RECENT ADVANCES IN THE PdI_2-CATALYZED CARBONYLATIVE SYNTHESIS OF HETEROCYCLES FROM ACETYLENIC SUBSTRATES: A PERSONAL ACCOUNT

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Abstract. *Carbonylation has emerged as the most powerful and sustainable route for the direct incorporation of a carbonyl group into an organic substrate, with formation of high value added molecules starting from readily available substrates and CO, under the catalytic action of a metal complex. With the appropriate catalyst and reaction conditions, starting from suitably functionalized substrates it is possible to synthesize a plethora of heterocyclic derivatives by a carbonylation approach. In this account, I will focus on the most recent achievements realized in my laboratory on the synthesis of heterocycles starting from acetylenic substrates by different types of carbonylations, catalyzed by a very simple and efficient catalytic system, based on palladium iodide in conjunction with potassium iodide.*

Contents

1. Introduction

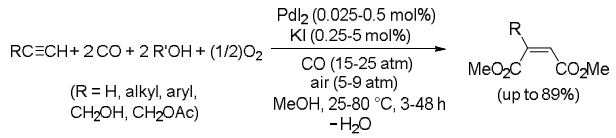
Carbon monoxide is a cheap, abundant, and readily available C-1 source. The possibility to activate CO for its efficient incorporation into an organic substrate has therefore attracted the interest of both academic and industrial chemists for many years. Nowadays, a process like this, called carbonylation, is considered the most attractive and sustainable way for the direct synthesis of carbonyl compounds starting from readily available substrates (alkenes, alkynes, alcohols, amines, and so on), thanks to the elevated atom economy and the continuous development of catalytic systems able to promote the process under mild conditions and with high selectivity.[1-17]

Our research group has been interested for a long time in developing efficient carbonylation methods aimed at synthesizing either already known molecules, but with improved catalytic performances, or new high value added compounds of applicative and/or pharmaceutical interest. In this account, we will review our most recent achievements in the application of the carbonylation reactions developed in our laboratory to the synthesis of important functionalized heterocyclic derivatives.

2. PdI_2-catalyzed oxidative heterocyclization-alkoxycarbonylation

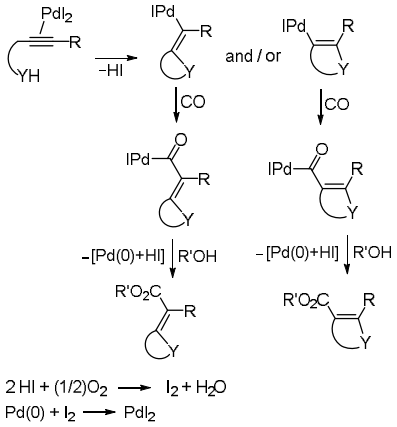
In 1992, we introduced a very simple catalytic system, consisting of PdI_2 in conjunction with KI (corresponding to K_2PdI_4 plus additional iodide ligands), as an efficient catalyst for the direct synthesis of dimethyl 2-(hydroxymethyl)maleate from propargyl alcohol.[18] The method was subsequently further optimized and generalized to the use of different alkyl- and arylacetylenes, to give the corresponding maleic diesters in high yields and with unprecedented catalytic efficiencies for this kind of reaction (Scheme 1).[19] The process, corresponding to an oxidative dialkoxycarbonylation of the triple bond, was carried out in MeOH as the reactant and solvent, at 25-80 °C and under pressure of CO (15-25 atm) and air (as source of oxygen, used as external oxidant; 5-9 atm) for 3-48 h.

With acetylenic substrates bearing a suitably placed nucleophilic group, the PdI_2-catalyzed oxidative alkoxcarbonylation process can take place with concomitant heterocyclization, thus leading to carbonylated heterocycles. We reviewed this kind of chemistry in 2012,[12] so we will describe here our most recent achievements in this field.



Scheme 1. PdI_2-catalyzed oxidative carbonylation of terminal alkynes to maleic diesters.

A possible pathway leading to heterocycles from functionalized alkynes through PdI_2-catalyzed oxidative carbonylation is shown in Scheme 2, and corresponds to a sequential heterocyclization-alkoxycarbonylation process (in this and in the following Schemes anionic iodide ligands are omitted for clarity). Thus, intramolecular nucleophilic attack by the nucleophilic group to the triple bond, activated by coordination to PdI_2, takes place, in either an *exo* or an *endo* mode, to afford the corresponding heterocyclic vinylpalladium intermediates. Carbon monoxide insertion then occurs, followed by intermolecular nucleophilic displacement by an external alcohol. This leads to the formation of the final carbonylated heterocycle (without incorporation of CO into the cycle) and Pd(0). The latter is then reoxidized to PdI_2 trough oxidative addition of I_2, formed in its turn by oxidation of 2 mol of HI (formally also deriving from the carbonylation process) with oxygen.



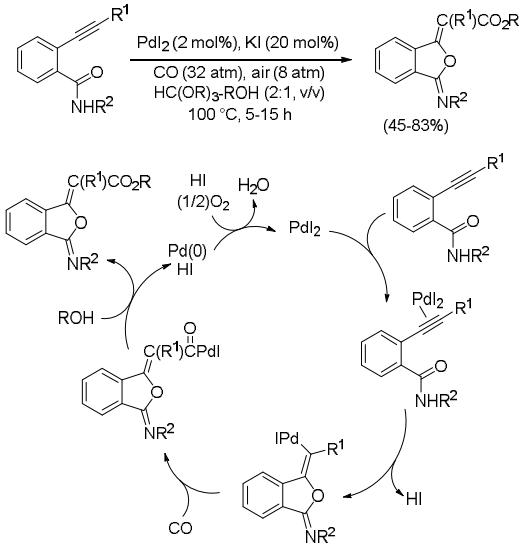
Scheme 2. PdI_2-catalyzed oxidative heterocyclization-alkoxycarbonylation of acetylenic substrates bearing a suitably placed nucleophilic group YH (Y=O, NR") to give carbonylated heterocycles without CO incorporation into the cycle.

