

Chuan-Feng Chen · Yun Shen

Helicene Chemistry

From Synthesis to Applications

 Springer

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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.

Beijing, China

Chuan-Feng Chen
Yun Shen

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Abbreviations

A	Adenine
Ac	Acetyl
acac	Acetylacetonyl
AFM	Atomic force microscopy
AIBN	2,2'-azobis(2-methylpropionitrile)
BCP	2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BINAPO	[1,1'-binaphthalene]-2,2'-diylbis(diphenylphosphine oxide)
BINOL	1,1'-bi-2-naphthol
B_{\max}	The maximum brightness
BP	Benzophenone
Bphen	Bathophenanthroline
CAN	Ceric ammonium nitrate
CBP	4,4'- <i>N,N'</i> -dicarbazolebiphenyl
CD	Cyclodextrin (only for α -CD, β -CD, γ -CD)
CD	Circular dichroism
CE	Cotton effect
CIE	Commission Internationale de l'Eclairage
CLSM	Confocal laser scanning microscopy
cod	1,5-cyclooctadiene
Cp	Cyclopentadienyl
CP	Circularly polarized
CPL	Circularly polarized luminescence
Cy	Cyclohexyl
dba	Dibenzylideneacetone
DBU	1,5-diazabicyclo[5,4,0]-5-undecene
DCE	1,2-dichloroethane
DCM	Dichloromethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DFT	Density functional theory

DIPA	Diisopropylamine
DMA	<i>N,N</i> -dimethylacetamide
DMAP	<i>N,N</i> -4-dimethylaminopyridine
DME	1,2-dimethoxyethane
DMF	<i>N,N</i> -dimethylformamide
dmsO	Dimethyl sulfoxide
DNA	Deoxyribonucleic acid
DNT	1-methyl-2,4-dinitrobenzene
dppb	1,4-bis(diphenylphosphino)butane
dppf	1,1-bis(diphenylphosphino)ferrocene
dppm	1,1-bis(diphenylphosphino)methane
dppp	1,3-bis(diphenylphosphino)propane
ee	Enantiomeric excess
EL	Electroluminescence
ENDOR	Electron nuclear double resonance
EPR	Electron paramagnetic resonance
ESR	Electron spin resonance
F8BT	Poly[9,9-dioctylfluorene-co-benzothiadiazole]
FVP	Flash vacuum pyrolysis
G	Guanine
g_{lum}	Dissymmetric factor
HAT-CN	Dipyrazino[2,3- <i>f</i> :2',3'- <i>h</i>]quinoxaline-2,3,6,7,10,11-hexacarbonitrile
HELIXOL	2,2'-dihydroxyhelicene
HELOL	2,2'-bihelicenyl-1,1'-diol
HOMO	Highest occupied molecular orbital
HPLC	High performance liquid chromatography
I_D	Drain current
ITO	Indium-tin oxide
LAH	Lithium aluminum hydride
LB	Langmuir–Blodgett
LDA	Lithium diisopropylamide
LLC	Lyotropic liquid crystalline
LUMO	Lowest unoccupied molecular orbital
<i>m</i> -CPBA	Meta-chloroperbenzoic acid
MOM	Methoxymethyl
MS	Molecular sieve
MW	Microwave
N/D	Not determined
NA	Not available
NBS	<i>N</i> -bromosuccinimide
NEXAFS	Near edge X-ray absorption fine structure
Nf	Nonafluorobutanesulfonyl
NIR	Near infrared
NIS	<i>N</i> -iodosuccinimide
NMP	<i>N</i> -methyl-2-pyrrolidinone

