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Focus Review Article

$(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ as a Heterogeneous Reusable Catalyst for Organic Reactions: Mini-Review

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Abstract: Over the last decade, polyoxometalates (POMs) have attracted extensive attention as homogeneous and heterogeneous catalysts used for organic transformation. The most important feature of POMs is the possibility of the catalyst design at atomic/molecular levels. They could also be used as multifunctional catalysts, based on different metal atoms and heteroatoms in their structure, counter cations, and second structures. In this review, application of the Keplerate-type giant nanoporous isopolyoxomolybdate $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}\text{-}(CH_3COO)_{30}(H_2O)_{72}]$, denoted $\{Mo_{132}\}$ was reviewed in the synthesis of many organic reactions as a heterogeneous solid acid catalyst, which significantly improved the synthesis condition of various organic reactions in the recent years from 2013 to 2019.

Key words: Polyoxometalates (POMs), Nanocatalyst, Nanoporous, Organic reactions.

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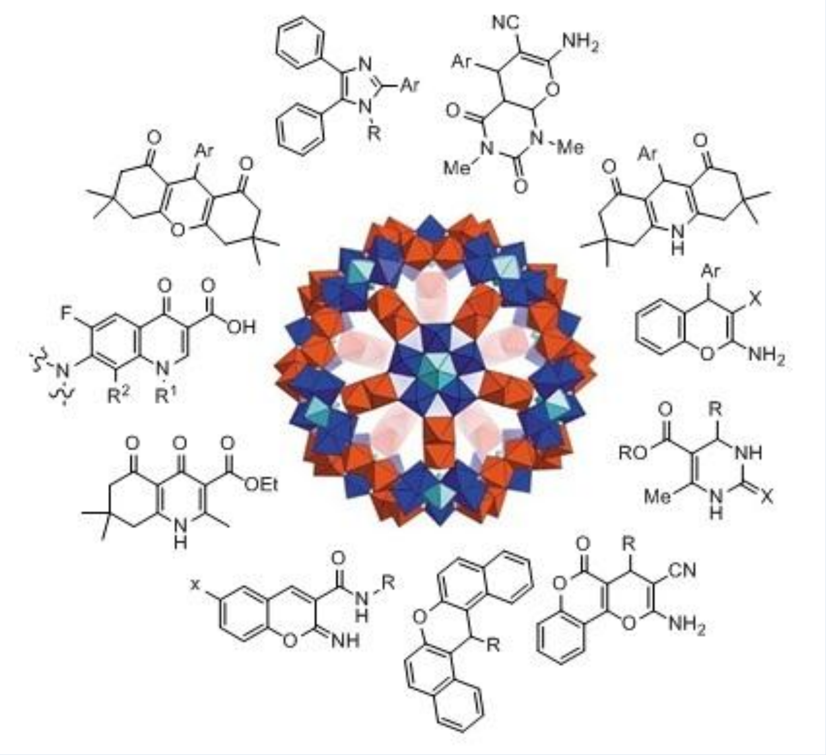
Graphical Abstract:



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Biography:

Ahmad Nakhaei was born in 1987 in Zahedan, Sistan and Baluchestan, Iran. He obtained his B.Sc. degree in applied chemistry from Sistan and Baluchestan University, Zahedan, Iran, in 2010. He received his M.Sc. degree in 2012 in organic chemistry from Payame Noor University, Mashhad, Iran, under the supervision of Dr. Hooshang Vahedi and Ph.D degree at Islamic Azad University, Mashhad, Iran, in 2015 under the supervision of Prof. Abolghasem Davoodnia. His research interests are in the area of the synthesis of heterocyclic compounds, catalysis, synthetic methodology, and computational chemistry.

