eISSN 2581-8996
ONLINE
INTERNATIONAL JOURNAL OF ADVANCED RESEARCH IN MULTIDISCIPLINARY SCIENCES (IJARMS)
A BI-ANNUAL, OPEN ACCESS, PEER REVIEWED (REFEREED) JOURNAL
Volume 08, Special Issue 03, Nov 2025

Environmentally sustainable: Glycerol- boric acid, good promoter in various organic synthesis due to green and mild catalytic properties

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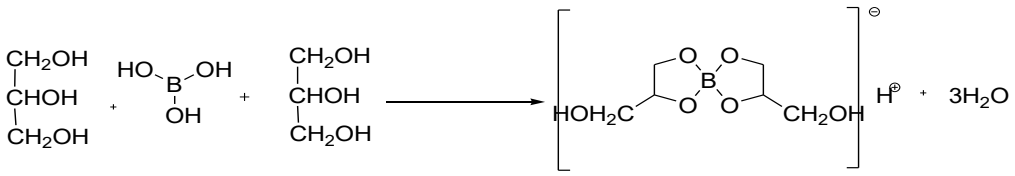
Received: 08 November 2025, Accepted: 20 November 2025, Published online: 30 November 2025

Abstract

Glycerol is a colorless, odourless and viscous liquid. It is a simple trihydric alcohol. Glycerol is widely used as a solvent because it enhances the rate of an organic reaction. Glycerol can be considered as 'organic water'. Glycerol form strong hydrogen-bond, which facilitate it to dissolve a wide range of organic and inorganic compounds into it. Boric acid is a weak acid, its complex with polyhydroxy compounds is stronger due to chelate formation and it increases the acidity of the medium by the release of H^+ ions.



Boron Chelate complex

Boron chelate complex in water

Keywords – Glycerol, boric Acid, Environmentally sustainable, Heterocycles, Water, Green chemistry

Introduction

A careful overview of the literature expose that chemist involved in the synthesis totally focused to maintain the green chemistry protocols.[1] Majority of organic transformation are carried out in the liquid phase.[2] The solvent play an important role in the reaction due to direct contact between reactants it also determines procedures for the work up and reuse or decline.[3] Taking into consideration the effect of chemical processes on nature, the investigation for new strategies for the alternative of volatile organic reaction medium. In the last few years, water gained extra attention in the solution phase chemistry.[4] But now a day ionic liquids, polyethylene glycol and supercritical fluids are being frequently used.[5] There are several properties of glycerol which fulfill the criteria of green solvent such as low toxicity, high boiling point, low-flammability, low vapor pressure biodegradability and high solubility of polar organic compounds.[6] These above properties prompted us to use it as a green solvent in organic synthesis. Glycerol[7] is by-product[8] of biodiesel.[9]

Azizi et.al. reported[11] the synthesis of α-aminophosphonates in glycerol. Authors reported a three-component Kabachnik–Fields reaction from amines, phosphites and carbonyl compounds. In this reaction Glycerol play the role of a promoting medium. **(Scheme-IV.1)**

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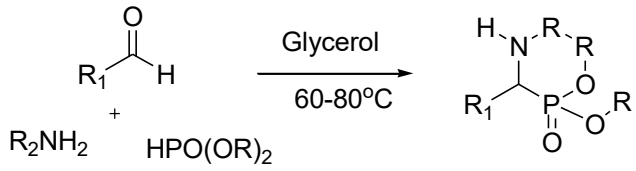
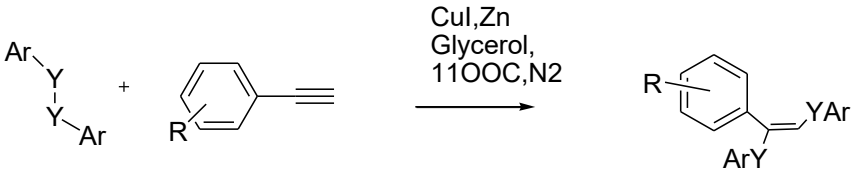
(Scheme-IV.1)



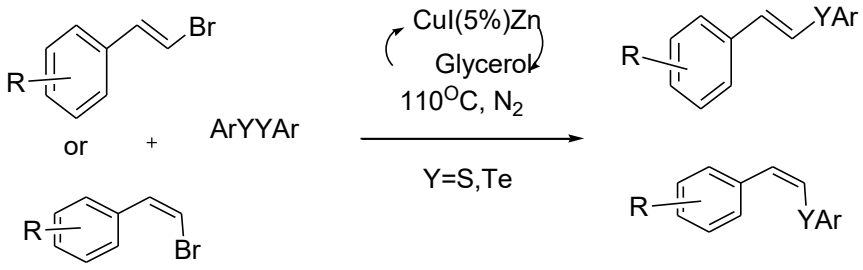
Gonçalves and co-worker[12] synthesized and reported the antioxidant activity of (E)-1, 2-Bis-chalcogen alkenes using CuI/Zn/glycerol as a catalyst system. The copper-catalyzed addition of diaryl dichalcogenides to terminal alkynes furnished stereoselectively (E)-bis-chalcogen alkenes with good yields. The catalyst system was recovered and used several times without significant loss of its catalytic activity. **(Scheme-IV.2)**

