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Atroposelective synthesis of sterically hindered stereochemically complex BINOL derivatives *via* central-to-axial chirality induction

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A sequential strategy is proposed for the atroposelective construction of new families of sterically hindered BINOL derivatives bearing multiple stereogenic elements and featuring up to four stereogenic centers. The sequence begins with an organocatalyzed regio- and enantioselective mono-dihydrobenzofurannulation of commercially available 2,7-dihydroxynaphthalene establishing two stereogenic carbon atoms, followed by highly atroposelective copper-catalyzed aerobic oxidative homo- or cross-couplings fixing the axial chirality thanks to a nearly perfect induction of chirality. In addition, the resulting BINOL derivatives serve as promising precursors for the synthesis of either complex spiroheterocycles by axial-to-central conversion of chirality, heterohelicene-like molecules by axial-to-helical conversion of chirality, or an atropisomeric naphtho[2,1-*b*]furan scaffold *via* 1,2-aryl migration, further underscoring the potential of this new atroposelective strategy based on a practical central-to-axial chirality induction.

Introduction

The preparation of optically active BINOL derivatives is extremely important in organic chemistry, owing to their widespread applications in enantioselective catalysis, chiral recognition, and the development of optical materials.[1–6] In recent years, the advances in enantioselective oxidative coupling have led to the development of elegant methodologies for the synthesis of optically active BINOL derivatives.[7] Typically, Cu(II),[8–12] V(V),[13–17] Fe(III)[18–21] and Ru(IV)[22,23] coordinated with suitable chiral ligands are used as catalysts, as well as more recently in electrochemical cross-couplings.[24,25] Therefore, the synthesis of optically active chiral BINOL derivatives remains a very attractive area of research.[26–29]

Among various derivatives, the 8,8′-disubstituted BINOL family is distinctive due to its pronounced steric hindrance.[30,31] This leads to a greater dihedral angle and a more restricted rotation around the axis, making them key precursors for the construction of helically chiral compounds.[32–40] As shown in Scheme 1a, chiral helicenoids constructed from sterically hindered 8,8′-disubstituted BINOL derivatives exhibit excellent photoelectric properties and catalytic performance.[33–36] Moreover, helical structures are of great importance in areas such as molecular recognition and circularly polarized luminescence (CPL).[37–43] However, unlike the thriving development of the synthesis of other axially chiral biaryls, the stereoselective construction of highly sterically hindered 8,8′-disubstituted BINOL derivatives has remained relatively underexplored, probably due to the challenges associated with the difficulty of achieving high stereocontrol in such congested systems. As depicted in Scheme 1b, the current strategies involve either using simple achiral 8-substituted naphthol precursors, followed by oxidative coupling and chiral resolution,[33–35,40–42] or direct enantioselective oxidative couplings.[44,45] The former strategy is the most widely used but is time-consuming and labor-intensive, and the latter has only sporadic reports and faces limitations such as low enantiomeric excess or the need for additional coordinating groups. It is speculated that the changes in reactivity brought by the remote steric hindrance may impose higher requirements on the enantioselective catalytic system. In contrast to previous strategies, we design herein a catalytic atroposelective synthesis *via* a central-to-axial chirality induction strategy. This approach pioneered by Meyers in 1982 has been only utilized to date in several specific cases with modest to good atroposelectivities.[46–51] Here we propose the generation of the key centrally chiral 2-naphthol precursor through a regio- and enantioselective functionalization of phenols followed by an atroposelective oxidative coupling reaction triggering the stereogenic axis with chiral induction (Scheme 1b).

