Centrally Chiral Arenes:

From Concept to Catalytic Enantioselective Synthesis

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Compared to the well-established axial, planar, and helically chiral arenes, central chirality in arene derivatives arising out of unsymmetrically substituted arene rings is a relatively underexplored research topic. However, this counterintuitive concept is indeed fascinating. With inherent challenges associated with their enantioselective synthesis, desymmetrization of prochiral and *meso*-compounds has recently emerged as a straightforward approach to such centrally chiral arenes. This article aims to give an overview of this concept along with the state-of-the-art syntheses, including our own endeavors in this direction.

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Introduction

CENTRALLY CHIRAL ARENEs is a concept that instantly triggers curiosity due to the presence of an inherent molecular plane of symmetry in arenes: How can such flat species be chiral? Chemists are long acquainted with axial,[1] helical,[2] and planar chiral arenes[3] (Figure 1) as well as their enantioselective syntheses and applications in various facets of Chemistry – from catalysts and ligands to natural products, synthetic drugs, and functional materials.[4]

Although lesser known and counterintuitive, the concept of central chirality in arenes is indeed exciting. There are two possible scenarios. Arenes bearing one or more chiral centers close to their planar framework are extremely common, and their enantioselective synthesis is routine (Scenario-1, Figure 1). However, this class of chiral compounds can hardly be classified as centrally chiral arenes since the arene part plays little role in dictating the stereogenicity of the molecule. In other words, the chirality of these compounds is not dependent on the presence or the position of substituent(s) on the arene ring.

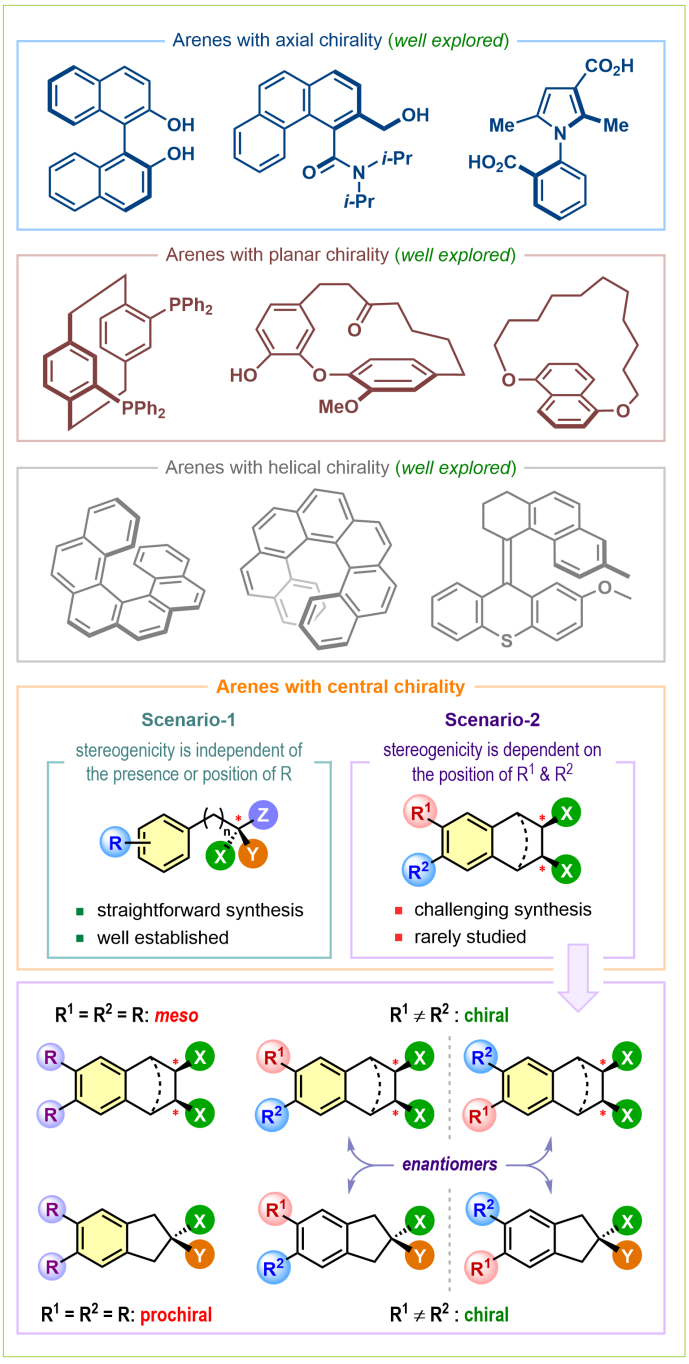


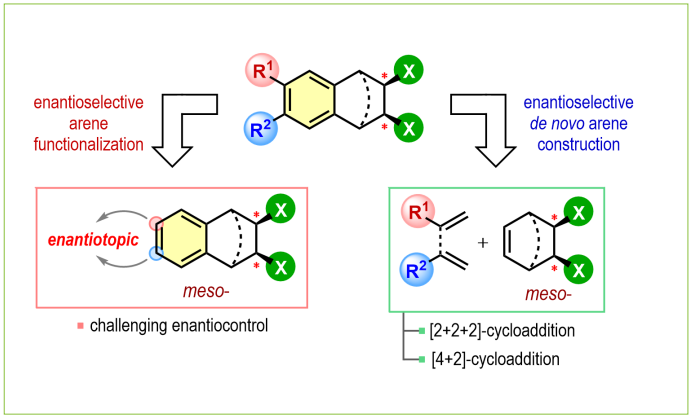
Figure 1. Chiral arenes

In contrast, another class of arene derivatives can be considered whose central chirality arises out of unsymmetrical substitution on the arene ring ($R^1 \neq R^2$) (Scenario-2, Figure 1). These molecules become either prochiral or *meso* if the arene ring is symmetrically substituted ($R^1 = R^2$) or unsubstituted ($R^1 = R^2 = H$). Their stereochemical behavior is fascinating: Not only the chirality of these arenes depends on the substituent(s) remote from the stereocenter(s) (e.g., R^1 & R^2) but also an exchange in the position of these substituents results in enantiomeric arenes. It is this class of molecules we refer to as centrally chiral arenes, and their enantioselective synthesis is the topic of discussion in this article.

