

QUINOXALINE SYNTHESIS AND STRUCTURE-ACTIVITY RELATIONSHIP OF ANTI-CANCER ACTIVITY

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DOI: <https://doi.org/10.5281/zenodo.23801469>



How to cite this Article: Goldi Maurya¹, Prof. (Dr.) Shobhit Prakash Srivastava^{2*} (2026). Quinoxaline Synthesis And Structure-Activity Relationship Of Anti-Cancer Activity. European Journal of Pharmaceutical and Medical Research, 13(11), 181–189.

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Article Received on 29/09/2026

Article Revised on 19/10/2026

Article Published on 01/11/2026

ABSTRACT

Quinoxaline is a privileged pharmacophore that has broad-spectrum applications in the fields of medicine, pharmacology and pharmaceuticals. Similarly, the sulfonamide moiety is of considerable interest in medicinal chemistry, as it exhibits a wide range of pharmacological activities. Therefore, the therapeutic potential and biomedical applications of quinoxalines have been enhanced by incorporation of the sulfonamide group into their chemical framework. The present review surveyed the literature on the preparation, biological activities and structure-activity relationship (SAR) of quinoxaline sulfonamide derivatives due to their broad range of biomedical activities, such as diuretic, antibacterial, antifungal, neuropharmacological, antileishmanial, anti-inflammatory, anti-tumor and anticancer action. The current biological diagnostic findings in this literature review suggest that quinoxaline-linked sulfonamide hybrids are capable of being established as lead compounds; Quinoxaline derivatives have been used as anticancer, anticonvulsant, anti-inflammatory, antidiabetic, antioxidant, antibacterial, anti-TB, antimalarial, antiviral, anti-HIV, and many other uses. Various substituted quinoxalines are significant therapeutic agents in the pharmaceutical industry. This review spotlights on the chemistry, physiochemical characters, synthesis, pharmaceutical products, and medicinal chemistry of various anticancer quinoxaline derivatives that were developed in the last period. Modification in their structure has offered a high degree of diversity that has proven useful for the development of new therapeutic agents having improved potency and lesser toxicity.

KEYWORDS: Quinoxaline, Synthesis, structure-activity relationship, Anti-Cancer activity.

INTRODUCTION

1. Quinoxaline

Heterocyclic scaffolds hold a pivotal place in medicinal chemistry and are one of the largest areas of research in organic chemistry due to their wide spectrum of biological activities. Therefore, continuous efforts have been undertaken to explore their therapeutic potential in the field of design and development of new drugs. Quinoxaline is a privileged, ubiquitous and versatile nitrogen-containing heterocyclic motif, which exhibits a broad spectrum of medicinal, pharmacological and pharmaceutical applications. Quinoxaline, also known as benzopyrazine, was formed by the combination of pyrazine and benzene^[1] rings at the carbons 2 and 3 of the pyrazine ring. Heterocycles containing nitrogen have great importance in the pharmaceutical field including

uses in drug discovery, synthesis, and development processes. Their unique ring systems, often incorporating atoms like nitrogen, oxygen, or sulfur, enhance molecular stability and reactivity. Nitrogen-containing heterocycles are particularly significant, as nitrogen contributes to key interactions with enzymes and receptors, improving drug-likeness and pharmacokinetic properties. These N-heterocyclic compounds are widely found in drugs for treating various conditions,^[2] such as antibiotics and anticancer agents, underscoring their broad therapeutic relevance. Quinoxaline, a nitrogen-containing heterocyclic compound, is recognized for its chemical stability and versatile framework, making it a valuable scaffold in medicinal chemistry. Structurally, quinoxaline consists of a fused benzene and pyrazine ring, providing a rigid planar core. The 2- and 3-

positions on the quinoxaline ring are highly amenable to chemical modifications, allowing for the development of derivatives with tailored biological activities. Substitutions at these positions influence the electronic properties of the scaffold, enabling fine-tuning of binding affinities to specific targets. For instance, 2,3-bis-substituted quinoxalines have been optimized for anticancer activity by enhancing interactions with topoisomerases and tubulin polymerization sites. Green

chemistry approaches, such as microwave-assisted synthesis and recyclable catalysts.^[3]

Quinoxaline is defined as a weakly basic bi-cyclic compound $C_8H_6N_2$, having fused benzene and pyrazine rings. Quinoxaline is a nitrogen-containing heterocyclic compound and is an indispensable structural unit for both chemists and biochemists. The structure is as shown in **Figure 1**.^[4]

