T. Hayashi

The author presented on this page has recently published his ***25th article*** *since 2000 in Angewandte Chemie:* “High Performance of a Palladium Phosphinooxazoline Catalyst in the Asymmetric Arylation of Cyclic *N*-Sulfonyl Ketimines”: C. Jiang, Y. Lu, T. Hayashi, *Angew. Chem. Int. Ed.* **2014**, *53*, 9936–9939; *Angew. Chem.* **2014**, *126*, 10094–10097.

Tamio Hayashi

Date of birth:	February 16, 1948
Position:	Principal Scientist, Institute of Materials Research and Engineering (IMRE) Professor, National University of Singapore (NUS)
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Education:	1970 BS, Kyoto University 1975 PhD with Makoto Kumada, Kyoto University 1976–1977 Postdoctoral position with Louis S. Hegedus, Colorado State University
Awards:	**1991** IBM Japan Science Prize; **2003** The Chemical Society of Japan Award; **2004** Thomson Scientific Research Front Award; **2007** Ryoji Noyori Prize, Society of Synthetic Organic Chemistry, Japan; **2008** Arthur C. Cope Scholar Award, American Chemical Society; **2010** Medal with Purple Ribbon (Shiju Hosho) from the Emperor of Japan; **2013** Foundation Lectureship Award in Organic Chemistry, Federation of Asian Chemical Societies
Current research interests:	1) Synthetic organic chemistry: Selective organic synthesis catalyzed by transition-metal complexes, particularly new carbon–carbon bond-forming reactions. 2) Organometallic chemistry: Mechanistic understanding of catalytic reactions by characterization of key intermediates and kinetic studies. 3) Catalysis: Asymmetric catalysis, development of catalytic asymmetric reactions and design of new chiral ligands for metal-catalyzed reactions.
Hobbies:	Sailboat racing; watching sports

My favorite saying is … “Curiosity makes us young”.

My favorite drink is … green tea from Japan, Taiwan, or China.

If I could be any age I would be … 18 years old as a university student. However, I would not like to study for the entrance examination again!

My favorite time of day is … the morning, when taking a relaxing bath before going to work.

My favorite way to spend a holiday is … to stay in the bed, half sleeping and half musing.

The secret of being a successful scientist is … to believe I am a successful scientist (even if I am not).

My favorite name reaction is … the Claisen condensation, which produces β-ketoesters by the reaction of esters containing α-hydrogen atoms with a base such as sodium ethoxide. This is the best reaction for teaching students about the driving force of chemical reactions.

The principal aspect of my personality is … I never worry.

My favorite painter is … Hokusai Katsushika, a Japanese ukiyo-e painter, famous for his series *Thirty-Six Views of Mount Fuji.*

My favorite musician is … Takuro Yoshida, a Japanese singer-songwriter. He is the most charismatic musician of my generation.

My favorite books are … novels by Haruki Murakami, particularly *Hard-Boiled Wonderland and the End of the World.*

The natural talent I would like to be gifted with is … a long attention span.

My motto is … “Keep smiling”.

The biggest challenge facing scientists is … to give nonscientists a real appreciation of science.

Looking back over my career, I … have had a lot of luck with great teachers and dedicated co-workers.

Last time I went to the pub … it was a few weeks ago to entertain visitors from Japan in a Japanese-style pub in Singapore.

Has your approach to publishing your results changed since the start of your career?

At the initial stage of my university career as an assistant professor, all the research projects came mainly from my personal curiosity, which is not always relevant to the quality or novelty of the research topics. As the years passed, I recognized the importance of my publication list for the future careers of my co-workers as well as myself. I came to be more conscious of the possibility of better publications when starting a new project, although I sometimes feel uncomfortable with those who care too much about their publication list. Currently I assume that publication in the best journals is one of the ways of demonstrating how broadly and deeply we understand the research project.

What do you think the future holds for your field of research?

I have been studying and working in essentially the same research field for 40 years. The research area is the use of transition-metal complexes as catalysts for selective organic transformations, particularly for catalytic asymmetric reactions. This research area has developed very quickly and extensively over the last two decades, and now it is in a mature stage. However, the fact that it is mature does not mean it will start to decline soon, and the upward curve should continue for at least another 20 years. Many new types of catalytic reactions of fundamental interest will appear, some of them will be applied to the practical production of useful chemicals, and the application will be extended to broader adjacent research areas.

