



## Cross-coupling of vinyl ethylene 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 vinyl ethylene 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.

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### Introduction

The 4-hydroxylprenylarene motif appears in a wide range of biologically active natural products,<sup>1</sup> 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),<sup>2</sup> but the transformation is not effective. 4-Hydroxylprenyl group could also be introduced by Wittig olefination<sup>3</sup> (Eq. 1b) and Stille coupling<sup>4</sup> (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,<sup>5</sup> arylstannanes,<sup>6</sup> aryl-Grignard reagents,<sup>7</sup> arylbismuth,<sup>8</sup> and arylsiloxanes<sup>9</sup> (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.<sup>10</sup> Nevertheless, a pre-prepared palladium pincer complex as catalyst and

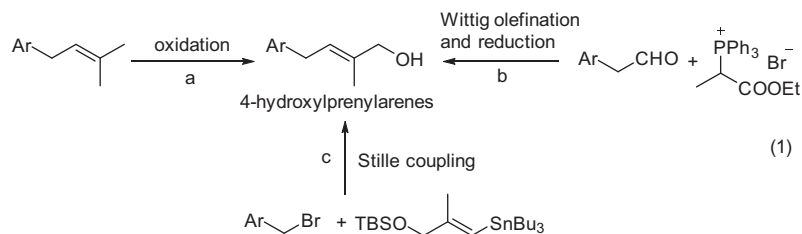
excess base are required for the process. Therefore, the development of practical and greener methods for the synthesis of 4-hydroxylprenylarenes and their derivatives is highly appealing.

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.<sup>11,12</sup> Recently, we reported palladium-catalyzed cross-coupling of allylic donors with arylboronic acids to afford allyl–aryl coupling products in high efficiency.<sup>13</sup> We also demonstrated that the allyl–aryl coupling could be catalyzed by palladium nanoparticles (PdNPs) generated in situ from Pd(OAc)<sub>2</sub> without any ligands and additional stabilizers in pure water at ambient conditions.<sup>13c</sup> On the other hand, we have recently found that vinyl ethylene 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.<sup>14,15</sup> Based on our continuous effort to the development of practical and greener allyl–aryl coupling process, we herein will represent PdNPs-catalyzed<sup>16</sup> allyl–aryl coupling of VECs with arylboronic acids to form 4-hydroxylprenylarenes and their derivatives (Scheme 1, Eq. 3).<sup>17</sup> The cross-coupling process could be carried out effectively catalyzed by PdNPs generated in situ from the reaction of arylboronic acids with Pd(OAc)<sub>2</sub> in pure water at ambient conditions.

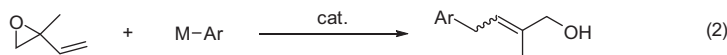
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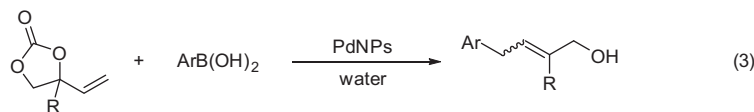
## General approaches to 4-hydroxyprenylarenes



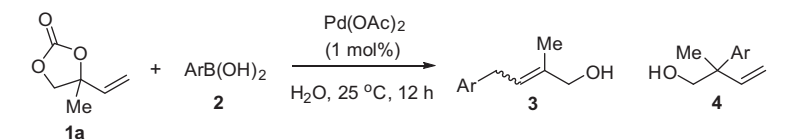
## Coupling of methylvinylepoxyde with arylmetal reagents



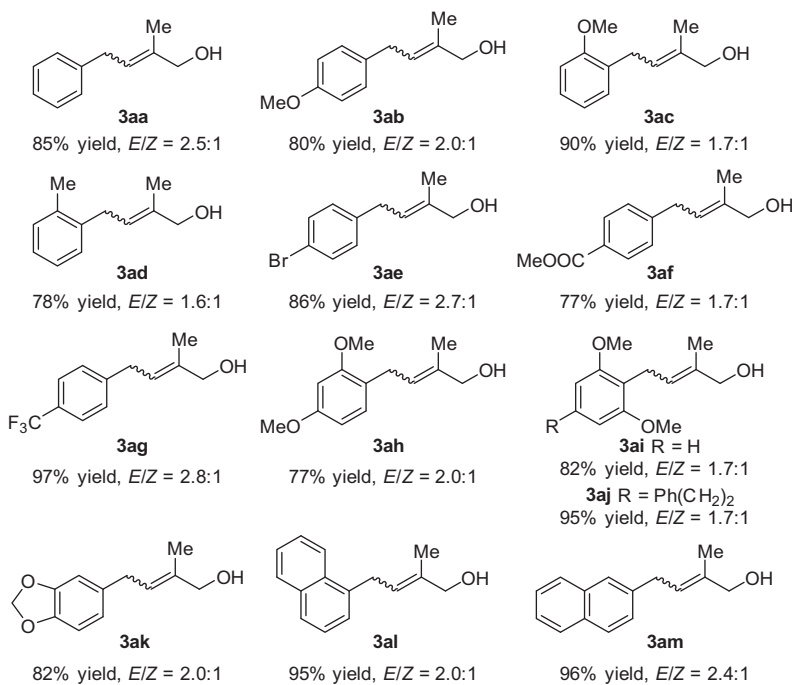
## Coupling of VECs with arylboronic acids (this work)



Scheme 1. Synthetic approaches to 4-hydroxyprenylarenes.



**2a**, Ar = Ph; **2b**, Ar = 4-MeO C<sub>6</sub>H<sub>4</sub>; **2c**, Ar = 2-MeO C<sub>6</sub>H<sub>4</sub>; **2d**, Ar = 2-Me C<sub>6</sub>H<sub>4</sub>;  
**2e**, Ar = 4-Br C<sub>6</sub>H<sub>4</sub>; **2f**, Ar = 4-MeOOC C<sub>6</sub>H<sub>4</sub>; **2g**, Ar = 4-CF<sub>3</sub> C<sub>6</sub>H<sub>4</sub>; **2h**, Ar = 2,4-diMeO C<sub>6</sub>H<sub>4</sub>;  
**2i**, Ar = 2,6-diMeO C<sub>6</sub>H<sub>4</sub>; **2j**, Ar = 2,6-diMeO-4-(2-phenylethyl)C<sub>6</sub>H<sub>4</sub>;  
**2k**, Ar = 3,4-OC<sub>2</sub>H<sub>4</sub>OC<sub>6</sub>H<sub>4</sub>; **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)<sub>2</sub> (0.005 mmol), H<sub>2</sub>O (1.0 mL), 25 °C, 12 h. The yields are of isolated materials. The ratios of **3/4** and *E/Z* were determined by <sup>1</sup>H NMR of the crude reaction mixture. All the examples gave linear products **3** predominantly (**3:4** > 20:1).

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