(Scheme-IV.2)



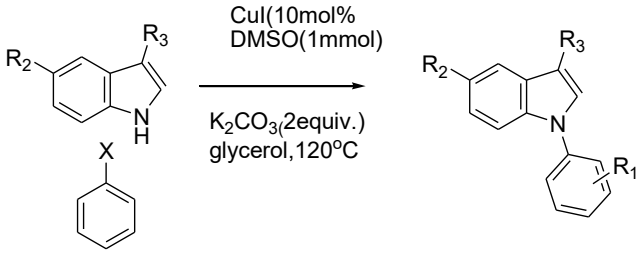
Same research group[13] extended the scope of this catalyst system on the coupling of diphenyl disulfide and diphenyl ditelluride with (Z)-(2-bromovinyl)benzene and (E)-(2-bromovinyl)benzene. These strategies once again found to be highly efficient, cost effective and environmentally more acceptable. **(Scheme-IV.3)**

(Scheme-IV.3)



As an extension of the copper/glycerol catalytic system Bhanage and co-worker[14] used this system for cross-coupling of indoles with aryl halides in which DMSO play the role of an additive. The protocol has various attractive features like low catalyst loading, excellent yield and recyclable catalyst system. **(Scheme-IV.4)**

(Scheme-IV.4)



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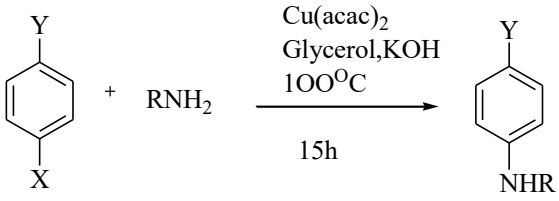
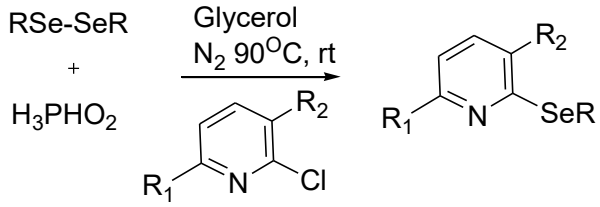
In the same area Khatri *et. al.* reported[15] the coupling reaction of aryl halides with several aromatic and cyclic amines by using glycerol embedded copper catalyst. **(Scheme-IV.5)**

(Scheme-IV.5)



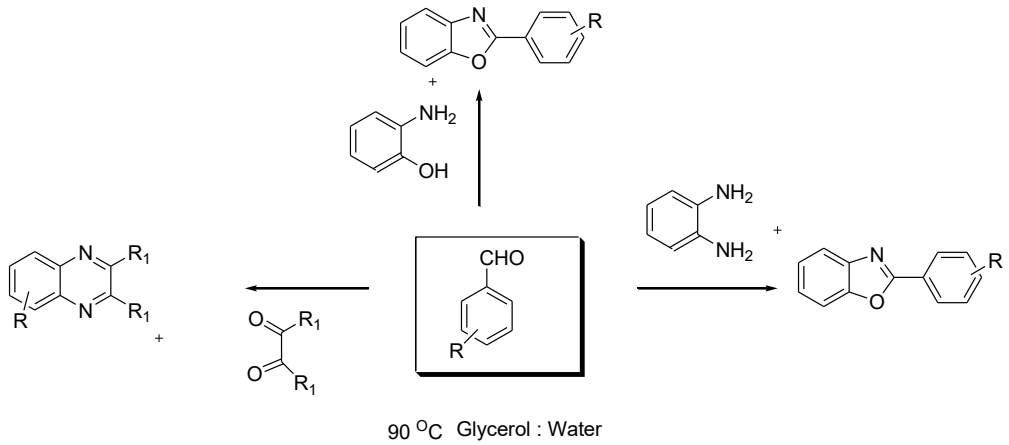
Thurow group[16] has been associated to the glycerol with hypophosphorous acid and used for the synthesis of 2-organylselanyl pyridines. In this reaction glycerol was used as solvent and hypophosphorous acid as a reducing agent. Both were recovered and reused several times in the same reaction. **(Scheme-IV.6)**

(Scheme-IV.6)



On the other hand Telvekar *et. al.*reported[17] the catalyst-free synthesis of benzimidazole quinoxaline, and benzoxazole ring system in glycerol–water system at 90 °C . **(Scheme-IV.7)**

(Scheme-IV.7)



