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Pd-catalyzed decarboxylative alkynylation of alkynyl carboxylic acids with arylsulfonyl hydrazides via desulfinative process

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Abstract

In the presence of Pd(II)/P-ligand catalytic system, decarboxylative alkynylation of alkynyl carboxylic acids and arylsulfonyl hydrazides by desulfinative coupling could present either aryl alkynes in satisfactory yields by judiciously selecting palladium catalysts or modulating phosphine ligands under mild conditions. The reported coupling reactions are very practical as they do not require the protection of inert gas or oxygen and tolerant to many functional groups.

Keywords Pd-catalyzed, decarboxylative alkynylation, alkynyl carboxylic acids,

arylsulfonyl hydrazides

Introduction

Functionalized aryl and heteroaryl alkynes are highly valuable classes of compounds, which are not only important tools, structural elements in material sciences and chemical biology, but also versatile building blocks in contemporary organic synthesis.[1] Such compounds are commonly formed by the coupling of aryl or heteroaryl halides with terminal acetylenes catalyzed by palladium and other transition metals, commonly termed as Sonogashira cross-coupling reaction. It is one of the most important and widely used sp^2–sp carbon–carbon bond formation reactions in organic synthesis, frequently employed in the synthesis of natural products, heterocycles, biologically active molecules, molecular electronics, dendrimers and conjugated polymers or nanostructures.[2]

Recently, the direct alkynylation of (hetero)aromatic compounds has appeared as an alternative to the Sonogashira reaction by using the alkynyl reagents prepared from terminal alkynes, such as alkynyl halides,[3] benziodoxolone-based hypervalent iodine reagents,[4] or arylsulfonylacetylenes.[5] Alkynyl carboxylic acids are employed as alkyne synthons yet demonstrate a sharp discrepancy in reactivity and selectivity compared to terminal alkynes and related. It offers a novel method to obtain alkyne products using aldehyde as precursor which are more accessible and cheaper than alkyne related. One attractive alternative synthetic strategy to access internal alkynes that has emerged recently is the transition-metal catalyzed decarboxylative cross-coupling of aryl halides with alkynyl carboxylic acids catalyzed by palladium, [6]

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nickel[7] or copper.[8] Recently, Lee et al. reported palladium-catalyzed decarboxylative coupling of alkynyl carboxylic acids with aryl/alkenyl tosylates as pseudohalides for the synthesis of aryl alkynes/enynones.[9] Nagarkar et al. reported Pd-catalyzed decarboxylative Sonogashira reaction with arene diazonium tetrafluoroborate under ligand and co-catalyst free conditions. [10] Organometallic compounds such as arylboronic acid,[11] aryl silanes [12] and triarylbismuth reagents[13] have also been employed in the palladium or nickel-catalyzed decarboxylative Sonogashira coupling reaction with alkynyl carboxylic acids. However, the use of boronic acids possess some difficulty to purify and stoichiometry due to the formation of boroximes, likewise the use of aryl silanes possess some difficulty in preparation and require the introduce of fluoride or hydroxide ion to activate organosilanes.[14] Although many coupling methods have been described, however, the desulfinative & decarboxylative coupling Sonogashira reaction was still obscured. In view of the recent progress in desulfinative coupling, it is highly desirable to develop new strategies of decarboxylative alkynylation for more convenient and efficient Csp−C bond formations.

Commercial aryl sulfonyl/sulfinate compounds[15] are recognized as the new aryl sources that are universally utilized in desulfinative arylation reactions recently.[16] Notably, owing to the features of good stability, versatile transformation models, compatible with water and free of unpleasant odor, arylsulfonyl hydrazines are regarded as particularly favorable aryl precursors in desulfination reactions by C−S bond cleavage. Pd-catalyzed desulfinative cross-coupling of arylsulfonyl hydrazides

