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The Photochemical Approach to Helicenes

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1.1 Introduction

In this chapter, the authors have decided to follow the nomenclature recommendations of IUPAC [1] for class names of organic compounds, which classifies *helicenes* as “*ortho*-fused polycyclic aromatic or heteroaromatic compounds in which all rings (minimum five) are angularly arranged so as to give helically shaped molecules, which are thus chiral.” Therefore, the following text includes [*n*]helicenes where $n \geq 5$ and the photoreaction is the very last step of their preparation, unless stated otherwise.

Two basic photo-approaches (oxidative photocyclodehydrogenation and photoinduced elimination; for details, see Section 1.2) were used for the preparation of all helicenes listed in this chapter. The photochemically created bonds are highlighted in red in all figures. Non-oxidative photochemical approaches are discussed in specific cases.

At the beginning of the chapter, some general features are mentioned, including the mechanism of the photocyclization, reaction conditions, attempts at asymmetric photosynthesis, and the synthetic approach to starting materials. The appropriate helical structures and their preparations are described in sections on carbo-, aza-, thia-, and phosphahelicenes and other helicenes. Helicene-like molecules, including dihydrohelicenes, are discussed separately, as well as photochemical transformations of helicenes.

1.2 General Features

Historically, the photocyclization of stilbenes [2, 3] was discovered during the investigation of their *cis/trans* photoisomerization [4], but the reaction was not used synthetically until Mallory found that iodine catalyzed this reaction in 1964 [5, 6].

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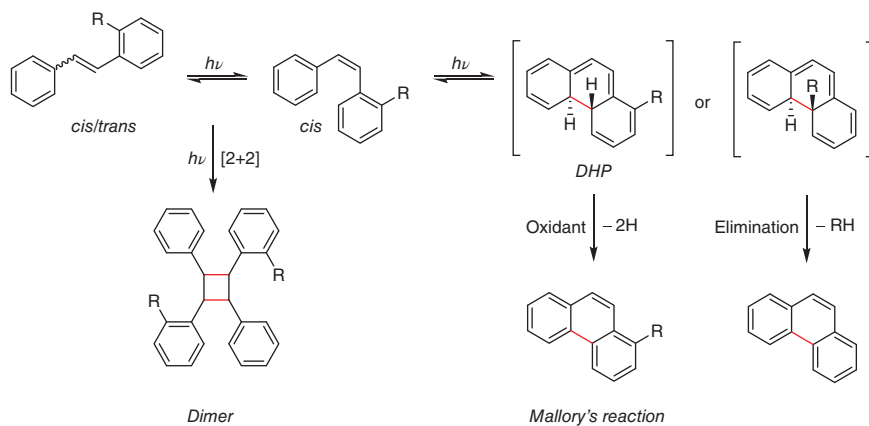


Figure 1.1 Photochemical reaction pathways for stilbene derivatives.

From the mechanistic point of view, the *cis/trans* photoisomerization of stilbenes is very fast with a high quantum yield, allowing stilbenes to be used as an isomeric mixture (Figure 1.1), although only the *cis*-isomer is capable of cyclization. The symmetry-allowed photoreaction typically takes place from the singlet S_1 state by a conrotatory process according to the Woodward–Hoffmann rules. Thus triplet sensitizers do not sensitize the photocyclization, and triplet quenchers (such as oxygen) do not quench it. The unstable 4a,4b-dihydrophenanthrene (DHP) intermediate possesses *trans*-configuration [7] and can, unless trapped, relax back to the stilbene. In the presence of an oxidant, DHP forms a phenanthrene derivative. This type of photocyclization is called the *Mallory reaction* [8]. If the stilbene contains suitable leaving groups ($R = \text{OMe}, \text{Cl}, \text{Br}$, etc.) in *ortho*-position, the elimination reaction producing cyclization product can take place (in the absence of an oxidant) [9–11]. Photocyclizations are typically carried out at concentrations of 10^{-3} M and lower to avoid the competing photodimerization [12]. The proposed photocyclization mechanism is also applicable to aza-, thia-, and other stilbene derivatives.

Originally, air was used as an oxidant until Mallory discovered that oxidative trapping occurs much faster when iodine (5 mol%) is used together with air [5]. It was proposed that iodine is photochemically cleaved into radicals reacting with hydrogen to form hydrogen iodide, which is then reoxidized to iodine by oxygen [13]. Other oxidants (e.g. selenium radicals, TCNE, TCNQ, chloranil, etc.) were investigated by Laarhoven without any practical significance for photocyclization of helicenes [14].

Higher amounts of hydrogen iodide may contribute to side reactions including double bond saturation of stilbenes [13]. In 1986, Katz developed new photocyclization conditions using propylene oxide as a hydrogen iodide scavenger under inert conditions [15, 16]. As a consequence, the iodide could not be reoxidized by air, and its stoichiometric amount is needed. Accordingly, it allows for a higher concentration of starting material in the reaction mixture without the undesired formation of dimers. When speaking about photocyclodehydrogenation leading to [*n*]helicenes, these conditions are sometimes familiarly referred

to as *Katz's conditions*. Other cyclic ethers (such as THF) are often used as HI scavengers too.

The previously mentioned conditions provide [*n*]helicenes in strictly racemic mixtures (1 : 1 ratio of (*P*)- and (*M*)-enantiomer). Although attempts to lead photocyclizations asymmetrically using circularly polarized light sources [17–23], chiral solvents [24–26], or cholesteric liquid crystals [27, 28] were made, the obtained results (% ee) were more or less at the level of experimental error and did not have any practical importance. Thus, the photochemical approach has to be followed by an optical resolution to obtain helicenes in their optically pure forms. The nonracemic helicenes are often photochemically accessible as corresponding diastereomers with (photo-stable) chiral auxiliaries (providing up to >99% de), which can be synthetically cleaved or transformed after cyclization [29–31]. Eventually, such diastereomers might be separated using standard chromatographic methods. When an enantiomerically pure [6]helicene moiety was a part of the precursor, nonracemic [*n*]helicenes (*n* = 8–11, 13) were obtained [32]. Other asymmetric photosyntheses to enantioenriched metallocene helicenes were developed by Katz [33–35]. Some studies suggested that only one chiral auxiliary is not sufficient, and a better result might be obtained with the chiral substitution at the most sterically hindered position [36]. The same phenomenon was observed by Carbery and Pearson [37]. For an overview see Ref. [26] and the references therein.

Conventional (Figure 1.2a) and transition metal-catalyzed (Figure 1.2b) methods of preparation of stilbene-like molecules as a common starting material for the photochemical synthesis of helicenes are described in the literature [38, 39], including several other synthetic procedures. In practice, the Wittig reaction (and its variations) and Pd-catalyzed cross-coupling reactions belong to commonly used methods.

The most widely used sources of UV–vis light for continuous irradiation in laboratory experiments are commercially available mercury lamps (low, medium, and high pressure) [40]. Their spectral irradiance is strongly dependent on the mercury vapor pressure. The lamp also produces a considerable amount of infrared radiation and heat. Therefore, cooling-water circulation must be utilized to protect the reaction solution from heating. Recently, new energy-efficient light sources like light-emitting diodes (LEDs) [41–43] (Figure 1.3d) became available, thus avoiding the use of optical filters and reducing consumption costs.

Photoreactors with an *immersion well* (Figure 1.3a) and *external chamber (merry-go-round)*, (Figure 1.3b) are the most common types of photochemical equipment on a preparative laboratory scale. Both reactor types are well established and in widespread utilization. The use of quartz allows light of all wavelengths above about 200 nm to enter the reaction mixture. For some photoreactions, higher yields can be obtained by employing Pyrex glass. This excludes from the reaction mixture light of wavelengths below about 300 nm and thereby protects the forming products from further photochemical degradation.

Following the experiments by Mallory [6], Scholz [44], and Martin [45], the batch setup of photocyclization of stilbene derivatives under UV–vis irradiation has become one of the most popular methods for the synthesis of helicenes [13]. This is

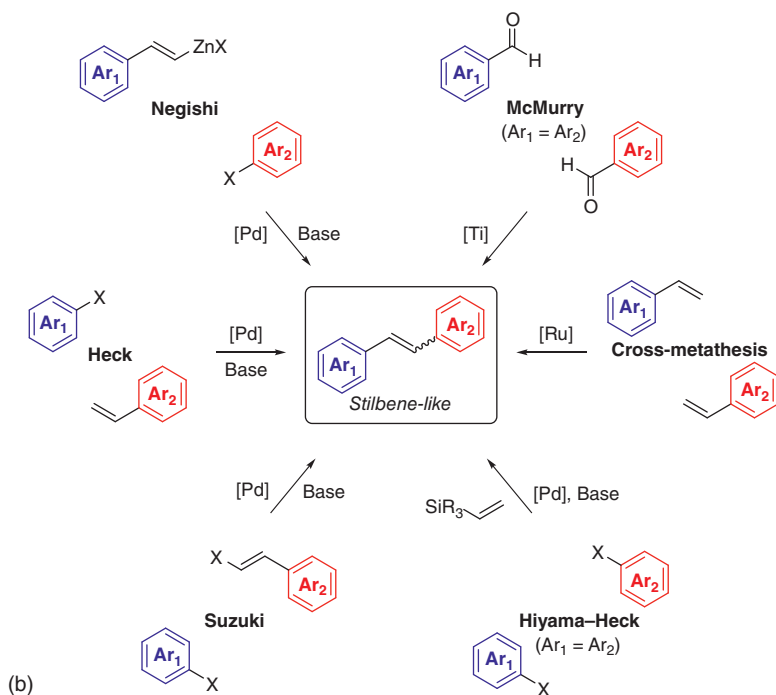
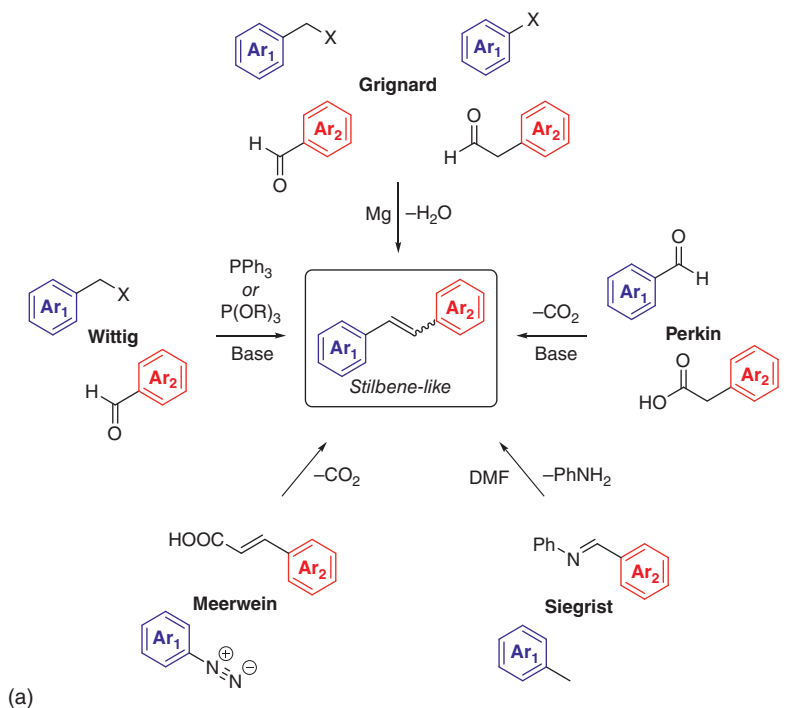


Figure 1.2 Commonly used preparations of stilbene-like molecules by conventional (a) and metal-catalyzed (b) procedures.

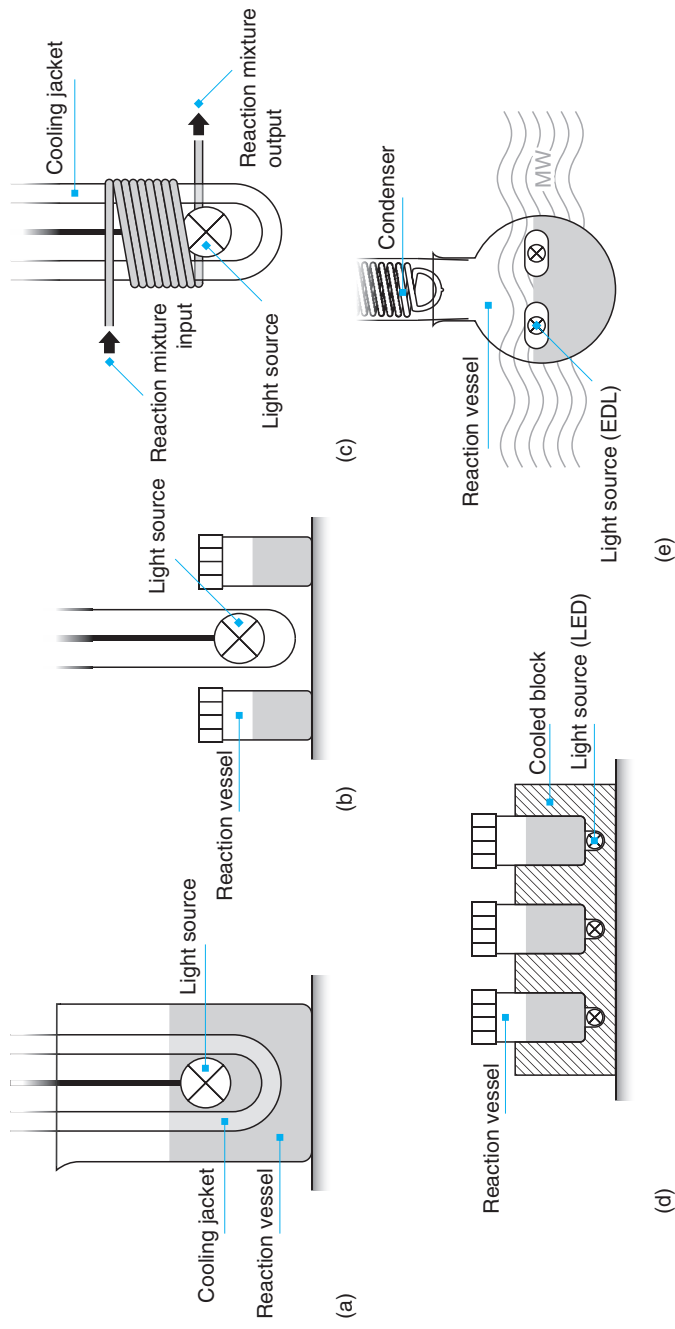


Figure 1.3 Common photoreactor types: (a) immersion well, (b) external chamber, (c) continuous-flow, (d) LED-type, and (e) electrodeless discharge lamps.

mainly due to the synthetic accessibility of the stilbene precursors and functional group tolerance under the reaction conditions (pH, temperature, etc.). However, the development of this setup is limited by the necessary dilution of the reaction mixture ($\sim 10^{-3}$ mol·l⁻¹) to prevent the undesired [2 + 2] cycloaddition, requiring large volumes of pure solvents and prolonged reaction times (>15 hours).

