unique chemoselectivity, regioselectivity, and stereoselectivity [5,18-29]. POMs can exhibit one or two types of acid catalytic properties because of their multiple active sites, including acidic protons with Brønsted acidity, or/and metals with Lewis acidity. Apparently, protons can act as Brønsted acids to promote acid-catalyzed reactions [30,31]. POMs substituted by metals with strong Lewis acidity exhibited excellent Lewis acid catalytic activity [32,33]. Furthermore, POMs can be modified to possess both Brønsted and Lewis acid activity, such as cationic functionalized POMs catalysts, and POMs supported on non-precious metal support [34].

Although the application of POMs as acid catalysts in organic reactions is a relatively mature field, it continues to be attractive due to the following outstanding properties: POMs exhibit stronger Brønsted acidity than traditional mineral acids such as $H_2SO_4$, $HNO_3$, and HCl [35]. POMs exhibit *pseudo*-liquid behaviors, which result in high catalytic activities and unique selectivities [36]. POMs can be reasonably designed on molecular and atomic scales, leading to tunable acidity, redox potential, and enhanced stability [37,38]. Up to now, multifarious outstanding reviews about the development of POMs acid-catalyzed organic reaction. For example, in 2003, Kozhevnikov *et al.* reviewed Friedel-Crafts acylation and related reactions catalyzed by HPAs [39]. In 2015, Yang and his co-workers published an integrated review on the POMs-catalyzed reaction [21]. They summarized the development of POMs in a more comprehensive manner, with reaction types as a clue. In 2021, Song *et al.* summarized the latest progress of the use of POMs-based heterogeneous catalysts in acid catalysis [20]. Nevertheless, there is no review exclusively focusing on POMs acid-catalyzed organic reactions. During the past seven years, some intriguing works about POMs acid-catalysis have been reported, and these researches have yet to be summarized. Considering the importance of POMs acid-catalysis, we present a review that emphasizes its significance and widespread applications in organic synthesis in the past several years (mainly from 2015 to 2022). This review includes the application of POMs for (1) C–C bond formation reactions, (2) C–N bond formation reactions, (3) C–O bond formation reactions, (4) heterocyclic synthesis reactions, (5) cyanosilylation and hydrolysis reactions. Various POMs catalysts exhibit Brønsted acidity, Lewis acidity or both Brønsted and Lewis acidity in above reactions.

* Corresponding authors.
*E-mail addresses:* cwhu@bit.edu.cn (C.-W. Hu), erick@ecut.edu.cn (G.-P. Yang).

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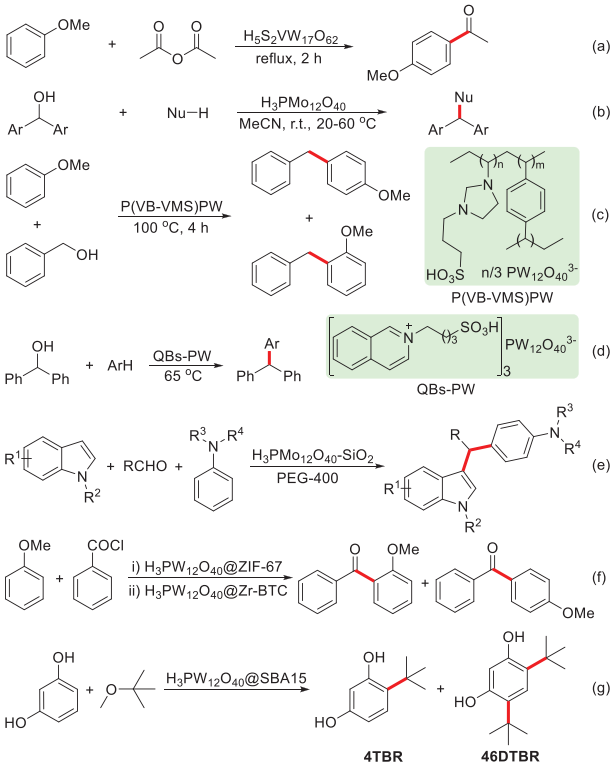
## 2. C–C bond formation

The construction of C–C bonds has emerged as one of the most intriguing areas of organic chemistry, as proved by the 2010 Nobel Prize in chemistry award [40,41]. The C–C bond formation reactions lay a foundation for the construction of the carbon skeleton of organic molecules. Related reactions are widely used in organic synthesis, material science, pesticide and natural product synthesis, and many other fields [42–44]. Recently POMs have been explored as catalysts in C–C bond formation reactions. Due to its strong and versatile solid acid nature, POMs can facilitate the reaction at lower concentrations and temperatures, and therefore become key catalysts in the development and commercialization of several C–C bond formation methods including Friedel-Crafts reactions, dehydrative coupling reactions, Claisen rearrangement and C=C bond formation.

### 2.1. Friedel-Crafts reactions

The Friedel-Crafts (FC) acylation/alkylation is widely used for C–C bond formation. Despite the fact that numerous solid acid catalysts such as zeolites, clays, and Nafion-H have been developed for the reactions, solid POMs catalysts with strong and versatile acidity are attractive for this type of reaction [39].

In 2014, Onda *et al.* prepared a series of POMs ($[S_2V_xM_{18-x}O_{62}]^{(4+x)-}$ and $[AsV_xM_{12-x}O_{40}]^{(3+x)-}$ (M = Mo, W; $x$ = 0-2)) with their protonated form in aqueous-organic solutions by modifying and optimizing the extraction conditions [45]. The acidity of the protonated POMs decreases with increasing total charge or with the increasing number of vanadium atoms in the POMs. Their catalytic ability was investigated in the Friedel-Crafts acylation of anisole with ethyl pyruvate (Scheme 1a). The use of $H_5S_2VW_{17}O_{62}$ led to a higher yield than that achieved with $H_3PW_{12}O_{40}$ and other POMs in this study, giving the desired product in 72% yield. Other types of organic reactions, including the Pinacol rearrangement, acetal formation, and acylation of ethylpyruvate were also successfully catalyzed by these protonated POMs. They exhibited greater catalytic ability than commercially available POMs such as $H_3PM_{12}O_{40}$ and $H_4SiM_{12}O_{40}$ (M = Mo, W). Hu *et al.* found $H_3PMo_{12}O_{40}$ could be used as a bifunctional catalyst, the protons play a critical role in the activation of alcohol, while the polyanion was advantageous for stabilizing the carbocation species. Based on the special catalytic activity of $H_3PMo_{12}O_{40}$, the reaction of various nucleophiles such as 2-naphthols, indoles, benzofuran, and benzothiophene, epoxides (or diols, aldehydes) with diarylmethanols have achieved the green and efficient synthesis of a series of valuable organic molecules (Scheme 1b) [46,47].




**Scheme 1.** POMs-catalyzed Friedel-Crafts reaction for C–C bond formation.

Some POMs-based heterogeneous materials as solid acid catalysts have been developed for the Friedel-Crafts reaction to achieve good recovery and recyclability besides high activity. In 2014, Wang *et al.* prepared a new heteropolyanion-based acidic ionic liquid-functionalized mesoporous copolymer P(VB-VMS)PW by anion-exchange of 1,3-propanesulfonate poly(*N*-vinylimidazole-*co*-divinylbenzene) with $H_3PW_{12}O_{40}$ (Scheme 1c) [48]. This catalyst exhibits a superior yield to benzylating products for the benzylation reaction of arenes with benzyl alcohol under solvent-free conditions (96.7%). The superior acid catalysis performance result from the copolymeric structure, suitable mesoporosity, and enhanced acidity of $HO_3S$-functional groups due to the existence of polyanions. Moreover, the $HO_3S$-functionalized organic-inorganic ionic liquids based on polyoxometalates (QBs-PW) were also achieved by Ezzat Rafiee *et al.* (Scheme 1d) [49]. The materials showed promising catalytic activity for C–C coupling between benzhydrol and aromatic compounds at neat reaction.

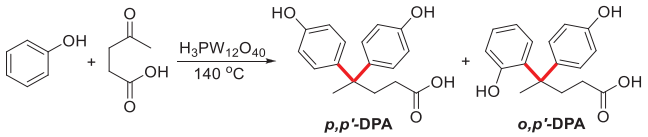
Immobilization of heteropoly acids (HPAs) on suitable supports are an effective method to recycle POMs. In 2015, Manojit Pal *et al.* described an aza-Friedel-Crafts reaction for the synthesis of 3-arylmethyl/diarylmethyl indoles using silica-supported $H_3PMo_{12}O_{40}$ ($H_3PMo_{12}O_{40}$-$SiO_2$) as a heterogeneous catalyst (Scheme 1e) [50]. Various indoles, aldehydes, and *N*,*N*-disubstituted anilines could be converted to indole derivatives in PEG-400 with good yields. This catalytic system represents a greener and safer method to construct 3-arylmethyl/diarylmethyl indoles, and may be used to the synthesis of more complex indole derivatives.

