

Go Green with Green Catalysis: A Focus and Review on Advancement of Biocatalysts

Suman¹, Sheetal², Suprita³, Susheel Gulati⁴, Rajvir Singh⁵

Department of Chemistry and Biochemistry CCSHAU Hisar

Abstract: Green chemistry is a sustainable approach to explain latest research topics and expresses an area of scientific discoveries about pollution awareness. Green chemistry is the future chemistry which is simple, efficient and benign in all steps of particular synthesis processes. The most simple and safe way to apply green chemistry in various field of life is to utilizes a set of principles that gives a backbone for the advancement of chemistry carried out a number of challenges to those who applied chemistry in medicine industry, education and research.

Keywords: Green chemistry, environment friendly, biocatalyst, and economic

1. Introduction

Green synthetic approach and development is one of the alternative to reduce the threat of climate change lies at the doorstep of our planet (Thomas *et al.*, 2004). Meeting the needs of the present generation without compromising the ability of future generations to meet their own needs (Brundtland 1987). In future, we have to substitute fuel based materials with bio-derived sources to minimize the environment degradation and their adverse effects on living beings. In early 1990's the US Environmental Protection Agency (EPA) coined the term "Green Chemistry" which is grown from a small idea and change into a large view to the scientifically based environmental protection. Researchers and chemical industries must have to consider the principles of green chemistry proposed by Paul Anastas and John C. Warner (1998). In recent years has attracted attention as this is promoter of innovative chemical technologies that reduces the use or generation of hazardous substances. The first book of green chemistry were published in 1990's including the journal of clean processes and and green chemistry explains a new approach to reduces threats to health and environment. This new area of research is also known as:

- Design by Benign Chemistry
- Atom Economy
- Clean and Safe Chemistry

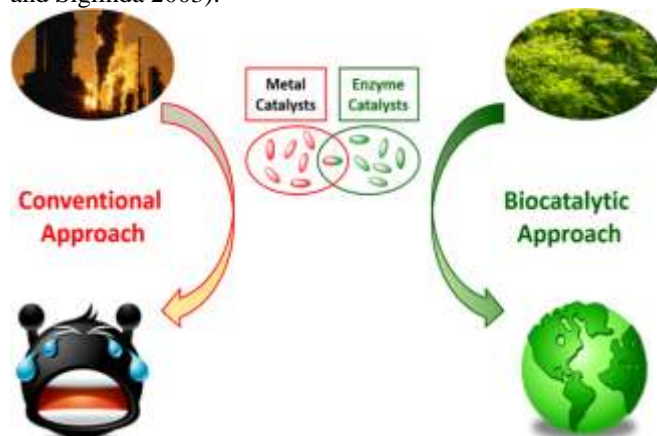
2. Basic Principles of Green Chemistry

Anastas and James C. Warner (1998) proposed a set of 12 principles which represents the green chemistry as a sustainable approach.



3. Biocatalyst

"The greenness of a chemical transformation can only be assessed on the context of its application and practice" (Glaze 1987). In this article we have focused on the catalyst which plays an important role in almost all types of chemical reactions. Biocatalyst is a magical intermediate which is helpful to overcome the negative environmental effects due to various hazardous and toxic chemicals used in synthetic pathways. The utilization of catalysis to achieve the goals of green chemistry has met with tremendous success (Gabriele and Siglinda 2003).



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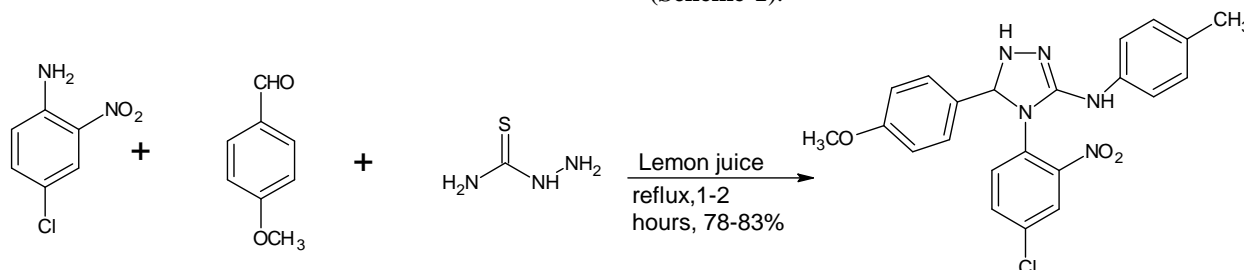
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The growing interest in Biocatalyst is mainly because of its environmentally benign characters. Best of literature survey a number of green catalysts are included in this article. The following examples show a broad use of biocatalysts in synthesis of organic compounds.

3.1 Using fruit Juices

Sachdeva *et al.*, 2013 reported the multi-component synthesis of substituted -2H-1,2,3-triazoles derivatives using lemon juice in ethanol by the reaction of 4-chloro-2-nitro aniline and 4-methoxy aldehyde with thiosemicarbazide in maximum yield. They found that lemon juice plays a role of biocatalyst which provides a non hazardous and mild conditions which are basic principles of green chemistry (**Scheme-1**).

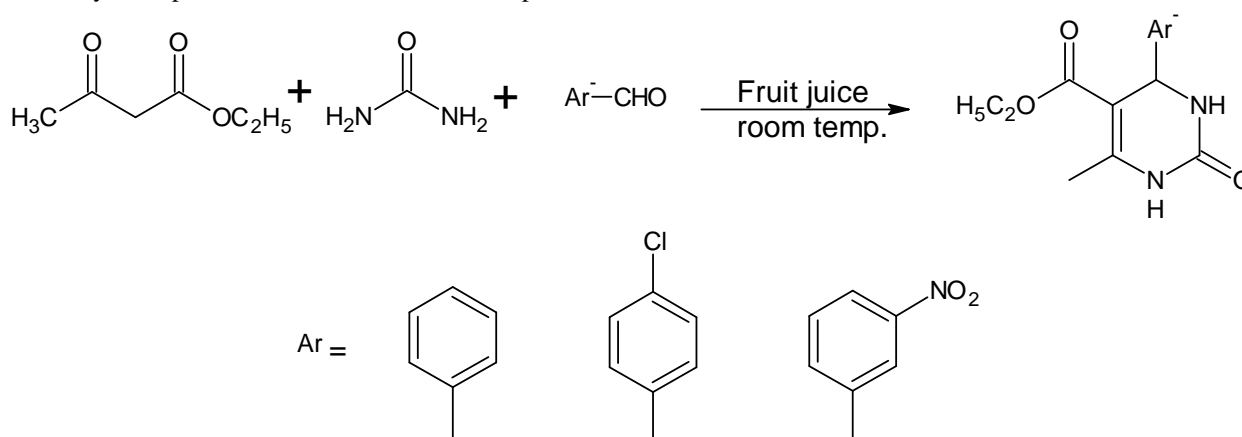


R= OH, OCH₃, CH₃, Cl

Scheme - 1

Dihydropyrimidinone have been synthesized by Patil *et al* (2011). These derivatives synthesized by reacting aldehydes, 1,3-dicarbonyl compounds with urea at room temperature

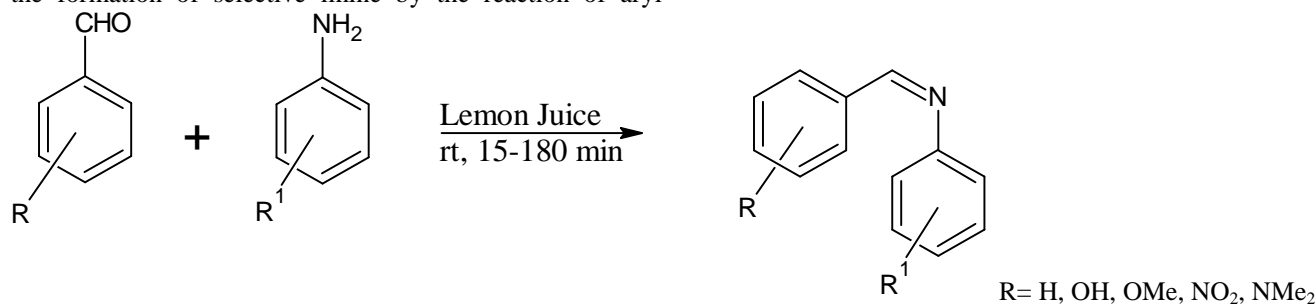
under solvent free conditions. This is a one-pot multi-component system reaction where lemon juice or pineapple acts as a green catalyst (**Scheme - 2**).



Scheme - 2

Patil *et al* (2012) reported the synthesis of Schiff Base by using lemon juice (*Citrus limonium*) as an effective and mild acid catalyst for condensation reaction. This synthesis shows the formation of selective imine by the reaction of aryl

aldehyde and aromatic primary amine. This method provides a cost effective idea and benefits from the elimination of production of acidic waste (**Scheme - 3**).



R¹= H, Me, OMe, Br, NO₂

Scheme - 3

A green procedure for Knoevenagel condensation was reported by Deshmukh *et al* (2012). They showed that lemon juice (*Citrus limonium*) act as environmentally benign acid catalyst for the reaction between aldehydes and

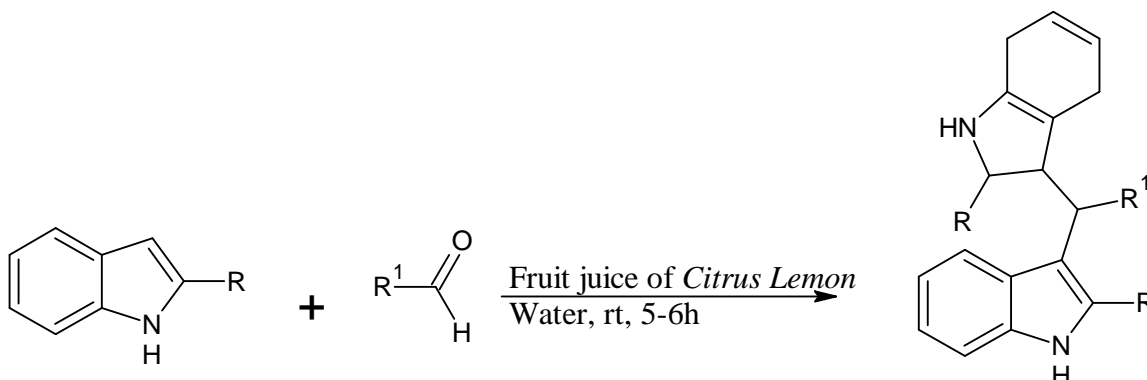
malanonitriles. The mixture were stirred at room temperature for 30-120 minutes. This is new procedure by lemon juice qualifying it is a green method (**Scheme - 4**).



Scheme- 4

Pal *et al* (2013) reported the biocondensation of indoles and aldehydes for the synthesis of bis-, and tris (indoyl) methanes. This reaction proceeds indoles and aldehydes were treated in lemon juice (*Citrus limonium*) mixture at pH

3 in stirring at room temperature for 5-6 hour. This method is suitable in term of short reaction time, reaction procedure is very simple and attained better yield of product (Scheme - 5).

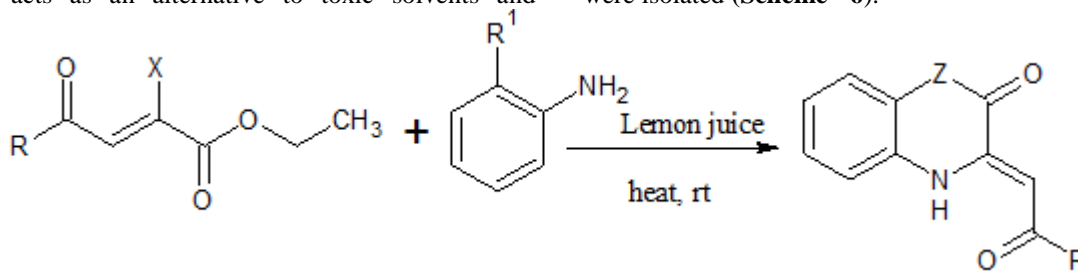


R= H, Me
 R¹= aryl, heteroaryl, alkyl

Scheme – 5

Petronijevic *et al* (2017) reported ecofriendly and clean one-pot synthesis of 3,4-dihydro-2(1H)-quinoxalinones and 3,4-dihydro-1,4-benzoxazine-2-ones. Lemon juice (*Citrus limonium*) acts as an alternative to toxic solvents and

catalysts. This reaction proceeds by substituted ester keto ester and substituted amines with lemon juice and reflux for 24h. After simple work up the newly synthesized products were isolated (Scheme - 6).