Therefore, finding an efficient protocol for the photocyclization of stilbene derivatives in a flow mode (Figure 1.3c) would be useful for the synthesis of helicenes on a gram scale. The photochemical transformations conducted under continuous-flow conditions are commonly characterized by shorter reaction times, higher yields, increased selectivities, easier purification, improved productivities, and high photonic and energy efficiencies compared with the conventional batch methods [46]. The equipment requirements are a special tubing (fluorinated ethylene propylene [FEP], which is highly transmittable, flexible, and anticorrosive) wound around the light source and a diaphragm pump.

Collins et al. reported the first example of the [5]helicene preparation by the photochemical continuous-flow strategy under visible light in the presence of Cu complex formed in situ [47]. In comparison to the traditional setup in a batch reactor, the flow method under photocatalytic conditions prevented the product from overannulation and enabled its gram-scale preparation. The same group used it also for the synthesis of pyrene–helicene dyads [48]. Rueping et al. [49] used a photo-flow methodology for the synthesis of [5]- and [6]helicenes with different substitution patterns. Murase et al. [50] accomplished the synthesis of amide-type aza[6]helicene in high yield by photocyclization of boron hydroxamate complex using a continuous-flow reactor in order to minimize its decomposition. Sýkora et al. [51] prepared 2-bromo[6]helicene as a key intermediate for helicene functionalization utilizing a continuous-flow photoreactor. Finally, Církva et al. [52] synthesized [6]helicenes fluorinated at terminal rings in the same setup.

A special photochemical reactor utilizing electrodeless discharge lamps (EDLs; Figure 1.3e) was also designed [53, 54]. It generates UV irradiation when placed in a microwave (MW) field. This methodology was used for the preparation of [6]helicene derivatives. Next to low costs, the arrangement in which the EDLs are placed inside the reaction vessel has several other advantages, such as simultaneous UV and MW exposure of the sample, enabling the performance of photochemistry at high temperatures.

1.3 Photochemical Preparation of Carbohelicenes

This part is further divided into oxidative and eliminative photocyclization according to the mechanism of the reactions. More details on photocyclizations toward carbohelicenes can be found in reviews [8, 13, 14, 26, 55–60] and a book chapter [61].

1.3.1 Oxidative Photocyclizations of Unsubstituted Carbo[*n*]helicenes

The first preparation of helicene molecule by photocyclization reaction was reported by Martin in 1967 on the preparation of [7]helicene (**3**) [45]. Since then,

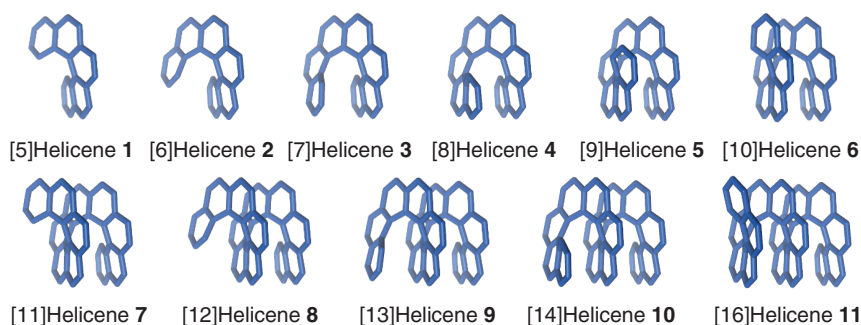


Figure 1.4 Unsubstituted carbo[*n*]helicenes.

photocyclization has become one of the most important methods for the synthesis of helicene homologs, from [5]- to [16]helicenes (Figure 1.4) and, of course, their derivatives.

[*n*]Helicenes can be photochemically formed from olefinic precursors of [*a*] + [*b*] + [*c*] structure, where “[*a-c*]” denotes the number of *ortho*-fused benzene subunits and “+” stands for the vinylene linker(s).

In the case of [5]helicene (**1**), great attention must be paid to the design of precursors due to possible benzo[*ghi*]perylene formation (see Section 1.6), which was observed by Dietz [44, 62], who attempted the synthesis of **1** using the [2] + [2] or [3] + [1] strategy. Using the [1] + [1] + [1] photocyclization strategy fails as well, as Liu and Katz prepared [5]helicene only in small amounts (6% yield) [63]. A possible solution to this problem was recently shown by Collins [47], who used copper(I) complexes as photocatalyst and [2] + [2] under visible light irradiation to prepare [5]helicene in 57% yield.

In the case of [6]helicene (**2**), several strategies have been investigated. Martin reported on [1] + [2] + [1], [2] + [1] + [1], and [4] + [1] cyclization leading to **2** with yields up to 80% [64, 65]. On the other hand, photocyclizations of [3] + [2] precursors by Laarhoven [66] and Kagan [22] provided low yields due to poor regioselectivity of the reaction.

[7]Helicene (**3**) reported by Martin [64, 65] and Laarhoven [66] employed [2] + [1] + [2] and [4] + [2] precursors, respectively; however, due to poor regioselectivity of the reaction, only low yields of the desired products were obtained. Consequently, Laarhoven irradiated [3] + [3] stilbene under an inert atmosphere, yielding up to 50% of **3** [66]. However, the best result was obtained in the case of a [1] + [3] + [1] cyclization published by Ben Hassine and Marinetti, who prepared [7]helicene in 90% yield [67].

The preparation of [8]helicene (**4**) included several strategies, such as [4] + [1] + [1], [4] + [3], and [6] + [1], all regioselectively yielding helicene in up to 85%, as published by Kagan and Martin [17, 23, 32, 65, 68]. The same authors furnished also [9]helicene (**5**) using [4] + [1] + [2], [4] + [4], or [6] + [2] starting materials with yields up to 74% [17, 23, 32, 65]. More recently, a triple photocyclization was proposed for a precursor containing two phenylene and two naphthylene

units linked together with vinylene spacers ([2] + [1] + [1] + [2]) [69]. The resulting [9]helicene was isolated in 67% yield. [10]Helicene (**6**) was prepared by [4] + [1] + [3], [4] + [3] + [1], and [6] + [3] photodehydrogenation in 79% yield [17, 32].

Martin [32, 70] reported a regioselective photocyclization of [3] + [3] + [3] and [6] + [4] stilbene-like molecules that yielded [11]helicene (**7**) in up to 54%, which was later increased to up to 80% using the [4] + [1] + [4] or [4] + [3] + [2] strategy [17, 70]. In the same works, [2] + [6] + [2], [3] + [4] + [3], and [4] + [3] + [3] starting materials served as precursors for the synthesis of [12]helicene (**8**), which was obtained in 42% yield. A comparable yield was obtained in the case of higher [13]helicene (**9**) using regioselective [4] + [3] + [4] and [8] + [4] precursors, respectively [17, 32, 71]. Moreover, it was found that [6] + [6] stilbene [72] is not synthetically practical, probably due to attractive π - π dispersive interactions. [14]Helicene (**10**) was obtained in moderate yields using regioselective irradiation of [3] + [6] + [3] or [4] + [4] + [4] precursors [70].

The recently published [2] + [1] + [1] + [2] + [1] + [1] + [2] method proposed by Murase and Fujita to synthesize the longest carbohelicene to date, the [16]helicene (**11**), was based on sextuple photocyclization of a single-strand oligo(arylene-vinylene) precursor [69]. The key to the successful synthesis of **11** was the rational design of the precursor, in which the phenylene and naphthylene units are arranged in a way that disfavors side reactions (benzoanthracene formation or overannulation). Additionally, only readily available aromatic precursors were used, further improving the practicality of this approach. However, the bulky TIPSO (triisopropylsilyl ether) substitutions at the peripherals of the olefin were necessary to increase the solubility of the precursor prior to photocyclization. **11** was then prepared by their subsequent removal in 7% yield.

The Mallory reaction was studied using Hückel molecular orbital (HMO) calculations, which provided a remarkably accurate description of its regioselectivity [44]. Usually, only one product is formed, even when the formation of several others looks plausible. The reaction favors such ring structures that are curved toward helicenes. Laarhoven evaluated reactivity parameters such as free valence numbers (F_{rs}^*) [14, 73] and localization energies (L_{rs}^*) [44] for a large number of examples. He found a good correlation between these two parameters, although the use of just free valence numbers was more convenient as only one calculation was needed to evaluate all cyclization modes of one particular compound. Upon the analysis of the excited state calculations, Laarhoven derived three simple rules [14] to determine the product and regioselectivity of the proposed reaction, in which the sum of the free valence numbers of atoms r and s is involved ($\sum F_{rs}^*$):

- (i) Photocyclizations do not occur when $\sum F_{rs}^* < 1.0$.
- (ii) When two or more ways of cyclization are possible in a single compound, only one product arises if $\Delta(\sum F_{rs}^*) > 0.1$; otherwise more products are formed.
- (iii) The second rule stands when either only planar or only nonplanar products (penta- or higher helicenes) can arise. When both planar and nonplanar products can be formed, the planar aromatic is generally the main product ($\sum F_{rs}^* > 1.0$).

When helicenes become larger than five benzene rings, they become nonplanar. The formation of planar S-shaped molecules becomes the major side reaction or even the main reaction. This led Katz's group to the development of various strategies to facilitate the synthesis of helicenes by photocyclization. A bromine substituent was used as a protecting group preventing a photocyclization in this position [15].

1.3.2 Oxidative Photocyclizations of Substituted Carbo[*n*]helicenes

Substituted carbo[*n*]helicenes have been studied from the very beginning of helicene chemistry to the present day, and it was found that the substituents can in some cases have a significant influence on the course of the photocyclization reaction. For example, it was found that nitro, acetyl, or dimethylamino substituents are not suitable for the photocyclization because they enhance intersystem crossing to the triplet excited state [74].

Substituted [*n*]helicenes can be synthesized in the same way as unsubstituted ones. With a *meta*-substituent at the styryl group (Figure 1.5), two isomers can be formed (1- and 3-substituted helicenes) [75], while *meta*-substituted distyrylnaphthalene derivatives lead to a mixture of three products [76]. To increase the formation of 1-substituted helicenes, the blocking group, e.g. an additional *ortho*-bromo-substituent, has to be introduced to the styryl group [30]. Finally, 2-substituted [*n*]helicenes [19, 51, 75] can be synthesized from *para*-substituted derivatives and 4-substituted [*n*]helicenes [19, 30, 77, 78] from *ortho*-substituted derivatives with no obstacles for regioselectivity of the reaction.

Like [5]helicene, its derivatives may be poorly photochemically available due to rapid overannulation into benzo[*ghi*]perylene. This phenomenon can be hindered by the introduction of functional groups at C₁ [79–82] or C₂ [37, 63, 67, 83–85] positions of the [5]helicene backbone (see Figure 1.6). In some cases, however, rearrangement or elimination may occur [79]. To prevent the overannulation, Matsuda found that the introduction of cyano groups to ethylene moieties using the [1] + [1] + [1] cyclization strategy could eliminate the degeneracy of unoccupied molecular orbitals; therefore 5,10-dicyano[5]helicene derivatives **13a–c** have been prepared in high yields [86]. This phenomenon was also observed by Durola [88]

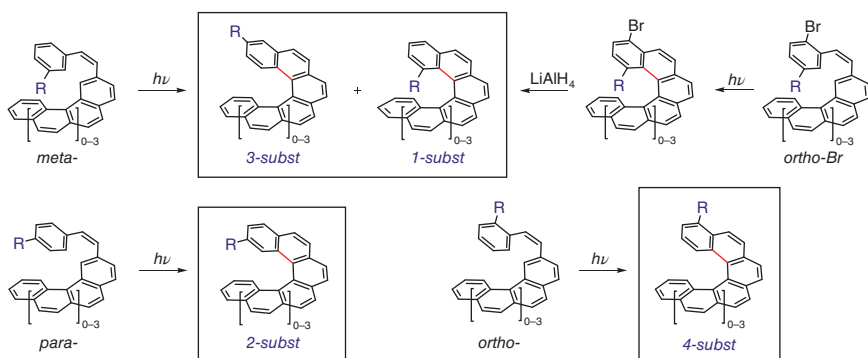


Figure 1.5 Photocyclization of substituted carbo[*n*]helicenes.

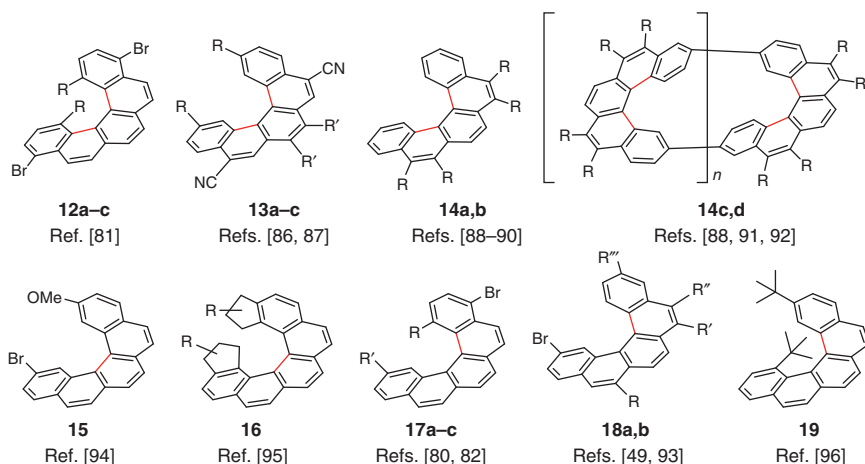


Figure 1.6 Representative examples of substituted carbo[5]helicenes. **12a**: R = F; **b**: R = Me; **c**: R = OMe; **13a**: Ref. [86] R, R' = H; **b**: Ref. [86] R = H, R' = OMe; **c**: Ref. [87] R = OMe, R' = H; **14a**: Refs. [88, 89] R = CO₂Et; **b**: Ref. [90] R = anhyd; **c**: Refs. [88, 91] R = CO₂Et, *n* = 1; **d**: Ref. [92] R = CO₂Et, *n* = 2; **16**: R = OSiMe₂*t*-Bu; **17a**: Ref. [80] R = F, R' = Br; **b**: Ref. [80] R = F, R' = Me; **c**: Ref. [82] R = CO₂Me, R' = H; **18a**: Ref. [49] R = Me, R' = OMe, R'' = OMe, R''' = H; **b**: Ref. [93] R' = CN, R, R'' = H, R''' = OMe.

and Frimer [97] for the preparation of [5]helicene tetraesters **14a** and dianhydride **14b**. This finding then led to the preparation of cyclobis[5]helicene macrocycles **14c,d** with stable lemniscular, or figure eight, shapes [37, 88, 91, 92]. Helicenes **15** and **16** were used for the preparation of the first helically chiral phosphane ligands [85], helical donor–acceptors [94], and helical metallocenes [95]. Recently, during photocyclization, Mallory discovered an unusual skeletal rearrangement of 1-styrylphenanthrene with *tert*-butyl groups to form [5]helicene derivative **19** in addition to the expected *tert*-butyl-substituted [5]phenacene [96].