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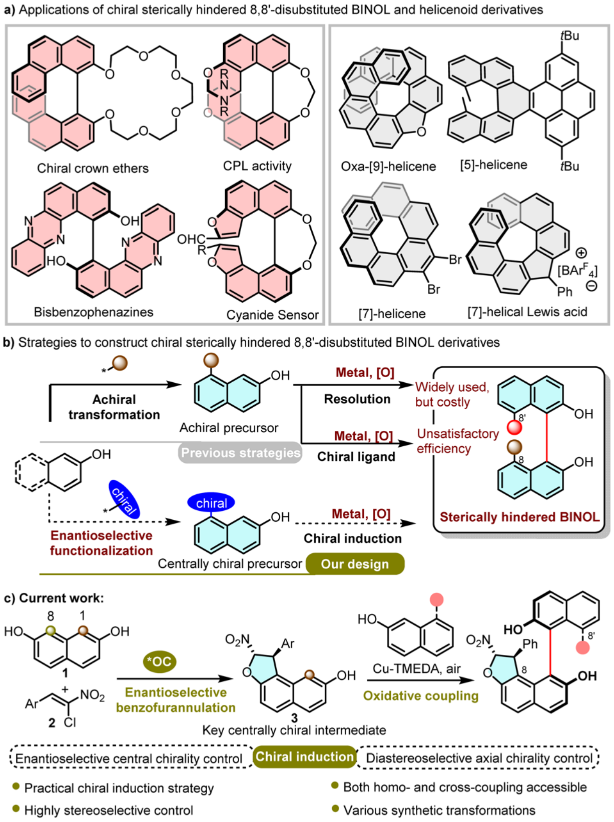
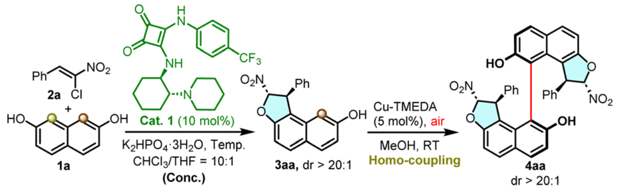


Scheme 1 Application of steric hindrance in BINOL derivatives and their synthesis.

To implement this chirality induction strategy, cheap and commercially available 2,7-dihydroxynaphthalene **1** was selected as the starting material. Its two unique 1,8-reactive sites offer more opportunities for reaction design and the installation of a chiral moiety *via* enantioselective transformations. Building on our previous work,[52–57] the key centrally chiral dihydrobenzofuran **3** could be constructed through an enantioselective domino Michael/*O*-alkylation reaction with α-chloronitroalkenes **2** (Scheme 1c). By controlling the reaction conditions and leveraging steric effects, we were able to ensure a totally regio- and enantioselective mono-functionalization. Subsequently, we hypothesized that by using commercially available Cu-TMEDA as the achiral oxidative coupling catalyst, either homo-coupling of the chiral intermediate **3** or cross-coupling with other naphthol derivatives could be insured in a high atroposelective manner. The success of this design would provide a new practical strategy for the preparation of sterically hindered 8,8′-disubstituted BINOL derivatives embedding various stereogenic centers that are otherwise difficult to access.[58,59]

Results and discussion

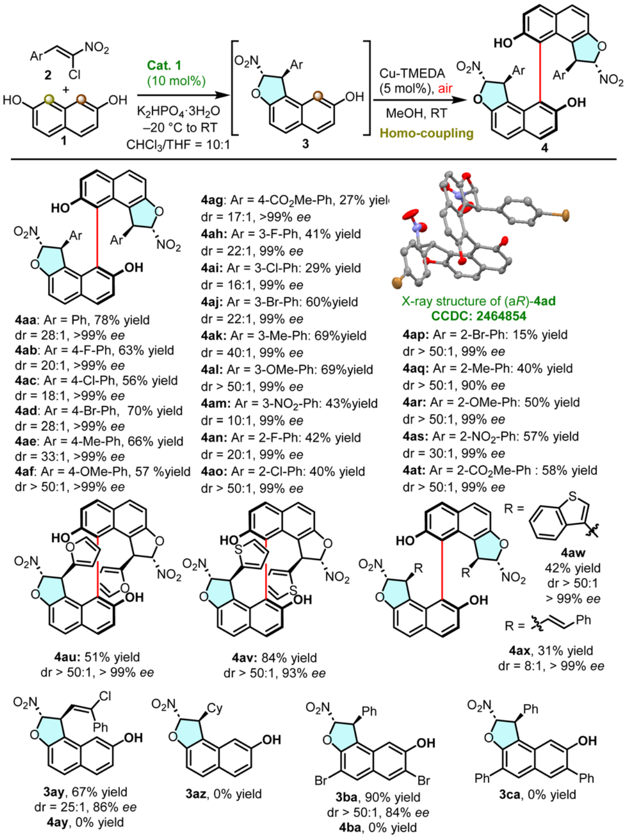
Table 1 Optimization of the reaction conditions for chirality induction[a,b]