NMR	Nuclear magnetic resonance
NP	Nanoparticle
NPB	4,4'-bis(1-naphthyl- <i>N</i> -phenylamino)-biphenyl
NR	No reaction
NT	1-methyl-4-nitrobenzene
OFET	Organic field-effect transistor
OLED	Organic light-emitting diode
OPV	Organic photovoltaic
OR	Optical rotation
PA	Picric acid
PAH	Polycyclic aromatic hydrocarbon
<i>p</i> -BQ	<i>p</i> -benzoquinone
PEDOT	Poly(3,4-ethylene dioxylthiophene)
PLED	Polymer light-emitting diode
PMMA	Polymethylmethacrylate
PPA	Polyphosphoric acid
PSS	Photostationary state (Chapter 10)
PSS	Poly(styrenesulfonate) (Chapter 12)
<i>p</i> -Tol	<i>p</i> -tolyl
Py	Pyridyl
rt	Room temperature
SOMO	Singly occupied molecular orbital
STM	Scanning tunneling microscope
T	Thymine
TAPA	2-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy)propionic acid
TBAF	Tetra- <i>N</i> -butylammonium fluoride
TBBD	<i>N</i> 4, <i>N</i> 4', <i>N</i> 4'-tetra([1,1'-biphenyl]-4-yl)-[1,1'-biphenyl]-4,4'-diamine
TBDMS	Tert-butyldimethylsilyl
TCTA	Tris(4-(9 <i>H</i> -carbazoyl-9-yl)phenyl)amine
<i>T</i> _d	Decomposition temperature
TEA	Triethyl amine
Tf	Trifluoromethanesulfonyl
TFA	Trifluoroacetic acid
TFAA	Trifluoroacetic anhydride
<i>T</i> _g	Glass transition temperature
THF	Tetrahydrofuran
tht	Tetrahydrothiophene
TIPS	Triisopropylsilyl
<i>T</i> _m	Melting temperature
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMP	Lithium 2,2,6,6,-tetramethylpiperidide
TMS	Trimethylsilyl
TNT	2-methyl-1,3,5-trinitrobenzene
TPBi	1,3,5-tris(1-phenyl-1 <i>H</i> -benzo[d]imidazol-2-yl)benzene

TS	Transition state
Ts	<i>p</i> -toluenesulfonyl
UV–vis	Ultraviolet–visible
VAZO	1,1'-azobis(cyclohexanecarbonitrile)
V_g	Gate voltage
$\eta_{c,max}$	The maximum current efficiency
$\eta_{p,max}$	The maximum power efficiency
μ	Carrier mobility
μ_e	Electron mobility
μ_h	Hole mobility

Part I

What Are Helicenes?

Chapter 1

Introduction to Helicene Chemistry

Abstract In this chapter, a brief introduction to helical structure and helicene is first given followed by the nomenclature. The historical development is discussed in detail, and some landmarks such as the first reported helicene, the demonstration of helical structure by X-ray analysis, the first large-scale synthesis by Diels-Alder addition, and the contributions of leading research groups at different times are highlighted. This book is aimed to become a primer for beginners who want to enter this area and also a useful manual for researchers and graduate students. Literatures from 2012 to early 2016 are covered and important discoveries before 2012 are emphasized as well. At last, helicene-related books or review articles published before 2016 are summarized. If readers are interested in a specific topic, more details could be obtained from them.

Keywords Helicene · Helicene chemistry · Historical overview · Nomenclature · Objectives and literature coverage

1.1 Introduction

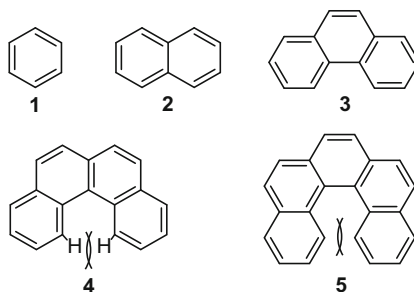
Helical structures are very common in our daily life and microscopic world. For example, at macroscopic level, the beautiful Sunflower Galaxy (Messier 63) photographed by Hubble Telescope (Fig. 1.1) [1], the violent tornadoes formed by rotating air, the transitory whirlpools generated by boat paddle, the vines entwined with trees, at microscopic level, the famous DNA double helix in a cell, the foldamers in supramolecular chemistry, they all bear different types of helical forms. From an energy standpoint, the helical structures stabilize the systems to some degree.

If benzene rings are added one by one to a benzene molecule at the ortho-positions as shown in Fig. 1.2, it would be easy to predict that molecules with more than three rings would cause great steric hindrance. Therefore, the skeletons spiral up and come into helical shapes to decrease the van der Waals interaction.

