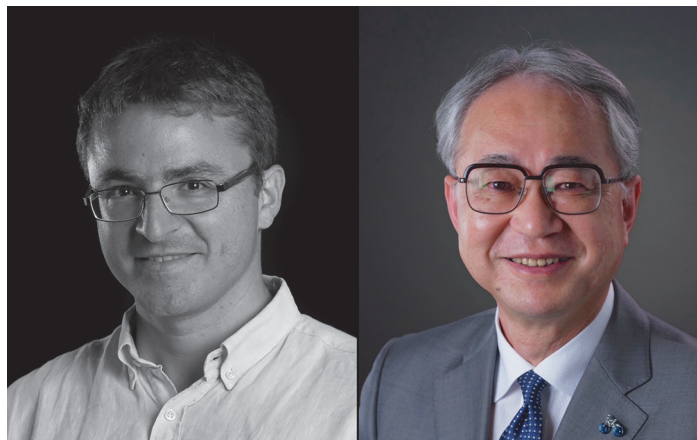


Cluster Preface: Special Issue Honoring Masahiro Murakami's Contributions to Science

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Ruben Martin (left) was born in Barcelona in 1976. After receiving his PhD at the Universitat de Barcelona with Prof. Antoni Riera, he moved in January 2004 to the Max-Planck-Institut für Kohlenforschung, Mülheim, as a Humboldt postdoctoral fellow with Prof. Alois Fürstner, where he worked on iron cross-coupling reactions. In May 2005, he undertook further postdoctoral studies at the Massachusetts Institute of Technology with Prof. Stephen L. Buchwald where he developed new metal-catalyzed C–C and C–N bond-forming reactions. In September 2008, he initiated his independent career as an Assistant Professor at ICIQ (Tarragona). In July 2013, he was promoted to Associate Professor and subsequently to ICREA Research Professor. His research interests concern the discovery and development of synthetically useful organometallic methodologies.

Masahiro Murakami (right) studied chemistry at the University of Tokyo under the supervision of Professor Mukaiyama, receiving his doctoral degree in science in 1984. He started his career with a research assistant position to Professor Mukaiyama at the same place. In 1987, he moved to Kyoto University to take a research assistant position to the late Professor Yoshihiko Ito (1937–2006). He took a leave from May in 1991 to March in 1992 to work for Professor Albert Eschenmoser at ETH Zürich as a post-doctoral fellow. He then returned to Kyoto, being promoted to Associate Professor in 1993 and Professor in 2002. In March 2022, he retired from Kyoto University. His research interests include the development of synthetically useful, yet mechanistically interesting, organic sections, and the utilization of photo-energy for organic synthesis.

Masahiro Murakami was born into a poor rice-farming family in 1956, 11 years after the end of World War II. Although the economic difficulties encountered after this period made it difficult to raise a family, his parents offered him the highest level of education. He studied chemistry at the University of Tokyo under the supervision of Prof. Teruaki Mukaiyama, and received his doctoral degree in science in 1984. He subsequently began his independent career as a research assistant to Prof. Mukaiyama at the Uni-

versity of Tokyo. In 1987, he moved to Kyoto University to take a position as an assistant professor to Prof. Yoshihiko Ito. He took leave from May 1991 to March 1992 to work for Prof. Albert Eschenmoser at ETH-Zürich as a postdoctoral fellow. He then returned to Kyoto University, being promoted to associate professor in 1993 and to professor in 2002. In March 2022, he retired from Kyoto University in adherence with the age-mandatory rules implemented by Japanese employers.

Masahiro Murakami's commitment to education and research began in 1985. During this time, he mentored more than 150 students, many of whom made their way into industry and academia, building successful careers. Among them, more than thirty became professors at academic institutions. His rigorous but heartfelt supervision and training encouraged students to pursue research at the highest level. The contributions originating from Murakami's laboratories are certainly countless, and it would be difficult, if not impossible, to appropriately highlight them and judge their impact on the scientific community. Masahiro Murakami has demonstrated that there are no invincible projects and taught us to think imaginatively instead of using preconceived ideas in order to seek new boundaries in chemical research. In this manner, his legacy includes concepts that today we adopt as general knowledge, such as the development of catalytic techniques for the functionalization of strong sigma carbon-carbon bonds, cycloaddition reactions, torquoselective transformations, annulation events, skeletal rearrangements and light-induced processes, among many others.

