

Preyssler catalyst: a heterogeneous polyacidic catalyst for the efficient synthesis of diverse bioactive heterocyclic scaffolds

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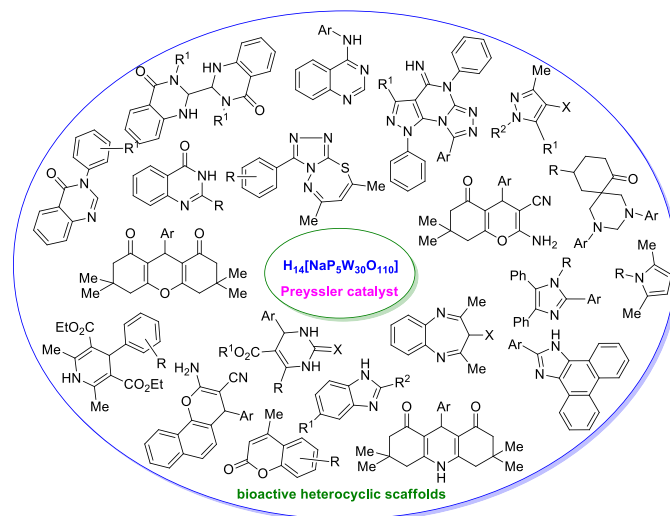
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Abstract

Synthesis of biologically promising heterocyclic scaffolds under greener conditions is one of the most promising areas of research today in organic chemistry. Heterogeneous catalysis has received greater attention versus homogeneous catalysis as it is much more beneficial in terms of reusability of the catalysts. Among many others, various heteropoly acids have been used as efficient heterogeneous catalysts for diverse organic transformations. In the present review, we have summarized the literature related to the synthesis of various biologically promising heterocyclic scaffolds utilizing a catalytic amount of one such efficient and reusable heteropoly acid, the Preyssler catalyst.



Keywords: Heterogeneous catalysis, heteropoly acids, Preyssler catalyst; reusable catalysts

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1. Introduction

Heterocycles are very common in naturally occurring and natural-product-inspired bioactive compounds.¹ Many commercially available drug molecules contain heterocyclic skeletons.² More than half of the known organic compounds consist of heterocyclic skeletons. A large number of synthetic heterocyclic scaffolds have been found to possess a wide range of promising pharmacological efficacies which include anti-cancer,³ anti-malarial,⁴ anti-tubercular,⁵ anti-microbial,⁶ anti-asthmatic,⁷ anti-inflammatory,⁸ anti-histaminic,⁹ anti-hypertensive,¹⁰ anti-depressant,¹¹ anti-rheumatic,¹² anti-diabetic,¹³ anti-Alzheimer's, anti-Parkinson's, anti-

Huntington's disease,¹⁴ as well as many other activities.¹⁵⁻¹⁷ Realizing the importance of heterocyclic scaffolds, a large number of methods have been reported for the synthesis of structurally-diverse heterocyclic scaffolds.¹⁸⁻²⁵ In all of the methods, the screening of suitable catalysts played an important role.

In recent times, heterogeneous catalysis has received great attention. The main advantage of heterogeneous catalysts is the easy isolation of the catalysts from the reaction mixture following product formation. In many cases, the heterogeneous catalysts were recovered simply by filtration and, following washing and drying, the same catalysts were recycled a number of times with almost equal efficiency.²⁶⁻²⁸ A large number of heterogeneous catalysts have been employed to carry out various organic transformations under environmentally benign conditions.²⁹⁻³⁵ Among many others, a number of heteropoly acids were also employed as efficient heterogeneous catalysts for various organic transformations.³⁶⁻³⁹ These have been used for bulk productions in the pharmaceutical, flavor and food industries.⁴⁰ Heteropoly acids are well-defined molecular clusters having metal-oxygen octahedra as the basic structural units.⁴¹ Among various heteropoly acids, the catalytic efficacies of Keggin ($H_3[PW_{12}O_{40}]$),^{42,43} Dawson ($H_6[P_2W_{18}O_{62}]$)^{44,45} and Venturolo ($H_3[PO_4(WO(O_2)_2)_4]$)⁴⁶ catalysts have been studied extensively. During the last two decades, another heteropoly acid, the Preyssler catalyst ($H_{14}[NaP_5W_{30}O_{110}]$)⁴⁷, has also received considerable attention, and employed as an efficient heterogeneous catalyst for various organic transformations. It showed excellent catalytic efficacies for esterification,⁴⁸⁻⁵² alkylation,^{53,54} oxidation,⁵⁵⁻⁵⁸ *N*-oxidation of pyridine,⁵⁹ protection of alcohols,^{60,61} synthesis of lactones,⁶² aspirin,⁶³ synthesis of 1,2,4-triazino[4,3-*b*][1,2,4,5]tetrazines,⁶⁴ and bis-coumarins,⁶⁵ etc. Silica-supported Preyssler catalyst was also found to efficiently catalyze many organic transformations, including esterification of salicylic acid^{66,67} and alcohol,⁶⁸ alkylation of benzene,⁶⁹ photodegradation of methyl orange,⁷⁰ oxidation of benzyl alcohols,⁷¹ and synthesis of carbamato alkylnaphthols.⁷² In 2020, Saneinezhad *et al.* employed silver-nanoparticles-decorated Preyssler-functionalized cellulose biocomposite as a novel and efficient catalyst for the synthesis of a series of structurally diverse 2-amino-4*H*-pyrans and spirochromenes in aqueous ethanol under reflux.⁷³ Preyssler catalyst is a strong Brønsted acidic catalyst with 14 acidic protons. Moreover, high hydrolytic stability, high thermal stability, ease of separation, reusability, corrosiveness, high oxidation potential are some of the extra advantages of this heterogeneous heteropolyacid.

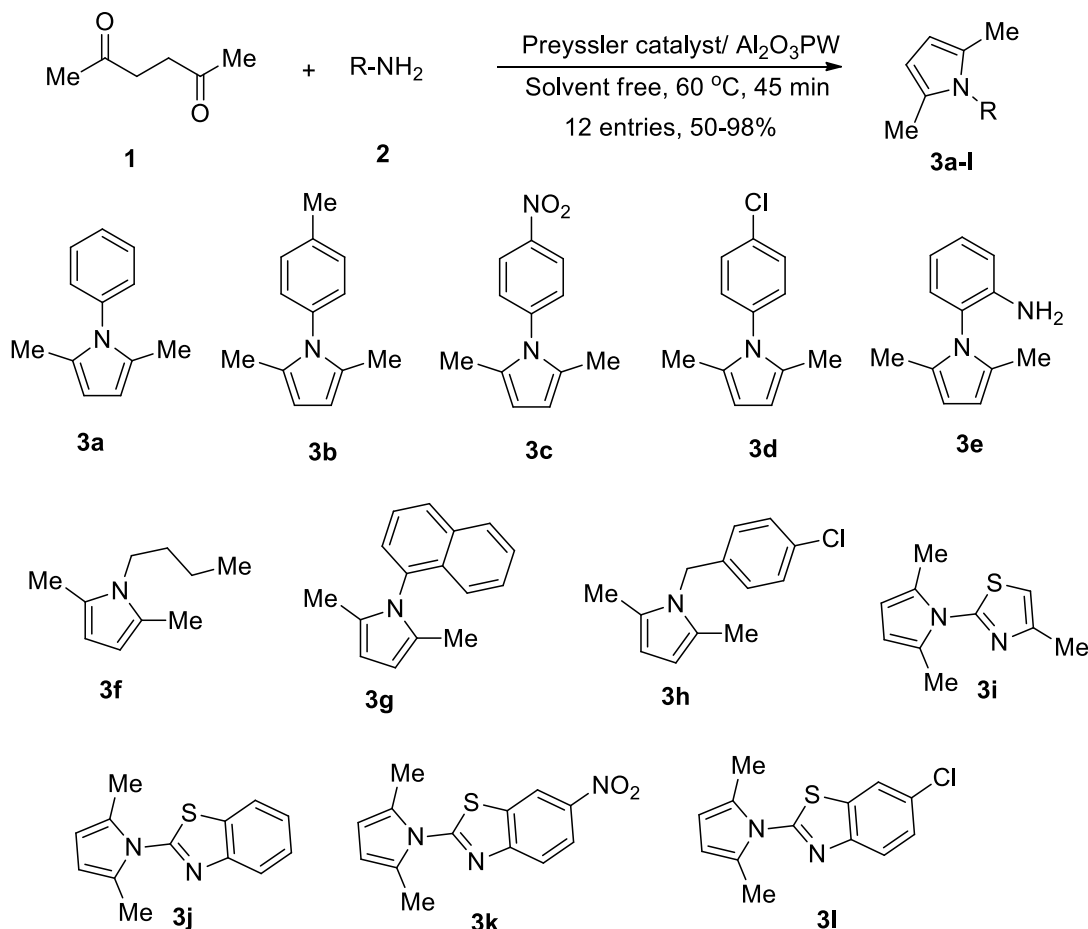
The Preyssler catalyst can be synthesized by following the hydrothermal synthesis method mentioned in the literature.^{74,75} In most cases, after completion of the reaction, the catalyst was recovered quantitatively, and recycled for several runs without any notable loss in its catalytic activities.

The following section deals with the latest developments in the synthesis of various biologically relevant heterocyclic scaffolds utilizing a catalytic amount of Preyssler catalyst or solid-supported Preyssler catalyst under diverse reaction conditions.

