

Catalytic Arylation Methods

The book Catalytic Arylation
Methods by Anthony J. Burke
and Carolina Silva Marques differs
in its conception from many other
monographs on a specific topic because it
is not an edited book but one entirely written

by two authors. As a result, the book shows a high degree of consistency and quality. The title already reminds one of the related book *Modern Arylation Methods*, also published by Wiley-VCH, and edited by Lutz Ackermann (Göttingen), which gives a broad overview of different modern aspects in arylation chemistry. The present book concentrates on major developments in arylation reactions in the last few decades, as well as including significant historical and preliminary work. The clear arrangement of the content has been achieved by subdivision into nine chapters, each one dealing with the arylation of a certain functional group.

The introductory chapter describes the different, mostly palladium-catalyzed, cross-coupling reactions that have gained a prominent position among arylation reactions since the award of the Nobel Prize for their invention. It covers their history and the various name reactions, followed by descriptions of recent developments and applications.

The following chapter reviews couplings with N-, O-, and S-nucleophiles, which have come to the fore through the Buchwald–Hartwig reaction. The importance of these couplings is evident from their application on the industrial scale, due to the important role of aryl amines as moieties in many compounds that are used for pharmaceutical, agricultural, and other purposes. These two chapters are complemented by Chapter 8, which describes α -arylations, an important tool for the assembly of $C(sp^3)$ – $C(sp^2)$ bonds from common classes of carbonyl compounds. The development of this particular area has led to the derivation of novel and efficient catalyst systems.

In Chapter 3, the authors describe the decarboxylative cross-coupling of carboxylic acid derivatives, which has emerged especially during the recent decade. The reasons can be found in the versatility, ease of use, and widespread application of carboxylic acids and their derivatives; the release of CO_2 as a by-product is an attractive feature—at least in the context of coupling chemistry.

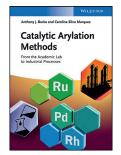
The extensive Chapter 4 discusses an extremely active and dynamic field: C–H arylation reactions as a route for potentially "green" arylation chemistry. As well as the formation of C–C bonds between two unsaturated fragments, formally releasing only hydrogen, also the addition of C_{Aryl}–H bonds to unsaturated substrates, thus affording, for example,

(aromatic) ring systems, plays a significant role. That is followed by a group of three chapters on related topics: the conjugated addition of aryl nucleophiles to α,β -unsaturated molecular moieties (Chapter 5), the arylation of imines, especially for the synthesis of chiral amines (Chapter 6), and the addition of aryl nucleophiles to carbonyl compounds such as aldehydes or ketones (Chapter 7). The latter case might appear to be trivial in view of the well-known reactive properties of carbonyl compounds, for example in Grignard reactions, but the application of transition metal catalysts allows one to perform e.g. also asymmetric syntheses, and to use easy-to-handle aryl nucleophiles such as aryl boronic acids.

The final chapter is somewhat exotic compared with the ones described so far, which dealt with aryl group transfer, as it is concerned with catalytic cycloaddition reactions for the de novo construction of aromatic systems. The chapter centers around the [2+2+2] cycloadditions and [3+2] cycloadditions ("click reactions") that have been adopted as reliable and indispensable reactions in the toolbox of synthetic chemists, and therefore definitely belong in a book such as this. In particular, [2+2+2] cycloadditions have emerged as strategic reactions for the skillful assembly of complex structures from simple unsaturated starting components.

The book's subtitle already indicated the authors' intention to combine the presentation of recent ground-breaking research with its practical application in the synthesis of aromatic compounds for pharmaceutical or other industrial purposes. In addition to the popular and most frequently used catalyst systems and metals, the authors also discuss metals and their compounds that are less often applied or researched, some of which might promise hitherto unknown catalytic arylation possibilities in the future. The inclusion of selected experimental procedures at the end of each chapter is a special bonus, because the reader can get a quick overview of the practical performance of a certain reaction, or an idea for a solution to his or her own synthetic problems, without having to immediately look up the original literature. However, some of the reactions and their products are shown in the "landscape" format, which is sometimes less reader-friendly; in many cases it should have been possible to use the normal "portrait" format. The schemes and figures are, in general, clearly arranged and informative. However, in very few cases (e.g., in schemes 1.54 or 9.8), more significant mistakes in the representation of reaction products or catalysts have slipped in.

In this book, Anthony J. Burke and Carolina Silva Marques have accomplished a readable and very instructive overview of recent developments in catalytic arylation reactions. The authors focus on



Catalytic Arylation Methods From the Academic Lab to Industrial Processes. By Anthony J. Burke and Carolina Silva Marques. Wiley-VCH, Weinheim, 2014. 528 pp., hardcover, © 162.00.—ISBN 978-3527335183



the major developments, provide details where necessary, and offer readers an easy and convenient

way of becoming immersed in this especially active field of research.

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International Edition: DOI: 10.1002/anie.201509471
German Edition: DOI: 10.1002/ange.201509471