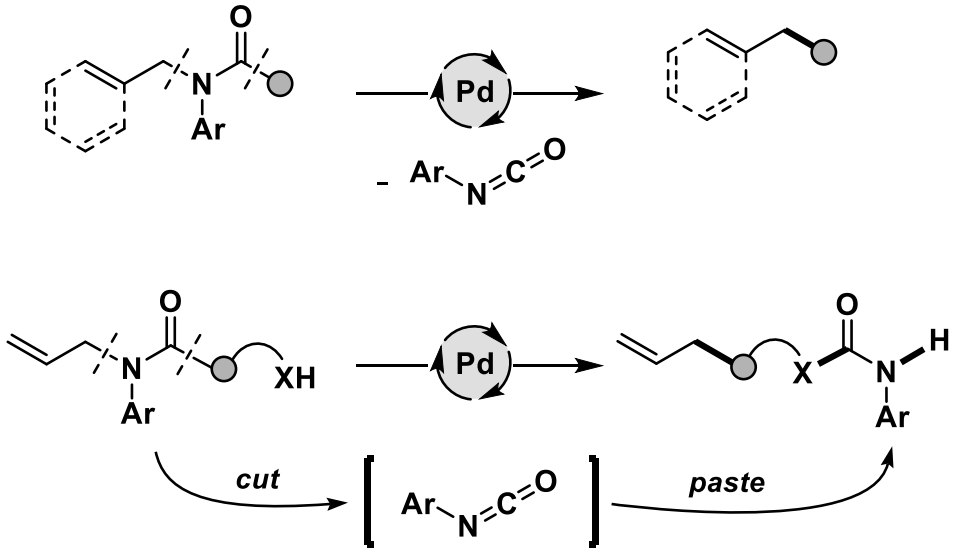
Palladium-Catalyzed Unimolecular Fragment Coupling of Amides via Elimination and Translocation of Isocyanate

([1]*Graduate School of Engineering, Osaka University*, [2]*ICS-OTRI*)
○Ryoma Shimazumi,[1] Takuya Kodama[1,2] Mamoru Tobisu[1,2]
Keywords: *deisocyanation; migration; intramolecular coupling reaction; amide; palladium catalyst*

Unimolecular fragment coupling (UFC) is a useful method for forming new bonds from readily available starting materials via elimination of small molecules. A catalytic decarboxylation reaction of esters[1)] is a typical example of UFC. If amides, instead of esters, can be used in a catalytic UFC, it would serve as powerful bond-forming methods using abundant amine and carboxylic acid building blocks. However, such a UFC of amides have not been reported to date.

We have developed palladium-catalyzed UFC reactions of amides for forging new carbon–carbon and carbon–heteroatom bonds via the elimination of isocyanate. In addition, we have also developed an amide group migration reaction in which the eliminated isocyanate is trapped by a pendant nucleophile.[2)]



1) Weaver, J. D.; Recio, A.; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846.
2) Shimazumi, R.; Tanimoto, R.; Kodama, T.; Tobisu, M. *J. Am. Chem. Soc.* **2022**, *144*, 11033.