2. Synthesis of Bioactive Heterocycles Using Preyssler catalyst

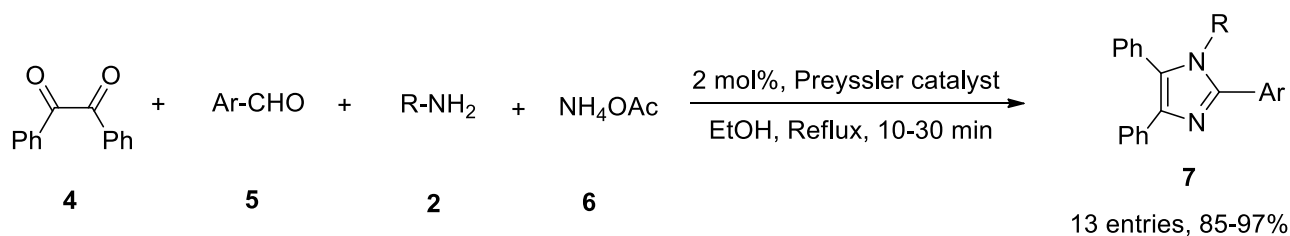
2.1. Synthesis of bioactive N-heterocycles using Preyssler catalyst

2.1.1. Synthesis of pyrroles. Portilla-Zúñiga *et al.* prepared a novel, bifunctional Preyssler heteropoly-acid-supported mesoporous alumina. Using a catalytic amount of this catalyst, they synthesized a series of pyrrole derivatives (**3**) from the reactions of acetylacetone (**1**) and various aromatic as well as aliphatic amines (**2**) under solvent-free conditions at 60 °C (Scheme 1).⁷⁶ The catalyst here acts as a strong Brønsted acid which activates the carbonyl group thereby facilitating the attack by the amine.



Scheme 1. Synthesis of pyrroles in the presence of Preyssler catalyst under neat conditions.

2.1.2. Synthesis of 1,2,4,5-tetrasubstituted imidazoles. Only 2 mol % Preyssler catalyst was found to be necessary for the synthesis of a series of 1,2,4,5-tetrasubstituted imidazoles (**7**) in one-pot, four-component reactions of benzil (**4**), aromatic aldehydes (**5**), amines (**2**) and ammonium acetate (**6**) in ethanol under reflux (Scheme 2).⁷⁷

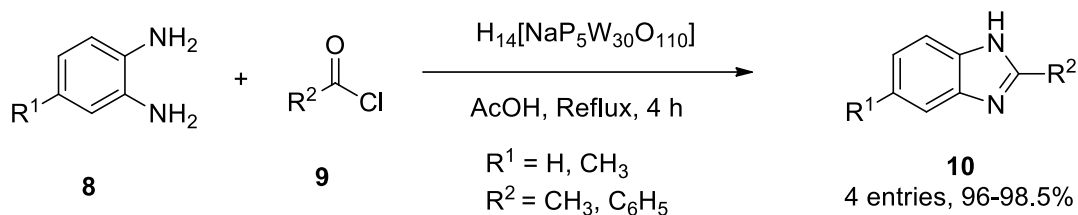


Ar = C₆H₅, 4-Cl-C₆H₄, 4-CH₃O-C₆H₄, 4-CH₃-C₆H₄, 4-OH-C₆H₄, 2-OH-C₆H₄, 4-Br-C₆H₄, 4-NO₂-C₆H₄
R = CH₃C₆H₄, CH₃, C₆H₅

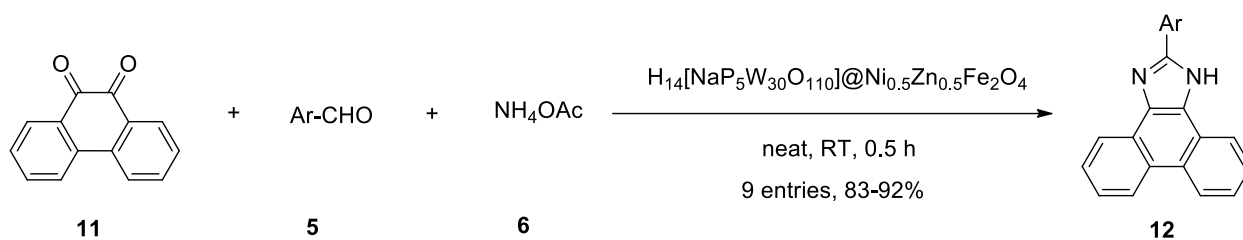
Scheme 2. Synthesis of 1,2,4,5-tetrasubstituted imidazoles in the presence of Preyssler catalyst.

2.1.3. Synthesis of 2-substituted benzimidazoles. In 2018, Heravi *et al.* synthesized 2-substituted benzimidazoles (**10**) from the reactions of *o*-phenylenediamines (**8**) and benzoyl or acetyl chlorides (**9**) in the presence of Preyssler heteropoly acid in acetic acid (as solvent) under reflux (Scheme 3).⁷⁸ Some other

Preyssler-type catalysts such as $H_4[PMo_{11}VO_{40}]$, $H_5[PMo_{10}V_2O_{40}]$ and $H_6[P_2W_{18}O_{62}]$ were also found to be efficient for this reaction, and afforded the desired products in excellent yields. Synthesis of 2-aryl-1*H*-phenanthro[9,10-*d*]imidazoles (**12**) was achieved *via* one-pot, three-component reactions of phenanthrene-9,10-dione (**11**), aromatic aldehydes (**5**) and ammonium acetate (**6**) in the presence of a catalytic amount of Preyssler heteropoly acid-immobilized magnetic nanoparticles, under solvent-free conditions at room temperature (Scheme 4).⁷⁹



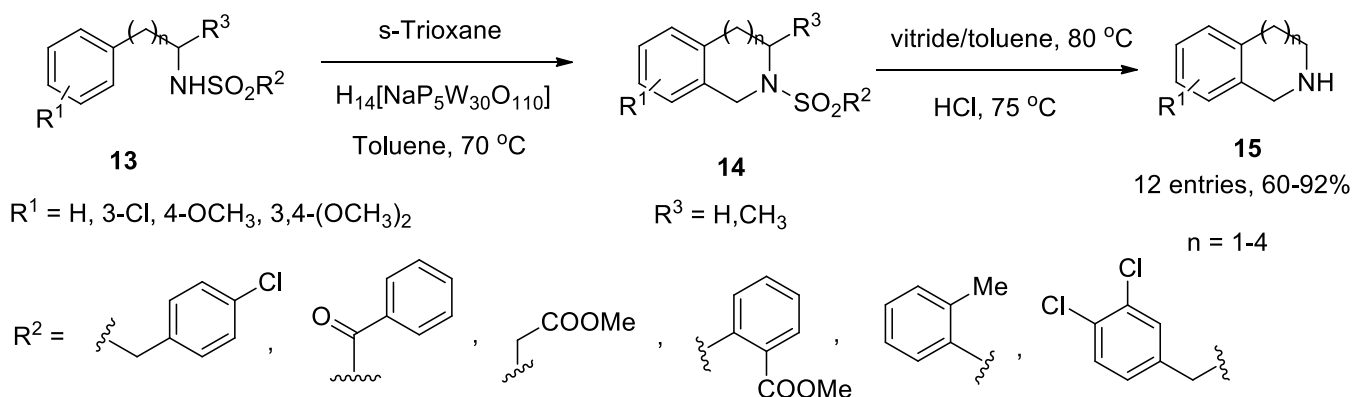
Scheme 3. Synthesis of 2-substituted-benzimidazoles in the presence of Preyssler catalyst.



Ar = C_6H_5 , 4- $\text{NO}_2\text{C}_6\text{H}_4$, 3- $\text{NO}_2\text{C}_6\text{H}_4$, 4- CNC_6H_4 , 2- ClC_6H_4 , 4- ClC_6H_4 , 4- OMeC_6H_4 , 4- MeC_6H_4 , 4- $\text{CH}_3\text{CONHC}_6\text{H}_4$

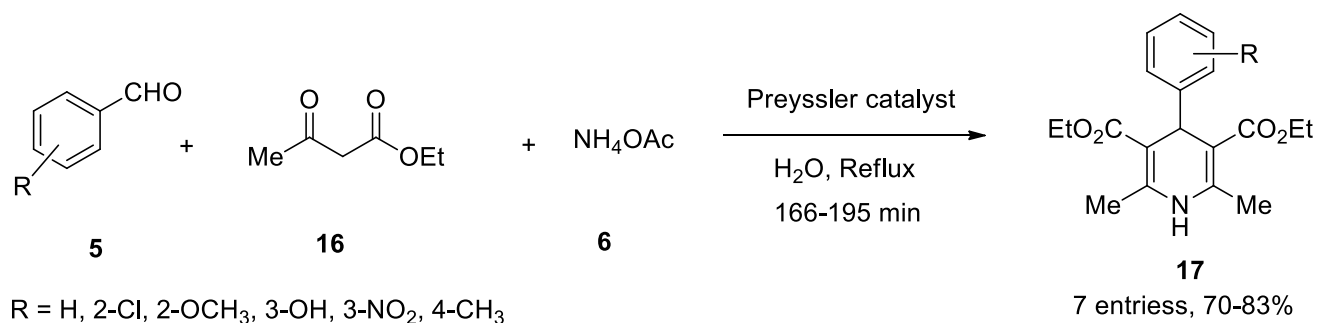
Scheme 4. Synthesis of 2-aryl-1*H*-phenanthro[9,10-*d*]imidazoles using Preyssler heteropoly acid-immobilized magnetic nanoparticles.

2.1.4. Synthesis of *N*-sulfonyl-1,2,3,4-tetrahydroisoquinoline and related analogs. A series of *N*-sulfonyl-1,2,3,4-tetrahydroisoquinoline and related analogs (**15**) were synthesized *via* the intramolecular sulfonamidomethylation reaction between compounds **13** and trioxane in the presence of Preyssler catalyst in toluene at 70 °C (Scheme 5).⁸⁰ Desulfonation of compounds **14** was carried out in the presence of acid in toluene, under reflux, which afforded the corresponding compounds **15** with good-to-excellent yields.

