

Palladium-catalyzed aerobic dehydrogenative C(sp³)-N bond formation reaction with 1,3-diene derivatives

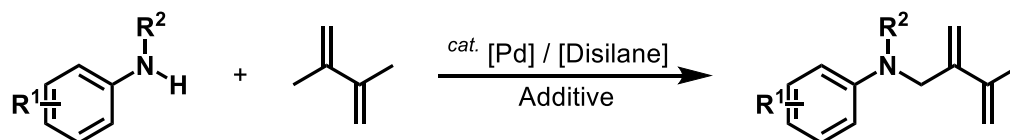
(¹ *Fac. Chem. Matl. & Bioeng., Kansai Univ.*, ² *Grad. Sch. Eng., Kyoto Univ.*)

○Kazuki Tabaru,¹ Tetsuaki Fujihara,² Kazuyuki Torii,¹ Yasushi Obora¹

Keywords: Dehydrogenative coupling; Pd complex catalyst; 1,3-Diene; Disilane

Functionalization of unsaturated hydrocarbons is one of the most important organic reactions.¹ 1,3-Dienes have emerged as attractive compounds which can be readily transformed into another molecular in a wide range of organic transformation, especially Diels-Alder reaction and polymerizations.² In synthetic and material chemistry, the use of complicated 1,3-dienes realizes the development for further applications to products such as construction of pharmaceutical molecules and an improvement of property of polymers. At present, the most common methods for preparing 1,3-dienes are based on classical organic reactions with stoichiometric by-products. Transition metal-catalyzed coupling reactions have also required unfavorable steps during the preparation of starting materials. Therefore, the most straightforward functionalization of 1,3-dienes which can bypass prefunctionalizations of substrates is desirable. During the past decade, dehydrogenative coupling has represented a powerful tool in green chemistry because of a high atom- and step-economical transformation. Especially, dehydrogenative C–N bond formation reaction has been taken considerable efforts in the field of organic chemistry. Although various nitrogen included nucleophiles reacted with unsaturated hydrocarbons to form the coupling product, dehydrogenative coupling with 1,3-dienes, which are one of the useful chemical feedstocks, has been unprecedented.³

In this study, we developed palladium-catalyzed dehydrogenative coupling of 1,3-dienes with aromatic amines using molecular oxygen as a terminal oxidant. Amines are preferable to be introduced to allylic position where C(sp³)-N bond is formed and the 1,3-diene group remains during the transformation. Employing disilanes combined with carboxylic acids allowed the reaction to achieve the excellent yield with high chemoselectivity. Spectroscopic studies revealed the role of additives in the reaction. Furthermore, density functional theory calculation supports a plausible reaction pathway.



1) (a) K. Torii, A. Kawakubo, X. Lin, T. Fujihara, T. Yajima, Y. Obora *Chem. Eur. J.*, **2021**, 27,4888. (b) K. Tabaru, M. Nakatsuji, S. Itoh, T. Suzuki, Y. Obora, *Org. Biomol. Chem.*, **2021**, 19, 3384.

2) K. Torii, K. Tabaru, Y. Obora, *Org. Lett.*, **2021**, 23, 4898.

3) K. Tabaru, T. Fujihara, K. Torii, Y. Obora, *67th Symposium on Organometallic Chemistry*, Online, **2021**, PC-34.