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# Chiral Phosphoric Acid Catalyzed [3 + 2] Cycloaddition and Tandem Oxidative [3 + 2] Cycloaddition: Asymmetric Synthesis of Substituted 3-Aminodihydrobenzofurans

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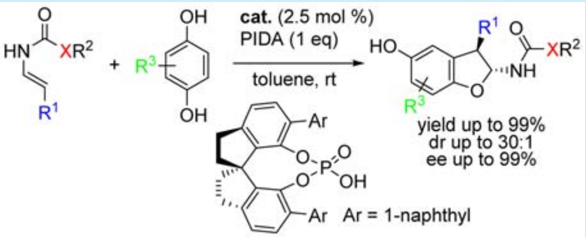
Ⓢ *Supporting Information*

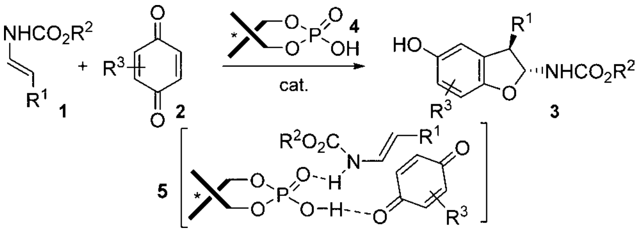
**ABSTRACT:** Asymmetric [3 + 2] cycloaddition of quinones with ene- and thioene-carbamates was achieved by chiral phosphoric acid catalysis, providing the corresponding 3-amino-2,3-dihydrobenzofurans in excellent yields with moderate to good diastereoselectivities and excellent enantioselectivities. An asymmetric tandem oxidative cycloaddition protocol starting from hydroquinones was also accomplished with phenyliodine(III) diacetate and a chiral phosphoric acid in the same reaction vessel.



Chiral 2,3-disubstituted 2,3-dihydrobenzofurans are common fragments in a number of biologically active molecules and natural products.[1,2] For their preparations, the [3 + 2] cycloaddition of quinones with electon-rich olefins represents one of the most convergent approaches.[3] Although the first [3 + 2] cycloaddition with quinones was reported in 1978,[4] very few enantioselective versions have been developed to date. In 1999, Engler et al. disclosed the first asymmetric example using a titanium−TADDOLate complex as catalyst.[5] More recently, Jørgensen[6a] and Shi[6b] reported elegant enantioselective organocatalytic [3 + 2] cycloadditions using *N*-tosyl-*p*-benzoquinone imines as 1,3-dipoles. Only one example using benzoquinone has been described.[6a] Despite these notable contributions, the search for a new catalytic enantioselective process that employs the benzoquinones as 1,3-dipole partners has yet to be developed.

Chiral phosphoric acids[7] are well-known as effective bifunctional organocatalysts in the activation of imines in various enantioselective transformations.[7] However, activation of carbonyl compounds such as quinones has been less successful and generally requires the presence of an imine functionality and/or stronger Brønsted acid catalysts.[6b,8,9] Some of our recent investigations were devoted to the chemistry of secondary ene-carbamates in enantioselective transformations.[10] Mechanistic studies have shown that hydrogen-bonding activation of ene-carbamates by the Lewis base of phosphoric acid was crucial to achieve high asymmetric induction.[10] On the basis of these studies, we envisioned that a dual activation of the dipole and dipolarophile with **4** (TS **5**) might enable the development of enantioselective inverse electron demand [3 + 2] cycloaddition with simple quinones and phosphoric acid catalysts (Scheme 1). Herein, we report our results on the chiral phosphoric acid catalyzed [3 + 2] cycloaddition of quinones with ene-carbamates and thioene-carbamates, affording 2-amino-3-alkyl-2,3-dihydrobenzofuran-5-ols in high yields with moderate to good diastereoselectivities and excellent enantioselectivities (up to 99% ee). We also describe the first enantioselective tandem oxidative processes combining phenol oxidation with an enantioselective [3 + 2] cycloaddition catalyzed by chiral phosphoric acids.

