



Review

Recent update on catalytic activity of N-heterocyclic carbene supported on graphene nanosheets: A mini review

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ABSTRACT

This mini review examines the latest advancements (2013- up to 2024) in the catalytic properties of N-heterocyclic carbene (NHC) complexes that are supported on graphene nanosheets, emphasizing their importance in improving catalytic efficiency across a range of organic reactions. It explores various innovative strategies, such as the development of ferrocene-tethered NHC-copper complexes and pyrene-tagged NHC-palladacycle complexes, which exhibit exceptional effectiveness in processes like the Suzuki-Miyaura cross-coupling and the N-alkylation of anilines. Importantly, these hybrid materials demonstrate outstanding recyclability, with certain catalysts retaining high activity over numerous cycles, thereby addressing sustainability issues in catalysis. The interactions between NHC complexes and graphene, particularly through π - π stacking, are critical for stabilizing the catalysts and enhancing their performance. Furthermore, the review highlights how these approaches align with green chemistry principles, showcasing high carbon efficiency and minimal environmental impact. The findings indicate that NHC-supported catalysts not only propel advancements in catalysis but also aid in the creation of environmentally friendly synthetic methods. In summary, this mini review offers a thorough overview of the progress made in NHC-supported catalysts, highlighting their potential for practical applications in organic synthesis and their contribution to fostering sustainable practices within the chemical industry.

1. Introduction

Carbenes are carbon compounds with two coordination number that are electron-deficient, characterized by the presence of two non-bonding electrons on the carbon atom [1,2]. The pursuit of a stable carbene was historically viewed as an unrealistic goal, until Wanzlick demonstrated that the presence of vicinal amino substituents could significantly enhance the stability of carbenes [3,4]. At that time, the isolation of a 'monomeric' carbene was not accomplished [5–7]. The first isolation of a 'monomeric' N-Heterocyclic Carbene (NHC) was reported in 1991 by Alfred L. E. in their work with 1,3-dimethylimidazol-2-ylidene [8]. NHCs boast a significant history, having been first isolated in the 1990s [8–12]. They have since emerged as crucial components in synthetic

chemistry, attributed to their distinctive electronic characteristics and adaptability [13–17]. Their significance is underscored by their function as organocatalysts and ligands in organometallic complexes, enabling a diverse array of catalytic reactions with exceptional regioselectivity and stereoselectivity [18,19]. The progress in their development has coincided with advancements in organometallic chemistry [20–22]. NHCs act as effective σ -donors, providing stabilization to reactive intermediates [23–25]. NHCs can donate a pair of electrons from their lone pair to the empty molecular orbital of a metal center, forming a coordinate bond. The σ -bond formed is a result of this electron donation, and it enhances the electron density around the metal center and increasing the electron density around a metal, and leads to enhancing its reactivity. They are employed in various catalytic processes,

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improving both reaction efficiency and selectivity [26–32]. The structures of the most frequently used carbene ligands are illustrated in Fig. 1. The achievements of NHCs are frequently linked to their robust σ -electron-donating characteristics, which facilitate the formation of strong NHC-metal bonds and inhibit the breakdown of the catalyst. NHCs are effective electron donors, meaning they can donate electrons to a metal center through σ -bonding. This donation increases the electron density around the metal. In addition, the strong σ -donor ability of NHCs leads to the formation of stable NHC-metal bonds. This stability is crucial for efficient catalysis, as it enables the metal to remain bound to the NHC during the catalytic cycle. NHCs help prevent the metal from undergoing deactivation or breakdown during the catalytic process. This contributes to the longevity and effectiveness of the catalyst, making it more reliable and efficient over time. Therefore, the strong electron-donating ability of NHCs ensures stable metal complexes that enhance the performance and longevity of catalysts in various chemical reactions.

NHCs have become essential instruments in synthetic chemistry, celebrated for their adaptability and effectiveness across a variety of chemical processes [33–35]. These stable carbenes, noted for their distinctive electronic characteristics, greatly improve the reactivity of different substrates and intermediates [36,37]. Recent research has shed light on the function of NHCs in enhancing transition metal catalysis, especially in cross-coupling reactions, where they act as ligands that facilitate the creation of metal complexes [38–43]. For example, the application of NHCs in palladium-catalyzed reactions has been thoroughly documented, showcasing enhanced reaction rates and selectivity in the production of biaryl compounds [44–46]. NHCs have also found applications in asymmetric catalysis, demonstrating their capability to facilitate enantioselective transformations [47,48]. Their effectiveness in stabilizing reactive intermediates has paved the way for innovative catalytic systems, particularly in C–H activation and functionalization reactions [49–51]. Research conducted by Bode and his team highlights the potential to tailor NHCs to adjust steric and electronic characteristics, thereby providing improved control over the results of chemical

reactions. NHCs have extended their utility beyond catalysis into the realm of materials science, especially in the creation of metal-organic frameworks (MOFs) and coordination polymers [52–54]. They play a significant role in designing materials with adjustable properties suitable for gas storage and separation. Furthermore, their ability to stabilize organometallic complexes has paved the way for the synthesis of intricate organic molecules, highlighting their potential in synthetic pathways that were once limited by the instability of conventional organometallic reagents. The progress in NHC chemistry is enhanced by cutting-edge synthetic techniques, particularly the application of NHCs in the development of various molecular frameworks via processes like NHC-mediated carbene transfer and cyclopropanation. In summary, the growing range of NHC applications in synthetic chemistry highlights their significance as adaptable reagents, facilitating numerous reactions and playing a crucial role in the advancement of contemporary chemical synthesis. Furthermore, Fig. 2 shows different application fields that NHC have been used.

Graphene, consisting of a single layer of carbon atoms arranged in a two-dimensional lattice, has attracted considerable interest in recent years due to its exceptional electrical, thermal, and mechanical properties [55]. Graphene oxide (GO), a modified variant of graphene characterized by the presence of oxygen-containing functional groups, has emerged as a significant subject of interest in materials science due to its exceptional properties and wide-ranging potential applications [56]. The functionalization of GO improves its solubility and compatibility with different substrates, positioning it as an excellent candidate for the development of advanced hybrid materials. A notable advancement in this area is the integration of NHCs onto the surfaces of GO, which has demonstrated considerable potential by merging the remarkable electronic and mechanical characteristics of graphene with the diverse chemistry of NHCs. NHCs are recognized for their strong σ -donor abilities and their capacity to stabilize reactive intermediates, which can significantly enhance the catalytic activity and selectivity of transition metal complexes, thereby improving performance across

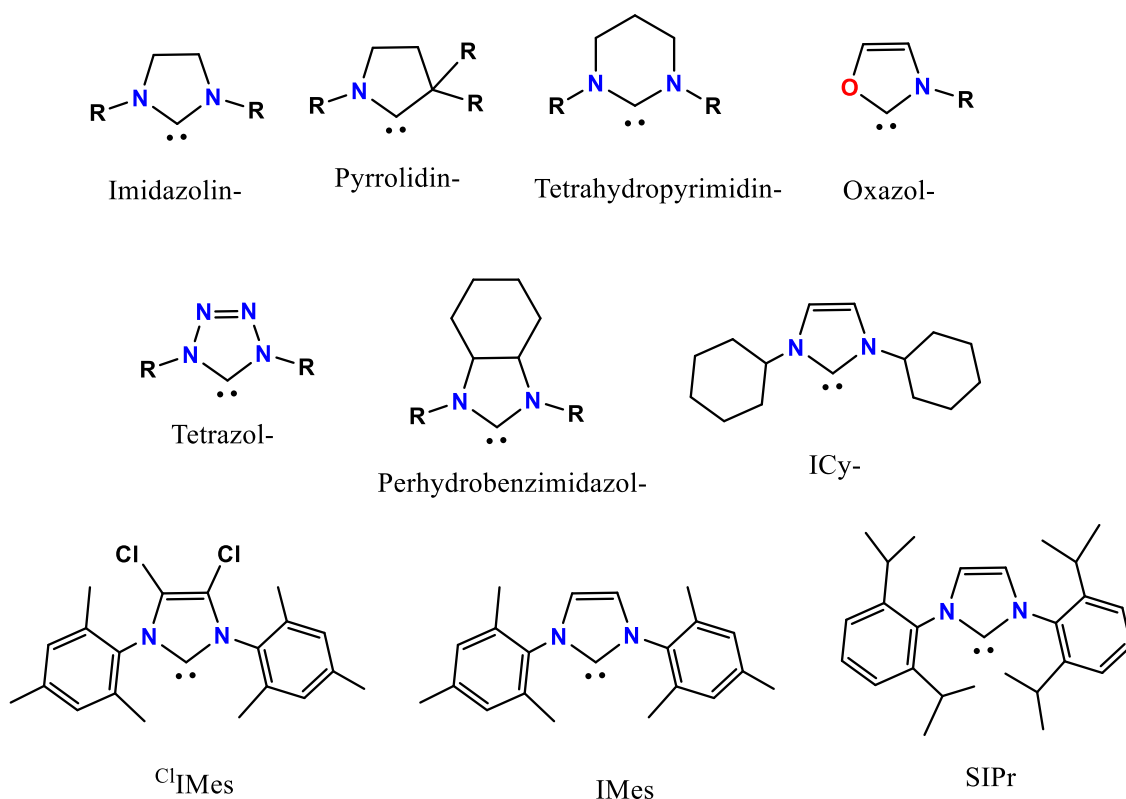


Fig. 1. Chemical structure of some N-heterocyclic carbene.

