Available online at **www.joac.info**

ISSN: 2278-1862

Journal of Applicable Chemistry

2019, 8 (2): 565-573

(International Peer Reviewed Journal)

Facile and Green Syntheses of Substituted-5-arylidene-2,4-thiazolidinediones using Polymer Supported DABCO as an Eco-Friendly Catalyst in Aqueous Medium

Bhikan J. Khairnar[1], Pravinsing S. Girase[1] and Bhata R. Chaudhari[1,2]*

1. Department of Chemistry, JET's Z. B. Patil College, Dhule (MS), **INDIA**
2. Department of Chemistry, SSVPS's ACS College, Shindkheda, Dhule (MS), **INDIA**

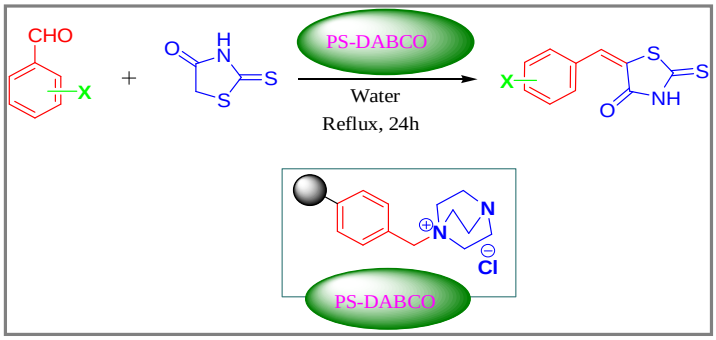
Email: brc155@gmail.com, brc15@rediffmail.com

Accepted on 7th February, 2019

ABSTRACT

An efficient, high-yielding and rapid protocol has been developed for the synthesis of 5-benzylidene rhodanine derivatives via C-C bond forming reaction of aryl aldehydes and rhodanine by using PS-DABCO as green reusable heterogeneous catalyst in water as reaction solvent. Absence of unwanted products, general applicability, reusability of the catalyst, non-chromatographic purification procedure, green synthesis avoiding toxic reagents and improved and operational simplicity make this protocol a useful, greener, cost effective and practical for both academic as well as industrial purposes.

Graphical Abstract



Keywords: C-C bond formation reaction, 5-benzylidene rhodanine, Polymer supported DABCO, Heterogeneous catalyst

INTRODUCTION

Heterocyclic chemistry is of great importance to the medicinal chemists because the steady growth of interest in heterocyclic compounds is related with their increasing therapeutic activity [**1**]. The structural and therapeutic diversity coupled with commercial viability of small heterocyclic molecules

have fascinated to organic and medicinal chemists [2]. One very interesting and promising class of heterocycles is the 2-thioxothiazolidin-4-one ring (Rhodanine) system. Rhodanine derivatives have demonstrated wide range of interesting biological and pharmacological activities, which include antimicrobial [3], antiviral [4], antidiabetic [5], anticancer [6], antidiarrheal [7], anticonvulsant [8], anti-malarial [9], anti-HIV [10], antitubercular [11] and anti-inflammatory [12] activities. Additionally, rhodanine based compounds have also been popular as small molecule inhibitors such as aldose reductase [13], inhibitors of hepatitis C virus (HCV) protease [14], inhibitors of uridine diphospho-N-acetyl muramate/L-alanine ligase [15] and inhibitors of various enzymes such as bacterial β-lactamase and Mur ligases [16], Rhodanine represents an significant scaffold in drug discovery and the effect of its derivatives on plant physiology has been well documented.

