Asymmetric Catalysis

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Highly Enantioselective [3+2] Coupling of Indoles with Quinone Monoimines Promoted by a Chiral Phosphoric Acid**

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Abstract: *Highly enantioselective [3+2] coupling of 3-substituted indoles with quinone monoimines promoted by a chiral phosphoric acid has been reported. A large variety of benzofuroindolines were prepared in moderate to good yields (up to 98%) with generally excellent enantioselectivities (up to 99% ee).*

Fused indolines are important building blocks for a large number of natural products and phamarceuticals.[1] Consequently, diverse successful strategies have been developed to construct fused indolines.[2] Among these transformations, dearomative annulation of indoles is the most straightforward method and has attracted much attention.[3]

The benzofuroindoline core is a unique motif found in some important natural alkaloids,[4–6] such as diazonamides[4] and azonazine[5] (Figure 1). Since diazonamide A has been found to be a very potent anticancer agent owing to its high antitumor activity ($IC50 < 5$ nm),[4b,c] it has received considerable attention from chemists for the synthesis of these benzofuroindoline skeletons.[4f–k]

In 2012, Bisai et al.[6a] reported Lewis acid catalyzed Friedel–Crafts alkylations of 3-hydroxy-2-oxindoles, and it provides access to benzofuroindolines in three steps. Soon after, Vincent[6b] and co-workers reported $FeCl_3$-mediated Friedel–Crafts hydroarylation of electrophilic N-acetyl indoles with phenols to afford 3,3-disubstituted indolines, followed by oxidation to yield the desired benzofuroindolines. In addition, direct construction of benzofuroindolines by

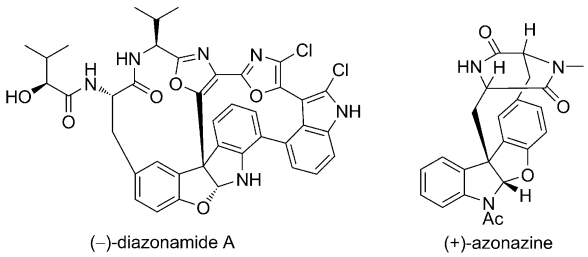

Figure 1. Representative benzofuroindoline natural products. Ac = acetyl.

[3+2] coupling of 3-substituted indoles with quinone derivatives were also demonstrated by several groups.[6c–m] For an example, in 2011, Chen and co-workers employed a Brønsted acid catalyzed direct [3+2]coupling of β-carbolines with qinones as a key strategy in the formal synthesis of (+)-haplophytine.[6j] In 2003, MacMillan et al. described an enantioselective synthesis of a benzofuroindoline by an addition/cyclization cascade of 3-phenol-substituted indole with acrolein promoted by a chiral imidazolinone catalyst.[6l] Recently, we employed a Lewis acid to promote [3+2] coupling of 3-substituted indoles with quinone monoacetals and a quinone imine ketal through which various benzofuroindolines and tetrahydroindolo[2,3-b]indoles were prepared in moderate to good yields.[6m] Meanwhile, we also attempted an enantioselective variant using a chiral phosphoric acid as a catalyst. However, only 33% *ee* was obtained. To the best of our knowledge, these are the only two examples of the enantioselective construction of benzofuroindolines.

Quinones and quinone monoimines are excellent electrophiles. In recent years, quinones and quinone monoimines have attracted increasing attention in asymmetric reactions.[7] In 2010, Jørgensen et al. reported a highly enantioselective α-arylation of aldehydes through nucleophilic addition of aldehydes to quinones or quinone monoimines followed by aromatization.[7a] In addition, asymmetric transformations involving activation of quinones by chiral organocatalysts were also demonstrated.[7b–j]

Chiral phosphoric acids are versatile catalysts for many asymmetric reactions.[8] In particular, many efficient strategies for asymmetric C3 functionalization of indoles and functionalization of enamines (enamides) by phosphoric acids have been well established.[3a,g,j,k,o,9] Herein we report a highly enantioselective [3+2] coupling of 3-substituted indoles with quinone monoimines promoted by a chiral phosphoric acid. This reaction provides a large variety of benzofuroindolines with moderate to high yields in generally excellent enantioselectivities.