**Scheme 1. Catalytic Enantioselective [3 + 2] Cycloaddition Synthesis of 2-Amino-3-methyl-2,3-dihydrobenzofuran-5-ol**



We started our investigations with the reaction between (*E*)-*N*-(benzylprop-1-en-1-yl)carbamate (**1a**), benzoquinone (**2a**), and 10 mol % of (*R*)-BINOL-derived phosphoric acid catalyst **4** in $CH_2Cl_2$ at rt (Table 1). In all cases, full conversions with a suitable *trans*-selectivity were obtained; the enantioselectivity, however, varied dramatically (entries 1−6, Table 1). As such, the steric bulk of the aromatic substituents of the BINOL backbone has a significant influence on the selectivity of the reaction. For instance, the bulky (*R*)-3,3′-bis(2,4,6-triisopropylphenyl)-BINOL phosphoric acid (**4d**) achieved the targeted product in a good *trans*/*cis* diastereoselectivity (dr = 6:1) and a high ee value (85%) of the major *trans*-diastereomer. On the other hand, chiral (*R*)-spirophosphoric acid catalyst **4f**, incorporating a simple naphthyl group, gave much better enantioselectivity (entries 6 vs 2−4). After a survey of reaction conditions by varying the solvents, temperatures, and stoichiometries (see Supporting

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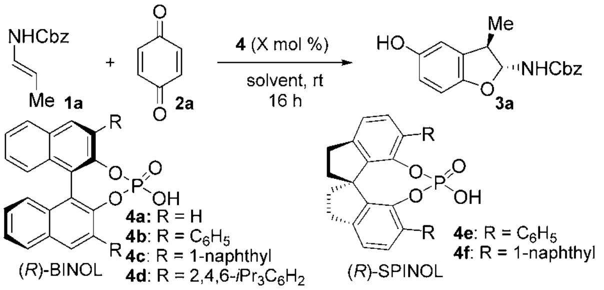
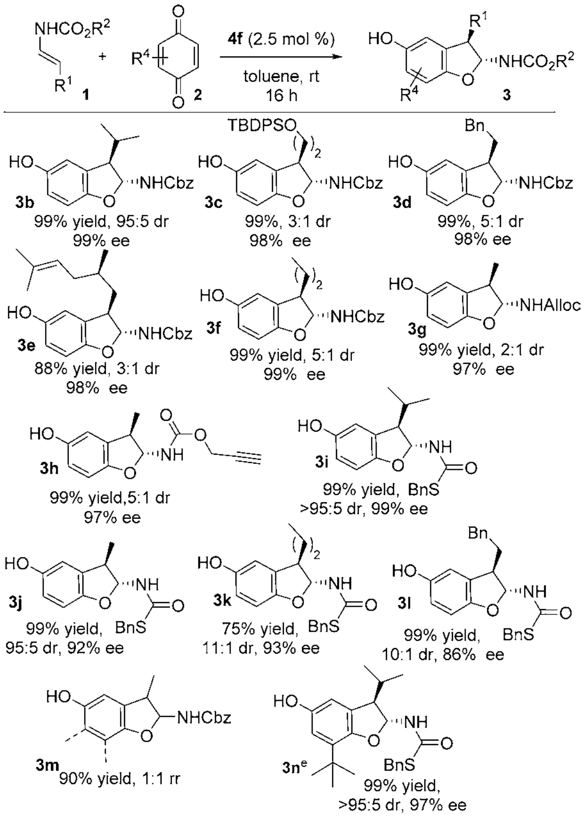
**Table 1. Optimization of Catalytic Enantioselective [3 + 2] Cyclization**



| entry | cat. | X | solvent | yield (%)[a,b] | dr[c,d] | ee (%)[e] |
|---|---|---|---|---|---|---|
| 1 | **4a** | 10 | $CH_2Cl_2$ | 95 | 6:1 | <5 |
| 2 | **4b** | 10 | $CH_2Cl_2$ | 99 | 6:1 | 49 |
| 3 | **4c** | 10 | $CH_2Cl_2$ | 99 | 6:1 | 52 |
| 4 | **4d** | 10 | $CH_2Cl_2$ | 99 | 6:1 | 85 |
| 5 | **4e** | 10 | $CH_2Cl_2$ | 99 | 6:1 | 65 |
| 6 | **4f** | 10 | $CH_2Cl_2$ | 99 | 6:1 | 97 |
| 7 | **4f** | 10 | $CH_2Cl_2$ | 80 | 6:1 | 95[f] |
| 8 | **4f** | 5 | $CH_2Cl_2$ | 99 | 6:1 | 97 |
| 9 | **4f** | 2.5 | $CH_2Cl_2$ | 99 | 6:1 | 97 |
| 10 | **4f** | 1 | $CH_2Cl_2$ | 67 | 6:1 | 97 |
| 11 | **4f** | 2.5 | toluene | 99 | 6:1 | 99 |
| 12 | **4f** | 2.5 | toluene | 82[g] | 6:1 | 91 |

