**Category**

**Synthesis of Heterocycles**

**Key words**

**ruthenium catalysis**

**indoles**

**C–H functionalization**

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Ruthenium-Catalyzed Regioselective C2 Alkenylation of Indoles and Pyrroles via C–H Bond Functionalization
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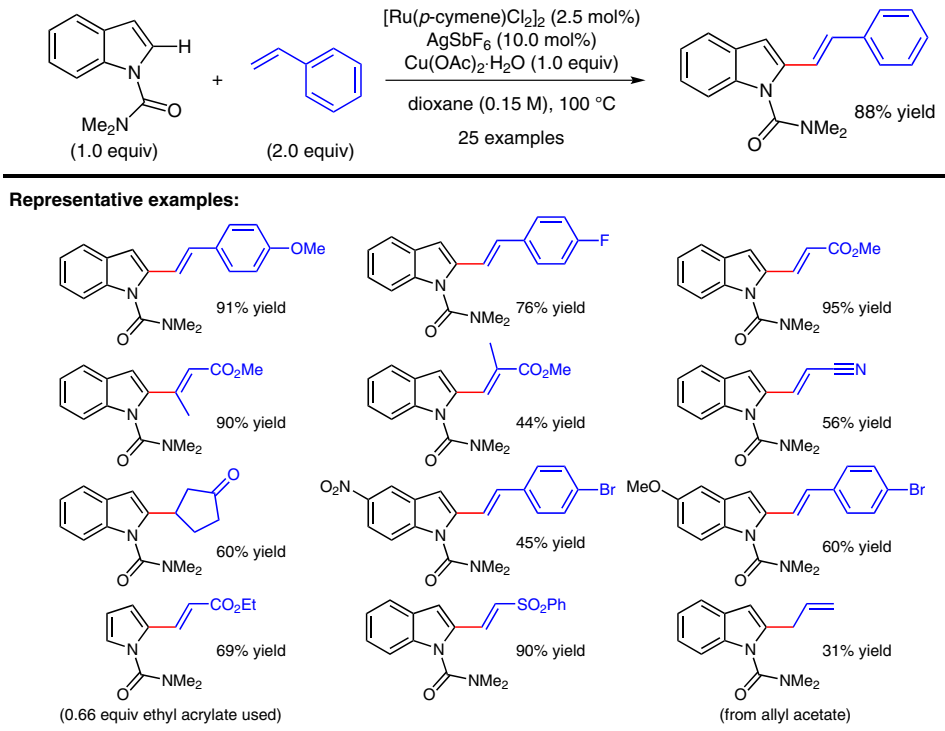
# C2-Substituted Indoles via Ruthenium-Catalyzed C–H Bond Functionalization




**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 C2 indole functionalization including directed *ortho* metalation (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.

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