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One-Pot Palladium-Catalyzed Carbonylative Sonogashira Coupling using Carbon Dioxide as Carbonyl Source

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Carbonylation coupling reaction has emerged as a powerful and versatile strategy for the construction of carbonyl-containing compounds in modern synthetic chemistry over the past years. Carbon dioxide, a renewable one carbon molecule, has become one of the most attractive and promising alternative carbonyl sources due to its highly abundance, nontoxicity and stability in comparison with CO in recent years. However, in most cases, a two-chamber technique was generally necessary to allow the CO-producing and CO-consuming processes to perform successfully because of the complexities and incompatibility of reaction conditions, when carbon dioxide was utilized as carbonyl source. Herein, a practical one-pot protocol using carbon dioxide as the carbonyl source for the palladium-catalyzed carbonylative Sonogashira coupling has been established, providing an expedient and practical route to a wide range of functionalized alkynones and indoxyls under mild reaction conditions. By finding a suitable catalytic system, the method allowed the CO-generating and CO-consuming processes to proceed in one pot, wherein carbon monoxide was generated in situ from the reduction of carbon dioxide in the absence of any fluoride reagents. Simple and safe operation, readily available substrates, good functional group tolerance and mild reaction conditions are the features of the method.

Introduction

Palladium-catalyzed carbonylation reactions represent a powerful and versatile tool for the preparation of many fine chemicals,[1] such as aldehydes, carboxylates, heterocycles, hydrocarbon fuels, and the construction of bioactive natural products, pharmaceutical agrochemical compounds containing carbonyl structural motif[2] over the past few years. Traditionally, carbon monoxide (CO) was used as the carbonyl source in the transformations. However, the high toxicity, flammability as well as the difficulties in handling of CO might remain to be formidable problems, which have limited its applications in the carbonylative coupling. To circumvent these issues, various CO surrogates, such as formates,[3] formamides,[4] aldehydes,[5] pivaloyl chloride,[6] and metal carbonyls,[7] have been exploited in recent years.[8] However, the transition metal catalyst, strong base and high temperatures are generally employed in order to release CO successfully in these cases, which inspire the development of efficient and sustainable CO surrogates. Carbon dioxide (CO_2) has recently been regarded as a more attractive and promising one-carbon source because of its highly abundance, nontoxicity and stability in comparison with CO,[9] which renders the replacement of CO with CO_2 as the carbonyl source highly valuable in synthetic chemistry. Actually, the exploitation of catalytic methods for the reduction of CO_2 to CO have been well documented in the presence of appropriate reductants in recent years,[10] including the photo- and electrochemical catalytic approaches. However, due to the complexities and incompatibility of reaction conditions between the CO-producing and CO-consuming process, the direct application of CO_2 as the carbonyl source to catalytic carbonylation coupling in a one-pot manner still remain a significant challenge.

To address these problems, a two-chamber technique, which can allow the CO-producing and CO-consuming processes to take place separately, has been developed by Skrydstrup and coworkers.[11] For example, recently, they reported a low-pressure, low-temperature and near-stoichiometric hydroformylation efficient operation on a diverse array of terminal olefins without the need for expensive equipment by decoupling the syngas formation and consumption *via* a two-chamber reactor.[11c] By using the technique, several elegant processes for the carbonylation reactions using CO_2 as the CO source have been successfully demonstrated (Scheme 1, a).[12] Skrydstrup and Gee *et al.* reported that silacarboxylic acids, which were produced from CO_2 and chlorosilane in the presence of lithium, could be utilized as efficient CO releasing molecules and further applied in the carbonylation process.[12a–d] The merges of fluoride-catalyzed reduction of CO_2 by using stoichiometric amount of disilane and aminocarbonylations have also been reported respectively by the groups of Skrydstrup, Sundararaju and He.[12e–g] Additionally, Fleischer and coworkers proved that *N*-formyl saccharin derived from CO_2 could also be used as CO surrogate and applied in the Pd-catalyzed alkoxycarbonylation of alkenes.[12h] Moreover, photocatalysis is also effective for the reduction of CO_2 and applied in

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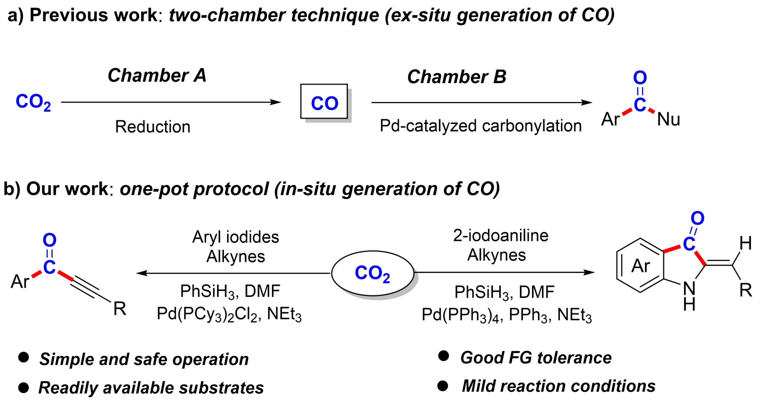


