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Review

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Recent Developments on Palladium-Catalyzed Carbonylation Reactions in Renewable Solvents

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Palladium-catalyzed carbonylation reaction has surfaced as a robust tool for insertion of the carbonyl group into organic molecules, and in the last decades enormous progress has been made. Nowadays, a plethora of methodologies is available to synthesize all kinds of carbonyl compounds. However, the focus has shifted during recent years to address rising concerns related to developing safe, cost-efficient, and more sustainable methodologies. The use of different carbon monoxide (CO) precursors/sources, avoiding handling of highly toxic and flammable gaseous carbon monoxide, and substituting nonrenewable solvents for those derived from renewable feedstock have contributed to aim these goals. In this review, we will discuss the advent of the application of renewable solvents to improve the sustainability and environmentally benign nature of Pd-catalyzed carbonylation reactions.

Keywords: palladium-catalyzed, carbon monoxide, carbonylation reactions, renewable solvent, sustainability

1. Introduction

Growing concern over the impact of chemical processes, associated with the rising price of oil, as well as, the need to search for greener, sustainable, and economically viable chemicals, has prompted the scientific community around the world to develop new cost-efficient, environmentally benign and efficient synthetic protocols to minimize waste generation and attend the demand for chemical products from an ever-increasing population.[1-5] Solvents are present in most chemical processes and generally account for the primary source of the wasted mass of fine chemical and pharmaceutical industry. The reason is mainly due to the required large quantities of organic solvent during synthesis and purification of complex molecules, making it a cause of primary environmental concern due to their toxic, flammable, and/or corrosive properties, as well as the issues associated with health and/or safety.[6-10] Although the development of new solvent-free alternative processes could offer eco-friendly solutions, running a reaction in a solvent is often essential to facilitate mass and heat transfer. In addition, the appropriate choice of solvent can also facilitate the reaction, improve the reactivity and selectivity, or the position of chemical equilibria.[11,12] In recent years, environmental directives and legislation have been driven significant progress towards a more sustainable reaction media. There are two general strategies to find a suitable material that can act as an alternative solvent and, therefore, lessening the environmental impact of the processes. The first strategy is the substitution of conventional hazardous volatile organic solvents by nonvolatile alternatives that show better environmental, health and safety properties. The second strategy is the replacement of solvents produced from fossil resources with renewable solvents, i.e., solvents emanating from renewable feedstock.[13,14] Nonetheless, one question arises: which criteria must be taken into account to measure how green and sustainable a solvent is? To this end, Gu and Jérôme[15] inspired by the 12 well-known principles of green chemistry published by Anastas and Warner in 1998,[16] proposed twelve criteria that a green and sustainable solvent should exhibit: availability, price, recyclability, grade, synthesis, toxicity, biodegradability, performance, stability, flammability, storage and renewability.[17] There is

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no perfect green and sustainable solvent that meets all those criteria and therefore choices have to be made if the solvent is crucial to a process.[18,19] To help researches to select more sustainable practices, many pharmaceutical companies and collaborative groups such as Innovative Medicines Initiative (IMI)-CHEM21 and ACS Green Chemistry Institute Pharmaceutical Roundtable (GCI-PR) have elaborated solvent selection guides based on its properties.[20-27] In the last 15-20 years, significant efforts have been made to find innovative and greener reaction media.[28-33] In such way several environment-friendly tunable and smart solvents such as supercritical fluids, room temperature ionic liquids and renewable solvents have been proposed for better solutions.[2,15,34-49]

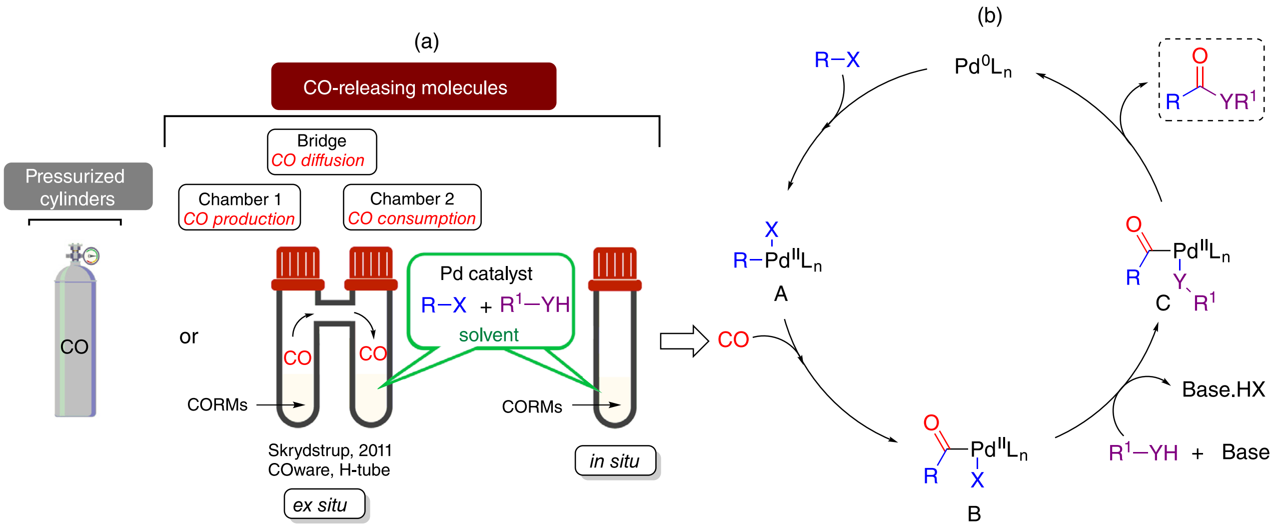
Transition metal-catalyzed carbonylation reactions have become a powerful synthetic way to insert a variety of carbonyl-based functional groups.[50-65] The carbonyl insertion can be achieved mainly by using carbon monoxide pressurized cylinders in the presence of CO detectors to protect the operator. However, the challenge associated with this strategy is the requirement for handling large volumes of gaseous, corrosive, odorless and highly toxic CO from a pressurized cylinder (Scheme 1a). Extensive research on this field led to the advent of CO-releasing molecules (CORMs) for generating CO gas *in* and *ex situ* during the reaction (Scheme 1a).[51,55,66] In such a way, different methodologies based on Pd-catalyzed carbonylation reactions have been reported[67-78] to prepare highly valuable compounds, such as aldehydes, ketones, carboxylic acids, and their derivatives. Recent attention has shifted to improving the overall sustainability of the carbonylation reactions using greener and more sustainable solvents.[79] The fact that these reactions have been used to prepare a range of important pharmaceutical and industrial products makes the development of renewable methodologies for carbonylations a task of great importance.

Palladium-catalyzed carbonylation reactions usually involves coupling of a suitable organic halide (or pseudohalide) and a nucleophile in the presence of CO.[80] The three-component reaction follow a common pathway (Scheme 1b). The first step involves the oxidative addition of Pd^0 catalyst into the aryl halide, resulting in the intermediate Pd^{II}-aryl halide complex **A**. Subsequently, intermediate **A** undergoes coordination with CO accompanied by ligand displacement and 1,1-insertion generates the acyl-palladium complex **B**, susceptible to attack by nucleophiles in the presence of a base to afford the intermediate complex **C**. The carbonylated product is then formed through reductive elimination of **C** and restoring the catalytically active Pd^0 species.

In face of the growing significance of the carbonylation reactions, in this review, we are focusing on the most recent developments in the design of enabling green strategies for carbonylation reactions employing safer and environmentally benign solvents. To facilitate the reader's understanding, the article has classified according to the renewable solvent used, in the following order: 2-methyltetrahydrofuran, gamma-valerolactone, carbonates, deep eutectic solvents, bio-polyethylene glycol, anisole and water. In addition, the carbonylation reactions that do not fit in any of these solvents or that fit in more than one is compiled in the Miscellaneous sub-section.

2. Renewable Solvents

In the past decades, much attention has been devoted to renewable feedstock to produce high-value chemicals products and replace those derived from



Scheme 1. (a) Carbonylation reaction with gas-pressurized cylinders and with CORMs; (b) general mechanism of palladium-catalyzed carbonylation reaction.

fossil raw materials.[2,15,49] Renewable solvents, such as ethanol, 2-methyltetrahydrofuran, gamma-valerolactone, (*R*)-(+)-limonene, *p*-cymene, dimethyl and propylene carbonates, eucalyptol, deep eutectic solvents and many others have been recently proposed as alternative green media for organic reactions.[2,15,49,80-83] Such molecules are derived from vegetable, animal or mineral raw materials, and carbon dioxide, using chemical and physical processes that are safer for the environment and humans. Moreover, because their conception is compatible with sustainable development, renewable solvents are expected to provide a positive environmental balance (volatile organic compound reduction, biodegradability, non-ecotoxicity) to improve safety aspects. The processes involved in solvent production must be eco-compatible and the selection of renewable raw materials depends on their availability, cropping cycle, physicochemical properties and cost.[49]

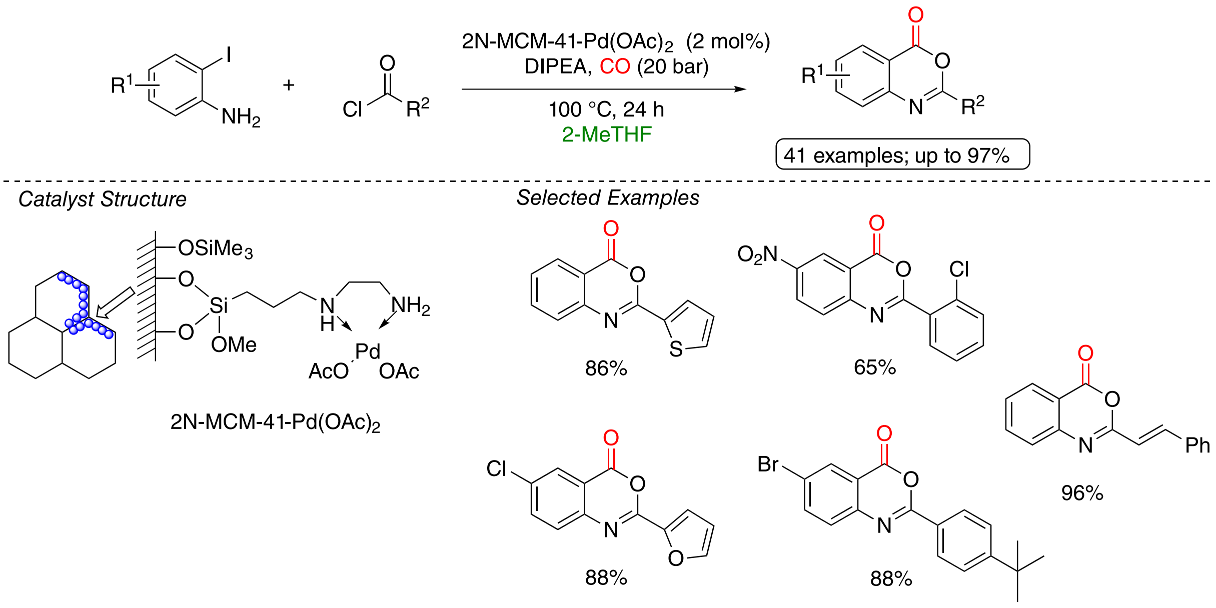
2.1. 2-Methyltetrahydrofuran (2-MeTHF)

2-MeTHF is a commercially available solvent with a broad application in organic synthesis that is produced from renewable resources (e.g., furfural or levulinic acid).[84,85] The use of this solvent in industrial and academic research has been gained popularity in recent years as an alternative to commonly employed tetrahydrofuran (THF) in several synthetic procedures because of its low toxicity and high biodegradability.[86,87] Besides its advantages with respect to environmental impact, several critical aspects of 2-MeTHF make it an interesting medium to study chemical syntheses: (*i*) the low solubility in water favors a clean work-up, allowing recovery of the product; (*ii*) it is highly stable towards acids and bases; (*iii*) it is not easily oxidized; (*iv*) it can be dried without the need to use dangerous drying agents; (*v*) it has a higher boiling point compared to THF, which can be advantageous in some instances.

Due to environmental and economic concerns, the use of 2-MeTHF as an ecofriendly solvent increased in recent years. Taking this into account, Cai and co-workers[88] reported in 2020 a novel, efficient and green methodology for the synthesis of 2-substituted 4*H*-3,1-benzoxazin-4-one derivatives from readily available 2-iodoanilines and acyl chlorides through a heterogeneous palladium catalyzed cyclocarbonylation reaction (Scheme 2). The reaction proceeded efficiently for a broad range of substrates, affording 41 compounds with 64-97% yields. Recycling studies were carried out for eight cycles giving excellent reproductible yields without an apparent decrease in catalytic activity. The significant improvement of this new methodology reported by Cai and co-workers[88] comes from replacing common toxic solvents, e.g., THF and *N*,*N*-dimethylformamide (DMF) with renewable 2-MeTHF and from the use of a heterogeneous catalyst that could be easily recovered via a simple filtration process.

2.2. Gamma-valerolactone (GVL)

GVL has become the most popular bio-derived platform chemical.[89-91] It can be easily produced from lignocellulosic biomass in a multistep process.[89-93] The excellent properties of GVL allow it to be used as a renewable fuel or as a biomass-based solvent. GVL offers several interesting chemical-physical characteristics that make it an ideal sustainable alternative to conventional polar aprotic



Scheme 2. Heterogeneous Pd-catalyzed cyclocarbonylation of 2-iodoanilines with acyl chlorides in 2-MeTHF.

solvents. For instance, GVL is a stable liquid, non-toxic, safe to store; its polarity is quite similar to those of the most common solvents, has a high boiling/flash point, high solubility in water and its vapor pressure is 0.65 kPa at 25 °C. Notably, it increases only to 3.5 kPa.[94] Due to its very low toxicity, GVL has found applications as a reaction medium in the synthesis of pharmaceuticals.[89-91]

Aminocarbonylations reactions have gained particular importance in the last years. However, these reactions are routinely carried out in conventional organic solvents such as, DMF, toluene and 1,4-dioxane.[73,95-97] In 2016, Mika and co-workers[98] described the first application of GVL as an alternative biomass-based medium for Pd-catalyzed aminocarbonylation reactions. The *tert*-butylamine, and iodobenzene as model substrates and its 4-substituted benzene derivatives were converted to the corresponding 2-ketocarboxamides with high conversions and chemoselectivities (Scheme 3). The application of GVL as an alternative solvent for Pd-catalyzed aminocarbonylation reactions allowed a greener procedure for this synthetically relevant transformation.

