Green Synthesis of Pyrazoles: Recent Developments in Aqueous Methods

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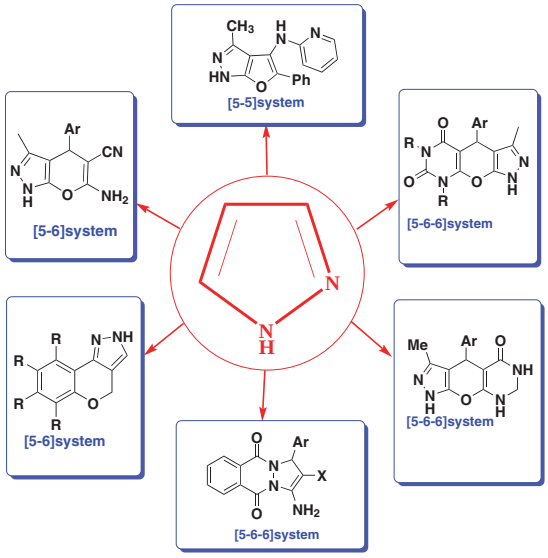

Received: 02.06.2023
Accepted after revision: 03.07.2023
Published online: 05.07.2023 (Accepted Manuscript), 07.08.2023 (Version of Record)
DOI: 10.1055/a-2123-8102; Art ID: SO-2023-06-0040-RV

Crowd-Reviewed

Abstract Organic syntheses by adopting green protocols such as sonochemical procedures, microwave technologies, solvent-free conditions, green solvents, heterogeneous catalysis particularly nanocatalysts, ionic liquids have replaced traditional procedures due to concerns pertaining especially to the environment. The heterocycle, pyrazole, due to its multifaceted applications, has been the target of chemists and therefore various synthetic approaches have been developed to synthesize pyrazole-containing molecules. In the present compilation, we have summarized recent water-based research work on the synthesis of pyrazoles.

Keywords green chemistry, environment friendly, water-based synthesis, pyrazoles

1 Introduction

There is great concern in the utilization of chemicals and polymers for production processes, which have detrimental effects on public health and the global environment. For the wellbeing of society and humans, various environmentally benign organic transformations are being devised with advantages such as chemical waste minimization, atom economy, energy saving, easy workup, alternative catalysts and procedures, and chromatography-free isolation of the products. The utilization of ecofriendly synthetic techniques like 'green chemistry' has come into consideration for the synthetic chemist to develop products with these desired qualities.[1–5]

The green approaches that are generally considered for organic synthetic reactions are: (i) the use of green solvents, such as nature's solvent water, as a reaction medium instead of organic solvents, (ii) reactions in the solid state without the use of solvent, (iii) using catalytic amount of organometallic reagents instead of stoichiometric amounts, and (iv) biosynthetic processes. For the synthesis of heterocyclic compounds, many green methods have been applied,[6–9] performing the reactions at ambient temperature and using alternative energy sources are the methods of choice.

Organic reactions are mainly performed in organic solvents thus giving rise to large amounts of solvent waste that are hazardous to aquatic organisms and pollute underground water. The use of aqueous media, a non-polluting abundant solvent, for organic syntheses is a very important

area of green chemistry receiving special attention in the past three decades.[10–14]

The present compilation elaborates the water-based synthesis of pyrazoles, including fused examples, with and without a catalyst. Pyrazole is a versatile ring among heterocyclic compounds as pyrazole compounds are involved in a plethora of applications, including industrial, medical, pharmaceutical, and agricultural uses and as polymers, luminophores, dyes, etc.[15] Pyrazole-containing compounds have various therapeutic and pharmaceutical properties and represent important building blocks for, insecto-acaricidal, antibacterial, antidepressant, analgesic, antiviral, anticancer, antioxidant, anti-HIV, cyclooxygenase-2 (COX-2) inhibitor, anti-inflammatory, antiproliferative drugs.[16–26] Many of the de-

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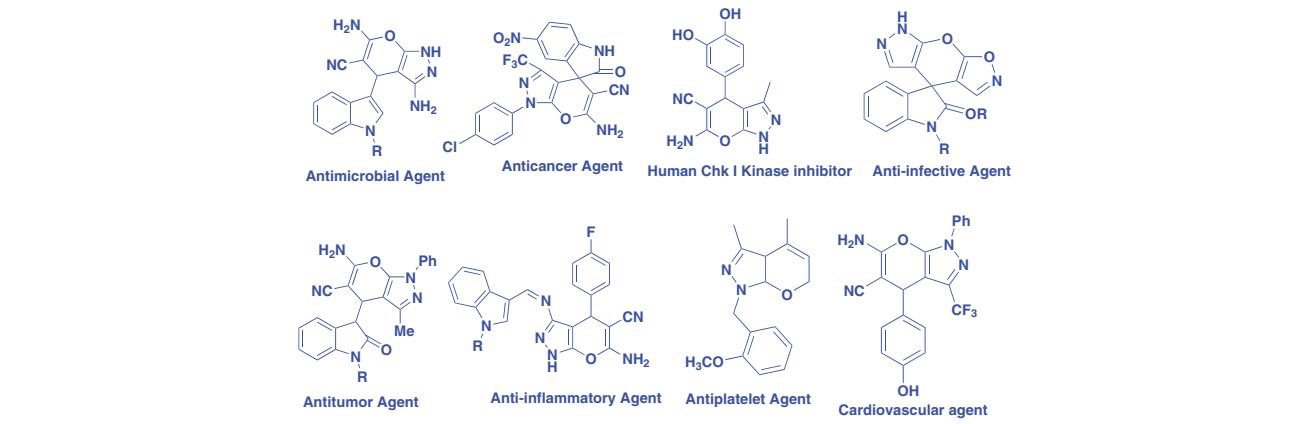


Figure 1 Medicinally important pyrazole derivatives

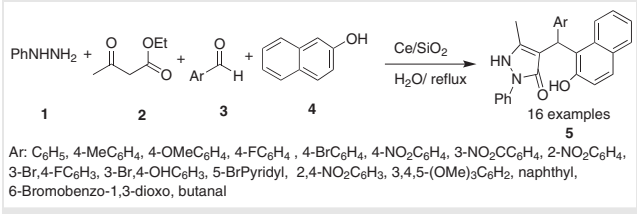
rivatives are of great interest due to their pharmacological properties, for instance, celecoxib {4-[5-(4-methylphenyl)-3-(trifluoromethyl)pyrazol-1-yl]benzenesulfonamide} acts as inhibitor of COX-2 and reduces side effects in the gastrointestinal tract. Methylthio pyrazole epothilone B shows strong antitumor activity. Functionalized pyrazoles and suitably substituted pyrazoles such as pyranopyrazole, benzopyranopyrazoles, pyrazolopyrimidines, furopyrazoles, tetrahydrobenzo[*b*]pyrans and many others show a wide range of biological activities (Figure 1).[27–30]

Due to multifaceted applications of pyrazole derivatives, a number of methods for the synthesis of pyrazoles have been performed using Al_2O_3/clay (montmorillonite K10),[31] Amberlyst-70,[32] polymer-bound PTSA,[33] silica-supported sulfuric acid (H_2SO_4·SiO_2),[34] $Sc(OTf)_3$,[35] and sulfamic acid[36] as catalysts. Various environmentally benign protocols using green solvent have also been reported in the literature including synthetic methods using water as solvent.

This review compiles recent work on the water-based syntheses of pyrazole derivatives (from 2015 till 2022) to facilitate scientists working, or intending to work, in this important field.

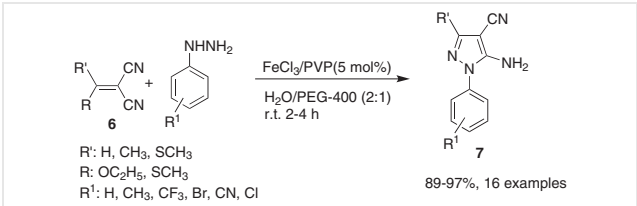
2 Synthesis of Polyfunctionalized Pyrazoles

In 2016, Kantam, Trivedi, and co-workers reported the synthesis of pyrazolones **5** in 85–92% yield by the multicomponent reaction of $PhNHNH_2$ (**1**), ethyl acetoacetate (**2**), 2-naphthol (**4**), and an arylaldehyde **3** using the heterogeneous Lewis acid CeO_2/SiO_2 (0.9%) as a catalyst (Scheme 1).[37] All the newly synthesized pyrazoles **5** were evaluated for *in vitro* antimicrobial activity. For antibacterial activity, the derivatives containing halogen and nitro groups were found to be more useful. For antifungal activity, the dinitro-substituted pyrazolone derivatives were found to be even better than the standard drug, ketoconazole.



