



Review

Construction of axially chiral compounds *via* catalytic asymmetric radical reactionDong Liang^a, Wenjing Xiao^a, Sami Lakhdar^{b,*}, Jiarong Chen^{a,*}^a CCNU-uOttawa Joint Research Centre, Key Laboratory of Pesticides & Chemical Biology Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, China^b CNRS/Université Paul Sabatier, Laboratoire Hétérochimie Fondamentale et Appliquée, Toulouse 31062, France

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ABSTRACT

The chemistry of axially chiral compounds has emerged as a subject of increasing interest due to their widespread presence in natural products, bioactive molecules, advanced materials, and chiral ligands/catalysts. On the other hand, catalytic asymmetric radical-based transformations provide a complementary platform for the construction of enantiomerically enriched molecules that are in growing demand in the chemical and pharmaceutical industries. In recent years, considerable research efforts have been devoted to the development of catalytic asymmetric radical reactions for the construction of axially chiral compounds based on the unique reactivity modes of diverse radicals. In this review, we critically illustrate these recent achievements according to different radical precursors and catalytic activation modes. Wherever possible, special emphasis is also placed on the discussion of mechanistic features underlying these works and substrate scopes. This review should be of great interest to the experts in this area, but also serve as a helpful starting point for new researchers in this field.

1. Introduction

Molecular chirality is one of the most underlying elements for modern drug discovery as many mirror-image compounds may differ significantly in biological activity, pharmacodynamics, pharmacokinetics, and toxicity. Unlike central chirality (the central atom has different substituents), axial chirality, which refers to the stereoisomerism generated by the paired nonplanar arrangement of different groups around a chiral axis, including atropisomers, chiral allenes, spiranes, spiroindanes, etc, lacks a stereocenter but exists as an enantiomer (Fig. 1a) [1]. Due to their widespread appearance in many natural products, bioactive molecules, optically pure materials, and their wide applications as chiral ligands and organocatalysts in enantioselective catalysis (Fig. 1b), the significance of axially chiral compounds has been increasingly recognized and appreciated in many disciplines of sciences [2–7]. With the evolvement of asymmetric catalysis, a variety of transition metal-catalyzed and organocatalytic approaches have been developed for the construction of structurally diverse axially chiral compounds in an enantioselective manner [8–20]. Mechanistically, the vast majority of these catalytic methods rely on general ionic pathways. To enrich the pool of axially chiral compounds, it is still highly desirable to develop new, cost-effective, more efficient, and sustainable methods for their

construction.

Given the structural diversity and unique reactivity modes of radical species, radical-based transformations have enjoyed considerable development in organic synthesis over the past decades [21–23]. In contrast to the traditional ionic approaches, the construction of axial chirality based on radical pathways is far less developed mainly because of the lack of general methods for the generation of highly reactive radical intermediates and difficulty in the stereocontrol of radical reactions [24–31]. In recent years, with the devolvement of transition-metal catalysis, organocatalysis, and photocatalysis, remarkable advances have been made in the field of catalytic asymmetric radical reactions. These strategical developments have thus stimulated the invention of a range of radical-involved approaches for the assembly of axially chiral compounds that are often not easy to obtain by conventional ionic methods. These impressive advances opened up a new window for the application of enantioselective radical reactions, and provides a potentially new avenue for asymmetric construction of axially chiral compounds. Therefore, in this review, we will present the recent advances in radical-involved catalytic asymmetric construction of axially chiral compounds. Wherever possible, special emphasis is also placed on the discussion of reaction mechanisms and substrate scopes according to different radical precursors and catalytic activation modes.

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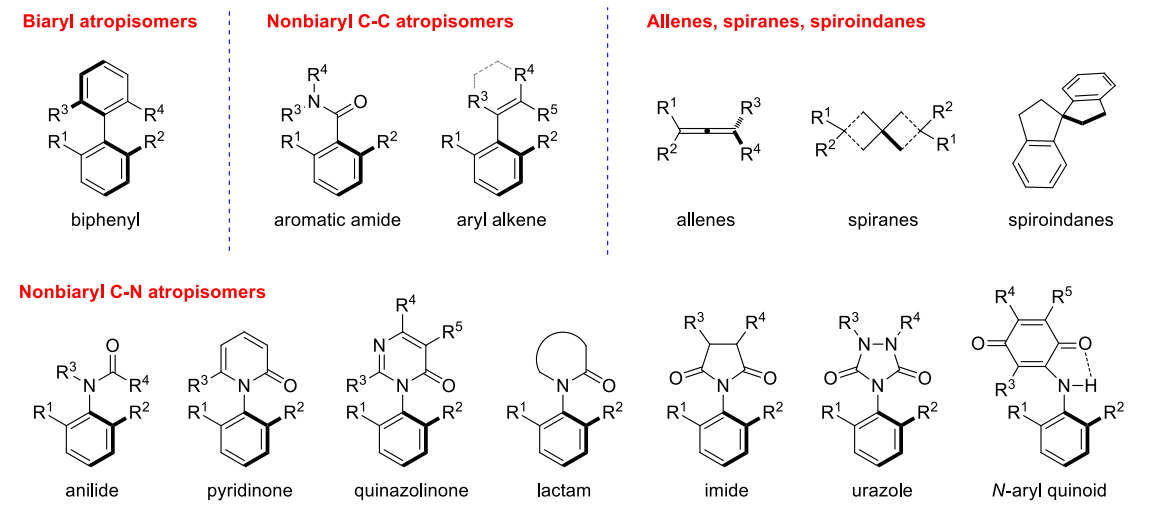
E-mail addresses: sami.lakhdar@univ-tlse3.fr (S. Lakhdar), chenjiarong@mail.ccnu.edu.cn (J. Chen).<https://doi.org/10.1016/j.gresc.2022.06.003>

