Atroposelective Synthesis of Axially Chiral Biaryldiols via Organocatalytic Arylation of 2-Naphthols

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S *Supporting Information*

ABSTRACT: The first phosphoric acid-catalyzed asymmetric direct arylative reactions of 2-naphthols with quinone derivatives have been developed, providing efficient access to a class of axially chiral biaryldiols in good yields with excellent enantioselectivities under mild reaction conditions. This approach is a highly convergent and functional group tolerant route to the rapid construction of axially chiral compounds from simple, readily available starting materials. The excellent stereocontrol of the process stems from efficient transfer of stereochemical information from the chiral phosphoric acid into the axis chirality of the biaryldiol products. Preliminary results demonstrate that the biaryldiols can act as efficient chiral ligands in asymmetric transformations.

Axially chiral C_2-symmetric BINOL and its derivatives have been extensively evaluated as versatile chiral ligands/catalysts in asymmetric transformations.[1] Their well-established conversions to the corresponding BINAP[2] and phosphoric acids[3] further expand their synthetic utility in various domains of asymmetric catalysis (Figure 1). As a result, the construction of these scaffolds has attracted considerable attention, and relatively practical methods have already been achieved.[1] Recent studies have disclosed that the nonsymmetric BINOL derivatives (biaryldiols) can also be used as efficient chiral ligands or catalysts.[4] Notably, this motif is a prominent feature of many biologically active natural products,[5] such as vancomycin, knipholone, and gossypol (Figure 1). Compared with the successful application and synthesis of C_2-symmetric BINOLs, the application of these biaryldiols remains largely underexplored with respect to asymmetric synthesis and natural products synthesis, probably due to a lack of reliable synthetic routes.[1a]

In this context, there have only been a few synthetic attempts toward enantioselective synthesis of these axially chiral biaryldiols, which include direct metal-catalyzed asymmetric oxidative cross-coupling reactions[6] and kinetic resolutions[7] (Scheme 1). Although oxidative cross-coupling reactions represent a straightforward way to access nonsymmetric biaryldiols from achiral precursors, current catalytic systems can only give products with certain specific substitution patterns in high enantioselectivity. Over the past several decades, the kinetic resolution of racemic starting materials has been one of the most powerful and reliable strategies for the synthesis of enantiopure compounds in both academia and industry. However, the catalytic kinetic resolution of these axially chiral biaryldiols is surprisingly underdeveloped,[8]
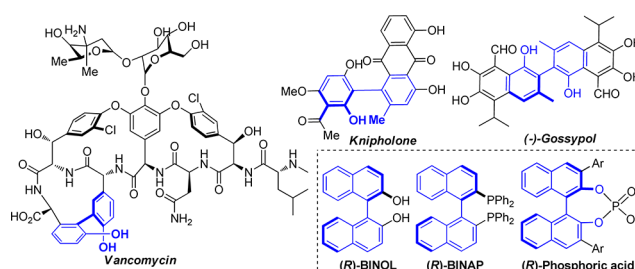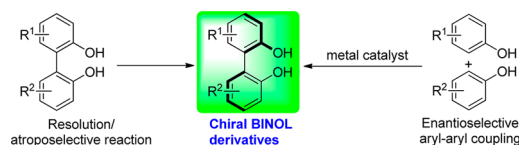

Figure 1. Selected natural products and ligands/catalysts involving axially chiral biaryldiols.

**Scheme 1. Existing Strategies for Atroposelective Synthesis of Axially Chiral Biaryldiols**

and has been limited to no more than 50% yield. More recently, Akiyama achieved a significant breakthrough by using phosphoric acid to enable asymmetric atroposelective bromination, providing a more useful avenue to access these types of axially biaryldiol skeletons.[9] Despite these successful results, the development of an efficient and highly enantioselective strategy for facile access to axially chiral biaryldiols would greatly expand the application scope and is still in great demand.

