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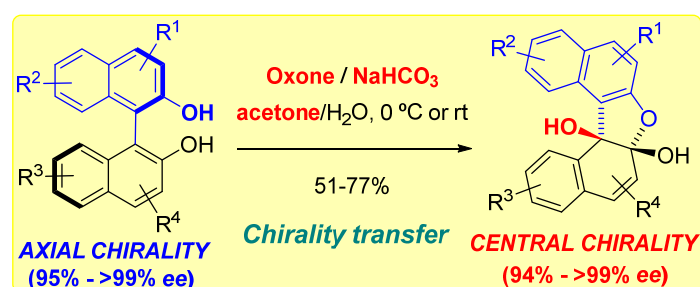
Chirality transfer from the oxidative dearomatization of axially chiral binols with Oxone under mild conditions

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Supporting Information Placeholder



ABSTRACT: Easily accessible axially chiral substituted binols (95 to >99% *ee*), undergo an oxidative dearomatization process with the system Oxone / NaHCO₃ / acetone, under mild conditions, to afford pentacyclic hemiacetalic *cis*-diols (94 to >99% *ee*), bearing two new stereogenic centers, through an efficient axial-to-central chirality transfer.

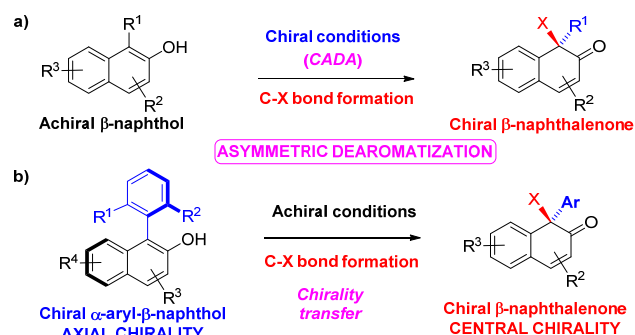
Dearomatizations of phenols and naphthols have been studied intensively for a long time,¹ providing an efficient method to transform planar achiral substrates into three-dimensional structures through an *sp*²-to-*sp*³ change in geometry on one of the *sp*²-hybridized carbon centers. These dearomatized compounds contain a highly functionalized cyclohexadienone skeleton, which is a useful handle framework often appear in biologically active natural products and pharmaceuticals.²

In particular, dearomatization of 2-naphthols³ allows the installation of a new stereogenic center at the C-1 position of the naphthyl core for the rapid construction of functionalized β-naphthalenones, used feasibly for further transformations into diverse bioactive molecules and natural products. A variety of compounds bearing oxygen-, nitrogen-, halogen- and carbon-substituents can be prepared depending on the reactants used. With respect to the enantioselective version of this process, the catalytic asymmetric dearomatizations (CADA) of planar achiral β-naphthols into chiral β-naphthalenones has emerged as a powerful tool during the past decade (Scheme 1a).⁴ CADA of β-naphthols has received intense attention, and a series of elegant works has been realized in this emerging field, including asymmetric formation of C-O, C-halogen, C-N, C-S and C-C bonds.⁵ In these works, different cyclic ketone frameworks are efficiently constructed in high yields and enantioselectivities.

Another interesting area in this field could be the axial-to-central chirality transfer⁶ from dearomatization of α-aryl-β-naphthols, with axial chirality, into β-naphthalenones, showing central chirality (Scheme 1b). Nevertheless, this synthetic strategy has been limited, first by the need of multistep procedures during the preparation of enantiopure biaryls and second by the

risk of racemization in the dearomatization. Thus, the use of easily accessible enantiopure biaryls and milder conditions to achieve dearomatizations are basic requirements for the development of the axial-to-central chirality transfer strategy for synthesis of chiral β-naphthalenones.⁷

