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Article

Sulfonic Acid Functionalized Organic/Inorganic Templates used for Various Organic Transformations

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ABSTRACT

The main intention of this review is to summarize, some of the recent advances in a sulfonic acid-functionalized organic/inorganic templates, such as melamine tri sulfonic acid, β-cyclodextrin sulfonic acid, and cellulose sulfonic acid, are belongs to sulfonated organic templates and hybrid templates; on the other hand, the sulfonated inorganic acids are phospho sulfonic acid, boron sulfonic acid, and tungsto sulfonic acid. All these sulfonated templates are most stable, recyclable, heterogeneous nature, and bio-degradable polymeric catalysts in organic synthesis. In this review, preparation, and application of sulfonated templates in organic synthesis are investigated.

Key words: Heterogeneous acid catalysis, various organic transformations, Environment friendly

1. INTRODUCTION

The significant increase in the rate of chemical reaction in the presence of addition substance is called as catalyst this process is called as catalysis. Catalysis has played an important role in reduction of byproducts, toxic waste, and reduction of poisonous gases from chemical processes in our environment. In addition catalysis is one of the most importances for the synthesis of medicinally potent heterocyclic compounds. Chemical transformation can be more efficient and selective using catalyst in that way eliminating unwanted products [1,2]. In general, the catalysts are mainly two types, one is homogeneous [3], another one is heterogeneous [4]. Homogeneous acid catalysts are HCl, $ClSO_3H$, HBr, CH_3COOH, CF_3COOH, CF_3SO_3H, H_2SO_4, and HF which are widely used in many significant organic transformations as well as important industrial processes, but they have some disadvantages in handling, trouble work-up procedures, water sensitive, corrosiveness, and production of toxic waste [5]. After completion of the reaction, such acids are usually destroyed in water quenching stage need subsequent neutralization. Furthermore, the recovery of the catalyst from the reaction mixture is difficult. Hence, the researchers are focused toward heterogeneous recyclable solid acid (HRSA), catalysts such as per fluorinated ion exchange polymers and Nafion [6,7] were prepared to solve this problem [8]. Afterward, there are many solid acids that were prepared such as solid acid zeolite [9], sulfated zirconia [10], phospho sulfonic acid (PSA) [11] phosphotungstic acid [12] silica sulfonic acid [13], tungstate sulfuric acid [14], alumina sulfuric acid [15,16], molybdate sulfuric acid [17], SiO_2-Pr-SO_3H [18], phosphomolybdic acid [19], amberlyst-15 [20], and MCM-41-SO_3H [21], were used for the synthesis of various organic transformations. These HRSAs have many advantages over conventional homogeneous acid catalyst such as such as mildness, easy to handling in reactions, cost-effective, selective transformations, easy to separate form reaction mixture, ecofriendly, and also reduced plant corrosion problems in chemical industry. On the other hand, the biodegradable, polymer-supported, and recyclable solid acid catalysts such as PEG-SO_3H, Cellulose-SO_3H, Chitosan-SO_3H, and beta-cyclodextrin-sulfonic acids are developed for the synthesis of biologically heterocyclic compounds as well as a wide range of industrial important organic intermediates.

Nowadays, the researchers are mainly focused toward eco-friendly, green solvents (i.e., water, PEG, and ethylene glycol) easy to synthesize, reusable, and easy to handle catalysts. Thus, supported catalysts, reagents, and scavengers have drawn much attention of researchers [22]. The utility of supported catalysts is well-recognized with their advantages such as ease of workup, simple separation of products from the catalysts, and economy. The majority of the sulfonated organic templates are biodegradable catalysts expect MSTA. The biodegradable, polymer supported that recyclable solid acid catalysts are an important one in the synthesis of heterocyclic compounds due to the high reactivity. Polymer supported catalysts have been employed as stoichiometric reagents and catalysts in organic synthesis [23,24]. However, their development and applications in organic synthesis are undergoing a tremendous renaisstance at present, which is undoubtedly being fueled by the special requirements of combinatorial and green chemistry [23,24]. The all polymer supported catalysts were best example of solid supported organic solid acid catalyst that is functionalized with strong acidity, non-corrosiveness, and non-volatility and also recognized as a good surfactant. Therefore, many efforts have been made by researchers constantly to introduce novel recyclable, biodegradable, and polymer-supported catalyzed organic synthesis using Cellulose-SO_3H, Chitosan-SO_3H, PEG-OSO_3H, beta-cyclodextrin-sulfonic acids that are more economical, efficient, and biocompatible with the environment and also these

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catalysts can be easily separate and reused several times without losing its catalytic activity.

On the other hand, the sulfonated inorganic templates are denoted as HSRAs these catalyst to facilitates various organic transformations a significant area of research. Consequently, many researchers were introduce new and novel HSRAs catalyzed organic synthesis using PSA, boron sulfonic acid (BSA), alumina sulfuric acid (ASA), and tungstate sulfuric acid (TSA), which are more efficient, economical and eco-friendly with the environment. Furthermore, these catalysts can be recovered and reused many times, without decreasing their activity. The present article is intended to review briefly the recent research progress made concerning the synthesis of different organic compounds catalyzed by sulfonated organic/inorganic templates.

2. ORGANIC TEMPLATES

2.1. Melamine Tri Sulfonic Acid (MTSA) [25]

MTSA has been developed as a heterogeneous solid acid catalyst for the synthesis of a various organic transformations and heterocyclic compounds. MTSA can be easily prepared by adding melamine (3.12 g) to chlorosulfonic acid (5 mL) under stirring condition with removal of the liberated HCl gas under reduced pressure. Then, the reaction was kept at this condition for 30 min at room temperature. The mixture was triturated with n-hexane (10 mL) and then filtered. The solid residue was washed with n-hexane (10 mL) and dried under vacuum. MTSA (7.9 g, 87%) was obtained as a white solid, which was stored in a capped bottle. MTSA is a solid, heterogeneous catalyst and after completion of an organic transformation, it can be recovered and reused several times without loss of its catalytic activity.

2.1.1. Synthesis of coumarins

Coumarins and their derivatives are important class of oxygen containing heterocyclic compounds preparation of these compounds are significant area for organic and medicinal chemistry owing to the various biological properties such as antibacterial [26], inhibitor of HIV-1 protease [27], anticancer [28], inhibition of platelet aggregation [29], and inhibitor of steroid 5-reductase [30] and. Furthermore, coumarins are widely used as additives in food, agrochemicals, cosmetics, perfumes, pharmaceuticals [31], and also in the preparation of optical brightening agents, insecticides, dispersed fluorescent, and tunable dye lasers [32]. Based on this importance of coumarins, Shirini *et al*. [33] in 2010 have developed an efficient and eco-friendly synthesis of coumarins through the condensation of various phenols, resorcinols, and naphthols with ethyl acetoacetate or methyl acetoacetate in the presence of MTSA as a heterogeneous recyclable solid acid catalyst in solvent free at 80°C (Scheme 1). In addition, the authors also carried out a comparison of MTSA with various acid catalysts such as $InCl_3$, [bmim] [HSO_4], $HClO_4$-SiO_2, and Wells-Dawson Heteropolyacid. It was found that MTSA is best suited catalyst for the Pechman condensation.

2.1.2. Synthesis of chemoselective oxathioacetalyzation of aldehydes

Oxathiolanes are important protecting groups for aldehydes due to their considerable stability under acidic and basic conditions. The construction of Oxathiolanes are by the reaction of aldehyde with 2-mercaptoethanol. The mercaptoethaol is another significant protecting reagent for aldehydes. There are numerous reagents were used for the synthesis of targeted compounds such as p-TsOH [34], HClO4 [35], ZrCl4 [36], TMSOTf [37], TBAB [38], OTAB [39], NBS [40], MeS2/Br2 [41], PPS/SiO2 [42], PAS [43], TaCl5/SiO2 [44], ASA [45]. However, these reported methods suffer from such as long reaction time, vigorous reaction conditions, the occurrence of side reactions, and unavailability of the reagents, as well as poor yields of the desired product. Due to this Shirini *et al*. [46] reported chemoselective high yield oxathioacetalyzation (Scheme 2) in the presence of MTSA.

2.1.3. Synthesis of triazolo[1,2-a]indazole-triones and some 2H-indazolo[2,1-b]phthalazine-triones

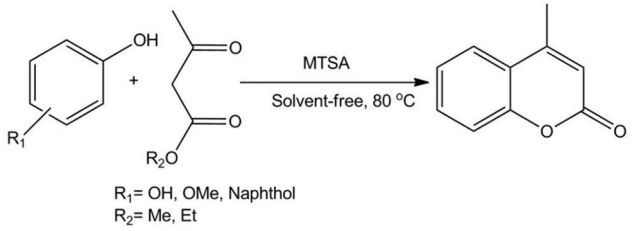
Triazolo[1,2-a]indazole-triones and 2H-indazolo[2,1-b]phthalazine-triones are an important class of nitrogen containing heterocyclic compounds and also important class of natural and non-natural products, many of which exhibit useful biological activities and clinical applications [47,48]. Khazaei *et al*. have developed a solvent-free synthesis of Triazolo[1,2-a]indazole-triones and 2H-indazolo[2,1-b] phthalazine-triones, through the condensation of various aldehydes, β-ketones (dimedone or 1,3-cyclohexanedione) urazole and phthalhydrazide in the presence of MTSA as a heterogeneous recyclable solid acid catalyst in solvent free at 80–100°C (Scheme 3) [49].

2.1.4. Synthesis of crossed-aldol condensation

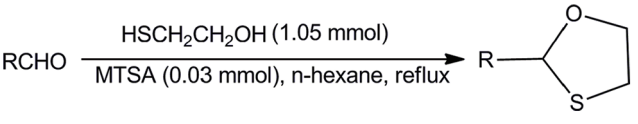
Crossed-aldol condensation is one of the most significant method for the carbon-carbon bond formation and the synthesis of α, β-unsaturated carbonyl compounds and also important precursors to potentially bioactive pyrimidines derivatives [50], intermediates of agrochemicals, perfumes, and pharmaceuticals [51]. Crossed-aldol condensation is typically carried out using strong acid or base [52]. However, this procedure suffers from reverse and side reactions resulting in low yields of the products. Various methods for the synthesis of this type of reactions have been developed. Various metal complexes ions, such as Co(II), Fe(II), Mn(II), Ni(II), and Zn(II), were used as catalysts [53], but all the reported yields were <38%. On the other hand, the other methods such as silica sulfuric acid [54], SiO_2-Pr-SO_3H [55], $LiClO_4$ [56], polymer supported sulfonic acid (NKC-9), and carbon based solid acid [57] have also been used to synthesis of this reaction. The reported methods are effective but it contains various drawbacks such as requirement of long reaction times, hazards, explosive, use of solvent, and formation of side-products. Therefore, Shirini *et al*. [58] reported efficient and eco-friendly synthesis of crossed-aldol condensation of various aromatic aldehydes and cyclic ketones in the presence of MTSA under solvent free at 75°C (Scheme 4). Furthermore, they also comparison with other reported methods such as silica sulfuric acid [54], I_2 [59], SiO_2-Pr-SO_3H [55], and NKC-9 [57], among all of them, MTSA is the best suited catalyst for this reaction.

2.1.5. Protection alcohols, phenols, aldehydes, and amines

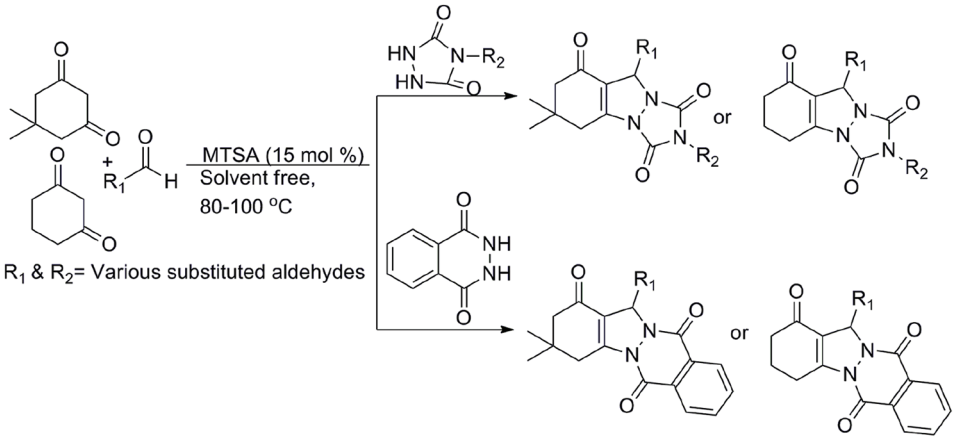
Shirini *et al*. [25] have been developed efficient and eco-friendly procedure for the protection of alcohols, phenols, aldehydes, and amines using MTSA under solvent-free condition at room temperature (Scheme 5). In this method, they used a wide range of substrates are protected by the corresponding reagents such as alcohols, phenols are



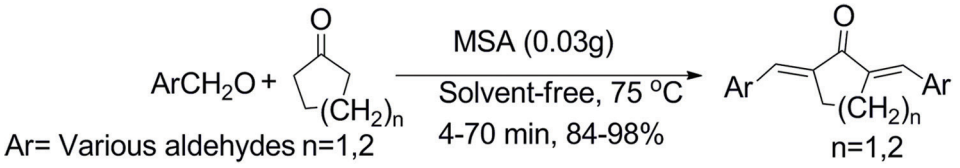
Scheme 1: Synthesis of coumarins catalyzed by MTSA.



Scheme 2: Synthesis of oxathiolanes catalyzed by MTSA.



Scheme 3: Synthesis of triazolo[1,2-a]indazole-triones and some 2H-indazolo[2,1-b]phthalazine-triones catalyzed by MTSA.