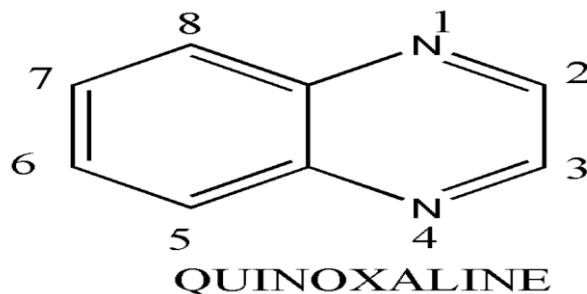


Figure 1: Structure of Quinoxaline.^[4]

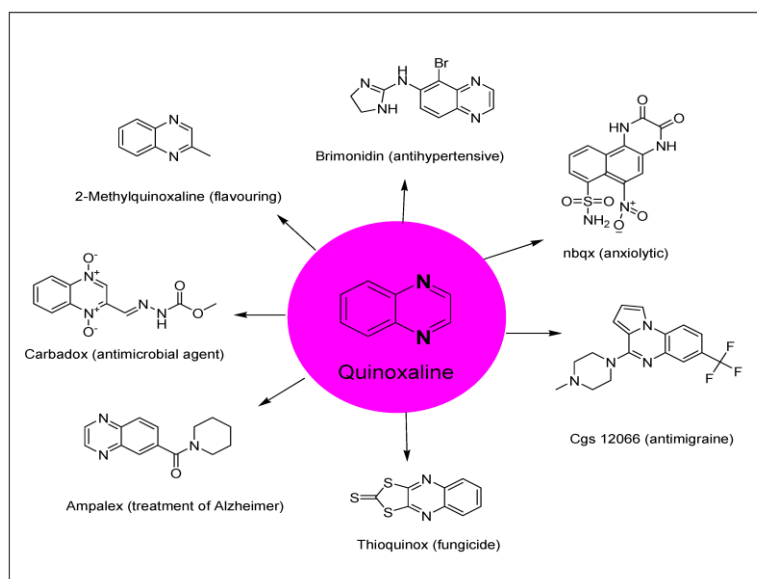
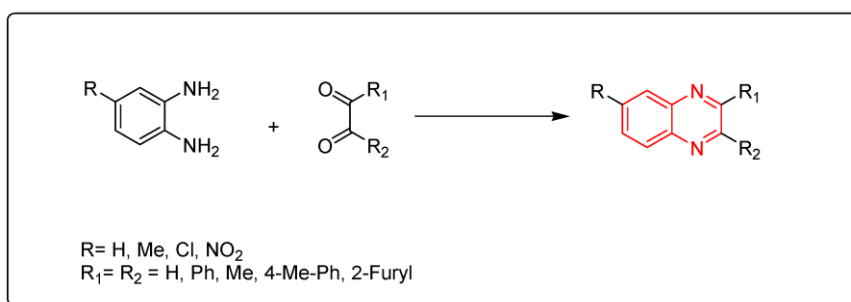


Figure 2. Quinoxaline and examples of its pharmacological activities.^[5]

2. Condensation of *o*-Phenylenediamine and 1,2-Dicarbonyl Derivatives

Korner and Hinsberg in 1884 synthesized the first derivative of quinoxaline through a condensation of *o*-

phenylenediamine with a 1,2-dicarbonyl derivative. Various derivatives were obtained from this reaction (**Scheme 1**)^[6]

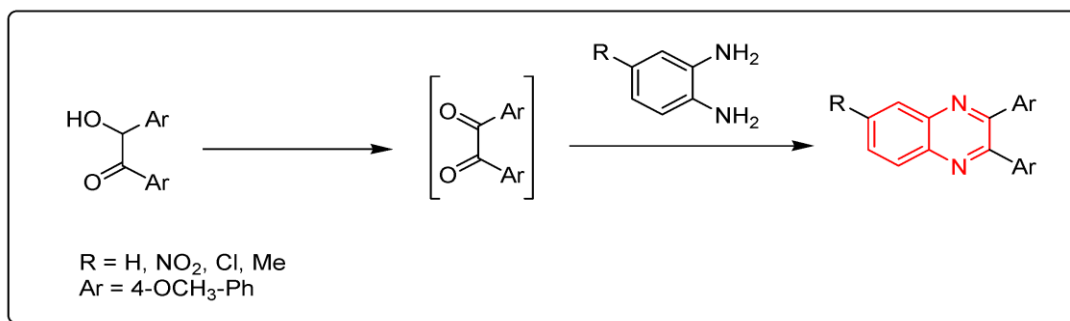


Scheme 1. Synthesis of quinoxaline by the condensation technique: diamine (1 mmol), dicarbonyl (1 mmol), glycerol (5 mL), water (2 mL), 90 °C, 4–6 min, yield (85–91%).