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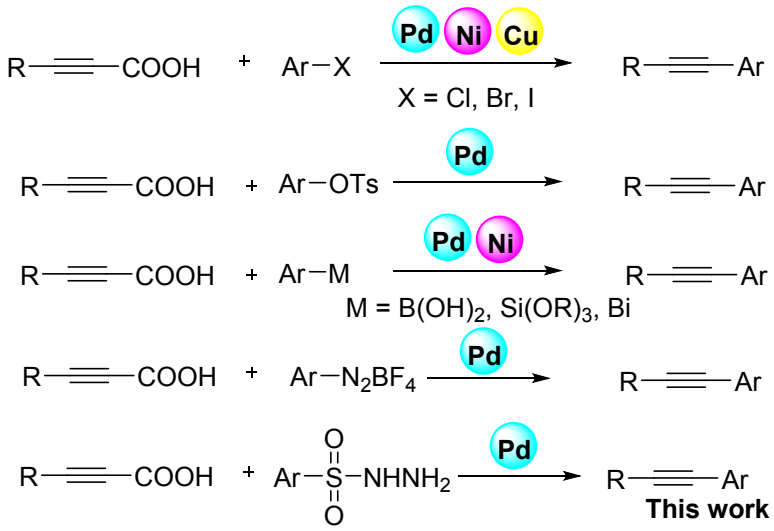
have been well studied these years. Tian et al. first employed arylsulfonyl hydrazides as aryl sources in Heck-type coupling reactions via desulfitation processes.[17] Subsquently, arylsulfonyl hydrazides were employed as aryl sources in Hiyama[18] coupling, Suzuki[19] coupling, homocoupling,[20] iodination[21] and addition[22]. It is noted that the groups of Dong and Zhou reported palladium-catalyzed desulfitative Sonogashira coupling of arylsulfonyl hydrazides with terminal alkynes.[23] However, the development of new-type Pd-catalyzed decarboxylative & desulfinative cross-coupling[24] of arylsulfonyl hydrazides was still highly desirable. Herein we reported the example of decarboxylative & desulfinative coupling of alkynyl carboxylic acids with arylsulfonyl hydrazides with good to excellent efficiency.



Scheme 1 Transition-metal-catalyzed cross-coupling of alkynyl carboxylic acids to afford aryl alkynes

Results and Discussion

With our continuous interest on the oxidative palladium-catalyzed cross-coupling,[25] we initially tried to investigate the decarboxylative & desulfinative coupling of corresponding alkynyl carboxylic acid derivatives with arylsulfonyl hydrazides (Table

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1). To our delight, when phenylpropiolic acids and phenylsulfonyl hydrazide was stirred in DMA in the presence of $Pd(OAc)_2$ and K_2CO_3 under air, the alkynylated product was obtained although in low yield (Table 1, entry 1). It is noteworthy that significant improvement was achieved when PPh_3 was employed as ligand (Table 1, entry 2). The screening of trialkyl phosphine ligands, such as PCy_3, P(*t*-Bu)$_3$ and P(*n*-Bu)$_3$, gave modest yields (Table 1, entries 3−5). We then screened the combination of $Pd(OAc)_2$ and some common triaryl phosphine ligands including P(*o*-tol)$_3$ or P(*p*-tol)$_3$, no better results were obtained (Table 1, entries 6−7). To our delight, among the triaryloxy phosphine ligands tested ($P(OPh)_3$, $P(OMe)_3$), $P(OPh)_3$ was shown the best efficiency (Table 1, entries 8−9). Interestingly, TFP (trifurylphosphine) could also be an efficient ligand with a slightly low efficiency (Table 1, entry 10). We also tried to use the $Pd(OAc)_2$ with the nitrogen ligand, however, the use of 1,10-phenanthroline (phen) did not work (Table 1, entry 11). Various palladium catalyzed systems were then examined. Application of $Pd(PPh_3)_4$ as catalysts yielded traces of desired product (Table 1, entry 12). It was observed that most of the Pd(II) catalysts could successfully promote the reaction (Table 1, entries 13−17). Therefore, $PdCl_2$ and $Pd(TFA)_2$ in combination with $P(OPh)_3$ was applied with less effective affording alkynylated product in yields varying between 66% and 73% (Table 1, entries 13−14). The introduction of various palladium with phosphine ligands ($Pd(dppe)Cl_2$, $Pd(PPh_3)_3Cl_2$ and $Pd(dppp)Cl_2$) slightly increased the yields (Table 1, entries 15–17). Among the Pd(II) catalysts tested, $Pd(dppf)Cl_2$ was the most effective affording the addition product in 88% yield (Table 1, entry 18). (Optimization table of bases and

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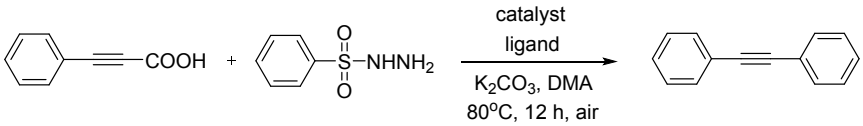
solvents was putted in SI section) Clearly, desired product was not generated in the absence of a palladium catalyst or an base (Table 1, entries 19−20). We subsequently explored the effect on the reaction yield of other variations such as temperature, solvents, concertrtion, use of various bases, etc. The details were summarized in the Supporting Information (Table SI).