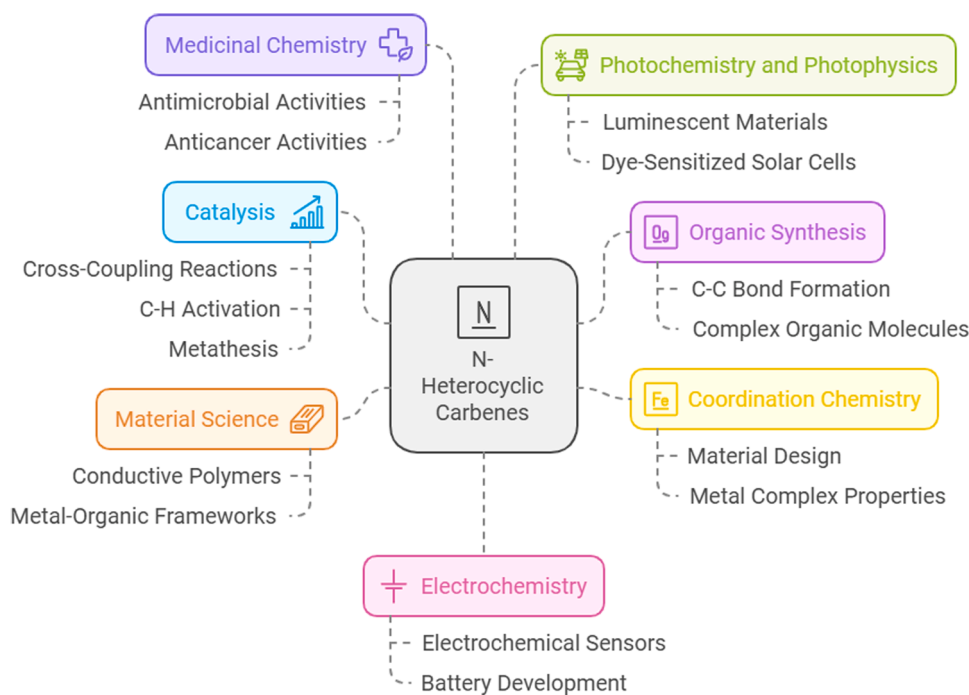


Fig. 2. Diverse application of NHC.

various chemical reactions [57–61].

Recent research has shown that NHC-functionalized GO can support a range of processes, including catalysis, sensing, and energy storage [62–64]. By adjusting the electronic and steric properties of NHCs on the GO framework, scientists have observed increased stability and reactivity of catalysts, facilitating efficient organic transformations. This hybrid material not only capitalizes on the superior attributes of graphene but also harnesses the unique features of NHCs to develop innovative platforms for catalysis and functional materials. As the field progresses, it is crucial to comprehend the relationship between NHC and GO to enhance their synergistic properties and broaden their uses in synthetic chemistry and other areas. Tethering NHC (N-Heterocyclic Carbene) ligands to graphene involves several techniques, primarily aimed at functionalizing the graphene surface for enhanced properties in applications like catalysis, sensing, and electronics. Here are the most common approaches: 1-Covalent Bonding: 1a-Direct Attachment: NHCs can be directly attached to the graphene surface via covalent bonds. This often involves reactions between the NHC and functional groups on modified graphene (e.g., epoxy, carboxyl groups). 1b-Click Chemistry: Utilizing click chemistry (like azide-alkyne cycloaddition) allows for efficient and selective attachment of NHCs to graphene. This approach often uses intermediates that have been previously functionalized onto the graphene surface. 2-Functionalization of GO: 2a-Reduction Methods: Graphene oxide can be reduced to create defects or functional groups that can be reacted with NHCs. The reduction can also enhance the electronic properties of graphene while providing sites for tethering. 2b-Esterification or Amidation: Carboxylic groups on GO can be converted to esters or amides with NHC-containing molecules through esterification or amidation reactions, creating strong bonds between the ligand and graphene. 3- Self-Assembly: 3a-Monolayer Formation: NHCs can be designed to form self-assembled monolayers on graphene surfaces. This method exploits the strong π - π interactions and electrostatic attractions between the ligands and the graphene. 4-Chemical Vapor Deposition (CVD): For larger scale production, CVD can be used to grow graphene while simultaneously depositing NHC ligands in a controlled manner, resulting in a hybrid material with specific properties. 5- Pyrolysis of Precursor Materials: Precursor materials containing both graphene and NHC functional groups can be pyrolyzed to convert them into

graphene with embedded NHC ligands. This method allows for significant control over the ligand distribution. Each of these methods offers unique advantages and can be selected based on the desired properties of the graphene-NHC composite (Fig. 3).

This review seeks to consolidate recent discoveries regarding the synthesis, characterization, and functional applications of NHCs supported on GO, paving the way for future investigations into their capabilities in advanced catalytic systems, nanocomposites, and sensor technologies. By connecting these two exceptional materials, we aim to offer insights into how their integration can foster advancements in both fundamental research and practical applications. This review seeks to examine the recent progress in graphene-NHC systems between 2013 and 2024, focusing on their synthesis, characterization, and potential applications in catalysis, sensors, and more, while also discussing the fundamental mechanisms that contribute to their enhanced performance.

1.1. Catalytic activity of N-Heterocyclic carbene-graphene in carbon-carbon coupling reaction

The quest for effective strategies in carbon-carbon (C–C) bond formation remains a central focus in synthetic organic chemistry, impacting fields such as pharmaceuticals, agrochemicals, and materials science [65–67]. NHCs have gained recognition as potent ligands in catalysis, especially in reactions mediated by transition metals, owing to their distinctive electronic characteristics and capacity to stabilize reactive intermediates. When these carbenes are immobilized on graphene, they create a hybrid material that significantly enhances catalytic efficiency. The integration of graphene, known for its remarkable electrical conductivity and extensive surface area, aids in the distribution and stability of NHCs, resulting in heightened reactivity and selectivity in C–C coupling reactions. Recent research has shown that NHC-graphene composites can markedly increase catalytic performance in essential coupling reactions, including Suzuki, Sonogashira, and Heck reactions. This introduction explores the critical function of NHC-modified graphene in promoting C–C bond formation, emphasizing their mechanistic insights, advantages over conventional catalysts, and potential for future advancements in sustainable organic synthesis.

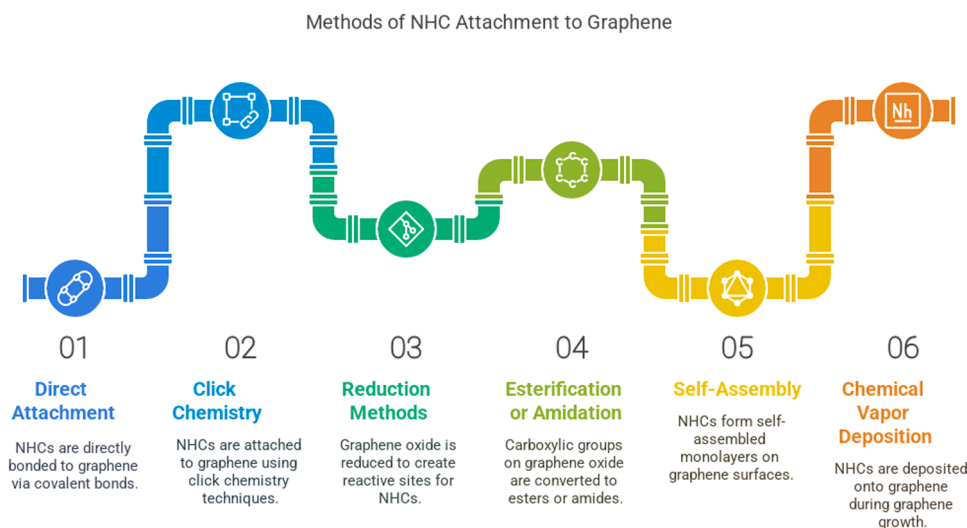


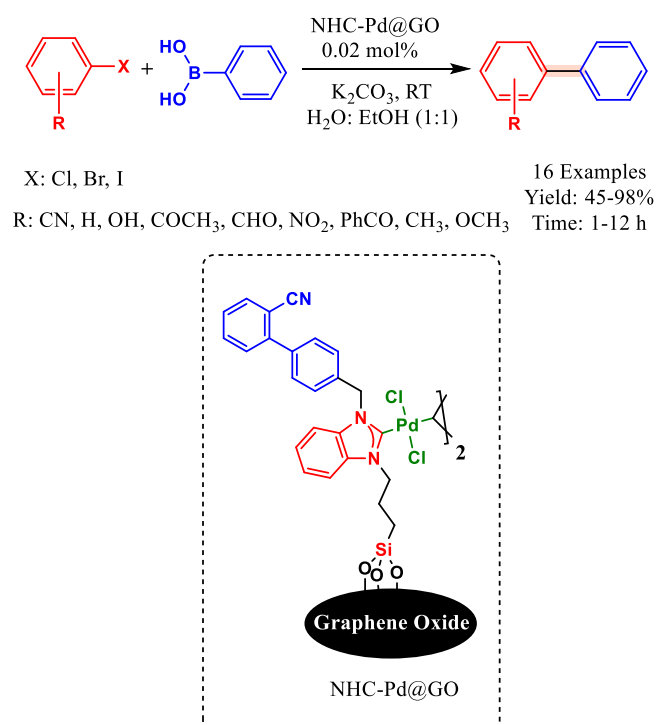
Fig. 3. Most common approaches to tethering NHC ligands to graphene.

