

## Recent Trends in the Catalysis of Cross Coupling and Carbonylation Reactions Using Pd(II)-N-Heterocyclic Carbene-Stabilized Complexes

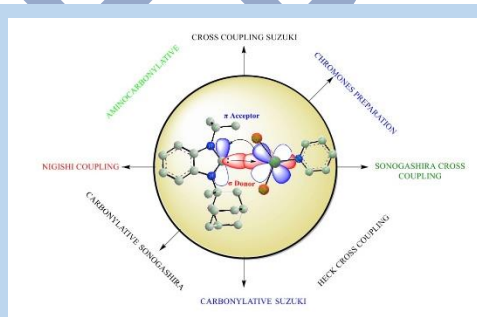
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**Abstract:** Carbonylation processes and couplings catalyzed by transition metals have advanced significantly in the production of practical materials and in commercial applications. Choosing the right ligand is very important in these reactions. Even though this field has developed a lot in recent years, most commonly used ligands are phosphine-based compounds that have many problems such as difficult synthesis, harmful effects, high cost, and the poor stability under air or moisture conditions. On the other hand, there are many numerous benefits with N-heterocyclic carbene (NHC) ligands synthesis. These include lower cost, strong sigma donor, and easy to synthesize. Also, NHCs can be created from many N-heterocyclic rings, their stability toward air and moisture and lack of toxicity make them a useful ligand precursor. An overview of using NHC as donor ligands with palladium to aid the catalyzing of different coupling and carbonylation reactions that can be used in production of bioactive compounds and other medications.



**Keywords:** Cross Coupling Reactions, Carbonylation Reactions, NHCs Donor Ligands, N- Heterocyclic Carbene.

### Introduction

Transition metal-catalyzed cross coupling and carbonylation reactions have become very popular in the last decade due to its importance for making useful materials in organic chemistry and for industrial processes [1]. This field is still challenging and interesting because there is a lot of work to improve the conditions used in these reactions for synthesis of organic compounds and in industrial applications. Today, cross-coupling and carbonylation reactions are widely used in different stages of chemical production and industries such as, fine chemicals, agrochemicals, pharmaceuticals, petrochemicals, polymers, and dyes [1-2]. For this reason, researchers are trying to develop better catalysts that are more active, reliable, cheaper, and environmentally friendly [1-3]. One of the most commonly used ligands are phosphine-based compounds, but they have some drawbacks like being expensive and not stable in air or moisture [2-3]. In particular, and contrary to phosphine ligands, the N-heterocyclic carbene (NHC) ligands are advantages of low cost, strong sigma donation, and simple synthesis. Although, vast numbers of N-heterocyclic rings can be used to produce NHCs, they are more useful as ligand precursors due to their stability against air and moisture and their non-toxic nature properties. [3]. Scientists are now interested in studying N-heterocyclic carbene (NHC) ligands. These ligands have strong  $\sigma$  donation and good  $\pi$  back donations, making them flexible for designing

ligands which are suitable for different reactions [4]. Also, they are cheaper and easier to make. Even though many N-heterocyclic rings have been reported in the literature for making NHCs [5], they are more useful as ligand precursors since they are stable in air and moisture and are not toxic [5-6]. This work will discuss the use of NHC ligands in both cross-coupling and carbonylation reactions.

### Coupling Reactions

Carbon-carbon bond formation is a versatile process in organic chemistry that helps in synthesizing different kinds of molecules, that can be used in a lot of industries, like petrochemicals, medicine, plastics, and dyes. Some of these molecules include different functional groups as biaryls, aromatic esters, amides, ketones, and amino acids [1-7]. For example, Biaryls are special kind of molecules that are used as building blocks for new materials, such as strong rigid-rod polymers, molecular wires, control light materials, and liquid crystals [7-8].

There are many types of cross-coupling reactions that have been studied, but some of the most effective and well-known ones are the Suzuki-Miyaura [9], Heck-Mizoroki [10], and Sonogashira [11] reactions.

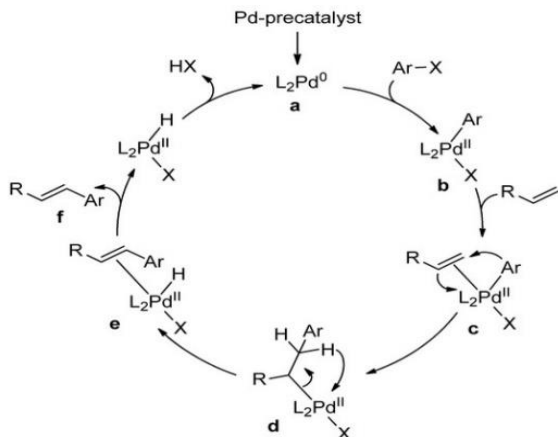
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Most of these reactions prefer to use palladium as efficient catalysts although the cost of palladium catalysts,

one of the reasons is the catalytic cycle of these reactions, the catalytic cycle usually involves three main steps: Oxidative addition, Transmetalation (or Insertion in Heck) and Reductive elimination [6]. In these steps the palladium can easily change the oxidation state between Pd(0)  $\leftrightarrow$  Pd(II) better than different metal complexes as shown in catalytic cycle of Mizoroki–Heck cross coupling reaction Figure. 1 [6].

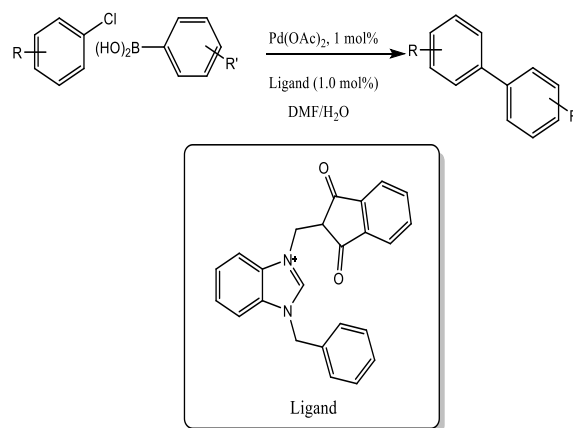


**Figure (1):** Overall catalytic cycle for the Heck olefination reaction [6].

These reactions are used to form simple molecules as well as the complex molecules. In order to construct new, intricate molecular structures, they are also highly helpful in the creation of specially designed ligands that can bond to metal ions. Also, these structures can act as catalysts in various chemical reactions, making them very useful in organic chemistry [12].

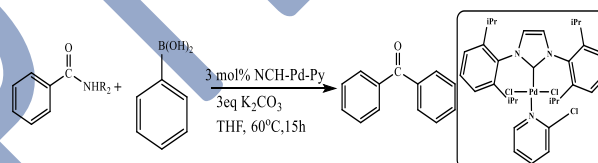
### Suzuki-Miyaura cross-coupling reactions

Since the discovery of Suzuki-Miyaura coupling reaction, many different types of palladium complexes both heterogeneous and homogeneous, have been used for this reaction with various kinds of substrates that have different functional groups. In the literature, several methods for synthesis Pd-NHC complexes have been described by using NHC salts and Pd(OAc)<sub>2</sub> in order to create efficient catalysts for the Suzuki-Miyaura reaction. For example, bulky phenanthryl NHC ligands were made, and then palladium complexes were formed right there to help catalyze the Suzuki-Miyaura coupling of different aryl and vinyl chlorides with organoboron compounds at room temperature. This method produced tri- and tetra-ortho-substituted products in high yields under mild conditions [13]. Another example is the work by Kayser and Co-worker who made active palladium-NHC catalysts from benzimidazolium salts and Pd(OAc)<sub>2</sub> using in situ generation (Scheme 1). They investigated the prepared catalysts in the Suzuki-Miyaura coupling of various aryl and vinyl chlorides with boronic acid in DMF/H<sub>2</sub>O as solvent [14].



