

## CBC SEMINAR ANNOUNCEMENT



**Professor Takahiro Nishimura**  
**Kyoto University**

### Group 9 Metal-Catalyzed Asymmetric Arylations and Alkynylations

Recent progress of rhodium-catalyzed asymmetric addition of organoboron reagents to electron-deficient alkenes provides one of the most reliable methods available for the synthesis of chiral carbonyl compounds, where a variety of aryl and alkenyl groups are introduced with high enantioselectivity.<sup>1</sup> Since the first report on the asymmetric addition of arylboronic acids to conjugated enones by use of a Rh/binap catalyst in 1998,<sup>2</sup> this type of asymmetric catalysis has been extended to the addition to a wide variety of electron deficient alkenes. In this context, we have recently developed asymmetric arylations of electron deficient alkenes, which are catalyzed by rhodium<sup>3</sup> and iridium<sup>4</sup> complexes coordinated with chiral diene ligands. In this seminar, some of the recent results will be presented. The results of the cobalt-catalyzed asymmetric alkynylation of conjugated enones or oxabenzonorbornadienes will also be presented.<sup>5</sup>

1. For reviews, see: (a) Hayashi, T.; Yamasaki, K.; Chem. Rev. 2003, 103, 2829. (b) Christoffers, J.; Koripelly, G.; Rosiak, A.; Rössle, M. Synthesis 2007, 1279. (c) Edwards, H. J.; Hargrave, J. D.; Penrose, S. D.; Frost, C. G. Chem. Soc. Rev. 2010, 39, 2093. (d) Tian, P.; Dong, H.-Q.; Lin, G.-Q. ACS Catal. 2012, 2, 95.
2. Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. J. Am. Chem. Soc. 1998, 120, 5579.
3. (a) Asymmetric Synthesis of (Triaryl)methylamines by Rhodium-Catalyzed Addition of Arylboroxines to Cyclic N-Sulfonyl Ketimines, Nishimura, T.; Noishiki, A.; Tsui, G. C.; Hayashi, T. J. Am. Chem. Soc. 2012, 134, 5056. (b) Rhodium/chiral diene-catalyzed asymmetric methylation of N-sulfonylarylimines with trimethylboroxine, Nishimura, T.; Ashouri, A.; Ebe, Y.; Maeda, Y.; Hayashi, T. Tetrahedron: Asymmetry 2012, 23, 655. (c) Effect of Chiral Diene Ligands in Rhodium-Catalyzed Asymmetric Addition of Arylboronic Acids to  $\alpha,\beta$ -Unsaturated Sulfonyl Compounds, Nishimura, T.; Takiguchi, Y.; Hayashi, T. J. Am. Chem. Soc. 2012, 134, 9086.
4. (a) Iridium/Chiral Diene-Catalyzed Asymmetric 1,6-Addition of Arylboroxines to  $\alpha,\beta,\gamma,\delta$ -Unsaturated Carbonyl Compounds. Nishimura, T.; Yasuhara, Y.; Sawano, T.; Hayashi, T. J. Am. Chem. Soc. 2010, 132, 7872. (b) Electronic tuning of chiral diene ligands in iridium-catalyzed asymmetric 1,6-addition of arylboroxines to  $\delta$ -aryl- $\alpha,\beta,\gamma,\delta$ -unsaturated ketones. Nishimura, T.; Noishiki, A.; Hayashi, T. Chem. Commun. 2012, 48, 973.
5. (a) Cobalt-catalyzed conjugate addition of silylacetylenes to  $\alpha,\beta$ -unsaturated ketones. Nishimura, T.; Sawano, T.; Ou, K.; Hayashi, T. Chem. Commun. 2011, 47, 10142. (b) Cobalt-catalyzed asymmetric addition of silylacetylenes to oxa- and azabenzonorbornadienes, Sawano, T.; Oh, K.; Nishimura, T.; Hayashi, T. Chem. Commun. 2012, 48, 6106.

**Date:** 7<sup>th</sup> September 2012 (Friday)  
**Time:** 11:00am – 12:30pm  
**Venue:** NTU SPMS CBC Building Level 2,  
Conference Room  
**Host:** Assoc Professor Tan Choon Hong