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Recent advances in the synthesis of multiple helicenes

Zhen Chen,^{a,b} Wei-Chen Guo^{a,b} and Chuan-Feng Chen[✉]^{a,b}

Multiple helicenes, as helically twisted polycyclic frameworks with extended π -conjugated systems, have attracted growing attention due to their unique topologies, tunable chiroptical properties, and potential applications in chiral materials and organic electronics. In this review, we provide a systematic overview of the recent advances in the field of multiple helicenes and propose a concise classification strategy that classifies them into linear, cyclic, and cross-linked types. Based on this classification, we further summarize and highlight a range of efficient synthetic strategies that facilitate the construction of multiple helicenes. We hope this review will provide the design inspiration of multiple helicenes and further be helpful for the development of helicene chemistry.

1 Introduction

Helicenes are a class of compounds characterized by their unique twisted stereo helical structures, formed by *ortho*-fused aromatic or heteroaromatic rings.^{1–4} This unique chirality, structural variety, and optical/electronic properties endow helicenes with remarkable physicochemical properties, making them highly attractive for applications in various fields, including asymmetric catalysis, chiral recognition, and chiral optical materials.^{5–11}

Depending on the number of helical units present in the molecule, helicenes can be broadly classified into two categories:

single helicenes containing one helical unit and multiple helicenes incorporating two or more helical units within a single molecule. Compared to single helicenes, multiple helicenes exhibit more distinctive properties. First, multiple helicenes possess more complex stereo-structures, owing to the incorporation of multiple helical units within a single molecule. The spatial orientation and connectivity of these helical structures can vary significantly, giving rise to a wide range of molecular topologies. This structural diversity introduces new dimensions to stereochemistry and conformational control, far beyond what is achievable with single helicenes. Second, the presence of multiple helical units in one molecule results in multi-chirality, where each helical unit can independently adopt a P or M configuration. This gives rise to a complex set of stereoisomers with distinct chiral properties, including multiple diastereomers and enantiomers. This also leads to

^aBeijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: cchen@iccas.ac.cn

^bUniversity of Chinese Academy of Sciences, Beijing 100049, China



Zhen Chen

Zhen Chen received his BS degree from the University of Science and Technology of China in 2021 and MS degree from the same University of Science and Technology of China in 2024 under the supervision of Prof. Zhenhua Gu. In 2024, he joined the laboratory of Prof. Chuan-Feng Chen at ICCAS to pursue his PhD degree in chemistry. His research focus is on the design of B,N embedded hetero-helicene TADF materials and their application in CP-OLEDs.



Wei-Chen Guo

Wei-Chen Guo received his BS degree from China University of Petroleum (Beijing). In 2021, he joined the laboratory of Prof. Chuan-Feng Chen at the Institute of Chemistry, Chinese Academy of Sciences, to pursue his PhD degree in chemistry. His research interest is on high-performance circularly polarized electroluminescent materials based on B,N embedded hetero-helicenes.



unique molecular packing, solid state chirality and self-assembly behaviours. Third, multiple helicenes generally feature larger π -conjugated systems than their single helicene counterparts. The extended conjugation facilitates stronger electronic communication throughout the molecule, resulting in unique optical absorption, emission properties, and electronic characteristics. These properties make them promising candidates for applications in optoelectronic materials, molecular electronics, and spintronics.

The synthesis of complex multiple helicenes presents significant challenges due to their inherent strain and the need for precise stereochemical control. To overcome these obstacles, several powerful synthetic strategies have been developed (Fig. 1). Oxidative coupling reactions, particularly Scholl reactions and photocyclization, have proven highly effective for constructing extended π -systems and forming multiple rings simultaneously. Transition metal-catalyzed $[2 + 2 + 2]$ cycloadditions offer an atom-economical route to build helical scaffolds, often with good stereoselectivity. Friedel–Crafts alkylation/acylation provides a versatile method for intramolecular cyclization, enabling the closure of helical units. More recently, intramolecular borylation reactions have emerged as a valuable tool, allowing the formation of strained boron-bridged helical structures that are difficult to access using other approaches. These methods collectively provide a robust toolbox for accessing diverse multiple helicene architectures.

Since the first synthesis of double [5]helicene in 1959,¹² the field of multiple helicenes has witnessed rapid and substantial development. Numerous molecular architectures have been reported,^{13–15} encompassing bis-, tris-, tetra-, penta-, and hexa-helicenes, with diverse geometric arrangements such as S-shaped, X-shaped, M-shaped, fan-shaped topologies and so on. Despite the rapid expansion and growing structural diversity of multiple helicenes, there remains a lack of a unified and systematic classification method to organize these multiple helicene structures. Furthermore, the synthetic strategies developed for constructing multiple helicenes—although often elegant and efficient—have not been comprehensively sum-

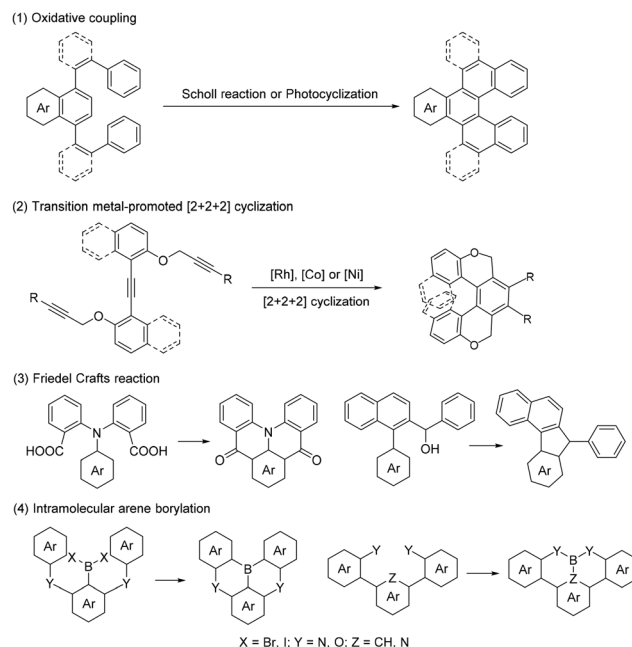


Fig. 1 Several synthetic methods toward multiple helicenes.

marized in a way that highlights their potential applicability across different helicene structures.

In this review, we aim to present a systematic overview of the recent advances in the field of multiple helicenes, and we propose a concise and intuitive classification strategy based on their overall stereostructural characteristics, grouping them into linear, cyclic, and cross-linked categories. This framework not only facilitates a clearer understanding of these complex multiple helicenes but also serves as a guide for future molecular design. Additionally, we summarize and highlight various and efficient synthetic approaches to drive the development, property modification, and application enhancement of multiple helicenes with diverse stereochemical architectures. Through this review, we aim to provide a solid foundation for further exploration and innovation in the field of multiple helicene chemistry, particularly in the development of advanced chiral π -conjugated materials.



Chuan-Feng Chen

Chuan-Feng Chen has been working as a full professor of organic chemistry at the Institute of Chemistry, Chinese Academy of Sciences, since 2001. His current research interests include supramolecular chemistry based on synthetic macrocyclic hosts and organic cages, chiral organic light-emitting materials and helicene chemistry.

2 Linear multiple helicenes

Linearly extended multiple helicene structures are constructed by simplifying each helical unit into a “linear helix,” which retains the conjugated backbone while disregarding the three-dimensional helical distortion. These linear helices are then connected *via* aryl cores, such as benzene or naphthalene rings, to form a linearly extended molecular architecture. Analogous to the approach used in higher-order single helicenes, where linear extension is achieved by increasing helicity, in linear multiple helicenes the linear helix is elongated by increasing the number of helicene units.



2.1 Double helicenes

S-shaped double helicenes represent the simplest structural form of linear multiple helicenes, in which each component is fused at the terminal. In recent years, such double helicene compounds have been reported successively. Transition-metal-catalyzed cyclization is a prevalent method for synthesizing helicenes and has recently been used for the synthesis of S-shaped double helicenes. In 2018, Tanaka's group achieved the asymmetric synthesis of an S-shaped double helicene using gold catalysis with (*R*)-BINAP as a chiral phosphine ligand¹⁶ (Fig. 2a). This intramolecular asymmetric hydroarylation yielded the S-shaped double [6]helicene **1** in 29–34% yields and with 64–66% ee.

Besides hydroarylation, [2 + 2 + 2] cycloaddition can also be utilized for synthesizing S-shaped double helicenes. In 2019, Tanaka's group reported a rhodium-catalyzed asymmetric

hydroarylation for synthesizing S-shaped double helicenes¹⁷ (Fig. 2b). In the presence of rhodium and the chiral ligand (*R*)-difluorophos, the reaction afforded (–)-**2** and *meso*-**2** S-shaped double [6]helicenes in 45% total yield, with the (–)-**2** isomer exhibiting 73% ee. Both configurations were confirmed by single-crystal X-ray diffraction. Due to steric clashes between the terminal naphthalene rings, the helical chirality of these S-shaped double [6]helicenes is unstable, leading to epimerization between (–)-**2** and *meso*-**2** and eventual racemization at room temperature. In 2020, the same group further reported a highly diastereo- and enantioselective intramolecular double [2 + 2 + 2] cycloaddition catalyzed by a chiral rhodium(i) complex¹⁸ (Fig. 2c). This reaction yielded S-shaped double [6]helicene (–)-**3** with stable helical chirality (>99% ee). The introduction of two additional fused benzene rings significantly enhanced the configurational stability of the helicene. Additionally, Tanaka's group achieved the asymmetric syn-

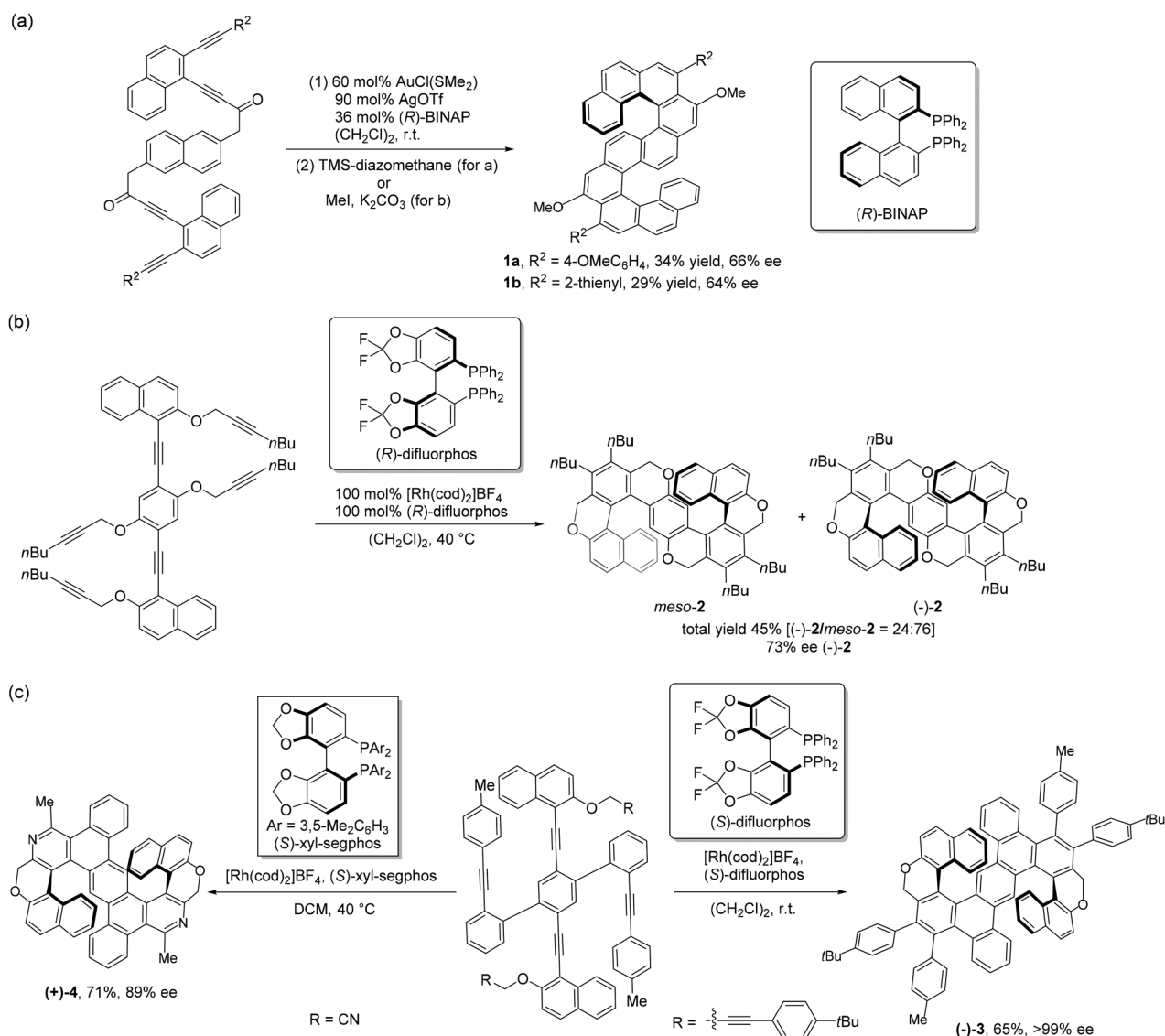


Fig. 2 Transition metal catalyzed synthesis of S-shaped double helicenes.

thesis of nitrogen-incorporated S-shaped double helicenes¹⁹ (Fig. 2c). In 2021, by introducing a cyano group into the substrate, they accomplished the asymmetric synthesis of a pyridine-embedded S-shaped double [6]helicene **4** via a cationic rhodium(i)/axially chiral biaryl bisphosphine complex-catalyzed intramolecular [2 + 2 + 2] reaction, affording the target product (+)-**4** in 71% yield with 89% ee.