Scheme 1. Pd-catalyzed carbonylation reactions using carbon dioxide as carbonyl source

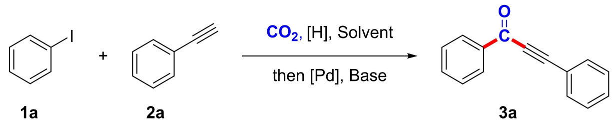
carbonylation with this strategy.[13] Although great progress has been made in this research field, the two-chamber technique was necessary in these cases to enable the CO-producing and CO-consuming process performing smoothly. Moreover, the pre-preparation of carboxylation reagents such as silacarboxylic acids and *N*-formyl saccharin, or a catalytic amount of fluoride reagents were required. To our knowledge, the one-pot green technique for the carbonylation reactions with CO_2 as the carbonyl source, in which CO is generated in situ, has remained unexplored but is more desirable and appealing due to the operation convenience. With our continuous interest in developing efficient methods for the transformation of CO_2,[14] we envisioned that the CO-producing and CO-consuming might be conducted simultaneously in one chamber through finding a suitable catalytic system between the CO_2 reduction and the carbonylative coupling. Herein, we reported a new one-pot method for the Pd-catalyzed carbonylation of aryl iodides/2-iodoaniline, alkynes and CO_2 under mild reaction conditions, wherein CO was acted as intermediate and generated in situ under the fluoride-free conditions in the presence of phenylsilane. A wide array of alkynones and indoxyls were obtained, which are important building blocks found in numerous biologically active compounds and valuable intermediates widely utilized in cycloadditions for the efficient synthesis of heterocycles, such as oxazole, pyrazole, etc.[1,2]

Results and Discussion

Our initial studies were directed towards finding an appropriate combination of reductant and catalyst by employing iodobenzene (**1 a**) and phenyl acetylene (**2 a**) as the model substrates, and the representative optimization conditions were summarized in Table 1. To our delight, when the reaction was performed *via* a two-step, one-pot procedure with phenylsilane as reductant, $Pd(PCy_3)_2Cl_2$ as the catalyst and NEt_3 as the base in *N*,*N*-dimethyl formamide (DMF) at 60 °C, the desired product **3 a** could be obtained with 63 % yield (entry 1). No better results were obtained when Et_2SiH_2, Ph_3SiH and $PhSi(OEt)_3$ were examined (entries 2–4) in comparison with $PhSiH_3$. Notably, in contrast to the previous report,[12g] the introduction of a fluoride inhibited the formation of the desired product, which might be due to the reason that fluoride was not conducive to the carbonylation reaction (entry 5). Moreover, we observed the amount of reductant had great impact on the reaction. Decreasing the amount of $PhSiH_3$ led to lower yields, whereas the result was not improved when it was further increased to 6 equivalents (entries 6–8). Among the palladium precursors investigated, including $Pd(PPh_3)_2Cl_2$, $Pd(dppp)Cl_2$, $Pd(OAc)_2$, $PdCl_2$ and $Pd(PPh_3)_4$, $Pd(PCy_3)_2Cl_2$ gave the best result (entries 9–13). However, the yield of product **3 a** decreased when the combination of $PdCl_2$ and PCy_3 was used as the catalyst system (entry 14). During the screening of bases, NEt_3 was found to be the best out of a variety bases such as DBU, DABCO and NEt(*i*Pr)$_2$ (entries 15–17). Further experiments were carried out to test the influence of the stirring time of CO_2 reacting with reductant (entries 18–20). Finally, The optimal result was obtained when the stirring time was increased to 3 h, affording the desired product with 79 % isolated yield, while a further increase demonstrated to be not beneficial.

With the optimized reaction conditions in hand, the generality of the one-pot palladium-catalyzed carbonylative Sonogashira coupling by the use of CO_2 as carbonyl source was then investigated with a variety of terminal alkynes (Scheme 2). In general, various alkynes containing various substituents including electron-donating and electron-withdrawing on the phenyl groups were all tolerated under the optimized reaction conditions (**3 a**–**3 j**). Notably, aryl alkynes with electron-donating groups (**3 b**–**3 e**) gave the corresponding products in higher yields than those with electron-withdrawing groups (**3 f**–**3 j**), which revealed that the electronic nature of the substituents had significant influence on this transformation. Moreover, *meta*-substituted substrates, such as 1-ethynyl-3-methylbenzene (**2 k**), 1-ethynyl-3-methoxybenzene (**2 l**), 1-ethynyl-3-fluorobenzene (**2 m**), 2-ethynylnaphthalene (**2 o**), and *ortho*-substituted aryl acetylene (**2 n**) also could undergo the reaction smoothly, affording the corresponding products with atisfactory yields. It was worth mentioning that 3-ethynylthiophene (**2 p**) could also be employed in this one-pot transformation, albeit with moderate yield. Moreover, aliphatic terminal alkynes such

Table 1. Optimization of reaction conditions.[a]