An initial *exo* heterocyclization was observed in the case of 2-alkynylbenzamides, whose PdI_2-catalyzed oxidative carbonylation led, under suitable conditions, to the selective formation of 3-[(alkoxycarbonyl)methylene]isobenzofuran-1(3*H*)imines through *O*-cyclization, as depicted in Scheme 3.[20] Products were obtained in fair to high yields (45-83%) in the presence of trialkyl orthoformate as co-solvent, necessary to avoid the hydrolysis of the imino group under the reaction conditions. Some of the newly synthesized hetereocycles were successfully tested as potential herbicides.[21]

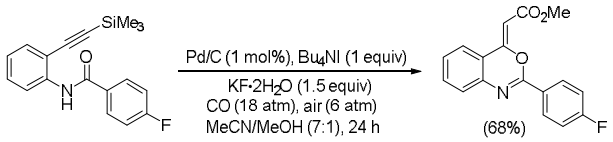
In a similar way, 4-fluoro-*N*-[2-((trimethylsilyl)ethynyl)phenyl]benzamide was converted into (*Z*)-4-[(methoxycarbonyl)methylene]-2-(4-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazine in 68% yield (Scheme 4).[22] In this latter reaction, the active catalytic species PdI_4^{2-} was formed in situ by oxidation of Pd/C with oxygen in the presence of iodide ligands, and the trimethylsilyl group of the substrate was lost during the carbonylation process.

Endo cyclization was observed with 3-yne-1,2-diols.[23] In this case, the heterocyclization-alkoxycarbonylation was accompanied by dehydration, with the C-1 hydroxyl acting as internal nucleophile (Schemes 5 and 6). In particular, starting from substrates bearing a secondary alcoholic function at C-1, dehydrative aromatization occurred, with formation of furan-3-carboxylic esters in good to excellent yields

(56-93%) (Scheme 5), while 2-methyl-3-yne-1,2-diols underwent dehydration from the methyl group at C-2, with selective formation of 4-methylene-4,5-dihydrofuran-3-carboxylic esters in fair to good yields (55-70%) (Scheme 6).[23]



Scheme 3. Synthesis of 3-[(alkoxycarbonyl)methylene]isobenzofuran-1(3*H*)imines by PdI_2-catalyzed oxidative *exo O*-heterocyclization-alkoxycarbonylation of 2-alkynylbenzamides.

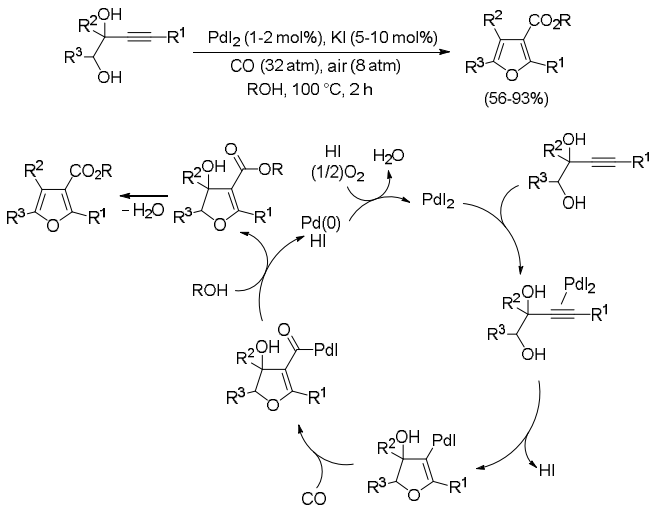


Scheme 4. Synthesis of (*Z*)-4-[(methoxycarbonyl)methylene]-2-(4-fluorophenyl)-4*H*-benzo[*d*][1,3]oxazine by PdI_2-catalyzed oxidative *exo O*-heterocyclization-alkoxycarbonylation of 4-fluoro-*N*-[2-((trimethylsilyl)ethynyl)phenyl]benzamide.

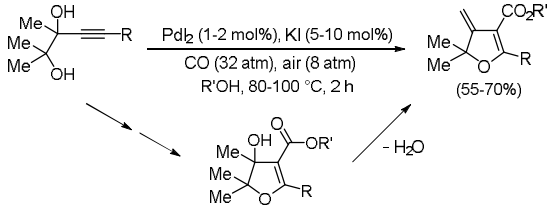
The method was then extended to *N*-Boc-1-amino-3-yn-2-ols, for the synthesis of pyrrole-3-carboxylic esters.[24] As shown in Scheme 7a, the PdI_2-catalyzed oxidative carbonylation of these substrates led to a mixture of Boc-protected and *N*-unprotected pyrrole-3-carboxylates, which could be easily and quantitatively converted into the *N*-unprotected heterocycles by subsequent treatment with an alkoxide. Interestingly, starting from substrates bearing two geminal alkynyl substituents at C-2, *N*-deprotection and water regioselective addition to the triple bond of the second alkynyl group were observed under the reaction conditions, with selective formation of 4-acylpyrrole-3-carboxylic esters (Scheme 7b).

N-substituted indole-3-carboxylic esters were synthesized in fair to good yields (50-84%) by PdI_2-catalyzed oxidative carbonylation of 2-alkynylanilines bearing an internal triple bond and a secondary amino group.[25] Also in this case, *N-endo* cyclization was followed by alkoxycarbonylation to give the final heterocyclic derivatives (Scheme 8).