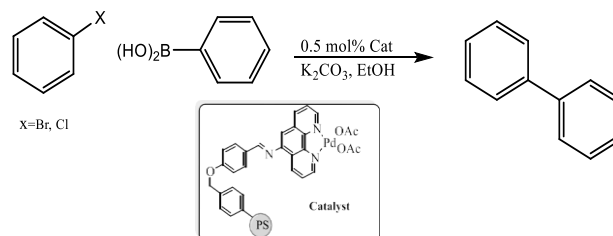
**Scheme (1):** In situ generation of active palladium-NHC catalysts based on Pd(OAc)<sub>2</sub> and benzimidazolium salts [14].

Numerous studies at the new Pd(II)-NHC and Pd(II)-NHC-pyridine complexes as catalysts have been checked for the Suzuki coupling process between aryl boronic acids and various aryl halides and activated aryl chlorides [15–18]. One notable study about the Suzuki-Miyaura coupling of amides with different aryl boronic acids using a palladium-NHC-pyridine complex that works well even in air and moisture [19]. In this method, 3% of the catalyst, 15 hours stirring at 60°C were used and gave much better results compared to other known Pd/phosphine catalysts when it comes for activating the N-C bond in amides.



**Scheme (2):** A stable catalyst for the Suzuki-Miyaura coupling of amides with various aryl boronic acids is the palladium-NHC-pyridine complex [19].

Besides that, many different types of palladium-based catalysts were used to help carry out various Suzuki-Miyaura reactions. For instance, palladium nanoparticles attached to PVC were used as good catalysts for these reactions at room temperature in water [20]. In 2005, Gao and their team showed that using iron oxide nanoparticles as a support for Pd-NHC complexes worked well for these reactions [21]. Another example involved a recyclable catalyst made from a simple Merrifield Resin that held a phenanthroline-palladium (II) complex. This catalyst was effective in catalyzing the reactions with only 0.5 mol% at normal temperature as in Scheme 3 [21].



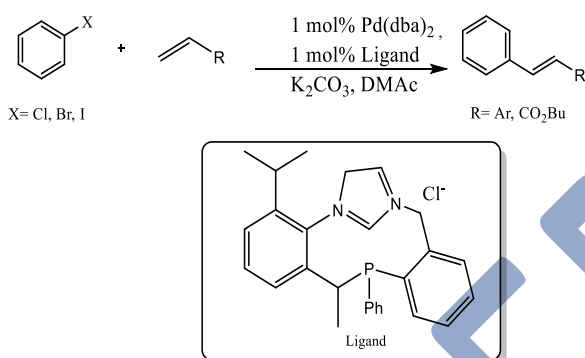
**Scheme (3):** As effective catalysts for Suzuki-Miyaura reactions, recyclable catalysts made of a basic Merrifield Resin supported phenanthroline-palladium (II) complex were used [21].

### Mizoroki-Heck coupling reactions

In last years, imidazolium and benzimidazolium-based NHC compounds have become popular as starting materials for creating stable carbene ligands and carbene metal complexes. These NHCs are especially useful when paired with palladium to form organometallic catalysts used in homogeneous catalysis, and a lot of research has been done in this field [23-25]. The

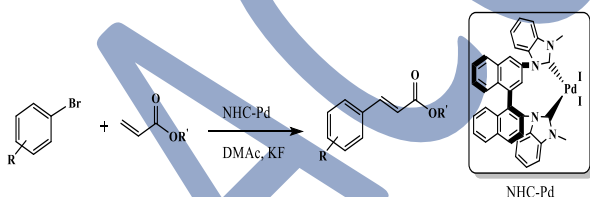
effectiveness of NHCs as ligands in these reactions comes from their ability to be modified in ways that adjust their size and electronic behavior by changing the structure of the heterocyclic part [26]. The strength of carbon-palladium bonds in Pd-NHC complexes made these compounds more stable, which avoiding the formation of inactive palladium black during the catalytic process [23]. Even though there have been many improvements in making and using Pd-NHC catalysts for different chemical reactions, this issue is still quite difficult to solve [27-30].

Recently, a new method was developed to make Pd-NHC-phosphine complexes right where they are needed for Heck reactions. This method uses a special type of catalyst made from a triaryl phosphine-linked imidazolium salt and a palladium (0) compound called Pd(dba)<sub>2</sub>. This catalyst works very well for coupling a wide range of aryl bromides and iodides with acrylates, as shown in scheme 4. It also works well when coupling para-bromotoluene with different styrene compounds. The reason this catalyst is so effective is because of the large groups attached to the N-phenyl ring of the phosphine-linked NHC ligands, as reported in reference [31].



**Scheme (4):** The generation of Pd-NHC-Phosphine complexes in situ for the Heck reactions [31].

Surprisingly, some examples in the literature mentioned the use of bis-carbene complexes made from chelating diazolum salts. One of these examples showed high efficiency for the synthesized Pd(II)-NHC complexes, which have a regular cis-chelating, bidentate structure in the Heck-type reaction (Scheme 5) [32].



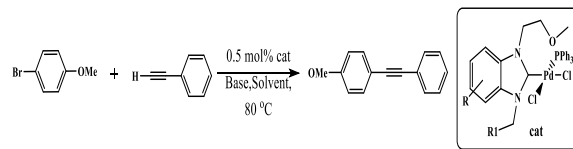
**Scheme (5):** Synthesized Pd(II)-NHC complexes, which has a 'normal' cis-chelating, bidentate structure in the Heck-type reaction [32].

In another study, the relationship between catalytic activity and softness in Mizoroki-Heck reactions—in which aryl bromides react with styrene or acrylate compounds to form diarylethene and cinnamic acid derivatives—was examined using DFT calculations on 1,3-propanediyl bridged bis(N-heterocyclic carbene) palladium (II) complexes. According to the study, catalytic activity rises with softness, but the +I effect of N-substituents on the ligands had no effect [33].

### Sonogashira coupling reactions

are in general, the Sonogashira coupling reactions, which are the main way to make internal alkynes, are carried out using palladium complexes along with copper salts and an excess amine as a base [34]. However, when copper(I) co-catalysts are present, they can form some copper(I) acetylides on their own, which causes alkynes to undergo oxidative homo-coupling [34-35].

Many researchers have worked hard to prevent these homocoupling reactions. One approach has been to create new types of active palladium complexes that work better as catalysts in the Sonogashira reaction. Pd (II)-NHC complexes have been seen as a useful solution to avoid the issues caused by copper salts (Scheme 6) [36-37]. Internal alkynes are important parts of active molecules and materials and play a significant role as essential parts in synthesis chemicals used in many medicines [38].



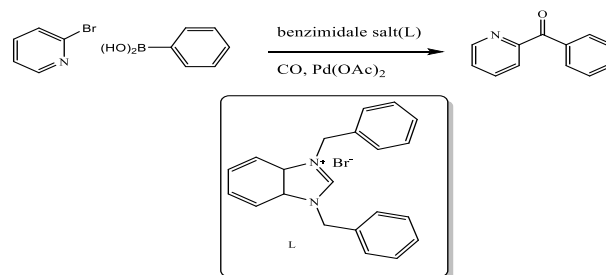
**Scheme (6):** Synthesized Phosphate-Pd (II)-NHC complexes, which has bidentate structure in the Sonogashira reaction [38].

### Carbonylation reactions

The process of adding a carbonyl group to alkynes using nucleophiles that can donate protons was first discovered in the 1930s [39-40]. This method can make a lot of useful chemicals for different purposes. The kind of nucleophile used affects what products can be made. These consist of different α,β-unsaturated carboxylic acids, esters, and amides that are chains, branched, and cyclic [41-42]. In the future, carbonyl reactions like Suzuki and Sonogashira carbonylation reactions were also added to the list of carbonyls coupling reactions. Carbonylation reactions make many useful things, like diaryl ketones, alkynones, chromones, aryl esters, and aryl amides. These species (moieties or intermediates) are the first steps to make other compounds that are important for medicine. Most reactions that join carbon and oxygen together use carbon monoxide as the starting material. Possible Palladium is the most common catalyst for carbon-carbon bonds formation from carbon monoxide and other carbon-containing molecules. Many other metals can do this, but palladium is the best.