Fig. 1.1 The sunflower galaxy [2]



Fig. 1.2 Structures of molecules with different numbers of benzene rings



Such are helicenes [3–10], one type of polycyclic aromatic compounds with non-planar screw-shaped structures composed by ortho-fused aromatic rings.

The nomenclature was proposed by Newman and Lednicer in 1956 [3]. For hexahelicene (Fig. 1.3), “A systematic name is phenanthro[3, 4-c]phenanthrene. However, a proposal to create the systematic name **helicene** for nuclei of the continuously coiled type is at present being considered by American and International Nomenclature committees. The prefixes, penta, hexa and hepta, etc., would be used for five, six and seven, etc., ring compounds.”

This proposal was accepted quickly and widely used in the literatures after 1950s. Another simple method was also accepted: $[n]$ helicene, where n means the number of aromatics ring in the helical skeleton, and other rings fused to the backbone should not be counted [4, 6–10]. This method would be adopted in this

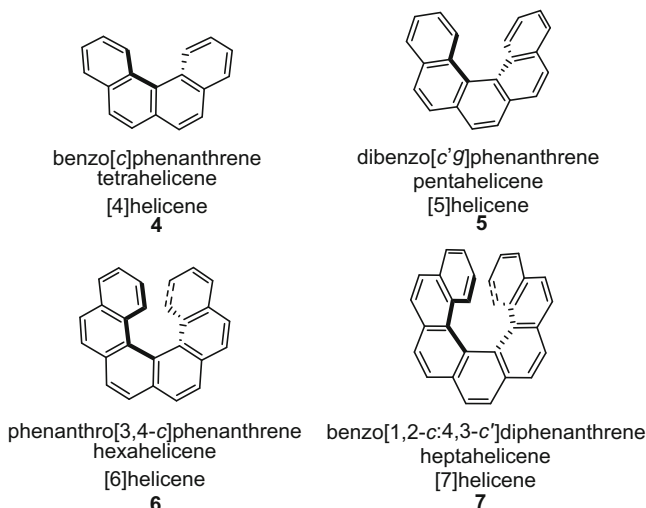


Fig. 1.3 Nomenclature of helicenes

book when the name of a helicene is referred to. In addition to the carbohelicenes that are formed all by benzene rings, if heteroatoms, like O, N, S, P, Si, present on the backbones (generally named heterohelicenes), they are named oxa-, aza-, thia-, phospho-, sila[n]helicenes (or silahelicenes), respectively [4–7, 11, 12].

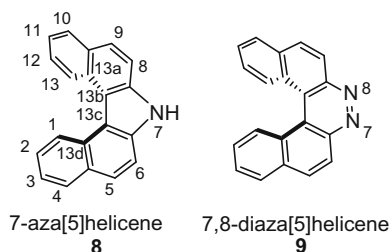
Besides the structures mentioned above, two helicene moieties connected by a single bond are named bihelicenyls; two helicenes fused together are called double helicenes; and the helicenes where an aliphatic chain or other fragments that form a bridge to link the terminal rings are helicenophanes [4, 6, 7, 13, 14].

1.2 A Historical Overview

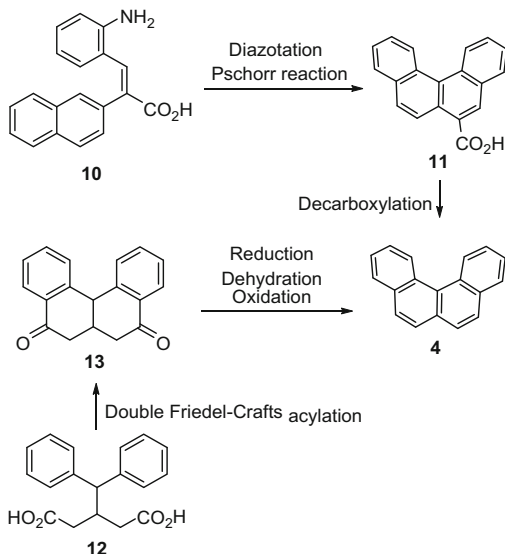
Although the systematical nomenclature was proposed in 1956, the first two helicenes (Fig. 1.4), 1,1-dinaphto-2,2-imin **8** and 1,1-dinaphto-2,2-*ortho*-diazin **9**, could date back to 1903, when Meisenheimer and Witte studied the reduction of 2-nitronaphthalene [15].