Scheme 1 Synthesis of pyrazolones using CeO_2/SiO_2 in water

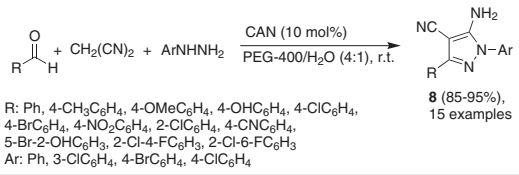
Elnagdy and Sarma, in 2019, performed the room temperature reaction of different arylhydrazines with malononitrile derivatives using the homogenous catalyst $FeCl_3$-PVP (5 mol% $FeCl_3$) in water/PEG-400 (2:1) medium for 2–4 h for the synthesis of several 5-amino-4-cyanopyrazoles in high 89–97% yield (Scheme 2).[38]



Scheme 2 $FeCl_3$/PVP-catalyzed synthesis of pyrazoles in H_2O/PEG-400

The ceric ammonium nitrate (CAN) catalyzed synthesis of substituted polyfunctionalized pyrazoles **8** was been achieved by Bhosale and co-workers in 2019 starting from aromatic aldehydes, malononitrile, and arylhydrazines in PEG-400/H_2O, where polyethylene glycol (PEG) plays the role of solvent as well as promoter (Scheme 3).[39]

In 2021, Shahbazi-Alavi and co-workers reported the CeO_2/CuO@GQDs@NH_2 nanocomposite catalyzed reaction of $PhNHNH_2$, dimethyl acetylenedicarboxylate, and arylaldehydes at ambient temperature in water solvent to obtain the bispyrazole derivatives **9** in good yields (82–94%) (Scheme 4).[40] Initially, the reaction was attempted in the



Scheme 3 Synthesis of polyfunctionalized pyrazoles using CAN/PEG-400/H_2O

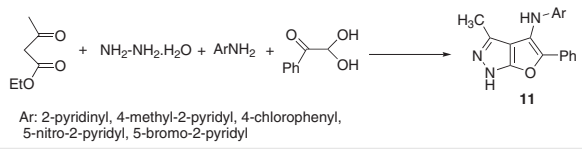
presence of PTSA, Et_3N, CeO_2/CuO, CeO_2/CuO@GQDs, and CeO_2/CuO@GQDs@NH_2 nanocomposite, the use of different concentrations of the catalyst under different solvents was also examined. The best results were obtained using CeO_2/CuO@GQDs@NH_2 nanocomposite catalyst in water.

Also in 2021, Bansal and co-workers reported an environment friendly aqueous synthesis of tetrasubstituted pyrazoles **10** in the presence of cetyltrimethylammonium bromide (CTAB) by using arylaldehydes, ethyl acetoacetate, and $PhNHNH_2$ or $NH_2NH_2{\cdot}H_2O$ in one pot (Scheme 5).[41] This is green and efficient synthetic protocol that can be used to prepare sulfinic esters which will have good applications in the future.

3 Synthesis of Fused Pyrazoles in Water without a Catalyst

3.1 Fused [5-5]System (3 Heteroatoms): Furo[2,3-*c*]pyrazoles

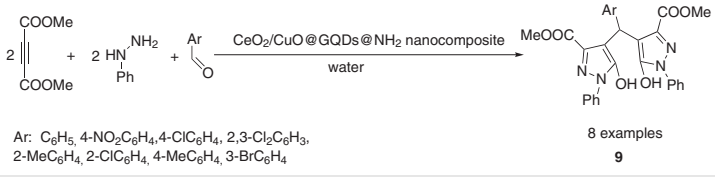
Olyaei and co-workers synthesized new fused furopyrazoles **11** using a four-component system without the use of a catalyst at room temperature (Scheme 6).[42] This domino reaction when applied to amines with electron-withdrawing groups furnished the unexpected bis(pyrazole-5-ol) products.



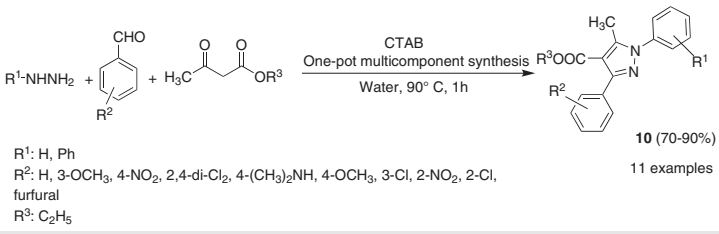
Scheme 6 Synthesis of some new 1*H*-furo[2,3-*c*]pyrazole-4-amines in water

3.2 Fused [5-6]System (3 Heteroatoms): Pyrano[2,3-*c*]pyrazoles

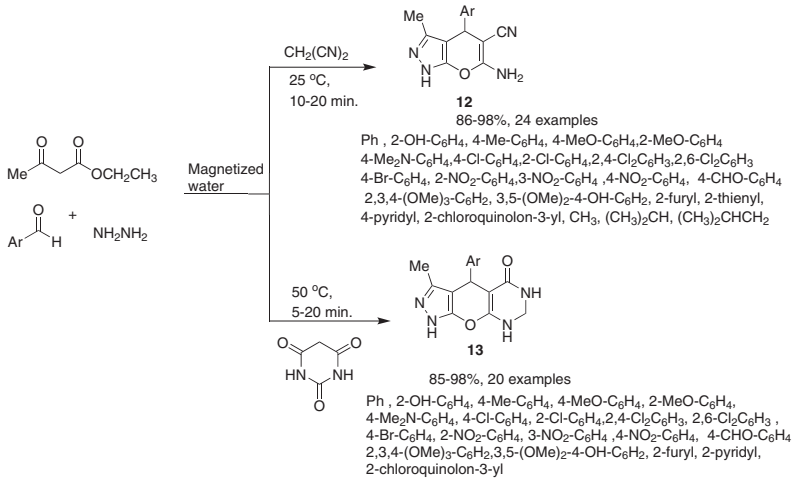
The reaction of ethyl acetoacetate, aromatic aldehydes, and hydrazine with malononitrile or barbituric acid (pyrimidinetrione) under magnetized water gave pyrano[2,3-*c*]pyrazoles **12** or pyrano[4′,3′:5,6]pyrazolo[2,3-*d*]pyrimidines **13**, respectively (Scheme 7).[43] The reaction was unsuccessful in nonpolar solvents and gave a poor yield in polar-protic solvents (EtOH, MeOH). It was suggested that hydrogen bond interactions at the organic-water interface are responsible for the stabilization of the intermediate. This reaction has a wide applicability for differently substituted (hetero)arylaldehydes, such as furan-2-, thiophene-2-, pyridine-4-, and 2-chloroquinolone-3-carbaldehydes.



Scheme 4 The use of CeO_2/CuO@GQDs@NH_2 nanocomposite catalyst for synthesis of bispyrazoles



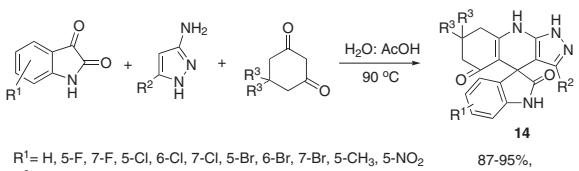
Scheme 5 CTAB-mediated synthesis of tetrasubstituted pyrazoles



Scheme 7 Magnetized water as solvent in the synthesis of pyrano[2,3-*c*]pyrazoles and pyrano[4′,3′:5,6]pyrazolo[2,3-*d*]pyrimidines

3.3 Fused [5-6-6]System (3 Heteroatoms): Pyrazolo[3,4-*b*]quinolones

In 2018, Rong and co-workers synthesized spiro[indoline-3,4′-pyrazolo[3,4-*b*]quinoline]-2,5′(6′*H*)-diones **14** using isatins, 3-aminopyrazole, and cyclohexane-1,3-dione or dimedone as reactants with H_2O/AcOH (4:1) as the solvent system at 90 °C for 5–7 h (Scheme 8).[44] The use of lower temperature was unsuccessful and the use of a single solvent, such as water or acetone gave poor yields.

