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Cross-coupling of vinylethylene carbonates with arylboronic acids catalyzed by in situ generated palladium nanoparticles in water

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ABSTRACT

A practical and greener method of the cross-coupling of vinylethylene carbonates (VECs) with arylboronic acids has been described. The coupling reaction was catalyzed by in situ generated palladium nanoparticles (PdNPs) without any ligands and additional stabilizers in water under ambient conditions to provide useful 4-hydroxylprenylarenes and their derivatives in good to high yields.

Introduction

The 4-hydroxylprenylarene motif appears in a wide range of biologically active natural products,[1] yet efficient methods for the introduction of 4-hydroxylprenyl group into aromatic rings are largely unexplored. The approaches to 4-hydroxylprenylarenes include selective oxidation of prenylarenes (Scheme 1 Eq. 1a),[2] but the transformation is not effective. 4-Hydroxylprenyl group could also be introduced by Wittig olefination[3] (Eq. 1b) and Stille coupling[4] (Eq. 1c). However, multi-steps syntheses are required whether for arylacetaldehyde or the organostannane reagent. More practical methods have been accomplished through transition metal-catalyzed cross coupling of isoprene oxide with arylmetallic compounds, including arylmercurates,[5] arylstannanes,[6] aryl-Grignard reagents,[7] arylbismuth,[8] and arylsiloxanes[9] (Scheme 1, Eq. 2). However, those arylmetallic compounds are moisture sensitive and need to be pre-prepared. In addition, toxic metallic byproducts are generated for the transformations using some of the arylmetallic compounds. Szabó and co-workers reported only one example for Pd-catalyzed cross-coupling of vinyl epoxides with arylboronic acids to form 4-hydroxybut-2-enylarenes in high efficiency.[10] Nevertheless, a pre-prepared palladium pincer complex as catalyst and excess base are required for the process. Therefore, the development of practical and greener methods for the synthesis of 4-hydroxylprenylarenes and their derivatives is highly appealing.

Transition metal-catalyzed cross-coupling of allylic electrophiles with arylboronic acids is one of most practical methods for the formation of valuable allyl–aryl coupling compounds.[11,12] Recently, we reported palladium-catalyzed cross-coupling of allylic donors with arylboronic acids to afford allyl–aryl coupling products in high efficiency.[13] We also demonstrated that the allyl–aryl coupling could be catalyzed by palladium nanoparticles (PdNPs) generated in situ from $Pd(OAc)_2$ without any ligands and additional stabilizers in pure water at ambient conditions.[13c] On the other hand, we have recently found that vinylethylene carbonates (VECs) as readily accessible and stable allylic donors could be successfully applied to the Pd-catalyzed asymmetric decarboxylative cycloadditions with unsaturated electrophiles to construct quaternary stereocenters in very high efficiencies.[14,15] Based on our continuous effort to the development of practical and greener allyl–aryl coupling process, we herein will represent PdNPs-catalyzed[16] allyl–aryl coupling of VECs with arylboronic acids to form 4-hydroxylprenylarenes and their derivatives (Scheme 1, Eq. 3).[17] The cross-coupling process could be carried out effectively catalyzed by PdNPs generated in situ from the reaction of arylboronic acids with $Pd(OAc)_2$ in pure water at ambient conditions.

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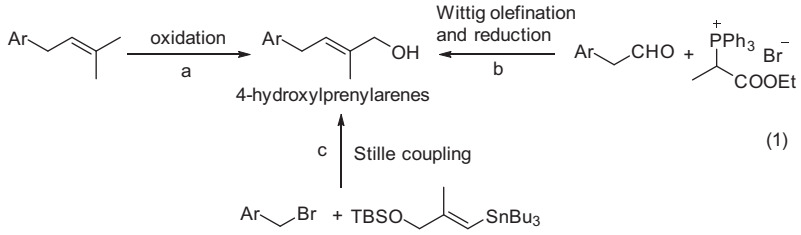
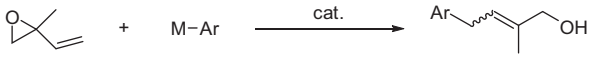
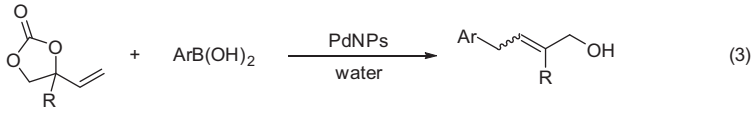
General approaches to 4-hydroxylprenylarenes



