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

Significance: The use of ambident nucleophiles in C–H functionalizations allows the generation of more than one product from a single precursor. The authors report that a simple switch in the palladium catalyst used enables the synthesis of 2-aminooxazolines 2a or imidazolidinones 2b from olefin 1 via C–O and C–N formation, respectively. This study represents the first successful report of achieving selective C–O over C–N bond formation using ambident urea nucleophiles under palladium catalysis.

Comment: Mechanistic studies demonstrate that the formation of 2a and 2b occurs via two diverging mechanistic pathways, the former of which involves olefin isomerization, followed by amino-palladation, while the latter invokes allylic C–H oxidation in the reaction mechanism. In all examples, diastereoselectivities of >20:1 are observed. The products 2a and 2b can be conveniently converted into syn aminoalcohols and syn diamines, respectively.