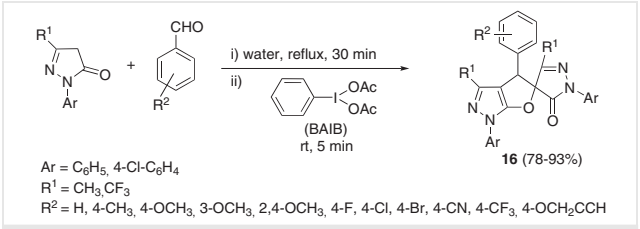


Scheme 8 Preparation of spiro[indoline-3,4′-pyrazolo[3,4-]quinoline]-2,5′(6′*H*)-diones in water/acetone

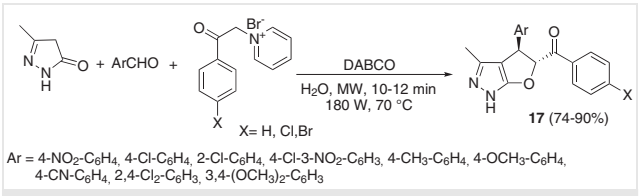
4 Synthesis of Fused Pyrazoles in Water Using a Catalyst

4.1 Fused [5-5]System (3 Heteroatoms): Furo[2,3-*c*]pyrazoles

In 2018, Atmakur and co-workers reported the reaction of arylaldehydes and 1,3-disubstituted pyrazolones in refluxing water for 30 min followed by the addition of [bis(acetoxy)iodo]benzene (BAIB) and stirring for 5 min at room temperature to give spirofuropyrazoles **16** (Scheme 9).[45] Also in 2018, Yazdani-Elah-Abadi and co-workers reacted arylaldehydes, 1,3-disubstituted pyrazolones, and 1-(2-aryl-2-oxoethyl)pyridinium bromide employing the catalyst 1,4-diazabicyclo[2.2.2]octane (DABCO) and microwaves to give furopyrazoles **17** (Scheme 10).[46]



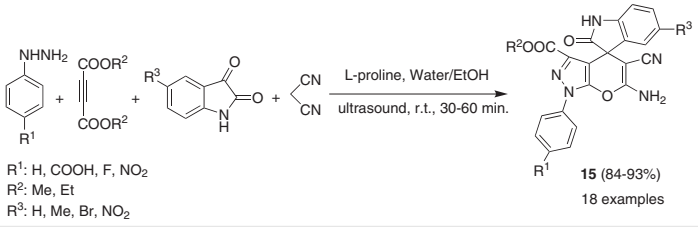
Scheme 9 BAIB-mediated fusion of pyrazolones with aldehydes



Scheme 10 DABCO-mediated synthesis of furopyrazoles

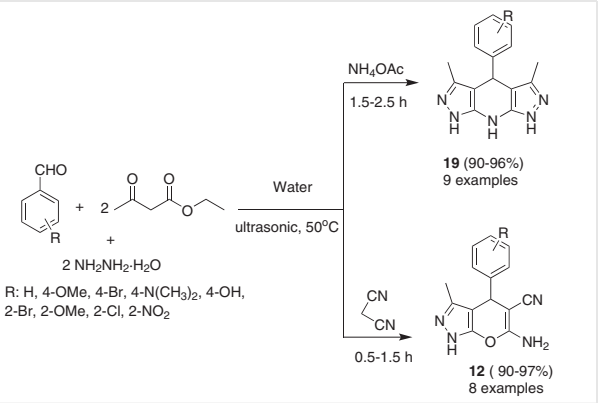
4.2 Fused [5-6]System (3 Heteroatoms): Pyrano[2,3-*c*]pyrazoles

Banerjee and co-workers used ZrO_2 nanoparticles as a reusable catalysts for the multicomponent synthesis (r.t., 2–10 min) of dihydropyrano[2,3-*c*]pyrazoles **12** in 90–98% yield (Scheme 36).[47] Ablajan and co-workers utilized L-proline as a catalyst in the synthesis of spiro[indoline-3,4-pyrano[2,3-*c*]pyrazole] derivatives **15** in 84–93% yields (Scheme 11). EtOH/H_2O (1:1) was used as the solvent and the reaction was performed under ultrasonication to obtain the target compounds within 60 min.[48]



Scheme 11 Synthesis of spiro[indoline-3,4-pyrano[2,3-*c*]pyrazole]s under ultrasound using L-proline

In 2015, Jonnalagadda and co-workers reacted arylaldehydes, ethyl acetoacetate, and $NH_2NH_2{\cdot}H_2O$ with ammonium acetate or malononitrile at 50 °C under ultrasonication to give pyrazolopyridines **19** and pyranopyrazoles **12**, respectively, as pure products that did not require chromatography (Scheme 12).[49]



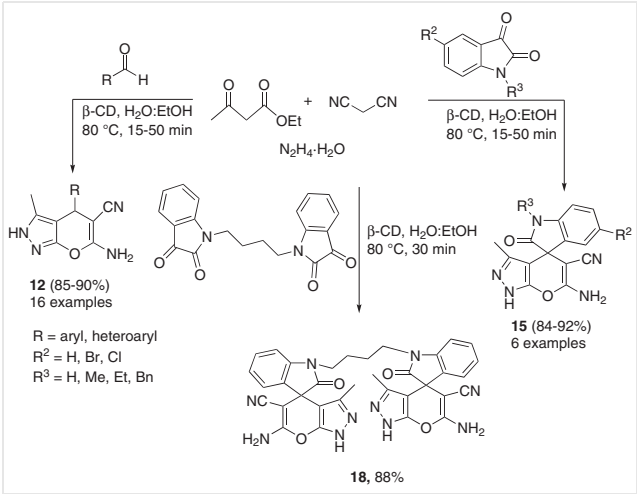
Scheme 12 Ultrasonication for annulation

Various nanoparticles have been applied as catalysts for the synthesis of fused pyranopyrazoles. Fe_3O_4@SiO_2 core-shell NPs were used by Soleimani, Jafarzadeh, and co-workers for the construction of fused pyrazoles in H_2O/EtOH (Scheme 20).[50]

The application of biodegradable β-cyclodextrin (β-CD) as a catalyst in the four-reactant domino synthesis of pyrano[2,3-*c*]pyrazoles **12** and spiro[indoline-3,4-pyrano[2,3-*c*]pyrazole] products **15** and **18** was explored by Dalal and co-workers in 2015. The reaction progressed successfully with ethyl acetoacetate, malononitrile, $NH_2NH_2{\cdot}H_2O$, and aldehydes (aryl or hetaryl)/1,5-disubstituted isatins/1,1-(butane-1,4-diyl)bis(indoline-2,3-dione) in H_2O/EtOH (9:1) at 80 °C (Scheme 13).[51]

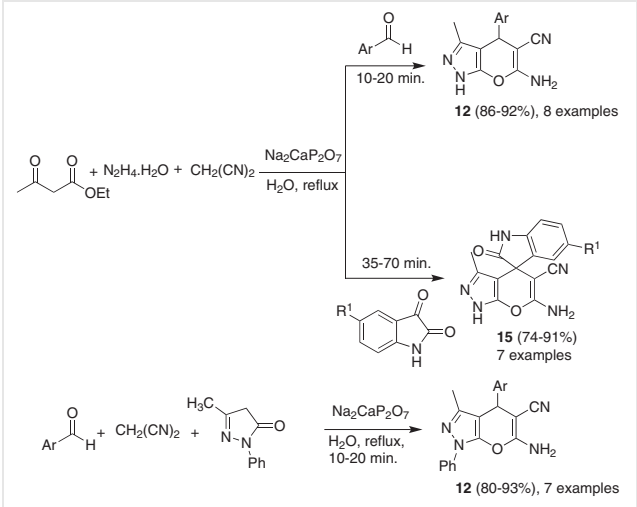
In 2016, Khojastehnezhad and co-workers prepared Preyssler-heteropoly acid ($H_{14}NaP_5W_{30}O_{120}$) supported silica coated $NiFe_2O_4$ magnetic NPs ($NiFe_2O_4$@SiO_2-Preyssler/NFS-PRS) and employed it for the synthesis of 25 pyrano[2,3-*c*]pyrazole derivatives **12**[52] under green conditions using water as a solvent (Scheme 36).

The preparation and application of nanostructured diphosphate, $Na_2CaP_2O_7$, was performed by Maleki, Khojastehnezhad, and co-workers in 2016 for the synthesis of dihydropyrano[2,3-*c*]pyrazoles **12** and spiro[indoline-3,4-

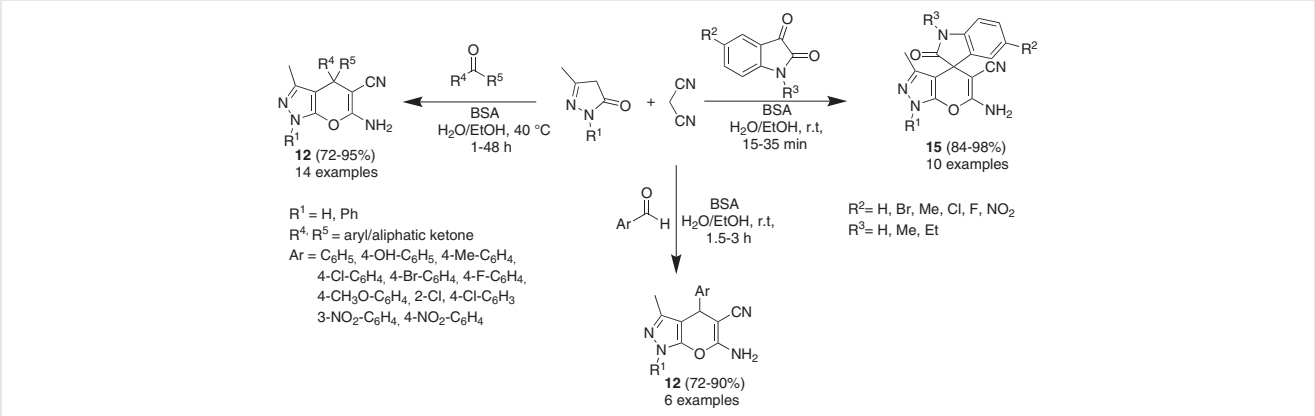


Scheme 13 β-Cyclodextrin-mediated annulations

pyrano[2,3-*c*]pyrazole]s **15** (Scheme 14).[53] All the reactions were performed under reflux with water as the solvent. The catalytic approach is efficiently extendable to a wide variety of aromatic aldehydes to produce only the expected product.