Abolghasem Davoodnia was born in 1971, Mashhad, Iran. He studied chemistry at Tehran University, Tehran, Iran, where he received BSc in 1994. He received his MSc degree in organic chemistry in 1997 from Ferdowsi University of Mashhad, Mashhad, Iran, under the supervision of Professor Majid M. Heravi and completed his PhD in organic chemistry in 2002 under the supervision of Prof. Mehdi Bakavoli at the same university. Currently, he is working as a professor at the Chemistry Department, Mashhad Branch, Islamic Azad University, Mashhad, Iran. He has published over 150 peer-reviewed articles in ISI journals. His current research interest is on heterocyclic chemistry, catalysis and new synthetic methodologies.

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1. Introduction

Polyoxometalates (POMs) are a large class of metal oxide cluster compounds, consisting of transition metal atoms bridged by oxygen atoms. POMs have been studied extensively because they possess interesting electronic and molecular properties, such as wide-ranging redox potentials, acidities, polarities, and solubilities. Based on their attractive properties, POMs have also been used in a variety of differentvarious application, including, catalysis, biomedicine, magnetism, nanotechnology, and materials science [1]. There has been a growing interest during the last few years in the synthesis of nanotubularusing materials containing POMs such as POM-based titanium nanotubes [2] and POM-organic hybrid nanotubes [3]. These new types of nanotubes possess the functional properties of POMs as well as some of the key advantages associated with tubular systems, including, for example, enhanced catalytic and photochemical properties [2].

Müller *et al*. [4] reported the discovery of giant nanosized porous Keplerate-type POMs. The Keplerate and giant nanosized porous POMs possess unique features and properties that could allow them to be considered as the basis for a new area of nanochemistry and nanomaterials science [5]. These materials have also found numerous application in fundamental and applied sciences, where they have been used to model passive cation transport through membranes, as well as being evaluated in terms of their encapsulation, nanoseparation chemistry, magnetic, and optical properties [6].

As a result of our interest in the development of environmentally friendly methods for the synthesis of organic compounds using reusable catalysts [7-32], we are demanded to review previously reported evidences of the application of $\{Mo_{132}\}$ as heterogeneous solid acid catalyst in the synthesis of various organic reactions. The {Mo_{132}} compound was reported for the first time by Muller and coworkers [4]. Based on theoretical calculations, a diameter of 2.9 nm was reported for this giant ball (Figure 1) [4]. The characterization of the molybdenum cluster of this material was reported for the first time by Polarz and coworkers using TEM [5]. The TEM picture image clearly showed that the clusters possessed a periodic structure with an average diameter of approximately 3 nm. This experimentally determined diameter was in good agreement with the theoretical value for the inner diameter of the ball-shaped POM [4]. With attention to the high catalytic activity of {Mo_{132}} and many other advantages reported by Muller and co-workers, in this review we wish to encourage other scientists to apply this material in the other aspects of chemistry, as well.

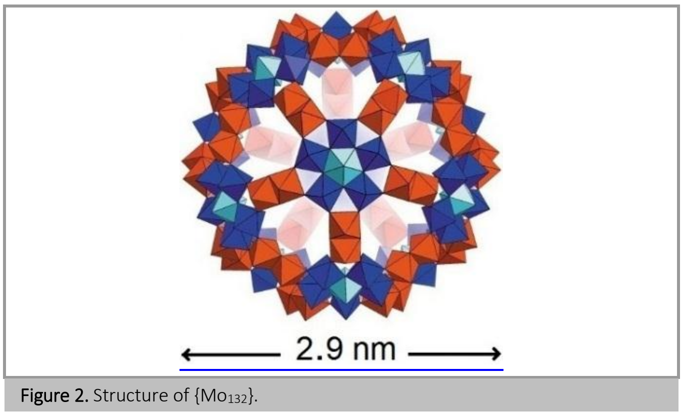


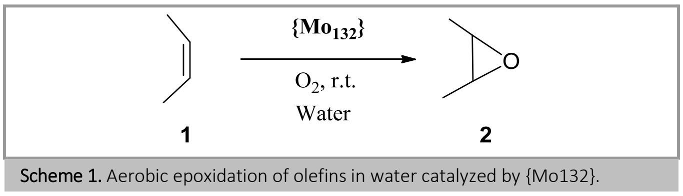
Figure 2. Structure of {Mo_{132}}.

