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# Enantioselective construction of triaryl-substituted all-carbon quaternary stereocenters *via* organocatalytic arylation of oxindoles with azonaphthalenes†

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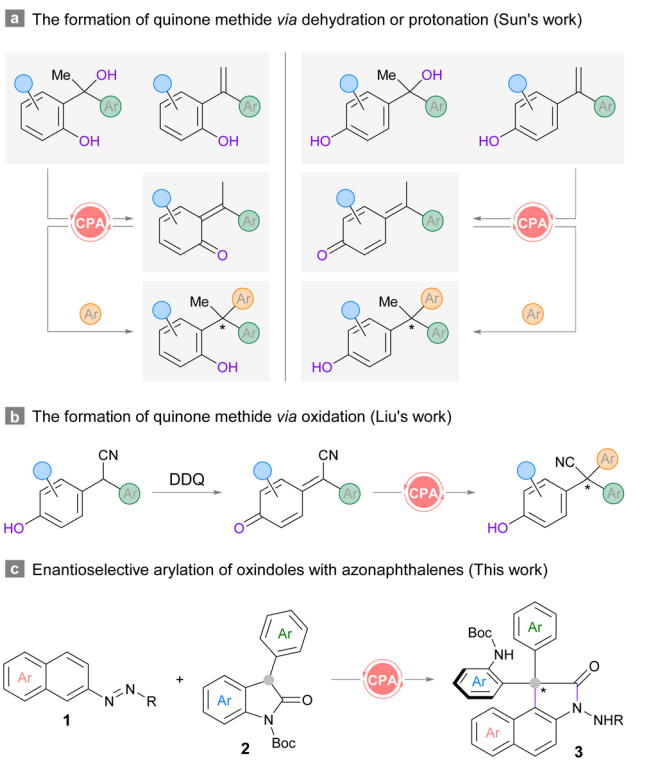
Azonaphthalenes have been verified as a class of effective arylation reagents in a variety of asymmetric transformations. Here a highly efficient approach to construct triaryl-substituted all-carbon quaternary stereocenters through chiral phosphoric acid-catalyzed enantioselective arylation of 3-aryl-2-oxindoles with azonaphthalenes is disclosed. This chemistry is scalable and displays excellent functional group tolerance, furnishing a series of 3,3-disubstituted 2-oxindole derivatives in good yields with excellent enantiocontrol. Preliminary mechanistic data suggest that the initially formed direct addition intermediate undergoes intramolecular annulation under acidic reaction conditions.

## Introduction

Structures that contain all-carbon quaternary centers are widely found in natural products and pharmaceutical molecules.[1,2] The development of highly efficient and enantioselective approaches to construct congested centers has been a long-standing challenge due to the steric repulsion encountered in installing the carbon appendages.[3] Although diverse synthetic strategies have been elegantly devised in the last decade,[4] the realization of enantioselective versions remains difficult. A more challenging scenario arises when the stereocenters contain triaryl-substitution, where the subtle difference between the three arene substituents could hinder stereodifferentiation.[5,6] Therefore, straightforward routes to prepare specifically functionalized frameworks with triaryl-substituted all-carbon quaternary stereocenters are always desirable.[5,6] The unique electronic nature of *ortho*- or *para*-quinone methides[7] renders a convenient platform to forge such carbon centers by means of bifunctional chiral phosphoric acid (CPA) catalysis.[8] A series of pioneering contributions have been made by the Sun group in utilizing racemic tertiary alcohols or 1,1-diarylethylenes as the precursors for *ortho*- or *para*-quinone methides in various heteroarylation reactions (Scheme 1a).[5] In Liu's protocol, racemic 2,2-diarylacetonitriles were used for enantioselective oxidative cross-coupling with (hetero)arenes (Scheme 1b).[6] Despite the




Scheme 1 Representative catalytic asymmetric construction triaryl-substituted all-carbon quaternary centers and our design.

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robustness of these routes, an *ortho*- or *para*-hydroxyl group should be installed at one of the aromatic rings in the diaryl substrates for *in situ* generation of the reactive quinone methide intermediates. In this context, the exploration of novel strategies which could accommodate substrates with diverse structures remains meaningful and necessary.