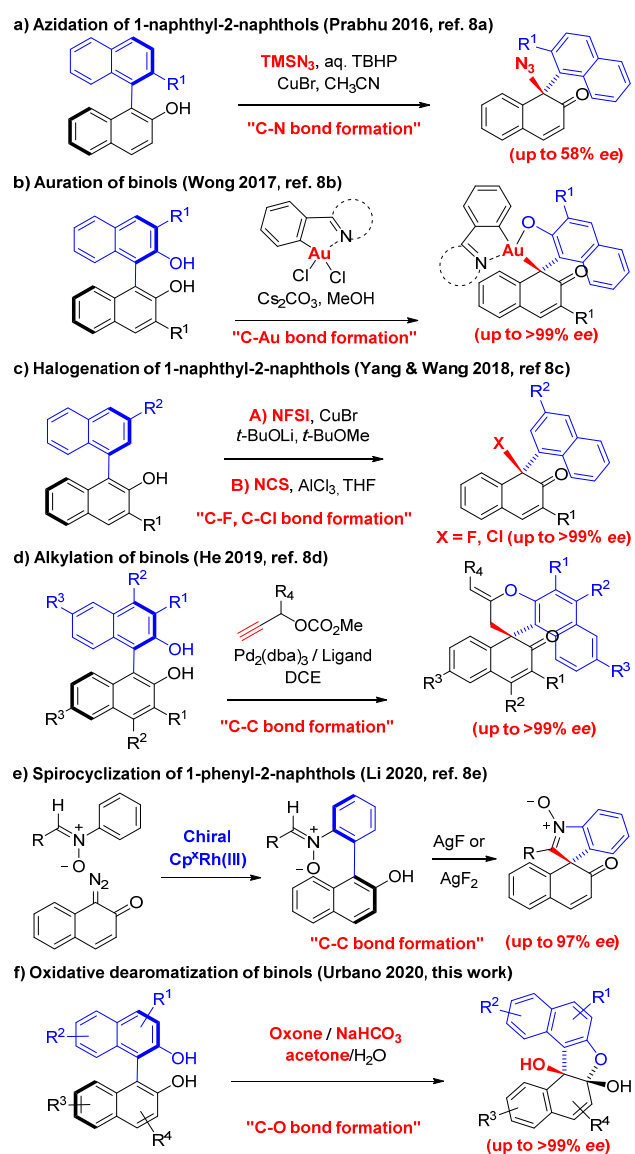
Scheme 1. Asymmetric synthesis of β-naphthalenones: a) Catalytic asymmetric dearomatizations (CADA) of achiral β-naphthols. b) Axial-to-central chirality transfer from axially chiral α-aryl-β-naphthols.



In recent years, only a few examples of asymmetric dearomatizations of α-aryl-β-naphthols and binols into chiral β-naphthalenones, through an axial-to-central chirality transfer, have been reported so far (Scheme 2).⁸ In 2016,^{8a} Prabhu reported the azidative dearomatization of 1-naphthyl-2-naphthols with TMSN₃, CuBr and TBHP to afford chiral quaternary azides, showing 58% *ee* (Scheme 2a). One year later,^{8b} stable

BINOL/gold(III) complexes with central chirality (*ee* up to >99%) were synthesized by dearomatization of binols with cyclometalated gold(III) dichloride complexes and CsCO₃ (Scheme 2b). In 2018,^{8c} Yang & Wang described the asymmetric fluorinative dearomatization of axially chiral 1-naphthyl-2-naphthols using NFSI, CuBr and *t*-BuOLi, to give fluorinated β -naphthalenones with *ee* up to 95% (Scheme 2c). Using NCS and AlCl₃, the chlorinated derivatives were obtained with *ee* up to >99%. Later,^{8d} He disclosed an axial-to-central chirality transfer via dearomatization of binols with a wide range of propargyl carbonates under Pd catalysis to afford chiral spiro-compounds with optical purities up to >99% (Scheme 2d). In 2020,^{8e} Li has reported the synthesis of nitrones with an all-carbon quaternary center (*ee* up to 97%) by the Ag-mediated dearomatization of 1-phenyl-1-naphthols prepared in situ by chiral Rh(III) catalysis from nitrones and quinone diazides (Scheme 2e).