[a] General conditions: **1a** (0.12 mmol), **2a** (0.10 mmol), and cat. (*x* mol %) in solvent (0.1 M) at rt for 16 h. [b] Yield of isolated pure product after column chromatography. [c] Determined by $^1$H NMR. [d] Absolute configuration (2*R*,2*R*) was determined by X-ray crystal structure analysis of tosylated **3a** (see Supporting Information). [e] Determined by HPLC analysis on a chiral stationary phase. [f] At 0 °C. [g] (*Z*)-**1a** was used instead of (*E*)-**1a**.

**Scheme 2. Scope of the Enantioselective [3 + 2] Cyclization[a–d]**



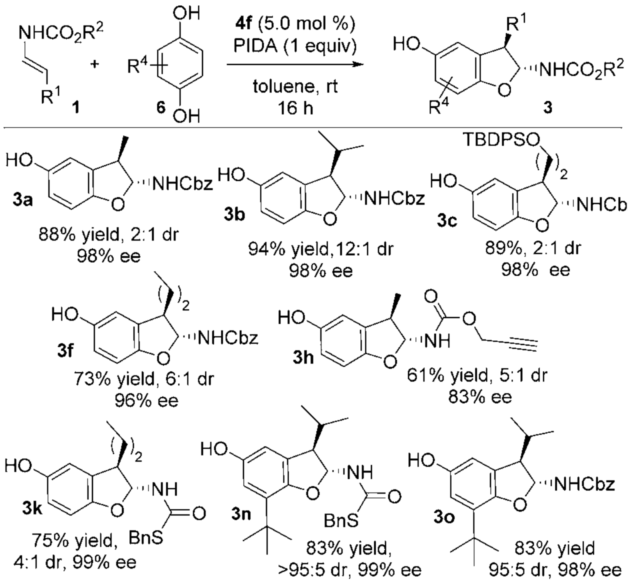
[a] General conditions: **1** (0.12 mmol), **2** (0.10 mmol), and **4f** (2.5 mol %) in toluene (0.1 M) at rt for 16 h. [b] Yield of isolated pure product after column chromatography. [c] Enantioselectivity determined by HPLC analysis on a chiral stationary phase. [d] Diastereoselectivity determined by $^1$H NMR. [e] Regioselectivity determined by HSQC and HMBC NMR analysis (see Supporting Information).

Information), the optimal conditions were identified to perform the reaction in toluene at rt in the presence of 2.5 mol % of catalyst **4f** (entry 11). Under these conditions, **4f** afforded cycloadduct **3a** in 99% yield with good diastereoselectivity and 99% ee.

