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# Copper-Catalyzed Enantioselective Ring-Opening of Cyclic Diaryliodoniums and *O*-Alkylhydroxylamines

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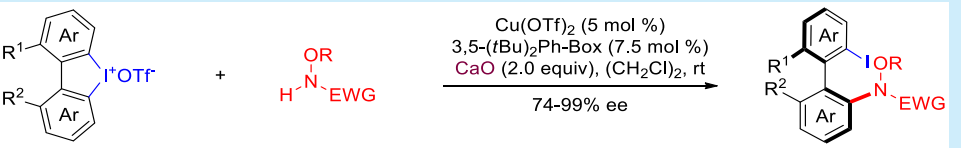
Supporting Information



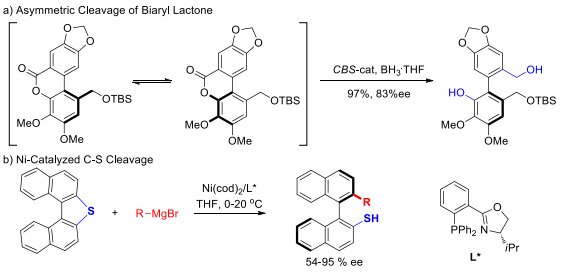

**ABSTRACT:** A preparation of 2-hydroxyamino-2′-iodobiaryls via the Cu-catalyzed enantioselective ring-opening reaction of cyclic diaryliodonium salts with *O*-alkylhydroxylamines is reported. 3,5-Di(*tert*-butyl)phenyl bis(oxazoline) was found to be the optimal ligand, and up to 99% ee values were achieved. The use of CaO as the base dramatically improved the yields and inhibited the side reactions. Finally, synthetic applications of these hydroxylamines were briefly demonstrated.



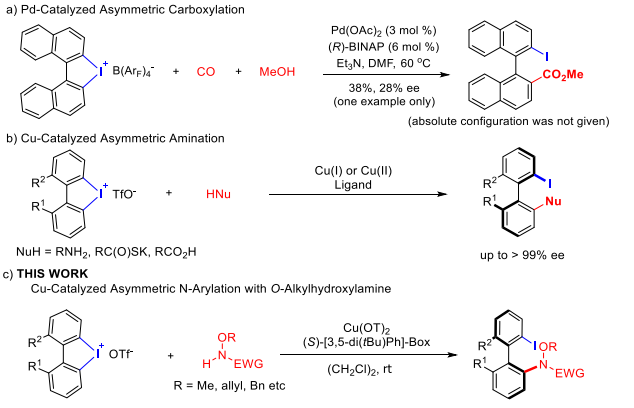
Since the observation of "non-free rotation" of 6,6′-dinitrodiphenic acid by Christie and Kenner,[1] axial chirality as a new stereogenic element has come to the attention of chemists and later on became one of the privileged chiral units of chiral ligands and catalysts in asymmetric catalysis. Furthermore, mastigophorene, vancomycin, blumeanine, and other related natural products containing axially chiral biaryl units were isolated.[2]

The applications of biaryl axial chirality in asymmetric catalysis and its existence in biological active molecules urged chemists to develop new practical methods to access these highly valuable scaffolds. Besides the aryl−aryl cross-coupling[3] and oxidative couplings,[4] elegant methods including de novo asymmetric aryl ring construction,[5] desymmetrization or resolution,[6] as well as point-to-axial chirality transfer[7] have been developed for the diverse preparation of optically active atropisomers. Recently, organo-catalysis became a robust method for the atropisomers syntheses.[8] The asymmetric ring-opening of Bringmann's lactones, which undergo fast dynamic equilibrium of their (R)- and (S)-isomers, is a very powerful strategy in the construction of axially chiral compounds (Scheme 1a).[9] Remarkably, inspired by this fast dynamic equilibrium, the Akiyama and Wang groups realized the dynamic kinetic resolution of biaryls via *N*,*O*-acetal intermediates by either chiral phosphoric acid or chiral iridium catalysis.[10] In 2002, Hayashi and coworkers demonstrated a Ni-catalyzed asymmetric C−S bond cleavage/ring-opening reaction of dibenzo[*b*,*d*]thiophenes (Scheme 1b).[11] Later on, the same group studied a palladium-catalyzed ring-opening of cyclic diaryliodonium, where they showed one example for an asymmetric trial with 38% yield and 28% ee (Scheme 2a).[12,13] Recently, Gu and coworkers realized the Cu-catalyzed highly enantioselective ring-opening amination, thiolation, and oxygenation reactions of cyclic diaryliodonium (Scheme 2b).[14] More than 1 year later, Zhang and coworkers reported a very