Scheme 4: Synthesis of crossed-aldol condensation catalyzed by MTSA.

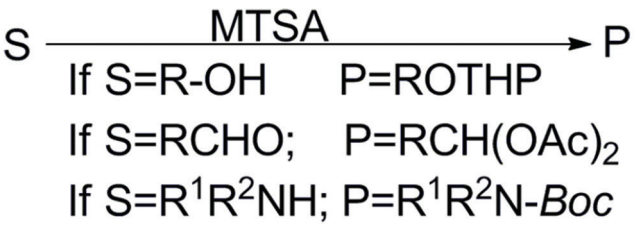
protected by 3,4-dihydro-2H-pyran, aldehydes were protected by acetic anhydride, and amines are protected by di-tert-butoxypyrocarbonate [$(Boc)_2O$]. All the products were obtained with high yields with short reaction times. In addition, these results are comparison with other reported methods such as p-toluene sulfonic acid [60], copper methanesulfonate/HOAc [61], and silica sulfuric acid [62], among all of these, MTSA is superior than reported one.

2.1.6. N-formylation of amines

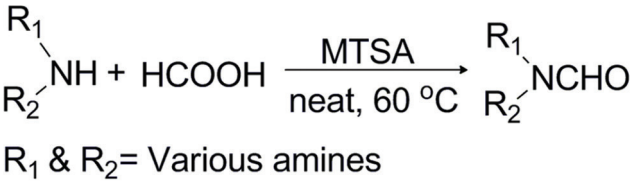
The formyl group is most significant amino protecting group in peptide synthesis [63]. Formamides are important intermediates in organic synthesis that have been used in the synthesis of biological active compounds, for example, substituted imidazoles [64], nitrogen-bridged heterocycles [65], fluoroquinolones [66], and 1,2-dihydroquinolines [67]. In general, syntheses of formamides are the reaction of amines with formic acid, in the presence of various catalyst, such as Amberlite IR-120 [68], In [69], nano-MgO [70], I_2 [71], VB1 [72], and sulfonic acid supported on hydroxyapatiteencapsulated-c-Fe_2O_3 nanocrystallites [73]. These methods are appropriate for certain synthetic conditions; however, the majority of these reported procedures are connected with one or more disadvantages such as expensive reagents, low selectivity, longer reaction times, tedious work-up procedure, and large amounts of catalysts which would ultimately result in the generation of large amounts of toxic waste. Yang *et al*. [74] reported a novel, mild, and efficient method for the N-formylation of amines using amines and formic acid in the presence of MTSA as a catalyst (Scheme 6) and also these results are comparison with other literature methods such as I_2, in, nano-MgO, $ZnCl_2$, among all of these, MTSA is shows best results.

2.1.7. Synthesis of β-acetamido ketones

β-Acetamido ketones are important building blocks for various biologically and medicinally valuable compounds [75-80]. For example, they are precursors of molecules such as 1,3-amino alcohols [75-77] and γ-lactams [78], as well as biologically attractive compounds such as nikkomycins or neopolyoxins [76,79]. Moreover, it is reported that β-acetamido ketones can act as a glucosidase inhibitors [80]. Due to



Scheme 5: Protection alcohols, phenols, aldehydes, and amines catalyzed by MTSA.



Scheme 6: N-formylation of amines with formic acid in the presence of MTSA.

the importance of these compounds various methods are reported for the synthesis of β-Acetamido ketones such as heteropolyacids [81], $ZrOCl_2.8H_2O$ [82], $CoCl_2$ [83], and polyaniline-supported salts [84]. However, the reported methods have some drawbacks such as low yields, long reaction times, the use of toxic or expensive catalysts, the use of large amount of catalyst, harsh reaction conditions, tedious work-up procedure, and performance the reaction under certain special conditions so that Zare *et al*. [85], search for finding a protocol for the preparation of β-acetamido ketones (Scheme 7) which are not associated with the above-mentioned disadvantages.

2.1.8. Synthesis of 7-alkyl-6H,7H-naphtho[10,20:5,6]pyrano-[3,2-c]chromen-6-ones

Chromenes are naturally occurring chemical compounds [86-89], and poses various biological and therapeutic properties such as

antimicrobial [90,91], antioxidant [92,93], ant rhinovirus [94], anticancer [95,96], and antihypertensive activity [97]. Due to the importance of chromenes, Wu *et al*. [98] have been developed efficient neat chemical synthesis of chromenes in the presence of MTSA (Scheme 8). He also studied various molar percentage of MTSA and reaction temperature he found 2 mol % of MTSA at 120°C this is the best condition for the synthesis of biologically potent chromenes.

2.1.9. Synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones

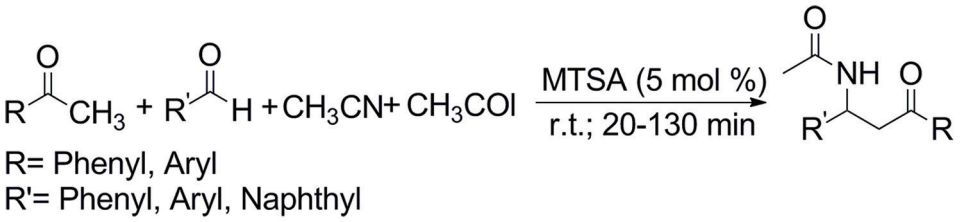
Biginelli reported the first synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones, through a one-pot three component condensation of an aldehyde, a b-ketoester and urea in 1893 [99]. Nowadays, the synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones has attracted the attention of many synthetic chemists due to their wide range therapeutical and pharmacological properties, such as antitumor, anti-inflammatory, antiviral, and antibacterial properties [100]. Furthermore, many alkaloids containing dihydropyrimidine as the core unit, exhibiting interesting biological properties, have been isolated from marine sources [101-103]. The researchers are developed various methods for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones some of them $H_3PW_{12}O_{40}/SiO_2$ [104], $Cu(OTf)_2$ [105], NH_2SO_3H [106], 12-molbdophosphoric acid [107] [bmim]BF_4-immobilized Cu(II) acetylacetonate [108], and [bmim] [$FeCl_4$] [109]. On the other hand, in spite of their potential utility, the practical application of most of these reagents suffers from disadvantages such as the use of expensive or less easily available reagents, long reaction times, vigorous reaction conditions, high temperatures, unsatisfactory yields, and tedious manipulations to isolate the products. Therefore, Shirini *et al*. [110] have been discovered an inexpensive, facile, and efficient reagent for the preparation of 3,4-dihydropyrimidin-2(1H)-ones/thiones in the presence of MTSA (Scheme 9).

2.1.10. Trimethylsilylation of alcohols and phenols are promoted by MTSA

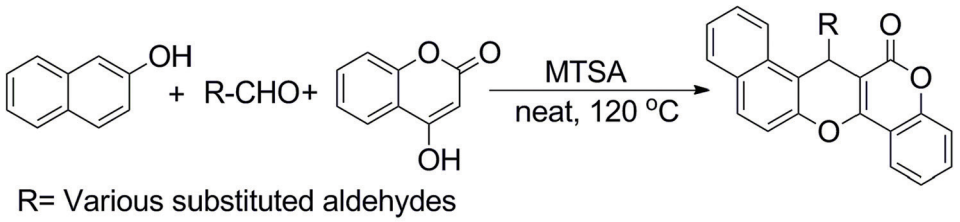
The protection of hydroxyl groups by the formation of silyl ethers has been extensively used in organic synthesis [111]. The silylation of alcohols and phenols is very significant attention in multistep organic synthesis [111]. There are numerous reagents which have been used protection, hexamethyldisilazane (HMDS), a commercially available, stable, and cheap, reagent, is selected as one of the best reagent for the silylation. Its handling does not require special precautions and the workup is not facile because the by-product of the reaction is ammonia, which is simple to remove from the reaction medium. However, the low silylating power of HMDS is the main drawback to its application. Hence, there are a variety of catalysts for the activation of this reagent such as 1,3-dichloro-5,5-dimethylhydantoin [112], $TiCl_2(OTf)$–SiO_2 [113], $NaHSO_4$–SiO_2 [114], NBS [115], $CuSO_4$ [116], ZnO [117], and I_2 [118]. However, the accessible methodologies are associated with one or more disadvantages such as harsh reaction conditions, for example, treatment with air sensitive reagent such as trichloroisocyanuric acid at CH_2Cl_2 for 4 h, heating at 85°C in PhMe catalyzed by alumina-supported heteropolyoxometalates,15 heating in CH_3CN in the presence of 25 mol% $Fe(HSO_4)_3$ at reflux for 1.7 h; prolonged reaction time; and requirement for hazardous and carcinogenic organic solvents such as CH_3CN, CH_2Cl_2, PhMe; use of toxic, costly, or air sensitive catalysts [119]. Thus, Yan *et al*. [120] have been developed environmentally benign, high-yielding, and clean approaches for the silylation of hydroxyl groups in the presence of recyclable solid acid MTSA (Scheme 10). In addition, he studied comparison of reported methods to the present method this is the best one for the silylation of alcohols and phenols. Furthermore, he used to study the recyclability of the catalyst up to three runs, the catalyst is effectively working.

2.1.11. Synthesis of aryldithienylmethanes

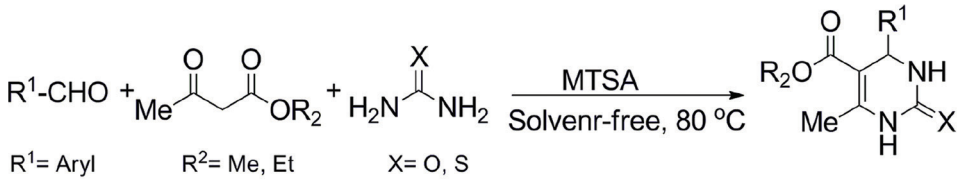
Dithienylmethanes are significant building blocks for the synthesis of a variety of functionational porphyrins and its analogs [121], which can be used in materials science [122]. Subsequently, the synthesis of dithienylmethanes by the reaction of aldehydes with thiophene under various catalysts such as trifluoroacetic acid [121a], NaHSO4- SiO2



Scheme 7: Synthesis of β-acetamido ketones in the presence of MTSA.



Scheme 8: Synthesis of 7-alkyl-6*H*,7*H*-naphtho[10,20:5,6]pyrano-[3,2-c]chromen-6-ones catalyzed by MTSA.



Scheme 9: Synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones in the presence of MTSA.

[123] BF3·Et2O [121a], TiCl4 [121b], and Hence, a mild, efficient, and green chemical method using for the synthesis of dithienylmethanes in the presence of heterogeneous reusable catalyst MTSA (Scheme 11). Furthermore, he studied the different molar percentage of catalyst and different temperatures he found the best method for the synthesis of targeted compounds 20 mol % of catalyst at 84°C and also he used to study the comparison with reported methods.

3. HYBRID TEMPLATES

3.1. Synthesis of β-Cyclodextrin Sulfonic Acid, β-Cyclodextrin-n-propyl Sulfonic Acid, β-Cyclodextrin-n-butyl Sulfonic Acid

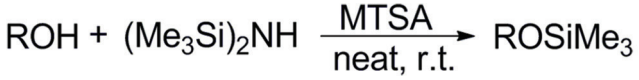
A mixture of β-cyclodextrine (5.00 g, 4.5 mmol) in $CHCl_3$ (20 mL), chlorosulfonic acid (1.00 g, 9 mmol) was added dropwise at 0°C during 2 h. After addition was completed, the mixture was stirred for 2 h to remove HCl from reaction vessel. Then, the mixture was filtered and washed with methanol (30 mL) and dried at room temperature to obtain sulfonated β-cyclodextrine as white powder (5.28 g). The $–SO_3H$ content was measured by titration method and showed 0.52 mequiv./g.

3.1.1. Synthesis of 3,4-dihydropyrimidine-2(1H)-one/thiones

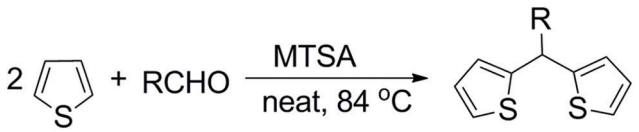
The biginelli dihydropyrimidine synthesis [124], first described in 1891, consists of the condensation of urea, aldehyde, and a 1,3-ketoester. This condensation reaction has been used for the synthesis of dihydropyrimidin-2-ones, which have fascinated significant interest because of their wide applications as antihypertensive agents, calcium channel blockers, a-1a-antagonists, and neuropeptide Y (NPY) antagonists [125,126]. In addition, some bioactive alkaloids such as batzelladine B containing the dihydropyrimidine unit have been isolated from marine sources, which show anti-HIV activity [102]. However, this method suffers from the drawbacks such as the lower yields of the desired products (20–40%) particularly in case of substituted aldehydes and loss of sensitive functional groups during the reaction. There are several methods developed and these methods have some drawbacks such as long reaction time, high catalyst loading, use of toxic solvents, and laborious work up procedures. Based on the above drawbacks, Asghari *et al*. [127] in 2011 developed a highly efficient and neat method for the synthesis of 3,4-dihydropyrimidine-2(1H)-one/thiones in presence of β-cyclodextrin sulfonic acid (Scheme 12). Furthermore, Gong *et al*. [128] also reported for the synthesis of 3,4-dihydropyrimidine-2(1H)-ones in the presence of β-cyclodextrin-propane sulfonic acid.

