Abstract: The copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction provides 1,4-disubstituted-1,2,3-triazoles regioselectively, and has found utility in drug discovery, medicinal chemistry, organic synthesis and bioconjugation. 1,2,3-triazoles can be decomposed into highly reactive synthetic intermediates via multiple degradation pathways. Our research group has been interested in the thermal decomposition of the 1,2,3-triazole with rhodium to gain access to the rhodium carbenoid, and the spontaneous decomposition of the 1,2,3-triazole into the ketenimine intermediate when sulfonyl azides are employed. Both species can undergo nucleophilic addition and/or rearrangement reactions to yield N-heterocycles such as pyridines, pyrroles and indoles. Our research group seeks to utilize these highly reactive intermediates and expand the known nucleophile scope to synthesize N-heterocycles including indolizines and dihydroisoquinolines.