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a) Various types of axially chiral molecules



b) Selected examples of axially chiral natural products, materials, ligands and organocatalysts

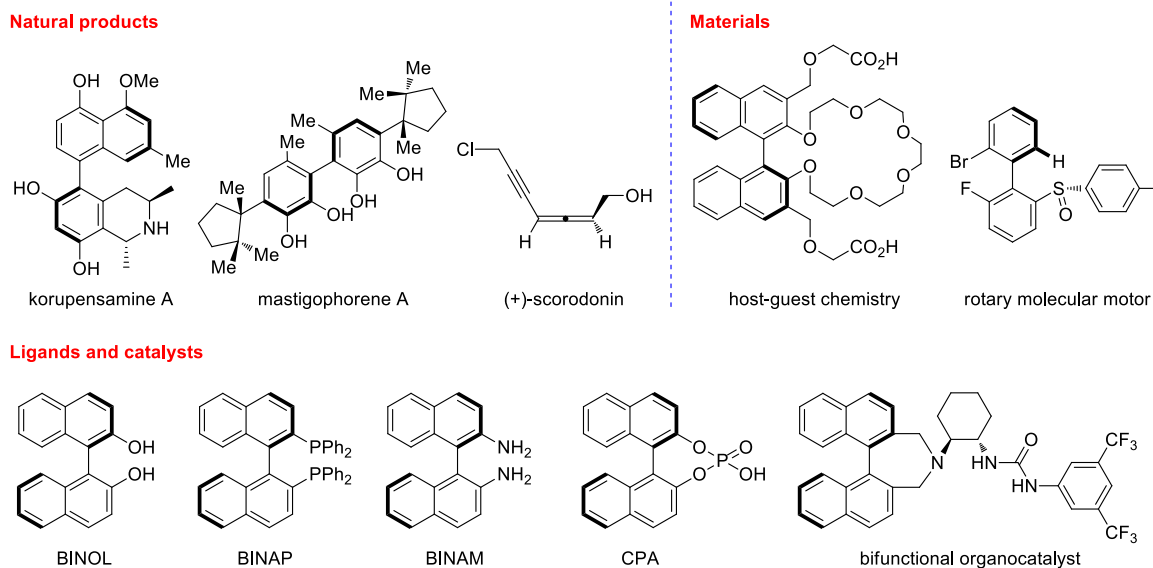


Fig. 1. Overview of axially chiral compounds.

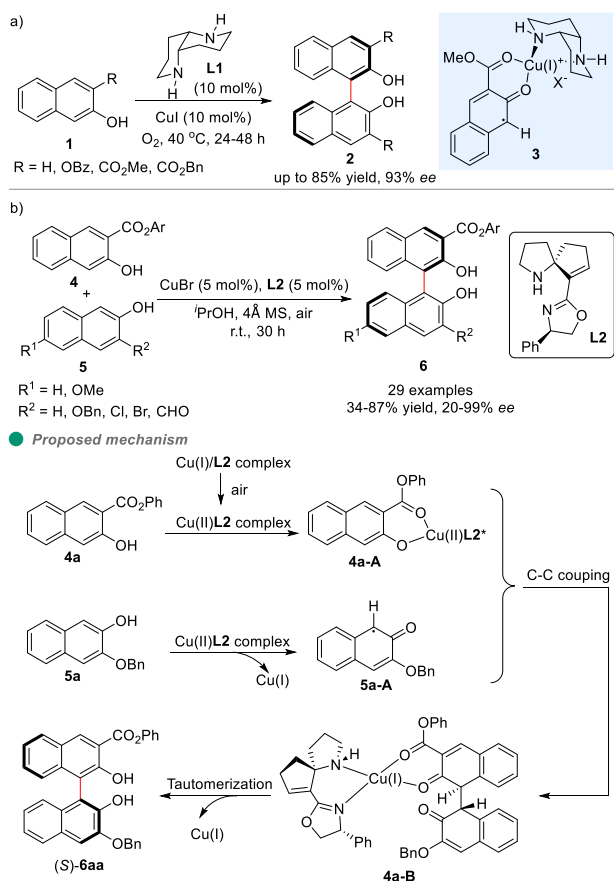
2. The catalytic asymmetric construction of atropisomers via radical pathways

Atropisomerism, arising from three-dimensional compounds with rotationally restricted σ -bond, constitute the most-represented subclass of axial chirality, and atropisomers can be divided into (hetero)biaryls atropisomers, nonbiaryl C-C atropisomers and nonbiaryl C-N atropisomers according to the different units linked at the ends of the shaft [32]. In contrast to well-developed ionic strategies, so far, only two types of atropisomers, (hetero)biaryls atropisomers and axially chiral styrenes, have been constructed through a radical pathway. Therefore, in this section, the radical-involved construction strategies for these two types of atropisomers are described according to different catalytic methods.