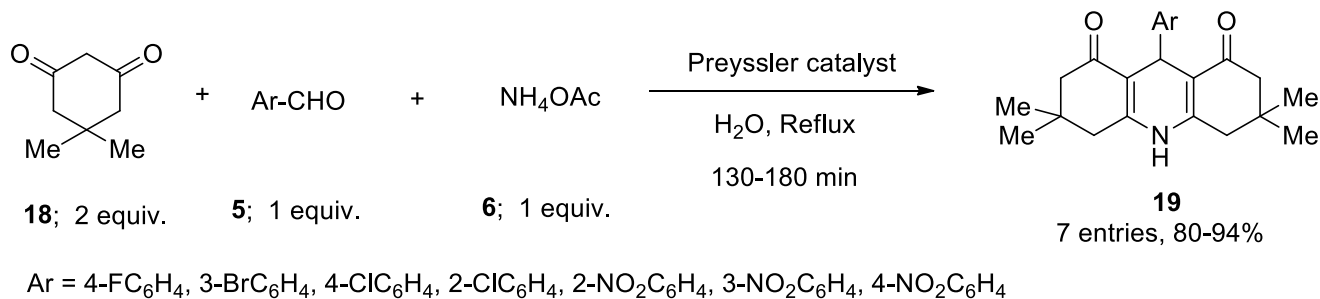


Scheme 5. Synthesis of *N*-sulfonyl-1,2,3,4-tetrahydroisoquinolines using Preyssler catalyst.

2.1.5. Synthesis of highly substituted 1,4-dihydropyridine and acridine derivatives. Gharib *et al.* utilized a catalytic amount of Preyssler heteropoly acid as an efficient heterogeneous catalyst for the synthesis of a series of highly substituted 1,4-dihydropyridine derivatives (**17**) from the reactions of various aromatic aldehydes (**5**), ethyl acetoacetate (**16**) and ammonium acetate (**6**) in the presence of water under reflux (Scheme 6).⁸¹ All of the synthesized compounds were isolated pure and afforded excellent yields. After completion of the reaction, the catalyst was recovered easily and reused for four successive runs. Under the same optimized-reaction conditions, the same group was also able to synthesize a series of acridine derivatives (**19**) in good-to-excellent yields from the pseudo-four-component reactions between two equivalents of dimedone (**18**), one equivalent of aromatic aldehyde (**5**), and one equivalent of ammonium acetate (**6**) (Scheme 7).

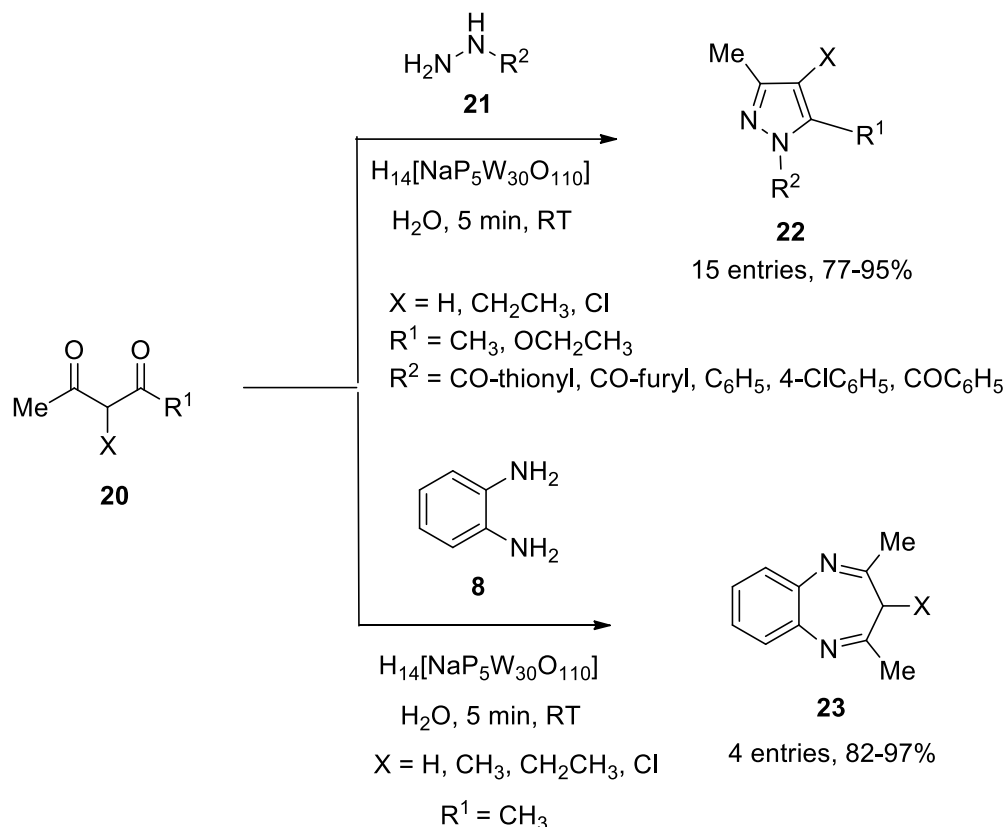


Scheme 6. Synthesis of 1,4-dihydropyridine derivatives using Preyssler catalyst in water.



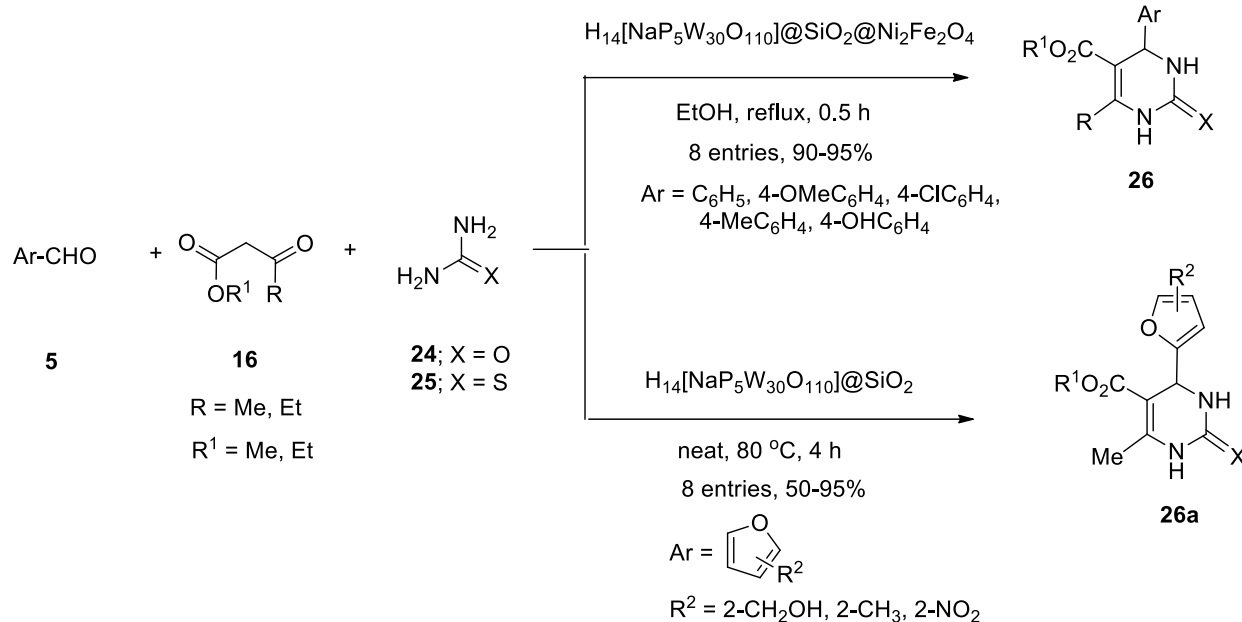
Scheme 7. Synthesis of acridine derivatives using Preyssler catalyst in water.

2.1.6. Synthesis of pyrazoles. Gharib *et al.* reported a facile protocol for the efficient synthesis of a series of pyrazole derivatives (**22**) from the reactions of various hydrazine derivatives (**21**) and 1,3-diketones (**20**) in the presence of Preyssler heteropoly acid ($\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$) as catalyst in water at room temperature (Scheme 8).⁸² The solid heterogeneous catalyst was recovered easily and reused for five successive runs. The catalytic activity of a number of other heterogeneous catalysts, such as $\text{H}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$, $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ and $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$, were also evaluated, however, all of them afforded lesser yields than the Preyssler catalyst. Under the same optimized reaction conditions, the synthesis of a series of diazepine derivatives (**23**) was also achieved in good yields from the reactions of *o*-phenylenediamine (**8**) and various 1,3-diketones (**20**) (Scheme 8).



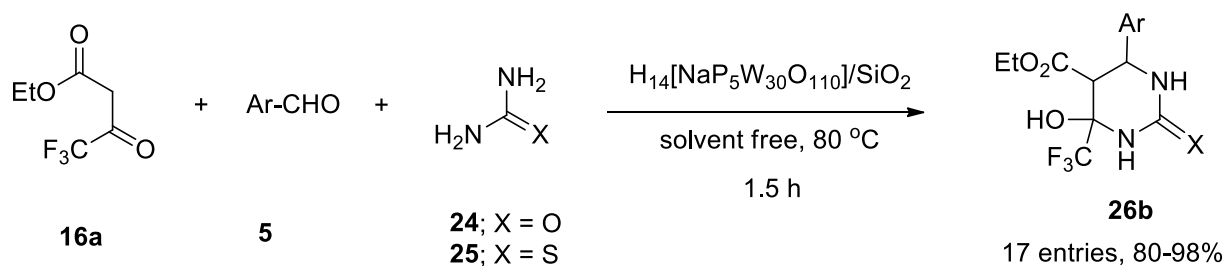
Scheme 8. Synthesis of pyrazoles and diazepines in the presence of a Preyssler catalyst.

2.1.7. Synthesis of 3,4-dihydropyrimidin-2(1H)-ones. Eshghi *et al.* was able to support Preyssler heteropoly acid on silica-coated NiFe_2O_4 nanoparticles. The synthesized catalyst was characterized using FT-IR, TEM, SEM, EDS, XRD and VSM analyses.⁸³ Using the same magnetic nanomaterials as catalysts, they synthesized a series of 3,4-dihydropyrimidin-2(1H)-ones (**26**) *via* one-pot, three-component reactions of aromatic aldehydes (**5**), ethyl acetoacetate (**16**) and urea (**24**) or thiourea (**25**) in ethanol under reflux (Scheme 9). The used magnetic catalyst was recovered easily by using a simple bar magnet and reused for five successive runs with almost equal efficiency. Portilla-Zuñiga *et al.* demonstrated the synthesis of another series of 3,4-dihydropyrimidin-2(1H)-ones (**26a**) *via* one-pot Biginelli reactions of furfurals (**5**), β -ketoesters (**16**), and urea (**24**) or thiourea (**25**) using a catalytic amount of silica-supported Preyssler heteropoly acid as catalysts under solvent-free conditions at 80 °C (Scheme 9).⁸⁴



Scheme 9. Synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones using Preyssler heteropoly-acid-supported silica-coated NiFe_2O_4 nanoparticles.