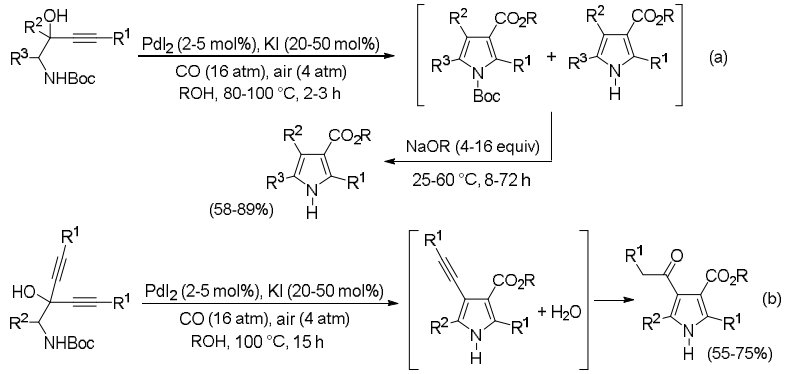
In the case of 2-alkynylanilines bearing an internal triple bond and a primary amino group, 1-(dimethoxymethyl)indole-3-carboxylic esters were formed by performing the carbonylation process in the presence of trimethyl orthoformate, through the formation of *N*-(dimethoxymethyl)-2-alkynylanilines as intermediates.[25] *N*-unsubstituted indole-3-carboxylic esters were then obtained by a simple acidic treatment of the reaction mixture (Scheme 9).



Scheme 5. Synthesis of furan-3-carboxylic esters by PdI_2-catalyzed oxidative *endo O*-heterocyclization-alkoxycarbonylation-dehydration of 3-yne-1,2-diols bearing a secondary alcoholic function at C-1.



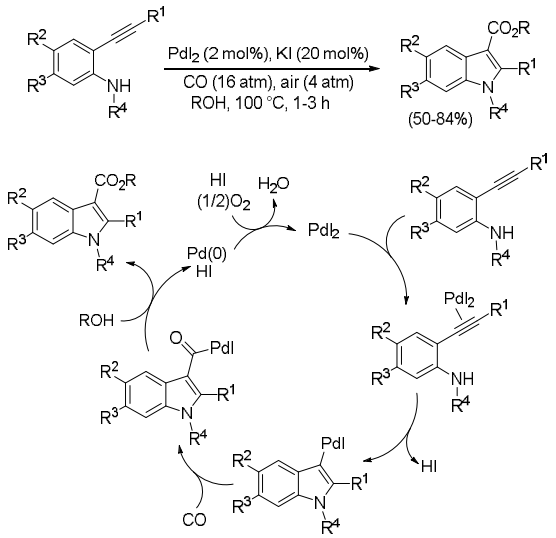
Scheme 6. Synthesis of 4-methylene-4,5-dihydrofuran-3-carboxylic esters by PdI_2-catalyzed oxidative *endo O*-heterocyclization-alkoxycarbonylation-dehydration of 2-methyl-3-yne-1,2-diols.



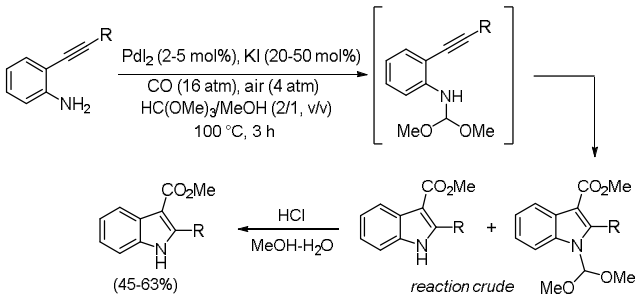
Scheme 7. Synthesis of (a) pyrrole-3-carboxylic esters and (b) 4-acylpyrrole-3-carboxylic esters by PdI_2-catalyzed oxidative *endo N*-heterocyclization-alkoxycarbonylation of 1-amino-3-yn-2-ol derivatives.

In some cases, the PdI_2-catalyzed oxidative carbonylative heterocyclization of alkyne derivatives may occur with CO incorporation into the cycle (oxidative cyclocarbonylation). As shown in Scheme 10, the process usually begins with the formation of a carbamoylpalladium species, deriving from the reaction between an amino group (present in the substrate at a suitable position with respect to the triple bond) and

PdI_2, followed by CO insertion. Triple bond insertion and alkoxycarbonylation then take place, to give the final heterocyclic product and Pd(0), which is reoxidized to PdI_2 by oxygen.



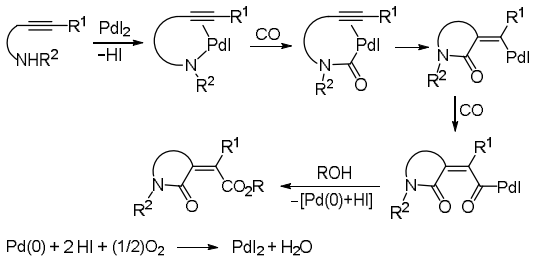
Scheme 8. Synthesis of *N*-substituted indole-3-carboxylic esters by PdI_2-catalyzed oxidative *endo* *N*-heterocyclization-alkoxycarbonylation of 2-alkynylanilines bearing an internal triple bond and a secondary amino group.



