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An Overview of Biological and Synthetic Aspects of Thiazole Derivatives in Heterocyclic Chemistry

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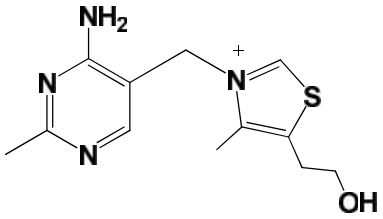
***Abstract*— These overviews signify a study covering the literature on thiazole derivatives in heterocyclic chemistry. This brief analysis as well provides a revise on current reports and demonstrates the utility and the effectiveness of this approach. The data on the process of synthesis, chemical reactions, and biological activity of these heterocycles available over the preceding years are assessing here. In the last few decades, a lot of effort has been prepared on thiazole ring to discover novel compounds associated to this scaffold. This review presents the advanced improvement on the proposed and growth of diverse thiazole derivatives. It is known as the building block in organic synthesis, which provides as an important outline for the improvement of diverse therapeutic agents and illustrate a broad variety of activities. These articles furnish a widespread explanation of the synthetic and biological value of thiazole engaged in the design and synthesis of diverse type of compounds encloses fused heterocyclic rings with more importance on latest literature.**

***Index Terms*—Heterocyclic System, Pharmacologically Active, Thiazole.**

I. INTRODUCTION

Thiazole is the constituent of azole heterocycles that too contain pyrazoles, imidazoles, isoxazoles, and oxazoles. Thiazole is aromatic, heterocyclic organic compound that hold together a nitrogen atom and sulfur atom as component of the aromatic five-membered molecular ring composition, C3H3NS. It is produce in a diversity of specific products, frequently fused with benzene ring, which are well-known as benzothiazoles. Thiazole is structurally correlated to imidazole in which sulfur is replaced by nitrogen and oxazole in which sulfur replaced by oxygen.

Thiazole is an apparent to light yellow liquid with a boiling point of 116-118oC. Its specific gravity is 1.2 and it is sparingly soluble in water, soluble in alcohol and ether and sparingly soluble in organic solvents and dyes. The odor of thiazole is like to pyridine. It is used as an intermediate to create synthetic drugs, fungicides and dyes. A thiazole ring is found naturally in the necessary vitamin B1 (Thiamine) 1 (Fig.-1.1). Thiamine is a water soluble vitamin. It helps the body to liberate energy from carbohydrates throughout metabolism. It also helps in the normal execution of the nervous system by its function in the synthesis of neurotransmitters, such as acetylcholine. Thiazole is a parent material for various chemical compounds including sulfur drugs, biocides, fungicides, dyes, and chemical reaction accelerators. Commercial significant thiazoles include mostly thifluzamide, tricyclazole, and thiabendazole are sell for control of different agricultural pests. Thiazoles and their derivatives have fascinated ongoing attention over the years since of their diverse biological activities. Thiazole, mainly the 2-amino thiazole nucleus has been included into a broad array of therapeutically fascinating contender.



Thiamine
Fig.-1.1

Epothilones (**Fig.-1.2**) are anti-tumor agents[2] that reveal greater stimulus against Taxol-resistant tumor cell lines.

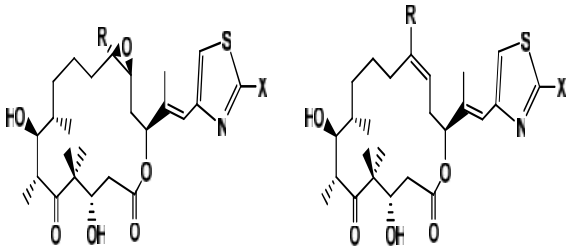


Fig.-1.2

Among the extensive array of heterocyclic compounds survey, thiazoles have played an vital position in therapeutic chemistry. Literature reviews illustrate that compounds with thiazole nucleus take hold of a wide range of pharmacological activities. The thiazole ring system is found in a diverse range of natural products and purposeful materials. Thiazoles also play a vital role in the biochemistry of life as being a part of vitamin B1 which plays the key role in the metabolism. Thiazoles are always being included into pharmaceutical compounds contained by the flavorings, perfumes and agrochemicals.