Friedel–Crafts cyclization is another effective strategy for synthesizing double helicenes. In 2020, Chi's group reported a novel S-shaped double [6]helicene containing two embedded *p*-quinodimethane (*p*-QDM) units²⁰ (Fig. 3a). By converting an aldehyde-bearing precursor into an alcohol and subsequently inducing Friedel–Crafts cyclization, the double [6]helicene precursor **5a** was synthesized. Subsequent deprotonation with potassium *tert*-butoxide and oxidation with *p*-chloranil yielded the S-shaped double [6]helicene **5b** in 62% yield. This compound exhibited open-shell diradical character, providing insights for designing stable helicenes with diradical properties.

In 2022, Eli Zysman-Colman's group reported their work on the synthesis and properties of a S-shaped [4]double helicene with thermally activated delayed fluorescence²¹ (Fig. 3b). The synthesis involved a Cu-catalyzed Ullmann coupling reaction between resorcinol and methyl 2-iodobenzoate, yielding intermediate **6** in 43% yield. Hydrolysis then afforded compound **7** in 43% yield. Hydrolysis then afforded compound **7** in 43% yield. Hydrolysis then afforded compound **7** in 43% yield.

quantitatively, followed by conversion of the carboxylic acid to an acyl chloride and Friedel–Crafts cyclization catalyzed by AlCl₃, yielding the S-shaped double [4]helicene **8** in 36% yield.

Similar to S-shaped helicenes, M-shaped helicenes also exhibit a linear molecular structure. In 2022, Yang's research group synthesized a boron–nitrogen–sulfur-doped double [5]helicene with circularly polarized luminescence and thermally activated delayed fluorescence properties²² (Fig. 4).

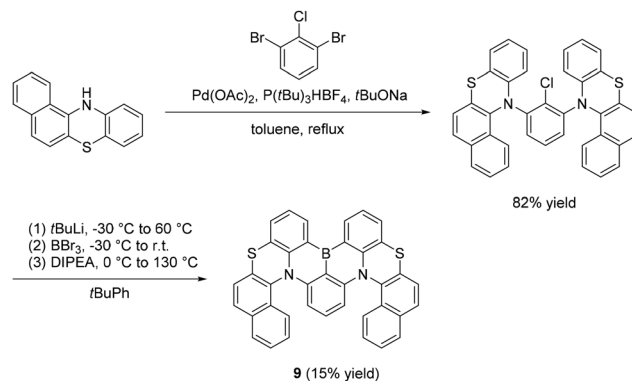


Fig. 4 Synthetic routes to the M-shaped double helicene **9**.

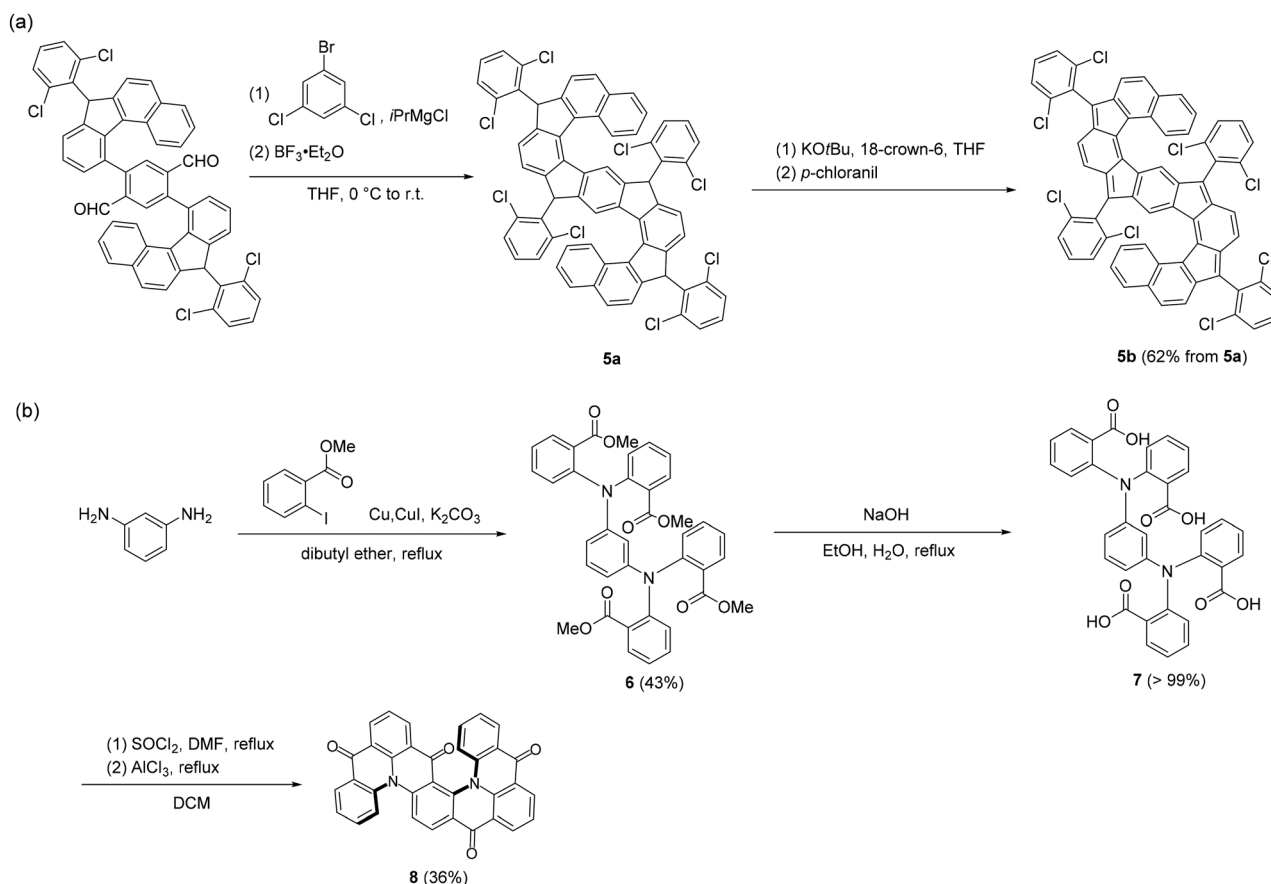


Fig. 3 Synthesis of S-shaped double helicenes via a Friedel–Crafts reaction.



Consequently, compound **9** was prepared from 12*H*-benzo[*a*]phenothiazine and 2-chloro-1,3-dibromobenzene *via* Buchwald–Hartwig coupling and electrophilic borylation reactions, in a total yield of 12%. This study highlights the significant potential of helicene-based emitters for CP-OLED applications.

2.2 Other linear multiple helicenes

In addition to double helicenes, other multiple helicenes also include linear structural types. In 2021, Nuckolls' research group reported the utilization of perylene diimide in the synthesis of chiral spiral nanoribbons through coupling and ring formation reactions²³ (Fig. 5a). Compound **10** is a linear triple

helicene, while compounds **11** and **11-iso** are linear quadruple helicenes. To synthesize helicene **10**, the precursor helicene **12**, which contains two perylene diimide (PDI) units, was initially transformed into the bis(pinacolato)diboron-substituted helicene **13**. Subsequent Suzuki–Miyaura cross-coupling reactions, followed by a regioselective photocyclization sequence, led to the formation of the linear triple helicene **10** in an overall yield of 44% in two steps. For the preparation of **11**, two successive Suzuki–Miyaura couplings between aryl bromide **14** and the bis-Bpin reagent **15** were carried out while retaining the *N*-methyliminodiacetic acid (MIDA) protecting group in the substrate. This was followed by two photocyclization steps to produce the bis-MIDA boronate intermediate.

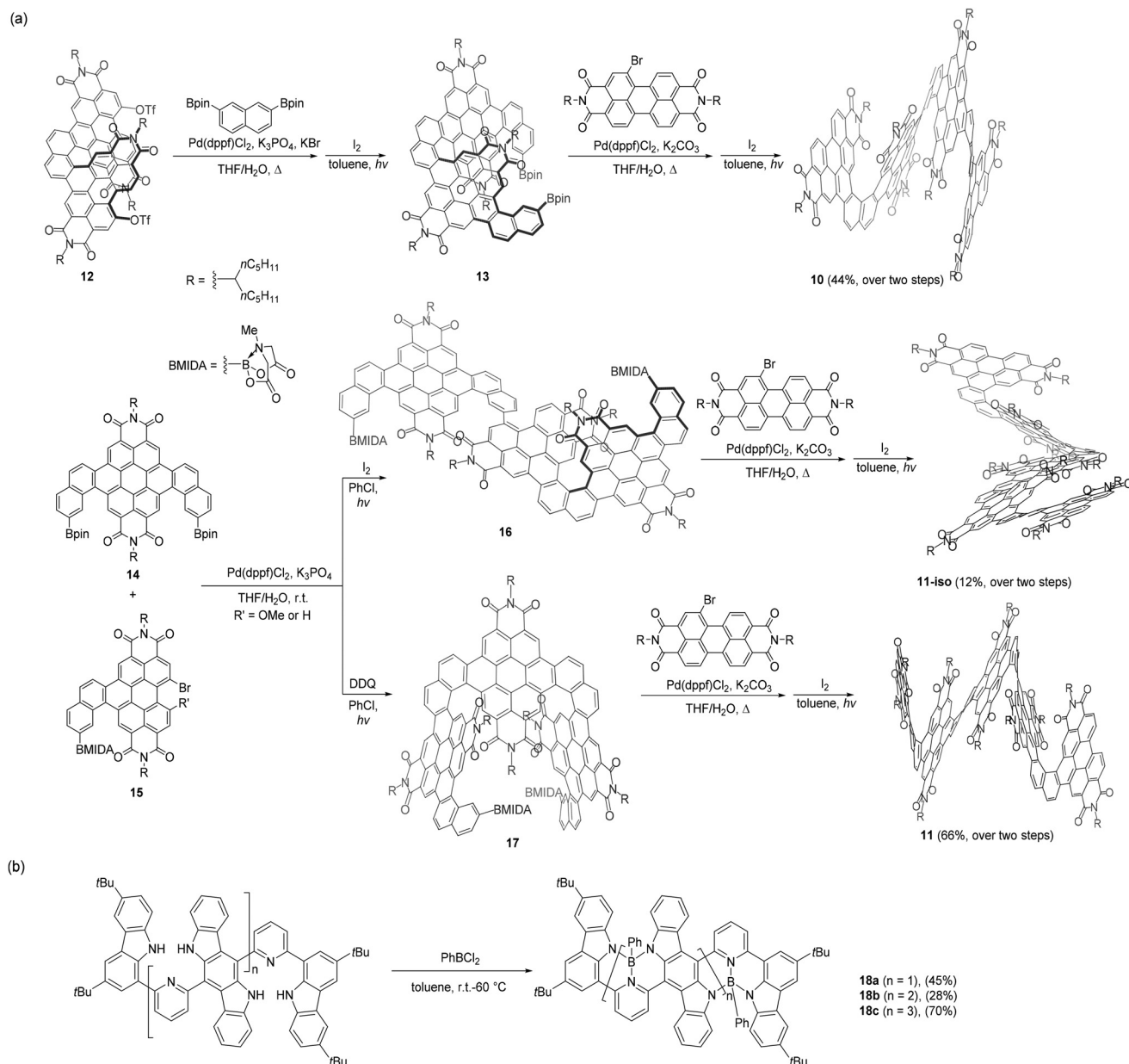


Fig. 5 Synthetic routes to other linear multiple helicenes.