The same photocyclization strategies as for carbo[6]helicene (**2**) were chosen for the preparation of its derivatives (Figure 1.7) [49, 85, 108, 109]. The choice of strategy depends on the availability of starting compounds and the method of preparation (see Section 1.2). Based on the literature, the most common photocyclization strategy is [4] + [1] [19, 30, 51, 78, 106, 110–117]. Meier used oxidative photocyclization [1] + [2] + [1] to prepare [6]helicenes **20b–e** and **23a,b** bearing four to six alkoxy chains with good solubility and processability for applications in materials science [99, 102]. The same reaction led to [6]helicenophanes **20f,g** with methylenedioxy chains [100]. Církva synthesized racemization-stable [6]helicenes **21** and **26** fluorinated at terminal rings to study their physicochemical properties [52]. It is worth noting that a [3] + [2] method for the preparation of helicene **22** with alkoxy groups [101] in 3,3' positions has been successful, although this method is not very common. Other substances, such as optically active 1,8-naphthalimide with [6]helicene scaffold [103] **24**, diastereopure [6]helicene binaphthol hybrid [104] **25**, 2,2'-bis-[6]helicenyl [106] **27**, and paracyclophane [6]helicene derivative [107] **28** have been also successfully synthesized.

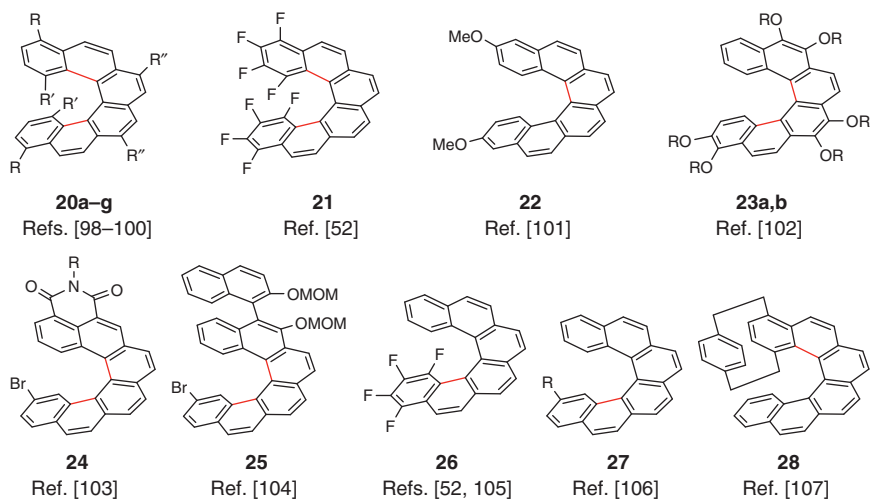


Figure 1.7 Representative examples of substituted carbo[6]helicenes. **20a**: Ref. [98] R = Br, R'' = OMe, R''' = H; **b**: Ref. [99] R = R'' = OMe, R' = H; **c**: Ref. [99] R = R'' = *O*-dodecyl, R' = H; **d**: Ref. [99] R = R'' = *O*-(2-ethylhexyl), R' = H; **e**: Ref. [99] R = R'' = *O*-(2-butylhexyl), R' = H; **f**: Ref. [100] R = O(CH₂)₈O, R' = R'' = H; **g**: Ref. [100] R = O(CH₂)₁₀O, R' = R'' = H; **23a**: R = C₆H₁₃; **b**: R = C₁₂H₂₅; **24**: R = CH₂*t*-Bu; **27**: R = [6]helicen-2-yl.

[7]Helicene derivatives are usually prepared by the same photocyclization strategies as unsubstituted ones (Figure 1.8) [33, 98, 105, 115, 125]. Notable examples include [7]helicene phosphines **29b** [118], methoxy- and cyano[7]helicenes **30a–c** [119, 120], [7]helicene fused with hexafluorocyclopentene **31** [123], the important synthetic synthon bromo[7]helicene **32a** [15], and diastereopure [7]helicene binaphthol hybrid **33a,b** [104]. Also, a simple method for producing dimethyl bifunctionalized [7]helicene precursor **34** [124] was discovered by Howarth. It is important to mention that the [3] + [1] + [1] to **35a,b** [122] and [5] + [1] to **36a–j** [78, 110] strategies were newly used, while the [4] + [2] method for synthesis of [7]helicene derivatives has so far not been utilized. In the case of [8]helicene derivatives, the tetrafluoro[8]helicene **37** [105] and dimethoxy-dibromo[8]helicene **38** [16] were prepared using [2] + [3] + [1] and [1] + [4] + [1] strategies, respectively.

1.3.3 Oxidative Photocyclizations of Benzocarbo[*n*]helicenes

To investigate the effect of fused benzene rings on helicene helicity, several benzo-carbo[*n*]helicenes (*n* = 5–7) were synthesized [14]. At the same time, the influence of benzene rings on the course of the photocyclization reaction was also studied (Figure 1.9).

Several benzocarbo[*n*]helicenes differing in the location of the benzo fusion on helicene have been prepared. Martin and Laarhoven prepared a series of benzo[5]helicenes, such as **39a** [126, 131, 132]. Recently, the substituted derivative of maleic anhydride **39b** was synthesized by Wang [90]. Many other aromatic

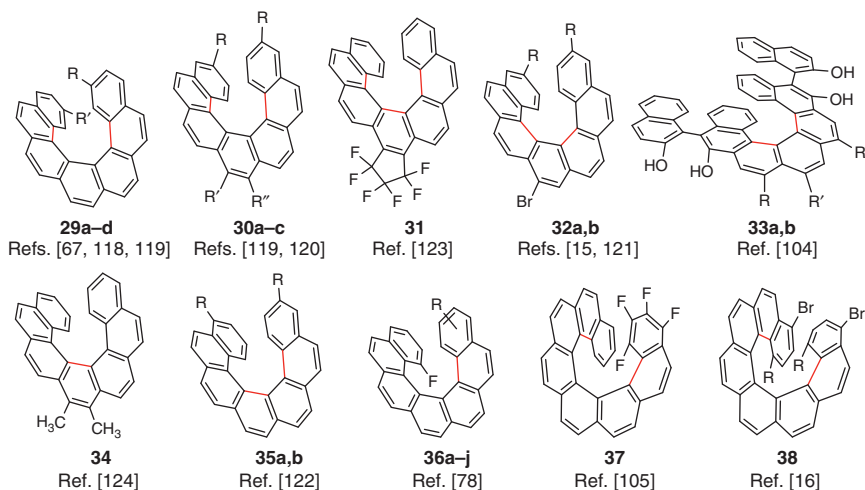


Figure 1.8 Representative examples of substituted carbo[7]- and [8]helicenes. **29a**: Ref. [67] R = OMe, R' = H; **b**: Ref. [118] R = POPh₂, R' = H; **c**: Ref. [67] R = R' = Me; **d**: Ref. [119] R = R' = OMe; **30a**: Ref. [119] R = OMe, R' = R'' = OEt, **b**: Ref. [120] R = H, R' = R'' = CN; **c**: Ref. [120] R = R' = H, R'' = CN; **32a**: Ref. [15] R = H; **b**: Ref. [121] R = CH₂OTHP; **33a**: Ref. [104] R = CN, R' = H; **b**: Ref. [104] R = H, R' = Br; **35a**: Ref. [122] R = Me; **b**: Ref. [122] R = CO₂Et; **36a**: Ref. [78] R = H; **b-d**: Ref. [78] R = 2' to 4'-OMe; **e-g**: Ref. [78] R = 2' to 4'-CO₂Me; **h-j**: Ref. [78] R = 2' to 4'-CN; **38**: Ref. [16] R = OMe.

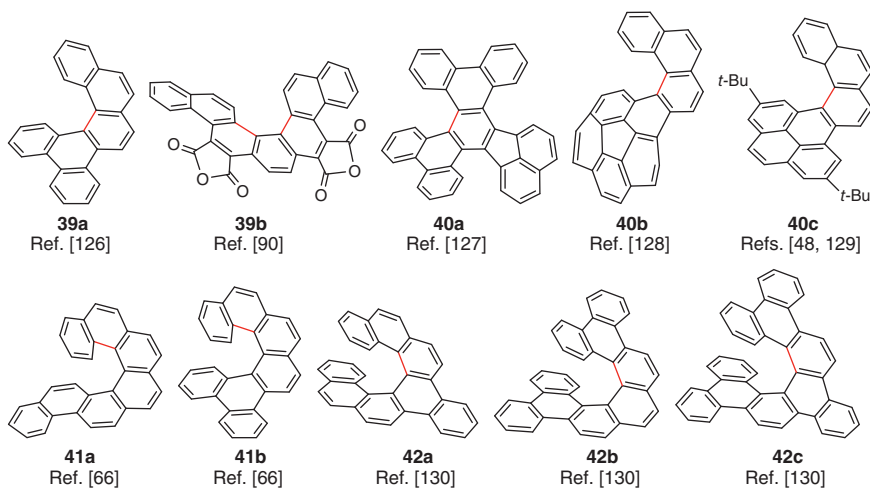


Figure 1.9 Representative examples of benzocarbo[n]helicenes.

building blocks can be introduced into the benzo[5]helicene structures. For example, acenaphthylene derivative **40a** [127], corannulene hybrid **40b** [128], and pyrene-cored helicenes **40c** were investigated [48, 129]. Also, Laarhoven prepared several benzo[6]helicenes **41a,b** [66] and benzo[7]helicenes like **42a-c** [130] with varying numbers (one to three) of benzo groups on the helicene skeleton.

1.3.4 Oxidative Photocyclizations of Multiple Carbo[n]helicenes

The fusion of two or more helicene moieties together into one polycyclic framework leads to the formation of multiple helicenes, which have received considerable attention in recent years [133–135]. In the following text, they are categorized by the number of their helicene moieties (Figure 1.10).

The simplest double helicene **43a** was first prepared by Martin in 1983 [131]. More recently, Sarkar synthesized a bis(butyloxycarbonyl)double[5]helicene **43b** in an excellent 87% yield [136]. The contorted quadruple [5]helicene **43c** was obtained by Nuckolls in a sixfold photocyclization of the olefin precursor [140]. Watanabe prepared a triple [5]helicene **43d** in moderate yield through the double [2] + [1] + [2] strategy from 1,3,5-tris[2-(2-naphthyl)vinyl]benzene [141]. The first documented double [6]helicene **44a** was synthesized in a moderate yield by Laarhoven and Cuppen already in 1971 [142, 143]. Other double [6]helicenes (e.g. **44b**) were synthesized in even higher yields [77, 144, 145]. The double [7]helicene was obtained by Martin in 1974 [77]. Recently, Durolo reported on the synthesis of *meso* double [7]helicene **45** in 83% yield from maleate-bridged chrysene trimer [137]. Wang afforded perylene diimide-embedded double [8]helicene **46a**, which represents the highest photochemically prepared double carbohelicene reported thus far [138]. Perylene diimide (PDI) is an increasingly popular functionality in

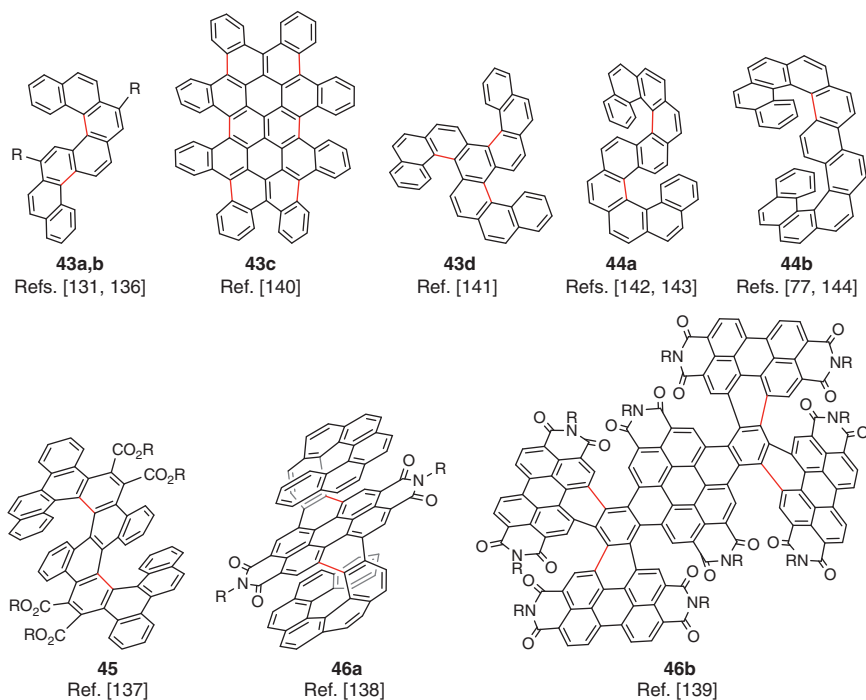


Figure 1.10 Representative examples of multiple carbo[n]helicenes. **43a**: Ref. [131] R = H; **b**: Ref. [136] R = CO₂Bu; **45**: Ref. [137] R = C₈H₁₇; **46a**: Ref. [138] R = CH(C₅H₁₁)₂; **b**: Ref. [139] R = CH(C₅H₁₁)₂.

helicene chemistry, as demonstrated by Nuckolls, who prepared helicene-based molecules with two PDI units [146–148]. These helicene-based structures exhibit the largest electronic circular dichroism (ECD) in the visible range of any molecule [148]. Recently, triperylene hexaimides with a three-bladed propeller-shaped π backbone [149] and pentaperylene decaimide dual-core sixfold [5]helicene **46b** were prepared by Wang in high yields using quadruple photocyclization [139].

