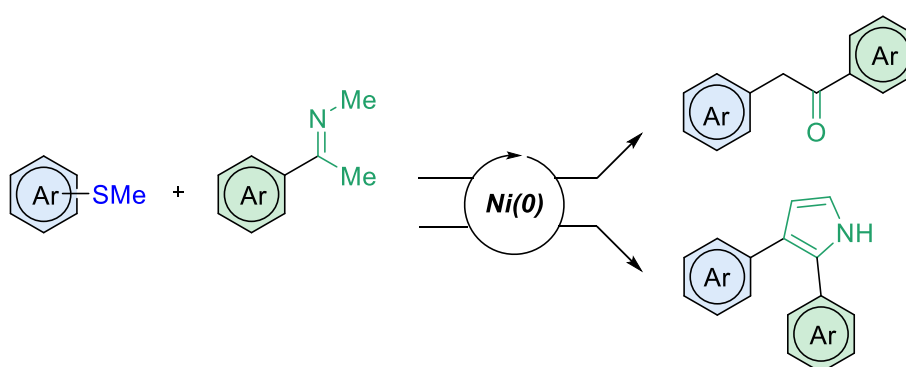


Ni-Catalyzed Cross-Coupling between Aryl Thioethers and Aryl Imines

Valentina Gasser¹, Tristan Delcaillau¹, Bill Morandi¹

¹Institute of Organic Chemistry, ETH Zürich, Vladimir-Prelog-Weg 3, 8093 Zürich
valentina.gasser@org.chem.ethz.ch

The use of aryl thioethers as cross-coupling partners has proved to be a viable alternative in comparison to the more reactive aryl halides. Our group has developed several methodologies employing aryl thioethers in such reactions, such as the amination of aryl thioethers,¹ the reversible functional group metathesis of aryl nitriles and aryl thioethers,² as well as the Ni-catalyzed cyanation of aryl thioethers.³



The Pd-catalyzed cross-coupling between aryl thioethers and aryl imines was reported by the Yorimitsu group in 2016, using SingaCycle-A1 as the catalytic system.⁴ In this work, we have devised a more cost-efficient strategy using catalytic amounts of Ni(COD)₂/dcype.⁵ A wide variety of benzyl phenyl ketones was synthesized upon hydrolysis of the generated imine intermediate. This strategy tolerates a broad range of electron-rich as well as -poor functional groups, including a never-before reported citronellol-derivative. In the presence of a strong base (KOtBu) and DMF, the benzyl phenyl imine product was further reacted to give a 2,3-diarylpyrrole derivative. This methodology combines the milder reactivity of aryl thioethers and the nickel catalyst, giving access to a diverse substrate scope.

[1] Delcaillau, T.; Bismuto, A.; Müller, P.; Morandi, B. *ACS Catal.* **2020**, *10*, 4630–4639.

[2] Delcaillau, T.; Boehm, P.; Morandi, B. *J. Am. Chem. Soc.* **2021**, *143*, 3723–3728.

[3] Delcaillau, T.; Woenckhaus-Alvarez, A.; Morandi, B. *Org. Lett.* **2021**, *23*, 7018–7022.

[4] Gao, K.; Yorimitsu, H.; Osuka, A. *Angew. Chem. Int. Ed.* **2016**, *55*, 4573–4576.

[5] Gasser, V.; Delcaillau, T.; Morandi, B. *manuscript in preparation*.