

Pd-Catalyzed Decarbonylative Suzuki–Miyaura Cross-Coupling of Pyramidalized *N*-Mesyl Amides by a Tandem *N*–C(O)/C–C Bond Activation

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Streszczenie

The Suzuki–Miyaura biaryl cross-coupling is the pivotal technology for carbon–carbon coupling in pharmaceutical, polymer, and agrochemical fields. A long-standing challenge has been the development of efficient precursors for the decarbonylative cross-coupling of amide bonds. Herein, we report a highly chemoselective palladium-catalyzed Suzuki–Miyaura cross-coupling of *N*-mesyl amides for the synthesis of biaryls by a tandem *N*–C(O)/C–C bond activation with high selectivity for decarbonylative cleavage. The results demonstrate the first example of a decarbonylative coupling (–CO) of amide bonds activated by an atom-economic, low-cost, and benign *N*-pyramidalized mesyl group (>30 examples). The reaction shows high generality and functional group tolerance and can be applied in late-stage functionalization of pharmaceuticals. Notably, *N*-mesyl amides are significantly more reactive than other classes of amides in the decarbonylative Suzuki cross-coupling manifold. Density functional theory (DFT) studies demonstrate considerably lower barrier for rate-limiting transmetalation using *N*-mesyl amides. The study establishes *N*-mesyl amides as versatile precursors for Suzuki–Miyaura cross-coupling to afford valuable biaryls and opens the door to deploy *N*-mesyl amides in challenging cross-couplings of amides by decarbonylation.

Słowa kluczowe

Amides, Column chromatography, Cross coupling reaction, Nuclear magnetic resonance spectroscopy, Silica

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