J. Barluenga

*J. Barluenga has recently published his **35th article** since 2000 in Angewandte Chemie:*
"Sequential Five-Component Construction of the Cyclopenta[e][1,3]oxazine Skeleton using Stable 2-Azetine Derivatives": J. Barluenga, A. Gómez, J. Santamaría, M. Tomás, *Angew. Chem.* **2010**, *122*, 1328–1330; *Angew. Chem. Int. Ed.* **2010**, *49*, 1306–1308.

José Barluenga

Date of birth:	July 27, 1940
Position:	Professor of Chemistry, University of Oviedo (Spain)
Education:	1963 BS University of Zaragoza (Spain) 1966 PhD with Prof. V. Gómez Aranda, University of Zaragoza 1967–1970 Postdoc with Prof. H. Hoberg, Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr (Germany)
Awards:	**1989** Research Award of the "Alexander von Humboldt" Foundation, (Germany); **1990** Solvay Award (Spain); **1991** 1st Dupont Award (Spain); **1996** Iberdrola Award for Science and Technology (Spain); **1999** 1st Gold Medal from the Spanish Society of Chemistry; **2000** Doctor Honoris Causa, University of Alcalá de Henares (Spain); **2001** 1st National Award of Chemical Science and Technology "Enrique Moles" (Spain); **2002** Foundation García-Cabrerizo Award (Spain); **2005** Hermanos Elhuyar-Hans Goldschmidt Award (Germany–Spain); **2005** Rey Jaime I de Investigación Award (Spain); **2009** Silver Medal of Principado de Asturias (Spain); **2009** Doctor Honoris Causa, University of La Rioja (Spain)
Current research interests:	Transformations without assistance from transition metals: "carbon–carbon" and "carbon–heteroatom" coupling reactions; Enantioselective carbo- and heterocyclization reactions; Synthetic methodologies based on transition-metal reagents, stoichiometric, and catalytic processes; Design and synthesis of new molecular probes for tracing (in vivo) and treatment of amyloidal diseases; Bioactive compounds: preparation of new molecules with antitumoral properties
Hobbies:	Nature watching, cooking, history, and sports

If I could be anyone for a day, I would be … Christopher Columbus at the time he reached America for the first time.

If I were not scientist, I would be … a veterinary surgeon.

My favorite subject at school was … physics.

When I was eighteen I wanted to be … a chemist.

The most significant scientific advance of the last 100 years has been … catalysis, all types of catalysis.

My science "heroes" are … Antoine-Laurent Lavoisier, Emil Fischer, and Karl Ziegler.

If I could have dinner with three famous scientists from history, they would be … Santiago Ramón y Cajal, Albert Einstein, and Linus Pauling.

I chose chemistry as a career because … of the influence of my high school chemistry teacher. As time goes by I see him as a generous and friendly teacher who was enthusiastic about the growth of his pupils and was truly devoted to his work.

In my spare time I … read novels and listen to music.

The secret of being a successful scientist is … There is no doubt! The excellence and commitment of the students in your research group.

The best advice I have ever been given is … "Where there's a will there's a way".

My ultimate goal is to … contribute to the development of science in a broad sense and, more specifically, to the visibility of my country.

I would have liked to have discovered … olefin metathesis.

The part of my job which I enjoy the most is … discussions with my students at the blackboard in my office.

The most groundbreaking discovery in science in the past 100 years has been … molecular biology.

My favorite book is … "Don Quixote" (Full title: "The Ingenious Hidalgo Don Quixote of La Mancha") by Miguel de Cervantes.

How is chemistry research different now than it was at the beginning of your career?

In the late 1960s, it was very difficult to start a scientific career in Spain. That was true in many regards and for different reasons. Not only because of the economic situation but, to a great extent, there was a lack of scientific tradition that hampered the progression of those singular and few people that went abroad to improve their knowledge. Most of them did not return and decided to remain at the more scientifically advanced institutions. At that time, as a young Professor, I began my independent research program (1970), following a long postdoctoral stay in Germany. After a decade, the context for research changed dramatically and things became easier. To put it in simple words, and by taking into account the striking change of coordinates in Spain along this time, the difference is huge. Now one can safely say that only the capacity of our brain is the key limiting factor.

Has your approach to chemistry research changed since the start of your career?

