

Asymmetric conjugate addition of arylboronic acids and aryltrialkoxysilanes: new reactions in palladium catalysis

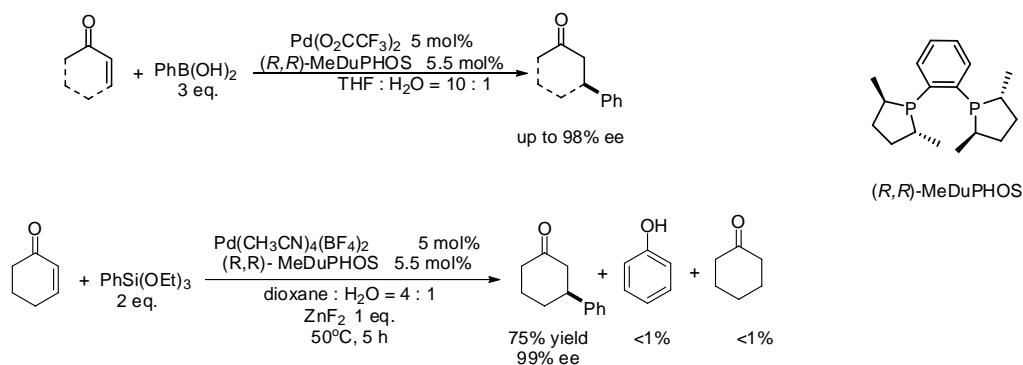
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The asymmetric transition-metal catalyzed conjugate addition of organometallic reagents to α,β -unsaturated carbonyl compounds is of great importance for the enantioselective formation of carbon-carbon bonds.¹ The well established copper-catalyzed conjugated addition of dialkylzinc reagents² and Grignard reagents³ allows the introduction of alkyl substituents in very high yields and enantioselectivities. A complementary protocol for the introduction of aryl moieties is the rhodium-catalyzed asymmetric conjugate addition of arylboronic acids⁴ and arylsiloxanes.⁵

The use of palladium-based catalysts has been limited for the competitive formation of the corresponding Heck coupling product. Nevertheless, there are example of palladium-catalyzed conjugate addition of arylboronic acids⁶ and aryltrialkoxysilanes.⁷

Our research was aimed to the development of the first example of asymmetric palladium-catalyzed conjugate addition of arylboronic acids⁸ and aryltriethoxysilane (Scheme 1).⁹ The conjugate addition of arylboronic acids proceeds smoothly affording excellent yields and enantioselectivities for a large variety of cyclic and acyclic α,β -unsaturated carbonyl compounds. In the addition of aryltriethoxysilanes instead the formation of side products arising from a palladium-catalyzed transfer hydrogenation was observed. The careful optimization of the reaction conditions, aimed to the enhancement of the transmetalation step, however, led to almost complete suppression of the side reaction.



Scheme 1.

¹ P. Perlmutter *Conjugate Addition Reactions in Organic Synthesis*; Tetrahedron Organic Chemistry Series 9; Pergamon: Oxford, 1992.

² Feringa, B. L.; Naasz, R.; Imbos, R.; Arnold, L. A. *In Modern Organocopper Chemistry*; Krause, N., Ed.; Wiley-VCH: Weinheim, Germany, **2002**; pp 224–258.

³ López, F.; Minnaard, A. J.; Feringa, B. L. *Acc. Chem. Res.* **2007**, *40*, 179.

⁴ Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829.

⁵ Oi, S.; Taira, A.; Honma, Y.; Inoue, Y. *Org. Lett.* **2003**, *5*, 97.

⁶ (a) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 2768. (b) Nishikata, T.; Yamamoto, Y.; Gridnev, I. D.; Miyaura, N. *Organometallics* **2005**, *24*, 5025.

⁷ (a) Denmark, S. E.; Amishiro, N. *J. Org. Chem.* **2003**, *68*, 6997. (b) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Chem. Lett.* **2003**, *32*, 752.

⁸ Gini, F.; Hessen, B.; Minnaard, A. J. *Org. Lett.* **2005**, *7*, 5309.

⁹ Gini, F.; Hessen, B.; Feringa, B. L.; Minnaard, A. J. *Chem. Commun.* **2006**, 710.