Catalyst-Controlled C–O versus C–N Allylic Functionalization of Terminal Olefins

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The divergent synthesis of syn-1,2-aminoalcohol or syn-1,2-diamine precursors from a common terminal olefin has been accomplished using a combination of palladium(II) catalysis with azaphilic Lewis acid co-catalysis. Palladium(II)/bis-sulfoxide catalysis with a silver triflate co-catalyst leads for the first time to *anti*-2-aminooxazolines (C–O) in good to excellent yields and selectivities. Simple removal of the bis-sulfoxide ligand from this reaction results in a complete switch in reactivity to afford *anti*-imidazolidinone products (C–N) in good yields and excellent selectivities. Mechanistic studies suggest the divergent C–O versus C–N reactivity from a common ambident nucleophile arises due to a switch in mechanism from allylic C–H cleavage/functionalization to olefin isomerization/oxidative amination.