X= OH, ONa
 R= cyclopropyl, alkyl, substituted aryl

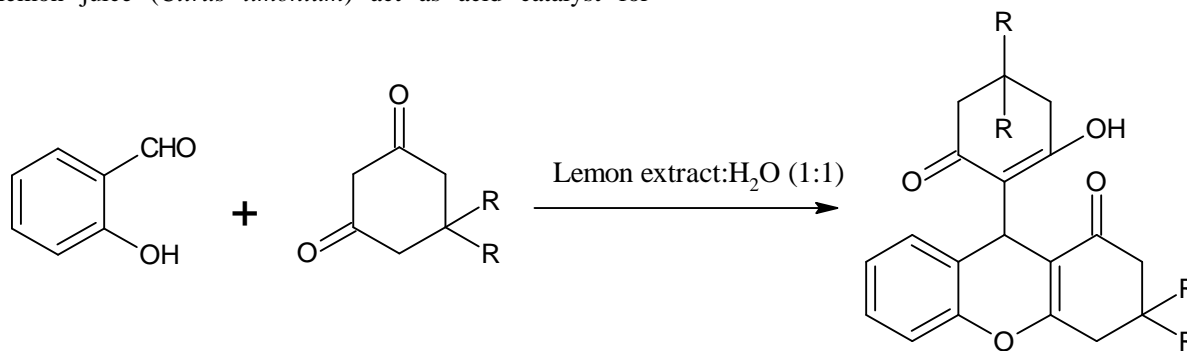
R¹= NH₂, OH

Z= NH, O

Scheme – 6

Morbale *et al* (2015) reported green and economic method for the synthesis of benzopyran synthesis. They found that lemon juice (*Citrus limonium*) act as acid catalyst for

cyclocondensation of salicylaldehyde and cyclic 1,3-diketones for benzopyran formation (Scheme-7).



R= CH₃, H

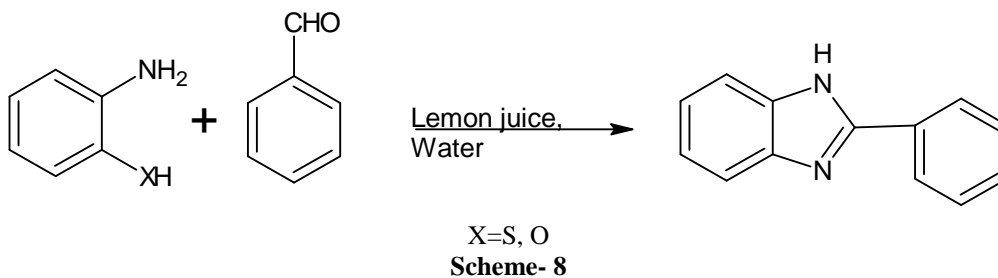
Scheme-7

Patil *et al* (2017) reported the multi-component synthesis of substituted benzthiazole and benzoxazole derivatives using

lemon juice in water by the reaction of 2-aminothiophenol or 2-aminophenol, aryl aldehyde and lemon water mixture

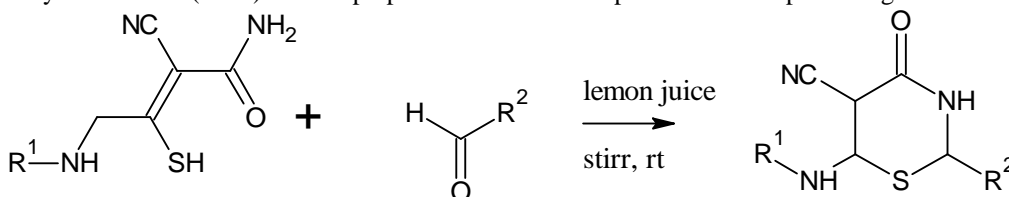
(1:1) was added in reaction vessel. They found that lemon juice plays a role of biocatalyst which provides non

hazardous and mild conditions which are basic principle of green chemistry (**Scheme-8**).



An efficient and greener approach has been developed for the synthesis of 6-arylamino-5-cyano-2,3-dihydro-1,3-thiazin-4(1H)-ones, using Lemon juice (*Citrus limonium*) as a natural catalyst by Ishak *et al* (2017). It was prepared via

condensation of 3-arylamino-2-cyano-3-mercaptoacrylamides with several of aldehydes. The reaction proceeded in ecofriendly manner with excellent yields (**Scheme-9**). Most of the synthesized compounds were reprints effective promising antimicrobial activity.

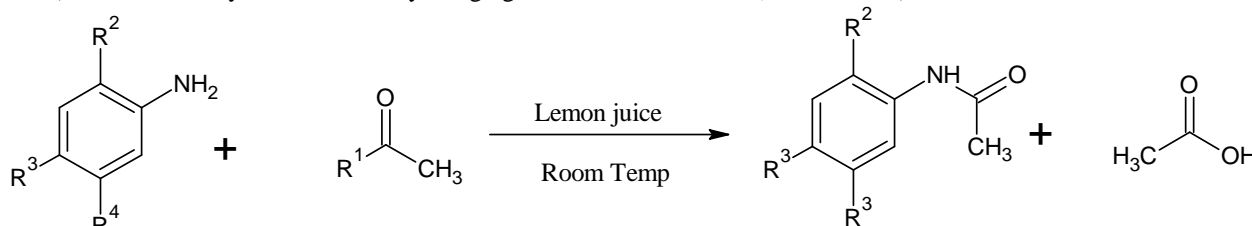


R¹ = Ph, Ph-CH₂
 R² = Ph, Ph-CH₃, Ph-Cl, Ph-NO₂, Ph-OCH₃

Scheme-9

Chavhan *et al* (2016) reported the acetylation of different amines and salicylic acid by using lemon juice (*Citrus limonium*) and acetic anhydride as an acetylating agent. This

reaction proceeds under normal reaction condition with formation of product in high yield. This method reduce the chemical wastage and more convenient than other reported methods (**Scheme - 10**).

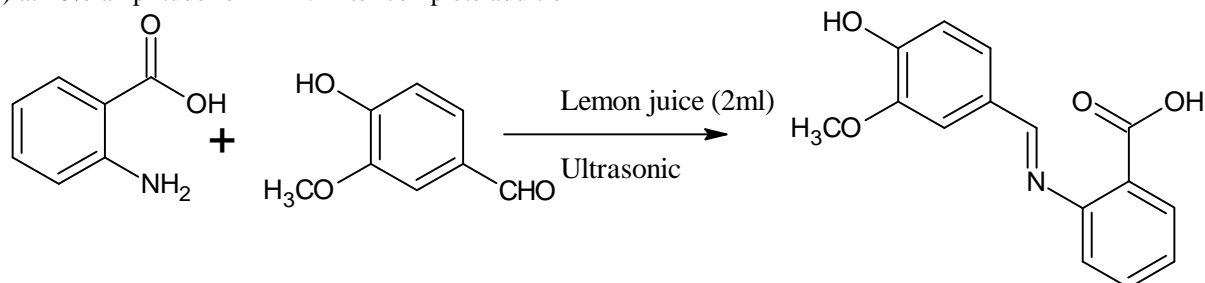


R¹ = CH₃COO
 R₂, R₃, R₄ = NH₂, NO₂, CH₃, OH

Scheme - 10

Bakhat (2015) reported a lemon juice catalysed ultrasound assisted, ecofriendly synthesis of schiff's base. A mixture of o-benzoic acid and 4-hydroxy-3-methoxy benzaldehyde was taken in sonication flask and then 2ml lemon juice was added drop wise under sonication probe (ACE probe, 20KHz) at 40% amplitude for 2min. After complete addition

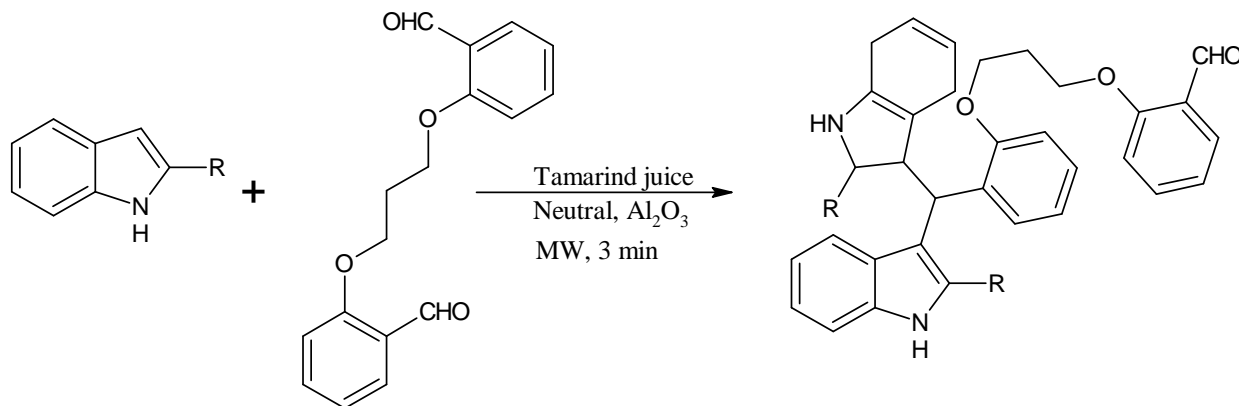
of lemon juice, the reaction mixture was again exposed to acoustic cavitation for further 10 min, by keeping all the parameter constant. The completion of reaction was measured by TLC. The recrystallization was done by ethanol and a white solid pure product was obtained (**Scheme - 11**).



Scheme 11

Tamarind (*Tamarindus indica*) fruit act as a biocatalyst for synthesis of bis-, and tris (indoyl) methanes and tetraindolyl compounds. This novel pathway of synthesis was first time reported by Pal (2013). Excellent yield of product have been

obtained by reaction of indoles with aldehydes by using microwave irradiation under solvent free conditions (**Scheme - 12**).

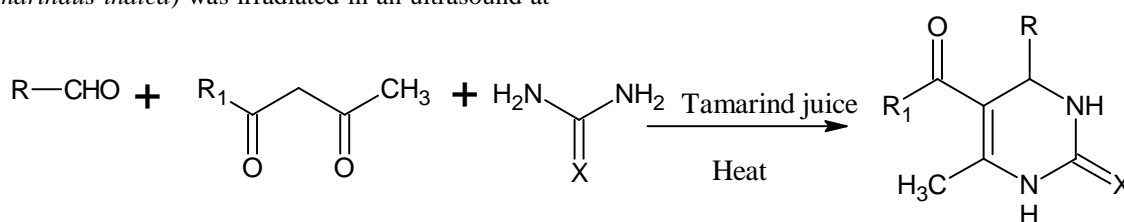


R= H, Me

Scheme - 12

Nazeruddin *et al* (2014) reported the synthesized the dihydropyrimidinone derivatives by reacting between aldehyde, ethylacetoacetate, urea/thiourea and 1ml tamarind juice (*Tamarindus indica*) was irradiated in an ultrasound at

100W for few minutes. Microwave synthesis shows advantage over conventional heating by time, extent of chemicals used and by yield (**Scheme - 13**)



X= O, S

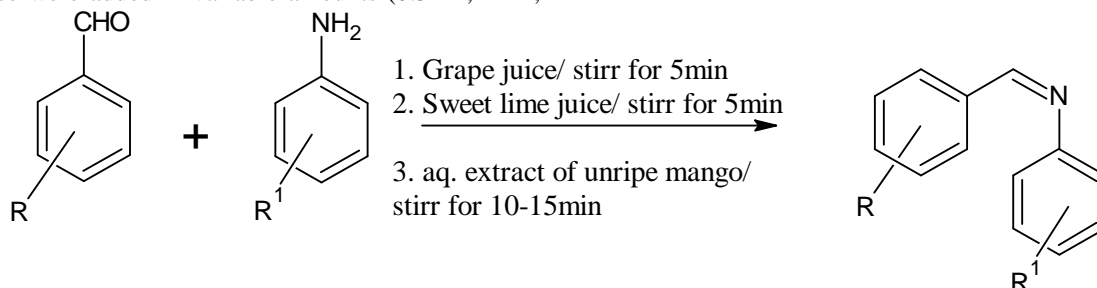
R= Ph, Ph-OMe, Ph-OH, Ph-NO₂, Ph-Cl,

R₁= OEt

Scheme - 13

Yadav and Mani (2015) reported the green synthesis of Schiff bases with grape juice (*Vitis Linata*), sweet lemon juice (*Citrus Limetta*) and extract of unripe mango (*Mangifera indica*) under solvent free conditions. This reaction proceeds by stirring method, when the equimolar amount of benzaldehyde and aniline was taken in different beakers. In those reaction mixtures natural acid catalyst i.e. grapes juice were added in variable amounts (0.5 ml, 1 ml,

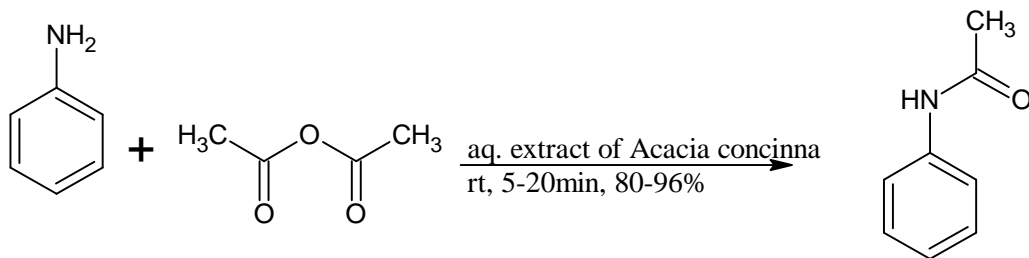
1.5 ml, 2.0 ml, 2.5 ml) and then kept for 5-10 minutes. Further each reaction mixture was stirred for 2 - 4 minutes at room temperature pale yellow solid crude product was appear after completion of reaction which was washed with distilled water and purified by recrystallization with minimum amount of ethanol. The same procedure is repeated with sweet lemon juice and aqueous extract of mango (**Scheme - 14**).