2. Application of {Mo_{132}} in organic transformation

{Mo_{132}} as an outstanding and heterogeneous catalyst has been used in many organic reactions. In the following parts, application of this catalyst in various organic transformations is discussed.

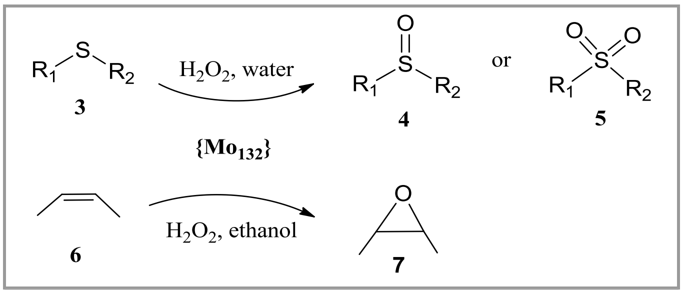
2.1. Olefins and sulfides oxidation

Epoxidation of olefins is an important reaction in the laboratory as well as in chemical industry [33-35], because epoxides are widely used as raw materials for epoxy resins, paints, surfactants, and are intermediates in organic syntheses [36]. Rezaeifard *et al.* [37] reported the aerobic epoxidation of olefins **1** by the aid of {Mo_{132}} as catalyst in water at ambient temperature. All the epoxides are prepared at short reaction time and high yields (Scheme 1).



Scheme 1. Aerobic epoxidation of olefins in water catalyzed by {Mo132}.

Also, Rezaeifard and co-workers reported selective oxidation of sulfides **3** to sulfoxides **4** and sulfones **5** in water and epoxidation of olefins **6** in ethanol with hydrogen peroxide catalyzed by Keplerate nanoball polyoxomolybdate {Mo_{132}} under heterogeneous conditions (Scheme 2). The reaction has been carried out in high yields and mild situation. In addition, catalyst reused several times without any appreciable decrease in catalytic activity and selectivity [33].



Scheme 2. Oxidation of sulfides and olefins using H_2O_2 catalyzed by a {Mo_{132}} nanoball.

2.2. Application of {Mo_{132}} in the synthesis of heterocyclic compounds

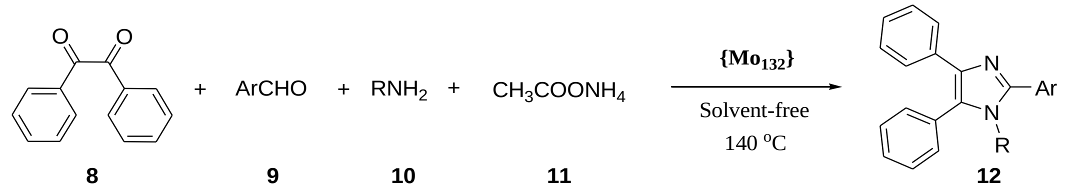
For the first time, in this research study, the {Mo_{132}} applied as heterogeneous catalyst in the synthesis of heterocyclic compounds [38]. This material improved the reaction condition in the synthesis of various heterocyclic compounds compared to the previously evidences as discussed in the following sections.

2.2.1 Imidazoles synthesis

The imidazole ring system is a nitrogen-containing substructure that plays an important role in numerous biochemical processes. This system can be found in a large number of natural products and pharmacologically active compounds [39-41]. Multisubstituted imidazoles showed interesting biological properties, including antibacterial [42], analgesic [43] and glucagon receptor antagonism [44] activity. Several substituted imidazoles have also been reported as inhibitors of p38 MAP kinase [45] and B-Raf kinase [46]. Many procedures were introduced for synthesis of these compounds [47-51]; however, they need to be improved. So, we have decided to present a new synthesis methodology for the 1,2,4,5-tetrasubstituted imidazoles **12** by the reaction of Benzyl **8**, aromatic aldehyde **9**, primary amine **10**, ammonium acetate **11**, and {Mo_{132}} as catalyst (Scheme 3) [38].