Beyond any reasonable doubt, Masahiro Murakami leaves behind an unperishable footprint, both from a scientific and human standpoint. Therefore, the SYNLETT editorial team decided to create a permanent tribute to Masahiro Murakami by way of a Special Issue Cluster that includes contributions from eminent scientists in different areas of

expertise. Specifically, we have contributions from authoritative experts, ranging from technologies occurring via two-electron manifolds to one-electron endeavors that operate via radical intermediates. Thus, Akiyama reports an interesting photoinduced technique to access α -hydroxy-amino ketones by harnessing the propensity of benzothiazoline to generate acyl radical precursors.¹ Andersson describes an enantioselective catalytic hydrogenation of α,β -unsaturated amides with iridium complexes supported by modular P,N-ligands.² Fernández describes an interesting platform that leverages the synthetic potential of alkylideneboranes as reaction intermediates for forging C–C bond linkages.³ You and Gu include a powerful platform towards axially chiral 1-arylisquinolines via Ir-catalyzed atroposelective hydroarylation events.⁴ An elegant photoinduced Barbier-type reaction of aziridines and azetidines with simple aldehydes is described by Yu and Gui, providing an interesting entry point to 1,*n*-amino alcohols.⁵ Furthermore, Harran describes a powerful synthetic endeavor that leverages the synthetic utility of in situ generated prototropic isomers of 2-acetyl-3-methylpyrrole.⁶

Meanwhile, Ohta and Hayashi describe an expeditious route to fused λ^5 -phosphinines, including detailed explorations into their interesting properties as fluorophores.⁷ Hong provides a complementary tool towards γ -aryl compounds by using bifunctional arylsulfonium reagents in the context of photoinduced processes.⁸ This Cluster also includes an approach to highly reactive cyclobutenes by means of a 1,2-aryl or alkyl shift of in situ generated Rh(II) carbene intermediates by Huo and Wang.⁹ Ito, Kubota and Isshiki make use of a mechanochemical silver-catalyzed platform for accessing γ -fluorinated ketones from *tert*-cyclobutanols.¹⁰ Following their interest in amination reactions, Jiao and co-workers describe a direct route to aminotetrazoles from very simple amide congeners in an essentially one-pot operation by means of C–C bond cleavage.¹¹ Koskinen includes an interesting Knoevenagel/transesterification sequence followed by an allylative Pd-catalyzed cyclization reaction as a platform to access chromenopyrrolidinones.¹² The modularity of in situ generated Rh carbenes is additionally covered by Lacour, showing the potential of *N*-substituted oxazolidines as a vehicle for preparing eight-membered 1,3,6- or 1,4,6-oxadiazocines in a regiodivergent manner.¹³

This Cluster also includes a contribution from Lee on the synthesis of 2-sulfonylthiazoles via heteroaryl C–H sulfonylation without recourse to the utilization of halogenated derivatives,¹⁴ whilst Fensterbank, Ollivier and Lemièrre describe a Ni-catalyzed coupling of organosilicates as a platform to rapidly and reliably construct sp^2 – sp^3 architectures.¹⁵ Li reports a Rh-catalyzed regioselective *N*-reverse prenylation of indoles under neutral conditions by using triphenyl phosphite ligands.¹⁶ Ma describes a technique for accessing heteroaryl nitriles with CuCN via Rosenmund–von Braun reactions.¹⁷ Following up his interest in chiral-at-

Ru catalysts, Meggers includes a rather compelling enantioselective intramolecular cyclopropanation of *trans*-cinnamyl diazoacetates.¹⁸ On the other hand, Mordini and Calamante describe a direct arylation approach to rapidly access benzothiadiazole-based fluorophores and discuss their utilization in luminescent solar concentrators.¹⁹ Morita and Krause make use of a recyclable permethylated β -cyclodextrin *N*-heterocyclic carbene–gold complex for rapidly accessing benzofurans and indanes.²⁰ Murai reveals a two-step process that allows access to *P*-chirogenic phosphine oxides in high enantiomeric ratios by promoting an axis-to-center transfer reaction on treatment with Grignard reagents. Lee reports a catalytic iminocarboxylation technique for accessing densely substituted *N*-acyl pyrroles via intermolecular acyl transfer reactions.²² Nakao describes a new protocol for the catalytic denitrative generation of open-shell species from simple nitroalkanes by using 9-fluorene as a single-electron-transfer catalyst.²³ Following up their interest in carbon-labelling, Neumann and Skrydstrup describe a Ni-catalyzed carbonylative coupling of alkyl zincs with α,α -difluorobromoacetamides by using near-stoichiometric CO.²⁴