Scheme - 14

An ecofriendly and cost effective protocol was reported by Mote *et al* (2010) for the synthesis of acetanilide. The reaction proceeds by reacting aromatic primary amines and acetic anhydride, catalysed by aqueous extract of pods of *acacia concinna* fruit as a green catalyst. This catalyst shows

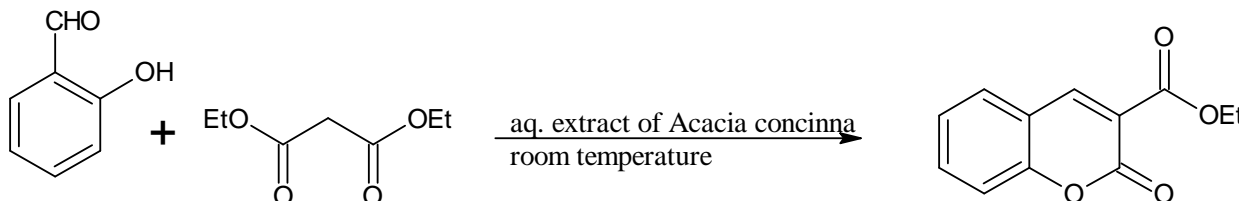
highly acidic nature (pH 2.1) and high solubility of reactant by hydrogen bond formation in aqueous solution. This type of unique protocol shows the economic and green pathways (**Scheme - 15**).



Scheme-15

An aqueous extract of *Acacia concinna* pods has been reported as a biocatalyst by Shafqat *et al* (2017) for Knoevenagel Condensation. A equimolar mixture of salicylaldehyde and malonic ester and aqueous extract of *Acacia concinna* were taken in a round bottom flask and

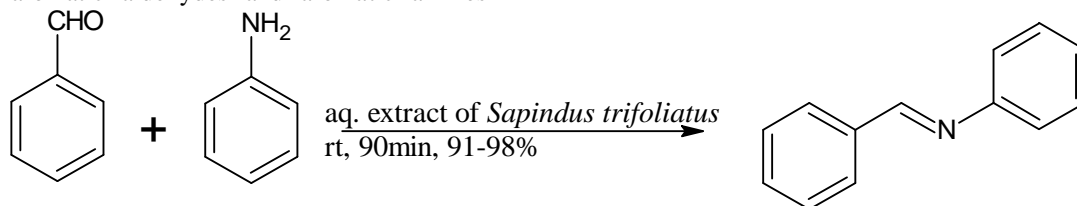
heated along with stirring at boiling water bath for 2h. After completion of the reaction, the reaction mixture as cooled at room temperature, the solid product was filtered off and recrystallized to get pure product (**Scheme - 16**).



Scheme - 16

The aqueous extract of the pericarp of *Sapindus trifoliatus* acts as a biocatalyst in the synthesis of al-damines in a chemoselective manner. This reaction occurs by stirring the mixture of aromatic aldehydes and aromatic amines in

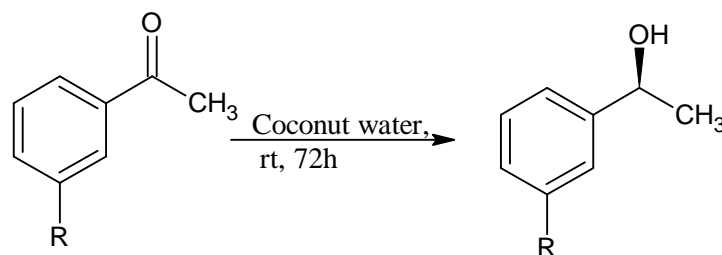
presence of this fruit extract (**Scheme - 17**). This method provides a valuable reaction pathway against conventional method reported by Pore *et al* (2010).



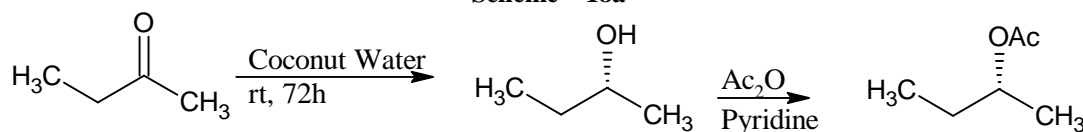
Scheme - 17

Fonseca *et al* (2009) reported the most sustainable reduction of aliphatic and aromatic aldehydes and ketones by using coconut juice (*Cocos nucifera*) as a biocatalyst. Thus, when the various carbonyl compounds were treated with freshly prepared coconut and the mixture was shaken at room temperature for 72 h, produced alcohols (**Scheme - 18a**),

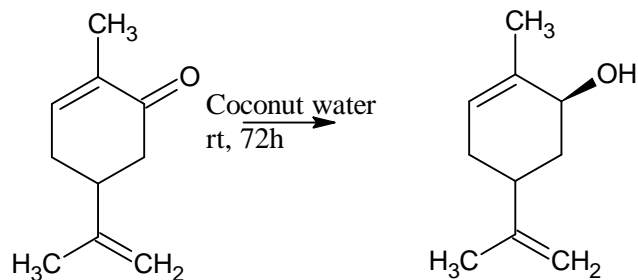
(**Scheme - 18b**), (**Scheme - 18c**), (**Scheme - 18d**). Fonseca and co-workers also reported the hydrolysis of ester (**Scheme - 19a**), amide (**Scheme - 19b**) and anilides (**Scheme - 19c**) by using coconut juice. This bioconversion provides a significant role of green chemistry.



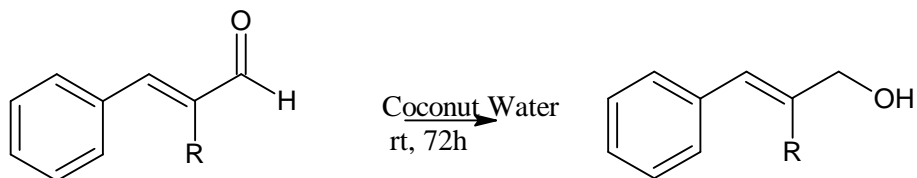
R= H, OCH₃
Scheme - 18a



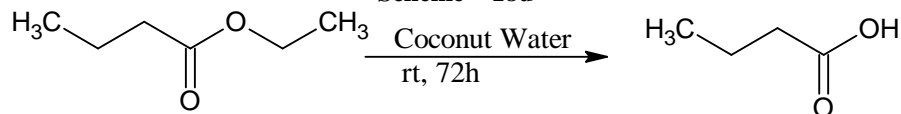
Scheme - 18b



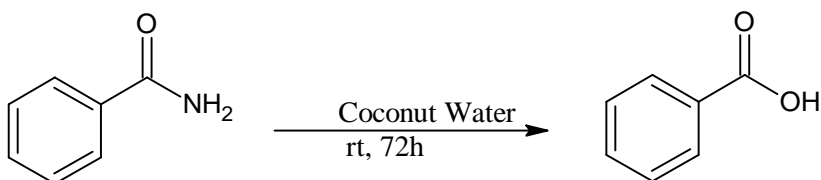
Scheme – 18c



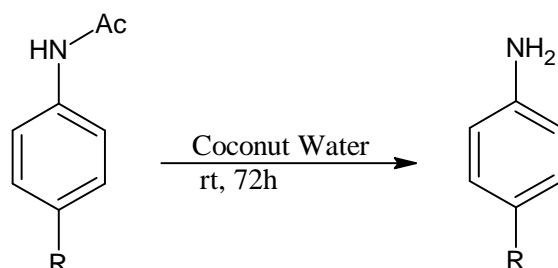
Scheme – 18d



Scheme – 19a



Scheme – 19b

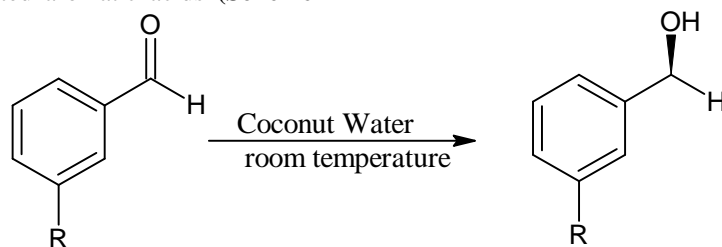


R= OH, H

Scheme – 19c

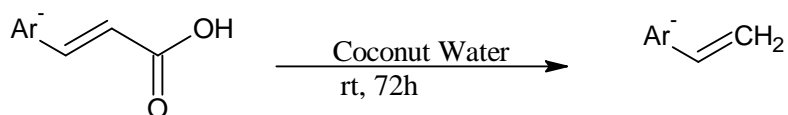
Misra *et al* (2012) reported a new greener alternatives for bioreduction of aromatic aldehydes (Scheme – 20a). and decarboxylation of substituted aromatic acids (Scheme –

20b) using coconut water as a biocatalyst. This is an effort towards the energy efficient, eco-friendly transformation of interesting organic molecule.



R= H, OH, OMe, Me

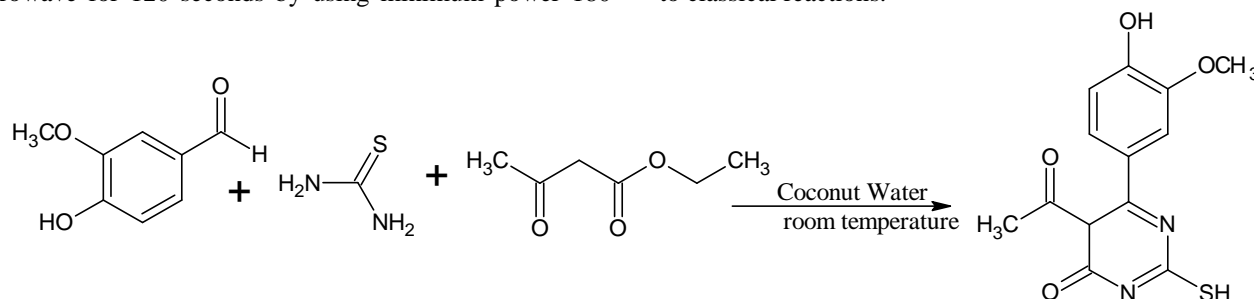
Scheme – 20a



Scheme – 20b

Hajite (2017) reported the synthesis of vanillin derivative using coconut water as a green catalyst. Thus, when equimolar amount of vaniline, ethylacetoacetate, thiourea and 5ml coconut water and carried out the reaction in microwave for 120 seconds by using minimum power 180

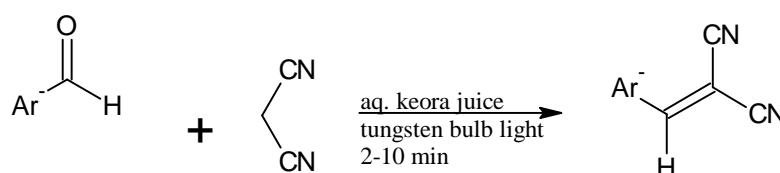
watts. After a simple work up and recrystallization is done by proper solvent, the pure product with a good yield was obtained (**Scheme – 21**). This method is very simple, economical, mild and environmentally benign as compared to classical reactions.



Scheme – 21

Pal (2016) reported the synthesis of arylidene malonitrile by Knoevenagel condensation reaction of aldehydes and malanitrile under visible light produced by tungsten bulb.