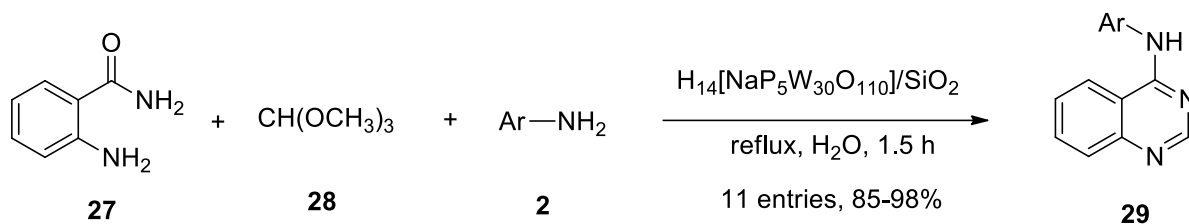
Sathicq *et al.* prepared a series of highly substituted hexahydropyrimidines (**26b**) in good-to-excellent yields from the reactions of ethyl trifluoroacetoacetate (**16b**), substituted benzaldehydes (**5**) and urea (**24**) or thiourea (**25**), using Preyssler heteropoly acid encapsulated in a silica framework, under solvent-free conditions at 80 °C for 90 minutes (Scheme 10).⁸⁵ The Preyssler catalyst embedded in the silica matrix is insoluble in polar media. This aids the easy removal of the products from the reaction mixture without affecting the catalytic activity of the catalyst.



Ar = C_6H_5 , 4- OMeC_6H_4 , 4- ClC_6H_4 , 4- BrC_6H_4 , 4- $\text{NO}_2\text{C}_6\text{H}_4$, 2-thienyl, 3-furyl, 2-furyl, pyrrolyl, cinnamyl

Scheme 10. Synthesis of highly substituted hexahydropyrimidines using Preyssler heteropoly acid encapsulated in a silica framework as catalyst.

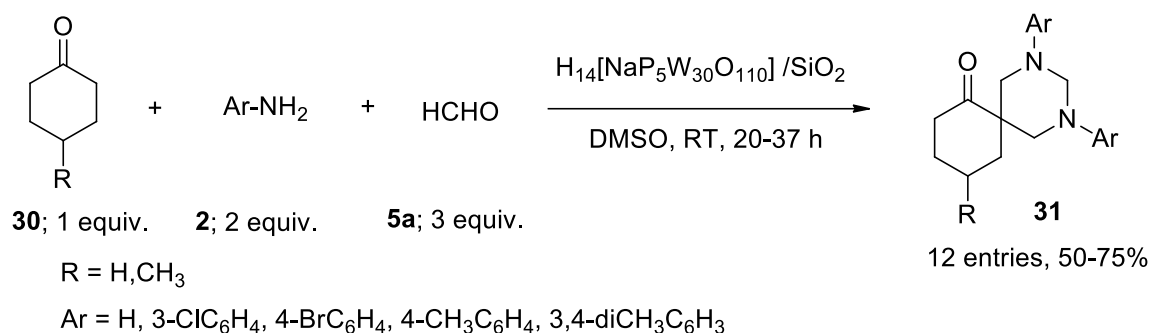
2.1.8. Synthesis of quinazolin-4-arylamines. Using the same silica-supported Preyssler catalyst, the same group also synthesized a series of quinazolin-4-arylamines (**29**) from the reactions of 2-aminobenzamide (**27**), orthoester (**28**) and substituted anilines (**2**) in water under reflux (Scheme 11).⁸⁶ After completion of the reaction, the heterogeneous catalyst was recovered easily and recycled for five successive runs without any significant loss of its catalytic activities.



Ar = C₆H₅, 2-BrC₆H₄, 4-ClC₆H₄, 4-MeC₆H₄, 3,4-di-MeC₆H₃, 4-NO₂C₆H₄,
2-NO₂C₆H₄, 2-OCH₃C₆H₄, 3-OCH₃C₆H₄, 4-OCH₃C₆H₄

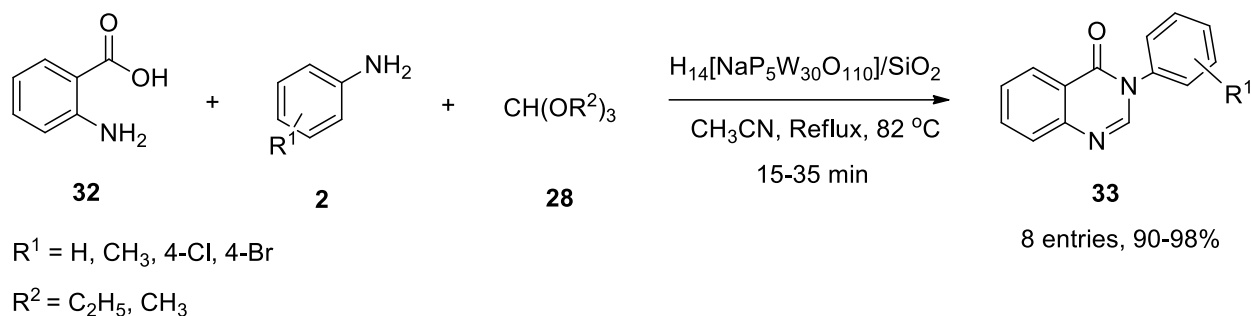
Scheme 11. Synthesis of quinazolin-4-arylamines using silica-supported Preyssler catalyst in water.

2.1.9. Synthesis of 1,3-diaryl-5-spirohexahydropyrimidines. Heravi *et al.* synthesized a series of 1,3-diaryl-5-spirohexahydropyrimidine derivatives (**31**) from one-pot, pseudo-six-component reactions of one equivalent of ketones (**30**), two equivalents of anilines (**2**) and three equivalents of formaldehyde (**5a**) in the presence of a catalytic amount of silica-supported Preyssler catalyst in DMSO at room temperature (Scheme 12).⁸⁷ The catalyst was recovered successfully and recycled five times without any significant loss in its catalytic activity.



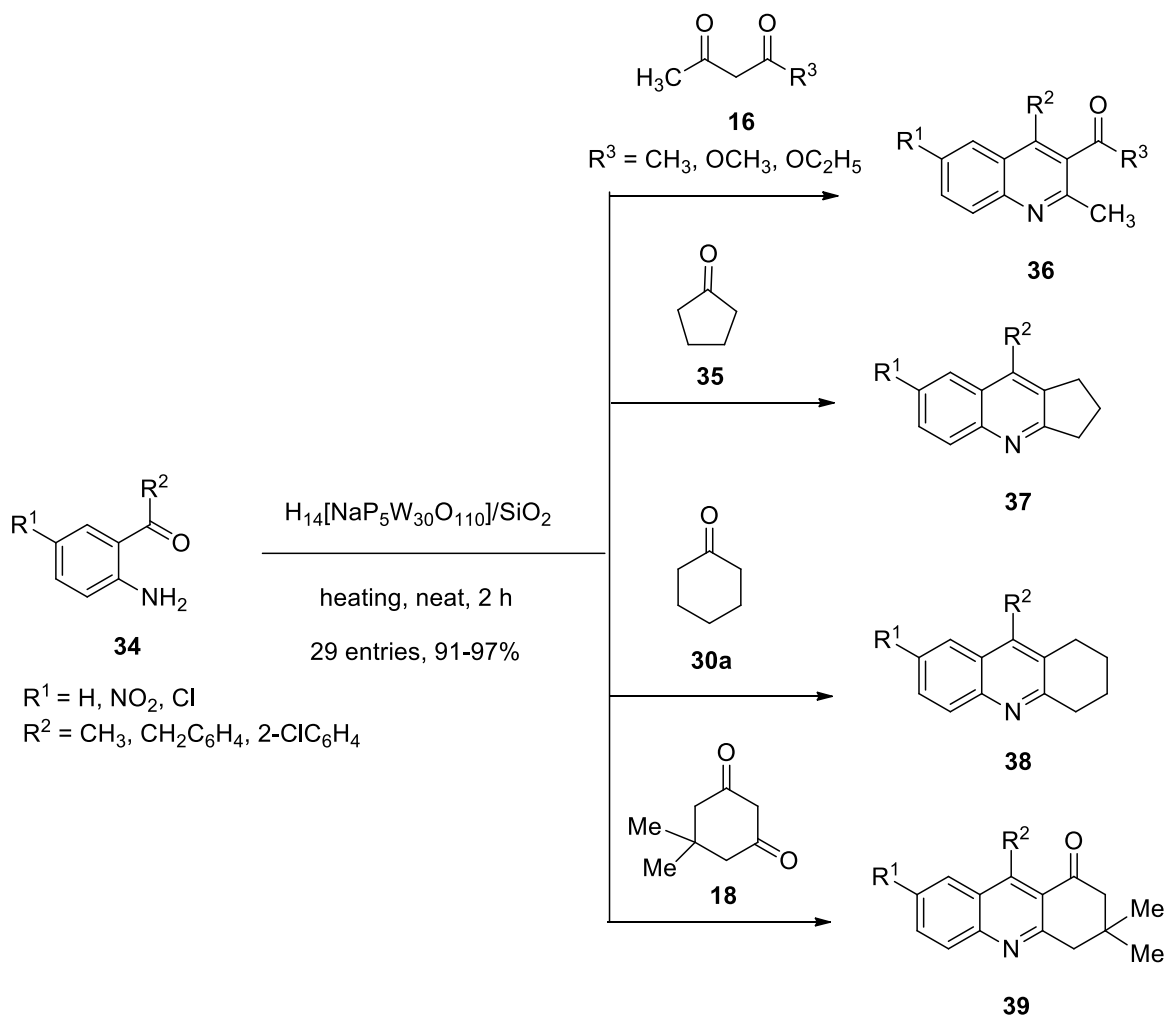
Scheme 12. Synthesis of 1,3-diaryl-5-spirohexahydropyrimidines using silica-supported Preyssler catalyst.