Quinones have long served as useful synthetic precursors to construct densely functionalized aromatic rings.[10] Their application in asymmetric organocatalysis has been on the increase as an expedient means to deliver a range of optically enriched compounds.[11] Motivated by this progress and the recent development of synthesis of axially chiral compounds,[12] we envisioned that 2-naphthols could directly react with quinones to afford the chiral biaryldiols, providing the possibility to develop a direct enantioselective arylation strategy to construct axially chiral nonsymmetric biaryldiols. As shown in Scheme 2, we postulated that conjugated addition intermediates **A** could be generated from 2-naphthols and quinones and then aromatized with efficient central-to-axial chirality exchange[6e,12l,13] as a result of the restricted rotation, to yield the final axially chiral compounds. This entails several challenges: (1) the selection of
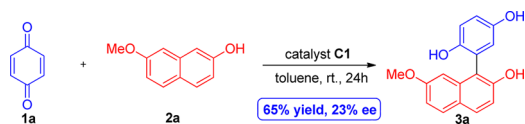
Scheme 2. Our Strategy for Atroposelective Synthesis of Axially Chiral Biaryldiols via Direct Arylation of 2-Naphthols
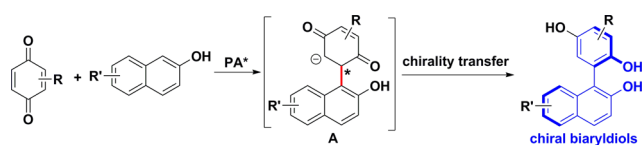
**Scheme 3. Initial Results for Direct Synthesis of Biaryldiols**

a reasonable catalyst to increase the reactivity, to efficiently control C/O chemoselectivity of the 2-naphthols; (2) the choice of a chiral catalyst to efficiently induce stereocontrol in the conjugated addition step; (3) the use of mild reaction conditions to transfer the chirality and obviate the axial rotation. As part of our ongoing interest in asymmetric synthesis of axially chiral compounds[14] and phosphoric acid catalysis,[15] here we describe the novel chiral phosphoric acid-catalyzed, highly enantioselective, direct arylative reactions of 2-naphthols and quinone derivatives, providing a new synthetic route toward axially chiral biaryldiols bearing multiple substituent patterns. Such structural motifs are important components of various biologically active natural products[5] and should have the potential for application in asymmetric catalysis.[4]

We initiated our studies by evaluating the reaction between quinone **1a** and 2-naphthol **2a** in toluene at room temperature in the presence of the typically used phosphoric acid catalyst, **C1** (Scheme 3). The reaction proceeded smoothly and afforded the desired axially chiral biaryldiol **3a** in good yield, albeit with poor enantioselectivity (23% ee). However, despite making great efforts toward optimization of the reaction conditions, we could not improve the enantioselectivity by using the current model reaction.

To improve the reaction results, we modified the design of the quinone substrate to provide it with a potential for hydrogen bond formation with catalysts. Specifically, we installed an ester group into the quinone skeleton to facilitate access of the catalyst to the ketone−ester moiety[16] for multiple H-bonding, enabling the simultaneous activation of a nucleophile and an electrophile in a suitable spatial configuration. Quinone derivative **1b** was tested for this reaction using **C1** as catalyst, and the enantioselectivity was improved up to 57% ee (Table 1, entry 1). Based on this promising result, a detailed optimization study was done, first with different catalysts (**C1−C9**). Several BINOL-, SPINOL-, and VAPOL-derived catalysts were investigated and displayed remarkable effects on the outcome of the reaction (Table 1, entries 1−9). Clearly, phosphoric acid catalysts with a very bulky substituent at the 3,3′-position gave rise to good enantiocontrol. Almost no ee of product **4a** was obtained with VAPOL-derived **C6** as the catalyst, most likely because the catalyst **C6** had less interaction with reactants. Of the solvents tested for the reaction catalyzed by **C1** (Table 1, entries 10−13), dichloromethane (DCM) proved optimal with respect to enantioselectivity (Table 1, entry 10). Conducting the reaction at different temperatures provided the desired improvement in enantioselectivity, and we found that the best results—up to 90% yield and 93% ee—were obtained at −78 °C (Table 1, entry 16). Lower catalyst loading has a negative effect on the results, while

