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Chiral Phosphoric Acid-Catalyzed Enantioselective Aza-Friedel–Crafts Alkylation of Indoles with γ-Hydroxy-γ-lactams

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Abstract: An enantioselective aza-Friedel–Crafts reaction of indoles with γ-hydroxy-γ-lactams using a chiral phosphoric acid catalyst is reported. The approach described herein provides an efficient access to 5-indolylpyrrolidinones in good to quantitative yields and excellent enantioselectivities (up to >99% *ee*). The results suggest that the reaction may proceed *via* *N*-acyliminium intermediates associated with the chiral phosphoric acid anion.

Keywords: alkylation; asymmetric synthesis; aza-Friedel–Crafts reaction; chiral phosphoric acids; organocatalysis

Chiral 5-indolylpyrrolidinones are a class of compounds found in a number of natural products and synthetic molecules with a wide array of biological activities, offering synthetic utility as structural motifs and pharmacological potential.[1] The aza-Friedel–Crafts (aza-FC) reaction represents one of the most straightforward approaches for the stereoselective construction of these structures.[2] Although the catalytic asymmetric variant of the transformation has been demonstrated using α-iminoalkyl-glyoxylate[3] and imines derived from aromatic[4] as well as aliphatic aldehydes,[4a,d,h,5] only limited success was achieved using cyclic aliphatic imines.[1i,6,7] The tendency of cyclic aliphatic imines to isomerize into enamine derivatives under acidic conditions renders the catalytic enantioselective development of this transformation much more difficult.[6c,8] The first example of an enantioselective intermolecular FC reaction with cyclic *N*-acyliminium ions has been recently developed by Jacobsen et al. using a thiourea-Schiff base catalyst and TMSCl.[9] Subsequently, Rueping et al.,[10] Zhou et al.[11] and You et al.[12] described chiral Brønsted acid-catalyzed FC reactions involving more stable iminium intermediates, including 2-alkyl and non-isomerizable iminiums. More recently, Huang and co-workers observed a different regioselectivity for the reaction of indoles with α,β-unsaturated γ-lactam-derived *N*-acyliminium ions in the presence of a chiral phosphoric acid catalyst, exclusively giving chiral *N*-alkylated indoles with good enantioselectivities.[13] Therefore, the development of novel catalytic enantioselective methods to construct 5-indolylpyrrolidinones still remains a challenging and attractive field of research.

Asymmetric counterion-directed catalysis (ACDC) introduced by List[14] has recently been proved to be an efficient strategy for enantioselective reactions that proceed *via* cationic species and chiral counteranions.[8–16] The use of chiral phosphoric acids as stereodirecting counteranions was inspired by the high efficiency of these bifunctional Brønsted acid catalysts for various enantioselective transformations.[17] Based on this idea, we hypothesized that the combination of a chiral phosphoric acid and a γ-hydroxy-γ-lactam would result in an effective catalytic iminium salt[18] to undergo enantioselective aza-FC alkylation of indoles.

Our initial studies involved a reaction of indole **1a** and γ-hydroxy-γ-lactam (5-hydroxy-*N*-phenyl-2-pyrrolidinone, **2a**) in the presence of a chiral phosphoric acid catalyst (**4**) in dichloromethane (DCM) at room temperature. Catalysts with various substitution patterns at the 3,3′-positions of BINOL were screened, all of which gave the desired C3-alkylated product **3a** in excellent yields and no *N*-alkylation by-product was observed. The 9-phenanthryl-substituted catalyst (**4e**, entry 5) was found to be the best in terms of yield and enantioselectivity. A solvent screening study

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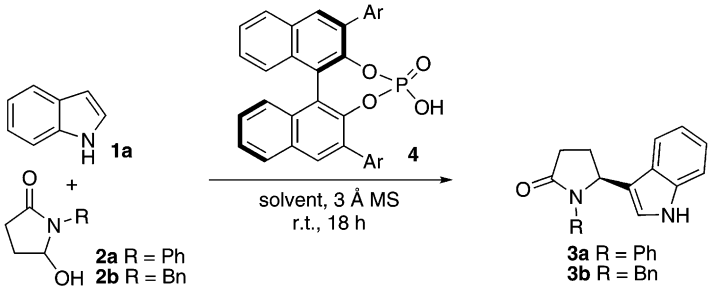
Table 1. Optimization studies the chiral phosphoric acid-catalyzed aza-FC reaction between indole **1a** and hydroxylactam **2**.[a]