As I have already mentioned, my personal experience might not be of general application. At the beginning of my career, my proposals were severely restricted by some important circumstances. These were primarily economic reasons, but also I (and many others) had to set a daily fight for the most obvious things required to carry out a research program. Fortunately, nowadays, we have access to all the facilities available at a top international laboratory, so we are able to target problems within the regular schemes of a worldwide advanced laboratory.

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

From what I have already said, my initial goal was to be able to conduct a modest but innovative research program that would give rise to results deserving publication and, importantly, visibility at an international level, according to the standards of publication at that time. At some point in my career the surrounding conditions allowed me to move one step forward. Thus, I started to be more selective and ambitious with respect to the scientific goals I want to reach, but always, as from the very first moment, keeping a high standard of exigency and, of course, quality.

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

Personally, I truly think that the only limit is our imagination and our ability to combine. It is always difficult to make predictions because we all go in search of what is yet unknown. Just to give an example, can you think of many people, early in the 1980s, who were able to foresee the evolution of the metathesis reaction and its enormous impact for selective organic synthesis? Anyway, one may speculate that at the borderline of physics and biology there are still enormous possibilities to advance science, without missing our identity as chemists.

Have you changed the main focus of your research throughout your career and if so why?

One must always be aware of his own situation, and so at the beginning I had to postpone some research initiatives. Then, after a long career, my curiosity has prompted me to explore and enjoy approaching new and diverse problems, and I would say always with passion and enormous dedication. Should my intelligence have been at the level of my enthusiasm for chemistry, I would have reached major milestones in my career long ago.

What has been you biggest influence/motivation?

I believe that in my case much is owed to a significant dedication to the reading of scientific literature, and then to reflect on its relevance for my research. So, if on this basis you properly combine a certain degree of circumspection and a bit of intuition to attempt to tackle chemical problems that you consider of interest, you will get the answer.

What advice would you give to up-and-coming scientists?

Just the advice that I think was the best offered to me: “Where there’s a will there’s a way”. Sometimes the results will not be on your side. This is the right time for you to be fully devoted to your work, and to give all you bring inside yourself. Also, you should train your students to try to be at the top level, asking them to fulfill the highest possible standards of intellectual demands.

What is the secret to publishing so many high-quality papers?

There are no secrets! You must always try to undertake your daily work with passion, dedication, and cope with standards of intellectual innovation and significance. To do so you certainly need to attract the most talented and enthusiastic students. Many times they provide the true power and inspiration behind those publications, and I am certainly grateful to all of them.

My 5 top papers:

