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SHORT COMMUNICATION

(E)-N-(pyren-1-ylmethylene)benzenamine: efficient promoter for additive-free palladium catalyzed aerobic oxidative coupling of arylboronic acids and terminal alkynes

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Abstract

A highly productive protocol for the synthesis of internal alkynes by the carbon–carbon cross-coupling reactions of electronically different arylboronic acids with substituted phenylacetylenes was described by employing (E)-N-(pyren-1-ylmethylene)benzenamine with $Pd(OAc)_2$. The influence of reaction parameters such as solvent, base and reaction temperature in this carbon–carbon cross-coupling reaction was also investigated. The substrate scope could be expanded to electron-poor alkynes, for which the conventional Sonogashira reaction gives poor yields. Moderate to excellent yield was obtained in the oxidative Sonogashira-type coupling reaction.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s11696-020-01156-8) contains supplementary material, which is available to authorized users.

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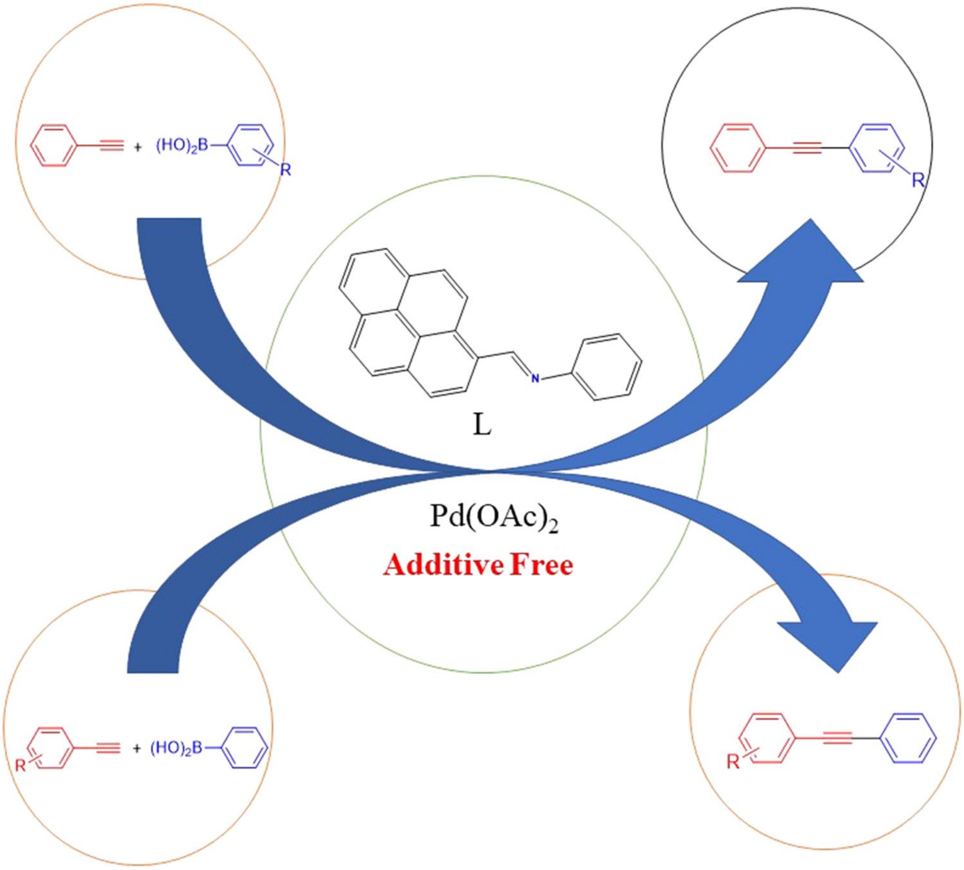
Graphic abstract



Keywords Schiff base · Palladium-catalyzed · Oxidative Sonogashira-type · C–C coupling · Diaryl acetylenes