### Carbonylative Suzuki-Miyaura coupling reactions

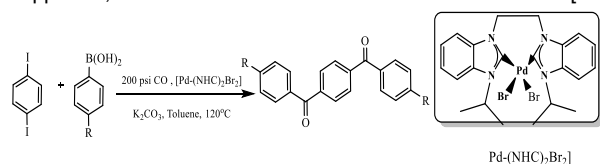
Because of their favorable thermal, optical, and electrochemical characteristics, biaryl ketones are highly valuable organic molecules. And these advantages make them useful in biological and medical areas, such as medicine dosing, tracking DNA activity, internal radiation measurements, and sun protection. Pd-NHCs complexes can be used to create these types of compounds. For example, Hamdi and his team recently showed that Pd-NHCs complexes can be made in real time from Pd (OAc)<sub>2</sub> and a benzimidazole NHC salt [43-46]. This method was used to speed up effectively a reaction called carbonylative Suzuki coupling, where aryl boronic acids react with 2-bromopyridine under safe, inert conditions [47-48]. This process helped the synthesis of unsymmetrical aryl pyridine ketones, as shown in Scheme 7.



**Scheme (7):** Pd-NHC complexes are produced in situ using benzimidazole NHCs salt as a ligand precursor and Pd(OAc)<sub>2</sub> [47].

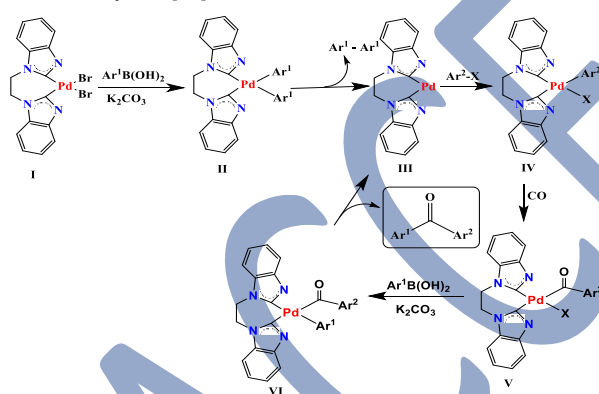
The useful chemicals from butterflies that used in drug delivery were made using a special chemical process called

carbonylative Suzuki–Miyaura coupling. This process involved combination of aryl boronic acids with aryl halides using a specific type of catalyst called bridged bis(*N*-heterocyclic carbene)palladium(II) complexes. These catalysts were tested and showed high effectiveness even with small amounts. The reactions with aryl bromides favored making the carbonylated product when a higher pressure of carbon monoxide is supported, as shown in Scheme 8 [49].



**Scheme (8):** Carbonylative Suzuki–Miyaura coupling reaction of aryl diiodides with aryl boronic acids and aryl iodides with aryl diboronic acids by the palladium complex [49].

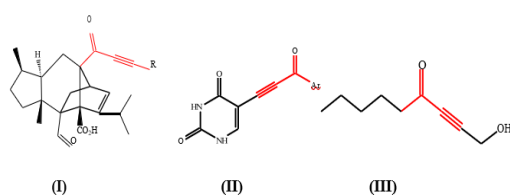
The proposed mechanism for this reaction was illustrated from kinetic study as shown in Scheme 9. The palladium (0) active species III is formed through two steps starting from the chelate dibromido pre-catalyst Pd(II) II by transmetalation of palladium complex I with aryl boronic acid in the presence of strong base such as  $K_2CO_3$ , then diaryl were removed by reductive elimination step. Next step is oxidative addition of aryl halide to the Pd(0) species produce the palladium (II) intermediate IV. Formation of the acyl Pd intermediate V was reached by insertion of CO gas into the Ar–Pd bond. Followed by transmetalation of V with aryl boronic acid in the presence of  $K_2CO_3$  forms the Pd intermediate VI. The last step is a reductive elimination of the diaryl ketone with the regeneration of the Pd(0) active catalyst III [49].



**Scheme 9:** A proposed mechanism for the carbonylative Suzuki–Miyaura coupling reaction catalyzed by the chelate bis(*N*-heterocyclic carbene) palladium(II) complex [49–50]

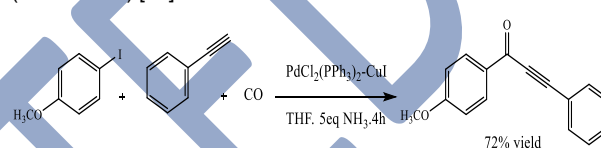
### Carbonylative Sonogashira Reactions

Ynones are compounds that contain both an acetylene group and a carbonyl group. These compounds are important because they have specific structures that are found in many natural products and chemicals used in agriculture. Some Ynones show useful biological effects, like fighting cancer or preventing fungal growth. These active compounds can be found in different organisms or made in factories (Figure 2).



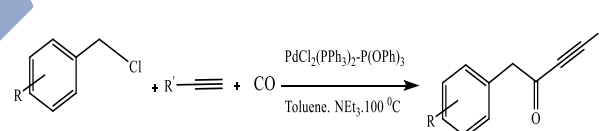
**Figure (2):** (I) Anti-cancer cytotoxic uracil analogue, (II) Antifungal isolated from fermentation of schnoodle benzoin, (III) Antifungal sordaricin analogue.

Ynones are also seen as important in making medicines like bryostatin 1, which has been used in different medical treatments. These include helping with HIV-1 latency and the virus reservoir in patients who are on antiretroviral therapy, treating severe Alzheimer's disease, and cancer treatment plans [53–55]. Making ynones usually involves many steps, which can create unwanted byproducts and result in lower amounts of the final product [55]. A better way to make ynones is the carbonylative Sonogashira coupling reaction, where aryl halides are joined with terminal alkynes using palladium-based catalysts. This method allows ynones to be made in a single step under mild conditions [55]. Researchers have tested this reaction using different types of palladium catalysts [56–58]. For example, using 5 mol% of  $PdCl_2(PPh_3)_2$  along with 2 mol% of CuI as a supported catalyst, they were able to carry out the carbonylative Sonogashira coupling between para-methoxy-1-iodobenzene and phenylacetylene. This was achieved in the presence of 2 equivalents of 0.5 M aqueous ammonia, 1 atm of carbon monoxide, to produce the corresponding  $\alpha,\beta$ -alkynones (Scheme 10) [56].



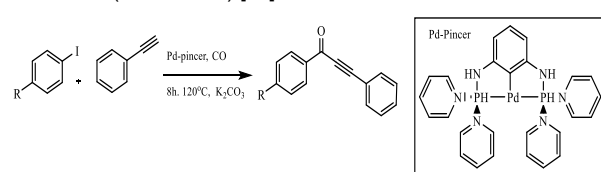
**Scheme (10):** Copper-palladium acts as a cocatalyst in the carbonylative Sonogashira coupling reaction between aryl iodides and terminal alkynes [56].

M. Beller and his group created a new catalyst system that uses an efficient method without copper for the Sonogashira carbonylative coupling reaction. This process combines benzyl chlorides with terminal acetylenes in presence of triethylamine as a base at 100 °C temperature. The reaction involves a mixed catalyst made of  $Pd(PPh_3)Cl_2$  and  $P(OPh)_3$ , along with carbon monoxide, to form the desired alkynone products (Scheme 11) [58].



**Scheme (11):** Sonogashira carbonylative coupling of benzyl chlorides with terminal acetylenes in presence of triethylamine as a base and mixed  $Pd(PPh_3)Cl_2/P(OPh)_3$  as catalyst [58].

