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Highly Enantioselective Friedel–Crafts Reaction of 4,7-Dihydroindoles with Imines by Chiral Phosphoric Acids: Facile Access to 2-Indolyl Methanamine Derivatives

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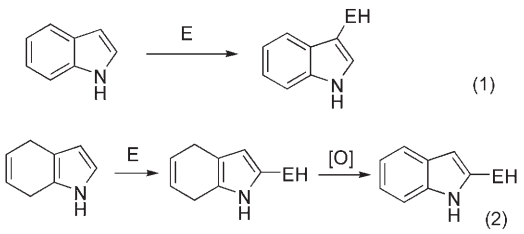
The Friedel–Crafts reaction represents one of the most important reactions for the formation of carbon–carbon bonds and direct derivatization of aromatic compounds in organic synthesis.[1] The enantioselective Friedel–Crafts reaction has attracted considerable interest and witnessed significant progress recently.[2] As indoles are probably the most widely distributed heterocyclic compounds in nature and exist extensively in biologically active natural products and pharmaceutical compounds, the enantioselective Friedel–Crafts reaction of indoles is no doubt one of the most extensive areas of research.[3] Due to the dramatic difference in reactivity between the 2- and 3-position of indole, most of the current studies on the enantioselective Friedel–Crafts reaction of indoles lead to 3-substituted indole derivatives ([Eq. 1], Scheme 1).[4] Developing a highly enantioselective synthesis of 2-substituted indole derivatives represents a challenging task, especially for indoles without substituents on 1- and 3-positions. Recently, Çavdar and Saraçoğlu found that reaction of 4,7-dihydroindole with α,β-unsaturated compounds led to 2-substituted indole derivatives following oxidation of the alkylation products.[5] More recently, Evans et al. and Pedro et al. have realized the asymmetric version of this reaction by utilizing chiral Lewis acid catalysts,[6] providing easy access to enantioenriched 2-substituted indole derivatives ([Eq. 2], Scheme 1). To the best of our knowledge, this strategy has not been utilized in enantioselective organocatalytic reactions. As part of our continuing efforts on the chiral phosphoric acid catalyzed Friedel–Crafts reaction of indoles with imines,[7–9] we recently realized the asymmetric Friedel–Crafts reaction of 4,7-dihydroindoles with imines. The reaction proceeds smoothly to afford the 2-substituted products in good yields with excellent enantiomeric excesses. In addition, 2-indolyl methanamine derivatives, which are a popular structure core in many biologically active natural and unnatural products,[10] can be synthesized by a one-pot procedure involving the Friedel–Crafts reaction of 4,7-dihydroindoles with imines and oxidation of the products with *p*-benzoquinone. Herein, we report our preliminary results.



Scheme 1. Routes to 3- and 2-substituted indoles via Friedel–Crafts reactions.

We first examined the reaction between 4,7-dihydroindole **2a**[5] and imine **3a** catalyzed by different chiral phosphoric acids **1** (Table 1). In the presence of 10 mol% of the chiral phosphoric acids **1** in toluene at −60 °C, reaction of **3a** with 1.5 equivalents of **2a** all gave the desired product **4aa** with *ee* values from 35 to 99%. It should be noted that all the reactions were complete within 10 min. Chiral phosphoric acid **1b** bearing two triphenylsilyl groups at the 3 and 3′ positions of the binaphthyl scaffold proved to be the optimal catalyst, affording the product **4aa** in 93% yield with 99% *ee* (entry 2, Table 1).

We further optimized the reaction conditions by using chiral phosphoric acid **1b** as the catalyst. The results are summarized in Table 2. We first investigated the effect of the reaction temperature. In general, lowering the temperature results a slight decrease of the reaction rate but a slight increase of the enantioselectivity (96 to 99% *ee*, from room temperature to −60 °C, entries 1–4, Table 2). Excellent enantioselectivity (98% *ee*) was attained when the reaction was

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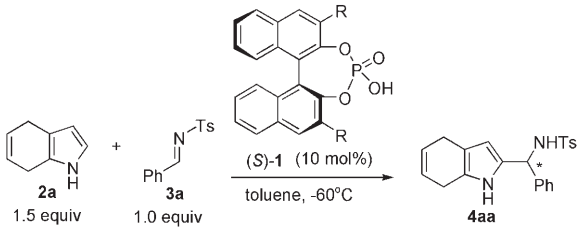
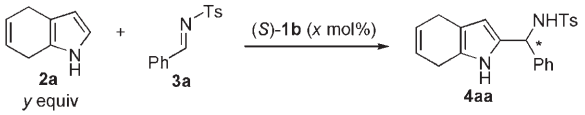
Table 1. Screening of phosphoric acids **1** in enantioselective Friedel–Crafts reaction.