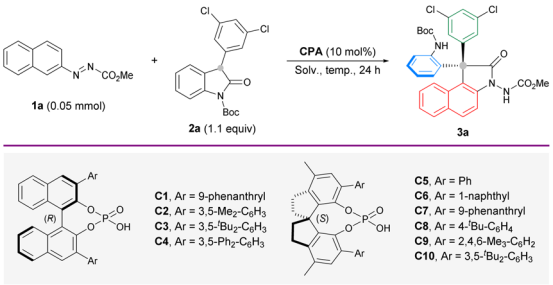
C3-substituted oxindoles exist extensively in biologically active compounds,[2,9] and they are also appreciated as fundamental building blocks[10] and reaction intermediates[11] due to the wide range of synthetic opportunities. Accordingly, the synthesis and transformation of C3-substituted oxindoles as well as their derivatives receive intense research focus, especially in the total synthesis of complex molecules. We contemplated a scheme to construct sterically congested triaryl-substituted quaternary stereocenters by harnessing the verified nucleophilicity of 3-aryl-2-oxindoles, which would necessitate suitable electrophilic arenes as the arylation reagents. Our previous finding proved that the umpolung of the nucleophilic aromatic rings could be realized by installing an azo substituent at the C2-position of naphthalene as the directing and activating group in the presence of a CPA catalyst.[12a] This strategy has also been applied in the construction of diverse axially and centrally chiral structures by our and other groups.[12,13] This success led us to consider the union of azonaphthalenes and C3-aryl-2-oxindoles for the enantioselective construction of triaryl-substituted all-carbon quaternary stereocenters. The recruitment of a bifunctional CPA catalyst should be able to control the configuration of the stereogenic carbon center when both reacting partners are brought together. However, the regioselectivity might be complicated by the steric size of oxindole nucleophiles, directing arylation at more accessible sites on azo-arene substrates.

Herein we report an organocatalytic enantioselective arylation of C3-aryl-2-oxindoles with azonaphthalenes. The reaction develops through sequential nucleophilic addition at the *ortho*-carbon and skeletal rearrangement. The latter is initiated by the electrophilic interception at the hydrazine nitrogen under acidic conditions. The *in situ* polarity inversion of the nitrogen on the azo-group enables an overall intermolecular annulation between the two substrates to provide oxindoles harbouring a triaryl-substituted all-carbon quaternary stereocenter (Scheme 1c). This protocol also enriches the current synthetic toolbox of 3,3-diaryl-2-oxindoles, which mostly generates racemic analogues through substrate-specific reactions, including Friedel–Crafts type arylations, cyclizations and rearrangement reactions,[11c,14] or from pre-functionalized substrates.[15]

## Results and discussion

Our initial attempt of enantioselective arylation was performed with azonaphthalene **1a** and 3-aryl-2-oxindole **2a** as the model substrates in the presence of catalyst (*R*)-**C1**. Delightfully, the reaction performed in toluene at 25 °C gave an annulated product **3a** in 31% yield and 35% ee (Table 1, entry 1), which features a change in the original connectivity of the substrates.

Table 1 Optimization of reaction conditions[a]