This highly enantioselective synthesis of **3a** can also be expanded to reactions with a broad range of (*E*)-ene-carbamates **1b–h** and moderate to high diastereoselectivity (up to 95:5) with excellent enantioselectivity (97–99% ee) obtained (Scheme 2) under these conditions. Representative ene-carbamates with linear alkyl substituents (**1c–e,g**) participated in this [3 + 2] cycloaddition; the corresponding *trans*-2-amino-3-alkyl-2,3-dihydrobenzofuran-5-ol (**3c–e,g**) was isolated in high yield with excellent enantiomeric excess (98–99% ee) albeit with moderate diastereoselectivity (*trans*-isomer is the major product). On the other hand, (*E*)-ene-carbamate **1b** bearing a bulky *i*-Pr group at the *β*-position afforded the 2,3-*trans*-dihydrobenzofuran **3b** in an excellent diastereoselectivity (95:5 dr) with 99% yield and 99% ee. A variety of functional groups installed on the ene-carbamate such as silyl ether (**1c**), olefin (**1g**), and even a triple bond (**1h**) were well-tolerated. Meanwhile, chiral ene-carbamate derived from (*S*)-citronellal proceeded smoothly to give cycloadduct **3e** in 88% yield with 98% ee. Use of carbamate protecting groups, such as allylcarbamate (Alloc), propynyl carbamate, and ethylcarbamate, was found to participate in the reaction with similar diastereo- and enantioselectivities. The diastereoselectivity is profoundly influenced by protecting groups. For instance, the thiocarbamate protecting **1j** yielded desired cycloadduct **3j** in a higher diastereoselectivity than carbamate **1a**. These high selectivities prompted us to explore other thioene-carbamates **1i–n**. In all cases, excellent yields and diastereo- and enantioselectivities were observed for a broad range of substrates (**3i–l,n**). This current cycloaddition was extended to other benzoquinones. Reaction of 2-methyl-1,4-benzoquinone (**2b**) with **1a** gave cycloadduct **3m** as an inseparable complex mixture of regioisomeric and diastereomeric products. Using the unsymmetrical quinones, we were able to produce a single regioisomer. For instance, 2-(*tert*-butyl)-1,4-benzoquinone (**2c**) provided the corresponding 2,3-dihydrobenzofuran (**3n**) in high yield with excellent regio-, diastereo-, and enantioselectivity. Unfortunately, the cycloaddition reaction failed with 2,6-dimethylbenzoquinone (**2d**).

We then tried the possible development of a one-pot tandem reaction combining hydroquinone oxidation and enantioselective [3 + 2] cycloaddition.[3f,g,6a,11,12] Since most of the benzoquinones are obtained by oxidation of the corresponding hydroquinones, development of such an oxidative tandem process would significantly increase the versatility and synthetic efficiency of this enantioselective [3 + 2] cycloaddition. However, this stimulating approach is quite challenging due to potentially oxidizable enamides,[13] intermediates, and catalyst. Although great progress has been made in combination of an oxidative dearomatization reaction and asymmetric organocatalyzed desymmetrization processes, no example of a phosphoric acid catalyzed asymmetric one-pot tandem oxidative dearomatization−cycloaddition has been fully described.[12d] Following the pioneering work of Gaunt[12b] and Jørgensen[6a] on the phenyliodine(III) diacetate (PIDA)-promoted asymmetric oxidative dearomatization processes, we initially examined the reaction of **1a** and hydroquinone **6** with PIDA as the oxidant (see Supporting Information). Using our previously optimized conditions, **3a** was obtained in moderate yield with low diastereo- and enantioselectivity (50% ee, 3:1 dr). This poor selectivity is due to the formation of acetic acid in the reaction media, which might disturb the H-bonding interaction of substrates with the phosphoric acid catalyst.[10d] Meanwhile, an increase of the catalyst loading from 2.5 to 5% was found to boost the enantioselectivity to 98% ee (**3a**, Scheme 3) while maintaining moderate levels of diastereoselectivity. Other representative chiral 2,3-dihydrobenzofuran samples are listed in Scheme 3. In general, cycloadducts **3** were isolated in excellent yields and enantioselectivities. Although a good diastereoselectivity was preserved with the ene-carbamate and thioene-carbamate bearing an isopropyl group **1b**, a loss of diastereoselectivity was observed with the thioene-carbamate **1k**, albeit with higher ee. The reaction exhibited a high degree of tolerance toward various acid- or oxidation-labile groups such as silyl ether **3c** and propargyl **3h**. Most remarkably, the tandem oxidative [3 + 2] cycloaddition worked well with substituted hydroquinone, whose corresponding quinones are not commercially available. This was shown as the 2-(*tert*-butyl)benzene-1,4-diol (**6b**) being converted into the *trans*-3-amino-2,3-dihydrobenzofurans **3n** and **3o** in excellent yields and diastereo- and enantioselectivities. Moreover, note that no dioxygenation of ene-carbamates was observed, thus sustaining the high chemo- and regioselectivity of this tandem oxidative cycloaddition.[13]