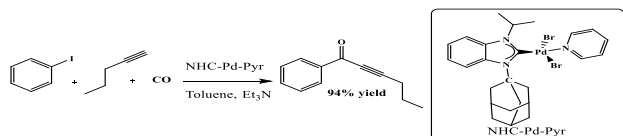
Despite some issues, scientists have kept working on producing different palladium complexes to fix problems and come up with better solutions. These problems include a lot of catalyst needs, the low effectivity of the catalyst, long time reactions, high temperatures, and high levels of CO pressure [59–61]. Recently, as part of this ongoing work, a new type of palladium complex called an amino phosphine palladium pincer complex was made and then used as a good catalyst for the Sonogashira and Suzuki–Miyaura reactions in propylene carbonate (Scheme 12) [62].



**Scheme (12):** Sonogashira carbonylative coupling of aryl iodide with terminal acetylenes by amino phosphine palladium pincer as catalyst [62].

In earlier studies, a series of heterolytic (NHC)–pyridine palladium (II) complexes based on novel pre-ligands based on *N*-substituted *N*-heterocyclic carbene (NHC) shown

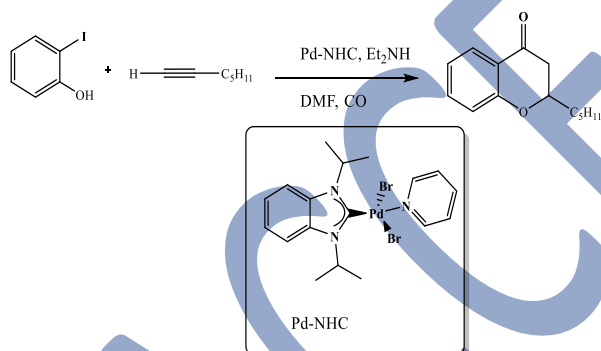
exceptionally high catalytic selectivity and activity in carbonylative Sonogashira coupling processes. The DFT quantum mechanical analysis of the frontier orbitals for these complexes shows that the species are softened by bulky alkyl groups donating. This refers likely to the steric and electronic characteristics of the bulky alkyl groups. This is equivalent to the complexes' highest catalytic efficiency when dealing with soft substrates (Scheme13) [63].



**Scheme (13):** Pyridine-NHC-Pd Catalyzes Aryl Iodide-Aryl Alkyne Carbonylative Sonogashira Coupling Reactions [63].

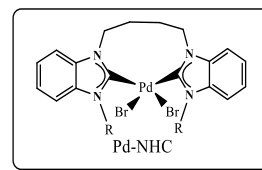
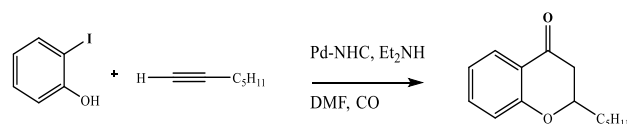
#### Cyclocarbonylative Sonogashira coupling reactions

Chromones, especially flavones, Chromones, especially flavones, are important compounds and very useful, especially in medicine and drug-making, that encourage many scientists and researchers to study [64-67]. These compounds can be prepared using the Cyclocarbonylative Sonogashira coupling a reaction. The studies about using Pd-NHC complexes in this type of reaction are not many. One example is that, when these complexes support the preparation of chromones and flavones, by reacting to ortho-functionalized aryl iodides with terminal aryl alkynes as shown in Scheme14. However, these palladium complexes work well with aryl alkynes but not so well with terminal alkyl alkynes. To improve their performance, they often need to be used with other compounds like pyridine or NHC as helper ligands [68].



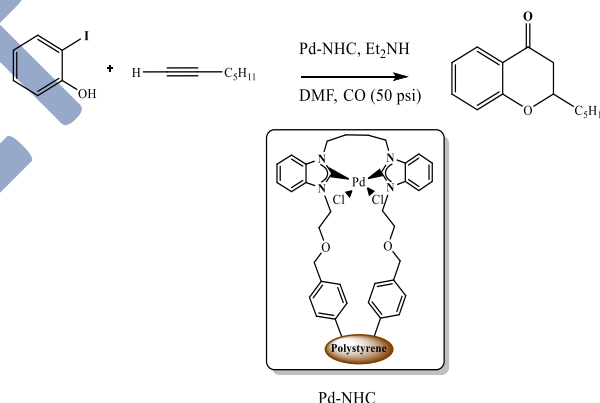
**Scheme (14):** Pd-NHC complexes for the catalytic cyclocarbonylative of ortho-functionalized aryl iodides with terminal aryl alkynes, which results in the synthesis of chromones and flavones [68].

Bioactive chromones and flavones were produced via catalytic and one-pot regioselective methods employing phosphine-free Cyclocarbonylative Sonogashira coupling reactions between 2-iodophenols and aryl alkynes or other alkynes. These reactions were aided by new dibromides (NHC) palladium (II) complexes. Bridged N,N'-substituted benzimidazolium salts were formed into palladium complexes. In Cyclocarbonylative Sonogashira coupling methods, the generated compounds showed strong catalytic activity and outstanding stability even with little amounts of catalyst. To control the regioselectivity of these reactions, dimethylamine was used as the base and DMF as the solvent. (Scheme 15) [69].



**Scheme (15):** Using bridging bis(N-heterocyclic carbene) palladium (II) complexes as catalysts, 2-iodophenol and phenylacetylene undergo cyclocarbonylative Sonogashira coupling reactions [69].

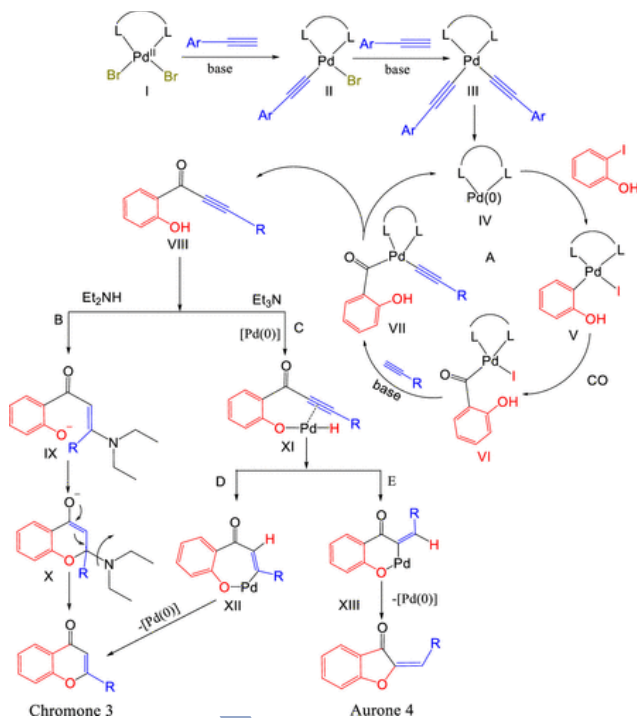
On the other hand, it is well known that it is important to immobilize catalysts on different supports such as nanoparticles, clays or some polymers to manufacture recoverable and reusable catalysts. [70-74]. In the same context, other studies showed that chelating bis(N-heterocyclic carbene) ligand precursors and their palladium (II) complexes were successfully supported on different supports one of these examples is immobilization of Pd-NHC complexes on Co-MOF 74 microrods to catalyze cross coupling reactions [75]. Other bridging heterogenous Pd-NHCs complexes were attached to Merrifield's resin through covalent bonding. These attached complexes are very stable because of the strong chelate effect from the ligand. These systems work very well as catalysts in preparing different flavones and alkynones. They support a variety of aryl iodides and a broad set of aryl and alkyl alkynes in both carbonylative and cyclocarbonylative Sonogashira coupling processes. Additionally, they are quite reusable (Scheme16) [76].



**Scheme (16):** Robust Pd-NHC2@M, as a supported catalyst, and carbonylative Sonogashira coupling of distinct aryl iodides with different aryl alkynes [76].