Ji *et al.* utilized the zeolite imidazolate framework (ZIF-67) structure as a support for $H_3PW_{12}O_{40}$ ($H_3PW_{12}O_{40}$@ZIF-67) and develop a highly active, stable, reusable, and environmentally friendly heterogeneous catalyst for the Friedel-Crafts acylation of anisole with benzoyl chloride (Scheme $1f_i$) [51]. Zhang *et al.* synthesized a stable and efficient catalyst for acylation of anisole with benzoyl chloride by niching $H_3PW_{12}O_{40}$ into a Zr-based metal-organic framework ($H_3PW_{12}O_{40}$@Zr-BTC). Heteropoly anions were shown to stabilize the structure of the metalorganic framework, likely due to their anionic templating effect (Scheme $1f_{ii}$) [52].

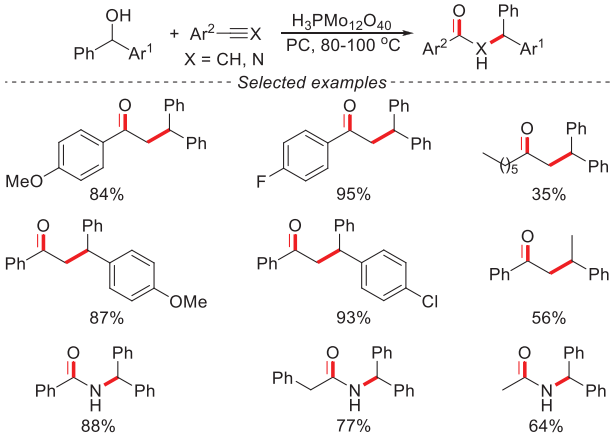
Pezzotta *et al.* immobilized $H_3PW_{12}O_{40}$ onto Santa Barbara Amorphoustype silica (SBA-15) to obtain selective catalysts ($H_3PW_{12}O_{40}$@SBA15) for the resorcinol *tert*–butylation with methyl-tertbutyl ether (Scheme 1g) [53]. They found that the product distribution change depended on the catalyst surface chemistry: 4TBR selectivity can be increased by adjusting the fraction of Brønsted acid sites *versus* Lewis acid sites at the catalyst surface. This work provided a potential direction for the design of catalysts for selective Friedel-Crafts alkylation reactions.

### 2.2. Dehydrative coupling reactions

HPAs and their ionic liquid (IL) salts are attractive for the C–C bond formation *via* the dehydrative coupling reaction. For example, Sathitsuksanoh *et al.* use $H_3PW_{12}O_{40}$ as an efficient catalyst for the




**Scheme 2.** $H_3PW_{12}O_{40}$-catalyzed levulinic acid-phenol condensation reaction.




**Scheme 3.** $H_3PMo_{12}O_{40}$-catalyzed carbohydroxylation of terminal alkynes with benzylic alcohols.

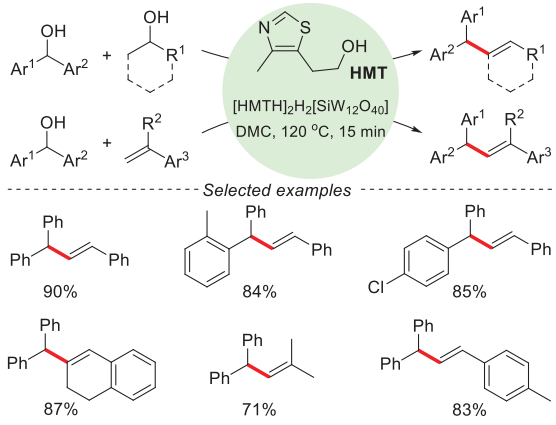
levulinic acid-phenol condensation reaction (Scheme 2) [54]. The results demonstrated that increasing reaction temperature not only accelerated the condensation rate but also it shifted the regioselectivity toward the desired *p,p′*-DPA. This work provides a potential production route for *p,p′*-DPA from biomass.

Hu *et al.* have published several papers on the $H_3PMo_{12}O_{40}$-catalyzed dehydrative coupling reaction for C–C bond construction from diarylmethanols and various nucleophiles [55–57]. For example, they developed a $H_3PMo_{12}O_{40}$-catalyzed carbohydroxylation of terminal alkynes with benzylic alcohols under mild conditions, which provided an efficient and atom-economical method to construct substituted $\beta$-arylethyl ketones (Scheme 3) [55]. This protocol use cheap $H_3PMo_{12}O_{40}$ as catalyst and non-volatile propylene carbonate (PC) as green solvent, the yield and turnover number (TON) up to 95% and 520, respectively.

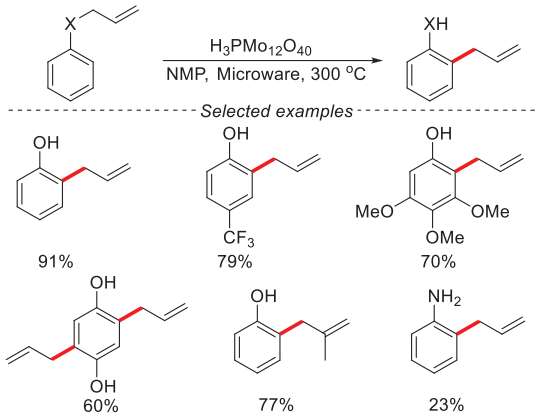
Inspired by the excellent catalytic activity of HPAs in the dehydrative coupling reaction, Hu's group used the *N*-methyl-2-pyrrolidinone (NMP) as precursors to prepare a non-corrosive heteropolyacid-based recyclable ionic liquid, exhibited excellent catalytic performance and reusability in the direct dehydrative coupling of alcohol and alcohol (or olefin) to synthesize various polysubstituted olefins [56]. From the standpoint of environmental sustainability, they further used the inexpensive, nontoxic and biomimetic precursor 5-(2-hydroxyethyl)–4-methylthiazole (HMT) for the synthesis of HPAs-based ionic liquids $[HMTH]_2H_2[SiW_{12}O_{40}]$ (Scheme 4) [57]. This acidic ionic liquid was found to be an efficient heterogeneous catalyst for the direct dehydrative coupling of alcohols with alcohols (or alkenes) in good to excellent yields with dimethyl carbonate (DMC) as a green solvent. Such findings may pave the way for the development of new green chemistry transformations.

### 2.3. Claisen rearrangement

POM catalysts also work for the Claisen rearrangement. Xie *et al.* reported a microwave-accelerated Claisen rearrangement of allyl aryl ethers catalyzed by $H_3PMo_{12}O_{40}$ in NMP at temperatures ranging from 220 °C to 300 °C (Scheme 5) [58]. The catalytic system was also applied in the rearrangement of allyl thiophenol ether, allyl aniline, propynyl phenol ether, and a substituted propenyl phenol ether. This method was found to be useful for preparing several intermediates previously reported in the literature using precious metal catalysts such as Au(I), Ag(I) and Pt(II).




**Scheme 4.** Direct dehydrative coupling of alcohol and alcohol (or olefin).

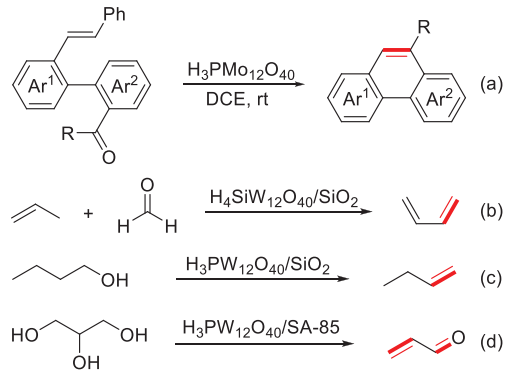



**Scheme 5.** $H_3PMo_{12}O_{40}$-catalyzed Claisen rearrangement.

### 2.4. C=C bond formation

Alkenes play essential roles in organic synthesis due to their active chemistry properties; POMs catalysts receive considerable attention for the C=C bond formation. The carbonyl-olefin metathesis (COM) is one of the most powerful alternatives to the construction of a C=C bond [59]. Recently, Lin *et al.* disclosed a $H_3PMo_{12}O_{40}$-catalyzed COM reaction for the construction of phenanthrene derivatives (Scheme 6a) [31]. The current annulations could realize carbonyl-olefin, carbonyl-alcohol, and acetal-alcohol *in situ* COM reactions and feature mild reaction conditions, simple manipulation, and scalability, making this strategy a promising alternative to the traditional Lewis acid-catalyzed COM reaction.