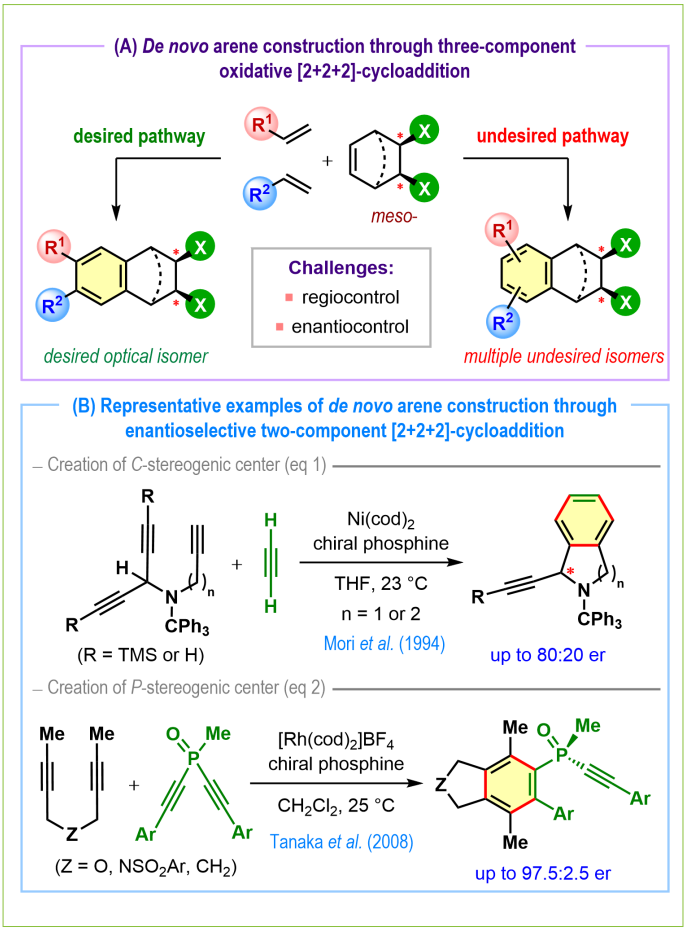
Due to the presence of stereodetermining substituents on the arene ring away from the stereocenter(s), the enantioselective synthesis of these centrally chiral arenes can be challenging. Two direct synthetic strategies can be envisaged – each of them involves the breaking of symmetry elements present in the starting material, i.e., through the desymmetrization of prochiral or *meso*-compounds. As illustrated in Scheme 1, these strategies involve either (1) an enantioposition-selective installation of a substituent or a functional group to the pre-existing symmetrical arene framework where the enantioinduction takes place during the C(sp^2)–H substitution step (i.e., enantioselective arene functionalization) or (2) forging the unsymmetrical arene ring in the enantioselectivity-determining step (i.e., enantioselective *de novo* arene construction).

Regioselective introduction of a substituent in arenes in itself is a challenging transformation: Multiple steps are usually required to install the desired substituent, which often leads to limited substitution patterns on the arene ring. Many of these arene substitution reactions require harsh reaction conditions. Moreover, functional groups already present on the arene ring may influence the reactivity and dictate the regioselectivity of such substitution reactions. These aspects render the enantioselective arene substitution strategy complicated. The absence of any functional group on the centrally chiral target arenes adds an additional layer of difficulty for the enantioinduction.

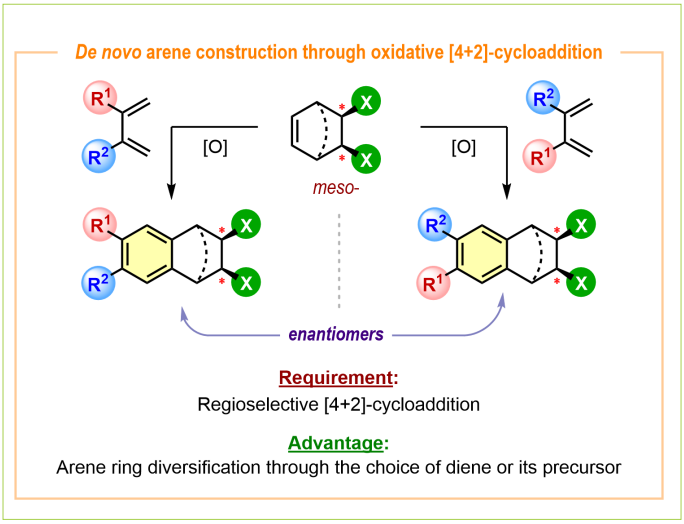
On the other hand, enantioselective *de novo* arene construction[5] from a symmetrical (prochiral or *meso*) arene precursor perhaps constitutes the most direct approach, having the potential to reduce the number of synthetic steps. Judicious implementation of this strategy



Scheme 1. Desymmetrization strategies for the enantioselective synthesis of centrally chiral arenes



Scheme 2. *De novo* construction of centrally chiral arenes through [2+2+2]-cycloaddition: (A) Strategies and (B) representative examples



Scheme 3. Enantioselective strategy for the *de novo* construction of centrally chiral arenes through [4+2]-cycloaddition

can exhibit better regiocontrol and substitution patterns on the arene ring. These advantages make the *de novo* arene construction a powerful and efficient strategy for the enantioselective synthesis of centrally chiral arenes. However, despite its popularity for the synthesis of axial and planar chiral arenes,[5] enantioselective *de novo* construction of centrally chiral arenes is scarce.