Notably, iodine-mediated photocyclization predominantly yielded compound **16** as the major product, which exhibited resistance to further conversion to **17** even at elevated temperatures. Conversely, photocyclization using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an oxidant selectively generated **17** as the primary product. Finally, by employing synthetic procedures similar to those for NP4H, two-step transformations from **16** and **17** resulted in the isolation of the linear quadruple helixes **11-iso** and **11** in 12% and 66% yields, respectively. This strategy emphasizes the precise regulation of regioselective photocyclization and the sequential construction of complex helical structures using boronate protection techniques. These conjugated chiral molecules exhibit intriguing chemical, biological, and chiral characteristics.

In 2024, Yang's group reported one kind of linear multiple helixene²⁴ (Fig. 5b). They utilized a new synthetic approach to create a series of boron-bridged helically twisted donor- π -acceptor (D- π -A) conjugated systems. By employing sequential Suzuki coupling reactions, they prepared precursor compounds containing multiple carbazole and pyridine groups. Subsequent electrophilic borylation reactions led to the formation of helical nanobelt compounds **18a-c** in 45%, 28%, and 70% yields, respectively. These boron-nitrogen-doped multiple helixenes exhibited bright red to near-infrared (NIR) emission, opening up avenues for developing advanced materials with tailored optoelectronic properties, especially in the challenging NIR spectral region. This accomplishment underscores the promise of boron-mediated helical structures in diversifying the functionality of π -conjugated systems.

3 Cyclic multiple helixenes

Cyclic multiple helixenes are defined by a cyclic structure made up of multiple helixene units. This structure can be constructed by connecting helixene units end-to-end to form a closed-ring conjugated system or by bridging the termini to create rings, which then twist into multiple helixene configurations. The closed-ring architecture and intrinsic cavity of cyclic multiple helixenes make them promising for applications in molecular recognition and photoelectric fields. As a result, research interest in these compounds has surged in recent years.

In 2017, Osuka's group unexpectedly synthesized a closed hexathia-double [9]/[5]helixene *via* Scholl oxidation of an *o*-phenylene-bridged hexathiophene precursor²⁵ (Fig. 6a). This process involved a 1,2-aryl migration of a thiophene-linked benzene unit, forming new C-C bonds between α - and β -carbon atoms of adjacent thiophene units. The macrocyclic double helixene **19** was achieved in 66% yield. The oxidative cyclization demonstrated high selectivity, primarily producing the double helixene. This unique asymmetric double-helical structure marks a significant advancement in helixene chemistry by introducing a novel non-planar π -conjugated framework, enhancing structural diversity in the field.

By employing "head-to-head" and "tail-to-tail" connection, two individual helical olefin units are integrated into cyclic

molecules, effectively anchoring the end of the helical olefin to minimize racemization and stabilize the helical configuration. In 2017, Durola's group successfully synthesized a double helixene with a macrocyclic structure²⁶ (Fig. 6b). The macrocyclic compound **20** was thus synthesized *via* a quadruple Perkin condensation reaction involving diphenylglyoxalic acid and terephthalic acid in a diluted solution, resulting in 21% isolated yield. Subsequent quadruple oxidative photocyclization reactions produced the double helixene **21** with a closed macrocyclic architecture in 54% yield. Analysis using X-ray crystallography confirmed its unique non-planar geometry. This study showcased a systematic approach to building intricate helical frameworks through the consecutive condensation and photocyclization processes, broadening the scope for designing novel topologically distinct π -conjugated systems.

In 2024, Zhang's group successfully synthesized a persistent chiral cyclic double helixene using a cove-region bridging strategy²⁷ (Fig. 6c). The double helixene produced through this approach exhibits a compact 3D cavity. The synthesis of this target compound was achieved by leveraging the structure of a known double heterohelixene. In the spiro-phenazine (SPZ) molecule, the presence of steric hindrance in the cove region causes the two benzene rings connected to the phenazine (PZ) unit to orient either upwards or downwards relative to the PZ unit, resulting in the formation of (*P,P*) and (*M,M*)-enantiomers. To bridge the cove region of SPZ, dibromo-SPZ (DBrSPZ) was initially synthesized as a crucial intermediate. Subsequently, a lithium-halogen exchange reaction was conducted at -78 °C using *n*-BuLi as the lithiating agent. The macrocyclic structures of **22** and **23** were successfully obtained in 56% and 49% yields, respectively, by reacting the prepared dilithium reagent with terephthaloyl/isophthaloyl dichloride. Subsequently, using BH₃ and Et₃SiH as reducing agents in two sequential reduction steps, the double helixene **24** was obtained in a total yield of 17%. The macrocyclic structural features endow these compounds with persistent chirality. Moreover, the cyclic double helixenes possess excellent luminescence properties, including thermally activated delayed fluorescence and circularly polarized luminescence.

4 Cross-linked multiple helixenes

Cross-linked multiple helixenes feature three-dimensional frameworks with the multiple helixene units converging at a central node to form cross or fan-like structures through shared aryl units. This class of compounds include various subclasses, which vary based on the number of spiroene units and the specific aryl units in the common connecting portion.

4.1 X-shaped double helixenes

X-shaped double helixenes consist of two helixene units connected through a distinct cross-linking, forming a spatially crossed configuration resembling the letter "X". This structure often involves shared aromatic rings or bridged connections, resulting in a complex double-helical topology. Recently,



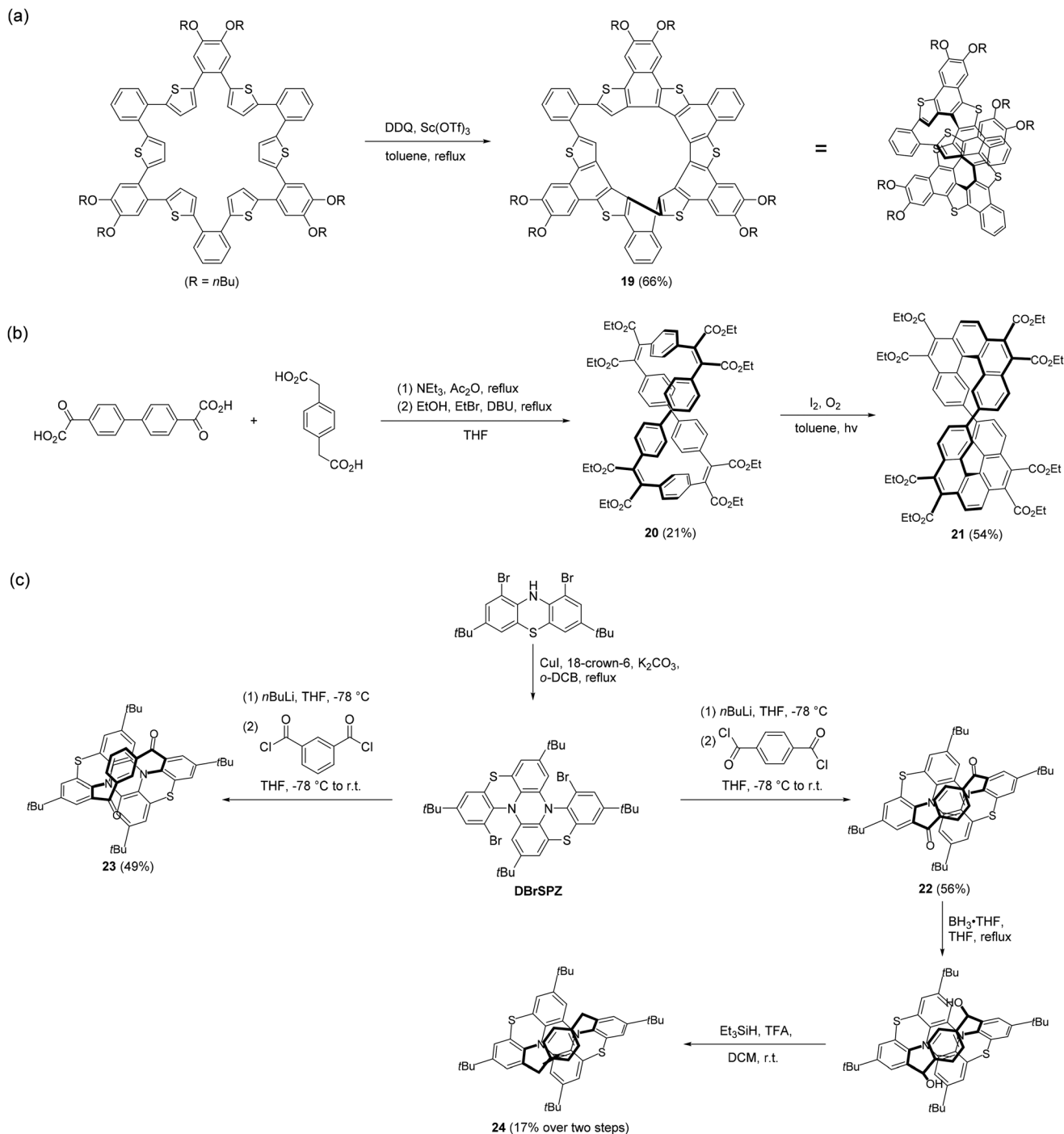


Fig. 6 Synthetic routes to cyclic multiple helicenes.

numerous reports have detailed the synthesis of X-shaped double helicenes.

The synthetic approach of utilizing benzene rings as aromatic cores to create X-shaped cross-conjugated double helicenes by connecting two molecular fragments through a common benzene ring has gained considerable attention and has been extensively documented in recent literature. In 2019, Zhang and colleagues utilized a palladium-catalyzed Suzuki

coupling reaction in conjunction with a highly regioselective intramolecular Scholl reaction to produce boron–nitrogen-doped double [5]helicene **25** and boron–nitrogen-doped double [6]helicene **26** in 83% and 49% yields, respectively²⁸ (Fig. 7a).