Internal alkynes moiety has wide application in daily life and is encountered as building blocks in numerous medicines, natural products, dendrimers (Agou et al. 2009), macrocycles (Liu et al. 2009), optoelectronic materials (Balsukuri et al. 2015), fine chemicals (Dasaradhan et al. 2015; Prabhu and Ramesh 2016), etc. Hence, reaction protocols that provide an efficient access to internal alkynes are greatly desirable. Many synthetic protocols are reported for the generation of diaryl acetylenes. The palladium-catalyzed and CuI co-catalyzed coupling reaction of aryl halides and terminal acetylenes, also known as the Sonogashira reaction, is competent and unequivocal methodology for the construction of C(sp^2)–C(sp) bond (Chinchilla and Nájera 2011; Karak et al. 2014). However, from literature reports it is inferred that the use of copper salts which can yield undesired diynes in air or O$_2$ by the Glaser–Hay-type homo-coupling of alkynes. In addition, highly sensitive and potentially explosive copper acetylides can also form, thereby decreasing the productivity of the reaction. Though different ligand systems have been used for the palladium-catalyzed Sonogashira reaction under copper free conditions (Chinchilla and Nájera 2007; Fortman and Nolan 2011; Singh and Verma 2011; Sabounchei et al. 2013; Yang et al. 2014; Prabhu and Pal 2015a), some of the main drawbacks of these systems include their availability, high price, laborious and time consuming strategies for synthesis of ligands and corresponding palladium complexes, unstability of ligands, use of inert atmosphere and Schlenk-line techniques, etc. Further, electron-deficient alkynes are not effective substrates in Sonogashira reaction as poor yields are generally observed. These enforce the researchers to develop new, stable, cost-effective and efficient catalytic systems as modifications of the traditional Sonogashira protocol. In recent years, oxidative coupling of terminal alkynes with arylboronic acids mediated by transition metals has transpired as an alternate option for the traditional Sonogashira coupling reaction. This oxidative cross-coupling reaction offers copious superiority, such as mild reaction conditions, carrying out the reaction in the absence of inert atmosphere and high functional group tolerance, many air- and water-stable boronic acid derivatives are commercial available or can be easily prepared, boron residues can be easily removed after the reaction, the reagents and by-products are generally non-toxic, thus explaining the growing attraction in this synthetic methodology. There are some interesting reports on the oxidative coupling between terminal acetylenes with arylboronic acids catalyzed by iron (You et al. 2012), copper (Mao et al. 2008; Pan et al. 2009; Rao et al. 2010; Yasukawa et al. 2011; Li et al. 2012) nickel (Troung et al. 2014; Prabhu and Lakshmipraba 2017) palladium (Zou et al. 2003; Mitsudo et al. 2010; Zhou et al. 2010; Nie et al. 2011; Li et al. 2013; Lu et al. 2014; Xu et al. 2016) or gold (Qian and Zhang 2011) as an alternative to the traditional Sonogashira reaction. However, in most of these reports, additives were required for good yields of the desired product. Although compelling results have been obtained, the development of a milder protocol for this transformation, especially under additive-free conditions, continues to be a central goal of current research in chemistry.

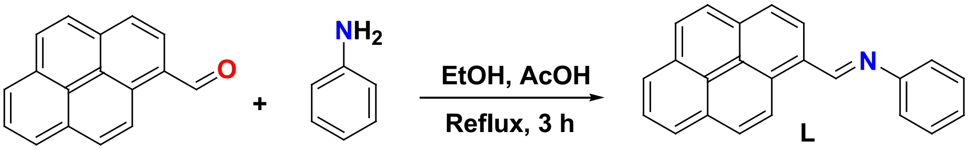
Schiff bases draw considerable attention as ligands due to their ease in preparation, stability and high coordination capacity towards various transition metals (Das and Linert 2016). Further, the steric and electronic properties of Schiff bases could be tuned easily by selecting appropriate substituents on the aldehyde or amine (Abu-Dief and Mohamed 2015). In this paper, we report a straightforward and effectual protocol for the aerobic oxidative Sonogashira reaction of substituted arylboronic acids and electronically different phenylacetylenes by utilizing $Pd(OAc)_2$/(E)-N-(pyren-1-ylmethylene)benzenamine system in the absence of any silver additive. Diverse reaction parameters such as solvent, base and reaction temperature were sequentially optimized for this C(sp^2)–C(sp) coupling reaction before evaluating the scope of the coupling partners. Though there are reports on the synthesis and characterization of Schiff bases derived from 1-pyrenecarboxaldehyde (Shree et al. 2019; Shellaiah et al. 2013), our screening on the literature has revealed that no attention has been paid to explore the Pd-catalyzed synthesis of diaryl acetylenes by the oxidative Sonogashira coupling reaction using (E)-N-(pyren-1-ylmethylene)benzenamine (L).

