

Pd-induced double C—H bond activation in annulative syntheses of bipyrrrole boomerangs: mechanistic insights from NMR spectroscopy and computation.

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Streszczenie

1, n-Dipyrrolylalkanes can be efficiently converted into extensively π -conjugated bipyrrroles by Pd^{II}-mediated annulative double C-H activation, and this approach might be further developed into tandem processes involving further cyclization of substituents or oxygenation of pyrrolic α -positions. Herein, the mechanism of these transformations is explored using NMR spectroscopy and DFT calculations. The kinetics of the annulation are found to depend on the conjugation extent and donor-acceptor character of the pyrroles, as well as on substitution and the linker length. Combined experimental and theoretical evidence indicates that a change of the rate-determining step occurs for the most electron-deficient substrates. The unprecedented double α -oxygenation of bipyrrroles is found to be a stepwise process, involving α -acetoxyated intermediates.

Adres publiczny

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<https://www.acs.org/content/acs/en.html>