3.1.2. Synthesis of 3-indolyl-3-hydroxy oxindoles and 3,3-di(indolyl)indolin-2-ones

Indole derivatives are nitrogen containing various heterocyclic compounds, among them 3-substituted 3-hydroxyoxindoles are contains in many natural products and it possess biological activities [129] such as antiviral [130], anticancer [131], anti-HIV [132], antitumor [133], anticonvulsants [134], antifungal [135,136], anti-angiogenic [137], anti-Parkinson's disease therapeutic [138], and effective SARS coronavirus 3CL protease inhibitor [139]. Due to the importance of these compounds, the researchers are developed a number of reported methods for the synthesis of 3-indolyl-3-hydroxy oxindoles and 3,3-di(indolyl)indolin-2-ones. These reported methodologies produce good results in many instances. However, some of the synthetic strategies suffer from expensive reagents, metal catalyst, long reaction time, harsh reaction condition, environmentally hazardous, tedious work-up procedure, unsatisfactory yield, and use of homogeneous catalyst which are difficult to separate from the reaction mixture and reuse. Hence, Tayade *et al*. [140] developed an efficient aqueous medium for the synthesis of 3-indolyl-3-hydroxy oxindoles and 3,3-di(indolyl)indolin-2-ones in the presence of β-cyclodextrin sulfonic acid (Scheme 13).



Scheme 10: Trimethylsilylation of alcohols and phenols is catalyzed by MTSA.



Scheme 11: Synthesis of dithienylmethanes in the presence of MTSA.

3.1.3. Synthesis of 2,3-dihydroquinazolin-4(1H)-one

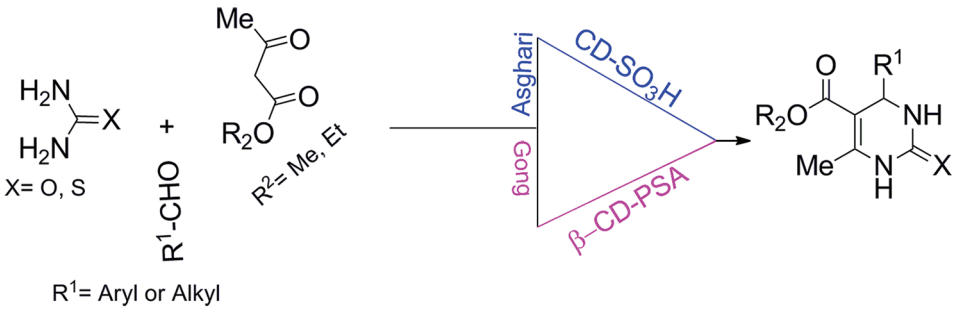
Quinazolinone derivatives are an important class of nitrogen containing fused heterocycles due to their wide range of potential pharmacological and biological properties [140-143]. The importances of these compounds are for the synthesis of drug molecules and natural products [144,145]. Recent years, the researchers are reported numerous methods for the preparation of 2,3-dihydroquinazolin-4(1H)-ones. The literature methods have drawbacks such as low yields, expensive catalysts, high reaction temperature, long reaction times, tedious procedures for preparation of catalysts, and tedious work-up conditions (column chromatography). Hence, Wu *et al*. have been developed an efficient, simple, easy work-up, and environmentally benign protocol using a recyclable catalyst and a green solvent for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-one in the presence of β-cyclodextrin sulfonic acid (Scheme 14a and b).

3.1.4. Synthesis of 1-amidoalkyl-2-naphthols

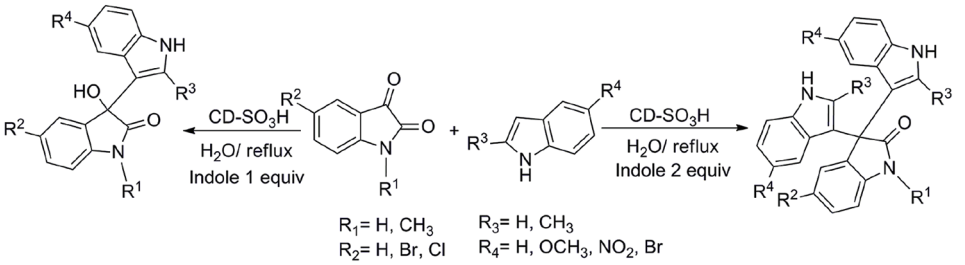
Compounds bearing 1,3-amido oxygenated functional groups are ubiquitous to a variety of biologically important natural products and potent drugs including a number of nucleoside antibiotics and HIV protease inhibitors such as ritonavir, lopinavir, and the hypotensive [146]. In addition, the bradycardiac effects of these compounds have been evaluated [147]. The importance of amidoalkyl naphthols has attracted renewed attention for their synthesis and various improved procedures have been developed using various catalyst as well as addition energies (i.e., microwave, ultrasonication). However, these reported procedures suffer from one or more shortcomings such as use of toxic organic solvents, prolonged reaction time, low yield, requirement of excess of reagents or catalysts, and harsh reaction conditions. Therefore, introducing neat method and utilizing eco-friendly catalysts which can simply be recycled at the end of the reactions have been receiving permanent attention. The necessity for an environmentally benign procedure with a heterogeneous and reusable catalyst is encouraged to develop a safe alternative method for the synthesis of 1-amidoalkyl-2-naphthols in the presence of β-cyclodextrin-butane sulfonic acid (β-CD-BSA) (Scheme 15) [148].

3.1.5. Synthesis of dihydropyrano[2,3-c]pyrazole

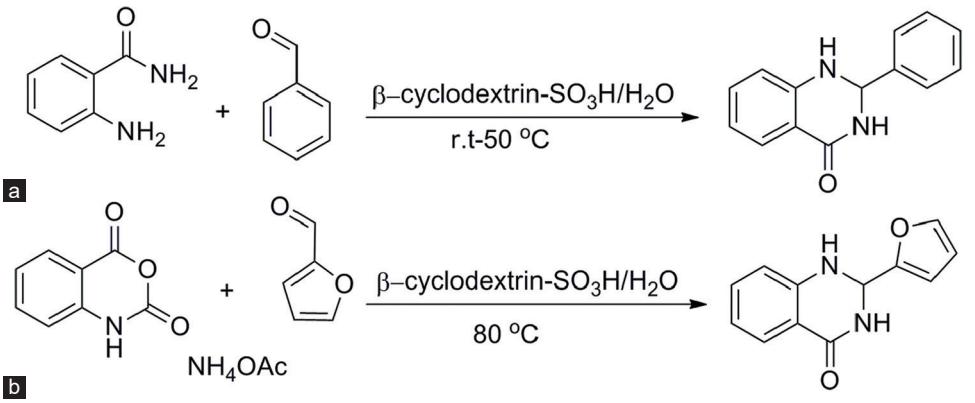
The nitrogen and oxygen fused heterocycles; pyranopyrazoles are ubiquitous and have been denoted as "core structures" in drug discovery. The dihydropyrano [2,3-c] pyrazoles show a various biological properties such as anti-inflammatory [149b], antitumor [149a], analgesic [149c], and antimicrobial [149d]. In addition, these compounds act as insecticides and molluscidal agents [150]. Due to the most potent biological properties of these compounds are prepared using various catalytic methods that have been developed. The reported methods show some disadvantages such as high catalyst loading, harsh reaction condition, and use to toxic solvents. Hence, Chaudhari *et al*. [151] have been developed highly efficient and agues



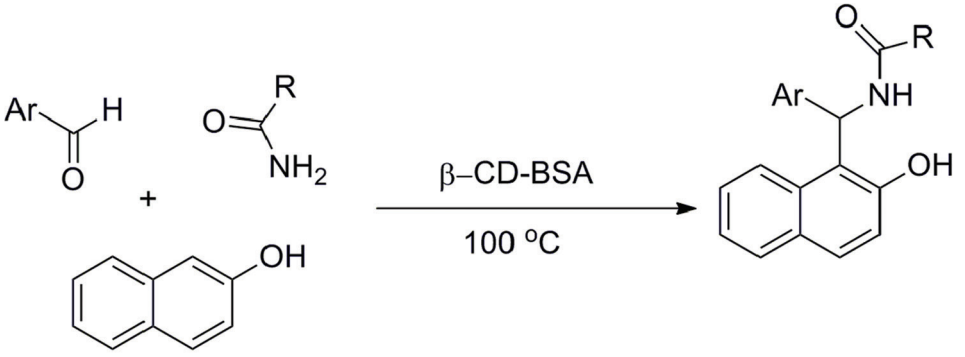
Scheme 12: Synthesis of 3,4-dihydropyrimidine-2(1H)-one/thiones in the presence of β-CD-SO_3H.



Scheme 13: Synthesis of 3-indolyl-3-hydroxy oxindoles and 3,3-di(indolyl)indolin-2-ones in presence of β-CD-SO_3H.



Scheme 14: (a and b) Synthesis of 2,3-dihydroquinazolin-4(1*H*)-one in the presence of β-CD-SO_3H.



Scheme 15: Synthesis of 1-amidoalkyl-2-naphthols in the presence of β-CD-SO_3H.

synthesis of dihydropyrano[2,3-c]pyrazole derivatives involve a four-component coupling of aromatic aldehyde, malononitrile, ethyl acetoacetate, and hydrazine hydrate in the presence of β-cyclodextrin sulfonic acid (Scheme 16).

3.1.6. Synthesis of 4-thiazolidinones

Thiazolidinones are an important S, N, and O containing heterocyclic compounds which possess diverse potent biological activities such as antibacterial [152,153], anti-tubercular [154], anti-inflammatory [155], anticonvulsant [156,157], anticancer [158,159], antifungal [160], antihistaminic [161,162], antiviral [163], and cardiovascular effects [164]. The most potent biological properties of these

compounds are prepared using various catalytic methods that have been developed. The reported methods show some disadvantages such as tedious workup procedures, high catalyst loading, and use to toxic solvents. Hence, Chaudhari *et al*. [151] have been developed highly efficient method for the synthesis of 4-thiazolidinones in presence of β-cyclodextrin sulfonic acid (Scheme 17).

3.1.7. Synthesis of 2H-indazole [2,1-b]phthalazinetriones

The construction of nitrogen, sulfur, oxygen, and phosphorus containing heterocyclic compounds are great interest due to their wide range of applications. Among them nitrogen containing heterocycles are showed most potent biological properties. Phthalazines are significant nitrogen contacting heterocyclic compounds which contain good medicinal and pharmacological activities such as anticonvulsant, cardiotonic, and vasorelaxant [165-167]. Owing to the importance of this compounds the researchers have been developed various catalytic methods for the construction of Phthalazine and its derivatives. The reported methods shown various disadvantages such as expensive catalyst, harsh reaction conditions, and non-recyclable catalysts. To solve this problem, Atar *et al*. [168] have been developed a green protocol for the synthesis of 2H-indazole [2,1-b]phthalazinetriones in the presence of β-cyclodextrin sulfonic acid (Scheme 18).

4. CELLULOSE SULFONIC ACID (CSA)

4.1. The Synthesis and Importance of CSA

Cellulose (5.00 g) in 20 ml of n-hexane, the mixture is magnetically stirred and 1.00 g of chlorosulfonic acid (9 mmol) added dropwise at 0°C over 2 h. HCl gas is immediately evolved. After completion of the addition the mixture is stirred for 2 h at room temperature. Then, the mixture is filtered and the collected solid washed with 30 ml of acetonitrile and dried at room temperature to afford 5.25 g of CSA as a white powder 33. CSA is non-hygroscopic, non-explosive, and stable at room temperature.

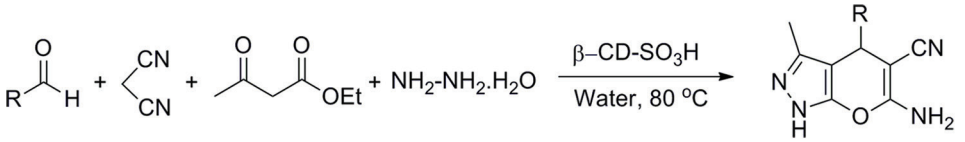
CSA is one of the significant heterogeneous solid acid catalysts which has a good performance as an inexpensive biopolymer-based catalyst and can be easily separated without contaminating the products. Syntheses of various kind organic reactions using CSA have many advantages such as inexpensive catalyst, simple work-up procedure, environmental friendly, outstanding yield of the products with high purity, solvent-free reaction shorter reaction times, and conditions and it can be recovered and reused several times without loss of its catalytic activity.

4.1.1. CSA catalyzed oxidation of sulfides and thiols by hydrogen peroxide

The oxidation of sulfur to sulfoxide is one of the most important for the synthesis of drug, drug metabolism, and bio conjugates compounds [169,170] and also the removal of excess of sulfur form reaction mixture various methods has developed by oxidation using various catalytic methods [169-171]. However, the reported methods have shown some disadvantages such as long reaction time, high catalyst loading, and harsh reaction conditions. Due to the above drawbacks in mind Ahmad *et al*. [172] have developed simple and high yielding for the oxidation of thiols and sulfides in the presence of CSA (Scheme 19).

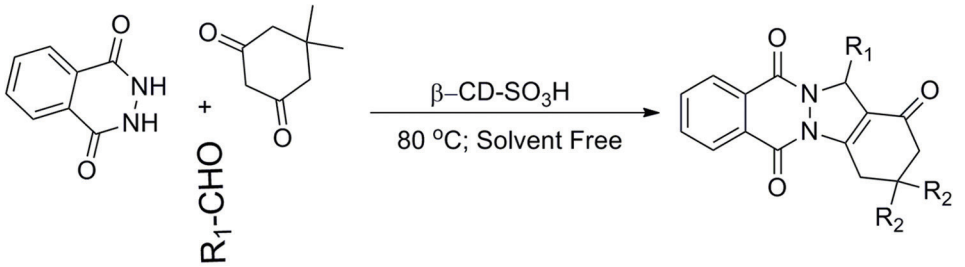
4.1.2. Synthesis of dihydropyrano [2,3-c] pyrazole

Pyrazoles are an important class of nitrogen containing heterocycles that have attracted a great attention due to the discovery of the considerable properties exhibited by a great number of their derivatives. Compounds containing a pyrazole design are having a



Scheme 16: Synthesis of dihydropyrano[2,3-c]pyrazoles in the presence of β-CD-SO_3H.