Thiazoles enclose N=C-S nucleus has been working as take part in pharmaceutical carry out due to their extensive biological activities like fungicidal, anti TB, anti cancer, anti

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microbial, and anti-inflammatory. The substituted thiazoles compounds have numerous typical pharmacological features such as

· Relative constancy and easiness of starting materials
· construct in biocidal unit
· improved lipid solubility with hydrophilitcity
· Simple metabolism of compounds

II. BIOLOGICAL ASPECTS OF THIAZOLES:

The extensive range of biological activities demonstrate by thiazole nucleus has prompt the improvement in the investigated in the field of heterocyclic chemistry. The position of explore and progress in this area is go faster and there appear to be almost no limit to the number of attractive ring systems that can be formed in the laboratory nowadays with an arrangement of initiative and urgency. The heterocyclic systems by five atoms, once measured chemical peculiarity are now just as effortlessly achieve as their six- and seven-membered equivalent. A speedy expansion in this area represents a fascinating combine of pure and applied heterocyclic chemistry.

Thiazoles and their derivatives have been commonly revealed as a essential part of new and structurally varied natural products with synthetic compounds that display a broad diversity of biological activities. The excellent range of anti-tumor, anti-viral, and antibiotic activities as well as their existence in peptides or capacity to unite to proteins, DNA, and RNA have been account. The thiazole ring has been recognized as an essential characteristic of natural products. Besides thiazoles are normally emerge in peptide research. Thiazoles can also provide as a confined formyl group that can be enlightened in the late stages of a complex natural product synthesis.

Literature review expose that thiazole derivatives might be used as a template for the improvement and designing of more effective therapeutic agents through modification or derivatization. These result recommended that derivatives of thiazole have fascinated interest of chemist in the field of drugs and pharmaceuticals. All this information was active strength to grow new thiazole derivatives with broad structural variation. Thus thiazole moiety takes part and necessary position in medicinal chemistry. Thiazole and its derivatives have been regularly exposed as a basic component of new and structurally various natural products with synthetic compounds that expose a wide assortment of biological activities.

Furthermore, thiazole derivatives are important synthetic counterpart that can be used in the preparation of other fused ring compounds such as oxazoles, pyrazoles, pyrimidines, oxazepines etc. Research in this area is very dynamic and is directed towards the synthesis of compounds with better pharmacological profile. Thiazole derivatives mostly 2-amino thiazole ring system is a valuable constituent in medicinal chemistry which is used in the cure of allergies3, hypertension4, inflammation5, diabetes6, anesthetic7, analgesic8, cancer9, tuberculosis10 and HIV11. 2-aminothiazoles are employing as legends of estrogen receptors12 as well as novel class adenosine receptor antagonists13. 2-Aminothiazoles are also recognized mainly as biologically active pharmacophores with a widespread activity of intermediates in the synthesis of anti-biotics and dyes. Apart from this, thiazole derivatives have expected considerable interest and the concern is to be sure a 'privileged scaffold' found in compounds active against a array of goal including estrogen receptors as well as novel class adenosine receptor antagonists.

Thiazoles have broadly been engaged as effective γ-secretase inhibitors to hinder Alzheimer's disease,14 - glycogen synthase kinase-3β(GSK-3 β) inhibitors,15 active metabotropic glumate subtype-5 (mGlu5) receptor antagonist with anxiolytic activity,16 transient receptors potential vanilloid-1 (TRPV-1) antagonists,17 CCR-4 antagonists,18 hepatitis-C virus (HCV) NS5B polyemerase inhibitors and hepatitis-B virus (HBV) inhibitors19. Thiazoles are creature a basic part of numerous biologically active molecules such as ritonavir20 (1.001) (anti-retriviral drug), sulfathiazole (1.002) (anti-microbial drug), abafungin (1.003) (anti-fungal drug) with trade name abasol cream, tiazofurin (1.004) (anti-neoplastic drugs) have been widely investigate21.