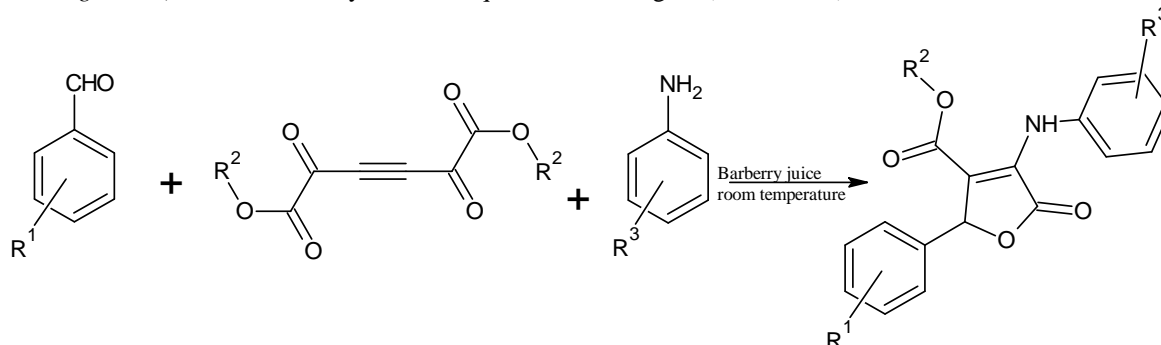
Aqueous extract of keora fruit can catalyze the Knoevenagel condensation with a good yield of products. Aqueous extract of keora is acidic and hence it could be work as acid catalyst for reaction (**Scheme-22**).



Scheme-22

A mild and environmentally benign synthesis of 3,4,5-substituted furan-2(5H)-ones was reported by Hazeri *et al* (2016) employing aqueous extract of seedless barberry (*Berberis integerrima*) as a biocatalyst. The equimolar

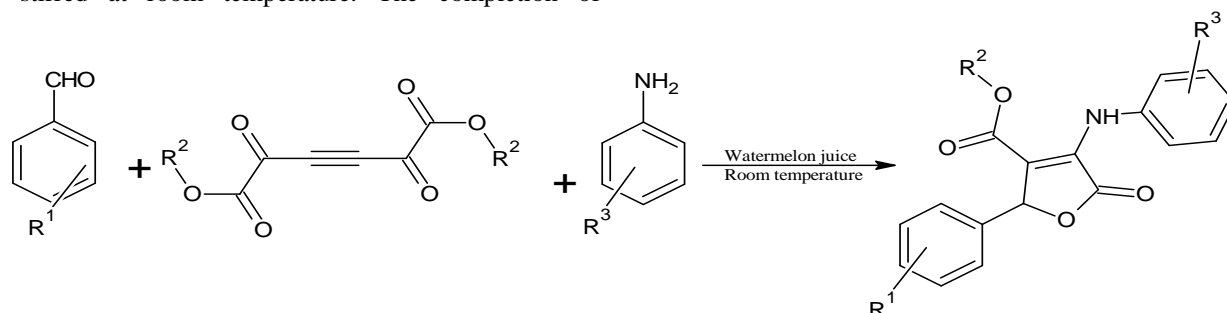
amount of substituted aldehyde, substituted amine and dialkylacetylene dicarboxylate and 5ml of barberry juice were stirred at room temperature. This method prevents the generation of waste rather than the conventional chemical reagent (**Scheme-23**).



Scheme-23

Adrom *et al* (2016) reported an efficient multicomponent synthesis of 3,4,5- substituted Furan-2(5H)-ones catalysed by watermelon juice. The equimolar amount of substituted aldehyde, substituted amine and dialkylacetylene dicarboxylate and 5ml of water melon juice of watermelon were stirred at room temperature. The completion of

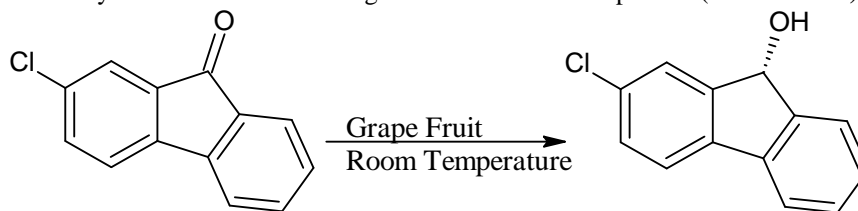
reaction was checked by TLC, after that the reaction products were collected by filtration. Thus, the products were washed with water/ethanol (50:50) to give the pure compound. The catalyst remained in the water/ethanol filtrate (**Scheme 24**).



Scheme- 24

Xie *et al.*, 2012 reported a simplified green chemistry approaches in organic transformation. Grape fruit which is an efficient and mild biocatalyst for some selected organic

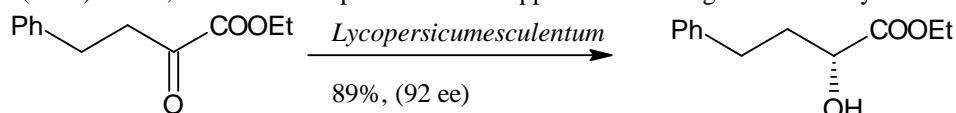
reactions in solvent-free conditions. This catalyst is stereoselective in the biotransformation of chloro-polycyclic aromatic compounds (**Scheme – 25**).



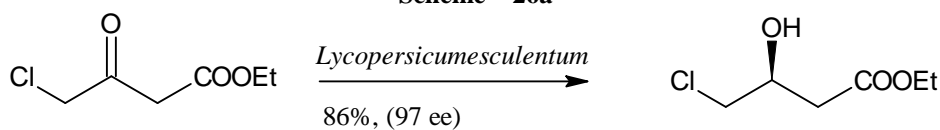
Scheme – 25

Asymmetric reduction of Ketones by using Tomato juice (*Lycopersicon esculentum*) as a biocatalyst is reported by Phukan and Devi (2012). Thus, this reaction provides a

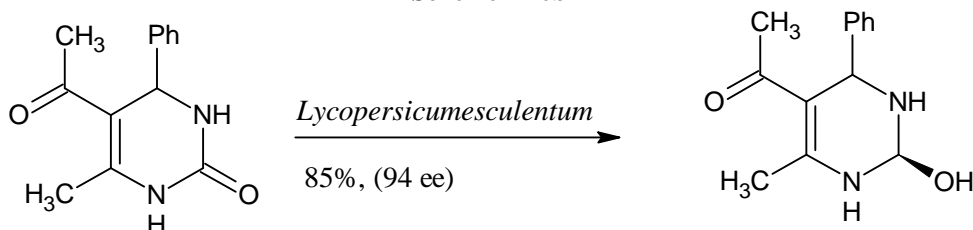
biocatalytic preparative method of asymmetric alcohols (**Scheme – 26a**), (**Scheme – 26b**) and (**Scheme – 26c**). This technique is more ecofriendly and provides an important approach towards green chemistry.



Scheme – 26a



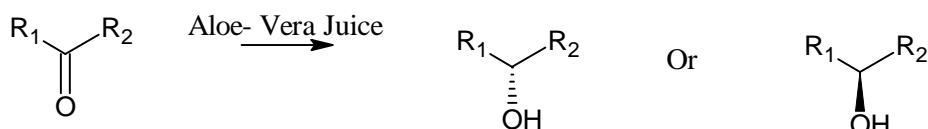
Scheme – 26b



Scheme – 26c

Fast microwave assisted bioreduction of aromatic and aliphatic aldehydes and ketones by using Aloe vera juice (**Scheme - 27**). Microwave-assisted synthesis was used in

the biotransformation of these organic compounds which acts as a very useful intermediates in various organic reactions. This simple, efficient and ecofriendly method was reported by Leyva *et al* (2012).

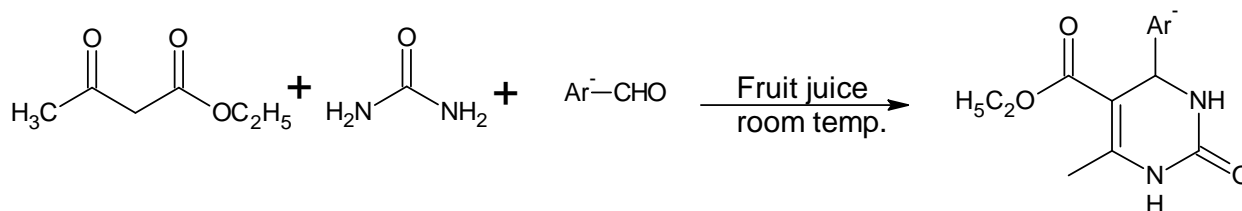


R1, R2 = H, Aliphatic, Aromatic, Saturated, Unsaturated, Cyclic etc

Scheme-27

Pranamik and Pathan (2014) reported the synthesis of Dihydropyrimidinone (DHPM) derivatives via one-pot multicomponent cyclocondensation namely Biginelli reaction employing urea, ethylacetoacetate with a series of

different derivatives of benzaldehyde in fruit juice (viz. orange juice, lime juice, amla juice) at room temperature (**Scheme-28**). They found that all the fruit juices are totally non-polluting, inexpensive and 100% biodegradable.



Ar = Ph-CH₃, Ph-Cl, Ph-OCH₃

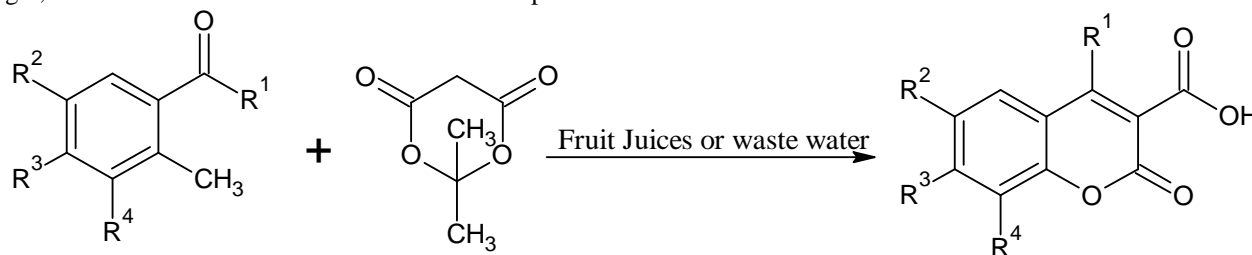
Scheme-28

Fiorito *et al* (2016) reported a great contribution to the green chemistry by using crop-derived products, like juices obtained from edible fruits and vegetables and waste waters

deriving from agriculture and industrial processing. They described the juices waste water promoted synthesis of coumarin-3-carboxylic acid (**Scheme-29**), and synthesis of

cinnamic acids (**Scheme-30**) with high purity. The Knoevenagel condensation have been accomplished by using substituted aldehyde and Meldrum's acid as substrates, both are mixed in the aqueous medium represented by lemon, grapefruit, carrot, pomegranate, kiwi, vinegar, tomato and buttermilk waste water. The process

was carried out for 24h under magnetic stirring at room temperature. Pure product have been isolated as solids after filtration in very good yields and the biocatalysts were recovered after filtration from all reaction media reused without any loss of activity.

