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Enantioselective synthesis of C3 substituted benzofuroindolines via catalytic asymmetric [3 + 2] cyclization of 3-substituted indoles with *p*-benzoquinones

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ABSTRACT

An efficient catalytic asymmetric [3 + 2] cyclization of 3-substituted indoles with *p*-benzoquinones has been realized using a binol-chiral phosphoric acid. A large variety of C3 substituted benzofuroindolines compounds were achieved in moderate to high yields (up to 91% yield) and excellent enantioselectivities (up to 94% ee).

Benzofuroindolines skeletons are part of the key structural core of fused indolines, which constitute the scaffolds of many important natural alkaloids [1–3], such as the very potent anticancer agents diazonamides [2] and azonazine [3], due to their moderate antitumor activity (Fig. 1). Consequently, constructing a benzofuroindoline core, especially in a catalytic asymmetric fashion, has become a fascinating-goal in the synthetic chemistry community. Although there are several elegant examples of organocatalytic cyclization for the construction of benzofuroindolines, there are few catalytic asymmetric methods for the synthesis of benzofuroindolines [4]. MacMillan [5b], Zhang [5l], Tang [5o], and Zhong [5p] independently reported methods for the preparation of benzofuroindolines through enantioselective cycloaddition reactions. As a result, exploring alternative strategies for the highly enantioselective construction of benzofuroindoline skeletons with diverse substitution and fusion patterns is completely desirable.

Quinones are extraordinary flexible starting materials of electron-deficient particles with multiple sites and modes, and they can be potentially used for reactions with electron-rich unsaturated species. Exploring the selectivity of these reactive molecules is an interesting strategy. Yadav and co-workers described a strategy involving the conjugate addition of indoles for *p*-benzoquinone to the synthesis of 3-indolylquinones by $InBr_3$ [6a], $Bi(OTf)_3$ [6b], or microwave irradiation [6c]. Nayak [6d], Li [6e], Wang [6f], and Song [6g] independently reported a direct coupling approach with 2-substituted indoles and 1,4-benzoquinone to construct 3-indolylquinones compounds by $CuBr_2$, iodine reagents and $Fe(OH)_3$, Recently, Shi and co-workers accomplished an elegant cascade 1,4-addition/alcohol elimination reaction involving 2,3-disubstituted indoles and quinone imine ketals, the 3-indolyquinone derivatives were generated in high yields and excellent stereoselectivities [6h]. Zhong and co-workers developed an enantioselective cyclization reaction with *p*-benzoquinone and 2,3-disubstituted indoles to construct benzofuroindolines bearing two vicinal tetrasubstituted carbon stereogenic centers by utilizing a chiral phosphoric acid catalyst [6l]. In Zhong's work, 3-methyl indole and *p*-benzoquinones underwent a 1,4-addition reaction to form 2-indolylquinone derivatives, using chiral binol-derived phosphoric acid and DCE as the solvent. Howerer, in our study, when CH_3CN was employed as the solvent in such reactions, a cyclization reaction occurred instead of the 1,4-addition reaction. We reasoned that the nature of the solvent has a direact impact on the reaction outcome. It is possible that the highly polar solvent CH_3CN is conducive to the cyclization reaction, while the less polar solvent DCE is conducive to the 1,4-addition reaction. We conducted experimental studies based on this interesting strategy of controlling the chemoselectivity by switching the solvent, and

