

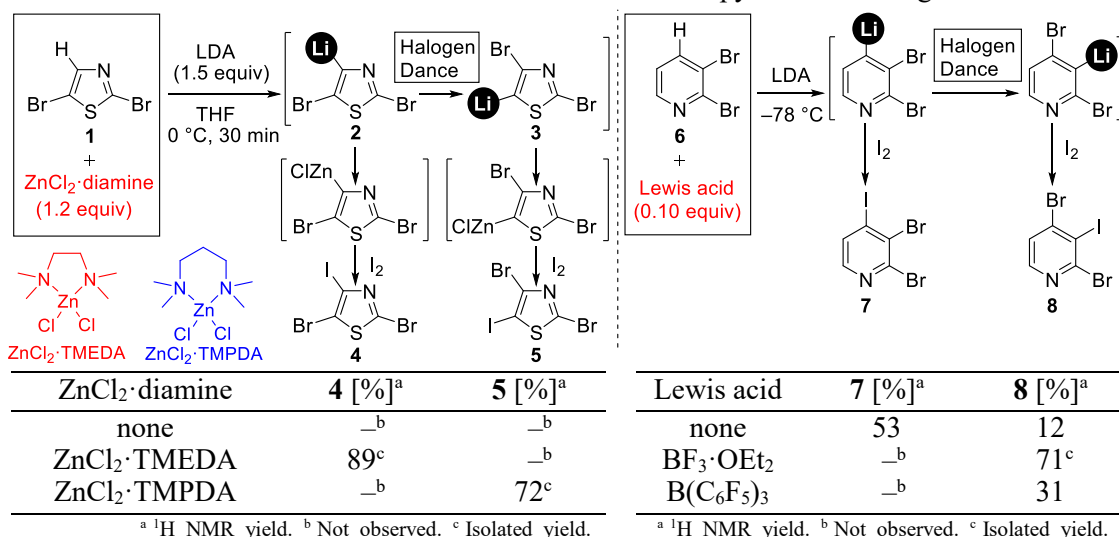
In Situ Transmetalation and Lewis Acid-Catalyzed Halogen Dance of *N*-Heteroarylolithiums

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Selective syntheses of multiple structural isomers are of importance to expand a chemical space. We have developed a new in situ transmetalation,¹ which enables selective trapping of unexplored *N*-heteroarylolithiums in halogen dance² to synthesize multiple structural isomers.

We achieved a method to use unexplored *N*-heteroarylolithiums by trapping transient azolylolithiums or facilitating halogen dance of pyridylolithiums. We focused on deprotonation of 2,5-dibromothiazole (**1**) with LDA which provided complex mixture at 0 °C. These results indicated that the possible organolithiums **2** and **3** were transient species. After screening of zinc halide diamine complexes to trap these organolithiums, ZnCl₂·TMEDA proved effective for the selective trapping of the first generated organolithium **2**, providing thiazole **4** in 89% yield after iodination. The use of ZnCl₂·TMPDA gave thiazole **5** in 72% yield, exclusively. The contrasting result was realized by a slower transmetalation of ZnCl₂·TMPDA. In contrast, halogen dance of lithiated pyridine **6** was sluggish, and subsequent iodination provided iodopyridines **7** and **8** in 53% and 12% yields, respectively. After optimization, a catalytic amount (0.10 equiv) of BF₃·OEt₂ drastically promoted halogen dance to afford pyridine **8** in 71% yield, whereas B(C₆F₅)₃ was less effective. We will discuss mechanistic insight into each reaction and the difference between bromoazoles and bromopyridines in halogen dance.



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