1.3.5 Eliminative Photocyclizations of Carbo[*n*]helicenes

In addition to oxidative photocyclization, an eliminative approach can also be used to prepare carbo[*n*]helicenes (see Figure 1.1). In these cases either methanol or hydrogen halides, such as HF, HCl, HBr, and HI, were eliminated. The loss of TfOH was also observed.

The triple [5]helicene **47** (Figure 1.11) was synthesized in moderate yield by Watanabe through an acid-promoted double [2] + [1] + [2] photochemical strategy with the elimination of methanol [141]. The PDI-[6]helicene hybrid **48** was prepared in 94% yield by Nuckolls using the same method [150]. A photocyclodehydrofluorination reaction where pentafluorostilbene precursor gave a modest yield

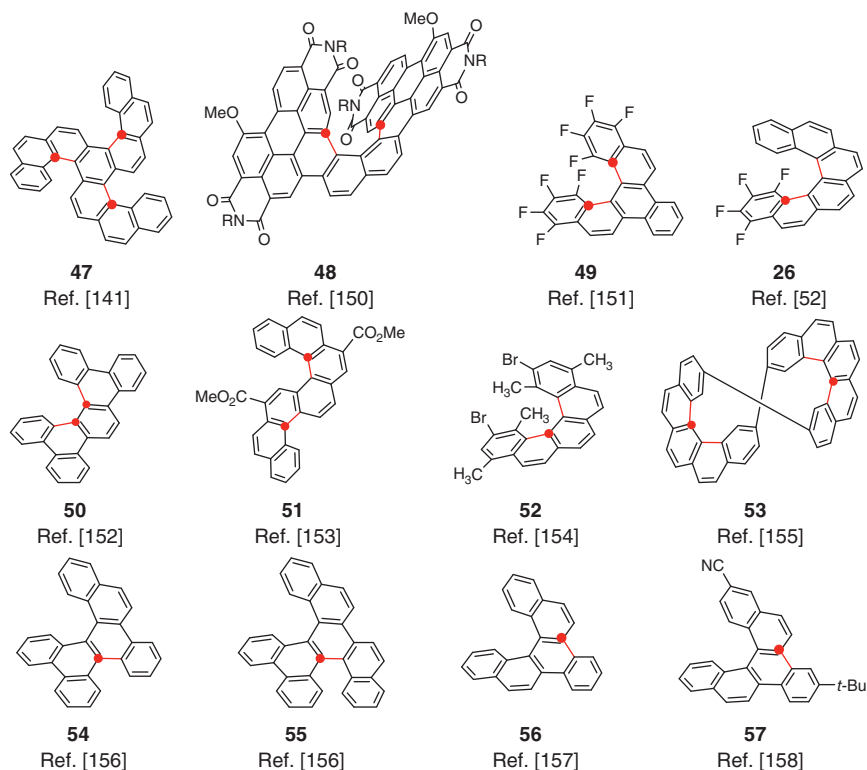


Figure 1.11 Carbo[*n*]helicenes formed by eliminative photocyclization. The red dot indicates an atom with a leaving group (i.e. OCH₃, F, Cl, Br, I, TfO); **48**: Ref. [150] R = CH(C₅H₁₁)₂.

of fluorinated benzo[*i*][5]helicene **49** was reported by Twieg and Li [151]. Církva found that pentafluorophenyl derivative can provide the fluorinated [6]helicene **26** by dehydrofluorination reaction, however, in low yield [52]. Morin worked on photochemical cyclodehydrochlorination, yielding dibenzo[5]helicene **50** in 79% [152].

The eliminations of HBr and HI are far less common. The former was employed in the preparation of double helicene derivative **51** [153], while the latter was used to prepare [5]helicene derivative **52** [154]. Thulin and Wennerström prepared *propellicene*, bis-2,13-[5]helicenylene **53**, in 70% yield from diiodo derivative of paracyclophane-tetraene [155]. It was shown that the strain in *propellicene* can sometimes help to avoid the overannulation to benzo[*ghi*]perylene. Alabugin reported the preparation of fused helicenes from the alkynyl precursors using a photocyclization–dehydroiodination sequence. This new approach led to dibenzo[5]helicene **54** [156] and double helicene **55** [156] in high yields. Yorimitsu achieved a synthesis of benzo[5]helicene **56** in 59% yield by photoinduced cyclization with a loss of TfOH [157]. The derivative **57** was prepared analogously [158].

1.4 Photochemical Preparation of Heterohelicenes

1.4.1 Azahelicenes

Along with parent carbo[*n*]helicenes, the most studied and probably the most abundant group of helicenes, which are easily accessible via a photochemical approach, are *azahelicenes*. They contain one or more nitrogen atoms, usually as a part of *pyridine* (*quinoline*) or *pyrrole* (*carbazole*) moiety, while keeping the aromaticity along the helical backbone untouched. A special case, photochemically accessible *azahelicenes* containing quaternary nitrogen atoms (*azoniahelicenes*), is also discussed in this part. Principles of photochemistry using Mallory's or Katz's approach and preparation of starting material remain similar to general procedures described previously and will not be described herein unless stated otherwise. In general, iodine might be a less satisfactory oxidant than oxygen due to possible charge-transfer complex formation with azastilbenes [159, 160], which act as competitive light absorbers or singlet quenchers, but it is still frequently used.

Whereas the tendency to form packed (helical) or less strained (benzoanthracene) structures during photocyclization can be reasonably explained (based on free-valence atom indexes of the Hückel model [14, 161], Wiberg bond indexes [162, 163], or influence of solvent polarity [162]; see details in Section 1.3), the selectivity of a photoreaction in the context of nitrogen atom position remains unclear. The regioselectivity of photodehydrocyclization of 3-pyridyl stilbenes is markedly higher than in the case of *meta*-substituted carbostilbenes, providing 2-azaphenanthrenes [164, 165] or eventually 3-aza[*n*]helicenes in greater yields than the respective products of ring closure in the other available position (cf. **66a** vs. **66b** [166] in Figure 1.14). However, in the case of diazastilbenes, this observation based on molecular orbitals calculations [164, 167, 168] can be suppressed by

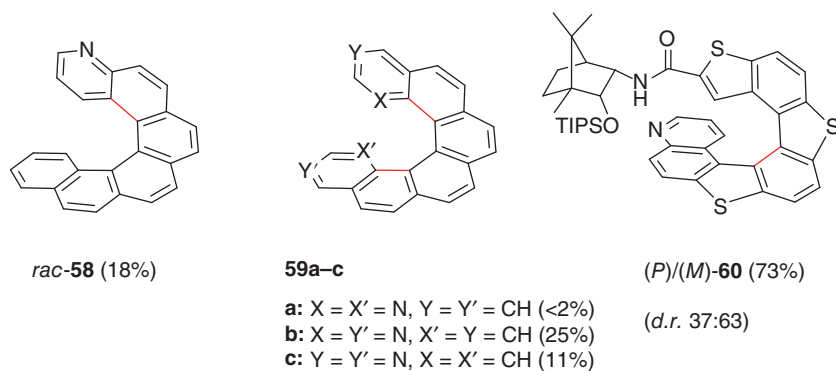


Figure 1.12 First photochemical approaches to azahelicenes **58–60**.

a molecular design in which the electrostatic repulsion of lone electron pairs at nitrogen atoms predominates. Moreover, the observation of Carrona when synthesizing **62a,c** [163] or **63a,b** [169] (Figure 1.13) was opposite to the previously mentioned with the predominant generation of 1-aza[5]helicenes. Similarly, it insufficiently explains the ratio of regioisomers formed in the case of **59** [170] (Figure 1.12), where the higher-yielding isomer was 1,14-diazahelicene **59b** rather than 3,14-diazaisomer **59c**.

The photochemical approach to aza[*n*]helicenes can be compartmentalized into two main subgroups. While the first group uses the light-induced closure of stilbene-like moiety with C=C double bond substituted with various aromatic N-heterocycles (Figures 1.12–1.17; some examples from Figure 1.18), the second one utilizes photocyclization of arylimines or hydroxamic acids (Figure 1.19).

The first photochemical approach to 4-aza[6]helicene (**58**, Figure 1.12) was published by Martin in 1969 [171], while the first diazahelicene was not photochemically synthesized until 1994 [170] when Staab reported on the synthesis of **59a**. Unfortunately, instead of the desired 1,16-diaza[6]helicene (**59a**) when applying Katz's conditions [16], he isolated 1,14- (**59b**) and 3,14-diaza (**59c**) derivatives in 25 and 11% yields, respectively, with less than 2% yield of **59a**. To overcome the lack of regioselectivity, Staab prepared **59a** by intramolecular coupling published therein. The hybrid aza-thiahelicenes prepared by Tanaka in 1997 belong to one of the first asymmetric photochemical approaches [36]. The chiral auxiliary derived from *D*-camphor allowed the preparation of a diastereomeric mixture of **60** separable via standard chromatography and opened a way to isolate other pure enantiomers of such helicene hybrids.

It was Carrona who started extensive research on the photochemical preparation of aza[5]helicenes and studied their optical properties. In 2005, he reported on a series of various azahelicenes **61a–i** [172] (Figure 1.13) using Pyrex-filtered irradiation by visible light and neither iodine nor propylene oxide as an oxidant or HI scavenger. Thanks to the modified reaction conditions, he was able to reach excellent yields of up to 98% in some cases. Other [5]helicene derivatives (**62–64**) were

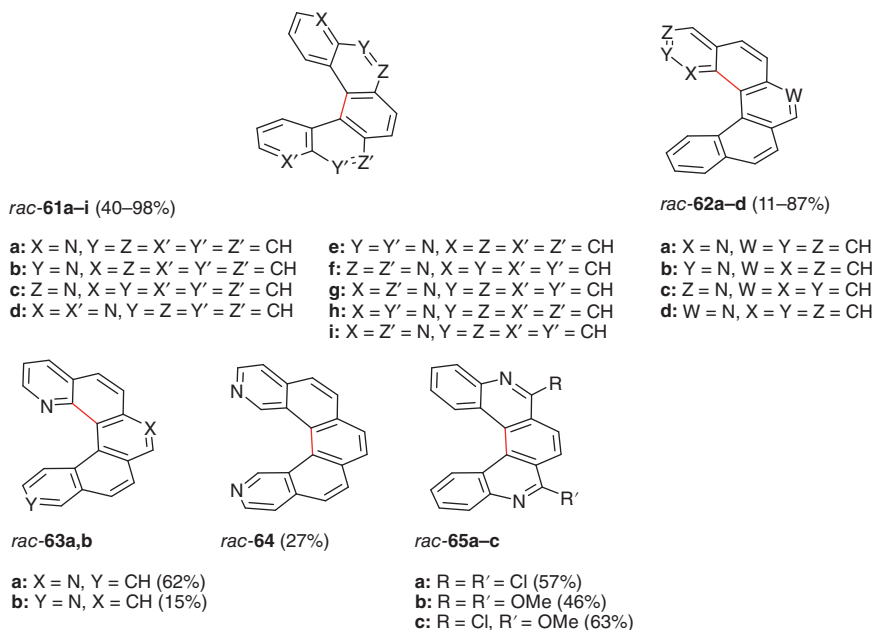


Figure 1.13 Photochemically prepared aza[5]helicenes **61–65**.

obtained after UV or vis light irradiation [162, 163, 169]. Among all reported structures, the author surprisingly observed no benzo[ghi]perylene formation except for the attempts to prepare 2-aza[5]helicene regardless of the starting stilbene used (for details see Section 1.6).

Photochemically prepared diazahelicenes with an appropriate position of nitrogen atoms can be alkylated to corresponding *viologens*, as shown by Clennan [173, 174] and Brichacek and Patterson, who studied gold heli-viologen [175].

Also, Dehaen, who introduced diversely functionalized diaza[5]helicenes **65**, (Figure 1.13) [176], observed the tendency of methoxy derivative **65b** to form an azabeno[ghi]perylene after prolonged irradiation, unlike the case of 6,9-dichloro-5,10-diaza[5]helicene **65a**. This helicene was transformed by Buchwald–Hartwig amination with a chiral amine, providing (*P,S,S*)/(*M,S,S*)-diastereomers separable via standard chromatographic methods. In 2013, the author extended his work to diazadithia[7]helicene derivatives [177]. Based on his synthetic strategy, Dias and Skabara later published a synthesis of phenoxazine-functionalized [5]helicenes as novel thermally activated delayed fluorescence (TADF) materials for use in functional devices [178].

2-Aza- [179] and 5-aza[6]helicene [180] (**67** and **68**, Figure 1.14) were prepared photochemically by Abbate using visible light. Ben Hassine [166] used UV irradiation to prepare 3-aza[6]helicene (**66a**), while also managing to isolate its 1-aza derivative **66b** as a minor product. The chiral aza[6]helicenes (*P*)/(*M*)-**69a**, prepared and separated to optical antipodes by Crassous [41], served as a photoinitiator in photoinduced polymerization of (meth)acrylates. This is a remarkable example

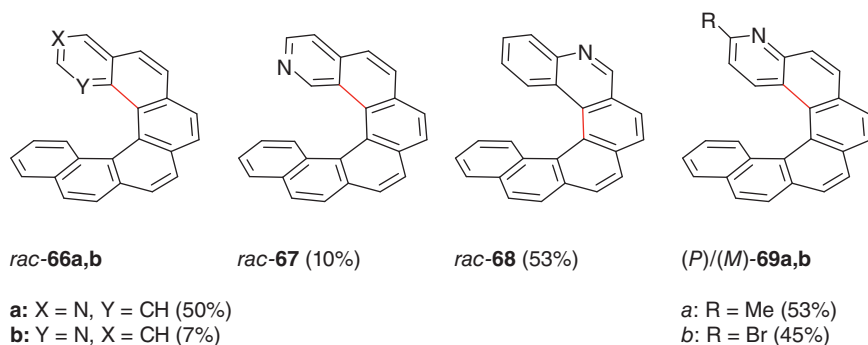


Figure 1.14 Photochemically prepared aza[6]helicenes **66–69**.