Scheme 2. Examples of asymmetric dearomatization of α -aryl- β -naphthols via axial-to-central chirality transfer.

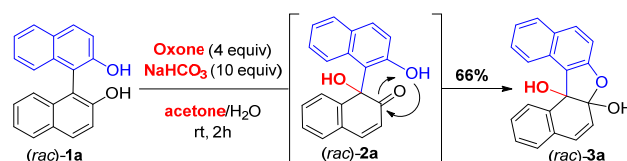


Herein, we report an efficient axial-to-central chirality transfer from the oxidative dearomatization of easily accessible enantiopure substituted binols using the system Oxone / NaHCO₃ / acetone to give pentacyclic hemiacetalic *cis*-diols, with two stereogenic centers, showing optical purities up to >99% (Scheme 1f). To the best of our knowledge, this is the first example describing the oxidative dearomatization of unprotected binols and the first general application of the axial-to-central chirality transfer to an oxidative dearomatization process.⁹

Very recently, we have developed a quite general highly site-selective oxidative dearomatization of substituted phenols and naphthols into the corresponding *ortho*-quinols or epoxy *ortho*-quinols using, as the final oxidant, dimethyldioxirane generated in situ with the system Oxone / NaHCO₃ / acetone.¹⁰

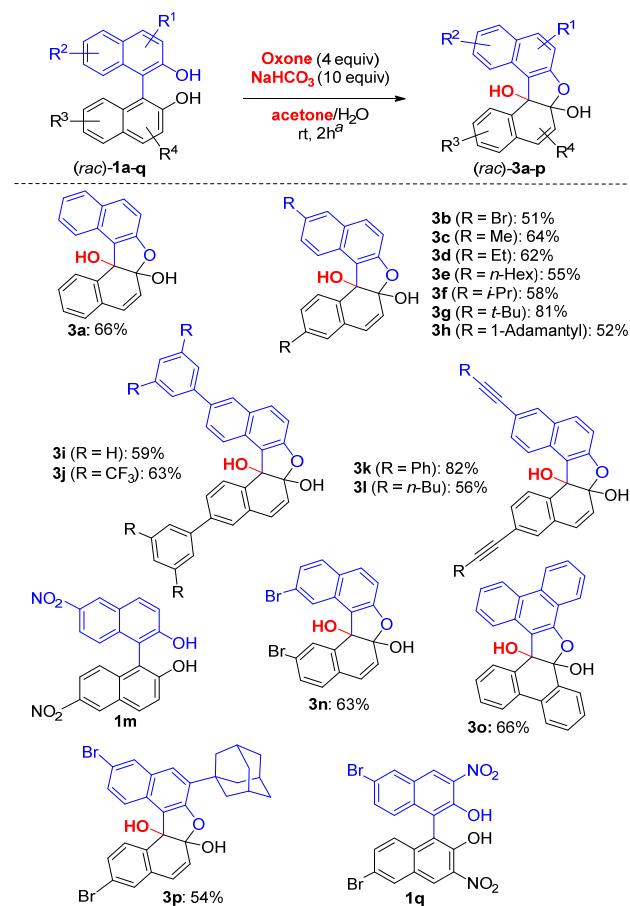
When this oxidative dearomatization was performed with commercially available racemic binol (*rac*)-**1a** using 4 equiv of Oxone and 10 equiv of NaHCO₃ in acetone and water at rt for 2 h, the pentacyclic hemiacetalic *cis*-diol (*rac*)-**3a** was obtained, as the only product, with 66% yield (Scheme 3). Compound (*rac*)-**3a**, with two new stereogenic centers, was probably formed from *ortho*-quinol intermediate (*rac*)-**2a**, initially formed after oxidative dearomatization of (*rac*)-**1a**, followed by an intramolecular nucleophilic addition of the phenolic OH to the carbonyl group of (*rac*)-**2a** promoted by the basic medium. The *cis* arrangement of the two hydroxyl groups of (*rac*)-**3a** was demonstrated after a NOESY experiment (see Supporting Information).