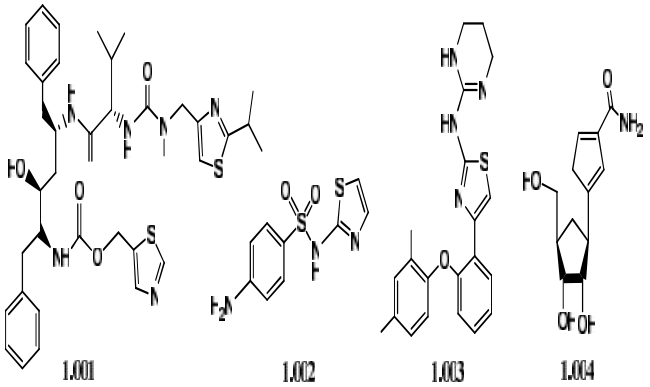


Fig.-1.3

III. THIAZOLE NUCLEUS PRESENT IN DRUGS

Various thiazole derivatives, revealed in (Fig.-1.4), are extremely pharmacologically active molecules. Meloxicam (1.005) is a non-steroidal anti-inflammatory compound (NSAID) investigates by Boehringer Ingelheim and used to treat arthritis, dysmenorrhes, fever and also acts as an analgesic22. Dasatinib (1.006) was developed by Bristol Myers Squibb as an ABL/SCR family tyrosine kinase inhibitor for the treatment of chronic myelogenous leukaemia. It is currently being assessed for use in the treatment of metastatic melanoma23. Cefotaxime (1.007) is a third generation cephalosporim antibiotic with widespread spectrum action associated with both gram positive and gram negative bacteria24. Nizatidine (1.008) was developed by Eli Lilly and is a histamine H2 receptor antagonist to reduce the production of stomach acid25. It is used in the treatment of peptic ulcer disease and gastroesophageal reflux disease.

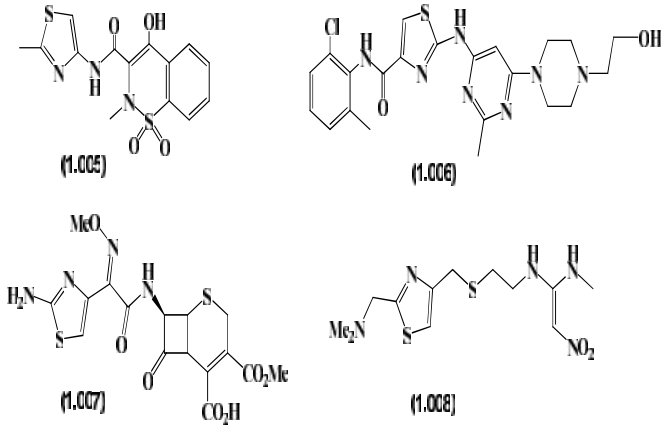
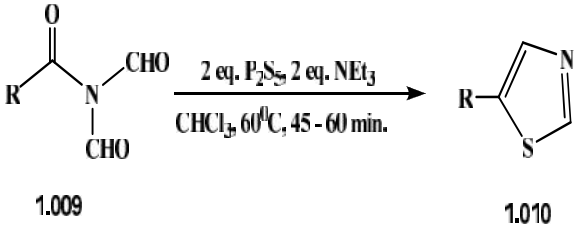


Fig.-1.4

IV. SYNTHETIC ASPECTS OF THIAZOLES

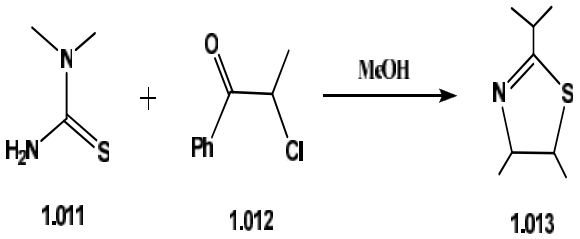
The remarkable physiological properties allied with these molecules essential the flexibility in the method of their synthesis, and this can be the reason for literature to be full with extensive range of methods for their synthesis. Some of the reported methods for the synthesis of thiazoles are illustrate below:

Reaction of phosphorus pentasulfide and triethylamine in chloroform, with N, N-diformylaminomethyl aryl ketones (1.009) gives 5-arylthiazoles (1.010) in good yield. (Scheme-1.1).[26]



