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# A Concise Review on Synthesis and Applications of Helicenes

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## Abstract

Helicenes can be recognized as helical-shaped π-conjugated molecular structures composed of sequential ortho annulated aromatic rings with thermal stability and intrinsic chirality. Helicenes are generally characterized by their distinctive supramolecular structural design and unusual optical characteristics. Helicenes have been utilized on a broad range of potential applications, such as liquid crystals, material dyes, asymmetric synthesis, molecular switches, polymers, and photorefractive materials, nanomaterials via self-assembly, biological recognition, as well as photovoltaics, and light-emitting devices.

*Keywords:* Helicenes, Synthesis, Dyes, Polymers; Catalysis.

## 1. Introduction

Smart materials have been designed for high technical applications, such as sensors, electrically conductive polymers, liquid crystals, linear actuators, molecular switches, biologically active fibers, photovoltaics and light-emitting devices [1-12]. So, with smart materials technology, the environment can be changed by activating the material's functions. Some of these materials are multifunctional materials that can be activated by electrical stimuli so as to produce its geometry change or property change. Also, it can be activated by the advent of nanotechnology, ranging from carbon nanotubes, graphene, inorganic nanoparticles, conducting polymers, and so on [13-22].

Helicenes are polycyclic aromatic molecules containing non-planar twisted structures produced by ortho-fused aromatic rings (Fig. 1). Meisenheimer and Witte have reported the first synthesis of helicenes at the beginning of the 20th century (Fig. 2) [23, 24].

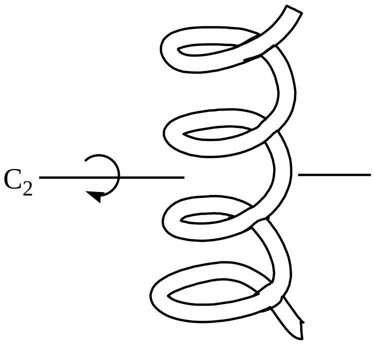

Fig. 1. Cylindrical helix with C2 axis.

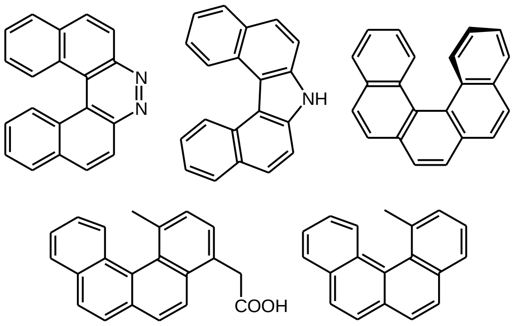

Fig. 2. Some Helicenes and heterohelicenes molecular structures.

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It has been reported the preparation of hexahelicenes in the 1950s. However, the investigation of helicenes has been done slowly during the periods of the first seventy years of the 20th century. In the 1990s, Diels-Alder synthetic chemistry has been employed to prepare a diversity of helicenes derivatives. At the end of the 20th century, other novel approaches including organometallic catalysis and other theoretical studies have been used to synthesize helicenes with enhanced yields and enantioselectivity [25-27].

Helicenes have been used in a diversity of potential applications such as liquid crystals, material dyes, asymmetric synthesis, molecular switches, polymers, and photorefractive materials, nanomaterials via self-assembly, photovoltaics, and light-emitting devices, biological applications, and linear actuators. Many earlier reviews have been published on describing the synthesis and characteristics of helicenes and heterohelicenes. This review briefly will explain the different synthetic approaches, reactions, characteristics, and applications of helicenes and substituted helicenes[28-34].

## 1. Nomenclature and numbering of Helicenes

In the 1950s, it was the first time to launch the helicene terminology using a number [n] indicating the number of aromatic moieties, in front of the helicene name such as; hexahelicene or [27] helicene for phenanthro[3,4-c]phenanthrenes. It was also proposed the numbering of carbohelicenes (Fig. 3) [35, 36].