2.1. The catalytic asymmetric construction of (hetero)biaryl atropisomers via radical pathways

Optically pure 1,1'-bi-2-naphthols (BINOLs) and their derivatives as auxiliaries and ligands have been used in numerous enantioselective synthesis, especially exemplified by 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), BINOL-derived phosphoric acid, *etc.* [33–35].

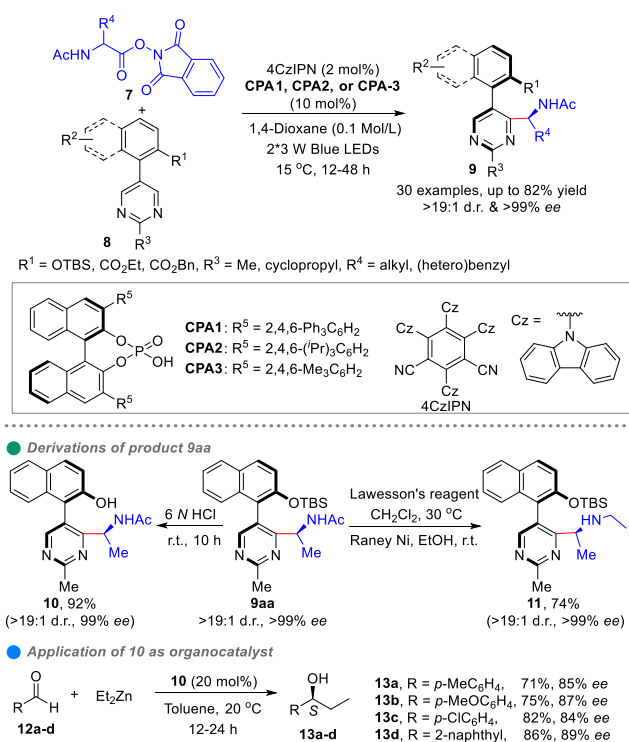
Undoubtedly, the direct catalytic asymmetric oxidative coupling of 2-naphthol derivatives is one of the most straightforward methods to access BINOLs in terms of reaction efficiency and step economy [36]. In 2001, the Kozłowski group reported an efficient copper-catalyzed enantioselective oxidative coupling of 2-naphthol derivatives **1** providing the biaryl product **2** in up to 93% *ee*, with chiral 1,5-diaza-*cis*-decalin **L1** as a ligand (Scheme 1a) [37]. The key to the success of this transformation is the generation of radical intermediate **3** possessing a Cu(I) tetrahedral coordination sphere through a SET process. Recently, Tu and co-workers developed a novel chiral 1,5-*N,N*-bidentate ligand based on the spirocyclic pyrrolidine oxazoline skeleton and with this ligand realized an interesting copper-catalyzed asymmetric aerobic oxidative cross-coupling reaction of 2-naphthols at ambient temperature (Scheme 1b) [38]. Notably, the catalytic system enabled the efficient preparation of a series of previously difficult-to-synthesize *C*₁-symmetric BINOL products **6** in generally good yields (up to 87%) with excellent enantioselectivity (up to 99% *ee*) by tuning the electronic effects of the substituents of 2-naphthol substrates. The mechanistic studies indicated that the Cu^I/L2 complex was oxidized in the presence of air, giving the Cu^{II}/L2 complex. Then, the Cu^{II}/L2 complex was coordinated to substrate **4a** to provide the intermediate **4a-A**. At the same time, the radical



Scheme 1. Catalytic asymmetric oxidative coupling of 2-naphthol.

species **5a-A** was obtained through SET oxidation from the Cu^{II}/L2 complex and substrate **5a**. Subsequently, the radical species **5a-A** underwent a radical-anion coupling process with intermediate **4a-A** to form intermediate **4a-B**. Finally, the chiral cross-coupling product (*S*)-**6aa** was afforded after tautomerization of intermediate **4a-B**. Except for copper catalysis, a series of strategies of chiral iron catalysis [39,40], and dinuclear vanadium catalysis [41] have also been developed for the enantioselective oxidative coupling reaction of 2-naphthol derivatives to prepare multi-substituted BINOLs with high optical purity.

