





K. Maruoka

The author presented on this page has published his 25th article since 2000 in Angewandte Chemie: "Catalytic Asymmetric Alkynylation of C1-Substituted C,N-Cyclic Azomethine Imines by Cu<sup>1</sup>/Chiral Brønsted Acid Co-Catalyst": T. Hashimoto, M. Omote, K. Maruoka, Angew. Chem. **2011**, *123*, 9114-9117; Angew. Chem. Int. Ed. 2011, *50*, 8952 – 8955.

## Keiji Maruoka

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http://kuchem.kyoto-u.ac.jp/yugo/english/index.html Homepage: **Education:** 1976 Undergraduate degree, Kyoto University

1980 Ph.D. with Prof. Hisashi Yamamoto, University of Hawaii

2001 Inoue Prize for Science; 2002 Ichimura Prize for Science; 2004 Synthetic Organic Awards:

Chemistry Award of Japan; 2004 Nagoya Silver Medal; 2006 Award of the Minister of Education, Culture, Sports, Science and Technology; 2007 Chemical Society of Japan Award; 2007 Novartis Lectureship Award; 2010 Chunichi Cultural Prize; 2011 Arthur C. Cope Scholar

Award; 2011 Medal of Honor with Purple Ribbon

Design of high-performance organocatalysts for sustainable chemical transformations with the **Current research** aim of large-scale production of useful materials in the chemical and pharmaceutical industries. interests:

**Hobbies:** Fishing and cooking

#### The most important thing I learned from my parents is ... persistence is power.

My favorite place on earth is ... Hawaii.

like refereeing because ... I can know about the very latest research findings and it gives me a good opportunity to study my own and related fields.

The most significant scientific advance of the last 100 years has been ... the computer.

The greatest scientific advance in the next decade will be ... hopefully photovoltaic power generation.

What I look for first in a publication is ... the authors' originality and creativity.

If I won the lottery, I would ... like to use the whole prize to help the smooth recovery of the Tohoku areas from the natural disaster.

If I could have dinner with three famous scientists from history, they would be ... Marie Curie, Karl Ziegler, and R. B. Woodward.

And I would ask them ... about the scientific advances they expect in chemistry in the 21st century.

chose chemistry as a career because ... of its similarity to sophisticated cooking in terms of ideas, concepts, creativity, and sensitivity.

If I were not a scientist, I would be ... a chef in a first-class Japanese restaurant in Kyoto.

My most exciting discovery to date has been ... the "Maruoka Catalysts" and the "Simplified

My greatest achievement has been ... the large-scale production of artificial amino acids for pharmaceutical use with the Simplified Maruoka Catalyst.

The most exciting thing about my research is ... the occurrence of very unexpected results.

My favorite food is ... raw fish that is freshly prepared with my 25-year-old fish-slicing knife.

The best stage in a scientist's career is ... the moment of his greatest discovery or achievement in

The best advice I have ever been given is ... life looks like a kind of transition state in chemical

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

At the beginning of my career, I was interested in many research topics in Lewis acid chemistry, and was very enthusiastic about the publication of my new findings in renowned chemistry journals such as *J. Am. Chem. Soc.* and *Angew. Chem.* Later, particularly when I got an independent professorship position at Hokkaido University, the final goal of my research was to write high-level review articles after several years. To do so, careful thinking about the original ideas, basic concepts, the design of new catalysts, and the development of new methods is of the utmost importance.

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

Organocatalysis has recently emerged as a field of research providing practical alternative or complementary technologies to the more traditional transition-metal-catalyzed systems. During the last ten years, a wide variety of organocatalysts, including chiral organocatalysts, have been devised and applied to various organic transformations. Some of the catalysts are highly sophisticated and have been successfully used in industrial reactions. However, organocatalysis is still in its infancy compared to traditional transition-metal chemistry, and hence there is a need to devise several kinds of new privileged organocatalysts to further expand the scope of this exciting field.