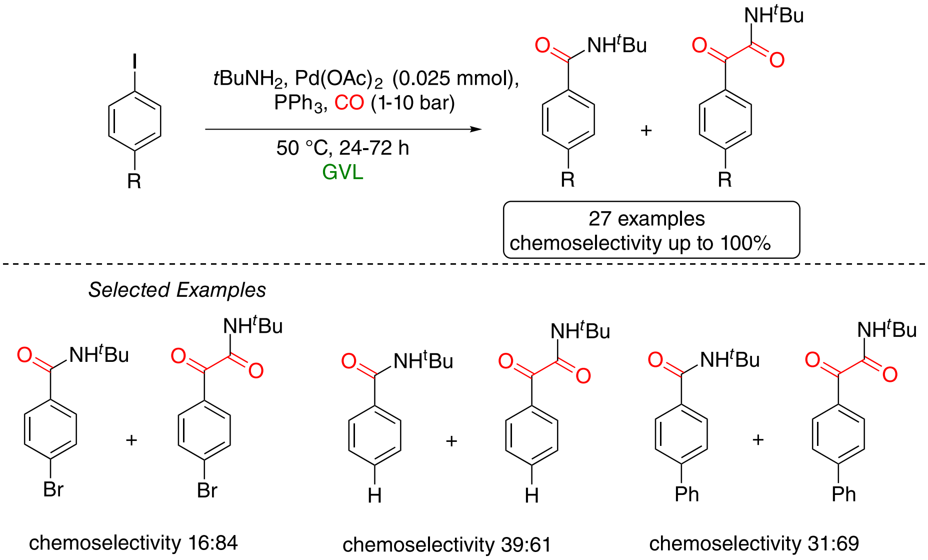
Later in 2020, the same group reported[99] the phosphine-free Pd-catalyzed aryloxycarbonylation reactions of different aryl iodides using γ-valerolactone as a renewable and environmentally benign reaction medium and K_2CO_3 as an inorganic base. The results obtained in GVL were superior compared with those obtained in common organic solvents such as *n*-octane, toluene, 1,4-dioxane, DMF and dimethyl sulfoxide (DMSO). Concerning the scope of the reaction, a wide range of aryl iodides and substituted phenols, bearing both electron-donating and withdrawing groups, could be successfully applied to this protocol, to afford the corresponding products in moderate to high yields (60-99%). The present protocol has also been extended to the alkoxycarbonylation of aryl iodides with several alcohols (Scheme 4).

4(3*H*)-Quinazolinones are privileged heterocyclic cores that display a vast spectrum of biological activities.[100] In 2017, Cravotto and co-workers[101] reported a green synthesis of 4(3*H*)-quinazolinones in GVL under microwave irradiation via four-component carbonylative coupling reactions of *o*-iodoanilines, carbon monoxide, trimethyl orthoformate and a variety of amines (Scheme 5). The heterogeneous Pd/β-cyclodextrin cross-linked catalyst showed to apply to a wide range of amines, providing 4(3*H*)-quinazolinones in good to excellent yields.

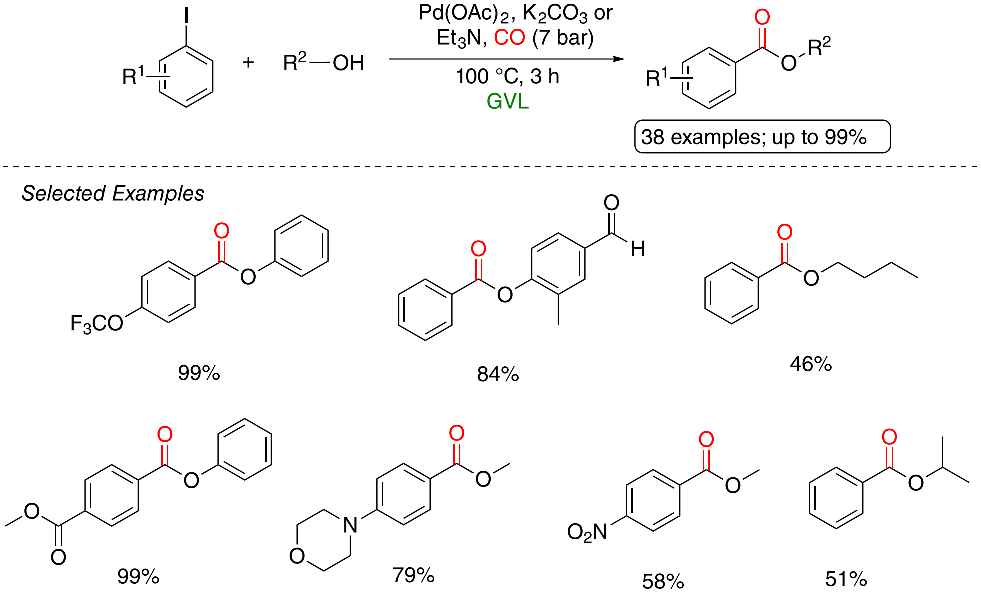
The main advantage of using GVL as a solvent appears to be the possibility of efficiently isolating the crude product from the reaction mixture. According to the authors, when GVL was used, the crude product could be efficiently isolated via precipitation by adding a small amount of water after heterogeneous catalyst recovery, minimizing waste production. Notably, the catalyst could be recycled five times with only a slight decrease in yields being observed (Figure 1). Interestingly, the GVL was recycled up to four times, without detriment on yields (Figure 1). Moreover, this green protocol avoids toxic solvents such as MeCN and can easily be scaled up to the gram scale.

2.3. Carbonates - dimethyl carbonate and propylene carbonate

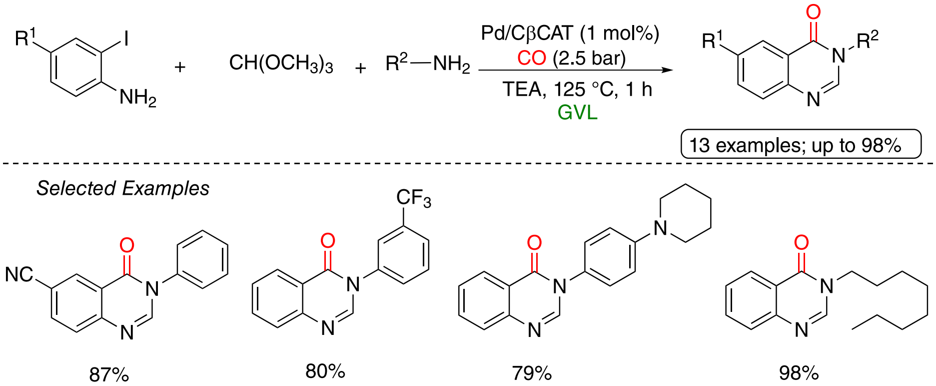
Organic carbonates are a renewable chemical with numerous and growing applications such as their use as solvents in industry or as additives for plastics.[80,102] Synthesis of organic carbonates from CO_2 as economical,



Scheme 3. Application of GVL as an alternative biomass-based medium for synthesis of 2-ketocarboxamides.



Scheme 4. Pd-catalyzed aryloxy- and alkoxycarbonylation of aromatic iodides in GVL as bio-based solvent.



Scheme 5. Microwave-assisted, green synthesis of 4(3*H*)-quinazolinones under CO pressure in GVL.

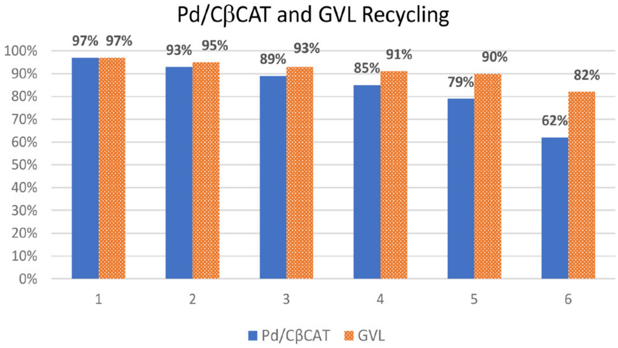
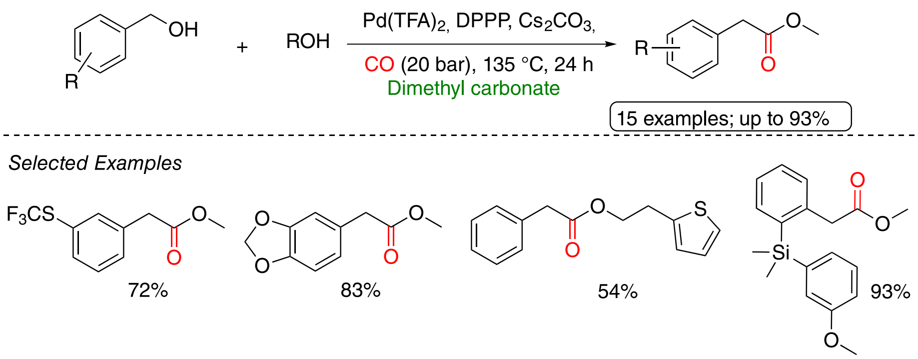


Figure 1. Catalyst and solvent recycling (adapted from reference 102).

non-toxic and abundant raw material is one of the most significant opportunities for the use of CO_2 in the chemical industry.[103] In general, they can be divided into linear carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC) and cyclic carbonates, where the most relevant is propylene carbonate (PC).[80-82] The employment of organic carbonates as environmentally friendly solvents offers various benefits and advantages such as, low cost, low (eco)toxicity and being entirely biodegradable.

Organic carbonates have the potential to replace many reactions that require nonrenewable polar aprotic solvents. In 2018, Wu and co-workers[104] reported the first transition metal-catalyzed direct carbonylation of benzyl alcohols in dimethyl carbonate as reaction media (Scheme 6). Carbonylation of benzyl alcohols was achieved by the combination of $Pd(TFA)_2$ (TFA: trifluoroacetate) and 1,3-bis(diphenylphosphino)propane (DPPP) as the catalytic system in DMC to furnish the desired alkyl arylacetates in good to excellent yields. The salient features of the strategy include its broad substrate scope and avoiding the use of any halogen additives.

According to them, DMC has a dual role in acting as a solvent and *in situ* activator. As a mechanistic proposal (Scheme 7), the authors believe that a mixed carbonate is generated through the reaction of benzyl alcohol with DMC in the presence of Cs_2CO_3. Meanwhile, the active

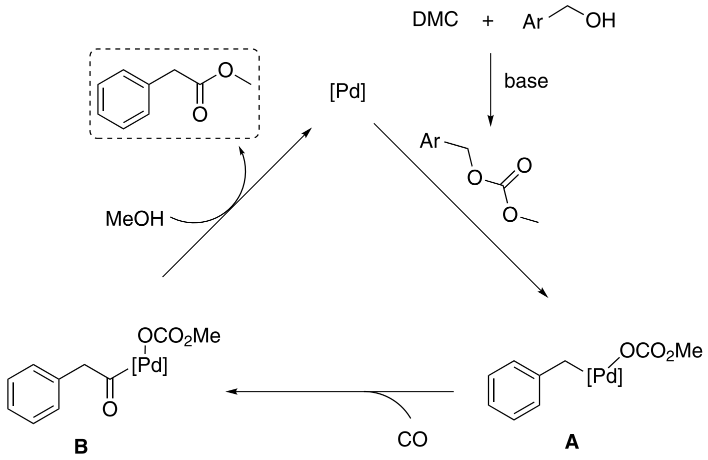


Scheme 6. Palladium-catalyzed carbonylation of benzyl alcohols in organic carbonates.

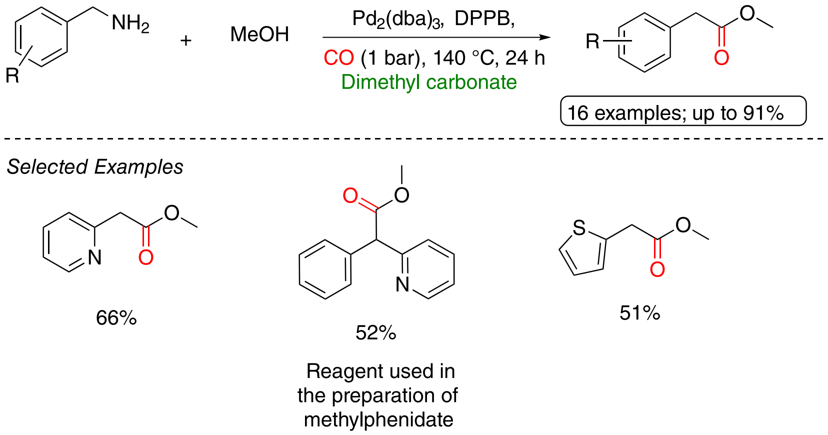
palladium complex **A** is formed after the oxidative addition of benzyl methyl carbonate with the palladium catalyst. The palladium complex undergoes coordination and insertion of CO to afford acylpalladium **B**. The final product can be eliminated after the nucleophilic attraction of alcohol to the acylpalladium intermediate.

In a recent study,[105] the same group found DMC as an effective solvent for the palladium-catalyzed carbonylative direct transformation of benzyl amines. By using dimethyl carbonate as a green solvent, methyl 2-arylacetates can be synthesized in moderate to excellent yields from different benzyl amines without any additive or even base (Scheme 8). The new methodology was further utilized for the synthesis of methyl 2-phenyl-2-(pyridin-2-yl) acetate in 52%, which can be further easily reduced to the methylphenidate, a drug used in the treatment of attention deficit hyperactivity disorder (ADHD) and narcolepsy.[106]

The synthesis of 1,2,3-triazole-5-carboxamides by



Scheme 7. Reaction pathway for alkyl arylacetates synthesis.