In 2020, Yasuda's group successfully doped boron and nitrogen atoms into a helicene framework at the *para*-position, forming B- π -B and N- π -N patterns around the central benzene ring²⁹ (Fig. 7b). This modification imparted unique physico-



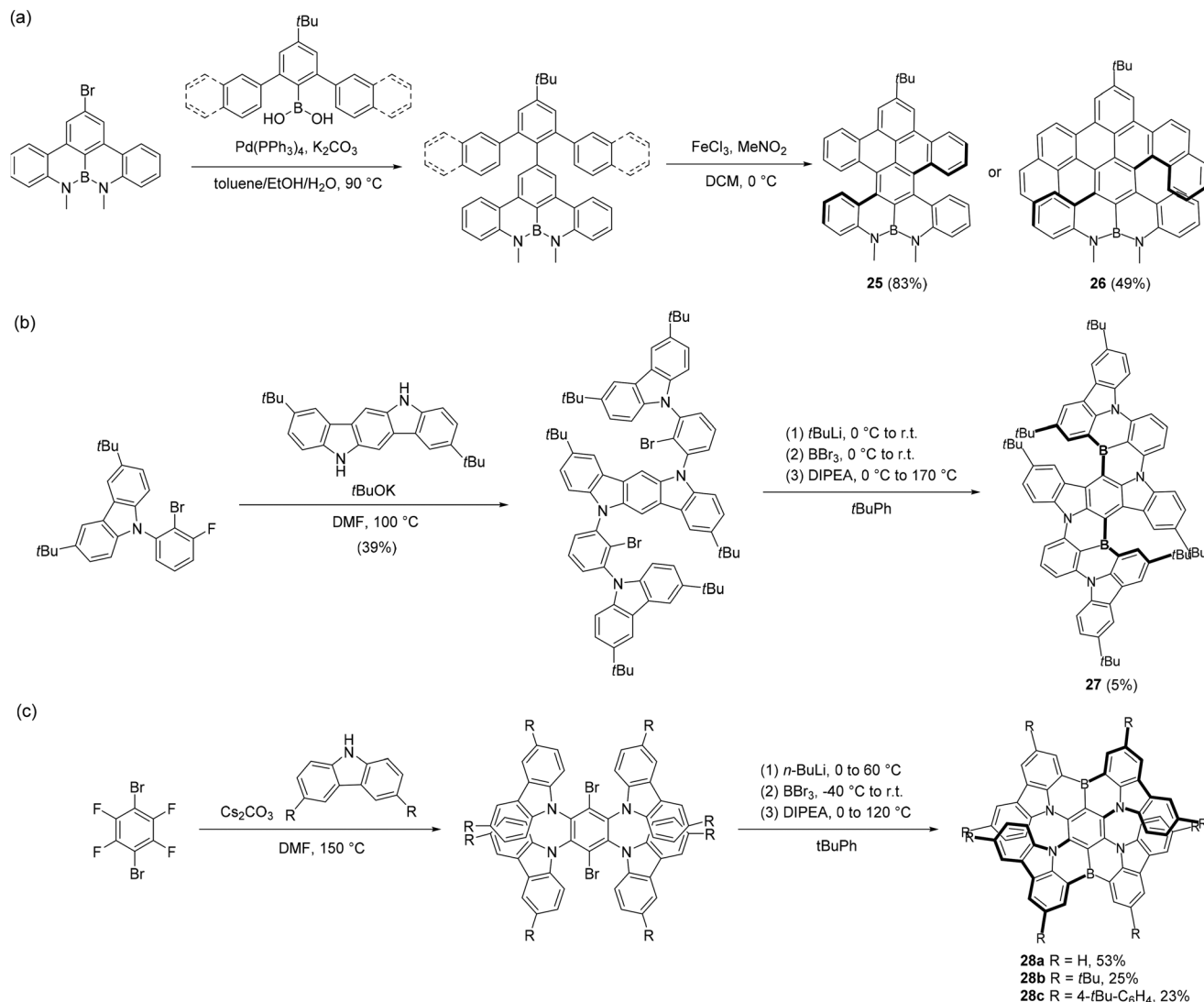


Fig. 7 Synthetic routes to X-shaped B,N-embedded double heterohelices.

chemical properties to the boron–nitrogen-doped helicenes. The team initially used carbazole derivatives and indolocarbazole as starting materials, achieving 39% yield of an intermediate *via* nucleophilic substitution. Then, boron nitrogen doped double [6]helicene **27** was obtained by lithium chloride exchange and electrophilic boron acylation, in 5% yield.

In 2021, Wang's group synthesized three B,N-embedded double hetero[7]helicenes with X-type structures³⁰ (Fig. 7c). The starting material was 1,4-dibromo-2,3,5,6-tetrafluorobenzene, which underwent aromatic nucleophilic substitution reactions with carbazole and its derivatives to yield the corresponding intermediates. Subsequently, by lithium-halogen exchange and electrophilic boration reactions, a “one-pot method” was employed to efficiently incorporate non-bonded boron and nitrogen atoms into the helical skeleton, producing the B,N-embedded double hetero[7]helicenes **28a**, **28b**, and **28c** in 53%, 25%, and 23% yields, respectively. Single-crystal X-ray diffraction analysis revealed that **28b** has a unique

double-helix structure with overlapping aromatic rings at the termini. The multiple resonance effects induced by the non-bonded boron and nitrogen atoms in the compounds lead to orbital separation, which is beneficial for improving the absorption asymmetry factor of this type of helicene. This compound demonstrates excellent chiral optical properties, underscoring the significant research value of X-type double helicenes in structural studies.

In 2023, Duan's group synthesized a B,N-doped double helicene with pure red emission featuring an X-shaped crossed topology³¹ (Fig. 8a). The synthetic route for B–N bond-embedded hetero-[*n*]helicene **29** involves three reaction steps: starting with nucleophilic substitution, followed by a Suzuki–Miyaura coupling reaction, and culminating in a one-pot borylation/cyclization reaction that delivered the target compound in 45% yield. Substantial steric hindrance between benzene rings induced the formation of a double-helical motif comprising [6]-helicene and [7]-helicene units, with fusion occurring



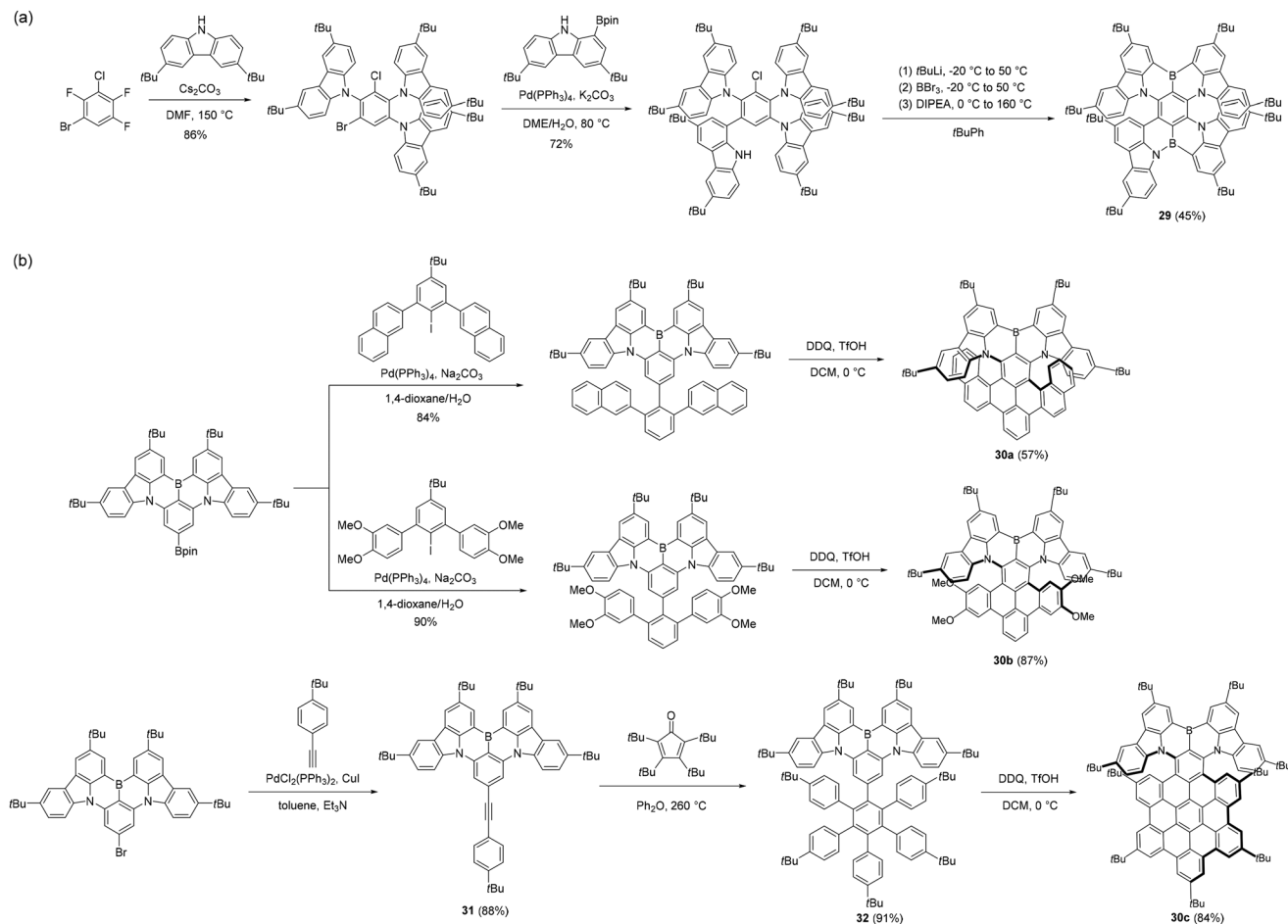


Fig. 8 Synthetic routes to X-shaped B,N-embedded heterohelices.

at the benzene hubs to construct the X-shaped crossed architecture. This strategy, achieved through modification of the **28b** scaffold to incorporate a B–N covalent bond, effectively reduced the electron-withdrawing strength of the boron atom and the electron-donating strength of the *para*-positioned nitrogen atom, ultimately yielding the exclusively red-emitting double helicene compound.

In 2024, Tan's group reported their work on the synthesis of B,N-doped nanographenes³² (Fig. 8b). With *DtBuCzB-Bpin* as the starting material, the double helicenes **30a** and **30b** were synthesized in 57% and 87% yields, respectively, by Suzuki coupling followed by a Scholl reaction. For product **30c**, the precursor **31** was obtained in 88% yield *via* Sonogashira coupling between BN-Br and 4-*tert*-butylphenylacetylene. Subsequently, Diels–Alder cycloaddition between **31** and 2,3,4,5-tetraarylcyclopenta-2,4-dien-1-one afforded precursor **32** in 91% yield. Treatment of **32** with DDQ and TfOH at 0 °C for 0.5 hours gave double [6]helicene **30c** featuring a hexabenzocoronene structure in 84% yield.

The oxidative cyclization of triphenyl-type precursors *via* Scholl reactions has become a powerful method for constructing X-shaped double helicenes. In 2019, Narita and colleagues

synthesized π -extended X-shaped double helicenes fused with pyrene units³³ (Fig. 9a). The synthesis began with tetrabromoterphenyl, which underwent Suzuki cross-coupling with 2-pyrenylboronic ester, yielding **33** in 85% yield. A subsequent Scholl reaction mediated by DDQ produced the target double [7]helicene **34** in 10% yield. Single-crystal X-ray analysis revealed significant helical overlap at the molecule's termini, along with pronounced intramolecular and intermolecular π – π interactions due to extended π -conjugation. In 2020, Hu's group synthesized furan-incorporated oxa-double[7]helicenes³⁴ (Fig. 9b). Using a similar approach, they substituted boronic acid with benzofuran derivatives, achieving intermediate **35** in 87% yield. Subsequent oxidative annulation yielded the X-shaped double [7]helicene **36** in 34% yield. **36** displayed stable twisted conformations at both helical ends.

In 2024, Dou and colleagues synthesized two boron-doped X-shaped double[6]helicenes³⁵ (Fig. 9c). They employed Suzuki coupling of boron-containing units with a triphenyl-derived diboronate precursor, achieving the helicene precursors **37a** and **37b** in 62% and 10% yields, respectively. Precursor **37a** underwent stepwise Scholl oxidation to produce the X-shaped double [6]helicene **38a** in 6% overall yield, while precursor **37b**