Before 1950s, reports on helicene were rare, where the names usually appeared as dibenzonaphthalene, tribenzonaphthalene, benzophenanthrene, dibenzophenanthrene, tribenzophenanthrene, etc. [16]. The research mainly focused on the synthetic methods. According to the key step, namely the step to construct helicene backbone, three strategies were developed, including Pschorr reaction, Friedel–Crafts acylation, and Diels–Alder addition.

Fig. 1.4 The first two helicenes and numbering

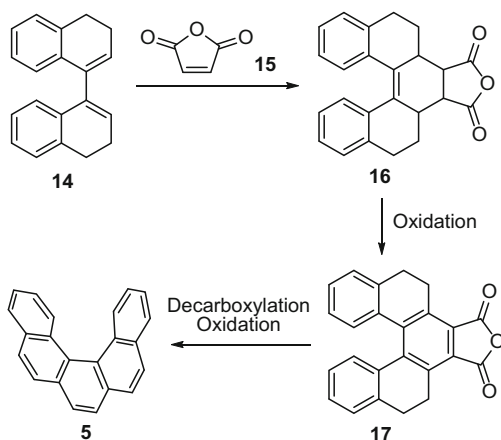
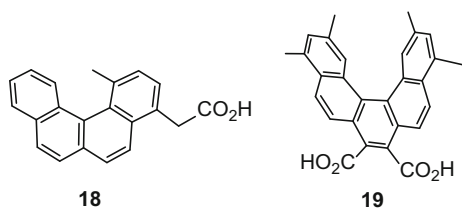


Scheme 1.1 Synthesis of [4]helicene



In 1912, Weitzenböck and Lieb prepared the first carbo[4]helicene from 2-naphthylacetic acid and 2-nitrobenzaldehyde [17]. By condensation and reduction, diarylethene **10** could be obtained, which was diazotized and treated with copper powder followed by decarboxylation to give helicene **4** (Scheme 1.1). Utilizing similar procedure, Weitzenböck and Klingler synthesized the first carbo[5]helicene **5** in 1918 [18]. Friedel-Crafts acylation was used as well, by which Newman and Joshel prepared [4]helicene from 3-benzhydrylglutaric acid **12** (Scheme 1.1) [19]. In addition, by virtue of Diels-Alder reaction between tetrahydro-1,1'-dinaphthyl **14** and maleic anhydride, Clar synthesized [5]helicene **5** via the following route with decarboxylation, reduction, dehydration, and oxidation (Scheme 1.2) [20]. Based on these synthetic methods, several derivatives of helicenes had been prepared during these 50 years [21–33].

The next landmark was in 1952, McIntosh et al. for the first time demonstrated that [5]helicene had a helical structure by X-ray crystallographic analysis, resulted from the steric hinderance between two terminal rings which prevented the skeleton

Scheme 1.2 Synthesis of [5] helicene**Fig. 1.5** Two partially resolved helicene acids

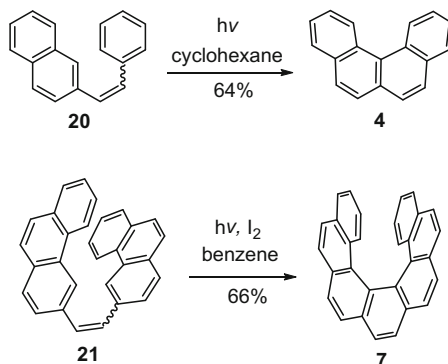
from assuming a coplanar configuration and had little effect on the benzene ring structures [34]. This screw-shaped structure rendered the molecule chiral.