Parmar and group disclosed[18] the domino/Knoevenagel–hetero-Diels–Alder (DKHDA) reaction in glycerol using thiopyrano[2,3-b]quinoline-3-carbaldehyde and 5-pyrazolone as substrates. Many attractive features are attached with this strategy like reaction rate, yields, and the use of hazardous catalysts or solvents. **(Scheme-IV.8)**

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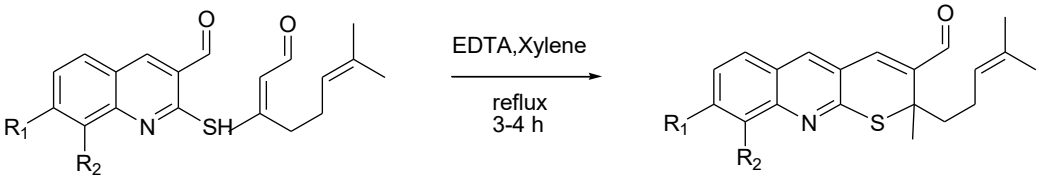
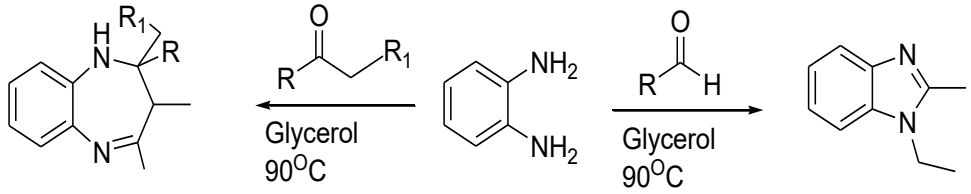
(Scheme-IV.8)



Alves and co-worker[19] reported benzodiazepines and benzimidazoles in glycerol. This catalyst-free methodology for the synthesis of target nucleus in good yields by the condensation of o-phenylenediamine with several aldehydes and ketones in which glycerol was used as asolvent. Glycerol can be reused without any purification for further same reactions. **(Scheme-IV.9)**

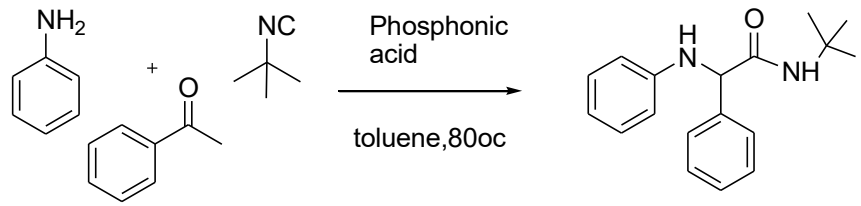
(Scheme-IV.9)



Boric acid is a water soluble weak lewis acid water soluble catalyst.[20] It is a fine catalyst and plays a significant role in organic reactions.[21] This catalyst was found to be effective in various organic transformations such as esterification of hydroxycarboxylic acids. Michael addition and bromination.[22]

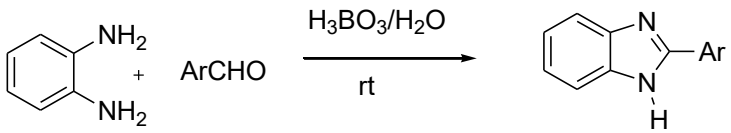
Kumar *et. al.* extended[23] the scope of boric acid and synthesized the 2-arylamino-2-phenylacetamides by using aldehydes, amines, and isocyanides as a model substrate in water. Only 10 mol % of catalyst was found to be sufficient to obtain the target product in excellent yield. **(Scheme-IV.10)**

(Scheme-IV.10)



Heravi and co-workers synthesized,[24] benzimidazoles from *o*-phenylenediamine with aldehydes using the boric acid catalyst under mild reaction conditions in aqueous media. **(Scheme-IV.11)**

(Scheme-IV.11)



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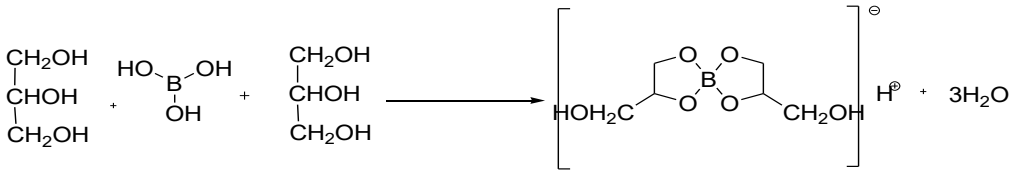
In literature reported that boric acid and glycerol leads to the formation of a boron chelate complex in water.[25]



Boron chelate complex in water

CONCLUSION

We have focused a new strategy for the synthesis of various nucleus, which has several attractive features such as easy handling, easy work-up and the involvement of a simple procedure. Moreover, the use of mild catalyst- **boric acid** and a green solvent-water makes the adopted route for the synthesis of a target nucleus extremely environment friendly

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