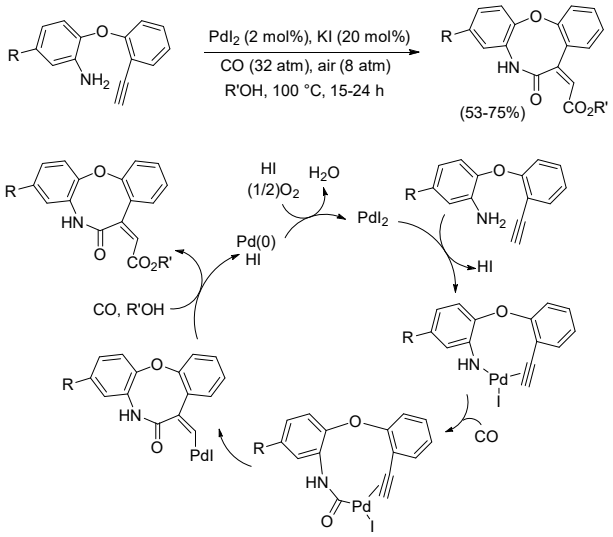
Scheme 9. Synthesis of *N*-unsubstituted indole-3-carboxylic esters by PdI_2-catalyzed oxidative *endo* *N*-heterocyclization-methoxycarbonylation of 2-alkynylanilines bearing an internal triple bond and a primary amino group, carried out in the presence of trimethyl orthoformate, followed by acidic treatment.

In an interesting example of this kind of reactivity, ζ-lactam derivatives were selectively obtained starting from 2-(2-alkynylphenoxy)anilines (Scheme 11).[26] The cyclocarbonylation-alkoxycarbonylation mechanism, occurring through the formation of a carbamoylpalladium iodide species followed by 8-*exo*-*dig* intramolecular triple bond insertion, was corroborated by theoretical calculations. The novel eight-membered lactam derivatives synthesized by this method showed a promising antitumor activity in vitro against both estrogen receptor-positive (MCF-7) and triple negative (MDA-MB-231) breast cancer (BC) cell lines, without noticeable effects on normal MCF-10A breast epithelial cell viability.[26]

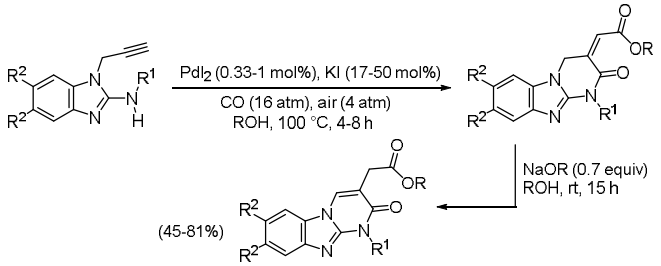
In another recent example, benzimidazopyrimidinone derivatives were synthesized from propynylbenzimidazolamines by PdI_2/KI-catalyzed oxidative cyclocarbonylation-alkoxycarbonylation followed by base-promoted double bond isomerization, as shown in Scheme 12.[27]



Scheme 10. PdI_2-catalyzed oxidative cyclocarbonylation-alkoxycarbonylation of acetylenic substrates bearing a suitably placed amino group to give carbonylated heterocycles with CO incorporation into the cycle.



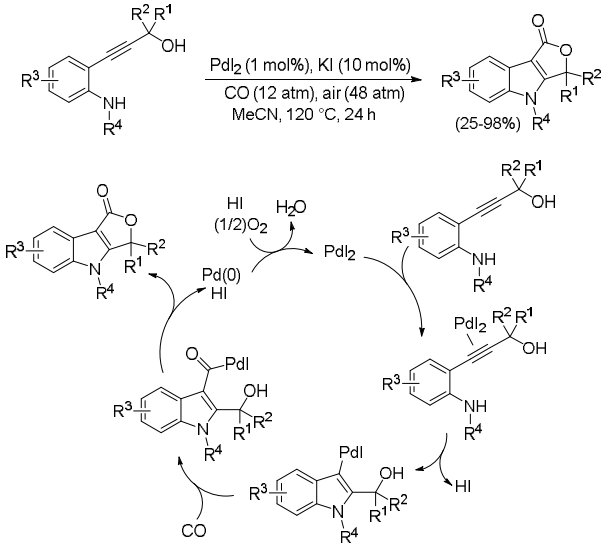
Scheme 11. Synthesis of (*Z*)-(6-oxo-5,6-dihydro-12-oxa-5-azadibenzo[*a*,*d*]cycloocten-7-ylidene)acetates by PdI_2/KI-catalyzed oxidative cyclocarbonylation-alkoxycarbonylation of 2-(2-ethynylphenoxy)anilines.



Scheme 12. Synthesis of 2-(2-oxo-1,2-dihydrobenzo[4,5]imidazo[1,2-*a*]pyrimidin-3-yl)acetic esters from 1-(prop-2-yn-1-yl)-1*H*-benzo[*d*]imidazol-2-amines by PdI_2/KI-catalyzed oxidative cyclocarbonylation-alkoxycarbonylation followed by base-promoted double bond isomerization.

With acetylenic substrates bearing two suitably placed nucleophilic groups, an initial heterocyclization, triggered by the first nucleophile, may be followed by carbon monoxide insertion and intramolecular trapping by the second nucleophilic group. The overall process thus results in a double

cyclization (heterocyclization followed by cyclocarbonylation), with formation of two cycles and three new bonds in a single operation. Fused furo[3,4-*b*]indol-1-ones were prepared by this strategy, starting from 2-(hydroxypropyn-1-yl)anilines, as shown in Scheme 13.[28] 5-*Endo-dig N*-cyclization was followed by CO insertion and intramolecular nucleophilic displacement by the hydroxyl (possibly, through the formation of a palladacycle followed by reductive elimination) to give the final products in modest to excellent yields.