2.1. O-Phenylenediamine and In Situ Produced 1,2-Dicarbonyls

Quinoxalines were synthesized via catalytic iodine, which was used to accelerate the oxidative cyclization

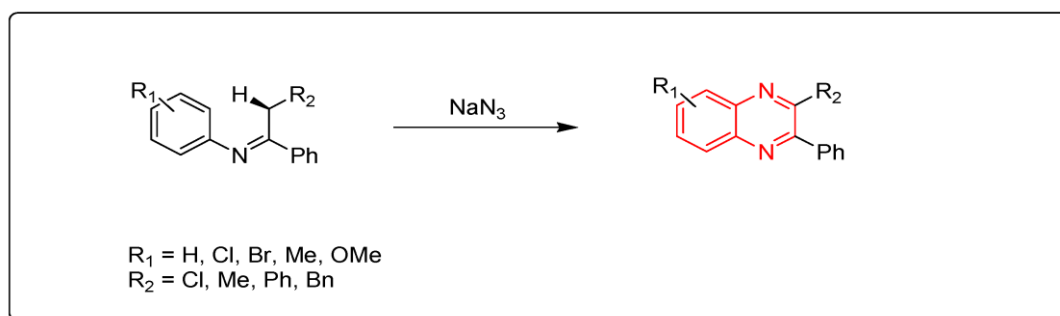
cascade between different 1,2-diamino compounds and hydroxyl ketones ([Scheme 2](#))^[7]



Scheme 2. Synthesis of quinoxaline from o-phenylenediamine and in situ generated 1,2-dicarbonyl derivatives: o-phenylenediamine (1 mmol), hydroxyl ketone (1 mmol), I₂ (0.25 mmol), DMSO (2 mL), RT, 12 h, yield (80–90%).

2.3. Metal-Catalyzed Cyclization of Imines and Azides

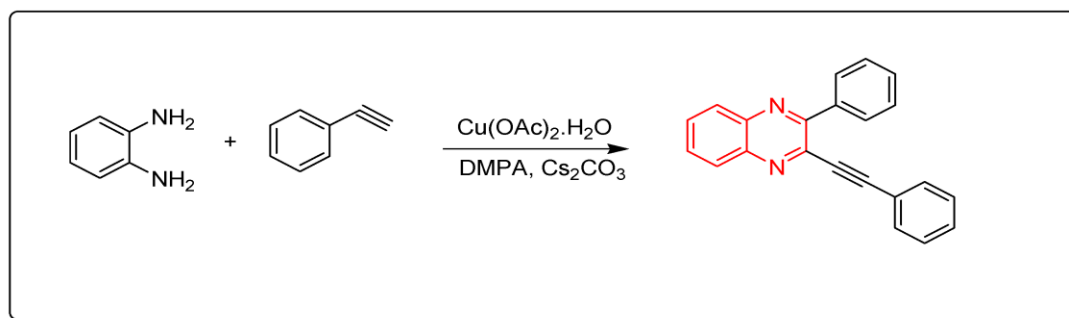
Ketimines and azides were used to create quinoxalines. This is a metal-catalyzed cyclization reaction that produces quinoxaline derivatives ([Scheme 3](#))^[8]



Scheme 3. Synthesis of quinoxalines from imines and azides: imine (1 mmol), sodium azide (3 mmol), (diacetoxyiodo)benzene (3 mmol), CuO (1 mmol), ethylacetate, Rt, 16 h, yield (35–80%).