Among various *de novo* arene construction strategies reported so far, [2+2+2]-cycloadditions[6] and [4+2]-cycloadditions[7] are possibly the most well-studied. However, controlling the regioselectivity of a three-component [2+2+2]-benzannulation can be tricky and can result in multiple undesired isomers along with the desired one (Scheme 2A). In contrast, a two-component [2+2+2]-benzannulation can prevent most of these undesired pathways due to restricted conformation of the starting diyne.

Utilizing this strategy, Mori *et al.* reported a Ni-catalyzed enantioselective desymmetrization of prochiral triynes through a two-component [2+2+2]-cycloaddition reaction in 1994 to construct the arene ring with moderate enantioselectivity (Scheme 2B, eq 1).[8] In 2008, Tanaka *et al.* reported a rhodium-catalyzed enantioselective desymmetrization of prochiral diynyl phosphine oxides through a two-component [2+2+2]-cycloaddition reaction to deliver arene derivatives bearing an adjacent *P*-stereogenic center, with high enantioselectivity (Scheme 2B, eq 2).[9]

However, in both these cases, the stereogenicity does not depend on the substitution pattern on the newly formed arene ring.

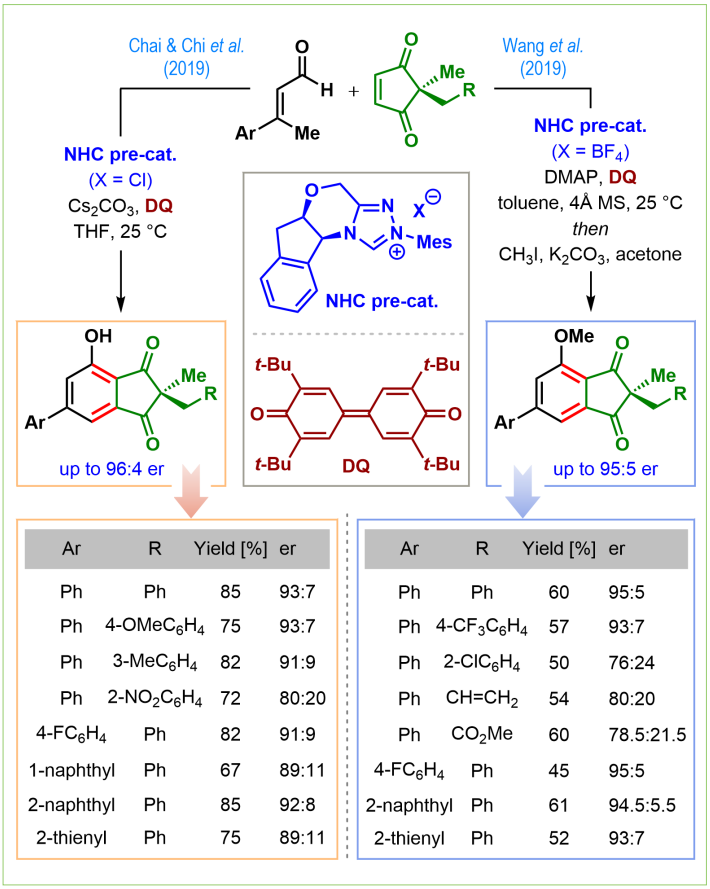
As opposed to the [2+2+2]-cycloaddition strategy discussed above, in the case of oxidative [4+2]-cycloaddition reactions, poor regiocontrol would result in two enantiomeric products (Scheme 3). Therefore, the regioselectivity of the [4+2]-cycloaddition step is the key to high enantioselectivity. At the same time, the desired substitution pattern on the newly formed arene ring can be achieved through the choice of diene or its precursor. The latter feature makes the oxidative [4+2]-cycloaddition strategy more versatile and modular for the synthesis of centrally chiral arenes. Nonetheless, despite obvious merits, such enantioselective oxidative [4+2]-cycloaddition reactions remained unexplored until recently.

In 2019, Chai and Chi group,[10] as well as Wang group,[11] independently applied this *de novo* arene construction strategy for the desymmetrization of prochiral cyclopentene-1,3-diones (Scheme 4). This *N*-heterocyclic carbene (NHC)-catalyzed reaction with α,β-unsaturated aldehydes proceeds via a cascade Michael/aldol sequence to effect an overall formal [4+2]-cycloaddition. The resulting indane derivatives, containing an all-carbon quaternary stereocenter, were obtained with moderate to good enantioselectivities. While Chai and Chi *et al.* directly isolated the hydroxy-functionalized arenes (phenols),[10] Wang *et al.* chose to convert the products to the corresponding methyl ether before isolation.[11]

Regardless of the fairly good level of enantioselectivity achieved, the scope of this NHC-catalyzed desymmetrization reaction is limited only to the construction of *meta*-(hetero)aryl-substituted phenols starting from β-(hetero)aryl crotonaldehydes (Scheme 4).

Although enantioselective *de novo* construction of centrally chiral unfunctionalized arenes remains unknown, the application of oxidative [4+2]-cycloaddition strategy for the *de novo* construction of unfunctionalized achiral arenes was reported in 2015 by Lee *et al.*[12] (Scheme 5). This proline-catalyzed Diels-Alder reaction of 1,4-naphthoquinones or 1,4-anthracenedione with α,β-unsaturated aldehydes proceeds via a dienamine intermediate.[13] The resulting cycloadducts were found to undergo spontaneous aerobic oxidation to produce achiral arenes such as anthraquinones and tetracenediones in moderate to excellent yield.

