N-HETEROCYCLIC CARBENE-CATALYZED CONCERTED NUCLEOPHILIC AROMATIC SUBSTITUTION OF ARYL FLUORIDES BEARING *α, β*-UNSATURATED CARBONYL MOIETY

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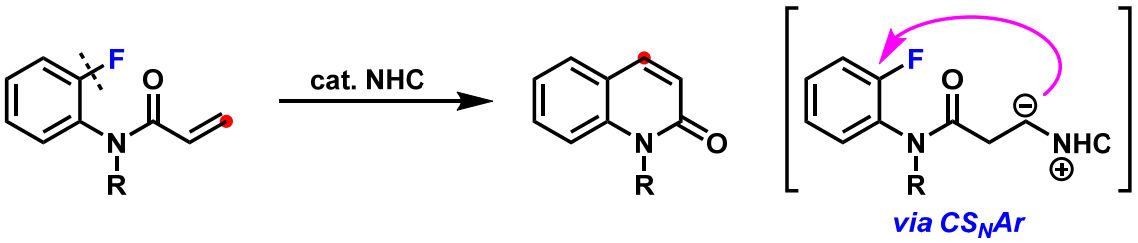
Since first isolated by Arduengo in 1991,[1] N-heterocyclic carbenes (NHCs) have widely been used with various applications, such as ligands and catalysts. In the context of organocatalysts, NHCs can activate *α,β*-unsaturated carbonyl compounds through conversion of the electrophilic *β* carbon into a nucleophilic one.[2] This NHC's peculiar feature led us to hypothesize that a structural optimization of the NHC catalyst should enhance the nucleophilicity of the carbanion intermediate, which allows for the reactions with less reactive electrophiles. Based on this hypothesis, we have developed NHC-catalyzed intramolecular cyclization of acrylamides having a 2-fluorophenyl group on the nitrogen through nucleophilic aromatic substitution. This type of nucleophilic aromatic substitution normally requires electron-withdrawing groups on the benzene ring to stabilize the Meisenheimer intermediate.[3] In contrast, this NHC-catalyzed reaction can be applied to electron-rich aryl fluorides. DFT calculations revealed that this cyclization proceeds via concerted nucleophilic aromatic substitution mechanism.[4]



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