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Chiral Brønsted Acid-Catalyzed Asymmetric Friedel−Crafts Alkylation of Pyrroles with Nitroolefins

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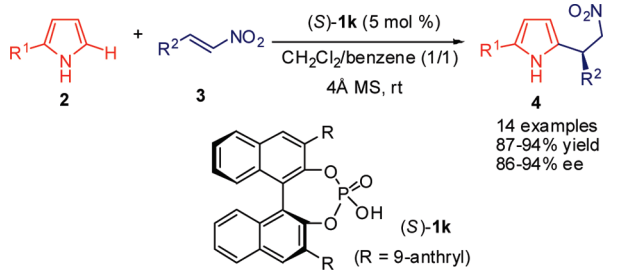
Received June 17, 2009



A highly efficient Friedel−Crafts reaction of pyrroles with nitroolefins by a chiral phosphoric acid was realized. With 5 mol % of catalyst, reactions conducted at rt afforded the 2-substituted or 2,5-disubstituted pyrroles in up to 94% ee for a wide range of substrates.

Friedel−Crafts alkylation is one of the most efficient methods for the derivatization of aromatic compounds.[1] Asymmetric Friedel−Crafts reactions provide an efficient way to synthesize optically active aromatics bearing benzylic chiral centers and have thus attracted considerable interest and witnessed significant recent progress.[2] Pyrroles exist extensively as the structure core of biologically active natural products[3] and pharmaceuticals.[4] However, the enantioselective Friedel−Crafts alkylations of pyrroles are relatively less explored.[5] Meanwhile, the asymmetric Friedel−Crafts reaction employing nitroolefin as the electrophilic partner is very attractive[6,7] since the nitro group of the products allows the subsequent versatile transformations.[8] Consequently, the efficient asymmetric Friedel−Crafts reactions between pyrroles and nitroolefins are very useful and highly desirable in organic synthesis. Surprisingly, only two asymmetric catalytic protocols have been documented in the literature by Trost and Du, and in both cases chiral zinc complexes were used as the efficient catalyst.[9] As part of our ongoing program in exploring chiral Brønsted acids as suitable catalysts for asymmetric Friedel−Crafts alkylation reactions,[10] we recently found that the chiral phosphoric acids[11,12] were efficient catalysts for the asymmetric Friedel−Crafts

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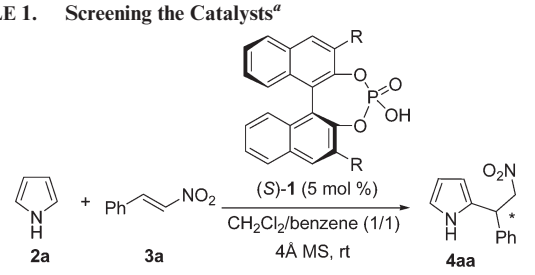
DOI: 10.1021/jo9013029 Published on Web 07/29/2009

TABLE 1. Screening the Catalysts[a]



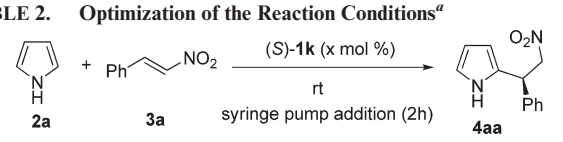
entry	(*S*)-**1**, R	time	yield (%)	ee (%)[b]
1	(*S*)-**1a**, H	2 d	79	2 (*R*)
2	(*S*)-**1b**, Ph	2 d	81	4 (*R*)
3	(*S*)-**1c**, 4-$NO_2C_6H_4$	2 d	80	13 (*S*)
4	(*S*)-**1d**, biphenyl	2 d	83	24 (*S*)
5	(*S*)-**1e**, 3,5-$(CF_3)_2C_6H_3$	2 d	72	1 (*R*)
6	(*S*)-**1f**, 1-naphthyl	2 d	79	6 (*S*)
7	(*S*)-**1g**, 2-naphthyl	2 d	73	4 (*S*)
8	(*S*)-**1h**, 2,4,6-$(iPr)_3C_6H_2$	2 d	77	3 (*R*)
9	(*S*)-**1i**, $SiPh_3$	2 d	76	5 (*S*)
10	(*S*)-**1j**, 9-phenanthryl	16 h	89	33 (*R*)
11	(*S*)-**1k**, 9-anthryl	15 h	93	87 (*R*)
12[c]	(*S*)-**1k**, 9-anthryl	3 h	93	88 (*R*)
13	none	2d	15[d]	0