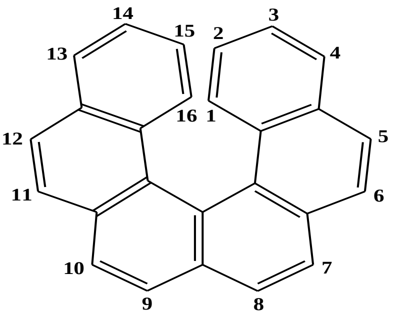


Fig. 3. Numbering of carbohelicenes.

Carbohelicene contains only benzene rings in their backbone structure, while heterohelicene compounds include one or more heteroatom such as aza[n]helicenes, or [n]oxahelicenes. The double helicene term refers to two similar or different fused screw moieties. Bihelicenyls includes two different helicene screw structures linked by a single bonding, and helicenophanes includes helicenes with two terminal moieties are connected by aliphatic chains (Fig. 4) [37].

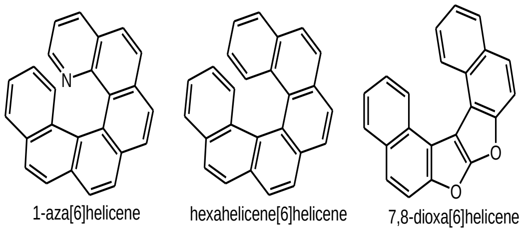
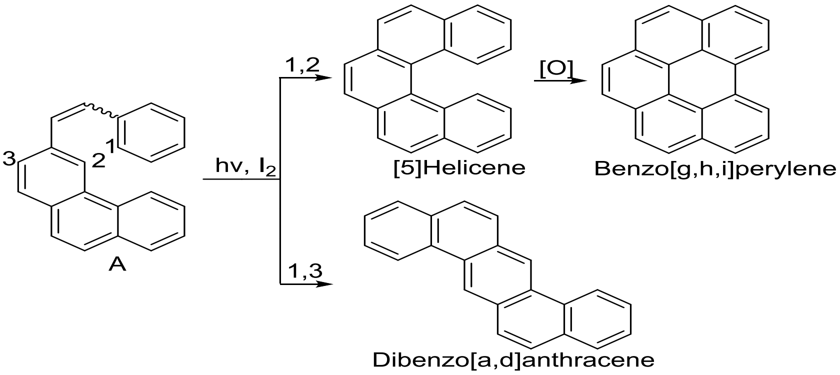


Fig. 4. Nomenclature of carbohelicenes.

## 2. Synthetic approaches

### 2.1. Photocyclization strategy

The photocyclization synthetic strategies of carbohelicene are a very significant approach for the production of many helicenes as formally reported by Martin et al In 1967s. This is a result of the simply synthesized stilbenes precursors using Wittig olefination reaction. The photocyclization process can occur at either C-2 or C-3 of precursor A to produce isomers that sometimes cannot be separated (Scheme 1). The cyclization process also forms a hydrogen iodide byproduct that may reduce the double bond. Katz et al. have reported an effective bromine directed photocyclization approach to form helicenes selectively high yield [38]. The same research group has also reported an additional extraordinary approach for the photo-induced production of helicenes by applying excess propylene oxide in addition to a stoichiometric quantity of iodine under inert gas to improve both obtained yields and to avoid the photo-reduction of the double bonds as a side reaction. The later synthetic approach has been considered as a typical practice for the photo-induced cyclization of stilbenoids. Furthermore, bromine can be used to functionalize these brominated helicenes [39-41].

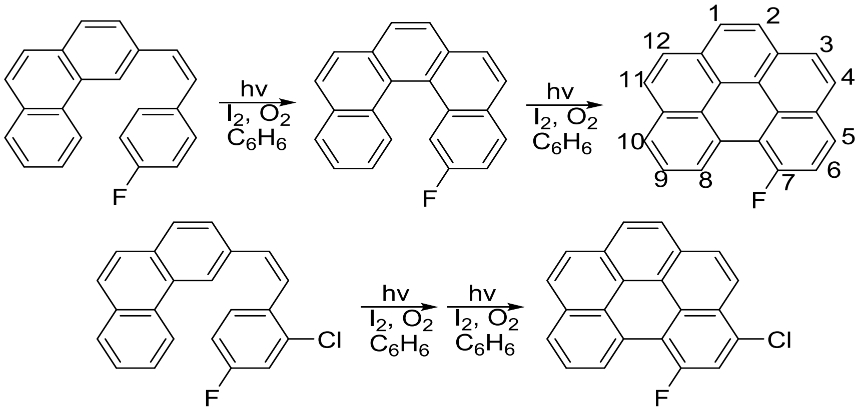


Scheme 1. Photocyclization at either C-2 or C-3 of the precursor A.