Table 1. Optimization of the Reaction Conditions[a]
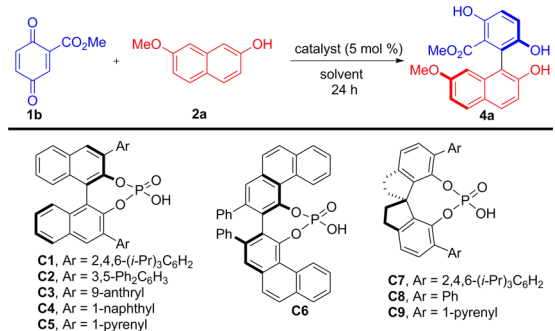
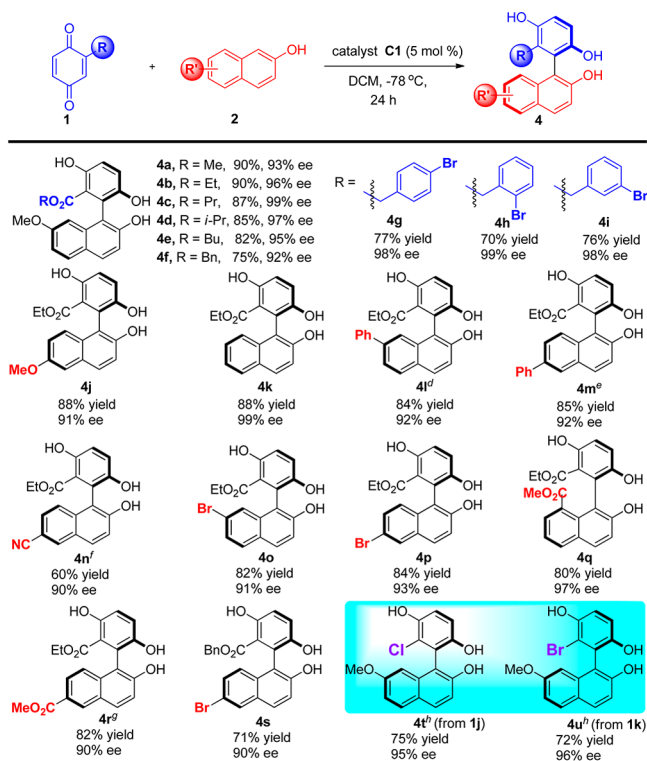| entry	catalyst	solvent	T(°C)	yield (%)[b]	ee (%)[c]
1	**C1**	toluene	25	90	57
2	**C2**	toluene	25	85	3
3	**C3**	toluene	25	87	6
4	**C4**	toluene	25	85	3
5	**C5**	toluene	25	83	10
6	**C6**	toluene	25	83	0
7	**C7**	toluene	25	88	-41
8	**C8**	toluene	25	81	-4
9	**C9**	toluene	25	87	-7
10	**C1**	DCM	25	92	72
11	**C1**	DCE	25	90	65
12	**C1**	CHCl₃	25	89	70
13	**C1**	EtOAc	25	84	57
14	**C1**	DCM	0	92	80
15	**C1**	DCM	-40	92	85
16	**C1**	DCM	-78	90	93
17[d]	**C1**	DCM	-78	88	85
18[e]	**C1**	DCM	-78	90	93
19[f]	**C1**	DCM	-78	85	88
20[g]	**C1**	DCM	-78	89	93

[a]Reaction was carried out with 2-methoxycarbonyl-1,4-benzoquinone (**1b**, 0.10 mmol), 7-methoxy-2-naphthol (**2a**, 0.12 mmol), and catalyst (5 mol%) in 2 mL of solvent for 24 h under Ar, unless noted otherwise. [b]Isolated yield based on **1b**. [c]ee values determined by HPLC analysis using a chiral stationary phase. [d]Using 2.5 mol% **C1**; [e]10 mol% **C1**; [f]1 mL of DCM; [g]3 mL of DCM, 48 h.

higher loading does not improve the chemical yield or stereoselectivity (Table 1, entries 17, 18). The reaction concentration has a fair influence on the chemical yield and enantioselectivity. When more concentrated solution was employed, the chemical yield and ee of the product decreased (Table 1, entry 19).