2.4. Cyclocondensation of o-Phenylenediamine and Aromatic Alkynes

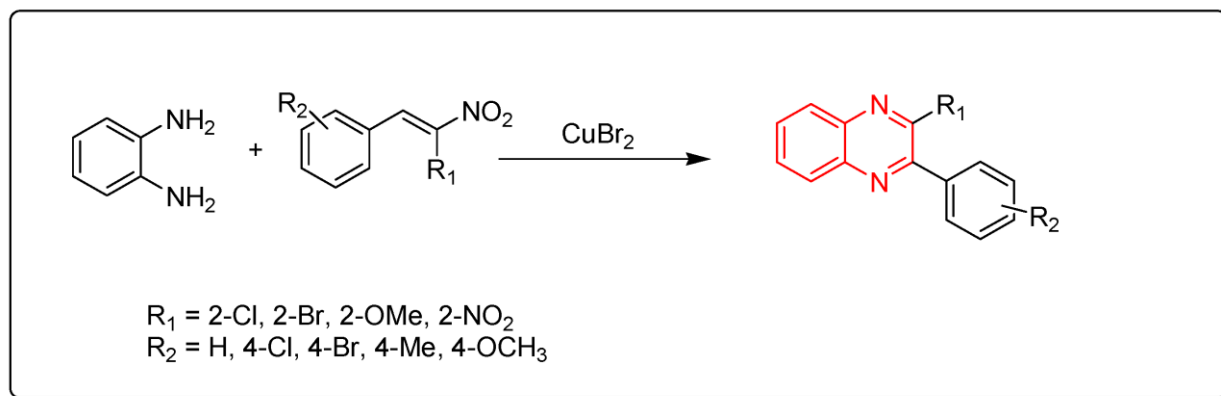
Quinoxalines were synthesized via cyclocondensation of phenylene diamine and aromatic alkynes in the presence of Cu(OAc)₂ as a catalyst ([Scheme 4](#))^[9]



Scheme 4. Synthesis of quinoxalines from aromatic alkynes and amines: o-phenylenedia mine (0.25 mmol) in toluene, phenyl acetylene (1 mmol), Cs₂CO₃ (0.75 mmol), Cu(OAc)₂.H₂O (10 mol % from the o-phenylenediamine), DMPA (0.75 mmol), 70 °C, 8 h, yield (86%).

2.5. Cyclocondensation of o-Phenylenediamine and Nitro-Olefins

Using CuBr_2 as a catalyst, phenylenediamine and nitro-olefins reacted to produce quinoxalines (**Scheme 5**)^[10]

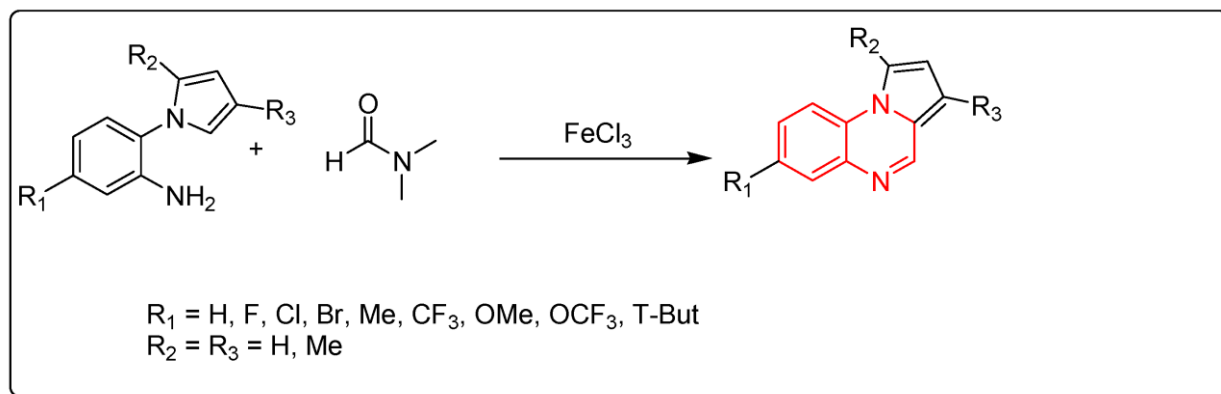


Scheme 5: Synthesis of quinoxalines from nitro-olefins and amines: phenylenediamine (1 mmol), nitro-olefins (1 mmol), CuBr_2 (1 mmol), ethanol, 110 °C, 2–4 h, yield (35–90%).

2.6. Cyclocondensation of Aromatic Amines and DMF

A new strategy for the preparation of pyrrol [1,2-a]quinoxaline derivatives was described by using ferric

chloride as a Lewis acid and an initiator for a straightforward reaction. DMF solvent was used as a source of carbon (**Scheme 6**)^[11]