Scheme 13. Synthesis of 3,4-dihydrofuro[3,4-*b*]indol-1-ones by PdI_2/KI-catalyzed oxidative *N*-cyclization-cyclocarbonylation of 2-(hydroxypropyn-1-yl)anilines.

On the other hand, 5-*exo-dig O*-cyclization, followed by cyclocarbonylation, allowed an innovative synthesis of dihydrofurofuranones with significant antitumor activity in vitro against breast cancer (BC) cell lines, including the most aggressive MDA-MB-231 and MDA-MB-468 cells, starting from 4-yne-1,3-diols (Scheme 14).[29]

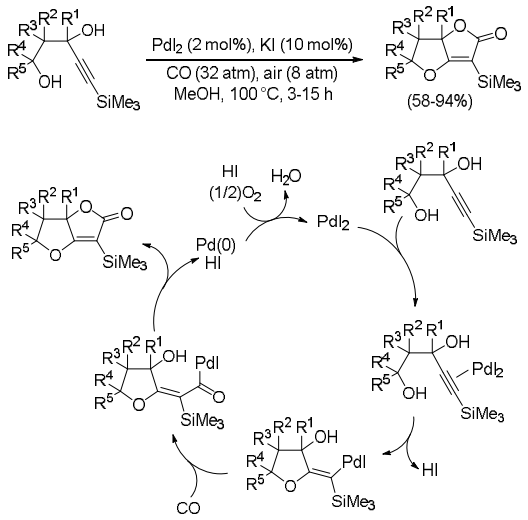
3. PdI_2-catalyzed oxidative aminocarbonylation-heterocyclization

The PdI_2/KI catalytic system is also able to catalyze a different kind of oxidative carbonylation of acetylenic substrates, when employed with terminal alkynes and in the presence of a secondary basic and nucleophilic secondary amine. In this case, in fact, the formation of an alkynylpalladium specied takes place, thanks to the basic properties of the amine, followed by CO insertion and nucleophilic displacement by the same amine (now acting as nucleophile) to the ensuing alkynoylpalladium iodide intermediate, to give 2-ynamides (Scheme 15).[30]

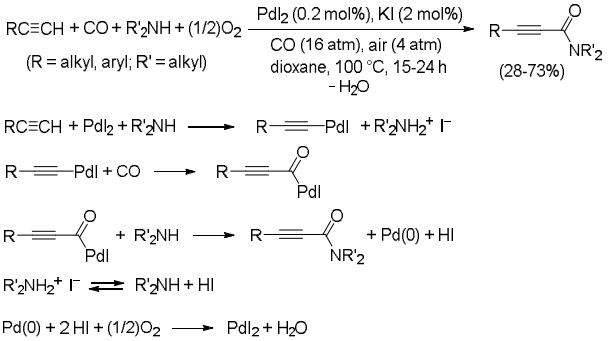
This reactivity may lead to heterocyclic derivatives when applied to acetylenic substrates bearing a suitably placed nucleophilic group, as the functionalized 2-ynamide intermediate may undergo either intramolecular conjugate addition (Scheme 16, path *a*) or intermolecular conjugate addition followed by heterocyclization (Scheme 16, path *b*). We reviewed this kind of chemistry in 2012,[12] so we will describe here our most recent achievements in this field.

Path *a* of Scheme 16 was followed by 2-ethynylbenzamides, when allowed to react with CO, amines, and O_2, in the presence of the PdI_2/KI catalytic system in MeCN as the solvent at 100 °C and under 40 atm of a 4:1 mixture of CO-air. These substrates were smoothly converted into 3-[(dialkylcarbamoyl)methylene]isoindolin-1-one derivatives by sequential oxidative aminocarbonylation-intramolecular conjugate addition (Scheme 17),[20] which were useful precursor for the preparation of novel spiro(isoindole-1,5'-isoxazolidin)-3(2*H*)-ones with antitumor activity in vitro on three human cancer cell

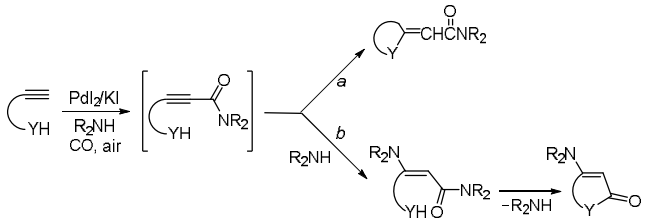
lines (neuroblastoma SH-SY5Y, HT-29 colorectal adenocarcinoma and HepG2 hepatocellular carcinoma cells).[31]



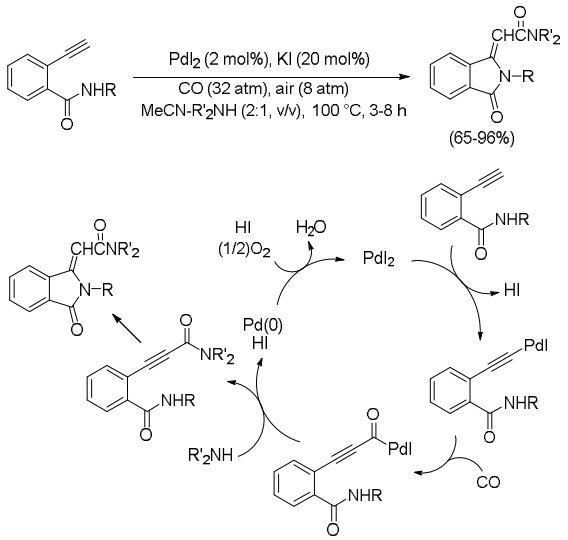
Scheme 14. Synthesis of 3-(trimethylsilyl)-6,6*a*-dihydrofuro[3,2-*b*]furan-2(5*H*)-ones by PdI_2/KI-catalyzed oxidative *O*-cyclization-cyclocarbonylation of 4-yne-1,3-diols.