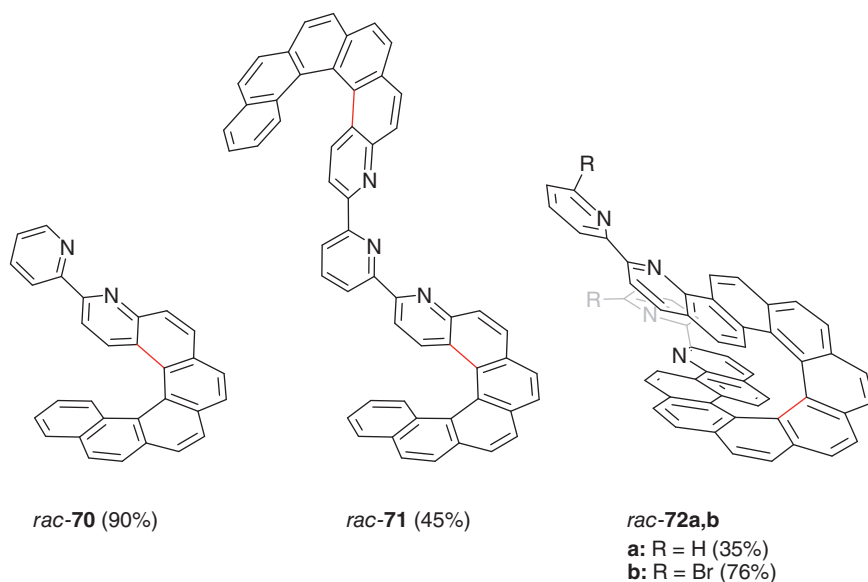


Figure 1.15 Helicopodands **72** and helicenes adopting bipy- **70** and terpy-structures **71**.

of chiral properties introduced to polymer films by the photoinitiator through photopolymerization processes. Recently, Srebro-Hooper and Crassous published a synthesis of enantiopure bis-(4-aza[6]helicene-3-yl) adopting a 2,2'-bipy structure suitable for transition metal complexation [181]. It was accessible via Negishi coupling of 3-bromo-4-aza[6]helicene **69b**. A reversible protonation resulted in the tuning of the photophysical properties of the bipyridyl derivative. Other helicenes **70–72** adopting bipy- [182] and terpy-structures [183] and *helicopodands* [184] that were obtained photochemically are depicted in Figure 1.15. Their protonation and transition metal complexes were also studied [182, 183, 185–187].

The photochemically prepared diaza[7]helicenes with protected –OH groups served for the synthesis of polyaromatics bearing pyridon moieties at the terminal rings [188]. It was shown that some of such racemic derivatives self-assembled via

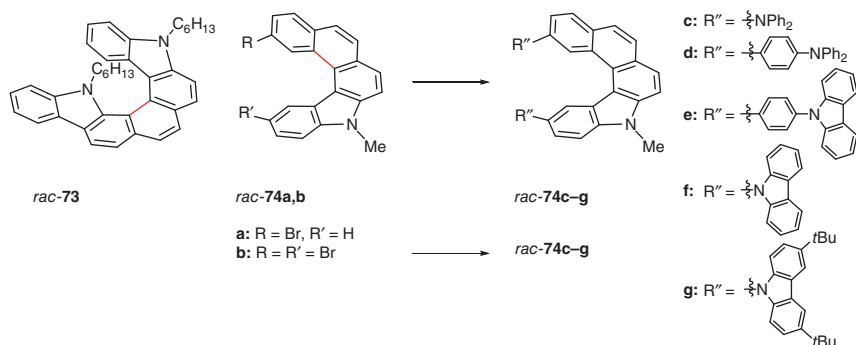


Figure 1.16 Helicenes **73–74** with carbazole subunits for OLED applications.

hydrogen bonding enantiospecifically in solution and diastereoselectively in solid state.

Pyrrole (carbazole) moiety represents another frequently used motif in aza-helicene chemistry. Carbazole belongs among popular functional units in conjugated systems owing to its planarity and easy N–H bond substitution for other functional groups. Although the first pyrrolo[5]helicene synthesized by Meisenheimer and Witte [189] as early as 1903 is among the oldest helical structures ever, the photochemical approach leading to such helicenes was not published until 2012 when Liu reported a diazahelicene **73** (Figure 1.16) as a deep-blue dopant in organic light-emitting diode (OLED) [190]. In 2013, Ben Hassine prepared pentacyclic **74a** [191], taking advantage of a possible further transformation due to the presence of reactive bromine at the terminal benzene core. However, the reactivity was not exploited until 2016, when Chow and coworkers prepared a series of helical diamines **74c–g** [192], which were synthesized from photochemically prepared dibromo derivative **74b**. In this study, diamino derivatives were studied as materials suitable for use in OLED devices, as they exhibited a favorable range of photophysical and redox properties as well as thermal stability.

It was primarily Bedekar who succeeded in the preparation of various aza[*n*]helicenes ($n > 5$) with carbazole moiety by double photocyclodehydrogenation reaction from both symmetric (**75a–d**, **78**, Figure 1.17) [193] and asymmetric (**75e–i**) [194] bis-stilbene precursors including synthesis of bi-azahelicenes **76** and **77** [195]. In the same fashion as mentioned earlier (cf. Refs. [176, 177]), a carbazole–quinoline hybrid was prepared photochemically by Dehaen [196]. Among others, Liu prepared **79a** [197] and **79b** [198].

A specific group of nitrogen-containing helicenes is azoniahelicenes. The photochemical approach to these compounds dates back to the late 1980s and is mostly connected to the work of Arai, who unsuccessfully attempted a synthesis of the first quinolinizinium-containing [5]helicene [199]. In fact, he identified the corresponding azoniabenz[*ghi*]perylene in the reaction mixture after additional photocyclization, as discussed later.

Soon after, Arai et al. published a series of azoniahelicene structures endowed with quaternary nitrogen either on an inner (**81** [200, 201]) or outer (**80** [202], **82**

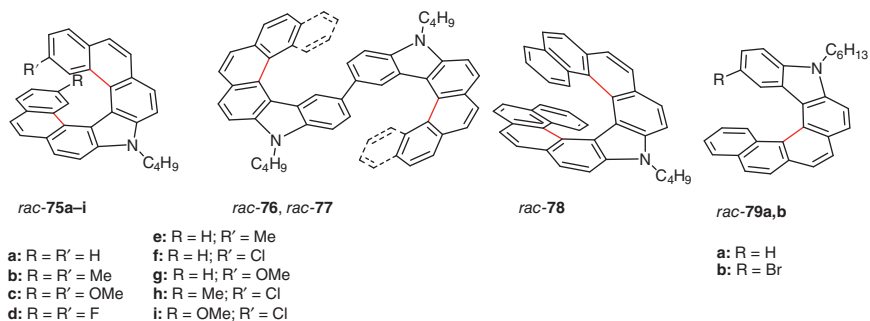


Figure 1.17 Carbazole containing azahelicenes **75–79** synthesized photochemically.

[203], **83–86** [204–206]) helix edge obtained upon photochemically induced quaternization or cyclodehydrogenation (Figure 1.18). The latter compounds were synthesized using stilbene-like precursors, which were typically prepared by dehydration of secondary alcohols followed by additional Knoevenagel condensation of suitably substituted quinolininium derivative with aromatic aldehydes.

The phenomenon of the undesired formation of benzo[ghi]perylene was observed only in the case of unsubstituted 6a-azonia[5]helicene [199] and partially in the case of **82a** [203] (where perylene was the minor product). Employing bulky substituents (**82b,c,f,g**) or thiophene(s) as a terminal ring(s) [204] (for example, in **83a–f**) avoids the formation of such by-products. When using monosubstituted precursors at one terminal ring, a mixture of [5]helicene/benzoperylene can be observed (e.g. **82e**), unlike in the case of kinetically driven helicene **82d** formation, where the helicene salt was isolated as a single product. Therefore, an efficient way to unsubstituted azonia[5]helicene or mono-methyl-substituted (e.g. **82h,i**) azonia[5]helicenes can be achieved by photocyclization of sterically demanding bromides (to form **82d,f,g**) and their subsequent debromination under mild conditions (see Figure 1.18).

Photochemically induced quaternization was used for the formation of compound **81** where the quaternary nitrogen is placed at the inner helix edge. To improve the yields, the Pyrex-filtered light was passed through aqueous nickel sulfate solution filter ($280 < \lambda < 360$ nm and $\lambda > 430$ nm) to rule out wavelengths corresponding to the absorption region of the product (around 410 nm) [207]. From the fundament of this chemical transformation, no oxidant is necessary. The stilbazoles as precursors of such azoniahelicenes are commonly synthesized by the condensation of 2-methylpyridine/quinoline with *o*-chlorobenzaldehyde or other 2-chloro aromatic aldehydes.

The results obtained from the preparation of azoniahelicenes showed that the N-heterocyclic subunit can be formed directly by the photochemical step. However, this is not the case of azahelicenes with pyridine or pyrrole subunits that are prepared almost exclusively from stilbene-like molecules with C=C double bond. Despite this, several examples can be found in the literature. In 1997, Howarth was the first who attempted to synthesize 8,11-diaza[7]heptahelicene photochemically from corresponding bisimine [124]. Unfortunately, the low yield of reaction conducted in pyridine using a Pyrex filter and propylene oxide discouraged researchers

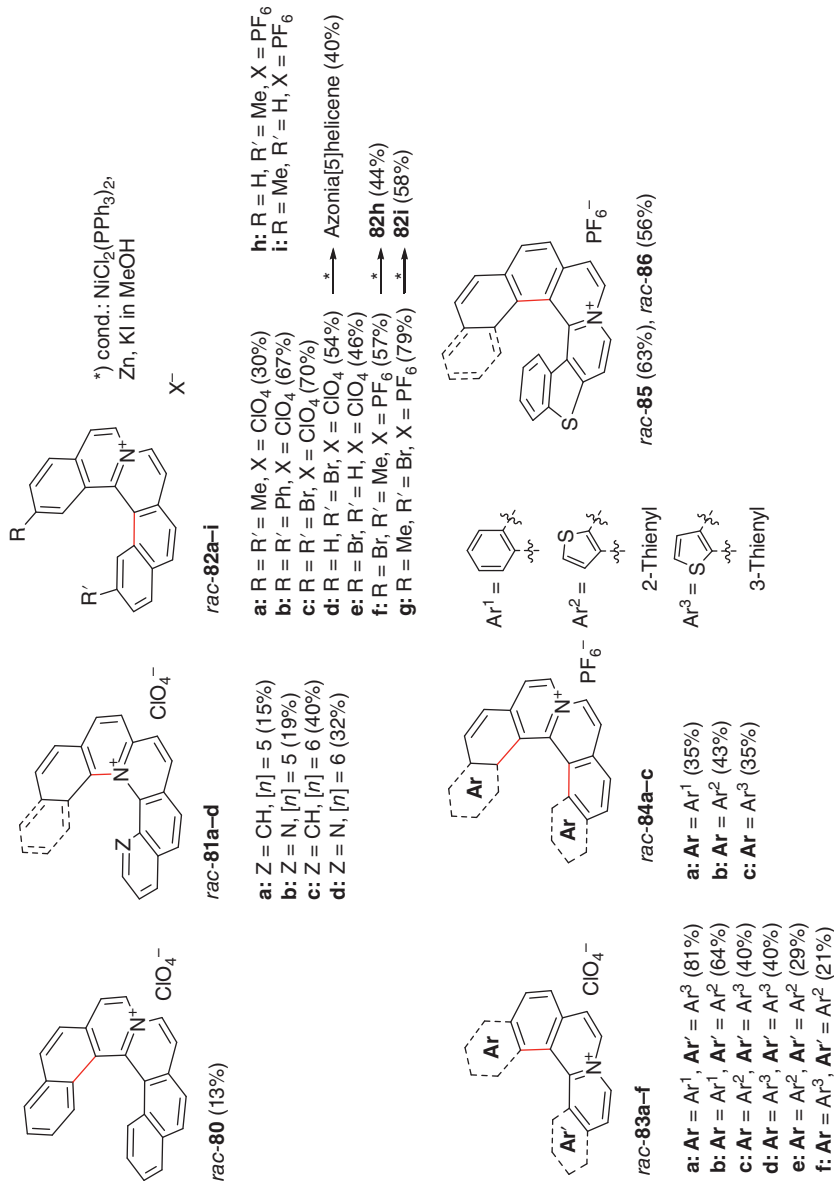


Figure 1.18 Photochemically synthesized azonia[n]helicenes **80–86**.

from further investigation of aromatic imines as precursors for azahelicenes. The poor reactivity of such imines is caused by the thermal instability of *Z*-conformers (short lifetime at room temp.) and unsuitable excited state (n, π^*) impeding cyclization from the (π, π^*) excited state [208–211]. Twenty years later, Murase came up with an idea to use hydroxamic acids as bidentate chelating ligands to circumvent this obstacle [50]. The boron complexes of *N*-phenylbenzohydroxamic acid **87** possessed a fixed *Z*-conformation diminishing the influence of the lone electron pair on the nitrogen atom, thus enabling successful photocyclization to *rac*-**88** upon N–O bond cleavage (Figure 1.19a). Recently, Alabugin, Cirkva, and Šýkora published Brønsted acid-promoted photocyclizations of arylimines (e.g. **89** and **91**) to various aza-PAHs, represented, among others, also by [5]helicenes **90** and **92** (Figure 1.19b) [212]. Unfortunately, higher aza[*n*]helicenes ($n \geq 6$) remained inaccessible using this protocol.