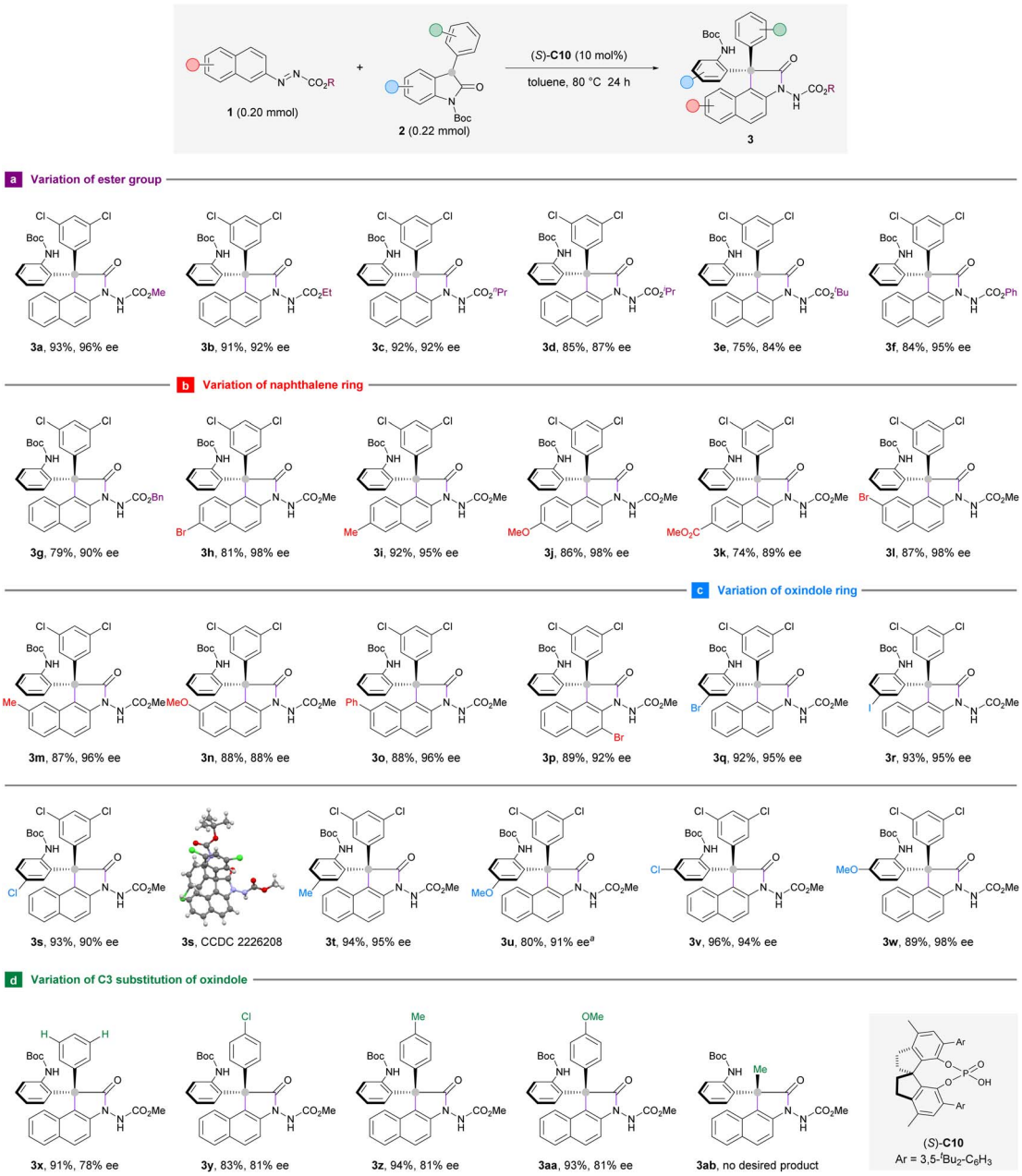

| Entry | CPA | Solv. | $T$ (°C) | Yield[b] (%) | ee[c] (%) |
|---|---|---|---|---|---|
| 1 | (*R*)-**C1** | Toluene | 25 | 31 | 35 |
| 2 | (*R*)-**C2** | Toluene | 25 | 29 | 20 |
| 3 | (*R*)-**C3** | Toluene | 25 | 30 | 20 |
| 4 | (*R*)-**C4** | Toluene | 25 | 27 | 8 |
| 5 | (*S*)-**C5** | Toluene | 25 | 40 | 9 |
| 6 | (*S*)-**C6** | Toluene | 25 | 38 | 17 |
| 7 | (*S*)-**C7** | Toluene | 25 | 43 | 60 |
| 8 | (*S*)-**C8** | Toluene | 25 | 39 | 14 |
| 9 | (*S*)-**C9** | Toluene | 25 | 36 | 31 |
| 10 | (*S*)-**C10** | Toluene | 25 | 44 | 70 |
| 11 | (*S*)-**C10** | $CH_2Cl_2$ | 25 | 44 | 35 |
| 12 | (*S*)-**C10** | $CHCl_3$ | 25 | 51 | 18 |
| 13 | (*S*)-**C10** | MeCN | 25 | 37 | 55 |
| 14 | (*S*)-**C10** | Dioxane | 25 | 17 | 50 |
| 15 | (*S*)-**C10** | Toluene | 50 | 76 | 89 |
| 16 | (*S*)-**C10** | Toluene | 60 | 88 | 85 |
| 17 | (*S*)-**C10** | Toluene | 70 | 88 | 91 |
| 18 | (*S*)-**C10** | Toluene | 80 | 89 | 96 |
| 19 | (*S*)-**C10** | Toluene | 90 | 91 | 90 |
| 20[d] | (*S*)-**C10** | Toluene | 80 | 93 | 96 |

[a] Reaction conditions: **1a** (0.05 mmol), **2a** (1.1 equiv.) and CPA (10 mol%) in solvent (1 mL) for 24 h unless noted otherwise. [b] Isolated yield. [c] The ee values were determined by chiral HPLC analysis. [d] **1a** (0.20 mmol) and **2a** (0.22 mmol) in solvent (4 mL).