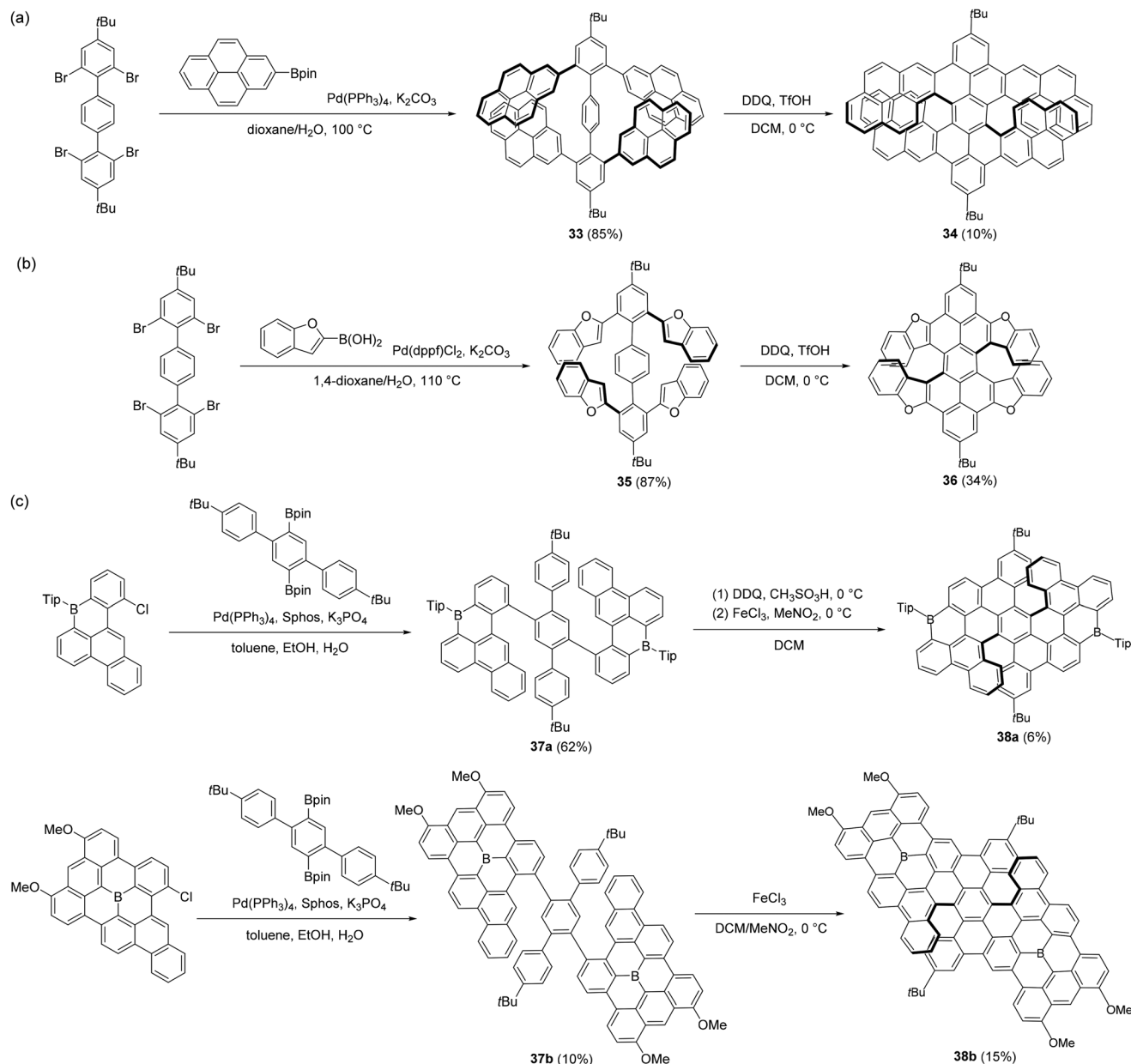


Fig. 9 Synthetic routes to X-type double helicenes using triphenyl compounds as precursors.

was subjected to one-pot Scholl cyclization, yielding the target compound **38b** in 15% yield. Detailed analyses revealed that boron induces delocalized electronic structures within the polycyclic π -system, allowing for tunable photophysical properties in both ground and excited states.

Perylene diimides (PDIs) have attracted considerable interest in organic optoelectronics due to their exceptional properties, including high charge carrier mobility, strong electron affinity, air stability, and versatile molecular design. Incorporating PDI as the aryl core in helicenes to create cross-conjugated helicene compounds is therefore of substantial research interest. In 2018, Wang's group synthesized double helicenes with thiophene heterocycles and a PDI core³⁶ (Fig. 10a). From the *ortho*-functionaliz-

ing PDI, they achieved tetrabromo-substituted intermediates **39a** and **39b** in 62% and 45% yields, respectively. Subsequent alkyne coupling and four-fold thiophene annulation produced the X-shaped double [5]helicenes **41a** and **41b**, which were then converted to products **42a** and **42b** via a desilylation reaction using Nu₄NF. In 2021, Lin's group introduced a skeleton-fusion strategy, constructing *ortho*- π -extended PDI-based double-[7]heterohelicenes by integrating a twisted PDI core with four fused heteroaromatic rings³⁷ (Fig. 10b). Using tetraiodo-substituted PDI as the substrate, intermediate **43** was obtained via aromatic nucleophilic substitution in 81% yield. Subsequently, a palladium-catalyzed intramolecular C–H activation reaction furnished the tetraindole-fused PDI double helicene in 51% yield.



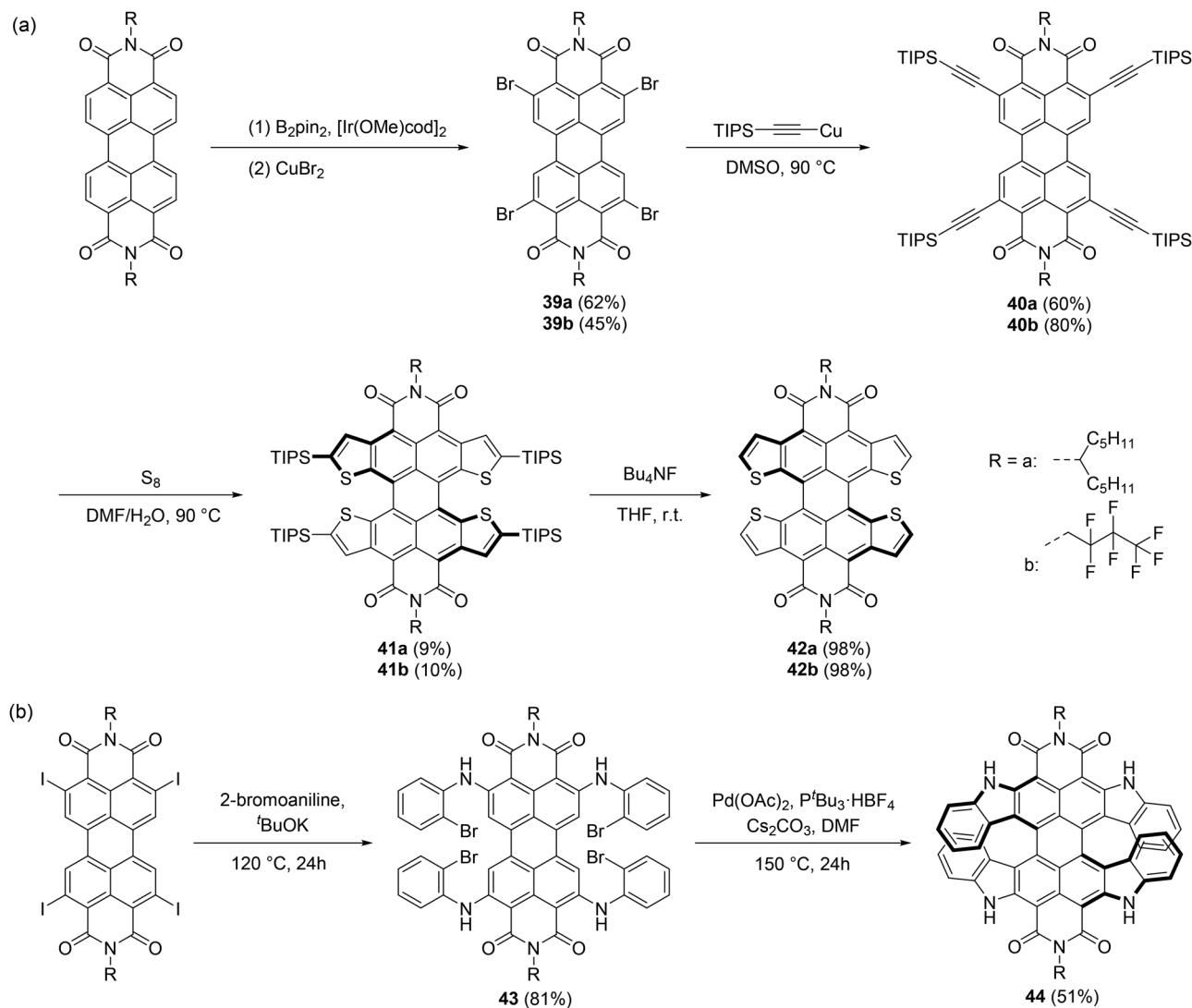


Fig. 10 Synthetic routes to X-type double helicenes with PDI as the core.

Utilizing perylene as the core is an effective strategy for synthesizing twisted nanographenes. In 2022, Qiu's group reported two π -extended chiral nanographenes featuring 29 benzene rings and two helical gaps³⁸ (Fig. 11a). Consequently, a highly congested perylene-core twisted graphene precursor was synthesized *via* Suzuki coupling between a perylene compound with four boronate ester groups and aryl iodides. Subsequent oxidative cyclization under Scholl reaction conditions showed that the highly strained precursor favored rearrangement to alleviate internal strain, resulting in two cross-shaped double helicene structural isomers **44a** and **44b** in a 5 : 2 ratio in a total yield of 53%. In 2023, Wang's group synthesized a double [6]helicene-type chiral nanographene using a similar synthetic strategy³⁹ (Fig. 11b). A Suzuki cross-coupling reaction yielded compound **45** in 88% yield. Subsequent cyclization at the *peri* position of perylene under standard Scholl reaction conditions (DDQ/TfOH) produced double [6]helicene **46** in 67% yield. Both the racemate and

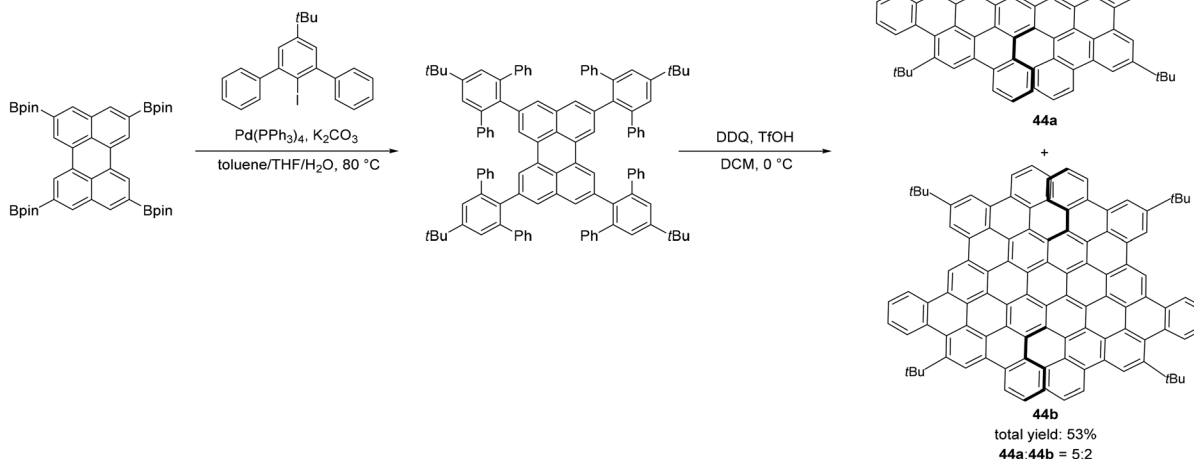
mesomer were detected, with a ^1H NMR-determined **46-*rac*** to **46-*meso*** ratio of 3 : 2. Notably, no cyclization at the bay positions of perylene or rearrangement products were observed, demonstrating the high regioselectivity of the Scholl reaction in this study.

4.2 Cross-linked triple helices

Helicene compounds featuring propeller-shaped triple helical structures were synthesized *via ortho*-annulation of three radially extending conjugated segments from a central benzene core. Steric interactions between adjacent units stabilize the triple helical topology.

In 2017, Watanabe *et al.* reported a method for synthesizing triple helicenes using triphosphonates and 2-naphthalaldehyde derivatives as precursors⁴⁰ (Fig. 12a). Through Arbuzov reactions, they synthesized the trialkenyl-substituted triple helixene precursors **47a** and **47b** in 48% and 87% yields, respectively. Photocyclization of the methoxy-containing pre-

(a)



(b)

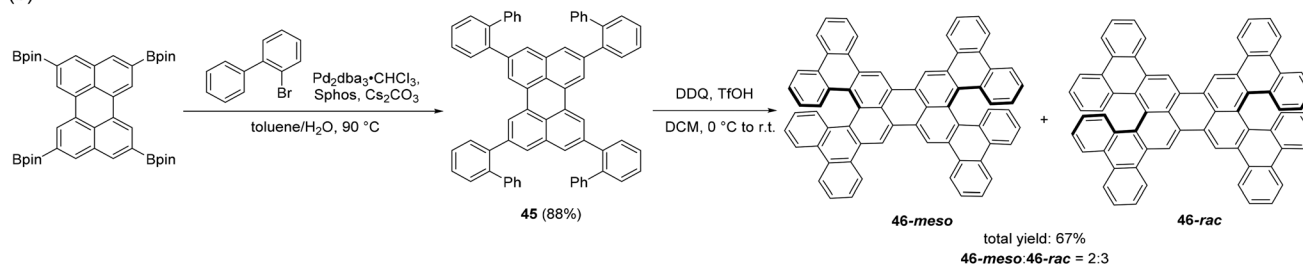


Fig. 11 Synthetic routes to X-type double helicenes with perylene as the core.

cursor **47a** via an eliminative pathway under a 450 W high-pressure mercury lamp produced the triple [5]helicene **48** in 37% yield. In contrast, the non-methoxy analogue underwent oxidative photocyclization, yielding the same product in 63% yield.