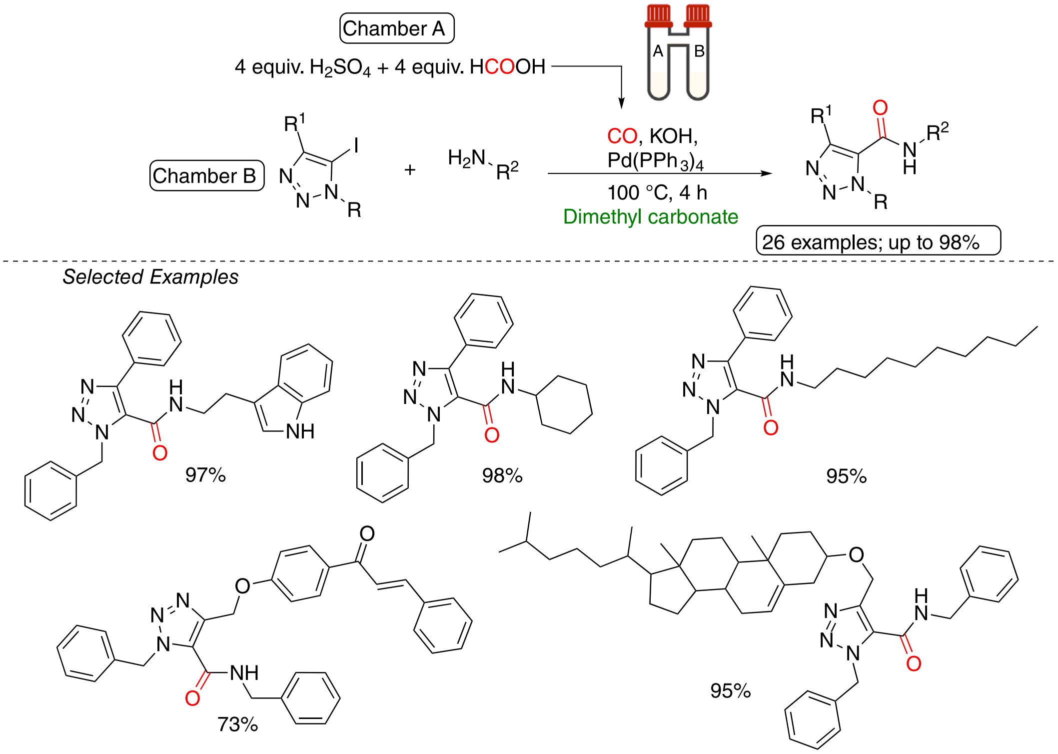
Scheme 8. Use of dimethyl carbonate in the synthesis of 2-arylacetates.

applying green solvents is still a challenge since the traditional routes for the synthesis of these frameworks usually involve the use of unsustainable and hazardous organic solvents such as, $CHCl_3$, 1,4-dioxane, DMF and DMSO.[107,108] To solve this problem, our group[67] proposed the use of DMC as a high biodegradability ecofriendly and low toxicity solvent. Employing this solvent in combination with a sealed two chamber reactor (COware) we developed a sustainable synthesis of 1,4,5-trisubstituted 1,2,3-triazole-5-carboxamides starting from 1,4-disubstituted-5-iodo-1,2,3-triazoles and easily accessible alkyl amines employing formic acid as an efficient, low-cost, and readily available carbon monoxide precursor (Scheme 9). Notably, the reaction proceeds efficiently in the presence of a simple and cost-efficient $Pd(PPh_3)_4$ catalyst, avoiding the use of other expensive phosphane ligands. This methodology was applied to a range of substrates, and as a result, densely functionalized 1,4,5-trisubstituted 1,2,3-triazole-5-carboxamides were obtained in good to excellent yields.

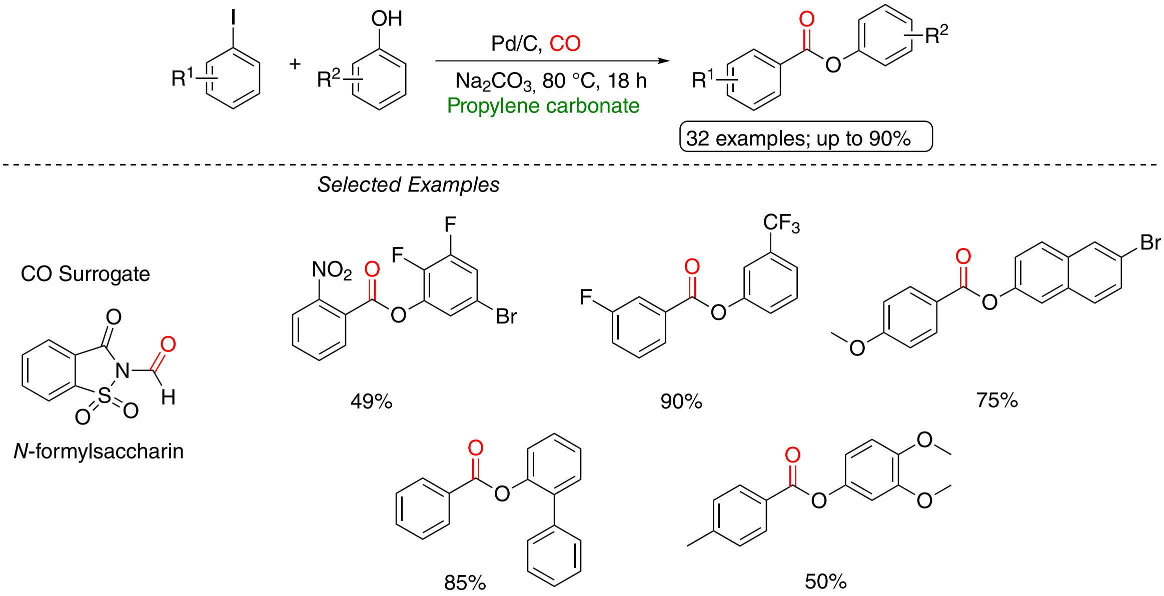
On the other hand, cyclic carbonates have gained prominence in the last years as an environmentally friendly solvent in carbonylation reactions. Favorable physicochemical properties of cyclic carbonates render it an efficient and eco-friendly reaction medium to carry out carbonylation reactions. This is mainly due to the high solubility of CO in cyclic carbonates.[109] Continuing the discussion, we highlight the various contributions made by Bhanage and co-workers[109-111] in the use of propylene carbonate as reaction media in different carbonylation reactions. In 2017, the authors proposed[110] the synthesis of phenyl esters, with the aid of palladium on activated charcoal (Pd/C) as an inexpensive heterogeneous catalyst, Na_2CO_3 as a base, *N*-formylsaccharin as a CO surrogate for *in situ* CO generation, in the presence of propylene carbonate as a sustainable polar aprotic solvent (Scheme 10). In this way, 32 phenyl esters were synthesized under mild, co-catalyst free, ligand-free and additive-free conditions, varying both aryl iodides and phenols. Interestingly, the recyclability test for the Pd/C catalyst provided satisfactory results with only a slight loss of the catalytic efficiency.

In a recent study,[111] the same group extended the approach towards aryl boronic acids for the synthesis of biaryl ketones via carbonylative Suzuki-Miyaura cross-coupling. The methodology was further utilized for the synthesis of (4-methoxyphenyl)(3,4,5-trimethoxyphenyl) methanone, as anti-neoplastic drug belonging to the phenstatin family.[112] The authors demonstrated that the heterogeneous catalyst Pd/C could be recycled up to five times with only a marginal decrease in catalytic activity.

In 2019, Bhanage and co-workers[109] disclosed a new carbonylative Sonogashira and Suzuki-Miyaura



Scheme 9. Pd-catalyzed aminocarbonylation of 1,4-disubstituted-5-iodo-1,2,3-triazoles.

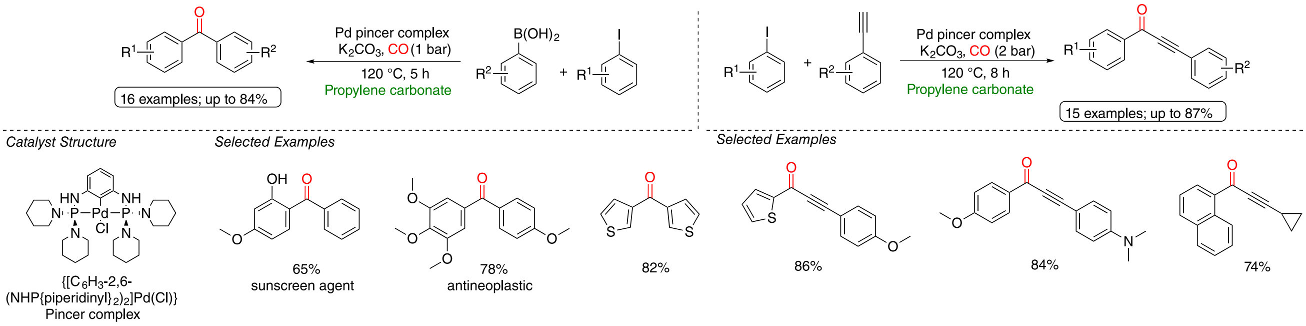


Scheme 10. Phenoxycarbonylation of aryl iodides by using immobilized Pd/C and *N*-formylsaccharin as an *in situ* CO source.

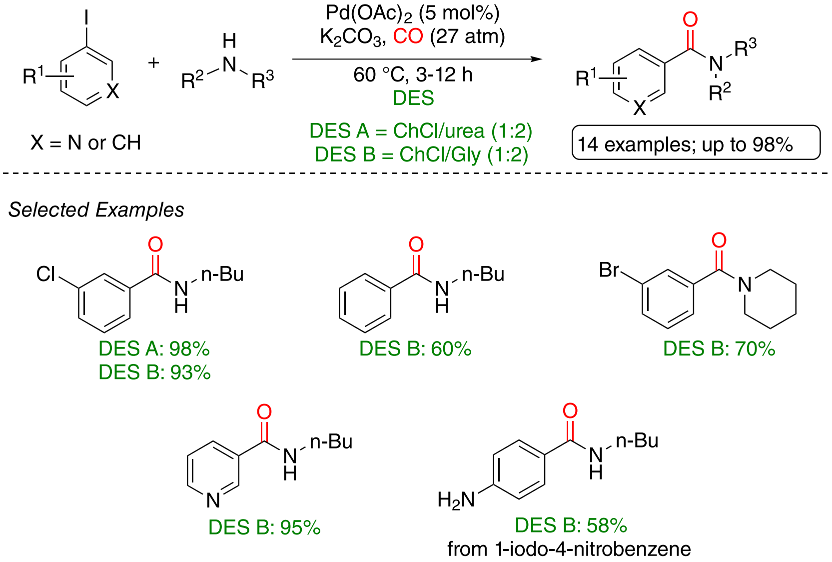
cross-coupling in propylene carbonate with recyclable palladium aminophosphine pincer complex {[C_6H_3-2,6-(NHP{piperidinyl}$_2$)$_2$]Pd(Cl)} as the catalyst (Scheme 11). A range of biaryl ketones and ynones could be synthesized in good yields, including the synthesis of an antineoplastic and a photostabilizer cum photoprotective agent.[112,113] Moreover, one of the more relevant features of this protocol was the superiority and robustness showed by the palladium pincer complex when compared with conventional palladium precursors such as $Pd(OAc)_2$ and $PdCl_2(PPh_3)_2$, which shows the efficiency and robustness of the pincer complex in effecting higher catalytic activity at low palladium loadings. Several sensitive functional groups were well tolerated, providing versatile access to several substituted biaryl ketones and ynones in high yields. The Pd-catalyzed carbonylative approach using propylene carbonate as a renewable solvent provided an alternative protocol to the synthesis of biaryl ketones and ynones, complementing the current methodologies that typically use hazardous, toxic, and unsustainable organic solvents.

2.4. Deep eutectic solvents

Deep eutectic solvents (DESs) have emerged at the beginning of this century as a new class of alternative green solvents to ionic liquids (ILs).[114-116] Although they share many physicochemical properties with ILs, including non-volatility, non-flammability, high viscosity, high thermal stability and tunable properties, the DES tend to be cheaper, are often biodegradable, biocompatible, non-toxic and easier to prepare than ILs.[117-122] They are defined as a mixture of two or more components, which may be solid or liquid, and that in a particular composition can self-associate, through hydrogen bond interactions to form a eutectic phase, which is a liquid at a temperature lower than 100 °C. They can be easily obtained by simply mixing one hydrogen-bond acceptors (HBAs) and one hydrogen-bond donors (HBDs) from cheap, renewable, and biodegradable starting materials in the proper ratio. DESs are a privileged class of new potential media for green technology and are widely used in the fields such as biomass processing, materials preparations,



Scheme 11. Palladium pincer-catalyzed carbonylative Suzuki-Miyaura and Sonogashira cross-coupling with high catalytic turnovers.



Scheme 12. Aminocarbonylation of (hetero)aryl iodides in deep eutectic solvents (DESs).

electrochemistry, extraction, and organic synthesis.[114] Typical examples reported in the literature[123-126] comprise choline chloride (ChCl) and urea, glycerol or other bio-based polyols, sugars and carboxylic acids as hydrogen-bond donors. When both components of DESs are derived from renewable sources, such as ammonium salts, amino acids, organic acids, sugar, they are so-called natural deep eutectic solvents (NADES).

The development of sustainable aminocarbonylation reactions has become a cornerstone of modern synthesis and has become one of the most important approaches to prepare amides. As a part of their efforts in developing a simple, phosphine-free and sustainable method to prepare amides, Salomone and co-workers[127] reported for the first time, in 2018, the aminocarbonylation reaction of (hetero)aryl iodides using a biodegradable deep eutectic solvents as environmentally benign and recyclable reaction solvents (Scheme 12). Through this strategy, 14 amides were synthesized in good to excellent yields by using as a eutectic mixture a ChCl/urea or ChCl/Gly (ChCl = choline chloride and Gly = glycerol).