Table 1. Optimization of palladium-catalyzed coupling of phenylsulfonyl hydrazide and phenylpropiolic acid [a]



entry	ligand	catalyst	yield (%) [b]
1	-	$Pd(OAc)_2$	15
2	PPh_3	$Pd(OAc)_2$	58
3	PCy_3	$Pd(OAc)_2$	47
4	P(*t*-Bu)$_3$	$Pd(OAc)_2$	41
5	P(*n*-Bu)$_3$	$Pd(OAc)_2$	53
6	P(*o*-tol)$_3$	$Pd(OAc)_2$	62
7	P(*p*-tol)$_3$	$Pd(OAc)_2$	71
8	$P(OPh)_3$	$Pd(OAc)_2$	75
9	$P(OMe)_3$	$Pd(OAc)_2$	50
10	TFP	$Pd(OAc)_2$	74
11	phen	$Pd(OAc)_2$	<5

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12	$P(OPh)_3$	$Pd(PPh_3)_4$	-
13	$P(OPh)_3$	$PdCl_2$	66
14	$P(OPh)_3$	$Pd(TFA)_2$	73
15	$P(OPh)_3$	$Pd(dppe)Cl_2$	79
16	$P(OPh)_3$	$Pd(PPh_3)_3Cl_2$	84
17	$P(OPh)_3$	$Pd(dppp)Cl_2$	**87**
18	**$P(OPh)_3$**	**$Pd(dppf)Cl_2$**	**88**
19	$P(OPh)_3$	$Pd(dppf)Cl_2$	- [c]
20	$P(OPh)_3$	-	-

[a] Reaction conditions: phenylpropiolic acid (1.0 mmol), phenylsulfonyl hydrazide (1.1 mmol), catalyst (0.05 mmol), ligand (0.1 mmol), K_2CO_3 (1.5 mmol), DMA (1 mL), 80 °C, 12 h, under air. [b] Isolated yields. [c] The reaction was done without K_2CO_3.

With the establishment of these optimum conditions, the scope of palladium-catalyzed desulfinative cross-coupling reaction was first evaluated (Table 2). First, 4-methoxy-phenylsulfonyl hydrazide was fixed as the substrate to test various substituted propiolic acids derivatives. Generally, introduction of methoxy, methyl, ethyl, *n*-butyl and nitro substituents into *para* positions of the benzene ring was well tolerated, and the reaction efficiency was marginally affected by such electronic perturbation (Table 2, **2a-2e**). Furthermore, the reaction efficiency was essentially not affected when a 3-methyl or 3-bromo group was introduced (Table 2,

