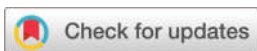


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RESEARCH ARTICLE



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Homoallyl alcohol as an allylation reagent for termination of the Catellani–Lautens reaction *via* retro-allylation†

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A palladium/norbornene-catalyzed *ortho*-amination/allylation of aryl iodides was developed for the construction of *ortho*-aminated allylbenzene by using *N*-benzoyloxyamine as the amination reagent and homoallyl alcohol as the allylation reagent. The reaction showed good functional group tolerance and broad substrate scope.

Introduction

Poly-substituted aromatics are ubiquitous scaffolds in pharmaceuticals, agrochemicals and organic materials.¹ The transition-metal-catalyzed cross-coupling reaction is one of the most effective approaches for preparing functionalized arenes.² However, these approaches typically only introduce one functional group in a single transformation, and multiple steps are required to construct densely functionalized arenes. In the past twenty years, palladium/norbornene (Pd/NBE) cooperative catalysis, which was initially reported by Catellani and further developed by Lautens, Dong, Liang, Luan, Gu, Zhou and others, has emerged as a powerful tool for expeditiously synthesizing highly substituted arenes (Scheme 1a).³ The Pd/NBE chemistry allows simultaneous functionalization of the *ipso* and *ortho* positions of simple aryl halides with different electrophiles and termination agents. A broad range of termination reactions, including Heck coupling,⁴ Suzuki coupling,⁵ alkyne annulation,⁶ C–N coupling,⁷ alkylation,⁸ hydrogenation,⁹ C–H activation,¹⁰ cyanation,¹¹ enolate coupling,¹² C–O coupling,¹³ carbene coupling,¹⁴ borylation,¹⁵ thio-

lation,¹⁶ selenation¹⁷ and alkylation,¹⁸ have been developed—and several structurally diverse poly-functionalized arenes were synthesized (Scheme 1b). Despite the broad scope of termination agents in these reactions, it is also highly desired to introduce new functional groups on the *ipso* positions of aryl halides to further meet the diverse goals of synthetic organic chemistry.

In 2006, the Oshima group first demonstrated that homoallyl alcohols can be used as a convenient and efficient source of allyl groups for palladium-catalyzed allylations of aryl halides.¹⁹ Recently, our group developed a palladium-catalyzed Heck cyclization/allylation with homoallyl alcohols to realize allylation of σ -alkylpalladium *via* retro-allylation.²⁰ Compared

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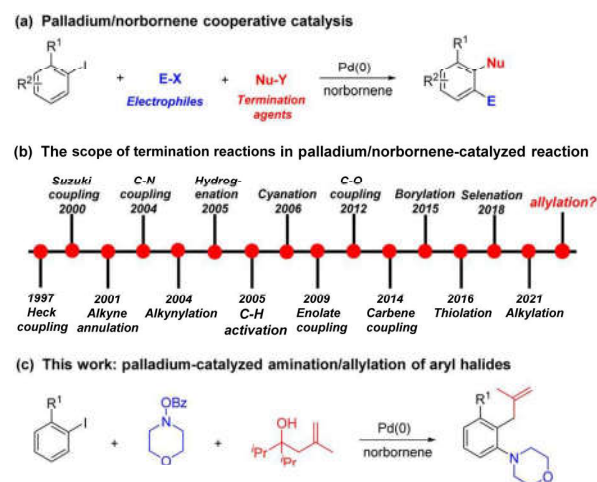
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Scheme 1 Design of the palladium-catalyzed amination/allylation reaction.