Another positive aspect of this work is the possibility of reusing the reaction system composed of $Pd(OAc)_2$ and ChCl/urea (1:2), which can be recycled for up to 5 cycles, albeit with a drop in the chemical yield of up to 34% (Figure 2). Interestingly, the recycling efficiency was improved when the authors used the less viscous ChCl/Gly (1:2) eutectic mixture and Pd/C (1 mol%) as the catalyst, in the presence of K_2CO_3. In this case, the chemical yield of the product dropped down to only 14% in the fourth cycle and up to 24% in the fifth cycle.

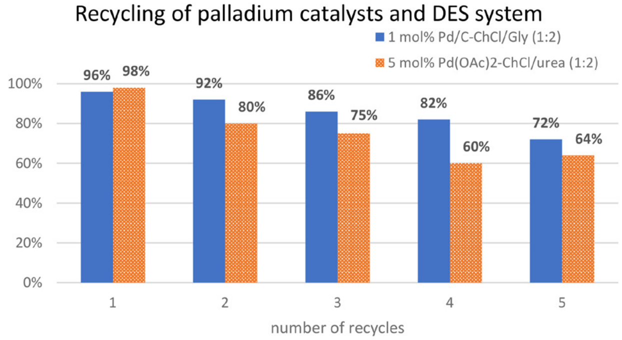


Figure 2. Recycling of $Pd(OAc)_2$ or Pd/C and DES in the coupling reaction between 1-chloro-3-iodobenzene and *n*-butyl amine (adapted from reference 127).

2.5. Bio-polyethylene glycol

The use of bio-polyethylene glycol (bioPEG) as an eco-compatible and readily biodegradable solvent in organic chemistry reactions has attracted great attention of organic chemists.[47] Furthermore, they form powerful recyclable systems, which offer an easy way to extract the product and recycle the reaction system.[128] However, PEG is produced primarily from ethylene glycol, and many other monomers are majorly obtained from petroleum or natural gas feedstocks.[129] Efforts to address this issue are a central part of sustainable development, and so researchers are now looking for alternative renewable raw materials to make monomers or polymers. It should be highlighted that the global market for ethylene glycol is approximately \$20 billion *per* year with around 15 million tonnes *per* year being produced.[130] Considering this, the development of new processes and the search for sustainable sources of ethylene glycol are of great interest. The sustainable ethylene glycol can be produced directly from sugar, starch, lignocellulosic biomass or via modified *E. coli*.[129,130] Additionally, second-generation bioethanol can be also used to afford the bio-based ethylene, an intermediate in the traditional synthesis of ethylene glycol.[131]

Bio-polyethylene glycols are becoming increasingly popular as alternative renewable solvents. In 2014, Cai and co-workers[132] reported a general protocol to access alkynyl ketones through the application of a $PdCl_2(PPh_3)_2$/PEG-2000/H_2O system for the carbonylative Sonogashira coupling reaction of aryl iodides with terminal alkynes (Scheme 13). Under the optimized reaction conditions, the reaction tolerated several terminal alkynes, including alkyl and aryl-substituted acetylenes and different aryl iodides. The synthetic approach was also applied to the preparation of flavones in a one-pot two-step reaction. As shown in Scheme 13, the synthesis of flavones takes place by sequential carbonylative coupling of 2-iodophenol with terminal alkynes to form α,β-unsaturated ketones, followed by intramolecular cyclization to afford the corresponding flavones with yields between 51-87%. The authors demonstrated that the catalytic system ($PdCl_2(PPh_3)_2$/PEG-2000/H_2O) could be recycled up to 6 times without any loss of activity in the reaction.

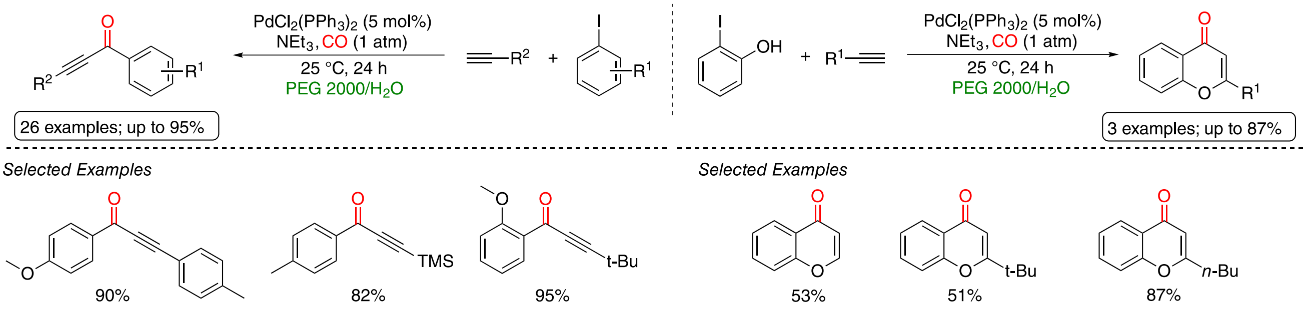
Two years later, Gautam and Bhanage[133] published the use of PEG-600 as a benign and recyclable solvent system as a safe alternative to toluene or DMF for carbonylative Sonogashira reactions (Scheme 14). The use of oxime palladacycles as a non-phosphine palladium catalyst at extremely low loading (10^{-5} mol%), resulting in high catalytic turnover numbers (TON's) and turnover frequencies (TOF's). By the method, 20 products were synthesized in good yields by combining different aryl iodides and alkynes. The reusability of the catalytic system was also evaluated. The use of PEG-600 as an environmentally benign system allowed the recyclability of the reaction system up to 4 times with only a marginal decrease in activity. Moreover, catalytic TON's and TOF's of the order of 10^4 could be maintained for all four cycles. In a comparative study with conventional palladium precursors, such as $Pd(OAc)_2$ and $PdCl_2(PPh_3)_2$, the oxime palladacycles afforded superiority in the conversion and selectivity results proving to be very efficient catalysts.

In 2016, Etemadi-Davan and Iranppor[134] reported the development of an efficient Pd-catalyzed carbonylative homo-coupling of aryl iodides using $Cr(CO)_6$ and dinuclear 1,3,2,4-diazadiphosphetidine oligomer ($[(PhNH)P_2(NPh)_2]_2NPh$) as a cheap, air-stable and heterogeneous ligand in PEG-400 at 90 °C (Scheme 15). The synthesis of symmetric diaryl ketones from a range of aryl iodides using $Cr(CO)_6$ as a carbon monoxide source provided yields up to 86%, allowing the use of a variety of electron-donating and electron-withdrawing substituents, as well as iodonaphthalenes and 2-iodothiophene. In addition, the applicability of this transformation can be further extended for unsymmetrical diaryl ketones synthesis using $PhB(OH)_2$ under identical condition, albeit with low yields compared with symmetric ketones and accompanied by the formation of biaryls by-products (Scheme 15).

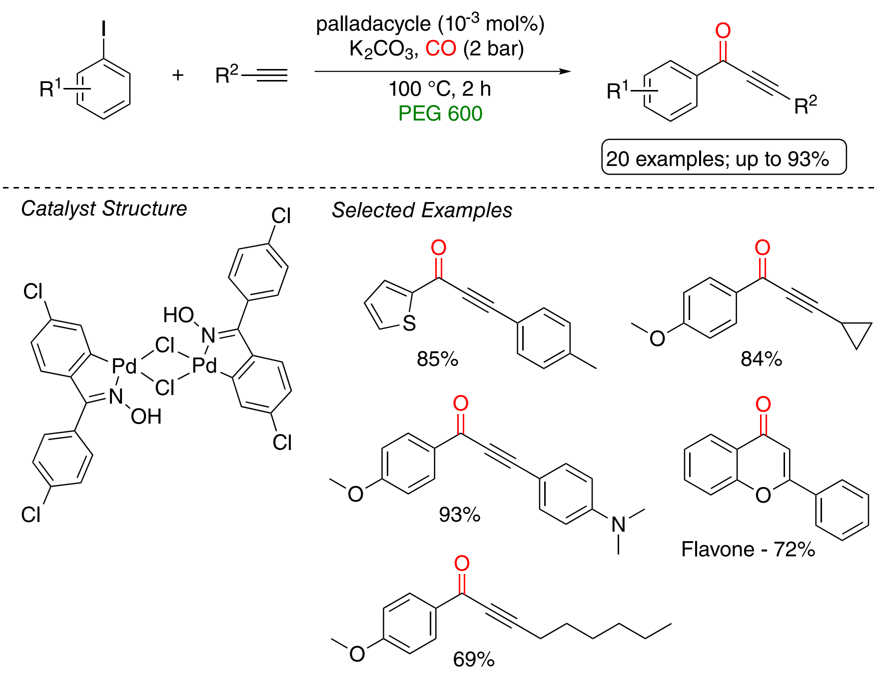
2.6. Anisole

A variety of different aromatic solvents once enjoyed widespread use as solvents, are now banned, once they pose an adverse effect on the human health and environmental. Obtained from renewable sources, such as lignin and guaiacol, anisole is a colorless, low cost, biodegradable and low toxicity liquid that occupies a prominent position in GlaxoSmithKline (GSK) solvent selection guide, and is highly recommended in organic reactions.[20,135-137] It is used as an intermediate in the pharmaceutical industry, cosmetics, as a flavoring agent in foods, as a solvent, and other applications.[138] As a consequence of its relevance in sustainable transformations, several works using anisole have been reported in the literature.

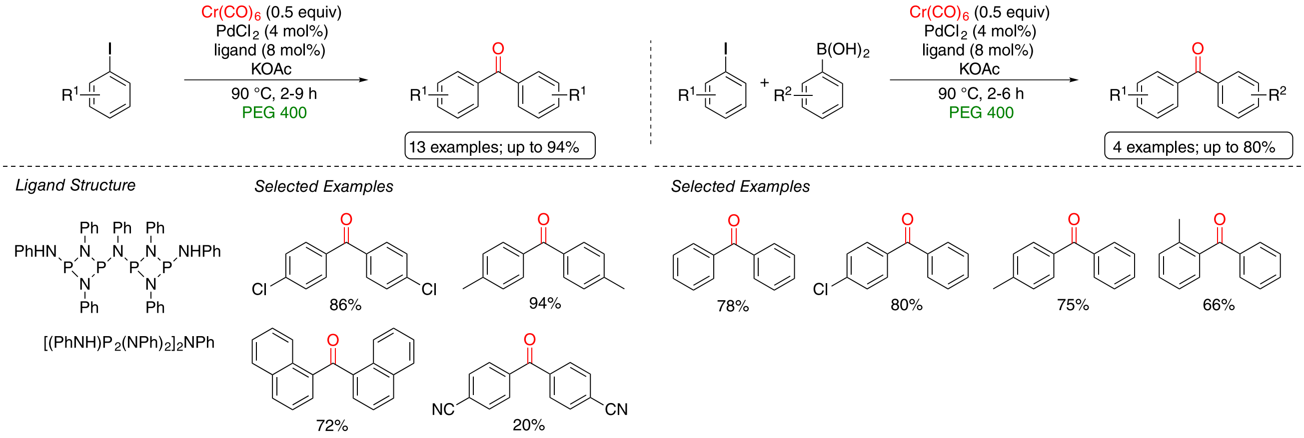
The first report to appear in the literature concerning the use of anisole as a solvent for a Pd-catalyzed carbonylative cross-coupling reaction was described in 1998 by Miyaura and co-workers.[139] They developed a straightforward and convenient route for the synthesis of unsymmetrical biaryl ketones, which are important building blocks in organic



Scheme 13. Synthesis of ynones by carbonylative Sonogashira reaction and flavones by carbonylation/cyclization from *ortho*-iodophenol and terminal alkynes.



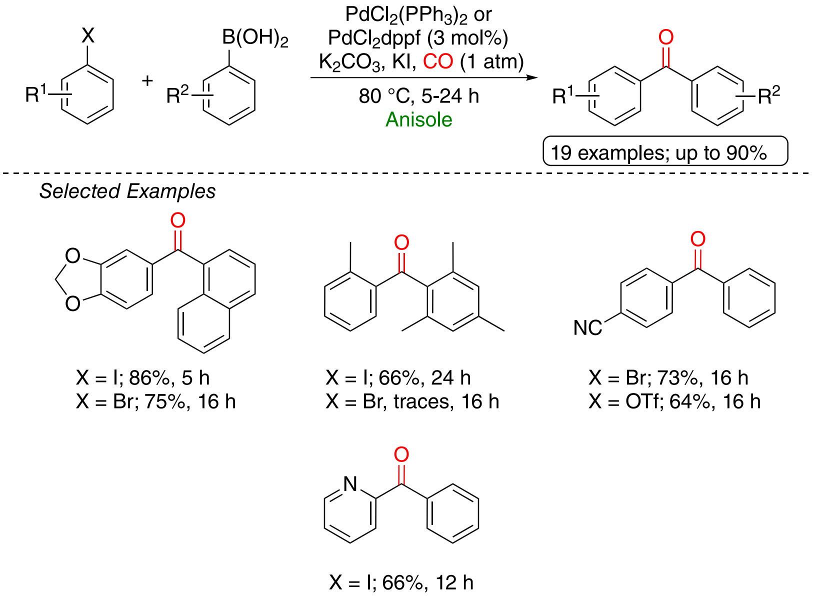
Scheme 14. Palladacycle oxime catalyzed carbonylative Sonogashira cross-coupling in PEG.