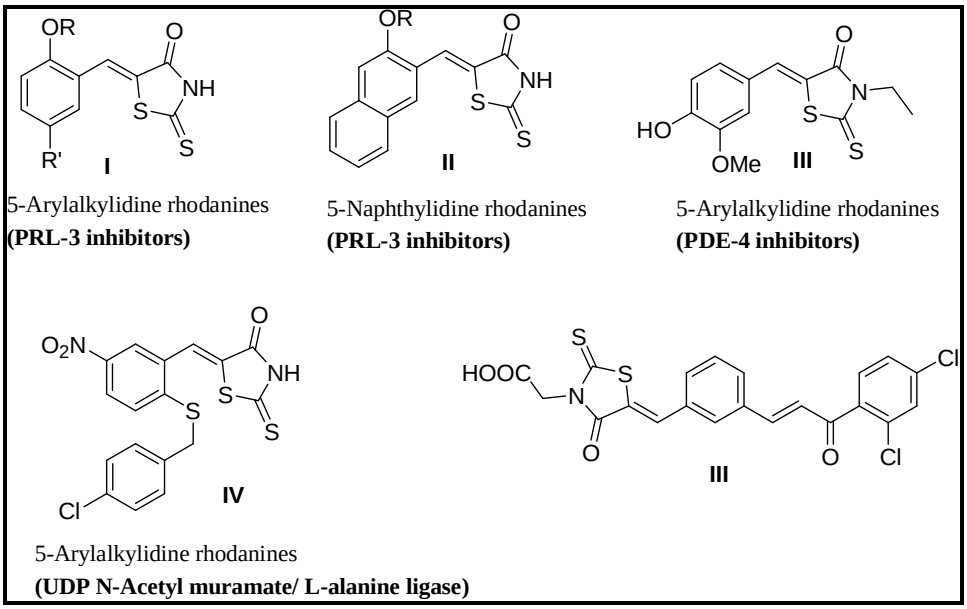


Figure 1. Representative drugs containing rhodanine motif.

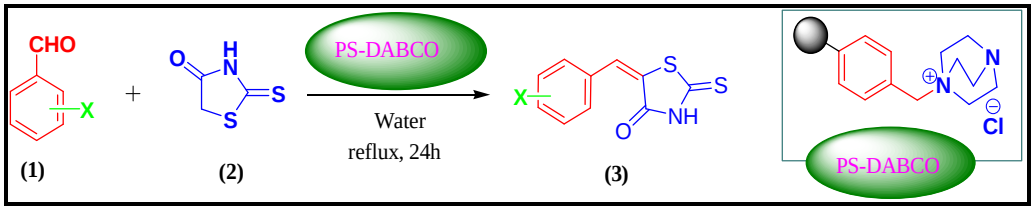
The Knoevenagel condensation is a basic reaction of aldehydes with active methylene compounds is an important and widely employed for C-C bond formation in the synthesis of fine chemicals and in synthesis of carbocyclic as well as heterocyclic compounds of biological significance, which is of paramount importance in organic synthesis. Substituted olefins obtained from the classical Knoevenagel condensation, form the basic building blocks of many pharmacologically important molecules [17]. Water solvent is abundant, inexpensive, benign and clean. Among various solvents, water is the most preferred solvent. The use of water as a reaction solvent is the important strategy commonly used toward greener chemistry. A wide range of reactions that can be piloted in or on water have been developed [18].

It is well known that the classical preparation of 5-Arylalkylidene rhodanines derivatives by Knoevenagel condensation of rhodanine with aldehydes in either basic or acidic catalyst environments using organic solvents, i.e. piperidine in EtOH[19], NH_4Cl in NH_4OH [20], NaOAc in acetic acid [21], NaOEt in acetic acid [22], $AlPO_4$-Zeolite in EtOH:H_2O [23], polyethylene glycol [24], L-tyrosine [25], phosphoryl chloride [26], tetrabutylammonium hydroxide [27], tetrabutyl-ammonium bromide [28] and 2-hydroxy ethylammonium acetate [29] have been used in this reaction. Each of these methods have their own advantages, but also many of them are confronted with one or more limitations such as the use of toxic solvents, expensive catalysts, tedious work-up procedures, low to moderate product yields, limited substrate scope and long reaction times, requirement of special apparatus and requirement of excess of catalysts. Therefore, the development of easy and modular synthetic strategy for this important class of compounds, especially under mild and environmentally benign reaction conditions, still represents a highly rewarding methodological

challenge in the rapidly growing field of diversity-oriented synthesis. Due to several possibilities of chemical derivatization of the rhodanine ring, rhodanine based compounds will probably remain a privileged scaffold in drug discovery.

Polymer supported heterogeneous taking basic nature and ionic liquid catalyst has been of great interest due to several advantages in organic synthesis over commonly used liquid bases, such as ease of products separation, isolation and reuse of the catalyst [**30**]. Literature survey revealed that, the DABCO based Ionic liquid or salts are shows good catalytic activities in various C-C and C-N bond forming reactions [**31, 32**]. Recently Y. Q. Yu and D. Z. Xu [**30**] have reported the use of PS-DABCO as base catalyst for one pot multicomponent synthesis of β-phosphonomalonates with very good activity.