1a **2a** **3a**

Entry	Catalyst [mol %]	[H] [equiv.]	Base [equiv.]	Yield[%][a]
1	$Pd(PCy_3)_2Cl_2$	$PhSiH_3$	NEt_3	63
2	$Pd(PCy_3)_2Cl_2$	$(Et)_2SiH_2$	NEt_3	trace
3	$Pd(PCy_3)_2Cl_2$	$(Ph)_3SiH$	NEt_3	n.d.
4	$Pd(PCy_3)_2Cl_2$	$PhSi(OEt)_3$	NEt_3	n.d.
5[b]	$Pd(PCy_3)_2Cl_2$	$PhSiH_3$	NEt_3	n.d.
6[c]	$Pd(PCy_3)_2Cl_2$	$PhSiH_3$	NEt_3	6
7[d]	$Pd(PCy_3)_2Cl_2$	$PhSiH_3$	NEt_3	34
8[e]	$Pd(PCy_3)_2Cl_2$	$phSiH_3$	NEt_3	61
9	$Pd(PPh_3)_2Cl_2$	$PhSiH_3$	NEt_3	16
10	$Pd(dppp)Cl_2$	$PhSiH_3$	NEt_3	49
11	$Pd(OAc)_2$	$PhSiH_3$	NEt_3	35
12	$PdCl_2$	$PhSiH_3$	NEt_3	47
13	$Pd(PPh_3)_4$	$PhSiH_3$	NEt_3	35
14[f]	$PdCl_2$	$PhSiH_3$	NEt_3	35
15	$Pd(PCy_3)_2Cl_2$	$PhSiH_3$	DBU	18
16	$Pd(PCy_3)_2Cl_2$	$PhSiH_3$	DABCO	10
17	$Pd(PCy_3)_2Cl_2$	$PhSiH_3$	$NEt(iPr)_2$	62
18[g]	$Pd(PCy_3)_2Cl_2$	$PhSiH_3$	NEt_3	37
19[h]	$Pd(PCy_3)_2Cl_2$	$PhSiH_3$	NEt_3	85(79)
20[i]	$Pd(PCy_3)_2Cl_2$	$PhSiH_3$	NEt_3	72

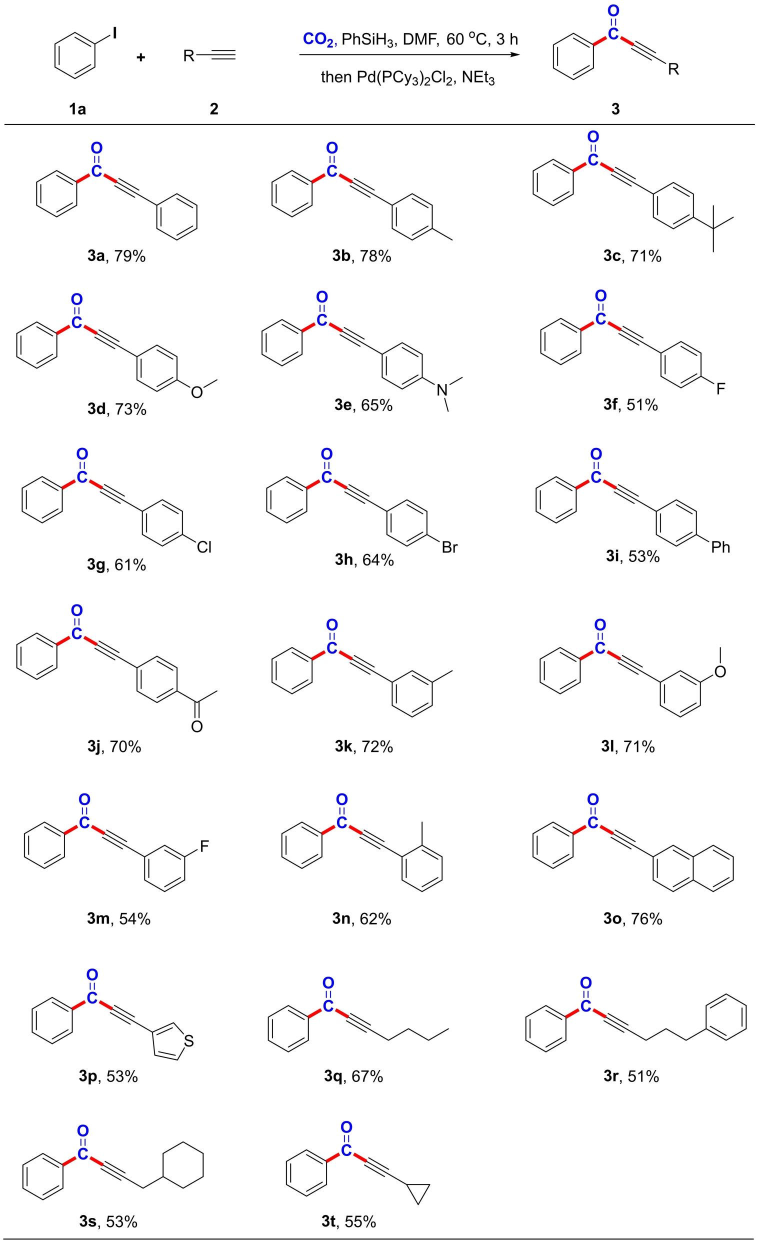
[a] Reaction conditions: The mixture of CO_2 (1 atm), [H] (0.8 mmol), DMF (2 ml) was first stirred at 60 °C for 2 h; then another mixture of **1 a** (0.2 mmol), **2 a** (0.3 mmol), [Pd] (0.01 mmol) and base (0.6 mmol) was added dropwise with syringe and stirred for overnight. The yield was GC yield with dodecane as the internal standard, the number in parentheses was the isolated yield. "n.d." was "not detected". [b] CsF (0.8 mmol) was added. [c] $PhSiH_3$ (0.4 mmol). [d] $PhSiH_3$ (0.6 mmol). [e] $PhSiH_3$ (1.2 mmol). [f] PCy_3 (0.04 mmol) was added. [g] The mixture of CO_2, $PhSiH_3$ in DMF was first stirred for 1 h. [h] The mixture of CO_2, $PhSiH_3$ in DMF was first stirred for 3 h. [i] The mixture of CO_2, $PhSiH_3$ in DMF was first stirred for 5 h.

