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Exploiting the Modularity of Ion-Paired Chiral Ligands for Palladium-Catalyzed Enantioselective Allylation of Benzofuran-2(3*H*)-ones

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Supporting Information

ABSTRACT: A highly enantioselective allylation of benzofuran-2(3*H*)-ones is achieved under Pd catalysis by taking full advantage of the structural modularity of ion-paired chiral ligands.

The design and synthesis of chiral ligands is inarguably a subject of central importance in the development of transition-metal-catalyzed stereoselective transformations because the chiral ligands play a crucial role in governing the reactivity and stereocontrolling ability of the corresponding metal complexes.[1] While much research has led to the discovery of broadly applicable ligands and their fruitful synthetic applications, adding a new entry to the list of such privileged ligand structures remains a great challenge, primarily owing to the enormous difficulty of ligand design from first principles. Over the past decade, the supramolecular approach to this important problem has proven to be effective by the elaboration of multicomponent chiral ligands and catalysts, which rely on the use of noncovalent interactions for the spontaneous assembly of relatively simple molecular components.[2−4] The inherent modularity of multicomponent ligands allows for the expeditious construction of structurally diverse and meaningful catalyst libraries, thus facilitating the identification of not only the optimal system for a particular asymmetric reaction but also a novel class of catalyst with promising generality.[5] However, the actual reaction manifold that has been explored in the application of this emerging strategy is still very limited. We recently introduced a conceptually new multicomponent chiral ligand, an ion-paired chiral ligand of type **1** (Figure 1),[6] assembled from an achiral cationic ammonium−phosphine hybrid ligand and a chiral binaphtholate ion through electrostatic interaction.[7,8] By exploiting the multitude of combinations created by the ammonium phosphines and chiral acids, this ion-paired ligand could serve as a powerful tool for developing hitherto difficult asymmetric bond-forming reactions, particularly those involving the precise control of anionic nucleophilic species. Herein, we report the successful realization of this unique possibility through the development of the first highly enantioselective allylation of benzofuran-2(3*H*)-ones.

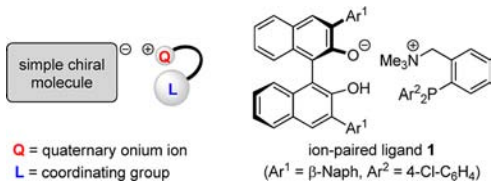

Figure 1. General concept of ion-paired chiral ligands (left) and first-generation ligand **1** (right).

Chiral benzofuran-2(3*H*)-ones possessing a quaternary stereocenter at their C-3 positions are important building blocks for a variety of natural products and potential pharmaceuticals.[9,10] Accordingly, the establishment of an efficient catalytic method for the asymmetric construction of this class of molecular architecture is much sought after and several notable contributions to fulfill this synthetic demand have been reported to date.[11] However, an enantioselective alkylation has never been developed despite its potential as a reliable yet straightforward strategy. In this study, we decided to pursue the development of a Pd-catalyzed protocol by the utilization of ion-paired chiral ligands with the expectation that they would be advantageous for the rapid identification of an optimal structure that allows the corresponding Pd complex to achieve rigorous enantiofacial discrimination of the prochiral enolate ions generated from 3-substituted benzofuran-2(3*H*)-ones. To this end, we first set out to examine the reaction of 3-benzylbenzofuranone **3a** with the synthetically attractive functionalized allylic methyl carbonate **4a** as a model system (Table 1).[12−15] An initial attempt with a catalyst prepared *in situ* from tris(dibenzylideneacetone)-dipalladium [$Pd_2(dba)_3$] and ion-paired chiral ligand **1** in toluene/H_2O (v/v = 20:1) at rt for 1 h resulted in the formation of the desired product **5a** in 79% isolated yield, albeit with low enantioselectivity (entry 1). It is essential to note that *O*-monoalkylated binaphthol was concurrently obtained, which indicates that the binaphtholate ion of **1** reacted with the allyl-Pd(II) intermediate during the course of the catalytic cycle. The intervention of this process could lead to the loss of stereocontrolling ability of the catalyst, which would account for the observed low ee value. Although this phenomenon manifested the drawback of the first-generation ligand **1**, we conceived it to be overcome toward expanded applicability by harnessing the modularity of the ion-paired ligand. This notion prompted us to attenuate the nucleophilicity of the chiral anion component of the ligand. After a screening of readily available chiral anions,[16] ligand **2a** having octahydrobinaphthol-derived chiral phosphate[17−19] was revealed to be a promising candidate for promoting the reaction with high stereoselectivity (entry 2). Optimizations then focused on modification of the chiral anion of **2** with regard to the structural feature of the 3,3′-substituents