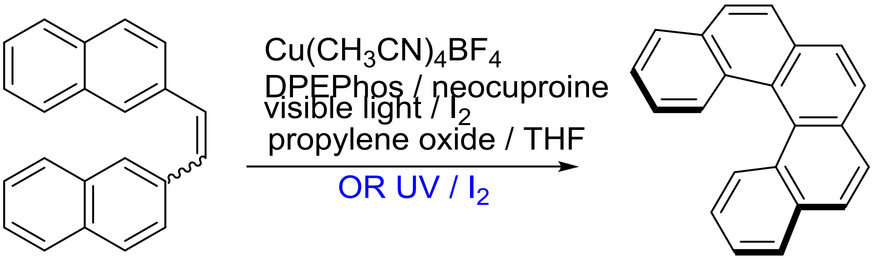
At the beginning of the 21st century, Koning et al have reported an additional precursor for the synthesis of pentahelicenes in high yield [42]. The mechanism was proposed to include proton abstraction using a strong base which results in enolate formation leading to photocyclization via isomerization [37, 43].

Mallory et al. have reported the oxidative photocyclization of l-fluoropentahelicene and two of its chlorine-functional derivatives to afford 8-fluorobenzoperylenes via fluorine atom migration. This unusual fluorine migration rearrangement process dominates at 0 $^oC$ in air-saturated benzene solution with iodine (Scheme 2) [44].

Photochemical cyclizations induced by copper sensitizer have been applied in the preparation of pentahelicene with avoiding the drawbacks related to the conventional UV light-mediated approach. This procedure has been established with a considerably high yield and large scale, shorter reaction period avoiding the production of any other side products. Also, the reaction does not employ any costly quartz glassware or dangerous UV lamps (Scheme 3) [45, 46].



Scheme 2. oxidative photocyclization of l-fluoropentahelicene and two of its chlorine-functional derivatives to afford 8-fluorobenzoperylenes

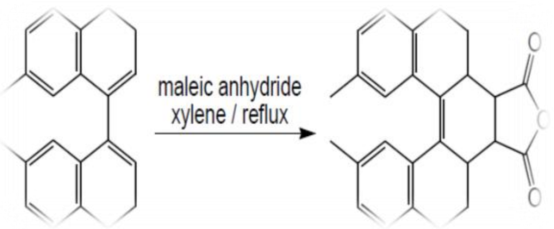


Scheme 3. Photochemical cyclization induced by copper sensitizer.

Generally, the photocyclization synthetic approach is hard to provide helicenes on a large scale, in addition, to be deficient with the introduction of several functional groups including amino and nitro functional groups that can speed up the intersystem crossing preventing the cyclization process. However, the photocyclization process is still considered a suitable technique for the production of a diversity of helicene derivatives in outstanding to the simple production of the stilbenoid precursors and mild reaction circumstances [37, 46-49].

### *1.1. Diels-Alder reactions*

Katz et al have described the preparation of helicenes on large scale in the 1990s using Diels-Alder chemistry. This synthetic strategy has been used to prepare pentahelicenes including two quinone fragments in practical yield and large-scale amounts from 4-benzoquinone and 4-divinylbenzene. Furthermore, the existence of 4 carbonyl functional substituents in the produced pentahelicenes tolerates the appropriate functionalization of the terminal aromatic rings [38-41, 50]. Using strong electron-withdrawing substituents on the dienophile and electron-donating groups on the diene usually leads to fast and effective Diels-Alder interactions. Nonetheless, the high sensitivity of these cycloaddition processes to the steric of the bulky groups at the terminal positions of the dienes reduces the reaction rate. Hence, dienes containing functional groups at the *β*-position is considered a better option to easily prepared helicenes. Vinyl-based dienes and 3,3',4,4'-tetrahydro-1,10-binaphthyl derivatives have been used broadly via Diels-Alder chemistry to synthesize helicenes. This Technique has been reported in the 1940s in the synthesis of coronene as the disubstituted pentahelicenes were formed in low yield (Scheme 4).