as *n*-butyl, 3-phenyl-propyl, 1- cyclohexyl-methyl and cyclopropane were all compatible with the standard reaction conditions, giving the corresponding products in moderate to high yields (**3 q**–**3 t**).

We subsequently turned our attention to the scope of this transformation with various aryl iodides. As shown in Scheme 3, aryl iodides bearing different electron-donating groups on the aryl ring, including 4-methoxy (**1 b**), 4-*t*butyl (**1 c**) and 4-morpholino (**1 d**), could furnish the corresponding products (**3 u**–**3 w**) in 63 %, 75 % and 80 % yields, respectively. Aryl iodides bearing electron-withdrawing groups, such as 4-chloro (**1 e**), 4-bromo (**1 f**), 4- trifluoromethyl (**1 g**), 4-acetyl (**1 h**) and 4-ester (**1 i**), could also undergo the reaction and delivered the corresponding products with moderate yields. Similarly, aryl iodides with electron-donating substituents gave higher yields in comparison with those with electron-withdrawing ones. Substituents at the *meta* and *ortho* positions were also assessed and all of them were compatible with the conditions, affording the desired products in moderate yields (**3 ac**–**3 ae**). Moreover, polysubstituted aryl iodides were also well-tolerated to give the corresponding alkynones (**3 af**–**3 ah**) in 71 %, 74% and 78 % yield, respectively. A fused ring containing aryl iodides could also enter into the reaction without difficulty, furnishing alkynone **3 ai** in 68 % yield. It is worth noting that other aryl halides including aryl bromide and aryl chloride exhibited very low reactivity, and only trace amounts of the desired product was detected by GC-MS analysis, and most of the starting materials were recovered.

Encouraged by the above results, we attempted to extend our methodology for the synthesis of indoxyls through a carbonylation / intramolecular cyclization process by using 2-iodoanilines as the coupling partner. Pleasingly, with the above slightly modified conditions, various indoxyls could be produced as well by using the $Pd(PPh_3)_4/PPh_3$ catalytic system, wherein PPh_3 might not only function as the ligand but also serve as the organocatalyst to promote the intramolecular cyclization of in-situ generated alkynones.[15a] As shown in Scheme 4, 2-iodoanilines with simple methyl- and methoxy-substituted on the phenyl ring proceeded smoothly to give the desired products **5 a**–**5 c** in moderate yields. Electron-withdrawing substituents (F, Cl, Br, CO_2Me, CN, CF_3) were also compatible with the standard reaction conditions, finishing the expected products in 52–72 % yields (**5 d**–**5 i**). The structure of product **5 d** was characterized by X-ray crystallographic analysis.[16]

Besides mono-substituted substrates, the substrate bearing 3,4-dimethyl on the aromatic ring could also be extended to the protocol, giving product **5 j** with 71 % yield. Heteroaromatic moieties could also be contained in substrate and allowing the formation of the desired product **5 k** in acceptable yields. However, the use of 2-iodoaniline protected by *N*-acetyl failed to yield the desired product **5 l**, but led to the formation of a small amount of unidentified product and most of the raw material could be recovered. Subsequently, various alkynes with 2-iodoaniline under standard conditions were examined. Alkynes containing electron-rich 4-methyl, 4-*t*-butyl or 4-*n*-amyl yielded the desired products **5 m**–**5 o** in 61–72 % yield, and