**Scheme 1. Asymmetric Ring-Opening Reactions**




**Scheme 2. Transition-Metal-Catalyzed Asymmetric Ring-Opening of Cyclic Diaryliodoniums**

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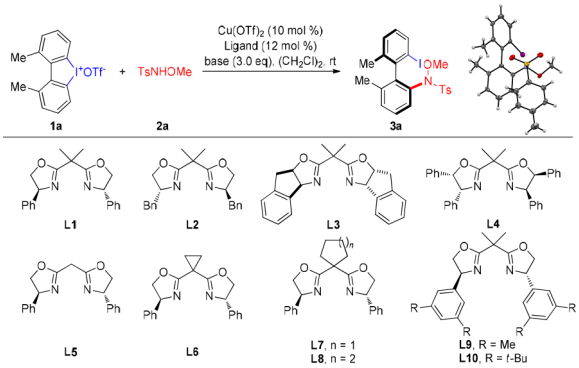
similar example of Cu-catalyzed asymmetric acyloxylation with cyclic diaryliodoniums (Scheme 2b).[15]

Notably, in the Cu-catalyzed asymmetric amination reaction, only the primary amine afforded high enantioselectivity. The secondary amines, including dialkyl amines or *N*-alkyl anilines, gave dramatically decreased ee values. Moreover, until now, trifluoromethanesulfonamide was the only amide that could be applied in this ring-opening reaction, with low conversion and reasonable enantioselectivity. Furthermore, the use of ammonia as the nucleophile was unsuccessful. In consideration of the strong derivatization capability of hydroxyamines, we report a Cu-catalyzed highly enantioselective ring-opening/amination of cyclic diaryliodoniums with *O*-alkylhydroxylamines (Scheme 2c).

We started our investigation by using diaryliodonium **1a** and *N*-methoxy-4-methylbenzenesulfonamide **2a** as the model substrates. With $Na_2CO_3$ as the base and Ph-Box **L1** as the ligand, the reaction afforded a complicated mixture, and the desired product **3a** was isolated in only 3% yield (Table 1, entry 1). With the use of $K_2CO_3$ in lieu of $Na_2CO_3$, an improved yield of **3a** was achieved, while the ee value dropped (entry 2). Disappointedly, replacing $K_2CO_3$ with $CaCO_3$ did not give the desired product (entry 3). During the investigation, one of the byproducts was characterized as 2′-iodo-6,6′-dimethyl-[1,1′-biphenyl]-2-ol, which was formed with $H_2O$ as the nucleophile. To remove a trace amount of $H_2O$ in the reaction system, CaO was employed as the base. Pleasingly, the reaction became much cleaner, and a drastic increase in yield was achieved, along with satisfactory stereoselectivity (entry 4). The enantioselectivity ranged from 35 to 72% with bis(oxazoline) **L2**–**L4** as the ligands (entries 5–7). Screening the ligand **L5** or spirobis(oxazo1ine) **L6**–**L8** showed that only **L7** gave comparable stereoselectivity to **L1** (entries 8–11). Further optimization focused on the modification on the aryl ring of bis(oxazoline). With 3,5-dimethylphenyl-substituted ligand **L9**, compound **3a** was formed in 95% ee (entry 12). A continued increase in the steric size of the aryl ring (**L10**) further improved the stereoinduction, and the ee value jumped to 99% (entry 13). Moreover, decreasing the loading of $Cu(OTf)_2$ to 5 mol % did not affect the overall outcome of this transformation (entry 14). The absolute configuration of **3a** was determined by single-crystal X-ray diffraction analysis (CCDC 1921712).

