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Synthesis of Functionalized Heterocycles via Oxidative Carbonylation

Qi Xing and Fuwei Li

Abstract With the assistance of a proper oxidant, carbonylation of two nucleophiles can take place directly in carbonylation conditions, which is defined as oxidative carbonylation. This process starts with the reaction of nucleophiles with the metal catalyst in oxidation state ($M^{(n+2)}$), followed by insertion of CO and subsequent reductive elimination, providing the carbonylated products and the metal catalyst in reduction state ($M^{(n)}$). The oxidant could reoxidize $M^{(n)}$ to $M^{(n+2)}$ to promote the catalytic cycle. Oxidative carbonylation avoids the difficult oxidative addition of R–X to metal catalyst, so this kind of carbonylation could proceed in mild conditions. What's more is that oxidative carbonylation doesn't need prefunctionalization of substrates. So, it's no wonder that considerable attention has been drawn to construct important carbonylated compounds through oxidative carbonylation. Particularly, much progress in synthesis of carbonylated heterocycles via oxidative carbonylation has been achieved in the past decades. Here, we summarized the main achievements in this area from 1982 to the beginning of 2015.

Keywords Catalytic • Heterocycles • Oxidative carbonylation • Synthesis

Contents

Q. Xing and F. Li (✉)
State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou, Gansu 730000, P. R. China
e-mail: fuweili@licp.cas.cn

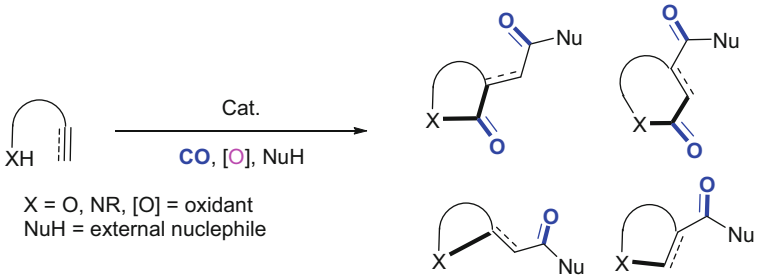
Carbonylated heterocycles as an important class of compounds can be found in many biologically active natural products. Therefore, many efforts have been devoted to developing improved methods for synthesis of these compounds (for selected reviews on synthesis of heterocycles, see [1–14]). CO as the simplest C-1 unit has been widely used to construct carbonylated compounds (for selected examples, see [15–26]). Heck and co-workers pioneered the carbonylation of organic halides with CO in 1963 [27]. In this work, the oxidative addition of organohalides to Pd(0) takes place firstly followed by coordination and insertion of CO, and finally reductive elimination occurs giving the carbonylated product. However, the π acidity of CO renders the CO-coordinated low-valence metal electron deficient, which makes oxidative addition of organohalides to Pd(0) difficult [28]. As a result, harsh conditions are often required for this kind of carbonylation. In addition, prefunctionalized substrates as electrophiles are needed for this reaction, which traduced the green chemistry principles. With the assistance of a proper oxidant, carbonylation of two nucleophiles can take place directly in carbonylation conditions, which is defined as oxidative carbonylation [29, 30]. This process starts with the reaction of nucleophiles with the metal catalyst in oxidation state ($M^{(n+2)}$), followed by insertion of CO and subsequent reductive elimination, providing the carbonylated products and the metal catalyst in reduction state ($M^{(n)}$). The oxidant could reoxidize $M^{(n)}$ to $M^{(n+2)}$ to promote the catalytic cycle. Oxidative carbonylation avoids the difficult oxidative addition of R–X to metal catalyst, so this kind of carbonylation could proceed in mild conditions. What's more is that oxidative carbonylation doesn't need prefunctionalization of substrates. So, it's no wonder that considerable attention has been drawn to construct important carbonylated compounds through oxidative carbonylation [18, 24, 26]. Particularly, much progress in synthesis of carbonylated heterocycles via oxidative carbonylation has been achieved in the past decades [13, 14]. Here, we summarized the main achievements in this area from 1982 to the beginning of 2015.

1 Synthesis of Heterocycles via Oxidative Carbonylation of Alkyne or Alkene Derivatives Incorporated with a Nucleophile (OH or NHR)

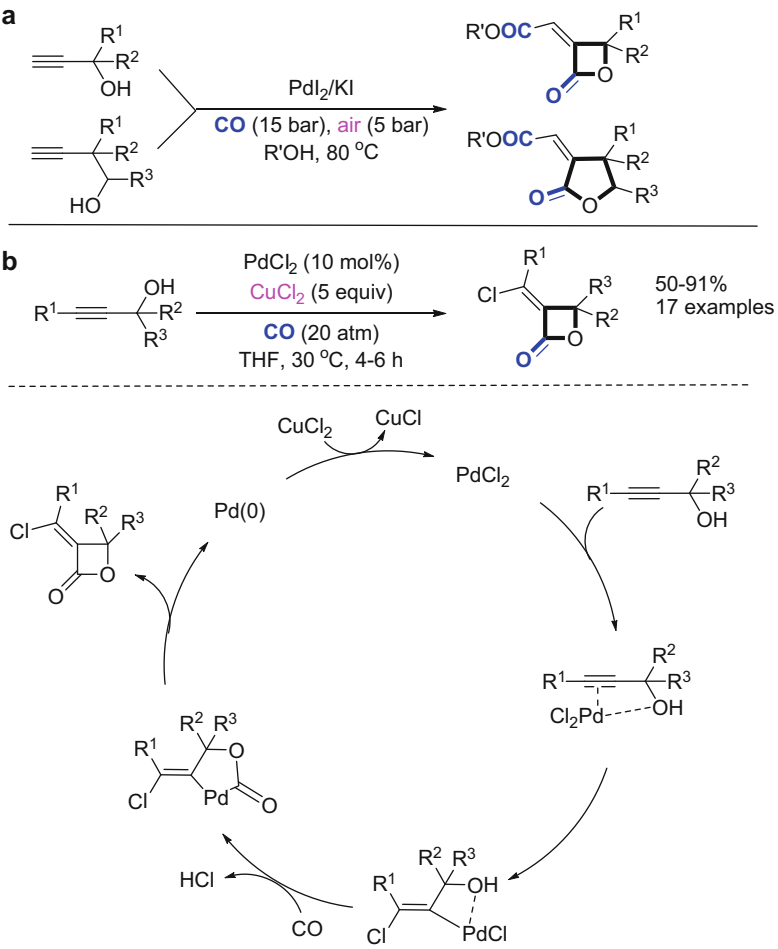
Cyclization of unsaturated substrates incorporated with a proper nucleophile is an efficient route to synthesize various carbonylated heterocycles (Scheme 1). Many advances in application of this methodology for synthesis of oxygen- or nitrogen-containing carbonylated heterocycles have been reported by different groups all around the world. Generally, this method provides endo-carbonyl or exo-carbonyl compounds as the main products depending on the type of substrates and reaction conditions. Meanwhile, different sizes and types of heterocycles are generated depending on the chain length of substrates and reaction regioselectivity.

1.1 Synthesis of Four-Membered Heterocycles via Oxidative Carbonylation of Alkyne or Alkene Derivatives Incorporated with a Nucleophile

Lactones are important skeletons in some biologically active natural products. Oxidative cyclocarbonylation of alkynols represents a powerful methodology for the synthesis of lactones. As early as 1994, Gabriele and co-workers reported a PdI_2-/KI-catalyzed oxidative carbonylation of tertiary α-hydroxyalkynes to give β-lactones stereoselectively with air as the oxidant [31]. Later, they extended this method to but-3-yn-1-ols to synthesize five-membered lactones (Scheme 2a) [32]. In 2003, Ma and co-workers developed a palladium-catalyzed cyclocarbonylation of 2-alkynols with $CuCl_2$ for the synthesis of (*Z*)-α-chloroalkylidene-β-lactones (Scheme 2b) [33]. Good regio- and stereoselectivities were obtained, and the optically active (*Z*)-α-chloroalkylidene-β-lactones could be obtained in high ee values using optically active propargylic alcohols.



Scheme 1 Oxidative carbonylation of unsaturated substrates incorporated with a nucleophile to carbonylated heterocycles

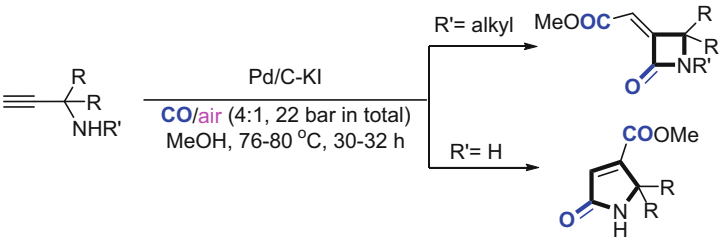


Scheme 2 Synthesis of four-membered lactones via oxidative carbonylation of alkynols

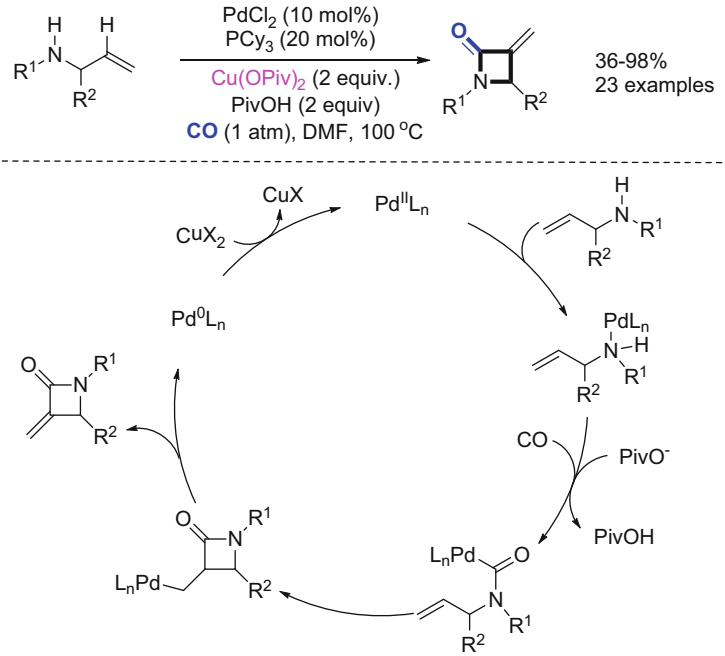
Later, the same group further studied this reaction: the scope of the reaction, mechanism, and the subsequent coupling reactions [34].

Similarly, oxidative cyclocarbonylation of alkynylamines provides lactams as the products. In 1995, Bonardi and co-workers reported a palladium-catalyzed oxidative carbonylation of 1-substituted prop-2-ynylamines [35]. This oxidative carbonylation method gave different products with different *N*-substituents. Using *N*-alkyl-substituted prop-2-ynylamines resulted in the formation of β-lactams, while γ-lactams were obtained with *N*-unsubstituted prop-2-ynylamines (Scheme 3).

Recently, the group of Lei developed an efficient method for the synthesis of α-methylene-β-lactams via palladium-catalyzed oxidative carbonylation of *N*-allylamines with $Cu(OPiv)_2$. A four-membered-ring transition state is supported by DFT calculations (Scheme 4) [36].



Scheme 3 Synthesis of lactams via oxidative carbonylation of prop-2-ynylamines

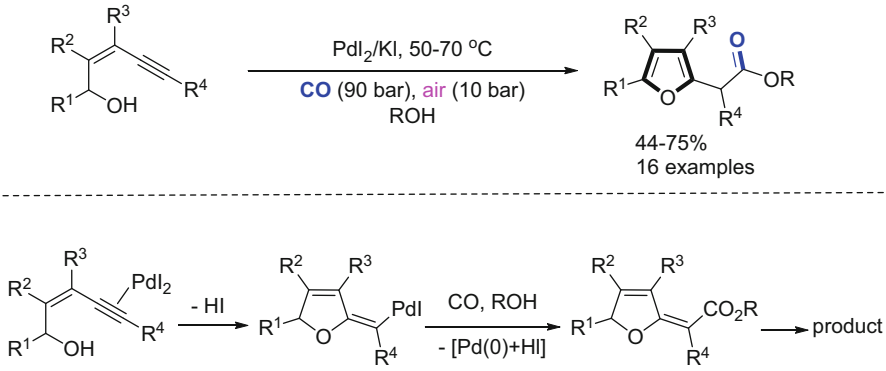


Scheme 4 Synthesis of four-membered lactams via oxidative carbonylation of *N*-allylamines

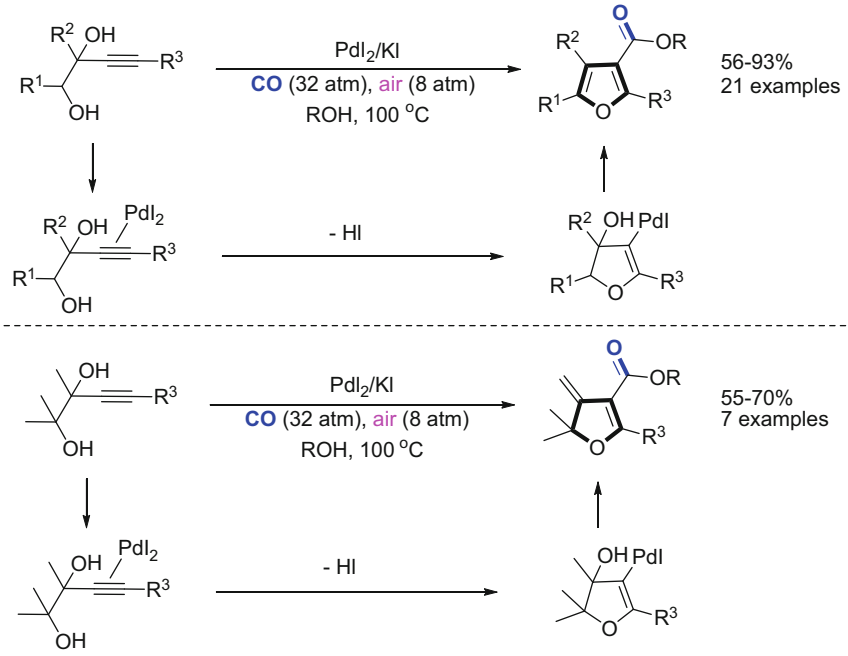
1.2 Synthesis of Five-Membered Heterocycles via Oxidative Carbonylation of Alkyne or Alkene Derivatives Incorporated with a Nucleophile

1.2.1 Synthesis of Five-Membered Oxygen-Containing Heterocycles via Oxidative Carbonylation of Alkyne or Alkene Derivatives Incorporated with a Nucleophile

Gabriele and co-workers reported the novel synthesis of furanacetic derivatives via oxidative carbonylation of acyclic (*Z*)-2-en-4-yn-1-ols [37, 38]. The cyclization–alkoxycarbonylation process occurs in an alcoholic media at 50–70°C and under



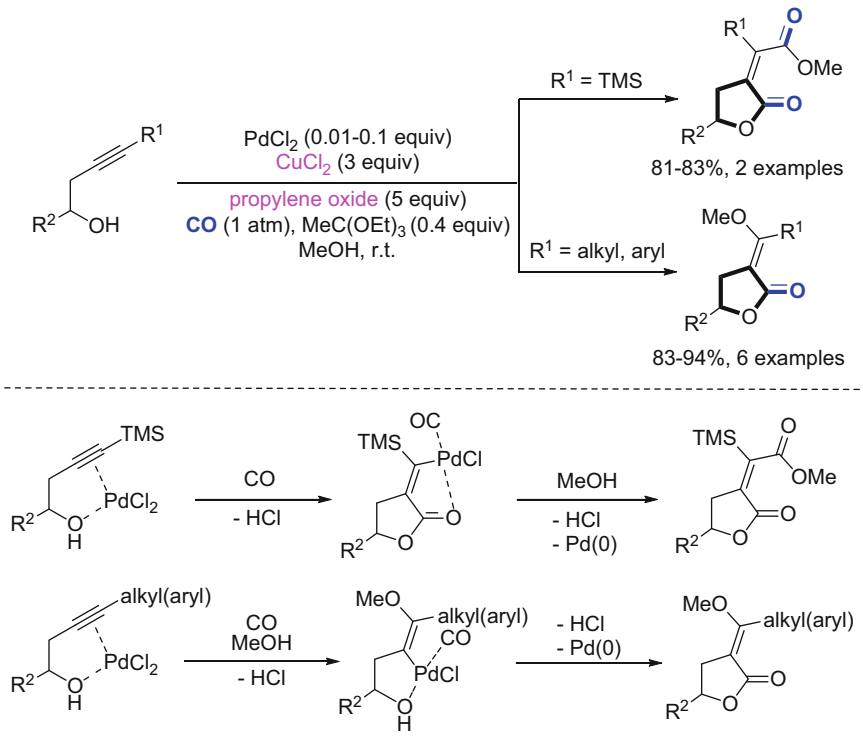
Scheme 5 Synthesis of furanacetic derivatives via oxidative carbonylation



Scheme 6 Synthesis of furanacetic derivatives via oxidative carbonylation

100 atm pressure of a 9:1 mixture of carbon monoxide and air with the catalysis of PdI_2/KI. With isolation of the nonaromatic precursors of the final product, a reaction mechanism was proposed accordingly (Scheme 5).