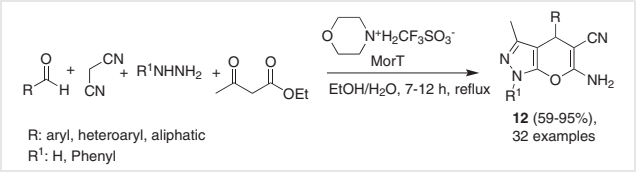
Scheme 14 Annulation to fused pyrazole system using $Na_2CaP_2O_7$



Scheme 15 Use of BSA biocatalyst for the synthesis of pyranopyrazoles and spiropyranopyrazoles

Several 5-substituted 6-amino-3-methyl-4-aryl-1,4-dihydropyrano[2,3-*c*]pyrazoles were synthesized by research groups by applying various catalysts. In 2016, the H. D. Patel group used the juice of *Citrus limon* (lemon juice) in aqueous ethanol[54] and also the organocatalyst thiourea dioxide (TUD) in water (Scheme 26).[55] The biocatalyst, bovine serum albumin (BSA), was used by Chaudhari and co-workers to produce different pyranopyrazoles **12** and spiro-pyranopyrazoles **15** (Scheme 15).[56]

Li, Su, and Zhou used the Lewis acid catalyst morpholine triflate (MorT) for the four-component reaction of aldehydes, malononitrile, hydrazine or $PhNHNH_2$, and ethyl acetoacetate to give pyrano[2,3-*c*]pyrazoles (Scheme 16).[57]

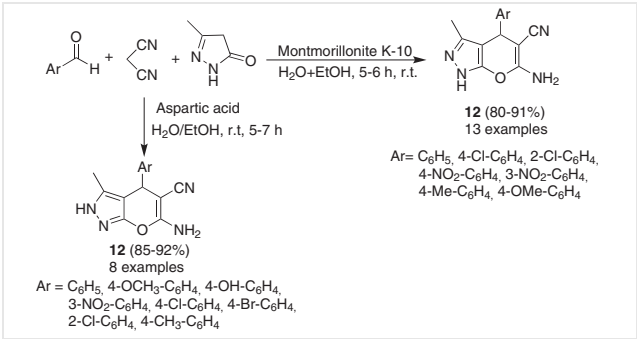


Scheme 16 Morpholine triflate in the synthesis of pyrano[2,3-*c*]pyrazoles

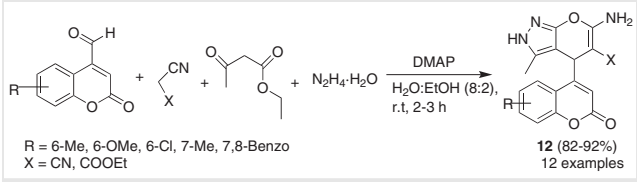
In 2017, Moeinpour and Khojastehnezhad reported the synthesis of 5-cyano-1,4-dihydropyrano[2,3-*c*]pyrazoles **12** in 86–94% yield in water using $Ni_{0.5}Zn_{0.5}Fe_2O_4$-PPA nanoparticles (0.03 g, 0.015 mmol H^+) as the catalyst.[58] The catalyst was recyclable at least up to six times (Scheme 36).

Similarly, in 2017, Ahad and Farooqui used arylaldehydes, malononitrile, and 3-methyl-1,4-dihydro-5*H*-pyrazol-5-ones for the synthesis of pyrano[2,3-*c*]pyrazoles **12** using aspartic acid as an efficient organocatalyst in $EtOH/H_2O$ solvent system (Scheme 17).[59]

Cyclocondensation of ethyl acetoacetate, $NH_2NH_2{\cdot}H_2O$, malononitrile, and chromene-4-carbaldehyde using the base catalyst 4-(dimethylamino)pyridine (DMAP) in $EtOH/H_2O$ at r.t. gave several coumarin-based dihydropyrano[2,3-*c*]pyrazole derivatives in 82–92% yield (Scheme 18).[60] A mechanism was proposed that explains this transformation and involves Knoevenagel condensation, intramolecular cyclization, and tautomerization.



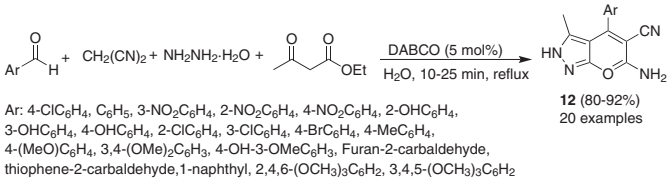
Scheme 17 Construction of dihydropyrano[2,3-*c*]pyrazoles



Scheme 18 Synthesis of coumarin-based dihydropyrano[2,3-*c*]pyrazoles using DMAP

Waghmare and Pandit reported a four-component cyclocondensation reaction using DABCO catalyst (5 mol%) in refluxing aqueous medium to give dihydropyranopyrazoles **12** (Scheme 19).[61] The reaction was unsuccessful with THF, ethyl acetoacetate, EtOH, MeCN and the percentage yield obtained was very poor.

Similarly, the Hazeri group applied Ag/TiO_2 nano films as heterogeneous catalysts in this reaction (Scheme 20).[62] Ghorbani-Vaghei and co-workers studied the use of $Fe_3O_4@SiO_2$

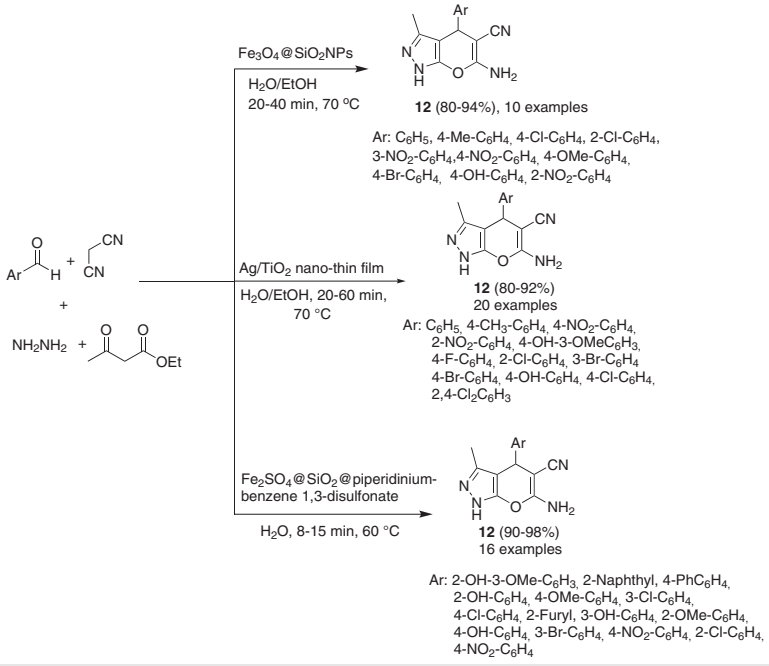


Scheme 19 DABCO catalyst in the construction of pyranopyrazoles

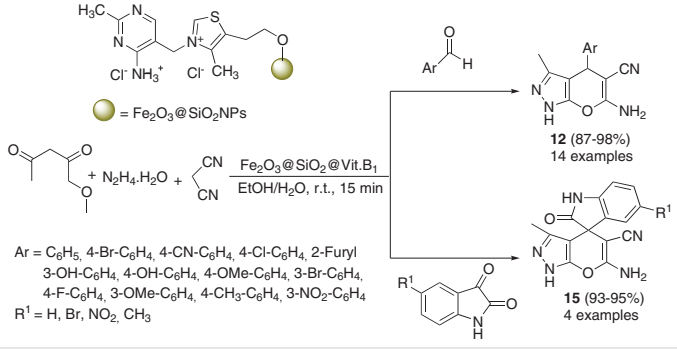
nanoparticle supported ionic IL, Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate in this reaction conducted in water (Scheme 20).[63]

In 2018, Nongkhlaw and co-workers reported the reaction of ethyl acetoacetate, $NH_2NH_2{\cdot}H_2O$, and malononitrile with variously substituted arylaldehydes or isatins using the Fe_2O_3@SiO_2 NPs functionalized by vitamin B1 in stirring aqueous ethanol at r.t. to give dihydropyrano[2,3-*c*]pyrazoles **12** and spiro[indoline-3,4-pyrano[2,3-*c*]pyrazole]s **15** (Scheme 21).[64]