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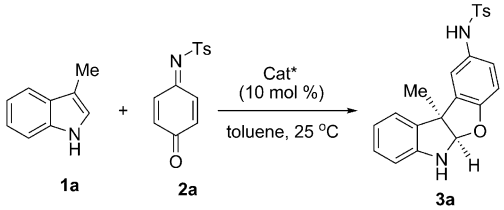
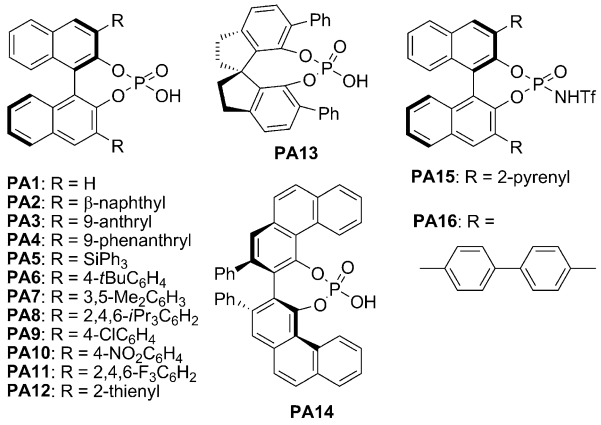
First, various chiral phosphoric acids were evaluated in the [3+2] coupling of 3-methyl indole (**1a**) with 4-methyl-*N*-(4-oxocyclohexa-2,5-dienylidene)benzenesulfonamide (**2a**) in toluene at 25 °C. As can be seen in Table 1, the chiral phosphoric acid **PA8**, which bears a 2,4,6-triisopropylphenyl group at the 3,3′-positions of binol, promoted the reaction efficiently to provide the benzofuroindoline **3a** in nearly quantitative yield with the highest *ee* value of 87% (Table 1, entry 8). Thus **PA8** was determined to be the optimal catalyst and used in subsequent investigations.

Next, the other reaction parameters were modified. When the temperature was lowered to 0 °C, the reaction proceeded for 5 hours to afford the desired product with almost quantitative yield and a slightly higher *ee* value (Table 2, entry 2). Then several other solvents were screened at 0 °C. Reactions in two chlorinated solvents gave good yields as well as good enantioselectivities (Table 2, entries 3 and 4). Meanwhile THF delivered a lower yield, although the *ee* value is good (Table 2, entry 5). To our delight, when acetonitrile was used, excellent yield and excellent enantioselection were obtained (Table 2, entry 6). Hence acetonitrile was identified as the most favorable solvent in the reaction. Moreover, lowering the catalyst loading to 5 mol% did not affect the result (Table 2, entry 7). However, further lowering the catalyst loading to 2 mol% led to a decrease in both the yield and *ee* value (Table 2, entry 8).

With the optimized reaction conditions in hand, the scope of the reaction was investigated. In the presence of 5 mol% of **PA8**, various 3-substituted indoles (**1**) were subjected to the [3+2] coupling with the quinone monoimines **2**. The results are summarized in Scheme 1. Generally, indoles bearing various electron-donating and electron-withdrawing groups on the benzene part are well tolerated in the reaction and afforded the corresponding benzofuroindolines in moderate to good yields with high *ee* values, except for 3-phenyl indole (**1t**), which exhibited lower enantioselection (80% *ee*). A better *ee* value (86% *ee*) was observed by employing 10 mol% of the catalyst **PA8**. For some indoles with bulkier substituents, lower yields were obtained even after a prolonged reaction time. When the quinone monoimine having an *ortho*-methyl substituent was employed, no desired reaction was observed, perhaps because of the decreased electrophilicity of this quinone monoimine. We also tried to prepare quinone monoimines with electron-withdrawing groups such as a chloro group in the *ortho*/*meta* position. However, we failed to synthesize these substrates. Finally, we tried to replace N-Ts by N-Boc and N-CBz. However, these quinone monoimines are very unstable and decomposed

Table 1: Screen of the chiral phosphoric acids.