1. "The Addition of Aromatic Amines to Alkenes in the Presence of Thallium(III) Acetate": V. Gómez Aranda, J. Barluenga, F. Aznar, *Synthesis* **1974**, 504–505.
   This paper is an early and representative contribution of research that was conducted in my laboratory in the 1970s, which dealt with the elusive addition of nitrogen-containing nucleophiles to alkenes. It was followed by a series of papers aimed at the functionalization of other types of unsaturated systems, and to the extension of this chemistry to allow the use of other sources of nucleophilic nitrogen, or even other heteroatoms as nucleophiles. A major breakthrough in this chemistry followed quickly and pioneered the use of metal catalysts to functionalize alkynes by reaction with amines ("Thallium(III) Acetate as Catalyst in the Addition of Aromatic Amines to Phenylacetylene": J. Barluenga, F. Aznar, *Synthesis* **1977**, 195–196).
2. "Transmetallation Reactions of Organomercury(II) compounds VII. Synthesis and Chemical Characterization of β-Hydroxy- and β-Aminolithium Derivatives": J. Barluenga, F. J. Fañanás, M. Yus, G. Asensio, *Tetrahedron Lett.* **1978**, 2015–2016.
   This paper describes the stabilization and chemical characterization of β-functionalized organolithium compounds. The conditions established in the paper made possible, for the first time, the use of these elusive and highly reactive reagents in selective organic synthesis. On this basis, subsequent studies addressed the potential of this protocol to provide smooth access to related reactive species, proving the generality of this approach and enabling a facile preparation of different polyfunctionalized synthons.
3. "IPy_2BF_4-Promoted Intramolecular Addition of Masked and Unmasked Anilines to Alkynes: Direct Assembly of 3-Iodoindole Cores": J. Barluenga, M. Trincado, E. Rubio, J. M. González, *Angew. Chem. Int. Ed.* **2003**, *115*, 2508–2511; *Angew. Chem. Int. Ed.* **2003**, *42*, 2406–2409.
   This article deals with the reactivity of the tetrafluoroborate of bis(pyridine)iodonium(I) as a mild source of iodonium ions. The enormous synthetic potential of the title reagent was evident from preliminary studies that were carried out in my laboratory in the mid 1980s, and its merits at iodinating a great diversity of aromatic compounds at room temperature were soon established. More recent studies addressed its utility to directly iodinate peptides or β-aryl alkylamine derivatives. Far from its ability to efficiently perform direct site-specific iodination reactions, the utility of the reagent to promote selective carbo- and heterocyclization events starting from proper unsaturated systems was also intensively studied. In this context, the iodination process is used to trigger an increase of molecular complexity and nicely complements the outcome of some metal-catalyzed cyclization reactions. The selected article provides a striking example for this concept.
4. "Alkenyl Fischer Carbene Complexes and α,β-Unsaturated Imine Derivatives: Synthesis of Azepines and Mechanistic NMR Studies": J. Barluenga, M. Tomás, A. Ballesteros, J. Santamaría, R. J. Carbajo, F. López-Ortiz, S. García-Granda, P. Pertierra, *Chem. Eur. J.* **1996**, *2*, 88–97.
   Early in the 1990s, I started a research program dealing with the chemistry of Fischer-type carbene complexes, mainly by using group 6 metals. From that moment, my laboratory has been actively engaged in this area, disclosing novel reactivity patterns for those complexes. Among them are various [4+3] and [5+2] carbo- and heterocyclization reactions. The selected contribution provides ground to comprehensively rationalize these transformations, which involve a key 1,2-migration of the pentacarbonyl metal fragment (another key paper: "First [4+3] Annulation of Alkynyl Fischer Carbene Complexes and Azadienes. X-ray Structure of a Metallated Zwitterionic Intermediate": J. Barluenga, M. Tomás, E. Rubio, J. A. López-Pelegrín, S. García-Granda, P. Pertierra, *J. Am. Chem. Soc.* **1996**, *118*, 695–696). Other advances in this field from our group include a series of [4+1] and [3+2] carbocyclizations with enolates and amines, and the design and achievement of asymmetric transformations. In this sense, a recent breakthrough is the asymmetric elaboration of the privileged skeleton of indolines from the reaction of indoles and alkynyl Fischer carbene complexes. Relevant results were obtained for the in situ preparation of Fischer carbene complexes of the late transition metals (groups 9–11) through transmetallation reactions. More recently, the chemistry of Fischer carbene complexes has moved into the alternative study of nonstabilized carbene complexes from group 6 metals. Previously, these could be termed as rarely described and studied reactive compounds in the literature.
5. "Metal-Free Carbon–Carbon Bond-Forming Reductive Coupling Between Boronic Acids and Tosylhydrazones": J. Barluenga, M. Tomás-Gamasa, F. Aznar, C. Valdés, *Nature Chem.* **2009**, *1*, 494–499.
   This chemistry is the result of the evolution of a long-standing synthetic target in my group. At some point, my interest in the preparation of dienes containing chiral information as building-blocks for [4+2] cycloaddition reactions, together with the scant number of alternatives to this end, prompted us to search for new cross-coupling approaches based on the reaction of amines with halodienes. This was a poorly documented process, particularly considering the well-established impact of related reactions with haloarenes. In this context we also explored the potential of different reaction cascades that involve a key C–N cross-coupling step to prepare several classes of privileged heterocyclic scaffolds. More recently, we turned our attention to the exploration of *N*-tosylhydrazones as convenient partners rather than haloarenes. In this synthetic scenario we have found that hydrazones can be safely used to mimic the reactivity of classes of diazocompounds, which are otherwise dangerous and difficult to handle. Ultimately, this finding has resulted in an unconventional metal-free approach to gentle trapping with boronic acid derivatives of the unstable intermediate species resulting from the decomposition of hydrazones. This is new chemistry that ultimately relies on simple carbonyl compounds, from which a rapid and spectacular evolution may be reasonably foreseen.

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