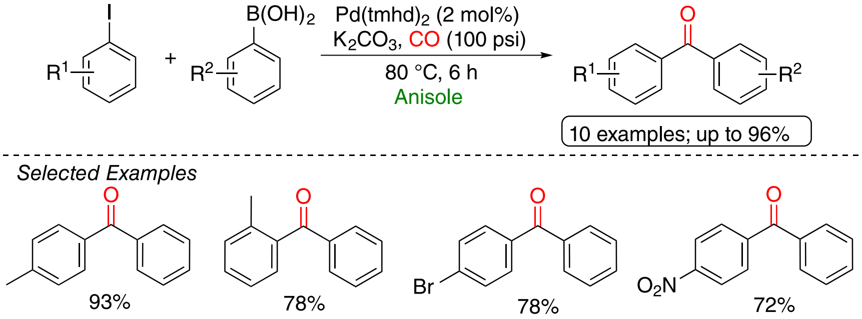
Scheme 15. Synthesis of symmetrical and unsymmetrical diaryl ketones via carbonylative homocoupling and via carbonylative Suzuki cross-coupling of aryl iodides.

chemistry.[140,141] The carbonylative cross-coupling reaction of several arylboronic acids with a set of aryl electrophiles has been successfully achieved in the presence of palladium catalyst and K_2CO_3 under an atmospheric pressure of carbon monoxide with good yields. Two different catalysts were employed, $PdCl_2(PPh_3)_2$ was used for aryl iodides and $PdCl_2$(dppf) was required for the aryl bromides or triflates in the presence of KI. The authors mention that the insertion of carbon monoxide into the Ar–Pd–I complex occurs more rapidly than into the Ar–Pd–Br complex. Thus, the addition of the iodine salt was necessary to exchange the bromine for the iodine atom in the intermediate complex to improve the selectivity of the reaction and reduce the formation of the non-carbonylated by-product biaryl. Although the aryl iodide provided better yields in shorter reaction times, good results were obtained starting from aryl bromides and triflates (Scheme 16).

Using the same strategy, in 2009, Bhanage and co-workers[142] reported a phosphane-free palladium-catalyzed carbonylative Suzuki coupling reaction of aryl and heteroaryl iodides. The influence of different solvents was evaluated. Notably, common organic solvents failed to provide the desired product in good yields, highlighting the unique potential of anisole as the reaction media. The combination of different aryl iodides with boronic acid derivatives led to the products with yields up to 96% at 80 °C, under 100 psi of carbon monoxide (Scheme 17). However, the use of anisole was not compatible with heteroaryl iodides. Unfortunately, this issue was only circumvented using hazardous toluene as the solvent. The



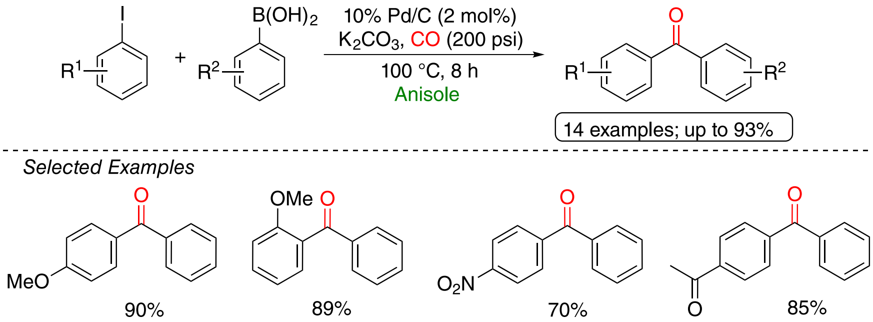
Scheme 16. Pd-catalyzed carbonylative cross-coupling reaction of arylboronic acids with aryl electrophiles in anisole.



Scheme 17. Phosphane-free Pd-catalyzed carbonylative Suzuki coupling reaction.

absence of any phosphane ligands makes this process very interesting.

The development of heterogeneous catalysts applied in carbonylative coupling reactions with anisole as solvent has presented highly promising results. Continuing the discussion of the synthetic routes for the synthesis of biaryl ketones, we highlight the various contributions made by different groups in the use of heterogeneous catalysts and anisole as reaction media for the carbonylative Suzuki coupling reactions. For instance, Bhanage and co-workers[143] disclosed an efficient protocol for the synthesis of biaryl and aryl heteroaryl ketones (Scheme 18). Here, catalytic amounts of Pd/C were used in combination with K_2CO_3 as a base and CO (200 psi) in the presence of anisole. Through this strategy, 14 compounds were synthesized in good yields, varying both aryl iodides and boronic acids (Scheme 18). The use of anisole was again restricted to aryl iodides. The major advance presented by this methodology is the possibility of reusing the catalyst up to 4 cycles with consistent results.

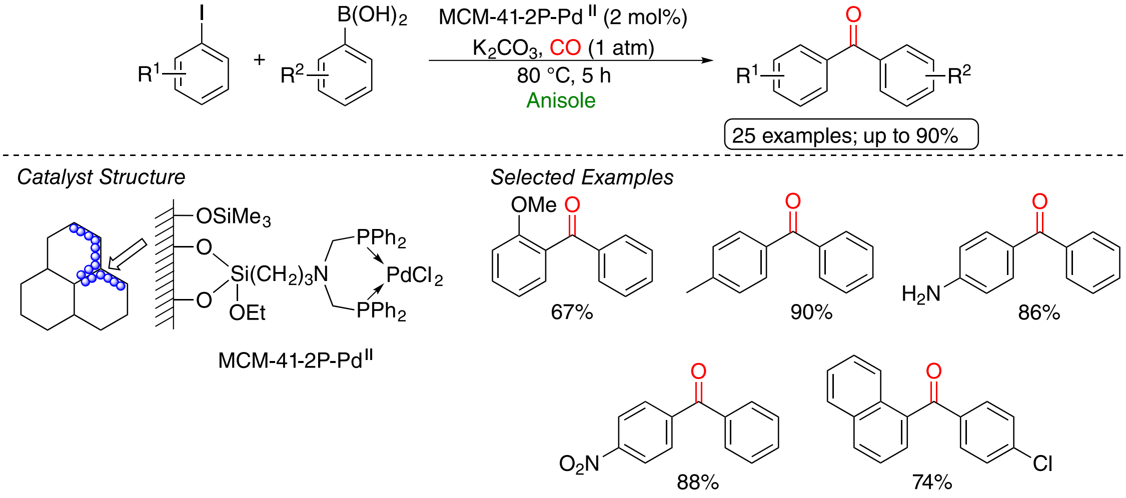


Scheme 18. Pd/C-catalyzed carbonylative Suzuki coupling reaction in anisole.

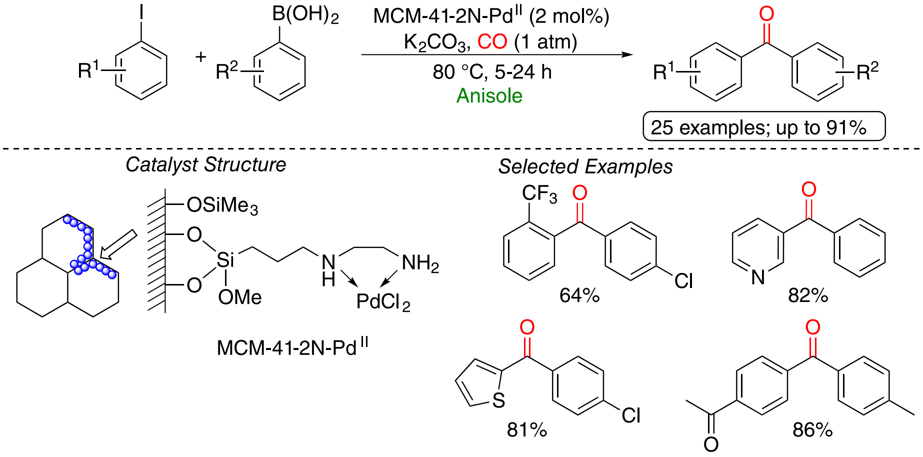
The use of Mobil Composition of Matter No. 41 (MCM-41) mesoporous material has proved to be attractive solid support for the immobilization of homogeneous catalysts.[144,145] MCM-41 has a regular pore diameter and a high surface area. Its large pore size (5 nm) allows large molecules, such as organic reactants and metal complexes, to pass through the pores to the surface of the channel, which may result in high catalytic activity.[146-148] Based on the possibility of employing the MCM-41 as a support, in 2009 Cai *et al.*[149] reported the first heterogeneous carbonylative Suzuki-Miyaura reaction of arylboronic acids with aryl iodides under an atmospheric pressure of CO in the presence of MCM-41-supported bidentate phosphine palladium(II) complex (MCM-41-2P-Pd^{II}) as catalyst (Scheme 19). In this way, 25 examples of unsymmetrical biaryl ketones were synthesized in good-to-high yields of 67-90%. The authors demonstrated that the supported catalyst can be recovered by simple filtration and reused at least 10 times without any decrease in activity.

Shortly thereafter, the same group[150] developed a novel, phosphine free, practical and economic catalyst system for the carbonylative Suzuki-Miyaura cross-coupling reaction by using 3-(2-aminoethylamino)propyl-functionalized MCM-41-supported palladium(II) (MCM-41-2N-Pd^{II}) as the catalyst in anisole under an atmospheric pressure of carbon monoxide (Scheme 20). Notably, the heterogeneous catalyst exhibited higher activity and selectivity than $PdCl_2(PPh_3)_2$ and can be reused at least 10 times without any decrease in its activity. Compared to the use of MCM-41-supported bidentate phosphine palladium(II) complex, the practical added bonus of using this new phosphine-free heterogeneous palladium catalyst was their rapid and simple assembly, in a two-step procedure from commercially available and cheap reagents.

In 2015, Guo and co-workers[151] used Pd/SiC (silicon carbide) as a high surface area catalyst for the carbonylative Suzuki coupling reactions of aryl iodides with boronic acids. The carbonylative coupling reactions led to the formation of the resulting unsymmetrical ketone products



Scheme 19. MCM-41-2P-Pd^{II}-catalyzed carbonylative Suzuki-Miyaura coupling reaction.



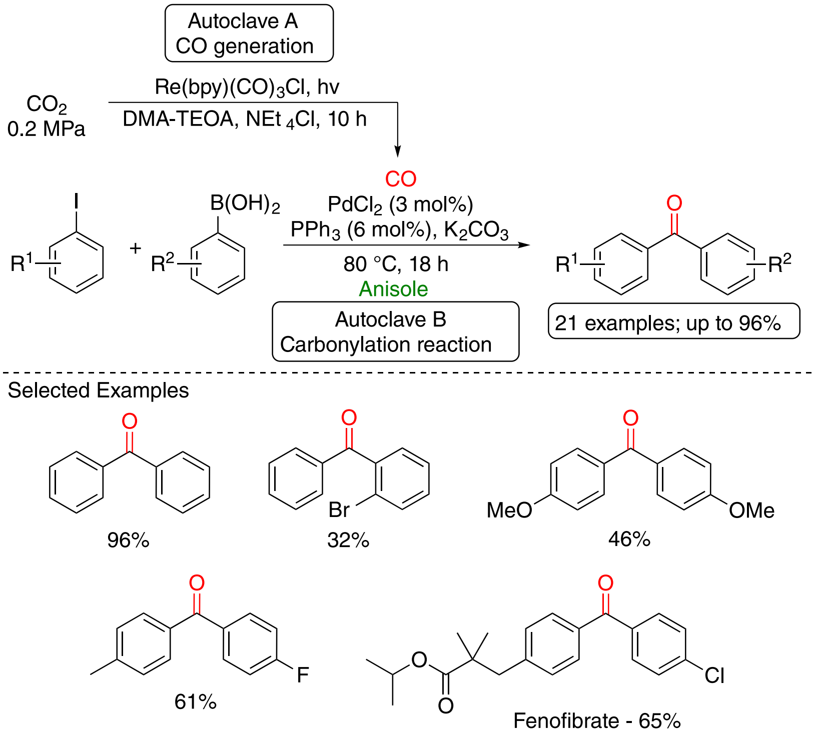
Scheme 20. Heterogenous palladium phosphine-free-catalyzed carbonylative coupling reaction.

with high conversion up to 97% and selectivity up to 99%. The authors emphasize that the catalyst could be filtered and recycled maintaining its catalytic activity up to 5 times.

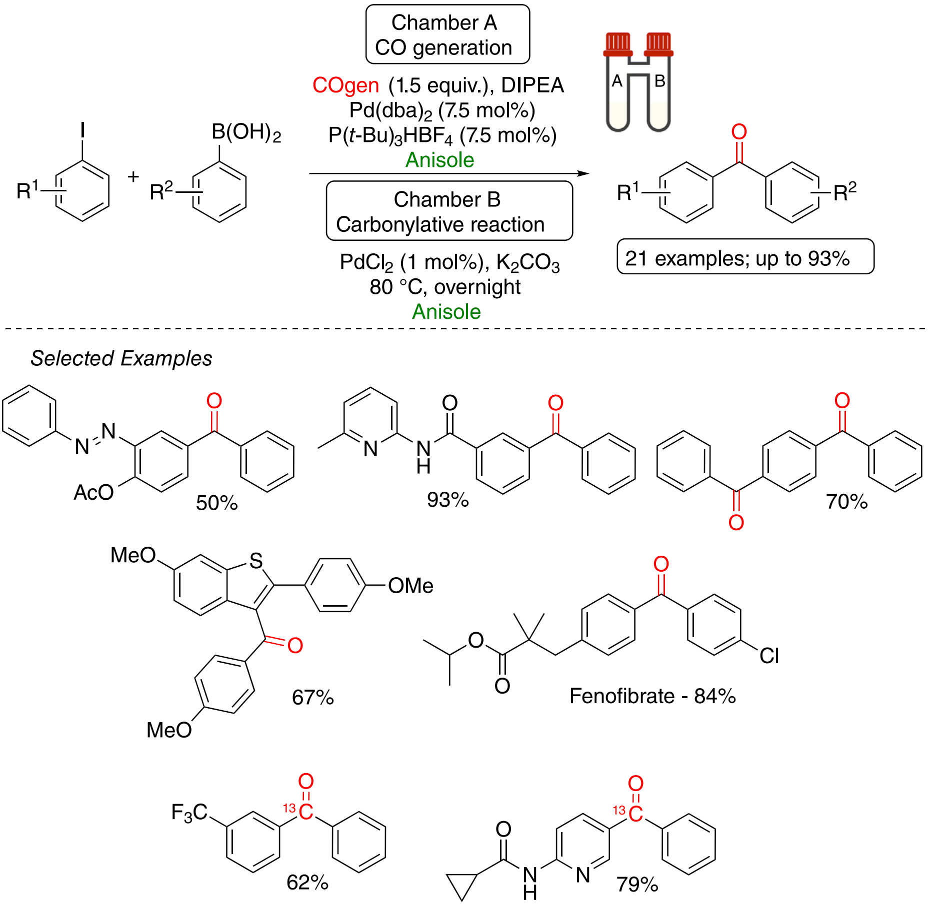
Recently He *et al.*[152] described an exciting methodology for generating carbon monoxide from the photochemical reduction of carbon dioxide (CO_2) and its application to the synthesis of biaryl ketones via carbonylative Suzuki-Miyaura reaction. $Re(bpy)(CO)_3Cl$ (bpy = 2,2'-bipyridine) was selected as the photoreduction catalyst since it is easily prepared and highly selective to CO production using a 500 W high-pressure mercury arc lamp (main peak wavelength 365 nm). All the reactions were carried out in autoclaves under 0.2 MPa of CO_2 (Scheme 21). Following the photocatalytic protocol for reductive functionalization of CO_2 with subsequent carbonylation using anisole as a renewable solvent, 21 different biaryl ketones were obtained in moderate to excellent yields. The feasibility of the protocol was extended successfully to the synthesis of fenofibrate, a hypolipidemic agent used to regulate lipoprotein cholesterol, total cholesterol, and triglycerides.[153]