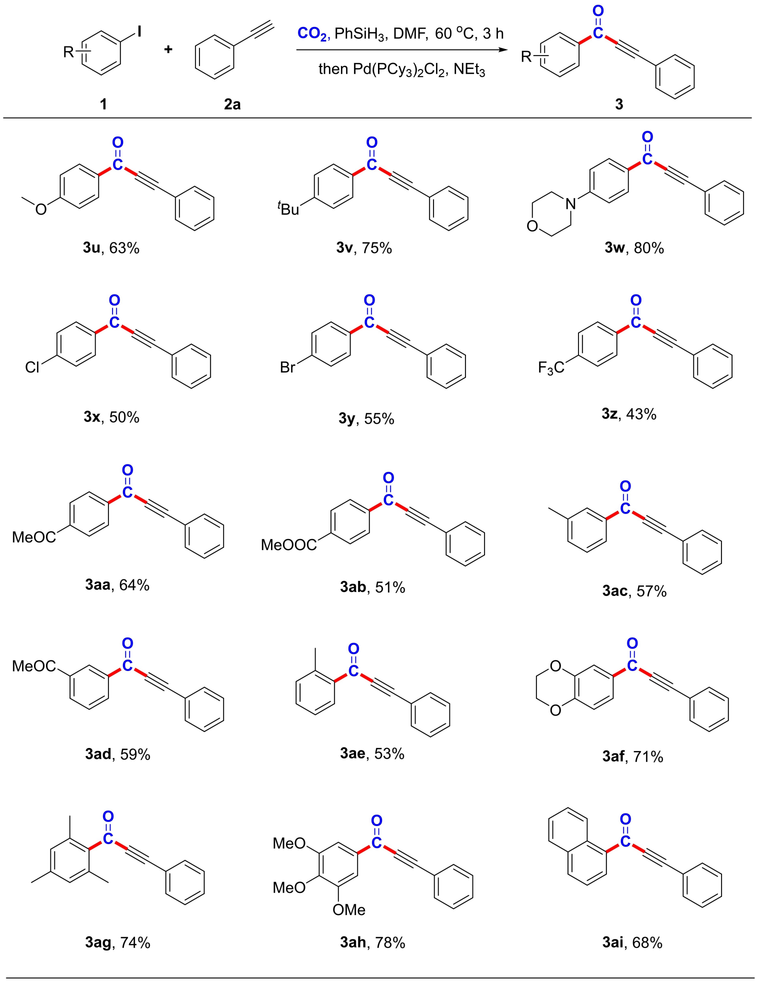


Scheme 2. Carbonylative synthesis of alkynones with various alkynes. Reaction conditions: the mixture of CO_2 (1 atm), $PhSiH_3$ (0.8 mmol), DMF (2 ml) was first stirred at 60 °C for 3 h, then another mixture of **1 a** (0.2 mmol), **2** (0.3 mmol), $Pd(PCy_3)_2Cl_2$ (0.01 mmol), NEt_3 (0.6 mmol) in DMF (1 mL) was added dropwise and stirred for overnight. The yield was the isolated yield.

electron-deficient 4-phenyl, 4-fluoro, 4-chloro, 4-bromo or 4-trifluomethyl derivatives yielded the desired products **5 p**–**5 t** smoothly. Moreover, *meta*-substituted substrates also could be subjected to the reaction conditions, and the desired products **5 u**–**5 w** were obtained in acceptable yields. In addition, alkyne containing pyridine heterocyclic was tested, and gave the product **5 x** with a moderate yield.

To further extend the application of this transformation, a series of heterocycles were prepared (Scheme 5). As expected, the treatment of **3 a** with $NH_2OH{\cdot}HCl$ in the presence of KOH at room temperature in a mixture solvent of $MeOH/H_2O$ (9 : 1) gave oxazole derivative **6** in 81 % yield. Moreover, pyrazole derivative **7** and **8** could be produced by conducting the reaction of alkynone and hydrazine at room temperature in DMF. The intermolecular cycloaddition at the triple bond could be readily achieved by the reaction of alkynone with $TMSN_3$ or S_8, generating triazole derivative **9** or *tetra*- substituted thiophene derivative **10**, which represented a useful structural motif found in numerous luminescent functional molecules.

Moreover, in order to unambiguously determine the source of C atom of carbonyl group in alkynone, an isotopic tracing experiment by replacing CO_2 with $^{13}CO_2$ under the standard conditions was conducted, and 99 % ^{13}C incorporation was found in the desired product (Scheme 6a). Subsequently, to get