Before this, Newman et al. [35] and Bell et al. [36] tested and verified the optical activity of helicene molecules in 1948 and 1949, respectively. Helicene acid **18** ($[\alpha]_D = +1.4 \pm 0.2^\circ$, *c*, 1 in CHCl₃) [35] was partially resolved by crystallization of the diastereomers formed by the reaction with *l*-menthol (Fig. 1.5); enantioenriched helicene diacid **19** ($[\alpha]_D = -47.2^\circ$, acetone) [36] was obtained by crystallization of the morphine salts. Both two groups found that the compounds displayed no optical activity after several hours at room temperature, which were thermally unstable and underwent racemization very fast.

The successful resolution of [6]helicene became a milestone achieved by Newman and co-workers by forming charge transfer complexes in 1955 [37] and 1956 [3]. This strategy opened the door of the chiroptical properties of helicenes. At this point, people started to know helicenes.

During 1966–1967, Mallory et al. [38], Carruthers [39], Scholz et al. [40], and Martin et al. [41] independently reported the first examples of helicenes synthesized by photochemical strategy, namely the oxidative cyclization of diarylethenes (Scheme 1.3). This greatly accelerated the development of helicene chemistry. Based on this method, helicenes bearing five to fourteen benzene rings with different functional groups had been obtained, and the spectral properties including UV,

Scheme 1.3 Synthesis of [4]helicene [40] and [7]helicene [41] by photochemical method



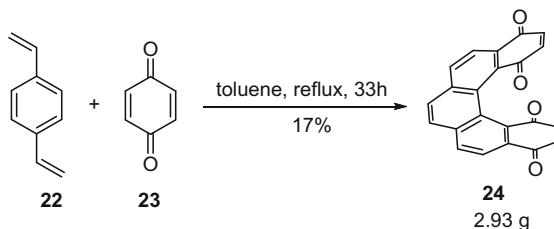
NMR, ORD, CD were systematically studied during the next two decades [40, 42–44]. Martin group made a great contribution to the exploration of this strategy [4]; Wynberg group expanded this method to heterohelicenes [11]; Laarhoven group carefully studied the mechanism of the photochemical procedure [6]. Katz and co-workers improved this method by adding propylene oxide to promote the effectiveness of the reaction, which became a standard reaction condition afterwards [45].

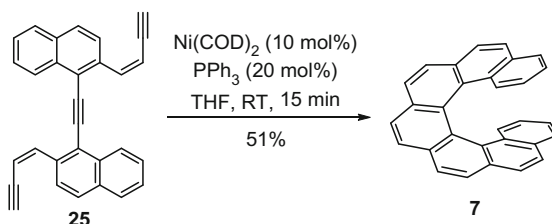
Another breakthrough was made by Katz and collaborator in 1990, utilizing the Diels-Alder reaction between the *p*-benzoquinone and diene to prepare the helicene quinone in large scale (Scheme 1.4) [46]. It resolved the problem that helicenes could not be prepared in quantity through photochemical procedures. From then on, the applications of helicene molecules began to be disclosed.

Compared with planar acenes, helicenes are not only π -conjugated systems, but also optically active [7, 10]. Therefore, the applications could be classified into two categories: one is based on the π -conjugated structure, like LB films [47], liquid crystals [48], optoelectronic material [49], functional polymers [50], and the other one is related to the helicity, including asymmetric catalysis [51–54], chiral recognition [55], chiroptical switches [56], nanoscience [57], and biological applications [58].

Meanwhile, the synthetic methods were greatly developed. For example, Starý and Stará groups developed intramolecular [2+2+2] cycloisomerization of triynes to construct helicene backbones (Scheme 1.5) [59]. When chiral ligands were used, asymmetric synthesis could be achieved with high enantioselectivity. Tanaka group utilized intermolecular [2+2+2] cycloaddition with chiral ligands and realized the