Scheme 4. Synthesis of coronene.

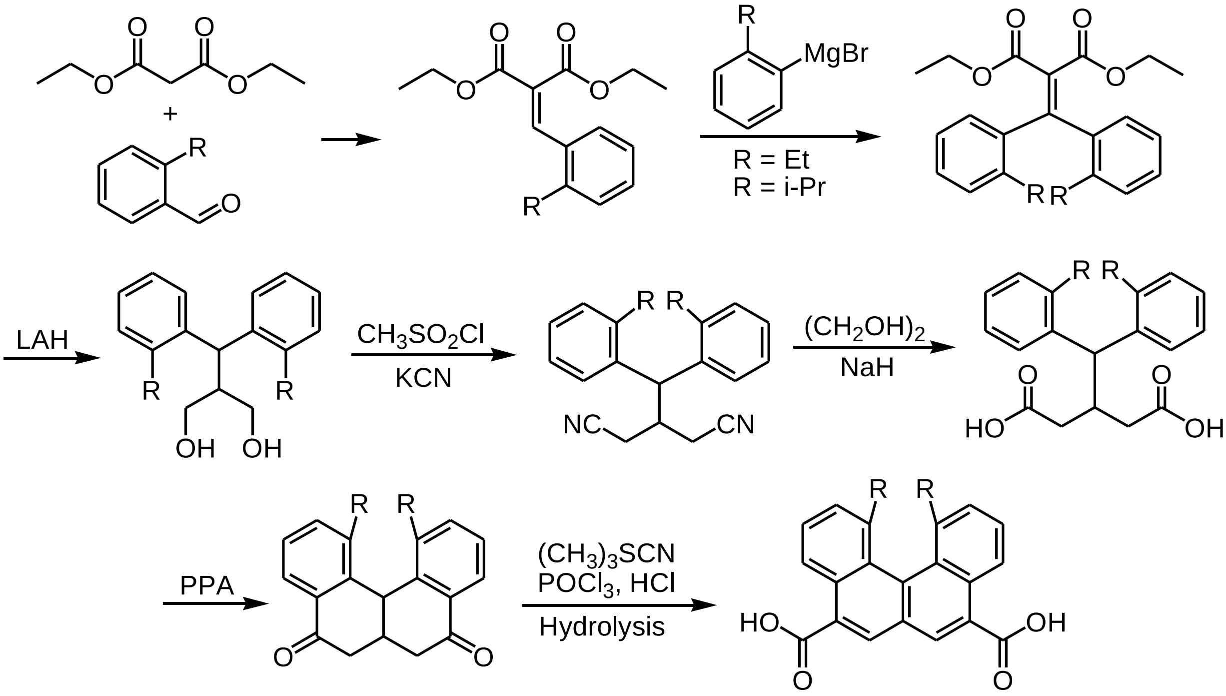
Minuti and co-workers also described the preparation of pentahelicenes in a 62% yield by reacting a diene with *p*-benzoquinone utilizing Pd/C as a catalyst. Tetrahydrobinaphthyls also have been used with benzyne to provide helicene derivatives in situ [37]. Overall, the Diels-Alder chemistry is an efficient approach to build helicenes on a large scale with reasonable yields. Additionally, the substituents on both dienes and dienophiles can also be employed to improve solubility, optical resolution, and adjusting their electronic characteristics. On the other hand, the reaction transformation progress is still limited because of the requested electron-donating groups on the diene [37].

### *1.2. Friedel-Crafts reactions*

Recently, Katz et al have reported Friedel-Crafts diacylation of phenanthrenes toward the preparation of nonracemic heptahelicenes. Reduction of 9,10-Phenanthrenequinone, followed by alkylation, and acetylation, provide 3,6-diacetyl-9,10-dialkoxyphenanthrenes in reasonable yield. These immediately give the corresponding heptahelicene-bisquinones followed by helicenyl camphorates [19].