Scheme 15. PdI_2/KI-catalyzed oxidative monoaminocarbonylation of terminal alkynes to 2-ynamides.

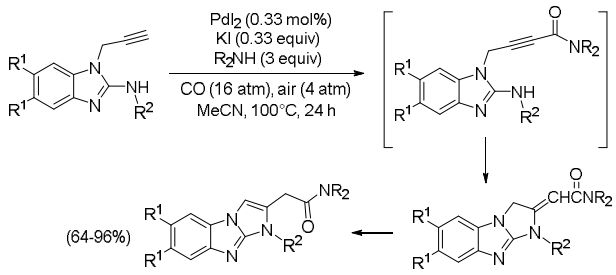


Scheme 16. PdI_2/KI-catalyzed oxidative aminocarbonylation of terminal alkynes functionalized with a suitably placed nucleophilic group YH: aminocarbonylation-intramolecular conjugate addition (path *a*) *vs.* aminocarbonylation-intermolecular conjugate addition-heterocyclization (path *b*).



Scheme 17. Synthesis of 3-[(dialkylcarbamoyl)methylene]isoindolin-1-ones from 2-ethynylanilines by sequential PdI_2/KI-catalyzed oxidative aminocarbonylation-intramolecular conjugate addition.

In a similar way, 1-(prop-2-yn-1-yl)-1*H*-benzo[*d*]imidazol-2-amines were recently converted into functionalized benzimidazoimidazoles, through sequential oxidative aminocarbonylation-intramolecular conjugate addition-isomerization, according to Scheme 18.[32]



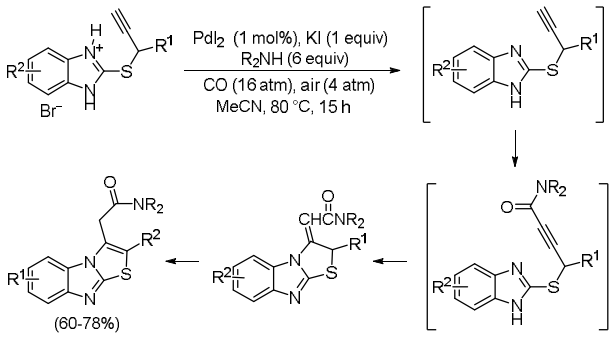
Scheme 18. Synthesis of 2-(1-alkyl-1*H*-benzo[*d*]imidazo[1,2-*a*]imidazol-2-yl)acetamides from 1-(prop-2-yn-1-yl)-1*H*-benzo[*d*]imidazol-2-amines by sequential PdI_2/KI-catalyzed oxidative aminocarbonylation-intramolecular conjugate addition-isomerization.

The nitrogen of an imidazole ring may also act as internal nucleophile in the intramolecular conjugate addition step. Thus, 2-prop-2-ynylsulfanyl-3*H*-benzimidazoles (obtained in situ from the corresponding benzimidazolium salts) were selectively converted into functionalized benzimidazothiazoles, according to Scheme 19.[33]

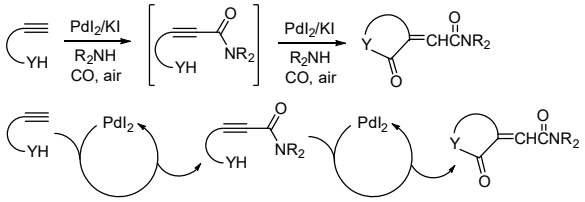
In some particular cases, the initial oxidative aminocarbonylation catalytic cycle is followed by a second catalytic cycle, corresponding to a PdI_2-catalyzed cyclocarbonylation. A process like this, depicted in Scheme 20, is an example of "auto-tandem catalysis", that is, a sequential catalytic process consisting of two concatenated catalytic cycles promoted by the same catalyst.[34]

A particularly interesting example of this kind of reactivity was reported by our research group in 2007, and consisted in the synthesis of oxazolidinone derivatives starting from propargyl amines in the presence of water as promoter.[35] More recently, we have shown that it is possible to carry out the reaction in the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate ($EmimEtSO_4$) as nonconventional solvent, with

the advantage of the recycle of the catalytic system.[36] As shown in Scheme 21, the cyclocarbonylation cycle took place through *N*-palladation, CO insertion, water attack with heterocyclization, and β-H elimination from the HO-C-PdI moiety.



Scheme 19. Synthesis of 2-(benzo[4,5]imidazo[2,1-*b*]thiazol-3-yl)acetamides from 2-prop-2-ynylsulfanyl-3*H*-benzimidazolium salts by sequential PdI_2/KI-catalyzed oxidative aminocarbonylation-intramolecular conjugate addition-isomerization.



Scheme 20. PdI_2/KI-promoted auto-tandem catalysis: oxidative aminocarbonylation of terminal alkynes functionalized with a suitably placed nucleophilic group YH followed by cyclocarbonylation.