With the optimal conditions in hand, the substrate scope of this amination reaction was tested (Scheme 3). The para substituents on the benzenesulfonamide moiety had little effect on the yield or stereoselectivity. For instance, compounds **3b**–**d** were formed in almost quantitative yield with 99% ee. 2-Chloro-*N*-methoxybenzenesulfonamide resulted in decreases in both yield and enantioselectivity (**3e**). 2,4,6-Trimethylphenyl and *β*-naphthyl sulphonamides smoothly coupled to **1a** to lead to **3f** and **3g** in high stereoselectivity. *O*-alkylhydroxyl-

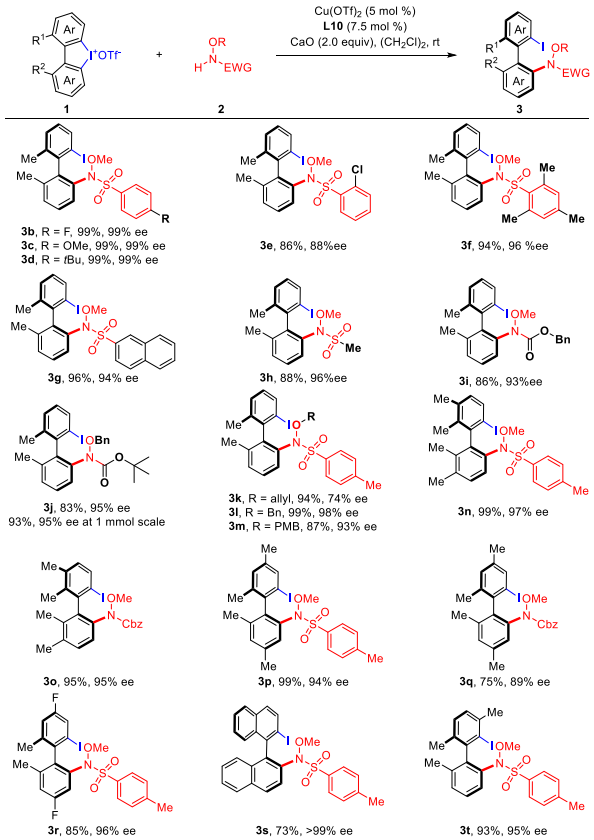
**Table 1. Reaction Condition Optimization**[a]




| entry | ligand | base | yield (%) | ee (%) |
|---|---|---|---|---|
| 1 | **L1** | $Na_2CO_3$ | 3 | 91 (*S*) |
| 2 | **L1** | $K_2CO_3$ | 17 | 72 (*S*) |
| 3 | **L1** | $CaCO_3$ | N.R. | |
| 4 | **L1** | CaO | 83 | 94 (*S*) |
| 5 | **L2** | CaO | 85 | 66 (*R*) |
| 6 | **L3** | CaO | 86 | 35 (*S*) |
| 7 | **L4** | CaO | 99 | 72 (*R*) |
| 8 | **L5** | CaO | 88 | 3 (*S*) |
| 9 | **L6** | CaO | 92 | 81 (*S*) |
| 10 | **L7** | CaO | 91 | 90 (*S*) |
| 11 | **L8** | CaO | 92 | 70 (*S*) |
| 12 | **L9** | CaO | 97 | 95 (*S*) |
| 13 | **L10** | CaO | 99 | 99 (*S*) |
| 14[b] | **L10** | CaO | 99 | 99 (*S*) |

[a]Unless otherwise stated, the reaction was conducted with **1a** (0.10 mmol), **2a** (0.12 mmol, 1.2 equiv), $Cu(OTf)_2$ (0.010 mmol, 10 mol %), Ligand (1.2 equiv to Cu), and base (3.0 equiv) in $(CH_2Cl)_2$ (2.0 mL) at rt for 24 h. [b]5 mol % of Cu(OTf)2, 7.5 mol % of **L10** and CaO (2.0 equiv) were used.