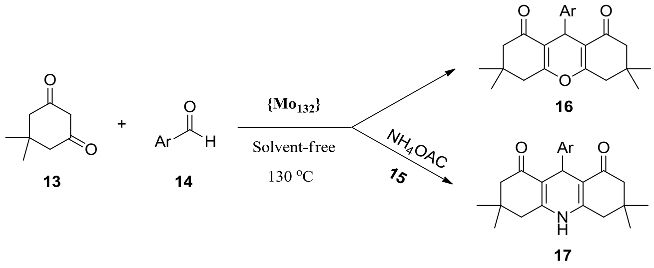
2.2.2. Acridines and xanthenes synthesis

Compounds derived from xanthenes and 1,4-dihydropyridines (1,4-DHPs) are of importance as they have various biological activities including, antibacterial [52], antiinflammatory [53], antimicrobial [54], antitubercular [55], neuroprotectant [56], and insecticidal activities [57]. A number of xanthenes found uses in laser



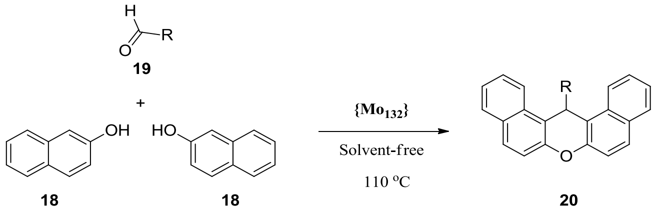
Scheme 3. $\{Mo_{132}\}$ catalyzed synthesis of 1,2,4,5-tetrasubstituted imidazoles.

technologies [58], dyes [59], and fluorescent materials for visualization of biomolecules [60]. 1,4-DHPs are also commercially used as calcium channel blockers for the cardiovascular diseases treatment, including hypertension [61]. Based on the mentioned benefits, we presented $\{Mo_{132}\}$ catalyzed reaction of dimedone **13**, and an aromatic aldehyde **14**, for the synthesis of 1,8-dioxo-octahydroxanthenes **16** or dimedone **13**, aromatic aldehyde **14**, and ammonium acetate **15** for the preparation of 1,8-dioxodecahydroacridines **17**. The method was very fast and the desired products were obtained only within a few seconds in high yields under solvent-free conditions at 130 °C (Scheme 4) [62].



Scheme 4. Synthesis of 1,8-dioxo-octahydroxanthenes and 1,8-dioxodecahydroacridines catalyzed by $\{Mo_{132}\}$.

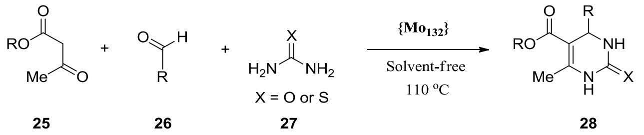
The next report of application of $\{Mo_{132}\}$ for the preparation of xanthenes presented by our group in the synthesis of 14-substituted-14*H*-dibenzo [*a*,*j*]xanthenes **20** *via* a mixture of β-naphthol **18**, and aromatic/aliphatic aldehyde **19** under solvent-free condition at 110 °C for 13-18 min (Scheme 5) [63]. By comparing our procedure with previous methods [64-69], the $\{Mo_{132}\}$ catalyst performed better for this reaction.



Scheme 5. $\{Mo_{132}\}$ catalyzed synthesis of 14-substituted-14*H*-dibenzo[*a*,*j*]xanthenes.

2.2.3. 1,4-Dihydropyridines synthesis

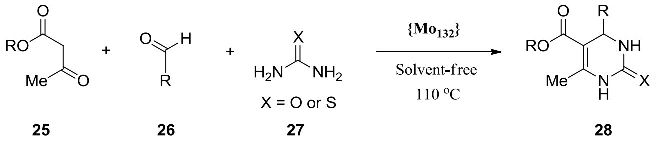
1,4-dihydropyridine plays significant roles in synthesis of valuable organic compounds that have various biological properties [70-72]. Many synthetic protocols were developed to accelerate the rate of 1,4-DHPs reaction and to improve the yield at the presence of various catalysts [73-76]. Despite all of these useful methods, further improvement of the synthesis process was essential. Accordingly, we introduced catalytic activity of $\{Mo_{132}\}$ in the synthesis of 1,4-DHPs **24** by the Hantzsch condensation of an aldehyde **21**, ethyl acetoacetate **22**, and ammonium acetate **23**. The procedure was very fast and mild without any undesired product (scheme 6) [77].



