Significance: A ruthenium-catalyzed method for the oxidative alkenylation of indoles which utilizes an N,N-dimethylcarbamoyl group to direct C–H functionalization is described. While several examples of ruthenium-catalyzed C2 alkenylation of indoles are known, in one case the scope of the coupling partners was limited to acrylates (V. Lanke, K. R. Prabhu Org. Lett. 2013, 15, 2818). In contrast, the substrate scope of the present report includes both electron-rich and -deficient styrenes, acylates, substituted acrylates, acrylonitrile, a vinyl sulfone, and cyclopentenone. A closely related method that utilizes oxygen as the terminal oxidant was recently reported (L.-Q. Zhang, S. Yang, X. Huang, J. You, F. Song Chem. Commun. 2013, 49, 8830).

Comment: Due to their inherent electronic character, indoles normally undergo electrophilic substitution reaction at C3. However, multiple methods exist for C2Indole functionalization including directed ortho metalia-tion (DoM) as well as creative palladium-, rhodium-, and ruthenium-based methods from the Gaunt, Ricci, Song, and Arrayás groups. The notable features of the present report include: 1. The observation that electron-rich indoles and/or electron-rich styrenes undergo reaction faster than their electron-deficient counterparts in competition experiments; 2. Pyrroles were identified as viable reaction partners in this chemistry; 3. Disubstituted alkenes, which can be challenging substrates for intermolecular Heck reactions, were shown to be viable. Attempted isolation of the putative ruthenium(II)-cyclometalated intermediate was not successful.