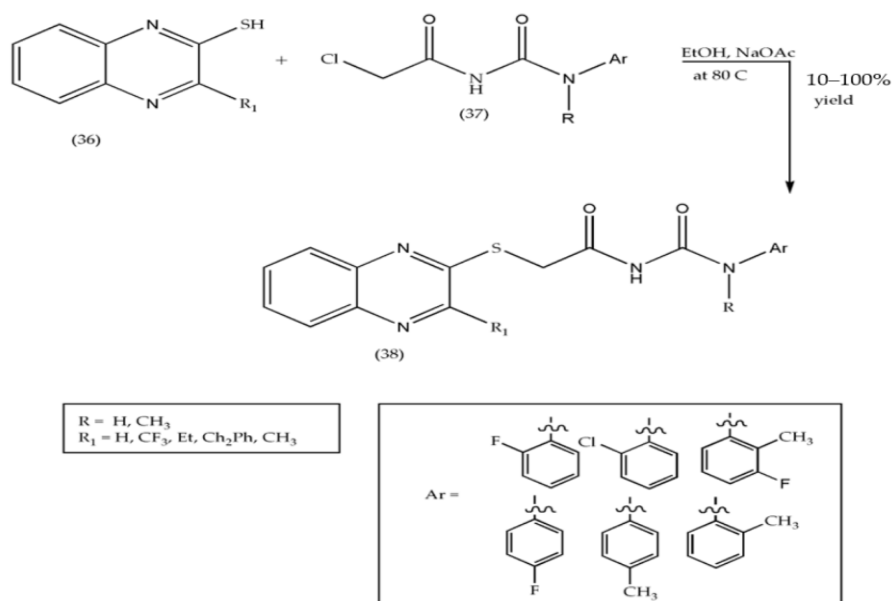
Scheme 6. Synthesis of quinoxalines from amines and DMF in Fe-mediated catalyst: aniline derivative (0.3 mmol), DMF (2 mL), FeCl_3 (0.3 mmol), TBPB (0.9 mmol), 120 °C, 5–12 h, yield (40–97%).

3. Synthetic Pathways to Prepare Biologically Active Quinoxaline Derivatives

3.1. Synthesis of Quinoxalin-2-Mercaptoacetyl Urea as Antiviral Agents

A pandemic situation in western Africa infected almost 28,000 individuals in 2014–2015 (WHO: Ebola situation report 2015). Even though vaccines are existing, it adversely affects some patients; therefore, it becomes requisite to formulate new antiviral drugs and vaccines. A series of quinoxaline-2 mercaptoacetyl urea analogs was devised by Loughran *et al.*^[12] and tested for their antiviral properties on Marburg, Ebola VP40 VLP budding assays in HEK293T cells. The reaction **Scheme 7** depicts the formulation of the target compound by alkylation of quinoxaline thiols with α -chloroacetamidoureas. The alkylating agents^[17] were attained via the reaction of commercially available

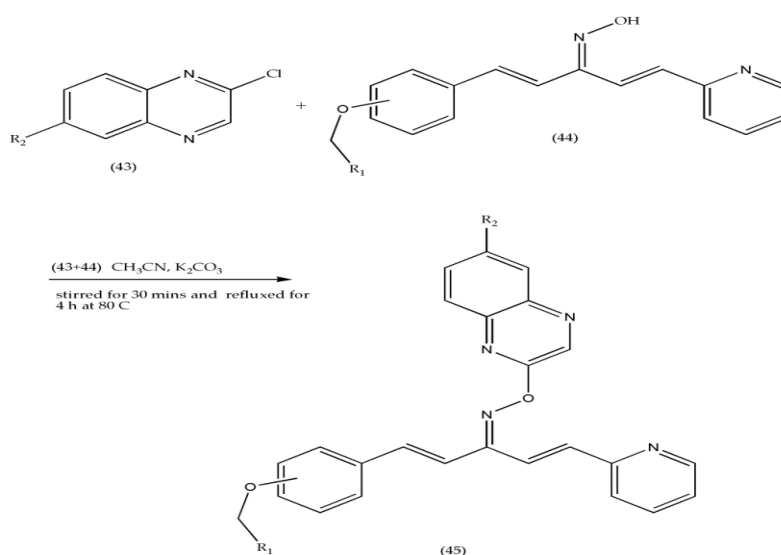
anilines or heteroaromatic amines (R-NH-Ar) with commercially available chloroacetyl isocyanate.^[13]

Scheme 7. Synthetic pathway to prepare quinoxalin-2-mercaptoacetyl urea.^[14]

3.2. The synthesized product quinoxalin-2-mercaptoacetyl urea showed improved potency as an RNA viral egress inhibitors and inhibited live virus egress (VSVM40). Synthesis of Penta-1,4-dien-3-one Oxime Containing a Quinoxaline Nucleus as Antiviral Agents