Entry	Conc. (M)	*T* (°C)	Yield of **3a**[c] (*ee*)	Yield of **4a**[c] (*ee*)
1	0.10	25	76 (88)	—
2	0.05	25	71 (90)	—
3	0.05	0	69 (93)	—
4	0.025	0	77 (94)	—
5	0.015	0	81 (94)	—
6	0.025	−20	69 (96)	—
7	0.003	−20	96 (94)	—
8[d]	0.003	−20	96 (94)	—
9	**0.003**	**−20**	**96 (94)**	**78[e](99)**
10[f]	0.003	−20	96 (94)	10[e] (99)

[a] Unless otherwise noted, reactions were conducted with **1a** (0.3 mmol), **Cat. 1** (10 mol%), **2a** (0.2 mmol) and base (0.4 mmol) in solvent. [b] Isolated yield. [c] Determined by HPLC on a chiral stationary phase. [d] **1a** (1.5 mmol) and **2a** (1 mmol). [e] Yield for 2 steps. [f] Under an argon atmosphere.

The initial endeavor of the domino Michael/*O*-alkylation process was conducted with 2,7-dihydroxynaphthalene **1a** and α-chloronitroalkene **2a** (Table 1). With bifunctional squaramide **Cat. 1** as a catalyst, the desired product **3aa** was obtained in 76% yield with 88% *ee* and over 20 : 1 *dr* in the presence of dipotassium hydrogen phosphate trihydrate as an inorganic base (entry 1). THF was added to enhance the solubility of 2,7-dihydroxynaphthalene **1a**, suppressing the second cyclization process. In order to further improve the yield and enantioselectivity, both low temperature and low concentrations were beneficial for this transformation (entries 2–7). Finally, in a highly diluted solution (0.003 M) at −20 °C, **3aa** was afforded in 96% yield with 94% *ee* (entry 7). In addition, the efficiency remained unchanged on a 1 mmol scale (entry 8). To simplify the process, **3aa** was used directly after short flash chromatography to remove the excess amount of 2,7-dihydroxynaphthalene, the catalyst and the inorganic base. To our delight, the atroposelective homocoupling was successful after a quick survey of oxidation catalysts (see Table S1 for details). With 5 mol% of commercially available di-*m*-hydroxo- bis[(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine)copper(II)] chloride (Cu-TMEDA) as a catalyst and air as a green oxidant, the desired C_2- symmetric BINOL derivative **4aa** featuring four stereogenic centers was obtained in 78% yield (for 2 steps) with 99% *ee* and, most importantly, as a single diastereomer (>20 : 1 *dr*, entry 9). The improvement of enantiomeric excess (96 to >99% *ee*) clearly indicated the beneficial role of the Horeau chiral amplification principle and the efficiency of central-to-axial chirality induction.[60,61] In addition, the importance of air was also proved, as the yield was dramatically decreased under an argon atmosphere, indicating that the combination of Cu-TMEDA and air is a practical catalytic system for oxidative cross-coupling of highly sterically hindered phenol derivatives.

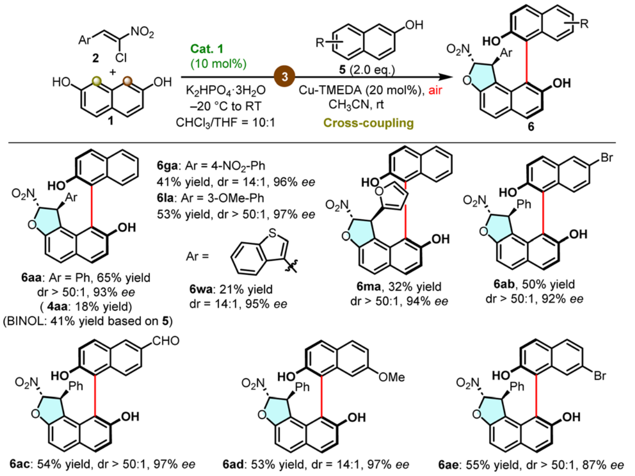


Scheme 2 Evaluation of substrate scope of homo-coupling. ^{a}Conducted on a 0.2 mmol scale, yield was reported for 2 steps, and **3** was used directly after flash chromatography.