Newman et al. was also the first to report the preparation of hexahelicenes using double Friedel-Crafts acylation approach. The cyclization reaction of malonic acid to the corresponding ketoacid that can be reduced to the carboxylic acid by applying the Huang-Minlon method, and consequently the acylation approach was established by means of stannic chloride was also reported. This acylation process was followed by reducing the ketone to afford hexahelicenes in reasonable yield. At the end of the 20th century [37, 51], Yamaguchi et al. have reported a related method to prepare disubstituted[4]helicenes (Scheme 4). Yamaguchi’s approach has been applied with functional groups as blocking groups to direct the acylation process to take place at a specific position and to decrease the racemization rate [52-54].

Another approach to tetrahelicenes have been reported with Friedel-Crafts acylation process, the diketones were reacted with a mixture of trimethylsilyl cyanide, phosphorus oxytrichloride, and HCl to provide the corresponding dinitriles that can be hydrolyzed in basic circumstances to afford dicarboxylic acids (Scheme 5) [55, 56].



Scheme 5. Synthesis of tetrahelicenes.

Gaucher et al. have recently described the production of 6, 11-diamino-[6]-helicenes using the Friedel-Crafts approach. Diarylnaphthalene was prepared via the Suzuki-Miyaura C-C coupling reaction, and then the product was subjected to bromination followed by cyanation to give the corresponding dinitriles [57]. The following dual cyclization process occurs in polyphosphoric acid to afford helicenes with two amino functional groups. In Friedel-Crafts strategies, two benzene rings can be produced in one step in reasonable yield. Blocking substituents are required to direct the cyclization process. Unsaturated polar bonds, such as cyano, carbonyl, and carboxyl, should be included in the starting material. Nonetheless, as a result of limited approaches to Friedel-Crafts-type precursors, this strategy is not so practical and only symmetric helicenes can be obtained [37].

### *1.3. Metal-induced cyclization*

Palladium-catalyzed coupling reactions have been used to produce helicenes. Novel chiral hexahelicenes bearing acetoxymethyl moiety have been obtained in 34% overall yield using the readily available and inexpensive naphthalene building blocks. Four steps have been applied including Pd-catalyzed Heck coupling reaction and oxidative photocyclizations [58, 59].

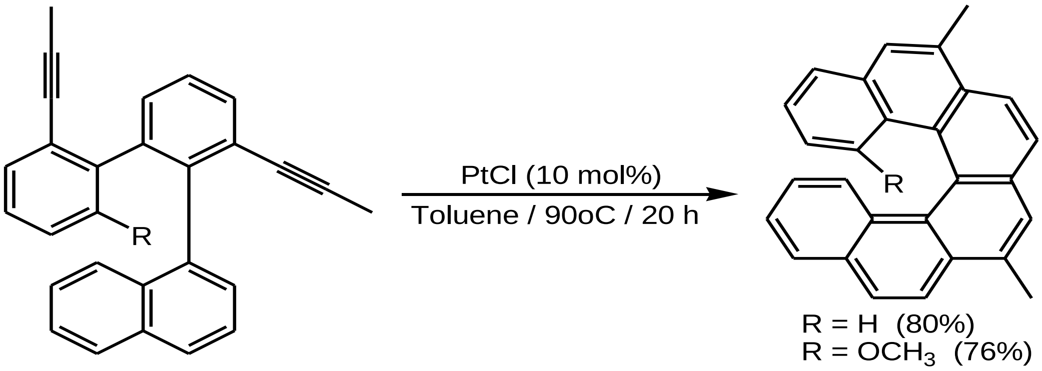
Dual C-H arylation reaction was applied in the preparation of different helicene derivatives in reasonable yields. The Pd-catalyzed coupling approach has been considered as a compatible method in the presence of electron-deficient groups at C-3 and C-12. Two methoxy substituents are necessary to direct the cyclization processes to give the targeted helicenes. However, heptahelicene could not be obtained using the Pd-catalyzed coupling chemistry [60, 61].

Metal vinyl ruthenium groups have been included in the molecular structure of hexahelicenes to considerably improve the chiroptical characteristics because of the strong electronic interactions between both metal and ligand. Collins et al. have described the preparation of helicenes in high yield by applying ring-closing metathesis RCM. There are two distinct methods have been used in this RCM approach [62]. The first method is rapid but needs high temperature that may lead to pyrolysis, while the second method takes place in mild circumstances including low temperature. The latter method allows the availability of sensitive substituents; however, it needs a longer time. Cobalt/Nickel-catalyzed intramolecular [2+2+2] cyclo-isomerization approach has been reported for the synthesis of helicenes and functionalized helicenes [63-65].