Minisci reaction refers to the radical substitution reaction between nucleophilic carbon radicals and electron-deficient nitrogen-containing aromatic heterocycles, which was first reported in 1971 [42]. As it can directly introduce various substituents such as alkyl, aryl, acyl, trifluoromethyl, and hydroxymethyl into electron-deficient heterocycles, the Minisci reaction has been widely used in both medicinal and organic synthetic chemistry [43–47]. Very recently, the Xiao group reported a novel visible-light-induced Minisci reaction of α -amino acid-derived redox-active esters (REA) **7** and 5-aryl pyrimidines **8**, providing access to catalytic asymmetric construction of axially and centrally chiral heterobiaryls **9** (Scheme 2) [48]. This metal-free radical reaction shows broad substrate scope and good functional group tolerance, producing compounds **9** featuring the union of a centrally chiral α -branched amine and an axially chiral heterobiaryl with excellent regio-, diastereo- and enantioselectivity (up to 82% yield; >19:1 d.r.; >99% ee). It is noteworthy that the protecting group TBS of the product **9aa** could be easily removed in the presence of 6 mol/L HCl, and the *N*-acetylated moiety in the product **9aa** also could be smoothly converted into secondary amine by treatment with Lawesson's reagent and Raney-Ni reagent. More importantly, hydroxy-free compound **10** could serve as a new chiral protonic ligand to promote the catalytic asymmetric addition of

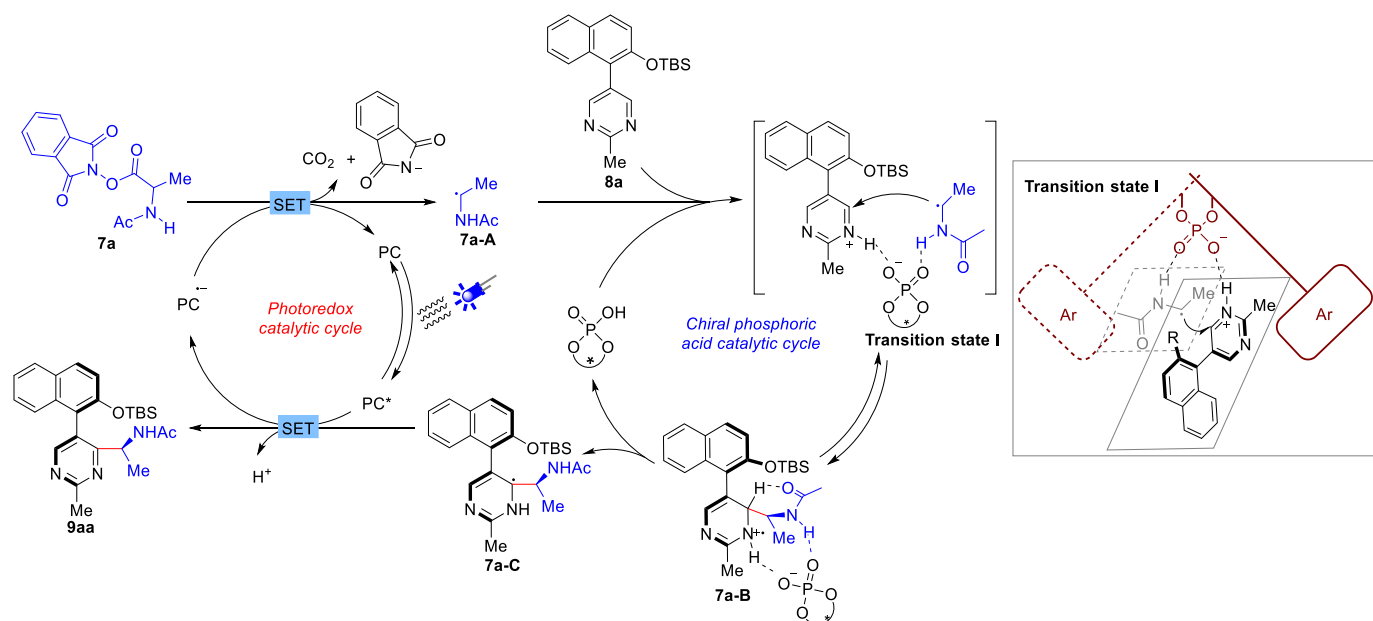


Scheme 2. The catalytic asymmetric construction of axially and centrally chiral heterobiaryls by Minisci reaction.

diethylzinc to aldehydes **12**, furnishing chiral secondary alcohols **13** with good yields (71%–86%) and excellent enantioselectivity (84%–89% ee).

Detailed mechanistic investigations suggested that the reaction begins with off-cycle SET oxidation of the mixture of **8a** and CPA-3 by the excited state photocatalyst, giving a reduction state photocatalyst to initiate the main cycle. Then, the reduced state photocatalyst could reduce the α -amino acid-derived REA **7a** via a SET process to generate α -aminoalkyl radical **7a-A** and ground state catalyst 4CzIPN. Subsequently, the radical intermediate **7a-A** undergoes chiral phosphoric acid-catalyzed radical addition to the pyrimidine **8a** to provide radical cation **7a-B** through transition state I. After deprotonation of radical cation **7a-B** with the amide carbonyl serves as an internal base, radical **7a-C** is generated and can be further oxidized by the excited state photocatalyst (PC*) via a SET process to generate product **9aa** upon rearomatization. Finally, the reduced state photocatalyst was formed again, closing the photoredox catalytic cycle (Scheme 3).