In 2020, Kandathil et al. introduced a novel and effective NHC-palladium(II) complex that is immobilized on GO, referred to as NHC-Pd@GO (Scheme 1) [68]. This heterogeneous catalyst was thoroughly characterized through a variety of techniques, including, ICP-OES, FTIR, EDS, FESEM, TGA, TEM, XRD, and BET. The NHC-Pd@GO catalyst demonstrated remarkable stability in air and moisture, proving to be highly effective in facilitating the Suzuki–Miyaura cross-coupling reaction between phenylboronic acid and different aryl halides (bromides, chlorides, and iodides). Optimal results for these organic transformations were achieved using aqueous ethanol and aqueous methanol as solvent systems, respectively, with minimal catalyst loading under mild reaction conditions. Additionally, the NHC-Pd@GO catalyst was easily recoverable and could be reused at least eleven times for the Suzuki–Miyaura cross-coupling and nine times for the reduction of nitroarenes, all while maintaining significant catalytic activity. The

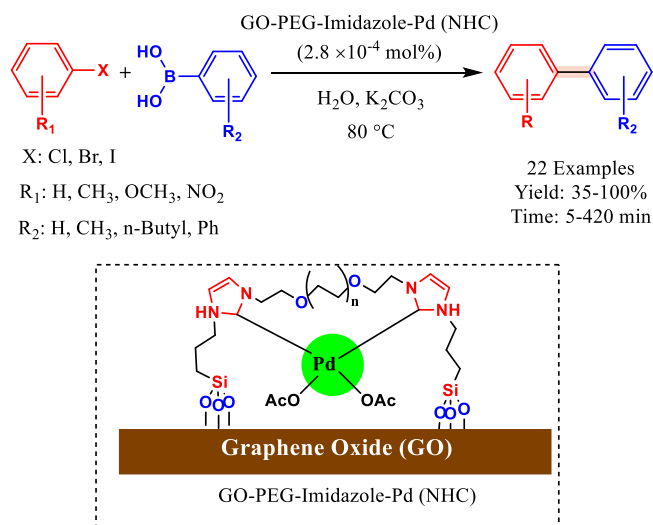
catalyst's stability and selectivity during recycling highlight its potential for practical applications in various organic transformations. The novel palladium complexes based on NHC can be synthesized and immobilized on GO using this protocol. These complexes are applicable in a range of organic transformations, including the Mizoroki–Heck reaction, Sonogashira–Hagihara coupling reaction, oxidation reactions, as well as Suzuki–Miyaura cross coupling and the reduction of nitroarenes.

In 2019, Heravi et al. demonstrated that GO can serve as an effective surface when immobilized with water-soluble poly(ethylene glycol)-imidazole, followed by the addition of PdCl₂ salt to create the desired catalyst (Scheme 2) [69]. The catalytic efficiency of this composite was evaluated in the Suzuki–Miyaura cross-coupling reaction under mild conditions. The catalyst's hydrophilic properties and the uniform distribution of palladium contributed to its enhanced catalytic performance in aqueous media. Furthermore, the Suzuki–Miyaura reaction was successfully carried out, and reduced reaction times, with no loss of activity observed even after seven consecutive cycles.

In 2019, Karami et al. synthesized a pyrene-tagged NHC palladacycle complex ([Pd]([C,N]C₆H₄CH₂NH(Et)](Imd-P)Br)] through the reaction of imidazolium salt with a dimer ([Pd₂[(C,N)C₆H₄CH₂NH(Et)]₂(μ-OAc)₂]). This complex was subsequently immobilized on reduced



Scheme 1. Suzuki–Miyaura cross coupling reaction catalyzed by NHC-Pd-GO.

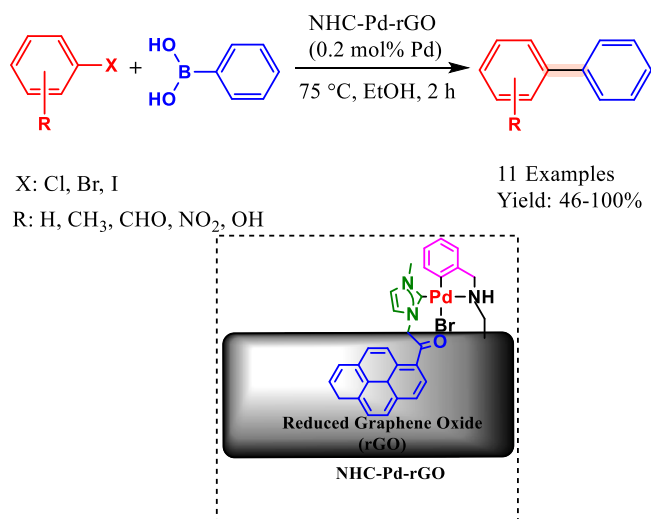


Scheme 2. Suzuki–Miyaura cross coupling reaction catalyzed by GO-PEG-Pd (NHC).

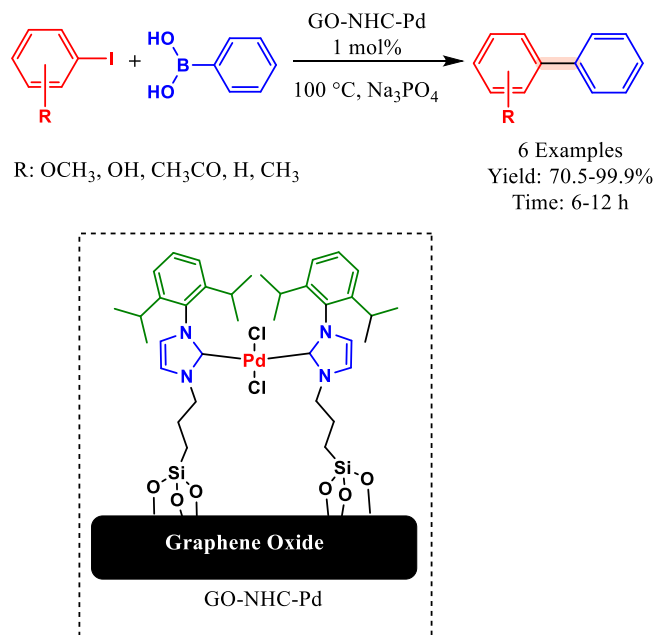
graphene oxide (rGO) using π - π stacking interactions (Scheme 3) [70]. The resulting hybrid compound ((NHC)Pd-rGO) was created in a single-step process. A variety of characterization techniques were utilized to analyze the compound, and computational studies were conducted to confirm the interaction between the palladium complex and rGO. The catalytic performance of both the molecular complex and the hybrid material was assessed in Suzuki–Miyaura cross-coupling reactions. Notably, the hybrid material exhibited improved catalytic activity compared to its homogeneous counterpart, indicating that rGO significantly enhances catalytic performance. Hot filtration tests demonstrated the heterogeneous nature of the catalyst, attributed to the strong interaction between pyrene and graphene. Furthermore, the hybrid (NHC)Pd-rGO material was shown to be recyclable up to six times without any loss in catalytic efficiency.

In 2017, Kim et al. introduced recyclable Pd-complexed GO catalysts featuring a bulky NHC ligand (GO/NHC-Pd) for a range of cross-coupling reactions conducted in an aqueous environment (Scheme 4, Scheme 5, Scheme 6) [71]. The synthesis of GO/NHC-Pd involved the combination of an NHC precursor with a trimethoxy-silane linker on the GO surface through a condensation reaction, followed by the chelation of Pd onto GO/NHC. These GO-based catalysts were utilized in three types of cross-coupling reactions Suzuki, Heck, and Sonogashira in the aqueous phase to assess their catalytic efficiency. Additionally, the reusability of the catalysts was evaluated through five consecutive cross-coupling reactions. Each step of the synthesis of GO/NHC-Pd catalyst was characterized using FT-IR and SEM analyses. Based on the pointed characterization analysis, the Pd (II) ions was coordinated on GO/NHC without the formation of Pd nanoparticles. The optimal inorganic bases identified for the Suzuki and Heck reactions were Na_3PO_4 and K_2CO_3 , respectively, tailored to specific reaction conditions. Various aryl iodide substrates were successfully cross-coupled in the aqueous phase, yielding GC results of 86–99.9 % for Suzuki reactions with phenylboronic acid and 55–97 % for Heck reactions with styrene. Furthermore, the GO/NHC-Pd catalyst demonstrated moderate yields of 55.4–69.9 % in coupling reactions involving several phenyl iodides and phenyl acetylene, using piperidine as a base. Ultimately, the GO/NHC-Pd catalysts were recycled during the Suzuki and Heck reactions, maintaining their performance over four consecutive cycles. This GO/NHC-Pd catalyst holds promise for further eco-friendly applications in the production of valuable pharmaceuticals.