2.1.10. Synthesis of 4(3H)-quinazolinones. Heravi *et al.* also employed a silica-supported Preyssler nanocatalyst for the synthesis of 4(3H)-quinazolinones (**33**) from the condensation reactions of anthranilic acid (**32**), substituted anilines (**2**) and orthoesters (**28**) (Scheme 13).⁸⁸ The heterogeneous catalyst was recovered easily and recycled for five successive runs without any loss in its catalytic activities.



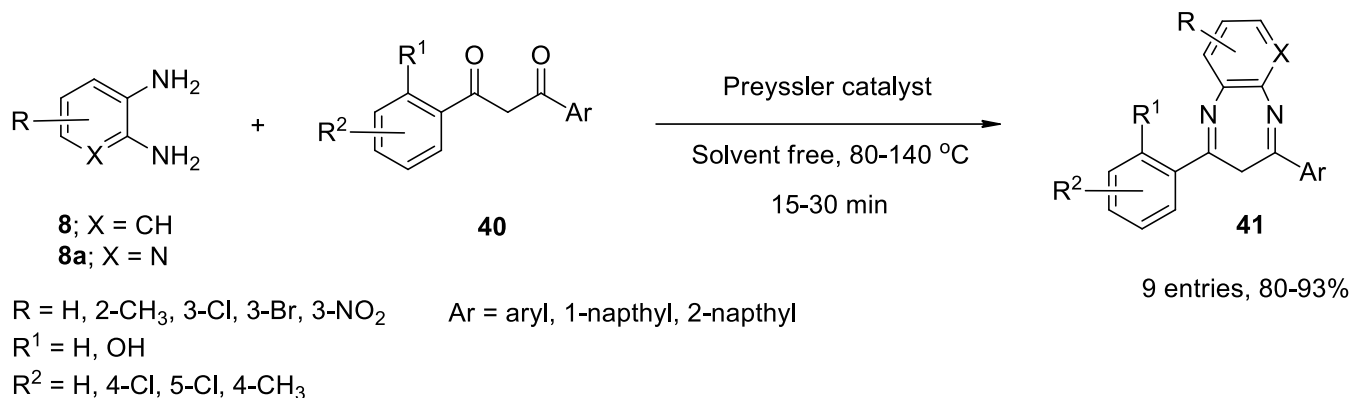
Scheme 13. Synthesis of 4(3H)-quinazolinones in the presence of silica-supported Preyssler catalyst.

2.1.11. Synthesis of quinolines. Quinoline derivatives have been found to possess a wide range of biological activities, which include anti-asthmatic, anti-inflammatory, anti-malarial, anti-hypertensive, anti-bacterial, and tyrosine kinase-inhibiting efficacies.⁸⁹ In 2014, Gharib *et al.* reported a facile protocol for the synthesis of wide range of quinoline derivatives (**36-39**) from the reactions of 2'-aminoacetophenone/benzophenone derivatives (**34**) and various C-H activated carbonyl compounds (**16,35,30a,18**) using a catalytic amount of Preyssler catalyst under solvent-free heating conditions (Scheme 14).⁹⁰ The same reaction afforded a little higher yields with silica-supported Preyssler nanoparticles $[\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]/\text{SiO}_2]$ as an efficient, reusable, heterogeneous catalyst under the same reaction conditions.



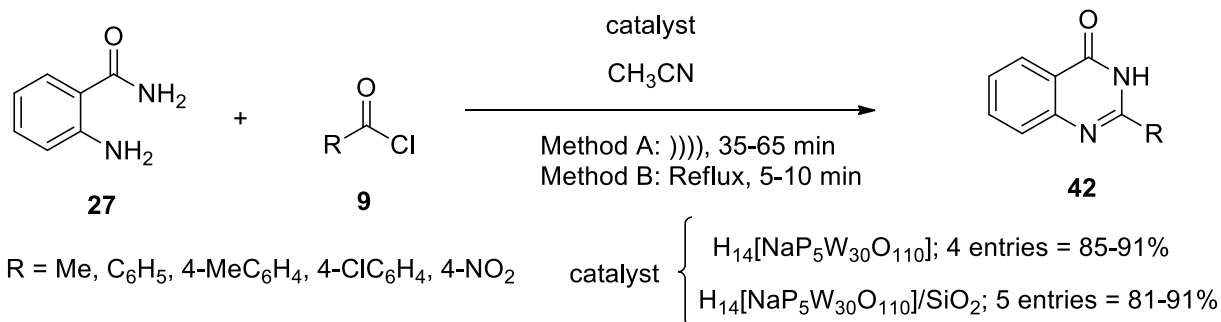
Scheme 14. Synthesis of quinolines using a silica-supported Preyssler catalyst under solvent-free conditions.

2.1.12. Synthesis of 1,5-benzodiazepines. Pasquale *et al.* synthesized a number of 1,5-benzodiazepine derivatives (**41**) from the reactions of *o*-phenylenediamines (**8**) or pyridine-2,3-diamine (**8a**) and 1,3-diaryl-1,3-propanediones (**40**) in the presence of Preyssler heteropoly acid as an efficient heterogeneous, reusable catalyst under solvent-free conditions at 80-140 °C (Scheme 15).⁹¹



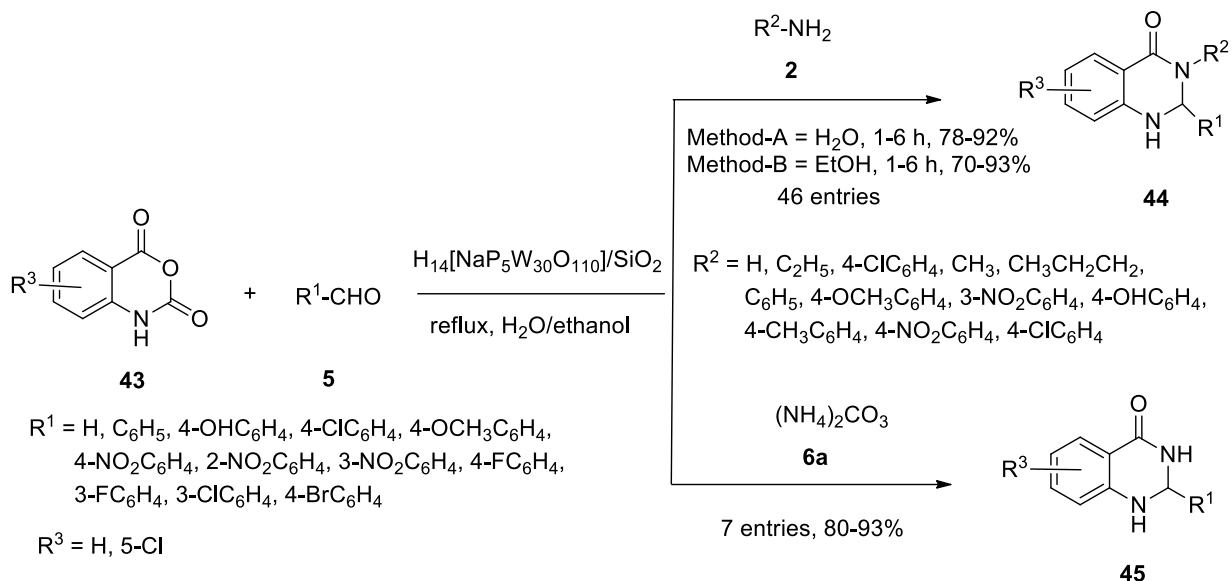
Scheme 15. Synthesis of 1,5-benzodiazepines in the presence of a Preyssler catalyst under neat conditions.

2.1.13. Synthesis of 4(3H)-quinazolinones. A series of 4(3H)-quinazolinones (**42**) was synthesized by Heravi *et al.* from the reactions with 2-amino-benzamide (**27**) and acyl chlorides (**9**) in the presence of Preyssler heteropoly acid as catalyst in acetonitrile under ultrasound-assisted conditions (Scheme 16).⁹² The same reactions required longer times when carried out under conventional refluxed conditions. Under the same optimized conditions, silica-supported Preyssler heteropoly acid was also found to be efficient and afforded the desired products in good-to-excellent yields.



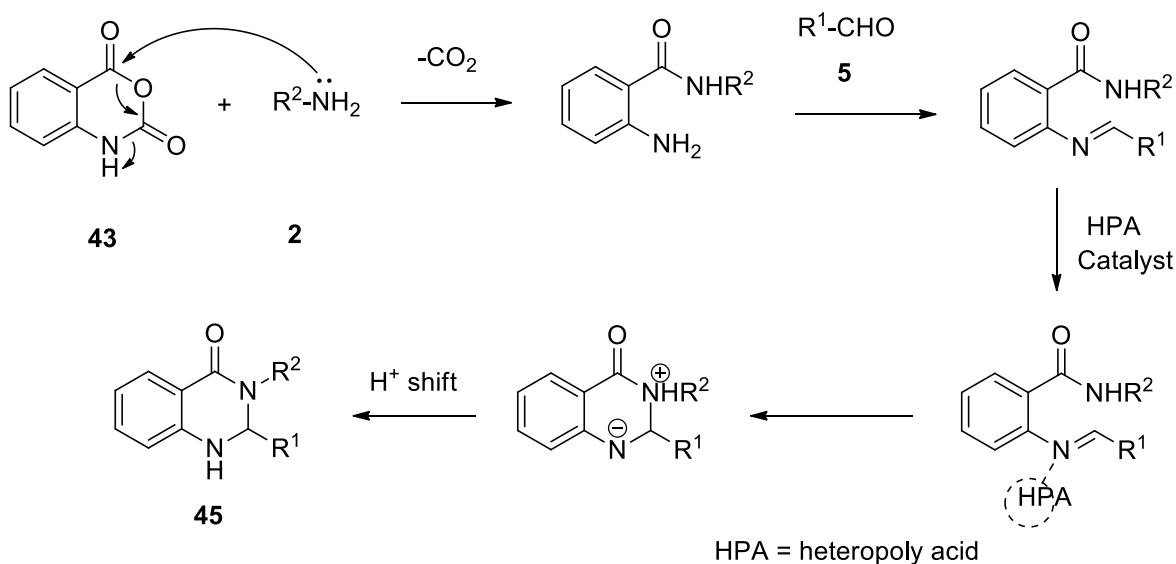
Scheme 16. Synthesis of 4(3H)-quinazolinones using Preyssler catalyst.