Gas-phase Prins condensation of alkyl olefins with formaldehyde is an ideal way to synthesize 1,3-dienes, which are widely used for the synthesis of rubbers, elastomers, and resins [60,61]. HPAs supported on silica are frequently used for Prins condensation. Various tungsten and molybdenum HPAs with Si, P, S and Al atoms in their structure efficiently catalyze isobutylene-formaldehyde and isobutylene-isobutanal condensations [62,63]. Recently, Kots *et al.* accomplished the direct one-step butadiene synthesis from propene and formaldehyde for the first time in a continuous flow fixed-bed reactor system (Scheme 6b) [64]. HPAs




**Scheme 6.** POMs-catalyzed C=C bond formation reactions.

supported on silica are shown to be promising catalytic systems for this process. Among different silica-supported HPAs, $H_4SiW_{12}O_{40}$ is selected as the most active and selective in gas-phase Prins condensation into butadiene.

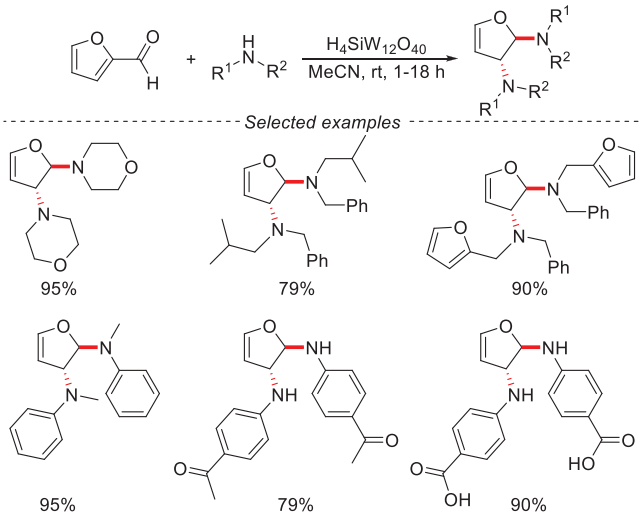
It is also worth mentioning that POMs present good catalytic activity for intramolecular dehydration of alcohols to alkenes [65]. HPAs supported onto the non-precious metal support were used as catalysts for the dehydration of *n*-butanol or ethanol [66,67]. For instance, the selective dehydration of 1-butanol to butenes over different silica-supported HPA catalysts was developed by Shee and co-workers in a continuous flow and isothermally operated fixed-bed reactor (Scheme 6c) [68]. The butanol conversion and butenes selectivity were up to 98.9% and 99.8%, respectively. The gas-phase dehydration of glycerin to acrolein was also achieved by the $H_3PW_{12}O_{40}$ supported on silica-alumina ($H_3PW_{12}O_{40}$/SA-85) (Scheme 6d) [69]. A synergistic effect between $H_3PW_{12}O_{40}$ and SA-85 for $H_3PW_{12}O_{40}$/SA-85 catalyst was observed in the dehydration of glycerin to acrolein. Moreover, the catalytic performance of regenerated $H_3PW_{12}O_{40}$/SA-85 catalyst was almost recovered compared to that of fresh $H_3PW_{12}O_{40}$/SA-85 catalyst. Thus, $H_3PW_{12}O_{40}$/SA-85 served as a stable, reusable, and highly active catalyst for the dehydration of glycerin.

The biomass conversion reactions related to the production of 5-(hydroxymethyl)furfural (HMF) involve the intramolecular dehydration of alcohols. Such reactions catalyzed by POMs have been well studied and are summarized in excellent reviews, which will not be discussed in this paper [18].

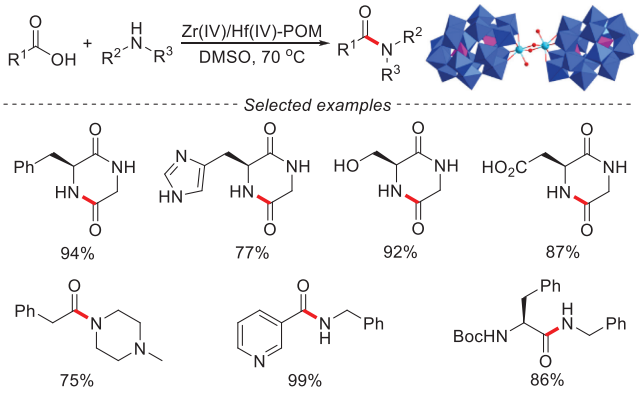
## 3. C–N bond formation

Structures containing C–N bonds are quite prevalent in the field of natural products, pharmaceutical agents, materials, synthetic intermediates, as well as coordination groups. Therefore, the development of the catalytic system for the formation of C–N bonds has become one of the hottest research goals in synthetic chemistry [70,71]. A series of POMs has been developed to construct C–N bonds.

Wang *et al.* employed $H_3PW_{12}O_{40}$ as an efficient and reusable catalyst for the construction of C–N bonds *via* nucleophilic substitution reactions [72]. Various alcohols react with sulfonamides, benzamide, and 4-nitroaniline smoothly, affording the amine derivatives in good yields. The very low catalyst loadings (*ca.* 0.6 mol%) and recyclability of the $H_3PW_{12}O_{40}$ made this protocol attractive. Recently, Lykakis and co-workers developed a $H_4SiW_{12}O_{40}$-catalyzed the three-component reaction of furfural and amines to synthesize trans-*N,N*-4,5-substituted-diaminocyclopenten-2-ones (Scheme 7) [73]. This catalytic reaction of the valuable furfural is characterized by low catalyst loadings




**Scheme 7.** The conversion of furfural to trans-*N,N*-4,5-diaminocyclopenten-2-ones.



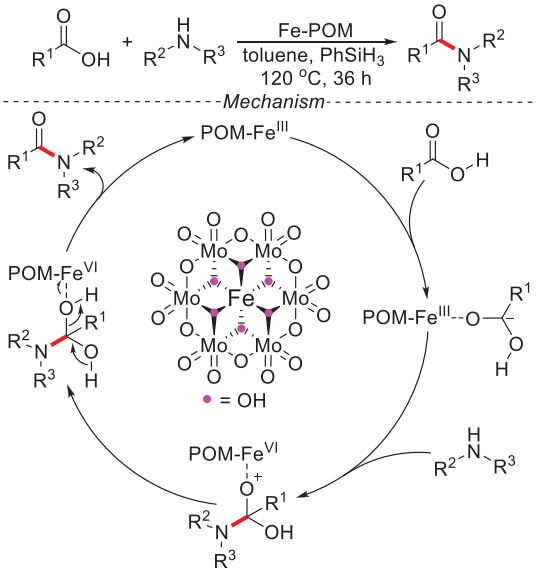

**Scheme 8.** Amide bond formation catalyzed by Zr(IV)- and Hf(IV)-substituted POMs. Color codes of crystal structure: W, blue; P, pink; O, red; Zr or Hf, turquoise.

(0.05 mol%), open air, without additives, short times, broad amines scope, and good to high isolated yields.

The formation of the amide bond is one of the most important reactions in organic chemistry because amides are ubiquitous building blocks in both synthetic and natural products [74,75]. POMs catalyzed the direct amide bond formation from free amines with carboxylic acid derivatives (such as acids, anhydrides or esters) has received increasing attention in recent years [76–78].

In 2019, a simple amide bond formation reaction directly from nonactivated carboxylic acids with free amines was reported [32,33]. Readily available Zr(IV)- and Hf(IV)-substituted POMs are shown to be catalysts for this transformation under mild conditions (Scheme 8). The catalytic system is compatible with a range of functional groups and heterocycles useful for medicinal, agrochemical, and material chemists. Mechanistic investigations revealed that the POM scaffolds can act as inorganic ligands to inhibit the hydrolysis of Zr(IV) and Hf(IV) Lewis acidic metals and preserve their activity to catalyze the amide bond formation. This work provides important insights for the development of catalysts based on POMs as inorganic ligands.

Recently, Yu *et al.* developed an efficient and environment-friendly amidation strategy by using a Fe-POM catalyst ($(NH_4)_3[FeMo_6O_{18}(OH)_6]$) that affords the amides in good yields (Scheme 9) [79]. A number of aryl and alkyl carboxylic acids could be easily converted to amides with a wide range of amines, including primary and secondary amines. Also, the diamides could be obtained *via* the cross-coupling of readily available amines and



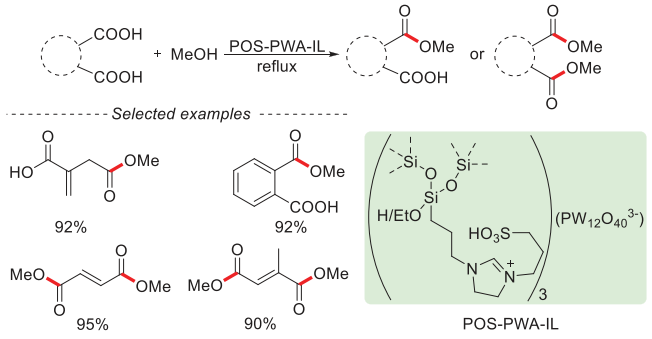

**Scheme 9.** Fe-POM-catalyzed amide bond formation.

carboxylic acids. Furthermore, the Fe-POM catalyst shows high activity and stability after several cycles.