Scheme 17: Synthesis of 4-thiazolidinones in the presence of β-CD-SO_3H.

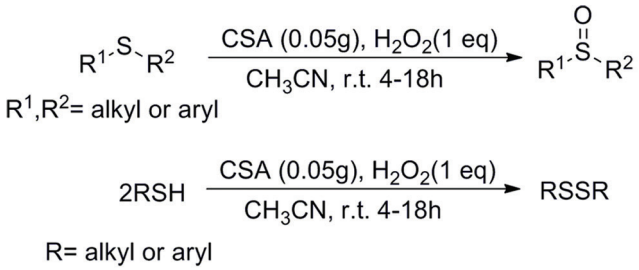


Scheme 18: Synthesis of 2H-indazole [2,1-b]phthalazinetriones in the presence of β-CD-SO_3H.

wide range of therapeutic areas, including oncological and metabolic diseases [173-176]. There are a number of pyrazole containing that compounds have been successfully commercialized. Various methods have been developed for the synthesis of pyrazoles some of them gave good results and some of them possess harsh reaction condition and use to toxic solvents. Hence, Nasseri *et al*. [177] have been developed highly efficient and aqueous synthesis of pyrazole and its analogs involves a two-component coupling of 1,3-diketone and hydrazines/ hydrazides in the presence of CSA (Scheme 20).

4.1.3. Synthesis of pyrimido and pyrazolo [4,5-b] quinolines

Quinolines and its derivatives are an important class of nitrogen containing heterocyclic alkaloids are important synthetic targets both in pharmaceutical industries and in academic laboratories [178] and also it shows various biological activities such as antitumor [179], DNA binding capability [180]. Furthermore, these compounds were mainly present as key structural motifs in a large number of bioactive drugs such as chloroquine, quinine, camptothecin, and Luotonine-A. Pyrimido quinolines are a class of naturally occurring fused uracils occupying a special place in synthetic and medicinal chemistry due to their wide range of pharmacological and biological properties. Pyrazolo quinoline derivatives are the important kind of fused heterocyclic compounds, possess significant bioactivities such as antimalarial, antiviral, and antibacterial activities, acting as potent remedies for treating at inflammatory disorders, restenosis, herosclerosis or demyelinating disorders, and cancers [181]. The researchers have been developed various catalyst for the synthesis of pyrazolo quinoline derivatives. The developed catalysts have some limitation such as moisture sensitive catalyst and additional energies like microwave, due the avoidance of these problems Azimi [182] have developed any efficient neat chemical synthesis of pyrimido and pyrazolo[4,5-b] quinolines in the presence of CSA (Scheme 21).



Scheme 19: CSA catalyzed oxidation of sulfides and thiols by hydrogen peroxide.

4.1.4. Synthesis of 3-substituted indoles

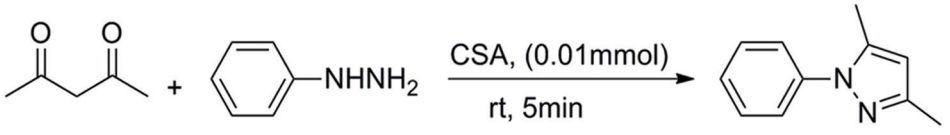
The indole is important nitrogen containing heterocyclic compound and it is widely present in a variety of biologically active compounds and has become an vital structural component in many pharmaceutical agents due to the immense structural diversity of biologically potent indoles [183,184]. The straightforward and direct method for the synthesis of 3-alkylated indoles involves the conjugate addition of indoles to α,β-unsaturated compounds in the presence of Lewis acids [185,186], protic acids [187,188], and metal complexes [189,190]. However, many of these procedures involved strong acidic conditions, longer reaction times, expensive reagents, and low yields of products. Due to the avoidance of this problems, Bathula *et al*. [191] have developed an efficient synthesis of 3-substituted indoles in the presence of CSA (Scheme 22).

4.1.5. Synthesis of 1,2-dihydro-1-aryl naphtho [1,2-e] [1,3] oxazine-3-one derivatives

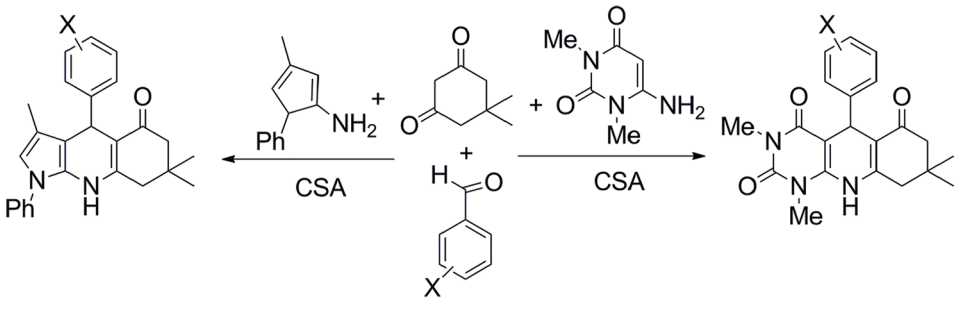
Oxazinone analogs are nitrogen and oxygen containing important heterocycles in the field of medicinal chemistry due to their significant biological activities [192,193]. Naphthalene condensed 1,3-oxazine-3-one derivatives have shown a broad spectrum of anti-inflammatory, antibacterial, analgesics, and muscle relaxant activities [194,195]. Based on this, importance of this various methods has been reported in the literature for the synthesis of naphthoxazinone derivatives, which include wet cyanuric chloride [196], acidic catalyst [197,198], using TiCl4 [199], pyridinium based ionic liquid [200], and ZnO nanoparticles [201]. However, these reported methods suffer from many disadvantages such as low yield, longer reaction time, tedious workup procedure, and harsh reaction conditions. To avoid these problems, Kawade *et al*. [202] have developed an efficient green chemical synthesis of 1,2-dihydro-1-aryl naphtho [1,2-e] [1,3] oxazine-3-one derivatives by the reaction of aldehyde, beta-naphthol and urea in the presence of CSA with microwave irradiation as well as neat conditions (Scheme 23).

4.1.6. Synthesis of bis-chalcones and bis-pyrazlone

Chalcones are significant pharmacophores of various natural products [203]. The official therapeutic agents incorporating this molecular scaffold include xanthohumol (antioxidant), 3-methoxy-



Scheme 20: Synthesis of dihydropyrano [2,3-*c*] pyrazole.

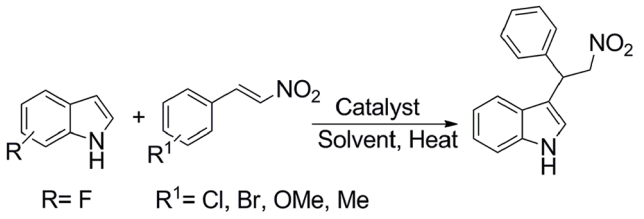


Scheme 21: Synthesis of pyrimido and pyrazolo [4,5-b] quinolines.

4-hydroxyloncocarpin (NADH:ubiquinone oxidoreductase activity inhibitor), and coumarin-chalcone (anticancer agents), respectively. Many functionalized derivatives were also used as NO production inhibitor, antitubulin, antidiabetic, peritoneal antiangiogenic, antiproliferative agents, and probe to study protein-dye interactions [204-208]. Chalcones are usually synthesized through Claisen-Schmidt condensation carried out in basic or acidic media under homogeneous conditions in the presence of various catalysts [209-214]. However, in spite of their possible value, many of the literature methods suffer from drawbacks such as use of expensive and toxic catalysts, refluxing in hazardous organic solvents for prolonged time, harsh reaction conditions with non-recyclable catalysts, high temperature, and low product yields. Hence, to avoid this problems, Siddiqui *et al*. [215] have been developed greener procedure for the synthesis of bis-chalcones and bis-pyrazolones in the presence of CSA (Scheme 24).

4.1.7. One-pot conversion of b-artemisinin to artemether

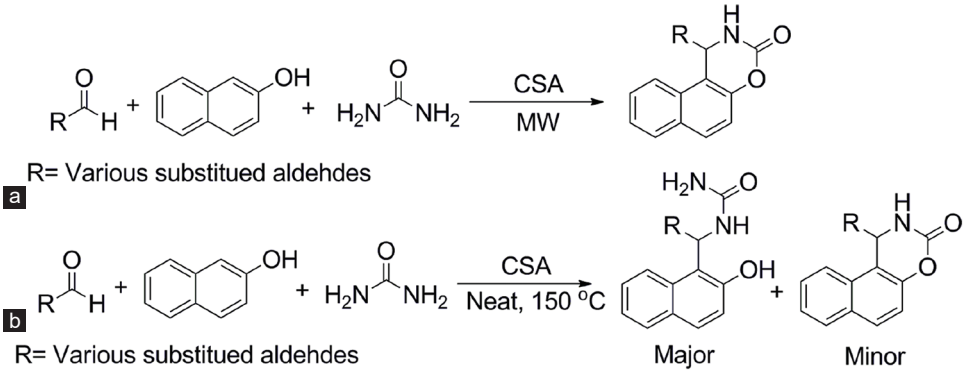
Malaria is one of the major diseases affecting people worldwide and causing the death of nearly 1–2 million people per year, mostly in African countries children. Artemisinin is one of the most significant treatments of human malaria. Artemisinin is a naturally occurring sesquiterpene lactone and its derivatives (dihydroartemisinin, artemether, and artesunate) are essential to modern malaria therapy, thus requiring an efficient synthetic route for these compounds. Over the past 10 years, the researchers are efforts an extensive synthetic have been directed towards the synthesis for artemether/arteether. This synthesis of artemether/arteether from Artemisinin involves mainly in two steps, that is, (i) first step involves the reduction of carbonyl group and (ii) in the second step etherification take place. The reported methodologies generate good yields but have some limitations such as the carcinogenic organic solvents such as benzene, toluene use of highly hazardous Lewis acid and pro acid, and use of column chromatograph in the separation of desired b-isomer. To avoid this problems, Kumar *et al*. [216] have been developed one-pot, environment friendly, and cost-effective process for preparation of methyl/ethyl ether derivative of artemisinin in the presence of $NaBH_4$/cellulose sulfuric acid (Scheme 25).



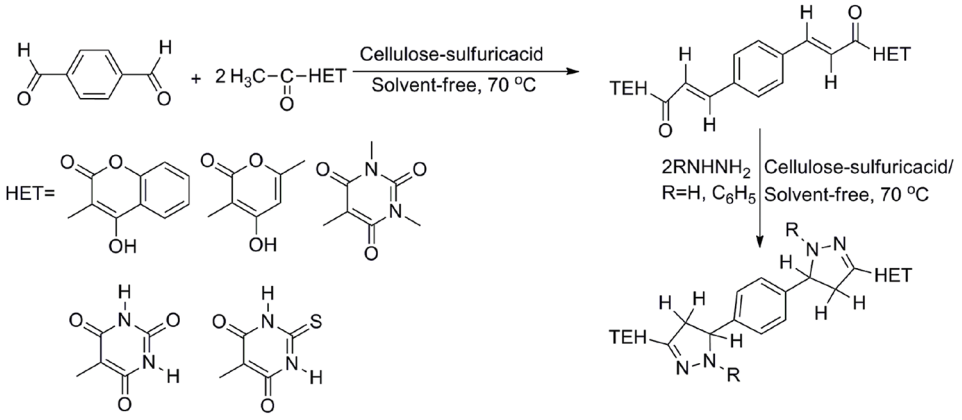
Scheme 22: Synthesis of 3-substituted indoles.

4.1.8. Conversion of aldehydes to gem-diacetates

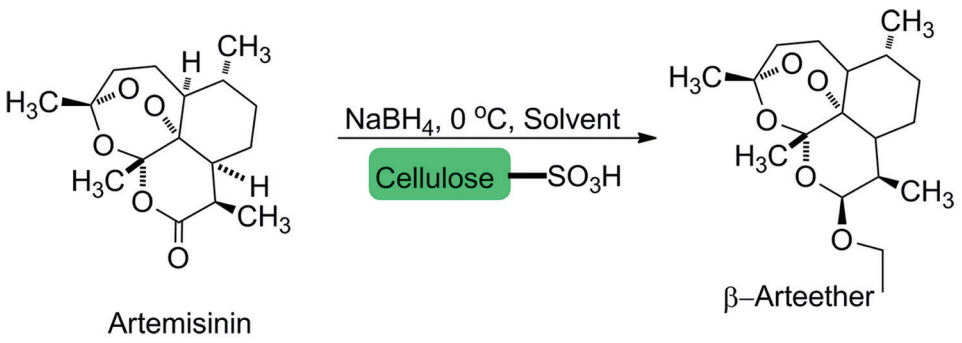
The protection of aldehydes to gem-diacetates (Acylals) is significant role in multistep organic synthesis [217]. In addition, acylals are important useful reagents to use as crosslinking reagents [218], acylals are good intermediates for nucleophilic substitution reactions [219], and also it shows good stability toward a various reaction methods. Due to this importance numerous methods have been presented using acid catalysts. Some of the reported methods show some disadvantages such as low product yields, harsh reaction conditions, number of purifications steps, and non-recyclables catalysts. To overcome above these drawbacks, Mehrjardi *et al*. [220] have been developed for an efficient ecofriendly and easy method for preparation of gem-diacetates



Scheme 23: (a and b) Synthesis of 1,2-dihydro-1-aryl naphtho [1,2-e] [1,3] oxazine-3-one derivatives.