Kinetic study of carbonylative sonogashira reactions and cyclo carbonylative Sonogashira reactions was used to collect data which correlated with DFT study of different Pd-NHC complexes. All of these data were used to propose the mechanism of cyclo carbonylative Sonogashira reactions [63, 69, 76]. Chromones and aurones were produced via carbonylative Sonogashira coupling reactions followed by the cyclization reactions. Initially, in the presence of the strong base, deprotonation of alkynes and the palladium (II) pre-catalyst (II) undergoes via substitution of the bromides by the acetylides to form the palladium (II) intermediate (III), followed reductive elimination of the dialkynes to generate the Pd (0) (IV) as the active catalytic species (Scheme 17, pathway A). The new palladium (II) intermediate (Ar-Pd-I) (V) is then formed via the oxidative addition of 2-iodophenol to the Pd (0). The acyl other palladium intermediate (VI) is generated by the insertion of carbon monoxide (CO) into the Ar-Pd bond. The next step is

substitution of the iodide acetylide to produce the palladium intermediate VII. Then reductive elimination in the presence of the strong base yields the carbonylative Sonogashira product VIII with the subsequent regeneration of the Pd (0) catalyst.[69] The production of aurones or chromones depends on the type of base used in the reaction. In the presence of diethylamine, the favored Michael addition to the intermediate VIII forms the Michael Adduct IX (Scheme 17, pathway B), which is usually stabilized in DMF as an ideal solvent in these reactions. [63,69]. This Michael adduct (IX) was observed and identified in the reaction mixture by gas chromatography–mass spectrometry (GC–MS) [ $m/z = 296.5$ ;  $C_{19}H_{22}NO_2$  ( $MH^+$ )]. The diethylamine is then eliminated to produce the cyclic enolate X, which is formed the corresponding chromone. When triethylamine was used as a base, no reaction was observed without catalysts. Furthermore, the palladium catalyzed reaction in the presence of triethylamine led to the production of a mixture of aurones and chromones [69]. In this case, it is suggested that the oxidative addition of O–H to the Pd(0) species generates the palladium intermediate XI (Scheme 17, pathway C). The subsequent insertion of the alkyne into Pd–H proceeds following two pathways to generate either the seven-membered metallacycle XII (pathway D) or the six-membered metallacycle XIII (pathway E) as intermediates. These undergo further reductive elimination to produce chromones and aurones, respectively.

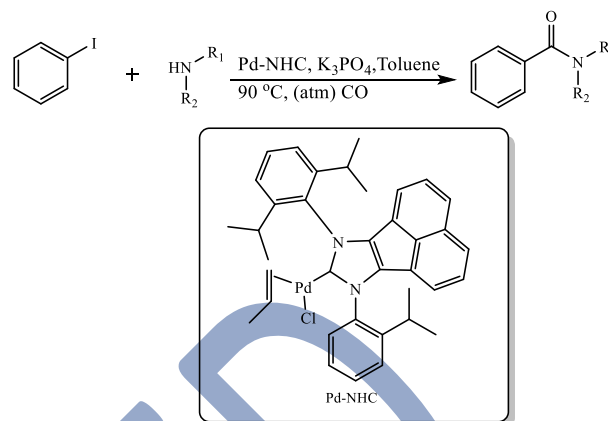


**Scheme (17):** Plausible Mechanism for the Cyclocarbonylative Sonogashira Coupling Reaction Catalyzed by Bridged-Bis(NHC)PdBr<sub>2</sub> Complexes; Production of Chromone [Pathway B or (C,D)], and Aurone (Pathway C–E) [69].

#### Alkoxy and amino carbonylative coupling reactions

Recently, palladium-catalyzed reactions that use aryl halides along with amines or alcohols as starting materials in the presence of carbon monoxide, have been widely used in big industries to make useful fine and bulk chemicals. This method is very flexible and allows the creation of many types of carboxylic acids and their related derivatives in a single step, and from common starting materials. The carboxylic acids and related compounds include straight, branched, and ring-shaped ones, [77–79]. Few studies discuss the use of Pd-NHC complexes for alkoxy carbonylation or amino carbonylation reactions. For instance, the production of bioactive amides

through the aminocarbonylation of different (hetero)aryl iodides with secondary amines using strong allylic palladium-NHC complexes as catalysts under normal CO pressure is shown in Scheme 18 [80].



**Scheme (18):** Allylic palladium-NHC complexes as a catalyst amino carbonylative coupling reactions [80].

#### Conclusion

After many years of quiet progress, scientists have recently worked on a new method to use Palladium (II) complexes with N-Heterocyclic carbene ligands as catalysts in coupling and carbonylation reactions. However, traditional protocols of using transition-metal complexes with phosphine ligands have some big problems. These difficulties of compounds synthesis, the harmful effects, the expensive costs, and poor stability in air and moisture are of the major problems faced by scientists. Recently, a new and promising method was developed. One of these methods is bridging between different pre-ligands that can create new bis-bridged Pd(II)-NHCs complexes which produce rigid and stable catalysts for cross coupling and carbonylative coupling reactions that can work at high temperature, additional to that, some workers innovated hybrid catalysts between NHCs pre-ligands and pyridine to produce new catalysts that have strong sigma donation and can receive electron by pi back donation which can produce efficient catalysts for many carbonylation reactions, in these types of Pd(II)-complexes the effect of steric effect was studied based on spectroscopic techniques correlate with DFT data which proved that bulky substituents can make the complexes soft and efficient for these carbonylative reaction with high selectivity and low loading. All of these types can be immobilized on different heterogenous support which produced new recoverable heterogenous Pd (II)-NHCs catalysts that were recycled around 12 times with high TON. These current trends in the synthesis of Pd (II)-NHCs complexes open new windows for making a useful compound that can be used in medicines, pharmaceuticals, and other industries via cross coupling reactions and carbonylative reactions under mild conditions, high yields, low cost, highly selectivity and ecofriendly.

#### Disclosure Statement

- **Ethics approval and consent to participate:** Not applicable
- **Consent for publication:** Not applicable
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- **Author's contribution:** The authors confirm contribution to the paper as follows: Conceptualization (Mansour W. and Bsharat O.); methodology ((Mansour W. and Bsharat O.);