Tetrahydrohelicenes have been easily prepared in moderate yield by applying CpCo(CO)2/PPh3 catalyst. Similar products were achieved in parallel yields and under ambient conditions using Ni(cod)2/PPh3 catalyst. Dehydrogenation of the formed tetrahydrohelicenes affords the corresponding helicenes [64, 66].

In a one-step reaction, anthra[11]helicene has been produced by means of double cyclo-isomerization including the construction of six novel aromatic rings. This approach is extremely practical due to high efficiency and modular assembly property that allows the functionalization of both the aromatic and alkyl fragments to give non-symmetric and multifunctional tetrahydrohelicenes [64].

Storch et al. have described an additional approach to produce hexahelicenes in high yields using dual [2+2+2] cyclo-isomerization of biphenylyl-naphthalenes allowing easily substitution at sterically hindered spots (Scheme 6) [67].



Scheme 6. Synthesis of hexahelicenes via dual [2+2+2] cyclo-isomerization of biphenylyl-naphthalenes.

Lithium stimulated cyclization of tribenzocyclyne was reported by Tessier et al. as an efficient method to benzo[5]helicene. Dianion also includes two cyclopentadienyl fragments that were obtained in high yield by lithium stimulated cyclization. In addition, the trimethylsilyl groups can be used to functionalize the produced helicenes [68].

McMurry coupling has been reported in the preparation of helicenes. The brominated BINOL has been formylated followed by cyclization using reduction of titanium trichloride and Zn-Cu in 1,2-dimethoxyethane as a solvent. However, McMurry coupling was not convenient due to low yield and severe conditions. These cyclization strategies are efficient because helicenes can be produced in low steps, high yields, and compatible functionalization. Therefore, the [2+2+2] cyclo-isomerization has been considered as a wide-ranging synthetic approach for helicenes [69].

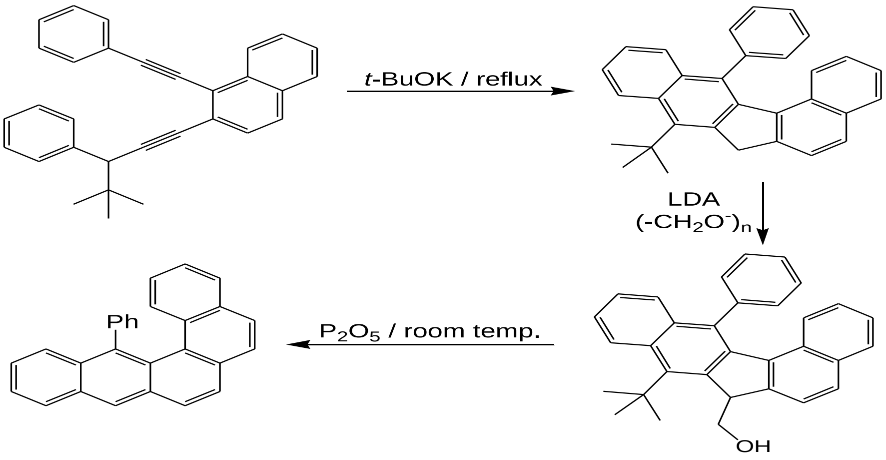
### *3.5. Radical Cyclizations*

The intramolecular radical addition approach for the preparation of helicenes has been reported with practical yields. Scheme 7 displays the synthesis of helicenes bearing aryl moieties by treatment with lithium diisopropylamide followed by reaction with paraformaldehyde. The product is then subjected to Wagner-Meerwein rearrangement in the existence of phosphorus pentoxide [70]. The radical cyclization approach is considered as a suitable and efficient method to produce helicenes due to the simple production of the used starting material and the reason for high yields. However, it has not been broadly used because of the low regioselectivity and less functional group compatibility [71-73].