Entry	**4a** [Ar]	**2** [equiv.]	*c* [mol/L]	Solvent	Yield [%][b]	*ee* [%][c]
1	**4a** C_6H_5	2	0.1	DCM	76	7
2	**4b** 9-anthracenyl	2	0.1	DCM	69	38
3	**4c** 2-naphthyl	2	0.1	DCM	80	60
4	**4d** 1-naphthyl	2	0.1	DCM	83	75
5	**4e** 9-phenanthryl	2	0.1	DCM	80	82
6	**4e**	2	0.1	1,2-DCE	87	88
7	**4e**	2	0.1	1,2-DCE	>99	91
8	**4e**	1.2	0.025	1,2-DCE	>99	95
9	**4e**	1.2	0.0167	1,2-DCE	>99	97
10	**4e**	1.2	0.0167	1,2-DCE	>99	98[d]
11	**4e**	1.2	0.0167	1,2-DCE	90	64[d,e]
12	**4e**	1.2	0.0167	1,2-DCE	>99	98[f]

[a] *General conditions:* indole **1a** (0.10 mmol, 1 equiv.), hydroxylactam **2a** and catalyst **4** (10 mol%) in a solvent.
[b] Isolated yields of **3a** after chromatography.
[c] Enantiomeric excesses were determined by chiral HPLC analysis.
[d] With 5 mol% of catalyst.
[e] Hydroxylactam **2b** was used to give **3b**.
[f] Without MS.

showed that the reaction proceeded with slightly higher enantioselectivity in 1,2-dichloroethane (entry 7). Interestingly, lowering both the concentration and amount of indole (from 2 to 1.2 equiv.) resulted in quantitative yield and pleasingly high enantioselectivity (entries 7–9). Moreover, the catalyst loading could be reduced to 5 mol% to give identical results (entries 10 *vs.* 11). Further studies revealed that the protecting group on the amide functionality of the hydroxylactams had an influence on the enantioselectivity, which was only moderate when **2b** was used (64% *ee*, Table 1, entry 11). Conveniently, similar results were observed in the absence of molecular sieves (MS) (entries 9 *vs.* 12).

After establishing the optimal reaction conditions (Table 1, entry 12), the scope of the reaction was examined (Table 2). It was found that the enantioselectivity was insensitive to the electronic property of the indole (Table 2, entries 1–9, 13, 15, and 16). Indeed, reactions of indoles substituted by electron-withdrawing and electron-donating groups at the 5-, 6- and 7-positions smoothly proceeded with high to excellent enantioselectivity. It is noteworthy that while a 2-alkylindole, namely 2-methylindole, provided **3k** with high enantioselectivity (90% *ee*, entry 9), the enantioselectivity of corresponding product **3l** dropped markedly when an aromatic counterpart was used (10% *ee*, entry 10). This also represents the first successful example of 2-alkylated indoles in the asymmetric aza-FC reaction. However, when a C-3-substituted indole was investigated (entry 11), only the *N*-alkylated regioisomer (**3m**) was observed with 20% *ee* (see the Supporting Information). The electron demand of the *N*-aryl group on hydroxylactams **2** was investigated by introducing a deactivating substituent at the *para* position. It was pleasing to find that uniformly high enantioselectivity and reaction yield were observed when a halogen was present (Br or I; entries 12–16). However, when hydroxylactam **2f**, which is strongly deactivating due to the presence of the nitro group, was used, a double alkylation product with the lactam ring being opened was obtained solely (Scheme 1).[19]