Entry[a]	**1**, R	Time [min]	Yield [%][b]	*ee* [%][c]
1	**1a**, phenyl	5	71	73
2	**1b**, $SiPh_3$	5	93	99
3	**1c**, 3,5-$(CF_3)_2C_6H_3$	5	67	35
4	**1d**, 4-NO_2-C_6H_4	5	73	68
5	**1e**, 1-naphthyl	5	79	83
6	**1f**, 2-naphthyl	5	81	61
7	**1g**, 9-anthryl	5	54	61
8	**1h**, 9-phenanthryl	5	79	49
9	**1i**, 2,4,6-(iPr)$_3C_6H_2$	10	75	97
10	**1j**, 4-biphenyl	10	60	68

[a] Reaction conditions: 10 mol% of **1**, 0.20 mol L^{-1} of **3a** in toluene at −60°C. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis (Chiralcel OD-H).

Table 2. Optimization of the reaction conditions.



Entry[a]	*y* [equiv]	Solvent	*x* [mol%]	*T* [°C]	Time	Yield [%][b]	*ee* [%][c]
1	1.5	toluene	10	RT	<5 min	70	96
2	1.5	toluene	10	0	<5 min	77	97
3	1.5	toluene	10	−40	5 min	91	98
4	1.5	toluene	10	−60	5 min	93	99
5	2.0	toluene	10	−40	5 min	96	98
6	1.1	toluene	10	−40	5 min	93	99
7	1.1	CH_2Cl_2	10	−40	30 min	69	99
8	1.1	THF	10	−40	9 h	trace	n.d.
9	1.1	Et_2O	10	−40	9 h	49	90
10	1.1	EtOAc	10	−40	9 h	71	94
11	1.1	toluene	5	−40	15 min	86	97
12	1.1	toluene	2	−40	40 min	86	94

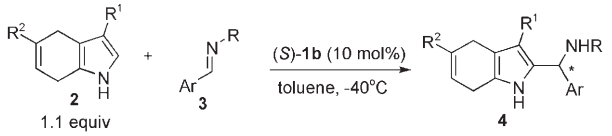
[a] Reaction conditions: *x* mol% of (*S*)-**1b**, *y* equivalents of **2a**, 0.20 mol L^{-1} of **3a**. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis (Chiralcel OD-H).

run at −40°C (entry 3, Table 2); this temperature was used to establish the best amount of 4,7-dihydroindole for the reaction. The reaction with 1.1 or 2 equivalents of 4,7-dihydroindole showed almost no effect on the outcome of the reaction (entries 3, 5, 6, Table 2). We found that reaction with 1.1 equivalents of 4,7-dihydroindole gave **4aa** in 93% yield with 99% *ee*.

Different solvents were then tested for the reaction of 10 mol% of **1b** and 1.1 equivalents of **2a** at −40°C. The reaction in CH_2Cl_2 afforded **4aa** with an excellent *ee* of 99% but in a moderate yield of 69% (entry 7, Table 2). A significant drop of both the reaction rate and enantioselectivity was observed for many other solvents tested such as THF, Et_2O, and EtOAc (entries 8–10, Table 2). Lower catalyst loadings were examined and 5 mol% or 2 mol% of **1b** also led to the desired product in excellent yields and enantioselectivities, respectively (entries 11 and 12, Table 2).

Under the above optimized reaction conditions (entry 6, Table 2), various substituted 4,7-dihydroindoles and imines were examined to test the generality of the reaction (Table 3).

Table 3. Enantioselective Friedel–Crafts reaction of 4,7-dihydroindoles with *N*-sulfonyl aldimines.