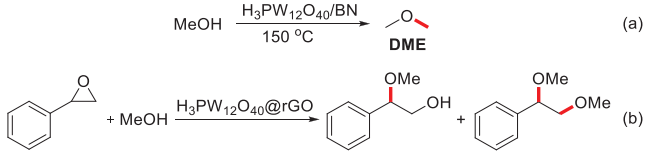
## 4. C–O bond formation

The C–O bond formation represents a fundamentally important transformation and plays an important role in modern organic synthetic chemistry due to the widespread application of oxygen-containing molecules in natural products, antimicrobial agents, biologically active compounds, herbicidal materials, and polymer [80,81]. To date, many POMs-based catalysts have attracted great attention to catalyze the C–O bond formation and the most common reactions include esterification [30,82-86], intermolecular dehydration of alcohols [87] and epoxide ring-opening reaction [88].

For esterification, Rajabi *et al.* prepared a Brønsted acidic, ionic liquid containing, heteropolyacid functionalized polysiloxane by condensation of 3-(1-(3-(trimethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium-3-yl)propane-1-sulfonate in the presence $H_3PW_{12}O_{40}$ (POS-PWA-IL) (Scheme 10) [89]. This compound exhibits excellent catalytic activity for the selective methyl esterification of dicarboxylic acids. The catalytic system showed a remarkable selectivity towards the formation of monoesters, especially in the case of aromatic dicarboxylic acids, which affords an eco-friendly and feasible method for the chemoselective esterification of a variety of dicarboxylic acids with a heterogeneous and reusable catalyst. Other studies on POMs-catalyzed esterification




**Scheme 10.** The selective methyl esterification of dicarboxylic acids catalyzed by POS-PWA-IL.




**Scheme 11.** POMs-catalyzed C–O bond formation reactions.

mainly focus on biomass transformations, biodiesel production, and so on, which have been summarized in excellent reviews but will not be discussed in this paper [6,90].

For intermolecular dehydration of alcohols, Gaigneaux and co-workers supported $H_3PW_{12}O_{40}$ on hexagonal boron nitride (BN) to get highly active catalysts in the gas-phase methanol-to-DME reaction at 150 °C (Scheme 11a) [91]. The support BN is able to increase the accessibility of $H_3PW_{12}O_{40}$ acid sites while preserving their strong acidity, which realized the BN-supported catalyst shows higher methanol conversion than the pure bulk activated $H_3PW_{12}O_{40}$ (showing 10.2% of conversion per milligram of $H_3PW_{12}O_{40}$ *vs.* only 6.3% reached with the pure $H_3PW_{12}O_{40}$).

Recently, Chi *et al.* developed a broad-spectrum hydrothermal approach to construct polyoxometalate-modified reduced graphene oxide (POM@rGO) foam, which worked as a monolith reactor for efficient continuous flow catalysis of epoxide ring-opening reactions (Scheme 11b) [88]. The $H_3PW_{12}O_{40}$@rGO monolith reactor shows excellent catalytic activity and durability for the epoxide ring-opening reactions with alcohols, achieving 99% conversion and 92% selectivity for the methanolysis product in 10 min under ambient conditions without stirring. Furthermore, the $H_3PW_{12}O_{40}$@rGO monolith reactor can continuously work at a high conversion level for 38 h with 99% conversion and over 90% selectivity, reaching a turnover number (TON) as high as 28,044.

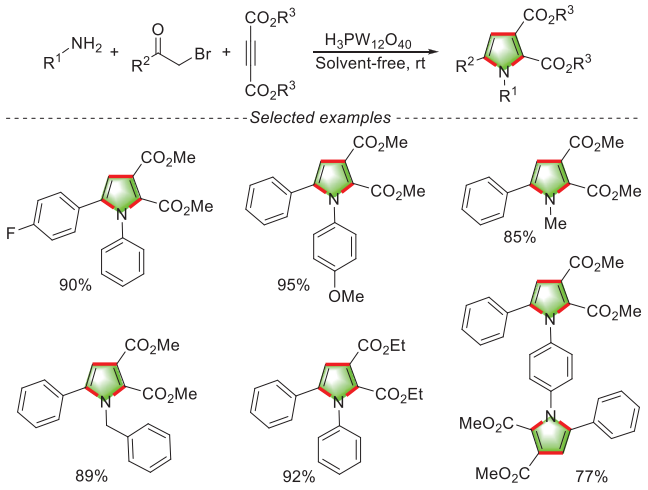
## 5. Heterocycles synthesis

Heterocycles constitute by far one of the largest groups of organic compounds. Various heterocyclic structures are widely found in biologically active natural products, organic materials, agrochemicals, and pharmaceuticals. Consequently, the preparation of heterocycles has undoubtedly been one of the most exciting areas of organic chemistry [92,93]. With increasing demands for a clean environment, researchers are in continuous pursuit of more efficient and green methods for the synthesis of heterocyclic compounds. POMs are believed to have extensive prospects of application for the synthesis of heterocyclics. Various heterocycles including five-membered heterocycles with one heteroatom, five-membered heterocycles with two heteroatoms, six-membered heterocycles with one heteroatom, six-membered heterocycles with two heteroatoms and other heterocycles could be synthesized *via* POMs-catalyzed cyclization reaction.

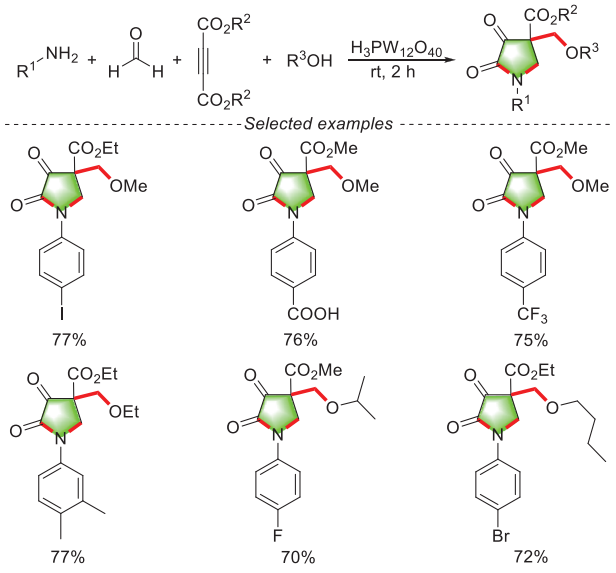
### 5.1. Five-membered heterocycles with one heteroatom

Pyrroles are heterocycles of great importance because of their interesting biological properties such as antibacterial, antioxidant, anti-inflammatory, and anticancer activities [94]. Khosropour and co-workers use $H_3PW_{12}O_{40}$ as a recyclable heterogeneous catalyst for the efficient synthesis of polysubstituted pyrroles (Scheme 12) [95]. Various amines, $\alpha$–bromo ketones and dialkyl acetylenedicarboxylate react smoothly to afford symmetrical and unsymmetrical polysubstituted bis-pyrroles under solvent-free conditions at room temperature, which makes this process attractive for the synthesis of these important heterocyclic compounds.

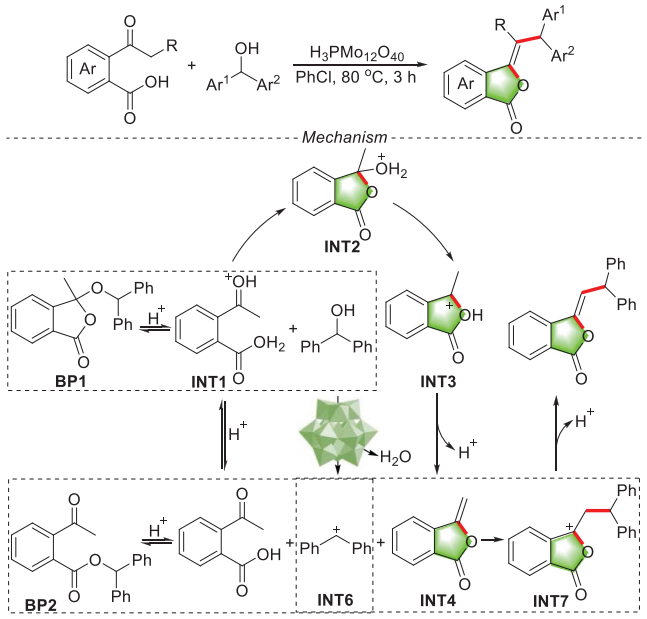
Mukhopadhyay *et al.* established an efficient protocol for the synthesis of dioxopyrrolidine scaffolds using $H_3PW_{12}O_{40}$ as an ef-



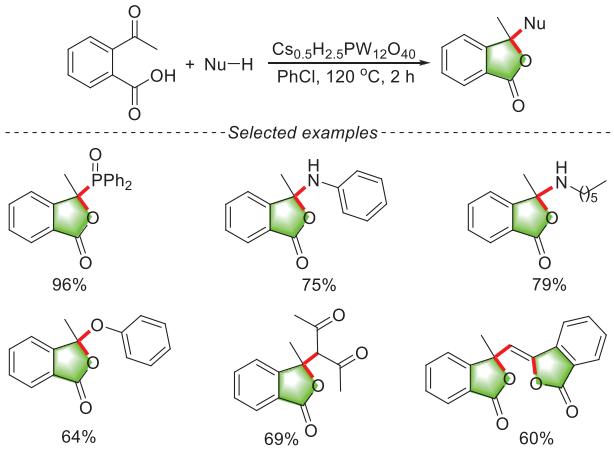

**Scheme 12.** $H_3PW_{12}O_{40}$-catalyzed synthesis of polysubstituted pyrroles.




**Scheme 13.** $H_3PW_{12}O_{40}$-catalyzed synthesis of dioxopyrrolidine scaffolds.




**Scheme 14.** Proposed mechanism for $H_3PMo_{12}O_{40}$-catalyzed cyclization reaction to synthesis (*Z*)-3-ylidenephthalides.