Scheme 6. $\{Mo_{132}\}$-catalyzed formation of 1,4-DHPs.

2.2.4. 3,4-dihydropyrimidin-2(1H)-ones/thiones synthesis

3,4-dihydropyrimidin-2(*1H*)-one/thione (DHPM) derivatives were first synthesized by Biginelli in 1891 [78]. Many scientists presented various methods of DHPMs [79-82] reported a wide range biological activities such as antiviral, antitumor, antibacterial and anti-inflammatory properties [83-86]. Also, these compounds have emerged as the integral backbones of several calcium channel blockers [87], antihypertensive agents [88], α_{1a}-adrenergic antagonists [89], and neuropeptide antagonists [90]. With attention to all of these unique properties, we decided to report a new facile synthesis of 3,4-dihydropyrimidin-2(*1H*)-ones/ thiones **28** *via* Biginelli reaction of β-ketoesters **25**, aromatic aldehydes **26**, urea or thiourea **27**, and $\{Mo_{132}\}$ as catalyst at 110 °C for 12-19 min (Scheme 7) [91].

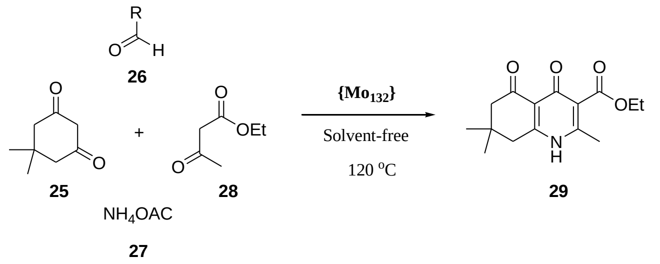


Scheme 7. $\{Mo_{132}\}$ catalyzed synthesis of DHPMs.

2.2.5. Polyhydroquinolines synthesis

polyhydroquinolines synthesis has attracted a great deal of attention due to their biological and pharmacological activities [92-94]. So, we reported

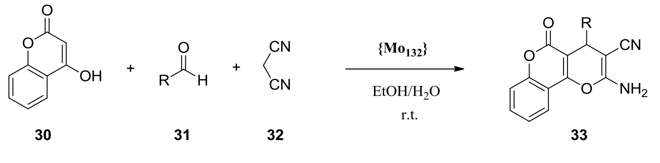
{Mo_{132}} catalyzed Hantszch condensation of dimedone **25**, an aldehyde **26**, ammonium acetate **27**, and ethyl acetoacetate **28** to prepare polyhydroquinoline **29** derivatives under solvent-free condition (Scheme 8) [95]. The presented method was fast and high yielding compared to the previously reported literatures [96-98].



Scheme 8. Synthesis of polyhydroquinolines catalyzed by {Mo_{132}}.

2.2.6. *Pyranochromenes synthesis*

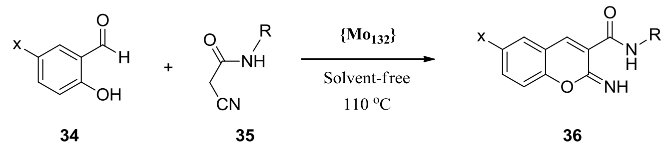
Synthesis of the dihydropyrano[3,2-*c*]chromenes **33** with biological and pharmacological properties such as spasmolytic, diuretic, anticoagulant, anticancer, and anti-anaphylactic activities [99-101] is currently of a great interest. Therefore, we introduced a new synthesis method for synthesis of these compounds by using the one-pot reaction of 4-hydroxycoumarin **30**, an aldehyde **31**, malononitrile **32**, and {Mo_{132}} as a new catalyst (Scheme 9) [102]. This new method presented a facile and fast synthesis pathway compared to the previously reports [103-105].