In this respect, PS-DABCO catalyst have gained much attention due to their recyclability and high reactivity giving higher yields with better atom economy. Owing to the economic appeal of heterogeneous base catalyst, their applications in C-C bond formation seems to be of great importance. Considering the advantages of the MCRs technique, in continuation of our earlier work on the synthesis of biologically active compounds by using heterogeneous catalyst [**32-39**] and an importance of 5-Arylalkylidene rhodanine molecules; herein, we have reporting a PS-DABCO catalyzed C-C bond forming reaction of aryl-aldehyde and rhodanine for synthesis of 5-Aryl-alkylidene rhodanine derivatives by Knoevenagel condensation in water as environmentally benign solvent (Scheme 1). However, to the best of our knowledge, no detailed investigation has been made on heterogeneous Polymer supported ionic liquid catalyzed synthesis of5-Arylalkylidene rhodanine derivatives by Knoevenagel condensation.



Scheme 1. PS-DABCO catalyzed synthesis of 5-Arylalkylidene rhodanine.

MATERIALS AND METHODS

Chemicals required for the synthesis were obtained from Aldrich, Spectrochem, Loba-Company. Reactions have been monitored by Thin Layer Chromatography on 0.2 mm precoated plates of silica gel G60 F254 (Merck). Visualization was made with UV light or with an iodine vapor. Melting point ranges were determined in one end open capillaries and are uncorrected. All yields were referred to isolated products after purification. The IR spectra were recorded on SHIMADZU-FTIR-8400 spectrophotometer using the KBr pellet method.^{1}H-NMR spectra were recorded on BRUKER AVANCE II 400MHz and ^{13}C-NMR spectra were recorded on BRUKER AVANCE II 100MHz Spectrophotometer in DMSO-d_6 using TMS as the internal standard. Mass spectra (ES-MS, *m/z*) were recorded on Water-Micro QUATTRO-II mass spectrophotometer.

General experimental procedure for the synthesis of 5-arylidene rhodanines: A 25 mL round bottom flask containing aryl aldehyde (**1a-l**) (1.0 mmol), rhodanine (**2**) (1mmol) in 5 mL ethanol then PS-DABCO (5.0 mol %) was added. The reaction mixture was sturred at reflux temperature for 24 h. The reaction progress was monitored by TLC. After the reaction was completed, it was diluted with ethanol (5 mL) and separate the catalyst by simple filtration, washed the residue (catalyst) with hot ethanol (2×5 mL) followed by concentrated under reduced pressure. The crude product was then purified by recrystallization in aq. Ethyl alcohol to give pure product. The selected products were

characterized by FTIR, NMR and Mass spectroscopy, whereas the remaining products characterized by their physical constants and are found to be in good agreement with the reported literature.

Spectral data for representative compound:

1). (*Z*)-5-(2-bromobenzylidene)-2-thioxothiazolidin-4-one (3e): Color: Brown crystalline solid, Yield: 80%, MP = 170-172°C, IR (cm^{-1}): 3170, 2887, 2339, 1680, 1437, 1245, 1033, 719, 522; **PMR** (400 MHz, DMSO-d_6) δ (ppm):13.9258 (br s, 1H), 7.7904 (dd, *J*=7.94 & 0.84 Hz, 1H), 7.7029 (s, 1H), 7.5515 (t, J=7.68 & 7.24 Hz, 1H), 7.4955 (dd, J=7.78 & 1.68 Hz, 1H), 7.4042 (ddd, J=7.72, 7.52, 1.76, 1.72 & 0.88 H, 1H); **CMR** (400 MHz, DMSO-d_6) δ (ppm): 195.51, 171.99, 169.02, 133.68, 132.48, 132.16, 129.35, 129.02, 128.83, 128.72, 125.71; **Mass** (ES-MS, m/z): 299.9 (100%) **(M-1)**, 297.9 (95%); **(ES+):** 300.9 (15%) **(M+1)**, 301.9 (12%).

2). (Z)-5-(3,4-dimethoxybenzylidene)-2-thioxothiazolidin-4-one (3i): Color: Light yellow solid, Yield: 84%, MP = 202-204°C, IR (cm^{-1}): 3180, 2360, 1635, 1481, 1230, 829, 596; **PMR** (400 MHz, DMSO-d_6) δ (ppm): 13.7137 (br s, 1H), 7.5423 (s, 1H), 7.1507-7.0740 (m, 3H), 3.8229 (s, 3H), 3.8065 (s, 3H); **CMR** (400 MHz, DMSO-d_6) δ (ppm): 195.42, 169.33, 151.16, 148.98, 132.24, 125.58, 124.59, 122.24, 113.33, 112.11, 55.68, 55.50; **Mass** (ES-MS, m/z): 280.0 (100%) **(M-H)**, 281.0 (15%), 282.0 (12%).