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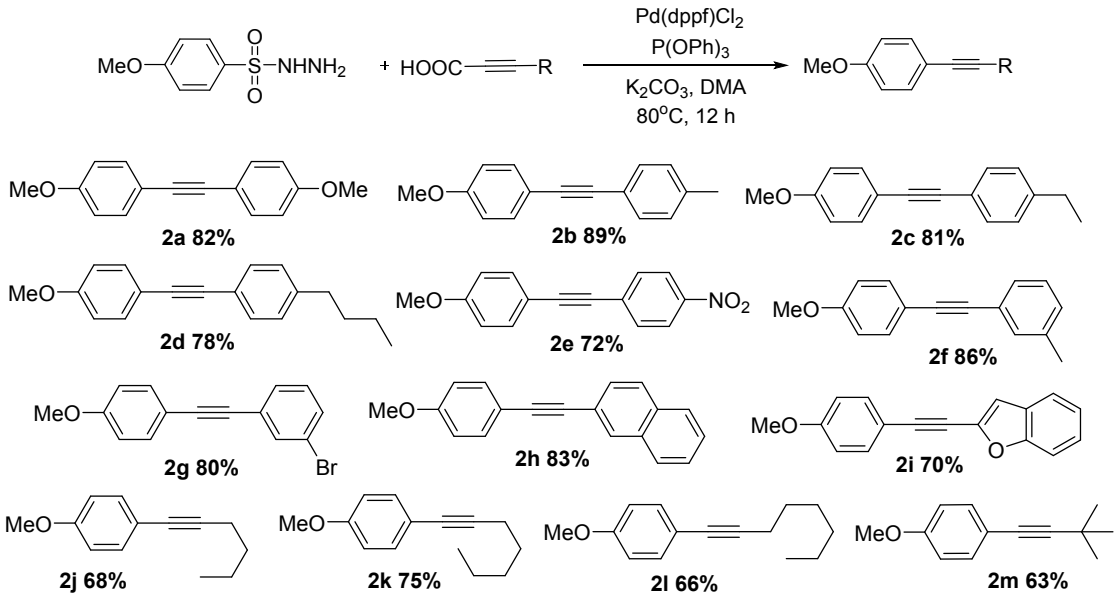
2f-2g). Halogen substituted phenyl propiolic acid was also reactive under this reaction condition without influence of C-Br bond (Table 2, **2g**). Fused-ring substrate such as naphthalen-2-yl propiolic acid was coupled with 4-methoxy-phenylsulfonyl hydrazide smoothly (Table 2, **2h**). The applicability of the method towards heteroaryl propiolic acid derivatives was also tested with good efficiency (Table 2, **2i**). The scope of the alkylpropiolic acids substrate was then examined, indicating that the reaction's broad feasibility. In general, various *n*-alkyl-substituted propiolic acids all underwent smooth coupling with 4-methoxy-phenylsulfonyl hydrazide under the standard conditions to afford the alkyne products in 66%-75% yields (Table 2, **2j-2l**). Furthermore, *t*-butyl-substituted propiolic acids coupled with comparably efficiency (Table 2, **2m**).

Table 2. Scope of Pd-catalyzed coupling of alkynyl carboxylic acids with 4-methoxy-phenylsulfonyl hydrazide [a,b]



[a] Reaction conditions: alkynyl carboxylic acids (1.0 mmol), 4-methoxy-phenylsulfonyl hydrazide

(1.1 mmol), $Pd(dppf)Cl_2$ (0.05 mmol), $P(OPh)_3$ (0.1 mmol), K_2CO_3 (1.5 mmol), DMA (1 mL), 80 °C, 12 h, under air. [b] Isolated yields.

We next examined the scope of the method with different arylsulfonyl hydrazide derivatives. As presented in Table 3, the desired products **3a-3b** were obtained in good yields with alkyl substituents like methyl, ethyl at 4-position of the phenyl ring. Likewise, the reaction exhibited good reactivity with substrates having no substituent (Table 3, **3c**). Various functional groups commonly utilized in organic synthesis were fully compatible with the simple cross-coupling method. Accordingly, substrates bearing methoxy, nitro, chloro, trifluoro methyl, acetyl, and ester functionalities at phenyl ring were all smoothly coupled in high yields (Table 3, **3d-3i**). The reaction delivered alkynylated aromatic compounds **3j-3k** in good yields having trifluoromethoxy or bromo substituent on the benzene moiety. Electron-rich substrates bearing methoxy (**3l**) and methyl (**3m**) substituents on the phenyl ring and arylsulfonyl hydrazide bearing electron deficient functional group such as trifluoromethyl (**3n**) at *meta*-position underwent the decarboxylative cross-coupling in good yields. As expected, the reaction furnished the desired product (**3o**) in good yield with 3-iodophenyl sulfonyl hydrazide. Substrates having *ortho*-methoxy (**3p**), *ortho*-methyl (**3q**), *ortho*-chloro (**3r**), or *ortho*-trifluoromethyl (**3s**) substituents at phenyl moiety gave slightly lower reactivity, presumably due to steric reason. The substrate scope of this transformation was further extended to the synthesis of fused ring and heteroaryl derivatives (Table 3, **3t–3u**), which were afforded in moderate yields. For the substrates bearing two sulfonyl hydrazide, the desired douple alkynylated products (**3v**) were obtained smoothly.