With optimized reaction conditions in hand, the generality of this chirality induction process was explored (Scheme 2). The tolerance of the *α*-chloronitroalkenes was investigated, revealing that both electronic and steric parameters influenced the reactivity, but with a uniform excellent double stereocontrol. The influence of *para*-substituents on the aryl group was first studied. It was found that halogen substitution could lead to good yields (**4ab**–**4ad**, 56–70% yield for 2 steps). Electron-donating substituents such as methyl (**4ae**) and methoxy (**4af**) groups were also tolerated well. When the *para*-position was substituted with an ester group (**4ag**), the yield decreased significantly, although the stereocontrol of the reaction was still good. The results of *meta*-substitutions were similar to those of *para*-substituted ones. Except for the chloro substitution (**4ai**), the products all achieved good yields (**4ah** and **4aj**–**4am**). When examining the substituent effect at the *ortho*-position, the steric effect played an important role. As expected, the bromo group (**4ap**) with the largest steric hindrance gave the lowest yield. Other groups with relatively smaller steric hindrance all achieved moderate yields (**4an**, **4ao**, and **4aq**–**4at**). In addition, heterocyclic substituents such as furan (**4au**), thiophene (**4av**), and benzothiophene (**4aw**) were all suitable, with the highest isolated yield of 84%. In addition to the aryl substituted chloronitroalkene, the alkenyl substituted counterpart also furnished the desired product **4ax** in 31% yield with 8 : 1 *dr* and 99% *ee.* Intriguingly, during the preparation of the alkynyl substituted chloronitroalkene, an additional hydrochlorination reaction of the carbon–carbon triple bond was observed. Under the optimized reaction conditions, the (3 + 2) cyclized product **3ay** was successfully isolated in 67% yield and 86% *ee*. However, the oxidative coupling product **4ay** remained undetected. Regrettably, the cyclohexyl substituted chloronitroalkene proved unable to undergo the initial (3 + 2) cyclization process. Furthermore, the 3,6-disubstituted 2,7-dihydroxynaphthalenes were also subjected to testing. The dibromo substituted cyclized product **3ba** was obtained in 90% yield with 84% *ee*. The coupling process was halted, presumably due to the steric hindrance and electron-withdrawing nature of the bromine atoms. Moreover, the diphenyl substituted 2,7-dihydroxynaphthalene was found to be incompatible with the cyclization process. The absolute configuration of **4ad** was determined to be *aR* by single crystal X-ray crystallographic analysis, and the configurations of the other compounds were assigned by analogy.[62]

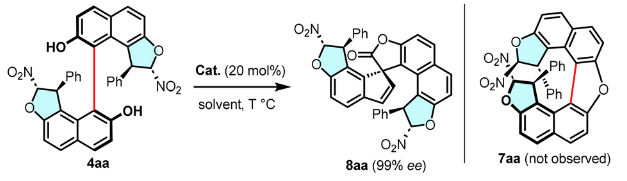
After achieving excellent chirality induction in homo-coupling, we wondered whether the cross-coupling reaction between chiral intermediates **3** and 2-naphthols **5** would be chemo- and stereoselective, as less hindered 2-naphthol may undergo self-coupling more easily. After the optimization of a series of reaction conditions, it was discovered that in acetonitrile, the Cu-TMEDA complex was also capable of facilitating the targeted selective cross-coupling reaction (see **TS-2** in the SI). When 2.0 equivalents of 2-naphthol **5a** were present, the homo-coupling of **3aa** was effectively inhibited. As a result, the sterically hindered non-C_2 symmetric BINOL derivative **6aa** was obtained in 65% yield and 93% *ee* (Scheme 3). Under these reaction conditions, **4aa** and BINOL (calculated based on **5a**) were isolated in 18% yield and 41% yield, respectively. Subsequently, a preliminary investigation of the substrate adaptability was carried out. Products with 3-methoxy (**6la**) and 4-nitro (**6ga**) substitutions on the aromatic ring of the nitroalkene moiety could be obtained with moderate yields and excellent ee values. For heterocyclic substitutions, such as benzothiophene (**6wa**) and furan (**6ma**), the yields of the products decreased slightly. In addition, the substituents on the 2-naphthol moiety also had less influence. For example, products with bromo (**6ab**) and formyl (**6ac**) substitutions at the 6-position, as well as methoxy (**6ad**) and bromo (**6ae**) substitutions at the 7-position, all showed good stereoselectivities in moderate yields. These preliminary results along with the adaptability of substituents indicate that chiral induction is also effective to construct more challenging non-C_2-symmetric BINOL derivatives.