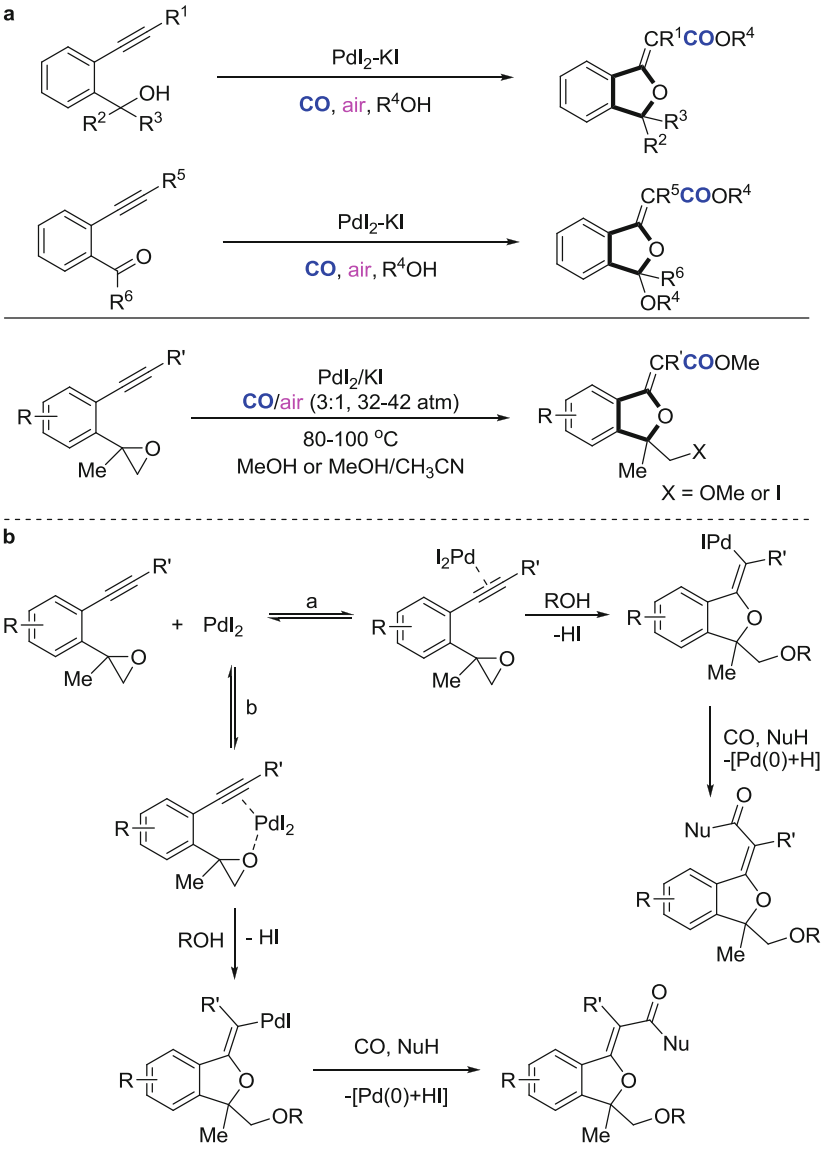
Similarly, as reported later by the same group, 3-yne-1,2-diols could be transformed into furan-3-carboxylic esters through a sequential 5-endo-dig heterocyclization–alkoxycarbonylation–dehydration process using air as the external oxidant. Under similar conditions, 4-methylene-4,5-dihydrofuran-3-carboxylates were obtained from 2-methyl-3-yne-1,2-diols (Scheme 6) [39, 40].



Scheme 7 Synthesis of oxygen-containing heterocycles via methoxycarbonylation of alkynoles

In 1991, Tamaru reported the palladium-catalyzed carbonylation of 3-butyne-1-ols. In this process, different substituents on acetylenic termini led to different courses of reaction. When the substituent is trimethylsilyl group, *cis* dicarbonylation proceeds selectively, while, with alkyl or aryl substituents, *trans* alkoxycarbonylation takes place selectively (Scheme 7). Recently, the group of Kato further developed methoxycarbonylation of terminal alkynes with bisoxazolines as the box ligands. In addition, they succeeded in applying this methodology to the synthesis of β-methoxyacrylate natural products [41, 42].

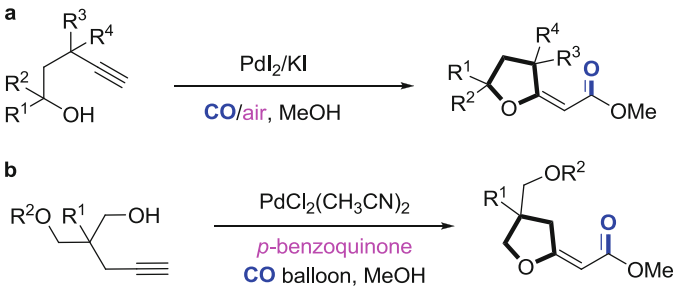
Palladium-catalyzed oxidative carbonylation of 2-alkynylbenzyl alcohols, 2-alkynylbenzaldehydes, and 2-alkynylphenyl ketones to 1-(alkoxycarbonyl)methylene-1,3-dihydroisobenzofurans and 4-(alkoxycarbonyl)benzo[*c*]pyrans was described by Costa and Gabriele et al. in 2004 (Scheme 8a) [43]. The reaction occurs through intramolecular attack by the nucleophilic oxygen atom (either already present in the starting material or generated in situ by ROH attack on the carbonyl group) on the triple bond coordinated to Pd(II) and subsequent alkoxycarbonylation. The presence of substituents in the position α to the alcoholic or ketonic hydroxy group leads to the selective formation of five-membered ethereal rings. In contrast, six-membered rings are preferentially formed in the absence of at least one of these substituents. Alternatively, different substituted alkynyloxiranes could also be converted into



Scheme 8 Synthesis of isobenzofurans via palladium-catalyzed oxidative carbonylation of 2-alkynylbenzyl alcohols, 2-alkynylphenyl ketones, and alkynyloxiranes

functionalized 1,3-dihydroisobenzofurans and tetrahydrofuran derivatives in fair to good yields by a cascade reaction, consisting of a sequential nucleophilic ring opening–heterocyclization–oxidative carbonylation process (Scheme 8b) [44].

As reported by Gabriele and co-workers, palladium-catalyzed oxidative cyclization–alkoxycarbonylation of 4-yn-1-ols under 100 atm of 9:1 mixture of



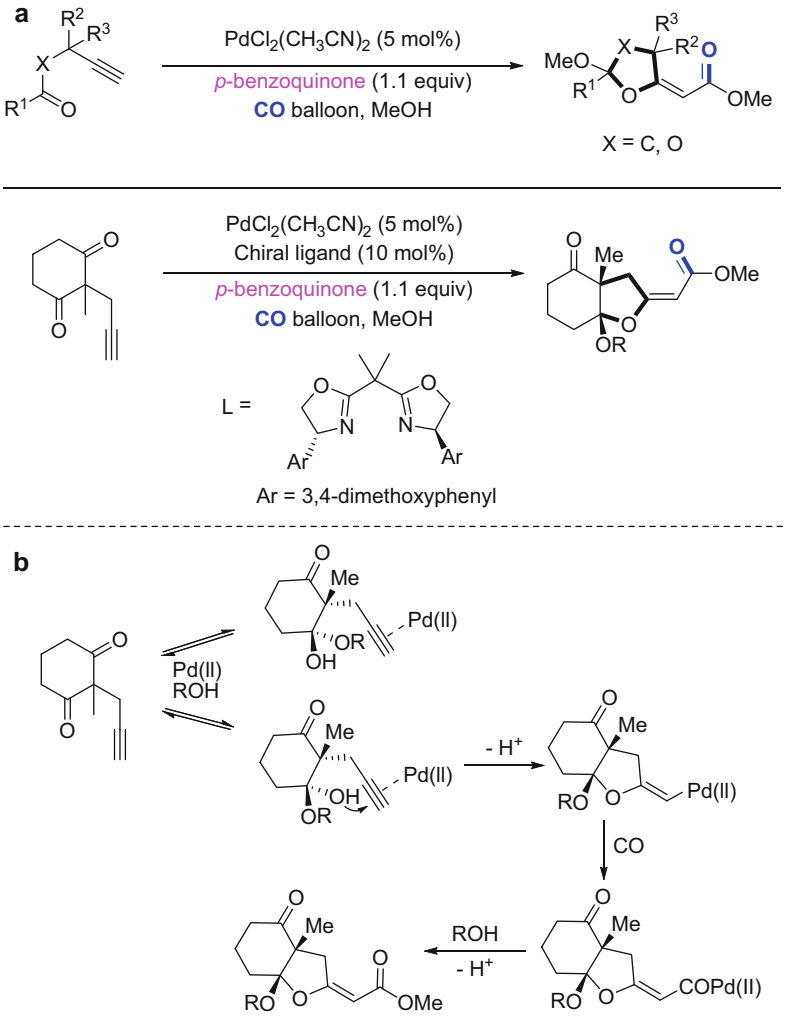
Scheme 9 Synthesis of tetrahydrofurans via oxidative carbonylation of 4-yn-1-ols

carbon monoxide and air could provide 2*E*-[(methoxycarbonyl)methylene]tetrahydrofurans in good yields (Scheme 9a). Meanwhile, the cycloisomerization–hydromethoxylation as a competing reaction could be easily prevented by increasing the KI excess [45]. Later, by using *p*-benzoquinone, Akita, Kato, and co-workers improved this method to be applicable to broader substrates with avoidance of KI and high pressure (Scheme 9b) [46]. Following this, they succeeded in performing the reaction in an asymmetric manner by applying chiral bisoxazolines as ligands [47, 48].

Besides alkynyl alcohols, alkynyl ketones could also underwent oxidative cyclocarbonylation to give carbonated heterocycles. Akita and Kato et al. developed palladium-catalyzed oxidative cyclization–carbonylation of 4-yn-1-ones affording cyclic ketals in moderate to good yields (Scheme 10a). The cyclic ketals can be easily converted into 2-cyclopentenones, which are useful intermediates of natural products [49]. Later, the same group extended this method to the cyclocarbonylation of propargylic acetates [50], propargylic esters [51], and 2-propargyl-1,3-dione [52, 53]. Furthermore, using chiral bisoxazoline ligands, they realized the asymmetric cyclization–carbonylation of 2-alkyl-2-propargylcyclohexane-1,3-diones successfully. Bicyclic-β-alkoxyacrylates were obtained in 51–74 % yields with 72–82 % enantiomeric excesses (Scheme 10b). This methodology was applied by Mukai and co-workers in the total synthesis of naturally occurring diacetylenic spiroacetal enol ethers [54]. A related mechanistic study including experiments and DFT studies was also done by Carfagna and co-workers [55].

In 2009, palladium-catalyzed carbonylation of 1,2-allenyl ketones was developed by the same group under a CO atmosphere with *p*-benzoquinone as the oxidant. Difuranylketones were obtained in moderate to good yields (Scheme 11) [56].

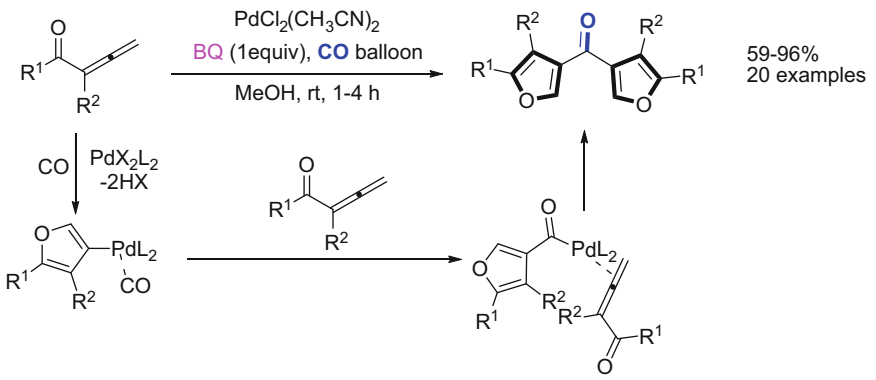
The group of Ma applied the $PdCl_2$-catalyzed chlorocyclocarbonylation of 2,3-allenols to the synthesis of 3-chloromethyl-2(5H)-furanones in mild conditions (Scheme 12). Optically active 3-chloromethyl-2(5H)-furanones could be obtained from readily available optically active 2,3-allenols. In addition, six-membered



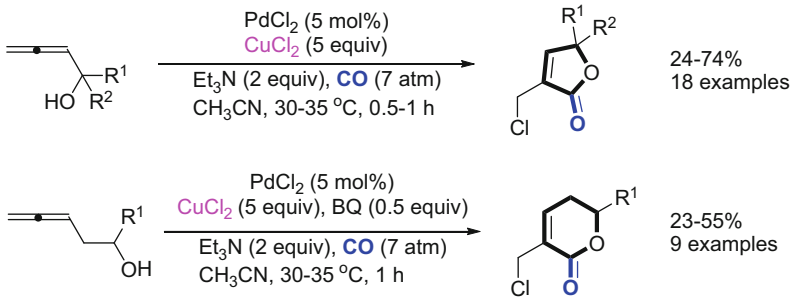
Scheme 10 Synthesis of five-membered oxygen-containing heterocycles via oxidative carbonylation of alkynones or propargylic acetates

3-chloromethyl-5,6-dihydropyran-2-ones could be prepared from 3,4-allenols in similar conditions [57].

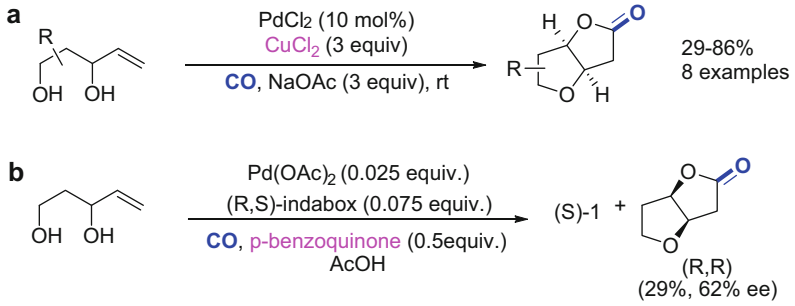
Yoshida and co-workers selectively prepared *cis* 3-hydroxytetrahydrofuran acetic acid lactones by an intramolecular palladium-catalyzed oxycarbonylation of 4-penten-1,3-diols under 1 atm of CO with $CuCl_2$ as the oxidant (Scheme 13a) [58]. The group of Gracza developed the asymmetric intramolecular oxycarbonylation of pent-4-ene-1,3-diols using chiral palladium(II) complexes. In the presence of $Pd(OAc)_2$-{(R,S)-indabox}, *p*-benzoquinone in acetic acid under an atmosphere of CO, the desired products were obtained in an enantiomerical manner



Scheme 11 Synthesis of difuranylketones via palladium-catalyzed carbonylative dimerization of allenyl ketones



Scheme 12 Synthesis of oxygen-containing heterocycles via oxidative carbonylation of allenols

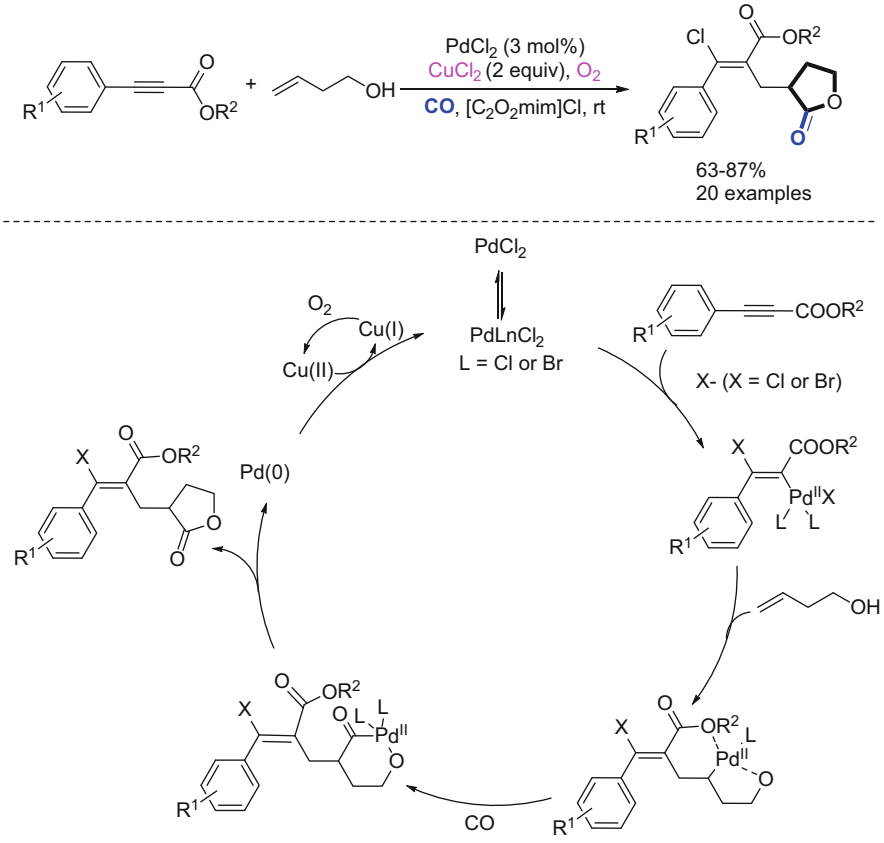


Scheme 13 Synthesis of cyclic lactones via oxycarbonylation of unsaturated diols

in low yields (Scheme 13b) [59]. Later, they extended the substrates to 4-benzyloxyhepta-1,6-diene-3,5-diols providing bicyclic lactones in good yields and with excellent threo-diastereoselectivity. However, the level of asymmetric induction is rather poor [60]. These methodologies were applied to the synthesis of

natural products such as kumausyne, crisamicin A, deoxynojirimycin, and so on [61–65].

