

Reactivity of Gem-Biszincio Reagents in Multicomponent Reactions



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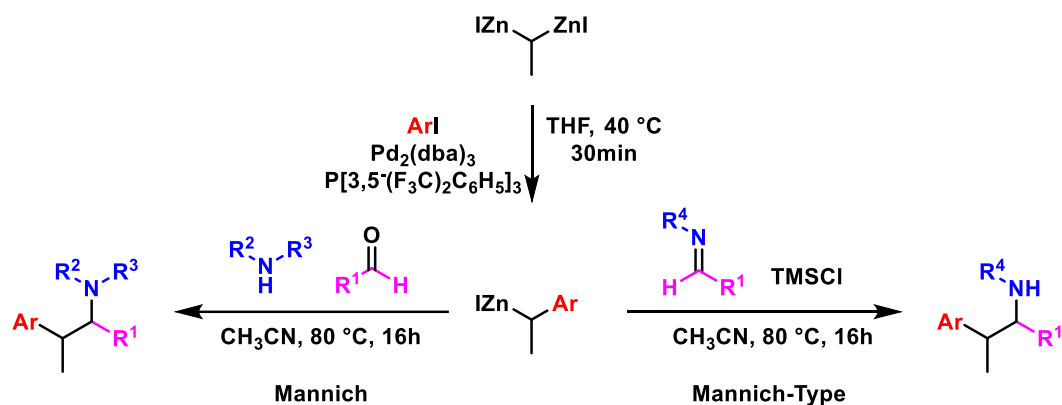
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Although 1,1-bimetallics reagents have been known for a long time, their reactivity as a dual nucleophilic species has received significant attention as a powerful and versatile tool only recently.¹ Successive functionalization with two different electrophiles proved to be possible from geminated homobimetallics. Thus 1,1-biszincio compounds were found to be valuable reagents for one pot transition metal catalyzed cross coupling/nucleophilic addition reaction sequences.² However, the use of the intermediate organozinc species in a subsequent multicomponent reaction, such as a Mannich reaction, has never been exploited.³

Therefore, we describe herein that a pallado-catalyzed cross coupling between a biszincio reagent and an aryl iodide affords excellent yields of a secondary benzyl zinc compound.⁴ Then an organometallic multicomponent Mannich reaction involving the newly formed organozinc reagent, an aromatic aldehyde and an amine leads to the straightforward generation of elaborated tertiary amines in excellent yields.

Moreover, additions of the secondary benzyl zinc species to a preformed imine affords the "secondary" Mannich product in moderate to excellent yields upon simple activation by TMSCl.

These methods prove complementary, leading to the possible preparation of both secondary or tertiary amines N-protected and free secondary amines in good yields.



- Cyclic/acyclic amine
- Access to densely substituted amines
- $R^2, R^3, R^4 =$ Alkyl, Aryl, Benzyl
- $R^1 =$ Aryl
- Access to primary amine
- Multicomponent reaction

References

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