RESULTS AND DISCUSSION

The polymer supported DABCO catalyst was synthesized by modification of the reported method in a single step from Merrifield peptide resin (2 % cross linked, 2.3 mmol Cl g^{-1}, Aldrich) and 1,4-diazabicyclo[2.2.2]octane (DABCO) [30-32].

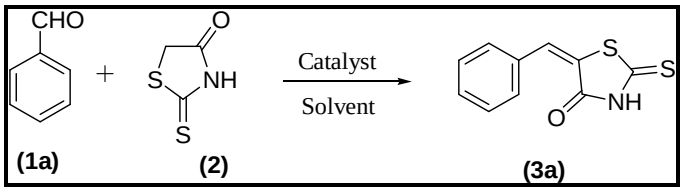
At the onset of the research, we made a conscious effort to develop a catalytic system that would address the limitations of the previously reported reactions. During the preliminary studies benzaldehyde (**1a**) and rhodanine (**2**) was in water used as a model system for this Knoevenagel condensation reaction. A series of experiments were performed to optimize various reaction parameters, such as the catalyst, catalyst loading, solvent, temperature and time (Table 1). The proposed transformation was first examined by treating a mixture of model reaction components with various heterogeneous metal and polymer supported catalysts were tested.

Among these heterogeneous catalysts examined PS-DABCO was found to be the best, providing excellent yields of the desired product **3a** (Table 1, entries 1-6). We further studied catalyst loadings ranging from 4 mol% to 6 mol%. The yield improved as the amount of PS-DABCO catalyst increased from 4 mol% to 5 mol% and became almost steady when the amount of catalyst was further increased beyond this (Table 1, entries 6-8). Only 36% product was obtained in absence of catalyst (Table 1, entry 1). As the solvent will have an impact on the overall process, the effects of various solvents were examined; amongst the studied solvents, we found that water was the best solvent for the model reaction(Table 1, entries 6, 9-12), without solvent the product was obtained only 64% (Table 1, entry 13). A study of the effects of temperature showed that the yield of **3a** increased with increasing reaction temperature from 90°C to 100°C. Thus 100°C is the optimum temperature (Table 1, entry 14). The reaction time was optimized at water refluxed temperature for 24 hours to give good yield of desired products (Table 1, entries 15, 16).

Having optimized reaction conditions in hand, we explored the substrate scope of the PS-DABCO catalyzed Knoevenagel reaction. Various substituted aldehydes containing different functional groups were investigated. Products containing electron-donating as well as electron withdrawing groups were obtained in good to excellent yield. More importantly, aryl aldehydes with bearing electron withdrawing groups as well as electron donating groups reacted efficiently and did not influenced

considerably effect on the yields of corresponding desired products. Satisfyingly a variety of communal functional groups, such as alkyl, ether, halo and nitro were tolerated note with standing of

Table 1. Effect of catalyst screening and loading on Knoevenagel reaction[a]

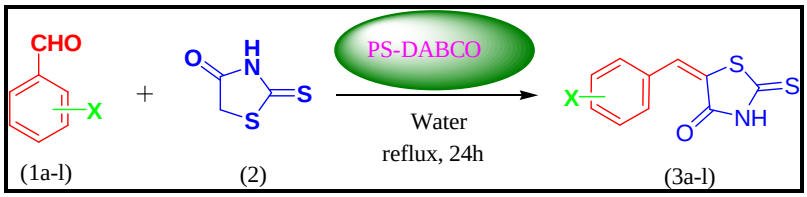


S. No.	Catalyst	Catalyst (mol%)	Solvent	Time (h)	Temp. (°C)	Yield (%)[b]
1	--	--	Water	24	100	36
2	Fe_3O_4	5	Water	24	100	82
3	$CuFe_2O_4$	5	Water	24	100	80
4	Nano-CuI	5	Water	24	100	86
5	PS-IMZ-Cl	5	Water	24	100	72
6	PS-DABCO	5	Water	24	100	91
7	PS-DABCO	4	Water	24	100	82
8	PS-DABCO	6	Water	24	100	91
9	PS-DABCO	5	Ethanol	24	78	88
10	PS-DABCO	5	AcOH	24	100	90
11	PS-DABCO	5	DMF	24	100	76
12	PS-DABCO	5	ACN	24	72	68
13	PS-DABCO	5	--	24	100	64
14	PS-DABCO	5	Water	24	90	72
15	PS-DABCO	5	Water	20	100	85
16	PS-DABCO	5	Water	26	100	91

[a]Reaction condition: Benzaldehyde (**1a**) (1.0 mmol) and rhodanine (**2**) (1.0 mmol), solvent (5 mL). [b]Isolated yields.