In 2013, Skrydstrup and co-workers[154] reported an air-tolerant approach to the carbonylative Suzuki-Miyaura coupling employing a stable solid CO precursor 9-methylfluoreno-9-carbonyl chloride (COgen) as the *ex situ* source of carbon monoxide in combination with a sealed two-chamber system (COware) (Scheme 22). The significant advantage presented by this methodology is the possibility of generating the CO *ex situ* by using a two-chamber reactor and a carbon monoxide precursor. Their method involves the use of 1.5 equivalents of the carbon monoxide precursor and $PdCl_2$ as the catalyst. The protocol afforded the desired benzophenones with excellent functional group tolerance and in good yields. It is essential to highlight that substituting the CO precursor, with its carbon-13 labelled version, afforded the corresponding carbon-13-labelled benzophenones. Furthermore, the approach enabled the synthesis of pharmaceutical fenofibrate with an 84% yield.[140]

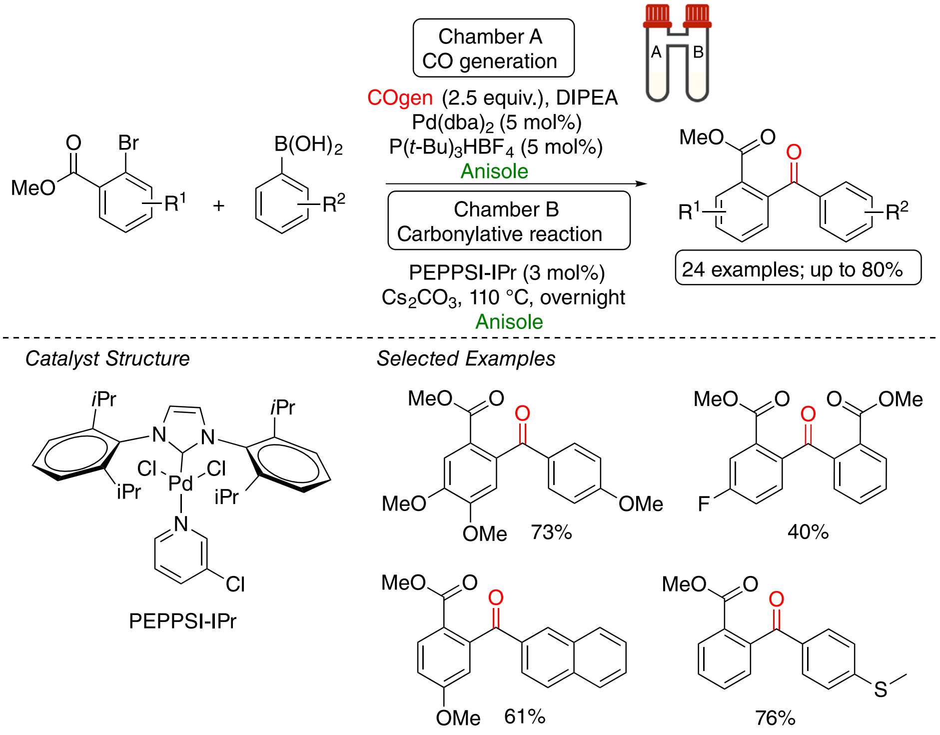
Despite the advances in the synthesis of biaryl ketones, only a few methods have been demonstrated to be applicable for the use of aryl bromides as electrophiles. Usually, these methods require using iodine salts as additives, or high-pressure CO gas, use of less accessible boronate esters instead of boronic acids, or the employment of solvents produced from fossil resources.[139,155-158] More recently, Bayer and co-workers[159] reported a different approach to the synthesis of 2-aroylbenzoate esters. The synthetic strategy was based on the use of a [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene](3-chloropyridyl)palladium(II) dichloride (PEPPSI-IPr) that catalyzes the formation of new C–C bonds, through Suzuki-Miyaura coupling of 2-bromobenzoate esters and aryl boronic acids, in the presence of anisole and COgen as an *ex situ* source of CO in a sealed two-chamber system (COware), to provide 2-aroylbenzoate esters in good yields (Scheme 23). The



Scheme 21. Photoreduction of CO_2 with subsequent carbonylation reaction to the synthesis of biarylketones.



Scheme 22. Synthesis of biarylketones using COgen as *ex situ* carbon monoxide source.



Scheme 23. Synthesis of 2-aroylbenzoate using COgen as *ex situ* carbon monoxide source.

authors reported that slow addition of the boronic acid was a strategy to favor carbonylative over non-carbonylative process in Suzuki-Miyaura couplings, once the slow addition favored the CO insertion step by decreasing the rate of transmetallation due to limited access to the organometallic nucleophile.

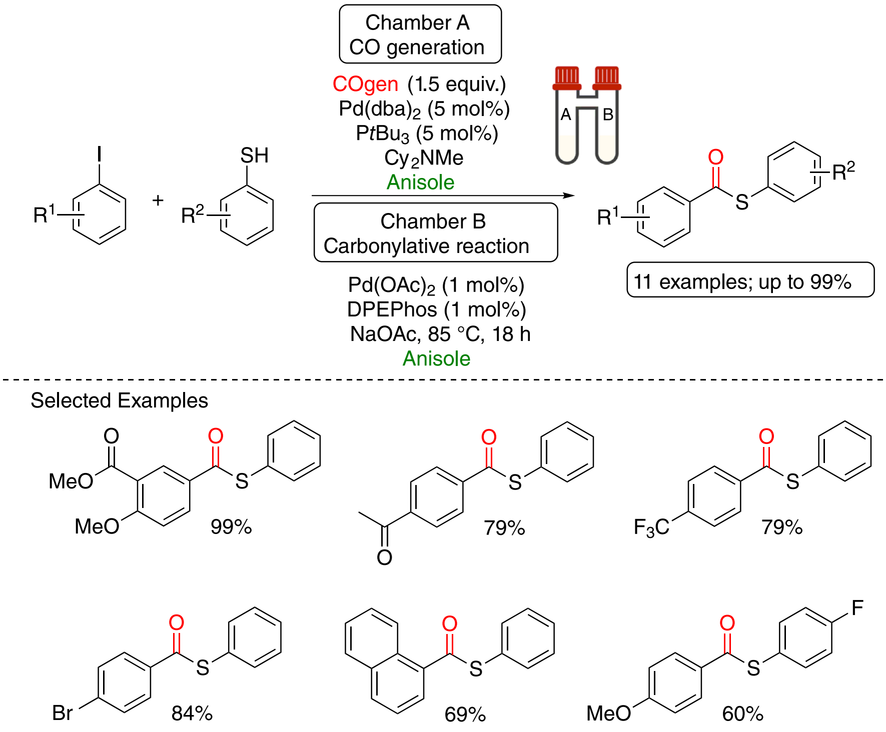
Carbonylation reactions can be regarded as one of the most attractive methods to be used for the synthesis of chalcogenoesters. Due to the rising potential of these classes of compounds, several research groups[160,161] have reported the use of innovative techniques for their preparation. The synthesis of chalcogenoester employing anisole as a reaction media is also highlighted in the literature.

In 2013, Skrydstrup and co-workers[162] developed one of the first protocols based on Pd-catalyzed thiocarbonylation of aryl iodides with stoichiometric carbon monoxide employing a catalytic system composed of $Pd(OAc)_2$ and (oxydi-2,1-phenylene)bis(diphenylphosphine) (DPEphos) (Scheme 24). The reaction is carried out in a two-chamber reaction vessel using (COgen) as the source of carbon monoxide. The authors found that the solvent system proved to be crucial for the efficiency and chemoselectivity of these transformations. When electron-deficient aryl iodides were used, switching the 1,2-dimethoxyethane (DME) to anisole was essential to improve the chemoselectivity and yield, since, in general, the non-carbonylated product thioesters were obtained as the major product. Furthermore, the present protocol allowed the synthesis of ^{13}C-labeling of an amide analogue of vortioxetine in excellent yield.[163]

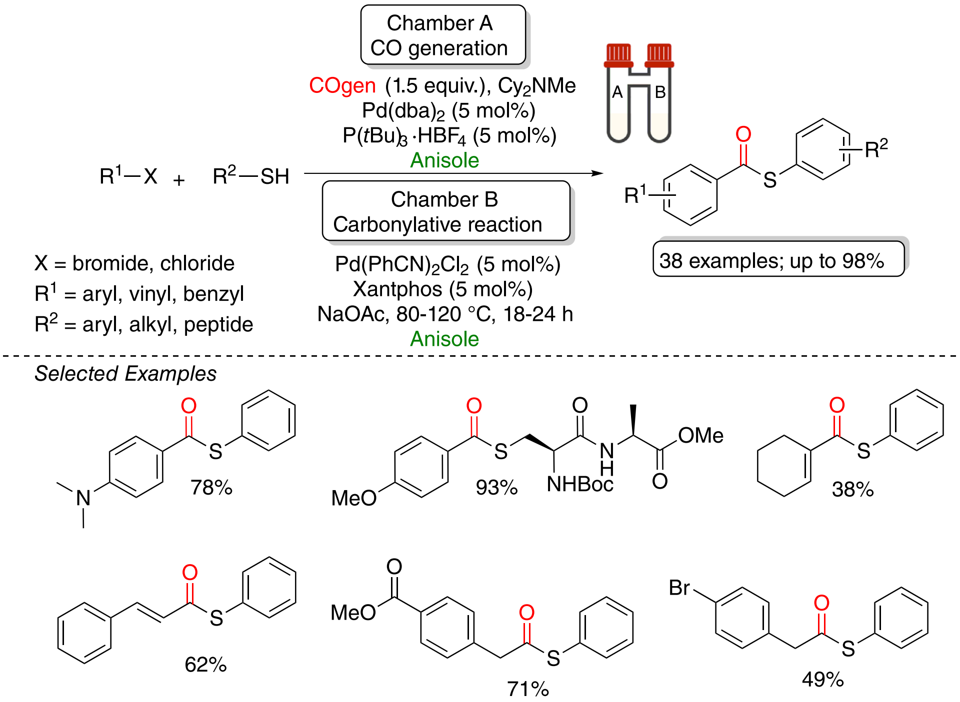
Later, another publication of the same group[164] reported a similar catalytic protocol for the synthesis of thioesters from aryl, vinyl, and benzyl bromides as well as benzyl chlorides (Scheme 25). The combination of bis(benzonitrile) palladium(II) chloride $[Pd(PhCN)_2Cl_2]$ and xantphos and anisole as a catalytic system and NaOAc as a weak base furnished the products in yields up to 98%. The choice of catalytic system and the use of anisole were fundamental to control the chemoselectivity in the reaction, to reduce the formation of the non-carbonylated thioester by-product.

Stefani and co-workers[165] have reported in 2020 a convenient carbonylative cross-coupling reaction of 2-iodoglycals with selenols in the presence of molybdenum hexacarbonyl $[Mo(CO)_6]$ as a reliable source of carbon monoxide (Scheme 26). This methodology afforded 23 thioesters and six selenoesters in moderate yields to excellent yield.

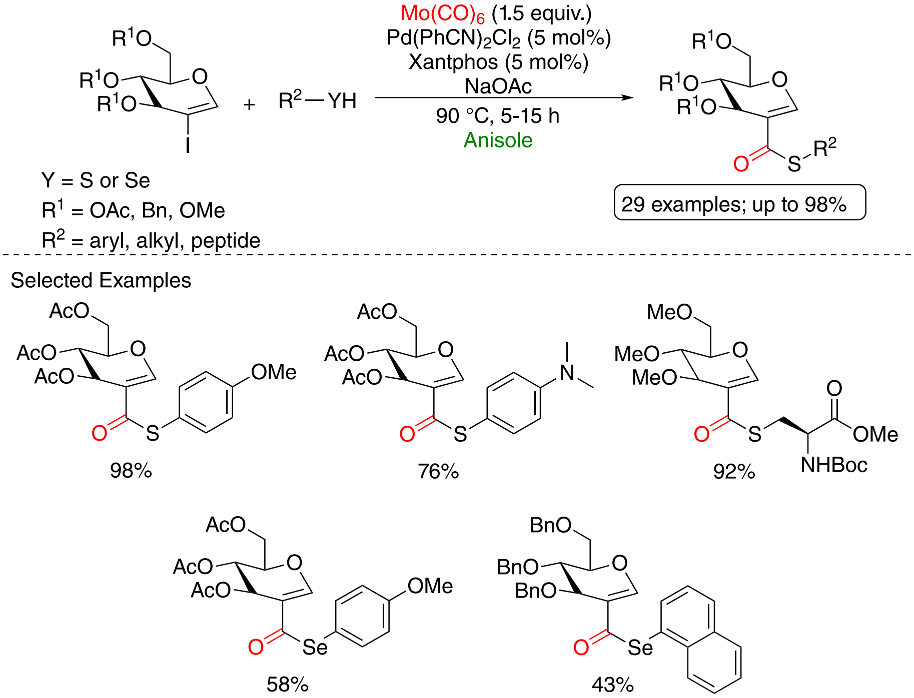
Malonates are fundamental building blocks and have often been applied for the manufacture of pharmaceuticals, vitamins, agrochemicals, dyes, and fragrance.[166] An efficient process for the synthesis of malonates through the Pd-catalyzed carbonylation of chloroacetates was proposed in 2012 by Li and co-workers.[167] The carbonylation reaction of chloroacetates with a set of alcohols has been successfully achieved in the presence of only 1 mol% of $[PdCl_2(PPh_3)_2]$ and Bu_4NI, in a reaction media composed



Scheme 24. Pd-catalyzed thiocarbonylation of aryl iodides in anisole.