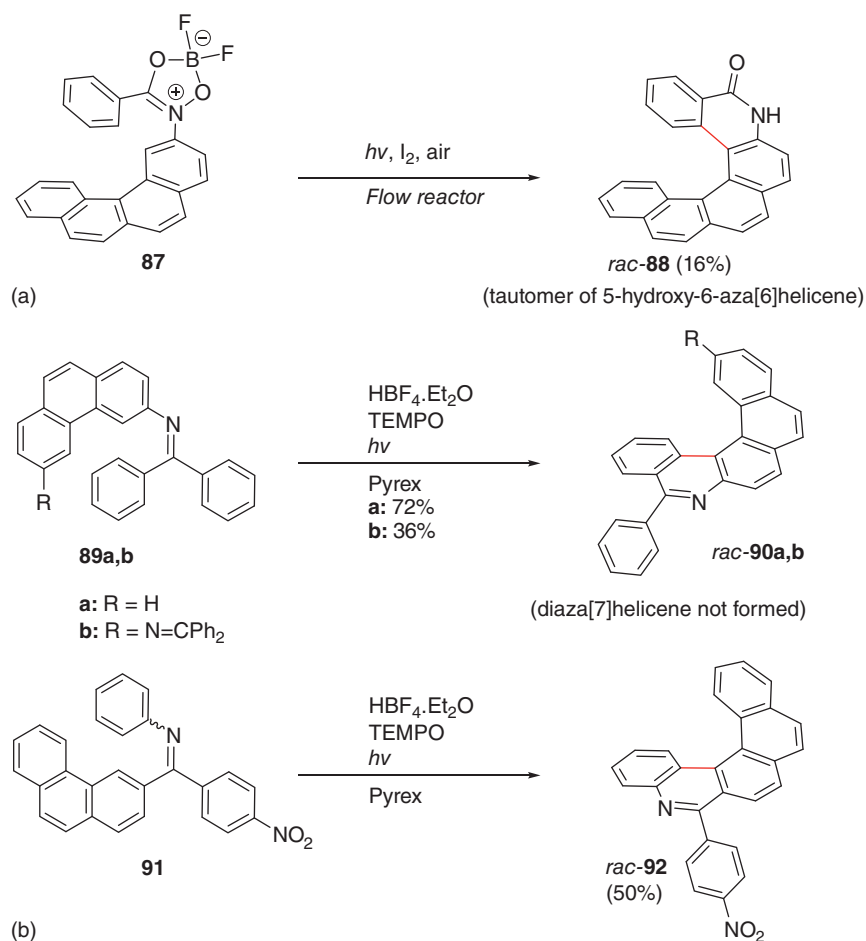


Figure 1.19 Photocyclization of (a) hydroxamic acids and (b) arylimines.

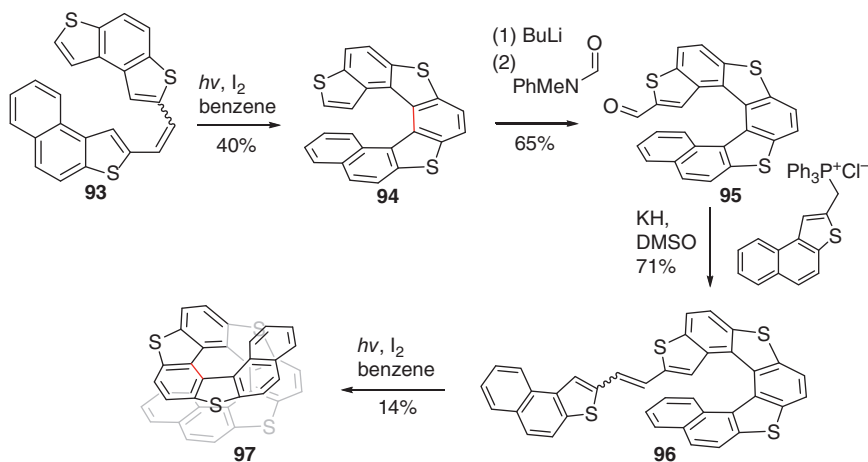


Figure 1.20 Preparation of tetrathia[11]helicene **97**.

1.4.2 Thiahelicenes

Thiahelicenes and other sulfur-containing derivatives make up a large part of helicene chemistry and therefore will be discussed separately. The first example of heterohelicene with thiophene replacing some of the benzenes in the original structure was published in 1968 by Wynberg and Groen, who synthesized dithia[6]helicene and trithia[7]helicene (Figure 1.20) [213]. The presence of five-membered rings in their structure has a significant impact on the shape of the molecule. The helix is more open, and, as a result, single enantiomers of these compounds are generally more prone to racemization than their carbohelicene counterparts [214–216]. On the other hand, the thiophene ring provides the possibility of easy derivatization of the thiahelicene backbone, which was used for the synthesis of longer derivatives by the same authors in 1971 [214, 215]. The main reaction in this sequence was the photocyclodehydrogenation of the asymmetrically substituted 1,2-benzothienylethene **93**, which formed helical compound **94** in 40% yield. The proton in the alpha position relative to the terminal thiophene ring was deprotonated in the presence of butyllithium, and the resulting carbanion was reacted with *N*-methyl phenyl formamide to give **95** in 65% yield. Subsequent Wittig reaction gave stilbene-type precursor **96**, which was irradiated by UV light for 12 hours in the benzene solution. The low yield of the reaction was caused by the fact that the reaction did not proceed to full conversion.

Long thiahelicenes with an alternating system of benzene and thiophene rings were also prepared with a similar approach (Figure 1.21) [217–219]. The starting material for the preparation of thia[5]- and [7]helicene was aldehyde **98**, which was used in the Wittig reaction to provide stilbene precursors **99** and **101**, respectively. These compounds then underwent the photocyclization reaction by 350 nm light to give tetrathia[7]helicene **100** and trithia[5]helicene **102**. Similarly, **102** was transformed to stilbenes **103** and **105** via formylation–Wittig reaction sequence, which were subsequently used as precursors for the preparation of pentathia[9]helicene

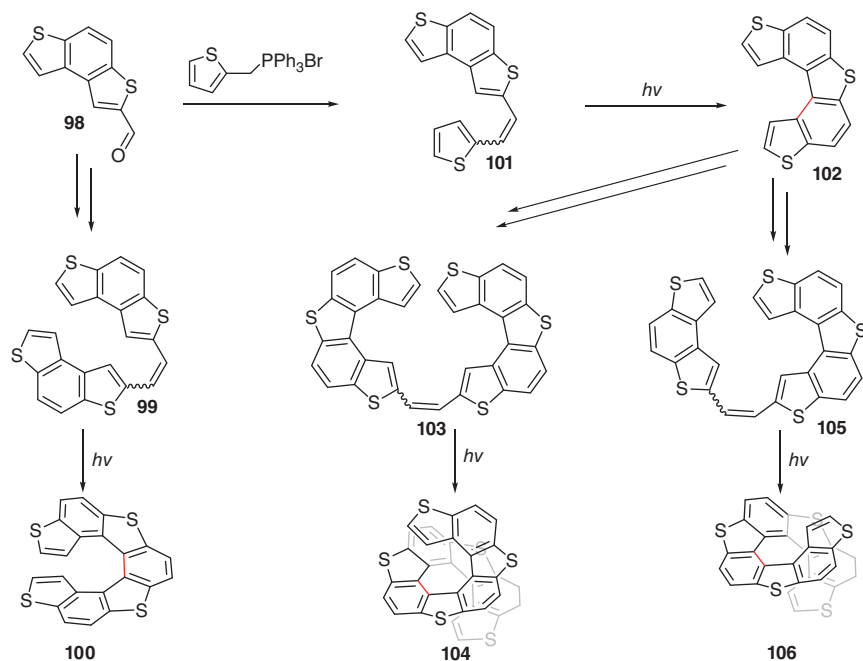


Figure 1.21 Preparation of alternate thia[η]helicenes **100**, **102**, **104**, and **106**.

106 and hexathia[11]helicene **104**, respectively. This approach was used for another series of substituted alternating thiahelicenes [220] and also for the preparation of even longer hexathia[13]helicene [221].

Other synthetic pathways for photochemical preparation of thiahelicenes have also been published. For example, 1,2-dithienylbenzenes can undergo the same cyclization procedure to yield naphthodithiophenes. This behavior was used for the synthesis of π -extended thiahelicenes, as shown in Figure 1.22 [222, 223]. Compound **107** underwent a threefold ring closure, providing thia[7]helicene **108** in 60% yield. The reaction, however, took 3 days of irradiation to observe full conversion, and the authors concluded that the precursor **107** can be more conveniently cyclized via Scholl reaction, providing the same product in higher yield within just 90 minutes. The same photochemical procedure was used in stepwise preparation of asymmetrically substituted thiahelicenes [224].

The aforementioned syntheses always produced thiahelicenes with sulfur atoms facing outward from the helical cavity as a result of the used precursors and their reactivity. The position of the sulfur can, however, be changed by using differently substituted thiophene precursors (Figure 1.23). Ben Hassine and coworkers observed that bisstilbene **109**, which was prepared by the double Wittig reaction, underwent the subsequent ring closure regioselectively to position 4 of the thiophene substituent [225]. Product **110** was isolated in 44% yield. On the other hand, other authors published a procedure where a similar precursor **111** differing only in the presence of two -COOH groups provided a mixture of two products in high

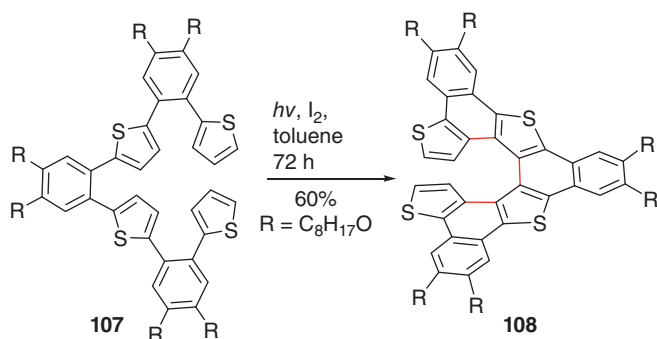


Figure 1.22 Preparation of tetrathia[7]helicene **108** via photocyclization of 1,2-diarylbzenes.

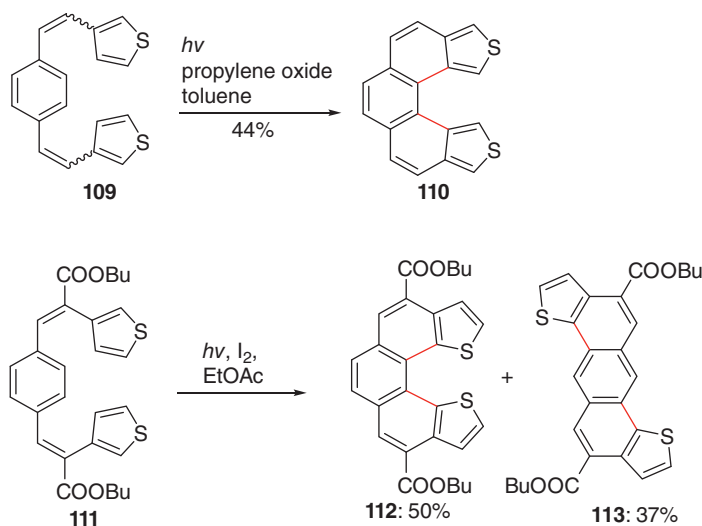


Figure 1.23 Examples of different regioselectivity in photocyclization of precursors **109** and **111**.

overall yield [136]. One was the desired dithiahelicene **112**, where both cyclizations proceeded selectively to position 2, and the other product (anthradithiophene **113**) with one thiophene ring reacted in position 2 and the other in position 5. These compounds were inseparable, and both regioisomers were distinguished by the means of NMR.

Aside from various other substituents that can be present during the photocyclization step of helicene preparation, chiral auxiliaries have been extensively studied for their possible influence on helicene formation. One of the first examples was published by Tanaka [226, 227], who studied the effect of chiral *exo*- and *endo*-bornane derivatives on the diastereoselectivity of the photocyclization reaction (Figure 1.24). The *exo* derivative **114a** ($R = H$) provided a very low excess of one diastereomer (10% *de*), although the diastereomers themselves were easily

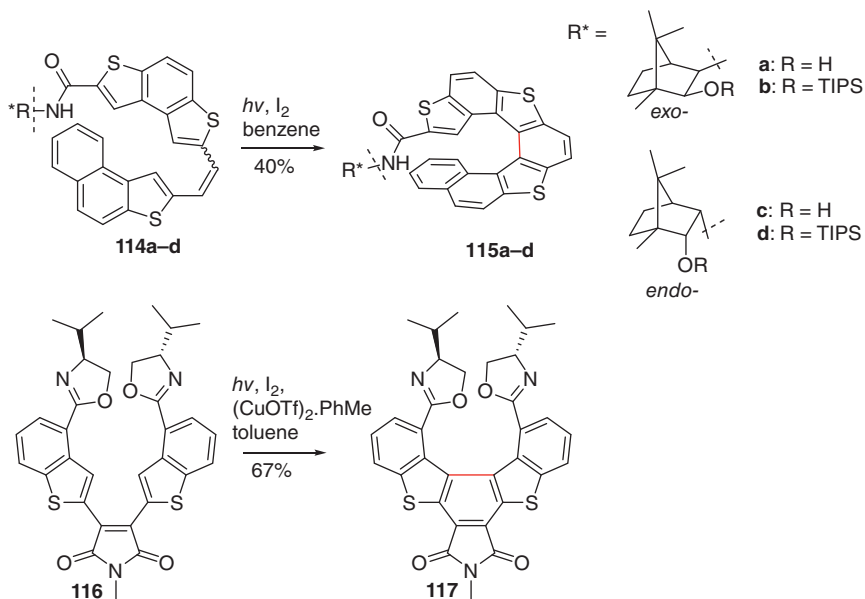


Figure 1.24 Chiral auxiliaries in photocyclization of thiahelicene precursors **114** and **116**.

separable by chromatography on silica gel. An improvement was observed upon triisopropylsilylation of the free hydroxyl (**114b**), which increased the diastereomeric excess to 36% *de*. The *endo* derivative **114c** showed no diastereomeric excess when free hydroxyl was used; however, upon triisopropylsilylation of the hydroxyl (**114d**), the diastereomers were observed in 75 : 25 ratio. The same approach was taken by Dehaen, who studied chiral oxazolines as auxiliaries [228]. The very presence of two oxazolines in the most sterically hindered positions of the precursor **116** provided the (*P,S,S*)-**117** with 32% *de*. The addition of copper salt $(CuOTf)_2$ PhMe, forming a complex of suitable geometry with the starting material, increased the diastereomeric excess to 100% *de*.

Molecules such as **119** and **121** (Figure 1.25) are made mainly of fused thiophenes and are members of the family of thiahelicenes as well. Simpler hexathia[7]helicene

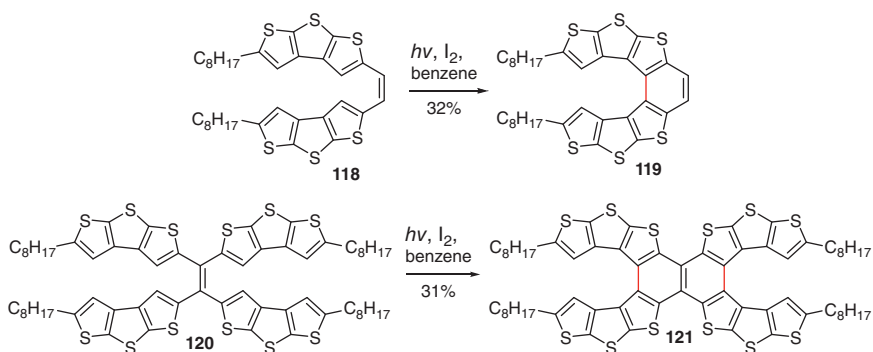


Figure 1.25 Preparation of thiahelicenes **119** and **121**.