With the optimal reaction conditions established, we set out to explore the substrate scope with various quinones and 2-naphthols as reactants (Table 2). The phosphoric acid-catalyzed direct arylation reaction proceeded smoothly with a variety of quinone esters to afford the desired products under mild reaction condition. All of the investigated reactions were complete within 24 h and gave products (**4a**−**4i**) in good yields (70−90%) and with excellent enantioselectivities (92−99% ee). For the use of 2-naphthols, the position and the electronic properties of the substituents on the aromatic ring appeared to have a very limited effect on stereoselectivity. Regardless of the type of substituents on the aromatic rings, bearing electron-withdrawing (Table 2, products **4n**−**4s**), electron-donating (Table 2, product **4j**), or neutral (**4k**−**4m**) groups at the different positions, the reactions of these 2-naphthols gave axially chiral biaryldiols with very high stereoselectivities and good reactivity. Notably, the use of a

Table 2. Substrate Scope of Direct Arylation Reaction[a,b,c]

4a, R = Me, 90%, 93% ee
4b, R = Et, 90%, 96% ee
4c, R = Pr, 87%, 99% ee
4d, R = i-Pr, 85%, 97% ee
4e, R = Bu, 82%, 95% ee
4f, R = Bn, 75%, 92% ee

4g 77% yield 98% ee

4h 70% yield 99% ee

4i 76% yield 98% ee

4j 88% yield 91% ee

4k 88% yield 99% ee

4l[d] 84% yield 92% ee

4m[e] 85% yield 92% ee

4n[f] 60% yield 90% ee

4o 82% yield 91% ee

4p 84% yield 93% ee

4q 80% yield 97% ee

4r[g] 82% yield 90% ee

4s 71% yield 90% ee

4t[h] (from 1j) 75% yield 95% ee

4u[h] (from 1k) 72% yield 96% ee

[a]Reaction was carried out with quinone derivatives 1 (0.10 mmol), 2-naphthols 2 (0.12 mmol), and catalyst C1 (5 mol%) in 2 mL of DCM at −78 °C for 24 h under Ar, unless noted otherwise. [b]Isolated yields based on quinone derivatives. [c]ee values determined by HPLC analysis using a chiral stationary phase. [d]Reaction at −20 °C, 72 h; [e]−78 °C, 48 h; [f]−25 °C, 10 mol% C1, 60 h; [g]−10 °C, 10 mol% C1, 48 h; [h]−40 °C, 24 h.

sterically hindered 8-substituted naphthanol also afforded the desired product 4q in excellent stereocontrol (97% ee) under the standard reaction conditions, demonstrating that the substrate scope is not limited to less bulky 2-naphthols. Changing the ester group to a more useful halogen group, such as Cl or Br, at the quinone moiety had almost no influence on the reaction efficiency and stereoselectivity, still giving excellent results (4t, 4u), which is very important for chiral ligands or catalyst design because halides are very reactive, allowing further modifications in many transition metal-catalyzed reactions.[17]

To demonstrate the utility of the direct arylative reaction, preparative-scale synthesis of products 4b and 4t was carried out. As displayed in Scheme 4, there was almost no change in the reactivity and stereoselectivity, suggesting that this method should have the potential for large-scale chemical production.

