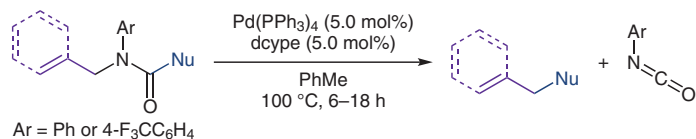
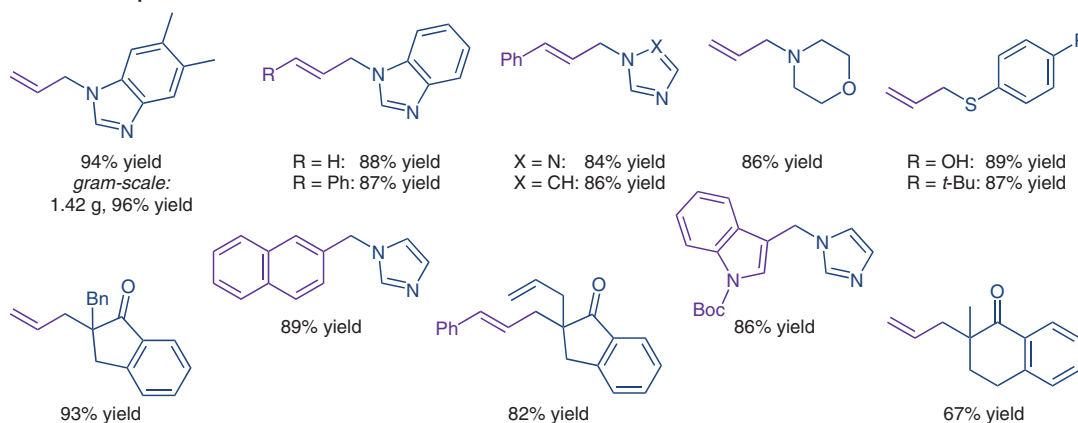


## Extrusion of Isocyanate from *N*-Allyl Amides Enables $\pi$ -Allyl Palladium Chemistry!

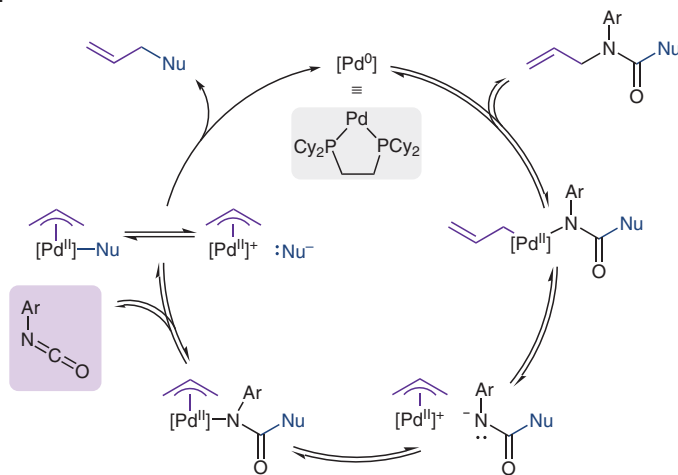


- 34 examples, up to 96% yield
- gram-scalable reaction
- C–N and C–S bond formation
- C–C bond formation with THF as solvent and K<sub>3</sub>PO<sub>4</sub> (1.0 equiv) as additive

### Selected examples:



### Proposed mechanism:



**Significance:** A palladium(0)-catalyzed unimolecular fragment coupling (UFC) reaction of *N*-allyl amides through the elimination of an isocyanate is reported. Recombination of the resulting fragments leads to C–N, C–C, and C–S bond formation in good to high yields. The synthetic value of this protocol is highlighted by the late-stage conversion of amides into allyl groups.

**Comment:** Besides Pd(PPh<sub>3</sub>)<sub>4</sub>, Ni(cod)<sub>2</sub> can also be used as the catalyst. Several control experiments under palladium catalysis were performed, supporting the shown mechanism. The use of nickel as transition metal eventually allowed the crystallographic characterization of the cationic  $\pi$ -allyl intermediate.