When intramolecular cyclocarbonylation was properly combined with an intermolecular cascade reaction, higher-value products could be obtained. For example, Jiang and Yang et al. reported a novel palladium-catalyzed cascade annulation in liquids to construct functionalized γ-lactones from alkynotes and homoallyl alcohol. This process included the carbonylation of the C(sp^3)–palladium bond. Ethyl, allyl, and phenyl alkynoates and substituted phenylpropiolic acid were allowed to react under the optimal conditions with good to excellent yields. In addition, both electron-withdrawing and electron-donating substituents on the aromatic ring were well tolerated. A possible reaction mechanism was proposed based on the experiment results and previous literature (Scheme 14) [66].



Scheme 14 Synthesis of γ-lactones via palladium-catalyzed cascade carbonylative annulation

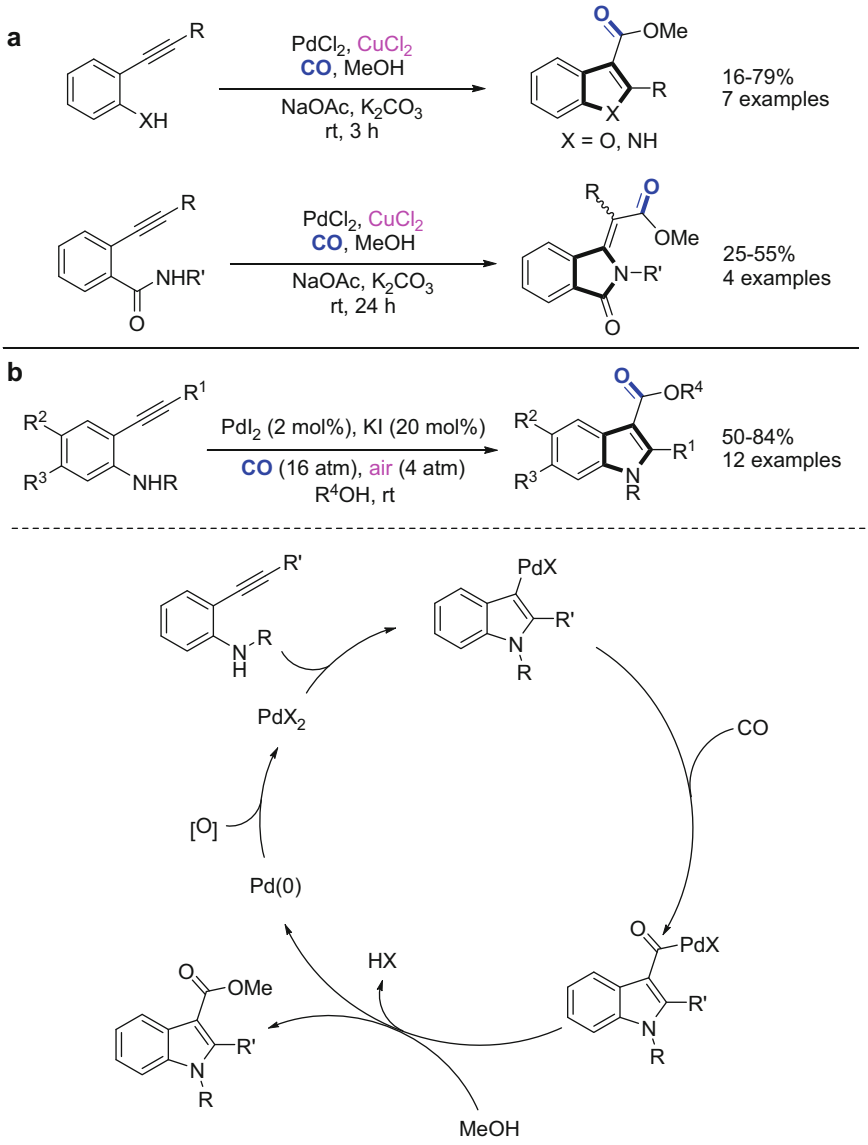
1.2.2 Synthesis of Five-Membered Nitrogen-Containing Heterocycles via Oxidative Carbonylation of Alkyne and Alkene Derivatives Incorporated with a Nucleophile

Comparing with other types of heterocycles, nitrogen-containing heterocycles represent privileged structures and show a variety of biological activities. Oxidative carbonylation of alkynylaniline derivatives represents an efficient approach to this kind of heterocycles. In 1994, Sakamoto and co-workers reported the sequential cyclization/carbonylation of 2-alkynylanilines and alkynylphenol in the presence of catalytic amount of palladium dichloride and copper dichloride. The corresponding indole-3-carboxylates and benzofuran-3-carboxylates were obtained in moderate yields. The reaction of 2-alkynylbenzamides gave 3-alkylidenisoindole derivatives (Scheme 15a) [67]. In 2012, Gabriele and co-workers applied the PdI_2/KI system to the oxidative carbonylation of 2-alkynylaniline derivatives with oxygen as the only oxidizing agent. A variety of 2-alkynylanilines bearing an internal triple bond and a second aryl amino group could be conveniently converted into *N*-substituted indole-3-carboxylic esters in fair to high yields. With the assistance of $HC(OR)_3$, the *N*-unsubstituted indole-3-carboxylic esters were obtained by the oxidative carbonylation of primary 2-alkynylanilines and subsequent acidic treatment (Scheme 15b) [68]. The reaction pathway started with the generation of the indolylpalladium complex from the reaction of ethynylanilines and palladium dichloride. Subsequently, the insertion of carbon monoxide into carbon–palladium bond gave the indolylacylpalladium species, which reacted with methanol to give the final products.

Recently, Mancuso and Gabriele et al. found that PdI_2-catalyzed oxidative carbonylation of 2-alkynylbenzamides underwent different reaction pathways depending on the nature of the external nucleophile and reaction conditions (Scheme 16). In the presence of a secondary amine as external nucleophile, 2-ethynylbenzamides are selectively converted into 3-[(dialkylcarbamoyl)methylene]isoindolin-1-ones through the intermediate formation of the corresponding 2-ynamide derivatives followed by intramolecular nucleophilic attack by the nitrogen of the benzamide moiety on the conjugated triple bond. On the other hand, in the presence of an alcohol R′OH as the external nucleophile and $HC(OR')_3$ as a dehydrating agent, 2-alkylnylbenzamides bearing a terminal or an internal triple bond underwent oxidative carbonylation to give 3-[(alkoxycarbonyl)methylene]-isobenzofuran-1(3H)imines selectively. This process started with the 5-exo-dig intramolecular nucleophilic attack of the oxygen of the benzamide moiety on the triple bond coordinated to the metal center followed by alkoxycarbonylation [69].

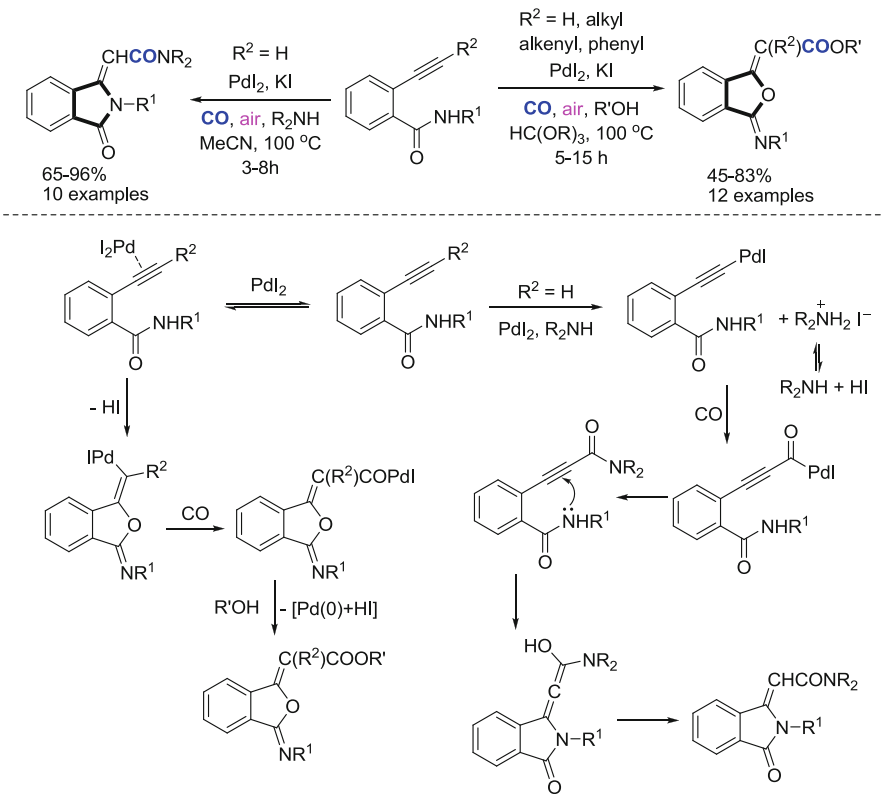
As reported by Gabriele and co-workers, 2-alkynylaniline imines could be converted into carbonylated indoles based on a multicomponent cascade reaction, involving ROH nucleophilic attack to the imine moiety, followed by a palladium-catalyzed heterocyclization/alkoxycarbonylation process. A number of indoles were obtained in good yields (Scheme 17) [70].

They also developed the direct synthesis of pyrrole-2-acetic esters by palladium-catalyzed oxidative carbonylation of (*Z*)-(2-en-4-ynyl)amines. They found that carbon dioxide effectively promotes this reaction by reversibly binding to the amino



Scheme 15 Palladium-catalyzed oxidative carbonylation for the synthesis of indoles and benzofurans

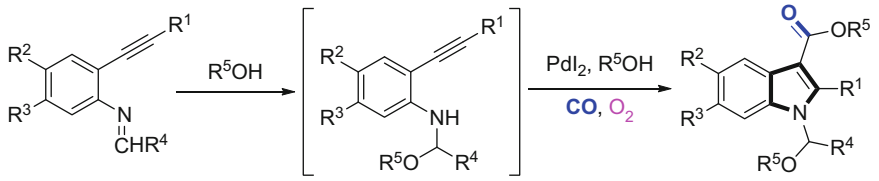
group, thus "freeing" the HI necessary for the reoxidation of Pd(0) (Scheme 18a) [71]. In 2012, PdI_2-catalyzed oxidative heterocyclization/alkoxycarbonylation of *N*-Boc-1-amino-3-yn-2-ols to functionalized pyrroles was developed by Gabriele. Reactions were carried out in alcoholic solvents at 80–100°C and under 20 atm (at 25°C) of a 4:1 mixture of CO–air, in the presence of Pd_2–KI catalytic system. By a basic



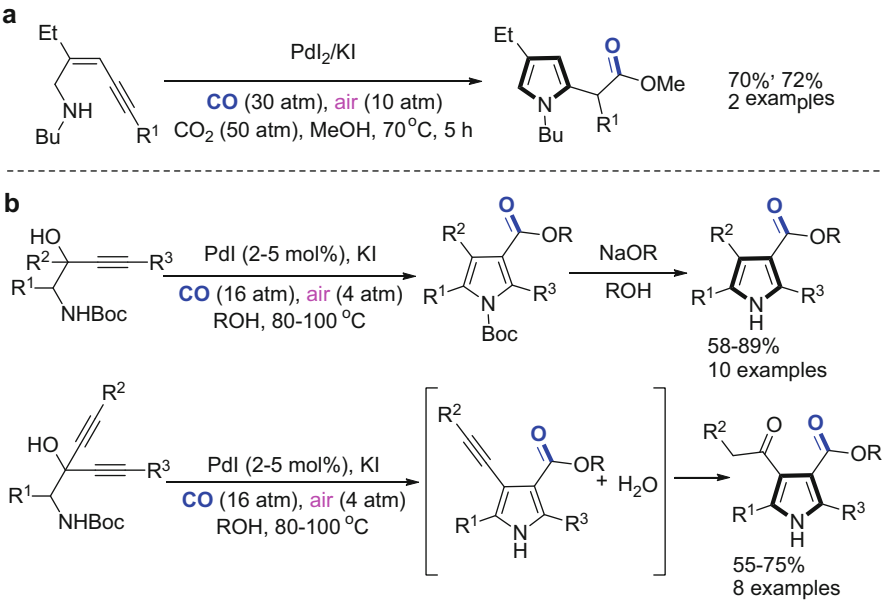
Scheme 16 Control synthesis of isoindolin-1-ones and isobenzofuran-1(3H)imines via oxidative carbonylation of 2-alkynylbenzamides

treatment, deprotected pyrrole-3-carboxylic esters were obtained in moderate to good yields. When the reaction was carried out on *N*-Boc-2-alkynyl-1-amino-3-yn-2-ols, bearing an additional alkynyl substituent α to the hydroxyl group, *N*-deprotection occurred spontaneously under the reaction conditions, together with regioselective water addition to the triple bond of the alkynyl substituent, providing polysubstituted and multifunctionalized pyrrole derivatives (Scheme 18b) [72].

In 2007, Tang and co-workers developed a palladium-catalyzed carbonylative annulation of 2-(1-alkynyl)benzenamines for the preparation of 3-(halo(substituted) methylene)-indolin-2-ones (Scheme 19). In the presence of PdX_2 and CuX_2, a variety of 2-(1-alkynyl)anilines underwent the carbonylative annulation reaction with CO smoothly to afford the target product in moderate to good yields. The reaction is proposed to start with the coordination of $PdCl_2$ with the triple bond and nitrogen, followed by *cis*- and *trans*-halopalladation to generate the corresponding vinylpalladium species. Afterward, the coordination and insertion of CO with the vinylpalladium species and subsequent reductive elimination provided the desired



Scheme 17 Synthesis of indoles via the multicomponent cascade reaction terminated by carbonylation

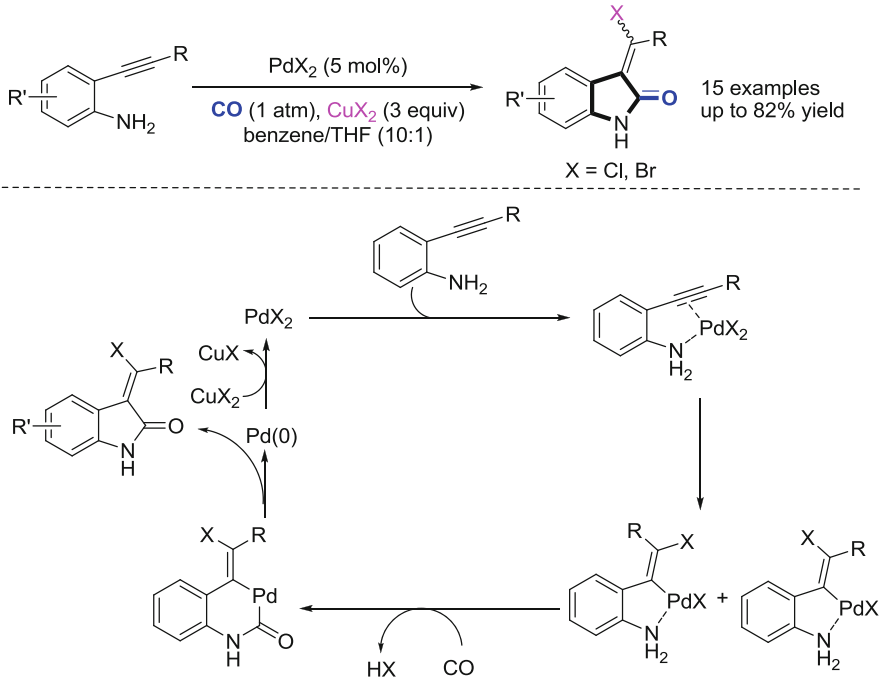


Scheme 18 Synthesis of carbonylated pyrroles via oxidative carbonylation

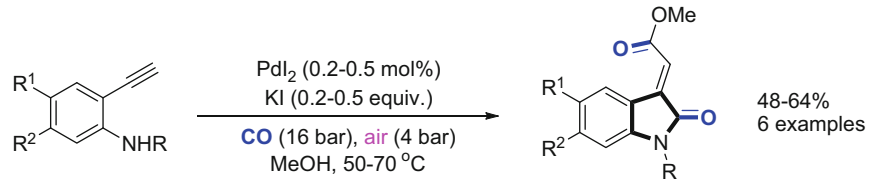
products and a Pd(0) species. Finally, the active Pd(II) species could be regenerated by the oxidative reaction of Pd(0) with CuX_2 [73].