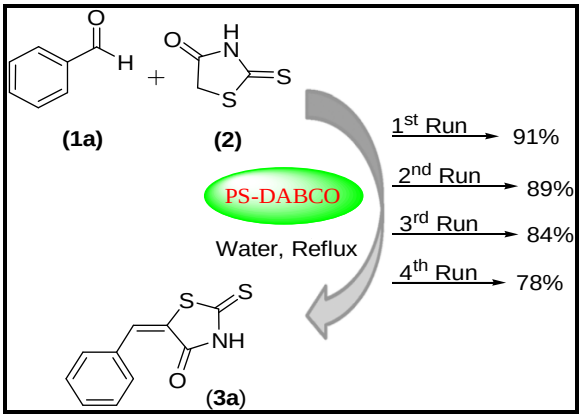
the *meta*- or *para*-position, however *ortho*- substituted benzaldehyde gave lower yields, maybe due to steric hindrance. All the obtained results are summarized in table 2. Formation of desired product was confirmed with the help of FT-IR, PMR and mass spectroscopic data.

Table 2. PS-DABCO catalysed synthesis of 5-benzylidene rhodanine[a]



Entry	Aldehyde (-X)	Product	Yield[b] (%)	MP. (°C) (Obt.) [ref.]
1	-H	**3a**	91	204-206 (202-204) [27]
2	2-Cl	**3b**	80	176-178 (180-182) [21]
3	3-Cl	**3c**	88	190-192
4	4-Cl	**3d**	91	228-230 (225-227) [27]
5	2-Br	**3e**	80	170-172
6	4-F	**3f**	90	226-228 (226-228) [21]
7	3-OMe	**3g**	90	244-246 (247) [40]
8	4-OMe	**3h**	84	248-250 (247-249) [21]
9	3,4-di-OMe	**3i**	84	202-204
10	2-NO_2	**3j**	80	212-214
11	3-NO_2	**3k**	88	262-264 (263-264) [27]
12	4-NO_2	**3l**	92	256-258 (255-257) [21]

[a]Reaction condition: (1) (1.0 mmol), (2) (1.0 mmol), PS-DABCO (5 mol%), water (5 mL), reflux, 24h. [b]Isolated yields.



Scheme 2. Recyclability study of PS-DABCO catalyst.

In terms of green chemistry principles, reusability of the catalyst is highly preferable. Hence the recyclability of the catalyst was studied taking PS-DABCO in the repeated experiments. In order to regenerate the catalyst, after the reaction it was separated from the reaction mixture by simple filtration and washed several times with deionized water and ethanol. Then it was dried at 100°C and reused for the further recycle reaction run. Interestingly, it was observed that the activity of catalyst did not more decreased for the first two consecutive recycles, while slight decrease in conversion was observed during third and fourth recycle. As shown in scheme 2. Therefore, the present catalyst is an interesting candidate for commercial exploitation and exhibited remarkable activity.

APPLICATION

The present method was environmentally benign. The procedure offers advantages in terms of better yields, short reaction times, mild reaction conditions, and reusability of the catalyst. The easy separation, high thermal stability of catalyst and an environmentally benign procedure makes this methodology useful contribution to the existing procedures available for the synthesis of 5-benzylidene derivatives as biologically and pharmaceutically relevant materials.

CONCLUSION

We have developed a new eco-friendly procedure for the synthesis of 5-arylidene rhodanines via condensation of aromatic aldehydes and rhodanine using PS-DABCO as a polymer supported ionic liquid catalyst under aqueous solvent conditions. The wide varieties of 5-benzylidene rhodanine were synthesized in good to excellent yields. The presented methodology includes an advantage such as simple procedure, non-chromatographic purification procedure, excellent yields and easy separation of catalyst and its reusable behavior. This approach therefore represents a precious addition to the existing processes for the synthesis of 5-arylidenerhodanines.

ACKNOWLEDGEMENTS

The author BJK is greatly thankful to Council of Scientific and Industrial Research (CSIR), New Delhi, India for providing the research fellowship. The authors are also thankful to the Principal, JET's Z.B. Patil College, Dhule for providing the laboratory facilities for this work.