Scheme 3. Oxidative dearomatization of binol (*rac*)-1a** into pentacyclic *cis*-diol (*rac*)-**3a** with Oxone through *ortho*-quinol intermediate (*rac*)-**2a**.**



In order to evaluate the scope of this oxidative dearomatization, several racemic binols (*rac*)-**1a-q** were used as starting materials (Scheme 4). Thus, under the conditions depicted in Scheme 4, the dibromo derivative **1b** afforded the pentacyclic *cis*-diol **3b** in 51% yield. When the reaction was performed on linear alkyl-substituted binols **1c-e**, the oxidative dearomatization process worked well and *cis*-diols **3c-e** were formed in yields ranging from 55 to 64%, whereas the presence of branched and sterically demanding alkyl substituents on the starting binols **1f-h** didn't avoid the oxidative dearomatization to be successful allowing to obtain pentacyclic derivatives **1f-h** in good yields (52-81%). In the case of phenyl- and bis(trifluorophenyl)-substituents, the corresponding *cis*-diols **3i-j** were obtained with 59 and 63% yield, respectively. Similarly, the presence of triple bonds on binols **1k-l** didn't affect the efficacy of the process which afforded pentacyclic derivatives **3k-l** in 56 and 82% yield, respectively. Nevertheless, when the process was tried on binol **1m**, bearing two nitro substituents, no reaction was observed. This result suggested that the presence of strong electron-withdrawing substituents on the starting binols could inhibit the process. On the other hand, the reaction of racemic binol **1n**, bearing two bromine substituents at 7 and 7' positions afforded the pentacyclic hemiacetalic *cis*-diol **3n**, in 63% yield (Scheme 4).

Scheme 4. Scope of the oxidative dearomatization of substituted racemic binols 1a-q with Oxone in acetone. ^aIsolated yields.



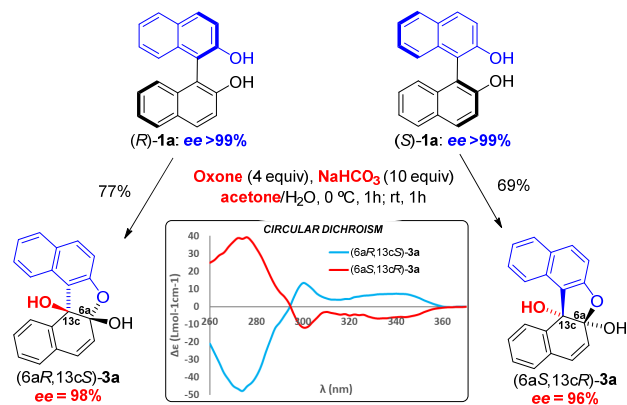
When the oxidative dearomatization was realized using 9,9'-biphenanthrene-10,10'-diol (**1o**), the heptacyclic *cis*-diol **3o** was obtained with a 66% yield. On the other hand, the reaction on the non-symmetric binol **1p** with one bulky 1-adamantyl substituent at C-3 afforded, as the unique product, pentacyclic *cis*-diol **3p**, in 54% yield. This result suggested that bulky substituents close to the reactive center could difficult the oxidation, directing the reaction to the other less sterically demanding 2-naphthol. Finally, when the reaction was tried on binol **1q**, with two nitro substituents at the 3 and 3' positions, no reaction was observed again evidencing that strong electron-withdrawing substituents clearly inhibited the reaction.

Next, we investigated the possible axial-to-central chirality transfer from the oxidative dearomatization of axially chiral enantiopure binols to the enantiomerically enriched pentacyclic hemiacetalic *cis*-diols showing central chirality.

