

Preface

Transition metal catalysis is a major driving force for development of new approaches in organic synthesis, medicinal chemistry, preparation of biologically active and pharmaceutical molecules, as well as in numerous applications related to material science and molecular electronics. Recent advances in green and sustainable chemistry emphasized the key role of waste-free chemicals production. Especially critical in fine chemicals synthesis is that high values of E-factor are not uncommon. Increasing demand in very complex molecular structures enforces implementation of sophisticated multistep synthetic procedures and further complicates the waste/product balance. On the other hand, so far most of the commodity chemicals remain to be produced by classical procedures, which are not green.

A fundamental solution to the problem is to develop novel synthetic processes that are “clean” by initial design. For carbon–heteroatom bond formation it is the hydrofunctionalization process that opens the possibility for environmentally friendly chemical transformations. Hydrofunctionalization of unsaturated organic molecules via direct addition of H-X to multiple bonds is an atom-economical addition reaction which does not produce wastes. In view of the need of green and sustainable chemical procedures, the role of the metal catalysis is crucial to control the reaction, in particular, regio-, stereo-, and enantioselectivity.

This volume highlights fascinating development of catalytic hydrofunctionalization chemistry toward selective formation of C–X bonds (X = N, P, O, S, Se). Discovery of new catalysts, impressive development of ligands, and optimization of reaction conditions have made it possible to access molecular complexity in 100% atom-economical manner. Broad scope of the reactions, high functional group tolerance for a variety of substrates, and superior control over alternative pathways of the addition process are characteristic trends in state-of-the-art catalytic hydrofunctionalization.

The mechanistic insight into the catalytic reactions is discussed for the key insertion step [1] and catalytic hydrochalcogenation reactions [2]. Two chapters of this volume review hydroamination reaction catalyzed by early/main group [3] and late [4] metal catalysts. Synthesis of organophosphorus compounds via addition

of P–H [5] and P(O)–H [6] bonds is described next. An important area of O–H bond addition to unsaturated molecules is highlighted in three chapters depending on the nature of the metal catalyst [7–9], followed by detailed overview of synthetic pathways to organic chalcogenides [10]. Most of the hydrofunctionalization processes covered in this volume were carried out under homogeneous reaction conditions. With a noticeable exception of sulfur and selenium species, where a significant contribution of heterogeneous pathway and competing homogeneous vs. heterogeneous routes were reported. Therefore, two chapters were devoted to C–S/C–Se bonds formation focusing on mechanistic aspects [2] and outstanding synthetic potential [10].

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