SYNTHETIC chemistry is almost unimaginable without three main group elements, namely, boron, silicon, and tin. When attached to a carbon atom of any hybridization, these functional groups serve as exceptionally versatile linchpins in synthesis, selectively transforming into an enormous breadth of C–C and C–X bonds. Therefore, the means to discover new methods to forge valuable C–Si, C–B and C–Sn bonds are always in high demand.

This doctoral thesis is focused on the development of novel techniques to make use of silicon-heteroatom interelement linkages to functionalize inert C–O & C–H bonds via either nickel catalysis or transition metal-free protocols. Our first effort on interelement linkages was focused on a nickel-catalyzed stannylation of aryl esters via sp2 C–O functionalization aided by silicon-tin nucleophiles. This protocol was distinguished with its wide scope and mild conditions, thus representing a useful entry to synthetically versatile aryl stannane building blocks. Following up our interest on interelement linkages, we developed a rather unusual site-selective sp2 C–H silylation of (poly)azines in the absence of transition metal. Our method is characterized by its mild conditions, wide substrate scope, switchable regioselectivity by subtle modulation of the solvent denticity and its application in late-stage functionalization in (poly)azine drugs. Our last project deals with the difunctionalization of alkynes with silylboranes in the absence of transition metals. It provides a new strategy for streamlining the synthesis of geminal dimetallic reagent with high stereoselectivity and preparative utility in organic synthesis. We hope that our transformations will inspire others for the development of cross-coupling reactions and functionalization techniques that make use of interelement linkages as coupling partners.