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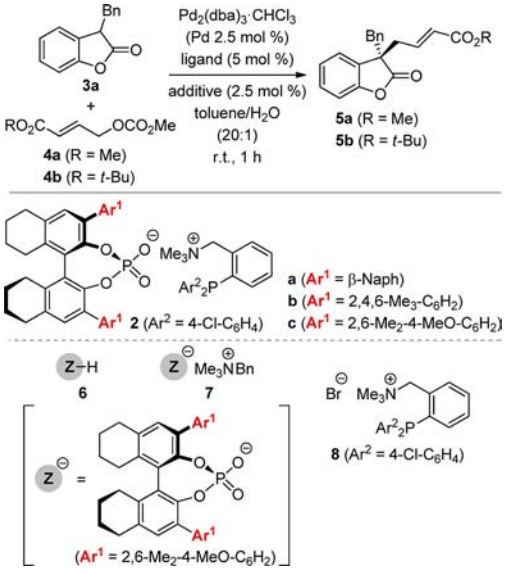
Table 1. Evaluation of Ion-Paired Chiral Ligands for Asymmetric Alkylation of Benzofuranone 3a with Allylic Carbonate 4[a]



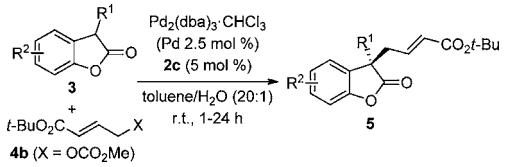
entry	ligand	additive	4	% yield	% ee[c]
1	**1**	none	**4a**	79[b]	22
2	**2a**	none	**4a**	78[b]	80
3	**2b**	none	**4a**	68[b]	82
4	**2c**	none	**4a**	91[b]	90
5	**2c**	none	**4b**	99[b]	92
6	$P(4\text{-Cl-}C_6H_4)_3$	**6**	**4b**	14[d]	<1
7	$P(4\text{-Cl-}C_6H_4)_3$	**7**	**4b**	30[d]	<1
8	**8**	**6**	**4b**	43[d]	−19

[a]Conditions: 0.20 mmol of **3a** and 0.20 mmol of **4** in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (Pd 2.5 mol %), ligand (5 mol %), and additive (2.5 mol %) in toluene (2.0 mL)/H_2O (0.1 mL) at rt for 1 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]NMR yield.

(Ar^1) by using well-established procedures; this uncovered that the introduction of the 2,6-dimethyl-4-methoxyphenyl group (**2c**) enabled a satisfactory level of stereochemical control (entry 4). Finally, we assessed the effect of the identity of allylic methyl carbonate **4** on the reactivity and selectivity and found that the alkylation proceeded smoothly with **4b** bearing *tert*-butoxycarbonyl functionality to give **5b** quantitatively with 92% ee (entry 5). To confirm the importance of ion pairing between the ammonium−phosphine hybrid ligand and the chiral phosphate ion in this stereocontrol, we also attempted the reaction with tris(4-chlorophenyl)phosphine as a ligand in the presence of either chiral phosphoric acid **6** or benzyltrimethylammonium phosphate **7** under otherwise identical conditions, which gave rise to racemic **5b** in low yield (entries 6 and 7). Furthermore, the use of achiral phosphinobenzylammonium bromide **8** with chiral phosphoric acid **6** led to the production of **5b** with low enantioselectivity (entry 8).[20]