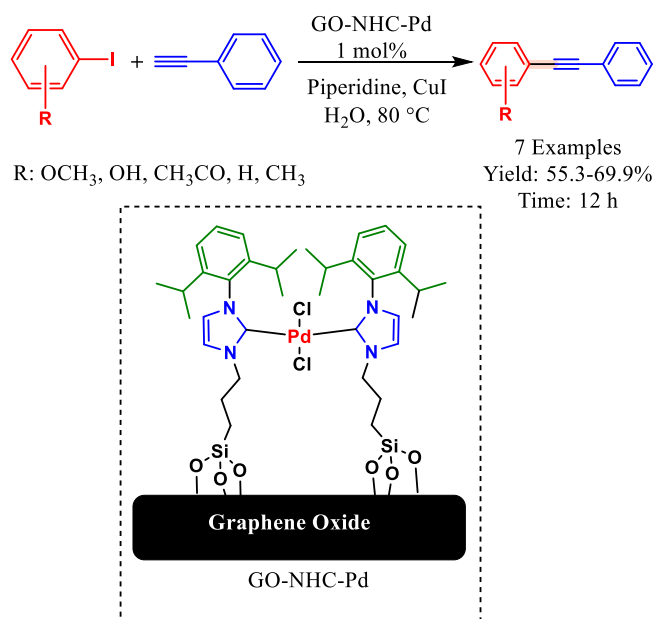
In 2014, Kazemi Movahed et al. developed an N–Heterocyclic carbene palladium complex that was immobilized on GO and incorporated into an ionic liquid framework (NHC-Pd/GO-IL) through a silylation reaction to modify the GO (Scheme 7) [72]. The resulting catalyst



Scheme 3. Suzuki-Miyaura cross coupling reaction catalyzed by NHC-Pd-rGO.



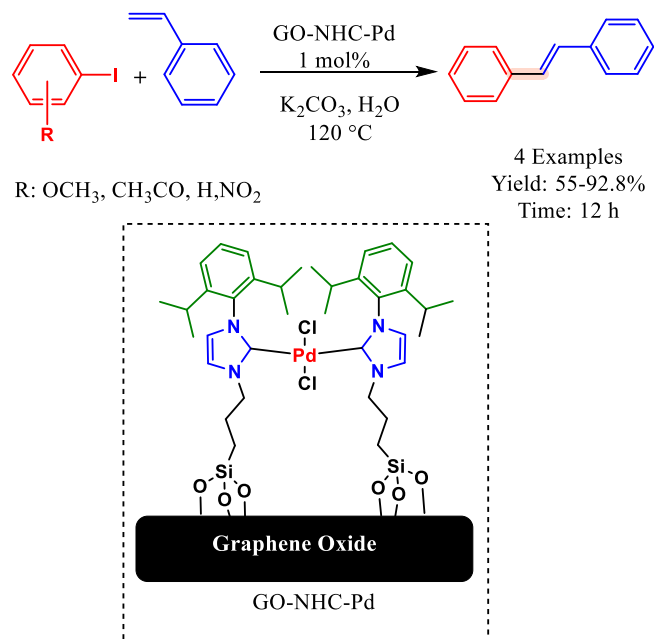
Scheme 4. Suzuki-Miyaura cross coupling reaction catalyzed by GO–NHC-Pd.



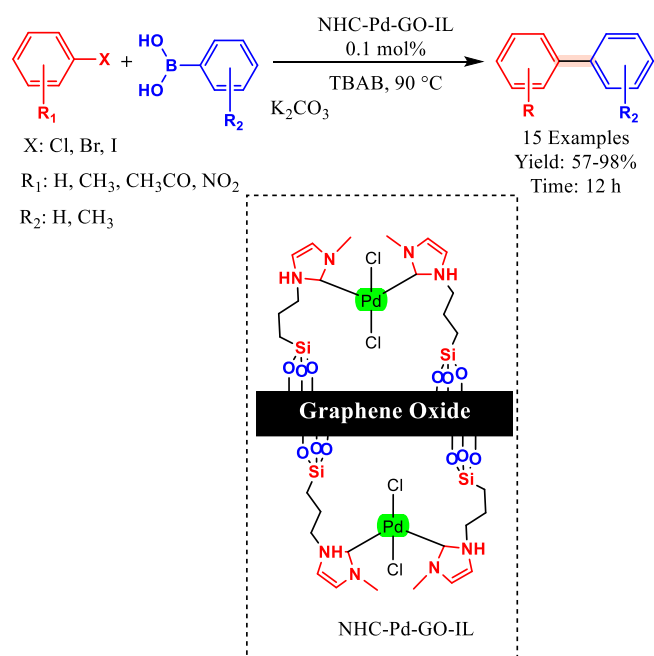
Scheme 5. Sonogashira cross coupling reaction catalyzed by GO–NHC-Pd.

demonstrated significant activity in the Suzuki reaction conducted in a volume ratio (1:1) of mixture of ethanol and water. The nanocomposite demonstrated excellent catalytic performance in the Suzuki coupling of various activated and deactivated aryl halides with aryl boronic acids (yield: 57–98 %). Leaching tests, including hot filtration and atomic absorption spectroscopy (AAS) analysis, suggest that the catalytic process is predominantly heterogeneous. This catalyst exhibits high reusability, allowing for multiple cycles of use without a significant loss in catalytic efficiency. Additionally, the TEM image of the recovered catalyst reveals a uniform distribution of Pd nanoparticles on the GO-IL sheets, with no signs of aggregation. Ongoing research in the laboratory is exploring further applications of this catalytic system in other palladium-catalyzed reactions.

In 2014, Park et al. developed a GO functionalized with an NHC precursor, specifically 3-(3-aminopropyl)-1-methylimidazolium



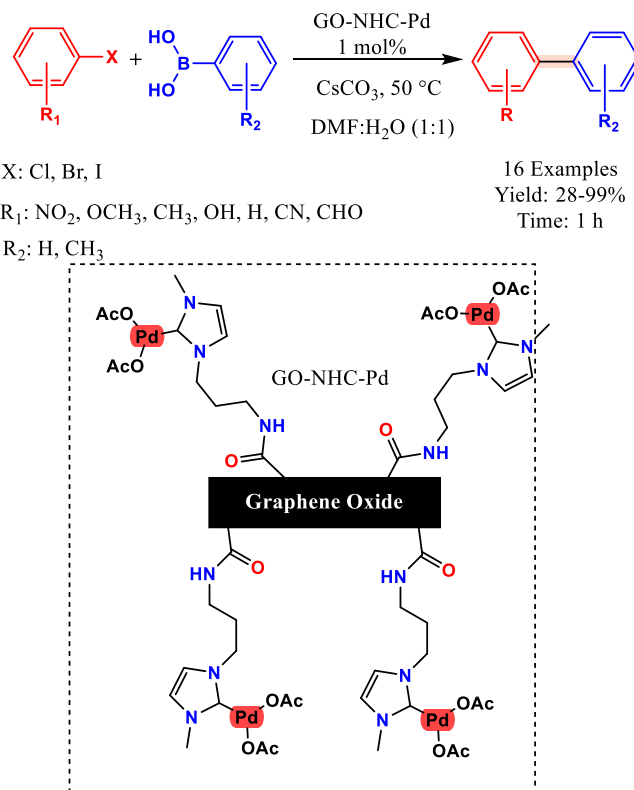
Scheme 6. Heck-Mizoroki cross coupling reaction catalyzed by GO-NHC-Pd.



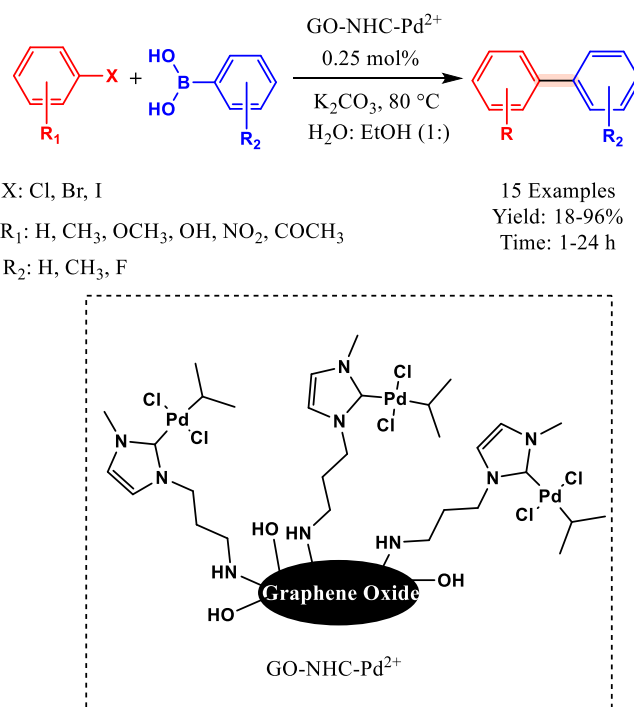
Scheme 7. Suzuki-Miyaura cross coupling reaction catalyzed by NHC-Pd-GO-IL.

bromide ([APMim][Br]), to facilitate the immobilization of a palladium catalyst (Scheme 8) [73]. The resulting GO-supported NHC precursor (IMGO) established a stable complex with Pd(OAc)₂, referred to as GO-NHC-Pd. This complex demonstrated remarkable catalytic performance and rapid reaction kinetics during the aqueous-phase Suzuki reaction involving aryl bromides and chlorides under relatively mild conditions (1 hour at 50 °C). Notably, the GO-NHC-Pd catalyst maintained its catalytic efficiency across multiple reuse cycles (5 runs) in the Suzuki reaction of aryl bromides.