Scheme 24: Synthesis of bis-chalcones and bis-pyrazlone.



Scheme 25: One-pot conversion of b-artemisinin to artemether.

using biodegradable CSA catalyzed (Scheme 26). This method is very convenient to conversion of aldehydes to acylals compared with reported catalyst.

4.1.9. Synthesis of 5H-dibenzo[b,i]xanthene-tetraones and spiro[dibenzo[b,i]xanthene-13,3'-indoline]-pentaones

5H-dibenzo[b,i]xanthene-tetraones and spiro[dibenzo[b,i]xanthene-13,3'-indoline]-pentaones are important oxygen containing heterocycles. These molecules show various biological activities such, antiviral, anti-inflammatory, and antimicrobial properties. Various methods have been reported for these molecules; the reported methods show limitations such as expensive catalyst and solvents, high catalyst loading, and low yields of the product. To avoid this problems, Azimi *et al*. [221] have been developed for an highly efficient method for the synthesis of 5H-dibenzo[b,i]xanthene-tetraones and spiro[dibenzo[b,i] xanthene-13,3'-indoline]-pentaones in the presence of biodegradable CSA (Scheme 27).

4.1.10. Heteroaryl substituted 1,4-dihydropyridines (DHPs)

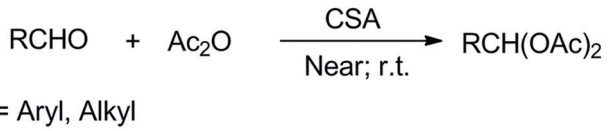
The DHPs are promising nitrogen heterocyclic compounds, it exhibits significant biological and pharmacological properties such as antifilarial, antifungal, antitubercular and also they serve as calcium channel modulators for the treatment of cardiovascular disorders [222,223]. Many methods have been reported for the synthesis of DHPs through the Hantzch method. Various catalytic reports have some disadvantages such as harsh reaction method, unwanted by products formation, low yields, and high work procedures. Hence, Mamaghani *et al*. [224] have been developed an alternative method for the synthesis of biologically potent heteroaryl dihyropyridines in the presence of biocompatible CSA (Scheme 28).

4.1.11. Synthesis of 5-hydroxymethylfurfural and 5-ethoxymethylfurfural (EMF)

Nowadays, the important abundant renewable biomass resource has received significant attention as an alternative feedstock for both fuels and chemicals through the biorefinery technology. Biomass is mainly consists of carbohydrates, which transformation to various chemical compounds and fuels. In general, the fructose is conversion to 5-hydroxy methyl furfural (HMF), using various homogeneous and heterogeneous acid catalysts. The conversion of HMF to5-EMF is most prominent reaction due to which is an excellent additive for diesel. Furthermore, various methods have been developed for the conversion of HMF to EMF these methods show disadvantages such as no recyclability of catalyst, and disposal of acids; to overcome this problems, Liu *et al*. [225] have been developed highly green method for the conversion of HMF to EMF in the presence of CSA (Scheme 29).

4.1.12. Diazotization-iodination of aryl amines

The halogen substituted aromatic compounds are important precursors for various carbon-carbon bond formations. Among all of them, the iodo substituted compounds are significant synthetic



Scheme 26: Conversion of aldehydes to gem-diacetates.

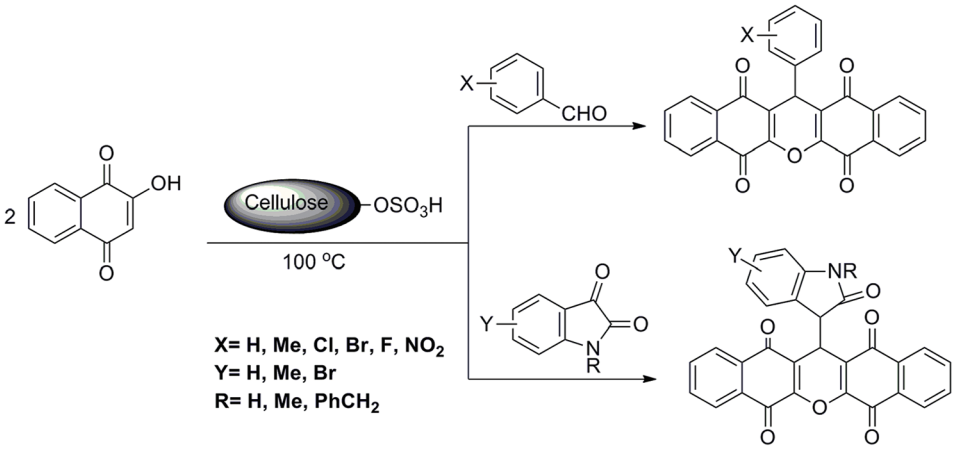
intermediates and also they have wide applications in medicine such as nuclear magnetic imaging and radioactivity label markers in radio-immunoassays [226,227]. The iodoarenes are usually synthesis from Sandmeyer reaction [228,229]; this reaction is complicated due to the numerous competing reactions. There are various methods have been reported for the iodation of amines the reported methods show some advantages and disadvantages such as highly expensive reagents and use of toxic solvents is commonly required. Hence, there is still significant interest in developing easy methods for synthesis of aryl iodides that require minimizing environmental pollution and low cost is preferable. Nemati *et al*. [230] have been developed green method for the synthesis of iodoarenes in the presence of biodegradable CSA (Scheme 30).

4.1.13. Synthesis of 3,4-dihydropyrimidinones/thiones and novel N-dihydro pyrimidinone-decahydroacridine-1,8-diones

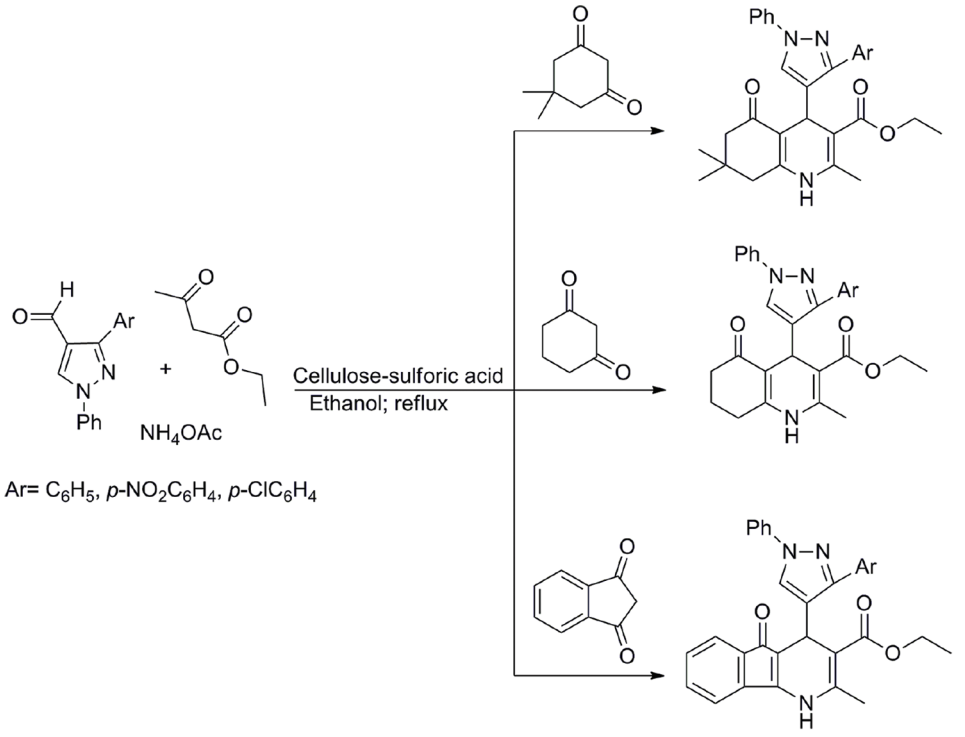
Multicomponent reactions are important for the construction of various organic transformations in one pot method. Among them, the construction of N, O, S heterocyclic compounds is prominent due to the diverse biological properties [231]. During the past 10 years, the researchers are efforts a wide-ranging synthetic methods have been developed towards the synthesis for artemether/arteether DHPs are belongs to nitrogen containing heterocycles compounds and it possess potent pharmaceutical activities; there are numerous reports are available for the preparation of DHPs. However, they have some limitations such as expensive catalyst, harsh reaction conditions, low yields, and toxic solvents. Hence, Rajack *et al*. [232] have been developed an highly efficient and green method for the synthesis of 3,4-dihydropyrimidinones/thiones and N-dihydro pyrimidinone-decahydroacridine-1,8-diones (Scheme 31).

4.1.14. Synthesis of quinoxalines

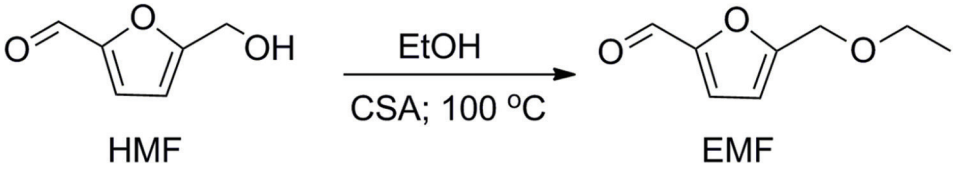
Quinoxalines and its derivatives have received significant attention from organic and medicinal chemists due to the wide range applications in various fields, such as organic semiconductors [233], combinatorial drug discovery libraries [234], electron luminescent materials [235], and DNA cleaving agents [236]. Furthermore, quinoxalines are structural similarities with coumarin ring system and its show potent biological properties. There are numerous homogeneous and heterogeneous catalytic methods have been developed for the synthesis of them but none of them gives satisfactory results. Consequently, Kuarm *et al*. have been developed a highly efficient, inexpensive, method for the



Scheme 27: Synthesis of 5H-dibenzo[b,i]xanthene-tetraones and spiro[dibenzo[b,i]xanthene-13,3'-indoline]-pentanones.



Scheme 28: Heteroaryl substituted 1,4-dihydropyridines.

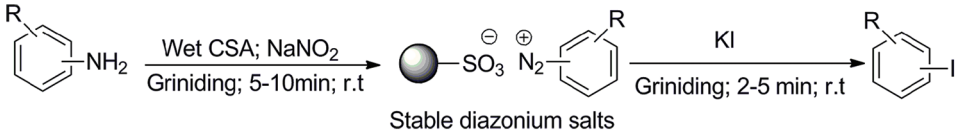


Scheme 29: Synthesis of 5-hydroxymethylfurfural and 5-ethoxymethylfurfural.

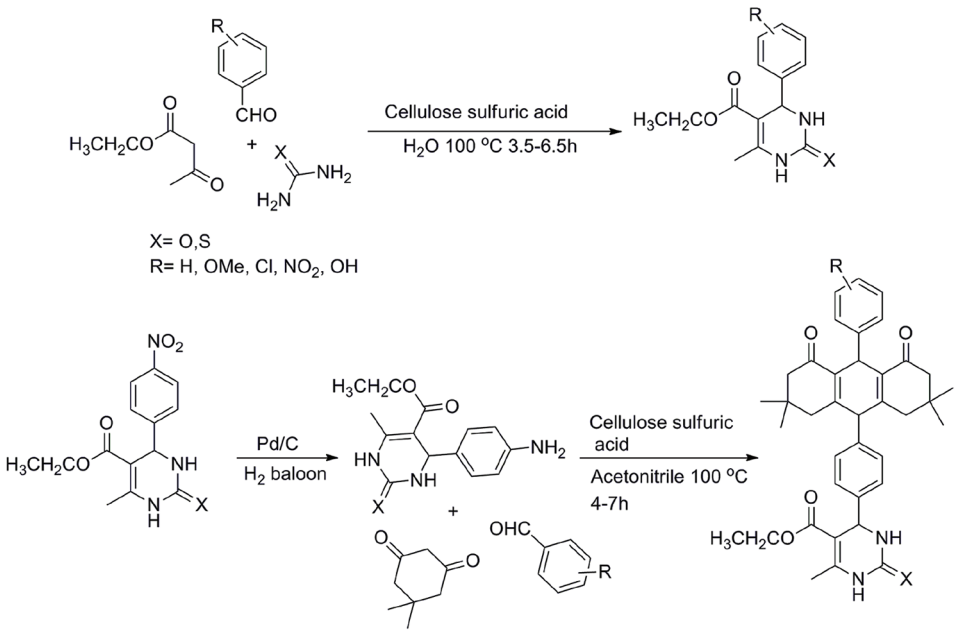
synthesis of quanoxilines in the presence of biodegradable cellulose sulfuric acid (Scheme 32) [237].

4.1.15. Protection of hydroxyl groups using HMDS

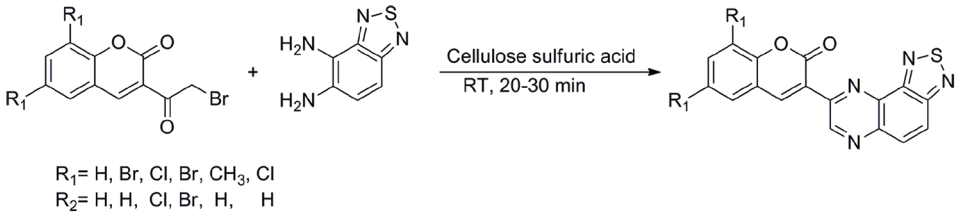
Protection of alcohols is an important factor during multistep organic synthesis. The alcohols are protected by various functional groups such as aceticanhydride, methyl iodide, tosyaltion, mesylation, and silylation; among all of them silylation is good protecting group than that of above mentioned due to the low viscosity, fine solubility in non-polar solvents, resistant to oxidation, and thermal stability. Furthermore, trimethylsilylation of hydroxy compounds is used to volatility of the compounds gas chromatography and as well as mass spectrometry [238]. There are numerous reported methods for the protection of hydroxy compounds with 1,1,1,3,3,3-HMDS; the reported methods suffer to increase the yield of the product and expensive catalyst as well as drastic reactions conditions. To solve



Scheme 30: Diazotization-iodination of aryl amines.