Using optimal ligand **2c**, the scope of the benzofuranone nucleophile **3** in the Pd-catalyzed asymmetric alkylation with **4b** was briefly investigated. As listed in Table 2, various C(3) substituents, including a functionalized one, were accommodated and high enantioselectivities were uniformly observed (entries 1−3). This allylation is also applicable to 5- or 6-substituted benzofuranones with a similar degree of enantiocontrol (entries 4−6).

Table 2. Substrate Scope of Asymmetric Alkylation of Bezofuranones 3 with Functionalized Allylic Carbonate 4b[a]



entry	3 (R^1, R^2)	5	% yield[b]	% ee[c,d]
1	**3b** (CH_2i-Pr, H)	**5c**	92	90
2[e]	**3c** (*i*-Pr, H)	**5d**	81	94
3	**3d** [$(CH_2)_2CO_2Me$, H]	**5e**	94	91
4	**3e** (Bn, 5-OMe)	**5f**	90	90
5	**3f** (Bn, 5-Cl)	**5g**	99	89
6	**3g** (Bn, 6-OMe)	**5h**	95	91

[a]Conditions: 0.20 mmol of **3** and 0.20 mmol of **4b** in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (Pd 2.5 mol %) and **2c** (5 mol %) in toluene (2.0 mL)/H_2O (0.1 mL) at rt unless otherwise noted. [b]Isolated yield of **5**. [c]Ee of **5** was determined by chiral HPLC analysis. [d]Absolute stereochemistry of **5g** has been established by X-ray crystal analysis (see Figure 2 and Supporting Information (SI) for details), and the stereochemistry of the remaining examples were assumed by analogy. [e]Conducted with 0.40 mmol of **4b** (2 equiv) in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (Pd 5 mol %) and **2c** (10 mol %).

The absolute configuration of the allylated product **5g** was determined to be *S* by single-crystal X-ray diffraction analysis (Figure 2). The synthetic utility of this class of chiral scaffold,

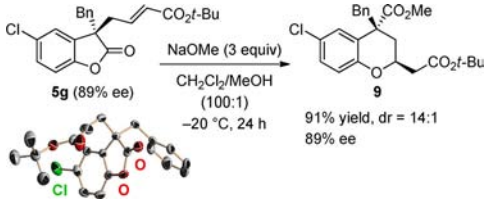


Figure 2. ORTEP diagram and derivatization of allylated bezofuranone **5g** (calculated hydrogens are omitted for clarity).

besides as a building block of natural products with a C(3)-quaternary benzofuranone core, can be illustrated by productive structural reorganization through the simultaneous utilization of the furanone and α,β-unsaturated carbonyl functionalities. For instance, treatment of **5g** with sodium methoxide triggered the ring opening and subsequent intramolecular oxy-Michael addition took place stereoselectively to afford benzopyran derivative **9** in 91% yield (dr = 14:1) without the loss of enantiomeric purity.

Next, we examined the feasibility of extending the present system to reactions with simple allylic carbonates. Thus, the allylation of **3a** with cinnamyl methyl carbonate **4c** was carried out in a similar manner using **2c** as a ligand. However, the reaction was rather slow, and the product **5i** was isolated in 79% yield with insufficient enantioselectivity (Table 3, entry 1). This result could be ascribed to the significant change in the structure and electronic property of the allyl-Pd(II) intermediate; hence, we undertook further optimization of the ligand **2**, which showed that the structural manipulation of the ammonium−phosphine component could provide a viable solution for realizing higher catalytic efficiency and stereoselectivity. For reactivity enhancement, replacement of the 4-chlorophenyl substituent on phosphorus (Ar^2) with the more electron-withdrawing 4-