In 2013, Shang et al. successfully immobilized an N-heterocyclic carbene-palladium complex (NHC-Pd²⁺) onto GO using a chemical bonding technique for the first time (Scheme 9) [74]. The resulting



Scheme 8. Suzuki-Miyaura cross coupling reaction catalyzed by GO-NHC-Pd.

Scheme 9. Suzuki-Miyaura cross coupling reaction catalyzed by GO-supported NHC-Pd²⁺.

composite, known as GO-supported NHC-Pd²⁺, was thoroughly characterized using transmission electron microscopy, XRD, XPS, and infrared spectroscopy. The study revealed that the GO-supported NHC-Pd²⁺ serves as an effective catalyst for Suzuki-Miyaura coupling reactions, achieving product yields between 83 % and 96 %.

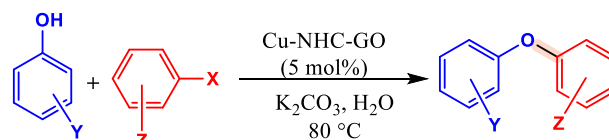
Furthermore, the catalyst demonstrated the ability to be easily recovered and reused for at least six consecutive cycles with minimal loss of catalytic performance (1st run: 94 % and 6th run: 90 %).

1.2. Catalytic activity of N-Heterocyclic carbene-graphene in heteroatom arylation and alkylation

The incorporation of heteroatoms into aromatic frameworks through methods such as arylation and alkylation is essential for the development of biologically active substances and advanced materials [75]. NHCs are recognized for their robust σ -donor characteristics and their ability to stabilize transition metals, making them highly effective ligands for facilitating these reactions [76]. When linked to graphene, NHCs form a composite that leverages the stability and adjustable properties of the carbene alongside the high surface area and conductivity of graphene. This synergy significantly enhances catalytic performance in heteroatom arylation and alkylation processes, allowing for efficient coupling with a diverse range of electrophiles. Recent progress in this field has shown that NHC-graphene hybrids not only accelerate reaction rates and improve selectivity but also expand the range of substrates that can be utilized compared to conventional homogeneous catalysts. This overview emphasizes the cutting-edge approaches in employing NHC-graphene systems for heteroatom functionalization, with a focus on their mechanistic insights and potential uses in the creation of pharmaceuticals, agrochemicals, and other specialty chemicals.

In 2023, Imanpour et al. developed GO that was modified with 1,1'-((ethane-1,2-diylbis(oxy))bis(ethane-2,1-diyl))bis(3-(3-(triethoxysilyl)propyl)-1H-imidazol-3-ium) chloride ionic liquid, serving as a 2e-donor NHC ligand to enhance the decoration and stabilization of copper species [60]. Copper chloride (CuCl) salt was anchored onto the ionic liquid-modified surface of graphene, resulting in a copper/N-heterocyclic supported GO composite. The ligand structure and final catalyst were characterized using various analytical techniques, including NMR, FTIR, TEM, TGA, CHN, SEM, and ICP-OES. The successful immobilization of Bis-Im-IL onto the GO was confirmed through the condensation reaction between the C-OH groups of GO and the alkoxy groups of the ionic liquid, as evidenced by FTIR analysis. The thermal stability of the material improved with the attachment of the ionic liquid to the graphene surface. TEM and SEM imaging revealed wavy-shaped sheets with folded edges for both pure and modified GO. The Cu-NHC/GO catalyst demonstrated significant activity in the O-arylation reactions of phenols with aryl halides, as well as in the O-arylation of azoles (including imidazole, triazole, and pyrazole) with aryl halides in water. This catalytic system achieved high product yields and maintained activity over 8 successful runs for O-arylation and 7 runs for N-arylation reactions (Schemes 10 and 11).

In 2022, Kujur et al. developed a novel N-heterocyclic carbene (NHC) copper(I) complex, designated as GO-NHC-Cu, which is supported on GO [77]. This complex was extensively characterized using a range of instrumental techniques, including FT-IR, XPS, FT-Raman, PXRD, HRTEM, FESEM, EDX, TGA, and ICP-OES. The catalytic performance of the supported complex was investigated in the N-alkylation of anilines with alcohols under solvent-free and aerobic conditions, resulting in the formation of monoalkylated products with yields ranging from good to excellent (20 products, 83–96 %). All synthesized products were isolated and characterized through ^1H and ^{13}C [^1H] NMR spectroscopy. The catalyst was easily recovered from the reaction mixture via simple filtration and demonstrated the ability to be reused for up to five consecutive cycles with minimal loss in catalytic efficiency. Control experiments confirmed that the reaction occurred under aerobic conditions. The green chemistry metrics for this reaction were found to be quite close to ideal values, including carbon efficiency (95.9 %), E-factor (0.15), atom economy (92.14 %), process mass intensity (1.15), and reaction mass efficiency (86.80 %). Notable features of this methodology include the catalyst's air stability, selectivity, recyclability, and the



Y: H, NO_2 , OH, Ph

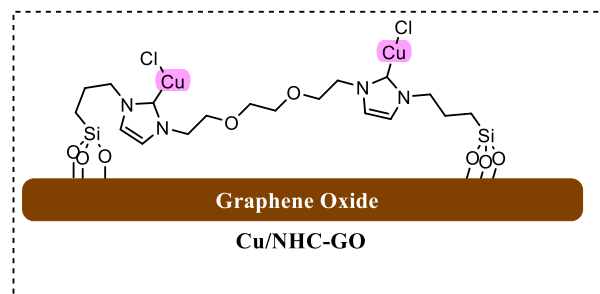
X: Cl, Br, I

Z: H, CH_3 , OCH_3 , CH_3CO , NO_2 , Br, I

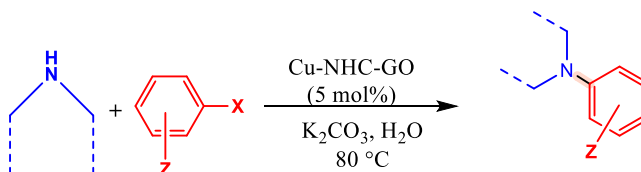
22 Examples

Yield: 50-97%

Time: 4-11 h



Scheme 10. O-Arylation reaction catalyzed by Cu-NHC/GO.



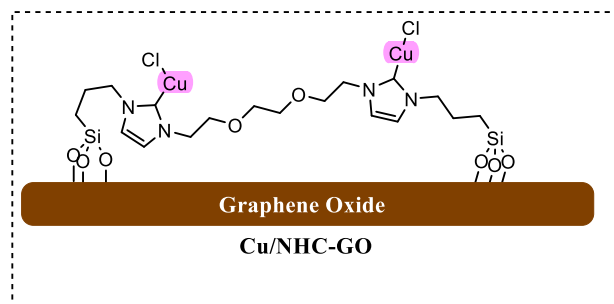
X: Cl, Br, I

Z: H, CH_3 , OCH_3 , CH_3CO , NO_2 , Br, I

16 Examples

Yield: 80-95%

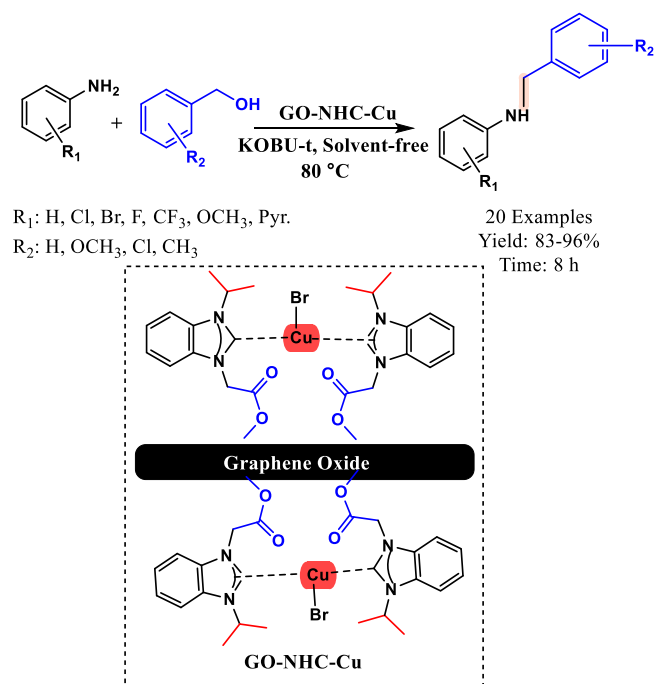
Time: 7-12 h



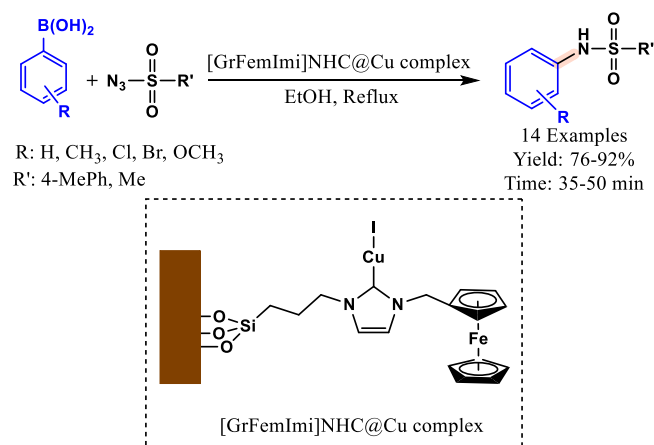
Scheme 11. N-Arylation reaction catalyzed by Cu-NHC/GO.

high yields of products achieved under solvent-free conditions (Scheme 12).