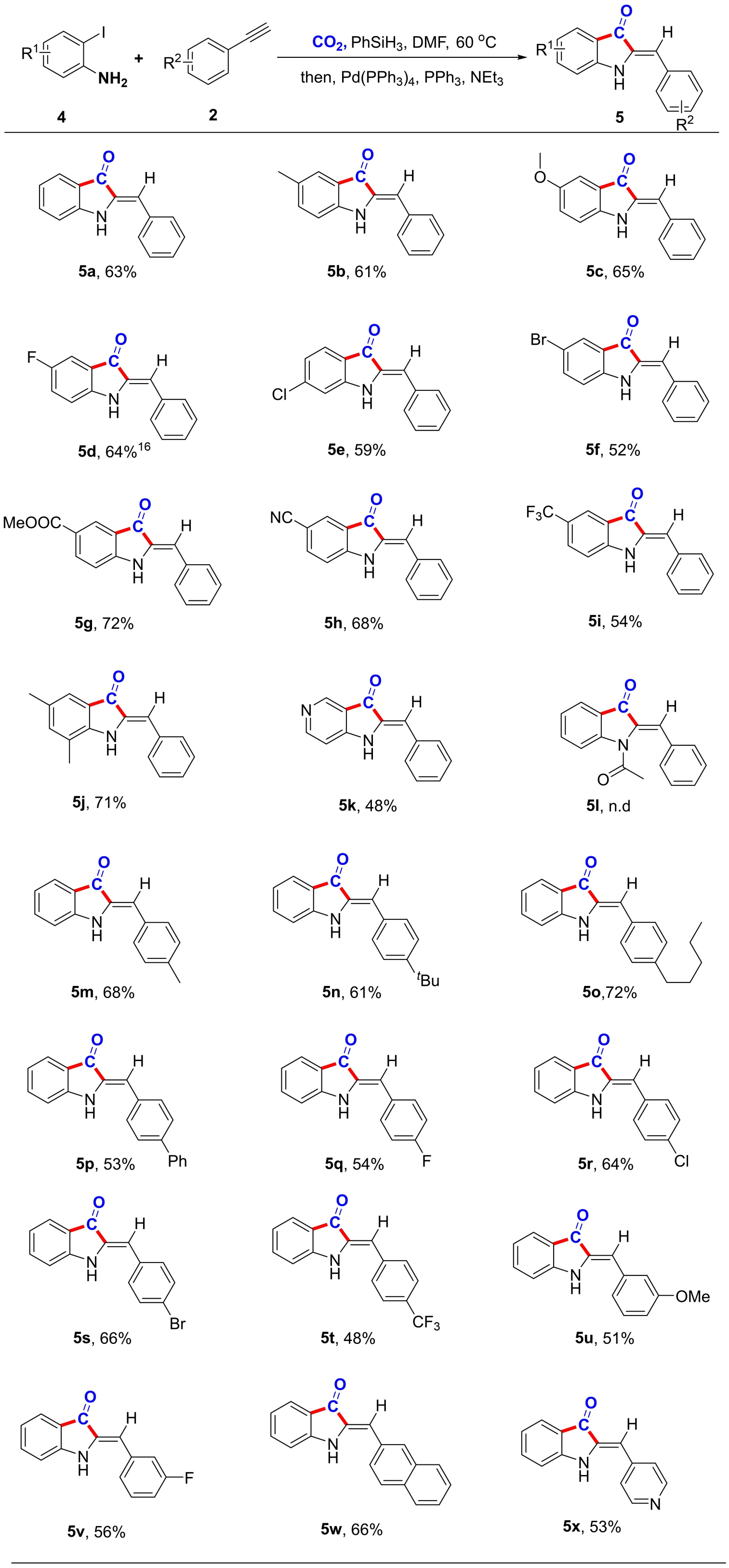
Scheme 3. Carbonylative synthesis of alkynones with various aryl iodides. Reaction conditions: the mixture of CO_2 (1 atm), $PhSiH_3$ (0.8 mmol), DMF (2 ml) was first stirred at 60 °C for 3 h, then another mixture of **1** (0.2 mmol), **2a** (0.3 mmol), $Pd(PCy_3)_2Cl_2$ (0.01 mmol), NEt_3 (0.6 mmol) in DMF (1 mL) was added dropwise and stirred for overnight. The yield was the isolated yield.

a deeper understanding of the cyclization process, several control experiments were designed. First, the reaction of CO_2 with **4a** and **2a** under the standard conditions without PPh_3 was carried out, trace amount of the desired product was observed together with the formation of a small amount of non-cyclized product (Scheme 6b). Then, when the intermediate **11** was synthesized and treated with PPh_3 and NEt_3 in DMF at 60 °C for 24 h, the reaction afforded **5a** with 55 % isolated yield and the intermediate **11** with 40 % recovered (Scheme 6c). In contrast, the product **5a** could not be obtained without the addition of PPh_3 (Scheme 6d). These results demonstrated that PPh_3 might not only serve as the ligand but also function as the organocatalyst to promote the intramolecular cyclization of in-situ generated alkynones.

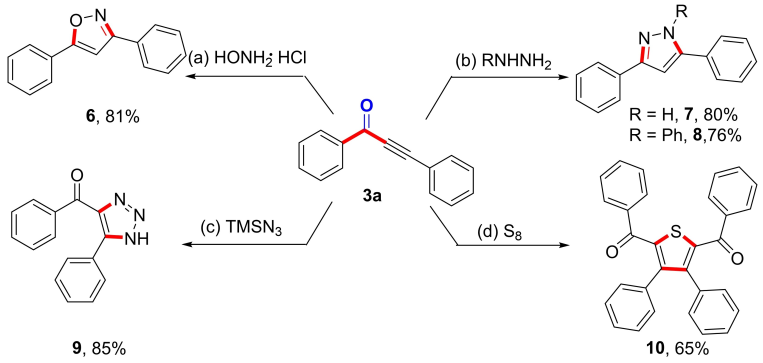
With respect to this transformation, a reaction mechanism was tentatively proposed based on the experimental results as well as the previous works,[15] as showed in Scheme 7. The reduction of CO_2 with the assistance of $PhSiH_3$ will generate CO and release $PhSiH_2OH$. And the generated CO can undergo the insertion with (σ-aryl)palladium species **B** derived from the oxidative addition of palladium(0) **A** with aryl halide **1** or **4** to form intermediate **C**. Then, the intermediate **C** will react with alkynes to give intermediate **D** and release HI in the presence of base, followed by the reductive elimination to afford product **3a** or intermediate **11**. Intermediate **11** can further react with PPh_3 to produce intermediate **E**, which undergoes the isomerization and intramolecular cyclization to yield the product **5a** and release PPh_3.