In 2018, Itami's group⁴¹ synthesized a C₃-symmetric, propeller-shaped triple [4]helicene with three heptagonal rings through a two-step process (Fig. 12b). The initial Suzuki coupling yielded precursor **49** in 68% yield, followed by a palladium-catalyzed intramolecular C–H arylation to achieve construction of the triple [4]helicene **50**. The reaction favored the formation of a heptacyclic system over the expected hexacyclic triple [6]helicene, likely due to steric repulsion among [6]helicene subunits in the intermediate. Computational analysis indicated that the incorporation of heptagonal rings significantly stabilized the helicity of the [4]helicene system.

In 2022, Zhang's team introduced two novel π -extended triple [5]helicenes⁴² (Fig. 12c). Their synthetic process involves precursor assembly, followed by nickel-mediated [2 + 2 + 2] cyclotrimerization, affording intermediates **51a** and **51b** in 70% and 60% yields, respectively. Then, a Scholl oxidative coupling reaction was carried out with FeCl₃ to generate the triple helicenes **52a** and **52b** in 60% and 70% yields, respec-

tively. Spectroscopic analysis, single-crystal X-ray diffraction, and DFT calculations verified the C₁-symmetric conformation in the crystalline state. In 2023, Liu *et al.* synthesized the triple helicene **53** using a one-pot sequence of Suzuki coupling and Knoevenagel condensation, achieving 26% yield⁴³ (Fig. 12d). Subsequent nitration with NOBF₄ produced the C₃-symmetric **54** in 40% yield. Notably, **54** formed hierarchical (PPP·PPM·MMP·MMM) tetrameric stacks in the solid state, exemplifying a rare social self-sorting behavior. This study establishes fundamental structure–property relationships in fused polycyclic helicene systems.

Synthesizing heterocyclic-containing triple helicenes remains a significant challenge. In 2021, You's group reported the synthesis of a furan-based triple oxa[7]helicene⁴⁴ (Fig. 13a). The process began with brominated benzofuran preparation, followed by alkynylation with propiolic acid to yield a diarylacetylene substrate. A subsequent [2 + 2 + 2] cyclotrimerization, catalyzed by octacarbonyldicobalt, produced the hexaarylbenzene precursor **55** in 56% yield. Finally, intramolecular cyclization using FeCl₃ and DDQ at 60 °C afforded the triple oxa[7]helicene **56** in 49% yield. Compared to previously reported double oxa[7]helicenes, the triple oxa[7]helicene showed both theoretical and experimental improvements in the lumine-



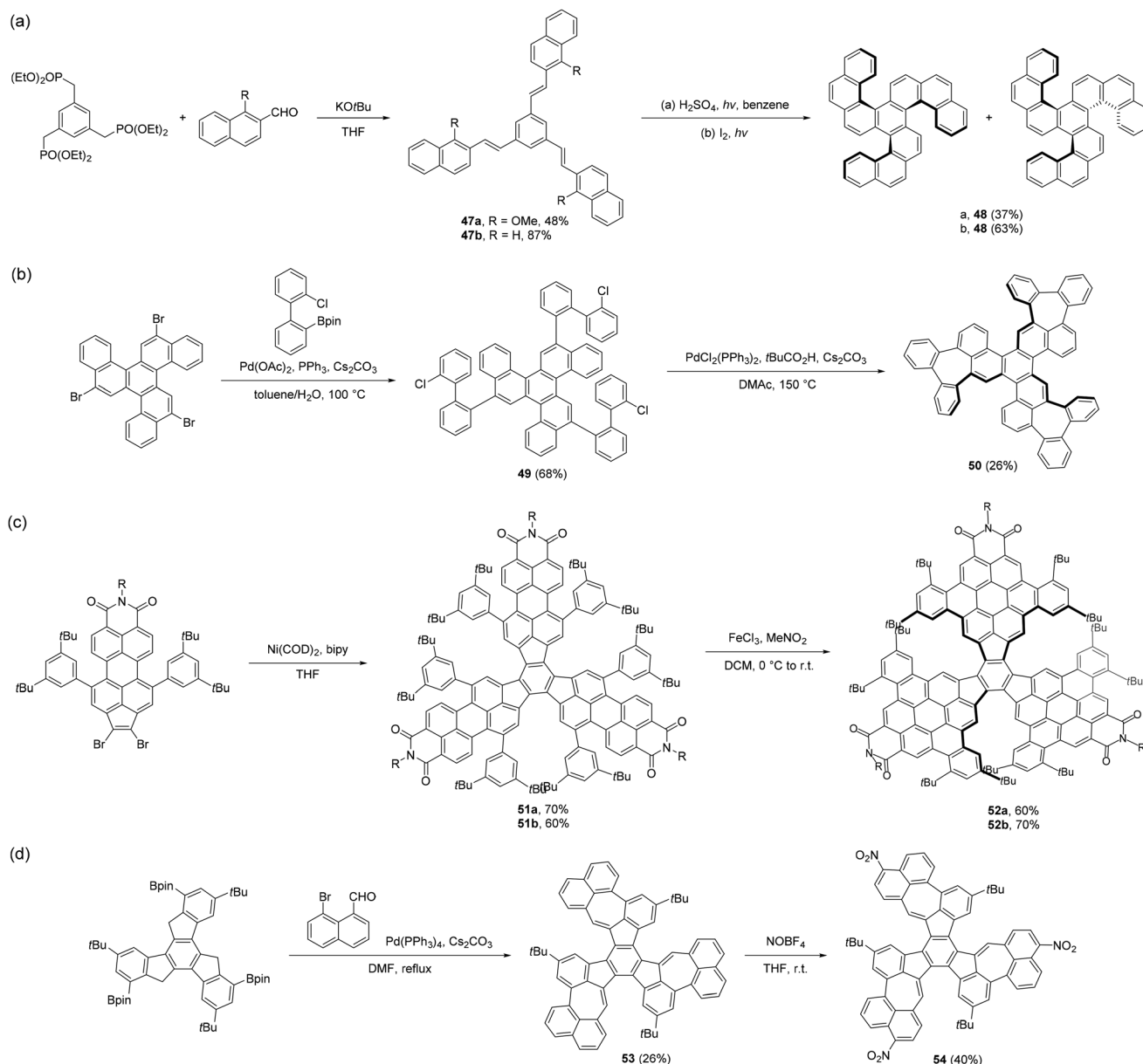


Fig. 12 Synthetic routes to cross-linked triple helicenes.

science dissymmetry factor, indicating that increasing helicene subunits could enhance the luminescence dissymmetry factor of heterohelicenes.

In 2022, Hu's group synthesized and characterized the first C3-symmetric triple oxa[6]helicene⁴⁵ (Fig. 13b). The synthesis of 57 involved two steps. Initially, a triple Suzuki–Miyaura coupling produced intermediate 58 in 75% yield. Then, in the presence of DDQ, the Scholl reaction was carried out in dichloromethane and trifluoromethanesulfonic acid (TfOH) to obtain the triple helicene 57 in 34% yield. Compared to the D3-symmetric triple oxa[7]helicene 56, the C3-symmetric variant showed parallel electric and magnetic transition dipole moments, enhancing luminescence dissymmetry and highlighting the importance of molecular symmetry in chiral

responses. Additionally, the synthesis of sulfur- and selenium-containing propeller-shaped triple helicenes has also been documented. In 2022, Wang's group⁴⁶ reported an efficient synthesis of four thiophene/selenophene-based triple[6]helicenes (Fig. 13c). The crucial step was the oxidative photocyclization of intermediates 61a–d in anhydrous toluene with iodine, producing the target propeller-shaped triple[6]helicenes 62a–d in 8–35% yields. Replacing sulfur with selenium in the molecular framework altered the racemic triple[6]helicenes' crystal packing due to the changes in intermolecular interactions. Spectroscopic and physicochemical analyses revealed that selenium substitution precisely modulates their luminescence property and molecular energy levels.



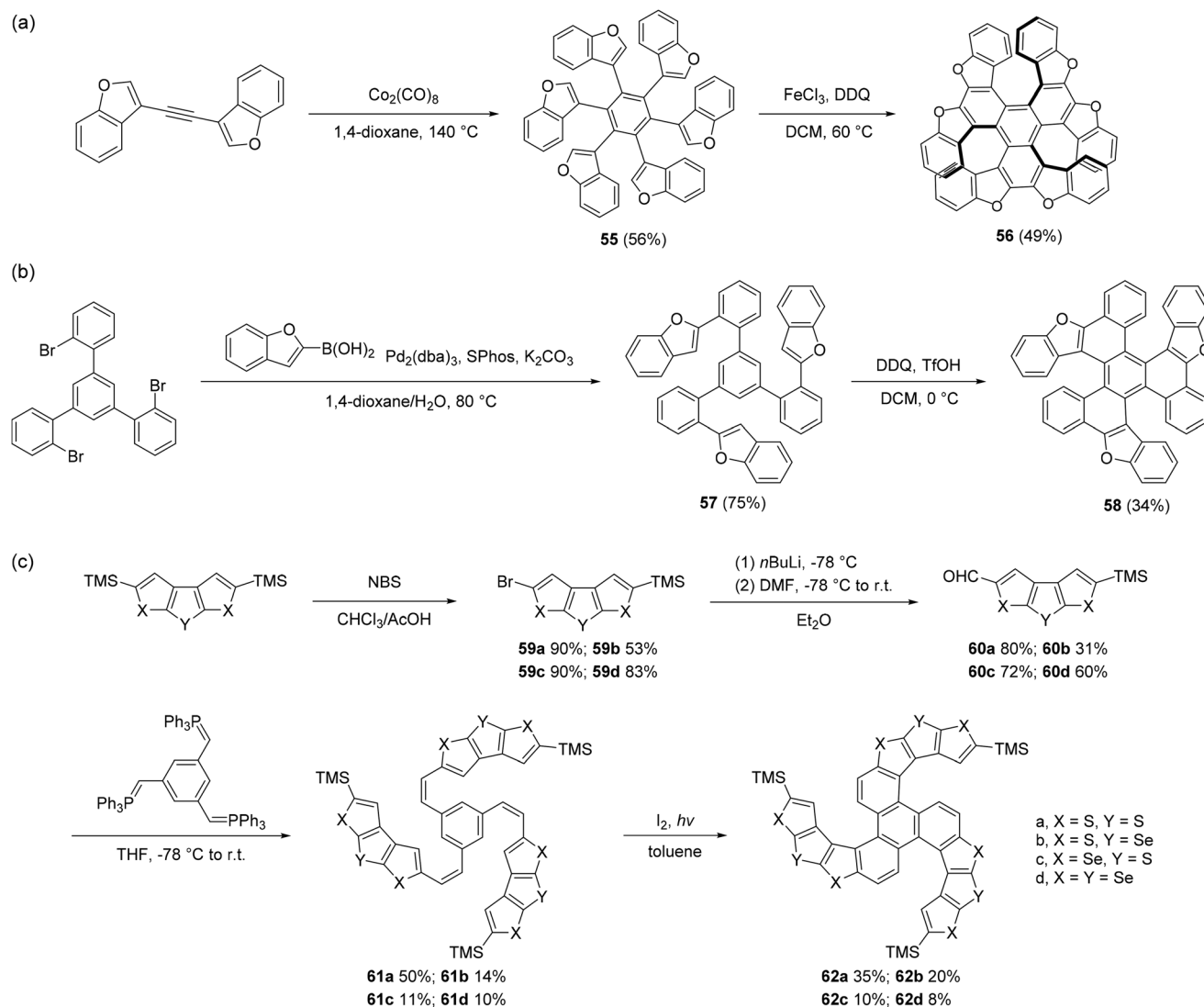


Fig. 13 Synthetic routes to heterocyclic-containing cross-linked triple helices.