Cobalt-catalyzed cross-couplings have been established as a robust tool for constructing complex organic molecules [49]. Although this area has been extensively studied, the development of efficient cobalt-catalyzed asymmetric radical-involved cross-coupling reactions to construct chiral compounds with excellent regio- and enantioselectivity is still highly desirable [50–53]. Quite recently, the Xiao and Lu group developed an interesting dynamic kinetic resolution (DKR) of racemic heterobiaryl triflates **14** with DHP reagents **15** by the merger of organic photoredox catalysis and asymmetric cobalt catalysts construction of axial chirality through a radical pathway (Scheme 4a) [54]. Furthermore, this radical DKR process could be extended to reductive cross-coupling reactions of more easily available starting materials, chlorides and iodides **17** (Scheme 4b). Under the optimized conditions, a wide variety of chiral heterobiaryl products **16** were obtained with high yields (up to 99% yield) and excellent enantioselectivities (up to 97% ee). Notably, these axially chiral heterodiaryl molecules **16** exhibit a pronounced aggregation-induced emission (AIE) effect.

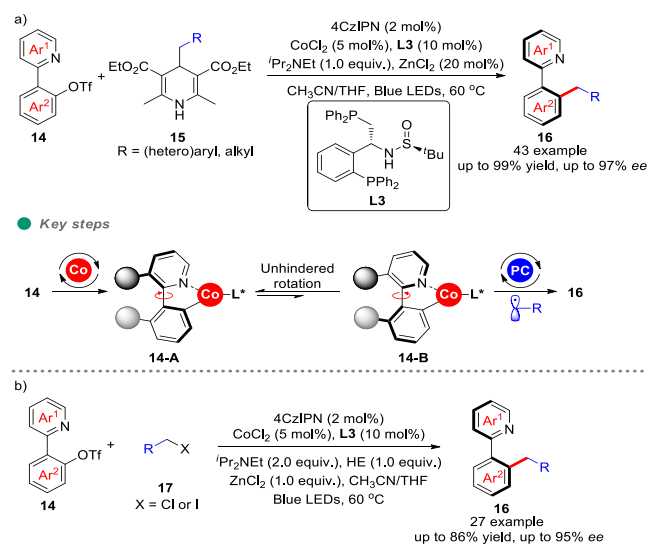


Scheme 3. Proposed mechanism.

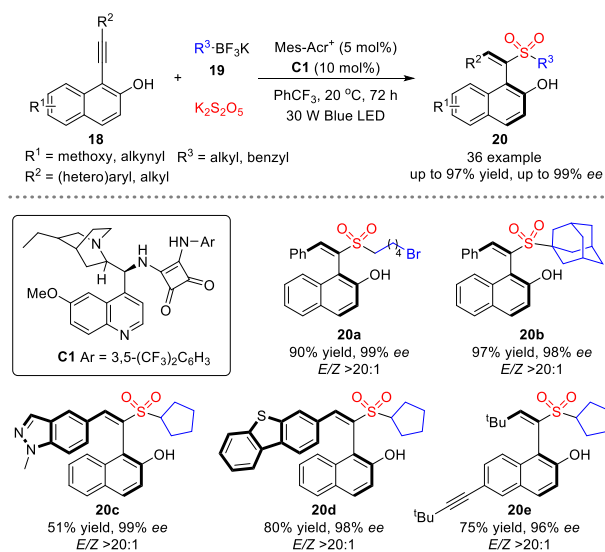
2.2. The catalytic asymmetric construction of axially chiral styrenes via radical pathways

Quite recently, Wu, Li, Ye and their co-workers documented a novel visible-light-induced catalytic asymmetric three-component radical reaction of 1-alkynynaphthalen-2-ols **18**, potassium alkyltrifluoroborates **19**, and potassium metabisulfite, giving sulfonyl-containing axially chiral styrenes **20** with good yield (up to 97%) and excellent enantioselectivity (93%–99% *ee*) (Scheme 5) [55]. By using cinchona alkaloid-substituted chiral squaramides as the organocatalyst, this protocol demonstrated good functional group tolerance and broad substrate scope with respect to each reaction component, accommodating a variety of substituents on the naphthalene ring and the potassium alkyltrifluoroborate. Remarkably, in addition to simple aryl-substituted alkynes, heterocyclic fused rings (**20c** and **20d**) and *tert*-butyl substituents (**20e**) could also participate in this three-component reaction smoothly, delivering the corresponding products with satisfactory results.