#### My 5 top papers:

- "Molecular Design of a C<sub>2</sub>-Symmetric Chiral Phase Transfer Catalyst for Practical Asymmetric Synthesis of α-Amino Acids": T. Ooi, M. Kameda, K. Maruoka, J. Am. Chem. Soc. 1999, 121, 6519-6520.
  - This was the starting point of designer chiral phase-transfer catalysts based on the chiral  $C_2$ -symmetric binaphthyl backbones, because almost all the previously reported elaborated chiral phase-transfer catalysts had been restricted to cinchona alkaloid derivatives, which unfortunately constituted a major difficulty in rationally designing and fine-tuning catalysts to attain sufficient reactivity and selectivity for various chemical transformations under phase-transfer-catalyzed conditions. A series of these binaphthyl-modified chiral phase-transfer catalysts are now referred to as Maruoka Catalysts.
- 2. "Practical Catalytic Enantioselective Synthesis of α,α-Dialkyl-α-Amino Acids by Chiral Phase-Transfer Catalysis": T. Ooi, M. Takeuchi, M. Kameda, K. Maruoka, J. Am. Chem. Soc. 2000, 122, 5228-5229. Nonproteinogenic  $\alpha,\alpha$ -dialkyl- $\alpha$ -amino acids have played a special role in the design of peptides with enhanced properties, not only because these amino acids possess stereochemically stable quaternary carbon centers, but also because their incorporation into peptides results in a significant influence on the conformational preferences, which eventually provides useful information for the elucidation of enzymatic mechanisms. This paper describes the first practical enantioselective synthesis of  $\alpha,\!\alpha\text{-dialkyl-}\alpha\text{-amino}$  acids by the enantioselective phase-transfer alkylation of the aldimine Schiff base of glycine and  $\alpha$ -substituted amino acid derivatives with 3,3'-bis(trifluorophenyl)bi-
- "Powerful Chiral Phase Transfer Catalysts for the Asymmetric Synthesis of α-Alkyl- and α,α-Dialkyl-αamino Acids": M. Kitamura, S. Shirakawa, K. Maruoka, Angew. Chem. 2005, 117, 1573–1575; Angew. Chem. Int. Ed. 2005, 44, 1549–1551.

naphthyl-modified chiral quaternary ammonium salts.

After the discovery of the first-generation phasetransfer catalysts, the so-called Maruoka Catalysts, the structural simplification and the catalyst efficiency

- were the two remaining important problems in the design of high-performance phase-transfer catalysts. In order to solve these intrinsic problems, we developed a new combinatorial design approach for the synthesis of a series of chiral phase-transfer catalysts from three different parts. Accordingly, by introducing trifluorophenyl substituents and a dibutylamino moiety to the chiral binaphthyl core structures, an exceedingly efficient, yet enantioselective phase-transfer catalyst was newly prepared and is now widely utilized as the Simplified Maruoka Catalyst for the large-scale production of various artificial amino acids.
- "anti-Selective Direct Asymmetric Mannich Reactions Catalyzed by Axially Chiral Amino Sulfonamide as an Organocatalyst": T. Kano, Y. Yamaguchi, O. Tokuda, K. Maruoka, J. Am. Chem. Soc. 2005, 127, 16408– 16409.
  - This paper demonstrated the first example of the rational design of chiral amino acid type organocatalysts with two functional groups at a remote position. Such a bifunctional organocatalyst allows the otherwise difficult *anti*-selective direct asymmetric Mannich reactions of aldehydes and  $\alpha$ -imino esters with an axially chiral amino sulfonamide catalyst. This reaction has also been successfully applied to the *syn*-selective direct asymmetric aldol reaction of two different aldehydes with high enantioselectivity.
- 5. "Enantioselective Base-Free Phase-Transfer Reaction in Water-Rich Solvent": R. He, S. Shirakawa, K. Maruoka, J. Am. Chem. Soc. 2009, 131, 16620–16621. As in biocatalyzed transformations, the development of certain organocatalytic reactions that would proceed in water under essentially neutral conditions without any promoters is quite attractive and challenging in terms of environmental awareness. In this paper, we demonstrated the base-free phase-transfer conjugate addition of 3-aryloxindoles to nitrostyrenes with a bifunctional phase-transfer catalyst in a water-rich solvent. This is the first example of asymmetric base-free phase-transfer reactions under essentially neutral conditions.

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