4.3 Cross-linked quintuple helices

Corannulene, as the smallest fragment of C_{60} , exhibits unique properties due to its bowl-shaped geometry and distinctive dynamic behavior, making it highly significant for constructing crossed, fan-shaped multiple helices. In 2018, Itami's group reported the synthesis of the first quintuple helix centered on corannulene⁴⁷ (Fig. 14a). Starting from pentaboronate-substituted corannulene, the target compound **63** was obtained in 76% yield *via* five Suzuki–Miyaura coupling reactions with 2-bromo-2'-chlorobiphenyl. Subsequently, in the presence of $\text{PdCl}_2(\text{PCy}_3)_2$ and DBU, **63** in DMAc solution was stirred at 140 °C for 3 days, resulting in the quintuple [6]helicene **64** in 10% yield.

Similarly, in 2019, using perylene diimide as a component, Wang and colleagues⁴⁸ synthesized a new cross-linked quintuple [6]helicene **66** featuring a nonplanar graphenoid structure (Fig. 14b). The synthesis of compound **66**

involved two key steps: first, a Suzuki–Miyaura coupling afforded the corannulene-core precursor **65** in 60% yield; subsequently, a photocyclization reaction afforded the target product **66** in 62% yield. Theoretically, **66** possesses eight possible stereoisomers. However, ^1H NMR analysis indicated that the photocyclization reaction produced two major diastereomers: (*P,P,P,P,P*)-**66** with D_6 symmetry and (*P,P,P,P,M*)-**66** with C_2 symmetry.

In 2024, Zhang and colleagues⁴⁹ adopted an alternative substrate strategy to synthesize two corannulene-centered quintuple helices (Fig. 14c). Using pentaiodocorannulene as the starting material, two types of aryl olefins underwent five Heck reactions, yielding two quintuple helixene precursors **67a** and **67b** in 26% and 38% yields, respectively. Under Mallory reaction conditions, these precursors were converted to the corresponding quintuple [6]helices **68a-1** and **68a-2** and the [7] helixene **68b**. Notably, **68b** is the highest reported helixene based on corannulene. X-ray crystallographic analysis revealed



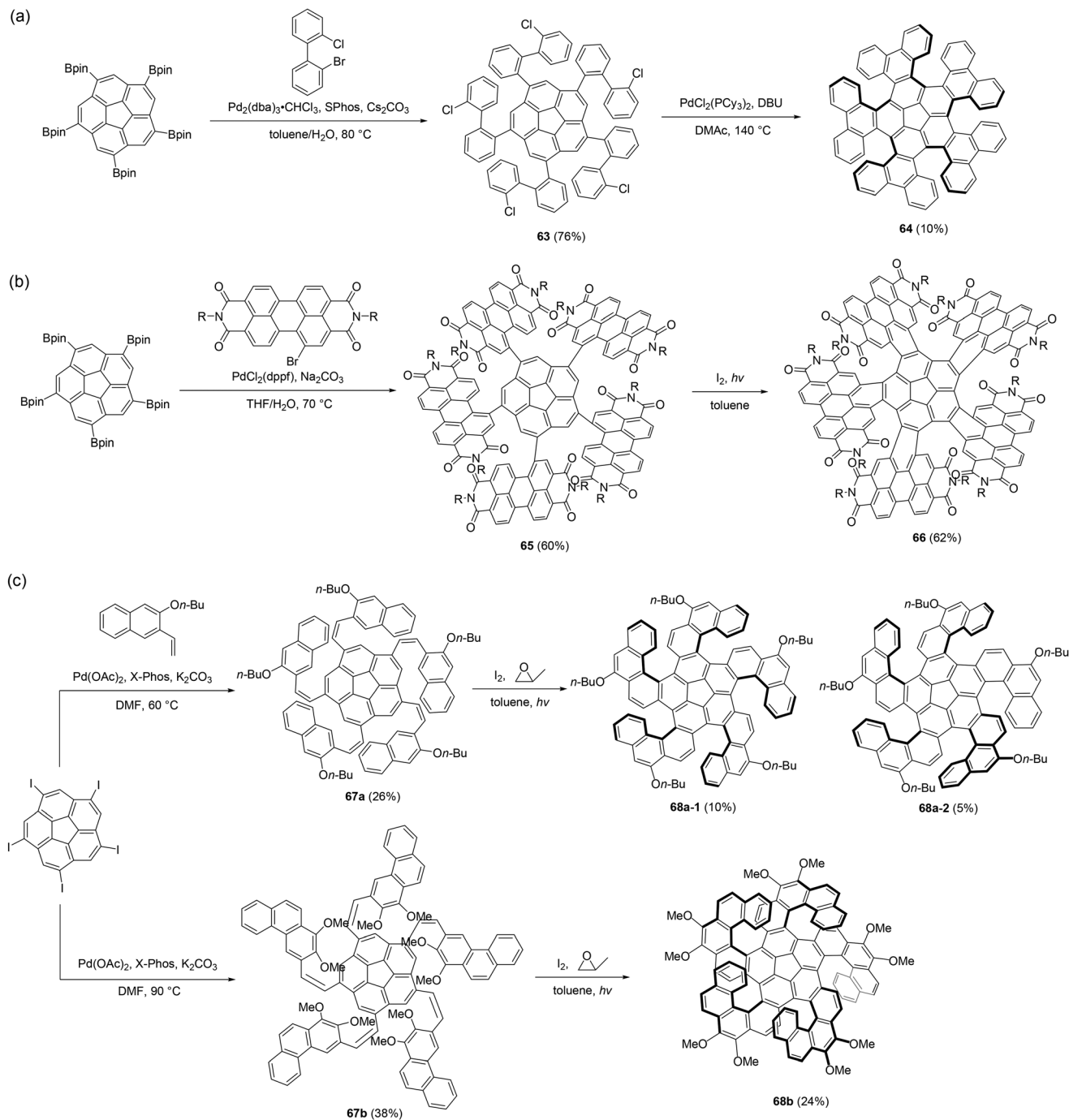


Fig. 14 Synthetic routes to cross-linked quintuple helicenes with corannulene as the core.

that **68a-1** adopts a propeller-like conformation with an intact corannulene core, whereas **68a-2** and **68b** exhibit quasi-propeller conformations.

Similar to corannulene, azabuckybowl also possesses a rigid bowl-shaped structure. Due to the unique photophysical properties arising from nitrogen atom doping in multiple helicene frameworks, the synthesis of cross-conjugated multiple helicenes with an azabuckybowl as the core has been reported

in recent years. In 2022, Zheng and coworkers⁵⁰ reported the first synthesis of a quintuple helicene centered on an azabuckybowl (Fig. 15a). Thus, **71** was synthesized from an azabuckybowl *via* a three-step reaction sequence. Initially, an iridium-catalyzed borylation reaction between the azabuckybowl compound and Bpin₂ afforded the pentaborylated precursor **69** in 75% yield. Subsequently, five consecutive Suzuki–Miyaura coupling reactions yielded precursor **70** in 52% yield. Finally, a

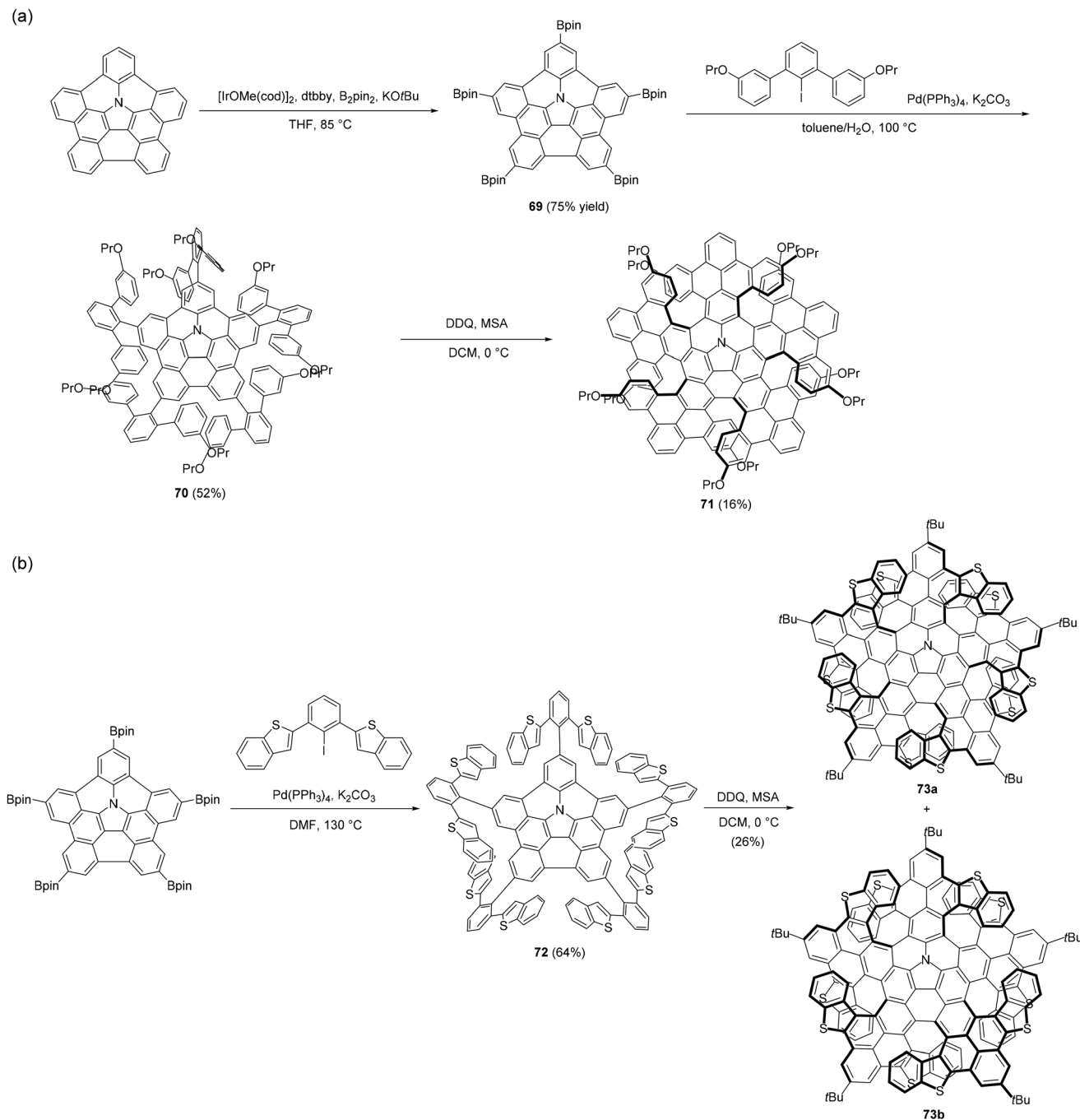


Fig. 15 Synthetic routes to cross-linked quintuple helicenes with azabuckybowl as the core.

Scholl reaction mediated by DDQ and methanesulfonic acid (MSA) produced the target quintuple [7]helicene **71** in 16% yield. It was found that **71** exhibits excellent photophysical properties and inherent chirality, indicating that nitrogen-embedded azacorannulene can serve as an outstanding nitrogen-doped core for constructing novel multiple helicenes with broad application potential. By using a similar synthetic strategy, in 2022, they⁵¹ obtained two conformational isomers of a quintuple [9]helicene centered on an azabuckybowl by introdu-

cing thiophene, representing the highest hetero-helicene reported in the field of multiple [*n*]helicenes (Fig. 15b). X-ray crystal structure showed that the quintuple [9]helicene includes not only the propeller-shaped conformational isomer **73a** but also an unforeseen quasi-propeller-shaped conformational isomer **73b**. This is the first time that different conformational isomers have been observed in high-order multiple helicenes (*n* > 8), which might be caused by the doping of heteroatomic sulfur in the helical skeleton.