REFERENCES

[1]. P. K. Maji, R. Ul Islam, S. K. Bera, Recent progress in metal assisted multicomponent syntheses of heterocycles, *Heterocycles*, **2014**, 89(4), 869-962.

[2]. T. Eicher, S. Hauptmann. The Chemistry of Heterocycles: Structure, Reactions, Synthesis, and Applications, Wiley-VCH: Weinheim, **2003**.
[3]. C. V. Kavitha, B. Basappa, S. N. Swamy, K. Mantelingu, S. Doreswamy, M.A. Sridhar, J. S. Prasad, K.S. Rangappa, Synthesis of new bioactive venlafaxine analogs: novel thiazolidin-4-ones as antimicrobials, *Bioorg. Med. Chem.***2006**, 14(7), 2290-2299.
[4]. R. Dayam, T. Sanchez, O. Clement, β-Diketo acid pharmacophore hypothesis. 1. Discovery of a novel class of HIV-1 Integrase inhibitors, *J. Med. Chem.***2005**, 48, 111-120.
[5]. R. Murugan, S. Anbazhagan, S. Lingeshwaran, S. S. Narayanan, Synthesis and in vivo antidiabetic activity of novel dispiropyrrolidines through [3+2] cycloaddition reactions with thiazolidinedione and rhodanine derivatives, *Eur. J. Med. Chem.***2009**, 44(8), 3272-3279.
[6]. S. Chandrappa, C. V. Kavitha, M. S. Shahabuddin, K. Vinaya, C. S. A. Kumar, S. R. Ranganatha, S. C. Raghavan, K. S. Rangappa, Synthesis of 2-(5-((5-(4-chlorophenyl)furan-2-yl)methylene)-4-oxo-2-thioxothiazolidin-3-yl)acetic acid derivatives and evaluation of their cytotoxicity and induction of apoptosis in human leukemia cells, *Bioorg. Med. Chem.,* **2009**, 17(6), 2576-2584.
[7]. M. V. Diurno, O. Mazzoni, G. Correale, I. G. Monterrey, A. Calignano, G. L. Rana, A. Bolognese, Synthesis and structure–activity relationships of 2-(substituted phenyl)-3-[3-(N,N-dimethylamino)propyl]-1,3-thiazolidin-4-ones acting as H1-histamine antagonists, *IL Farmaco*, **1999**, 54(9), 579-583.
[8]. N. Ergenc, G. Capan, Synthesis and anticonvulsant activity of new 4-thiazolidone and 4-thiazoline derivatives, *IL Farmaco* **1994**, 49(6), 449-451.
[9]. V. R. Solomon, W. Haq, K. Srivastava, S. K. Puri, S. B.Katti, Synthesis and antimalarial activity of side chain modified 4-aminoquinoline derivatives, *J. Med. Chem.,* **2007**, 50(2), 394-398.
[10]. R. K. Rawal, R. Tripathi, S. B. Katti, C. Pannecouque, E. DeClercq, Design and synthesis of 2-(2,6-dibromophenyl)-3-heteroaryl-1,3-thiazolidin-4-ones as anti-HIV agents, *Eur. J. Med. Chem.,* **2008**, 43(12), 2800-2806.
[11]. B. P. Mallikarjuna, B. S. Sastry, G. V. Suresh Kumar, Y. Rajendraprasad, S. M. Chandrashekar, K. Sathisha, Synthesis of new 4-isopropylthiazole hydrazide analogs and some derived clubbed triazole, oxadiazole ring systems; a novel class of potential antibacterial, antifungal and antitubercular agents, *Eur. J. Med. Chem.,* **2009**, 44(11),4739-4746.
[12]. A. Kumar, S. Sharma, A. Archana, K. Bajaj, S. Sharma, H. Panwar, T. Singh, V. K. Srivastava, Some new 2,3,6-trisubstituted quinazolinones as potent anti-inflammatory, analgesic and COX-II inhibitors, *Bioorg. Med. Chem..,* **2003**, 11(23), 5293-5299.
[13]. P. Fresneau, M. Cussac, J. M. Morand, Synthesis, activity, and molecular modeling of new 2,4-dioxo-5-(naphthylmethylene)-3-thiazolidineacetic acids and 2-thioxo analogues as potent aldose reductase inhibitors, *J. Med. Chem.,* **1998**, 41, 4706-4715.
[14]. K. Sudo, Y. Matsumoto, M. Matsushima, Novel hepatitis C virus protease inhibitors: thiazolidine derivatives, *Biochem. Biophys. Res. Commun.,* **1997**, 238, 643-647.
[15]. H. M. Soltero, E. E. Carlson, J. H. Phillips, Identification of inhibitors for UDP-Galactopyranose Mutase, *J. Am. Chem. Soc.,* **2004**, 126, 10532-10533.
[16]. C. J. Andres, J. J. Bronson, S. V. D Andrea, M. S. Deshpande, P. J. Falk, K. A. Grant-Young, W. E. Harte, H. T. Ho, P. F.Misco, J. G. Robertson, D. Stock, Y. Sun, A.W. Walsh, 4-Thiazolidinones: novel inhibitors of the bacterial enzyme MurB, *Bioorg. Med. Chem. Lett.,* **2000**, 10(8), 715-717.
[17]. F. Freeman, Properties and reactions of ylidenemalononitriles, *Chem. Rev.,* **1980**, 80, 329-350. (b) L. F. Tietze, Domino reactions in organic synthesis, *Chem. Rev.,* **1996**, 96, 115-136.
[18]. (a) S. Chitra, N. Paul, S. Muthusbramanian, P. Manisankar,A facile, water mediated, microwave-assisted synthesis of 4,6-diaryl-2,3,3a,4-tetrahydro-1*H*-pyrido[3,2,1-*jk*]carbazoles by a domino Fischer indole reaction–intramolecular cyclization sequence, *Green Chem.,* **2011**, 13, 2777-2785. (b) M.C. Pirrung, Acceleration of organic reactions through aqueous solvent effects, *Chem. Eur. J.,* **2006**, 12, 1312-1317.(c) U.M. Lindstrom, Org.reac. in water: Principles, Strategies and Applications (Blackwell Publishing: Oxford, U.K. **2007**), p. 60.