A few years later, the same group extended this strategy for the conversion of maleimides to phthalimides (Scheme 5).[14] Apart from the operational simplicity of these protocols, diversification of the



Ar	R	Yield [%]	er
Ph	Ph	85	93:7
Ph	4-OMeC$_6$H$_4$	75	93:7
Ph	3-MeC$_6$H$_4$	82	91:9
Ph	2-NO$_2$C$_6$H$_4$	72	80:20
4-FC$_6$H$_4$	Ph	82	91:9
1-naphthyl	Ph	67	89:11
2-naphthyl	Ph	85	92:8
2-thienyl	Ph	75	89:11

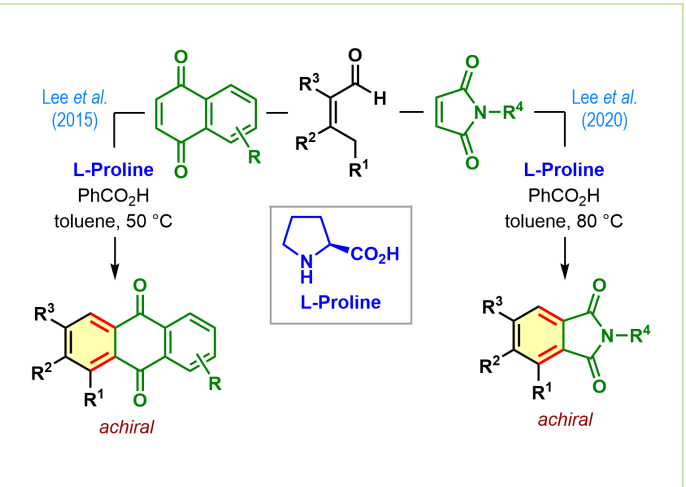
Ar	R	Yield [%]	er
Ph	Ph	60	95:5
Ph	4-CF$_3$C$_6$H$_4$	57	93:7
Ph	2-ClC$_6$H$_4$	50	76:24
Ph	CH=CH$_2$	54	80:20
Ph	CO$_2$Me	60	78.5:21.5
4-FC$_6$H$_4$	Ph	45	95:5
2-naphthyl	Ph	61	94.5:5.5
2-thienyl	Ph	52	93:7

Scheme 4. Oxidative formal [4+2]-cycloaddition for the enantioselective *de novo* construction of centrally chiral functionalized arenes

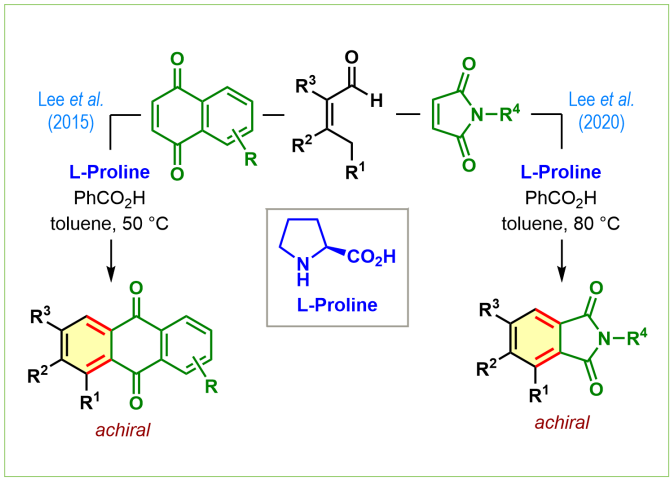
arene ring through the choice of α,β-unsaturated aldehydes marks a notable feature of this strategy.

Interestingly, enantioselective variants of these oxidative [4+2]-cycloaddition reactions have never been reported.

While enantioselective [4+2]-cycloaddition reactions are among the most well-studied reactions during the past half a century, they almost



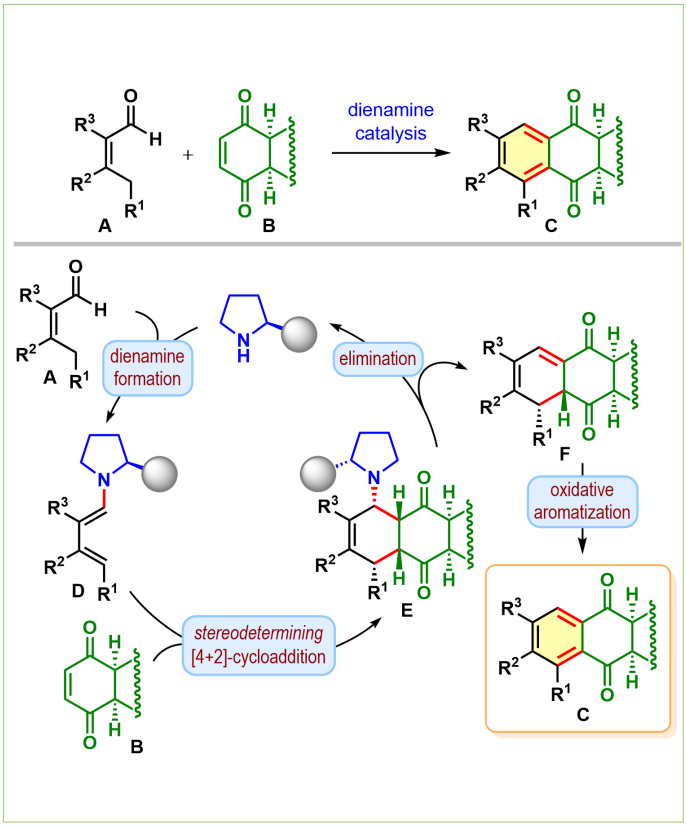
Scheme 5. Proline-catalyzed oxidative [4+2]-cycloaddition for the *de novo* construction of achiral unfunctionalized arenes