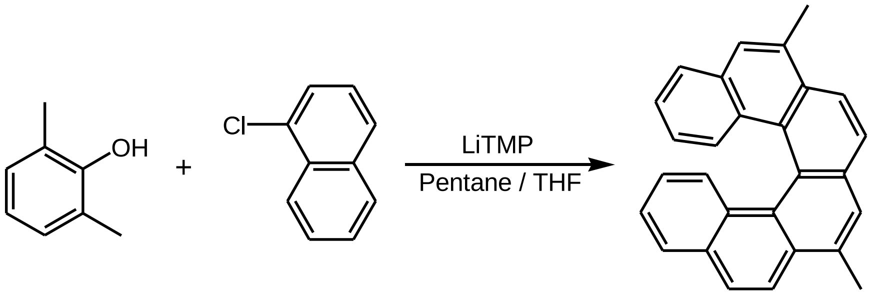
### *3.6. Other cyclization reactions*

The reaction of phenols with arynes has been studied using lithium tetramethylpiperidide (LiTMP) base to afford helicenes. The o-arylation process of applicable phenols was established using t-BuONa base and silver acetate (Scheme 8) [74].

Gingras et al. have reported the carbenoid coupling reaction of the bromonated 2, 2'-dimethyl-1, 10-binaphthyl in the existence of the suitable lithium reagent to prepare penta and heptahelicenes in moderate yields. The same research group has also reported an enhanced path to prepare functionalized helicenes using benzylic (dibromo) methine coupling reaction. 2,2'-Bis(dibromomethyl)-1,10-binaphthyl was obtained via brominating the disubstituted binaphthyl then ring-closing to provide 7,8-dibromo[5]helicene, followed by reduction to afford 7-bromo[5]helicene. In these routes, the used precursors are simply prepared by coupling reactions or from 1,10- binaphthyls. The used reagents are inexpensive; the reaction rates are tremendously fast with high yields [75]. Piers et al. have reported an appropriate one-step preparation of pentahelicenes in moderate yield via Li/Br metal exchange and quenching with one equivalent of hexafluorobenzene [76]



Scheme 7. Synthesis of helicenes bearing aryl moiety.



Scheme 8. Reaction of phenols with arynes toward helicenes.

Larock and co-workers have described an effective production of tetrahelicenes in reasonable to high yields via electrophilic-cyclization reaction under gentle reaction circumstances. Helicenes described above, have been prepared via building one benzene moiety employing 1,10-binaphthyls. Those reactions do not involve any costly noble metal-based organometallic catalysis and generally include low steps with moderate to high yields, and some reaction rates are tremendously fast. However, the majority of these approaches have been used to produce pentahelicenes that are not optically stable under ambient conditions [77, 78].

## 4. Applications of carbohelicenes

### *4.1. Asymmetric Catalysis*

Martin et al. have reported the substituted heptahelicenes as chiral auxiliaries in five distinct diastereoselective reactions [79-81].

In 1997, Reetz et al. have described the first catalytic reagent using helicene as a chiral ligand that has been applied in the reduction of itaconate under gentle conditions to give the corresponding diester in moderate yield and 39% ee [82].

In 2003, Yamaguchi et al. have used bihelicenol phosphite ligands to afford a quantitative yield and 96% ee [83].

The same research group in 1998, have also described that the optically pure macrocyclic amide bearing two tetrahelicene groups can be applied in the catalyzed-asymmetrical addition of diethyl-Zinc (Et2Zn) to aromatic aldehyde derivatives allowing the preparation of (R)-arylpropanol in 50% ee [15].

Katz et al. have established that (P, P, S)-Pentahelol with a helical engraves can be applied in the catalyzed-asymmetrical addition of Et2Zn to benzaldehyde, that is motivated by the substituted BINOL and vaulted biaryl ligand, to provide (S)-product in 81% ee [62].

The reaction was proposed to include the pentahelol-based intermediate, in which the Zn atom is bonded to pentahelol moiety and linked to benzaldehyde via coordination bonding. Accordingly, the Re-face of benzaldehyde is blocked by the bottom side of the helicene pushing Et2Zn to go into the engraves from the top side of the helicene. At the beginning of the 21st century, Soai et al. have established that hexahelicene could be applied for the autocatalysis among R2Zn and the pyrimidyl aldehyde as (P)-helicenes stimulate the generation of (S)-alcohol in high ee [63,64].