With the preparation of a series of sterically hindered BINOL derivatives, we attempted to transform them into the corresponding [7]-oxa-helicenes **7**.[63,64] However, in the presence of a stoichiometric amount of *p*-toluenesulfonic acid (TsOH) in refluxing toluene, the expected heterohelicene **7aa** was not observed. Surprisingly, the rearranged spirocyclic lactone **8aa** featuring five stereogenic centers was isolated in 16% yield instead.[65] After a series of investigations (Table 2, entries 2–6, Tables S3–S5 in the SI), it was found that a catalytic amount (20 mol%) of stronger trifluoromethanesulfonic acid (TfOH)



Scheme 3 Evaluation of substrate scope of cross-coupling. [a]Conducted on a 0.2 mmol scale. [b]Yield was reported for 2 steps.

Table 2 Optimization of the reaction conditions for the synthesis of spiro-cyclic products[a]

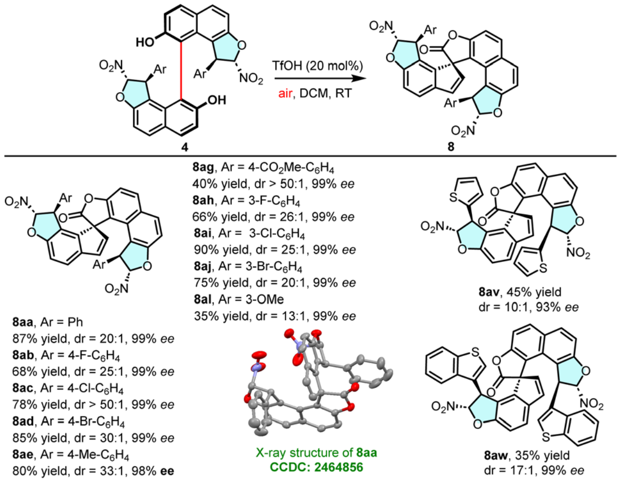


Entry	Cat.	Solvent	T (°C)	Yield of **8aa**[b]
1[c]	TsOH·H$_2$O	Toluene	120	16
2[c]	TsOH·H$_2$O	Toluene	25	0
3[c]	TsOH·H$_2$O	DCM	25	0
4[c]	CH$_3$SO$_3$H	DCM	25	9
5[c]	TfOH	DCM	25	Complex
6	**TfOH**	**DCM**	**25**	**87**
7	FeCl$_3$	DCM	25	66
8	TfOH	MeOH	25	0
9	TfOH	CHCl$_3$	25	Trace
10[d]	TfOH	DCM	25	Trace

[a] Unless otherwise noted, reactions were conducted with **4aa** (0.1 mmol) and **Cat.** (20 mol%) in solvent. [b] Isolated yield. [c] 100 mol% of **Cat.** was used. [d] Under Ar.