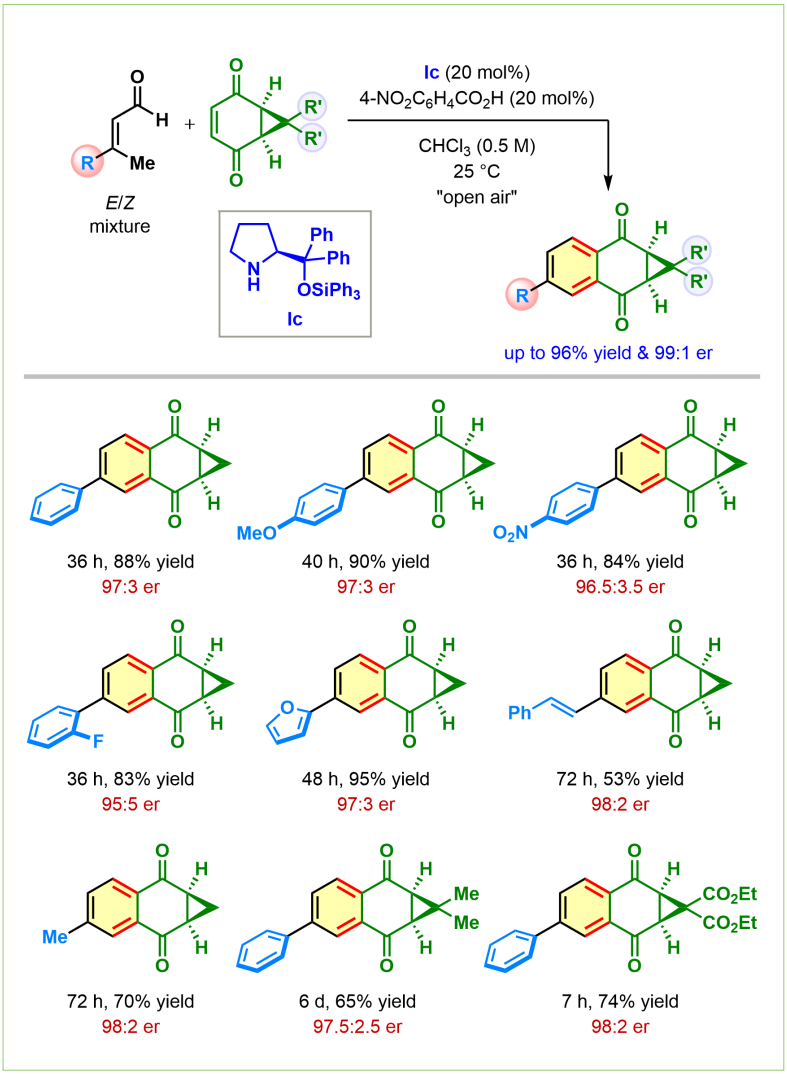
Scheme 6. Enantioselective [4+2]-cycloaddition reactions under dienamine catalysis

always result in the formation of at least one stereocenter at the reaction site.[15] In fact, enantioselective [4+2]-cycloaddition reactions under dienamine catalysis, first introduced by Serebryakov *et al.* in 1993[16] and later on popularized by Jørgensen *et al.*,[17] also generate stereocenter(s) at the reaction sites (Scheme 6).[18] In contrast, a completely stereoablative [4+2]-cycloaddition reaction for constructing centrally chiral arenes was unknown.

We recently reported the first example of this kind by desymmetrizing polycyclic *meso*-cyclohexenediones, which enabled the enantioselective *de novo* construction of centrally chiral unfunctionalized arenes (Scheme 7).[19]



Scheme 7. Catalytic hypothesis for the enantioselective *de novo* construction of centrally chiral unfunctionalized arenes



Scheme 8. Enantioselective *de novo* construction of centrally chiral unfunctionalized arenes through the desymmetrization of *meso*-*p*-homobenzoquinones

Our working hypothesis is shown in Scheme 7, and hinges on a chiral aminecatalyzed [4+2]-cycloaddition reaction of polycyclic *meso*-cyclohexenediones **B** with catalytically generated electron-rich dienamine intermediate **D** from a suitably substituted α,β-unsaturated aldehyde **A**. The facile elimination of the amine catalyst from the initially formed cycloadduct **E** was expected to produce the corresponding cyclohexadiene **F**, which on aerobic oxidation would furnish the desired chiral arene **C**. Notwithstanding the involvement of subsequent stereoablative steps, the diastereoselectivity of the [4+2]-cycloaddition step was deemed to be crucial in determining the regioselectivity and hence the configuration of the centrally chiral arene products.