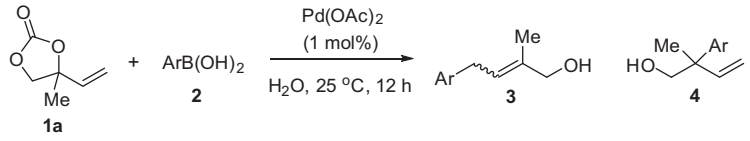
Coupling of methylvinylepoxide with arylmetal reagents



Coupling of VECs with arylboronic acids (this work)



Scheme 1. Synthetic approaches to 4-hydroxylprenylarenes.



2a, Ar = Ph, **2b**; Ar = 4-MeO C_6H_4; **2c**, Ar = 2-MeO C_6H_4; **2d**, Ar = 2-Me C_6H_4; **2e**, Ar = 4-BrC_6H_4; **2f**, Ar = 4-MeOOC C_6H_4; **2g**, Ar = 4-$CF_3C_6H_4$; **2h**, Ar = 2,4-diMeO C_6H_4; **2i**, Ar = 2,6-diMeO C_6H_4; **2j**, Ar = 2,6-diMeO-4-(2-phenylethyl)C_6H_4; **2k**, Ar = 3,4-OCH_2OC_6H_4; **2l**, Ar = 1-naphthyl; **2m**, Ar = 2-naphthyl

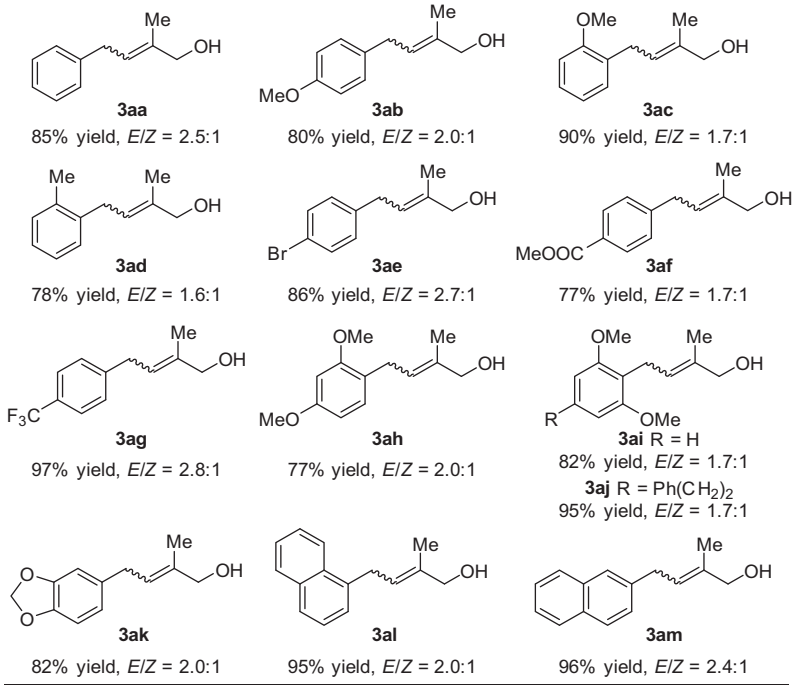


Figure 1. PdNPs-catalyzed cross-coupling of Me-VEC **1a** with arylboronic acids **2**. Reaction conditions: **1a** (0.5 mmol), **2** (0.75 mmol), $Pd(OAc)_2$ (0.005 mmol), H_2O (1.0 mL), 25 °C, 12 h. The yields are of isolated materials. The ratios of **3**/**4** and *E*/*Z* were determined by ^1H NMR of the crude reaction mixture. All the examples gave linear products **3** predominantly (**3**:**4** > 20:1).