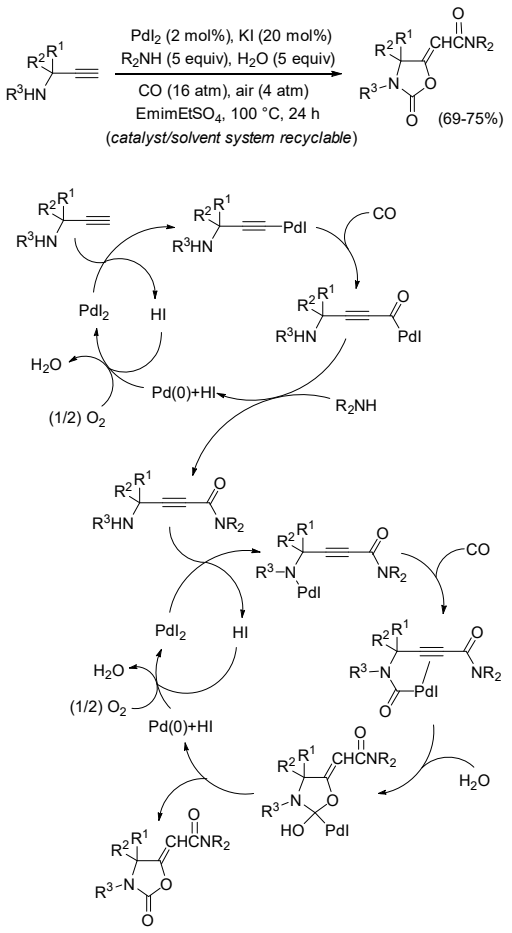
In another recent example, 2-(prop-2-ynylthio)imidazoles were converted into imidazothiazinone derivatives. In this case, the cyclocarbonylation cycle took place through *N*-palladation, CO insertion, triple bond insertion, protonolysis, and isomerization (Scheme 22).[37]

4. PdI_2-catalyzed non-oxidative carbonylations

The versatility of the PdI_2/KI calatytic system is further demonstrated by its capacity to efficiently promote the carbonylative synthesis of important heterocyclic derivatives under non-oxidative conditions. A particularly striking example was reported several years ago, and concerned the synthesis of benzofuran derivatives starting from readily available 1-(2-allyloxyphenyl)-2-yn-1-ols bearing an internal triple bond.[38-42] The process consisted in a concatenation of two catalytic cycles: the first one [catalyzed by Pd(0), either formed in situ or added as $Pd(PPh_4)_4$] corresponded to substrate deallylation; the second one (catalyzed by PdI_2) corresponded to 5-*exo-dig* heterocyclization-carbonylation-reduction. The reduction step of the allylalcoholic group of the intermediate deriving from heterocyclization-carbonylation probably occurred by its reaction with the H-Pd-I species (also deriving from the carbonylation step) followed by protonolysis of the corresponding π-allylpalladium complex, as exemplified in Scheme 23 for methoxycarbonylation. For a process like this, consisting of two concatenated catalytic cycles promoted by the same metal, but in two different oxidation states, we coined the term "sequential homobibetallic caytalysis".[38-42] We have recently found that the (benzofuran-2-yl)acetic esters thus synthesized possess an interesting anticancer activity in vitro, by inducing apoptosis in BC cells.[43]

Interestingly, starting from 2-(1-hydroxyprop-2-ynyl)phenols, bearing a free phenolic group and a terminal triple bond, a process starting with cyclocarbonylation took place, followed by alkoxycarbonylation

and reduction of the allylalcoholic moiety, with selective formation of coumarin-3-acetic esters (Scheme 24).[44] We have recently found that these derivatives possess a promising herbicidal activity.[45]

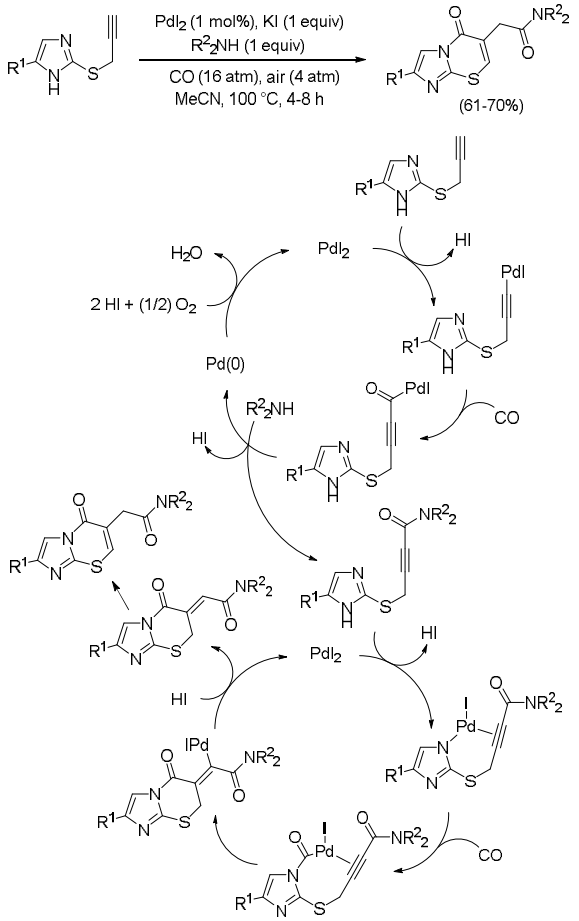


Scheme 21. Recyclable synthesis of 2-(2-oxooxazolidin-5-ylidene)acetamides by PdI_2/KI-promoted auto-tandem catalysis in $EmimEtSO_4$: oxidative aminocarbonylation of propargyl amines followed by water-promoted cyclocarbonylation.

Under nonoxidative conditions, a PdI_2-catalyzed cyclocarbonylation process may also occur by protonolysis of the vinylpalladium species ensuing from *N*-palladation, CO insertion, and triple bond insertion. This is exemplified by the synthesis of thiazafluorenone derivatives from 2-(propynylthio)benzimidazoles shown in Scheme 25, where a final double bond isomerization step accounted for the formation of the final products.[46] In this reaction, the use of an excess of CO_2 could assist the product formation, probably by favoring the protonolysis step.