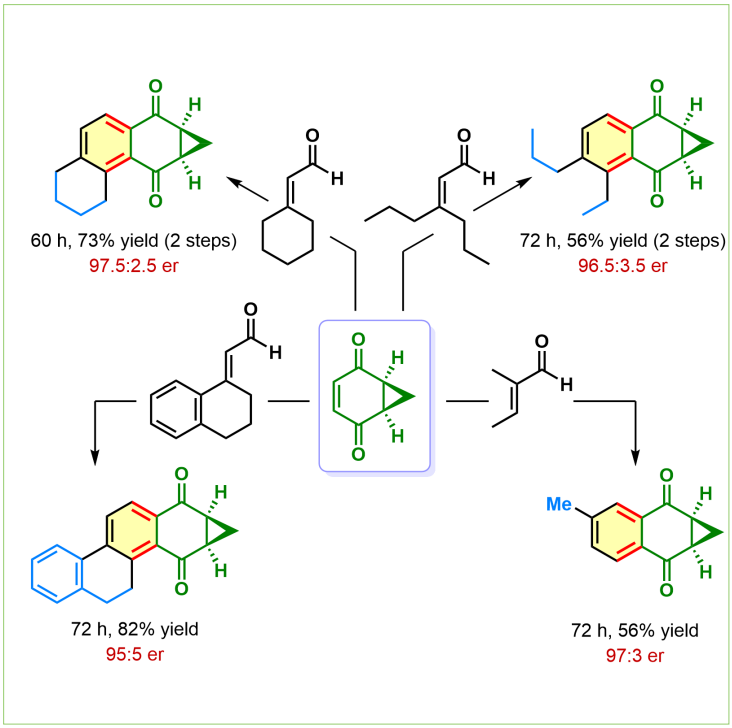
A systematic catalyst screening revealed triphenylsilyl-protected (*S*)-diphenylprolinol[20] **Ic** and 4-nitrobenzoic acid to be the optimum combination for the desymmetrization of our initially chosen substrate – *meso*-*p*-homobenzoquinone (Scheme 8).[19] In a majority of the cases, air was sufficient for the oxidative aromatization step, which was found to be spontaneous. Thus, using 20 mol% of the catalyst combination, the generality of this protocol was demonstrated.

Through the choice of α,β-unsaturated aldehydes, we could achieve the enantioselective synthesis of unfunctionalized centrally chiral *p*-homonaphthoquinones, bearing aryl, alkenyl, or alkyl group in various positions of the arene ring (Schemes 8-9).[19] The products were generally obtained in good yield with good to excellent enantioselectivities. In a few cases, aerobic oxidation was found to be sluggish, and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was required to facilitate the oxidative aromatization step.

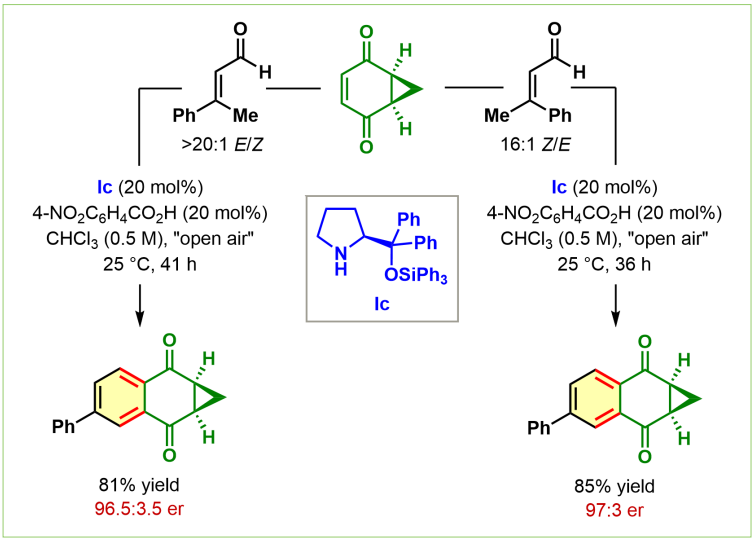
Since these reactions proceed via a dienamine intermediate, the efficiency, as well as the stereochemical outcome of this *de novo* arene construction reactions, were found to be independent of the geometry (*E*- or *Z*-) of α,β-unsaturated aldehydes, rendering the overall process stereoconvergent (Scheme 10).[19]

The scope of this oxidative [4+2]-cycloaddition reaction was further extended for the desymmetrization of tricyclic *meso*-*endo*-*norbornenoquinones* (Scheme 11).[19] Using the same catalyst (**Ic**) under nearly identical reaction conditions, this protocol was found to be amenable to a variety of *endo*norbornenoquinones. The resulting chiral methanoanthraquinones with diversely substituted arene rings were formed in excellent yield with outstanding enantioselectivities.

Apart from the arene ring diversification, the products could be transformed into higher chiral arene homologs. As illustrated in Scheme 12, we could convert one of the products to methanoanthracene or dihydromethanoanthracene derivatives in a two-step sequence[21] with retention of enantiopurity.[19] Enantioselective synthesis of these chiral arene derivatives would be challenging by other means.



Scheme 9. Arene ring diversification in *p*-homonaphthoquinones through the choice of α,β-unsaturated aldehydes



Scheme 10. Stereoconvergency in amine-catalyzed enantioselective *de novo* construction of centrally chiral arenes

In an attempt to rationalize the observed stereochemical outcome, four pre-transition state assemblies were considered for the [4+2]-cycloaddition step between the catalytically generated dienamine from (*S*)-**Ic** and *p*-homobenzoquinone (Scheme 13). Among them, only the ***endo* TS-1** was deemed to be both sterically and energetically favorable and explains the absolute stereochemistry of the centrally chiral arene products. This stereochemical model was supported by the density functional theory (DFT) study, which revealed the *endo*-**TS-1** to be 2.4 kcal/mol more stable than the competing *endo*-**TS-2**. This energy difference between the two competing diastereomeric transition states is in excellent agreement with the experimental outcome (calculated er = 98:2 vs observed er = 97:3).[19]

Although the objective of this article was to discuss centrally chiral arenes and their enantioselective synthesis, we cannot resist the temptation of mentioning a few words about the successful extension of this *de novo* arene construction strategy to axially chiral arenes.[22]