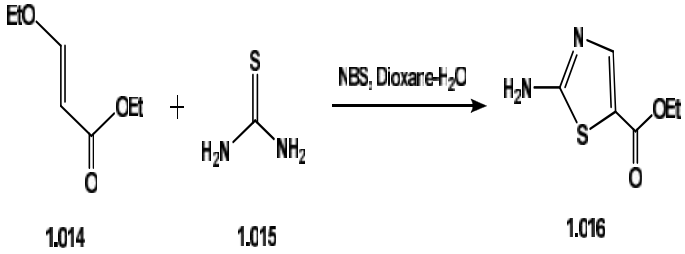
Scheme-1.1

The Hantzsch thiazole (1.013) synthesis is a reaction involving thioamide (1.011) and haloketones(1.012) (Scheme-1.2).[27]



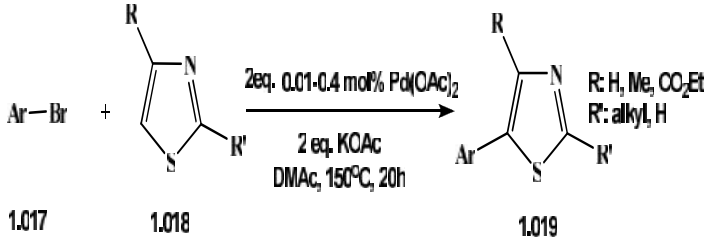
Scheme-1.2

Ethyl *β*-ethoxyacrylate **(1.014)** reacted with NBS followed by thiazole ring development with thiourea **(1.015)** to give ethyl 2-aminothiazole-5-carboxylate **(1.016) (Scheme-1.3).**[28]



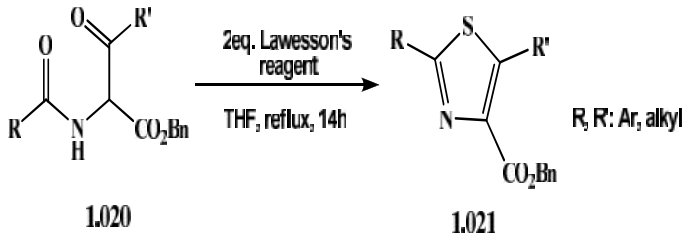
Scheme-1.3

Ligand-free Pd $(OAc)_2$ catalyzed direct arylation of thiazoles derivatives **(1.019)** with activated aryl bromides **(1.017)** under very low (0.1-0.001mol) catalyst concentration gives thiazole derivatives**(Scheme-1.4)**[29]**.**



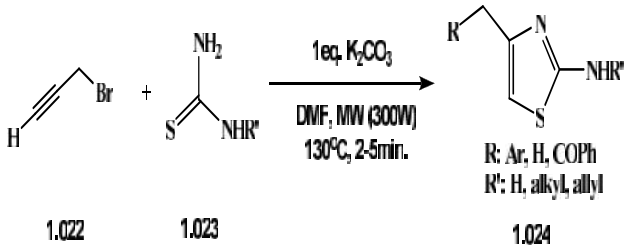
Scheme-1.4

Double acylation of a protected glycine provides intermediates α-amido-β-ketoesters **(1.020)** which was dehydrated to afford 1,3-oxazoles or reacted with Lawesson's reagent to give 1,3-thiazoles.**(1.021)(Scheme-1.5)**[30]**.**



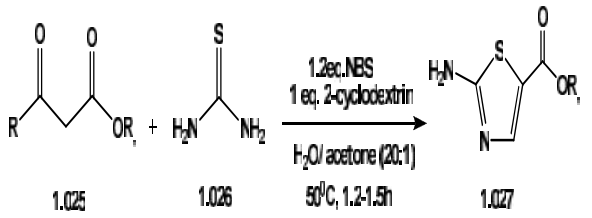
Scheme-1.5

A domino alkylation-cyclization reaction occurs by propargyl bromides **(1.022)** and thiourea **(1.023)** permits the synthesis of 2-aminothiazoles **(1.024).** Domino reactions were carrying out under microwave irradiation leading to preferred compounds in a few minutes and piercing yields **(Scheme-1.6)**[31]**.**