4. Conclusion

The PdI_2/KI catalytic system has shown to be a very versatile catalytic system for promoting the carbonylation reactions of functionalized alkynes leading to a variety of heterocyclic motifs starting from simple and readily available substrates.



Scheme 22. Synthesis of 6-(*N*,*N*-dialkylcarbamoylmethyl)imidazo[2,1-*b*][1,3]thiazin-5-ones by PdI_2/KI-promoted auto-tandem catalysis: oxidative aminocarbonylation of 2-(prop-2-ynylthio)imidazoles followed by cyclocarbonylation and isomerization.

It is able to catalyze oxidative carbonylation processes as well as nonoxidative carbonylations and, depending on the substrate particular structure and on reaction conditions, may favor either a cyclocarbonylative process (with incorporation of CO into the cycle) or a process in which CO is not incorporated into the formed cycle. Double bond cyclization (heterocyclization followed by cyclocarbonylation) has also been successfully achieved with this catalyst.

Further research in this field will be aimed, on one hand, on the application of these methodologies to the synthesis of novel and possibly more complex heterocyclic structures, whith applications in several fields of Science (such as, pharmaceutical chemistry, material science, and so on) and, on the other hand, on the possibility to heterogenize the catalytic system. This will allow an easier product recovery and purification from the carbonylation mixture associated with the possibility to recycle the catalyst, thus further improving the sustainability of the catalytic synthetic approach.

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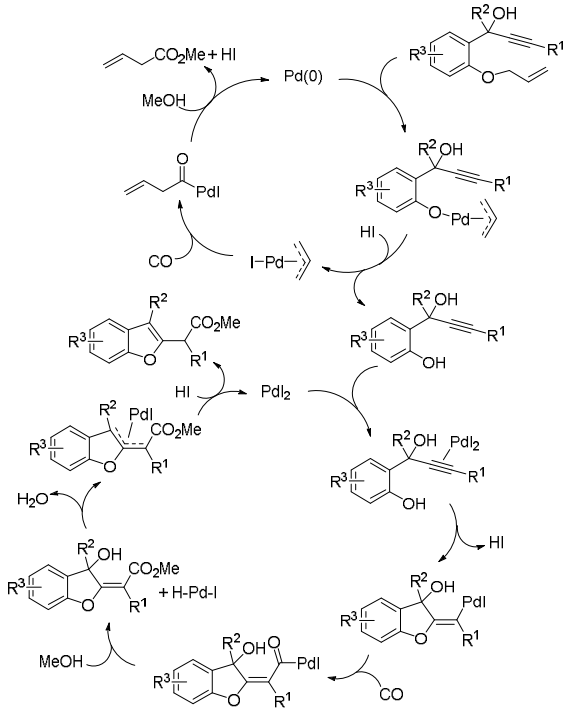
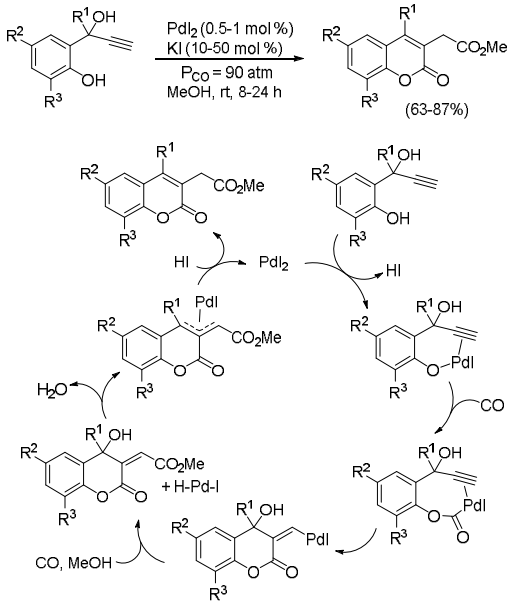
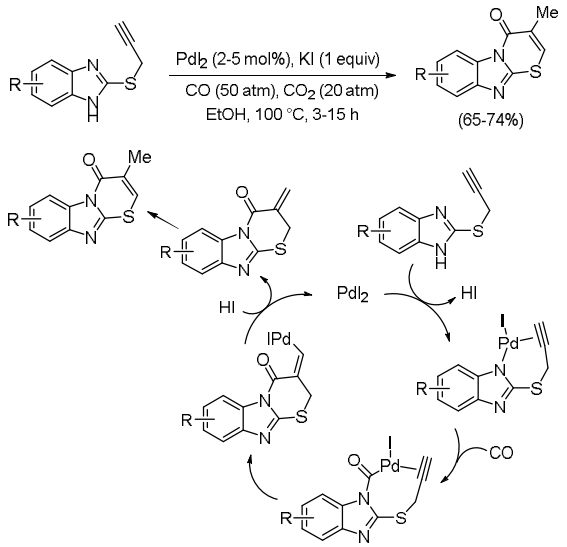


Scheme 23. Sequential homobimetallic catalysis leading to (benzofuran-2-yl)acetic esters from 1-(2-allyloxyphenyl)-2-yn-1-ols bearing an internal triple bond.



Scheme 24. Synthesis of coumarin-3-acetates from 2-(1-hydroxyprop-2-ynyl)phenols by PdI_2/KI-catalyzed cyclocarbonylation-alkoxycarbonylation-reduction sequence.



Scheme 25. Synthesis of 1-thia-4*a*,9-diazafluoren-4-ones by PdI_2/KI-catalyzed cyclocarbonylation of 2-(prop-2-ynylthio)-1*H*-benzo[*d*]imidazoles.

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