

Editorial



Organic Free Radicals

This special issue of CHIMIA presents contributions by selected speakers of the 11th International Symposium on Organic Free Radicals (ISOFR-11) organized in Bern from July 1st to July 5th 2012. This conference is organized every four years and was held for the last time in 2008 in Australia on Heron Island. It is dedicated to the discussion of new ideas and knowledge in the field organic free radicals. The symposium covers organic synthesis, polymer and material chemistry, as well as selected aspects of chemical biology.

The chemistry of organic free radicals was for a long time considered as an interesting curiosity without any particular significance. Indeed, radicals were associated with unselective reactions leading to a mixture of products. However, during the last 30 years, this situation has massively changed. Highly stereoselective radical reactions have been discovered demonstrating that such processes can be as stereoselective as the more established ionic and pericyclic reactions. Moreover, one of the major problems associated with free radical processes, *i.e.* the use of toxic heavy metals such as tin, could be efficiently overcome by the emergence of a wide variety of alternative processes. Many of these processes are also characterized by a very high level of atom economy (see for instance the atom and group transfer reactions), by mild reaction conditions, and by a unique functional group tolerance. At the same time, the exceptional reactivity of radicals has been used to develop efficient cascade processes, aromatic substitution, and C–H functionalization. Radical chemistry is now a unique tool to solve difficult synthetic problems encountered in the synthesis of complex targets such as natural products. The synthetic aspects of organic free radical chemistry are highlighted in the contributions of **Ryu** 'Free Radical-mediated Hydroxymethylation Using CO and HCHO', **Chiba** 'Mn(III)-Catalyzed Radical Reactions of 1,3-Dicarbonyl Compounds and Cyclopropanols with Vinyl Azides for Divergent Synthesis of Azaheterocycles', **Movassaghi** 'Radical-mediated Dimerization and Oxidation Reactions for the Synthesis of Complex Alkaloids', **Stephenson** 'Radical Carbon-Carbon Bond Formations Enabled by Visible Light Active Photocatalysts', **Procter** 'Recent Advances in the Chemistry of Sml₂–H₂O', **Zard** 'Some Aspects of the Radical Chemistry of Xanthates', **Studer** 'Transition-metal-free Oxidative Coupling Reactions for the Formation of C–C and C–N Bonds Mediated by TEMPO and its Derivatives', **Murphy** 'The Development of Organic Super Electron Donors', **Fensterbank**, **Goddard**, **Malacria** and **Ollivier** 'Homolytic Reduction of Onium Salts', **Gansäuer** 'Reductive Cleavage of 2,2,2-Trichloroethyl Esters by Titanocene Catalysis', **Gastaldi** 'Enzyme-triggered Radical Reactions: Another Approach For Tin-free Radical Chemistry', and **Severin** 'Ruthenium-catalyzed Atom Transfer Radical Addition Reactions'.

In parallel to this development, organic free radicals are playing a key role in material science as demonstrated by the development of controlled living radical polymerization and surface modifications. Recent progress in the field of initiation of polymerization processes are discussed in the paper of **Lacôte and Lalevé** 'NHC-Boranes are Air- and Water-tolerant Co-initiators for Type II Photopolymerizations' and **Lalevé** 'Photoredox Catalysis for Polymerization Reactions'.

Finally, the role of free radicals in biological processes is essential and probably still underestimated. Radicals are known to play a key role in aging processes including protein, nucleic acid, and membrane lipid degradation. Radicals are also involved in important enzymatic reactions, and other biological processes of importance in medicinal chemistry. The articles of **Giese** 'Radicals and Radical Ions as Intermediates of Electron Transfer Processes through Peptides', and **Chatgililoglu** 'Biomimetic Models of Radical Stress and Related Biomarkers' treat this aspect of organic free radical chemistry.

As a coordinator of this special issue of CHIMIA, I would like to thank all the authors of the articles who did a tremendous job on short notice to give you a flavor of the recent developments in the field of organic free radicals. Financial support to the ISOFR-11 Symposium by the Swiss National Science Foundation, the Division of Chemical Research of the Swiss Chemical Society, Actelion Pharmaceuticals, BASF, F. Hoffmann-La Roche, Novartis Pharma, Merck Serono, and Syngenta Crop Protection is gratefully acknowledged.

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The Editorial Board of CHIMIA is very grateful to the guest editor, Prof. Philippe Renaud, for organizing this issue illustrating the depth of interest in the growing research field of 'Organic Free Radicals'.

Cover: Three recent reactions described in this issue of CHIMIA developed by Procter (page 399), Movassaghi (page 389) and Chiba (page 377) demonstrating the power of organic free radicals in synthesis.