The reaction also failed with hydroxylactams having electron-rich aromatic rings such as *para*-methoxyphenyl. Additionally, the use of an *N*-protected indole, where hydrogen bonding with the catalyst was not possible, was investigated to support our proposed mechanism (Table 2, entry 18). The resulting product

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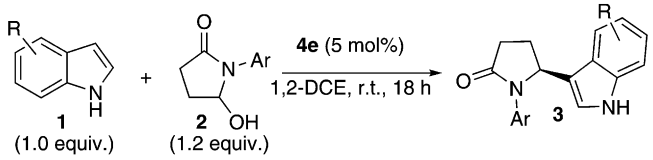
Table 2. Chiral phosphoric acid-catalyzed enantioselective synthesis of 5-indolylpyrrolidinones 3.[a]



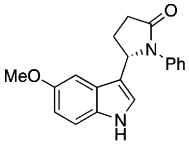
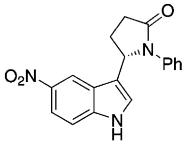
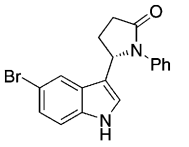
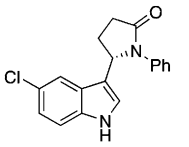
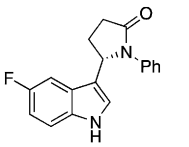
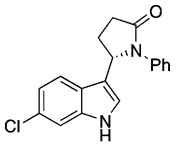
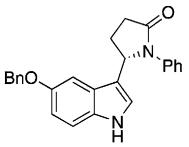
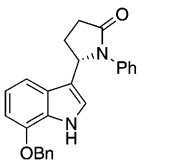
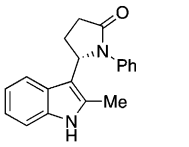
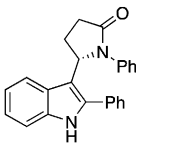
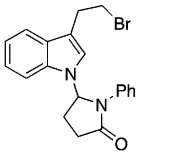
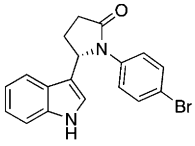
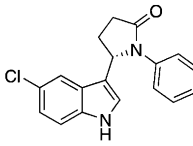
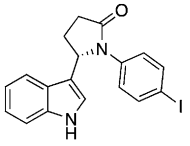
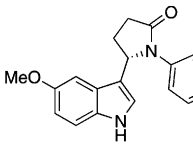
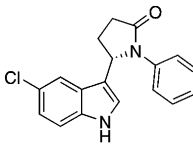
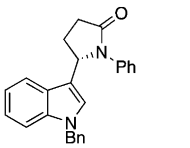
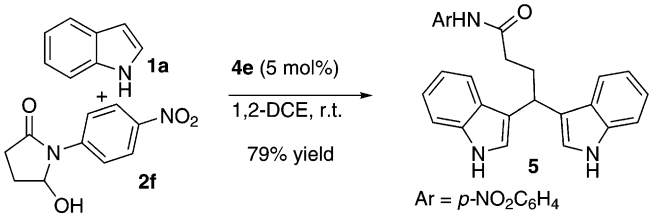
Entry	3		Yield [%][b]	*ee* [%][c]
1		**3c**	>99	97
2		**3d**	90	85
3		**3e**	80	92
4		**3f**	90	95
5		**3g**	>99	95
6		**3h**	>99	98
7		**3i**	>99	94
8		**3j**	63	>99
9		**3k**	90	90
10		**3l**	90	10

Table 2. (Continued)

Entry	3		Yield [%][b]	*ee* [%][c]
11		**3m**	84	20[d]
12		**3n**	62	83
13		**3o**	84	94
14		**3p**	60	93
15		**3q**	>99	97
16		**3r**	>99	97
17		**3s**	38	19

[a] *General conditions:* indole **1** (0.10 mol, 1.0 equiv,), hydroxylactam **2** (0.12 mmol, 1.2 equiv,) and catalyst **4e** (5 mol%).
[b] Isolated yields after chromatography.
[c] Enantiomeric excesses were determined by chiral HPLC analysis.
[d] The *N*-alkylated indole was formed instead of the C-3-alkylated product.



