





Michael P. Doyle

The author presented on this page has recently published his 10th article in Angewandte Chemie in the last 10 years:

"Highly Enantioselective Carbonyl – Ene Reactions of 2,3-Diketoesters: Efficient and Atom-Economical Process to Functionalized Chiral  $\alpha$ -Hydroxy- $\beta$ -Ketoesters": P. M. Truong, P. Y. Zavalij, M. P. Doyle, Angew. Chem. Int. Ed. **2014**, 53, 6468–6472; Angew. Chem. **2014**, 126, 6586–6590.

### Michael P. Doyle

**Date of birth**: October 31, 1942

Awards:

**Position**: Professor, University of Maryland

E-mail: mdoyle3@umd.edu

Homepage: http://www.chem.umd.edu/michael-p-doyle/ Education: 1960–1964 BS, College of St. Thomas, St. Pa

1960–1964 BS, College of St. Thomas, St. Paul, Minnesota 1968 PhD with Walter S. Trahanovsky, Iowa State University

1968 Postdoctoral position with Jan Roček, University of Illinois at Chicago

1995 Fellow, American Association for the Advancement of Science; Alexander von Humboldt Research Award; 1998 Paul Gassman Distinguished Service Award from the American Chemical Society (ACS) Division of Organic Chemistry; 2002 George C. Pimentel Award in Chemical Education, ACS; 2006 Arthur C. Cope Senior Scholar Award, ACS; 2009 Fellow,

Royal Society of Chemistry; Fellow, ACS; 2014 Hillebrand Award, Chemical Society of

Washington

**Current research** The major focus of our research is the development of highly selective and efficient catalytic **interests**: processes for the synthesis of biologically relevant compounds. Investigations are built upon

unique, highly efficient and selective, catalytic uses of dirhodium and other transition-metal catalysts. The fixed stereodefined geometry of dirhodium carboxamidates provides access to highly enantioenriched products in metal carbene reactions of diazoacetates and, together with their low oxidation potentials, also gives capabilities for highly selective Lewis acid catalyzed reactions and efficient chemical oxidations with high turnover numbers and high selectivities. We are developing enoldiazoacetates for catalytic highly stereoselective transformations that

include [3+3] cycloaddition reactions for the synthesis of heterocycles.

Hobbies: Gardening and history

#### I lose track of time when ... I'm solving a chemical problem.

n retrospect I would never again ... take a job that removes me from research.

My greatest achievement has been ... the design and development of chiral dirhodium carboxamidates for highly enantioselective metal carbone transformations and Lewis acid catalyzed reactions.

My worst nightmare is ... not completing what I set out to do. As a youngster it was coming to the final exam with the realization that I had never attended a lecture.

The most exciting thing about my research is ... the discovery of new chemical processes and how they occur.

The best advice I have ever been given is ... "you are of greater interest and value when you are passionate about the subject".

The worst advice I have ever been given was ... "burn your bridges" with reference to seeking my first job near the end of the hiring season.

When I'm frustrated, I ... look for other things to do.

My favorite author (fiction) is ... John Steinbeck.

My biggest motivation is ... discovery together with the persons with whom I work.

My favorite piece of music is ... the aria "Un bel dì vedremo", from Puccini's opera Madama Butterfly.

like refereeing because ... this gives me the opportunity to be aware of current developments in my areas of expertise and to maintain an understanding of the science.

The most significant scientific advance of the last 100 years has been ... the birth control pill.

The biggest problem that scientists face is ... denial of the validity of scientific discovery and the conclusions drawn from them.

f I won the lottery, I would ... set up a foundation to support the further development of the chemical sciences.

The most important thing I learned from my parents is ... unselfishness.

My favorite place on earth is ... wherever I can be with my children and grandchildren.



chose chemistry as a career because ... chemistry promised "better things for better living" and was a national priority.

My best decision was ... marrying my wife of now 50 years.

f I were not a scientist, I would be ... a lawyer; but the choice was not close.