Conclusions

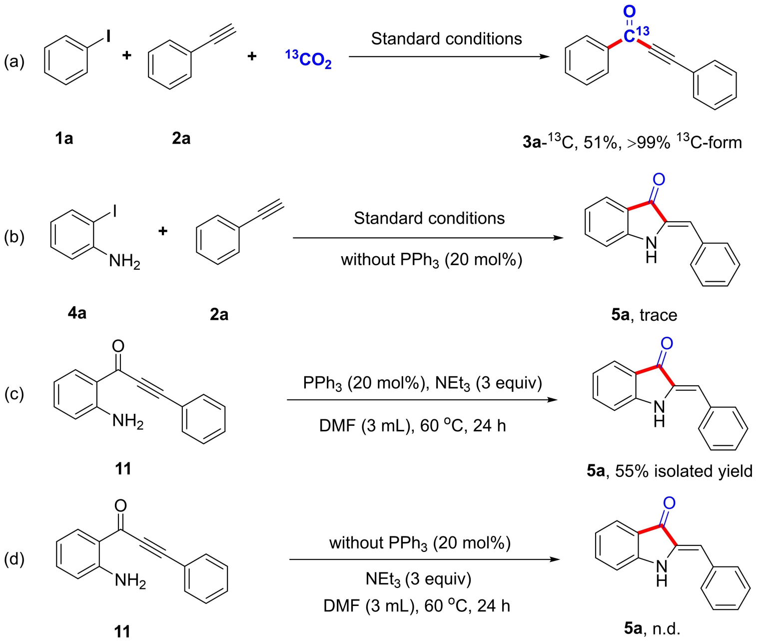
In summary, we have successfully developed a protocol for the palladium-catalyzed carbonylative Sonogashira coupling with CO_2 as the CO source, providing an efficient and practical route to a range of functionalized alkynones and indoxyls under mild reaction conditions. Notably, this method allowed the CO-generating and CO-consuming process to proceed in one pot, thus avoiding the use of two-chamber technique that requires a special apparatus. Simple and safe operation, readily available



Scheme 4. Carbonylative synthesis of indoxyls. Reaction conditions: the mixture of CO_2 (1 atm), $PhSiH_3$ (1.6 mmol), DMF (2 ml) was first stirred at 60 °C for 3 h, then another mixture of **4** (0.2 mmol), **2** (0.3 mmol), $Pd(PPh_3)_4$ (0.01 mmol), PPh_3 (0.04 mmol), NEt_3 (0.6 mmol) in DMF (1 ml) was added dropwise and stirred for 24 h. The yield was the isolated yield.



Scheme 5. The synthesis of heterocycles. Reaction conditions: (a) **3 a** (0.2 mmol), $NH_2OH{\cdot}HCl$ (4 equiv.), KOH (4 equiv.), $MeOH/H_2O$ (v : v = 9 : 1) (4 mL), room temperature; (b) **3 a** (0.2 mmol), $PhNHNH_2$ (0.3 mmol), room temperature, 1 h; (c) **3 a** (0.2 mmol), $TMSN_3$ (0.6 mmol), CuI (5 mol%), DMF : MeOH = 5 : 1, reflux, 24 h. (d) **3 a** (0.4 mmol), S_8 (3/8 mmol), KOH (1 equiv.), toluene (2.0 mL), 100 °C, 3 h.



Scheme 6. The isotopic tracing experiment and control experiments.