This interesting outcome encouraged us to screen different CPA catalysts. Having observed that BINOL-derived catalysts could not effectively improve the yield and enantioselectivity (entries 2–4), another subclass of CPAs based on a methyl-SPINOL skeleton (entries 5–10) was investigated. By focusing on the influence of the steric environment, (*S*)-**C10** with a bulky 3,5-di-butyl-phenyl group was found to afford the best enantiocontrol (70% ee) in 44% yield (entry 10). The much lower ee achieved with the BINOL-derived counterpart highlights the importance of both the backbone and sidearm components in enhancing reaction efficiency and stereoselectivity (entry 3). Subsequent optimization was conducted with the best-performing (*S*)-**C10**. Compared to toluene, other solvents dramatically hampered the enantioselectivity (entries 11–14). This remarkable solvent effect indicates the positive influence of a nonpolar solvent on the stereocontrol. It was noted that the yield remained very low at room temperature throughout the optimization process. As some unstable intermediates could be traced from thin-layer chromatography (TLC) analysis, we sought to drive better conversion by elevating the reaction temperature. A temperature gradient from 50 °C to 90 °C was explored (entries

15–19). As expected, the chemical yield saw substantial improvement. Surprisingly, the enantioselectivity increased significantly. From these attempts, 80 °C was identified as the most optimal temperature (entry 18) to furnish the desired arylation product **3a** in 89% yield and 96% ee. A slightly better yield (93%) was obtained when the reaction was performed on the 0.2 mmol scale (entry 20).

Having established the optimal reaction conditions, we turned to investigate the substrate scope of this enantioselective arylation reaction with respect to the azonaphthalene component. Aliphatic esters other than methyl ester were also compatible to deliver products **3b–g** in 75–92% yield and 84–95% ee (Scheme 2a). However, the yield and enantioselectivity decreased gradually as steric hindrance intensified from ethyl to *tert*-butyl groups (**3b–e**). In general, the position (C6 or C7) and electronic nature of the aryl substituents on azonaphthalene had limited influence on the enantioselectivities of arylation products (**3h–o**). It is worth pointing out that the reaction with C6-ester-substituted azonaphthalene (**3k**) proceeded in poorer yield (74%) and the formation of unidentified byproducts could be detected on the TLC. Remarkably, 3-bromoazonaphthalene was well-suited to this reaction system to deliver product **3p** in 89% yield and 92% ee

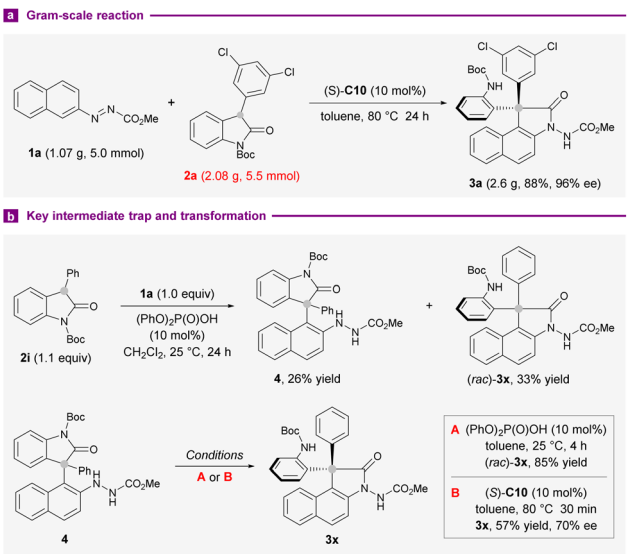



Scheme 2 Substrate generality of the CPA catalyzed enantioselective arylation reaction. Reaction conditions: **1** (0.20 mmol), **2** (0.22 mmol), (*S*)-**C10** (10 mol%) in toluene (4 mL) at 80 °C for 24 h under argon, unless noted otherwise. Yield of the isolated product is given. The ee values were determined by HPLC analysis using a chiral stationary phase. [a]Reaction was carried out at 25 °C for 48 h.

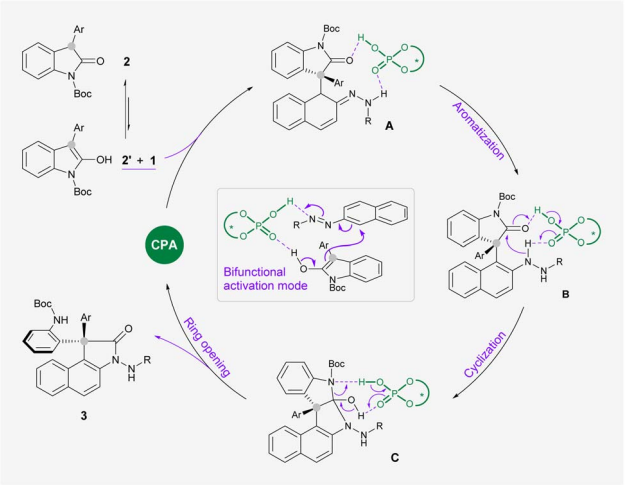
(Scheme 2b). This result suggests that the substrate–catalyst interaction is not interfered with by the presence of a bulky substituent adjacent to the azo group at the naphthalene ring.