All the chemicals used in this work were of analytical grade, available commercially and were used as received. Infrared spectra of ligands were recorded as KBr pellets on Perkin Elmer Spectrum RX I spectrophotometer. The NMR spectra were obtained on a Bruker Avance III NMR 400 MHz spectrometer operating at room temperature. ESI mass spectra were recorded on Elmer Clarus 900 C GC–MS spectrometer.

The Schiff base, L, was readily accessible in good yields by the condensation of 1-pyrenecarboxaldehyde with aniline in ethanol (Scheme 1). FT-IR, NMR (^{1}H and ^{13}C) and MS techniques were used to authenticate the purity and identity of L.

The FT-IR of free 1-pyrenecarboxaldehyde and aniline displayed bands due to the free aldehydic group (1700 cm^{-1}) and free $-NH_2$ group (3200 cm^{-1}), respectively. Disappearance of these bands in L indicated the formation of Schiff base. This was further confirmed by the appearance of a new stretching frequency at 1583 cm^{-1} in L. In the ^{1}H NMR spectra of L, the sharp singlet resonance at δ 9.65 ppm indicated the presence of azomethine proton and formation of the Schiff base (Kathiravan et al. 2014, Prabhu and Pal 2015b). This was further confirmed by the absence of the aldehydic proton of 1-pyrenecarboxaldehyde and $-NH_2$ protons of aniline in the ^{1}H NMR spectrum of L. The chemical shifts of the other aromatic protons of L are unexceptional. The ^{13}C NMR spectrum of L, the resonance at δ 158.97 ppm is attributed to the azomethine carbon (Kathiravan et al. 2014). Other carbons of the aromatic group resonate at expected regions. The GC–MS of L exhibited the molecular ion peak at m/z 339.

The unceasing procedure to discover different routes has made us interested in searching for a new methodology for the silver-free $Pd(OAc)_2$-L mediated aerobic oxidative Sonogashira coupling reaction. The generation of catalyst in situ is considered to be appealing because it eliminates the need for the additional tasks of prior synthesis and subsequent characterization of the corresponding metal-complex. In addition, it also provides the flexibility of selecting ligand to partner the available palladium salts based on the requirement of a specific cross-coupling catalysis reaction. The synthesis of 1-methoxy-4-(phenylethynyl)benzene by the coupling between phenylboronic acid and 4-ethynylanisole mediated by $Pd(OAc)_2$/L in air and in the absence of silver salts was first selected as a model system to establish the practical efficacy of the system. The solvent, base and reaction temperature were varied sequentially in order to determine the best reaction conditions. In order to identify a solvent which can enhance the yield of the desired product, initial investigation was implemented on the evaluation of different solvents (Fig. 1). It was inferred that the extent of product formation depended on the solvent used and



Scheme 1 Preparation of Schiff base

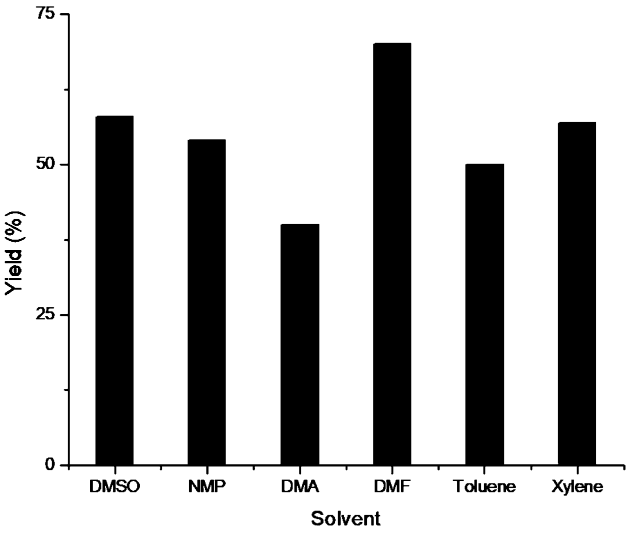


Fig. 1 Effect of solvent on product yield at 100 °C

among the various solvents screened, dimethylformamide (DMF) gave better results. When the reaction was carried out in other solvents such as dimethylsulphoxide (DMSO), N-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMA), toluene and xylene, relatively low but promising isolated yield of the desired internal alkyne was obtained. Therefore, DMF was chosen as relevant solvent for further coupling reactions.