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

I began my career at an undergraduate institution where resources were modest but undergraduate talent and motivation were high. When the experiments allowed conclusions to be reached, I began to write the manuscript with students assisting with the experimental section. At that time, I thought that including all experiments performed was the best way to achieve recognition of the results, and I must confess that I believed that anyone who reads the manuscript would understand the logic of the argument and the impact of the conclusions. To my good fortune, there were reviewers who could see a germ of substance and would guide me to refinement and focus. Today, manuscripts are more clearly focused; the introduction gives the reader the reason to continue, the results section clearly establishes the outcome, and the less important outcomes are in the Supporting Information.

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

Asymmetric catalysis continues to be the major focus of my research. At a recent workshop on "The Future of Asymmetric Catalysis" (July 2014 in Telluride, Colorado) there was consensus that the field is vibrant with a great amount left to accomplish. The field has changed dramatically over the past twenty-five years, however, and tomorrow's expectations are much greater and diverse than those of the past: even higher selectivities, lower catalyst loadings, uses of earthabundant metal catalysts, development of multicomponent reactions and cascade transformations. The speed with which an optically pure material can be accessed, whether by chromatographic separation or asymmetric synthesis, and the optimum method for synthesis (enzymatic, chemical catalysis) will become increasingly important, as will increasingly rapid access to relevant informa-

#### My 5 top papers:

- "Kinetics and Mechanism of the Oxidation of Human Deoxyhemoglobin by Nitrites": M. P. Doyle, R. A. Pickering, T. M. DeWeert, J. W. Hoekstra, D. R. Pater, J. Biol. Chem. 1981, 256, 12393–12398.
  - This and related publications established the oxidative mechanism for the interaction of alkyl nitrites and nitrite ions with hemoglobin and other heme iron proteins through rate determinations that defined the rate law and stereoelectronic influences, and they influenced subsequent understandings of the chemical biology of nitrite reactions with hemoglobin.
- 2. "Dirhodium(II) Tetrakis(carboxamidates) with Chiral Ligands. Structure and Selectivity in Catalytic Metal Carbene Transformations": M. P. Doyle, W. R. Winchester, J. A. A. Hoorn, V. Lynch, S. H. Simonsen, R. Ghosh, J. Am. Chem. Soc. 1993, 115, 9968–9978. The first full paper to describe the design and construction of chiral dirhodium(II) carboxamidate catalysts and intramolecular cyclopropanation and C-H insertion reactions of diazoacetates whose enantioselectivities and diastereoselectivities have not been surpassed by any other catalytic system.
- "Dirhodium(II) Caprolacatamate: An Exceptional Catalyst for Allylic Oxidation": A. J. Catino, R. E. Forslund, M. P. Doyle, J. Am. Chem. Soc. 2004, 126, 13622-13623.
  - Dirhodium(II) caprolactamate in combination with tert-butyl hydroperoxide effectively catalyzes the

- allylic oxidation of a variety of cycloalkenes and enones. Subsequent publications documented oxidations of cyclic alkenes and *N,N*-dialkylanilines, as well as benzylic, propargylic, and phenolic oxidations as effective and efficient methodologies.
- 4. "Cationic Chiral Dirhodium Carboxamidates are Activated for Lewis Acid Catalysis": Y. Wang, J. Wolf, P. Zavalij, M. P. Doyle, Angew. Chem. Int. Ed. 2008, 47, 1439–1442; Angew. Chem. 2008, 120, 1461–1464. This manuscript reports the preparation and applications of a set of cationic chiral dirhodium carboxamidates for asymmetric Lewis acid catalyzed transformations. Enhanced reactivity and selectivity were realized in both the hetero-Diels-Alder reaction and 1,3-dipolar cycloaddition of methacrolein to nitrones.
- "Highly Enantioselective Dearomatizing Formal [3+3] Cycloaddition Reactions of N-Acyliminopyridinium Ylides with Electrophilic Enolcarbene Intermediates": X. Xu, P. Y. Zavalij, M. P. Doyle, Angew. Chem. Int. Ed. 2013, 52, 12664–12668; Angew. Chem. 2013, 125, 12896–12900.

The synthesis of dihydroquinoline derivatives by [3+3] cycloaddition that occurs with highly enantioselective dearomatization of the pyridine ring was reported. Related highly enantioselective [3+3] cycloaddition reactions established the generality of this methodology for the synthesis of heterocycles.

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