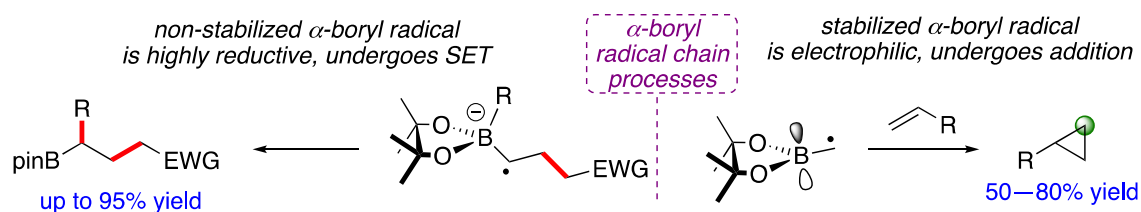


REACTIVITY AND SYNTHETIC UTILITY OF α -BORYL CARBON CENTERED RADICALS: TWO OPPOSING REACTION MANIFOLDS

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The vacant boron p-orbital in organoboranes has a stabilizing influence on a radical formally located on an adjacent carbon atom.¹ The stabilized radical precursor ICH₂Bpin performs atom transfer radical addition (ATRA) to terminal alkenes to furnish γ -iodoboronic esters. In an alternative manifold, occupying the vacant p-orbital on vinylboronic esters with a ligand eradicates any stabilization, and generates an excellent trap for electrophilic radicals.^{2–4} The mechanism appears to operate through a single electron transfer (SET) rather than an ATRA.



The investigations concluded with two operationally simple, one-pot protocols to affect an ATRA/ 1,3-cyclization to yield cyclopropanes or a three-component coupling reaction of an organolithium, electrophilic halide, and vinylboronic ester. The scope and mechanism of the two reactions will be discussed, outlining how this cyclopropanation is highly chemoselective and complementary to other cyclopropanation methodologies.

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