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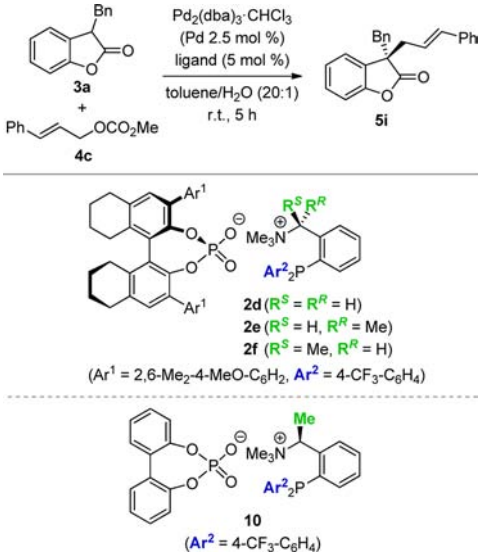
Table 3. Optimization of Ion-Paired Chiral Ligands for Asymmetric Alkylation of Benzofuranone 3a with Cinnamyl Carbonate 4c[a]



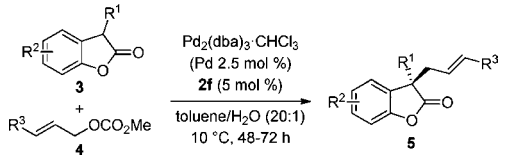
entry	ligand	% yield[b]	% ee[c]
1	**2c**	79	84
2	**2d**	97	85
3[d]	**2d**	94	88
4[d]	**2e**	96	78
5[d]	**2f**	99	95
6[d]	**10**	89	3

[a]Conditions: 0.20 mmol of **3a** and 0.20 mmol of **4c** in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (Pd 2.5 mol %) and ligand (5 mol %) in toluene (2.0 mL)/H_2O (0.1 mL) at rt for 5 h unless otherwise noted. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]Conducted at 10 °C for 48 h.

trifluoromethylphenyl group (**2d**) was beneficial (entry 2). This observation allowed us to perform the reaction at a lower temperature (10 °C), which resulted in a slight increase in the enantioselectivity without a detrimental effect on the reactivity profile (entry 3). More importantly, installation of chirality on the benzylic carbon of the ammonium−phosphine moiety was found to be associated with the stereocontrolling ability of the corresponding Pd catalyst. Although diminished enantioselectivity was observed with ligand **2e**, a pairing of the (*R*)-phosphate ion and (*R*)-1-(2-phosphinophenyl)ethylammonium ion (a mismatched chiral anion−cation combination) (entry 4), critical improvement in the stereoselectivity was attained with diastereomeric ligand **2f**, consisting of (*S*)-configured ammonium phosphine (a matched combination) (entry 5).[21−23] Noteworthy was that the attempted reaction with (*S*)-ammonium phosphine paired with achiral phosphate ion **10** as a ligand yielded **5i** in a nearly racemic form (entry 6). These results suggest that the chiral anion itself has a pivotal role in the asymmetric induction.

Subsequent experiments were conducted to explore the generality of this asymmetric allylation protocol, and the representative results are shown in Table 4.[24] With respect to the allylic carbonate electrophile **4**, the incorporation of different substituents, including fused aromatic and heteroaryl rings, was well tolerated (entries 1−3). In this catalytic system, unsubstituted allyl methyl carbonate also appeared to be a good candidate for an electrophilic partner (entry 4). With