2.1.14. Synthesis of substituted 2,3-dihydroquinazolin-4(1H)-ones. Gharib *et al.* synthesized a number of 2,3-dihydroquinazolin-4(1H)-one derivatives (**44**, **45**) from the reactions of isatoic anhydride (**43**), aldehydes (**5**) and primary amines (**2**) or ammonium carbonate (**6a**), respectively (Scheme 17).⁹³ The reactions were carried out in the presence of silica-supported nano-Preyssler catalyst, either in water or ethanol, under reflux conditions. Both solvents afforded the desired products in excellent yields.



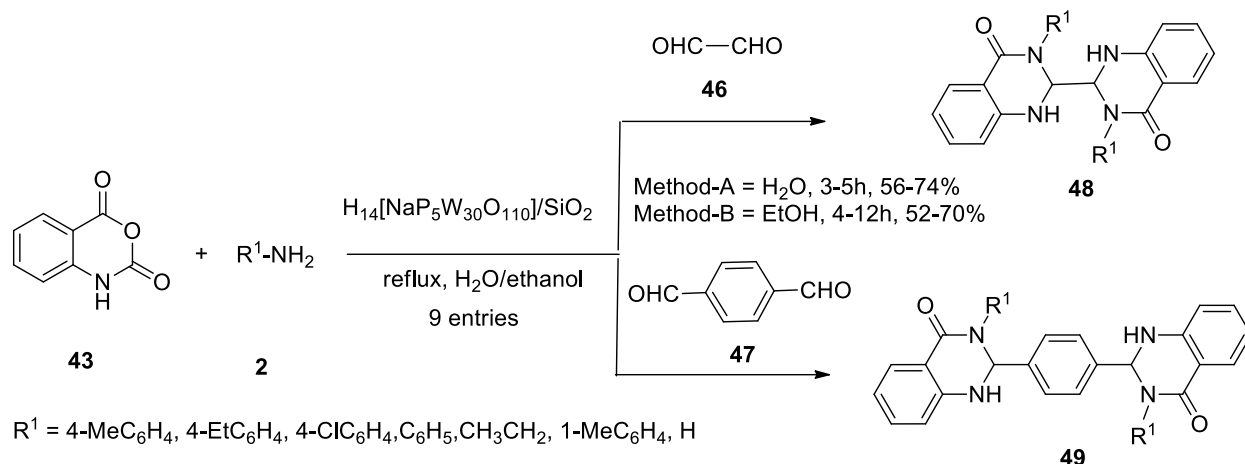
Scheme 17. Synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones in the presence of silica-supported Preyssler nanocatalyst.

A plausible mechanism for this reaction is presented in Scheme 18.



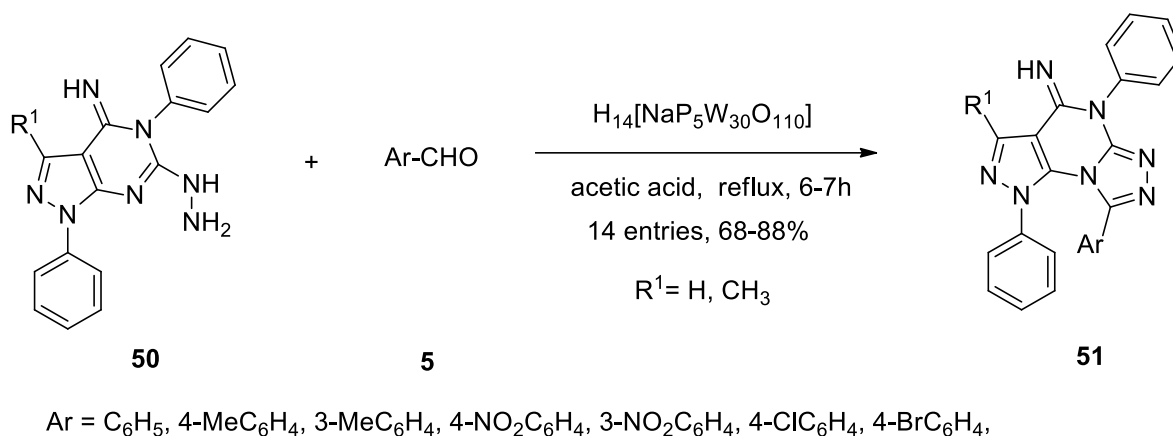
Scheme 18. Plausible mechanism for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones using silica supported Preyssler nanocatalyst.

Under the same optimized reaction conditions, the syntheses of *bis*(2,3-dihydroquinazolin-4(1*H*)-one) derivatives (**48,49**) were achieved from the reactions of isatoic anhydride (**43**), primary amines (**2**) and di-aldehydes (**46,47**) (Scheme 19).



Scheme 19. Synthesis of *bis*(2,3-dihydroquinazolin-4(1*H*)-one) derivatives using silica-supported Preyssler nanocatalyst.

2.1.15. Synthesis of 8-aryl-1*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[4,3-*a*]pyrimidine-4(5*H*)-imines. Seifi *et al.* prepared a series of 8-aryl-1*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[4,3-*a*]pyrimidine-4(5*H*)-imines (**51**) from the reactions of 6-hydrazino-1,5-diphenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine-4-imines (**50**) and aromatic aldehydes (**5**) using a catalytic amount of Preyssler catalyst in acetic acid under reflux (Scheme 20).⁹⁴ The catalytic activity of molybdenum-doped Preyssler catalyst [$\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$] and silica-supported Preyssler catalyst [$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]/\text{SiO}_2$] was also evaluated, however, they afforded lesser amounts of products.

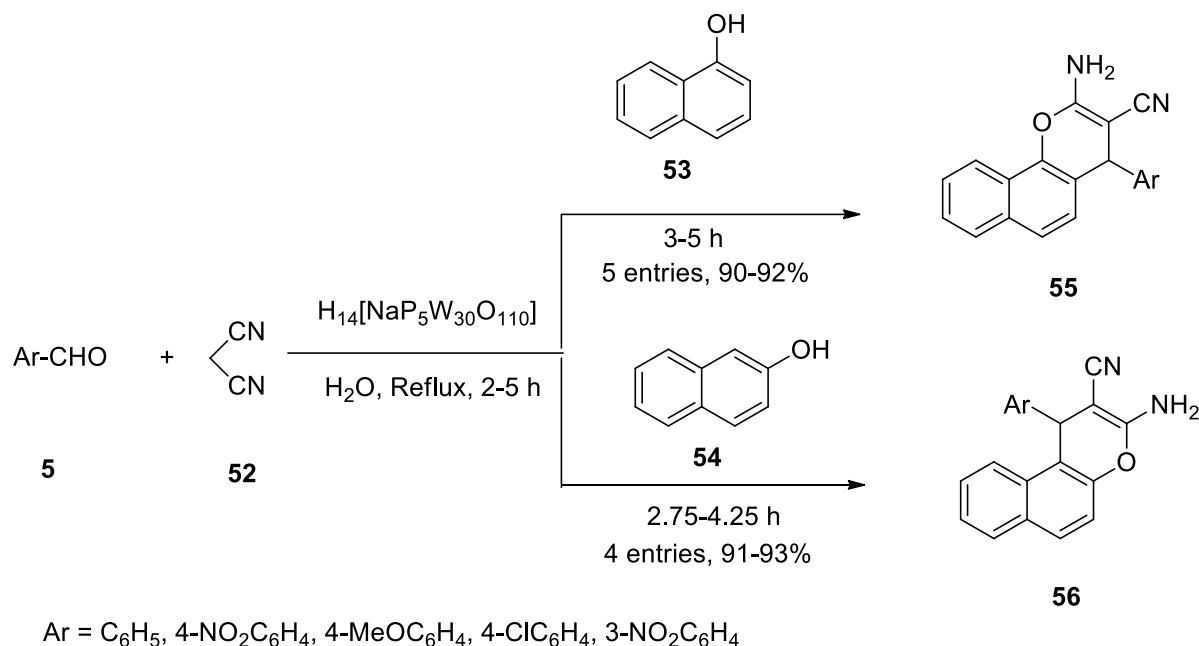


Scheme 20. Synthesis of 8-aryl-1*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[4,3-*a*]pyrimidine-4(5*H*)-imines using a Preyssler catalyst.