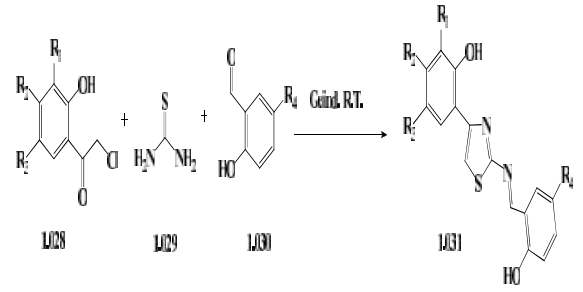
Scheme-1.6

Reaction between β-keto esters **(1.025)** with *N*-bromosuccinimide **(1.026)**, followed by cyclization using thiourea or selenoureа, in the presence of β-cyclodextrin in water at 50°C synthesized 2-Amino-4-alkyl- and 2-amino-4-arylthiazole-5-carboxylates **(1.027)** and their selenazole analogues respectivly **(Scheme-1.7)**[32]



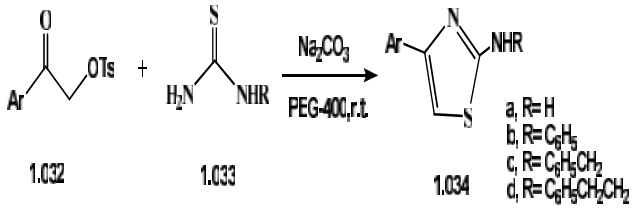
Scheme-1.7

One-pot synthesis of 2-{[4-substitutedphenyl)-thiazol-2-yl-imino]-methyl}-phenol **(1.031)** by the condensation with *α*-haloketones **(1.028)**, thiourea **(1.029)** and substituted *o*-hydroxybenzaldehyde **(1.030)** under environmentally solventless condition has been reported **(Scheme-1.8)**[33].



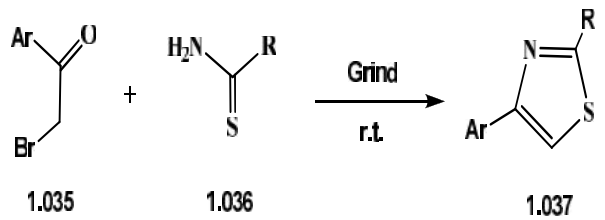
Scheme-1.8

Efficient Synthesis of the resultant 2-aminothiazoles **(1.034)** by the cyclocondensation reaction between α-tosyloxyketones (**(1.032)** and thioureas (**(1.033)** take place by simply used in PEG-400 [poly(ethylene glycol-400)] at room temperature in the presence of sodium carbonate **(Scheme-1.9)**[34].



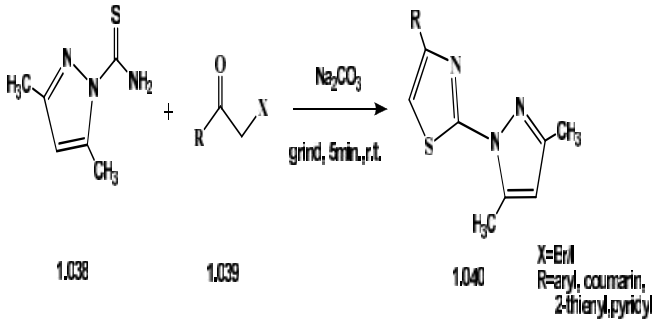
Scheme-1.9

A novel and proficient procedure for the synthesis of 2,4-disubstituted thiazoles**(1.037)** through a condensation reaction of *a*-halo carbonyl compounds **(1.035)** with thiourea or thioacetamide **(1.036)** at room temperature, under grinding**(Scheme-1.10)**[35].



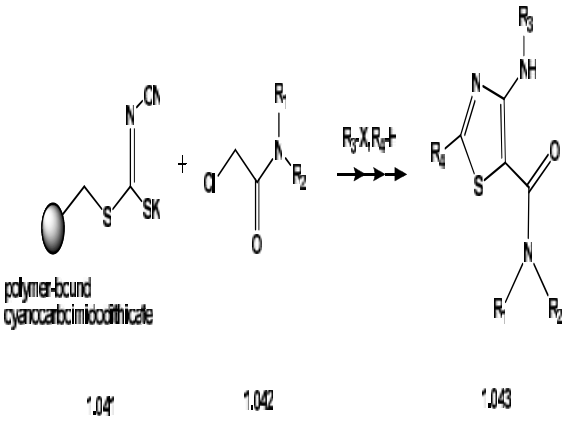
Scheme-1.10

An proficient and simplistic synthesis of 4-substituted-2-(3,5-dimethylpyrazol-1-yl)thiazoles **(1.040)** was achieved through grinding an equimolar mixture of *α*-haloketones **(1.039)** with 3,5-dimethylpyrazol-1-thiocarboxamide **(1.038)** by using sodium carbonate under the solventless conditions**(Scheme-1.11)**[36].



