Category

Synthesis of Heterocycles

Key words

benzo[b][1,4]oxazepines

domino reaction

palladium

bromoalkynes

isocyanides

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Palladium-Catalyzed Tandem Reaction of *o*-Aminophenols, Bromoalkynes and Isocyanides to Give 4-Amine-benzo[*b*][1,4]oxazepines

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Palladium-Catalyzed Synthesis of Benzo[b][1,4]oxazepines

Significance: Reported is the palladium-catalyzed synthesis of benzo[b][1,4]oxazepines **4** via the annulation of *o*-aminophenols **1** with bromoalkynes **2** and isocyanides **3**. Substrate-scope investigation revealed broad tolerance to variation of all components **1–3**, particularly across sterically and electronically differentiated aryl bromoalkynes **2**, with a reduction in yield noted for alkyl bromoalkynes (**4o**). Experiments demonstrating the competency of **5** under the standard reaction conditions are offered in support of the proposed mechanism.

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Comment: Building on their previous investigations into combining the nucleophilic addition of isocyanides **3** to bromoalkynes **2** with palladium catalysis (*Chem. Commun.* **2012**, 48, 3545), the current report extends this methodology allowing the synthesis of benzoazepines traditionally synthesized by multiple-step procedures. Taking advantage of the established addition of phenols to bromoalkynes (For furan synthesis, see: S. Wang et al. *Org. Lett.* **2011**, 13, 5968) the current report, intercepting intermediate **5**, appears to have exceptional scope.