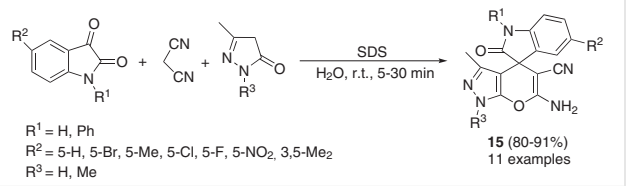
Deka and co-workers employed the sodium dodecyl sulfate (SDS) catalyst in water for the three-component room temperature synthesis of spiro[indoline-3,4-pyrano[2,3-*c*]pyrazole] s **15** in 80–91% yield (Scheme 22).[65]



Scheme 20 Catalytic synthesis of dihydropyrano[2,3-*c*]pyrazoles using: (i) Fe_3O_4@SiO_2NPs, (ii) Ag/TiO_2 nano-thin film, and (iii) Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonate

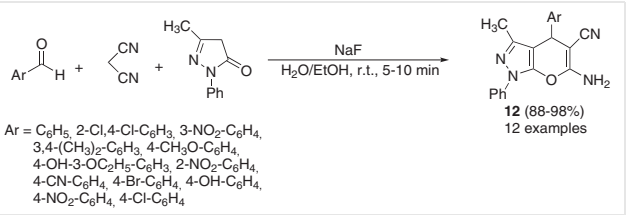


Scheme 21 Use of Fe_2O_3@SiO_2@VitB1catalyst in the synthesis of pyrano[2,3-c]pyrazoles in EtOH/H_2O



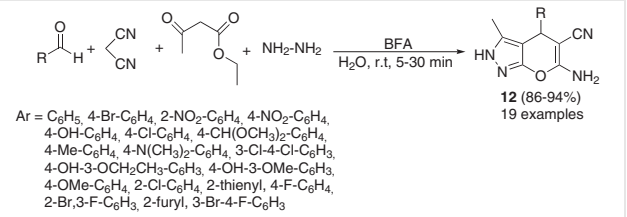
Scheme 22 Synthesis of spiro-pyranopyrazoles using SDS in water

The Kotha group reported the use of sodium fluoride in H_2O/EtOH using ultrasonic waves for 5–10 min for the synthesis of pyrano[2,3-*c*]pyrazoles **12** in 88–98% yield (Scheme 23).[66]



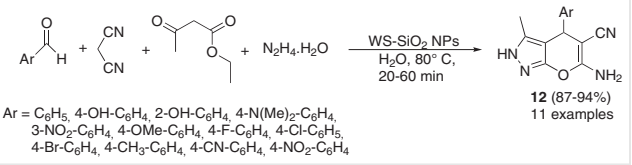
Scheme 23 NaF catalyst for the three-component synthesis of pyrano[2,3-*c*]pyrazole derivatives

Patil and co-workers reported the use of a green and ecofriendly natural catalyst, Bael fruit ash (BFA) in water at r.t. with (hetero)aryl aldehyde, ethyl acetoacetate, $NH_2NH_2{\cdot}H_2O$, and malononitrile for the synthesis of pyrano[2,3-*c*]pyrazoles **12** in 86–94% yield (Scheme 24).[67]



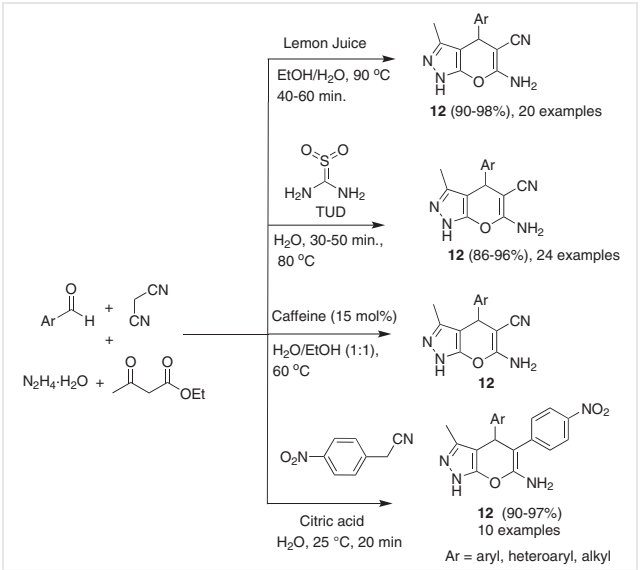
Scheme 24 Natural catalyst for the synthesis of fused pyranopyrazoles

In 2017, K. G. Patel and co-workers utilized the agricultural waste wheat straw and derived nano-silica from it and used it as a catalyst for the formation of fused pyranopyrazoles in aqueous medium at 80 °C. Different monosubstituted aromatic aldehydes were used successfully in this reaction (Scheme 25).[68]



Scheme 25 Use of WS-SiO_2NPs for the synthesis of fused pyranopyrazoles

Mohamadpour[69] used a caffeine catalyst while Pasha and co-workers used a citric acid catalyst for the reaction of arylcarbaldehydes with ethyl acetoacetate, $NH_2NH_2{\cdot}H_2O$, and malononitrile to give pyranopyrazoles (Scheme 26).[70]



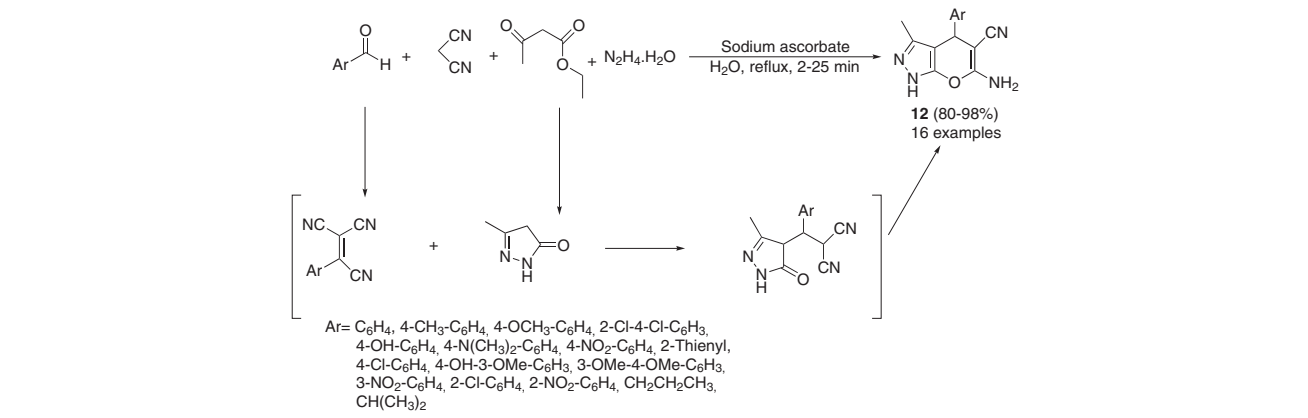
Scheme 26 Catalytic annulations for the preparation of fused systems

Kiyani and Bamdad used environmentally friendly heterogeneous catalyst sodium ascorbate in water for reaction of arylcarbaldehydes with ethyl acetoacetate, $NH_2NH_2{\cdot}H_2O$, and malononitrile to give pyranopyrazoles **12** (Scheme 27).[71]

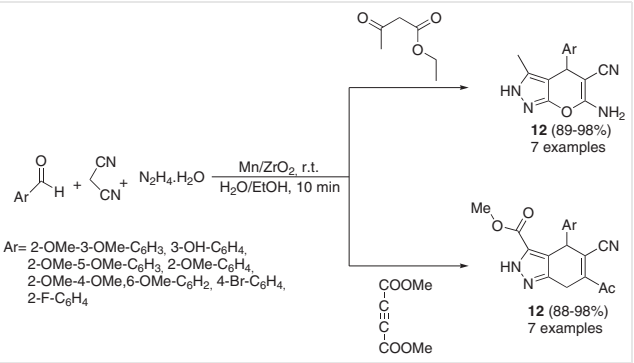
Garcia and co-workers constructed thirteen examples of dihydropyrano[2,3-*c*]pyrazole derivatives **12** from the reaction of *ortho/meta/para* monosubstituted aromatic aldehydes, malononitrile and pyrazolone by using the green and reusable catalyst montmorillonite K-10 in aqueous ethanolic solvent (Scheme 17).[72]

In 2016, Lavanya and co-workers reported the use of manganese-doped zirconia as an efficient catalyst for the ultrasound-assisted four-component water/ethanol r.t. synthesis of dihydropyrano[2,3-*c*]pyrazoles **12**. The tolerated various aromatic aldehydes containing electron-releasing or withdrawing groups without any effect on the yield of the products (Scheme 28).[73]