Scheme 31: 3,4-Dihydropyrimidinones/thiones and novel N-dihydro pyrimidinone-decahydroacridine-1,8-diones.



Scheme 32: Synthesis of quinoxalines.

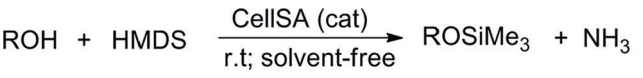
this problem, Shaterian *et al*. have been developed an environment friendly biodegradable CSA promoted for the protection of hydroxy to silylation (Scheme 33) [239].

4.1.16. Synthesis of 2-amino-4,6-diphenylnicotinonitriles

The occurrence of pyridines in nature and their essential role as flexible building blocks in the synthesis of natural products as well as biologically potent compounds has led to a continued interest in the laboratory synthesis of pyridine derivatives [240,241]. The majority of the pyridine nucleolus contacting derivatives shows multiple pharmacological activities. Due to the significance of these compounds, various methods are reported in the literature; but there are some limitations such as non-recyclable catalyst, toxic organic solvents, and low yields. Hence, Mansoor *et al*. [242] have been developed highly efficient green chemical synthesis of 2-amino-4,6-diphenylnicotinonitriles in the presence of recyclable natural polymer cellulose sulfuric acid catalyst (Scheme 34).

4.1.17. Synthesis of DHPs

DHPs are an important precursors in various biological properties; the important characteristic of these compounds the researchers has



Scheme 33: Protection of hydroxyl groups using HMDS.

been developed various catalytic methods these methods show some disadvantages such as low product yields, harsh reaction conditions, and use of expensive solvents. Therefore, Murthy *et al*. [243] have been developed inexpensive, efficient method for the synthesis of DHPs as well as they studied antimicrobial activity along with docking studies (Scheme 35).

4.1.18. Synthesis of -amino amide, 3,4-dihydroquinoxalin-2-amine, 4H-benzo[b][1,4]thiazin-2-amine and 1,6-dihydropyrazine-2,3-dicarbonitrile derivatives

Nowadays, science and technology are mainly focusing on sustainable and environmentally friendly resources and processes. In this view, biopolymers and functionalized biopolymers are most important attractive candidates to explore for the synthesis of various important

heterocyclic compounds. Three component Ugi-reactions is most significant method for the synthesis of various biologically potent nitrogen containing heterocyclic compounds. The synthesis of these compounds various methods has been developed these methods suffer from various drawbacks such as long reaction times, high reaction temperatures, and tedious workup procedures. To solve these drawbacks, Shaabani *et al*. have been developed an efficient green method for the synthesis of 1-amino amide, 3,4-dihydroquinoxalin-2-amine, 4H-benzo[b][1,4]thiazin-2-amine, and 1,6-dihydropyrazine-2,3-dicarbonitrile derivatives in the presence of CSA (Scheme 36) [244].

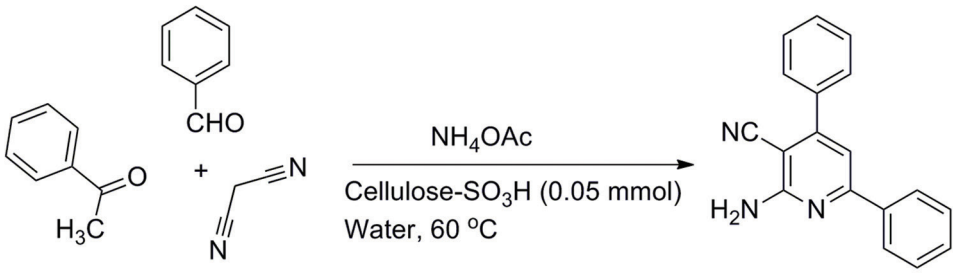
4.1.19. Synthesis of β-amino ketones through a Mannich reaction

The number of articles has been committed to the introduction and applications of valuable eco-friendly catalysts [245]. The most straightforward and useful strategies for the synthesis of such catalysts are the attachment of organic or inorganic materials to various solid supports. These catalysts have good advantages such as moisture resistance, greater selectivity, low toxicity, air tolerance, easier handling, and low cost which are some of the advantageous features of this method that make it a viable alternative to non-catalytic methods.

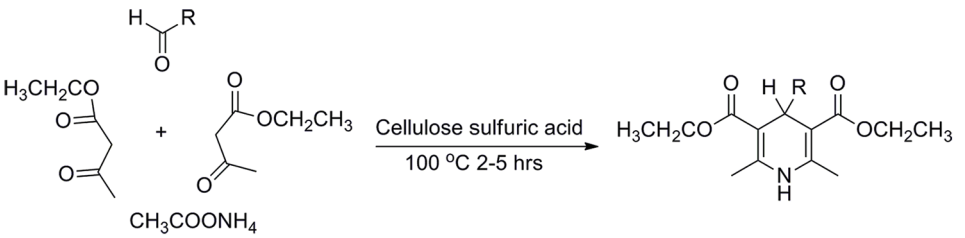
The Mannich reaction is an very important carbon–carbon bond-forming reaction in organic synthesis [246]. It is used for the synthesis of β-amino carbonyl compounds, which are important synthetic intermediates for various pharmaceuticals and natural products [247]. Various methods have been developed for this reaction but none of them was gave satisfactory results. Hence, Hayeniaz *et al*. [248] have been developed an alternative method for the synthesis of β-amino carbonyl compounds in the presence of CSA with significant yields (Scheme 37).

4.1.20. Synthesis of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols)

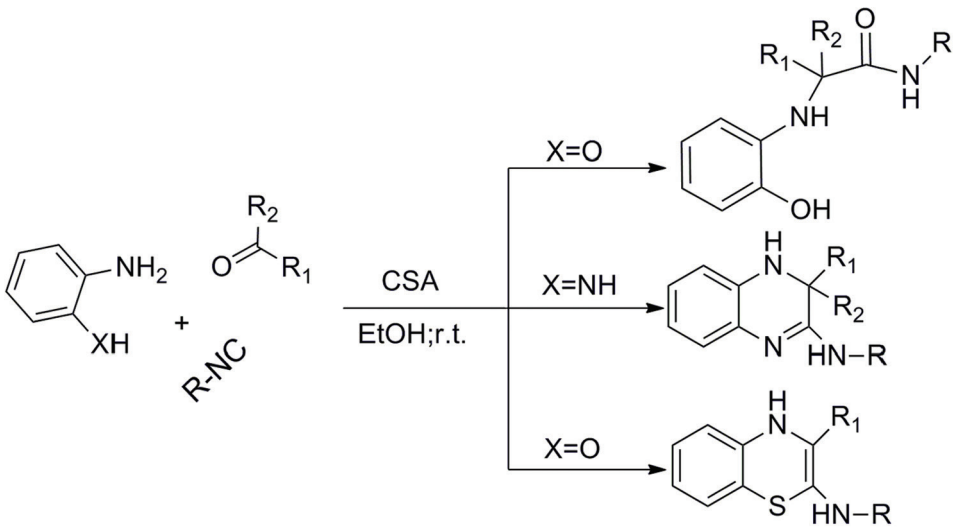
Pyrazlone compounds were rewarded much interest for their variety of biological activities such as antitumor [249] and cytokine inhibitors [250]. The compounds which are contains two pyrazolone ring can be used as extract ant for some metal ions, and ligands. Moreover, these compounds are applied as insecticides, pesticides,



Scheme 34: Synthesis of 2-amino-4,6-diphenylnicotinonitriles.



Scheme 35: Synthesis of 1,4-dihydropyridines.



Scheme 36: Synthesis of 1-amino amide, 3,4-dihydroquinoxalin-2-amine, 4H-benzo[b][1,4]thiazin-2-amine and 1,6-dihydropyrazine-2,3-dicarbonitrile derivatives in the presence of CSA.

and fungicides. The formation of these compounds involves the Knoevenagel synthesis of the corresponding arylidenepyrazolones and its base promoted Michael reaction and also one-pot tandem Knoevenagel-Michael reaction of arylaldehydes with two equivalents. Various reports are available in literature for the synthesis of these compounds but these methods show some disadvantages as well as advantages. Hence, Baghizadeh *et al*. [251] have been developed for the construction of C-C bond in the presence of CSA (Scheme 38).

5. INORGANIC TEMPLATES

5.1. PSA [11]

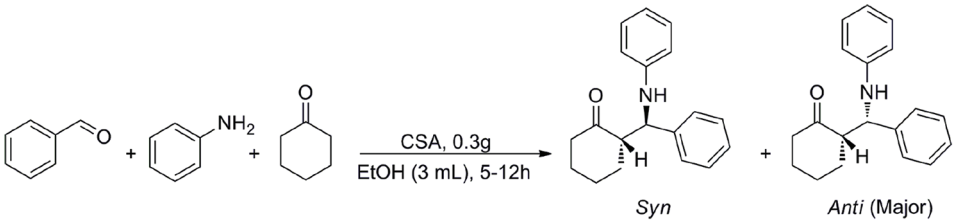
A 50 mL reaction flask was fitted out with a constant-pressure dropping funnel. DHAMP (7.5 mmol) was charged into the flask and chlorosulfonic acid (22.5 mmol) in CH_2Cl_2 (10 mL) was added dropwise over a period of 15 min at r.t. After completion of the addition, the mixture was agitated for 2 h, while the residual HCl was eliminated by suction. Then, the mixture was washed with excess amount of dried CH_2Cl_2. Finally, a solid white powder was obtained after drying.

5.1.1. Synthesis of indazolo [1,2-b]-phthalazinetriones

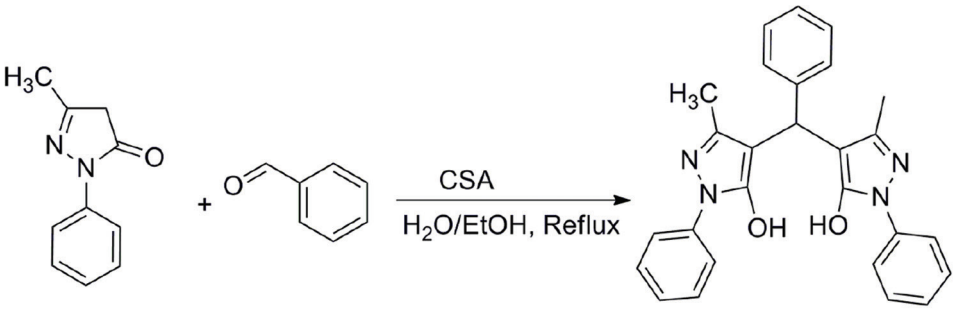
The construction of novel heterocyclic compounds is continuously great interest due to their wide range of various applications. Among them, phthalazine moiety containing heterocyclic compounds is interest because they show numerous pharmacological and biological activities. Phthalazine derivatives, which have two bridgehead nitrogen atoms in a fused ring system, possess cytotoxic, antimicrobial, anticonvulsant, antifungal, anticancer, and anti-inflammatory activities. Moreover, these compounds exhibited good promise as new luminescent materials or fluorescence probes. Several reports are available in literature for the synthesis of these compounds but the reported methods show some disadvantages as well as advantages. Hence, Kiasat *et al*. [252] have been developed for the construction of phthalazine derivatives in the presence of PSA (Scheme 39).

5.1.2. Synthesis of bis-(4hydroxycoumarin-3-yl) methanes

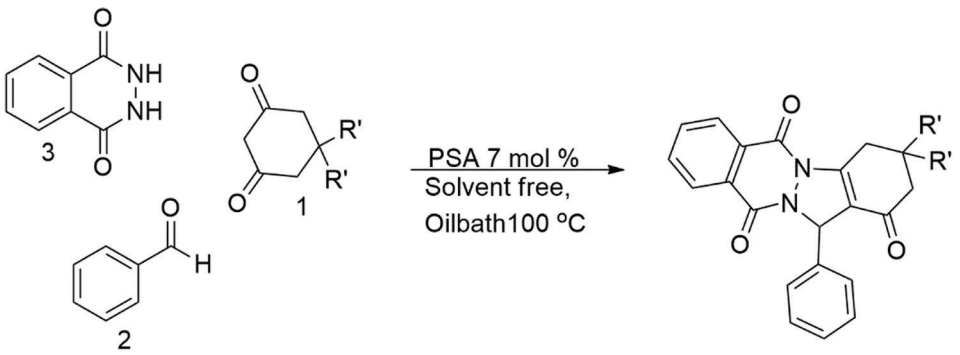
Biscoumarins have recognized significant attention of synthetic and medicinal chemists due to their large scale of pharmaceutical and biological activities. A number of biscoumarins have also been found to be urease inhibitors. Although some types of these compounds could be isolated from plants, attempts have been made to use alternative catalysts for biscoumarin synthesis. A literature examine revealed that a number of catalytic methods have been developed for the synthesis of biologically important biscoumarins derivatives, especially the bridge substituted dimers of 4-hydroxycoumarin, by the reaction of 4- hydroxycoumarin and various aldehydes. Although, each of the methods has its own disadvantages, such as harsh reaction conditions,



Scheme 37: Synthesis of β-amino ketones in the presence of CSA.



