Highly Selective Radical Relay 1,4-Oxyimination of Two Electronically Differentiated Olefins

**Significance:** Gutierrez, Glorius, and co-workers disclose an unprecedented 1,4-oxyimination of two electronically differentiated olefins with a class of bifunctional oxime carbonate reagents via an energy transfer strategy. The process enables the formation of three different chemical bonds (C–C, C–O, and C–N) in an orchestrated single operation. A wide scope of 1,4-oxyimination products was obtained in fair to good yields and with excellent functional group tolerance. Furthermore, the products were easily converted into biologically relevant δ-hydroxy-α-amino acids.

**Comment:** Mechanistic studies suggest an energy transfer step to promote the homolytic N–O bond cleavage of the oxime carbonate reagent to form O-centered alkoxycarbonyloxyl and N-centered iminyl radicals, which are of amphiphilic and electrophilic properties, respectively. In turn, the alkoxycarbonyloxyl radical undergoes a chemoselective double Giese-type addition to the olefin, followed by C–N bond formation with an oxime carbonate reagent that functions as a radical chain mediator.