Palladium Catalyzed Synthesis of Unsymmetrical 1,3-Diheteroarylbenzenes

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PURPOSE OF THE ABSTRACT
In this communication, we disclosed two novel approaches for the access to unsymmetrical benzene-1,3-diheteroaryl using palladium catalyzed direct arylation. This method has emerged as one of the most eco-friendly methods for the fast synthesis of complex molecules. Recently benzensulfonyl chlorides were introduced as a powerful arylating agent through metal catalyzed C-H bond activation1. Desulfitative direct arylation sometimes offered different regioselectivities, like the arylation of thiophene in the 2 position and the regioselective C2 arylation of benzofuran1-3.

The first synthetic route relies on the desymmetrization of benzene-1,3-disulfonyl dichloride through two successive palladium-catalyzed desulfitative arylations using two different heteroarenes. (Figure 1) The use of DEC as solvent was found to be critical to prevent the second arylation, allowing the synthesis of 3-heteroarylbenzenesulfonyl chlorides in high yields.4

The second synthetic pathway comes from the high chemoselectivity of desulfitative couplings, which tolerate C?Br bonds. Orthogonal C?H bond arylation sequence ?namely, palladium-catalyzed desulfitative arylation followed direct heteroarylation of aryl bromide? was performed from 3-bromobenzenesulfonfonyl chloride to afford unsymmetrical benzene-1,3-diheteroaryl in high yields.4 (Figure 2)
FIGURES

**Figure 1**
Pd-catalyzed desulfitative direct arylations of heteroarenes.

**Figure 2**
Orthogonal C-H bond arylation sequence.

KEYWORDS
C-H arylation | Catalysis | Desulfitative | Palladium

BIBLIOGRAPHY