4.4 Cross-linked hexapole helicenes

Hexabenzocoronene (HBC) is the smallest planar nanographene fragment, and its incorporation as a central motif in the synthesis of cross-shaped multiple helicene-type twisted nanographenes has been increasingly reported in recent years. The synthesis of such compounds primarily involves Co-catalyzed bis(aryl)acetylene [2 + 2 + 2] cycloaddition to construct precur-

sors, followed by oxidative cyclization. In 2018, Wang *et al.*⁵² reported the synthesis of cross-linked hexapole [7]helicenes with an HBC core (Fig. 16a). The synthetic route for obtaining **75a** and **75b** comprises two key steps: first, a $\text{Co}_2(\text{CO})_8$ -catalyzed [2 + 2 + 2] cycloaddition to build two precursors consisting of 25 benzene rings organized on a hexaphenylbenzene (HPB) scaffold; second, a Scholl reaction of the precursor in

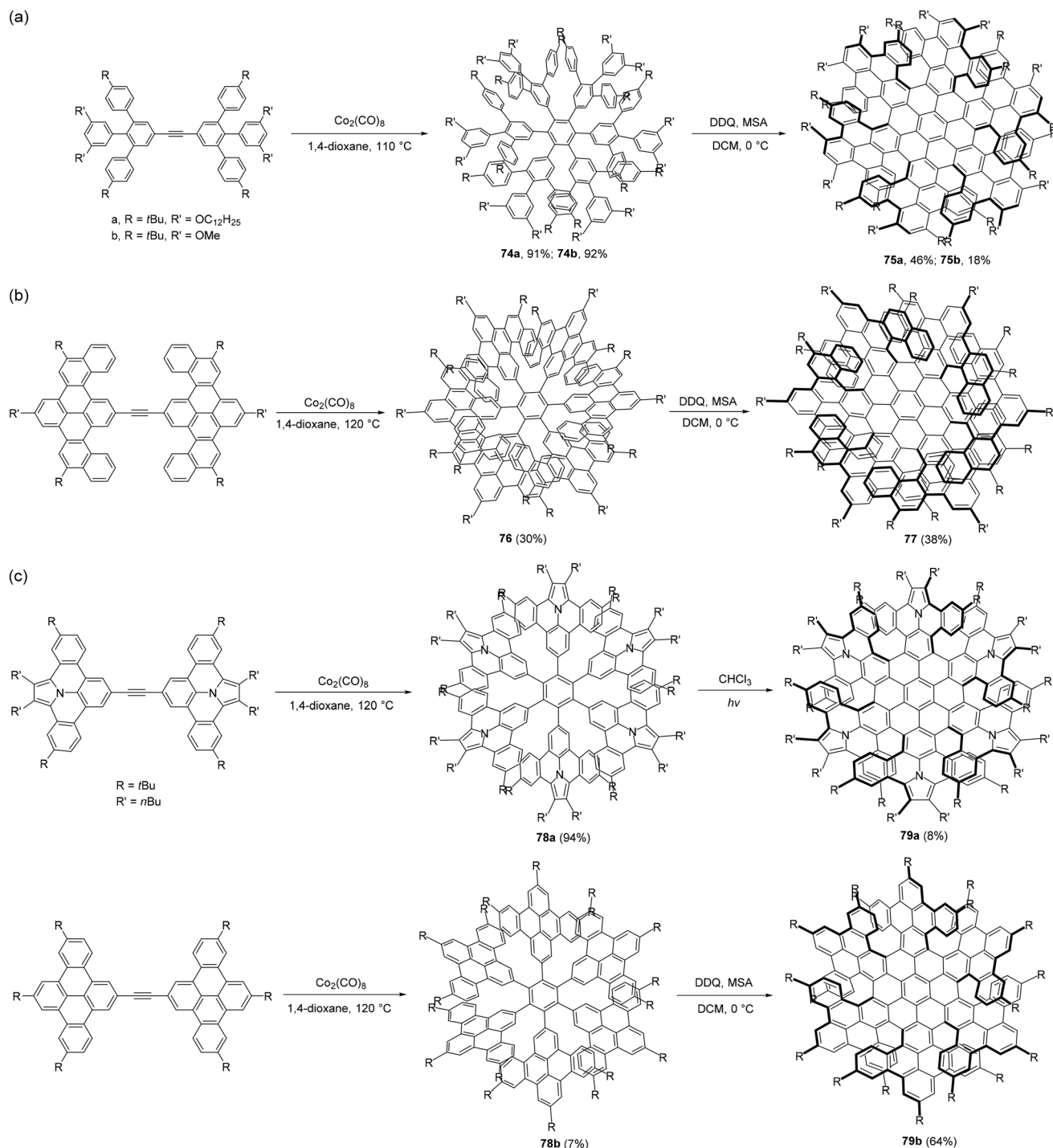


Fig. 16 Synthetic routes to cross-linked hexapole helicenes with hexabenzocoronene as the core.



the presence of MSA and DDQ, yielding **75a** in 46% yield and **75b** in 16% yield. X-ray crystallography revealed that **75a** adopts a propeller-shaped geometry, with six blades fused to the HBC core, each uniformly tilted.

Following a similar synthetic strategy, Wang's group reported a series of hexapole helicene compounds with propeller-shaped structures.⁵³ As shown in Fig. 16b, by using dinaphthopyrene (DPN) as the terminal arylacetylene units, a Co-catalyzed [2 + 2 + 2] trimerization afforded precursor **76** bearing six DPN fragments. Subsequent oxidative cyclization *via* a Scholl reaction yielded the hexapole [9]helicene **77** in 38% yield, representing the highest-order all-carbon multiple helicene reported to date. Single-crystal analysis showed that the six DPN blades are uniformly tilted, with an average dihedral angle (DA) of $\sim 32^\circ$. Due to severe steric repulsion between the crowded blades, the six aryl fragments at the periphery of the HBC core exhibit significant distortion, with an average non-planarity value of 0.128 Å. Furthermore, nitrogen-doped hexapole [7]helicenes were successfully synthesized by

employing nitrogen-containing aryl fragments as terminal arylacetylene units⁵⁴ (Fig. 16c). When precursors containing nitrogen moieties and their all-carbon analogs were subjected to Co-catalyzed trimerization, two helicene precursors **78a** and **78b** were obtained in 94% and 7% yields, respectively. However, the subsequent oxidative cyclization conditions differed. For precursor **78a**, photocyclization in CHCl_3 solution afforded the target compound **79a** in only 8% yield, whereas the other precursor **78b** underwent a traditional Scholl reaction, yielding the target molecule **79b** in 64% yield. Both products exhibited a propeller-shaped geometry with similar crystallographic parameters.

To further expand the π -conjugated system of such hexapole helicenes, Wang *et al.* reported the synthesis of π -extended hexapole [7]helicenes in 2019⁵⁵ (Fig. 17). The synthetic route involved two key steps: first, sixfold Diels–Alder addition between compound **80** and cyclohexenone to afford **81** containing six HPB units; second, a stepwise Scholl reaction by treatment with DDQ and TfOH at 0 °C for 1.5 hours to form an

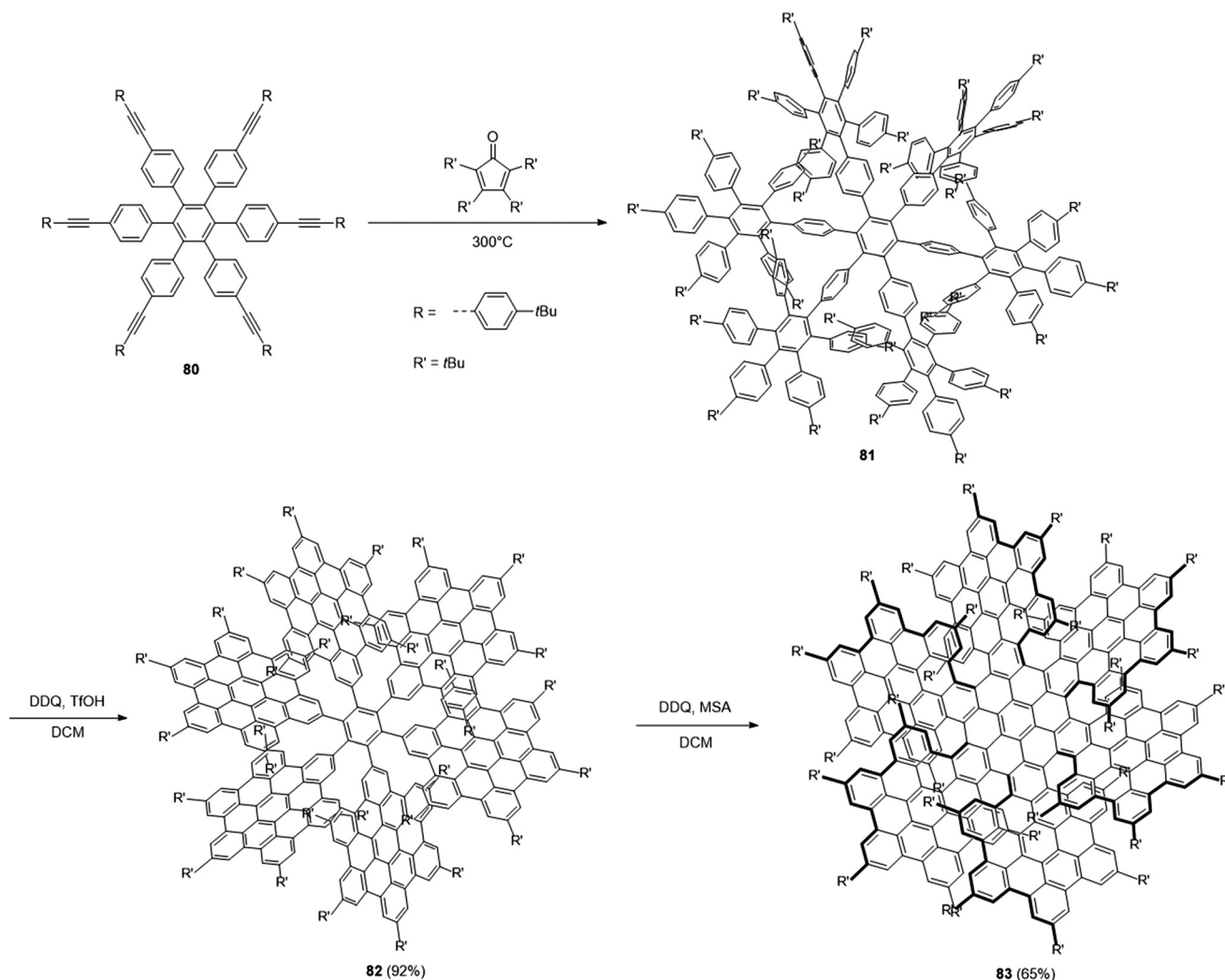


Fig. 17 Synthetic routes to π -expanded cross-linked hexapole helicenes.



intermediate **82** in 92% yield, followed by a second Scholl reaction in the presence of DDQ and MSA to form the central HBC core, yielding the hexapole [7]helicene **83** in 65% yield. The regioselectivity of the Scholl reactions was attributed to the *tert*-butyl substituents on the peripheral HBC fragments, which lowered the oxidation potential and facilitated the cyclization.

5 Conclusions and outlook

In summary, multiple helicenes represent a fascinating class of chiral polycyclic compounds with diverse and complex stereo-structures, emerging as promising candidates for advanced applications in chiral materials, optoelectronics, and molecular electronics. In this review, we proposed a concise and systematic classification of multiple helicenes into linear, cyclic, and cross-linked types, offering a structural framework to better understand their growing diversity. Based on this classification, we have systematically summarized the research progress in the synthesis methods of multiple helicenes with different stereo structures reported in recent years.

Looking ahead, the development of more general, modular, and stereoselective synthetic strategies will be crucial for accessing a broad range of multiple helicenes with various topologies and properties. In addition, a deeper understanding of relationships between structure and property, particularly how the topology influences chiroptical, electronic, and photo-physical behaviours, will be essential for rational molecular design. Furthermore, the integration of multiple helicenes into functional devices and supramolecular systems holds great promise for the development of advanced chiral materials.

We hope that this review will draw greater attention to the class of multiple helicenes and provide valuable guidance for their design and synthesis, thereby facilitating the development of novel molecules with diverse and unique properties and ultimately advancing not only the field of multiple helicenes but also the whole helicene chemistry.

Conflicts of interest

There are no conflicts to declare.

Data availability

No supporting data are included in this article.

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