A well-known plant virus is known as the Tobacco mosaic virus (TMV), which is known to infect nine plant species, including tobacco, tomato, pepper, and cucumbers^[15] Controlling plant diseases, once infected, is a severe problem faced by agriculture industries. Traditional antimicrobial agents and plant virucides have caused resistance in plant pathogens; therefore, a synthesis of safe agricultural chemicals is always in demand. The agricultural chemicals derived from natural products are environmentally friendly and have unique

bioactivities. synthesized a series of penta-1,4-dien-3-one oxime comprising a quinoxaline moiety, equivalent to curcumin isolated from plant *Curcuma Longa* L. The synthesized compounds displayed antibacterial and antiviral activities, with distinct activity against TMV. As revealed in **Scheme 8**, 2-chloroquinoxaline and penta-1,4-dien-3-one oxime ether^[16] were stirred for 30 min and refluxed for 4 h at 80 °C to get the target compound.^[17] The product is recrystallized with acetonitrile and dichloromethane. Some compounds demonstrated significant, beneficial, protective, and inactivation activity against TMV, with a 50% effective concentration (EC₅₀) of 287.1, 157.6, and 133.0 mg mL⁻¹, respectively. The findings were superior to or equal to those of ningnanmycin (356.3, 233.7, and 121.6 mg mL⁻¹, respectively).^[18]

Scheme 8: Synthetic pathway to prepare penta-1,4-dien-3-one oxime (24) with quinoxaline moiety.^[19]

4. Anticancer Quinoxalines

Kamble and colleagues (2016) created hybrid derivatives of quinoxaline molecules linked with coumarin to test their anticancer potential. Compounds **1** and **2** were tested against 60 cancer cell lines among these derivatives. Compound **1** showed a 55.75% growth inhibition (GI) against a melanoma (MALME-M) tumor

cell line. The SAR of these derivatives showed that unsubstituted aromatic rings ($R_1, R_2 = H$) have a higher activity than other substituents while the electron withdrawing group (Cl) produces higher activity than the electron withdrawing group (Br) and the electron releasing group (CH_3).^[20]

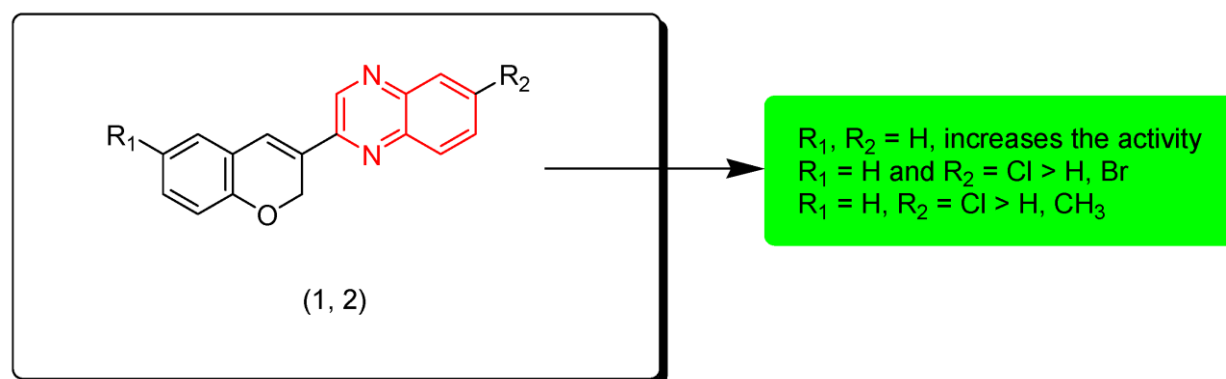


Figure 3: Anticancer quinoxaline 1 ($R_1 = H, R_2 = H$), 2 ($R_1 = H, R_2 = Cl$), and their SAR.

Ali and coworkers (2017) designed and synthesized some quinoxaline derivatives with a triazole ring. These derivatives were screened for their anticancer activity against leukemia cell lines Ty-82 and THP-1. Compound **3** was the highest active compound. It showed an excellent potency on the two cell lines Ty-82 ($IC_{50} = 2.5 \mu M$) and THP-1 ($IC_{50} = 1.6 \mu M$). The SAR of these derivatives showed that the aliphatic linker CH_2 at

the third position of quinoxaline is essential for the activity while N-linker decreases the activity. Electron releasing groups containing an oxygen atom (OCH_3, OC_2H_5) and phenyl substituents at R_2 decrease the activity while an isopropyl group ($CH(CH_3)_2$) increases the activity. Figure 5 shows the molecular structures of compound **3** and its SAR.^[21]