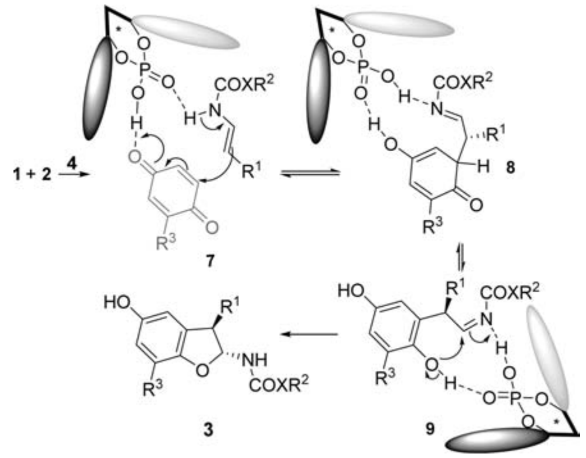
**Scheme 3. Scope of the Enantioselective Oxidative [3 + 2] Cyclization**[a−d]



[a]General conditions: **1** (0.12 mmol), **2** (0.10 mmol), and **5f** (2.5 mol %) in toluene (0.1 M) at rt for 16 h. [b]Yield of isolated pure product after column chromatography. [c]Enantioselectivity determined by HPLC analysis on a chiral stationary phase. [d]Diastereoselectivity determined by $^1$H NMR

The following control experiments were carried out to gain mechanistic insights. As shown in Table 1, the reaction with the (*Z*)-ene-carbamate (*Z*)-**1a** gave the same major diastereomer (*cis*/*trans* = 1:6) as that derived from (*E*)-ene-carbamate (*E*)-**1a**, albeit with lower enantioselectivity and yield (entry 12). Moreover, when the reaction was carried out in the presence of ethanol, apart from the cycloadduct **3a**, which was formed in a relatively small percentage, ethanol-trapping iminium intermediate **8** was mainly isolated (Scheme 2). On the basis of the above results and previous work,[6b] a plausible stepwise mechanism involving 1,4-Michael addition and intramolecular hemiaminalization is proposed in Scheme 4. Additionally, the use of a N-protected ene-carbamate, where hydrogen bonding with the catalyst was not possible, no cycloadduct was isolated. This highly suggests that the free NH group of the dipolarophile plays a crucial role in both reactivity and enantioselectivity. In light of these observations,[7,10] a tentative transition state model **7**, wherein the phosphoric acid forms hydrogen bonds with the dipole and dipolarophile, was proposed to explain the stereochemical outcome of the enantioselective [3 + 2] cycloaddition (Scheme 2). The enamide may preferentially add to the quinone from the *Re* face in a pseudo-intramolecular manner **6**, leading, after cyclization event, to (*R*,*R*)-2,3-dihydrobenzofuran **3**. The diastereomeric ratio (**3a**−**h**) varied with the steric demands of the ene-carbamates and the quinones, thereby suggesting a substrate-controlled diastereoselectivity.[14] However, whichever dipoles or dienophiles used, excellent diastereoselectiviy (**3i**−**n**) was obtained with thioene-carbamates. While the origin of this high diastereoselectivity awaits further study, transition state **9**, in which catalyst **4** might also control the configuration of the second stereogenic center, could be proposed. Thus, this catalyst-controlled process is supported by a loss of diastereoselectivity reaction **3k** in the presence of acetic acid (Scheme 3).

**Scheme 4. Plausible Reaction Mechanism**



In summary, a catalytic asymmetric [3 + 2] cycloaddition for a variety of ene- and thioene-carbamates was effectively achieved using quinones as the nitrogen source with a chiral SPINOL-phosphoric acid, giving *trans*-3-amino-2,3-dihydrobenzofurans in excellent yields with moderate to good diastereoselectivities and excellent enantioselectivities. The combination of oxidative dearomatization and enantioselective [3 + 2] cycloaddition in a single vessel is described. Under these conditions, 2,3-disubstituted 3-amino-2,3-dihydrobenzofurans were produced in excellent enantioselectivities (up to 99% ee). Ongoing work is directed toward gaining a greater understanding of the mechanism of this original reaction and expanding the scope of this methodology.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01593.

Experimental procedures, characterization data, copies of spectra, and crystallographic data (PDF)

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### Notes

The authors declare no competing financial interest.

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