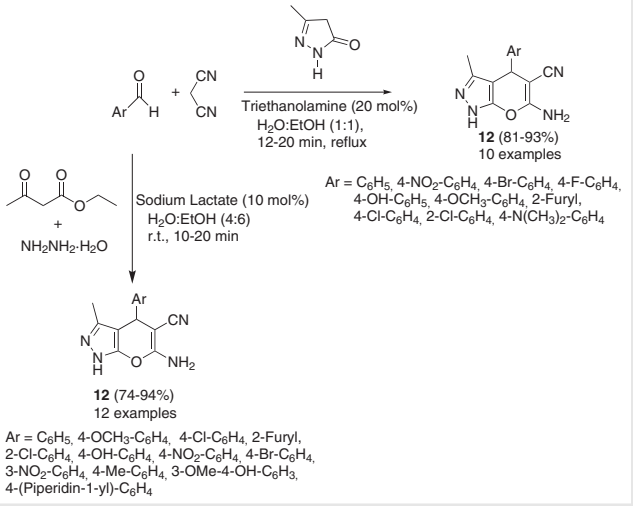
In 2019, Thore and co-workers used the reaction of arylaldehydes and malononitriles with 3-methyl-1,4-dihydro-5*H*-pyrazol-5-ones or ethyl acetoacetate using triethanolamine or sodium lactate catalyst, respectively, to give dihydropyrano[2,3-*c*]pyrazoles **12** (Scheme 29).[74] Khandebharad and co-workers reported a similar reaction using the recyclable organocatalyst sodium gluconate (Scheme 30).[75]



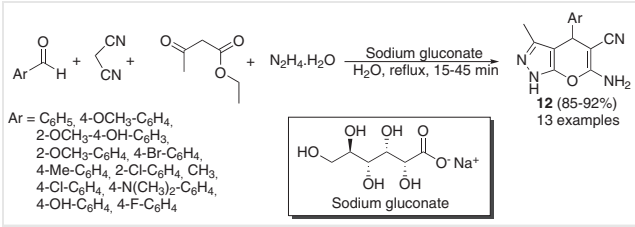
Scheme 27 Sodium ascorbate as heterogeneous catalyst in cyclocondensation reaction



Scheme 28 Mn/ZrO_2 catalyst for dihydropyrano[2,3-c]pyrazoles

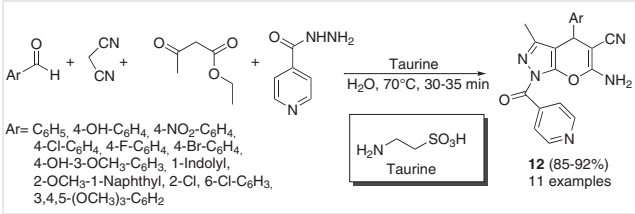


Scheme 29 Triethanolamine and sodium lactate catalyzed syntheses

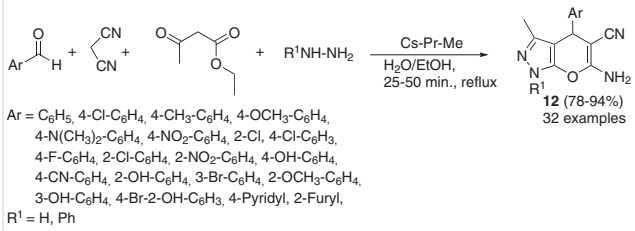


Scheme 30 Use of sodium gluconate as recyclable organocatalyst in pyrazoles synthesis

Chate and co-workers used the biocatalyst 2-aminoethanesulfonic acid (taurine) for the reaction of aldehydes, ethyl acetoacetate, and malononitrile with isoniazid to give new pyrazoles (Scheme 31).[76] Dekamin and co-workers used bifunctional organocatalyst melamine modified chitosan (Cs-Pr-Me) for the reaction of arylaldehydes, ethyl acetoacetate, hydrazine derivatives, malononitrile or 4-hydroxycoumarin (Scheme 32).[77]

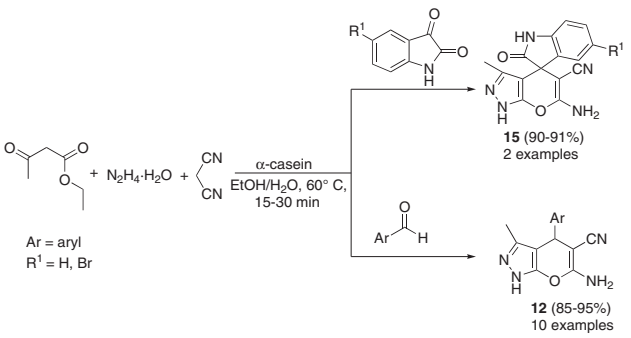


Scheme 31 Pyrazole ring formation reaction in the presence of taurine catalyst



Scheme 32 Melamine-modified chitosan catalyst for pyrazole construction

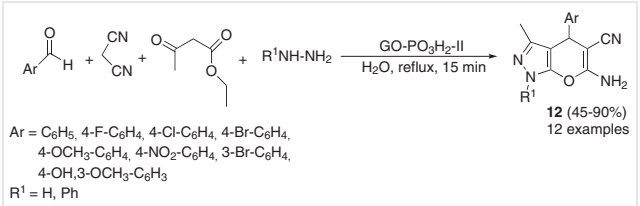
α-Casein has also been used for the synthesis of pyrazoles **12** and **15** in EtOH/H_2O at 60 °C by Maghsoodlou and co-workers in 2019 (Scheme 33).[78]



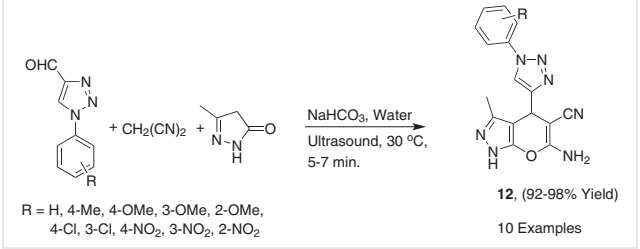
Scheme 33 Cyclocondensation in the presence of α-casein

Also in 2019, Abouzari-lotf and co-workers used phosphoric acid functionalized graphene oxide (GO-PO_3H_2-II) to catalyze the aqueous reaction of arylaldehydes, ethyl acetoacetate, and malononitrile with hydrazine or $PhNHNH_2$ (Scheme 34).[79] The nanocatalyst was compatible with various *meta*- and *para*-substituted arylaldehyde substrates.

Shingate and co-workers, in 2019, generated 1,2,3-triazolyl-substituted pyrano[2,3-*c*]pyrazoles **12** from the reaction of 1-aryl-4-formyl-1,2,3-triazoles, malononitrile, and 3-methyl-1,4-dihydro-5*H*-pyrazol-5-one with $NaHCO_3$ catalyst in water at 30 °C by using ultrasonic irradiation (Scheme 35).[80]

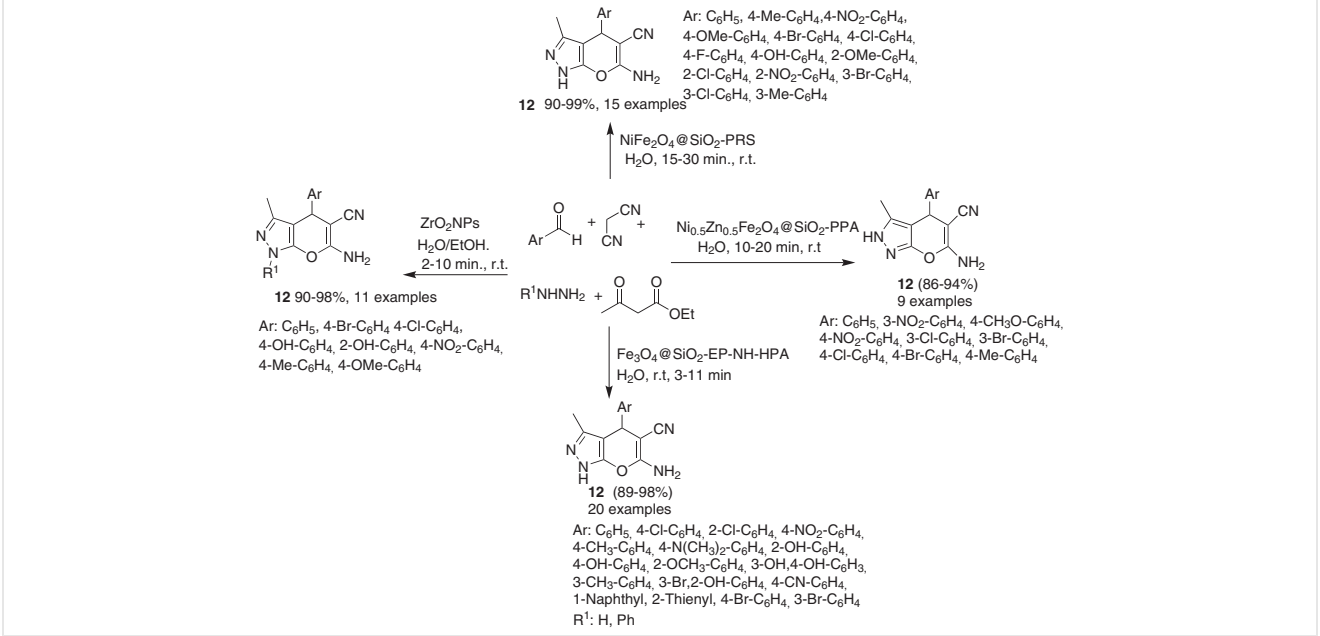


Scheme 34 Phosphoric acid functionalized graphene oxide catalyst for the construction of pyrazoles