Scheme 25. Pd-catalyzed thiocarbonylation of aryl, vinyl, and benzyl bromides reaction using COgen as *ex situ* carbon monoxide source and anisole as a solvent.

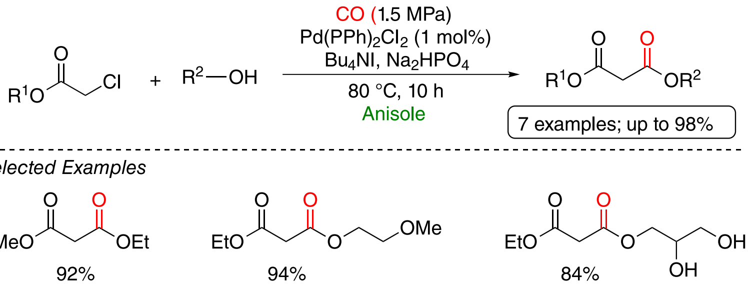


Scheme 26. Pd-catalyzed thio- and selenocarbonylation of 2-iodoglycals by using $Mo(CO)_6$ as an *in situ* CO source.

of a weakly alkaline (Na_2HPO_4/NaH_2PO_4) buffer and anisole with excellent selectivity and yields (Scheme 27). According to the authors, the combination of anisole as the solvent and the buffer was thoroughly effective in restraining the phase-transfer-catalyze substitution of diethyl malonate with ethyl chloroacetate, as well as for providing a suitable environment so that $[(PPh_3)_2PdI]^-[Bu_4N]^+$ can exist as a stable intermediate.

2.7. Water

Water is the most abundant liquid on earth. Apart from



Scheme 27. Palladium-catalyzed carbonylation of chloroacetate in anisole.

bio-based solvents, water also has found applications in several transformations.[43-45] Due to environmental and economic concerns, the use of water as a green solvent has been increasing in recent years.[168-170] Indeed, water offers many advantages because it is readily available, non-flammable, non-toxic, cheap, environmentally friendly, but its high polarity limits the solubility of non-polar compounds and is difficult to isolate water-soluble products.[39] Initially, water was not considered to be a suitable solvent for organic reactions, but this situation changed. Accordingly, to Simon and Li,[168] it is now well established that water's unique structure and physicochemical properties lead to particular interactions like polarity, hydrogen bonding, hydrophobic effect and *trans*-phase interactions that might significantly influence the reaction course.

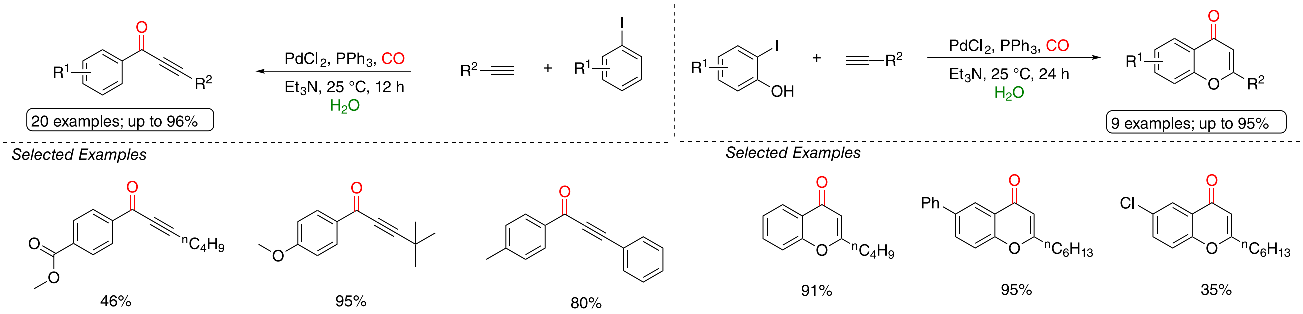
The application of an aqueous reaction medium for carbonylation reactions have been neglected mainly because water can react preferentially as a nucleophile. However, this scenario started to change in 2005, when Yang and co-workers[171] reported on the first Pd-catalyzed copper-free carbonylative Sonogashira reaction of aryl iodides with alkynes for the synthesis of alkynyl ketones using water as a solvent (Scheme 28). The reaction was carried out at room temperature under balloon pressure of CO with Et_3N as a base. Various substituted aryl iodides and aryl and alkyl alkynes were amenable substrates for the carbonylative Sonogashira cross-coupling reaction to afford the desired alkynyl ketones in good to excellent yields. The protocol was successfully applied to generate flavones, from iodophenols and terminal alkynes.

Inspired by the work of Yang and co-workers,[171] Ryu and co-workers[172] described an efficient carbonylative Sonogashira coupling between an iodobenzene and 1-octyne in water. Hence, the carbon monoxide was produced *ex situ* by the Morgan reaction (dehydration of formic acid by sulfuric acid) using a two-chamber reactor (COware). The desired alkynyl ketone was obtained in a high yield of 91%.

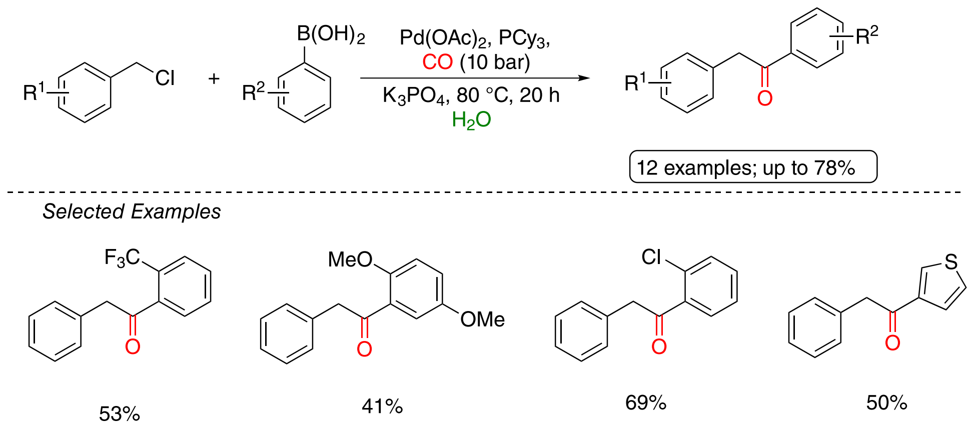
Furthermore, water has also found application for the synthesis of α-aryl acetophenones. To prepare this class of compounds in aqueous media, Beller and co-workers[173] developed a novel chemoselective protocol for the carbonylative Suzuki coupling of benzyl chlorides, an inexpensive and readily available starting material with aryl boronic acids at low pressure of carbon monoxide (Scheme 29). Water showed superior efficacy to typically used organic solvents for the desired α-aryl acetophenone product with better yield. Under optimal reaction conditions, 12 examples were obtained in moderate to good yields.

2.8. Miscellaneous

Renewable solvents have proven to be suitable for a variety of organic transformations. In this context, in 2020, Bayer *et al.*[79] delineated the first complete study fully dedicated to evaluating renewable solvents as an alternative green reaction media for Pd-catalyzed carbonylative couplings such as carbonylative cross-couplings, aminocarbonylations, and alkoxycarbonylations. It is noteworthy to mention that in this protocol not only



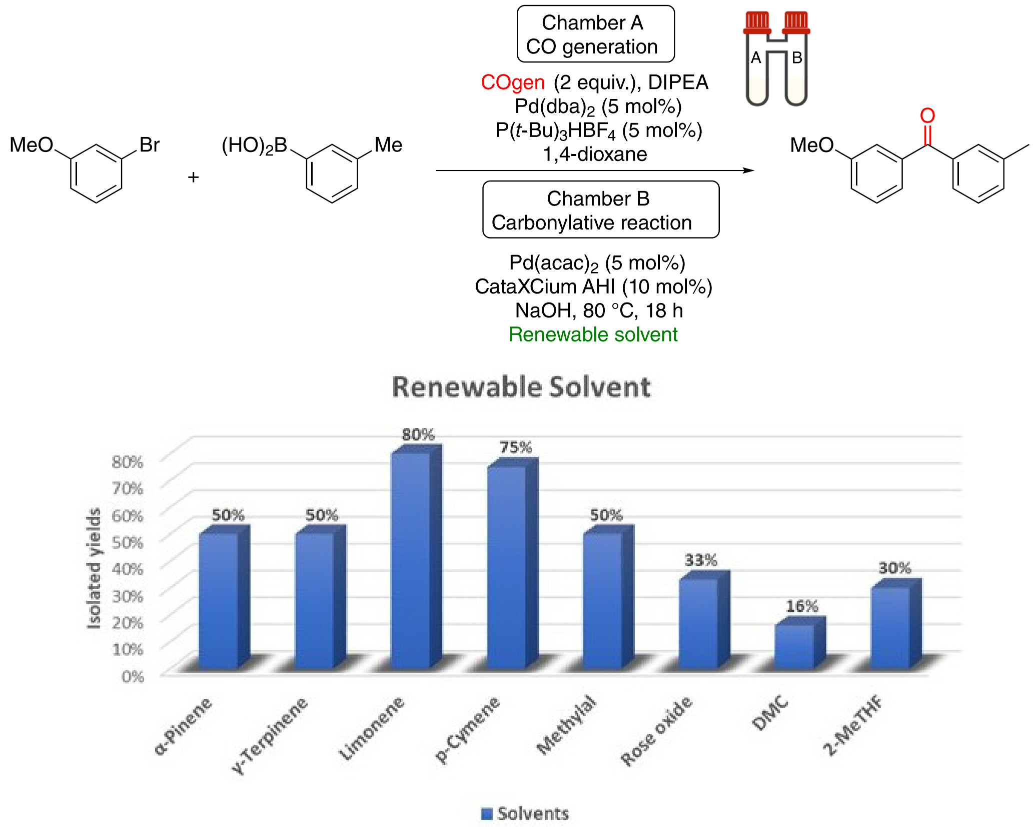
Scheme 28. Palladium-catalyzed carbonylative Sonogashira cross-coupling for the synthesis of alkynyl ketones and flavones by using water as a solvent.



Scheme 29. Palladium-catalyzed Suzuki carbonylation of different benzyl chlorides.

well-established renewable solvents, such as 2-MeTHF, GVL, limonene, *p*-cymene, DMC, DEC, ethylene carbonate (EC), PC, dimethosymehane (methylal) and diethoxymethane (ethylal) were evaluated, but also recently introduced biomass-derived solvents 1,1-dimethoxyethane (acetal), dimethyl isosorbide, γ-terpinene, α-pinene, eucalyptol, and rose oxide. It is noteworthy to mention that in this work the authors employed 1,4-dioxane solvent to generate carbon monoxide *ex situ* from COgen. Concerning this drawback, it is highly required that the generation of CO can also be carried out in a renewable solvent.

By using COgen as a precursor of carbon monoxide in combination with COware, the authors have developed an elegant Pd-catalyzed carbonylative coupling of aryl bromides and arylboronic acids for the preparation of biaryl ketones. In this reaction, eight organic solvents that currently can be 100% derived from bio-resources were evaluated (Scheme 30). Among these, the nonpolar ethers and carbonates (rose oxide, methylal, DMC) and polar ether 2-MeTHF provide the biaryl ketone in low yields (16-50%). In contrast, the nonpolar hydrocarbons solvents derived from citrus waste limonene and *p*-cymene and



Scheme 30. Screening of renewable solvents for carbonylative Suzuki cross-coupling (adapted from reference 79).

derived from coniferous plants γ-terpinene and α-pinene provided better yields.

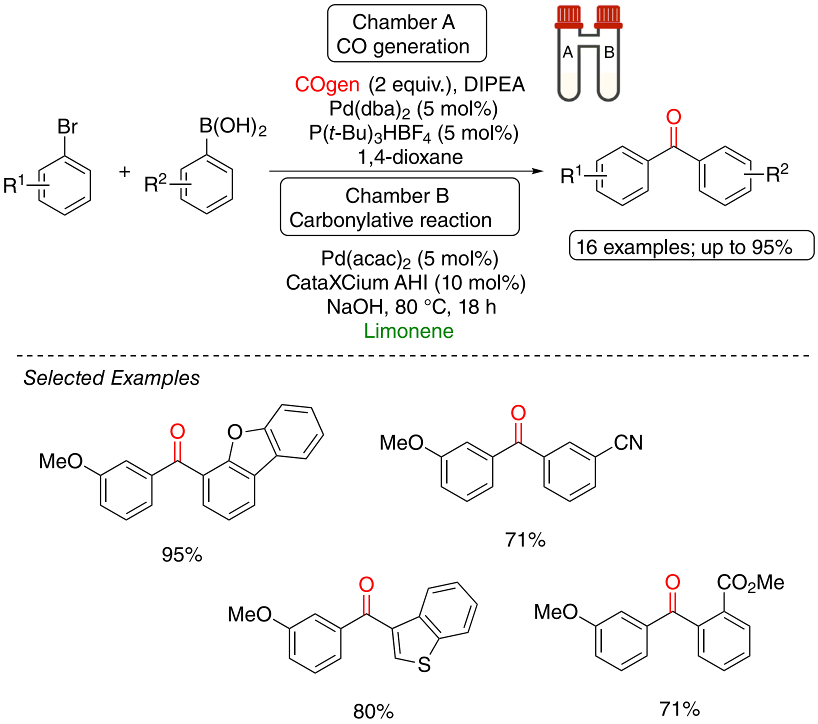
Limonene is identified to be slightly superior to *p*-cymene. The catalytic system showed tolerance to electron-withdrawing and electron-donating groups for both aryl bromides and aryl boronic acids (Scheme 31). It is noteworthy that limonene provided the same level as previously reported protocols using toluene as solvent.[155,156]

Encouraged by the excellent result detailed above, the authors examined the Pd-cacalyzed aminocarbonylation reaction of aryl bromides starting from *N*-methylaniline and 4-bromobenzonitrile.[79] This catalytic system showed to be well-adapted for most of the renewable solvents evaluated, giving the aminocarbonylated product in exceptional yields. Moreover, it was found that the side reactions such as hydroamination or Mizoroki-Heck coupling for solvents possessing double bonds were not observed. The investigation of optimum reaction conditions revealed that DMC, α-pinene and limonene were the top three best solvents (Scheme 32).