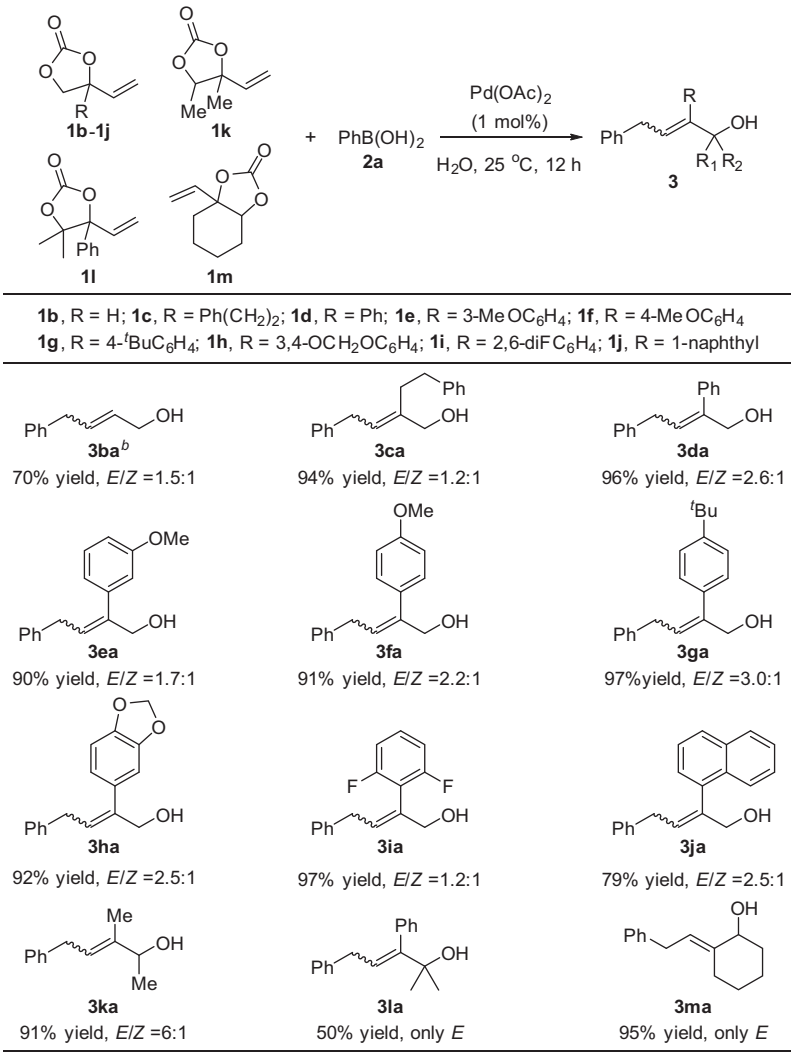
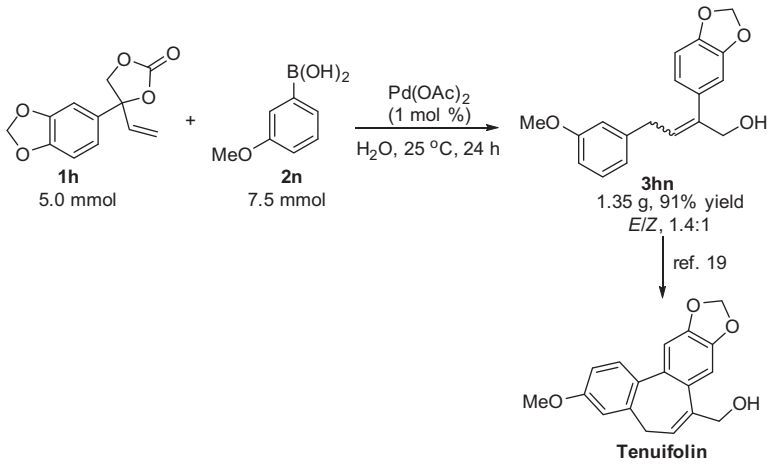


Figure 2. PdNPs-catalyzed cross-coupling of VECs **1** with phenylboronic acid (**2a**). As described for Fig. 1. [b]The ratio of linear and branched products is 5:1.