Scheme 1. Formation of bisindolyl by-product **5**.

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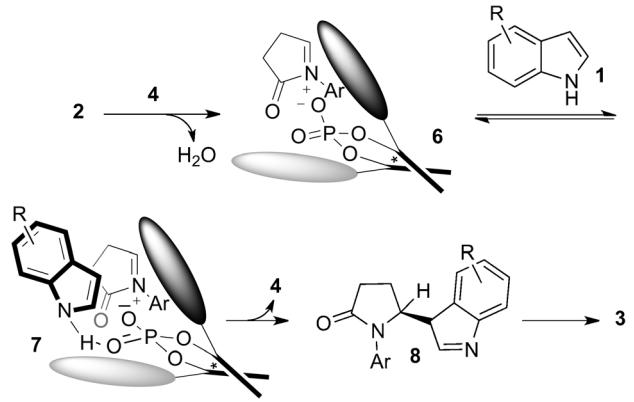


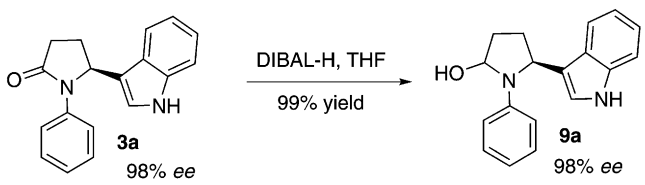
Scheme 2. Proposed mechanism and stereochemical issue.

(**3s**) was obtained in low yield and as an almost racemic mixture. The absolute configuration of compound **3a** was determined to be *S* by X-ray crystallography.[20]

Based on these observations, we surmise that the phosphoric acid-catalyzed FC alkylation may proceed *via* elimination of water from **2**, to form a chiral ion pair **6**, followed by hydrogen bonding between the NH site of indole and the Lewis basic phosphoryl oxygen (Scheme 2). Then, a pseudo-intramolecular *Si*-face attack of indole to the cyclic *N*-acyliminium carbon could occur *via* transition state **7**, leading to the isolated product *S*-**3**. This work is a good example of the dual activity of chiral phosphoric acids that allows: (i) generation of the catalytic iminium intermediate and (ii) the control of the face of attack by the ionic pair. However, what is remarkable about this catalytic system is the efficiency of the domino process, allowing the C–C bond formation to take place with high selectivity, and thus avoiding possible tautomerization.

Finally, the synthetic usefulness of products **3** was investigated using **3a** as an example to undergo a reduction to successfully afford 5-(indol-3-yl)-1-phenylpyrrolidin-2-ol **9a** which is suitable for further functionalizations (Scheme 3). Importantly, the product was isolated as one diastereomer with no erosion of *ee*.

In summary, we have described an efficient Friedel–Crafts alkylation of indoles and γ-hydroxy-γ-lactams using a chiral phosphate ion pair catalyst. The reaction proceeds with a great diversity of indole substrates with good to excellent enantioselectivities (up to 99% *ee*). A representative product has been transformed into a biologically active 3-(2-pyrrolidinyl)indole in two simple steps. Further work to strengthen the synthetic utility of optically active 5-indolylpyrrolidinones is underway.



Scheme 3. Elaboration of 3-(2-pyrrolidinyl)indole **9a**.

Experimental Section

General Procedure

To a stirring solution of *N*-phenylsuccinimidate **2** (1 equiv., 0.05 mmol) and indole **1** (1.2 equiv., 0.06 mmol), in dry 1,2-dichloroethane (3 mL) under argon was added catalyst 4**e** (0.005 mmol, 0.05 equiv.). The obtained mixture was stirred under an argon atmosphere at room temperature until completion of the reaction as judged by TLC monitoring (AcOEt/heptane 70/30). The solvent was removed under reduced pressure and the residue purified by flash chromatography over silica gel (AcOEt/*n*-heptane 40/60) to afford the corresponding 5-indolylpyrrolidinone **3**.

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[20] CCDC 901011 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.

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