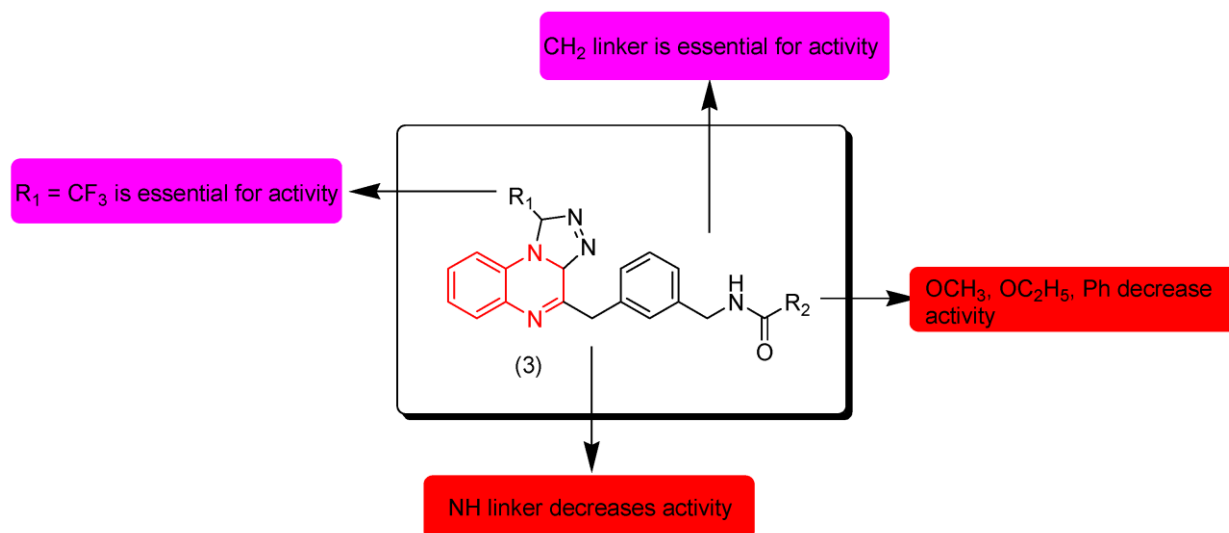


Figure 4: Anticancer quinoxaline 3 ($R_1 = CF_3, R_2 = CH(CH_3)_2$) and its SAR.

5. Quantitative Structure–Activity Relationship (QSAR) Modeling of Anticancer Quinoxalines

anticancer quinoxaline derivatives, a statistically verified 2D-QSAR model was developed by Abdullahi and coworkers (2023). By means of the created model, quinoxaline derivatives were virtually screened, and compound with a high inhibiting capacity ($pIC_{50} = 5.357$) was chosen as the model for the design, and five potential better VEGFR-2 inhibitory compounds (**26–**

30), having pIC_{50} values between 5.43 and 6.16, were created. The intended compounds were used as ligands in docking studies, and the active site residues of VEGFR-2 were discovered to have docking scores ranging from -171.384 to -182.241 kcal/mol, surpassing the score of -170.579 kcal/mol for the template ligand. MD simulation indicated that the ligands remained in the stable docked complex and that the molecules did not leave the VEGFR-2 active site during the 200 ns

simulation.^[22] shows the molecular structure of the model 25 and the designed derivatives while shows the

computed activities of these derivatives.^[23]

