

New carbon reactivity rules

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In this lecture, I will show how the catalytic generation of conceptually-novel radical carbenoids, carbyne equivalents, and metal-carbynoids enabled the discovery of new carbon reactivity towards C–H and C–C bonds. The metal or photocatalytic activation of tailored sources revealed new reactivity rules at carbon that have been under-appreciated, not only in the design and discovery of new chemical reactions, but also in their use to build molecular complexity through unexplored disconnection approaches.

Dr Marcos García Suero

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Marcos García Suero was born in Noreña (Asturias) in 1981. He graduated in Chemistry from the Universidad de Oviedo in 2003 and started organometallic chemistry research in the laboratory of Profs. José Gimeno and Pilar Gamasa. In February 2009, he obtained his PhD degree at the Institute of Organometallic Chemistry Enrique Moles and Department of Organic and Inorganic Chemistry (Universidad de Oviedo), where he worked under the direction of Prof. José Barluenga and Prof. Josefa Flórez on Fischer carbene chemistry. During the summer of 2005 he joined the laboratory of Prof. Andrew Myers at Harvard University working on the synthesis of novel tetracycline antibiotics as a PhD visiting student. In May 2010, he moved to the University of Cambridge to work with Professor Matthew Gaunt on copper catalysis and methionine bioconjugation as a Postdoctoral Marie Curie Fellow. In 2014, Dr Suero was awarded with the Starting Career Programme (SCP) at the Institute of Chemical Research of Catalonia by the ICIQ Scientific Advisory Board. The SCP provides a position for 4 + 3 years to establish a group and a research programme. After the first 4 years, Dr Suero has successfully passed the midterm evaluation and he has been recommended to continue under the SCP for three more years.

Over the last four years, the main goal of Dr Suero has been the development of catalytic strategies for the generation of conceptually-novel carbon species and study their reactivity towards organic matter. Key on the programme has been the use of novel catalytic activation modes and tailored reagents to unveil new carbon reactivity rules and unlock elusive and useful tools for chemical synthesis.

Educational/Professional Experience

From October 2014	Group Leader at the Institute of Chemical Research of Catalonia - ICIQ.
2010 - 2014	Postdoctoral Researcher. Advisor: Professor Matthew Gaunt , University of Cambridge (UK). <i>Development of new copper-catalyzed reactions and methionine bioconjugation with hypervalent iodine reagents.</i>
2003 - 2009	PhD studies. Advisors: Professors José Barluenga, Josefa Flórez, Universidad de Oviedo. Thesis title: Diastereoselective multicomponent cyclizations of Fischer alkoxycarbene complexes, lithium enolates and unsaturated organometallics. (2nd February 2009; Cum Laude).
2005 (3 months)	Internship in the group of Professor Andrew Myers, Harvard University (USA). <i>Total synthesis of novel tetracycline antibiotics.</i>
2002 - 2003	Undergraduate research internship. Advisor: Professor José Gimeno , Universidad de Oviedo . Synthesis of novel cumulenylidene ruthenium complexes with nonlinear optic properties.
1999 – 2003	BSc Chemistry, University of Oviedo.

Awards

2019 Leonardo Da Vinci Award 2019 (BBVA Foundation)

- 2019 Young Investigator Award EuChemS (Org Div)
- 2019 Thieme Chemistry Journal Award

2018 **JSP Travel Award** from the Swiss Chemical Society for the 53rd Bürgenstock Conference

2018 Merck Sigma-Aldrich Young Researcher Award from the Royal Spanish Chemical Society

2017-2019 SGR Emerging Group Recognition by the Generalitat de Catalunya (AGAUR)

Publications * indicates Dr Suero corresponding authorship

• Manuscript under preparation "New Synthesis of β -diazocarbonyl compounds enabled discovery of a rare intra-molecular Rh-catalyzed carbone C-H insertion". Liyin Jiang, Zhaofeng Wang, Melanie Armstrong, Marcos G. Suero*.

• J. Am. Chem. Soc **2019**, DOI: 10.1021/jacs.9b08632. Catalytic cleavage of C(*sp*₂)-C(*sp*₂) bonds with Rh-carbynoids. Zhaofeng Wang, Liyin Jiang, Pau Sarró, Marcos G. Suero*.

***Highlighted in Chemistry Views & Chemistry World

***Among the most read articles in September 2019

• *Chem. Sci.* **2019**, DOI: 10.1039/C9SC02749A. A transition-metal-free & diazo-free styrene cyclopropanation. Ana G. Herraiz, Marcos G. Suero*.

• *Synthesis*, **2019**, *51*, 2821. New Alkene Cyclopropanation Reactions Enabled by Photoredox Catalysis via Radical Carbenoids. Ana G. Herraiz, Marcos G. Suero*. Invited review by Prof. Paul Knochel for the Bürgenstock Conference Special Issue.

• *Nature*, **2018**, *554*, 86. Generating carbyne equivalents with photoredox catalysis. Zhaofeng Wang, Ana G. Herraiz, Ana M. del Hoyo, Marcos G. Suero*.