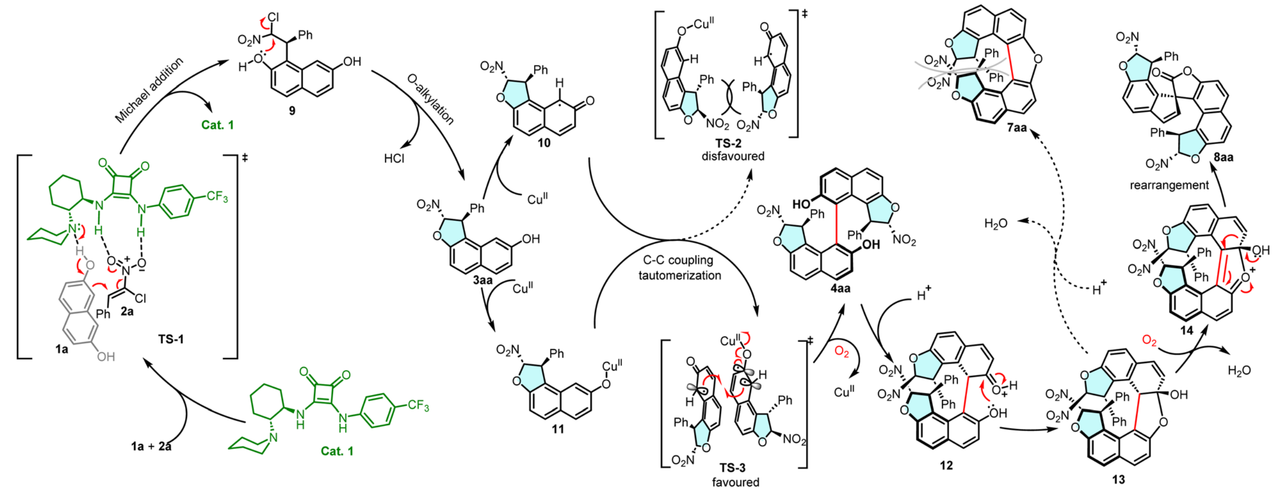
could afford the rearranged product **8aa** in 87% yield and 99% *ee*, *via* a rare example of axial-to-central chirality conversion.[66–73] In addition, ferric chloride as a Lewis acid catalyst could also promote this reaction, affording product **8aa** in 66% yield (entry 7). Subsequent investigations revealed that dichloromethane was the best solvent and air was essential for this rearrangement to proceed (entries 8–10).

Similarly, a preliminary investigation on the substrate adaptability of this peculiar rearrangement with axial-to-central chirality conversion was conducted. Overall, the rearranged products could be obtained in good yields with consistently excellent enantiomeric excesses (Scheme 4). Halogen substitutions at the *para*-position of the aromatic ring were well-tolerated, and the target products **8ab–8ad** were obtained in 68–85% yields. For the electron-donating methyl substitution, the yield of the product (**8ae**) was 80%. The product with a *meta*-methoxy substitution (**8al**) could be obtained with a moderate 35% yield but still with nearly perfect enantioselectivity (99% *ee*). In addition, products with *meta*-halogen substitutions (**8ah–8aj**) could also be obtained in good yields. For heterocyclic substitutions, illustrated as thiophene (**8av**) and benzothiophene (**8aw**), the yields of the products decreased to 45% and 35%, respectively but the *ee* remains high. The absolute configuration of the product **8aa** was determined by single crystal X-ray crystallographic analysis, and others were assigned by analogy.[62]



Scheme 4 Evaluation of substrate scope of spiro-cyclic products. [a]Conducted on a 0.2 mmol scale.

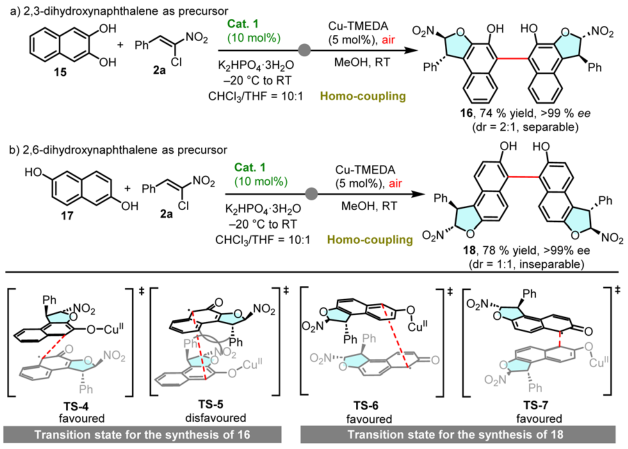
To explain the chirality induction process in BINOL derivatives **4** and **6** and the subsequent oxidative rearrangement with axial-to-central chirality conversion to spiro lactones **8**, a possible reaction pathway is proposed in Scheme 5. First, in the presence of bifunctional squaramide **Cat. 1**, hydrogen-bonding activation of both substrates **1a** and **2a** results in the transition state **TS-1** triggering enantioselective Michael addition to yield the adduct **9**. Subsequently, in the presence of the inorganic base, further *O*-alkylation is promoted to obtain the key centrally chiral dihydrobenzofuran **3aa**, with *trans* relative configuration. The remaining 2-hydroxynaphthalene moiety in **3aa** can be oxidized by Cu(II) to generate the radical intermediate **10**; meanwhile, another molecule of **3aa** can undergo ligand exchange to form intermediate **11**. In the subsequent C–C bond coupling step, two possible transition states, **TS-2** and **TS-3**, can be envisioned. However, **TS-2** involves significant steric hindrance between the two chiral dihydrobenzofuran moieties, making it energetically unfavorable. Therefore, the final oxidative coupling product **4aa** is obtained *via* a series of single-electron transfers through the more favorable transition state **TS-3**. The released Cu(I) can be oxidized to Cu(II) by oxygen to terminate the catalytic cycle. In addition, in the presence of a strong Brønsted acid, the tautomerized intermediate **12** can be