To further define the scope of our developed protocol, the optimal conditions were then applied to different oxindole derivatives with azonaphthalene **1a** as the standard arylation partner (Scheme 2c). The formation of triaryl-substituted stereocenters occurred smoothly, regardless of the identity of C5- or C6-substituents of the aromatic ring. Oxindoles that bear an electron-withdrawing (**3q–s** and **3v**) or electron-donating (**3t**, **3u**, and **3w**) group could afford the products with high yields and excellent stereoselectivities. Considering that the Boc-protecting group of **3u** would be labile at 80 °C, the reaction to prepare **3u** was carried out at 25 °C with an extended time (48 hours). Furthermore, the C3 position of oxindole could be occupied by a phenyl group (**3x**) or its 4-substituted analogues with electron-withdrawing (**3y**) or electron-donating (**3z** and **3aa**) functionalities. However, these reactions have afforded moderate enantioselectivities (78–81% ee). The introduction of a methyl group to this C3-position resulted in a messy reaction system and the target product **3ab** bearing a diaryl-substituted stereocenter could not be isolated (Scheme 2d). Product **3s** carrying a chloride substituent was crystalline, which allows unequivocal determination of the stereochemistry to be (*S*) at the all-carbon quaternary stereocenter by means of X-ray crystallographic analysis. The configurations of the other products displayed in this scheme were assigned by analogy.

We next examined the practicality and reliability of the present synthetic method by implementing a gram-scale reaction with **1a** (1.07 g) and **2a** (2.08 g) under standard reaction conditions. The isolation of 2.6 g of **3a** (88% yield) in 96% ee showed that the outcomes were largely preserved (Scheme 3a). To gain more mechanistic insights into the reaction, the coupling of **1a** and **2i** was conducted at 25 °C instead of 80 °C used in the substrate survey. An unstable




Scheme 3 Gram-scale synthesis and mechanistic investigations.




Scheme 4 Proposed reaction mechanism and stereocontrol mode.

arylation compound **4** and (*rac*)-**3x** could be separated in 26% and 33% yields, respectively. On subjection to 10 mol% diphenyl phosphate, **4** converted completely into **3x** after 4 hours at 25 °C (Scheme 3b). The application of standard conditions afforded **3x** with 70% ee instead, after 30 minutes. These results suggested the intermediacy of **4** in this intermolecular annulation reaction, and a secondary kinetic resolution could be operative during the transamidation step to improve the enantiopurity of the products.

On the basis of these experimental observations and previous literature, we proposed a reaction mechanism as outlined in Scheme 4. The bifunctional CPA catalyst simultaneously activates azonaphthalene **1** and oxindole **2′** which is in the enol form through multiple hydrogen bondings, which leads to a stereoselective nucleophilic attack at the α-carbon of **1** to form intermediate **A**. By comparing the conversion rate of intermediate **4** and the reaction rate of **1a** and **2i** under standard conditions, this arylation process is likely to be rate-determining (for more details, see the ESI†). The following rearomatization step reveals key intermediate **B**, which undergoes an acid-promoted intramolecular addition to a carbonyl group on oxindole. Subsequently, acid mediates the ring opening of **C** *via* cleavage of the C–N bond to release the observed product **3**.

## Conclusions

In summary, we have successfully developed a CPA-catalyzed asymmetric arylation of oxindole derivatives with azonaphthalenes as the electrophilic arylation reagents for efficient construction of triaryl-substituted quaternary stereocenters in good yields with excellent enantioselectivities. This protocol provided a general and practical method to prepare a variety of 3,3-disubstituted oxindole derivatives with fairly good functional group tolerance for both azonaphthalene and oxindole partners. The proposed reaction mechanism is supported by the isolation of a key intermediate and its conversion to the target product. The overall reaction

enantioselectivity could be enhanced by a secondary kinetic resolution. Efforts are currently underway in our laboratory to further investigate synthetic application and generality of this strategy.

## Data availability

All experimental and characterization data, as well as NMR spectra are available in the ESI.† Crystallographic data for compound **3s** have been deposited in the Cambridge Crystallographic Data Centre under accession number CCDC 2226208.

## Author contributions

B. T. & J. Z. conceived and directed the project. P. C. designed and performed the experiments. M.-J. L., J. K. C., S.-H. X. & X.-Z. R. helped with the collection of some new compounds and data analysis. B. T., P. C., J. K. C. & S.-H. X. wrote the paper. All authors discussed the results and commented on the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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