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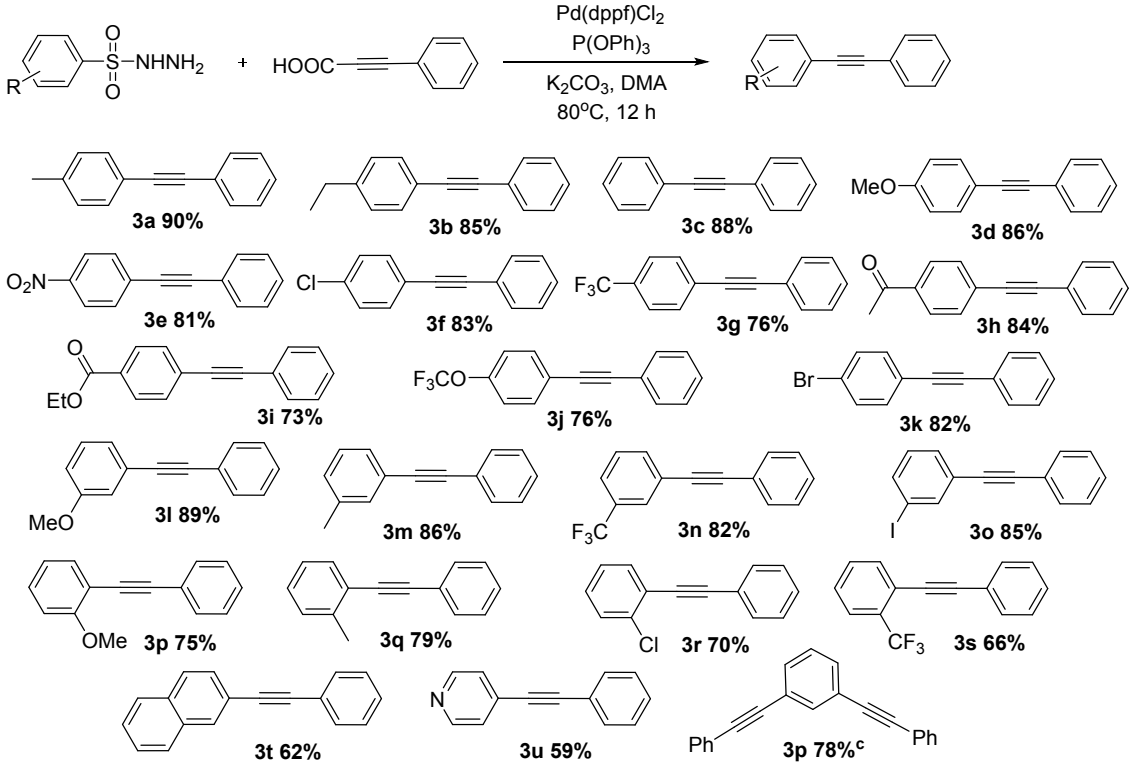
Table 3. Scope of Pd-catalyzed coupling of phenylpropiolic acid with arylsulfonyl hydrazide [a,b]



[a] Reaction conditions: phenylpropiolic acid (1.0 mmol), arylsulfonyl hydrazide (1.1 mmol), $Pd(dppf)Cl_2$ (0.05 mmol), $P(OPh)_3$ (0.1 mmol), K_2CO_3 (1.5 mmol), DMA (1 mL), 80 °C, 12 h, under air. [b] Isolated yields.[c] phenylpropiolic acid (2.0 mmol), benzene-1,3-disulfonyl hydrazide (1.0 mmol).

Preliminary studies were performed to gain insight into the reaction mechanism (Scheme 2). The cross-coupling reaction could not be terminated by radical scavenger (such as TEMPO), and decent yield of desired products were detected under standard conditions (Scheme 2, Eq 1). The radical pathway could be ruled out. Potassium 3-phenylpropiolate could coupled with phenylsulfonyl hydrazide under standard condtions in the yield of 85%, which indicate that carboxylic acid anion might be involved in this coupling process (Scheme 2, Eq 2). The replacement of phenylsulfonyl hydrazide with phenyl sulfonamide could not afford alkynylated