Scheme 9. Synthesis of dihydropyrano[3,2-*c*]chromenes catalysed by {Mo_{132}}.

2.2.7. *Functionalized 2-imino-2H-chromenes synthesis*

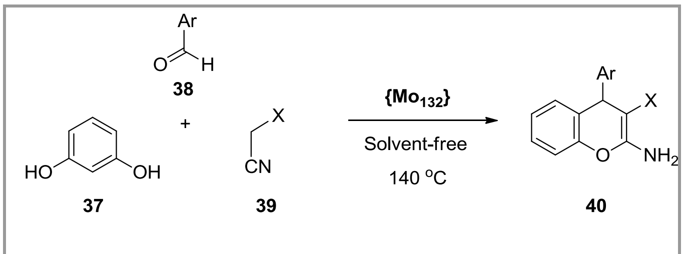
Functionalized 2-iminochromenes have been a subject of increasing interest and many of these compounds have been used as protein tyrosine kinase (PTK) inhibitors [106], anti-Alzheimer [107], antimicrobial [108], anticancer [109], and cytotoxic agents [110]. These compounds are also important intermediates in chemical synthesis [111]. The classic method for synthesis of these compounds is the reaction of salicylaldehydes with active methylene compounds prompted by catalysts such as potassium phthalimide [112], $NaHCO_3$ and Na_2CO_3 [113], polyethylene polyamine functionalized polyacrylonitrile fiber [114], and piperidine in the presence [115] or absence [116] of microwave irradiation. Davoodnia and coworkers reported the application of {Mo_{132}} as catalyst in the synthesis of *N*-alkyl-2-imino-2*H*-chromene-3-carboxamides **36**. This is done by reaction of salicylaldehydes **34** with *N*-alkyl-2-cyanoacetamides **35** using {Mo_{132}} under solvent-free conditions [117]. The reaction has been carried out at elevated temperature leading to a high yield of products **36** (Scheme 10).



Scheme 10. {Mo_{132}} catalyzed synthesis of *N*-alkyl-2-imino-2*H*-chromene-3-carboxamides.

2.2.8. *Functionalized 2-amino-4H-chromenes synthesis*

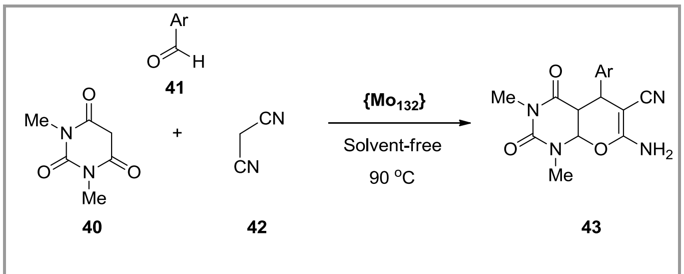
Functionalized 2-amino-4*H*-chromenes with pharmacological and biological activities which attracted chemist's attention [118-121]. The efficient synthesis of 2-amino-4-aryl-7-hydroxy-4*H*-chromenes **40** *via* a three-component cyclocondensation between resorcinol **37**, aromatic aldehydes **38**, and ethyl cyanoacetate or malononitrile **39** in the presence of {Mo_{132}} under solvent-free condition at 140 °C has been described by Davoodnia and co-workers (Scheme 11) [122].



Scheme 11. Synthesis of 2-amino-4-aryl-7-hydroxy-4*H*-chromenes catalyzed by {Mo_{132}}