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## References

- 1] Salih KS. Modern Development in Copper-and Nickel-Catalyzed Cross-Coupling Reactions: Formation of Carbon-Carbon and Carbon-Heteroatom bonds under Microwave Irradiation Conditions. *Asian Journal of Organic Chemistry*. 2022 Apr;11(4):e202200023.
- 2] Behzadi M, Boucher M, Robert J, Djukic JP. Kumada-Corriu Cross-Coupling Reaction Catalyzed by Cobalt Nanoparticles Arising from the Reductive Decomposition of a Cobaltacycle. *An-Najah University Journal for Research-A (Natural Sciences)*. 2025 Aug 30;39(3)
- 3] Neslihan Şahin. Palladium-N-heterocyclic Carbene Complexes: Synthesis, Characterization and Catalytic Application of C–H Activation for Carboxaldehyde Derivatives. *ChemistrySelect*. 2024, Volume9, Issue37 October 4, 2024. e202403032
- 4] Ma X, Wang H, Chen W. N-Heterocyclic carbene-stabilized palladium complexes as organometallic catalysts for bioorthogonal cross-coupling reactions. *The Journal of organic chemistry*. 2014 Sep 19;79(18):8652-8.
- 5] Hopkinson MN, Richter C, Schedler M, Glorius F. An overview of N- heterocyclic carbenes. *Nature*. 2014 Jun 26;510(7506):485-96.
- 6] Salih KS, Baqi Y. Microwave-assisted palladium-catalyzed cross-coupling reactions: Generation of carbon–carbon bond. *Catalysts*. 2019 Dec 18;10(1):4.
- 7] a. Doyle MG, Bsharat O, Sib A, Derdau V, Lundgren RJ. Enantioselective carbon isotope exchange. *Journal of the American Chemical Society*. 2024 Jul 5;146(28):18804-10. b. Doyle MG, Mair BA, Sib A, Bsharat O, Munch M, Derdau V, Rotstein BH, Lundgren RJ. A practical guide for the preparation of C1-labeled  $\alpha$ -amino acids using aldehyde catalysis with isotopically labeled CO<sub>2</sub>. *Nature Protocols*. 2024 Jul;19(7):2147-79.
- 8] Dagnaw WM, Hailu YM, Mohammed AM. Mechanistic insights into base-free nickel-catalyzed Suzuki-Miyaura cross-coupling of acid fluoride and the origin of chemoselectivity: a DFT study. *RSC Adv*. 2025 May 22;15(22):17241-17247. doi: 10.1039/d5ra01845e. eCollection 2025 May 21. PMID: 40406014
- 9] Reizman BJ, Wang YM, Buchwald SL, Jensen KF. Suzuki–Miyaura cross-coupling optimization enabled by automated feedback. *Reaction chemistry & engineering*. 2016;1(6):658-66.
- 10] Diao Y, Hao R, Kou J, Teng M, Huang G, Chen Y. Synthesis, structural characterization and catalytic activity of benzimidazole-functionalized Pd (II) N-heterocyclic carbene complexes. *Applied Organometallic Chemistry*. 2013 Sep;27(9):546-51.
- 11] Ezugwu CI, Mousavi B, Asrafa MA, Mehta A, Vardhan H, Verpoort F. An N-heterocyclic carbene based MOF catalyst for Sonogashira cross-coupling reaction. *Catalysis Science & Technology*. 2016;6(7):2050-4.
- 12] Shahnaz N, Banik B, Das P. A highly efficient Schiff-base derived palladium catalyst for the Suzuki–Miyaura reactions of aryl chlorides. *Tetrahedron Letters*. 2013 May 29;54(22):2886-9.
- 13] Song C, Ma Y, Chai Q, Ma C, Jiang W, Andrus MB. Palladium catalyzed Suzuki–Miyaura coupling with aryl chlorides using a bulky phenanthryl N-heterocyclic carbene ligand. *Tetrahedron*. 2005 Aug 1;61(31):7438-46.
- 14] a. Akkoc S, Sahin D, Muhammed MT, Yıldız M, İlhan İO. Synthesis, characterization, antiproliferative activity, docking, and molecular dynamics simulation of new 1, 3-dihydro-2 H-benzimidazol-2-one derivatives. *Journal of Biomolecular Structure and Dynamics*. 2024 Dec 9;42(21):11495-507. b. Bsharat O, Salama Y, Al-Hajj N, Al-Maharik N. Chiliadenus iphionoides: From chemical profiling to anticancer, antioxidant,  $\alpha$ -amylase, and  $\alpha$ -glycosidase activities. *PloS one*. 2025 Jul 1;20(7):e0327632.
- 15] Fortman GC, Nolan SP. N-Heterocyclic carbene (NHC) ligands and palladium in homogeneous cross-coupling catalysis: a perfect union. *Chemical Society Reviews*. 2011;40(10):5151-69.
- 16] Lei P, Meng G, Ling Y, An J, Szostak M. Pd-PEPPSI: Pd-NHC precatalyst for Suzuki–Miyaura cross-coupling reactions of amides. *The Journal of Organic Chemistry*. 2017 Jul 7;82(13):6638-46.
- 17] a. Han F, Xu Y, Zhu R, Liu G, Chen C, Wang J. Highly active NHC–Pd (ii) complexes for cross coupling of aryl chlorides and arylboronic acids: an investigation of the effect of remote bulky groups. *New Journal of Chemistry*. 2018;42(9):7422-7. b. Al-Hajj N, Bsharat O, Jaradat N, Abdallah L, Mousa M, Al-Maharik N. Assessing Salvia dominica L.: from chemical profiling to antioxidant, antimicrobial, anticancer,  $\alpha$ -amylase, and  $\alpha$ -glycosidase activities of the plant essential oil. *Chemical and Biological Technologies in Agriculture*. 2025 Dec;12(1):1-1.
- 18] Li G, Lei P, Szostak M, Casals-Cruaños E, Poater A, Cavallo L, Nolan SP. Mechanistic Study of Suzuki–Miyaura Cross-Coupling Reactions of Amides Mediated by Pd (NHC)(allyl)