**Scheme 15.** $Cs_{0.5}H_{2.5}PW_{12}O_{40}$-catalyzed synthesis of isobenzofuran-1(3*H*)-ones.

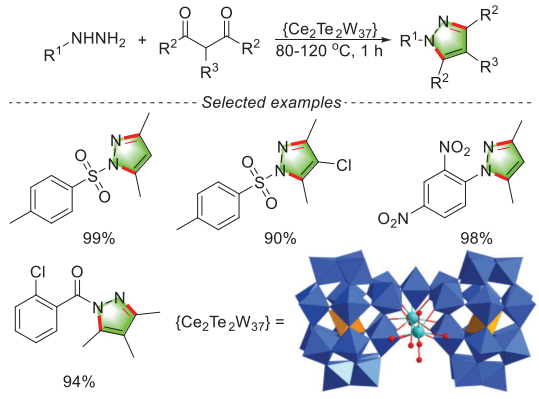
fective catalyst (Scheme 13) [96]. Various amines and dialkyl acetylene dicarboxylates react smoothly with formaldehyde and alcohol at room temperature, delivering the 4,5-dioxopyrrolidines in good yield. This protocol involves environment friendly, cost-effective methodology with a comparatively simple reaction mechanism.

Isobenzofuran-1(3*H*)-ones are important bicyclic lactones that are found in many natural products with broad pharmaceutical and biological activity [97–100]. Liu and co-workers developed a $H_3PMo_{12}O_{40}$-catalyzed cyclization and coupling reaction to regio- and stereoselective synthesis the (*Z*)-3-ylidenephthalides in good to excellent yields, which opens a new reaction space for the selective coupling of carbonyls or carboxyl with alcohols [101]. Detailed mechanistic studies and DFT calculations reveal that the reaction involves the well-known esterification and cyclization reactions, the corresponding by-product would reform the substrates to generate the desired product due to their different stability in the acidic reaction conditions (Scheme 14). This reaction features eco-friendly reaction conditions, facile scalability, and easy derivatization of the products to drugs and bioactive compounds.

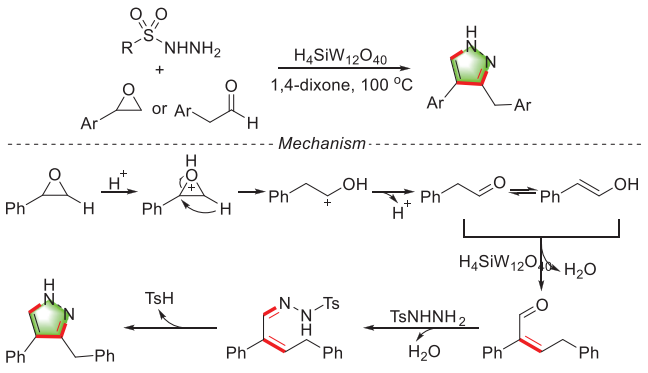
Recently, Yang *et al.* reported a $Cs_{0.5}H_{2.5}PW_{12}O_{40}$-catalyzed cyclization reaction for the synthesis of 3,3′-disubstituted isobenzofuran-1(3*H*)-ones *via* the carbonyl difunctionalization of 2-acylbenzoic acids (Scheme 15) [102]. Various functional groups could be introduced to the isobenzofuran-1(3*H*)-one skeletons *via* the C–P/C–N/C–O/C–C bond formation, which would provide opportunities for the synthesis of potential biologically active molecules.

### 5.2. Five-membered heterocycles with two heteroatoms

Pyrazoles are ubiquitous organic compounds with broad biological activities, such as analgesic, antifungal, and antitumor activities, and are also displayed applications in the preparation of metal-organic complexes, supermolecules, and ligands [103,104]. Owing to their prominent properties, extensive efforts have been made in the construction of pyrazole derivatives [105,106]. The synthesis of pyrazoles catalyzed by POMs is mainly the condensation of 1,3-dicarbonyl compounds or their analogues and hydrazine. Hu's group reported an efficient protocol for the synthesis of pyrazoles *via* condensation of 1,3-diketones with hydrazines/hydrazide employing $Cu_{1.5}PMo_{12}O_{40}$ as the catalyst [107]. A series of pyrazoles was constructed under mild conditions. Subsequently, they synthesized a new Dawson-like POMs




**Scheme 16.** Lewis acid-base synergistic catalyzed synthesis of pyrazoles. Color codes of crystal structure: W, blue; Te, orange; O, red; Ce, aqua.



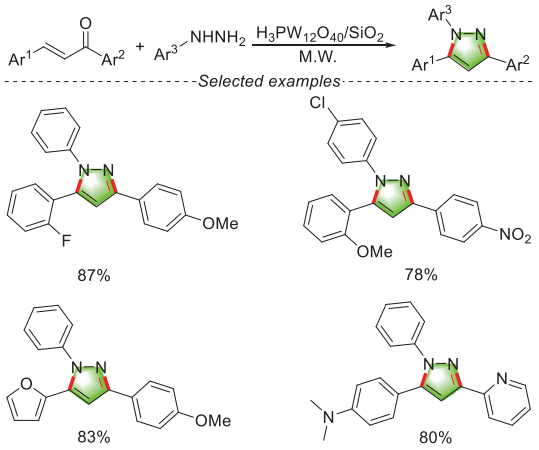

**Scheme 17.** Proposed mechanism for $H_4SiW_{12}O_{40}$-catalyzed cyclization of epoxides/aldehydes and sulfonyl hydrazides.

$(C_2H_8N)_{12}Na_2[H_{10}\{Ce(H_2O)_5\}_2(Te_2W_{37}O_{132})]\cdot 39H_2O$ ($\{Ce_2Te_2W_{37}\}$), which could be used as a bifunctional Lewis acid-base catalyst for the synthesis of pyrazoles and diazepines *via* the condensation of 1,3-diketones with hydrazines/hydrazides or diamines (Scheme 16) [108]. All the products were obtained in excellent yields (up to 99%) and with a high turnover number (up to 4347).

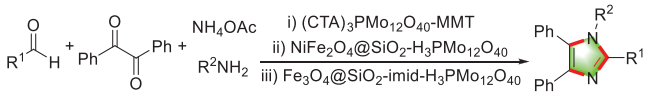
Yang *et al.* synthesized a range of new POMs to catalyze the condensation of 1,3-diketones with hydrazines/hydrazide for the synthesis of pyrazoles [109–114]. Lately, they developed a simple and efficient method for the synthesis of pyrazoles through $H_4SiW_{12}O_{40}$-catalyzed cyclization of epoxides/aldehydes and sulfonyl hydrazides (Scheme 17) [115]. Various epoxides/aldehydes were smoothly reacted with sulfonyl hydrazides to furnish regioselectivity 3,4-disubstituted 1*H*-pyrazoles. They studied the reaction mechanism through control experiments and DFT calculations. The epoxide undergoes Meinwald rearrangement and Aldol reaction to provide $\alpha,\beta$-unsaturated aldehyde, which condensation of hydrazides to generate pyrazole. Taken together with its operational simplicity, readily available reagents, and amenability to gram-scale synthesis, this green reaction will find practical applications for the synthesis of pyrazole derivatives.

Gu and co-workers the synthesis of 1,3,5-trisubstituted 1*H*-pyrazoles from $\alpha,\beta$-unsaturated aldehydes/ketones with hydrazine using catalyst $H_3PW_{12}O_{40}/SiO_2$ under microwave irradiation and solvent-free conditions (Scheme 18) [116]. The merits of the method included the environmental friendly reaction conditions, simple operation, extensive substrates, good yields, and reuse of the $H_3PW_{12}O_{40}/SiO_2$.