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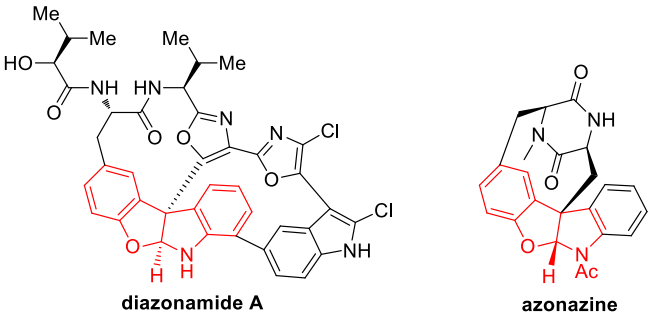
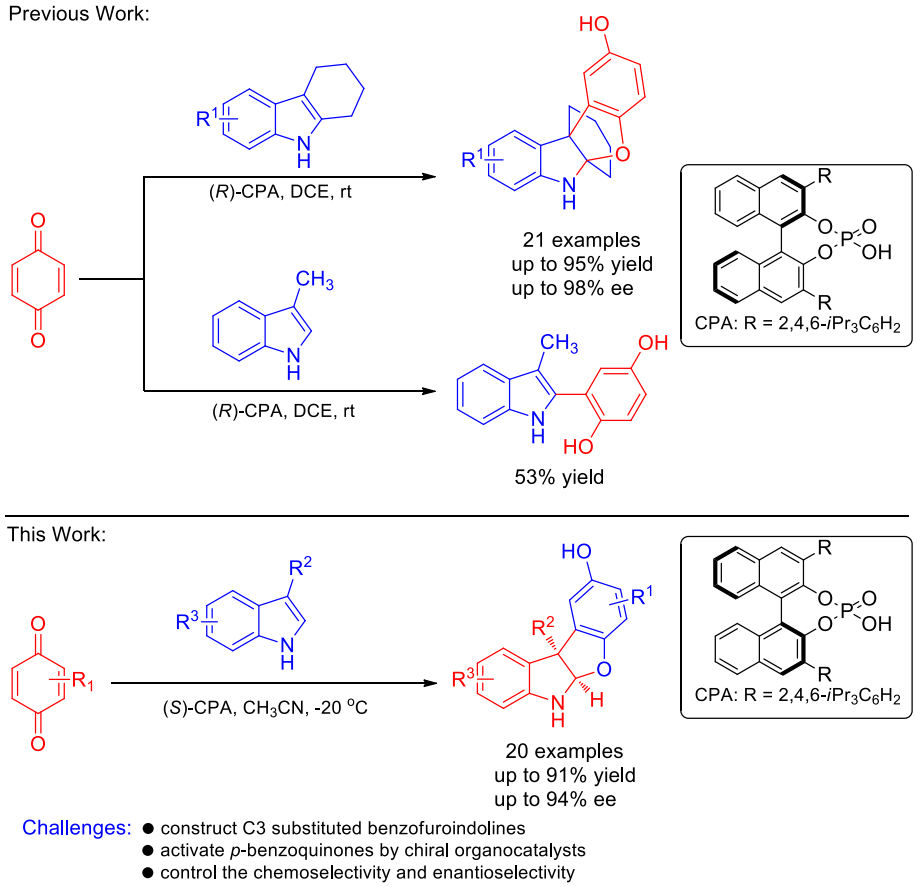


Fig. 1. Representative benzofuroindoline natural products.

we also hope to show an enantioselective [3 + 2] cyclization of 3-substituted indoles with *p*-benzoquinones to construct C3-substituted benzofuroindolines by bifunctional chiral phosphoric acid (CPA) [7–9]. We believe that this study will offer an opportunity for employing *p*-benzoquinone as a competent electrophile for diverse catalytic enantioselective transformations by solvent-controlled chemoselective [3 + 2] cyclization reactions, which is complementary to previous work by Zhong et al. [3i] (Scheme 1).