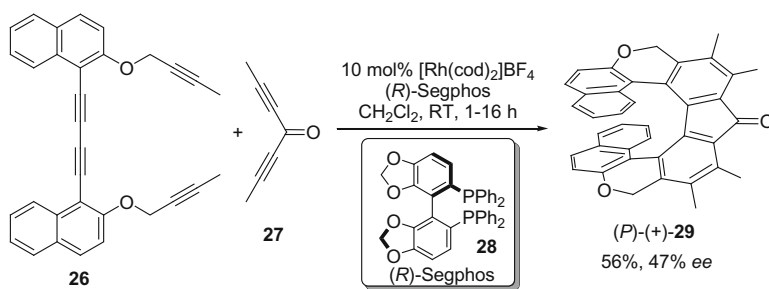
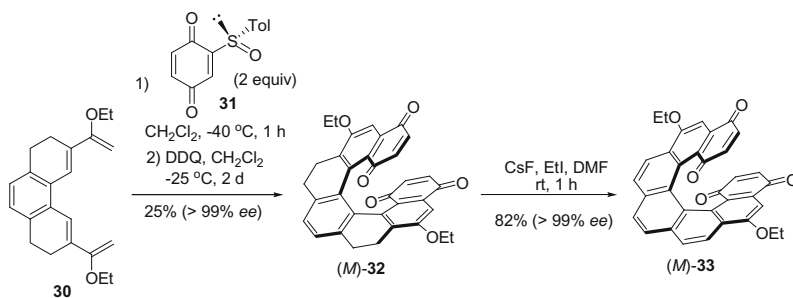
Scheme 1.4 Synthesis of [5]helicene bisquinone



Scheme 1.5 Synthesis of [7]helicene by intramolecular [2+2] cycloisomerization

enantioselective synthesis of long helicenes (Scheme 1.6) [60, 61]. Carreño and Urbano groups utilized chiral *p*-benzoquinone to prepare helicene quinones with high stereoselectivity (Scheme 1.7) [62]. Crassous, Autschbach, Réau, and colleagues had synthesized a variety of organometallic helicenes, which displayed optimized chiroptical properties (Fig. 1.6) [63].

Helicenes, as a member of polycyclic aromatic hydrocarbons (PAHs) for more than a century have been attracting more and more attentions to their physical properties, chemical reactivity, and synthetic challenges. The records of papers about helicenes are summarized in Fig. 1.7, which was obtained from *ISI Web of Knowledge*[®] website using *helicene** as the search term. It is obvious that the number of publications increased rapidly, especially after 2010. Undoubtedly,

**Scheme 1.6** Asymmetric synthesis of [9]helicene-like molecule**Scheme 1.7** Asymmetric synthesis of [7]helicene bisquinone

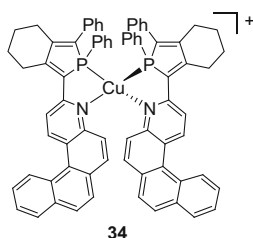


Fig. 1.6 Organometallic helicenes

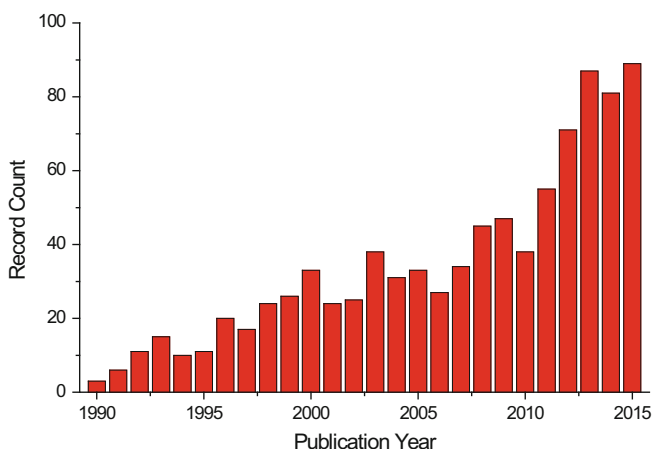


Fig. 1.7 Statistics of the literature published from 1990, retrieved on Oct. 21st, 2015

enormous progress has been witnessed in the past 20 years, and this active research field will get considerable development in the near future.

1.3 Objectives and Literature Coverage

This book is prepared to 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. Therefore, besides the general physical and chemical properties, we will focus on the practical synthetic methods as well, which have been widely accepted and used to prepare helicene in large scale via simple procedures. In addition, the frontiers of applications will be discussed in detail with regard to the helicity and the π -conjugated skeletons. The contents is based on the peer-reviewed journal papers from a thorough search of the literatures published between 2012 and early 2016, and important discoveries before 2012 will also be discussed here to give readers an overview of the progress of helicene chemistry.