- CiJ Precatalysts. ChemCatChem. 2018 Jul 19;10(14):3096-106.
- 19] Lei P, Meng G, Ling Y, An J, Szostak M. Pd-PEPPSI: Pd-NHC precatalyst for Suzuki–Miyaura cross-coupling reactions of amides. *The Journal of Organic Chemistry*. 2017 Jul 7;82(13):6638-46.
  - 20] Samarasimhareddy M, Prabhu G, Vishwanatha TM, Sureshbabu VV. PVC-supported palladium nanoparticles: an efficient catalyst for Suzuki cross-coupling reactions at room temperature. *Synthesis*. 2013 May;45(09):1201-6.
  - 21] Stevens PD, Fan J, Gardimalla HM, Yen M, Gao Y. Superparamagnetic nanoparticle-supported catalysis of Suzuki cross-coupling reactions. *Organic letters*. 2005 May 26;7(11):2085-8.
  - 22] Yang J, Li P, Wang L. Recyclable Catalysts for Suzuki–Miyaura Cross-Coupling Reactions at Ambient Temperature Based on a Simple Merrifield Resin Supported Phenanthroline-Palladium (II) Complex. *Synthesis*. 2011 Apr;2011(08):1295-301.
  - 23] Rajabi F, Thiel WR. An Efficient Palladium N-Heterocyclic Carbene Catalyst Allowing the Suzuki–Miyaura Cross-Coupling of Aryl Chlorides and Arylboronic Acids at Room Temperature in Aqueous Solution. *Advanced Synthesis & Catalysis*. 2014 May 26;356(8):1873-7.
  - 24] a. Zhang C, Liu J, Xia C. Aryl-palladium-NHC complex: efficient phosphine-free catalyst precursors for the carbonylation of aryl iodides with amines or alkynes. *Organic & Biomolecular Chemistry*. 2014;12(47):9702-6. b. Bsharat O, Salama Y, Al-Hajj N, Saed E, Jaradat N, Warad I, Al-Maharik N. Chemical profiling and biological assessment of essential oil from *Artemisia herba-alba*. *Scientific Reports*. 2025 Aug 27;15(1):31538.
  - 25] Chartoire A, Boreux A, Martin AR, Nolan SP. Solvent-free aryl amination catalysed by Pd (NHC)] complexes. *RSC Advances*. 2013;3(12):3840-3.
  - 26] Nguyen VH, Ibrahim MB, Mansour WW, El Ali BM, Huynh HV. postmodification approach to charge-tagged 1, 2, 4-triazole-derived NHC Palladium (II) complexes and their applications. *Organometallics*. 2017 Jun 26;36(12):2345-53. b. Warad I, Bsharat O, Tabti S, Djedouani A, Al-Nuri M, Al-Zaqri N, Kumara K, Lokanath NK, Amereih S, Abu-Reidah IM. Crystal interactions, computational, spectral and thermal analysis of (E)-N'-(thiophen-2-ylmethylene) isonicotinohydrazide as ONS-tridentate schiff base ligand. *Journal of Molecular Structure*. 2019 Jun 5;1185:290-9.
  - 27] Touj N, Al-Ayed AS, Sauthier M, Mansour L, Harrath AH, Al-Tamimi J, Özdemir I, Yaşar S, Hamdi N. Efficient in situ N-heterocyclic carbene palladium (ii) generated from Pd (OAc) 2 catalysts for carbonylative Suzuki coupling reactions of arylboronic acids with 2-bromopyridine under inert conditions leading to unsymmetrical arylpyridine ketones: synthesis, characterization and cytotoxic activities. *RSC advances*. 2018;8(70):40000-15.
  - 28] Lin YC, Hsueh HH, Kanne S, Chang LK, Liu FC, Lin IJ, Lee GH, Peng SM. Efficient PEPPSI-themed palladium N-heterocyclic carbene precatalysts for the Mizoroki–Heck reaction. *Organometallics*. 2013 Jul 22;32(14):3859-69.
  - 29] Fernando JE, Nakano Y, Zhang C, Lupton DW. Enantioselective N-Heterocyclic Carbene Catalysis that Exploits Imine Umpolung. *Angewandte Chemie*. 2019 Mar 18;131(12):4047-51. b. Bsharat O. 12C/13C isotope exchange for the synthesis of D-13C] phenylalanine by using 13C] CO2 and binol chiral aldehyde receptor. *Journal of Radioanalytical and Nuclear Chemistry*. 2025 May;334(5):3669-82.
  - 30] Romanov V, Tretyakov E, Selivanova G, Li J, Bagryanskaya I, Makarov A, Luneau D. Synthesis and Structure of Fluorinated (Benzo d] imidazol-2-yl) methanols: Bench Compounds for Diverse Applications. *Crystals*. 2020 Sep 4;10(9):786.
  - 31] Wang AE, Xie JH, Wang LX, Zhou QL. Triaryl phosphine-functionalized N-heterocyclic carbene ligands for Heck reaction. *Tetrahedron*. 2005 Jan 3;61(1):259-66.
  - 32] Xu Q, Duan WL, Lei ZY, Zhu ZB, Shi M. A novel cis-chelated Pd (II)–NHC complex for catalyzing Suzuki and Heck-type cross-coupling reactions. *Tetrahedron*. 2005 Nov 21;61(47):11225-9.
  - 33] Mansour W, Suleiman R, Iali W, Fettouhi M, El Ali B. Synthesis, crystal structure, and catalytic activity of bridged-bis (N-heterocyclic carbene) palladium (II) complexes in selective Mizoroki–Heck cross-coupling reactions. *Polyhedron*. 2021 Oct 1;207:115371.
  - 34] Chinchilla R, Nájera C. The Sonogashira reaction: a booming methodology in synthetic organic chemistry. *Chemical reviews*. 2007 Mar 14;107(3):874-922.
  - 35] Bakherad M, Kelvanloo A, Bahramian B, Jajarmi S. Copper- and solvent-free Sonogashira coupling reactions of aryl halides with terminal alkynes catalyzed by 1-phenyl-1, 2-propanedione-2-oxime thiosemi-carbazone-functionalized polystyrene resin supported Pd (II) complex under aerobic conditions. *Applied Catalysis A: General*. 2010 Dec 20;390(1-2):135-40.
  - 36] Touj N, Yaşar S, Özdemir N, Hamdi N, Özdemir İ. Sonogashira cross-coupling reaction catalysed by mixed NHC-Pd-PPh3 complexes under copper free conditions. *Journal of Organometallic Chemistry*. 2018 Apr 1;860:59-71. b. Bsharat O. Classical and modern methods for carbon isotope labeling. *Moroccan Journal of Chemistry*. 2024 May 8;12(3):1110-21.
  - 37] Ibrahim M, Malik I, Mansour W, Sharif M, Fettouhi M, El Ali B. Novel (N-heterocyclic carbene) Pd (pyridine) Br2 complexes for carbonylative Sonogashira coupling reactions: Catalytic efficiency and scope for arylalkynes, alkylalkynes and dialkynes. *Applied Organometallic Chemistry*. 2018 Apr;32(4):e4280.
  - 38] Santra S, Hota PK, Bhattacharyya R, Bera P, Ghosh P, Mandal SK. Palladium nanoparticles on graphite oxide: A recyclable catalyst for the synthesis of biaryl cores. *ACS Catalysis*. 2013 Dec 6;3(12):2776-89. 39] Roelen, O.; *Angew. Chem. A*. 60, 3, pp. 213, 1948.
  - 40] Gronnow MJ, Luque R, Macquarrie DJ, Clark JH. A novel highly active biomaterial supported palladium catalyst. *Green Chemistry*. 2005;7(7):552-7.
  - 41] Bolm C. Transition metals for organic synthesis. Beller M, editor. Weinheim: Wiley-VCH; 2004 Aug 25.
  - 42] Tsuji J. Organic synthesis with palladium compounds. Springer Science & Business Media; 2012 Dec 6.
  - 43] Aggarwal V. Transition Metals for Organic Synthesis. Vols. I, II Edited by M. Beller and C. Bolm. Wiley-VCH: Weinheim. 1998. 1030 pp. \$595.00. ISBN 3-521-29501-1.
  - 44] Huang B, Ban X, Sun K, Ma Z, Mei Y, Jiang W, Lin B, Sun Y. Thermally activated delayed fluorescence materials based on benzophenone derivative as emitter for efficient solution-