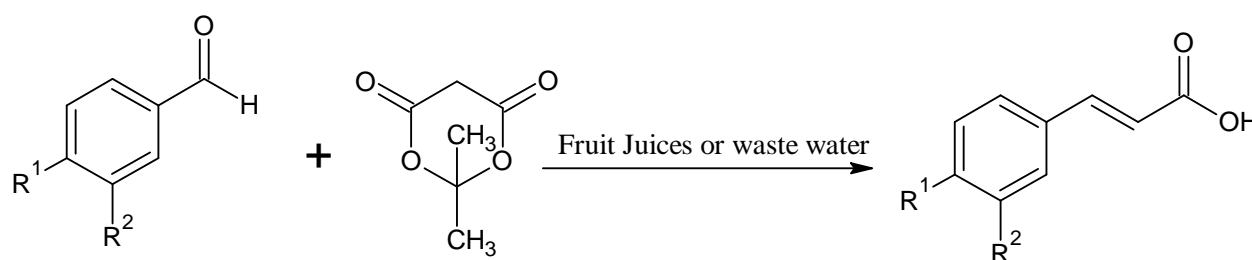


Scheme-29 (Table 1)

Table 1

S.No.	Carbonyl Compounds	Product (Scheme-29)	A %Y	B %Y	C %Y	D %Y	E %Y	F %Y	G %Y	H %Y	I %Y	J %Y
1	Salicylaldehyde	R ¹ =R ² =R ³ =R ⁴ =H	99	96	97	96	95	95	95	92	94	99
2	4-(Dimethylamino) salicylaldehyde	R ¹ =R ² =R ⁴ =H, R ³ =N(Et) ₂	99	99	92	93	94	96	96	97	91	96
3	4-nitrosalicylaldehyde	R ¹ =R ² =R ⁴ =H, R ³ =NO ₂	98	97	97	98	99	98	99	98	96	97
4	5-bromosalicylaldehyde	R ¹ =R ³ =R ⁴ =H, R ² =Br	99	97	99	99	98	95	97	99	99	98
5	2,4-dihydroxybenzaldehyde	R ¹ =R ² =R ⁴ =H, R ³ =OH	97	97	95	98	98	98	99	95	98	99
6	2-hydroxy-5-nitroacetophenone	R ¹ =Me, R ² =NO ₂ R ³ =R ⁴ =H	96	95	98	98	98	99	98	99	96	98
7	5-chloro-2-hydroxyacetophenone	R ¹ =Me, R ² =Cl R ³ =R ⁴ =H	98	97	99	99	96	98	99	96	97	98
8	2-hydroxy-4-methoxyacetophenone	R ¹ =Me, R ² =OMe R ³ =R ⁴ =H	96	95	98	98	98	99	98	99	96	98
9	2,5-dihydroxyacetophenone	R ¹ =Me, R ² =OH R ³ =R ⁴ =H	94	94	98	97	99	97	98	99	97	96
10	2,3,5-trihydroxyacetophenone	R ¹ =Me, R ² =OH R ³ =H, R ⁴ =OH	95	96	99	96	99	99	96	99	98	95
11	2-Hydroxyacetophenone	R ¹ =Me, R ² =R ³ =R ⁴ =H	94	98	98	94	97	98	99	99	97	95

A= lemon juice, B= grapefruit juice, C= carrot juice, D= pomegranate juice, E= kiwi juice, F= vinegar, G= tomato juice, H= limencello, I= olive mill waste water, J= buttermilk, %Y= Percentage Yield



Scheme-30 (Table 2)

Table 2

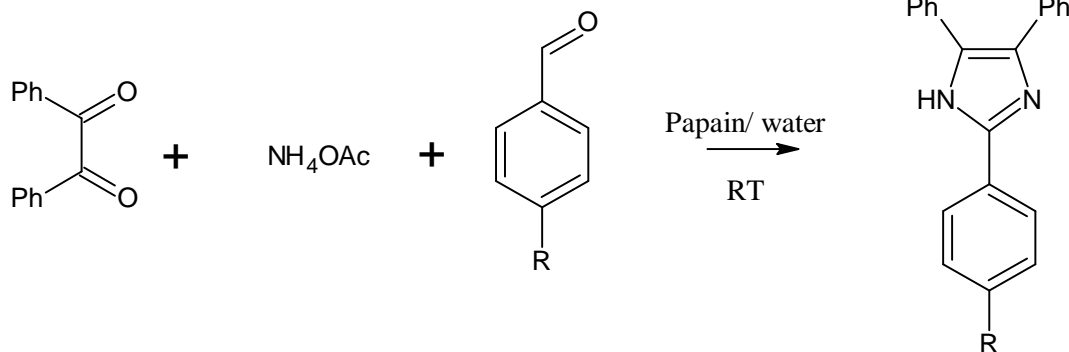
S.No.	Carbonyl Compounds	Product (Scheme-30)	A %Y	B %Y	C %Y	D %Y	E %Y	F %Y	G %Y	H %Y	I %Y	J %Y
1	Benzaldehyde	R ¹ =R ² =H	98	91	96	92	98	92	96	98	95	94
2	Vanillin	R ¹ =OH, R ² =OCH ₃	95	92	94	91	94	93	97	98	93	98
3	p-hydroxybenzaldehyde	R ¹ =OH, R ² =H	97	97	94	95	96	95	92	97	98	96
4	p-floro-benzaldehyde	R ¹ =F, R ² =H	92	95	94	95	97	97	93	98	97	99
5	p-chloro-benzaldehyde	R ¹ =Cl, R ² =H	93	95	98	95	96	95	98	99	99	95
6	p-bromo-benzaldehyde	R ¹ =Br, R ² =H	95	95	99	98	99	91	99	97	98	97
7	p-iodo-benzaldehyde	R ¹ =I, R ² =H	97	94	94	99	95	94	92	95	99	97
8	3,4-dihydroxybenzaldehyde	R ¹ =R ² =OH	98	99	96	99	97	98	91	98	96	97
9	p-nitrobenzaldehyde	R ¹ =NO ₂ , R ² =H	98	98	96	99	97	99	95	94	99	94
10	p-aminobenzaldehyde	R ¹ =NH ₂ , R ² =H	99	95	97	93	98	94	97	98	99	97
11	4(3,3-Dimethylallyloxy)-3-methoxybenzaldehyde	R ¹ =3,3-Dimethylallyloxy R ² =OCH ₃	95	99	97	92	99	96	97	97	96	99

A= lemon juice, B= grapefruit juice, C= carrot juice, D= pomegranate juice, E= kiwi juice, F= vinegar, G= tomato juice, H= limencello, I= olive mill waste water, J= buttermilk, %Y= Percentage Yield

3.2 Using Papain in water

Maske and Makhija, 2013 synthesized trisubstituted imidazoles by using papain (papaya latex) which is an inexpensive, mild and nontoxic biocatalyst. They perform the multicomponent synthesis from benzyl (10m mol),

ammonium acetate (20mmol), aromatic aldehyde (20mmol) and papain (150mg) in one pot and performed multicomponent reaction at room temperature. The recrystallization of product have been done by ethanol (**Scheme 31**).



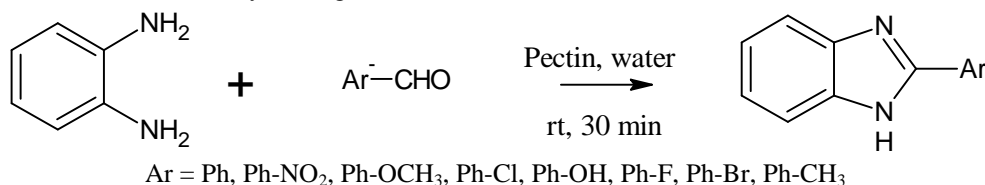
R= Ph, Ph-OMe, Ph-OH, Ph-Cl, Ph-NO₂, Ph-Me

Scheme 31

3.3 Using Pectin in aqueous media

Agarwal *et al.*, 2014 reported a mild and environmentally benign synthesis of benzimidazoles by using pectin as a green catalyst. The reaction was done by stirring substituted

benzaldehyde (10mmol), ortho-phenylene diammine (10mmol) and pectin (0.4gm) for 30 min at room temperature. This is a time and energy saving green method to synthesize benzimidazole with excellent yield (**Scheme 32**).



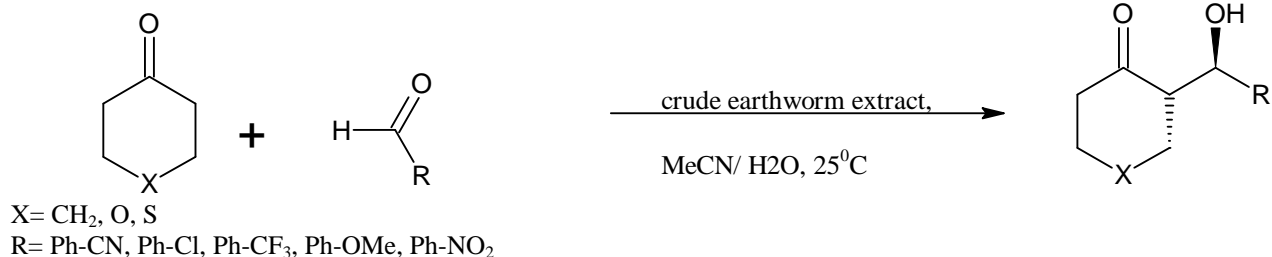
Ar = Ph, Ph-NO₂, Ph-OCH₃, Ph-Cl, Ph-OH, Ph-F, Ph-Br, Ph-CH₃

Scheme 32

3.4 Using Earthworm extract

Guan *et al.*, 2014 reported the great examples of green synthesis by using crude earthworm (*Eisema foetida*) extract. The biocatalyst plays an important role in synthesis of chiral β hydroxy carbonyl compounds via asymmetric Aldol reactions (**Scheme 33a**), synthesis of chiral β amino ketones by asymmetric Mannich reactions (**Scheme 33b**), synthesis of β nitro alcohols by Henry reactions (**Scheme**

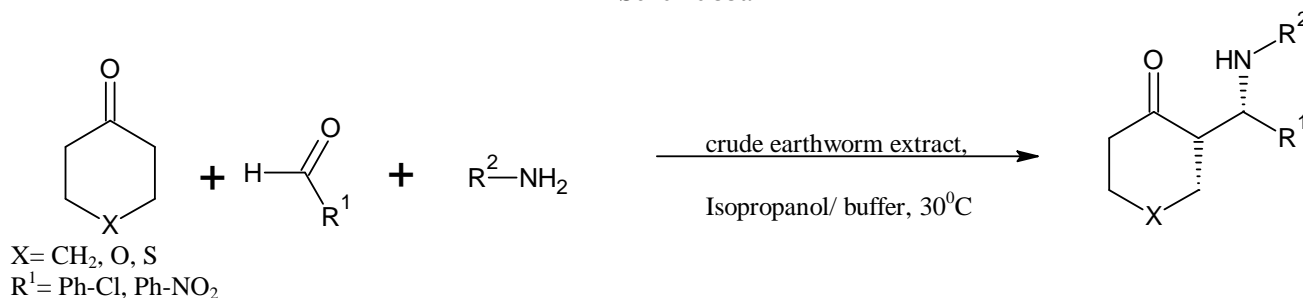
33c), synthesis of dihydropyrimidinones by Biginelli reactions (**Scheme 33d**), synthesis of aza-Diels-Alder reactions (**Scheme 33e**) and synthesis of coumarin derivatives by Domino process (**Scheme 33f**). The main advantages of using the crude earthworm extract as a catalyst are ecofriendly, environmentally benign, safe, cheap, easily accessible and stable.