Using methanol as the solvent, the 2-ethynylanilines underwent oxidative carbonylation to give (*E*)-3-(methoxycarbonyl)methylene-1,3-dihydroindol-2-ones in the presence of catalytic amount of PdI_2 in conjunction with KI. This reaction was completely stereoselective with no formation of (*Z*)-3-(methoxycarbonyl)methylene-1,3-dihydroindol-2-ones being observed (Scheme 20) [74].

In 2005, Costa and co-workers reported a cascade carboxylation–alkoxycarbonylation of *N*-alkyl-substituted dialkylpropynylamines in the presence of carbon dioxide and carbon monoxide. In this process, carbon dioxide and carbon monoxide were caused to react in sequence, providing oxazolidinone derivatives as the final products. In the absence of alkyl groups α to the triple bonds, the introduction of



Scheme 19 Synthesis of indolin-2-ones via oxidative carbonylation of 2-(1-alkynyl) benzenamines

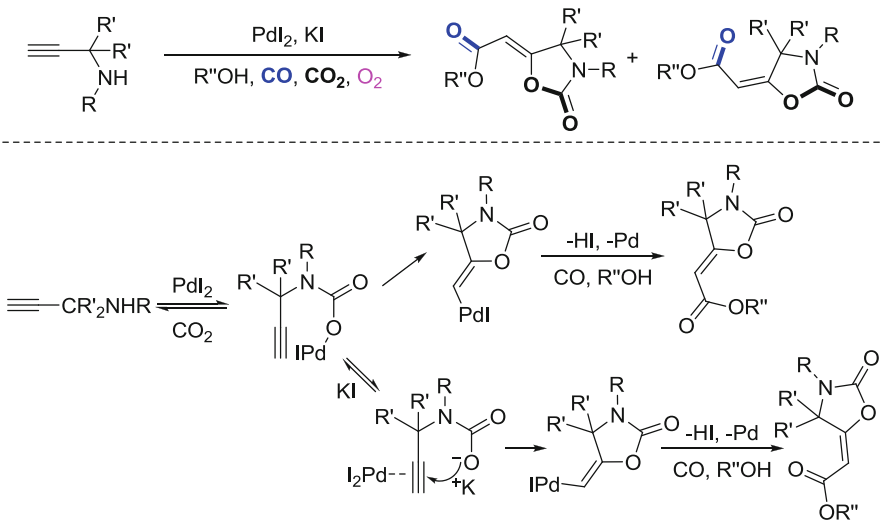


Scheme 20 Synthesis of indol-2-one derivatives via oxidative carbonylation of 2-ethynylanilines

carbon dioxide only and not that of carbon monoxide was observed under the similar conditions (Scheme 21) [75].

Notably, in the presence of water, α,α-disubstituted 2-ynylamines underwent sequential oxidative aminocarbonylation–cyclocarbonylation with the catalysis of PdI_2/KI, providing 2-oxazolidinone derivatives in good to excellent yields. In the case of α-monosubstituted propargylamine, the initially formed oxazolidinone derivatives underwent shift of the double bond into the cycle with formation of a 3H-oxazol-2-one derivative in good yields (Scheme 22) [76].

The group of Costa applied PdI_2-/KI-catalyzed oxidative carbonylation to prop-2-ynylamides under a mixture of CO and air for the synthesis of 5-(alkoxycarbonyl) methylene-3-oxazolines (Scheme 23) [77]. Under similar reaction conditions,

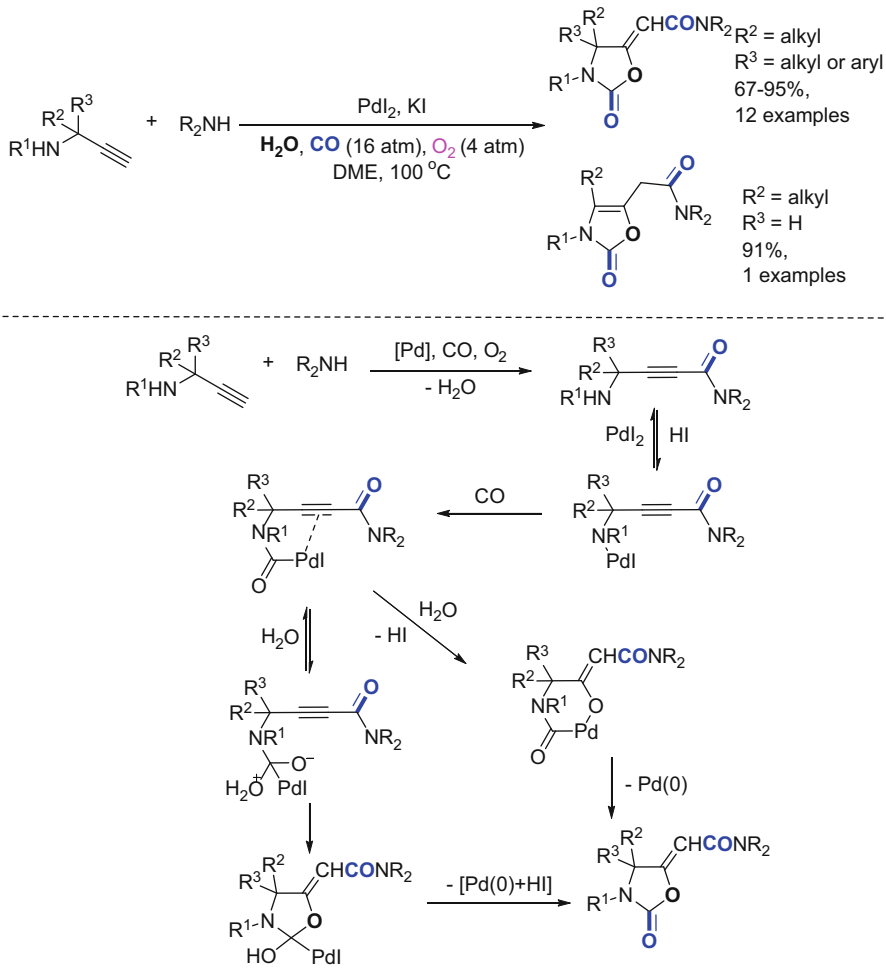


Scheme 21 Oxidative carbonylation of propargyl amines with carbon dioxide and carbon monoxide

4-yn-1-ones containing different substituents, prop-2-ynyl α-ketoesters, and prop-2-ynyl α-ketoamides underwent heterocyclization–alkoxycarbonylation to give tetrahydrofuran, dioxolane, and oxazoline, dihydropyridinone, and tetrahydropyridinedione derivatives in satisfactory yields [78].

By applying proper ligands and reaction conditions, these intramolecular cyclization/carbonylation reactions could be expanded to a cyclization/carbonylation/cyclization process, which would be a synthetically valuable method for direct preparation of ketones bearing two heterocycles. In 2011, Kato and co-workers developed a cyclization–carbonylation–cyclization (CCC-coupling reaction) coupling reaction of propargyl acetates and amides for the synthesis of ketones with two heterocyclic groups (Scheme 24a). The box ligands played an important role for this reaction by enhancing the electrophilicity of palladium(II) and thus promote coordination of the second triple bond in the second part of the tandem reaction [79]. In 2014, the same group applied this methodology to the CCC-coupling reaction of 2-alkynylanilines providing bis(1-benzyl-1H-indol-3-yl)methanones in good yields (Scheme 24b) [80].

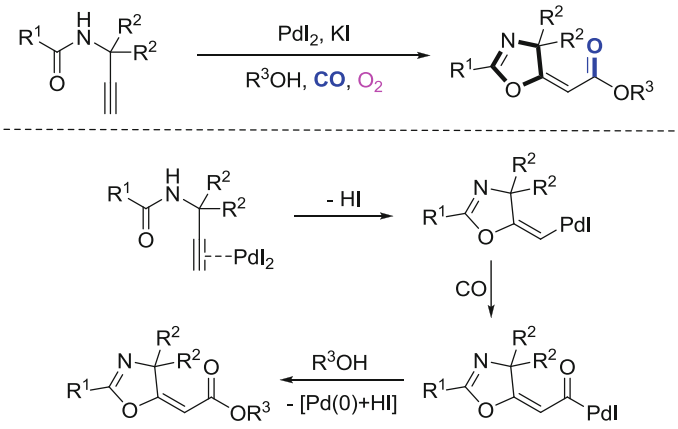
Intramolecular oxidative aminocarbonylation of alkenyl amine derivatives is also an efficient method for constructing complex heterocyclic products. In the presence of palladium and copper salts, *N*-tosylhomoallylamines furnished 3-methyl-2-pyrrolidones at 1 atm of CO and at room temperature (Scheme 25a) [81]. In 2003, Sasai and co-workers realized this reaction in an enantioselective manner using chiral spiro bis(isoxazoline) ligands (Scheme 25b) [82]. In 2009, the group of Lambert successfully prepared α-pyrrolidinyl ketones from *N*-tosylpentenamine and electron-rich aromatic nucleophiles via a tandem aminochlorocarbonylation/Friedel–Crafts acylation reaction (Scheme 25c). In the presence of Pd



Scheme 22 Synthesis of 2-oxazolidinones via water-promoted oxidative carbonylation of 2-ynylamines

(II) and indium(III) triflate, α-pyrrolidinyl ketones were obtained in moderate to good yields with $CuCl_2$ as oxidant and chlorine source [83]. This methodology was applied to the total synthesis of (±)-ferruginine, (±)-anatoxin-a, and 1,4-iminoglycitols [84–86].

In 2002, Bates and Sa-Ei reported the palladium(II)-catalyzed cyclocarbonylation of *O*-homoallylhydroxylamines in the presence of a base, methanol, and carbon monoxide with copper(II) as oxidant, providing isoxazolidines as the product (Scheme 26). An electron-withdrawing group on the hydroxylamine nitrogen was essential, and the products were obtained exclusively as *cis* isomers when carbamate groups were used [87].

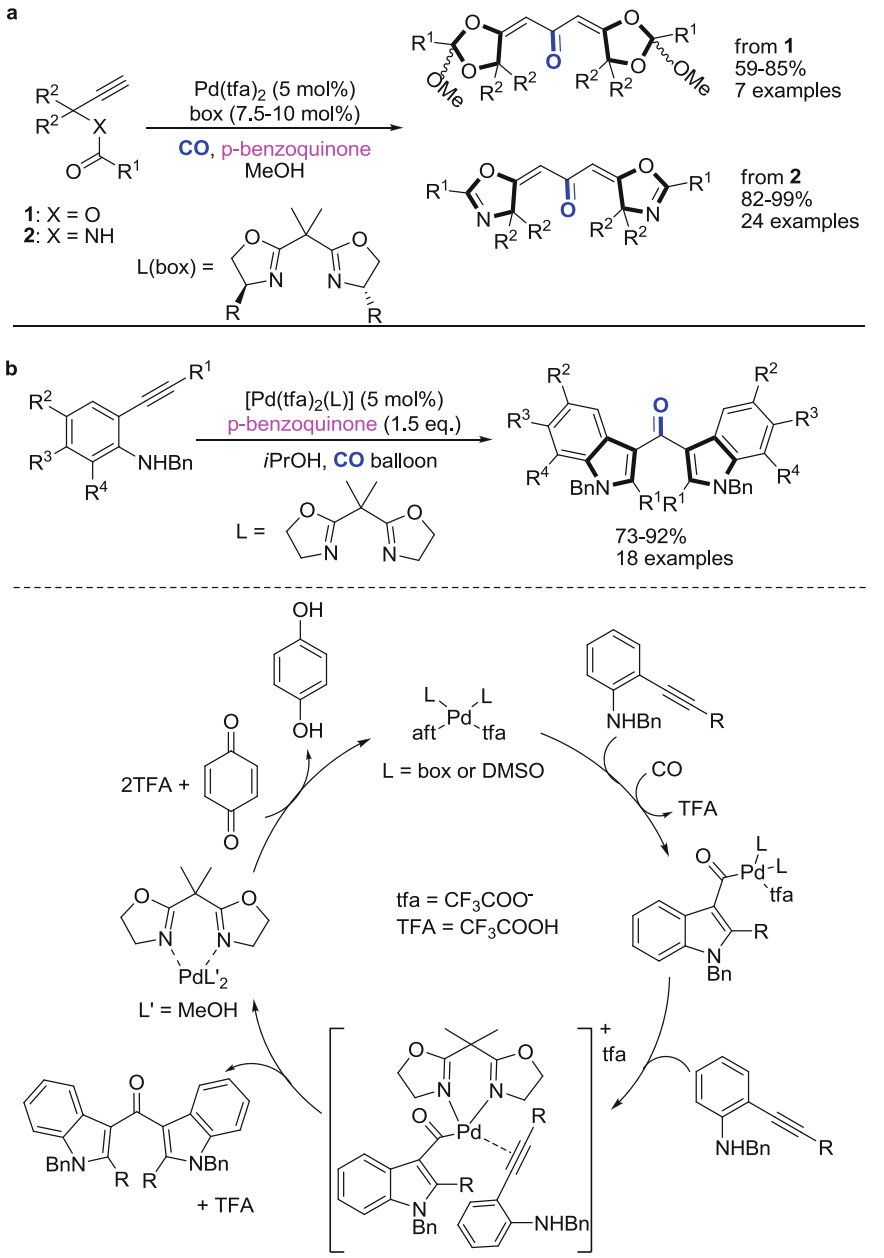


Scheme 23 Synthesis of oxazolines via oxidative carbonylation of prop-2-ynylamides

1.3 Synthesis of Six-Membered Heterocycles via Oxidative Carbonylation of Alkyne or Alkene Derivatives Incorporated with a Nucleophile

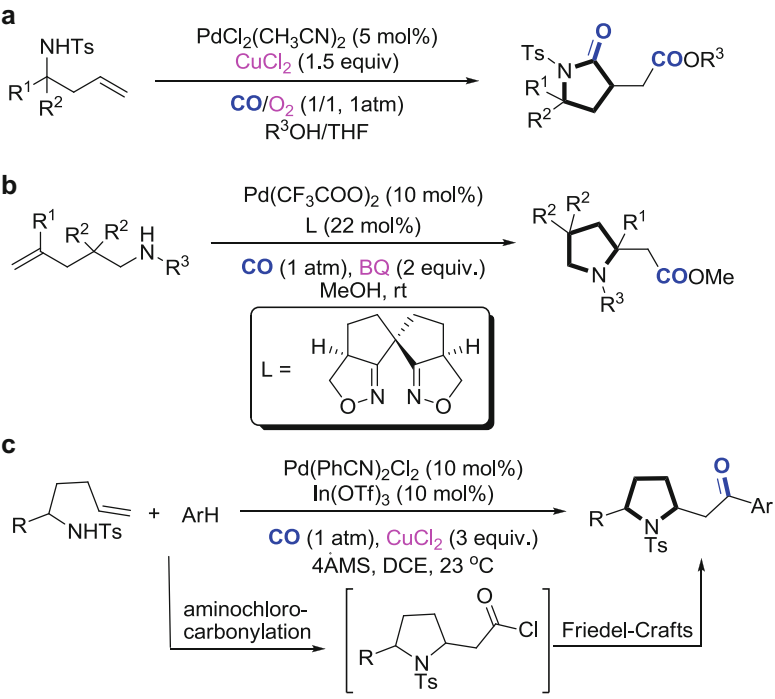
With proper substrates and reaction regioselectivity, six-membered heterocycles could be generated selectively. The groups of Gabriele and Costa made impressive studies in this respect. With the catalysis of palladium, 2-prop-2-ynyloxyphenols underwent a tandem oxidative aminocarbonylation–cyclization to provide 2,3-dihydrobenzo[1,4]dioxine derivatives (Scheme 27). Reactions were carried out in the presence of catalytic amounts of PdI_2 in conjunction with an excess of KI in DMA under 20 atm of a 4:1 mixture of CO/air. Under similar conditions, the reaction of 2-prop-2-ynyloxyanilines provides 3,4-dihydro-2H-benzo[1,4]oxazine as the product. For this reaction, the Z isomers were formed preferentially [88].