Results and discussion

Initially, in order to construct of 4-Hydroxylprenylarenes, 4-Me-VEC **1a** was chosen as a standard substrate. To our delight, the coupling reaction of Me-VEC **1a** with phenylboronic acid (**2a**) in the presence of $Pd(OAc)_2$ (1 mol%) at ambient temperature in pure water proceeded smoothly to afford coupling product **3aa** in 85% yield with a 2.5:1 of *E*/*Z* ratio (Fig. 1), and the branched product **4** was not observed as determined by ^1H NMR of the crude reaction mixture. The reaction mixture turned black after a few minutes. We find that the reaction in the initial stage produces PdNPs with an average particle size of 4.6 nm by transmission electron microscopy (TEM) analysis (see Supporting information). The particle size has no big change after completion of the reaction. These results indicated that $Pd(OAc)_2$ was reduced to form PdNPs by homo-coupling of phenylboronic acid, and the PdNPs are likely stabilized by phenylboronic acid.[13c] These simple and practical conditions were suitable for various arylboronic acids bearing different steric and electronic properties at the phenyl ring, providing 4-Hydroxylprenylarenes **3aa**–**ak** in good to high yields with 1.6–2.8:1 of *E*/*Z* ratios. The reactions with naphthylboronic acids were also performed well to give coupling product **3l** and **3m** in excellent yields. All the examples gave linear products **3** predominantly (**3**:**4** > 20:1). Notably, the allyl–aryl coupling product **3j** would be a useful precursor for the synthesis of natural product, radulanin A.[18]

After the successful realization of the formation of 4-hydroxylprenylarenes via cross-coupling of Me-VEC **1a**, we subsequently turned our attention toward the elaboration of the cross-coupling of substituted VECs with phenylboronic acid (**2a**). As shown Fig. 2, the reaction of H-VEC **1b** gave the coupling product **3ba** in 70% yield. In this case, the branched product was found in an 1:5 ratio to **3ba**. The 4-alkyl-substituted VEC **1c** was also tolerated in the reaction conditions to furnished coupling product **3ca** in 94% yield, but the poor *E*/*Z*-selectivity was observed. The cross-coupling reaction of Ph-VEC **1d** with **2a** proceeded smoothly to afford **3da** in 96% yield with a 2.6:1 of *E*/*Z* ratio. For the reactions of 4-aryl-substituted VECs **1e**-**i** bearing different steric and electronic nature, all performed well giving corresponding coupling products **3ea**-**ia** in high yields with moderate *E*/*Z* selectivities. The reaction efficiency for the 4-(1-naphthyl)-VEC **1j** was slightly decreased. 4,5-Dimethyl-VEC **1k** could also be converted into the coupling product **3ka** in 91% yield with high *E*/*Z*-selectivity. However, the reaction of 5,5-dimethyl-4-Ph-VEC **1l** gave coupling product **3la** in moderate yield, but only *E*-isomer was obtained. Significantly, the cross-coupling of VEC **1m** with **2a** afforded coupling adduct **3ma** in 95% yield with only *E*-isomer.



Scheme 2. Gram-scale transformation.

The synthetic utility of the present protocol was demonstrated by the gram-scale transformation. The reaction of VEC **1h** with 3-methoxylphenylboronic acid (**3n**) in 5.0 mmol scale proceeded smoothly to furnish coupling adduct **3hn** in 91% yield (1.35 g) (Scheme 2). The coupling product **3hn** would be a useful precursor for the synthesis of natural product, tenuifolin.[19]

Conclusion

In conclusion, we have developed an efficient method for the cross-coupling of VECs with arylboronic acids catalyzed by in situ generated PdNPs without any ligands and additional stabilizers in water at ambient temperature. The useful 4-hydroxylprenylarenes and their derivatives have been provided under the mild and practical conditions. Further studies will focus on gaining a better understanding of the reaction mechanism and finding reaction conditions for control of the *E*/*Z*-selectivity.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.06.022.

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