X= CH₂, O, S

R= Ph-CN, Ph-Cl, Ph-CF₃, Ph-OMe, Ph-NO₂

Scheme 33a

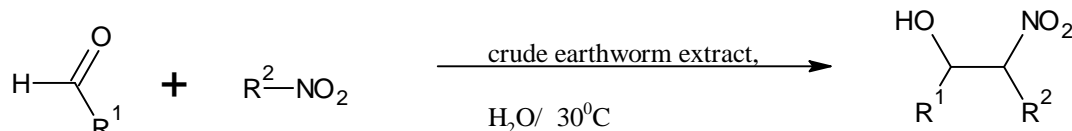


X= CH₂, O, S

R¹= Ph-Cl, Ph-NO₂

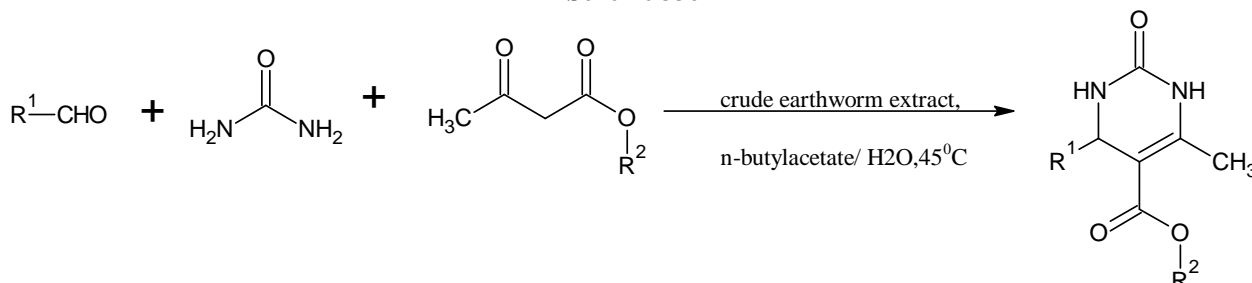
R²= Ph, Ph-Br, Ph-Cl, Ph-Me

Scheme 33b



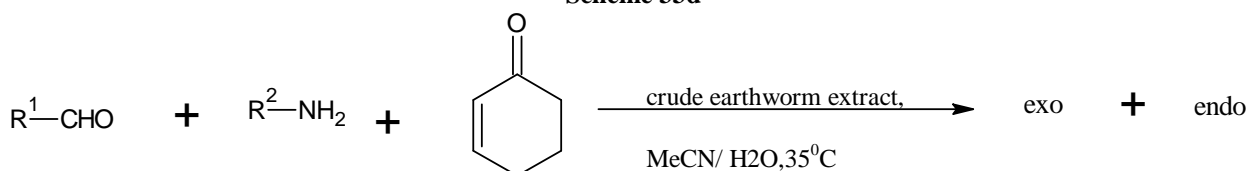
R¹= Ph-CN, Ph-NO₂
 R²= H, Me, Et

Scheme 33c



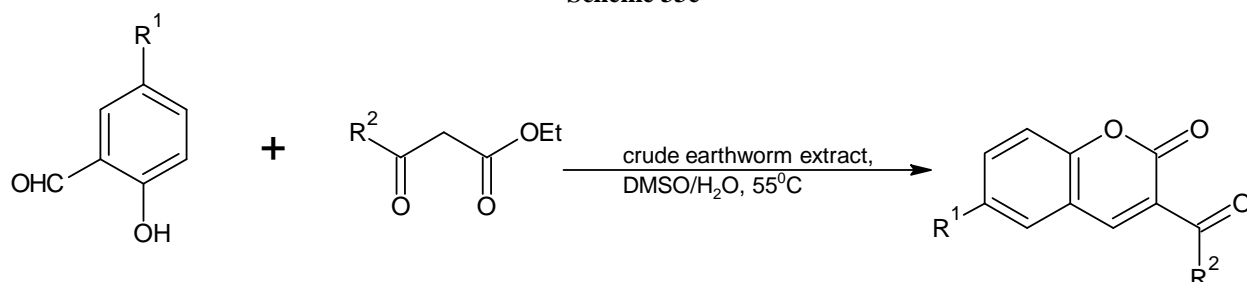
R¹= Ph-CN, Ph-NO₂
 R²= H, Me, Et

Scheme 33d



R¹= Ph-F, Ph-Cl
 R²= Ph, Ph-OMe

Scheme 33e



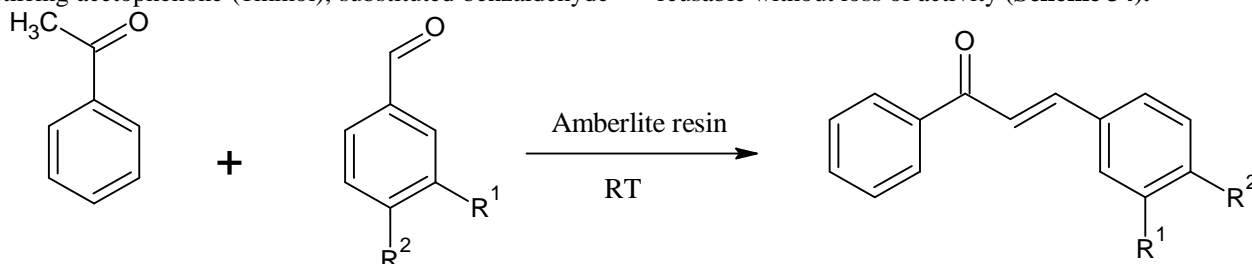
R¹= NO₂, Cl, OMe, H, 1-naphthol
 R²= Ph, Me, OEt

Scheme 33f

3.5 Using Amberlite Resin

Ezhilarasi *et al.*, 2015 designed a green chemical methods for the preparation of chalcones by using Amberlite Resin as an anion exchange medium. Thus the reaction was arrived by stirring acetophenone (1mmol), substituted benzaldehyde

(1mmol) and 30mmol basic resins at room temperature. The progress of reaction was measured by TLC and the product was purified by recrystallization. Chalcones are well known intermediates for synthesis of a large series of heterocyclic compounds. The product is easier to recover and the resin is reusable without loss of activity (Scheme 34).

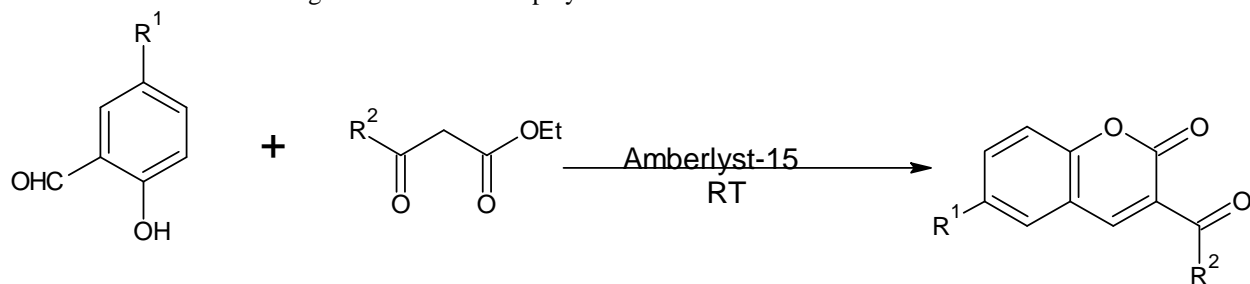


R¹= R²= H, CN, NO₂, CH₃

Scheme 34

Hussien *et al.*, 2016 synthesized coumarin derivatives via ketoester using Amberlyst-15 as a green and reusable Pechmann condensation using substituted phenols with β -catalyst (Scheme 35). They also found that synthesized

coumarin derivatives have biological activities and plays a momentousness role in the industrial fields.



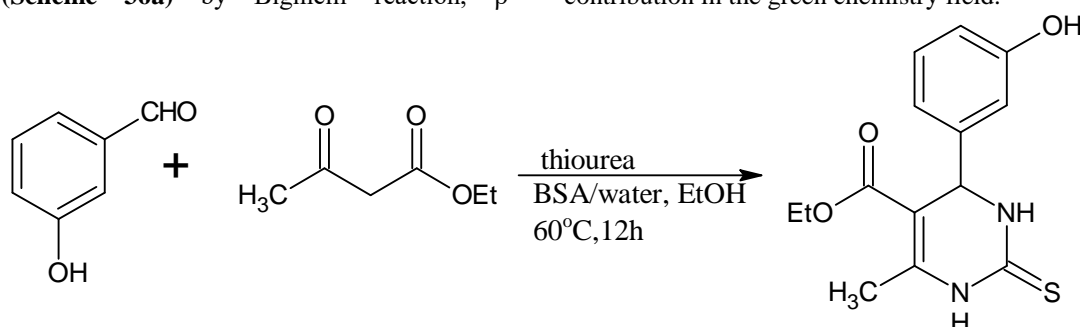
$R^1 = \text{NO}_2, \text{Cl}, \text{OMe}, \text{H}, \text{Br}, \text{CN}, \text{Me}$
 $R^2 = \text{Ph}, \text{Me}, \text{OEt}, \text{CH}_2\text{Cl}$

Scheme 35

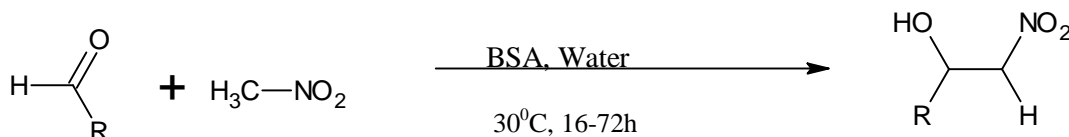
3.6 Using Bovine serum albumin

Albanese and Gaggero (2015) reported Bovine Serum Albumin (BSA) as a biocatalyst in organic synthesis. BSA in water plays an important role in the green synthesis of Monastrol (Scheme 36a) by Biginelli reaction, β -

nitroalcohols (Scheme 36b) by Henry reaction, addition of thiophenols into chalcones (Scheme 36c) by Thio-Michael addition reaction, sulphoxidation (Scheme 36d) and stereoselective reduction of β -hydroxy ketones (Scheme 36e). Hence the above examples carried out great contribution in the green chemistry field.

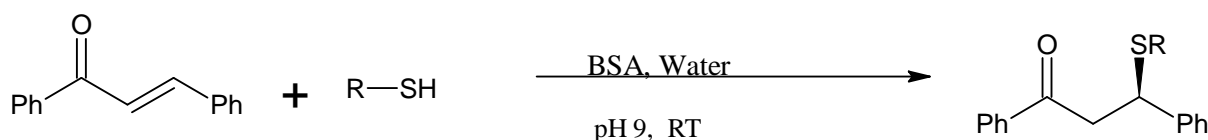


Scheme 36a



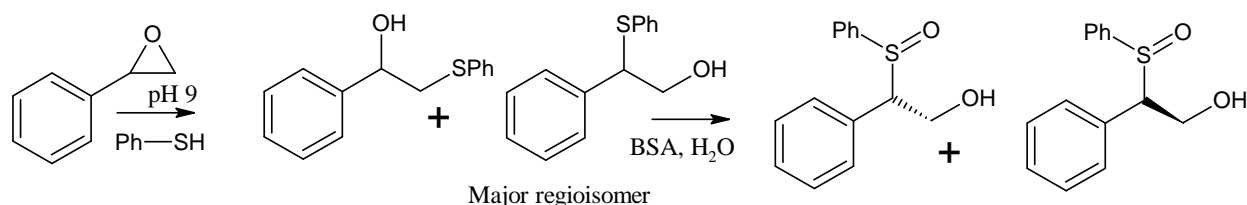
$R = \text{Ph-NO}_2, \text{Ph-CN}, 2\text{-pyridyl}, 3\text{-pyridyl}, 4\text{-pyridyl}, \text{Ph-Br}, 2\text{-Nf}, 1\text{-Nf}$

Scheme 36b

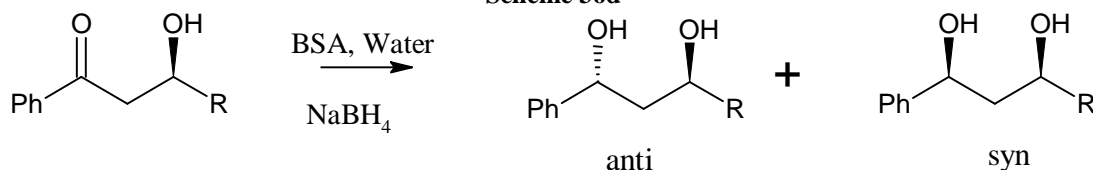


$R = \text{Ph}, \text{Ph-CH}_3, \text{Ph-OMe}, \text{Ph-NO}_2, \text{Ph-CH}_2, n\text{-C}_4\text{H}_9, n\text{-C}_8\text{H}_{17}, \text{C}_6\text{H}_5\text{-CO}$

Scheme 36c



Scheme 36d

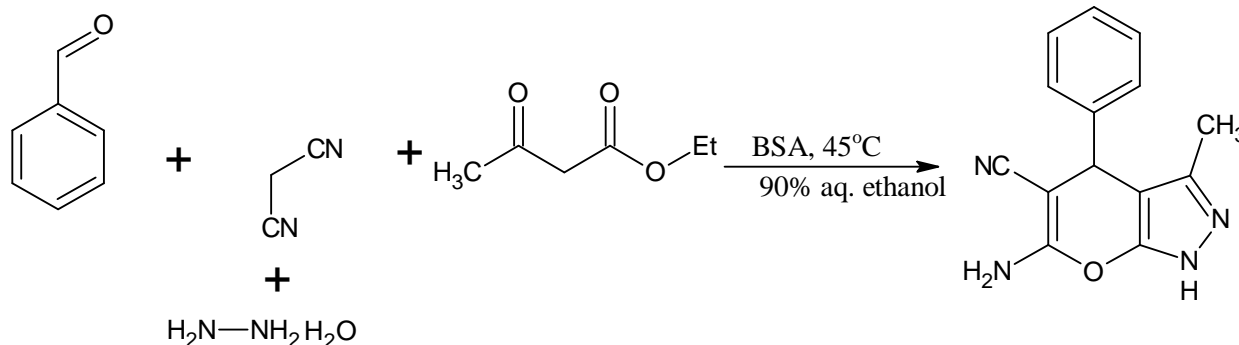


$R = \text{Ph}, \text{CH}_3, \text{Ph-Me}, \text{Ph-NO}_2, 4\text{-naphthyl}, \text{ferrocenyl}, 2\text{-furyl}, \text{Ph-OMe}, \text{Ph-OH}, (\text{CH}_2)_3\text{OH}$

Scheme 36e

Huang *et al.*, 2016 synthesized pyrano 2,3 pyrazoles from one-pot four component system by using BSA as an efficient and green biocatalyst. The reaction was carried out in presence of substituted benzaldehyde, malononitrile, hydrazine hydrate and ethyl acetoacetate in 90% aq ethanol

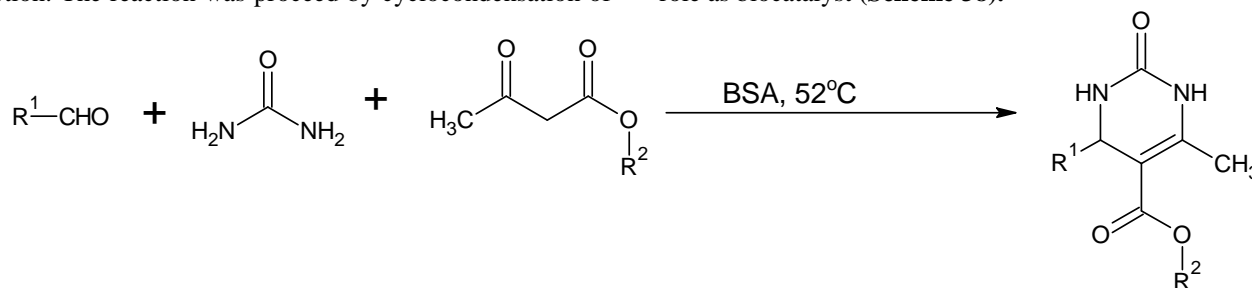
in presence of BSA. This catalyst could be used for five cycles without loss of catalytic activity. This is a novel, rapid, simple and environmentally benign pathway (**Scheme 37**).