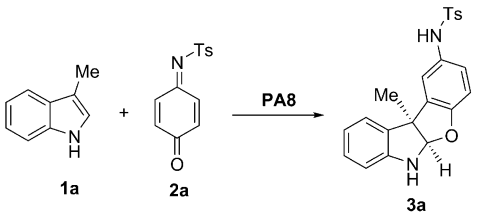




Entry[a]	Cat*	Solvent	*t* [h]	Yield [%][b]	*ee* [%][c]
1	**PA1**	toluene	2	50	57
2	**PA2**	toluene	2	73	17
3	**PA3**	toluene	2	93	47
4	**PA4**	toluene	6	50	13
5	**PA5**	toluene	24	90	67
6	**PA6**	toluene	2	77	28
7	**PA7**	toluene	12	65	49
8	**PA8**	toluene	2	99	87
9	**PA9**	toluene	6	49	37
10	**PA10**	toluene	48	56	43
11	**PA11**	toluene	5	36	17
12	**PA12**	toluene	12	43	21
13	**PA13**	toluene	2	90	83
14	**PA14**	toluene	12	95	47
15	**PA15**	toluene	24	33	21
16	**PA16**	toluene	72	71	23

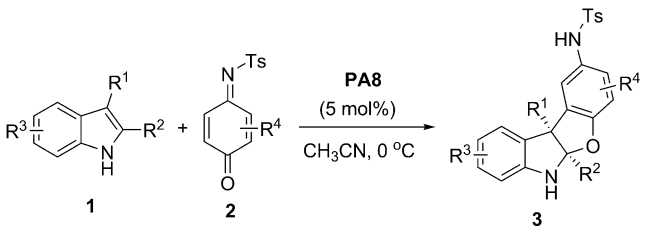
[a] Unless otherwise specified, the reactions were carried out with 0.20 mmol of **1a**, 0.30 mmol of **2a**, and 0.02 mmol of the chiral phosphoric acid in 2 mL of toluene at room temperature. [b] Yield of isolated product based on **1a**. [c] Enantiomeric excess was determined by HPLC analysis on a chiral stationary phase. Ts = 4-toluenesulfonyl, Tf = trifluoromethanesulfonyl.

Table 2: Optimization of the reaction conditions.



Entry[a]	Solvent	**PA8** (*x* mol%)	*T* [°C]	*t* [h]	Yield [%][b]	*ee* [%][c]
1	toluene	10	RT	2	99	87
2	toluene	10	0	5	99	89
3	CH_2Cl_2	10	0	5	98	93
4	$Cl_2CH_2CH_2Cl_2$	10	0	5	99	93
5	THF	10	0	6	80	90
6	CH_3CN	10	0	5	98	98
7	CH_3CN	5	0	5	98	98
8	CH_3CN	2	0	7	90	87

[a] Unless otherwise specified, the reactions were carried out with 0.20 mmol of **1a**, 0.30 mmol of **2a**, and **PA8** in 2 mL of the solvent. [b] Yield of isolated product based on **1a**. [c] Enantiomeric excess was determined by HPLC analysis on a chiral stationary phase.



1 + 2 → 3

3a 5h, 98% yield, 98% *ee*

3b 5h, 95% yield, 98% *ee*

3c 5h, 82% yield, 91% *ee*

3d 5h, 88% yield, 99% *ee*

3e 5h, 81% yield, 96% *ee*

3f 5h, 84% yield, 98% *ee*

3g 5h, 85% yield, 99% *ee*

3h 5h, 90% yield, 99% *ee*

3i 5h, 89% yield, 97% *ee*

3j 5h, 94% yield, 99% *ee*

3k 5h, 88% yield, 99% *ee*

3l 5h, 90% yield, 95% *ee*

3m 5h, 90% yield, 97% *ee*

3n 5h, 89% yield, 97% *ee*

3o 12h, 60% yield, 96% *ee*

3p 24h, 85% yield, 96% *ee*

3q 24h, 62% yield, 97% *ee*

3r 12h, 79% yield, 96% *ee*

3s 12h, 80% yield, 96% *ee*

3t 72h, 67% yield, 80% *ee*
72h,75% yield, 86% *ee*[a]