2a, R^1 = R^2 = H; **2b**, R^1 = H; R^2 = OMe; **2c**, R^1 = Me; R^2 = H; **2d**, R^1 = H; R^2 = F

Entry[a]	**2**	**3**, Ar, R	Time [min]	**4**, Yield [%][b]	*ee* [%][c]
1	**2a**	**3a**, C_6H_5, Ts	5	**4aa**, 93	99
2	**2a**	**3b**, 4-Me-C_6H_4, Ts	5	**4ab**, 89	99
3	**2a**	**3c**, 4-OMe-C_6H_4, Ts	20	**4ac**, 85	99
4	**2a**	**3d**, 4-Cl-C_6H_4, Ts	20	**4ad**, 82	98
5	**2a**	**3e**, 4-Br-C_6H_4, Ts	20	**4ae**, 84	99 (*R*)[d]
6	**2a**	**3f**, 4-CF_3-C_6H_4, Ts	20	**4af**, 90	>99
7	**2a**	**3g**, 3-NO_2-C_6H_4, Ts	20	**4ag**, 97	98
8	**2a**	**3h**, 2-Br-C_6H_4, Ts	80	**4ah**, 94	86
9	**2a**	**3i**, C_6H_5, Bs	10	**4ai**, 96	96
10	**2a**	**3j**, 4-Me-C_6H_4, Bs	40	**4aj**, 91	97
11	**2b**	**3a**, C_6H_5, Ts	10	**4ba**, 88	99
12	**2b**	**3b**, 4-Me-C_6H_4, Ts	5	**4bb**, 89	98
13	**2b**	**3f**, 4-CF_3-C_6H_4, Ts	10	**4bf**, 88	98
14	**2c**	**3a**, C_6H_5, Ts	10	**4ca**, 87	98
15	**2c**	**3c**, 4-MeO-C_6H_4, Ts	5	**4cc**, 88	98
16	**2c**	**3d**, 4-Cl-C_6H_4, Ts	5	**4cd**, 90	91
17	**2d**	**3a**, C_6H_5, Ts	30	**4da**, 83	92
18	**2d**	**3b**, 4-Me-C_6H_4, Ts	15	**4db**, 80	93

[a] Reaction conditions: 1.1 equivalents of **2**, 10 mol% of **1b**, −40°C, 0.20 mol L^{-1} of **3** in toluene. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis. [d] Determined by a single-crystal X-ray diffraction analysis.

The phosphoric acid catalyzed Friedel–Crafts reaction of 4,7-dihydroindoles with *N*-sulfonyl aldimines was found to be general with imines bearing different substituents. Substituted tosyl imines **3b–g**, containing either electron-donating groups or electron-withdrawing groups at the *para* or *meta* position of the phenyl ring, were tested in the reaction with 4,7-dihydroindole **2a**. In all cases, high yields and excellent enantioselectivities were achieved for the desired alkylation products (82 to 97% yields, 98 to >99% *ee*, entries 1–7, Table 3). When 2-Br-phenyl-substituted imine **3h** was used, a drop of the reaction rate and *ee* was observed, but the yield (94%) and *ee* (86%) of the product remained excellent (entry 8, Table 3). When the protecting group in **3** was changed from *N*-Ts to *N*-Bs, high enantioselectivities were

also acheived (96 to 97% *ee*, entries 9 and 10, Table 3). Substituted 4,7-dihydroindoles **2b–d**, containing either an electron-donating group or electron-withdrawing group (5-OMe, 3-Me, and 5-F, respectively), were tested in the reaction with different imines. In all cases, high yields and excellent enantioselectivities were achieved (80 to 91% yield, 91 to 98% *ee*, entries 11–18, Table 3).

To determine the absolute configuration of the product, crystals of enantiopure **4ae** were obtained and a single-crystal X-ray analysis revealed the configuration to be *R* (Figure 1).[11]