In 2019, Gajare et al. developed a ferrocene-tethered NHC-copper complex, referred to as the $[\text{GrFemImi}]\text{NHC@Cu}$ complex, which was anchored onto graphene. This was achieved through the covalent grafting of a ferrocenyl ionic liquid within the graphene matrix, followed by metallation with copper(I) iodide (Scheme 13) [78]. The characterization of the $[\text{GrFemImi}]\text{NHC@Cu}$ complex was conducted using various techniques, including FT-IR spectroscopy, Fourier transform Raman spectroscopy, CP-MAS ^{13}C NMR spectroscopy, TEM, TGA, EDX analysis, XPS, BET surface area analysis, and XRD analysis. According to the BET analysis, the catalyst exhibited a surface area of $20.23 \text{ m}^2/\text{g}$ and an average pore diameter of 43 \AA . Furthermore, the TEM micrographs revealed crumpling characteristics along with twisted nanosheets in a disordered phase. This innovative complex demonstrated effectiveness as a stable heterogeneous catalyst for the synthesis



Scheme 12. N-Alkylation of benzyl alcohols catalyzed by GO-NHC-Cu.



Scheme 13. Synthesis of N-aryl sulfonamide using GrFemImi]NHC@Cu.

of bioactive N-aryl sulfonamides from a range of aryl boronic acids and sulfonyl azides in ethanol via Chan-Lam coupling. Successful recyclability tests were conducted over six consecutive runs.

1.3. Catalytic activity of N-Heterocyclic carbene-graphene in reduction of nitroarenes

The conversion of nitroarenes to their respective amines represents a vital process in organic synthesis, with important ramifications for the manufacture of pharmaceutical intermediates, agrochemicals, and dyes [79]. Traditionally, this transformation is accomplished through various catalytic approaches; however, the investigation of novel catalytic systems is crucial for enhancing efficiency, selectivity, and sustainability. Recently, NHCs have emerged as prominent ligands in catalysis, especially when paired with transition metals, owing to their distinctive electronic characteristics and capacity to stabilize reactive complexes. The integration of NHCs with graphene results in a composite that improves catalytic efficacy by utilizing the high surface area and conductivity of graphene, which promotes more efficient electron transfer and

substrate interaction. Research indicates that NHC-graphene hybrids can significantly expedite the reduction of nitroarenes under mild conditions, offering benefits over traditional catalysts in terms of reaction rates and recyclability. This overview emphasizes the potential of NHC-graphene composites as cutting-edge catalytic systems for nitroarene reduction, showcasing their operational mechanisms and promising applications in green chemistry and industrial processes.

In 2020, Kandathil and colleagues utilized NHC-Pd@GO for the reduction of nitroarenes. This catalyst demonstrated the ability to be reused nine times in the reduction process while maintaining its catalytic activity without significant loss (Scheme 14) [68].

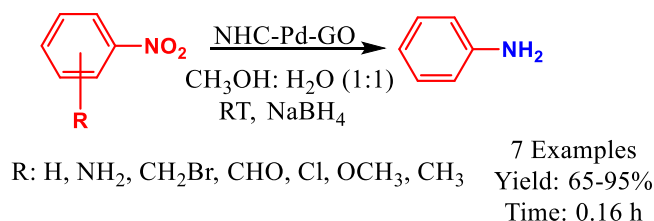
In 2018, Karami et al. documented the use of $[(\text{Pd}_2[(\text{C},\text{N})\text{C}_6\text{H}_4\text{CH}_2\text{NH}(\text{Et})_2]_2(\mu\text{-OAc})_2)]$ for the conversion of p-nitrophenol to p-aminophenol [70].

1.4. Catalytic activity of N-Heterocyclic carbene-graphene in hydration and hydrosilylation of alkynes

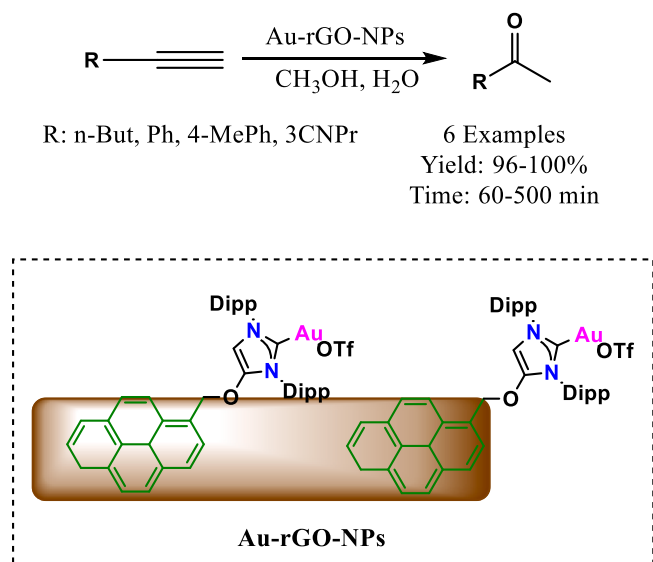
The hydration and hydrosilylation of alkynes are crucial reactions in organic synthesis, leading to the production of carbonyls and silanes, which are essential intermediates in the manufacture of fine chemicals, pharmaceuticals, and materials [80]. Historically, these reactions have relied on various catalysts, particularly transition metals; however, there is an increasing focus on creating more efficient and selective catalytic systems. NHCs have emerged as powerful ligands that can significantly boost the reactivity of metal catalysts. When combined with graphene, these carbenes produce hybrid materials that enhance catalyst stability and accessibility while utilizing graphene's outstanding electronic properties and large surface area. Recent research has shown that NHC-graphene composites demonstrate remarkable catalytic performance in both the hydration and hydro-silylation of alkynes, providing benefits such as milder reaction conditions, faster reaction rates, and improved selectivity for the target products. This introduction highlights the potential of NHC-graphene systems in facilitating these vital transformations, focusing on their mechanistic insights, advantages over conventional catalysts, and promising applications in synthetic organic chemistry.

In 2019, Ventura-Espinosa et al. reported the synthesis of ultra-small gold nanoparticles (AuNPs) through the treatment of precisely defined gold complexes with rGO, eliminating the need for any additional reducing agents [81]. These AuNPs are functionalized with NHC ligands, which facilitate the control of both size and morphology, thereby preventing aggregation. The AuNPs are directly anchored onto the surface of graphene, resulting in hybrid materials that combine metal nanoparticles with a carbon-based support. The catalytic performance of these AuNPs immobilized on graphene was evaluated in the hydration of alkynes, revealing significantly enhanced catalytic activity compared to the original molecular gold complexes, with the ability to be recycled up to ten times. It was noted that graphene plays a crucial role in stabilizing the NHC-functionalized AuNPs (Scheme 15).

In 2018, Ruiz-Botella and Peris successfully synthesized and characterized two pyrene-tagged NHC complexes of rhodium (I). These complexes were anchored onto rGO, resulting in the formation of two novel materials where the molecular complexes are held in place through π - π stacking interactions on the solid's surface [82]. The



Scheme 14. Reduction of nitroarenes using NHC-Pd@GO.

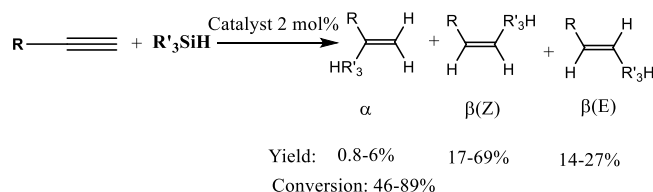


Scheme 15. Catalytic hydration of alkynes using NHC-functionalized AuNPs on r-GO.

catalytic performance of both the complexes and the solid hybrid materials was evaluated in the 1,4-addition of phenylboronic acid to cyclohex-2-one, as well as in the hydro-silylation of terminal alkynes. The findings indicated that the dimetallic complex exhibited superior catalytic activity compared to the monometallic complex in both homogeneous and solid-state reactions. Specifically, in the addition of phenylboronic acid to cyclohexanone, the solid containing the dimetallic catalyst demonstrated effective recyclability for up to five cycles with minimal loss of activity, whereas the monometallic catalyst quickly became inactive. Additionally, in the hydrosilylation of terminal alkynes, the use of the immobilized di-metallic catalyst enhanced selectivity towards the β (Z)-vinylsilane, although a decline in activity was observed after the second cycle (Scheme 16).

1.5. Catalytic activity of N-Heterocyclic carbene-graphene in the hydrogenation of alkynes

Hydrogenation, which involves the addition of hydrogen to unsaturated compounds, is a crucial chemical process extensively employed in the production of various organic molecules, such as pharmaceuticals, fine chemicals, and biofuels [83]. Conventional hydrogenation techniques typically depend on precious metal catalysts, which can be costly and less environmentally friendly. Recently, NHCs have gained attention as adaptable ligands that significantly improve catalytic efficiency in metal-catalyzed reactions, thanks to their distinctive electronic characteristics and robust σ -donor abilities. When combined with graphene, these NHCs create composite materials that leverage graphene's remarkable surface area and conductivity, resulting in enhanced catalyst stability and reactivity. The integration of NHCs with graphene not only boosts hydrogenation activity but also provides better control over selectivity and reaction parameters. Recent research indicates that NHC-graphene hybrids can effectively catalyze the hydrogenation of



Scheme 16. Hydrosilylation of terminal alkynes using NHC catalysts.

various substrates under mild conditions, offering notable benefits compared to traditional catalytic systems. This overview underscores the innovative capabilities of NHC-graphene composites in hydrogenation reactions, highlighting their mechanistic insights, improved performance, and potential future applications in sustainable organic synthesis.