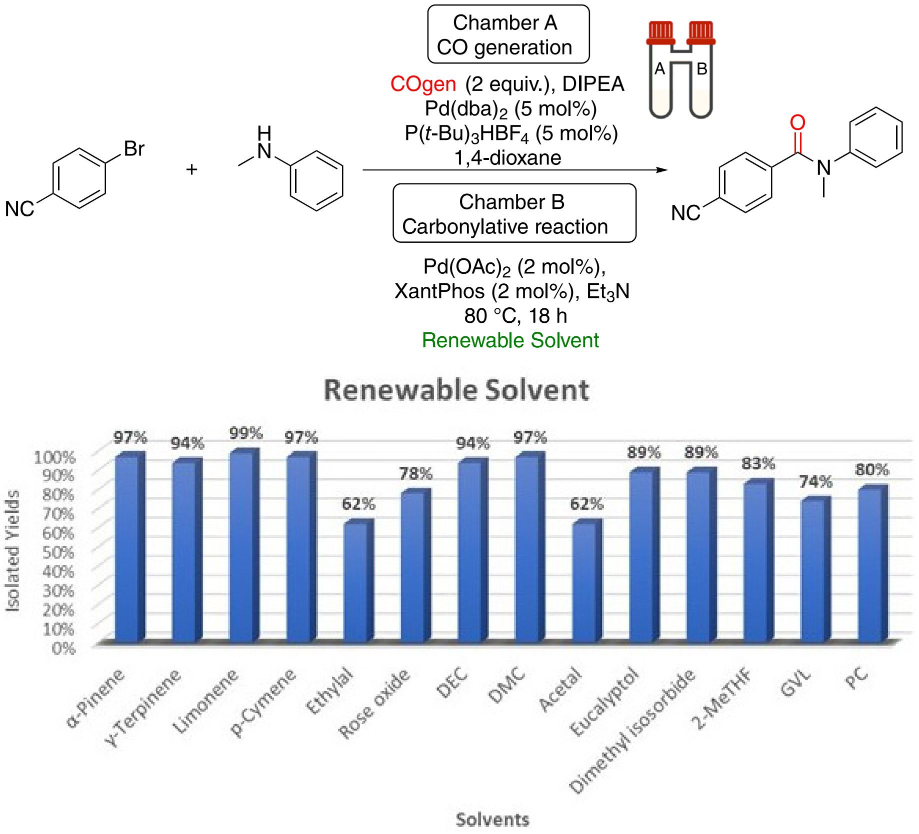
After optimization, aryl bromides were efficiently converted to the desired amides with catalytic amounts of $Pd(OAc)_2$, xantphos, Et_3N and COgen in DMC, α-pinene or limonene at 80 °C (Scheme 33). Under the optimized reaction conditions many functional groups were tolerated on the arene moiety, and various amines were also employed. According to the authors, the good results indicate that renewable solvents such as DMC, α-pinene and limonene can effectively replace 1,4-dioxane, toluene and THF commonly used in these reactions.[172-175] Furthermore, aminocarbonylation in renewable solvents can produce commercial drug trimetozine, a sedative agent, which has been used in the treatment of anxiety and an analogue of itopride used for the treatment of gastrointestinal symptoms.[176,177]

Using the same strategy, the authors[79] analyzed the application of renewable solvents for Pd-catalyzed alkoxycarbonylation. The application of renewable solvents in a combination of catalytic amounts of $Pd(dba)_2$, 1,1'-bis-(diisopropylphosphino)ferrocene (dippf), COgen, 2-bromonaphthalene with sodium *tert*-butoxide gave excellent results. However, it has been found that when nonpolar carbonate DMC was used, the side-product of methoxycarbonylation was isolated in 93% yield. According to them, this was the only example where the solvent was chemically transformed in the reaction. Moreover, it was found that the side product derived from the transesterification were not observed for the other carbonates (DEC, PC and EC). In all other solvents, the *tert*-butoxycarbonylation product was obtained in moderate to excellent yields (Scheme 34).

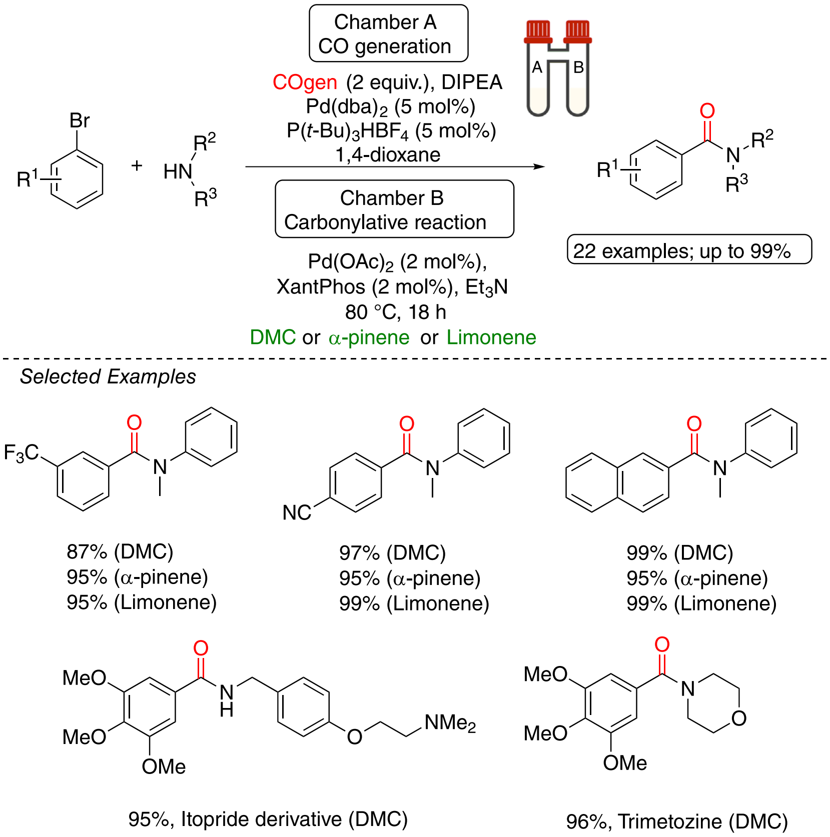
The scope of the reaction regarding the *tert*-butoxycarbonylation of aryl bromides was explored, using the top three best solvents 2-MeTHF, α-pinene, and γ-terpinene (Scheme 35). Acoording to the authors, the choice of solvent is dependent on the substrate. By using



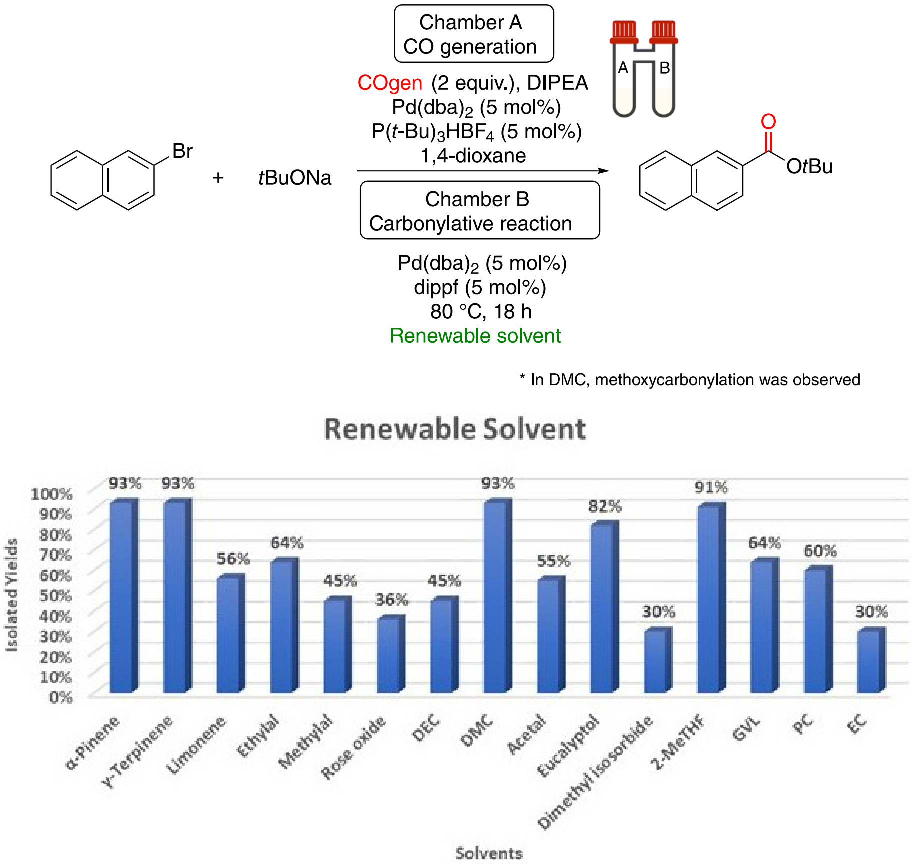
Scheme 31. Palladium-catalyzed carbonylative coupling of boronic acids and aryl bromides using the sustainable solvent limonene.



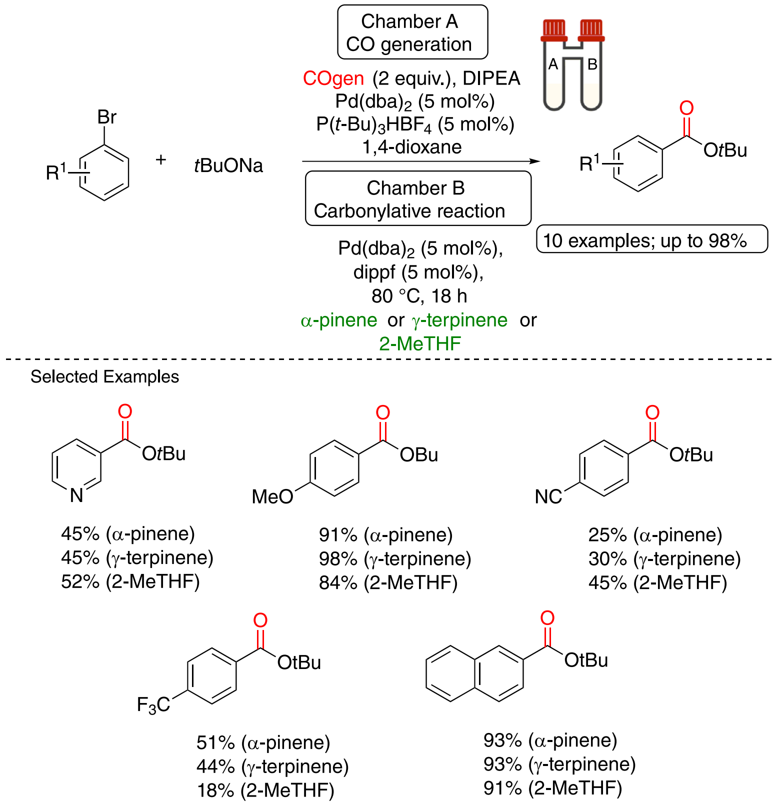
Scheme 32. Screening of renewable solvents for aminocarbonylation (adapted from reference 79).



Scheme 33. Palladium-catalyzed aminocarbonylation of aryl bromides using renewable solvents.



Scheme 34. Screening of renewable solvents for alkoxycarbonylation (adapted from reference 79).



Scheme 35. Palladium-catalyzed *tert*-butoxycarbonylation of aryl bromides using renewable solvents.

this catalytic protocol, the alkoxycarbonylated product could be obtained in similar or even better results than those of traditional solvents. Furthermore, this process improves sustainability by eliminating the need for toxic solvents such as hexafluoroisopropanol, THF, toluene, and dimethyl sulfoxide frequently used for alkoxycarbonylation reactions.[178-181]

3. Conclusions

During the last decades, palladium-catalyzed carbonylation reactions have emerged as robust and versatile synthetic tools to access a wide variety of carbonyl compounds. The significance of Pd-catalyzed carbonylation approaches is also evidenced by the fast-growing interest arising from both academia and industry in recent years. Tremendous advances have been made in the last years to development of more convenient and safer synthetic methods for handling the toxic pressurized carbon monoxide gas. For instance, the development of inexpensive carbon monoxide releasing molecules that allowed *in situ* or *ex situ* CO generation in an "on-demand" fashion has gained impetus over the last decades for carrying out carbonylation reactions. However, despite significant advances to carry out carbonylation reactions in a safer way, the use of renewable solvents which could well replace currently used fossil-based solvents as reaction media remains less explored. Nevertheless, over the last few decades, trends have been moving towards using renewable solvents derived from renewable raw materials on the development of new environmentally benign and highly efficient catalytic methodologies for organic transformations, since they have exceedingly zero or negligible impact on the environment and health. Hence, renewable solvents, have gained prominence as environmentally friendly solvents in various Pd-catalyzed carbonylative coupling reactions, such as carbonylative cross-couplings aminocarbonylations, alkoxycarbonylations, aryloxycarbonylations, thiocarbonylations and selenocarbonylations. The literature surveyed in this review showed that a diverse range of renewable solvents can be now efficiently used to access the carbonylated compounds with high yields. However, it is important to highlight again that there is no universal green solvent. Users must ascertain their best options based on prior chemistry, costs, eco-friendly benefits, and other factors. We believe that the emerging methodologies summarized in this review may help and inspire the scientific community to develop more efficient and eco-friendly Pd-catalyzed carbonylation reactions for a more sustainable future. Thus, there is no doubt that further progress will open for new synthetic routes and opportunities for organic chemists.

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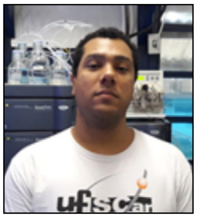

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