Thus, when commercially available enantiopure binol (*R*)-**1a** was submitted to the standard oxidative dearomatization conditions, 4 equiv of Oxone, 10 equiv of NaHCO₃ in acetone/H₂O at rt for 2 h, the pentacyclic *cis*-diol (6*aR*,13*cS*)-**3a**, showing a promising 93% *ee*,¹¹ was obtained (see SI). In order to enhance this optical purity, we perform the same reaction but at 0 °C for 1h and 1h at rt (Scheme 5). Under these conditions, enantiopure binol (*R*)-**1a** afforded pentacyclic *cis*-diol (6*aR*,13*cS*)-**3a** in 77% isolated yield with an excellent 98% *ee*, indicating that a very efficient axial-to-central chirality transfer had took place. Under the same reaction conditions, the oxidative dearomatization of enantiopure binol (*S*)-**1a** gave rise

to the corresponding enantiomer (6*aS*,13*cR*)-**3a** which was obtained with 69% yield and 96% *ee* (Scheme 5).

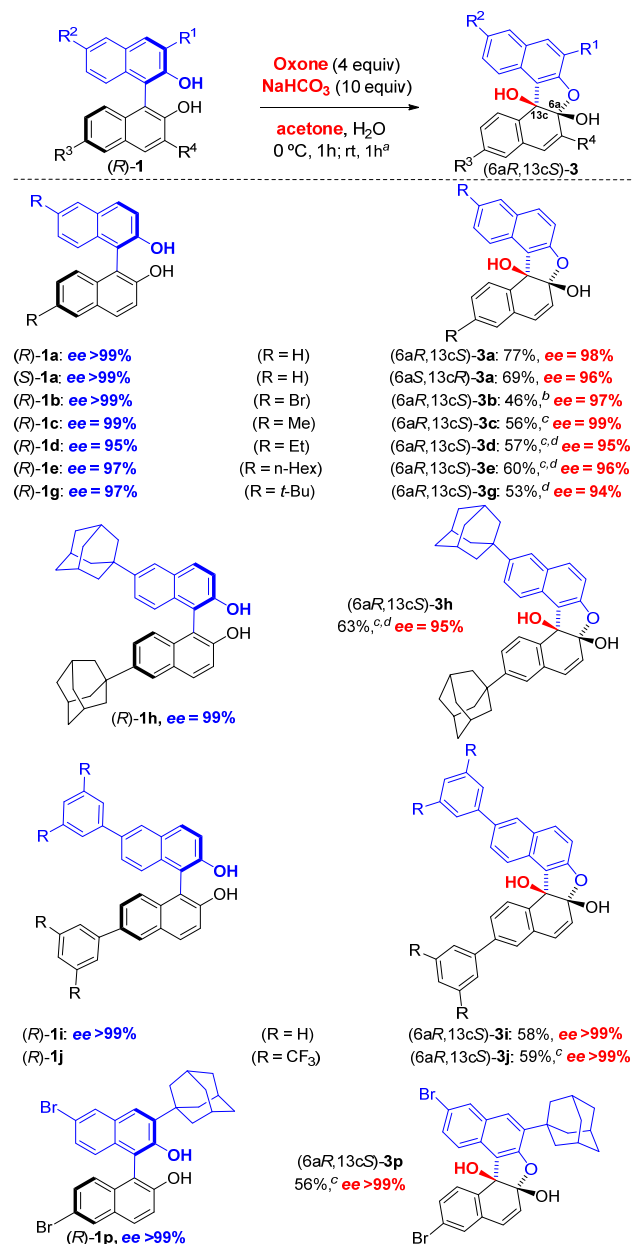
Scheme 5. Axial-to-central chirality transfer from the oxidative dearomatization of enantiopure binols (*R*)-1a** and (*S*)-**1a** into pentacyclic *cis*-diols (6*aR*,13*cS*)-**3a** and (6*aS*,13*cR*)-**3a** with Oxone in acetone.**



Due to the instability of hemiacetalic *cis*-diols **3**, we were not able to get suitable crystals to perform an X-ray study to determine their absolute configurations. We have tentatively assigned the (6*aR*,13*cS*) absolute configuration for all hemiacetalic *cis*-diols obtained from (*R*)-binols based on similar results on previous works,^{8a-d} suggesting that the phenolic OH is guiding the oxidation to the aromatic ring face of the adjacent ring.