[19]. N. Sachan, S. S. Kadam, V. M. Kulkarni,Synthesis, antihyperglycemic activity and QSAR of 5-benzylidene-2,4-thiazolidinediones, *Ind. J. Hetro. Chem.*, **2007**, 17, 57-62.
[20]. F. C. Brown, C. K. Bradsher, S. G. McCallum, M. Potter, Rhodanine derivatives of ketones, *J. Org. Chem.*, **1950**, 15, 174-176.
[21]. D. N. Pansare, D. B. Shinde, A facile synthesis of (Z)-5-(substituted)-2-(methylthio)thiazol-4(5H)-one using microwave irradiation and conventional method, *Tetrahedron Lett.*, **2013**, 55, 1107-1110.
[22]. D. N. Pansare, D. B. Shinde, A facile synthesis of (Z)-2-((5-(4-fluorobenzylidene)-4-oxo-4,5-dihydrothiazol-2-yl) amino) substituted acid using microwave irradiation and conventional method, *Open Chemistry Journal*, **2015**, 2, 40-46.
[23]. M. K. Lande, L. S. Gadekar, B. R. Arbad, $AlPO_4$-modified natural zeolite catalyzed facile synthesis of5-arylidene-2,4-thiazolidinediones, *Org. Chem. An: Ind. J.*, **2008**, 4, 458-461.
[24]. R. S. Mahalle, P. D. Netankar, S. P. Bondge, R. A. Mane, An efficient method for Knoevenagel condensation: a facile synthesis of 5-arylidenyl 2,4-thiazolidinedione,*Green Chem. Lett. Rev.*, **2008**, 1, 103-106.
[25]. G. Thirupathi, M. Venkatanarayana, P. K. Dubey, Y. BharathiKumari, Facile and green syntheses of substituted-5-arylidene-2,4-thiazolidinedionesusing L-tyrosine as an Eco-Friendly catalyst in aqueous medium, *Der Pharma Chemica*, **2012**, 4(5), 2009-2013.
[26]. S. Mohanty, S. Reddy, G, A. C.Karmakar, Phosphoryl chloride mediated synthesis of 5-arylidene-2,4-thiazolidinediones derivatives via aromatic bisulfite adducts, *Lett. Org. Chem.*, **2014**, 11(3), 197-202.
[27]. A. Khazaei, H. Veisi, M. Safaei, H. Ahmadian, Green synthesis of 5-arylidene-2,4-thiazolidinedione, 5-benzylidene rhodanine and dihydrothiophene derivatives catalyzed by hydrated ionic liquid tetrabutylammonium hydroxide in aqueous medium, *J. Sulfur Chem.*, **2014**, 35, 270-278.
[28]. J. F. Zhou, F. X. Zhu, Y. Z. Song, Y. L. Zhu, Synthesis of 5-arylalkylidenerhodanines catalyzed by tetrabutylammonium bromine in water under microwave irradiation, *Arkivoc*, **2006**, 14, 175-180.
[29]. L. Han, Z. Zhou, A rapid and green procedure for the synthesis of 5-arylidene rhodanine derivatives, *Modern Org. Chem. Res.*, **2016**, 1(1), 30-34.
[30]. Y. Q. Yu, D. Z. Xu, Polystyrene-supported DABCO as a highly efficient and recyclable heterogeneous catalyst for the one-pot synthesis of β-phosphonomalonates, *Tetrahedron*, **2015**, 71, 2853-2857.
[31]. (a) N. Seyyedi, F. Shirini, M. Safarpoor N. Langarudi, DABCO-based ionic liquids: green and recyclable catalysts for the synthesis of barbituric and thiobarbituric acid derivatives in aqueous media, *RSC Adv.*, **2016**, 6, 44630-44640. (b) T. Liu, Y. H. Lai,Y.Q. Yub, D.Z. Xua,A facile and efficient procedure for one-pot four-component synthesis of polysubstituted spiro pyrano[2,3-c]pyrazole and spiro 1,4-dihydropyridine catalyzed by a Dabco-based ionic liquid under mild conditions, *New J. Chem.*, **2018**, 42(2), 1046-1051.
[32]. B. J. Khairnar, D. V. Mane, B. R. Chaudhari, Heterogeneous PS-DABCO catalysed one pot four-component synthesis of Pyranopyrazole, *J. Applicable Chem.*, **2019**, 8(1), 425-434.
[33]. (a) B. J. Khairnar, B. M. Bhanage, Amidation of aryl halides with isocyanides using a Polymer-Supported Palladium-*N*-Heterocyclic Carbene complex as an efficient, phosphine-freeand heterogeneous recyclable catalyst, *Synthesis*, **2014**, 46, 1236-1242. (b) B. J. Khairnar, B. M. Bhanage, Amidation of aryl halides with isocyanides using a PS-Pd-NHC, *Synfacts*, **2014**, 10, 0771.
[34]. B. J. Khairnar, P. S. Girase, Z. A. B. Munshi, D. V. Mane, B. R. Chaudhari, Microencapsulated Copper (II) Acetylacetonate: an efficient, environmental benign and recyclable catalyst for microwave-promoted synthesis of amidoalkyl naphthol, *ejpmr*, **2017**, 4(11), 570-574.
[35]. B. J. Khairnar, P. S. Girase, D. V. Mane, B. R. Chaudhari, Heterogeneous Microencapsulated Copper (II) Acetylacetonate as green catalyst for synthesis of amidoalkyl naphthol, *Der Pharma Chemica*, **2016**, 8(17), 137-141.