Scheme 5 Proposed mechanistic pathways.

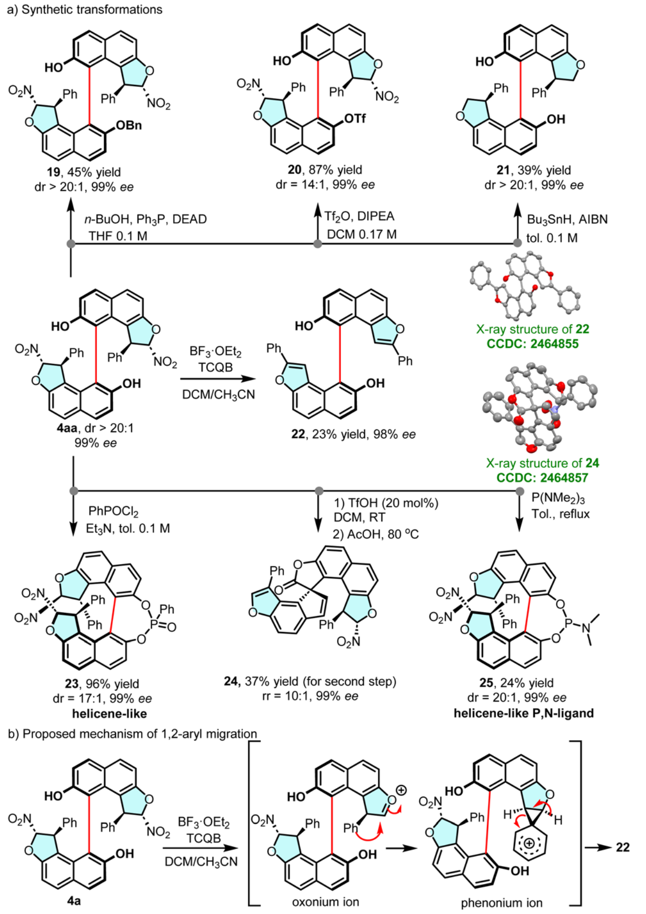
generated *in situ* and trapped by intramolecular addition to generate the hemiacetal intermediate **13** whose dehydration leading to oxa-helicene **7aa** is hampered for steric reasons. Therefore, the presence of dioxygen can promote the oxidation of **13** to the highly reactive oxonium ion intermediate **14**, triggering a 1,2-migration of the alkenyl part to yield the rearranged spirocyclic lactone **8aa.**

To further demonstrate the utility of this strategy, 2,3-dihydroxynaphthalene **15** was used as the starting material. Under standard conditions, the homo-coupled 3,3′-difunctionalized BINOL derivative **16** was obtained in 74% yield with 99% *ee* (Scheme 6). Although the atroposelectivity is modest ($dr = 2:1$), the two atropisomers bearing four stereogenic centers could be separated by column chromatography. When 2,6-dihydroxynaphthol **17** was used, the BINOL derivative **18** was obtained in 78% yield with low atroposelectivity ($dr = 1:1$) and 99% *ee* (Scheme 6). To account for this disparity in comparison with the high atroposelectivity exhibited by **4aa**, the corresponding transition states of the oxidative coupling process were postulated. As depicted in Scheme 6, within **Ts-5**, the two phenyl groups encounter steric hindrance. Consequently, **TS-4** is preferred, leading to a diastereomeric ratio of 2 : 1 for compound **16.** The closer proximity between both dihydrofuran moieties upon coupling as compared to the coupling leading to **4aa** might explain the lower diastereoselectivity in this case. In contrast, in **TS-6** and **Ts-7**, there is no steric hindrance since the chiral dihydrofuran moiety is situated at a higher distance from the coupling site. In consequence, almost no energy difference between **TS-6** and **TS-7** could account for the absence of diastereoselectivity in this case.