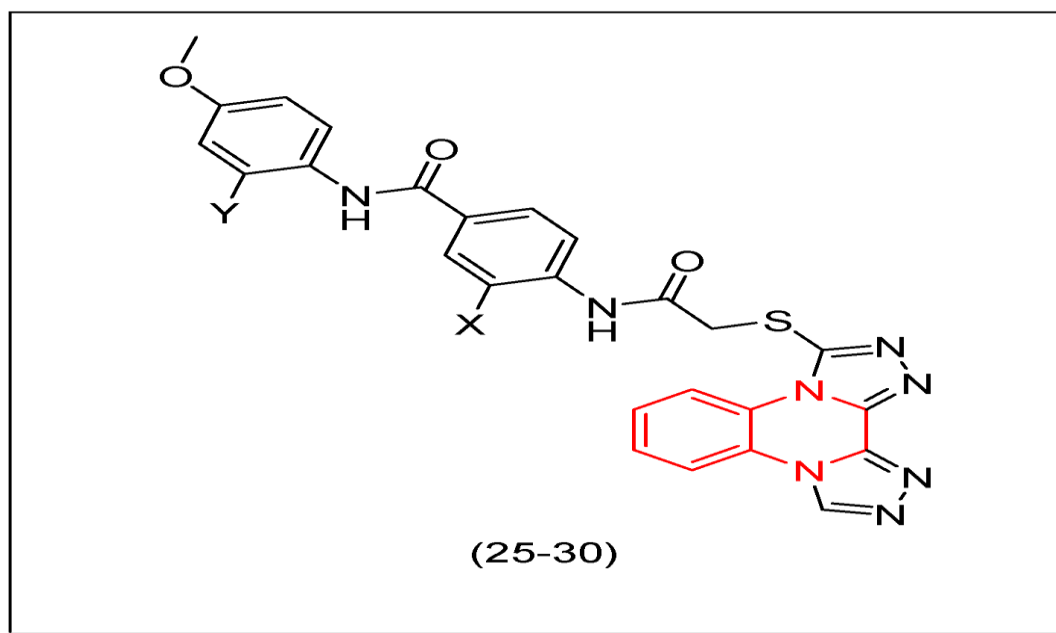


Figure 5: The molecular structure of the model 25 and the designed derivatives (26–30): 25 (Y = H, X = H), 26 (Y = H, X = CH₃), 27 (Y = H, X = OH), 28 (Y = H, X = OCH₃), 29 (Y = H, X = NH₂), 30 (Y = NH₂, X = NH₂).

6. Anti-proliferative agents^[24]

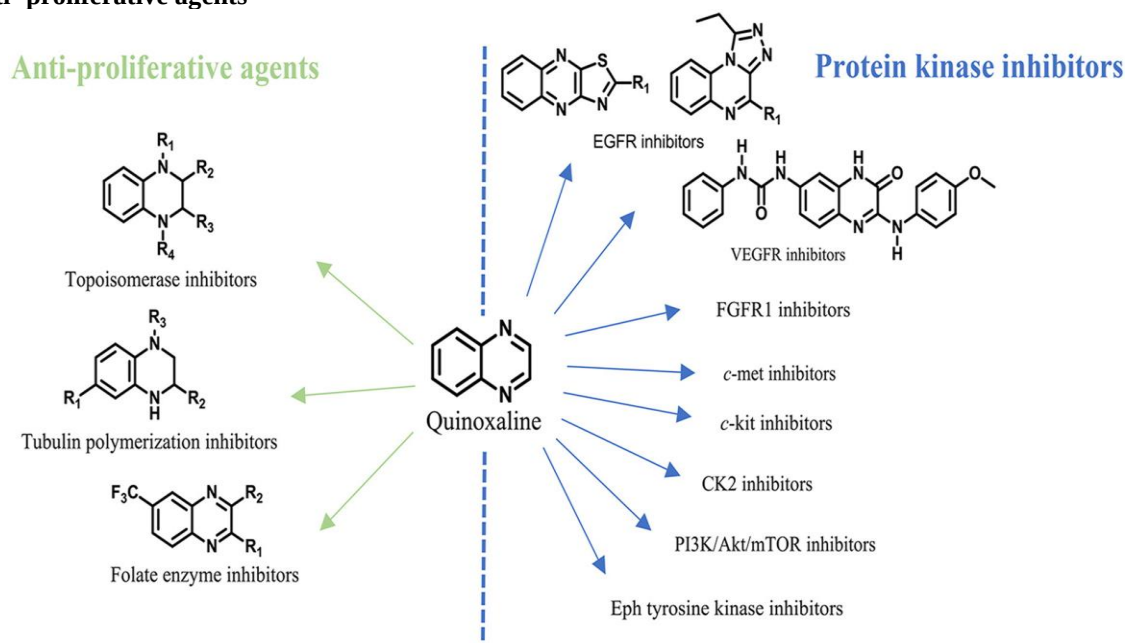


Figure 6: Anti-proliferative agents.^[25]

7. CONCLUSION

The present review showed the escalating interest of organic and medicinal chemists in the synthesis of quinoxaline scaffolds bearing a sulfonamide moiety to target a variety of diseases. The literature survey cited in this article highlighted and revealed that quinoxaline sulfonamide derivatives show a wide array of biological activities, such as antimicrobial, anti-convulsant, anti-inflammatory, anti-leishmania, anti-tumor and

anticancer. Ecofriendly and economical procedures for the synthesis of quinoxaline sulfonamide derivatives were also reported. The structure-based activity findings will be helpful for further modifications on the quinoxaline sulfonamide derivatives. In order to develop future potent therapeutic agents. Their ability to inhibit key enzymes and receptors and their structural adaptability have made them valuable in drug development. Despite these advancements, challenges

remain, particularly in improving their pharmacokinetic properties, such as bioavailability and metabolic stability, and overcoming drug resistance in cancer and microbial treatments. Future research should focus on optimizing drug-likeness, reducing toxicity, and exploring novel delivery systems to enhance their therapeutic impact. Additionally, expanding the application of quinoxaline derivatives into less-explored areas, such as neurological and metabolic disorders, offers further potential. With continued efforts in SAR optimization and innovative molecular designs.

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