2.2. Synthesis of bioactive O-heterocycles using Preyssler catalyst

2.2.1. Synthesis of substituted 2-amino-chromenes. Heravi *et al.* demonstrated a facile and efficient method for the synthesis of a series of 2-amino-3-cyano-4-aryl-4*H*-benzo[*h*]chromenes (**55**) from one-pot, three-component reactions of aromatic aldehydes (**5**), malononitrile (**52**) and α -naphthol (**53**) in the presence of a catalytic amount of Preyssler catalyst in water under reflux conditions (Scheme 21).⁹⁵ Under the same optimized reaction conditions, 3-amino-2-cyano-1-aryl-1*H*-benzo[*f*]chromenes (**56**) were also synthesized in excellent yields from the reactions of aldehydes (**19**), malononitrile (**52**) and β -naphthol (**54**). All the reactions

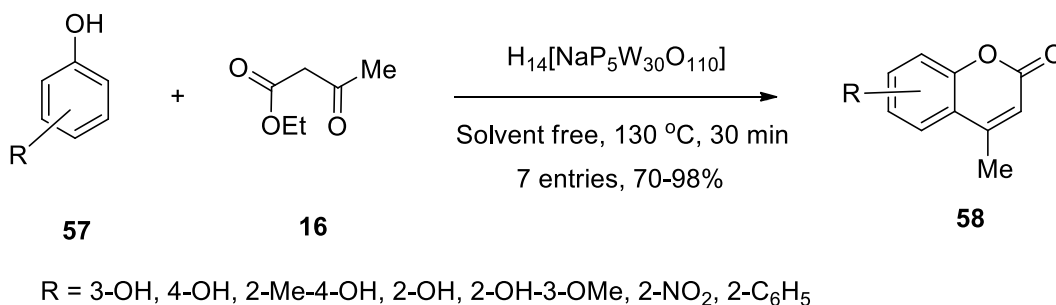
were completed within 4.5 hours. After completion of the reactions, the heterogeneous catalyst was recovered easily by filtration, and reused for three successive runs with almost the same catalytic efficiency.



Scheme 21. Synthesis of substituted 2-amino-chromenes in the presence of a Preyssler catalyst.

2.2.2. Synthesis of 4-substituted coumarins. Many methods have been reported for the synthesis of 4-methylcoumarins *via* Pechmann reactions between phenols and ethyl acetoacetate, employing various homogeneous as well as heterogeneous catalysts.

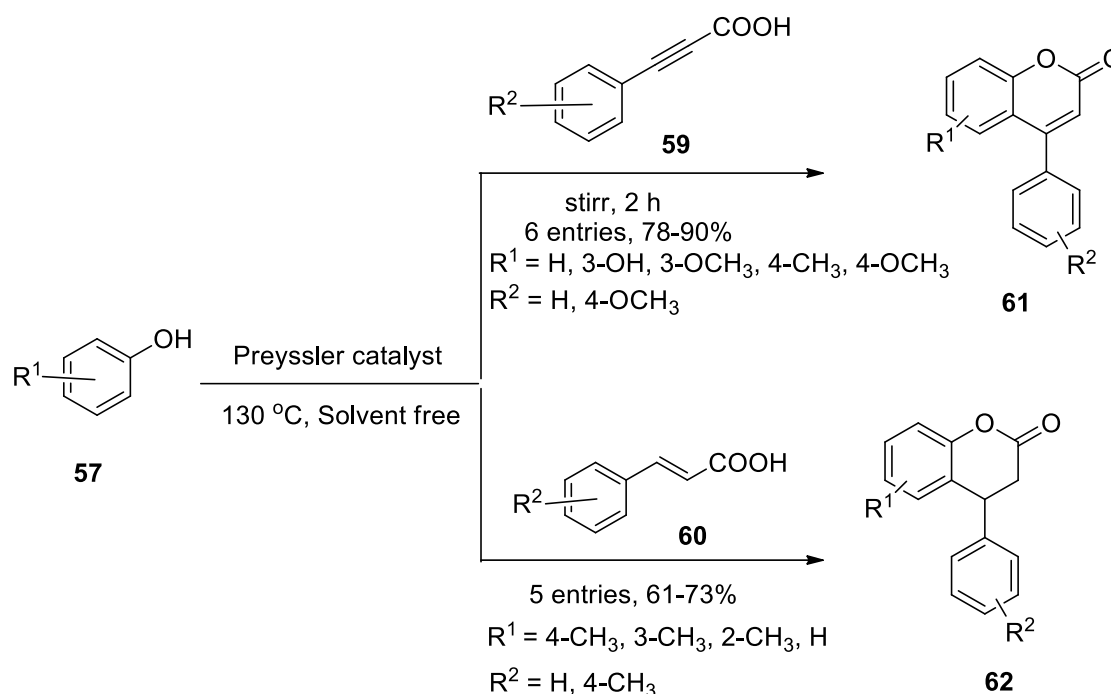
In 2007, Heravi *et al.* employed catalytic amounts of a Preyssler catalyst for the synthesis of a series of 4-methylcoumarin derivatives (**58**) by the reactions of substituted phenols (**57**) and ethyl acetoacetate (**16**) at 130 °C for 30 minutes under solvent-free conditions (Scheme 22).⁹⁶ The catalyst was recovered and reused for three successive runs without any notable loss in catalytic activity. A number of other heteropoly acids, including Keggin (H₃PW₁₂O₄₀) and Dawson (H₆P₂W₁₈O₆₂) catalysts, were also employed for this reaction, but afforded lower yields.



Scheme 22. Synthesis of 4-methylcoumarins using Preyssler catalyst under neat conditions.

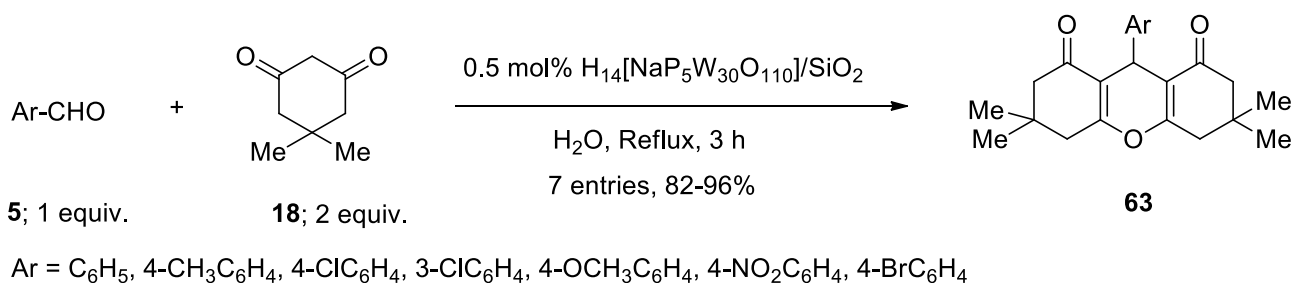
Using the same catalyst, Escobar *et al.* synthesized a series of 4-phenyl coumarins (**61**) from the reactions of substituted phenols (**57**) and 3-phenylpropionic acids (**59**) at 130 °C under solvent-free conditions

(Scheme 23).⁹⁷ Synthesis of 4-phenyl-3,4-dihydro-coumarins (**62**) were achieved from the reactions of phenols (**57**) and substituted cinnamic acid derivatives (**60**) under the same optimized reaction conditions.



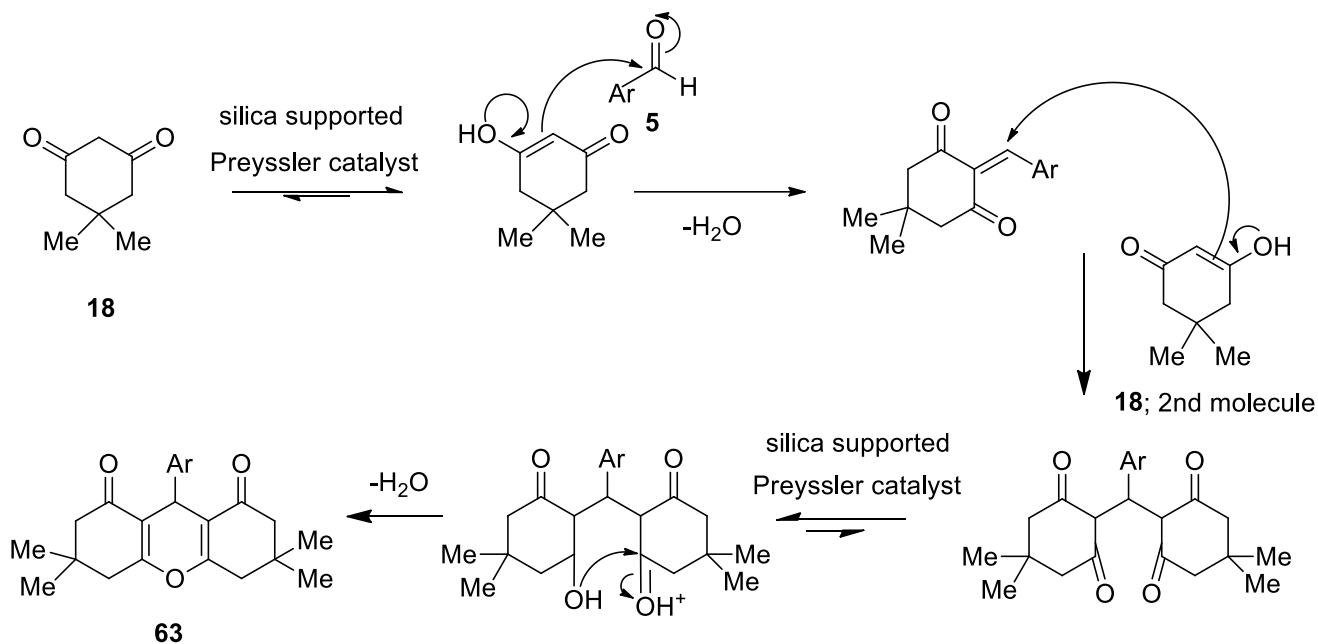
Scheme 23. Synthesis of 4-phenyl coumarins/3,4-dihydrocoumarins using Preyssler catalyst under neat conditions.