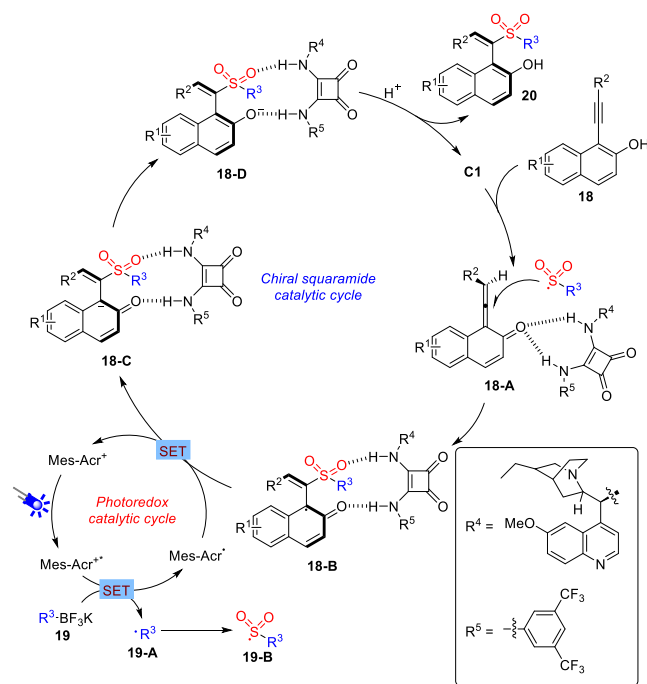
On the basis of detailed mechanism experiments and DFT calculation studies, a plausible radical process was proposed for this reaction. As shown in Scheme 6, the reaction began with SET oxidation of potassium alkyltrifluoroborate **19** by the excited state photocatalyst under visible light irradiation, giving the alkyl radical **19-A**. Next, **19-A** reacted with sulfur dioxide to form the alkylsulfonyl radical intermediate **19-B**. On the other hand, the allene intermediate **18-A** was formed in situ from 1-alkynynaphthalen-2-ol **18** in the presence of the chiral squaramide **C1**. Subsequently, the alkylsulfonyl radical intermediate **19-B** underwent radical addition to the central carbon of allene **18-A** to form the radical intermediate **18-B** in the presence of the chiral organocatalyst **C1**. The radical intermediate **18-B** would further be reduced by the reduced state photocatalyst to give the intermediate **18-C**, with the regeneration of the ground state photocatalyst. Ultimately, the resultant carbanion **18-C** underwent a sequential enol tautomerism and protonation process to produce the desired axially chiral product **20** with the assistance of a



Scheme 4. Cobalt/photoredox catalyzed asymmetric radical cross-coupling reaction for construction of axial chirality.



Scheme 5. Photoinduced asymmetric catalytic radical three-component reaction for construction of sulfonyl-containing axially chiral styrenes.



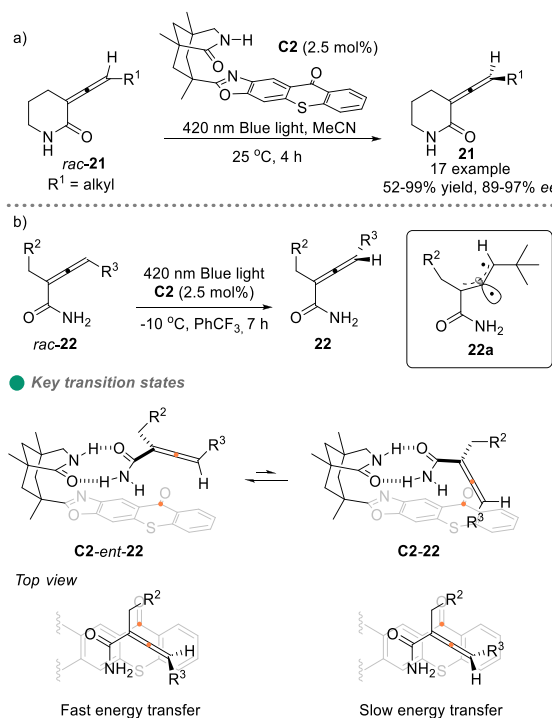
Scheme 6. Proposed mechanism.

chiral squaramide catalyst **C1**.

3. The catalytic asymmetric construction of chiral allenes via the radical pathway

Deracemization, which involves the selective conversion of a racemic mixture into a single enantiomer, is undoubtedly a direct and economical strategy for obtaining chiral compounds [56–58]. In 2018, the group of Bach disclosed an unprecedented catalytic enantioselective deracemization of allene lactams **rac-21** by a visible-light-driven triplet energy transfer process in the presence of chiral thioxanthone as a photosensitizer (Scheme 7a) [59,60]. This protocol efficiently converted a range of chiral racemic allene lactams **rac-21** into the corresponding single enantiomers **21** with excellent enantioselectivity (89%–97% *ee*). Quite recently, the Bach group extended this strategy to allene amides **rac-22** and carried out a detailed theoretical study on the reaction pathway through mechanistic experiments and DFT calculations (Scheme 7b) [61]. DFT calculation results show that there are significant differences in the binding properties between the two enantiomers and catalyst **C2**. Specifically, in contrast to the transition state **C2-ent-22**, the CH- π interaction between the hydrogen atom on the terminal allene carbon atom of transition state **C2-ent-22** and the external benzene ring of thioxanthone brings the alkene closer to the carbonyl chromophore, resulting in a faster triplet energy transfer. Therefore, transition state **C2-ent-22** can be rapidly processed and converted to another enantiomer through the diradical intermediate **22a**.