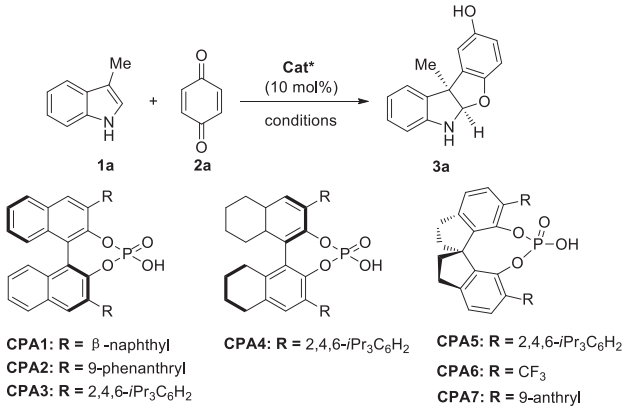
The studies were initiated by evaluating the reaction between 3-methyl indole (**1a**) and *p*-benzoquinone (**2a**) using various chiral phosphoric acids in acetonitrile at 25 °C. The reaction proceeded smoothly to give the desired **3a** product in a good yield with moderate enantioselectivity (Table 1, entry 1), Under the analogous conditions, **CPA1-CPA2** and **CPA4-CPA7** were a little lower enantioselectivity than **CPA3** for the reaction. As **CPA3** could bring about product **3a** in the highest enantioselectivity of 75% ee with good yield of 91% (Table 1, entry 3). These data suggest that the binol structure of chiral phosphoric acid is superior to the spiral structure of chiral phosphoric acid in both its reactivity and enantioselectivity. Therefore, binol-**CPA3** was determined to be the optimal catalyst, and it was used in the following investigations.

With the optimal reaction conditions determined, the screening of various parameters was modified. A variety of common organic solvents were screened based on the optimal reaction conditions (Table 1, entries 9–11). The results revealed that CH_3CN was better than the other solvents at 25 °C. When the temperature was reduced to 0 °C, the reaction took 2 days to generate the desired product with a 91% yield and slightly higher enantioselectivity of 80% (Table 1, entry 12). To our delight, when the temperature was reduced to −20 °C, the reaction proceeded well, generating benzofuroindoline **3a** in up to a 91% yield and 84% ee (Table 1, entry 13). When the temperature continued to decrease to −40 °C, the ee improved slightly to 89% (Table 1, entry 14), but the reaction time was extended to 7 days. Furthermore, when the catalyst loading amount was further reduced to 5 mol%, it resulted in a decrease in both the yield (77% yield) and ee value (70% ee) (Table 1, entry 15). Thus, the optimized reaction for the 3-methyl indole (**1a**) to *p*-benzoquinone (**2a**) included the reaction in CH_3CN and use of the 10% of **CPA3** at −20 °C.



Scheme 1. Previously reported reactions between indoles and 1,4-quinones and our designed strategy to access C3 substituted benzofuroindolines.

Table 1
Optimization of 3-methyl indole(1a) to p-benzoquinone (2a) by the chiral phosphoric acids.



Entry[a]	Cat*	Solvent	T(°C)	t (d)	Yield[%][b]	Ee[%][c]
1	**CPA1**	CH_3CN	25	1	80	57
2	**CPA2**	CH_3CN	25	1	73	17
3	**CPA3**	CH_3CN	25	1	91	75
4	**CPA4**	CH_3CN	25	1	50	13
5	**CPA5**	CH_3CN	25	1	90	67
6	**CPA6**	CH_3CN	25	1	77	28
7	**CPA7**	CH_3CN	25	1	65	49
9	**CPA3**	Toluene	25	4	83	41
10	**CPA3**	Mesitylene	25	7	60	43
11	**CPA3**	CH_2Cl_2	25	3	85	60
12	**CPA3**	CH_3CN	0	2	91	80
13	**CPA3**	**CH_3CN**	**−20**	**3**	**91**	**85**
14	**CPA3**	CH_3CN	−40	7	91	89
15[c]	**CPA3**	CH_3CN	−20	7	77	70

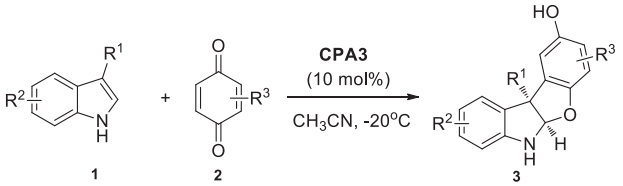
[a] Conditions: **1a** (0.20 mmol), **2a** (0.20 mmol) and 0.01 mmol of the chiral phosphoric acid in 2 mL of CH_3CN at room temperature. [b]Isolated yield based on **1a**. [c]Enantiomeric excesses were determined by HPLC analysis. [c]5 mol% CPA3 was used.

