

Electrophilicity scale of activated amides: ^{17}O NMR and ^{15}N NMR chemical shifts of acyclic twisted amides in N-C(O) cross-coupling.

Autorzy

Laura Ielo

Vittorio Pace

Wolfgang Holzer

Md. Mahbubur Rahman

Guangrong Meng

Roman Szostak

Michał Szostak

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The structure and properties of amides are of tremendous interest in organic synthesis and biochemistry. Traditional amides are planar and the carbonyl group non-electrophilic due to $n_{\text{N}} \rightarrow \pi^*_{\text{C=O}}$ conjugation. In this study, we report electrophilicity scale by exploiting ^{17}O NMR and ^{15}N NMR chemical shifts of acyclic twisted and destabilized acyclic amides that have recently received major attention as precursors in N-C(O) cross-coupling by selective oxidative addition as well as precursors in electrophilic activation of N-C(O) bonds. Most crucially, we demonstrate that acyclic twisted amides feature electrophilicity of the carbonyl group that ranges between that of acid anhydrides and acid chlorides. Furthermore, a wide range of electrophilic amides is possible with gradually varying carbonyl electrophilicity by steric and electronic tuning of amide bond properties. Overall, the study quantifies for the first time that steric and electronic destabilization of the amide bond in common acyclic amides renders the amide bond as electrophilic as acid anhydrides and chlorides. These findings should have major implications on the fundamental properties of amide bonds.

Słowa kluczowe

^{17}O NMR spectroscopy, cross-coupling, N-C(O) activation, transition-metal catalysis, twisted amides

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