In 2020, the groups of Bao and Zhang reported an elegant method for the synthesis of a range of valuable, but previously inaccessible axially chiral allenes by copper-catalyzed asymmetric radical difunctionalization of 1,3-enynes **23** with tertiary amyl alcohol (^tAmOH) as the solvent (Scheme 8) [62]. In this process, the alkyl radical **24-A**, generated via SET reduction of **24a**, undergoes radical addition to give the allenyl radical **24-B**. Detailed experimental and theoretical studies support that the newly formed allenyl radical **24-B** could react with Cu(II)CN complex through an outer-sphere cyanation pathway (group transfer) to afford the desired product **25** in an enantioselective manner. Under the optimal reaction conditions, a wide variety of readily available conjugate 1,

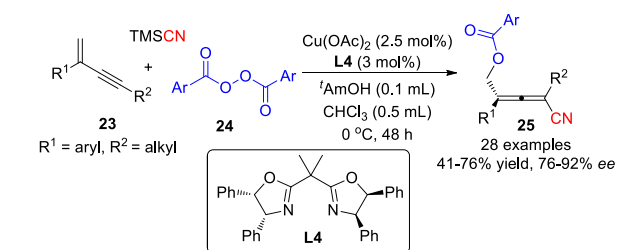


Scheme 7. Catalytic deracemization of racemic chiral allenes by sensitized excitation with visible light.

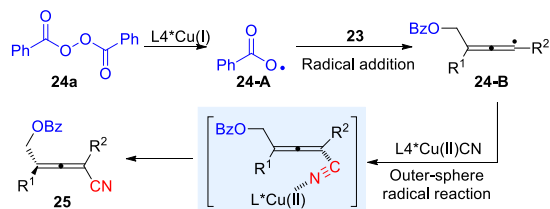
3-enynes **23** and phenyl-substituted peroxides **24** bearing electron-donating or electron-withdrawing groups were well tolerated to deliver the corresponding chiral allenes **25** with the high yields and enantioselectivities. Notably, perfluoroalkyl iodides (**25a** and **25b**), ethyl difluoroiodoacetate (**25c**), and cyclohexanecarboxylic peroxyanhydride (**25d**) can also participate in this process smoothly, affording the corresponding chiral allenes with good yields and with high *ee*.

Shortly thereafter, the Liu group disclosed a novel copper-catalyzed asymmetric coupling of terminal alkynes **28** with allenyl radicals derived from 1,3-enynes **26**, producing a variety of synthetically challenging tetrasubstituted axially chiral allenes **29** (Scheme 9) [63]. The key to the success of this three-component reaction is the subtle utilization of cinchona alkaloid-derived *N,N*, *P*-ligand to enhance the reducing ability of copper catalyst and achieve efficient enantioselective control over highly reactive allenyl radicals. Under the optimized conditions, a variety of 1,3-enynes including (hetero)aryl and alkyl alkynes as well as various radical precursors were proven suitable substrates, giving the corresponding cross-coupled products with high yields (up to 99% yield) and excellent enantioselectivities (up to 98% *ee*). Notably, bromide (**29a**), alkyl chlorides (**29b** and **29c**) and Togni's reagent **29d** were also compatible with the reaction respectively. As shown in the proposed mechanism, the *in situ*-formed alkynyl copper specie **28-A**, derived from Cu(I), **L5** and alkyne **28** in the presence of a base such as Cs₂CO₃, reduced radical precursor **27** to generate the Cu(II) **28-B** and alkyl radical intermediate **27-A**. The newly formed alkyl radical underwent radical addition to the alkene moiety of 1,3-enyne **26**, providing the propargyl radical **27-B** and its resonance structure trisubstituted allenyl radical **27-C**. Finally, the allene radical **27-C** reacted with the Cu(II) complex **28-B** to regenerate the Cu(I) complex and release the final tetrasubstituted axially chiral allene **29**.