A palladium-catalyzed cyclization–alkoxycarbonylation of 2-ethynylaniline derivatives to 4-*H*-3,1-benzoxazines, quinazoline-2-ones, and quinoline-4-ones was developed in 2004 [89]. In 2008, the group of Gabriele synthesized quinoline-3-carboxylic esters from 1-(2-aminoaryl)-2-yn-1-ols through palladium-catalyzed 6-endo-dig cyclization followed by dehydration and oxidative methoxycarbonylation under 80 atm of CO/O_2 (4:1) mixture. In addition, indole-2-acetic esters could also be obtained via 5-exo-dig cyclization and subsequent dehydrating methoxycarbonylation [90]. In 2011, they prepared isoquinoline-4-carboxylic esters and isochromene-4-carboxylic esters by palladium-catalyzed oxidative carbonylation of (2-alkynylbenzylidene)amine derivatives. Isoquinoline derivatives were obtained from (2-alkynylbenzylidene)(*tert*-butyl)amines through *N*-cyclization in the presence of dehydration agent, while isochromenes were obtained from *N*-(2-alkynylbenzylidene)-*N*′-phenylhydrazines through *O*-cyclization ensuing from water attack on the imino group (Scheme 28) [91].

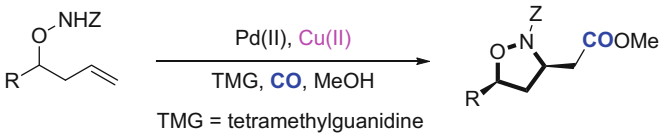


Scheme 24 Synthesis of ketones bearing two heterocycles through CCC-coupling reaction

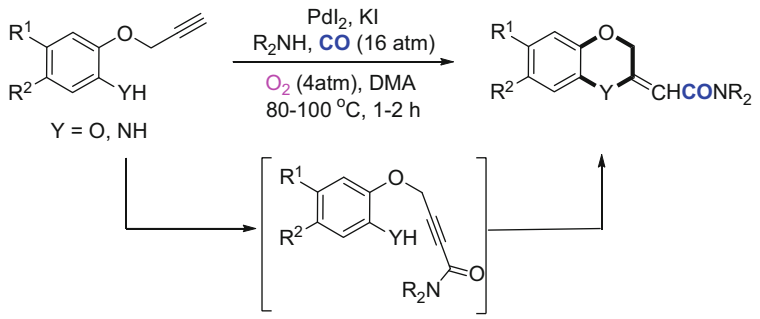
In 2008, Szolcsányi and co-workers applied Pd(II)-catalyzed aminocyclization/cyclocarbonylation of 2-(undec-1-en-6-ylamino)ethanol to the racemic synthesis of bicyclic piperidine alkaloids calvine and epicalvine (Scheme 29) [92].



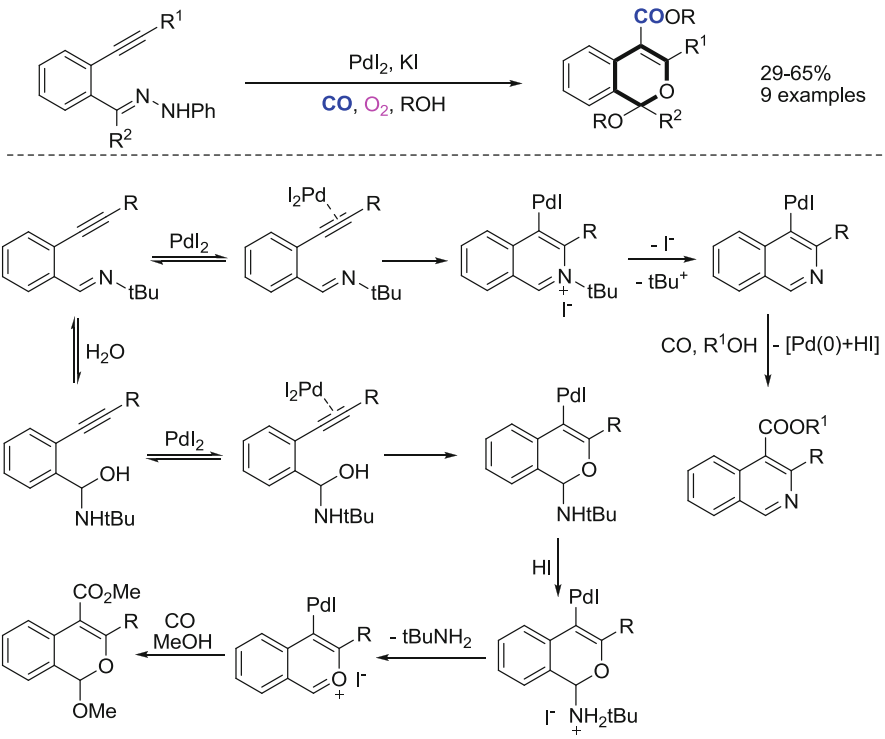
Scheme 25 Synthesis of pyrrolidine derivatives via oxidative carbonylation of alkenyl amine derivatives



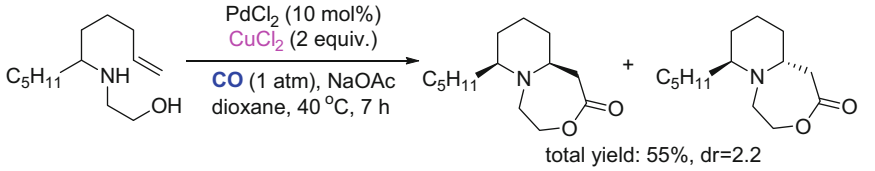
Scheme 26 Synthesis of isoxazolidines via carbonylation of *O*-homoallylhydroxylamines



Scheme 27 Synthesis of dioxine and oxazine derivatives via oxidative carbonylation

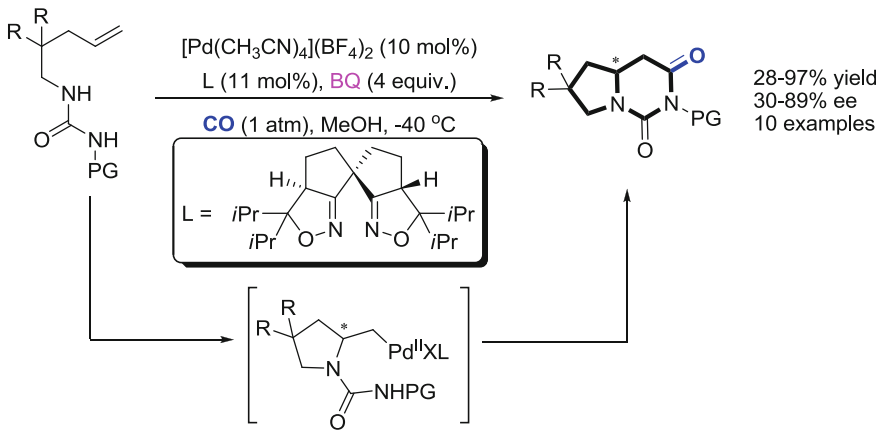


Scheme 28 Synthesis of isoquinolines and isochromenes via oxidative carbonylation of (2-alkynyl)benzylideneamine derivatives



Scheme 29 Racemic synthesis of calvine and epicalvine via carbonylation of 2-(undec-1-en-6-ylamino)ethanol

Sasai and co-workers realized an enantioselective synthesis of tetrahydropyrrolo [1,2-c]pyrimidine-1,3-diones via palladium-catalyzed intramolecular oxidative aminocarbonylation (Scheme 30). The use of a chiral spiro bis(isoxazoline) ligand (SPRIX) is essential to realize this reaction in an optically active form. Compared with other ligands, the low σ-donor ability of the isoxazoline coordination site and rigidity of the spiro skeleton make SPRIX the most suitable ligand for this reaction [93].



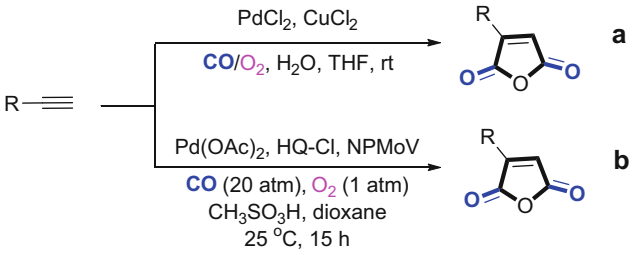
Scheme 30 Synthesis of cyclic β-amino acid derivatives via oxidative carbonylation of alkenyl ureas

2 Synthesis of Heterocycles via Oxidative Dicarbonylation of Alkynes

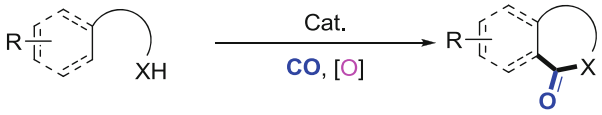
Under oxidative carbonylation conditions, maleic anhydrides can be formed from terminal alkynes via insertion of two CO molecules. In 1991, the group of Alper presented the $PdCl_2$-catalyzed dicarbonylation of terminal alkynes with formic acid and water, providing maleic anhydride derivatives as the major product (Scheme 31a) [94]. In 1999, Ishii and co-workers applied a triple catalytic system, Pd(II)/chlorohydroquinone/NPMoV, to the carbonylation of terminal alkynes (Scheme 31b). With dioxane as the solvent, maleic anhydrides were obtained as the major products [95]. What's more is that several methods have also been published from other groups with different oxidants [96–98].

3 Synthesis of Carbonylated Heterocycles via Oxidative Carbonylation with C–H Activation

Under proper oxidative conditions, carbonylation for synthesis of carbonylated heterocycles could be realized through C–H (sp^2 and sp^3) activation, in which case a heteroatom-containing group such as amine, amide, or hydroxyl group often acted both as directing group and nucleophile to participate in the reaction (Scheme 32). Generally, this method proceeded in an intramolecular way, and reports on the intermolecular multicomponent carbonylation with C–H activation are quite rare.



Scheme 31 Synthesis of maleic anhydrides via palladium-catalyzed oxidative carbonylation of alkynes

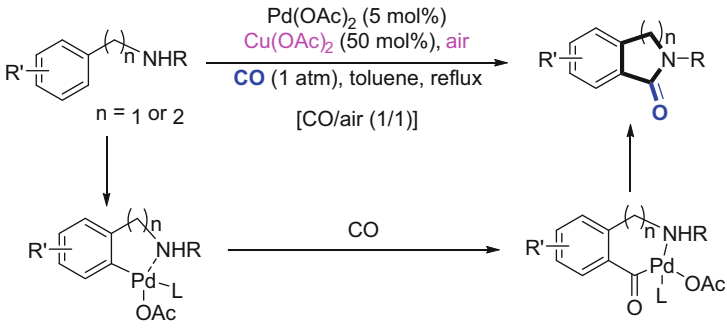


Scheme 32 Synthesis of carbonylated heterocycles via oxidative carbonylation with C–H activation

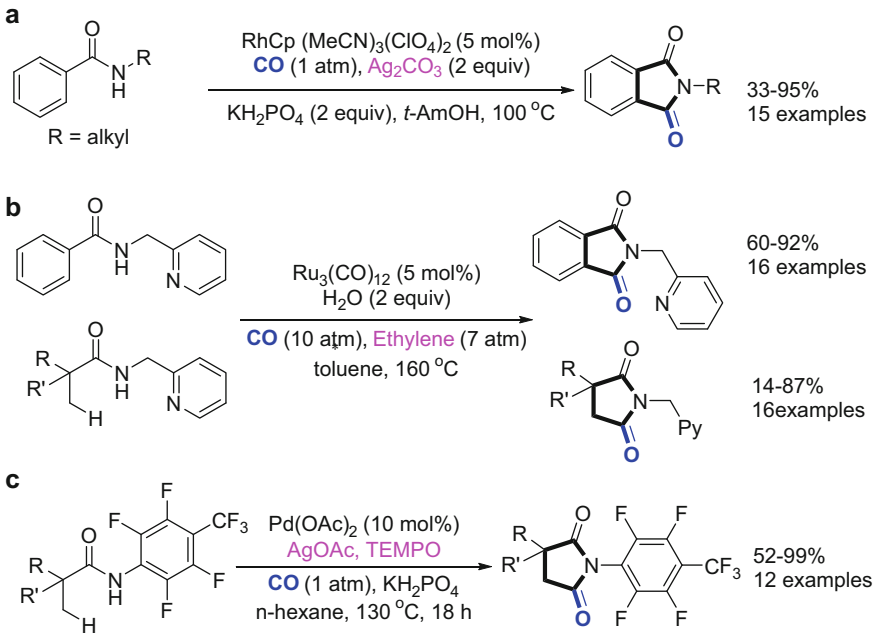
3.1 Synthesis of Five-Membered Heterocycles via Oxidative Carbonylation with C–H Activation

Orito and co-workers prepared a variety of five- or six-membered benzolactams by the direct aromatic carbonylation of secondary ω-phenylalkylamines using $Pd(OAc)_2$ and $Cu(OAc)_2$ in an atmosphere of CO gas containing air (Scheme 33) [99, 100]. In 2007, they applied this methodology to the synthesis of *N*-protected staurosporinones [101].

In 2011, Rovis and co-workers developed a rhodium(III)-catalyzed oxidative carbonylation of benzamides to form phthalimides with Ag_2CO_3 as the oxidant (Scheme 34a). C–H bonds of electron-rich aromatic amides showed better activity [102]. Chatani and co-workers found that utilizing a bidentate system, aromatic amides having a pyridin-2-ylmethylamine moiety could undergo cyclocarbonylation through C–H bond activation in the presence of catalytic amount of $Ru_3(CO)_{12}$ and CO (Scheme 34b). Phthalimides were obtained in moderate to good yields. In this process, ethylene acted as a H_2 acceptor [103, 104]. In 2011, they extended this methodology to the carbonylation of unactivated $C(sp^3)$–H bond of aliphatic amides with a regioselective preference for C–H bonds of methyl groups as opposed to methylene C–H bonds. In both cases, the presence of 2-pyridinylmethylamine moiety in the amide is crucial for the successful reaction. In 2010, Yu and co-workers reported palladium-catalyzed cyclocarbonylation of *N*-arylamides by $C(sp^3)$–H activation with AgOAc conjugated with a catalytic amount of TEMPO (Scheme 34c). The carbonylative C–H activation of arenes by using sulfonamide as a directing group was also reported by the same group [105, 106]. *N*-Methoxyamides also have the ability to facilitate C–H activation on



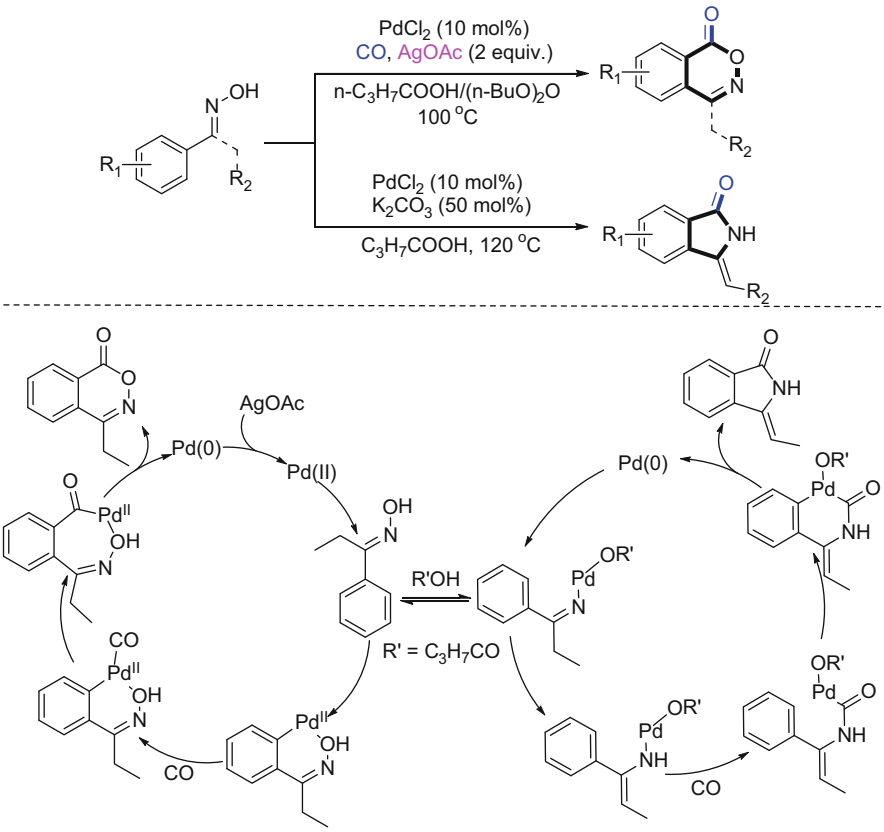
Scheme 33 Synthesis of benzolactams by direct carbonylation of ω-phenylalkylamines



Scheme 34 Synthesis of succinimide derivatives via carbonylative C–H activation of amides

sp^3 and sp^2 centers. In 2011, Booker-Milburn developed the carbonylative C–H activation of *N*-alkoxybenzamides in the presence of $Pd(OAc)_2$ and benzoquinone, providing substituted phthalimides in moderate to good yields [107].