Table 4. Substrate Scope of Asymmetric Alkylation of Bezofuranones 3 with Allylic Carbonates 4[a]



entry	**3** (R^1, R^2)	**4** (R^3)	**5**	% yield[b]	% ee[c,d]
1	**3a** (Bn, H)	**4d** (4-MeC_6H_4)	**5j**	95	92
2	**3a** (Bn, H)	**4e** (*β*-Naph)	**5k**	98	92
3	**3a** (Bn, H)	**4f** (2-thienyl)	**5l**	97	94
4	**3a** (Bn, H)	**4g** (H)	**5m**	93	80
5	**3h** (Me, H)	**4c**	**5n**	91	90
6	**3b** (CH_2*i*-Pr, H)	**4c**	**5o**	93	91
7[e]	**3c** (*i*-Pr, H)	**4c**	**5p**	98	96
8[e]	**3i** (*c*-Hex, H)	**4c**	**5q**	95	97
9	**3d** [$(CH_2)_2CO_2Me$, H]	**4c**	**5r**	91	90
10	**3e** (Bn, 5-OMe)	**4c**	**5s**	93	93
11	**3j** (Bn, 5-Me)	**4c**	**5t**	93	93
12	**3f** (Bn, 5-Cl)	**4c**	**5u**	91	91
13	**3g** (Bn, 6-OMe)	**4c**	**5v**	82	92

[a]Conditions: 0.20 mmol of **3** and 0.20 mmol of **4** in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (Pd 2.5 mol %) and **2f** (5 mol %) in toluene (2.0 mL)/H_2O (0.1 mL) at rt unless otherwise noted. [b]Isolated yield of **5**. [c]Ee of **5** was determined by chiral HPLC analysis. [d]Absolute configuration of the product **5n** was determined after conversion to the known compound (see SI for details), and the stereochemistries of the remaining examples were assumed by analogy. [e]Performed in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ (Pd 5 mol %) and **2f** (10 mol %) at rt.

nucleophile **3**, a series of C(3)-substituted benzofuranones were employable, constantly affording the corresponding alkylated products **5** of excellent enantiomeric purity (entries 5−9), although a higher catalyst loading and reaction temperature were required for substrates with sterically demanding appendages such as the 3-isopropyl and 3-cyclohexyl groups (entries 7 and 8). Also, the presence of a 5- or 6-substituent scarcely affected the stereochemical outcome of this successful alkylation (entries 10−13).

In conclusion, we have developed a catalytic and highly enantioselective allylation of 3-substituted benzofuran-2(3*H*)-ones for the first time through the identification of a new yet optimal ion-paired ligand featuring chiral phosphate in combination with an achiral or a chiral ammonium phosphine. This study not only offers a vital method for the construction of quaternary stereocenters at the 3-position of benzofuranones with rigorous enantiocontrol but also clearly demonstrates the vast potential of the modular ion-paired chiral ligand for the development of transition-metal-catalyzed asymmetric bond-forming reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Representative experimental procedures, analytical data for new compounds, and crystallographic data for **5g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(20) Although the origin of the opposite absolute stereochemistry was unclear, the asymmetric induction would stem from the *in situ* ion exchange between the bromide and phosphate ion. The validity of this assumption could be supported by the fact that the reaction with each 2.5 mol% of **2c** and **8** as ligands under otherwise similar conditions afforded **5b** in 81% yield with −17% ee (Figure S2 in the SI).

(21) Chiral ammonium phosphine was also readily prepared from commercially available (*R*)- or (*S*)-1-phenylethanamine in three steps. For details, see the SI.

(22) We ascertained that ligand **2f** was also effective for the reaction of **3a** with allylic carbonate **4b** under similar conditions shown in Table 1, affording **5b** in 96% yield with 90% ee.

(23) For the reaction of **3a** with **4b** in the presence of ligand **2c**, decreasing the reaction temperature to 10 °C was not effective to improve the enantioselectivity, resulting in the formation of **5b** with 92% ee (same value in the reaction at rt; see Table 1, entry 5).

(24) The present system was not effective for 1,3-disubstituted allylic substrates. For example, the reaction of benzofuranone **3a** with 1,3-diphenylallyl methyl carbonate or cyclohex-2-en-1-yl methyl carbonate did not proceed under the optimized conditions.