[36]. B. J. Khairnar, P. S. Girase, B. R. Chaudhari,A facile and green synthesis of "5-(3-methyl-7-substituted-4h-1, 4-benzothiazin-2-yl)-4-aryl-4h-1, 2, 4-triazole-3-thiols" under ultrasound irradiation, *Orient. J. Chem.*, **2013**, 29(1), 285-289.
[37]. B. J. Khairnar, R. S. Salunke, P. B. Patil, S. A. Patil, R. J. Kapade, P. S. Girase, B. R. Chaudhari, Synthesis and antimicrobial activity of some new 1, 4-benzothiazine containing thiosemi-carbazides and 1, 3, 4-oxadiazole derivatives, *E-J. Chem.*, **2012**, 9(1), 318-322.
[38]. B. J. Khairnar, B. R. Chaudhari, Microwave-promoted Zirconium (IV) Chloride as an efficient, environmentally benign and recyclable homogeneous catalytic system to synthesis of bis(indolyl)methanes, in PEG as a solvent, *J. Chem. Pharm. Res.*, **2015**, 7(5), 241-245.
[39]. B. J. Khairnar, D. V. Mane, M. S. Shingare, B. R. Chaudhari, Nano-Fe_3O_4 as a heterogeneous recyclable magnetically separable catalyst for synthesis of nitrogen fused imidazoheterocycles via double C-N bond formation, *Iran. J. Catal*., **2018**, 8(3), 155-163.
[40]. T. Swati, M. Srinivas, Green condensation reaction of aromatic aldehydes with rhodanine catalyzed by alum under microwave irradiation, *Der Pharma Chemica*, **2015**, 7, 100-104.