A contribution from Rovis shows the potential of electronically controlled Ru-catalyzed olefin metathesis with only electricity as a stimulus.²⁵ While decarboxylation techniques are certainly rare, Shigeno and Kondo provide an interesting endeavor that meets such a challenge, allowing access to dicarboxylated structures by harnessing the potential of combined Brønsted bases.²⁶ Itami and Yagi report the synthesis of a novel structurally constrained nanobelt via a Ni-mediated intramolecular aryl–aryl compound of a triflated prism[6]-arene.²⁷ In addition, Banwell describes the total synthesis of dysidealactams E and F as well as dysidealactone B.²⁸ Rueping and Yue describe a Ni-catalyzed technique for incorporating selenium atoms at sp^2 sites with aryl iodides as counterparts.²⁹ Following up on their interest in C–H functionalization, Chen and Zhao report a radical-based approach for accessing isoindolinones with ammonium persulfate as the oxidant.³⁰ Zhou and Yu describe the utilization of $Cp^*Rh(III)Cl_2$ catalysts for enabling a series of transfer hydrogenation events with isopropanol as the hydride source.³¹ Furthermore, Bissember and Stewart describe an expeditious route to (+)-chelonin A by leveraging the proclivity of triazoles to generate rhodium carbenoids in situ as a vehicle to construct the central morpholine motif.³²

This Cluster also offers elegant accounts that illustrate the potential of emerging methodologies as enabling tools to generate new molecular scaffolds of interest in both academic and industrial laboratories. In particular, Bach illustrates the potential of photochemical cascade (domino) reactions as a means to rapidly and reliably construct molecular architectures of utmost complexity in a single operation.³³ Similarly, Bower describes the potential of minimally activated cyclopropanes to generate active inter-

mediates by means of C–C bond cleavage as a vehicle for building up molecular complexity.³⁴ On the other hand, the versatility of Cp*Co(III) catalysis in a series of C–H amination events is nicely delineated by Chang, including detailed mechanistic investigations.³⁵ The recent advances in C(sp³)–H carboxylation reactions by utilizing carbon dioxide (CO₂) as the sole source of carbon is nicely reviewed by Das, including important take-home messages for practitioners and non-practitioners in the field.³⁶ Gevorgyan summarizes the potential of dual triplet ketone and transition-metal catalysis as a new platform for forging sp³ architectures by harnessing the propensity of multifaceted triplet ketones for enabling both hydrogen-atom transfer and single-electron transfer.³⁷ Meanwhile Kanai discusses the advances made in the context of catalytic dehydrogenation of saturated N-heterocycles, aliphatic alcohols and even the most problematic hydrocarbons.³⁸ Finally, Loh summarizes recent techniques aimed at promoting catalyst-free biocompatible reactions such as Mukaiyama reactions, click processes and applications on the functionalization of proteins.³⁹

'I was very much surprised when the SYNLETT editorial board members offered to publish a special issue in honor of my retirement! I was not sure if my scientific achievements deserved it. I was unable to make a quick decision and it took a while until I finally accepted the generous offer. I thank all the editorial board members, particularly Prof. Ruben Martin and Prof. Ben List, for their plan to recognize my work and for their dedication in bringing it to fruition. I am also immensely grateful to all the authors who have contributed to this special issue. In addition, I truly cannot thank enough my parents and Japanese society, which allowed me to pursue an academic career.' (Masahiro Murakami)

There are certain chemists that mark an era, and Masahiro Murakami is undoubtedly one of them. On the basis of his outstanding contributions, the new concepts he has discovered throughout his career and the cohort of students he has mentored, it is difficult to assess the enormous impact that Masahiro Murakami will have in the years to come. New generations of chemists certainly have an excellent role model to follow, and I am absolutely confident that Masahiro Murakami will continue to be an invaluable source of inspiration for discovering conceptually new processes that will drive research in catalysis. I sincerely hope that this SYNLETT cluster serves as a tribute to a chemist that we all, as a community, admire both as a scientist and as a human being.

Ruben Martin
Masahiro Murakami
May 2023

Conflict of Interest

The authors declare no conflict of interest.

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