After the reaction standard conditions were established (Table 1, entry 13), the substrate scope was explored by the reactions of various 3-substituted indoles (**1**) with various *p*-benzoquinones (**2**) (Table 2). First, a series of 3-substituted indole derivatives were investigated at the C5 and C6 positions. The study showed that the electronic nature and the position of substituents on the aromatic ring of C5 and C6 had no influence on the enantioselectivity (**3b**-**3f, 3i,** and **3l**). The sufficient distance between the C5 and C6 groups from the reaction site may explain why the selectivity had almost no effect. Under the same conditions, the C4 and C7 groups of 3-substituted indole derivatives, which are both electron-donating and electron-withdrawing, could react with *p*-benzoquinone, leading to a decrease in both the yield and ee values **(3g, 3h, 3j, 3k**). The yields of **3g, 3h, 3j,** and **3k** were presumably lower due to steric hindrance on the reaction site. Meanwhile, the C3-substituted substrates (**1a**, **1m**) gave the expected product with a good yield with 84–90% ee. This reaction was also applicable to 2,3-dimethyl indole **3n** and the product was obtained in 88% yield and 93% ee. For some of the substituted indoles with bulkier substituents (**1o**-**1q**), the products were generated with lower yields and ee values. When *p*-benzoquinone was employed with an orth-methyl substituent or *ortho*-chlorine substituent, there were poor outcomes (**1r**, **1s**). When the indole with a 3-phenyl substituent (**1t)** was employed, the desired reaction was not observed, perhaps due to steric hindrance on the reaction site. When the R^2 group of the substrate (**1u)** was a phenyl group, the reaction was tolerated in 58% yield with 83% ee. In addition, when the *p*-benzoquinone with a fluorine substituent (**2v**) was employed, resulted in trace amount of desired product, which may be due to the decreased electrophilicity of this benzoquinone. Furthermore, when 2-methyl indole and 2-phenyl indole (**1w**, **1x**) were investigated, a 1,4-addition reaction of benzoquinone occurred instead of the cyclization reaction (Scheme 2).