Takenaka et al. have recently described two novel categories of asymmetric catalysts from 1-azahelicene, that was oxidized by m-CPBA to afford the chiral pyridine N-oxides that function as a Lewis base in the catalyzed enantioselective ring-opening of meso-epoxide. The reaction was proposed to include a cationic species allowing the chloride anions to be added from the less hindered face [65].

Helicenes containing a 2-aminopyridinium terminal ring have been reported as an effective dual-hydrogen-bond donor catalyst at low temperature with high enantioselectivity. (M)-2-azahexahelicenes have been used as organo-catalysts in the asymmetric transferring reactions of the acyl group displaying good catalytic efficiency to give the (R)-derivative in 99% ee with 72% conversion using isopropylanhydride and diisopropylethylamine base.

### *4.2. Dye Materials*

Cyclo-pentadienes can be fitted into helicenes molecular structures or at their termini followed by deprotonation to provide tetra and pentahelicene dianions. Reacting these helicenes dianions with metal cations provide metallocenes with remarkable magnetic, conductive, and optical properties. The first optically active octaazaphthalocyanine-based helicene dyes have been reported by Katz and co-workers [66].

Afterward, Mandal et al. have reported an additional novel three pentahelicene-fused phthalocyanines that were described to produce dimeric assembled molecular structures over different concentrations [67].

Phthalocyanine-based helicenes display a broad absorption band at wavelength 525 nm. The absorbance spectra of those phthalocyanine-based helicene chromophores enclosed the whole visible regions demonstrating their capability to be applied as light-harvesting materials for photovoltaics purposes. Harima et al. established a new category of push-π-pull conjugated helical dyes using heterohelicenes building blocks. These helicenes-based dyes were prepared using a carboxylic group as an anchoring group in order to enhance the electron communication among both surface and dyes. Harima et al. established that the intramolecular charge transfer relied on the electron-acceptor moiety in the push-π-pull system. Therefore, to offer novel efficient organo-sensors, the used chromophores should exhibit a better light-harvesting property, strong interaction, and suitable arrangement on the titanium dioxide surface of the dye-sensitized solar cells [68,69].

### *4.3. Polymers*

The first ladder polymers included heptahelicene moiety attached by nickel salophen units with an extended π-conjugated system from the helicene into the entire polymer. These salophen ligands have been prepared from 1, 2-phenylenediamine. Because the two aldehyde functional substituents were located at different positions, two distinct polymers were produced with assist of the strong coordinating bonds among metal centers and ligands. Both polymers have average Mw (ca. 7000) with high solubility in a different range of organic solvents. Furthermore, their circular dichroism spectra were mainly the same as that of the used helicene precursor derivatives with just a minor shift to longer wavelength and other polymer displayed a larger circular dichroism spectral intensity at ca. 600 nm. Further new ladder polymer shaping 1D wires were made from fused-benzothiophene rings that have been reported by Nishide and co-workers. The conductivity of these produced one-dimensional wires could be significantly enhanced via structural doping. A rigid polymer based on thiaheterohelicenes was obtained via Suzuki coupling, oxidation, followed by intramolecular cyclization [70-72].

Lawesson’s reagents have been used to prepare helical polymers (Tg = $265^{O}$C) as reported by Wand and Douglas. A number of different dianhydrides have also been applied in the copolymerization processes to produce diads with helicene moieties. It has been described the preparation of cyclophanes and acetylene-helicene based polymers using Pd-catalyzed coupling reactions [73].

## 5. Conclusions

Helicenes are an attractive group of materials with distinctive helical shaped π-conjugated structures, unusual optical characteristics, and intrinsic chirality. During the 20th century, and the beginning of the 21st century, massive research work has been made in helicenes chemistry including diversity of synthetic approaches and a broad range of potential applications. These applications include liquid crystals, material dyes, asymmetric synthesis, molecular switches, polymers, and photorefractive materials, self-assembly, photovoltaics, and light-emitting devices, and biological applications.

## 6. Conflicts of interest

There are no conflicts to declare.

## 7. Acknowledgments

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