Scheme 38: Synthesis of 4,4'-(arylmethylene)bis(3-methyl-1-phenyl-1H-pyrazol-5-ols).



Scheme 39: Synthesis of indazolo [1,2-b]-phthalazinetriones.

long reaction time, and use of large excess of reagents, low yield and the use of toxic, corrosive, expensive, or non-reusable catalysts. Therefore, Kiasat *et al*. [253] have been developed for the production of biscoumarins derivatives in the presence of PSA (Scheme 40).

5.1.3. Synthesis of 14H-dibenzo[a,j]xanthenes and 1,8-dioxo-octahydro-xanthenes

Xanthenes and benzoxanthenes are an essential category of organic compounds which have in recent times received a great deal of attention from medicinal and organic chemists due to their wide-ranging of biological and therapeutic properties, including their, antibacterial, antiviral, and anti-inflammatory activities. In addition, these compounds are used in laser technologies, fluorescent material in the visualization of biomolecules, as well as being widely used as dyes.

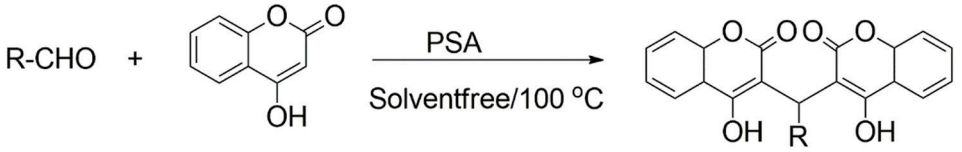
There are different methods and are various reagents are using for the synthesis of xanthene and benzoxanthenes have been reported in the literature, including cyclodehydration, cyclisation of polyclic aryl triflate esters, intermolecular phenyl carbonyl-coupling reactions of benzaldehydes and acetophenones, trapping benzynes by phenols, and cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone. However, each of the methods has its disadvantages, such as long reaction time, harsh reaction conditions, low yield, use of large excess of reagents, and the use of toxic, corrosive, expensive, or non-reusable catalysts. Therefore, Hajinasiri *et al*. [254] have been developed for the production of 14*H*-dibenzo[a,j] xanthenes and 1,8-dioxo-octahydro-xanthenesin presence of PSA with good yields (Scheme 41).

5.1.4. Synthesis of DHPs

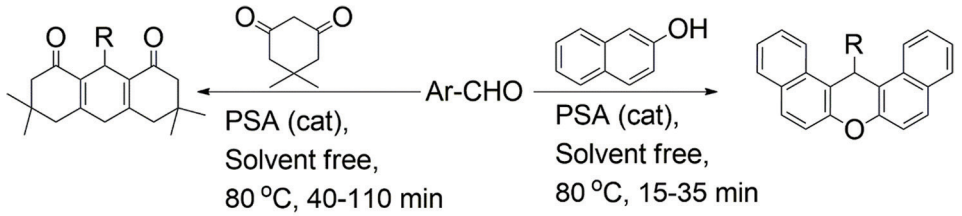
DHPs and its derivatives are significant category of organic compounds, due to these compounds have numerous medicinal characteristics including acting as cerebral anti ischemic agents in the treatment of Alzheimer's disease and as a chemo sensitizer in tumor therapy. On the other hand, 1,4-DHP compounds show an important parts in medicinal chemistry, for example, amlodipine, nifedipine, felodipine, and nicardipine, which are the best selling drugs used in the treatment of cardiovascular diseases. Due to the important properties of these compounds, the researchers have been established numerous catalytic methods these methods show some drawbacks such as low product yields, harsh reaction conditions, and use of expensive solvents. Therefore, Rezayati *et al*. [255] have been developed inexpensive, efficient method for the synthesis of DHPs in the presence of PSA (Scheme 42).

5.1.5. Synthesis of benzimidazole, benzoxazole, and quinoxaline

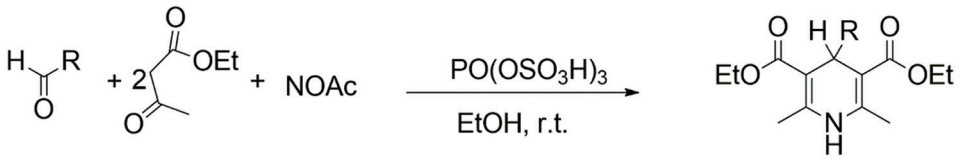
A vast number of benzimidazole and benzoxazole derivatives are found in a variety of natural products and wide range of biologically active compound, especially including antiviral, anti-ulcerative, antihypertensive, antimicrobial, anticancer properties (colon cancer therapies), and as kinase inhibitors. Furthermore, it used as an imperative pharmacophore in modern drug discovery and exhibit substantial activity against several viruses such as human cytomegalovirus (HCMV), HIV, Herpes (HSV-1), influenza, and RNA. Furthermore, the synthesis of quinoxaline, its derivatives has abundant significance in organic synthesis. Quinoxaline derivatives are very considerable class of nitrogen-containing derivatives and have been shown to possess a broad spectrum of biological activities such as antifungal, antibacterial, anti-inflammatory, antidepressant, anticancer, anthelmintic agents, and antitumor drugs. Furthermore, quinoxaline is a part of the chemical assemblies of various antibiotics such as Levomycin, Echinomycin, and Actinoleutin are known to inhibit the growth of Gram-positive bacteria and are also active agent for various transplantable tumor. Besides these, they have been also used as building blocks for the synthesis of organic semiconductors, extraction of metal cations, and application in dyes. Due to the essential properties of these derivatives, the researchers have been established various catalytic methods, these methods show some drawbacks such as harsh reaction conditions, low product yields, and use of expensive solvents. Therefore, Rezayati *et al*. [256] have been developed inexpensive, efficient method for the synthesis of synthesis of Benzimidazole, Benzoxazole, and quinoxaline derivatives in the presence of PSA (Scheme 43).



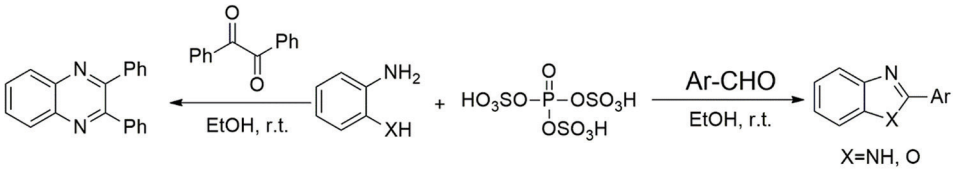
Scheme 40: Synthesis of bis-(4hydroxycoumarin-3-yl) methanes.



Scheme 41: Synthesis of 14*H*-dibenzo[a,j]xanthenes and 1,8-dioxo-octahydro-xanthenes.



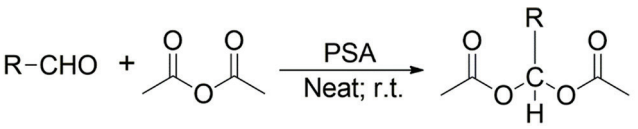
Scheme 42: Synthesis of 1,4-dihydropyridines.



Scheme 43: Synthesis of benzimidazole, benzoxazole, and quinoxaline.

5.1.6. Synthesis of acylals

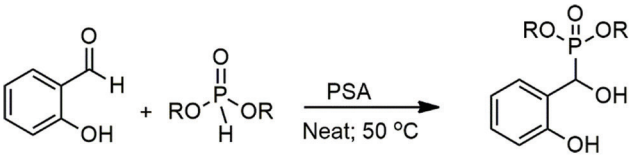
The protection of carbonyl group is an important step for a number of synthetic protocols. Reagents commonly used for protecting carbonyl groups include 2-mercaptoethanol, ethane dithiol, trialkyl orthoformate, acetic anhydride, and alcohols. Among these reagents, acetic anhydride is widely used for its robustness under neutral, basic, or acidic conditions. Acylals serve as important precursors for asymmetric allylic alkylation reactions, drug synthesis, and syntheses of 1-acetoxydienes and 2,2-dichlorovinylacetates (used for Diels–Alder reactions). Furthermore, acylals may also be used as cross-linking agents for cellulose in cotton. Moreover, though other methods show varying degrees of success, they have limitations such as prolonged reaction times, low yields, requirement of excess reagents or catalysts, use of toxic solvents, and laborious work-up procedures. Therefore, Kim *et al*. [11] have been developed alternate milder and environmentally sustainable procedures for the preparation of acylals (Scheme 44).



Scheme 44: Synthesis of acylals.

5.1.7. Synthesis of α-hydroxyphosphonates (HPPs)

HPPs are an important class of organophosphorus compounds because of their wide range of biological activities, including anticancer, antibacterial, antiviral, and anti-oxidant activities. In addition, HPPs are structural analogs of α-hydroxyphosphonic acids and can act as enzyme inhibitors for farnesyl protein transferase, human protein tyrosine phosphatase, purine nucleoside phosphorylase, 5-enolpyruvylshikimate-3-phosphate synthase, and human rennin. They also serve as useful precursors in the synthesis of other biologically important phosphonates such as α-amino, α-diketo, α-keto, α-halo, and α-acetoxy phosphonates. There are various catalytic methods available in literature; but some limitations such as harsh reaction conditions, low yields. Hence, Kim *et al*. [257], have been developed an inexpensive protocol for HPPs synthesis with easy accessibility, low toxicity solid acid catalyst, and the ability to proceed under neat condition and its anticancer activity (Scheme 45).



Scheme 45: Synthesis of α-hydroxyphosphonates.

5.1.8. Synthesis of α-aminophosphonates

α-Aminophosphonates are an significant precursors in various biological and medicinal properties; the important characteristic of these derivatives, the researchers have been developed various catalytic methods, these methods show some disadvantages such as low product yields, use of expensive solvents, and harsh reaction conditions,. Therefore, Suresh Reddy *et al*. [258] have been developed inexpensive, efficient method for the synthesis of DHPs as well as they studied antioxidant-studies (Scheme 46).

6. BSA

6.1. Synthesis of BSA [259]

A 50 mL suction flask was equipped with a constant pressure dropping funnel. The gas outlet was connected to a vacuum system through water adsorbing solution and an alkali trap. Boric acid (1.55 g, 25 mmol) was charged in the flask and chlorosulfonic acid (8.74 g, ca. 5 mL, 75 mmol in 5 ml CH_2Cl_2) was added dropwise over a period of 1 h at room temperature under N2(g). Hydrogen chloride evolved immediately. After completion of the addition, the mixture was shaken for 85 min, while the residual HCl was eliminated by suction. Then, the mixture was washed with diethyl ether to remove the unreacted chlorosulfonic acid (^{1}H NMR of BSA in Acetone-D6 show δ=12.218) and then add 14.4 g silica gel and stirred those. Finally, dried and grayish solid material was obtained (21.6 g, 95.66%).

6.1.1. Synthesis of benzimidazoles

Benzimidazole moieties are classified under several classes of drugs, based on the possible substitution at different positions of the benzimidazole nucleus. Benzimidazole derivatives exhibit significant activity against several viruses such as HIV, HCMV, HSV-1, RNA, and influenza. Furthermore, they have been also used to act as topoisomerase inhibitors, selective NPYY1 receptor antagonists, angiotensin II inhibitors, potential antitumor agents, and smooth muscle cell proliferation inhibitors. In addition, benzimidazoles are very important precursors in organic synthesis. Vitamin B12 constitutes a milestone in the chemistry of benzimidazoles. Bisbenzimidazole is DNA-minor grove binding agents possessing anti-tumor activity. Due to the importance of Benzimidazole moieties, the researchers have been developed various methods and these are have some advantages and disadvantages. Hence, Sajjadifar *et al*. [260] have developed ecofriendly method with high yields in the presence of BSA (Scheme 47).

6.1.2. Synthesis of 1,5-benzodiazepine

Benzodiazepines are interesting compounds because of their therapeutic properties. Many members of this family are, in fact, nowadays, widely used as tranquilizing and anticonvulsant agents. Due to the significant biological properties, various researchers have introduced various catalytic methods; these are having some drawbacks such as high temperature, reaction time, and tedious work up procedure, to overcome this, Sajjadifar *et al*. [261] have developed new catalytic method using BSA with good yields, short reaction times, and water as solvent (Scheme 48).

6.1.3. Synthesis of substituted benzenes

Polyarylated aromatic propellers have fascinated a great deal of interest in leading-edge carbon nanotechnology for increasing new efficient molecular rotors and new electroluminescent materials for flat-panel displays. These organic compounds have unique photo physical, chemical, and optical properties that make them useful as building blocks for material sciences. There are various reports regarding application of Π-conjugated polyaromatics, macromolecules. Due to this importance,

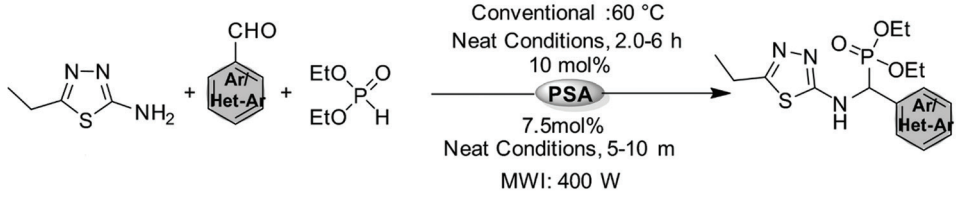
Safaei *et al*. [262] have been developed new catalytic method for the preparation of substituted benzenes in the presence of BSA (Scheme 49).