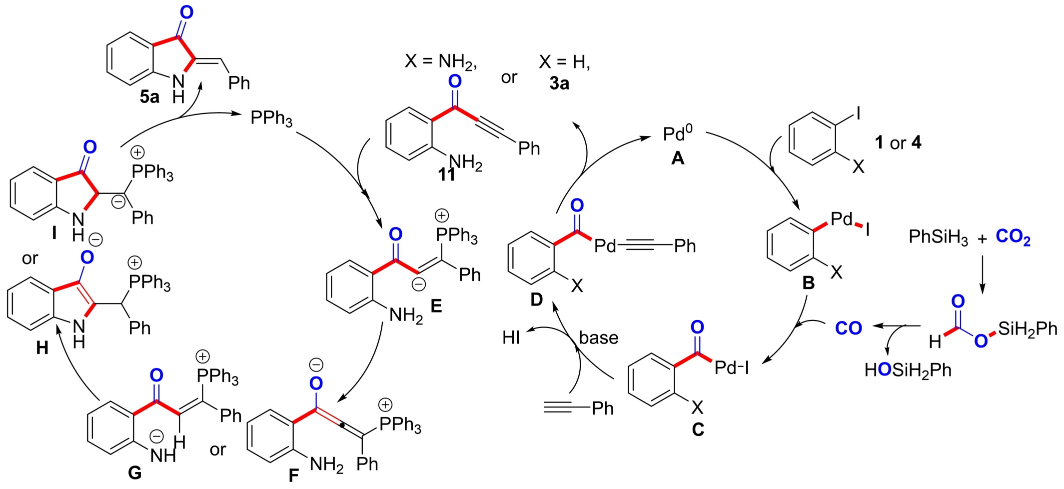
substrates, good functional group tolerance and mild reaction conditions were the features of this reaction. Further application of this strategy to the efficient conversion of CO_2 into valuable chemicals are underway in our laboratory.

Experimental Section

^1H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer in solutions of $CDCl_3$ or CD_3SOCD_3 with tetramethylsilane as an internal standard. The chemical shifts (δ) are referenced to signals at 7.26 and 77.0 ppm, respectively. Multiplicity was indicated as follows: s(singlet), d(doublet), t(triplet), q(quartet), m(multiplet). Coupling constants were given in Hertz (Hz). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Melting points were measured on a Büchi Melting Point B-545 instrument and were uncorrected. The data of HR-MS was conducted on a high-resolution mass spectrometer (LCMS-IT-TOF). Thin-layer chromatography was performed using Qingdao-Haiyang 600 mesh silica gel plates (GF254) and samples were made visual with short-wavelength UV light (254 nm). X-ray structural analyses were carried out an x-ray analysis instrument. All new compounds were characterized by ^1H NMR, ^{13}C NMR and HRMS. The known compounds were characterized by ^1H NMR and ^{13}C NMR. Unless otherwise stated, all manipulations were carried out by using standard Schlenk techniques, and all anhydrous solvents and reagents were commercially purchased and used without further purification.

General procedure for the Pd-catalyzed carbonylative Sonogashira coupling of aryl iodides, alkynes and CO_2

In a glove box, a solution of the phenylsilane (0.8 mmol) in DMF (2 mL) was added to a 25 mL Schlenk tube equipped with a Teflon



Scheme 7. Proposed reaction mechanism.

cap and a magnetic stirring bar. After the sealed tube was taken out of the glovebox, the mixture was subjected to vacuum for a while and CO_2 (1 atm) was introduced into the reaction vessel. After the reaction mixture was stirred at 60 °C for 3 h, a solution of aryl iodides **1** (0.2 mmol), alkynes **2** (0.3 mmol), $Pd(PCy_3)_2Cl_2$ (0.01 mmol), NEt_3 (0.6 mmol) in DMF (1 mL) was added dropwise and stirred for overnight. After completion of the reaction, the residual material was carefully quenched with water and extracted several times with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the product **3**.

General procedure for the one-step Pd-catalyzed carbonylative Sonogashira coupling of 2-iodoanilines, phenyl acetylene and CO_2

In a glove box, a solution of the phenylsilane (1.6 mmol) in DMF (2 mL) was added to a 25 mL Schlenk tube equipped with a Teflon cap and a magnetic stirring bar. After the sealed tube was taken out of the glovebox, the mixture was subjected to vacuum for a while and CO_2 (1 atm) was introduced into the reaction vessel. After the reaction mixture was stirred at 60 °C for 3 h, a solution of 2-iodoanilines **4** (0.2 mmol), alkynes **2** (0.3 mmol), $Pd(PPh_3)_4$ (0.01 mmol), PPh_3 (0.04 mmol), NEt_3 (0.6 mmol) in DMF (1 mL) was added dropwise and stirred for 24 h. After completion of the reaction, the residual material was carefully quenched with water and extracted several times with ethyl acetate. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the product **5**.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Pd-catalyzed · carbonylative Sonogashira · carbon dioxide · simple and safe operation

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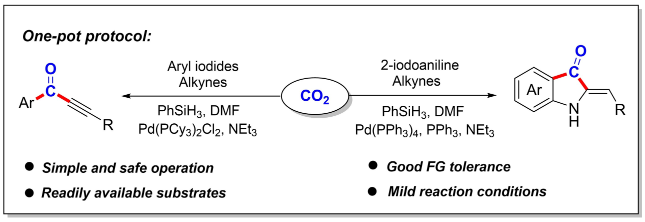

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One-Pot Palladium-Catalyzed Carbonylative Sonogashira Coupling using Carbon Dioxide as Carbonyl Source

One-pot synthesis: We report a practical one-pot protocol using carbon dioxide as the carbonyl source for the palladium-catalyzed carbonylative Sonogashira coupling, providing an efficient and practical route to a wide range of functionalized alkynones and indoxyls under mild reaction conditions.