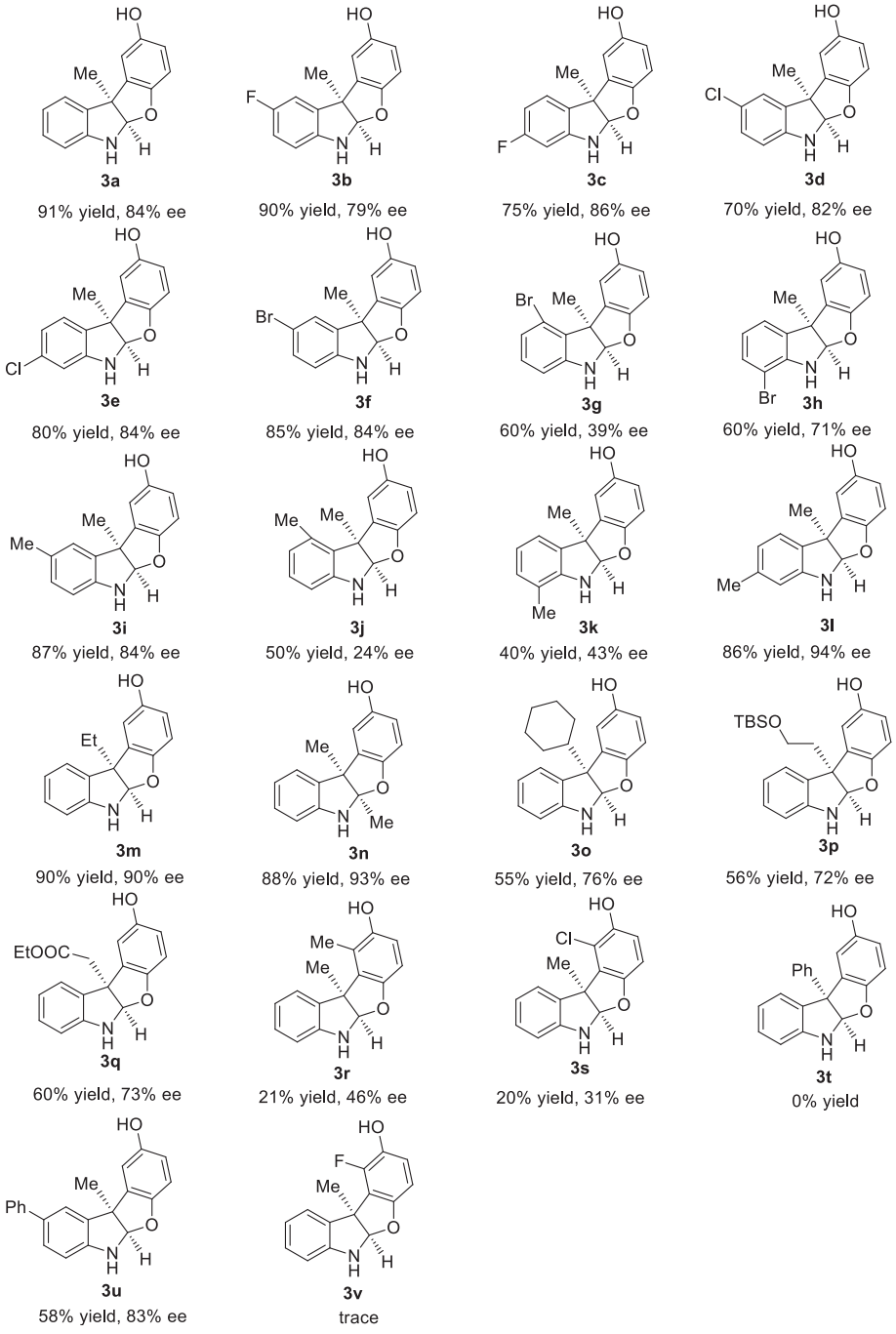
We also performed a preparative scale reaction to demonstrate the practical features of this process. The reaction of **1a** and **2a** was carried out on a gram scale with 10% catalyst **CPA3** in CH_3CN, As shown in Scheme 3, the reaction proceeded well to afford the corresponding product 3a in 85% yield and 70% ee.

To probe the reaction mechanism, 1,3-dimethyl indole (**1y**) was investigated to [3 + 2] cyclization reaction under standard

Table 2
Scope of CPA3-catalyzed asymmetric [3 + 2] cyclization of indoles 1 to *p*-benzoquinone 2.