Imidazoles as an important class of organic compounds have a wide range of biological and medical applications [117]. The most common method for the preparation of imidazoles is the condensation of benzil, aldehydes, $NH_4OAc$, and amines in the presence of acid catalysts [118,119]. HPAs-based heterogeneous catalysts with strong acidity and recyclability are attractive for this reaction [120]. For example, Masteri-Farahani *et al.* synthesize a $(CTA)_3PMo_{12}O_{40}$-MMT nanocomposite catalyst by immobilizing $H_3PMo_{12}O_{40}$ onto cetyltrimethylammonium ($CTA^+$) modified montmorillonite (MMT) clay, which exhibited remarkable catalytic activity for the synthesis of 2,4,5-trisubstituted imidazoles *via* the condensation of benzil, aldehydes, and $NH_4OAc$ in solvent-free conditions (Scheme $19_i$) [121]. The efficiency is due to the fact that the presence of $CTA^+$ species makes the nanocomposite catalyst hydrophobic and facilitates the accessibility of hydrophobic reactants to active sites in the course of the reaction. Maleki *et al.* prepared a magnetically-recoverable catalyst ($NiFe_2O_4@SiO_2–H_3PMo_{12}O_{40}$) by supporting $H_3PMo_{12}O_{40}$ onto silica-coated $NiFe_2O_4$ nanoparticles, which were used as a heterogeneous and recyclable catalyst for the one-pot synthesis of tri- and tetra-substituted imidazoles under solvent-free conditions (Scheme $19_{ii}$) [122]. Esmaeilpour *et al.* developed an efficient method using $Fe_3O_4@SiO_2$-imid-$H_3PMo_{12}O_{40}$ as a magnetic catalyst for the synthesis of polysubstituted imidazoles under solvent-free conditions and microwave irradiation in excellent yields (Scheme $19_{iii}$) [123].



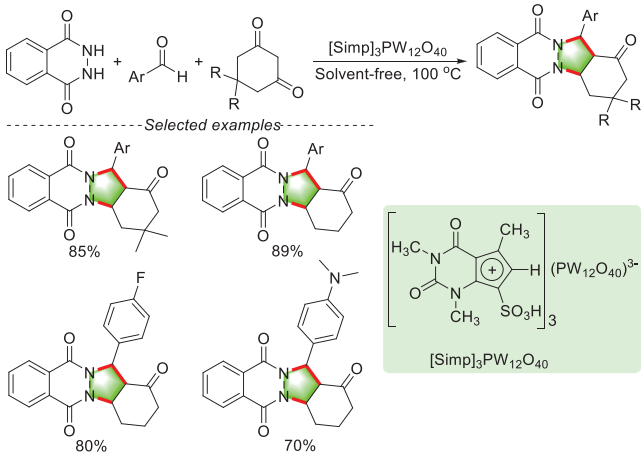

**Scheme 18.** Synthesis of 1,3,5-trisubstituted 1*H*-pyrazoles catalyzed by $H_3PW_{12}O_{40}/SiO_2$.



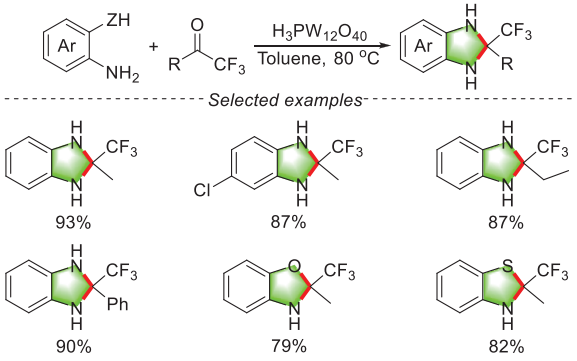

**Scheme 19.** The condensation of benzil, aldehydes, $NH_4OAc$ and amines.

The POMs-catalyzed three-component reactions of dimedone, aldehyde, and phthalhydrazide to give 2*H*-indazolo[2,1-*b*]phthalazine-triones have attracted the interest of chemist [124,125]. Tayebee and co-workers prepared a heteropolyacid-based ionic liquid $[Simp]_3PW_{12}O_{40}$ nanoparticle *via* the reaction of ionic liquid 3-sulfonic acid 1-imidazolopyridinium hydrogen sulfate $[Simp]HSO_4$ with $H_3PW_{12}O_{40}$ (Scheme 20) [126]. This compound can serve as a homogeneous catalyst for the synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones *via* the contraction of dimedone, phthalhydrazide and aromatic aldehydes.

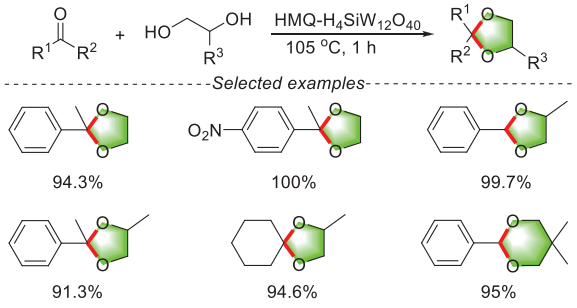
In 2018, Hu's group reported $H_3PW_{12}O_{40}$-catalyzed cyclization of 1,2-phenylenediamines and trifluoromethyl ketones to synthesize trifluoromethylated heterocycles (Scheme 21) [127]. In the presence of 1 mol% of $H_3PW_{12}O_{40}$, various benzimidazolines, benzoxazolines, and benzothiazolines bearing a $CF_3$ group were obtained in excellent yields. The synergistic effect of proton and polyanion in $H_3PW_{12}O_{40}$ was vital for the reaction. This efficient




**Scheme 20.** $[Simp]_3PW_{12}O_{40}$-catalyzed synthesis of 2*H*-indazolo[2,1-*b*]phthalazine-triones.



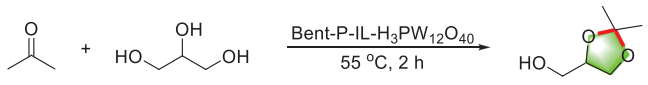

**Scheme 21.** $H_3PW_{12}O_{40}$-catalyzed synthesis of trifluoromethylated heterocycles.



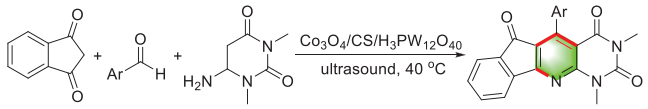

**Scheme 22.** HMQ-$H_4SiW_{12}O_{40}$-catalyzed acetalization of aldehydes/ketones.

and economical method is of great importance for practical applications.

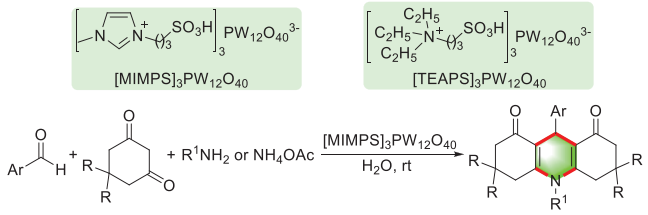
Acetals/ketals are important synthetic intermediates and can be used as starting materials in the production of flavors, disinfectants, and surfactants [128,129]. Acetals and ketals are generally prepared from carbonyl compounds and alcohols *via* the acetalization process in the presence of acid catalysts [130–133]. Due to their stronger acidity, POMs are superior candidates to catalyze the acetalization reaction [134,135]. In 2018, Gong *et al.* prepared a reusable heterogeneous catalyst by combining 8–hydroxy-2-methylquinoline (HMQ) with $H_4SiW_{12}O_{40}$ (HMQ-$H_4SiW_{12}O_{40}$) (Scheme 22) [136]. This catalyst displayed remarkable catalytic performance in the acetalization of ketones with glycol or 1,2-propylene glycol. The corresponding ketals obtained with high yield and 100% selectivity under the optimized reaction conditions. Moreover, the catalyst also exhibited excellent reusability and stability, which is a promising new type of heterogeneous acid catalyst for the synthesis of acetals/ketals.




**Scheme 23.** POMs-catalyzed acetalization of glycerol to solketal.




**Scheme 24.** $Co_3O_4$/CS/PWA-catalyzed synthesis of the indeno[2′,1′:5,6]pyrido[2,3-*d*]pyrimidines.




**Scheme 25.** The synthesis of 1,8-dioxo-decahydroacridine derivatives in water.

Lately, Sadjadi and co-workers prepared a highly selective catalyst by supporting $H_3PW_{12}O_{40}$ on the composite of bentonite and ionic liquid containing acidic polymer (Bent-P-IL-$H_3PW_{12}O_{40}$) (Scheme 23) [137]. This catalyst can selectively acetalize glycerol to solketal, which is potentially applied as beneficial fuel additives. It was found that the resulting catalyst could promote glycerol acetalization under the solvent-free condition at 55 °C to furnish solketal in 99% yield.