1.4 Books and Reviews on Helicene Chemistry

So far, dozens of book chapters and reviews have been published, and they are listed in Tables 1.1 and 1.2, respectively. Readers, if interested in a specific area, could find the related books or review articles to get more information.

Table 1.1 Book chapters on helicenes

Title	Author(s)	Year	Notes	Ref.
Polycyclic Hydrocarbons (Vol. I)	Clar, E.	1964	[4]-, [5]-, [6]helicenes and their derivatives prepared before 1964 via non-photochemical strategies	[16]
Photocyclization of Stilbenes and Related Molecules	Mallory, F. B., Mallory, C. W.	1984	Helicenes prepared by photochemical methods before 1980	[64]
Fascinating Molecules in Organic Chemistry	Vögtle, F.	1992	The properties and synthesis of helicenes	[65]
Classics in Hydrocarbon Chemistry: Syntheses, Concepts, Perspectives.	Hopt, H.	2000	The synthesis of helicenes	[66]
Cyclophane Chemistry for 21st Century	Sato, K., Arai, S.	2002	The synthesis of azahelicenes	[13]
Cotrimerizations of Acetylenic Addition Reactions	Agenet, N. et al.	2006	The synthesis of helicenes and helicene-like molecules by metal-mediated [2+2+2] triyne cycloisomerization	[67]
Functional Organic Materials: Syntheses, Strategies, and Applications	Rajca, A., Miyasaka, M.	2007	A review of helicenes including the synthesis and chiroptical properties	[68]
Dynamic Stereochemistry of Chiral Compounds: Principles and Applications	Wolf, C.	2008	Stereoselective synthesis of helicenes	[69]
Strained Hydrocarbons	Starý, I., Stará, I. G.	2009	A brief review of physicochemical properties, synthesis, and the applications of helicenes	[70]
Aromatic Ring Assemblies, Polycyclic Aromatic Hydrocarbons, and Conjugated Polyenes	Starý, I., Stará, I. G.	2010	A comprehensive review of synthetic methods	[59]
Transition-Metal-Mediated Aromatic Ring Construction	Tanaka, K.	2013	The synthesis of helicenes by metal-mediated reactions, especially the [2+2+2] cycloaddition	[71]
Helical Phosphorus Derivatives: Synthesis and Applications	Virieux, D. et al.	2015	The synthesis of phosphahelicenes and applications in asymmetric catalysis	[53]
Organic Photoredox Chemistry in Flow	Gilmore, K. et al.	2015	The synthesis of helicenes by continuous flow methods	[72]