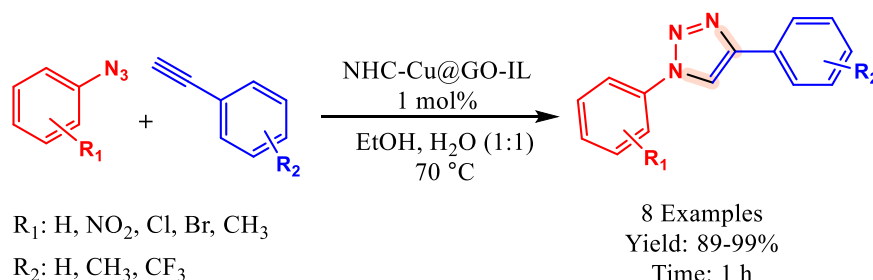
In 2018, Mollar-Cuni et al. successfully synthesized palladium nanoparticles (NPs) through the decomposition of precisely defined palladium complexes that were noncovalently attached to the surface of rGO [84]. Microscopic morphological analysis revealed that the palladium NPs were uniformly distributed across the support. Characterization via X-ray photoelectron spectroscopy indicated the presence of both Pd (2+) and Pd (0) oxidation states, along with NHC and bromo ligands. The catalytic performance of the NPs, both with and without the support, was assessed in the hydrogenation of alkynes. The supported palladium NPs exhibited significantly higher activity compared to their unsupported counterparts and demonstrated the ability to be recycled up to 10 times without a decline in catalytic efficiency. Notably, the composition of the palladium NPs varied with each catalytic cycle, suggesting a dynamic process that leads to the formation of different catalytically active species. In contrast, the unsupported palladium NPs displayed limited activity due to decomposition and were not recyclable. The investigation into the role of the support revealed its significant impact on the stability of the palladium NPs.

1.6. Catalytic activity of N-Heterocyclic carbene-graphene in the synthesis of triazoles and propargylamine

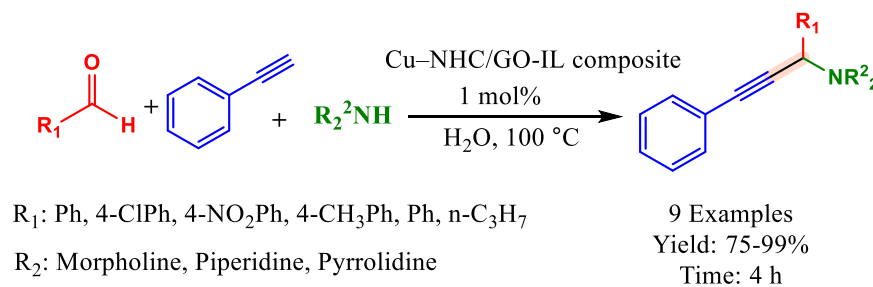
The synthesis of triazoles and propargylamines holds considerable significance in the field of organic chemistry, primarily due to their wide-ranging applications in the pharmaceutical and agrochemical sectors [85,86]. Triazoles are integral components of numerous biologically active molecules and can be produced using various methods, notably the Huisgen cycloaddition involving azides and alkynes. On the other hand, propargylamines are essential intermediates in the production of a variety of natural products and functional materials. Historically, these reactions have depended on metal catalysts, which may exhibit inefficiencies or necessitate harsh reaction conditions. The integration of NHCs into catalytic frameworks has emerged as a viable approach, significantly improving the reactivity and selectivity of metal catalysts due to their robust σ -donor characteristics and capacity to stabilize reactive intermediates. When combined with graphene, NHCs not only enhance catalytic efficiency through increased surface area and conductivity but also improve the stability and recyclability of the catalysts. Recent developments indicate that NHC-graphene composites can greatly expedite the synthesis of both triazoles and propargylamines, frequently under mild conditions. This introduction outlines the catalytic capabilities of NHC-graphene systems in these crucial synthetic processes, highlighting their mechanistic benefits and the potential for advancements in sustainable organic synthesis.

In 2018, Dabiri et al. developed a copper complex featuring NHC that was grafted onto GO and integrated with an ionic liquid framework [87]. This innovative catalyst successfully facilitated the synthesis of (i) 1,2,3-triazole derivatives through a 'Click reaction' (Scheme 17) and (ii) propargylamine derivatives (Scheme 18) via an A^3 coupling reaction' in aqueous environments. The characterization of the catalyst was performed using various techniques, including infrared spectroscopy, Raman spectroscopy, SEM, TEM, TGA analysis, EDX, XPS, and elemental analysis. Notably, the catalyst demonstrated the ability to be reused across ten reaction cycles with minimal loss of catalytic efficiency.

Water oxidation, which involves the transformation of water into oxygen, protons, and electrons, plays a vital role in energy conversion technologies, especially in solar fuel generation and artificial photosynthesis [88]. The development of effective catalysts for this process is crucial for improving the overall efficiency of these technologies and achieving sustainable energy outcomes. NHCs have emerged as



Scheme 17. Synthesis of 1,2,3-Triazole derivatives using NHC—Cu@GO-IL.



Scheme 18. Application of N—Heterocyclic Carbene-Graphene in Water Oxidation.

influential ligands that can significantly enhance the performance of metal catalysts due to their strong σ -donor characteristics and their capacity to stabilize high-valent metal species. When integrated with graphene, NHCs create nanocomposite materials that utilize graphene's unique electronic and structural attributes, including its high surface area and outstanding conductivity, to promote improved catalytic activity and stability. Recent research has shown that NHC-graphene hybrids can efficiently catalyze water oxidation reactions, demonstrating superior performance compared to conventional catalysts. These composites not only increase reaction rates and enhance oxygen evolution yields but also provide benefits in terms of catalyst recyclability and long-term stability. This overview underscores the promising potential of NHC-graphene systems in water oxidation, focusing on their operational mechanisms, the possibilities for integrated renewable energy applications, and the continuous progress in developing more efficient catalytic materials.

In 2020, Sánchez-Page et al. examined how the structural characteristics of graphene materials affect the local structure of -OH anchored Ir(I)-NHC complexes [89]. The study utilized two types of partially rGO, each with distinct sheet properties derived from the crystalline features of their original graphite. The primary distinctions between these materials were the size of the Csp^2 domains within their graphenic layers and the arrangement of functional groups on the basal planes and edges. The process involved anchoring N-methylimidazolium groups via the graphene -OH functional groups, leading to the creation of graphene-based hybrid materials. The structural variations of the support influenced the interaction between the supported iridium compounds and the graphene sheet. In the material with smaller graphene sheets, the oxygenated functional groups are positioned closer together, resulting in larger Csp^2 domains in the graphene layer. This configuration enhances the interaction with the supported iridium atoms, causing the displacement of the chlorido ligand from the first coordination shell. Conversely, the hybrid material with a more uniform distribution of oxygenated functional groups across the basal planes of the graphenic layer exhibits partial chlorido displacement. This variation significantly impacts the electrocatalytic performance of the iridium-based hybrid materials as water oxidation catalysts (WOCs), leading to enhanced catalytic activity while retaining coordinated chlorido ligands.

1.7. Application of N-Heterocyclic carbene-graphene in solid phase extraction

Solid phase extraction (SPE) is an essential method extensively utilized for the preparation and purification of samples in analytical chemistry [90]. It allows for the effective concentration and separation of target analytes from intricate matrices. The advancement of sophisticated sorbent materials is vital for improving the selectivity, sensitivity, and overall effectiveness of SPE techniques. NHCs have gained recognition as adaptable components in the creation of functional materials, owing to their robust coordination properties and stability. When integrated with graphene, NHCs can produce hybrid materials that leverage graphene's remarkable surface area, conductivity, and chemical adaptability, leading to customized sorbents with superior extraction capabilities. Recent studies have shown that NHC-graphene composites can greatly enhance SPE performance by boosting adsorption capacities and selectivity for a diverse array of analytes, such as pharmaceuticals, environmental contaminants, and biomolecules. These innovative materials promote quicker extraction kinetics and support the development of sustainable extraction methods. This introduction emphasizes the potential of NHC-graphene systems in solid phase extraction, detailing their operational mechanisms, benefits over conventional sorbents, and potential applications across various sectors, including environmental monitoring, food safety, and biomedical analysis.

In 2019, Aladaghlo et al. introduced an ultrasound-assisted technique for the dispersive solid phase extraction of trace amounts of triazole fungicides [91]. The sorbent utilized was derived from an NHC copper complex, which was supported on GO modified with ionic liquid. Characterization of the sorbent was conducted using various methods, including SEM, TEM, Raman and FT-IR spectroscopy, EDX, and elemental mapping. The extraction and sorption capabilities primarily rely on the complexation with Cu (I) ions. The parameters influencing the extraction process were systematically optimized. After desorption with ethanol, the fungicides were quantified using corona discharge ion mobility spectrometry. Under the optimized conditions (pH 7.0, 10 mg of sorbent, 3 min of extraction time, and ethanol as the desorption agent), the method demonstrated excellent linearity (greater than 0.994), repeatability ($\text{RSD} < 4.1\%$), low detection limits (0.18 ng. mL^{-1}), impressive preconcentration factors (468–476), and high

recovery rates from spiked environmental water samples (92–94 %). The sorbent maintained its effectiveness over more than five cycles without significant degradation in performance.