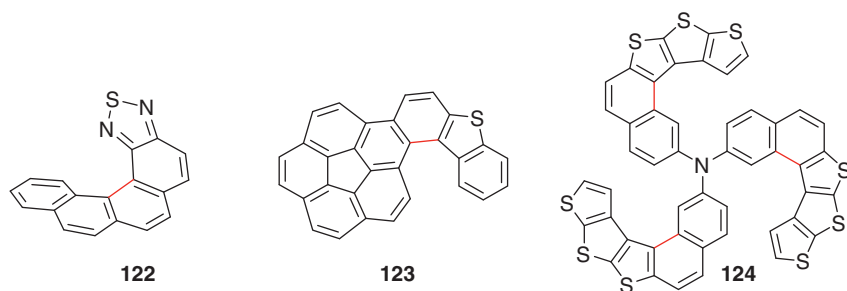
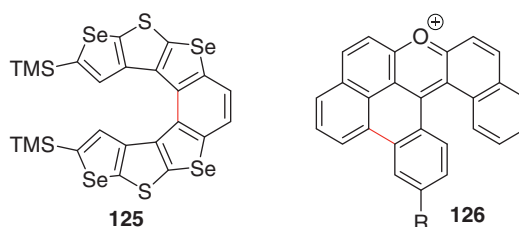


Figure 1.26 Structures of several thiahelicene-based derivatives.

Figure 1.27 Structures of other chalcogen-containing helicene derivatives.



was prepared via photodehydrogenation reaction in benzene in 32% yield [229]. A similar reaction sequence started with a tetraaryl substituted ethylene **120** (Figure 1.25), which served as a suitable precursor for the preparation of bishelicene **121** [230]. The racemic **121** was obtained in 31% yield, while its *meso* form was isolated in 30% yield.

The aforementioned transformations, despite being based on the same principle, can be easily used for the introduction of a variety of different functionalities into the helicene backbone (Figure 1.26). For example, thia-aza [36] **60**, thia-azonia **83–86** [204, 205] (mentioned in Section 1.4.1), or thiadiazole (**122**) [231] helicenes were prepared in this manner. This approach was also used for the preparation of thiahelicene derived from large aromatic corannulene (**123**) [232], as well as for the synthesis of propeller-shaped *trishelicene* based on triarylamine (**124**) [233].

Other chalcogens were also successfully introduced into helicene structure via photochemistry. For example, selenium derivatives (e.g. **125**, Figure 1.27) containing alternating selenophene and thiophene rings were prepared [234]. The aromatic *furan* or *pyran* rings containing helicenes are well-established and well-studied systems (for an overview see Ref. [235] and Refs. [12] and [13] therein); however, non-photochemical approaches prevail in their preparations. A solitary example of photochemical photocyclization of xanthylium salt (*pyrylium* ion) under acidic conditions was disclosed in the 1930s, which led to pentacyclic oxahelicene **126** [236–238].

1.4.3 Phosphahelicenes and Other Heterohelicenes

Phosphorus-containing helicene derivatives are valuable for their performance in different areas, with enantioselective catalysis being probably the most important

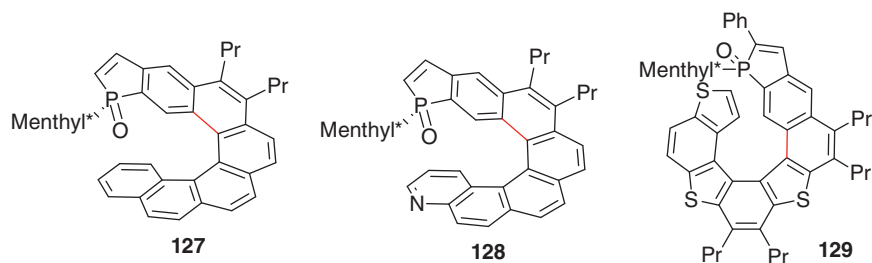


Figure 1.28 Structures of several phosphahelicene derivatives.

[239, 240]. The most significant contribution in this area of helicene chemistry was made by Marinetti and her coworkers, who studied the synthesis and applications of helicenes containing five-membered phosphole rings. These compounds can be prepared by a multitude of different approaches including photochemistry. The first photochemical approach was published in 2012 – the photocyclization of a suitable stilbene precursor provided phosphole-containing helicene **127** (Figure 1.28) [241]. The authors used the chirality on phosphorus, along with the *L*-menthyl group present in the structure, to form diastereomers easily separable by chromatography on silica gel. Subsequent formation of dimers of the product via [2 + 2] cycloaddition was found to significantly lower yields upon prolonged irradiation. This behavior was later found to be typical for the majority of these compounds and is discussed separately in Section 1.6. Phospholes based on other helicenes were later prepared, including different derivatives containing nitrogen (**128**) [242] or sulfur (**129**) [243]. Other helical compounds containing different functionalities on phosphorus atoms were also described in numerous instances [244–246].

Another way of utilizing photochemistry in the preparation of heterohelicenes involves the light-promoted synthesis of suitable building blocks prior to the non-photochemical formation of the helical backbone. Among various helical molecules accessible by this approach, metalla[*n*]helicenes [247, 248] and azaborahelicenes [249, 250] serve as typical examples.

1.5 Photochemical Preparation of Helicene-Like Molecules

In this part, only those screw-shaped molecules accomplished via photochemistry and containing non-aromatic rings will be discussed. The “helicene-world” is rich in systems possessing helical topology (known as *helicene-like molecules*, *helicenoids*, or *helicene-analogs*), and light might be used in different ways for their preparation, either for the generation of the catalytically active metal species promoting [2 + 2 + 2]-cyclootrimerization (e.g. in Refs. [251–256]) or simply for the preparation of molecular building blocks prior to the final non-photochemical cyclization (e.g. dioxepine[7]helicene-like [235]). Dihydrohelicenes may be formally included among these molecules too.

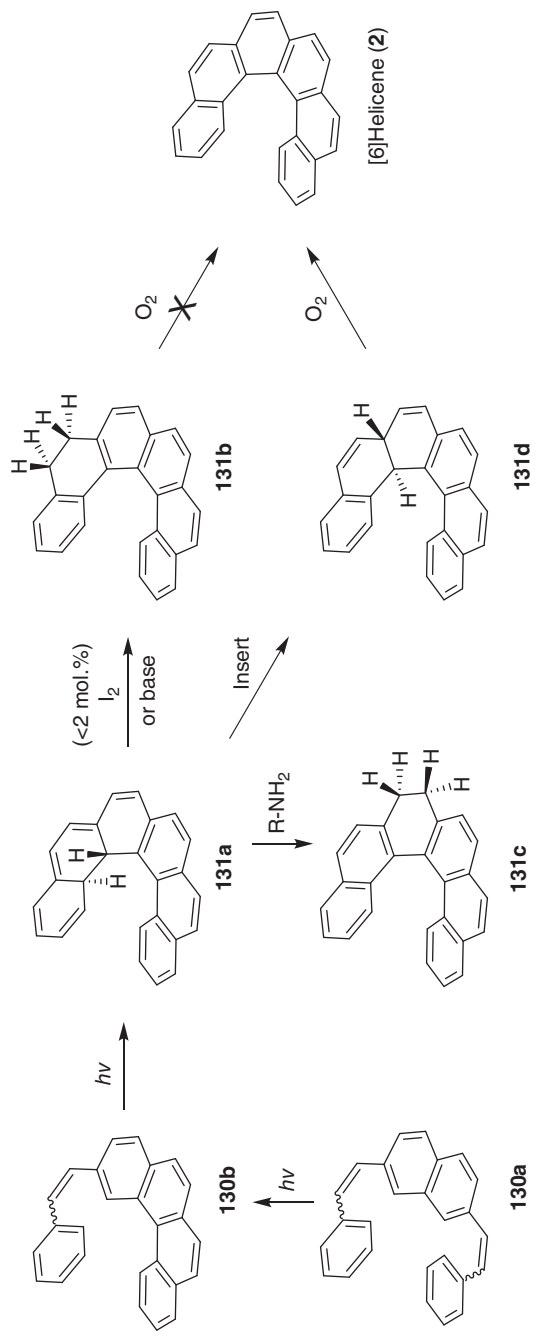


Figure 1.29 Photocyclizations leading to dihydro[6]helicenes 131.

The irradiation of 2,7-distyrylnaphthalene **130a** or 2-styrylbenzo[*c*]phenanthrene **130b** (Figure 1.29) under oxygen-free conditions and in the presence of a small amount of iodine (0.5–2 mol %) provided 5,6-dihydro[6]helicene (**131b**) in 60% yield as a consequence of H-shifts from the primarily formed cyclization product **131a** [257]. Interestingly, the substance **131b** was not easily oxidized to [6]helicene. Under anaerobic conditions, *trans*-6a,16d-dihydro[6]helicene **131d** was formed from **131a** by a suprafacial 1,5-H shift of one hydrogen [258]. Dihydrohelicene

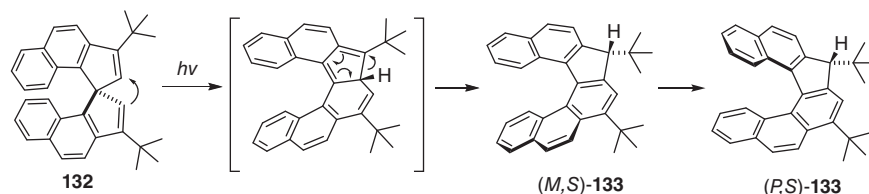


Figure 1.30 Other photochemical reactions to helicene analogs.

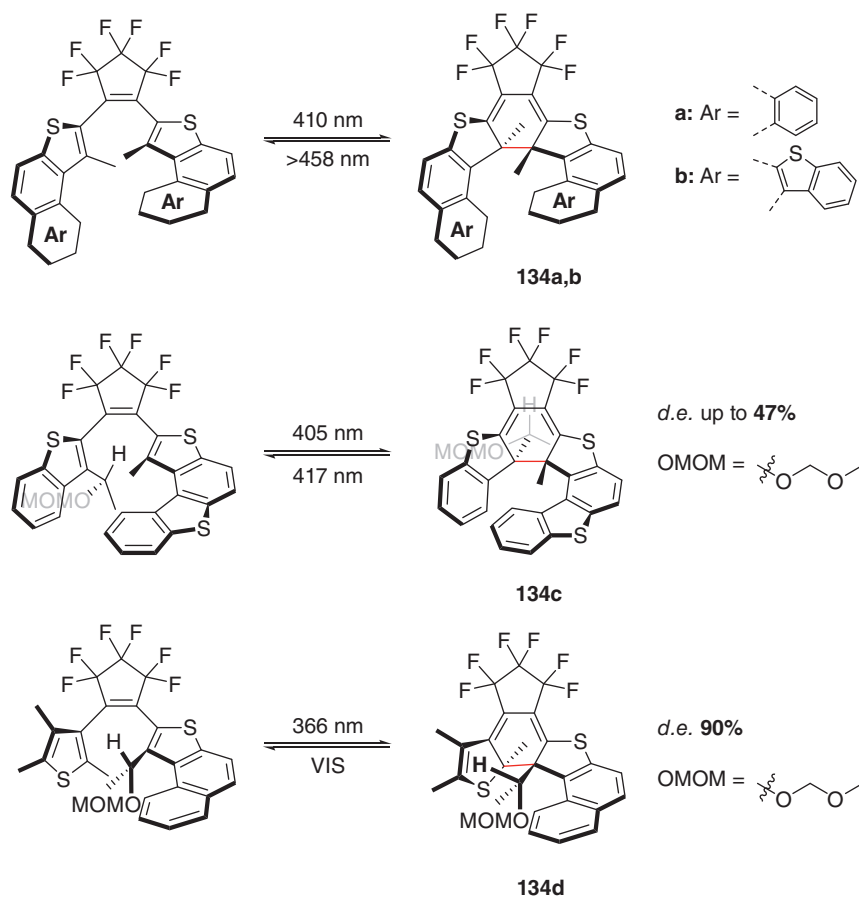


Figure 1.31 Photostationary states resulting in helicene-like structures.

131d was shown to be photolabile and easily oxidized to [6]helicene. Irradiation of 2-styrylbenzo[*c*]phenanthrene **130b** in alkylamines or basic alcoholic solutions resulted in the formation of a mixture of 5,6-dihydro- (**131b**) and 7,8-dihydro- (**131c**) [6]helicenes [259, 260]. In alkylamines, **131c** was the favored compound, whereas in basic alcoholic solutions compound **131b** predominated.

Shingu studied the stereospecific photochemical rearrangement of optically active *spiro*-compound **132** (Figure 1.30) that, after suprafacial 1,5-migration of the vinyl group, afforded 7,9-di-*tert*-butyl-9*H*-benzo[6,7]-indeno[2,1-*c*]phenanthrene (**133**), a helicene-like molecule [261]. The primary (*M,S*)-product epimerized to a more stable (*P,S*)-isomer.

Using photochemistry in the ring-closing reactions of other helicene-like molecules is rare and limited essentially to the preparation of *helicenoids* (e.g. **134a–d**, Figure 1.31) in their photostationary state (PSS). The photochromism of these systems was studied by Branda [262] and later on by Yokoyama et al. [263, 264]. Thanks to the allylic strain of the stereogenic carbon located at the periphery of the hexatriene moiety, Yokoyama prepared **134c,d** enantioselectively from their open forms [265]. Using the same strategy, Diederich et al. also succeeded in the preparation of other helicene-DAE (diarylethene) systems in PSS [266].

1.6 Photochemical Transformations of Helicenes

This part of the chapter discusses reactions where light is used to propel transformations of helicene skeleton, rather than for its preparation. The past couple of years has seen a surge in the development of photochemical methods for transformations of different substrates, and these methodologies are slowly finding their way into helicene chemistry as well.