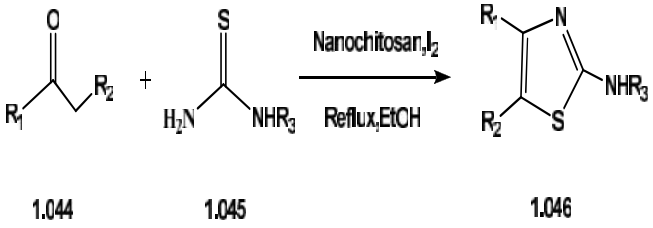
Scheme-1.11

An useful procedure for the solid-phase synthesis of 2,4-disubstituted 5-carbamoyl-thiazole derivatives **(1.043)** via the Thorpe-Ziegler type cyclization of 2- chloroacetamide **(1.042)** and polymer-bound cyanocarboimidodithioate **(1.041)**, which is derived from Merrifield resin was reported **(Scheme-1.12)**[37].



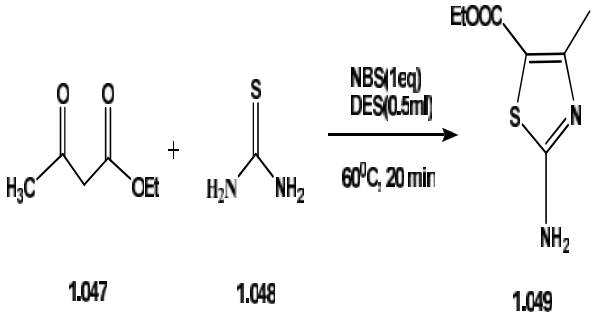
Scheme-1.12

Synthesis of 2-aminothiazoles **(1.046)** was reported through one-pot reaction of ketone **(1.044)** and thiourea **(1.045)** by employ biodegradable, green catalyst nanochitosan in mild condition**(Scheme-1.13)**[38].



One pot synthesis of 2-amino-thiazole **(1.049)** from the three-component reactions through active methylene compounds **(1.047)**, urea or thiourea **(1.048)** and N-bromosuccinimide (NBS) in the choline

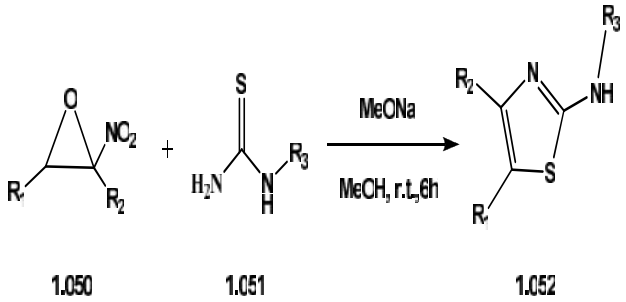
chloride–urea-based deep eutectic solvent (DES) **(Scheme-1.14)**[39].



1.047 1.048 1.049

Scheme-1.14

An effective synthesis of 2,4,5 -trisubstituted thiazoles **(1.052)** through the reaction between α-nitroepoxides **(1.050)** and thioureas **(1.051)** at room temperature in mild conditions **(Scheme-1.15)**[40].



1.050 1.051 1.052

Scheme-1.15

V. Conclusion

This overview has challenge to review the synthetic and biological aspects. In the last decade importance on thiazole nucleus has expended exponentially owing to their relevance in various diseases such as viral infection, cancer and cardiovascular disorders. Besides, thiazoles are important synthons for the preparation of other fused compounds, such as oxazoles, pyrazoles, pyrimidines, oxazepines etc. This proficient moiety has a lot scope as a number of diverse molecular targets are available for thiazole. This review aim to give a widespread account of the synthetic and biological value of thiazole working in the design and synthesis of different types of fused heterocyclic rings containing compounds with greater accent on current literature. This survey cover up all the synthetic and biological methodology published through **2016**.

Future Scope

Thiazole is versatile reactive intermediates to prepare variety of heterocycles as well as aromatic compounds. These reactive intermediates will be utilized to synthesize another bioactive heterocycles.

Acknowledgement

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