2.2.3. Synthesis of 1,8-dioxo-octahydroxanthenes. Many xanthene derivatives possess significant anti-inflammatory,⁹⁸ antiviral,⁹⁹ antiplasmodial,¹⁰⁰ etc., activities. 1,8-Dioxo-octahydroxanthenes (**63**) showed promising anticancer activities.^{101,102} Javid *et al.* synthesized these biologically significant scaffolds from the pseudo-three-component reactions between one equivalent of aldehydes (**5**) and two equivalents of dimedone (**18**) using a catalytic amount of silica-supported Preyssler catalyst in water under reflux conditions (Scheme 24).¹⁰³



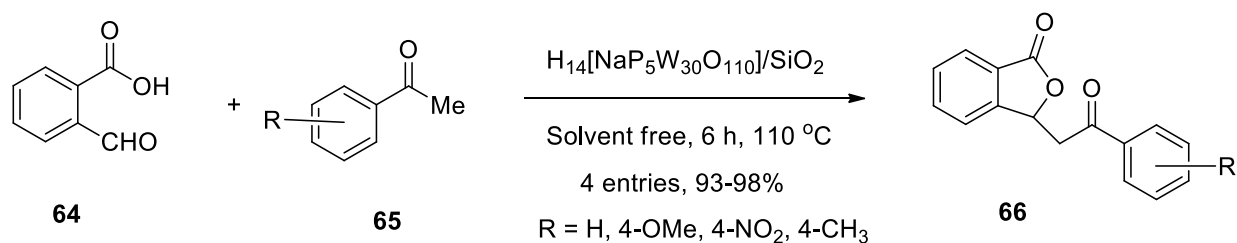
Scheme 24. Synthesis of 1,8-dioxo-octahydroxanthenes using silica supported Preyssler catalyst in water.

A plausible mechanism for the reactions is shown in Scheme 25.



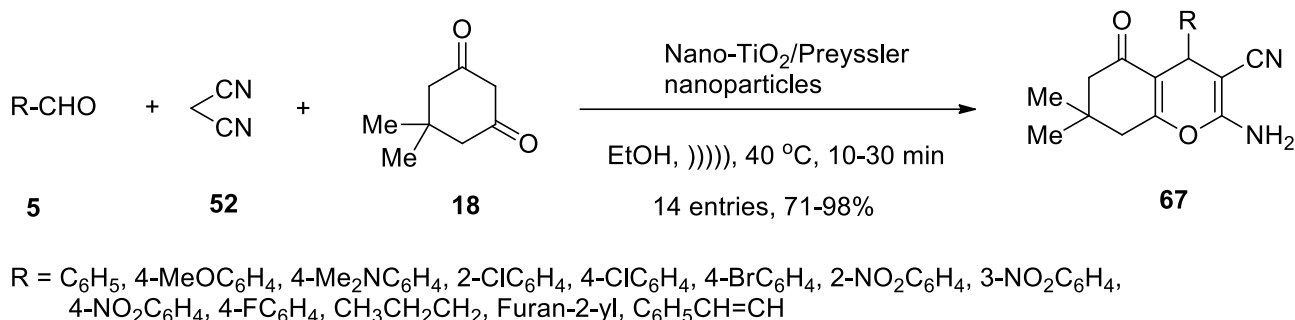
Scheme 25. Plausible mechanism for the synthesis of 1,8-dioxo-octahydroxanthenes using silica-supported Preyssler catalyst.

2.2.4. Synthesis of substituted isobenzofuran-1(3H)-ones. Starting from phthalaldehydic acid (**64**) and acetophenone derivatives (**65**), a series of substituted isobenzofuran-1(3H)-ones (**66**) was synthesized using a catalytic amount of silica-supported Preyssler catalyst under solvent-free conditions at 110 °C (Scheme 26).¹⁰⁴



Scheme 26. Synthesis of substituted isobenzofuran-1(3H)-ones using silica-supported Preyssler catalyst.

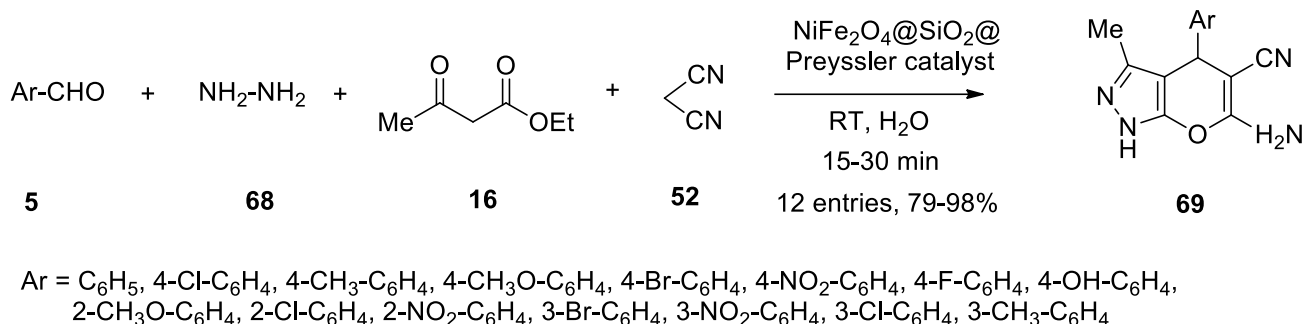
2.2.5. Synthesis of 2-amino-3-cyano-4H-pyrans or pyran-annulated heterocycles. Various 2-amino-3-cyano-4H-pyrans or pyran-annulated heterocycles possess a wide range of pharmacological activities.¹⁰⁵⁻¹⁰⁷ Numerous methods have been reported for the synthesis of structurally diverse pyran derivatives.¹⁰⁸⁻¹¹¹ A majority of these reported reactions were catalyzed by homogeneous catalysts. In 2014, Azarifar *et al.* reported a facile, efficient, and ultrasound-assisted protocol for the synthesis of 2-amino-3-cyano-4-aryl-5,6,7,8-tetrahydro-4H-chromenes (**67**) from the reactions of various aldehydes (**5**), malononitrile (**52**) and dimedone (**18**) utilizing a catalytic amount of nano-titania-supported Preyssler-type heteropoly acid as a heterogeneous catalyst, in ethanol, at 40 °C (Scheme 27).¹¹² After completion of the reaction, the solid catalyst was recovered and recycled for three successive runs without any loss in its catalytic efficiency. A series of aldehydes with electron-donating or electron-withdrawing substituents underwent reactions smoothly and afforded the desired products with excellent yields.



Scheme 27. Ultrasound-assisted synthesis of 2-amino-3-cyano-4-aryl-5,6,7,8-tetrahydro-4H-chromenes using nano-titania-supported Preyssler-type heteropoly acid as a catalyst.

2.3. Synthesis of bioactive N, O-heterocycles using Preyssler catalyst

2.3.1. Synthesis of pyrano[2,3-c]pyrazoles. In 2016, Javid *et al.* demonstrated a facile approach for the efficient synthesis of a series of pyrano[2,3-c]pyrazoles (**69**) *via* one-pot, four-component reactions of aromatic aldehydes (**5**), malononitrile (**52**), hydrazine hydrate (**68**) and ethyl acetoacetate (**2**) in the presence of a catalytic amount of silica-supported, nickel-ferrite functionalized, Preyssler catalyst in water at room temperature for 30 minutes (Scheme 28).¹¹³ The catalyst was recovered and reused for five successive runs with negligible loss of catalytic activities.



Scheme 28. Synthesis of pyrano[2,3-c]pyrazoles using silica-supported, nickel-ferrite-functionalized Preyssler catalyst in water.

2.4. Synthesis of bioactive N, S-heterocycles using Preyssler catalyst

2.4.1. Synthesis of 6,8-dimethyl-3-aryl-[1,2,4]triazolo[3,4-b][1,3,4]thiazepine derivatives. Hekmatshoar *et al.* utilized a Preyssler catalyst for the synthesis of 6,8-dimethyl-3-aryl-[1,2,4]triazolo[3,4-b][1,3,4]thiazepine derivatives (**71**) from the reactions of 3-aryl-4-amino-5-mercapto-1,2,4-triazole (**70**) and acetylacetone (**16a**) under solvent-free conditions at 90 °C (Scheme 29).¹¹⁴ The used catalyst was recovered quantitatively, and was recycled for four successive runs without any loss in its catalytic activities. During optimization of the protocol, the catalytic activities of a number of other heteropoly acids, such as H₁₄[NaP₅W₃₀O₁₁₀]/SiO₂ and H₃[PW₁₂O₄₀], H₃[PW₁₂O₄₀]/SiO₂, were screened, but were found to be less effective.

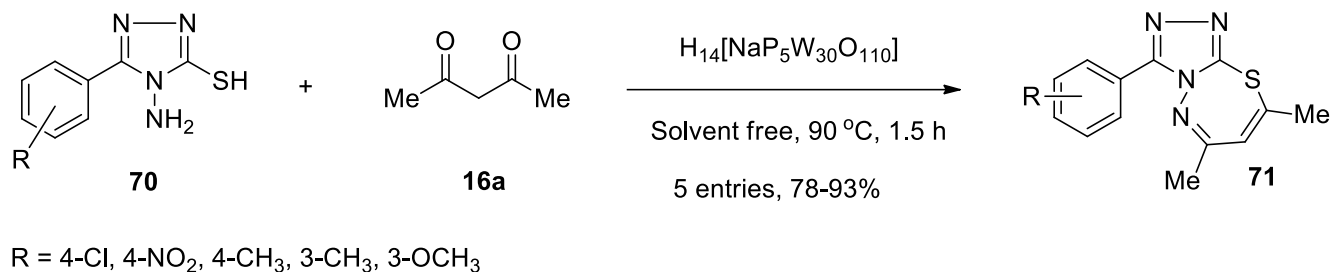


Figure 29. Synthesis of 6,8-dimethyl-3-aryl-[1,2,4]triazolo[3,4-*b*][1,3,4]thiazepines using a Preyssler catalyst.

3. Conclusions

The synthesis of diverse, biologically promising heterocyclic scaffolds is regarded as belonging among the forefronts of research today in organic chemistry. Heterogeneous heteropoly acids have received significant attention, and successfully employed, as efficient, reusable acidic catalysts for various organic transformations. The Preyssler catalyst ($\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$), particularly, has been used extensively for a variety of organic reactions. In most instances, the catalyst has been recovered easily and recycled several times with almost equal efficiency. The present review summarizes the literature related to the synthesis of various heterocyclic scaffolds under diverse reaction conditions, utilizing a catalytic amount of Preyssler heteropoly acid as catalyst. We strongly believe this review will help to promote the use of the Preyssler catalyst for many other organic transformations.

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This paper is dedicated to **Prof. György Keglevich**, pictured above. **Prof. György Keglevich** is the Head of the Department, Department of Organic Chemistry, Budapest University of Technology and Economics, Budapest, Hungary.

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