Recently, the group of Jiang developed a selective palladium-catalyzed carbonylation of C(sp^2)–H bonds with aromatic oximes for the synthesis of benzo[d][1,2] oxazin-1-ones and 3-methyleneisoindolin-1-ones (Scheme 35). For the production of [d][1,2]oxazin-1-ones, the N–OH group of the oximes acted as a directing group,

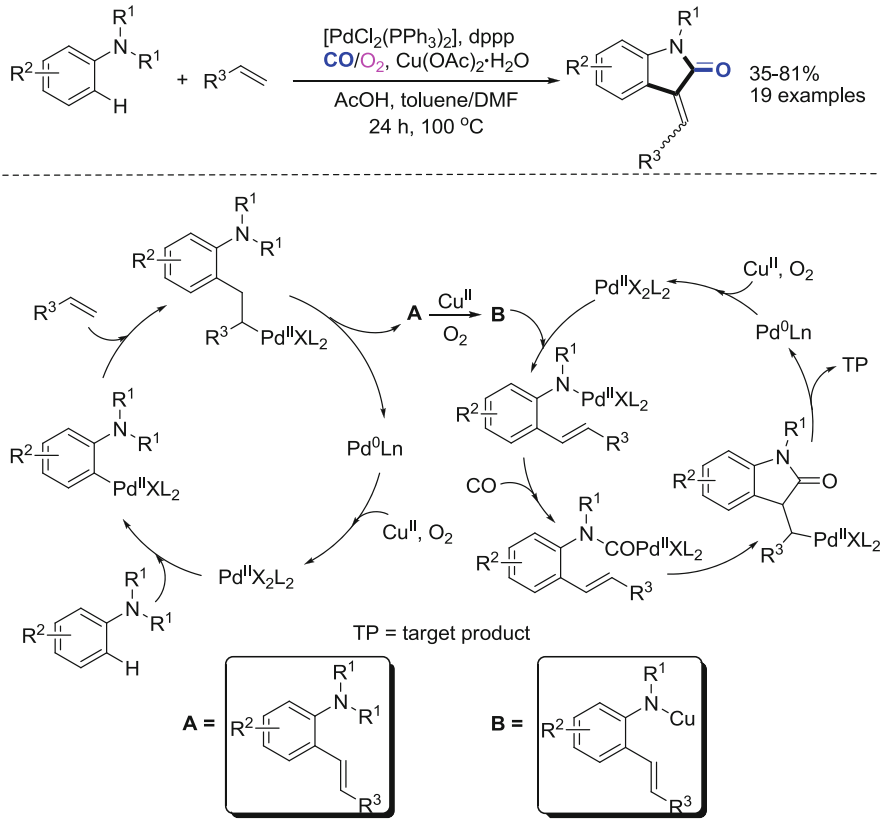


Scheme 35 Synthesis of different *N*-heterocycles via divergent carbonylation of aromatic oximes

while, in the presence of K_2CO_3, the N–OH group acted as an internal oxidant leading to the generation of 3-methyleneisoindolin-1-ones [108].

In 2013, Lei and co-workers successfully obtained 3-methyleneindolin-2-ones by palladium-/copper-catalyzed C–H alkenylation/*N*-dealkylative carbonylation of tertiary anilines in the presence of 1 atm of CO/O_2. Moderate to good yields were obtained (Scheme 36). Several experiments were carried out to explore the reaction mechanism. Based on the results, they proposed that the intermolecular selective *ortho*-alkenylation of *N*,*N*-dialkylanilines is the first and rate-determining step. In the presence of Cu(II) and O_2, the alkyl group leaves as aldehyde [109].

Recently, they further developed a palladium-catalyzed C–H double carbonylation of anilines to isatins in moderate to good yields (Scheme 37). The reaction proceeded under 1 atm of CO with $Cu(OPiv)_2$ as the oxidant. As they proposed, this process started with the activation of aryl N–H by the palladium complex, followed by insertion of CO to afford the carbamoyl intermediate. Subsequently, insertion of another CO and C–H activation occurred in succession generating a six-membered cyclic carbamoyl intermediate, which underwent reductive elimination to give the

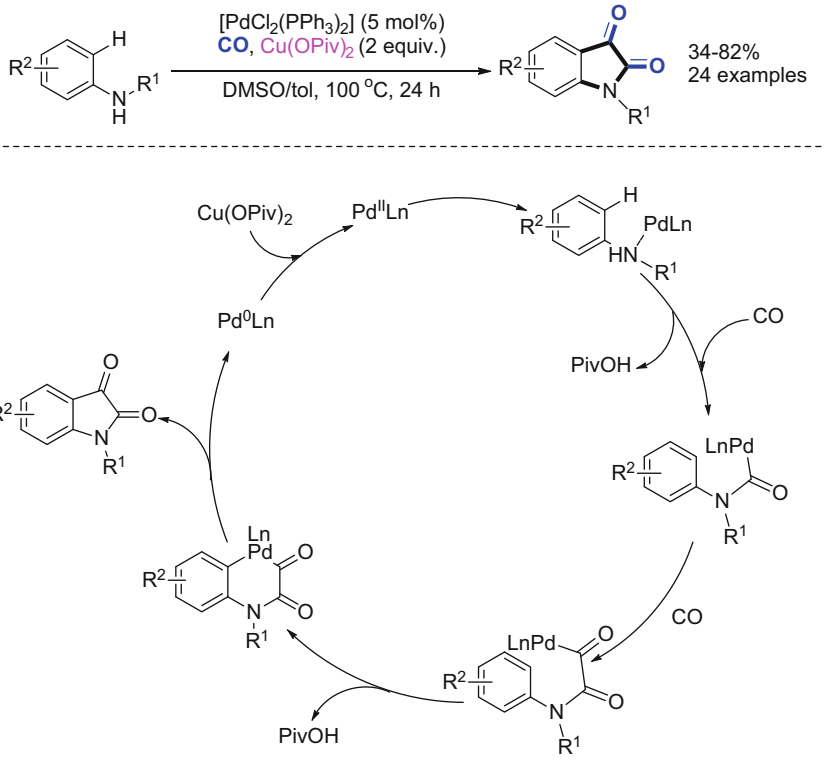


Scheme 36 Synthesis of indolin-2-ones via a cascade reaction of tertiary anilines with alkenes

product. Finally, the Pd^0 species is reoxidized to the Pd^{II} catalyst by Cu $(OPiv)_2$ [110].

3.2 *Synthesis of Six-Membered Heterocycles via Oxidative Carbonylation with C–H Bond Activation*

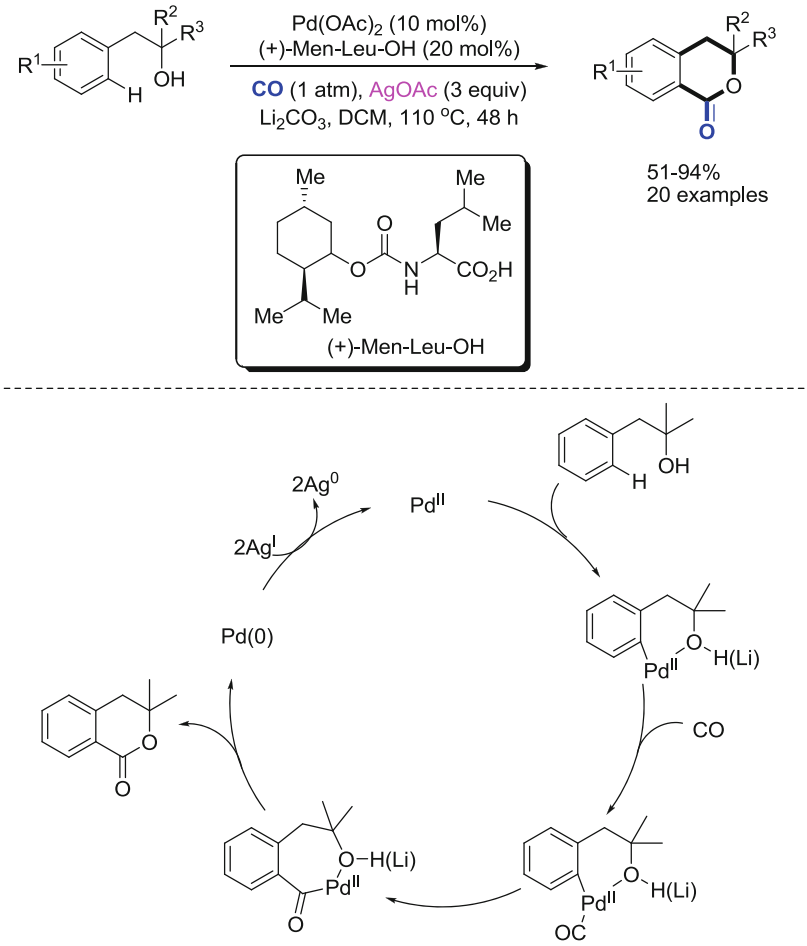
Hydroxyl group is also a good directing group for C–H activation; meanwhile, it could act as an intramolecular nucleophile to be incorporated into the final product. In 2011, Yu and co-workers realized the palladium-catalyzed C–H carbonylation of phenethyl alcohols using amino acid ligands to promote the reaction (Scheme 38). 1-Isochromanone derivatives were obtained in moderate to good yields. This transformation was used for the one-step synthesis of a histamine release inhibitor [111].



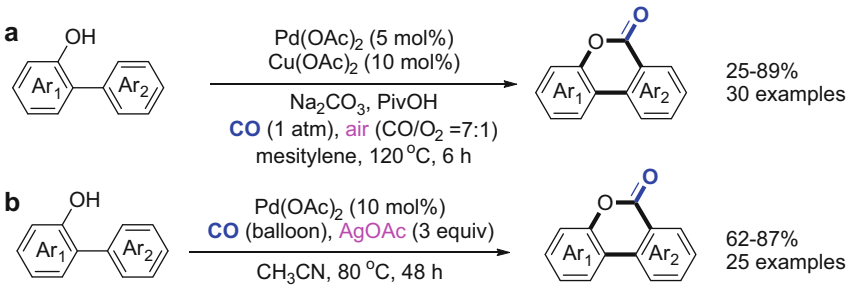
Scheme 37 Synthesis of isatins via oxidative double carbonylation of anilines

In 2013, the group of Shi developed palladium-catalyzed C–H bond activation/carbonylation of 2-arylphenol for the synthesis of dibenzopyranones (Scheme 39a). Various dibenzopyranones were prepared in the presence of $Pd(OAc)_2$ as a catalyst and $Cu(OAc)_2$ as a catalytic oxidant under an atmospheric pressure of CO and O_2. A series of deuterium labeling experiments were conducted. Based on the results, they proposed that the C–H activation step might go through a S_EAr mechanism, and the C–H activation might be involved in the rate-determining step [112]. Later, Chuang and co-workers realized the same reaction under acid–base-free and mild conditions with $Pd(OAc)_2$ as the catalyst and AgOAc as oxidant (39b). Benzopyrannone derivatives were obtained in good yields [113]. As displayed in both cases, substrates with electron-donating substituents showed better activity than the electron-withdrawing ones.

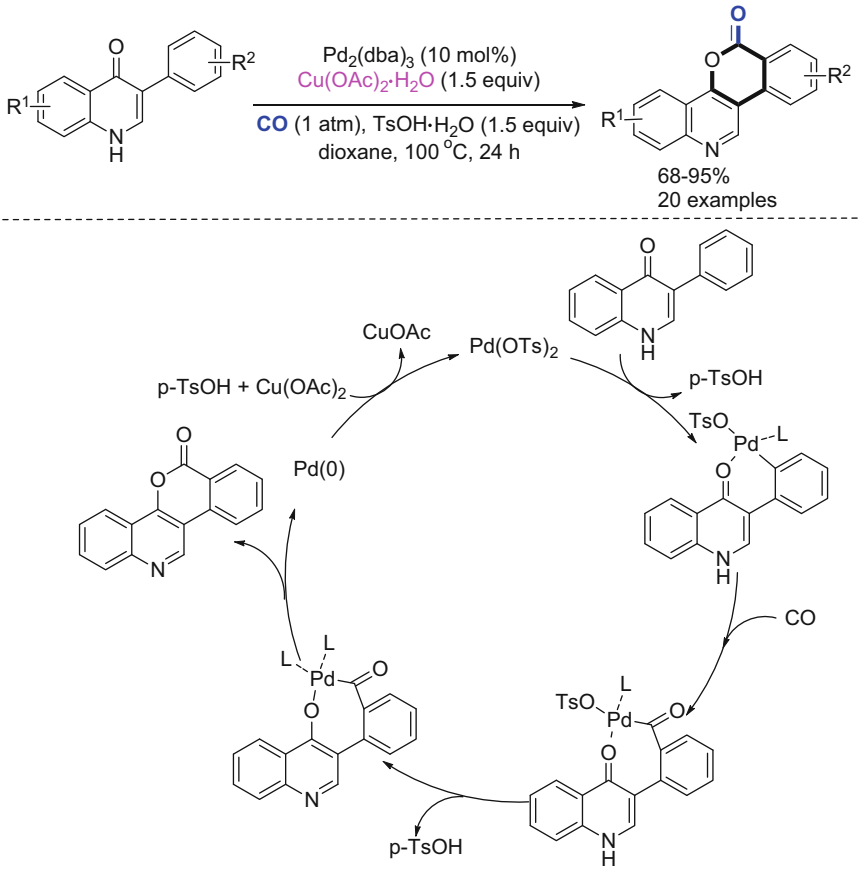
Recently, Jiang and co-workers reported a direct oxidative carbonylation of 3-phenylquinolin-4(1H)-one derivatives for the synthesis of polycyclic aromatic hydrocarbons (Scheme 40). This reaction proceeded under CO atmosphere with $Pd_2(dba)_3$ as the catalyst and $Cu(OAc)_2 \cdot H_2O$ as oxidant, providing polycyclic aromatic hydrocarbons in high to excellent yields. As they proposed, this oxidative carbonylation started with the reaction of $Pd_2(dba)_3$ with $Cu(OAc)_2$ and



Scheme 38 Synthesis of 1-isochromanones via oxidative carbonylation of phenethyl alcohols



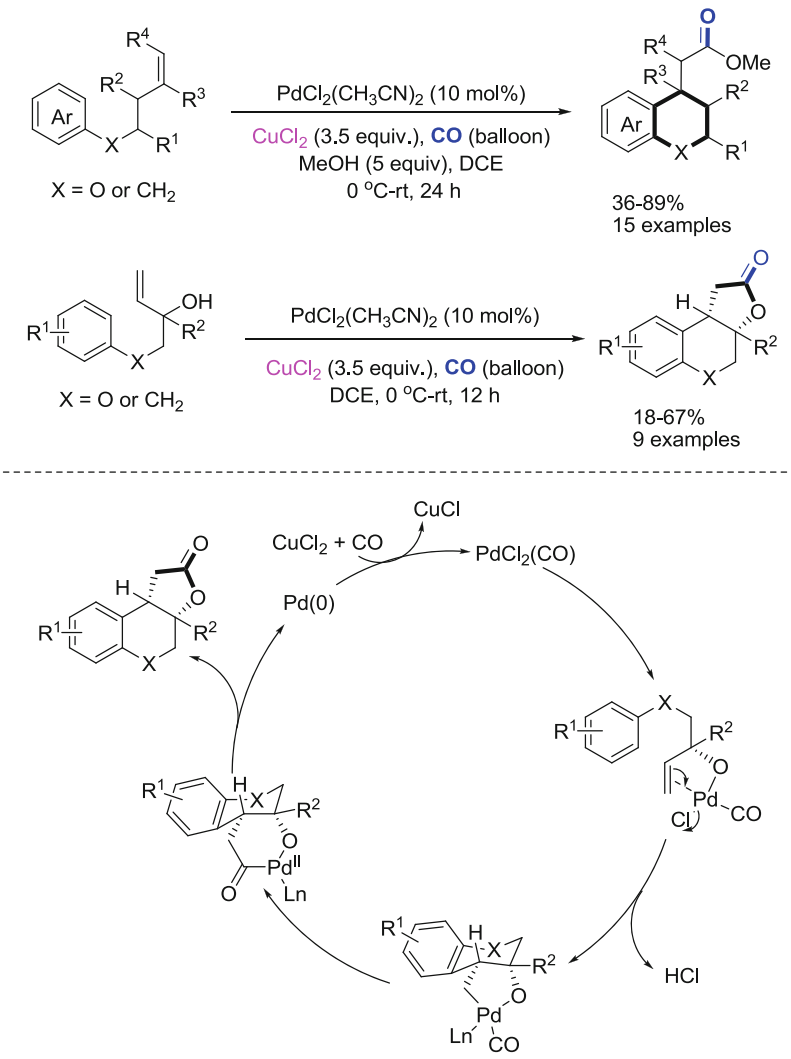
Scheme 39 Synthesis of benzopyranones via oxidative carbonylation of 2-arylphenols



Scheme 40 Synthesis of polycyclic aromatic hydrocarbons via oxidative carbonylation

