

Structures of highly twisted amides relevant to amide N—C cross-coupling: evidence for ground-state amide destabilization.

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Herein, we show that acyclic amides that have recently enabled a series of elusive transition-metal-catalyzed N—C activation/cross-coupling reactions are highly twisted around the N—C(O) axis by a new destabilization mechanism of the amide bond. A unique effect of the *N*-glutarimide substituent, leading to uniformly high twist (ca. 90°) irrespective of the steric effect at the carbon side of the amide bond has been found. This represents the first example of a twisted amide that does not bear significant steric hindrance at the α -carbon atom. The ^{15}N NMR data show linear correlations between electron density at nitrogen and amide bond twist. This study strongly supports the concept of amide bond ground-state twist as a blueprint for activation of amides toward N—C bond cleavage. The new mechanism offers considerable opp

Słowa kluczowe

amides, N—C activation, rotation, steric hindrance, twisted amides

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