2.2.9. *Pyrano[2,3-d]pyrimidines synthesis*

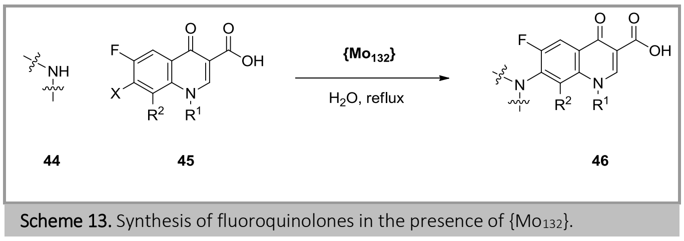
Pyrano[2,3-*d*]pyrimidines have shown pharmacological properties such as antitumor [123], cardiotonic [124-126], hepatoprotective [127], antihypertensive [128] and antibronchitic activity [129]. As shown in Scheme 12, three-component condensation reaction of 1,3-dimethylbarbituric acid, aromatic aldehydes, and malononitrile obtained pyrano[2,3-*d*]pyrimidines derivatives in high yields using catalytic effect of {Mo_{132}} under solvent-free conditions at 90 °C [130].



Scheme 12. Synthesis of pyrano[2,3-*d*]pyrimidines catalyzed by {Mo_{132}}.

2.2.10. Fluoroquinolones synthesis

Fluoroquinolones have been a class of important of synthetic antibacterial agents which are widely used in treatment of infectious diseases [131]. These compounds act with an excellent activity against gram-negative and comparatively moderate against gram-positive bacteria [132]. Mechanism of action of these compounds is based on inhibition of an enzyme which is essential for bacterial DNA replication (called DNA gyrase) [133]. Also some fluoroquinolones possess anticancer and even anti-HIV activities [134]. Therefore, we have reported fast synthesis of various antibacterial fluoroquinolone compounds **46** by the direct amination of 7-halo-6-fluoroquinolone-3-carboxylic acids **45** with variety of piperazine derivatives **44** and (4aR,7aR)-octahydro-*1H*-pyrrolo(3,4-b) pyridine **44** using {Mo_{132}} as a catalyst in high yield under refluxing water (Scheme 13) [135].

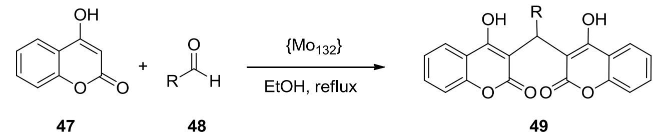


Scheme 13. Synthesis of fluoroquinolones in the presence of {Mo_{132}}.

2.3. Miscellaneous (carbon–carbon bond-forming)

Carbon-carbon bond-forming reactions are organic reactions in which a new carbon–carbon bond is formed. They are important in the production of many man-made chemicals such as pharmaceuticals and plastics [136]. Some examples of reactions which form carbon-carbon bonds are aldol reactions [137], Diels-Alder reaction [138], the addition of a Grignard reagent to a carbonyl group [139], a Heck reaction [140], a Michael reaction [141] and a Wittig reaction [142].

Coumarins are a large group of heterocycles with diverse and interesting biological activities [143-145]. These compounds are reported to possess significant anticoagulant [146], insecticidal [147], antihelminthic [148], hypnotic [149], antifungal [150], and HIV protease inhibition activities [151]. Biscoumarins, the bridge substituted dimers of 4-hydroxycoumarin, have enormous potential as anticoagulants [152]. A number of biscoumarins have also been found to be urease inhibitors [153]. Therefore developing methods of biscoumarin synthesis is important in the field of organic chemistry. We found that {Mo_{132}} is a useful catalyst for the synthesis of biscoumarins **49** by the mixture of 4-hydroxycoumarin **47**, aromatic or aliphatic aldehyde **48** in ethanol at reflux temperature as shown in Scheme 14 [154].



Scheme 14. {Mo_{132}} catalyzed synthesis of biscoumarins.

3. Conclusion

This review presented an overview of typical applications for the Keplerate-type giant nanoporous isopolyoxomolybdate $(NH_4)_{42}[MoVI_{72}MoV_{60}O_{372}-(CH_3COO)_{30}(H_2O)_{72}]$, denoted {$Mo_{132}$}, in multicomponent reactions. We found {Mo_{132}} as a very important green catalyst due to its stability, high solubility in water, non-toxicity, reusability, ease of handling, inexpensiveness, and high availability which enable this material to catalyze various transformations in the organic chemistry.

Acknowledgement

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