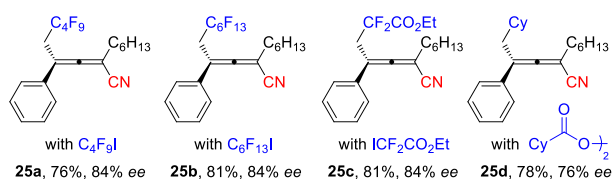
In 2021, the groups of Liu and Lin developed a copper-catalyzed asymmetric cyanation of allenyl radicals derived from benzyl alkynes **30** by using a novel chiral ligand Box^{OTMS} generated *in situ* from TMSCN and **L6** (Scheme 10) [64]. The key to the success of this transformation rests on the excellent site-selective hydrogen atom abstraction from the



● Key steps

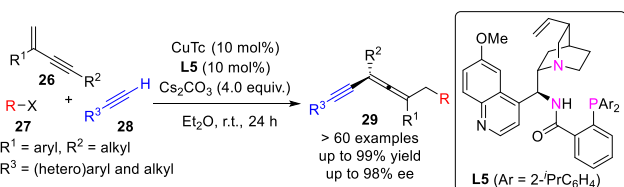


● Selected examples

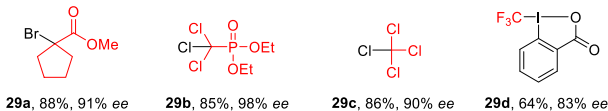


Scheme 8. Copper-catalyzed enantioselective radical 1,4-difunctionalization of 1,3-enynes.

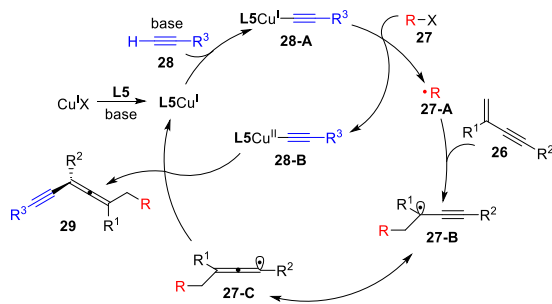
tertiary propargylic C–H bonds by $\text{L6}^*\text{Cu(II)}$ -bound nitrogen-centered radical (NCR). And DFT calculation results indicated that the coupling of propargylic radical with Cu(II) cyanide to provide the Cu(III) complex is the stereochemically determining step of the reaction. This protocol enables the synthesis of a wide variety of enantiomerically enriched trisubstituted allenyl nitriles **32** in good yields (up to 83% yield) with



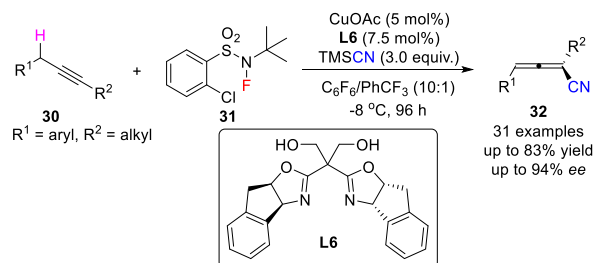
● Selected examples



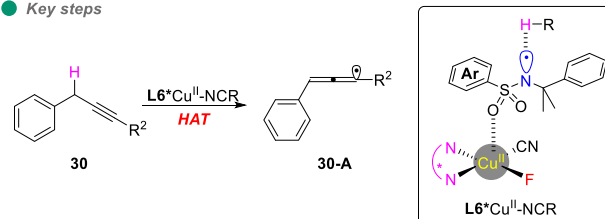
● Proposed mechanism



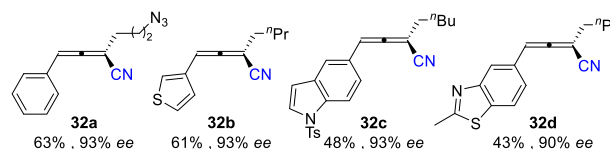
Scheme 9. Copper-catalyzed asymmetric coupling of allenyl radicals with terminal alkynes.



● Key steps



● Selected examples



Scheme 10. Copper-catalyzed enantioselective radical cyanation of propargylic C–H bonds.

excellent enantioselectivity (up to 94% ee). Importantly, azide on the aliphatic chain of the alkyne (**32a**) and heteroarenes such as thiophene (**32b**), indole (**32c**), and benzothiazole (**32d**) were all worked well and furnished the desired products with excellent enantioselectivity.

4. Conclusions

In recent years, considerable research efforts have been devoted to the development of catalytic asymmetric radical reactions for the construction of axially chiral compounds based on the unique reactivity modes of diverse radicals. In this review, we critically illustrate these recent achievements according to different radical precursors and catalytic activation modes. Despite these impressive advances, however, this field is still in its infancy. At the current stage, axially chiral compounds prepared *via* radical pathway are still restricted to only a few classes ((hetero)biaryl atropisomers, axially chiral styrenes, and chiral allenes). As a result, the scope of the radical precursors should be expanded, new powerful catalysts or chiral ligands should be designed, and new catalytic modes, especially the dual catalytic strategies, should also be explored. In addition, many potentially useful axially chiral frameworks have yet to be discovered, which is essential for asymmetric catalysis and drug discovery. We hope that this review will attract more attention to this field and serve as a helpful starting point for new researchers in this field.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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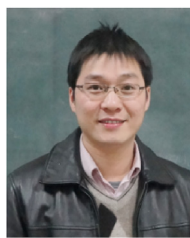
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