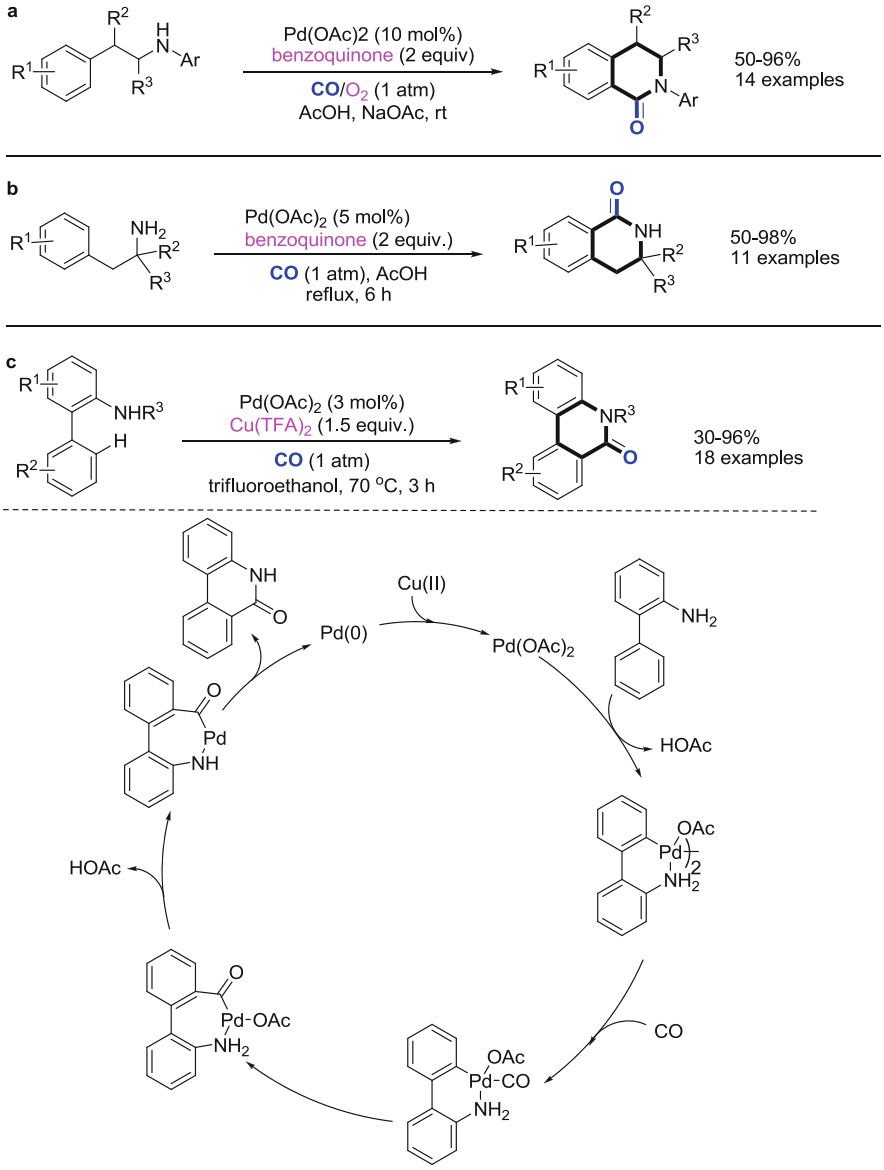
$TsOH \cdot H_2O$ to form $Pd(OTs)_2$. Subsequently, aryl C–H activation by $Pd(OTs)_2$ afforded the arylpalladium species, which further underwent CO insertion to form acylpalladium intermediate. Assisted by leaving *p*-TsOH, acylpalladium intermediate was transformed into the enolate intermediate followed by reductive elimination to give the final product [114].

Palladium-catalyzed intramolecular carbonylative cyclization of aryl alkenes and aryl alkenols for the synthesis of structurally diverse chromanes was developed by Yang and Gong et al. (Scheme 41). This reaction proceeded under the balloon pressure of CO with $PdCl_2(CH_3CN)_2$ as the catalyst and $CuCl_2$ as the oxidant. As they proposed, the mechanism for the carbonylative cyclization of alkenols includes an intramolecular nucleopalladation/CO insertion/reductive elimination process. The palladium(0) that resulted from reductive elimination would be reoxidized to palladium(II) by $CuCl_2$ [115].



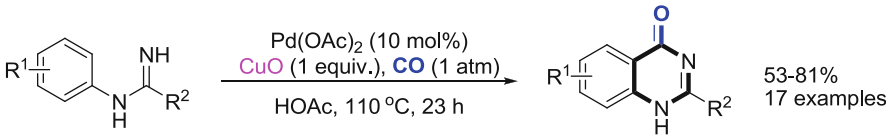
Scheme 41 Synthesis of chromanes via carbonylative cyclization of aryl alkenes/alkenols

By introduction of an aryl group onto the amine system, Gaunt and co-workers realized the C–H carbonylation of β-arylethylamine derivatives (Scheme 42a). The reaction proceeded in the presence of 10 mol% $Pd(OAc)_2$, 2 equivalents of benzoquinone, under 1 atm of CO and O_2, and with AcOH as solvent at room temperature. Dihydro-2-quinolone derivatives were obtained in moderate to good yields [116]. At almost the same time, Granell and co-workers reported the NH_2-directed carbocyclization of quaternary aromatic α-amino esters to six-membered benzolactams in the presence of catalytic amount of palladium with benzoquinone as the oxidant (Scheme 42b). The steric hindrance due to the R^2 and R^3 groups plays



Scheme 42 Synthesis of benzolactams via oxidative carbonylation with C–H activation

a crucial role in this process. Increasing the steric hindrance around the amino group prevents competitive acetylation. In addition, for the substrates used in this method, a strong bias to the six-membered lactams over five-membered ones was observed [117]. In 2013, the group of Zhang developed Pd(II)-catalyzed C–H carbonylation of biaryl-2-amine for the synthesis of phenanthridinones. The reaction proceeded in



Scheme 43 Synthesis of quinazolin-4(3H)-ones via carbocyclization of *N*-arylamidines

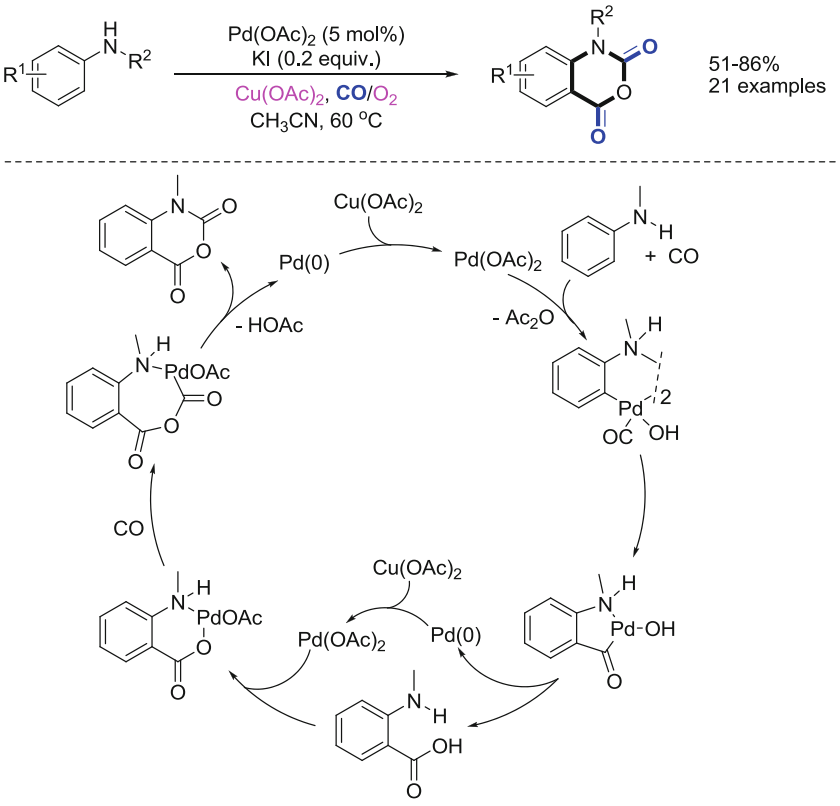
the presence of 3 mol% $Pd(OAc)_2$ and 1.5 equivalents of Cu(II) trifluoroacetate in trifluoroethanol. As they proposed, free-amine-assisted palladation of C–H bond occurs firstly to form the six-membered palladacycle intermediate, followed by CO coordination and insertion. Subsequently, a proton abstraction of the amino group may take place, and finally reductive elimination occurs to provide the desired products. The formed Pd(0) is reoxidized to Pd(II) by Cu(II) (Scheme 42c) [118].

Palladium catalysis has also been employed for the synthesis of quinazolin-4 (3H)-ones via intramolecular C–H carboamidation of *N*-arylamidines with CuO as the oxidant under atmospheric pressure of CO. Electron-rich substrates give better results than electron-deficient ones (Scheme 43) [119].

As reported by the group of Ren, isatoic anhydrides could be prepared efficiently through palladium-catalyzed regioselective C–H bond carbonylation of *N*-alkyl anilines (Scheme 44). A stoichiometric reaction of $Pd(OAc)_2$ with *N*-methylaniline under a CO atmosphere in the absence of $Cu(OAc)_2$ provided a palladium complex, which transformed into the isatoic anhydride in the presence of $Cu(OAc)_2$ and KI in CH_3CN under a CO atmosphere. Based on these results, a tentative mechanism including a dimeric palladium intermediate and *N*-methylanthranilic acid was proposed [120].

Quinolinones are another class of important six-membered nitrogen-containing heterocycles with numerous applications in drugs. Under oxidative conditions, the carbonylation of *N*-monosubstituted-2-vinylanilines provides 2(1*H*)-quinolinones, in which case the amino group was coupled directly with the terminal alkenyl group (Scheme 45). The optimal reaction conditions include 10 mol% $Pd(OAc)_2$, 50 mol% $Cu(OAc)_2$, solvent (CH_3CN), time (20 h), temperature (100°C), CO (2 bar), and air (0.7 bar). It was necessary for the aniline to be a secondary amine. As they proposed, the reaction started with the addition of the aniline nitrogen to the active Pd^{II} species to form a Pd–N bond followed by coordination and insertion of CO leading to a Pd–carbamoyl species. Then, insertion of the vinyl group into the Pd–CO bond could generate an alkylpalladium intermediate. Finally, β-hydride elimination occurred to provide the 2(1H)-quinolinone product. The resulted Pd^0 species is regenerated by Cu^{II} or O_2 to complete the catalytic cycle [121].

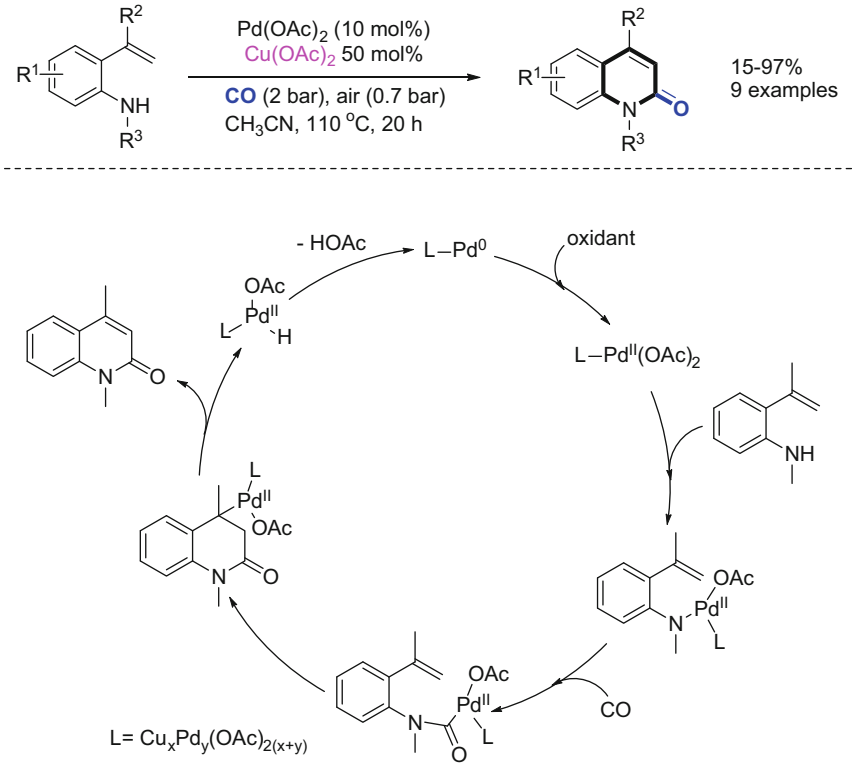
Recently, Wu and co-workers prepared 2-quinolinone derivatives in moderate to good yields by intermolecular carbonylative cyclization of *N*-aryl-pyridine-2-amines and internal alkynes with $Mo(CO)_6$ as a solid CO source. Various substituted 2-quinolinones were obtained from different kinds of internal alkynes and substituted *N*-arylpyridine-2-amines. As they proposed, the pyridine ring-assisted C–H activation took place firstly followed by the insertion of alkyne.



Scheme 44 Synthesis of isatoic anhydrides via oxidative carbonylation of *N*-alkyl anilines

Next, the coordination and insertion of CO and subsequent reductive elimination gave the desired product and Pd(0), which was reoxidized by BQ and/or AgOAc to active Pd^{II} (Scheme 46) [122].

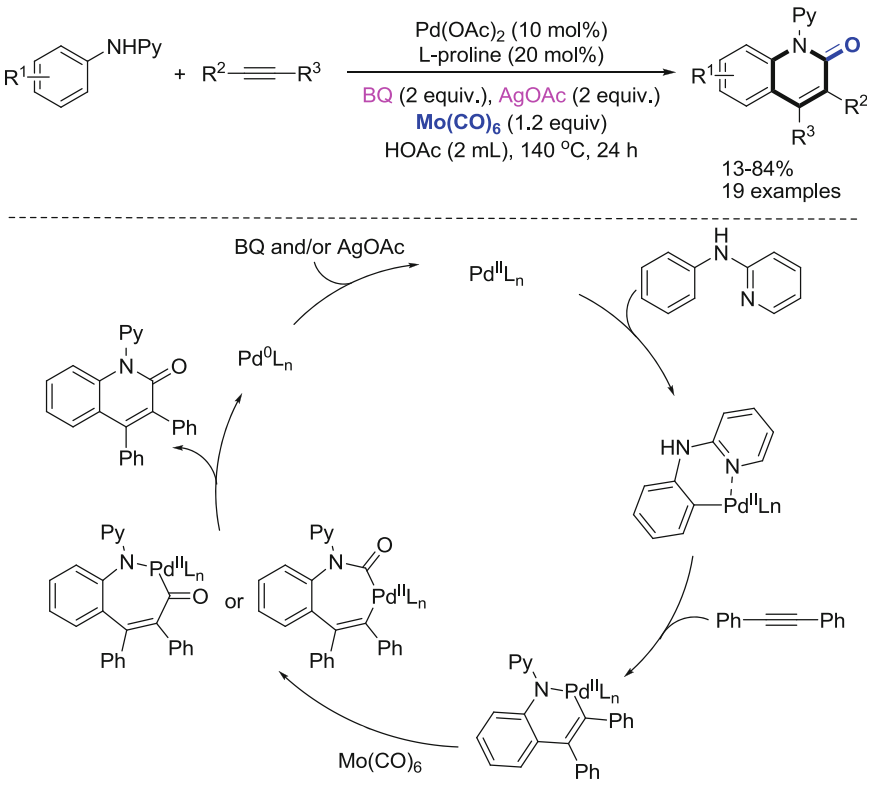
In 2009, Lloyd-Jones and Booker-Milburn et al. reported palladium-catalyzed C–H carbonylation of aryl urea derivatives with the urea moiety as directing group [123]. This reaction could proceed under 1 atm of carbon monoxide at room temperature, providing cyclic imidates in moderate to good yields. In their previous work, the *ortho*-palladate intermediate has been isolated from the reaction of the aryl urea with 1 equivalent of $[Pd(OTs)_2(CH_3CN)_2]$ in anhydrous THF. What's more is that conversion of the *ortho*-palladate into cyclic imidate by stoichiometric reaction with CO has been realized (Scheme 47a) [124]. In 2010, Yu and co-workers developed palladium-catalyzed carboxylation of *ortho*-C–H bond of anilides. As for benzanilides, the *ortho*-C–H bond of the aniline fragment was carboxylated selectively to give *N*-benzoylanthranilic acids, which underwent further cyclization by treating with Ac_2O to provide benzoxazinones in one pot (Scheme 47b) [125].