In carbon–carbon cross-coupling reactions, base is known to influence the yield of the product and the effects of various bases were then probed. Evident sensitivity to base used was noted in DMF. The results from the optimization of bases (Fig. 2) revealed that 1,8-diazabicycloundec-7-ene (DBU) had ranked the highest yield (99%) of the desired internal alkyne and was the best choice among other bases. Other organic bases (Et_3N, Bu_3N, pyridine) and inorganic bases (K_2CO_3, $KHCO_3$, K_3PO_4) were found to less efficient in this cross-coupling reaction.

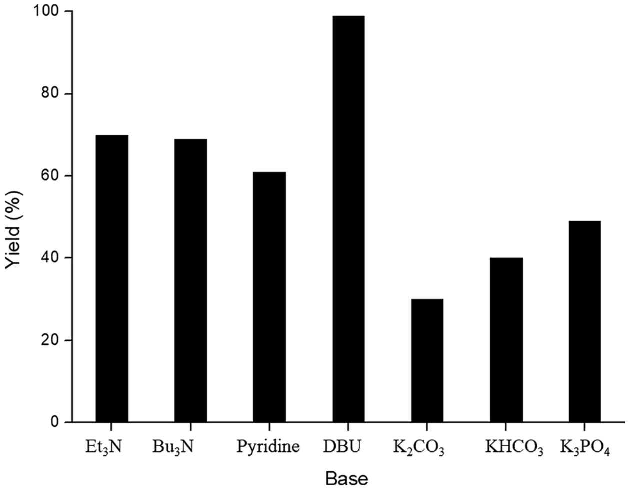


Fig. 2 Effect of base on product yield in DMF at 100 °C

The effect of temperature on the cross-coupling reaction was then probed. As the temperature of the reaction was decreased from 100 °C to 35 °C, a drop in the isolated yield of the product was observed (Fig. 3). At 100 °C, almost quantitative yield of the desired product was observed, whereas at 35 °C only < 10% of the desired product was obtained. Hence, for consequent experiments, DMF–DBU at 100 °C was considered to be optimal condition. Controlled experiments were also carried out in DMF at 100 °C. It was ascertained that in the absence of $Pd(OAc)_2$ or base, the desired product was not formed. Further, though $Pd(OAc)_2$–DBU in DMF could catalyze the oxidative Sonogashira coupling reaction in the absence of L, the efficiency was poor with only 30% yield of the product indicating that L acts as a promoter in this conversion. It is gratifying to say that under the given conditions the homo-coupling by-products of neither the internal alkyne nor the arylboronic acid were detected.

After authenticating the optimal reaction conditions (DMF, DBU, 100 °C, 3 h, in air), in order to comprehend the scope and feasibility of the oxidative Sonogashira reaction, the reaction of phenylboronic acid (as a representative arylboronic acid derivative) with a wide range of substituted phenylacetylenes with diverse electronic effects were surveyed (Table 1). For the ease of correlation of the results, all the coupling reactions were effectuated under identical reaction conditions. It was inferred that the protocol tolerated different functional groups giving the desired internal alkynes in good to excellent isolated yields when electron-donating, electron-neutral and electron-withdrawing substituents were present on the aromatic ring.