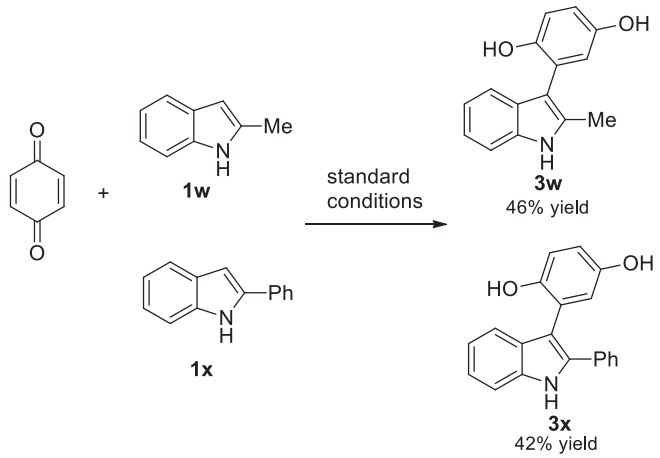


1 2 3

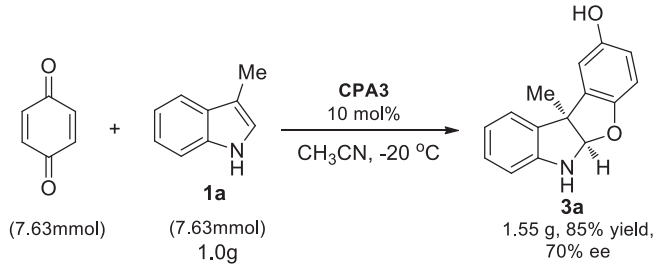


3a 91% yield, 84% ee
3b 90% yield, 79% ee
3c 75% yield, 86% ee
3d 70% yield, 82% ee
3e 80% yield, 84% ee
3f 85% yield, 84% ee
3g 60% yield, 39% ee
3h 60% yield, 71% ee
3i 87% yield, 84% ee
3j 50% yield, 24% ee
3k 40% yield, 43% ee
3l 86% yield, 94% ee
3m 90% yield, 90% ee
3n 88% yield, 93% ee
3o 55% yield, 76% ee
3p 56% yield, 72% ee
3q 60% yield, 73% ee
3r 21% yield, 46% ee
3s 20% yield, 31% ee
3t 0% yield
3u 58% yield, 83% ee
3v trace

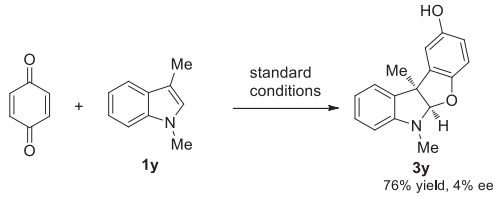
conditions, the corresponding product **3y** was obtained in 76% yield and 4% ee, thus implying that the N—H group of the 1,3-dimethyl indole play an significant role in the chirality induction through the formation of a H bond with the **CPA3** (Scheme 4). Thus a possible reaction pathway is illustrated in Scheme 5. It can be presumed that the NH group of **1n** and **2** was activated by the bifunctional phosphoric acid (*S*-**CPA3**) generated hydrogen bonding. In this model, the indole (**1n**) attacks the *p*-benzoquinones from the *Si* face preferentially as a result of less steric hindrance, resulting in a temporary intermediate having the formation of the first stereocenter **3S-A**, after a rapid enolization from (**3S)-A** to phenolic (**3S)-B**, this



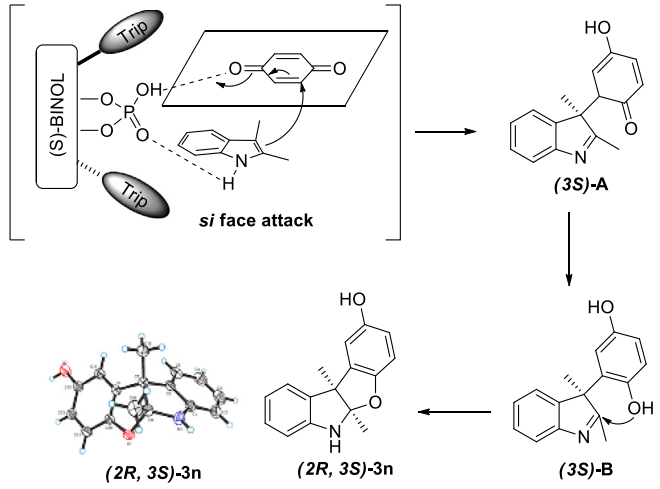
Scheme 2. Reactions of benzoquinone with 2-substituted indoles.



Scheme 3. Reactions on a Gram Scale.



Scheme 4. Reactions of benzoquinone with 1,3-dimethyl indole.



Scheme 5. Plausible reaction pathway.

intermediate further sponataneous cyclization generated **(2R, 3S)–3n**.

In conclusion, we have developed a catalytic enantioselective [3 + 2] cyclization of 3-substituted indoles with *p*-benzoquinones by chiral phosphoric acid, leading to a chemo-, diastereo- and enantioselective construction of diverse C3 substituted benzofuroindolines with moderate to good yields and with moderate to excellent enantioselectivity (up to 91% yield, up to 94% ee). A plausible reaction mechanism was also described. Notably, this reaction affords an opportunity to employ *p*-benzoquinone as a competent electrophile for diverse catalytic enantioselective transformations to construct a more structurally diverse group of benzofuroindolines.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2021.153233.

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