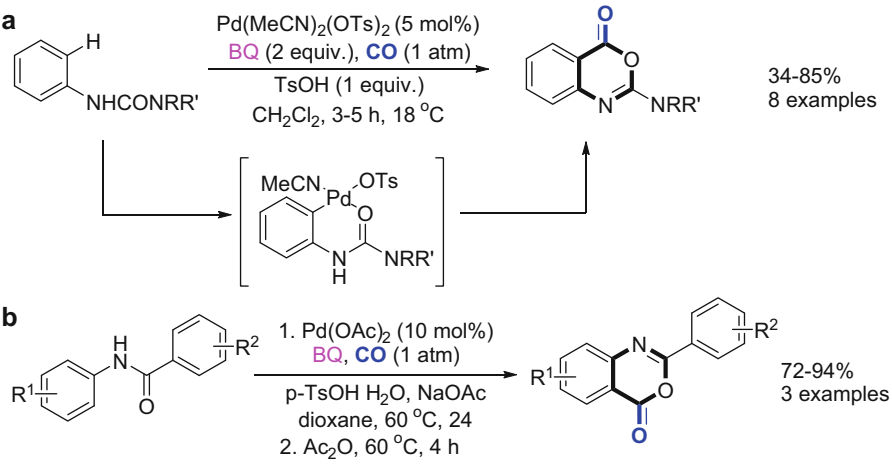
Scheme 45 Synthesis of 2(1H)-quinolinones via oxidative cyclocarbonylation of 2-vinylanilines

In 2013, the group of Guan developed a palladium-catalyzed alkenyl C–H bond carbonylation of enamides under balloon pressure of carbon monoxide with KI and Ac_2O as additives and $Cu(OAc)_2$ as oxidant (Scheme 48). A variety of substituted 1,3-oxazin-6-ones were obtained in good yields. Based on the reaction results employing a stoichiometric amount of $Pd(OAc)_2$, they proposed a reaction pathway, which started with the amide group-directed alkenyl C–H activation to form the vinylpalladium intermediate [126].

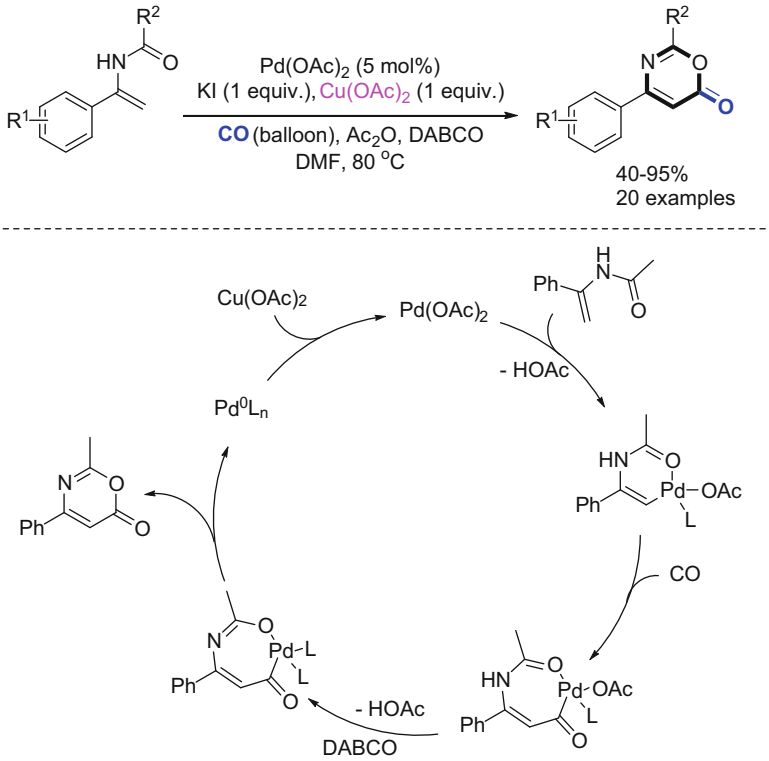
In 1998, Ryu and co-workers reported the δ-carbonylation of saturated alcohols to δ-lactones, in which lead tetraacetate (LTA) was used as a one-electron oxidant to generate the alkoxyl radicals (Scheme 49). Primary alcohols having primary δ-carbons, primary alcohols having secondary δ-carbons, secondary alcohols having primary δ-carbons, and secondary alcohols having secondary δ-carbons all underwent carbonylation to afford δ-lactones in moderate to good yields. The mechanism of this carbonylation involves (1) oxidation of a saturated alcohol by LTA to generate alkoxyl radicals, (2) conversion of this alkoxyl radical to a δ-hydroxyalkyl radical via a 1,5-hydrogen-transfer reaction, (3) generation of an acyl radical by CO trapping of the δ-hydroxyalkyl radical, and (4) oxidation and cyclization of the acyl radical to final δ-lactones [127].



Scheme 46 Synthesis of 2-quinolinone derivatives via oxidative carbonylation of *N*-aryl-pyridine-2-amines and internal alkynes



Scheme 47 Synthesis of benzoxazinones via C–H carbonylation of aniline derivatives

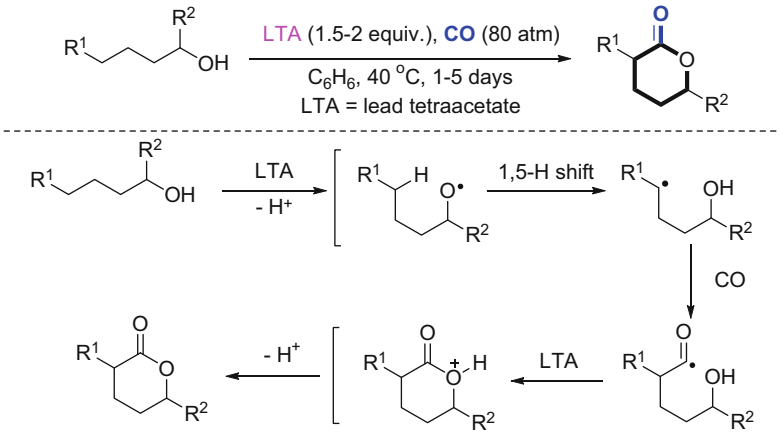


Scheme 48 Synthesis of 1,3-oxazin-6-ones via oxidative carbonylation of enamides

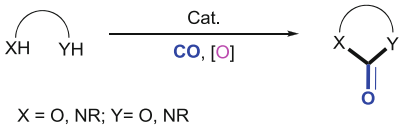
4 Synthesis of Carbonylated Heterocycles via Oxidative Carbonylation of Diamines, Amino Alcohols and Diols, and Related Compounds

As reported, oxidative carbonylation of amines or alcohols yields ureas or carbonate esters, respectively. Correspondingly, when applying this reaction to diamines, diols, or amino alcohols, cyclic ureas, cyclic carbonates, and oxazolidinones could be obtained as the products (Scheme 50). The only by-products are the reduced form of oxidant and protons, making this method an attracting approach to cyclic ureas, cyclic carbonates, and oxazolidinones, which are important classes of heterocycles with interesting biological activities.

Oxazolidinones are another important class of heterocycles showing interesting biological activities. An efficient method for the synthesis of this kind of compounds is the carbonylation of β-amino alcohols. In 1986, Tam reported palladium-catalyzed oxidative carbonylation of β-amino alcohols to oxazolidinones at 3 atm of CO with $CuCl_2$ as oxidant (Scheme 51a). Carbonylation of diols and aminodiols was also developed in similar conditions [128]. In 2000, Gabriele and co-workers

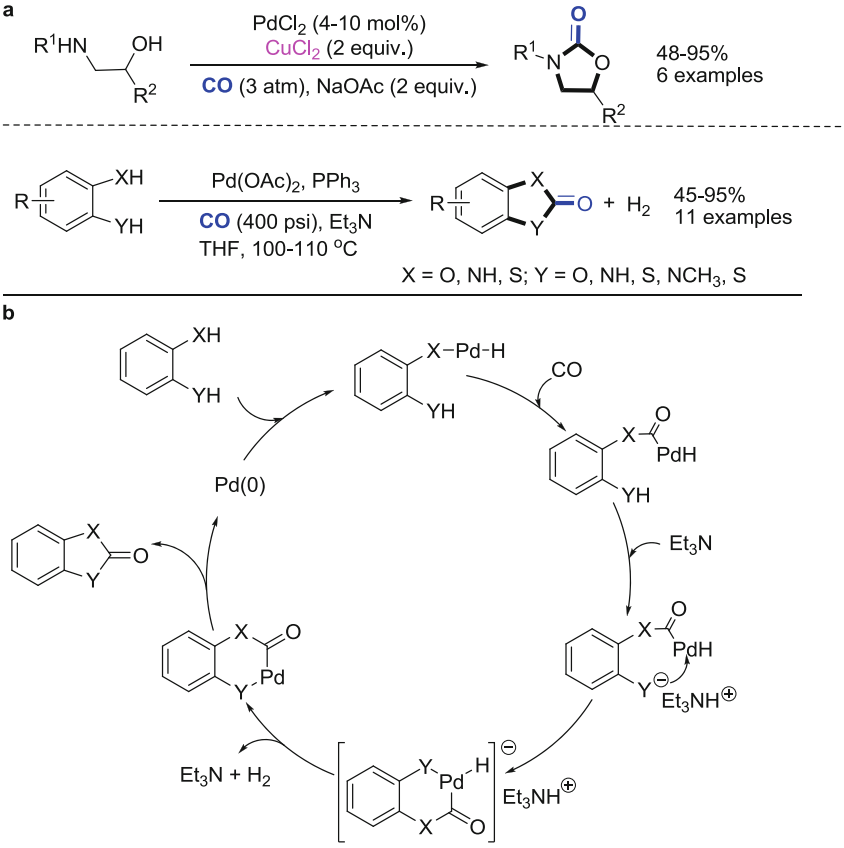


Scheme 49 Synthesis of δ-lactones via oxidative carbonylation of aliphatic alcohols



Scheme 50 Synthesis of carbonylated heterocycles via oxidative carbonylation of diamines, amino alcohols and diols

applied the PdI_2/KI catalyst system to the carbonylation of β-amino alcohols, generating 2-oxazolidinones in good yields. In this process, a large excess of both oxygen and iodide anions are essential. A KI/PdI_2 molar ratio of 200 with CO/O_2/air = 1/6/5 (60 atm total pressure) was used [129, 130]. In 2003, they improved this method to be carried out under relatively mild conditions (100°C and 20 atm of a 4:1 mixture of CO and air). The group of Xia made great progress in this methodology. They developed several efficient catalyst systems including $Pd(OAc)_2/I_2$ [131], $(NHC)Cu^I$ [132], salen–Co complex [133], (chitosan-*Schiff* base)cobalt (II) complex [134], and $Pd(OAc)_2$/[mmim]I [135] for this reaction providing 2-oxazolidinones in good yields. In addition, several recyclable catalyst systems were also developed by the same group, such as palladium on charcoal [136], Pd(Phen)Cl_2 stabilized by ionic liquid [137], and palladium on cross-linked polymer [138] for this reaction. Carbonylation of 2-amino-1-alkanols in an electrochemical way was developed by Feroci and Chiarotto using Pd(II) catalyst in combination with its anodic recycling at a graphite electrode. The reaction could be carried out at room temperature under atmospheric pressure of carbon monoxide [139]. In 2007, Lu and co-workers realized this reaction in a chiral way with the catalysis of selenium [140]. In 2011, Troisi and co-workers reported the synthesis of benzo-fused five-membered heterocycles via cyclocarbonylation of phenols, thiophenols, and anilines *ortho*-substituted by OH, SH, and NH groups in the presence of Et_3N,



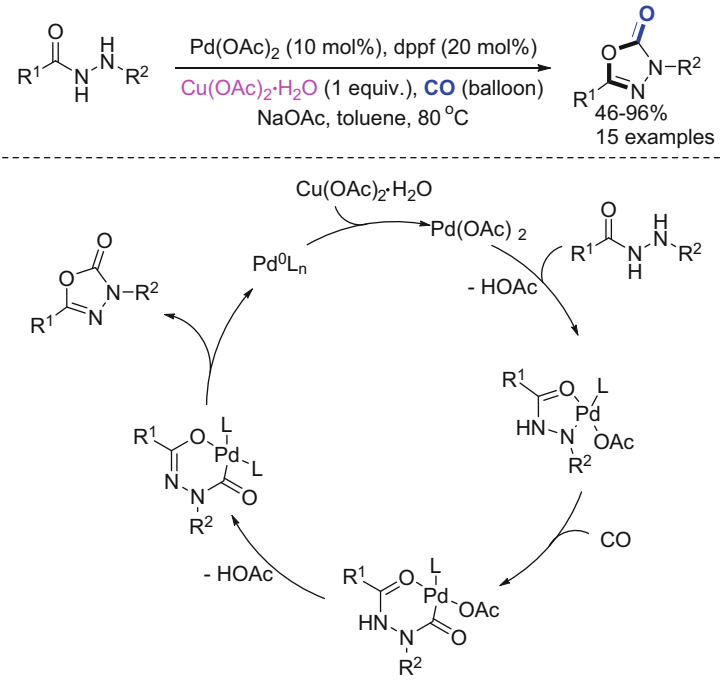
Scheme 51 Synthesis of oxazolidinone derivatives by oxidative cyclocarbonylation of β-amino alcohols

$Pd(OAc)_2$, and PPh_3 under CO pressure (Scheme 51b). For sulfonamides, o-hydroxybenzyl alcohol, and o-aminobenzyl alcohol, the corresponding six-membered heterocycles were obtained in moderate yields [141].

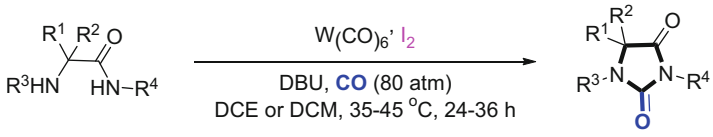
Very recently, Chen and co-workers developed a palladium-catalyzed oxidative cyclocarbonylation of hydrazides via the CO insertion between the amine group and the carbonyl group for the synthesis of 1,3,4-oxadiazol-2(3H)-ones (Scheme 52). In this process, the cyclocarbonylation took place between the amino group and carbonyl group under atmospheric pressure of CO [142].

The use of $W(CO)_6$ as the catalyst in the presence of I_2 as oxidant has been reported to promote the oxidative carbonylation of α-amino amides for the synthesis of hydantoins (Scheme 53) [143]. Later, the oxidative carbonylation of diamine diols to the cyclic urea core structure of the HIV protease inhibitor DMP 450 was also developed under similar conditions [144].

The oxidative carbonylation of diols allows for the synthesis of cyclic carbonates. Tam developed the stoichiometric oxidative carbonylation of 1,2-diols

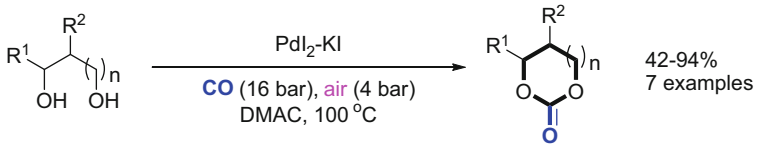


Scheme 52 Synthesis of 1,3,4-oxadiazol-2(3H)-ones via oxidative carbonylation of hydrazides

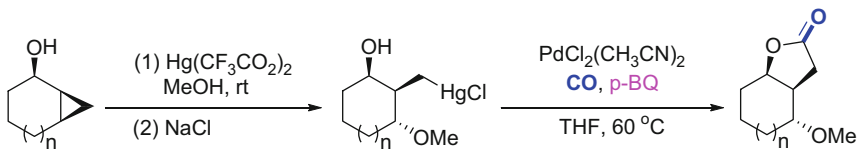


Scheme 53 Synthesis of hydantoins via oxidative carbonylation of α-amino amides

promoted by $PdCl_2$ in conjunction with 2 equivalents of AcONa to give [1,3] dioxolan-2-ones. He also reported a catalytic version of this reaction, but the substrate scope was limited, and the total catalytic turnover was low [128]. In 2009, Gabriele and co-workers applied their previously reported PdI_2–KI system to the oxidative carbonylation of 1,2- and 1,3-diols to produce five-membered and six-membered cyclic carbonates, respectively, with high catalytic efficiencies (Scheme 54) [145]. Later, the group of Li reported the synthesis of glycerol carbonate via the oxidative carbonylation of glycerol. $PdCl_2$(phen) was used as a catalyst with the aid of KI [146]. They evaluated the mechanism pathway based on PdI_2(phen) as the possible intermediate. A possible synergistic effect of I^- and 1,10-phenanthroline on the performance of the Pd complex was proposed. In 2011, Müller and co-workers adapted a bimetallic Wacker-type Pd/Mn redox catalyst



Scheme 54 Synthesis of cyclic carbonates via oxidative carbonylation of diols



Scheme 55 Synthesis of five-membered oxygen-containing heterocycles via oxidative carbonylation of organomercurials

system to the oxidative carbonylation of aliphatic polyols for the synthesis of cyclic carbonates [147].

Oxidative carbonylation of organomercurials offers another choice for the synthesis of carbonylated heterocycles. Kocovský and co-workers successfully synthesized *cis*- and *trans*-fused lactones via palladium-catalyzed oxidative carbonylation of organomercurials, which were obtained by the regioselective Hg (II)-mediated cleavage of cyclopropyl alcohols (Scheme 55) [148].

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