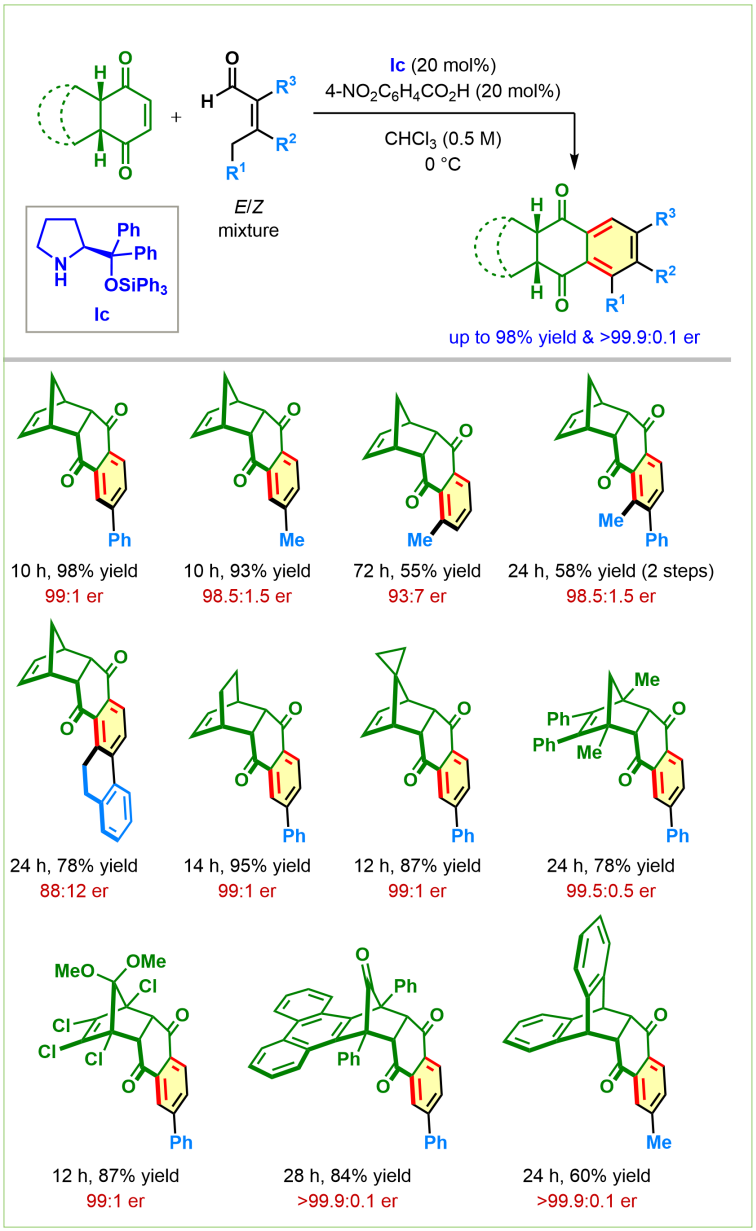
We were particularly interested in the desymmetrization of maleimide derivatives bearing a bulky *ortho-substituted* aryl group on the nitrogen center.[23] This class of compounds contains a plane of symmetry (σ), and their desymmetrization is typically carried out either through cycloaddition[24] or conjugate addition.[25] However, both these classes of reactions result in the generation of at least one stereocenter apart from the desired chiral C–N axis. In addition, the unsaturation present in maleimides is also lost in this process.

We reckoned that an oxidative [4+2]-cycloaddition between such an *N*-aryl maleimide and α,β-unsaturated aldehydes would lead to the *de novo* construction of an arene ring with concomitant obliteration of the σ-plane present in maleimide.

Using a combination of (*S*)-bis(3,5-dimethylphenyl)prolinol TMS-ether (**II**) and 2-fluorobenzoic acid as the catalyst, the resulting *N*-aryl phthalimide derivatives, bearing only a chiral C–N axis, were obtained with excellent enantioselectivities in most cases (Scheme 14).[22] However, due to the lower reactivity of maleimides compared to polycyclic *meso*-cyclohexenediones, the [4+2]-cycloaddition reactions with *N*-aryl maleimides turned out to be much slower. Moreover, the oxidative aromatization step was found to be sluggish and could only be accelerated in the presence of DABCO under an oxygen atmosphere.

Conclusion

In conclusion, we presented the counterintuitive concept of centrally chiral arenes along with scenarios under which such molecules are possible. The practical challenges as well as potential strategies for the enantioselective synthesis of such chiral arenes are also provided. Our desymmetrizing oxidative [4+2]-cycloaddition route to centrally chiral arenes is discussed in details in the backdrop of the existing literature. This operationally simple reaction is catalyzed by a diphenylprolinol silyl ether, doesn't usually require any external oxidant, and allows for the regioselective arene



Scheme 11. Enantioselective *de novo* construction of centrally chiral unfunctionalized arenes through the desymmetrization of *meso-endo*-norbornenoquinones

ring diversification simply through the choice of α,β-unsaturated aldehydes. This is the first example of enantioselective *de novo* construction of centrally chiral unfunctionalized arenes. The applicability of this strategy for constructing axially chiral arenes is also discussed at the end.