In order to evaluate the general efficiency of the axial-to-central chirality transfer, several easily accessible (*R*)-binols (*ee* 95 to >99%)¹² were prepared and submitted to the oxidative dearomatization conditions depicted in Scheme 6. Thus, the dibromo binol (*R*)-**1b** (*ee* >99%) afforded, in 46% yield for a 2 mmol scale, the pentacyclic *cis*-diol (6*aR*,13*cS*)-**3b** showing an excellent 97% *ee*. Next, we performed the reactions of alkyl-substituted binols (*R*)-**1c-e** being necessary to use 6 equiv of Oxone and 15 equiv of NaHCO₃ for the reactions to be completed. In the case of dimethyl binol (*R*)-**1c** (*ee* 99%), the reaction was carried out at 0 °C for 1 h and at rt for 1 h to afford pentacyclic *cis*-diol (6*aR*,13*cS*)-**3c** in 56% yield and 99% *ee*. In the case of diethyl and dihexyl binols, (*R*)-**1d** (*ee* 95%) and (*R*)-**1e** (*ee* 97%), respectively, the reaction was performed at rt for 2 hours giving rise to pentacyclic *cis*-diols (6*aR*,13*cS*)-**3d** and (6*aR*,13*cS*)-**3e**, which were obtained in 57-60% yields, showing enantiomeric purities of 95% and 96%, respectively. Next, the reaction of di-*tert*-butyl binol (*R*)-**1g** (*ee* 97%) was realized at rt for 2 hours rendering the pentacyclic *cis*-diol (6*aR*,13*cS*)-**3g** in 53% yield and 94% *ee*. In the case of the di(1-adamantyl) binol (*R*)-**1h** (*ee* 99%), the oxidative dearomatization was performed with 6 equiv of Oxone and 15 equiv of NaHCO₃ at rt for 2 hours affording pentacyclic *cis*-diol (6*aR*,13*cS*)-**3h** in 63% yield and 95% of enantiomeric purity. Under the conditions depicted in Scheme 6, the diphenyl binol (*R*)-**1i** (*ee* >99%) furnished *cis*-diol (6*aR*,13*cS*)-**3i** in 58% yield and *ee* >99%. On the other hand, the di(3,5-bis-(trifluoromethyl)-phenyl) binol (*R*)-**1j** reacted with 6 equiv of Oxone and 15 equiv of NaHCO₃ to give pentacyclic *cis*-diol (6*aR*,13*cS*)-**3j** in 59% yield and >99% *ee*. Finally, the oxidative dearomatization of the 3-(1-adamantyl)-substituted binol (*R*)-**1p** (*ee* >99%) took place after reaction with 6 equiv of Oxone and 15 equiv of NaHCO₃ to afford pentacyclic *cis*-diol (6*aR*,13*cS*)-**3p** in 56% yield and >99% *ee*.

Scheme 6. Scope of the asymmetric oxidative dearomatization of substituted binols (R)-1 with Oxone in acetone. ^a Isolated yields, **2 Mmol scale**. ^c 6 Equiv of Oxone, 15 equiv of NaHCO₃. ^d rt, 2h.



In summary, we have described a highly efficient axial-to-central chirality transfer from the oxidative dearomatization of easily accessible axially chiral binols (*ee* 95 - >99%) with the system Oxone/NaHCO₃/acetone into pentacyclic hemiacetalic *cis*-diols, bearing two stereogenic centers, with excellent optical purities (*ee* 94 - >99%) and under very mild conditions.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, characterization data, and copies of ¹H- and ¹³C-NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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