1.8. Application of N-Heterocyclic carbene-graphene in biosensor technology

Biosensor technology has attracted considerable interest in recent years due to its ability to deliver rapid, sensitive, and specific detection of biological analytes, including pathogens, toxins, and disease biomarkers [92,93]. The advancement of sophisticated sensing materials is essential for improving biosensor performance. NHCs have emerged as valuable components in this domain, owing to their distinctive electronic characteristics, adaptability, and capacity to form stable complexes with metal nanoparticles. When combined with graphene, a material celebrated for its superior conductivity and extensive surface area, NHCs can produce hybrid platforms that significantly enhance the electrochemical properties and sensitivity of biosensors. Recent research indicates that NHC-graphene composites can substantially improve detection limits and response times across various biosensing applications, such as glucose monitoring, biomarker detection, and pathogen identification. These composites enable the functionalization of graphene with biological recognition elements, promoting selective interactions with target analytes while ensuring high signal output. This overview underscores the innovative uses of NHC-graphene systems in biosensor technology, highlighting their operational mechanisms, advantages over traditional biosensing materials, and their potential to advance diagnostics in both medical and environmental sectors.

In 2024, Kim et al. identified fatal pathogenic organisms using various point-of-care tests (PoCTs) on clinical samples [57]. These PoCTs, which utilize portable electrical devices, offer a straightforward and rapid method for organism detection. Despite the high sensitivity of electrical PoCT devices in identifying pathogens in standard samples, their industrial application has been hindered by issues related to low reproducibility, sensitivity, and specificity, primarily due to nonspecific binding in the media. This study introduces a novel approach using a perpendicular NHC self-assembled monolayer (NHC-SAM) conjugated onto graphene micropattern field-effect transistors (NGMFETs) for pathogen monitoring. The interaction of two single bonds of NHC-SAM on graphene was analyzed through density functional theory (DFT) and surface analysis. Bioreceptors were attached to the side gate-modulated NGMFET, enabling ultra-stable on-site detection. The side-gated BNGMFET system demonstrated exceptional performance in detecting: i) SARS-CoV-2 spike protein S1 (limit of detection (LOD): approximately 10 pg mL^{-1}) in CTM, ii) *O. tsutsugamushi* antibodies (LOD: approximately 1 pg mL^{-1}), and iii) *Escherichia coli* (LOD: $10^\circ \text{CFU mL}^{-1}$) in serum. In comparison to commercial methods, this platform offers LODs that are 102 times higher for these pathogens in clinical samples, along with improved reproducibility. These findings suggest that side-gated BNGMFETs could serve as a universal PoCT solution during pandemics.

1.9. Future directions

As the investigation of NHCs supported on graphene nanosheets progresses, several promising future directions and research areas emerge that could significantly enhance both the theoretical and practical dimensions of catalytic science [94–96]. **Mechanistic Investigation:** Additional research is required to clarify the intricate mechanisms through which NHC-graphene composites boost catalytic performance. Gaining a deeper understanding of the electronic interactions and stabilization effects among NHCs, graphene, and metal centers will yield valuable insights for the development of more efficient catalytic systems [97]. **Broader Catalytic Applications:** Although existing studies have shown considerable effectiveness in specific reactions, including hydrogenation, water oxidation, and the functionalization of organic compounds, future investigations should assess the potential of

NHC-graphene catalysts across a wider array of catalytic processes. This encompasses complex transformations relevant to pharmaceuticals, biomass conversion, and renewable energy technologies [98]. **Enhancement of Composite Characteristics:** It will be vital to explore how different synthesis techniques, NHC configurations, and the NHC-to-graphene ratio affect catalytic performance. Optimizing these factors could result in improved stability, selectivity, and activity of the composites, making them more suitable for industrial use [99]. **Combination with Other Materials:** The potential benefits of integrating NHC-graphene composites with other nanomaterials, such as metal nanoparticles, metal-organic frameworks (MOFs), or additional two-dimensional materials, could further elevate catalytic performance. Investigating these hybrid systems may pave the way for the development of multifunctional catalysts [100]. **Practical Applications and Scalability:** There is an increasing demand for research focused on the scalability and practical implementation of NHC-graphene catalysts in industrial settings. Assessing their long-term stability, reusability, and performance under real-world conditions will be crucial for the successful application of these catalysts [101]. Table 1 highlights the advancements in the catalytic performance of NHCs ligands when anchored to different support, detailing various metals utilized and the specific catalytic transformations achieved in recent years.

2. Conclusions

The mini review on NHC supported on graphene nanosheets highlights notable progress in catalytic efficiency and sustainability achieved through these composite materials. The integration of NHC complexes with rGO significantly improves catalytic activity in various reactions, including Suzuki-Miyaura cross-coupling and N-alkylation, while also providing excellent recyclability, with some catalysts retaining their effectiveness over numerous cycles. The robust π - π stacking interactions between the NHC complexes and graphene play a vital role in the heterogeneous characteristics of these catalysts, which is essential for their application in industrial contexts. Additionally, the approaches discussed are in line with green chemistry principles, promoting high carbon efficiency and minimal environmental impact, thus making them ideal for eco-friendly applications in pharmaceutical manufacturing. In summary, the insights shared in this review emphasize the considerable

Table 1
Summary of key developments with the distinction of the metal and catalytic transformation using NHCs.

Entry	Metal	Catalytic Transformation	Key Development	Ref.
1	Gold (Au)	C-C Coupling Reactions	Enhanced selectivity in coupling reactions due to NHC support.	[102]
2	Palladium (Pd)	Cross-Coupling (Suzuki, Heck)	Improved catalytic activity and recyclability observed with NHC-graphene composites.	[103]
3	Copper (Cu)	Alkynylation Reactions	NHC-functionalized graphene showed higher efficiency and stability in alkynylation.	[104]
4	Silver (Ag)	Oxidation Reactions	Demonstrated significant oxidation capacity and product yield with NHC-Ag supported on graphene.	[105]
5	Iridium (Ir)	C-H Activation	NHC ligands on graphene increased the rate of C—H bond activation processes significantly.	[106]
6	Rhodium (Rh)	Hydroformylation	Optimized conditions led to higher yields in hydroformylation reactions using NHC-Rh/graphene catalysts.	[107]

potential of NHC-supported catalysts in enhancing both catalytic research and sustainable methodologies in organic synthesis. Several future challenges that researchers should consider them in the pointed topic are as follow: 1- Stability and Reactivity: 1a: Chemical Stability: Ensuring the NHCs maintain stability during catalytic reactions. 1b: Deactivation Mechanisms: Understanding how and why the NHCs may deactivate over time is crucial for improving their longevity. 2-Synthesis and Functionalization: 2a: Scalable Synthesis: Developing scalable and reproducible methods for synthesizing NHC-graphene composites. 2b: Functionalization Strategies: Identifying effective methods for functionalizing graphene to optimize the anchoring of NHCs without compromising their catalytic properties. 3-Catalyst Efficiency: 3a: Activity Enhancement: Finding ways to enhance the catalytic activity of NHCs on graphene, potentially through hybridization with other materials or optimizing the composition. 3b: Reaction Selectivity: Improving selectivity for desired products in various chemical reactions using these catalysts. 4-Environmental Sustainability: 4a: Green Chemistry Principles: Implementing sustainable and environmentally friendly practices in the synthesis of NHCs and their catalytic applications. 4b: Recyclability: Developing protocols for the recyclability of NHC-graphene catalysts to minimize waste. 5-Theoretical Understanding: 5a: Mechanistic Studies: Conducting more in-depth mechanistic studies to elucidate how the interactions between NHCs and graphene influence catalytic behavior. 5b: Computational Modeling: Utilizing advanced computational models to predict performance and guide the design of better catalysts. 6- Broader Applications: 6a: Diverse Reaction Types: Exploring the use of NHC-graphene composites in a wider variety of catalytic reactions beyond those currently studied. 6b: Commercial Viability: Assessing the potential for commercial applications and the economic feasibility of using these catalysts at scale. 7- Interdisciplinary Research: 7a: Collaboration across fields: Promoting collaboration between chemists, materials scientists, and engineers to address complex challenges in catalyst development. In our opinion, each challenge opens up new avenues for research and innovation, and addressing these will likely lead to significant advancements in the field of catalysis.

CRediT authorship contribution statement

Raed Muslim Mhaibes: Writing – review & editing, Supervision, Project administration. **Abdul Amir H. Kadhun:** Validation, Software, Methodology, Investigation, Data curation. **H.N.K. Al-Salman:** Visualization, Validation, Software, Resources, Methodology, Data curation. **Zaid H. Mahmoud:** Software, Methodology, Conceptualization. **Mustafa Mudhafar:** Software, Resources, Methodology. **Qais R. Lahhob:** Software, Resources, Methodology, Investigation. **Guang Shu:** Writing – review & editing, Writing – original draft, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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