The first transformations of this type, however, were observed as early as the late 1960s [44, 62, 267]. One of the typical by-products in photochemical preparations of [5]helicenes is their overannulation forming the corresponding benzo[*ghi*]perylene (Figure 1.32a). The starting stilbene-type molecule **135** initially forms the desired [5]helicene **1**, but under the reaction conditions, another photocyclodehydrogenation takes place to form **136**. In most cases, this process is undesired, and significant effort was put into avoiding this reaction. For example, some bromo- [63], cyano- [86], or phenylene- [132] substituted [5]helicenes do not undergo such cyclization, because the orbitals involved in the cyclization process are destabilized by the presence of the substituents. In other cases, however, different benzoperylene can be prepared in good yields, as shown in Figures 1.32b,c. For instance, dimethoxy benzoperylene **138** was isolated in 32% yield after irradiation of the bis(styryl)benzene **137** [86]. Similarly, π -extended derivative **140** was obtained in 89% yield from stilbene **139** [268].

A similar reaction can be conducted with certain aza- and azonia[5]helicenes as well. 2-Aza[5]helicene **62b** always undergoes overannulation to form the 7-azabenzoperylene **141**, irrespective of the starting stilbene precursor (Figure 1.33a) [172, 269]. Azonium stilbene precursors can be irradiated to give the

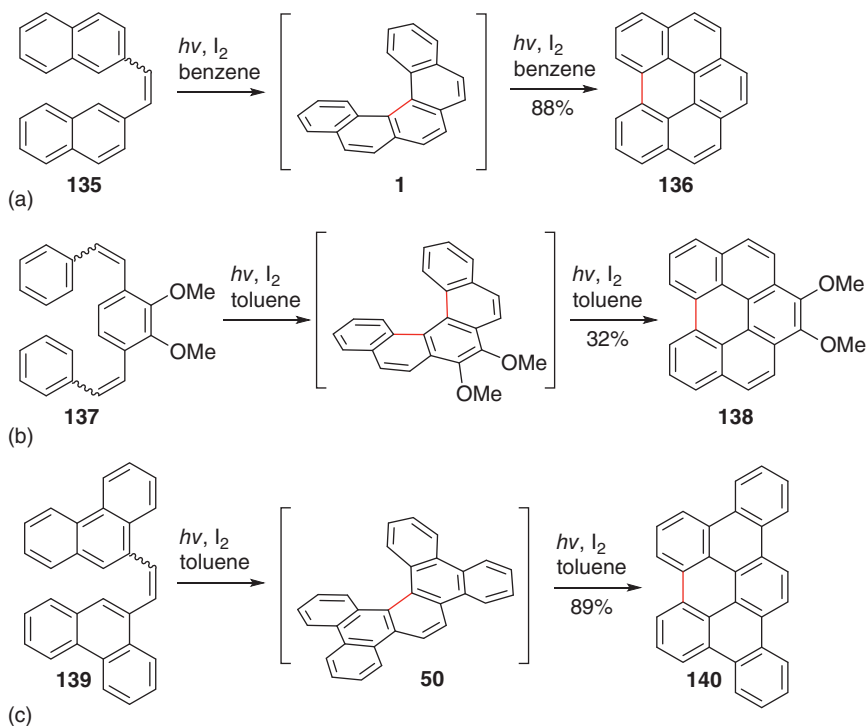


Figure 1.32 Preparation of (a) unsubstituted and (b, c) substituted benzo[ghi]perylenes from [5]helicenes.

respective azonia[5]helicenes, which subsequently undergo another ring closure to produce 2a-azoniabenz[ghi]perylene perchlorate **142** in low yield.

Photochemical transformations are not limited to [5]helicenes, as has been shown recently in several cases. [2 + 2]-Photocycloadduct **144** was formed from a phosphole-containing helicene derivative **143** (Figure 1.34a) [245]. The process is regioselective and takes place under both UV and X-ray irradiation, both in crystal and solution. This behavior of phosphahelicenes is rather general and has been observed on multiple occasions [241, 242]. A similar example was published by Církva and coworkers, who isolated cyclobutane **145** substituted by two benzo[c]phenanthrenes as a major product in an attempted synthesis of 1,2,3,4-tetrafluoro[6]helicene **26** (Figure 1.34b) [52]. One example of [4 + 2]-photocycloaddition was published by Storch and Sýkora, who irradiated 9,10-diketo[7]helicene **146** (Figure 1.34c) with UV light in the presence of 2,3-dimethylbut-2-ene to obtain helicene-based 1,4-dioxane **147** in good yield [270].

Storch and König studied both reductive and oxidative photochemical transformations of helicene derivatives [42]. They showed that bromohelicenes can generate helicenylyl radicals upon irradiation with blue light (Figure 1.35a, transformations of **32a** are shown as a representative example). This species can be subsequently trapped with a suitable trapping agent, ranging from various heterocycles (pyrrole,

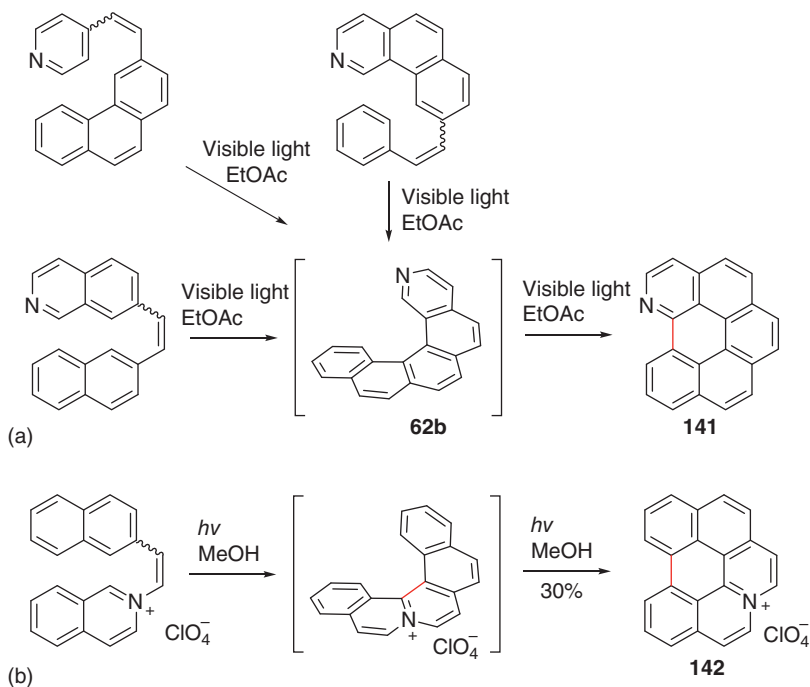


Figure 1.33 Preparation of (a) aza- and (b) azoniabenzo[ghi]perylenes.

thiophene, furan, indole) to heteroatomic compounds, such as triethyl phosphite, dimethyl disulfide, or bis(pinacolato)diboron to form helicenes **148a–h**. Three different examples of oxidative transformation of 2-methoxy[6]helicene **149** were also shown, yielding products **150a–c** with $-\text{Br}$, $-\text{CN}$, and $-\text{PO}(\text{OEt})_2$ groups regioselectively in position 6 (Figure 1.35b). The same authors also published a simple oxidation of twisted arylamines into respective *ortho*-diketones (**146**, **151–154**) by oxygen [270]. The arylamine sensitizes the formation of singlet oxygen, which then oxidizes the amine-substituted double bond via [2 + 2]-cycloaddition. The prepared diketones are shown in Figure 1.35c and can be easily transformed into π -extended nitrogen-containing heterohelicenes [270].

1.7 Conclusions

The photochemical approach to carbo[*n*]helicenes and their derivatives provides a wide range of helical molecules differing in their length or substitution patterns and conceptually represents the most explored area in this field. The current state of knowledge is, however, starting to reach its limit, especially in the photosynthesis of long ($n \geq 10$) or multiple carbo[*n*]helicenes. The limiting factors are mainly the growing complexity of the starting materials and, consequently, their decreasing solubility. Additionally, an increasing number of bonds formed in a single

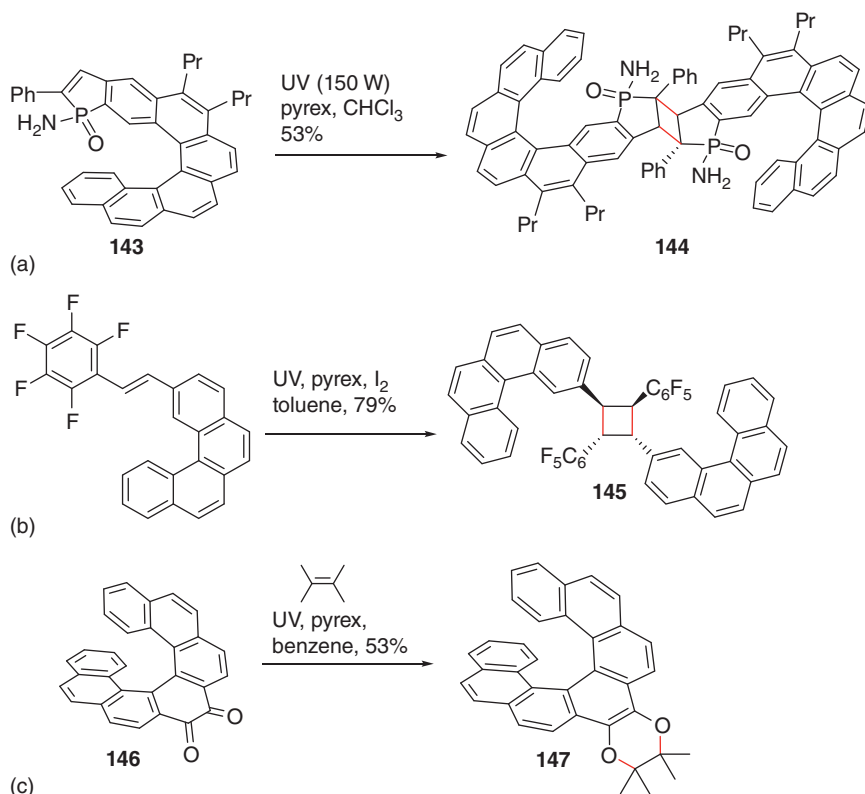


Figure 1.34 (a, b) [2+2]- and (c) [4+2]-Photocycloadditions of helicene molecules.

transformation typically lowers the yield of the reaction, limiting the applicability of the photochemical approach in the synthesis of complex helical structures.

Unlike carbohelicenes, the photochemical approach to hetero[n]helicenes is somewhat underdeveloped, despite the variability that these structures can offer. Thus, photosynthesis of long derivatives or helicenes with a higher number of heteroatoms in their backbone remains unexplored so far. Also, the preparation of helical structures with other heteroatoms (e.g. boron, silicon, etc.) that are commonly accessible with non-photochemical approaches remains elusive for photochemists.

The light-mediated transformations of helicenes represent significant interest in the recently emerging part of photochemistry. The results achieved in this area so far indicate an unexplored and potentially fast-growing field of photochemical research. The increasingly common LED-type photoreactors can play an important role in this field, as their development represents a major step forward in terms of their photoefficiency and availability of specific wavelengths.

Although the photochemical approach provides racemic helicenes only, it successfully competes with modern non-photochemical asymmetric syntheses requiring multistep reaction sequences or the use of economically demanding reagents/catalysts.

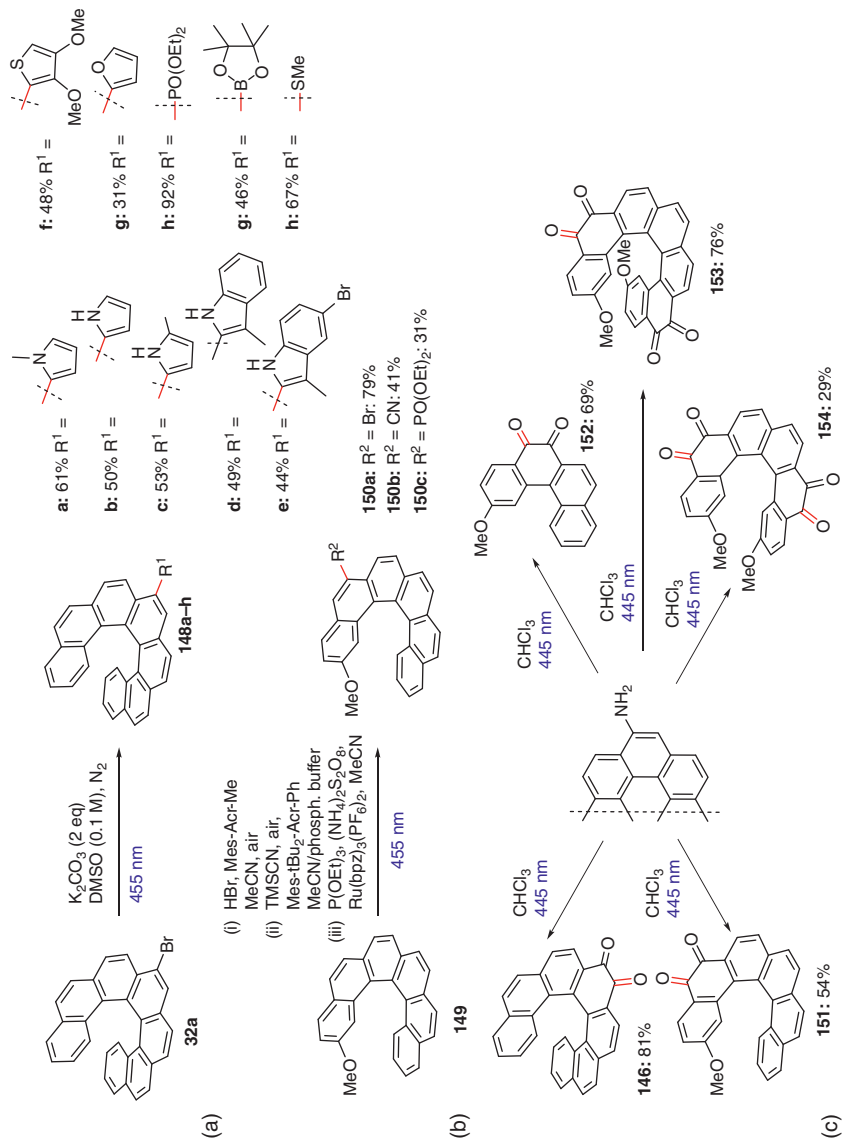


Figure 1.35 Photochemical (a) substitutions and (b, c) oxidative transformations of helicene backbone.

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