Scheme 6 Application of 2,3- and 2,6-dihydroxynaphthalenes.

The post-transformation of the sterically hindered BINOL derivative **4aa** was further investigated (Scheme 7a). First, mono-*O*-alkylated product **19** was obtained in 45% yield *via* a chemoselective Mitsunobu reaction preserving the stereochemical integrity. Similarly, the mono-triflate **20** was synthesized in 87% yield, which could be amenable to further cross-coupling reactions as needed. In the presence of tributyltin hydride, selective radical denitration gives the C_2-symmetric centrally and axially chiral dihydrobenzofurane **21** in 39% yield and no erosion of the enantiopurity was observed. Interestingly, in the presence of BF_3 and tetrachloro-1,4-benzoquinone (TCBQ), an unexpected aryl migration/aromatization reaction occurred, affording the atropisomeric naphtho[2,1-*b*]furan **22** in modest yield but with high stereocontrol.[74,75] A possible mechanistic interpretation for this 1,2 aryl migration is shown in Scheme 7b. The nitrodihydrofuran moiety could be oxidized to form the oxonium ion intermediate, which is then trapped by the phenyl group to generate a phenonium ion to complete the 1,2-aryl migration after rearomatization. The absolute configuration of the product **22** was confirmed by single crystal X-ray crystallographic analysis.[62] Moreover, in the presence of phenyldichlorophosphine oxide and triethylamine, an efficient axial-to-helical conversion of chirality occurred leading to the formation of heterohelicene-like molecule **23** in 96% yield. In addition, elimination of HNO_2 from spirolactone **8aa** obtained from BINOL **4aa** occurred in acetic acid providing the curved molecule **24** with maintained enantiopurity.[76] Finally, the



Scheme 7 Post-functionalization reactions.

heterohelicene-like *P*,*N*-ligand **25** was synthesized in the presence of hexamethylphosphinetriamine with maintained *ee.* The above synthetic post-transformations fully demonstrate the synthetic potential of the sterically hindered 8,8′-disubstituted BINOL derivatives obtained through central-to-axial chirality induction.

Conclusions

In summary, a highly atroposelective strategy for the synthesis of sterically hindered stereochemically complex 8,8′-disubstituted BINOL derivatives was developed through an efficient central-to-axial chirality induction. This process relies on a regio- and enantioselective mono-dihydrobenzofurannulation of commercially available 2,7-dihydroxynaphthalene controlling the central chirality, followed by a highly atroposelective copper-catalyzed aerobic oxidative coupling fixing the axial chirality and enabling access to new families of C_2 and non-C_2 symmetric BINOL derivatives featuring up to four stereogenic centers. In addition, simple post-transformations demonstrated the synthetic potential of these derivatives to access either spiroheterocycles by a rare axial-to-central conversion of chirality or heterohelicene-like or atropisomeric naphtho[2,1-*b*] furan compounds *via* intriguing rearrangement processes including a triple central-to-axial-to-helical conversion of chirality, which highlighted the versatility and synthetic utility of this new atroposelective methodology.

Author contributions

X. Bao and D. Bonne designed this project. Y. Yang, G. Bai, and M. Qin performed the chemical experiments and prepared the SI. Y. Yang and J. Wang participated in the preparation of the SI. J. Rodriguez and H. Wang supervised and directed the project. All authors discussed and participated in the preparation of the final manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

CCDC 2464854 (**4ad**), 2464855 (**22**), 2464856 (**8aa**) and 2464857 (**24**) contain the supplementary crystallographic data for this paper.[62a–d]

The data that support the findings of this study are available in the SI of this article, including the detailed experimental procedures, characterization data, and copies of the spectra of products (^{1}H, ^{19}F, ^{31}P, and ^{13}C NMR and HPLC). See DOI: **https://doi.org/10.1039/d5sc05212b**.

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