My 5 top papers:

1. "A Chiral Chelating Diene as a New Type of Chiral Ligand for Transition Metal Catalysts: Its Preparation and Use for the Rhodium-Catalyzed Asymmetric 1,4-Addition": T. Hayashi, K. Ueyama, N. Tokunaga, K. Yoshida, *J. Am. Chem. Soc.* **2003**, *125*, 11508–11509.
   A C_2-symmetric substituted bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) ligand was prepared by palladium-catalyzed asymmetric hydrosilylation of norbornadiene, and showed high catalytic activity and high enantioselectivity in the rhodium-catalyzed asymmetric conjugate addition of boronic acids to α,β-unsaturated ketones. Since this report, over 100 publications have appeared where chiral diene ligands are more efficient than conventional chiral phosphorus ligands.
2. "Catalytic Cycle of Rhodium-Catalyzed Asymmetric 1,4-Addition of Organoboronic Acids. Arylrhodium, Oxa-π-allylrhodium, and Hydroxorhodium Intermediates": T. Hayashi, M. Takahashi, Y. Takaya, M. Ogasawara, *J. Am. Chem. Soc.* **2002**, *124*, 5052–5058.
   The catalytic cycle of rhodium-catalyzed 1,4-addition of arylboronic acids to α,β-unsaturated ketones, which was first reported by Norio Miyaura in 1997, was studied by analyzing the intermediates. All three key intermediates were detected and characterized by ^{31}P NMR spectroscopy. This report provides us with a very rare example of mechanistic studies of transition-metal-catalyzed reactions where all the key intermediates are fully characterized.
3. "Asymmetric Synthesis Catalyzed by Chiral Ferrocenylphosphine–Transition Metal Complexes. I. Preparation of Chiral Ferrocenylphosphines": T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto, M. Kumada, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138–1151.
   A full paper on the synthesis of chiral ferrocenylphosphine ligands, which was initially reported in a communication in 1974. It is a compilation of all the chiral ferrocenylphosphine ligands including monophosphines (ppfa) and bisphosphines (bppfa), describing the functionalization on the ferrocenylmethyl side chain, which is unique to these ligands and makes fine tuning possible. These chiral ferrocenylphosphines were later used as the best chiral ligands in reactions such as palladium-catalyzed asymmetric cross-coupling to form allylsilanes, nickel-catalyzed cross-coupling to form axially chiral binaphthyls, and gold-catalyzed asymmetric aldol-type reactions.
4. "Dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II): An Effective Catalyst for Cross-Coupling of Secondary and Primary Alkyl Grignard and Alkylzinc Reagents with Organic Halides": T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, K. Hirotsu, *J. Am. Chem. Soc.* **1984**, *106*, 158–163.
   A palladium complex coordinated with 1,1′-bis(diphenylphosphino)ferrocene (dppf) was found to be an excellent catalyst for the cross-coupling of alkyl Grignard reagents with organic halides to give the coupling products with high selectivity without isomerization of the alkyl group or reduction of the halide by β-hydrogen elimination on the alkylpalladium intermediate. The X-ray analysis of [$PdCl_2$(dppf)] showed that the dppf complex has a wide P-Pd-P bite angle, and it was proposed that the wide bite angle promotes reductive elimination of the coupling product from a diorganopalladium intermediate.
5. "Catalytic Asymmetric Aldol Reaction: Reaction of Aldehydes with Isocyanoacetate Catalyzed by a Chiral Ferrocenylphosphine–Gold(I) Complex": Y. Ito, M. Sawamura, T. Hayashi, *J. Am. Chem. Soc.* **1986**, *108*, 6405–6406.
   This publication, which reported the first example of the use of a chiral gold complex as a catalyst for asymmetric organic reactions, was realized by collaboration with Professor Yoshihiko Ito, who is an expert in isocyanide chemistry. The design of the chiral ferrocenylbisphosphine ligand by introduction of a (dialkylamino)alkyl group onto the side chain was very successful in bringing about high catalytic activity and high enantioselectivity in the reaction of methyl isocyanoacetate with aldehydes giving enantiomerically enriched oxazoline carboxylates. The oxazolines are readily hydrolyzed into β-hydroxy-α-amino acids with high enantiomeric excess.

International Edition: DOI: 10.1002/anie.201409915
German Edition: DOI: 10.1002/ange.201409915