***Highlighted in the <u>cover</u> of Nature.

***Highlighted in <u>C&EN</u>, <u>Chemistry World</u>, <u>Nature News & Views</u>, and <u>La Vanguardia</u>.

***This process has been highlighted by medicinal chemists from Merck in a review of Science magazine as the latest of a series of very diverse, practical, and potentially impactful uses of photoredox techniques to assemble libraries of drug-like scaffolds for screening, and also in <u>Nature</u> <u>Reviews Drug Discovery</u> journal by medicinal chemists from Astra Zeneca and GSK.

For a video directed to the general public watch: Carbynes - The new piece of chemistry's Lego.

• *Nature*, **2018**, *562*, *563*. A protein functionalization platform based on selective reactions at methionine residues. Michael T. Taylor, Jennifer E. Nelson, Marcos G. Suero, Matthew J. Gaunt.

• Eur J. Org. 2017, 2122. Photoredox-catalyzed Cyclopropanation of Michael Acceptors. Ana M. del Hoyo, Marcos G. Suero*. Invitation to Special Issue on Photoredox Catalysis by Burkhard König (Guest Editor). -Among the most accessed articles in February 2017 – Selected as Very Important Paper – Highlighted in Chemistry Views.

• *Angew. Chem. Int. Ed.* **2017**, 56, 1610. A Stereoconvergent Cyclopropanation Reaction of Styrenes. Ana M. del Hoyo, Ana G. Herraiz, Marcos G. Suero*.

***Selected as Front Cover.

***Among the most accessed articles in December 2016.

• J. Am. Chem. Soc. **2014**, *136*, 8851. Cu-catalyzed Cascades to Carbocycles: Union of Diaryliodonium Salts with Alkenes or Alkynes Exploiting Remote Carbocations. F. Zhang, S. Das, A. Walkinshaw, A. Casitas, M. Taylor, M. G. Suero, M. J. Gaunt.

• J. Am. Chem. Soc. 2013, 135, 12532. Copper-Catalyzed Carboarylation of Alkynes via Vinyl Cations. A. J. Walkinshaw, W. Xu, M. G. Suero, M. J. Gaunt.

• Angew. Chem. Int. Ed. 2013, 52, 5799. Copper-Catalyzed Arylative Meyer–Schuster Rearrangement of Propargylic Alcohols to Complex Enones Using Diaryliodonium Salts. B. S. L. Collins, M. G. Suero, M. J. Gaunt.

• *J. Am. Chem. Soc.* **2013**, *135*, 5332. Copper-Catalyzed Electrophilic Carbofunctionalization of Alkynes to Highly Functionalized Tetrasubstituted Alkenes. M. G. Suero, E. D. Bayle, B. S. L. Collins, M. J. Gaunt.

• *Chem. Eur. J.* **2012**, 18, 7287. Enantioselective Multicomponent Synthesis of Fused 6–5 Bicyclic 2-Butenolides by a Cascade Heterobicyclisation Process. M. G. Suero, R. De la Campa, L. Torre-Fernández, S. García-Granda, J. Flórez. • Angew. Chem. Int. Ed. 2010, 49, 9720. Enantioselective Synthesis of 4-Hydroxy-2-cyclohexenones through a Multicomponent Cyclization. J. Barluenga, M. G. Suero, R. De La Campa, J. Flórez

• J. Org. Chem. 2009, 74, 7059. On the Mechanism of Cyclization of 5-Hexenylchromate Intermediates in the Reactions of Fischer Carbene Complexes with a Lithium Enolate and Allylmagnesium Bromide. P. Campomanes, J. Flórez, I. Pérez-Sánchez, M. G. Suero, T. L. Sordo, M. I. Menéndez,

• J. Am. Chem. Soc. 2008, 130, 2708. Diastereoselective Cyclopropanation of Ketone Enols with Fischer Carbene Complexes. J. Barluenga, M. G. Suero, I. Pérez-Sánchez, J. Flórez,

• *Chem. Eur. J.* **2006**, 12, 7225. Diastereoselective Multicomponent Cyclizations of Fischer Carbene Complexes, Lithium Enolates, and Allylmagnesium Bromide Leading to Highly Substituted Five- and Six-Membered Carbocycles. J. Barluenga, I. Pérez-Sánchez, M. G. Suero; E. Rubio, J. Flórez.

Patents

- Diazomethylation reagent and process for using it (EP17382063/WO2018146200) M. G. Suero, Z. Wang (ICIQ)
- Cyclopropanation reagent and method (EP19382720) M. G. Suero, A. G. Herraiz (ICIQ)

Fellowships

2010 - 2012	Marie Curie Intra-European Postdoctoral Fellowship – IEF (REA). Chemistry Department, University of Cambridge. Grant Agreement Number: PIEF-GA-2009-253650
2004 - 2008	Predoctoral fellowship , FPU (Spanish Ministry of Education). Facultad de Química, Universidad de Oviedo

Teaching Experience

From 2017	Master in Synthesis, Catalysis and Molecular Design, Course in Asymmetric Synthesis. Universitat Rovira i Virgili-ICIQ (Spain). 21 h/year.
2010 - 2012	Marie Curie Postdoctoral Fellow – The Foundations in Organic Synthesis, New Synthetic Methods, Stereoselective Synthesis. University of Cambridge, (UK). 27 h.