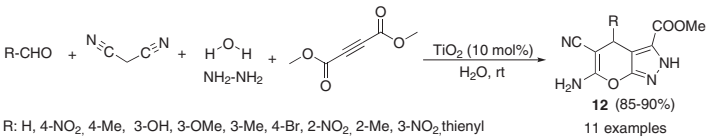


Scheme 35 Synthesis of triazolyl-substituted pyranopyrazole derivatives using ultrasound and base

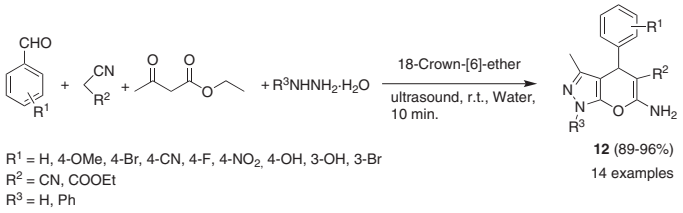
In 2020, Hosseini Mohtasham and Gholizadeh reported the synthesis of various pyrano[2,3-*c*]pyrazole compounds from the four-component system (arylaldehydes, ethyl acetoacetate, and malononitrile with hydrazine or $PhNHNH_2$) using natural mesoporous silica as a support for $H_3PW_{12}O_{40}$ immobilized on aminated epibromohydrin functionalized Fe_3O_4@SiO_2 NPs in aqueous medium at r.t. (Scheme 36).[81]



Scheme 36 Synthesis of dihydropyrano[2,3-*c*]pyrazole derivatives using nanocatalysts



Scheme 37 TiO_2-catalyzed one-pot synthesis of methyl pyrano[2,3-*c*]pyrazole-3-carboxylates

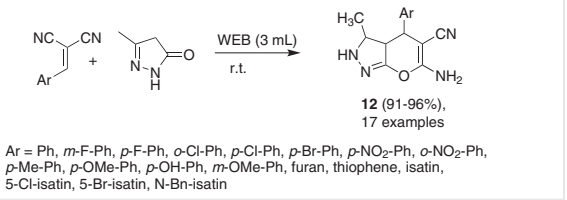


Scheme 38 Use of 18-crown-ether as catalyst for synthesis of pyrazoles

In 2020, Sangshetti and co-workers reported titanium dioxide (10 mol%) for the one-pot, four-component synthesis of methyl 6-amino-5-cyano-4-aryl-2,4-dihydropyrano[2,3-*c*]pyrazole-3-carboxylates **12** in 85–90% yield in water at r.t. in 30 min (Scheme 37).[82]

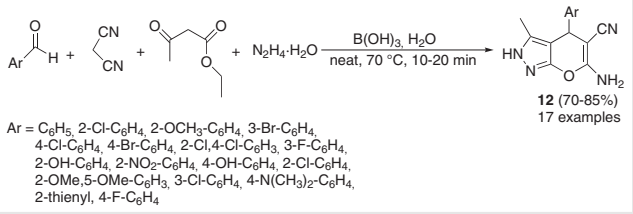
Nizam and co-workers, in 2020, used 18-crown-[6]-ether for the four-component synthesis of pyranopyrazoles **12** in 89–96% yield in water using ultrasonication within 10 min (Scheme 38).[83] The use of various solvents, such as MeOH, MeCN, DMF, DMSO, DCM, was examined but water was found to be the best.[83]

A two-component synthesis of pyrano[2,3-*c*]pyrazoles **12** was achieved using the natural waste, water extract of banana peels (WEB) by Chowhan and co-workers, in 2020, starting from arylidenemalononitriles and 3-methyl-1,4-dihydro-5*H*-pyrazol-5-one (Scheme 39).[84] The reaction was efficiently performed with various substituted arylidenemalononitriles possessing *ortho*-, *meta*-, or *para*-substituted aryl or hetaryl groups at room temperature and the products were obtained in excellent 91–96% yield.[84]



Scheme 39 Water extract of banana peels in the synthesis of fused pyrazoles

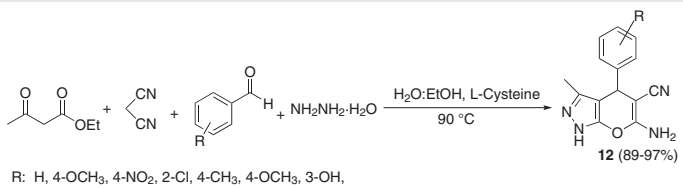
In 2017, Moosavi-Zare and co-workers utilized boric acid catalyst for the four-component reaction of arylaldehydes, ethyl acetoacetate, and malononitrile with $NH_2NH_2{\cdot}H_2O$ to give pyrano[2,3-*c*]pyrazole **12** at 70 °C within 20 min (Scheme 40).[85] The reaction is compatible with many electron-releasing and -withdrawing substituents on the arylaldehydes and also with halogen substituents



Scheme 40 Pyrano[2,3-*c*]pyrazole formation using boric acid catalyst

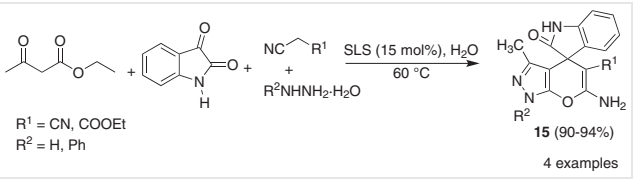
Zahoor and co-workers, in 2020, heated the aqueous ethanolic solution (9:1) of arylaldehydes, malononitrile, ethyl acetoacetate, and $NH_2NH_2{\cdot}H_2O$ at 90 °C with the natural catalyst L-cysteine (0.5 mol) to produce pyrano[2,3-*c*]pyrazoles **12** in excellent yields (Scheme 41).[86]

Dhakar and co-workers applied sodium lauryl sulfate (SLS) (15 mol%) in their work towards the four-component synthesis of spiro[indoline-3,4′-pyrano[2,3-*c*]pyrazole]s **15** using water as solvent (Scheme 42).[87] This micelle-promot-



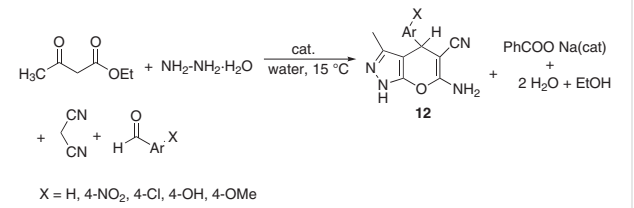
Scheme 41 Use of L-cysteine in the multicomponent synthesis of pyranopyrazoles

ed, surfactant-catalyzed reaction used isatin together with ethyl acetoacetate, hydrazine, and ethyl cyanoacetate as substrates.



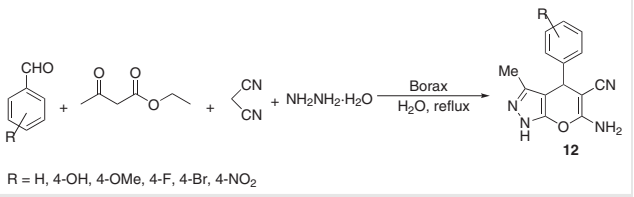
Scheme 42 Spiro[indoline-3,4′-pyrano[2,3-*c*]pyrazole]s by four-component sodium lauryl sulfate catalyzed reaction

The base catalyst sodium benzoate was applied by Habibi-Khorassani and co-workers in the synthesis of biologically active pyranopyrazoles **12** (Scheme 43).[88]



Scheme 43 Synthesis of pyranopyrazoles under basic condition

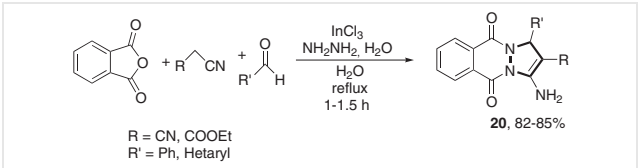
In 2021, Amiri-Zirtol and Amrollahi used sodium tetraborate pentahydrate (Borax) as an ecofriendly natural catalyst in the four-component reaction of arylaldehydes, malononitrile, ethyl acetoacetate, and $NH_2NH_2{\cdot}H_2O$ at reflux in aqueous solution to successfully give pyrano[2,3-*c*]pyrazoles in 85–95% yield (Scheme 44).[89]