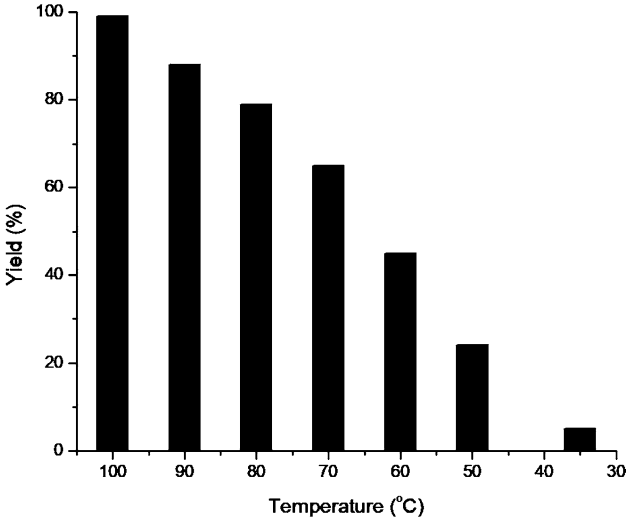
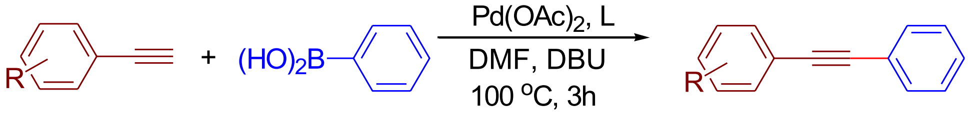
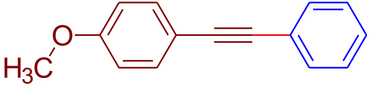
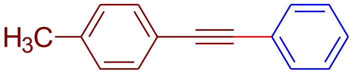
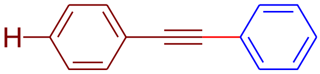
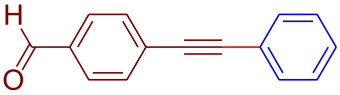
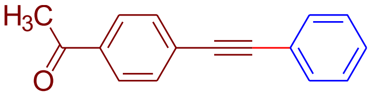
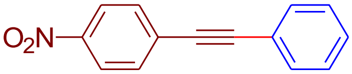
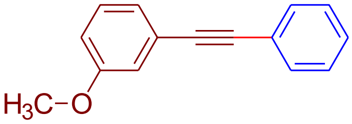
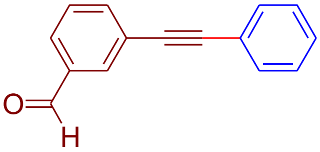
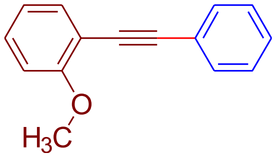
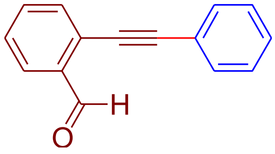


Fig. 3 Effect of reaction temperature on product yield in DMF at 100 °C

Table 1 C–C coupling reactions of phenylboronic acid with substituted phenylacetylene



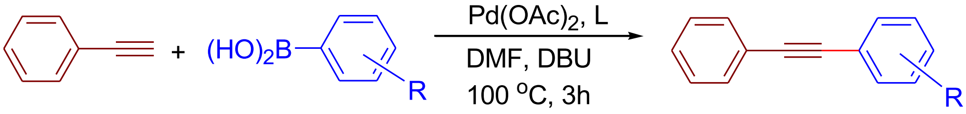
Entry	Product	Yield (%)[a]
1		99
2		97
3		94
4		90
5		87
6		83
7		93
8		85
9		80
10		76

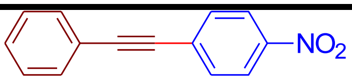
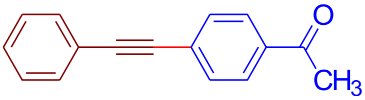
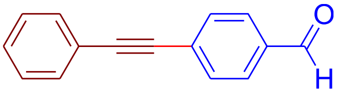
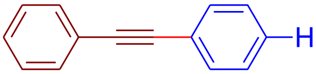
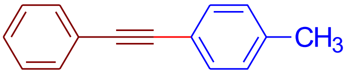
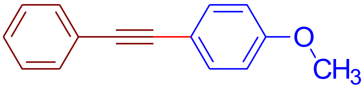
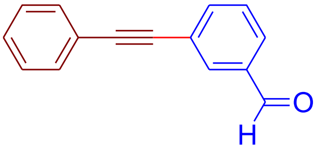
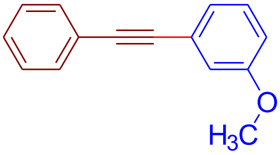
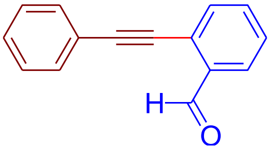
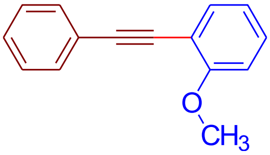
Phenylboronic acid (1.0 mmol), arylacetylene (1.2 mmol), $Pd(OAc)_2$ (1 mol%), L (1 mol%), DMF (5 mL), DBU (2.0 mmol) at 100 °C in air for 3 h

[a] Isolated yield after column chromatography (average of two independent runs)

Substituted phenylacetylenes bearing electron-donating groups (such as 4-methoxy or 4-methyl) reacted effortlessly with phenylboronic acid to afford greater isolated yield of the desired product when compared to phenylacetylene (entries 1-3). When electron-withdrawing groups (such as 4-formyl, 4-acetyl or 4-nitro) were present, the conversion is less when compared to that of phenylacetylene (entries 3-6). Utilization of 3-ethynylanisole and