6.1.4. Synthesis of xanthene derivatives

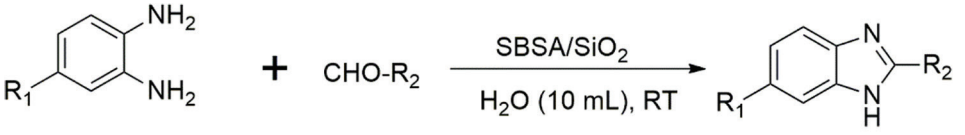
The construction of xanthenes and benzoxanthenes has gained substantial consideration in organic synthesis due to their wide range of biological and therapeutic properties. Because of this, the scientist in various chemical laboratories has been developed different methods for the synthesis of xanthene compounds, but some of these methods have some drawbacks. To overcome this drawbacks, Moghanian *et al*. [263] have been developed new green chemical method for the synthesis of xanthenes using BSA (Scheme 50).

6.1.5. Synthesis of aliphatic and aromatic 1H-indazolo[2,1-b] phthalazinetriones

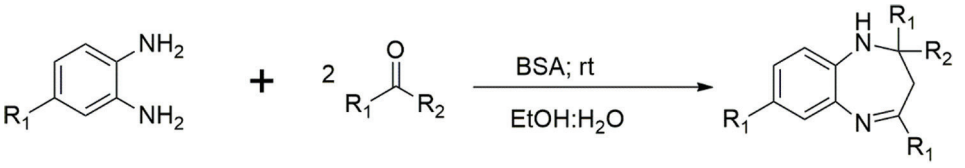
In recent years, amalgamation of nitrogen-containing heterocyclic compounds has received rising attention due to their applications to biologically active pharmaceuticals, agrochemicals, and functional



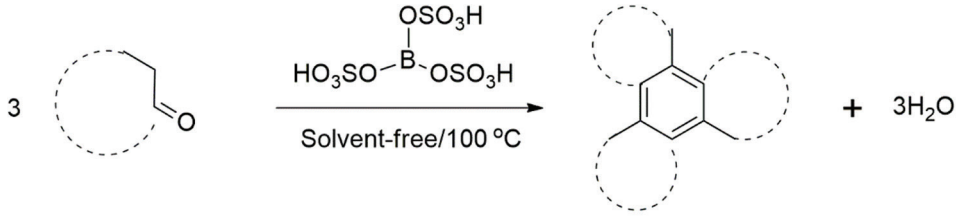
Scheme 46: Synthesis of α-aminophosphonates.



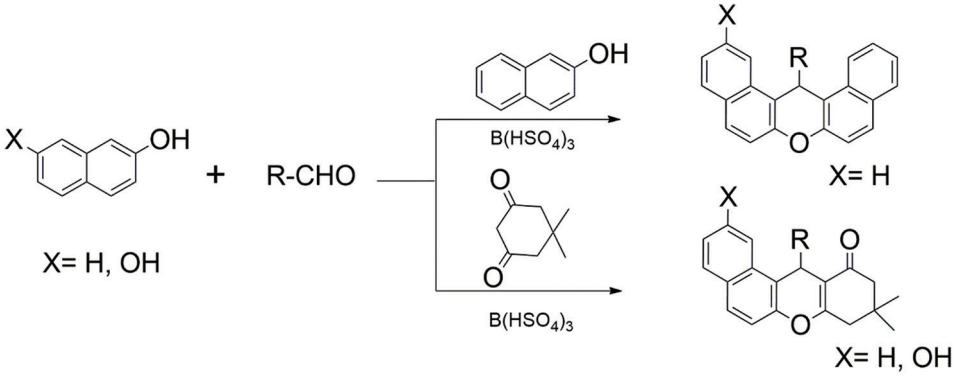
Scheme 47: Synthesis of benzimidazoles.



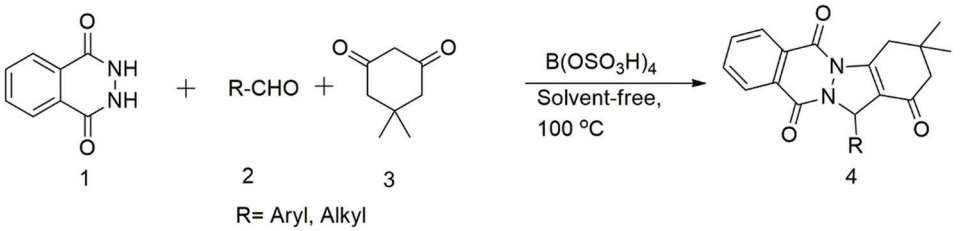
Scheme 48: Synthesis of 1,5-benzodiazepine.



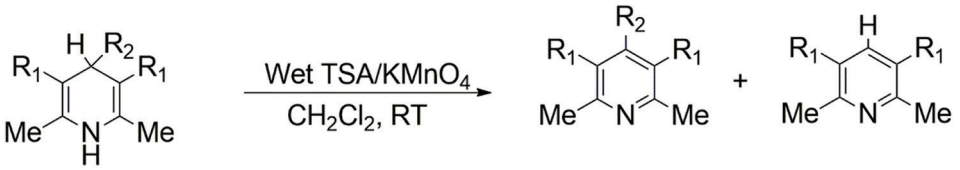
Scheme 49: Synthesis of substituted benzenes.



Scheme 50: Synthesis of xanthene derivatives.



Scheme 51: Synthesis of aliphatic and aromatic 1*H*-indazolo[2,1-b]phthalazinetriones.



Scheme 52: Synthesis of the rapid aromatization of hantzsch 1, 4-dihydropyridines.

materials. Due to this importance, various methods are available in the literature. Among them, some of them show advantages and disadvantages. To overcome this, Soheilizad *et al*. [264] have been developed one pot synthesis of phthalazinetriones in the presence of BSA (Scheme 51).

7. TUNGSTO SULFONIC ACID (TSA)

7.1. Preparation of TSA [265]

To a 0.2 mol chlorosulfonic acid (23.304 g, 13.31 mL) in 250 mL round button flask equipped with ice-bath 0.1 mol (29.38 g), anhydrous sodium tungstate was added gradually. After the completion of addition, the mixture was shaken for 1 h. A yellowish-with solid (TSA) of 40 g was obtained.

7.1.1. Synthesis of the rapid aromatization of hantzsch 1, 4-dihydropyridines

Karami *et al*. [265] have been reported simple, clean, and convenient method for the effective oxidation of 1,4-DHP with TSA to pyridine derivatives under mild and heterogeneous conditions (Scheme 52).

7.1.2. Synthesis of the N-nitrosation of secondary amines

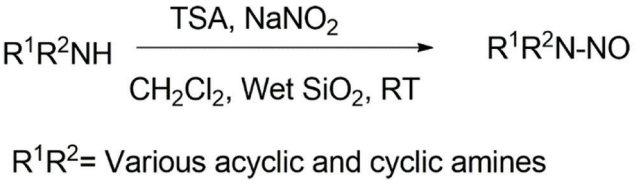
Nitrosation chemistry has been familiarized as an active area for biological and organic chemists. Their strong carcinogenic and mutagenic properties of N-nitrosamines have produced substantial attraction in this view. Various methods are developed for the synthesis of N-nitrosation of seconday amines but the reported methods have some drawbacks to overcome this, Karami *et al*. [266] have been reported novel method for the synthesis of Nitrosation of secondary amines in green chemical methods (Scheme 53).

7.1.3. Synthesis of deoximation

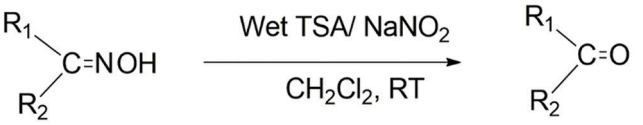
The cleavage of oximes to restore ketones and aldehydes is an essential reaction due to oximes serve as well-organized protective groups for ketones and aldehydes and extensively used for the purification and characterization of carbonyl compounds. There are numerous methods available in the literature but it have some drawbacks to solve it Karami *et al*. [267] have been developed new sustainable method for the deoximation (Scheme 54).

7.1.4. Synthesis of 9-aryl 1,8-dioxooctahydroxanthenes

Xanthenes and its derivatives have received significant attention in recent years due to their wide range of biological and therapeutic properties. Due to this importance various methods are available in literature, but some of them shows advantages



Scheme 53: Synthesis of the N-nitrosation of secondary amines.



Scheme 54: Synthesis of deoximation.

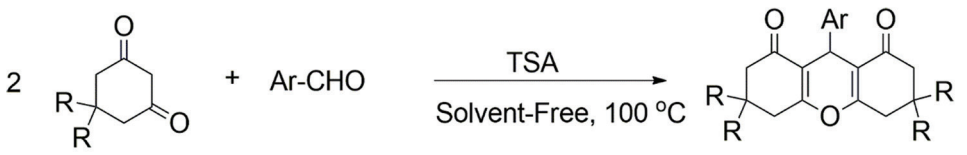
and disadvantages, due to this Karami *et al*. [268] have been developed innovate heterogeneous acid catalyst for the synthesis of xanthenes (Scheme 55).

7.1.5. Synthesis of dihydropyrimidine-thione

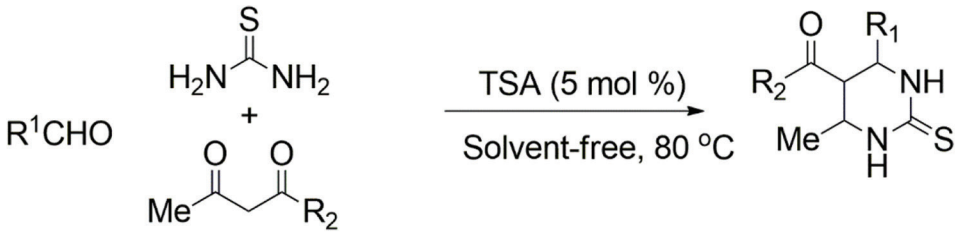
The usage of functionalized dihydropyrimidine-2(1H)-one/thione as strong calcium channel blockers, NPY antagonist, antihypertensive agents, due to their expanded properties such as antiviral, antibacterial, and antitumor properties, it can be concluded that these heterocyclic compounds play an important role in therapeutic, synthetic, and bioorganic chemistry. There are huge no of synthetic methods available in else ware, but some of methods shows long reaction times high temperature, and purification methods. Due to this, Karami *et al*. [269] have been developed new protocol for the synthesis of dihydropyrimidine-thione (Scheme 56).

7.1.6. Polycyclic aromatic phenazines and quinoxalines

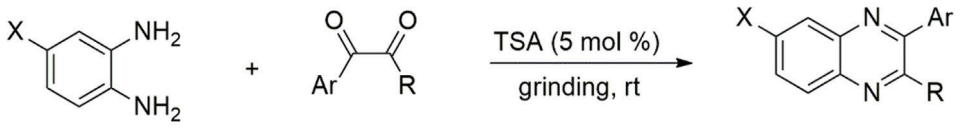
Quinoxaline derivatives are associated with a wide-ranging biological effects such as riboflavin (Vitamin B2), agonists and antagonists of various receptors, agents with high antibacterial or antiviral activities (e.g., echinomycin, lenomycin, and actinomycin). Due to the importance of these compounds, the researchers have developed various methods, but some of them have drawbacks, to overcome this, Karami *et al*. [270] have been reported new catalytic method for the synthesis of quinoxaline in green conditions (Scheme 57).



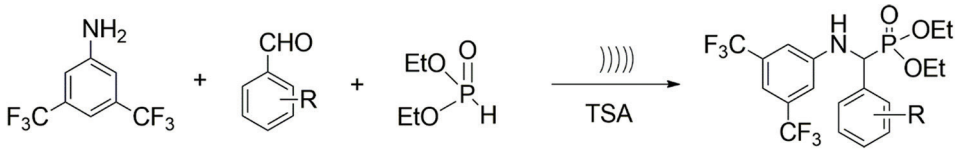
Scheme 55: Synthesis of 9-Aryl 1,8-dioxooctahydroxanthenes.



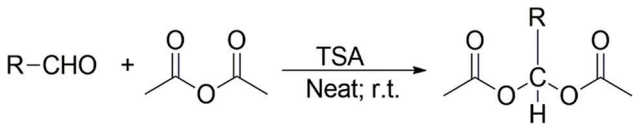
Scheme 56: Synthesis of dihydropyrimidine-thione.



Scheme 57: Synthesis of aromatic phenazines and quinoxalines.



Scheme 58: Synthesis of α-aminophosphonates.



Scheme 59: Synthesis for the protection of aldehydic carbonyl group.

7.1.7. Synthesis of α-aminophosphonates

The α-aminophosphonates are biomimetic to naturally occurring amino acids with an notable structure. They play a key role in current synthetic organic chemistry and medicinal chemistry. Due to the importance the researchers have been developed numerous methods among them, Reddy *et al*. [271] have been reported green chemical method for the synthesis of targeted compounds under ultrasonications (Scheme 58).

7.1.8. Synthesis for the protection of aldehydic carbonyl group

Selective protection of aldehydic carbonyl groups by conversion to their corresponding acylals is an important component of multistep organic syntheses. A crucial property of the acylals formed in this process is their stability in neutral, basic, and acidic media. There are various reports available in the literature, but some of them show drawbacks, such as long reaction time and high reagent volume and so on. To overcome this problem, Kim *et al*. [262] have been developed novel catalytic method for the protection and deportection of carbonyl compounds (Scheme 59).

8. CONCLUSIONS

This review summarizes the various heterogeneous acid catalyzed different organic transformations that are of importance due to their numerous properties. This review includes organic templates such as MTSA, hybrid templates such as β-Cyclodextrins and CSAs. After that, we have focused inorganic templates such as PSA, BSA, and TSA using various organic transformations. Beside the literature examples, our own synthetic results are also involved.

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