Table 1.2 Reviews on helicenes

Title	Author(s)	Journal name, year, starting page	Ref.
Some Observations on the Chemical, Photochemical, and Spectral Properties of Thiophenes	Wynberg, H.	Acc Chem Res, 1971, 65	[11]
Helicenes	Martin, R. H.	Angew Chem Int Ed Engl, 1974, 649	[4]
Chemistry of Heterochemistry	Kawazura, H., Yamada, K.	J Syn Org Chem Jpn, 1976, 111	[5]
Carbohelicenes and Heterohelicenes	Laarhoven, W. H., Prinsen, W. J. C.	Top Curr Chem, 1984, 63	[6]
Helical Molecules in Organic Chemistry	Meurer, K. P., Vögtle, F.	Top Curr Chem, 1985, 1	[73]
Synthesis and Properties of Helicenes	Oremek, G. et al.	Chem-Ztg, 1987, 69	[74]
Carbohelicenes, Heterohelicenes and Related Systems—Some Aspects of Synthesis and Reactions	Osuga, H., Suzuki, H.	J Syn Org Chem Jpn, 1994, 1020	[75]
Structure/Chiroptics Relationships of Planar Chiral and Helical Molecules	Vögtle, F. et al.	Eur J Org Chem, 1998, 1491	[76]
Syntheses of Functionalized and Aggregating Helical Conjugated Molecules	Katz, T. J.	Angew Chem Int Ed, 2000, 1921	[77]
Recent Developments in the Synthesis of Helicene-like Molecules	Urbano, A.	Angew Chem Int Ed, 2003, 3986	[78]
Unlocking the Potential of Thiaheterohelicenes: Chemical Synthesis as the Key	Collins, S. K., Vachon, M. P.	Org Biomol Chem, 2006, 2518	[79]
Photochemical Reactions as Key Steps in Organic Synthesis	Hoffmann, N.	Chem Rev, 2008, 1052	[80]
Azahelicenes and Other Similar Tri and Tetracyclic Helical Molecules	Dumitrascu, F. et al.	ARKIVOC, 2010, 1	[12]
Photochemical Oxidative Cyclisation of Stilbenes and Stilbenoids—The Mallory-Reaction	Jørgensen, K. B.	Molecules, 2010, 4334	[81]
Advances in the Synthesis of Helicenes	Dou, G.-L., Shi, D.-Q.	Chin J Org Chem, 2011, 1989	[82]
Helicenes: Synthesis and Applications	Shen, Y., Chen, C.-F.	Chem Rev, 2012, 1463	[7]
One Hundred Years of Helicene Chemistry. Part 1: Non-stereoselective Syntheses of Carbohelicenes	Gingras, M.	Chem Soc Rev, 2013, 968	[9]
One Hundred Years of Helicene Chemistry. Part 2: Stereoselective Syntheses and Chiral Separations of Carbohelicenes	Gingras, M., et al.	Chem Soc Rev, 2013, 1007	[10]
One Hundred Years of Helicene Chemistry. Part 3: Applications and Properties of Carbohelicenes	Gingras, M.	Chem Soc Rev, 2013, 1051	[8]

(continued)

Table 1.2 (continued)

Title	Author(s)	Journal name, year, starting page	Ref.
Applications of Helical-Chiral Pyridines as Organocatalysts in Asymmetric Synthesis	Peng, Z., Takenaka, N.	Chem Rec, 2013, 28	[51]
Metal-Catalyzed Annulation Reactions for π -Conjugated Polycycles	Jin, T. et al.	Chem Eur J, 2014, 3554	[83]
Helicene-based Transition Metal Complexes: Synthesis, Properties and Applications	Crassous, J. et al.	Chem Sci, 2014, 3680	[84]
Cationic Triangulenes and Helicenes: Synthesis, Chemical Stability, Optical Properties and Extended Applications of These Unusual Dyes	Lacour, J. et al.	Chem Soc Rev, 2014, 2824	[85]
Helical-Chiral Small Molecules in Asymmetric Catalysis	Narcis, M. J., Takenaka, N.	Eur J Org Chem, 2014, 21	[52]
Photochemical Reactions Applied to the Synthesis of Helicenes and Helicene-like Compounds	Hoffmann, N.	J Photochem Photobio C: Photochem Rev, 2014, 1	[86]
Synthesis, Double-Helix Formation, and Higher-Assembly Formation of Chiral Polycyclic Aromatic Compounds: Conceptual Development of Polyketide Aldol Synthesis	Yamaguchi, M. et al.	Chem Rec, 2014, 15	[55]
Helicene-like Chiral Auxiliaries in Asymmetric Catalysis	Marinetti, A. et al.	Dalton Trans., 2014, 15263	[54]
Enantioselective Helicene Synthesis by Rhodium-Catalyzed [2+2+2] Cycloadditions	Tanaka, K. et al.	Bull Chem Soc Jpn, 2015, 375	[61]
Circularly Polarized Luminescence from Simple Organic Molecules	de la Moya, S. et al.	Chem Eur J, 2015, 13488	[87]
Cyclophanes Containing Large Polycyclic Aromatic Hydrocarbons	Bodwell, G. J. et al.	Chem Soc Rev, 2015, 6494	[14]
Recent Advances in Stereoselective [2+2+2] Cycloadditions	Amatore, M., Aubert, C.	Eur J Org Chem, 2015, 265	[60]

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