

Palladium-NHC (NHC = N-heterocyclic Carbene)-Catalyzed Suzuki–Miyaura Cross-Coupling of Alkyl Amides.

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Streszczenie

We report the Pd-catalyzed Suzuki–Miyaura cross-coupling of aliphatic amides. Although tremendous advances have been made in the cross-coupling of *aromatic* amides, C–C bond formation from *aliphatic* amides by selective N–C(O) cleavage has remained a major challenge. This longstanding problem in Pd catalysis has been addressed herein by a combination of (1) the discovery of N,N-pym/Boc amides as a class of readily accessible amide-based reagents for cross-coupling and (2) steric tuning of well-defined Pd(II)-NHC catalysts for cross-coupling. The methodology is effective for the cross-coupling of an array of 3°, 2°, and 1° aliphatic amide derivatives. The catalyst system is user-friendly, since the catalysts are readily available and are air- and bench-stable. Mechanistic studies strongly support an amide bond twist and external $n_N \rightarrow \pi^*_{C=O/Ar}$ delocalization as a unified enabling feature of N,N-pym/Boc amides in selective N–C(O) bond activation. The method provides a rare example of Pd-NHC-catalyzed cross-coupling of aliphatic acyl amide electrophiles.

Słowa kluczowe

cross-coupling, Pd-NHCs, N–C activation, alkyl amides, amide resonance, twisted amides

Adres publiczny

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