3u 12h, 63% yield, 91% *ee*

3v 12h, 54% yield, 97% *ee*

3w 12h, 65% yield, 93% *ee*

3x 12h, 54% yield, 97% *ee*

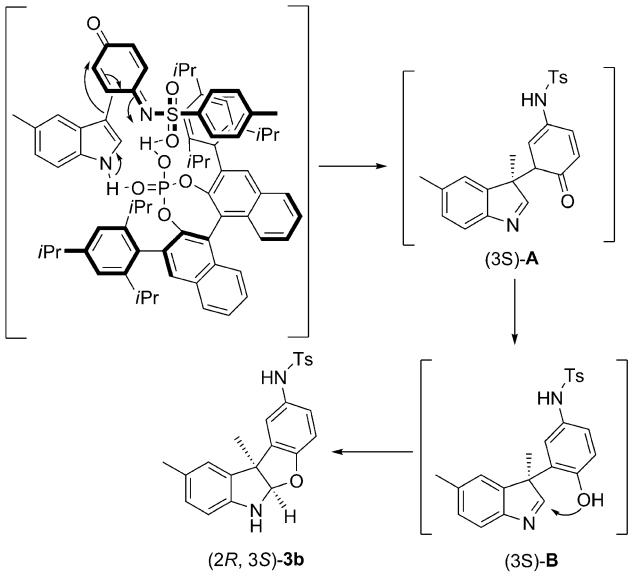
3y 72h, 0% yield

Scheme 1. Substrate scope. Reaction conditions: Unless otherwise specified, the reactions were carried out with 0.20 mmol of **1**, 0.30 mmol of **2**, and 0.01 mmol of **PA8** in 2 mL of acetonitrile at 0 °C. Yields shown are of the isolated products and based on **1**. Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase. [a] 10 mol% of **PA8** was employed. TBS = *tert*-butyldimethylsilyl.

quickly. Hence, it can be concluded that the scope of indoles was very good, but the scope of quinone monoimines was rather poor.

The absolute configuration of the benzofuroindoline **3b** was determined to be 2*R*,3*S* by an X-ray crystal structural analysis[10] (see the Supporting Information). Consequently, all of the other benzofuroindolines can be assigned absolute configurations by analogy.

Based on the absolute configuration of the product **3b**, a plausible reaction mechanism is proposed. As outlined in Scheme 2, first, the bifunctional phosphoric acid activated both the indole and quinone monoimine. 3-Methylindole attacked the quinone monoimine to give the intermediate (3*S*)-**A** which underwent aromatization immediately to give the phenol intermediate (3*S*)-**B**. Finally, spontaneous cyclization generated (2*R*,3*S*)-**3b**.



Scheme 2. Plausible reaction mechanism.

In conclusion, we have developed a highly enantioselective [3+2] coupling of 3-substituted indoles with quinone monoimines promoted by a chiral phosphoric acid. Through this transformation, a wide variety of benzofuroindolines were synthesized with moderate to good yields in moderate to excellent enantioselectivities. The absolute configuration of one product was determined as 2*R*,3*S* by an X-ray crystal structural analysis. Accordingly a plausible reaction mechanism was proposed.

Experimental Section

3-Substituted indole (**1**; 0.20 mmol) and quinone monoimine (**2**; 0.30 mmol) were placed in a flame-dried vial equipped with a magnetic stirring bar. Then 2 mL of CH_3CN was added to dissolve the mixture. The solution was cooled to 0 °C. Afterwards the chiral phosphoric acid (*R*)-**PA8** (0.01 mmol, 5 mol %) was added. The reaction mixture was stirred at 0 °C until no starting material was detected by TLC. The solvent was evaporated and the residue was subjected to chromatography (silica gel, petroleum ether/EtOAc 5:1→4:1) to afford the desired product **3**.

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[10] CCDC 1002543 (**3b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