Scheme 37

Sharma *et al* 2013 reported the benign synthesis of 3,4-dihydropyrimidin-2-(1H)-ones by multicomponent Biginelli reaction. The reaction was proceed by cyclocondensation of

substituted benzaldehyde, β -ketoester and urea in presence of Bovine Serum Albumin (BSA) which plays an important role as biocatalyst (**Scheme 38**).

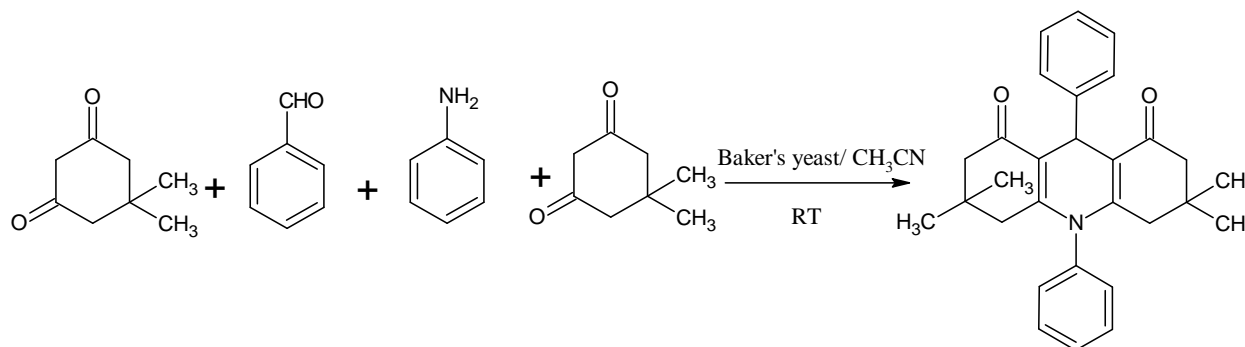


R¹= Ph-CN, Ph-NO₂, Ph-Cl, Ph-Br, Ph-OMe, Ph-Me
 R²= Me, Et

Scheme 38

3.7 By using Baker,s yeast (*Saccharomyces cerevisiae*)
 N-substituted decahydroacridine-1,8-dione derivatives, which are biologically important compounds were synthesized by Chate *et al.*, 2016 by using Baker,s Yeast as a green and reusable biocatalyst. The reaction was a one-pot

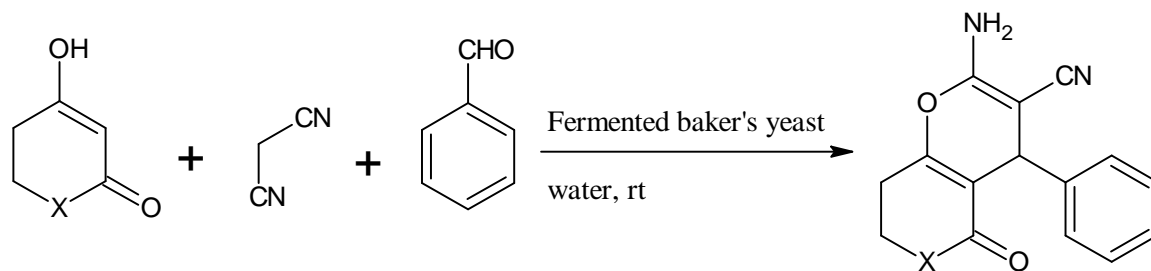
multicomponent route, the equimolar mixture of 5,5-dimethylcyclohexane-1,3-dione, benzaldehyde and aniline was dissolved in acetonitrile and add 1gm baker,s yeast per mmole reactants. The recovered baker,s yeast was used for 3-4 consecutive runs in this reaction without any significant loss in yield and activity (**Scheme 39**).



Scheme 39

Fermented baker,s yeast is an efficient catalyst for the synthesis of pyran derivatives in water at room temperature. A mixture of Baker,s Yeast (200mg), D-glucose (300mg), and phosphate buffer 5ml (pH 7.0) was taken in flask and stirred at room temperature for 24 hour. Dimedone , aryl

aldehyde and malanonitrile in equimolar quantity were added to it and the reaction was continued for 45 minutes. This environmentally concern synthesis was reported by Saha and Pal 2013 under (**Scheme 40**).

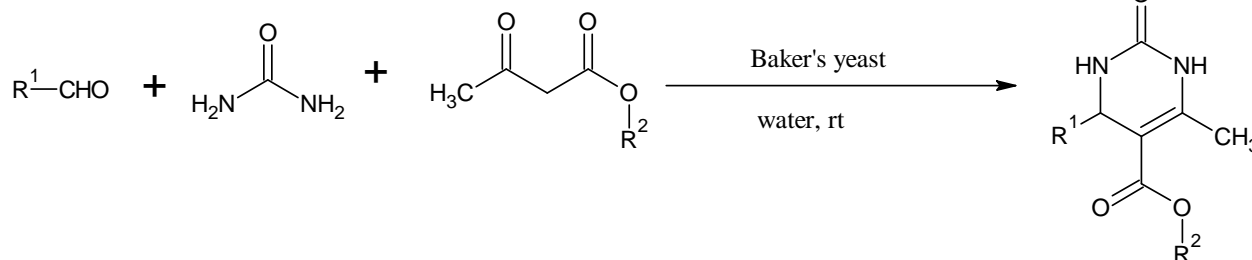


X= C or O

Scheme 40

Kumar and Maurya 2007 reported the synthesis of Dihydropyrimidin-2(1H)-ones by using Baker's Yeast as an effective and safe biocatalyst. It was observed that Biginelli cyclocondensation of substituted benzaldehyde, β -ketoester

and urea in presence of Baker's yeast reaction gives a good yield of compounds under fermenting conditions (Scheme 41).



R¹= Ph-CN, Ph-NO₂, Ph-Cl, Ph-Br, Ph-OMe, Ph-Me

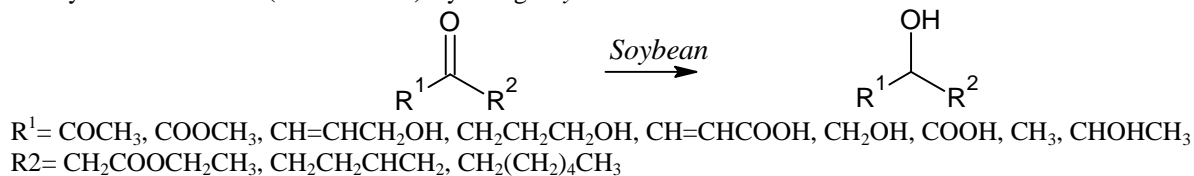
R²= Me, Et

Scheme 41

3.8 By using Soybean (*Glycin max*) as a versatile biocatalyst

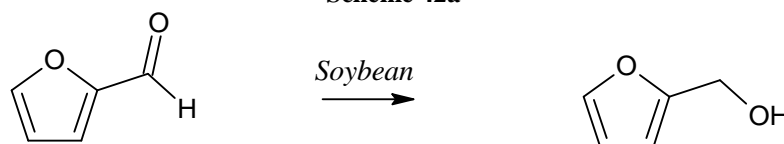
Bertini *et al* 2012 reported the reduction of a series of aliphatic aldehydes and ketones (Scheme 42a) and aromatic aldehydes and ketones (Scheme 42b) by using *Glycin max*

seeds (soybean). This type of biotransformation have received a great deal of attention. This work demonstrated that seeds of soyabean act as stereoselective biocatalyst in reduction of carbonyl compounds.



R¹= COCH₃, COOCH₃, CH=CHCH₂OH, CH₂CH₂CH₂OH, CH=CHCOOH, CH₂OH, COOH, CH₃, CHOCH₃
 R²= CH₂COOCH₂CH₃, CH₂CH₂CHCH₂, CH₂(CH₂)₄CH₃

Scheme 42a

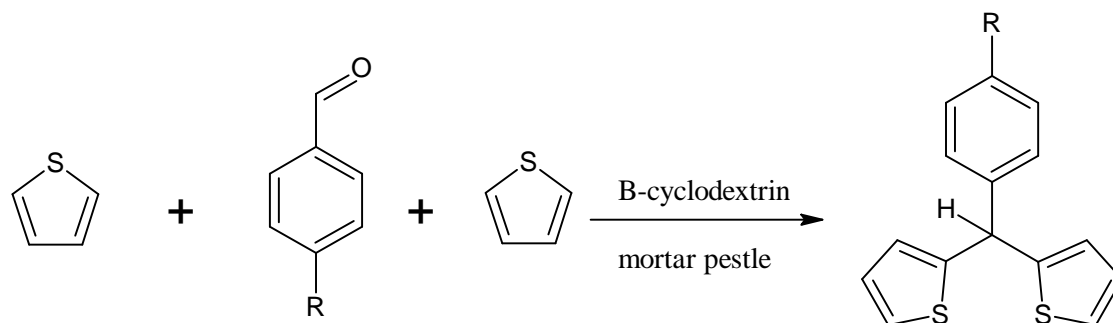


Scheme 42b

3.7 Using β cyclodextrin (plant culture) as a supramolecular catalyst

A novel synthesis of 2,2'(substituted aryl) methylene dithiophene by using β cyclodextrin (plant culture) as a supramolecular catalyst was reported by Chaudhari *et al* 2015. This is a simple and safe electrophilic substitution reaction of thiophene with aromatic aldehydes in mortal

pestle by grinding method. Thus, when a mixture of thiophene (2mmol), aromatic aldehydes (1mmol) and 0.5gm β -cyclodextrin were grinded in mortar pestle. The progress of reaction was measured by TLC. The solid obtained was extracted in diethyl ether by using separating funnel. Purified product was obtained by evaporating ether in air (Scheme 43).