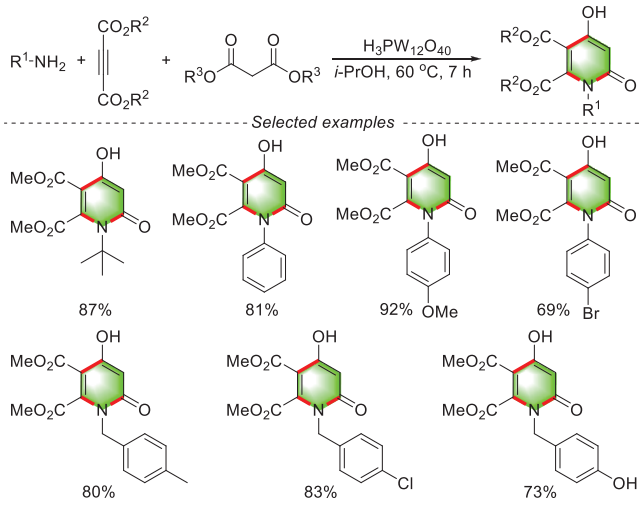
### 5.3. Six-membered heterocycles with one heteroatom

Pyridines and their analogues are key structural skeletons found in many natural and man-made compounds [138,139]. The synthesis of these compounds *via* the POMs-catalyzed multicomponent reactions has been well studied. For instance, a magnetically recoverable nanocomposite including $Co_3O_4$/chitosan/$H_3PW_{12}O_{40}$ ($Co_3O_4$/CS/$H_3PW_{12}O_{40}$) as a heterogeneous catalyst was prepared by Safari *et al.* (Scheme 24) [140]. The synthesis of the indeno[2′,1′:5,6]pyrido[2,3-*d*]pyrimidines was accomplished by the condensation of aldehydes, 1,3-indandione with 1,3-dimethyl-6-aminouracil in the presence of $Co_3O_4$/CS/$H_3PW_{12}O_{40}$ nanocatalyst under ultrasonic irradiation. Then, the catalyst was recovered with an external magnet and reused several times without significant loss of reactivity.

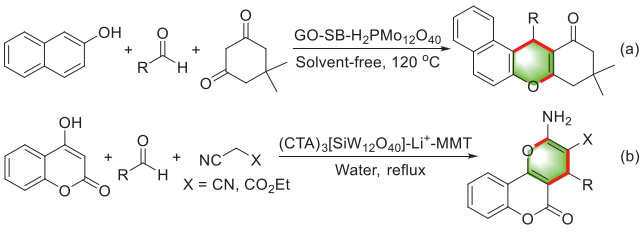
Vahdat's group prepared two nonconventional ionic liquids $[MIMPS]_3PW_{12}O_{40}$ and $[TEAPS]_3PW_{12}O_{40}$ as solid acid catalysts for the synthesis of 1,8-dioxo-decahydroacridine derivatives (Scheme 25) [141]. The sulfonated organic heteropolyacid salts effectively catalyze the condensation of 1,3-cyclohexanediones, aromatic aldehydes and aromatic amines or ammonium acetate in water and show good reusability.

Samzadeh-Kermani reported a $H_3PW_{12}O_{40}$-catalyzed reaction for the synthesis of 2-pyridone derivatives (Scheme 26) [142]. Various amines, acetylenic esters, and malonic esters or acid could convert to the corresponding 2-pyridones in good yield under mild reaction conditions.

4*H*-Pyran scaffolds are the key building block of numerous oxygen-containing heterocyclic natural products possessing diverse biological and pharmacological activities including anti-tumor, antifungal, anti-inflammatory, and so on [143]. Davoodnia and coworkers prepared a new Schiff base (SB) functionalized graphene




**Scheme 26.** $H_3PW_{12}O_{40}$-catalyzed synthesis of 2-pyridone derivatives.



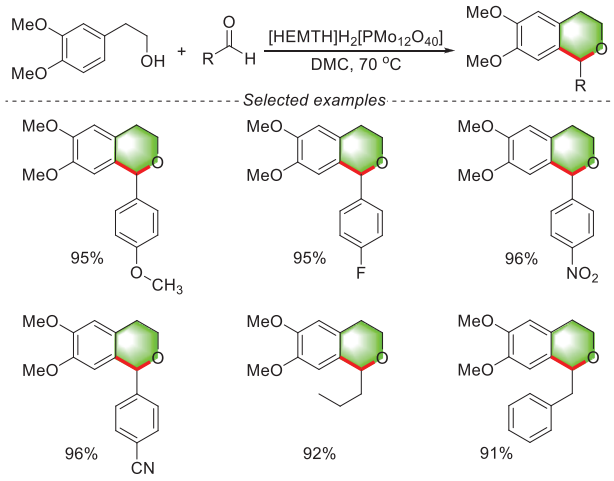

**Scheme 27.** HPA-based catalysts for the synthesis of 4*H*-pyran scaffolds.

oxide (GO) nanosheets containing $H_2PMo_{12}O_{40}^-$ anion, which performed well as a heterogeneous catalyst (GO-SB-$H_2PMo_{12}O_{40}$) for the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones by the reaction of $\beta$-naphthol, aldehydes, and dimedone under solvent-free conditions (Scheme 27a) [144]. Esmayeel *et al.* developed a simple and efficient method for the synthesis of functionalized 2-amino-4*H*-chromene in the presence of a catalytic amount of $(CTA)_3[SiW_{12}O_{40}]$-$Li^+$-MMT (Scheme 27b) [145]. The eco-friendly and reusability catalyst, aqueous conditions, operational simplicity and excellent yields are the most important advantages of this method.

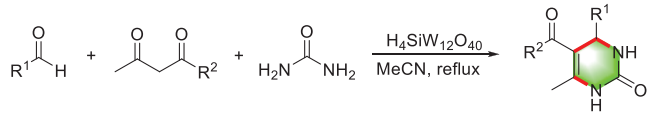
Isochroman is a prominent structure motif and is the core structure of numerous bioactive natural products [146]. Recently, Liu *et al.* prepared a recyclable and efficient heterogeneous catalyst based on the combining $H_3PMo_{12}O_{40}$ and vitamin B1 analogue 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazol-3-ium (HEMT), *i.e.*, [HEMTH]$H_2[PMo_{12}O_{40}]$ (Scheme 28) [147]. Oxa-Pictet-Spengler cyclization of arylethanols and aldehydes were catalyzed to afford various substituted isochromans in moderate conditions with excellent yields. This process using dimethyl carbonate (DMC) as a green solvent and the catalyst could be recycled eight times without significant loss of activity.

### 5.4. Six-membered heterocycles with two heteroatoms

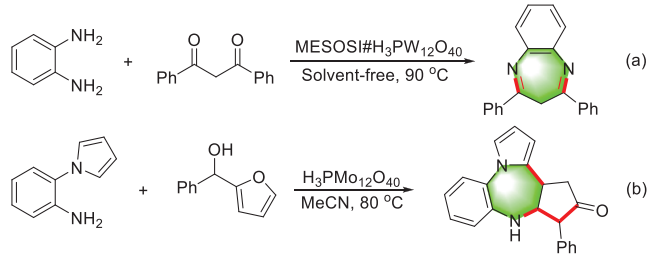
Dihydropyrimidinones (DHPMs) and their derivatives have been reported to possess a wide range of pharmaceutical and therapeutic properties such as antiviral, anticancer, antitumor, and antihypertensive activities [148,149]. The Biginelli reaction is one of the most powerful methods to construct DHPM scaffolds [150–152]. POMs have been utilized as strong solid acids to promote the Biginelli reaction [153]. For example, Hamdi and co-workers use $H_4SiW_{12}O_{40}$ as an excellent acid catalyst for the one-pot synthesis of 3,4-dihydropyrimidinones by the multicomponent condensation of aldehydes, $\beta$-keto esters, and urea (Scheme 29) [154]. HPAs-based heterogeneous catalysts such as $H_3PW_{12}O_{40}$-based ionic liquids, and HPAs supported on bentonite, were also used to catalyze the Biginelli reaction for the synthesis of DHPMs.




