

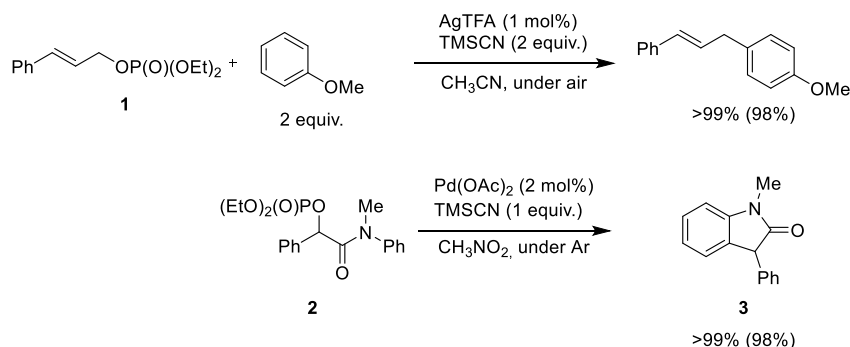


In situ Generated Silyl Cyanometallate-Catalyzed Friedel–Crafts-type Reaction

Hamdiye Ece, Taiga Yurino, Takeshi Ohkuma

The *C*-terminus of cyanide is known to strongly interact with some transition metal species to afford the stable metal cyanides. In the presence of excess amounts of cyanide, the corresponding cyanometallates are reversibly formed. Recently, we achieved allylic isocyanation catalyzed by Pd(II), using allylic phosphate as an electrophile.¹ The ate complexes $(\text{Me}_3\text{Si})[\text{Pd}(\text{CN})_3]$ and/or $(\text{Me}_3\text{Si})_2[\text{Pd}(\text{CN})_4]$ were generated *in situ* from $\text{Pd}(\text{OAc})_2$ and trimethylsilyl cyanide (TMSCN), and those served as both Lewis acid activating allylic phosphate and *C*-blocked cyanide reagents. In a similar manner, we also achieved Ag-catalyzed benzylic isocyanation.² In this case, $(\text{Me}_3\text{Si})[\text{Ag}(\text{CN})_2]$ is the active catalytic species. We hypothesized that those ate complexes could work as Lewis acid for Friedel–Crafts-type substitution in the presence of strongly nucleophilic compounds. Herein we report highly selective inter- and intramolecular Friedel–Crafts-type allylic and benzylic substitution in the presence of Ag(I) or Pd(II) salts with TMSCN.

We found that allylation of anisole undergoes regioselectively with combination of AgTFA (1 mol%) and TMSCN (2 equiv.) in CH_3CN under air, when allylic phosphate **1** is employed as an electrophile.³ $\text{Pd}(\text{OAc})_2$ was found to be a more suitable catalyst for the *para*-selective allylation of phenols. Mandelamide derivative **2** was transformed into the corresponding oxindole **3** through an intramolecular Friedel–Crafts-type benzylic substitution in high yield. In this case, $\text{Pd}(\text{OAc})_2$ (2 mol%) was more effective catalyst precursor. In all cases, both transition metal salt and TMSCN were necessary.



参考文献>

- 1) Yurino, T.; Tani, R.; Ohkuma, T. *ACS Catal.* **2019**, *9*, 4434-4440.
- 2) Yurino, T.; Tange, Y.; Tani, R.; Ohkuma, T.; *Org. Chem. Front.* **2020**, *7*, 1308-1313.
- 3) Yurino, T.; Ece, H.; Ohkuma, T. *Asian J. Org. Chem.* **2020**, *9*, 557-560.

発表者紹介

氏名 Hamdiye Ece
 所属 Graduate School of Chemical Science and
 Engineering
 学年 3rd Year Doctorate Degree Student
 研究室 Organic Synthesis