Activities as reviewer

Science, Nature, Chemical Science, Chemical Communications, Organic Letters, Journal of Organic Chemistry, Angewandte Chemie, Chem, Journal of the American Chemical Society.

Other information

- Professional member of RSQE, ACS.
- Member of the COST Action for C-H Activation in Organic Synthesis (CHAOS) (from 2016)

Institutional responsibilities

2015-2019 ICIQ Health and Safety Committee

From 2015 Member of the Master Thesis Examining Committee of the ICIQ-URV Master in Synthesis, Catalysis and Molecular Design.

Member of the Thesis Examining Committee of Sergio Sopeña de Fructos (ICIQ, 2018), Yangyang Shen (ICIQ, 2018), and Luca Buzzetti (ICIQ, 2018).

Supervision of Students and Postdoctoral Fellows at ICIQ

PhD students: Pau Sarró (2017–) Postdoctoral Marie Curie -IF Researchers: Liyin Jiang (2018–)

Alumni:

PhD students: Ana García Herraiz (President of examining committee: Prof. Ben Feringa, 20th September 2019), Finalist REAXYS PhD Prize 2019, 2019 Best PhD student RSEQ-Lilly Award, 1_{st} position in REAXYS RSEQ Early Researcher Award 2018)

Postdoctoral Researchers: Zhaofeng Wang (Suschem Postdoc Prize 2019, now PI College of Chemistry and Chemical Engineering in Hunan University (China)), Ana M^a del Hoyo (now project researcher at Novalix), Elham Etema (now postdoctoral researcher at USA); Undergraduate summer fellow: Ana Escobar (2015), Melanie Armstrong (2016), Eduardo da Concepción (2017), Marta Spasic (2018) Visiting researchers: Yuan Yuchao (2017).

Selected Presentations

2020 Invited Lectures to be presented at the "3rd International Symposium on Carbene and Nitrene Chemistry" San Antonio, Texas. Stanford University, Irvine University, Spanish-Italian Symposium on Organic Chemistry SISOC (Tarragona), Instituto de Química Orgánica General (CSIC, Madrid)

2019 Invited lectures to be presented at Max-Planck Institute for Coal Research, CIQUS, Universidad de Santiago de Compostela, University of Geneve.

- 2019 Young Investigator Workshop 2019, Vienne, Austria (invited lecture)
- 2019 Ludwig-Maximilians-Universität Munich, Germany (invited lecture)
- 2019 Intituto de Investigaciones Científicas de Sevilla, Spain (*invited lecture*)
- 2019 Universitat de Barcelona; Barcelona, Spain (*invited lecture*)
- 2018 International Conference on Organometallics and Catalysis (ICOC); Goa, India (*invited lecture*)
- 2018 UCB Pharma; Braine-L'Alleud, Belgium (*invited lecture*)
- 2018 XV Simposio de Jóvenes Investigadores, Toledo (invited lecture)
- 2018 Gordon Conference Stereochemistry; University Salve Regina, USA (poster presentation)
- 2018 53rd Bürgenstock Conference; Brunnen, Switzerland (invited poster and flash presentation)
- 2018 Janssen-J&J; Toledo, Spain (*invited lecture*)

2017 Research Conferences of the Master and PhD Programme UPV/EHU; Bilbao, Spain (invited lecture)

- 2017 Gregynog Synthesis Workshop; Newtown, Wales ("chalk talk")
- 2017 The University of Tokyo, Graduate School of Pharmaceutical Sciences, Japan (*invited lecture*)
- 2017 Gordon Conference Organic Reactions & Processes; Easton, USA (poster presentation)
- 2017 Spanish-Japanese Symposium on Modern Synthetic Methodology; Gijón (research seminar)
- 2017 2nd CHAOS Working Group Meeting; Sofia, Bulgaria (*invited lecture*)
- 2016 RSQE Biannual Congress in Organic Chemistry; Huelva, Spain (research seminar)
- 2014 University of Manchester, School of Chemistry (*invited lecture*)
- 2013 Invited lectures at Bayer (Berlin, Germany); Syngenta (Stein, Switzerland), Novartis (Basel, Switzerland) and J & J (Schaffhausen, Switzerland); Astex (Cambridge, UK)

Organization of Scientific meetings

2018 Chairman of the ICIQ-BASF seminar programme.

2018 Local organizer for the Cost Action CHAOS (C-H Activation in Organic Synthesis), Tarragona-ICIQ. September 19-21

Outreach activities and presentations

2018 <u>Carbynes – The new piece of chemistry's Lego</u>. This video explains our Nature paper to the general public

2018 Lecture to high-school students at ICIQ within the programme "Bojos por la Química"