**Scheme 3. Substrate Scope**[a]




[a]Reaction was conducted with **1** (0.10 mmol), *O*-alkylhydroxylamines **2** (0.12 mmol, 1.2 equiv), $Cu(OTf)_2$ (0.0050 mmol, 5.0 mol %), **L10** (0.0075 mmol, 7.5 mol %), and CaO powder (0.20 mmol, 2.0 equiv) in 1,2-dichloroethane (2.0 mL) at rt for 12 h.



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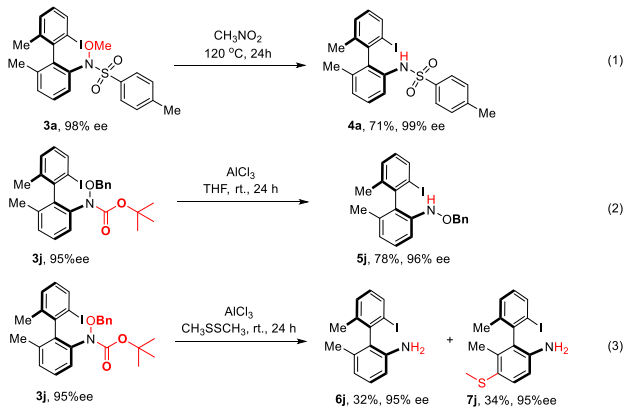
amines with *N*-methanesulfonyl, *N*-Cbz, or *N*-Boc protecting groups were also compatible substrates, and 96, 93, and 95% ee were achieved, respectively (**3h**−**j**). Subsequently, the reactivity by variation of the substituents on the oxygen atom was also investigated. Product **3k** with an *O*-allyl substituent was formed with 74% ee; however, high stereoinduction was still achieved for the *O*-Bn and *O*-PMB products (**3l** and **3m**). In a further experiment, the substituent effect on the diaryliodonium salts was studies. The reactions proceeded uneventfully with 5,5′-dimethyl-, 4,4′-dimethyl-, and 5,5′-difluoro-substituted diaryliodoniums (**3n**−**r**). Likewise, binaphthyl skeletons successfully underwent this Cu-catalyzed ring-opening reaction with a slight decrease in the yield (**3s**). For the nonsymmetric diaryliodonium, introducing an adjacent group (i.e., methyl) to the C−I bond was necessary for high regioselectivity. For instance, **3t** was isolated as a single regioisomer in 93% yield with 95% ee.

The utility of these products was further demonstrated by the modification of hydroxylamine functionality (Scheme 4).

**Scheme 4. Synthetic Applications**




Heating **3a** in $CH_3NO_2$ at 120 °C resulted in N−O bond selective cleavage to afford **4a** in 71% yield without losing the enantiopurity (eq 1). The chemoselective removal of the *tert*-butyloxycarbonyl (Boc) group proceeded uneventfully upon the treatment of **3j** with $AlCl_3$ in THF (eq 2). However, when $CH_3SSCH_3$ in lieu of THF was used as the solvent, primary amine **6j**, along with Friedel−Crafts thiolation product **7j** were isolated in 32 and 34% yield, respectively (eq 3).[16]

In summary, we have developed a Cu-catalyzed asymmetric ring-opening of cyclic diaryliodonium salts and *O*-alkylhydroxylamines. The base CaO played a pivotal role in the inhibition of the side reactions to get a high yield, and the ligand 3,5-di(*tert*-butyl)phenyl bis(oxazoline) showed the best stereoinduction. The products were readily manipulated to lead to aniline analogues with different degrees of substitution.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02267.

Experimental procedures, characterization of products, and spectroscopic data (PDF)

### Accession Codes

CCDC 1921712 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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