Table 2 C–C coupling reactions of arylboronic acids with phenylacetylene



Entry	Product	Yield (%)[a]
1	 	96
2	 	92
3	 	90
4	 	86
5	 	82
6	 	78
7	 	76
8	 	72
9	 	70
10	 	64

Arylboronic acid (1.0 mmol), phenylacetylene (1.2 mmol), $Pd(OAc)_2$ (1 mol%), L (1 mol%), DMF (5 mL), DBU (2.0 mmol) at 100 °C in air for 3 h

[a] Isolated yield after column chromatography (average of two independent runs)

3-ethynylbenzaldehyde (entries 7,8) as coupling partners, afforded the desired products with yields comparable to that of the corresponding para substituted derivatives (entries 1,4). Ortho substituted derivatives such as 2-ethynylanisole and 2-ethynylbenzaldehyde (entries 9, 10) were also compatible in the employed protocol. However, they resulted in slightly inferior yields than the corresponding para substituted derivatives (entries 1,4) which could be due to the steric effects as expected.

Additional coupling reactions were then effectuated in an inverted manner: i.e., with functionalized arylboronic acids and phenylacetylene (as a representative terminal acetylene derivative) to determine the generality of this catalytic method towards different arylboronic acids (Table 2). All the coupling reactions were carried out under identical reaction conditions for the ease of comparison of results. It was inferred that the substituted arylboronic acids reacted smoothly with phenylacetylene to furnish the corresponding internal alkynes in good to excellent yields, when electron-withdrawing (such as 4-nitro, 4-acetyl or 4-formyl), electron neutral and electron-donating (such as 4-methyl or 4-methoxy) substituents were present on the arylboronic acids. Fabulously, aryl boronic acids bearing electron-withdrawing groups afforded superior isolated yield of the desired product (up to 96%) when compared with those having electron donating groups. Utilization of 3-formylphenylboronic acid and 3-methoxyphenylboronic acid as coupling partners (entries 7,8) in this reaction resulted in the formation of the corresponding desired products in good yields. However, employment of 2-formylphenylboronic acid and 2-methoxyphenylboronic acid (entries 9,10) resulted in slightly reduced yields than for the corresponding para derivatives (entries 1,5) which may be due to steric effects.

The salient features of this protocol include simple and convenient reaction procedure, insensitivity towards air and moisture, non-necessity of any inert atmosphere, absence of silver additive, ease of handling of the reagents, lower reaction time, broad substrate scope and simple workup procedure. Though we have not carried out any mechanistic investigation, it is likely that L binds to the Pd-centre resulting in a cyclometallated complex which acts as the actual catalyst in this cross-coupling reaction (Han et al. 2011; Rao and Pal 2014). Further, though there are a few reports on the Pd-catalyzed oxidative Sonogashira reactions, a direct comparison of the present catalytic system with those reported earlier is difficult due to the differences in the reaction conditions such as solvent, base, temperature, reaction time and catalyst loading. However, in terms of isolated yields, the catalytic efficiency of the present protocol is found to be comparable or even slightly superior to some of the previously reports on oxidative Sonogashira cross-coupling reaction (Zou et al., 2003; Yang and Wu 2007; Lu et al. 2014).

Conclusions

In conclusion, a new facile protocol was developed using (E)-N-(pyren-1-ylmethylene)benzenamine as promoter for the silver-free palladium-catalyzed synthesis of internal alkynes by the C(sp^2)–C(sp) coupling reactions between arylboronic acids with substituted phenylacetylenes under aerobic conditions. The substrate scope could be extended to electron-neutral, electron-rich as well as electron-poor arylboronic acids and substituted phenylacetylenes to yield the desired products in satisfactory to excellent isolated yields. The substrate scope can include electron-deficient alkynes for which the traditional Sonogashira reaction does not proceed. This protocol provides the first examples of (E)-N-(pyren-1-ylmethylene)benzenamine as effective ligand for this palladium-catalyzed cross-coupling reaction. Further, such a strategy minimizes preparation and characterization of a metal complex which generally require specific conditions, laborious and time-consuming methods of synthesis. The scope, mechanism and synthetic applications of this catalytic reaction are under investigation in our laboratory.

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