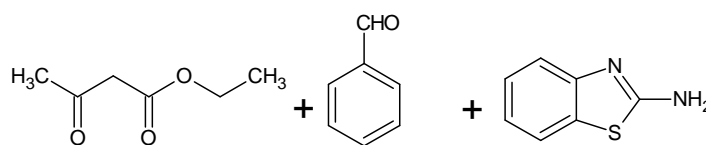


R= Cl, Br, OMe, Me, OH, NO₂

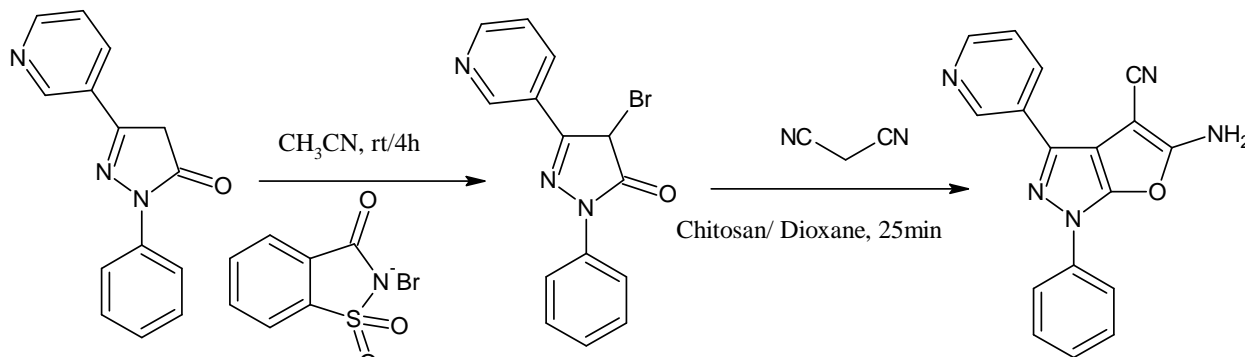
Scheme 43

3.8 Using Chitosan as a biocatalyst

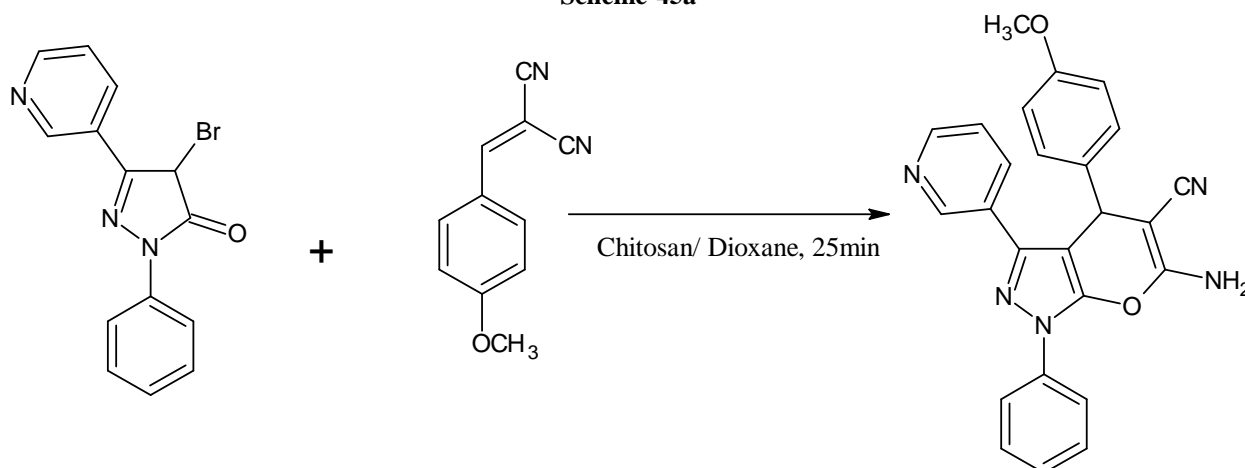
Sahu *et al.*, 2014 reported the synthesis of 4H-pyrimido [2,1-b] benzothiazole derivatives by using an efficient, reusable and biodegradable biocatalyst. This is a multicomponent reaction of substituted aromatic aldehydes dicarbonyl and 2-aminobenzothiazole/3-amino-1,2,4-triazole/urea/thiourea in 2% acetic acid in aqueous media with chitosan as green catalyst at 60-65 °C temp (Scheme - 44).



Scheme - 44

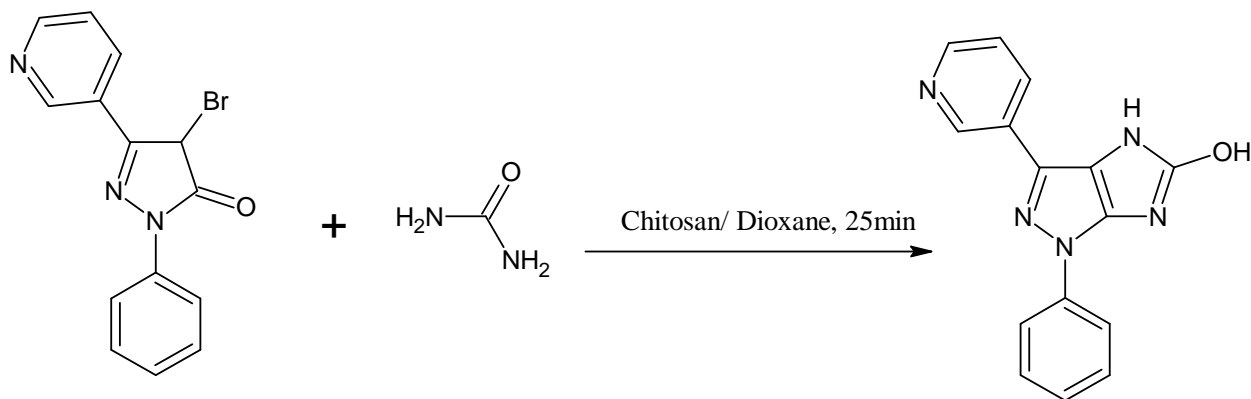


Scheme-45a

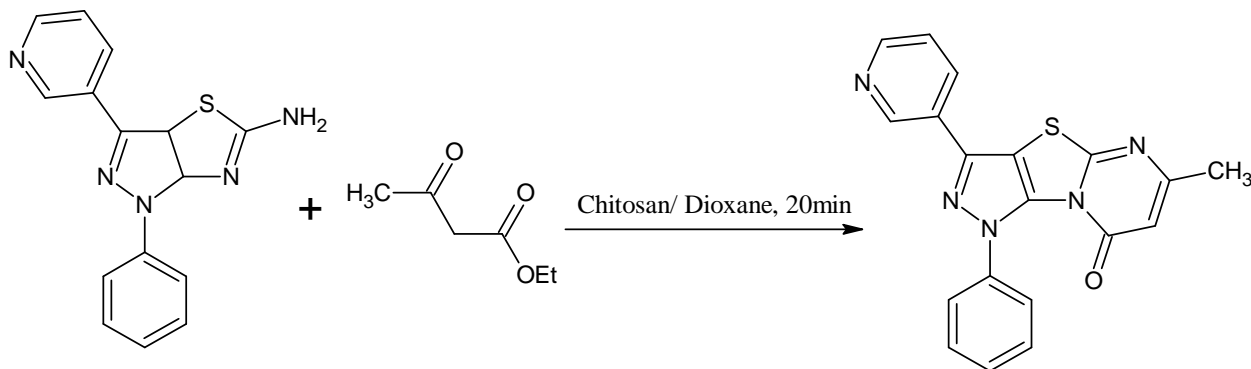


Scheme-45b

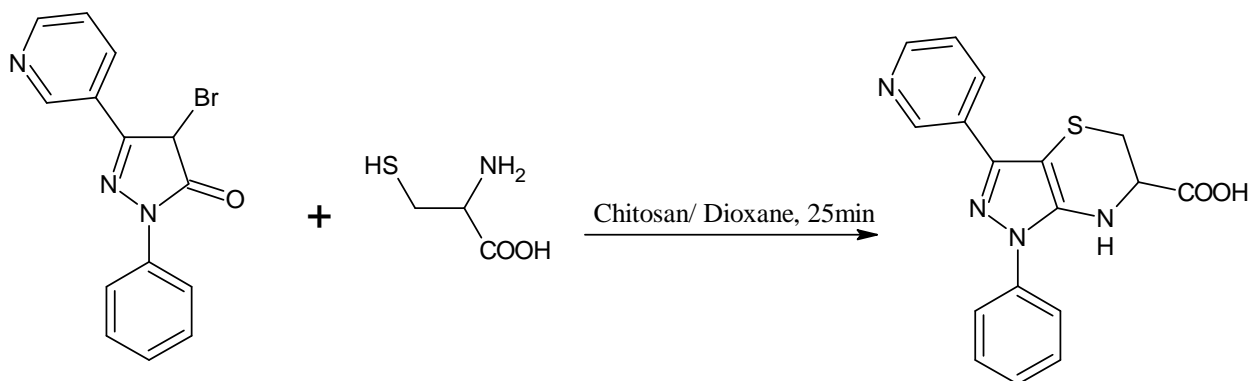
An ecofriendly synthesis of heterocyclic moieties condensed with pyrazole system was reported by Mohamed *et al* (2016). Thus the synthesis of 4-substituted 5-amino-1-phenyl-3-(pyridine-3-yl)-1H-furo[2,3-c] pyrazole (Scheme-45a), 6-imino-4-(methoxyphenyl)-1phenyl-3-(pyridine-3-yl)-1,4,5,6-tetrahydro-pyrano[2,3-c]pyrazole-5-carbonitrile (Scheme-45b), 1-phenyl-3-(pyridine-3-yl)-1,4-dihydroimidazo[4,5-c]pyrazo-5-ol (Scheme-45c), 5-substituted pyrazol[4,3-b]thiazole[3,2-a]pyrimidine-7-one (Scheme-45d), 1-phenyl-(pyridine-3-yl)-1,5,6,7-tetrahydropyrazolo[4,3-b][1,4]thiazine-6-carboxylic acid (Scheme-45e) and pyrazol[3,4-b]benzo[1,4]oxazine (Scheme-45f) were proceeded in presence of chitosan which is a green catalyst. The reactions were carried out by microwave irradiation as a green source of energy. Those synthesized compounds represent a broad spectrum of biological activities.



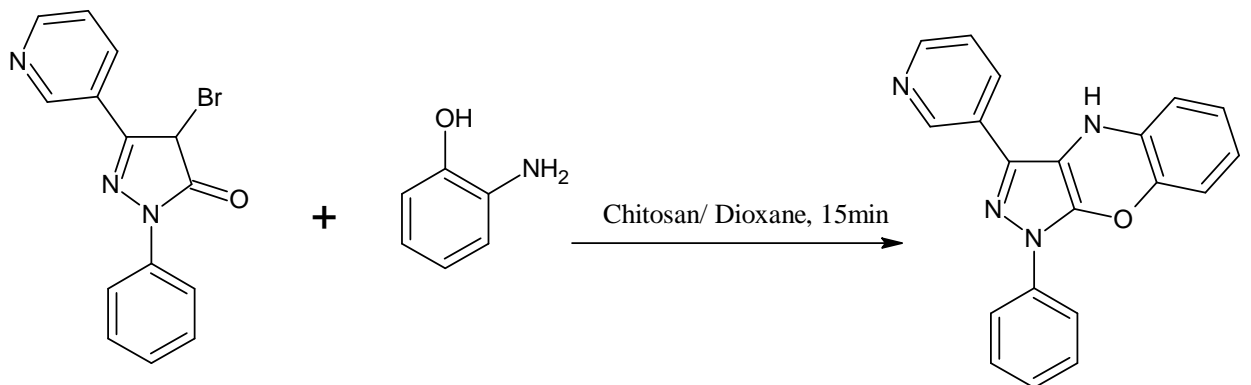
Scheme-45c



Scheme-45d



Scheme-45e

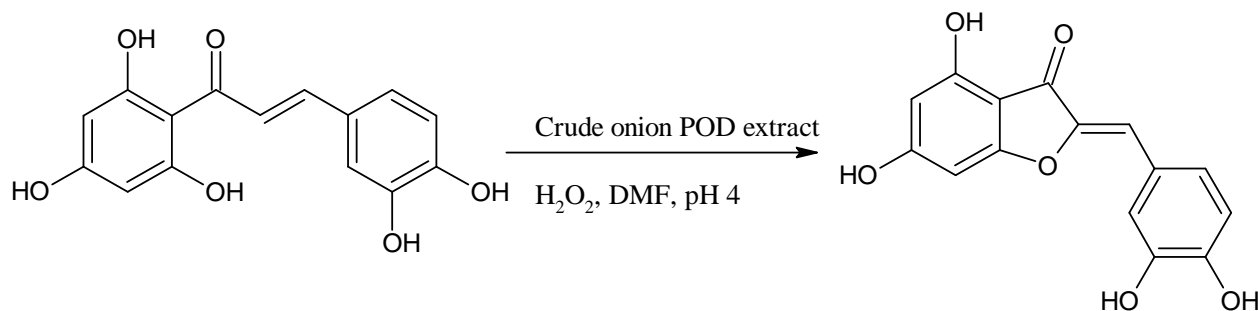


Scheme-45f

3.9 Using Crude Peroxidase from Onion Solid Waste

The cyclization of 2',3',4',4',6'-pentahydroxy-chalcone into aureusidin was reported by Moussouni *et al* (2010). That transformation was done by the crude peroxidase from onion solid waste as a biocatalyst. The onion used as the enzyme

source in that work were brown skinned onions (*Allium cepa*). The enzyme act as biocatalyst for the oxidative cyclization of 2'-hydroxy chalcone having a catechol moiety on one ring into the aurone scaffold, specifically PHC (polyhydroxychalcone) into aureusidin (Scheme - 46).



Scheme - 46

4. Future Prospects

This review summarizes most of the recent use of green catalysts at large scales in different areas of research and applied fields. This chemistry provides environmentally beneficial alternatives and thus reduces pollution. Used and exhausted vegetable oil has been used currently by researchers as a fuel for vehicles by making very less modifications in the cars of present use and a shocking result was found that by using vegetable oil, CO₂ emission has been reduced to almost 67% without compromising with the efficiency of the vehicle. Hence Green Chemistry is benign design of organic compounds and mechanisms of reaction for present and future.

5. Conclusion

It is clear that "Green chemistry" is not only the ways to synthesize the desired products economically and cleanly but it is also helps to save the environment. We must have to use this clean, benign and safe chemistry in our research. Government should also make some strict rules in governing industries to use ecofriendly ways of organic synthesis and production. It must be applied in the syllabus of U.G. and P.G. classes about green chemistry to aware the young generation.

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