**Scheme 28.** [HEMTH]$H_2[PMo_{12}O_{40}]$-catalyzed Oxa-Pictet-Spengler cyclization reaction.



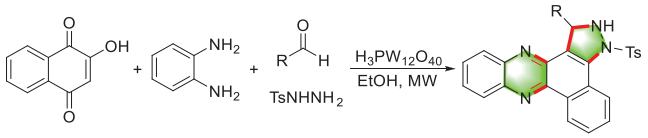

**Scheme 29.** $H_4SiW_{12}O_{40}$-catalyzed Biginelli reaction for dihydropyrimidinones.



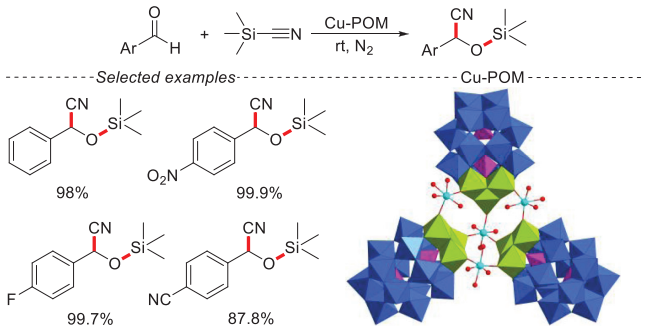

**Scheme 30.** POMs-catalyzed synthesis of benzodiazepines.

### 5.5. Other heterocycles

Benzodiazepines are an important class of bio-active heterocycles, which are widely applied as antiinflammatory, antitumor, and antifungal agents [155]. POMs-catalyzed the direct condensation of 1,3-diketones with diamines is an efficient method for the synthesis of benzodiazepines [156]. In 2020, Rodríguez-Castellón *et al.* prepared a series of solid acid catalysts using mesoporous silica (MESOSI) as support and $H_3PW_{12}O_{40}$ as active phase, which was incorporated by impregnation (MESOSI#$H_3PW_{12}O_{40}$) and inclusion (MESOSI@$H_3PW_{12}O_{40}$) (Scheme 30a) [157]. The potentiometric titration studies revealed that MESOSI#$H_3PW_{12}O_{40}$ catalysts exhibited greater acid strength than MESOSI@$H_3PW_{12}O_{40}$. The total acidity is strongly dependent on the method used to incorporate the heteropolyacid but almost independent of the $H_3PW_{12}O_{40}$ content. Although both series of catalysts (MESOSI@$H_3PW_{12}O_{40}$ and MESOSI#$H_3PW_{12}O_{40}$) are very active and highly selective in the synthesis of 3*H*-1,5-benzodiazepines in solvent-free conditions, the better catalytic performance of the latter is due to its higher acidic properties. D. Mane and co-workers developed a $H_3PMo_{12}O_{40}$-catalyzed domino reaction between furan-2-




**Scheme 31.** $H_3PW_{12}O_{40}$-catalyzed multicomponent condensation reaction.




**Scheme 32.** Cu-POM-catalyzed cyanosilylation of aldehydes. Color codes of crystal structure: W, blue; P, pink; Nb, Lime; O, red; Cu, turquiose.

yl(phenyl) methanol and 2-(1*H*-pyrrol-1-yl) aniline for the synthesis of 1,4-benzodiazepine scaffolds (Scheme 30b) [158].

A $H_3PW_{12}O_{40}$-catalyzed multicomponent condensation reaction between 2-hydroxynaphthalene-1,4–dione, *o*-phenylenediamine, aromatic aldehydes, and 4-methylbenzenesulfonohydrazide was developed by Mohebat *et al.* (Scheme 31) [159]. A novel series of 1*H*-benzo[*a*]pyrazolo[3,4-*c*]phenazine derivatives were prepared under microwave irradiation (MW) in EtOH. This reaction features the atom economy, inexpensive reagents, reusability of $H_3PW_{12}O_{40}$.

## 6. Cyanosilylation and hydrolysis reactions

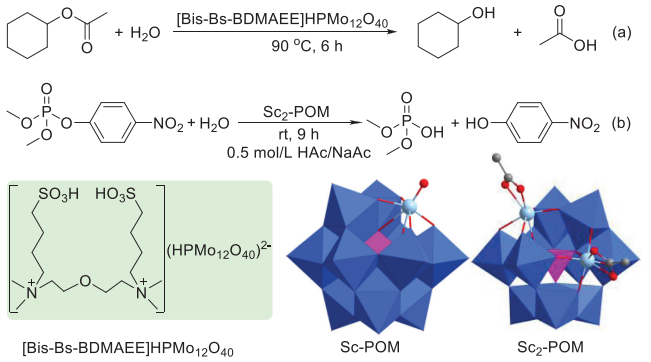
The diversity of POMs means that POMs can promote other acid-catalyzed reactions besides the aforementioned examples. In fact, some reactions have been well studied, which encouraged scientists to develop more reactions catalyzed by POMs [160].

### 6.1. Cyanosilylation of carbonyl compounds

The cyanosilylation of carbonyl compounds reaction is an important method to prepare cyanohydrins, which can be further converted into value-added chemicals such as $\alpha$–hydroxy acids, $\beta$-aminoalcohols and drug molecules [161]. Transition-metal-substituted POMs especially rare-earth-substituted POMs are charming catalyst candidates for the cyanosilylation of aldehydes/ketones with trimethylsilyl cyanide (TMSCN) due to the strong Lewis acidity of substituted metals [162–164]. A new transition-metal-substituted POM: $H_{19}[Cu_4(H_2O)_{15}(P_2W_{15}Nb_3O_{62})_3]\cdot 21H_2O$ (Cu-POM) is effective for the cyanosilylation reaction of aldehydes with TMSCN (Scheme 32) [165]. Under ambient temperature and solvent-free conditions, various aldehydes could convert into the corresponding products with excellent yield. The cycle experiment showed that Cu-POM can be reused for at least five cycles without significant loss of catalytic activity.

### 6.2. Hydrolysis reactions

Hydrolysis is one of the most classical acid catalytic reactions, POMs exhibited unique catalytic activity in hydrolysis reactions due to their designable acidity and stability [166,167]. In 2018, Liu *et al.* prepared a novel dual-$SO_3H$-functionalized $H_3PMo_{12}O_{40}$-based solid acid ([Bis-Bs-BDMAEE]$HPMo_{12}O_{40}$), which




**Scheme 33.** POMs-catalyzed hydrolysis reactions. Color codes of crystal structures: W, blue; P, pink; O, red; C, gray; Sc, pale blue.

was used in the hydrolysis of cyclohexyl acetate into cyclohexanol (Scheme 33a) [168]. Under the optimal conditions (catalyst dosage of 11.0 wt% (based on the mass of all reactants), 90 °C, 6 h), the conversion of cyclohexyl acetate and selectivity for cyclohexanol reached 90.56% and 94.86%, respectively. Moreover, the catalyst displayed good repeated utilization and could be reused five times at least, which developed an efficient and stable catalyst for the hydrolysis of cyclohexyl acetate to cyclohexanol.

Recently, Hu's group synthesized two novel Sc-substituted Keggin-type POMs $K_4[Sc(H_2O)PW_{11}O_{39}]\cdot 22H_2O\cdot 2CH_3COOK$ (Sc-POM) and $Na_7[Sc_2(CH_3COO)_2PW_{10}O_{38}]\cdot 10H_2O\cdot 2CH_3COONa$ ($Sc_2$-POM) (Scheme 33b) [169]. The two compounds can effectively catalyze the hydrolysis of nerve agent simulant, dimethyl 4-nitrophenyl phosphate (DMNP). 97% of DMNP could be convent to nontoxic products catalyzed by $Sc_2$-POM under optimal conditions. This study provided important guidance for the design and application of Sc-based hydrolysis catalysts and contributed the comprehension of the decontamination mechanism catalyzed by Lewis acidic centers.

## 7. Conclusion and outlook

POMs as a kind of green, inexpensive, and stable metal-oxide clusters can be employed as an efficient acidic catalyst for various organic reactions. In this review, we described the recent advances (mainly from 2015 to 2022) of POMs acid-catalyzed organic reactions including the C–C bond formation reactions, C–N bond formation reactions, C–O bond formation reactions, construction of heterocyclic reactions, cyanosilylation and hydrolysis reactions. In these reactions, POMs catalysts elegantly exhibit their strong and designable acidity and stability. The reviewed examples fully illustrate that the acid catalytic properties of POMs (such as Brønsted acid, Lewis acid, or bifunctional synergistic catalysis) can be tuned finely upon the consideration of satisfying the requirements of different reactions. In brief, POMs acid catalysts are inherently stable, effective, and designable. These advantages make POMs catalysts outstanding candidates for industrial acid catalysts.

It is found that these acid-catalyzed reactions have been mainly based on the Brønsted acidity of POMs, whereas the Lewis acid or bifunctional synergistic catalyzed reactions were very limited in this review. For Lewis acid catalysis, POMs substituted by metals can be regarded as metal complexes with multidentate oxo ligands. Theoretically, those catalyzed by organometallic complexes can probably be promoted by POMs catalysts with appropriate transition metals and inorganic oxygen ligands. The bulky inorganic ligands are likely to yield interesting results. In addition, POMs with both Brønsted acid and Lewis acid activity could make some cascade reactions proceed smoothly in one pot, and thus af-

ford simple schemes for organic synthesis. Thus, further expansion of POMs acid-catalyzed reactions will be highly expected.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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