- processed non-doped green OLED. *Dyes and Pigments*. 2016 Oct 1;133:380-6.
- 45] Bjerglund KM, Skrydstrup T, Molander GA. Carbonylative Suzuki couplings of aryl bromides with boronic acid derivatives under base-free conditions. *Organic Letters*. 2014 Apr 4;16(7):1888-91.
  - 46] Graham E, Rymarchyk S, Wood M, Cen Y. Development of activity-based chemical probes for human sirtuins. *ACS chemical biology*. 2018 Jan 31;13(3):782-92.
  - 47] Guy MR, Illarionov PA, Gurcha SS, Dover LG, Gibson KJ, Smith PW, Minnikin DE, Besra GS. Novel prenyl-linked benzophenone substrate analogues of mycobacterial mannosyltransferases. *Biochemical Journal*. 2004 Sep 15;382(3):905-12.
  - 48] Touj N, Al-Ayed AS, Sauthier M, Mansour L, Harrath AH, Al-Tamimi J, Özdemir I, Yaşar S, Hamdi N. Efficient in situ N-heterocyclic carbene palladium (ii) generated from Pd (OAc) 2 catalysts for carbonylative Suzuki coupling reactions of arylboronic acids with 2-bromopyridine under inert conditions leading to unsymmetrical arylpyridine ketones: synthesis, characterization and cytotoxic activities. *RSC advances*. 2018;8(70):40000-15.
  - 49] Mansour W, Fettouhi M, El Ali B. Novel and efficient bridged bis(N-heterocyclic carbene) palladium(II) catalysts for selective carbonylative Suzuki–Miyaura coupling reactions to biaryl ketones and biaryl diketones. *Appl Organometal Chem*. 2020;e5636.
  - 50] Tasch BO, Merkul E, Frank W, Mueller TJ. New three-component glyoxylation-decarbonylative stille coupling sequence to Acyl heterocycles under mild conditions. *Synthesis*. 2010 Jul;2010(13):2139-46.
  - 51] Whittaker RE, Dermenci A, Dong G. Synthesis of ynones and recent application in transition-metal-catalyzed reactions. *Synthesis*. 2016 Jan;48(02):161-83.
  - 52] Peng S, Wang Z, Zhang L, Zhang X, Huang Y. Streamlined asymmetric  $\alpha$ -difunctionalization of Ynones. *Nature Communications*. 2018 Jan 25;9(1):375.
  - 53] Wender PA, Hardman CT, Ho S, Jeffreys MS, Maclaren JK, Quiroz RV, Ryckbosch SM, Shimizu AJ, Sloane JL, Stevens MC. Scalable synthesis of bryostatin 1 and analogs, adjuvant leads against latent HIV. *Science*. 2017 Oct 13;358(6360):218-23.
  - 54] Marsden MD, Loy BA, Wu X, Ramirez CM, Schrier AJ, Murray D, Shimizu A, Ryckbosch SM, Near KE, Chun TW, Wender PA. In vivo activation of latent HIV with a synthetic bryostatin analog effects both latent cell "kick" and "kill" in strategy for virus eradication. *PLoS pathogens*. 2017 Sep 21;13(9):e1006575.
  - 55] Yang X, Ullah Z, Stoddart JF, Yavuz CT. Porous organic cages. *Chemical Reviews*. 2023 Apr 6;123(8):4602-34.
  - 56] Taylor CL, Bolshan Y. Metal-free Synthesis of Ynones from Acyl Chlorides and Potassium Alkynyltrifluoroborate Salts. *Journal of Visualized Experiments: Jove*. 2015 Feb 24(96):52401.
  - 57] Ahmed MS, Mori A. Carbonylative Sonogashira coupling of terminal alkynes with aqueous ammonia. *Organic Letters*. 2003 Aug 1;5(17):3057-60.
  - 58] Satapathy A, Gadge ST, Kusumawati EN, Harada K, Sasaki T, Nishio-Hamane D, Bhanage BM. Synthesis of Polyester Amide by Carbonylation–Polycondensation Reaction Using Immobilized Palladium Metal Containing Ionic Liquid on SBA-15 as a Phosphine-Free Catalytic System. *Catalysis Letters*. 2015 Mar;145(3):824-33.
  - 59] Brennfürer A, Neumann H, Beller M. Palladium-catalyzed carbonylation reactions of aryl halides and related compounds. *Angewandte Chemie International Edition*. 2009 May 25;48(23):4114-33.
  - 60] Bai C, Jian S, Yao X, Li Y. Carbonylative Sonogashira coupling of terminal alkynes with aryl iodides under atmospheric pressure of CO using Pd (II)@ MOF as the catalyst. *Catalysis Science & Technology*. 2014;4(9):3261-7.
  - 61] Ibrahim MB, Malik I, Shakil Hussain SM, Fazal A, Fettouhi M, El Ali B. Synthesis, crystal structures and catalytic activities of new palladium (II)–bis (oxazoline) complexes. *Transition Metal Chemistry*. 2016 Oct;41(7):739-49.
  - 62] Gautam P, Tiwari NJ, Bhanage BM. Aminophosphine palladium pincer-catalyzed carbonylative Sonogashira and Suzuki–Miyaura cross-coupling with high catalytic turnovers. *ACS omega*. 2019 Jan 17;4(1):1560-74.
  - 63] Mansour W, Suleiman R, Fettouhi M, El Ali B. Soft heteroleptic N-Heterocyclic carbene palladium (II) species for efficient catalytic routes to alkynones via carbonylative Sonogashira coupling. *ACS omega*. 2020 Aug 18;5(37):23687-702.
  - 64] Ibrahim M, Malik I, Mansour W, Sharif M, Fettouhi M, El Ali B. Efficient N-heterocyclic carbene palladium (II) catalysts for carbonylative Suzuki–Miyaura coupling reactions leading to aryl ketones and diketones. *Journal of Organometallic Chemistry*. 2018 Mar 15;859:44-51.
  - 65] Scattolin T, Nolan SP. Synthetic routes to late transition metal–NHC complexes. *Trends in Chemistry*. 2020 Aug 1;2(8):721-36.
  - 66] Ferreira A, Pousinho S, Fortuna A, Falcao A, Alves G. Flavonoid compounds as reversal agents of the P-glycoprotein-mediated multidrug resistance: biology, chemistry and pharmacology. *Phytochemistry Reviews*. 2015 Apr;14(2):233-72.
  - 67] Y. Kanzouai et al. Design, synthesis and characterization of new amide-linked chromone-isoxazole hybrids: in vitro anti-bacterial and antioxidant evaluation, DFT calculations, ADMET profiling, docking and molecular dynamics simulation *J Mol Struct* (2025), Volume 1325, 15 March 2025, 140972
  - 68] Xue L, Shi L, Han Y, Xia C, Huynh HV, Li F. Pd–carbene catalyzed carbonylation reactions of aryl iodides. *Dalton Transactions*. 2011 Jul 11;40(29):7632-8.
  - 69] Mansour W, Fettouhi M, El Ali B. Regioselective synthesis of chromones via cyclocarbonylative sonogashira coupling catalyzed by highly active bridged-bis (N-Heterocyclic Carbene) Palladium (II) Complexes. *ACS omega*. 2020 Dec 8;5(50):32515-29.
  - 70] Alwan GZ, Jawad EM, Kareem HH, Almansouri RJ. Biological Effect of Cobalt Oxide Nanoparticles Synthesized from (Cinnamon and Nigella sativa) Extracts and Chemical Method: A Comparative Study. *An-Najah University Journal for Research-A (Natural Sciences)*. 2025 Jul 15;39(3).
  - 71] Salameh S, Soboh S, Bsharat A, Maali R, Assali M, Ishtaiwi M, Hajjyahya M, Zarour A, Sawalha S. Preparation of Silver Nanoparticles/Polyvinyl alcohol Nanocomposite Films with Enhanced Electrical, Thermal, and Antimicrobial Properties.

- 72] Zyoud A, Jondi W, Mansour W, M. A. Majeed Khan, Hikmat S. Hilal. Modes of tetra(4-pyridyl) porphyrinatomanganese(III) ion intercalation inside natural clays. *Chemistry Central Journal* (2016) 10:12
- 73] Jondi W. Zyoud A, Mansour W, A Q Hussein, Hikmat S. Hilal. Highly active and selective catalysts for olefin hydrosilylation reactions using metalloporphyrins intercalated in natural clays. *React. Chem. Eng.*, 2016, 1194.
- 74] Badran I. Al-Ejlil M. Efficient adsorptive removal of methyl green using Fe<sub>3</sub>O<sub>4</sub>/sawdust/ MWCNT: Explaining sigmoidal behavior. *j.mtcomm*. Volume 41, December 2024, 110302.
- 75] Hacıfendioğlu D, Tuncel A. N-heterocyclic carbene-palladium complex immobilized on Co-MOF 74 microrods as a highly selective catalyst for Suzuki–Miyaura cross-coupling. N-heterocyclic carbene-palladium complex immobilized on Co-MOF 74 microrods as a highly selective catalyst for Suzuki–Miyaura cross-coupling. *Reac Kinet Mech Cat* 138, 1363–1380 (2025). <https://doi.org/10.1007/s11144-024-02777>.
- 76] Mansour W, Fettouhi M, Saleem Q, El Ali B. Robust alkyl-bridged bis (N-heterocyclic carbene) palladium (II) complexes anchored on Merrifield's resin as active catalysts for the selective synthesis of flavones and alkynones. *Applied Organometallic Chemistry*. 2021 May;35(5):e6195.
- 77] Wang T, Xu K, Wang W, Zhang AA, Liu L. Dinuclear NHC–palladium (II) complexes: synthesis, characterization and application to Suzuki–Miyaura cross-coupling reactions. *Transition Metal Chemistry*. 2018 May;43(4):347-53.
- 78] McNulty J, Nair JJ, Robertson A. Efficient carbonylation reactions in phosphonium salt ionic liquids: anionic effects. *Organic Letters*. 2007 Oct 25;9(22):4575-8. B. Badran I. From germolane to germylenes: a theoretical DFT study of thermal decomposition pathways and reactivity. *Journal of Coordination Chemistry*. 2024 Nov 1;77(20-21):2440-52.
- 79] Jayasree S, Seayad A, Gupte SP, Chaudhari RV. A novel palladium complex catalyst for carbonylation of alkynes under mild conditions. *Catalysis letters*. 1999 May;58(4):213-6.
- 80] Fang W, Deng Q, Xu M, Tu T. Highly efficient aminocarbonylation of iodoarenes at atmospheric pressure catalyzed by a robust acenaphthoimidazolidene allylic palladium complex. *Organic Letters*. 2013 Jul 19;15(14):3678-81.