Based on the experimental results, a possible reaction process is illustrated in Scheme 5. Chiral phosphoric acid C1 performed as a bifunctional organocatalyst to simultaneously activate 2-naphthols and quinone derivatives by multiple H-bonding and promote the first step of enantioselective conjugative addition

Scheme 4. Preparative Synthesis of 4b and 4t
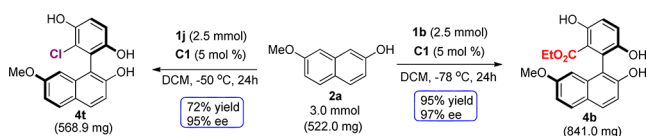
Scheme 5. Proposed Reaction Process
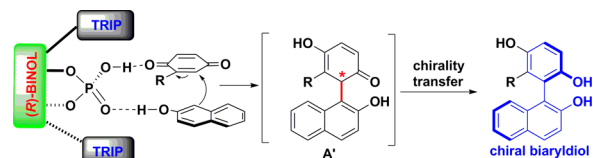
to form intermediate A'. The following step transfers its central chirality information to its axial chirality, affording the final chiral biaryldiol.[6e,12l,13] The ester moiety or halogen at the 2-position of the quinone might play a very important role to control the stereoinduction via additional interactions. These groups could also help to increase the stability of the obtained products. However, the exact role of these moieties remains unclear and deserves further investigations. To confirm the absolute configuration (AC) of compounds 4, ECD spectra were calculated by the TD-DFT method, which has been proven to be useful in predicting ECD spectra and assigning the AC of organic molecules. The R configuration could be reliably assigned to compound 4b. (For details, see Figure S1.)

An indication for the configurational stability of the product was obtained by heating a solution of 4b in DCE at 80 °C for 24 h. HPLC analysis showed that the ee was unaffected; thus, the obtained axially chiral compounds may have potential applications as asymmetric organocatalysts/ligands. To further investigate the utility of the obtained chiral biaryldiols, we verified the efficiency of (R)-4 as ligand for enantioselective addition of diethylzinc to aldehydes, which is one of the most reliable methods to prepare chiral sec-alcohols and also a standard reaction to test the reactivity and enantioselectivity of newly designed chiral ligands.[18] As shown in Table 3, the mixture

Table 3. Preliminary Application in Addition of Diethylzinc to Aldehyde[a,b,c]

4b 88% yield -96% ee

4p 90% yield -98% ee

(S)-BINOL 86% yield 89% ee
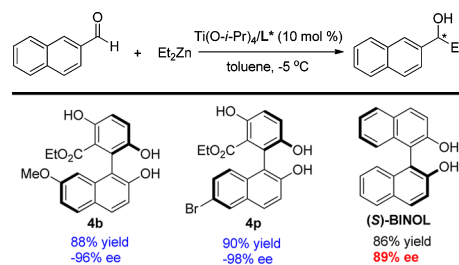
[a]For reaction conditions, see SI. [b]Isolated yields. [c]ee values determined by HPLC analysis using a chiral stationary phase.

prepared by allowing a toluene solution of 4b or 4p and titanium tetraisopropoxide to stand at −5 °C gave excellent chemical yields and ee's (96% or 99% ee). It should be noted that the enantioselectivity for this model reaction was just 89% ee with (S)-BINOL as chiral ligand under the same reaction conditions, further demonstrating the utility of the obtained nonsymmetrical biaryldiols.

In summary, we have successfully developed the first phosphoric acid-catalyzed asymmetric direct arylative reactions of 2-naphthols with quinone derivatives, giving efficient access to a class of axially chiral biaryldiols in good yields with excellent enantioselectivities under mild reaction conditions. This new, highly convergent and functional group tolerant approach allows for the rapid construction of axially chiral compounds from simple, readily available starting materials. The excellent

stereocontrol of the process stems from the efficient transfer of stereochemical information from the chiral phosphoric acid into the axis chirality of the biaryldiol products. Application of this strategy to other substrate classes, and mechanistic investigations addressing the intricacies of the chirality transfer, are currently underway in our laboratory and will be reported in due course.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b10152.

> Experimental procedures, characterization of all new compounds, and Figure S1 (PDF)

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Notes

The authors declare no competing financial interest.

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