



**Significance:** Glorius and colleagues report a regio- and chemoselective insertion of amidyl radicals into bicyclo[1.1.0]butanes (BCBs) through Ir(III)/Ir(IV) photoredox catalysis. This approach enables access to 2-oxa-4-azabicyclo[3.1.1]hept-3-enes, which, as shown by exit vector analysis, have a geometric resemblance to pyridine and pyrimidine derivatives. This similarity suggests their potential as isosteric mimetics of key heterocycles.

**Comment:** *N*-Amidocollidinium tetrafluoroborate salts with both electron-rich and electron-deficient aryl and heteroaryl substituents display similar reactivity. However, BCBs lacking carbonyl substituents or an aryl ring in the framework are not explored in the current study. Mechanistic investigations support a photoredox reaction pathway, and DFT analysis provides insight into the observed regioselectivity of the transformation.