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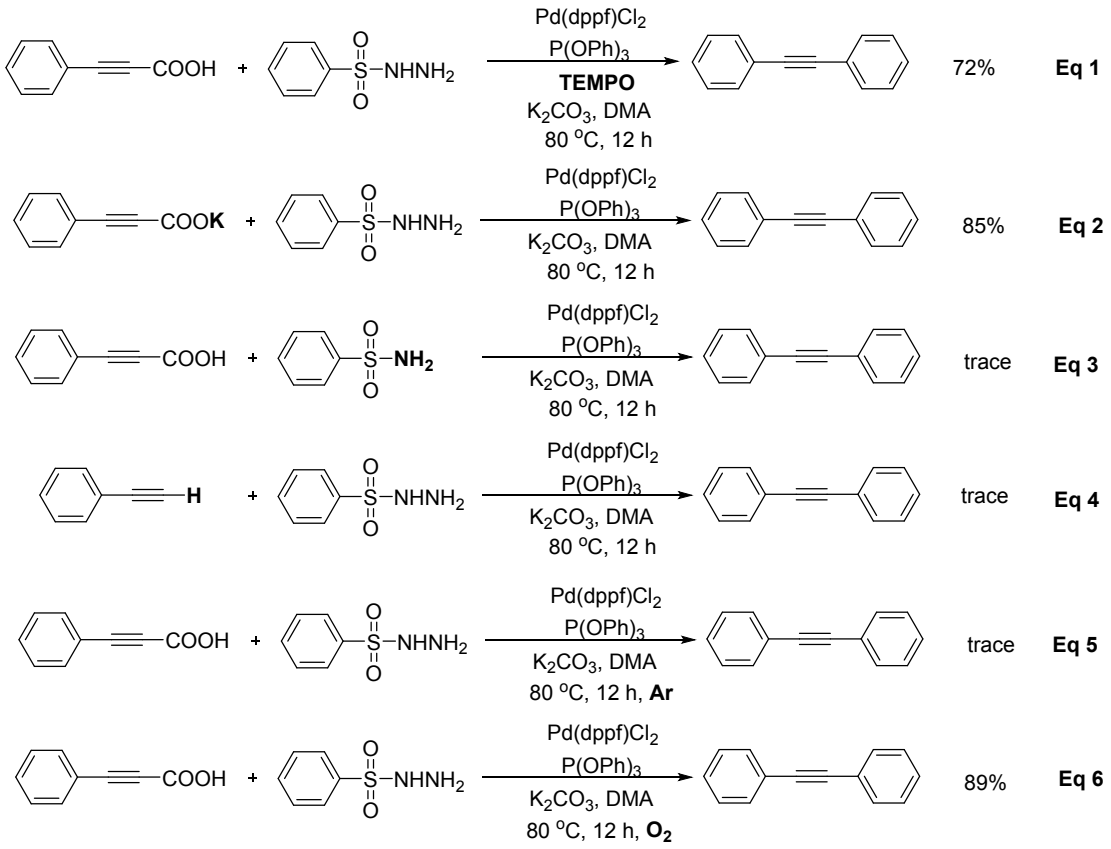
product, and the coupling of phenylsulfonyl hydrazide with phenylacetylene could not been proceeded either (Scheme 2, Eq 3 and Eq 4). The controlled experiments revealed that the cross-coupling transformation could be surpressed under the protection of argon, and the yield of alkynylated product was not enhanced under oxygen atmosphere, revealed that oxygen is indispensable for the reaction (Scheme 2, Eq 5 and Eq 6).



Scheme 2. Control experiments for decarboxylative & desulfinative coupling.

According to the above result, a tentative mechanism for palladium-catalyzed decarboxylative & desulfinative coupling was outlined in Scheme 3. The initial step would be the reaction of the ligand coordinated Pd(II)-complex with arylsulfonyl hydrazide gives an Pd(II) intermediate A by deprotonation, then (arylsulfonyl)diazene was generated via β-hydride elimination. Pd(II)-complex **B** was formed by another