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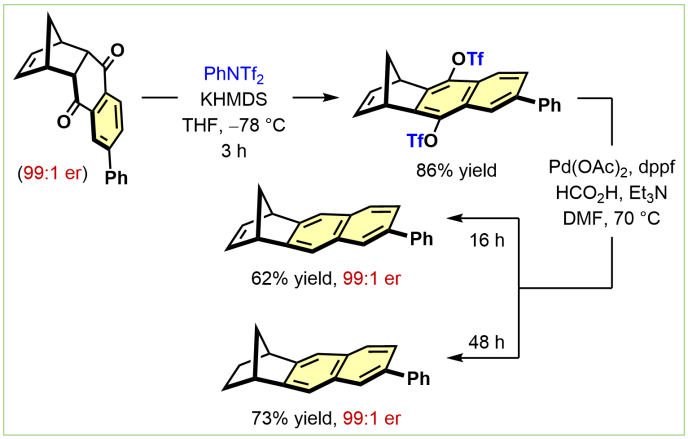
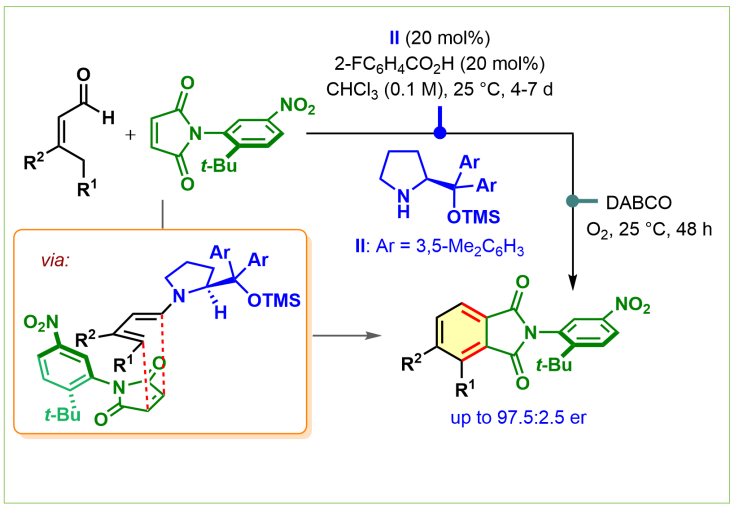
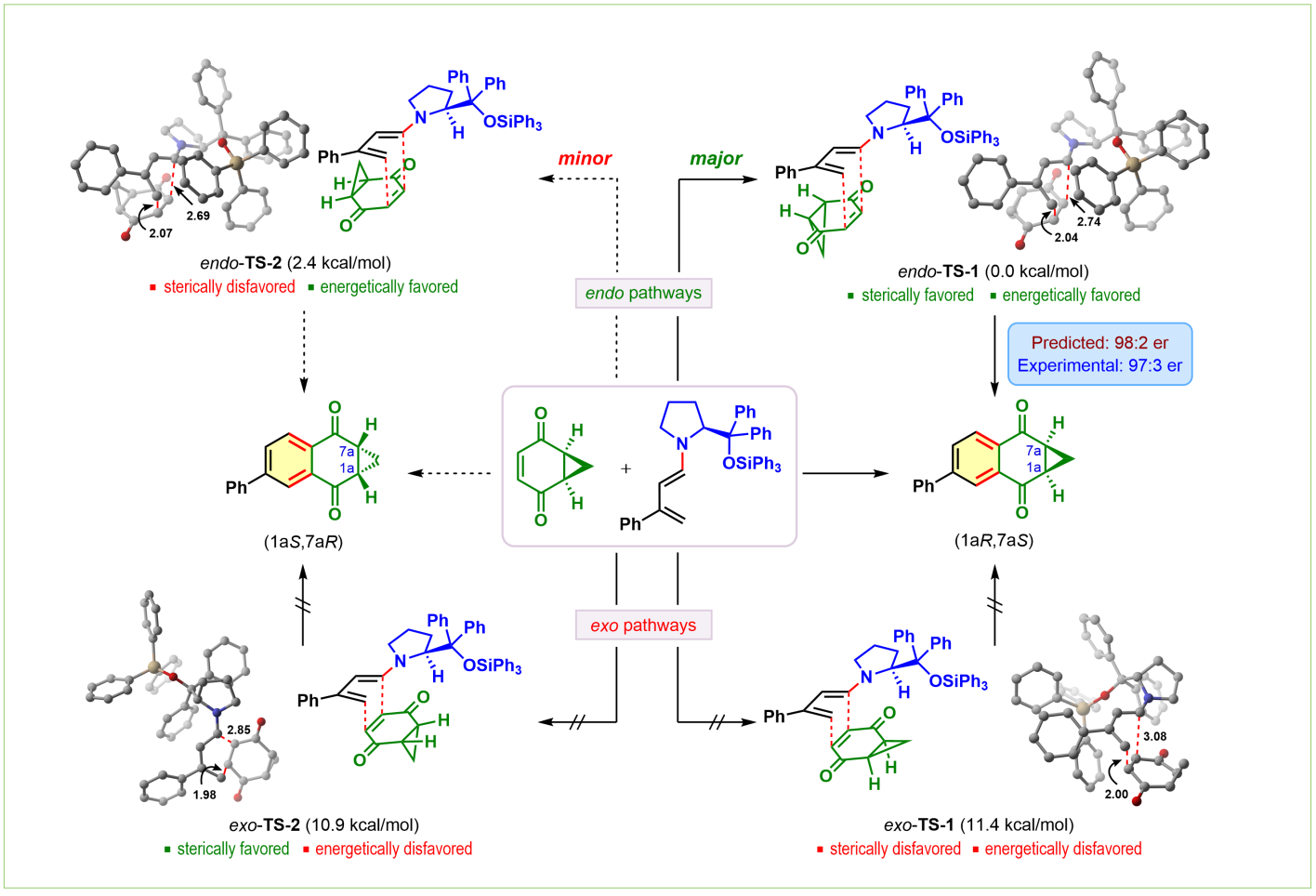


Scheme 12. Enantioselective synthesis of higher chiral arene homologs through product elaboration



Scheme 14. Construction of C–N axially chiral phthalimides by the *de novo* construction of the arene ring



Scheme 13. Rationalization of stereochemical outcome in enantioselective desymmetrization of *meso*-*p*-homobenzoquinones

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