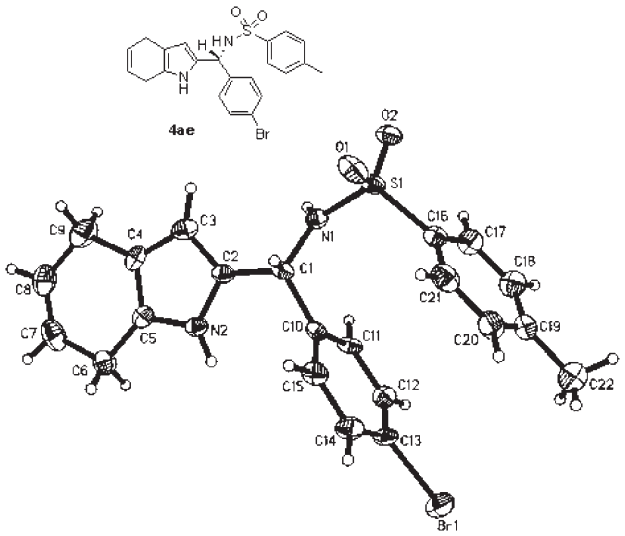
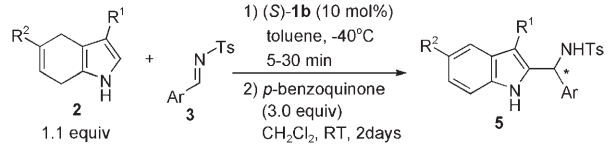


Figure 1. X-ray structure of (*R*)-**4ae**.

To demonstrate the suitability of the current methodology for the synthesis of 2-indolyl methanamine derivatives, we developed a one-pot procedure including the Friedel–Crafts reaction of 4,7-dihydroindoles with imines and further oxidation of the resulting products with *p*-benzoquinone (Table 4). To our delight, in all cases, the corresponding 2-indolyl methanamine derivatives were obtained smoothly in good overall yields with excellent enantioselectivities (74 to 88% yield, 98 to >99% *ee*).

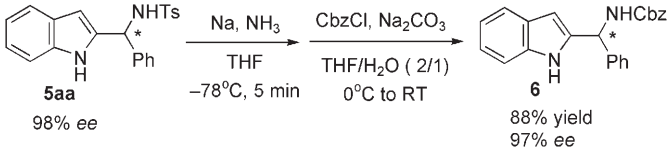
Table 4. One-pot synthesis of 2-indolyl methanamine derivatives.



Entry[a]	**2**	**3**, Ar	**5**, Yield [%][b]	*ee* [%][c]
1	**2a**	**3a**, C_6H_5	**5aa**, 88	99
2	**2a**	**3b**, 4-Me-C_6H_4	**5ab**, 81	98
3	**2a**	**3e**, 4-Br-C_6H_4	**5ae**, 79	99
4	**2b**	**3a**, C_6H_5	**5ba**, 74	>99
5	**2c**	**3a**, C_6H_5	**5ca**, 83	98

[a] Reaction conditions: see the Supporting Information for details. [b] Yield of isolated product. [c] Determined by chiral HPLC analysis.

As shown in Scheme 2, the tosyl group in **5aa** could be readily removed and converted to the carbobenzoxy (Cbz) group in an excellent yield (88%) without the loss of the optical purity.[12]



Scheme 2. Removal of the tosyl group in **5aa**.

In summary, we have developed the enantioselective Friedel–Crafts reaction of 4,7-dihydroindoles with imines by utilizing chiral phosphoric acids as efficient catalysts. The reaction features a metal-free approach, high efficiency of the catalyst, mild reaction conditions, high yields, and excellent enantioselectivities, and provides a practical method to synthesize highly enantiopure 2-(4,7-dihydroindolyl) and 2-indolyl methanamine derivatives.

Experimental Section

General procedure for the catalytic asymmetric Friedel–Crafts reaction (Table 3): In a dry Schlenk tube, *N*-sulfonyl imine **3** (0.20 mmol) and phosphoric acid **1b** (17.3 mg, 0.020 mmol) were dissolved in toluene (1 mL) under argon. The solution was stirred for 10 min at room temperature and then for another 5 min at −40 °C. Subsequently, 4,7-dihydroindoles **2** (0.22 mmol) were added in one portion at −40 °C. After the reaction was complete (monitored by TLC), saturated $NaHCO_3$ (3 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate (10 mL). The organic layer was washed with brine (5 mL), separated, and dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the residue was purified by column chromatography (ethyl acetate/petroleum ether 1/5 ~1/3) to afford the product **4**.

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Keywords: asymmetric catalysis · Friedel–Crafts reaction · imines · indoles · phosphoric acid

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[11] CCDC-672286 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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