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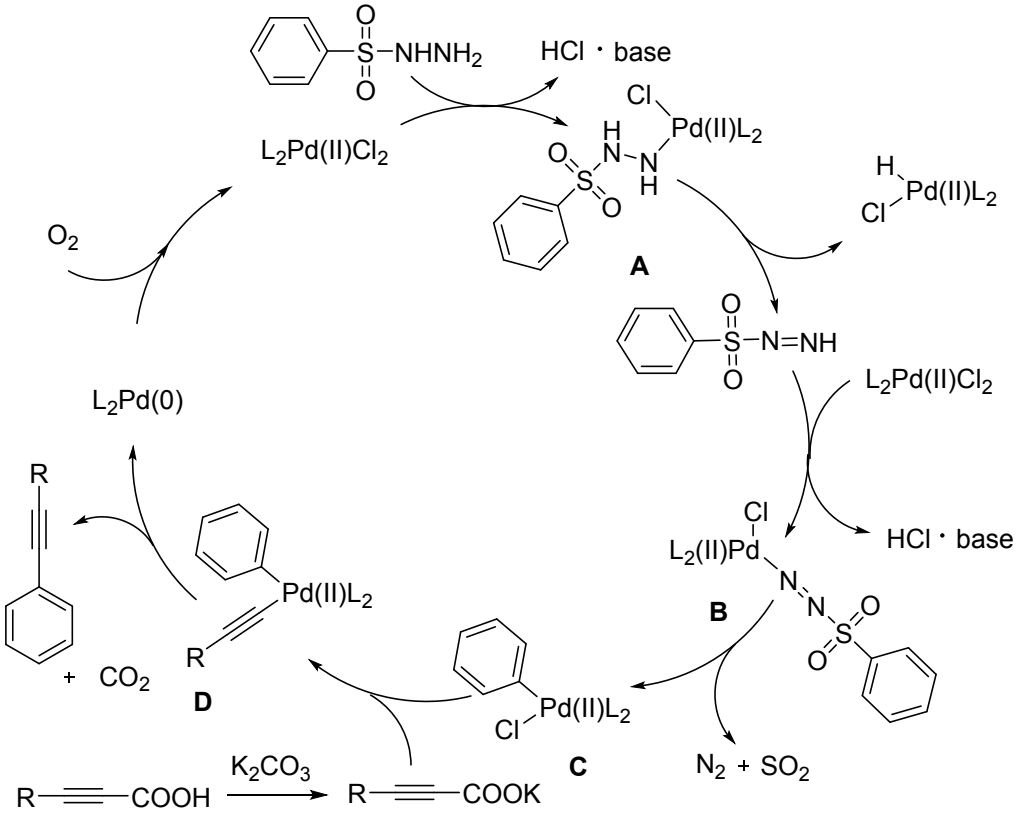
deprotonation with (arylsulfonyl)diazene, and providing ArPd(II)Cl intermediate (**C**) by liberation of N_2 and SO_2. Transmetallation of species **C** with the *in situ* generated potassium 3-propiolate gives intermediate **D**, which then undergoes reductive elimination to give the desired cross-coupling product with the release of CO_2. The Pd(II) species are then regenerated through the oxidation of the Pd(0) species with oxygen to complete the catalytic cycle.



Scheme 3. Possible Mechanism for Decarboxylative & Desulfinative Coupling

Conclusion

In conclusion, we have reported the first decarboxylative & desulfinative coupling with alkynyl carboxylic acids and arylsulfonyl hydrazides. This strategy provide new methods for the decarboxylative alkynylation by exploiting a decarboxylative & desulfinative process. We expect that these new synthetic methods will be of great

interest in the synthesis of versatile aryl alkynes building blocks and may enable the development of a broad range of Pd-catalyzed reactions through decarboxylative & desulfinative pathway.

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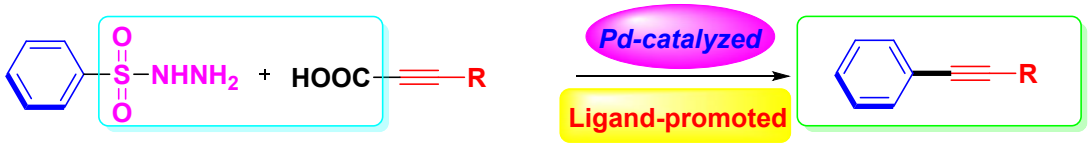
The decarboxylative alkynylation of alkynyl carboxylic acids and arylsulfonyl hydrazides by desulfinative coupling could present either aryl alkynes in satisfactory yields by judiciously selecting palladium catalysts or modulating phosphine ligands under mild conditions.



Decarboxylative & Desulfinative Alkynylation