

Preface

Compared with other chiral molecules, helicenes, comprised of *ortho*-fused aromatics, bear helicity and π -conjugated structures. Because of the highly contorted π -surfaces with superior chiroptical properties, synthetic challenges for the diversity of the skeletons, interesting interaction behaviors between themselves or with other (chiral) molecules, the helicene chemistry has been attracting more and more attention. Since the first report in 1903, it has been developed for more than 110 years. In 1950s, the helical structure was unambiguously demonstrated by X-ray crystallographic analysis. Moreover, the optical resolution was achieved and the relationship between the absolute configuration and chiroptical property was established. Some practical synthetic methods have been discovered, especially in the last three decades, such as metal-mediated [2+2+2] triynes cycloisomerization, Diels–Alder addition, and oxidative photocyclization. Some reactions render the preparation in gram scale, and some reactions could afford helicenes even in >99 % ee. Due to the advances in preparation, different applications have been discovered, including environmental-stimulus responsive molecular switches, asymmetric catalysis, molecular recognition, and organic electronic devices. Previously, we composed a review, *Helicenes: Synthesis and Applications*, in which the structures and properties were briefly introduced, nearly all the synthetic methods and applications developed before 2012 were summarized. However, since then, more than 350 peer-reviewed journal papers have been published, but there are only a few mini-reviews on specific topics among them. This motivated us to prepare this book *Helicene Chemistry: From Synthesis to Applications* to describe the recent progress. Moreover, we hope this book could be a primer for beginners who plan to enter this research area and also a useful manual for researchers and graduate students working in this area.

This book is composed of three parts. In Part I, we would like to make an introduction to helicenes. In Chap. 1, the nomenclature and the historical development are introduced. In Chap. 2, the structural features are presented in detail with crystal structures. The properties are classified by π -conjugated system and the helicity. The photophysical and electronic behaviors, chiroptical characteristics and

racemization process are discussed in different sections. In addition, other properties and helicenes with charges or open shells are listed at last. In Part II, the practical synthetic methods are summarized. For the nonselective methods, the widely accepted ones, such as oxidative photocyclization (Chap. 3), Diels–Alder addition and Friedel–Crafts-type reactions (Chap. 4), metal-mediated reactions (Chap. 5), and other methods (Chap. 6) are examined with advantages and disadvantages. The recent development of asymmetric synthesis is reviewed in Chap. 7 in three categories: (1) enantioselective approaches, (2) diastereoselective methods, and (3) strategies based on enantioenriched substrates. The reactivity of helicene skeletons, the direct C–H functionalization, the useful transformation of functional groups, and the helicene-based organometallics are discussed in Chap. 8. In Part III, selected hot research topics in the past 4 years are presented. In Chap. 9, the helicene-based organocatalysts and helical ligands used in the asymmetric catalysis are introduced. The chiral recognition, helicene-based sensors, and responsive switches are summarized in Chap. 10. And the applications of helicenes in biological realm are presented in Chap. 11. The circularly polarized luminescence and the organic electronic devices are discussed in Chap. 12. At last, the assembly behaviors of helicenes at interfaces and in organogels, LB films, and liquid crystals are reviewed. We sincerely hope the results selected and presented here will attract more chemists' attention and advance the development of helicene chemistry.

Finally, we would like to thank June Tang, from Springer for her kind invitation and help during the preparation of the book. We also thank Han-Xiao Wang and Wei-Bin Lin from our research group for literature analysis.

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Helicene Chemistry

From Synthesis to Applications

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2017, XIV, 272 p. 270 illus., 64 illus. in color., Hardcover

ISBN: 978-3-662-53166-2