

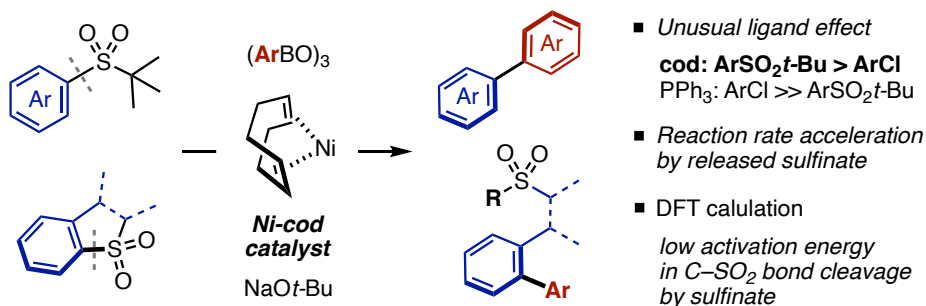
Ni-catalyzed Cross-Coupling Reactions of Aryl Sulfones

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Keywords: Ni catalysis, Sulfone, Suzuki–Miyaura cross-coupling, C–SO₂ bond activation, Sulfinate

Over the last decade, organosulfones have increasingly attracted attention as a valuable class of electrophiles in cross-coupling due to their ease of handling, bench-stability, and functional group tolerance. Arising from the pioneering work by Wenkert, various types of desulfonylative cross-coupling reactions of sulfones have been developed.¹ Our group has developed transition-metal-catalyzed desulfonylative cross-coupling reactions of alkyl or aryl sulfones with organometallic reagents to construct highly functionalized sp³ carbon centers in a modular manner. In the case of Suzuki–Miyaura type cross-coupling of aryl sulfones for biaryl synthesis, Moran, and Yorimitsu reported Pd-, and Pd/Rh-catalyzed systems.²

This presentation details a new Ni-catalyzed Suzuki–Miyaura cross-coupling of simple aryl sulfones with arylboroxines through carbon–sulfonyl (C–SO₂) bond activation. The utilization of the sulfonyl moiety as electron-withdrawing and directing groups provides a highly functionalized products via regioselective and iterative transformations, which are difficult to achieve with typical leaving groups. Moreover, cyclic arylsulfones can be employed in the ring-opening cross-coupling followed by a trapping with various electrophiles, producing π -conjugated structures bearing useful sulfur-containing functional groups. In contrast to a typical Ni-phosphine catalyst, this Ni-cod catalyst preferentially reacts with aryl sulfone over aryl chloride. And the sodium sulfinate released during C–SO₂ bond cleavage exhibits an unexpected rate-accelerating effect, as supported by mechanistic studies based on control experiments and DFT calculations.



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