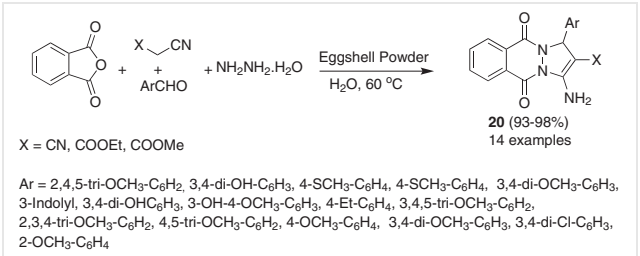
Scheme 44 Borax-mediated annulations to give pyrano[2,3-*c*]pyrazoles

4.3 Fused [5-6-6]System (2 Heteroatoms): Pyrazolo[1,2-*b*]phthalazines

1*H*-Pyrazolo[1,2-*b*]phthalazine-5,10-diones **20** can be efficiently obtained from isobenzofurandiones, malononitrile or alkyl 2-cyanoacetate, arylaldehydes, and $NH_2NH_2{\cdot}H_2O$. In 2017, Sreenivasareddy and co-workers used $InCl_3$ catalyst for this reaction in refluxing water for 1–1.5 h to give 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-diones **20** in 82–85% yield (Scheme 45).[90] In 2020, Jonnalagadda and co-workers used the heterogeneous catalyst eggshell powder, a biodegradable and inexpensive catalyst, for this reaction in water through Knoevenagel–Michael pathway with 98% atom economy and 100% carbon efficiency (Scheme 46).[91]



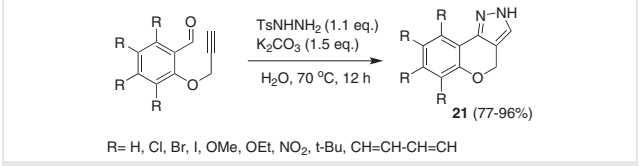
Scheme 45 $InCl_3$-catalyzed cyclocondensation to obtain pyrazolo[1,2-*b*]phthalazines



Scheme 46 Formation of derivatives of pyrazolophthalazines using eggshell powder

4.4 Fused [5-6-6]System (3 Heteroatoms): Benzopyranopyrazoles

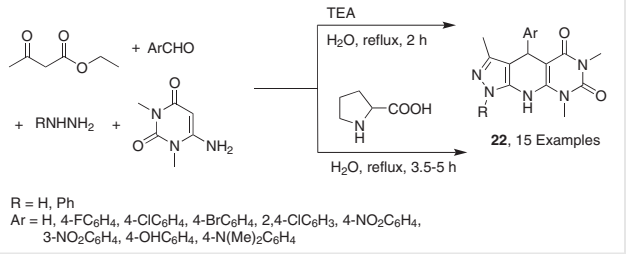
In 2018, Muthusamy and Gangadurai successfully synthesized chromeno[4,3-*c*]pyrazole derivatives **21** from propargylated salicylaldehydes and tosylhydrazine via intramolecular [3+2]-cycloaddition reaction in aqueous medium while heating at 70 °C for 12 h (Scheme 47).[92]



Scheme 47 Base-catalyzed preparation of benzopyranopyrazoles

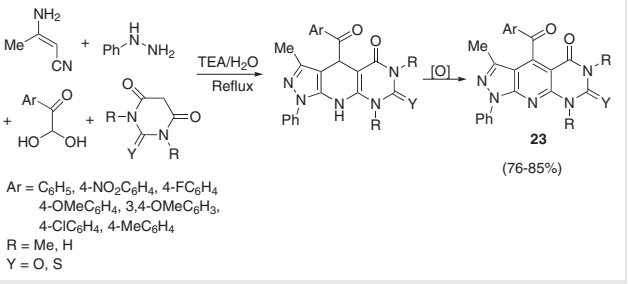
4.5 Fused [5-6-6]System (5 Heteroatoms): Pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidines and Pyrazolo[4′,3′:5,6]pyrano[2,3-*d*]pyrimidines

In 2016, Daraie and Heravi reported a simple and ecofriendly approach for the multicomponent production of many derivatives of pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidinediones **22** from the reactants ethyl acetoacetate, arylaldehyde, $NH_2NH_2{\cdot}H_2O$, and 6-amino-1,3-dimethyluracil catalyzed by triethylamine or L-proline in water as solvent (Scheme 48). The generality of this method was established by using various substituted arylaldehydes possessing either electron-donating or electron-withdrawing groups to successfully give products **22** in excellent yields (82–92% with TEA and 75–90% with L-proline).[93]



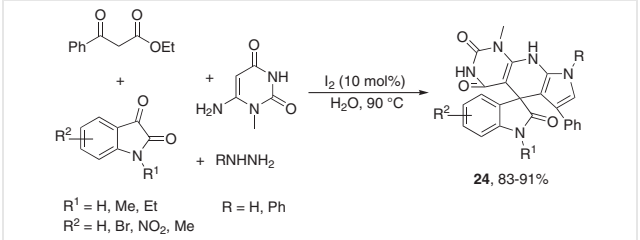
Scheme 48 TEA or L-proline catalyzed formation of pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidinediones

Polyfunctionalized pyrazolo[4′,3′:5,6]pyrido[2,3-*d*]pyrimidines **23** were conveniently obtained in aqueous medium by applying the multi-reactant approach. Derivatives of arylglyoxal, uracil, β-aminocrotonitrile, and $PhNHNH_2$ underwent the reaction efficiently in the presence of triethylamine catalyst under refluxing condition (Scheme 49). The protocol offered easy isolation and high yield of the products.[94]



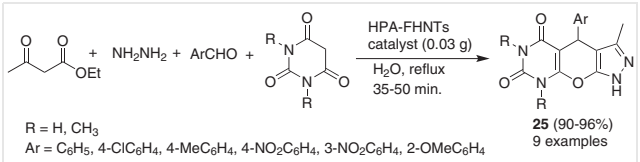
Scheme 49 TEA-mediated synthesis of polyfunctionalized tricyclic derivatives

Siddiqui and co-workers reported that the iodine (10 mol%) catalyzed reaction in aqueous medium of ethyl benzoylacetate, isatin, and 6-amino-1-methyluracil with $NH_2NH_2{\cdot}H_2O$ or $PhNHNH_2$ efficiently gave various substituted pyridopyrimidines **24** (Scheme 50).[95] Many Brønsted and Lewis acid catalysts, such as $FeCl_3$, I_2, $CoCl_2$, $Cu(OAc)_2$, HCl, and PTSA, were screened for this process. Among all the tested catalysts, molecular iodine was found to be best. The use of many solvents, such as $CHCl_3$, THF, MeOH, EtOH, MeCN, and water was also examined at various temperatures. The solvents MeOH, EtOH, MeCN, and water were successful, but water was the preferred solvent both in terms of environmental compatibility and yield. Furthermore, performing the reaction in the aqueous medium was also advantageous for the separation of the product as it was obtained just by filtration because of the solubility difference of the product and the reactants. Various isatin derivatives containing electron-donating or electron-withdrawing groups smoothly gave the products. The workup of the reaction involved only filtration, and chromatography or recrystallization was not needed.[95]



Scheme 50 Molecule iodine in the synthesis of substituted pyrazolopyridopyrimidines

Halloysite clay nanotubes (HNTs) were functionalized by γ-aminopropyltriethoxysilane and then immobilized by using phosphotungstic acid. The hybrid catalyst was used for the synthesis of fused tricyclic system containing pyrimidines, pyrans, and pyrazoles. This reaction was performed by refluxing ethyl acetoacetate, arylaldehydes, uracils, and hydrazine in water under microwave and ultrasonic conditions (Scheme 51). Using microwaves, the reaction was complete in 5 min, but the yield was low with many byproducts. Under ultrasonication, the reaction was complete within 15 min at 60 °C and the yield was excellent.[96]



Scheme 51 HPA-FHNTs catalyzed formation of pyrazolo[4′,3′:5,6]-pyrano[2,3-*d*]pyrimidine-5,7(6*H*,8*H*)-diones

5 Conclusion

The review is directed towards summarizing the literature on the synthesis of pyrazole derivatives (pyranopyrazole, spiro-pyranopyrazole, furopyrazole, pyrazolopyrimidine) using water as green solvent. The synthetic work on pyrazoles under water is mainly performed in the presence of catalysts. A wide variety of catalysts such as nanoparticles, nanothin films, Brønsted and Lewis acid catalysts, bases, amino acids, and natural catalysts have been applied to achieve the formation of the pyrazole nucleus. A little work has also been carried out under ultrasonication and microwave. It is to highlight that the reported work is inclined towards the synthesis of two fused pyrazole systems, furo[2,3-*c*]- and pyrano[2,3-*c*]pyrazoles. It is also found that the majority of the reactions are performed involving multicomponent reaction system. Surely, there is good deal of scope to work in this particular area and this focused compilation will be very advantageous for scientists interested in working in the area of green synthesis of pyrazoles.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgement

We are thankful to all the authors whose names are listed in the references and who have contributed to the green synthesis of pyrazole derivatives. We would like to thank all of the reviewers for their insightful comments.

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