[a] Reaction conditions: 3 equiv of **2a**, 5 mol % of (*S*)-**1**, 0.25 mol/L of **3a** in CH_2Cl_2/benzene. [b]Determined by chiral HPLC analysis (Chiralcel OD-H column). [c]A syringe pump was used to add **3a** for 2 h. [d]Conversion was determined by ^1H NMR.

alkylation reaction of nitroolefins with pyrroles, providing 2-substituted pyrrole derivatives with high ee values. To our knowledge, this study represents the first example of an enantioselective organocatalytic Friedel−Crafts reaction of pyrroles with nitroolefins. In this paper, we report our detailed studies on this subject.

We recently found that the (*S*)-**1k** bearing 9-anthryl groups could catalyze the reaction between 4,7-dihydroindole and nitroolefin with high yields and ee values.[10d] Since 4,7-dihydroindole is a substituted pyrrole derivative, the success of the reaction of 4,7-dihydroindole prompted us to explore simple unprotected pyrrole as a suitable electrophilic partner in the asymmetric Friedel−Crafts reaction with nitroolefins. We began our study by examining different chiral phosphoric acids in the Friedel−Crafts reaction between pyrrole **2a** and nitroolefin **3a** (Table 1). With 5 mol % of the catalyst and 4 Å molecular sieves (MS), all the catalysts led to alkylation product with good yields but mostly poor ee values. To our delight, chiral phosphoric acid (*S*)-**1k** bearing 9-anthryl groups was found to be the optimal catalyst, affording alkylation product **4aa** in 93% yield and 87% ee (entry 11, Table 1). The ee was further increased to 88% by adding the nitroolefin with a syringe pump over 2 h (entry 12, Table 1). Notably, the reaction between **2a** and **3a** could proceed slowly in the absence of the catalyst, affording **4aa** in 15% conversion in 2 d (entry 13, Table 1).

TABLE 2. Optimization of the Reaction Conditions[a]



entry	solvent	additive	*x* (mol %)	time (h)	yield (%)	ee (%)[b]
1	CH_2Cl_2/benzene	4 Å MS	10	2	94	89
2	CH_2Cl_2/benzene	4 Å MS	5	3	93	88
3	CH_2Cl_2/benzene	4 Å MS	2	6	91	81
4	CH_2Cl_2/benzene	4 Å MS	1	25	89	72
5	CH_2Cl_2/benzene	4 Å MS	0.5	48	66	23
6	CH_2Cl_2/benzene	3 Å MS	5	7	89	35
7	CH_2Cl_2/benzene	5 Å MS	5	6	91	45
8	CH_2Cl_2	4 Å MS	5	4	92	85
9	toluene	4 Å MS	5	5	93	83
10	CH_2Cl_2/toluene	4 Å MS	5	5	91	86

[a]Reaction conditions: 3 equiv of **2a**, *x* mol % of (*S*)-**1k**, 0.25 mol/L of **3a** in CH_2Cl_2/benzene. [b]Determined by chiral HPLC analysis (Chiralcel OD-H column).

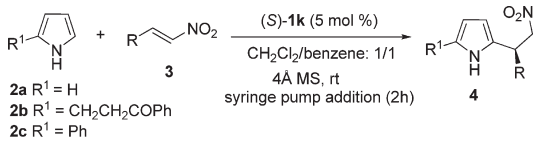
Then the reaction conditions were further optimized as summarized in Table 2. Increasing the catalyst loading to 10 mol % did not show notable beneficial effects. With 2 mol % of the catalyst, the reaction was also able to proceed to completion within 6 h with 81% ee (entry 3, Table 2). However, dramatic decrease of both the reaction rate and ee was observed with 0.5 or 1 mol % catalyst. Different molecular sieves were tested. Replacing 4 Å MS with either 3 Å MS or 5 Å MS led to the decrease of ee (entries 6 and 7, Table 2). Further examinations on the solvents showed that dichloromethane/benzene (1/1) was the best solvent combo in this reaction (entries 8−10, Table 2).

Under optimized reaction conditions, a wide array of nitroolefins **3** and pyrroles **2** were investigated in the asymmetric Friedel−Crafts alkylation reaction. The results are summarized in Table 3.

Several substituted nitroolefins **3b**−**e**, containing electron-donating groups, have been tested in the reaction with pyrrole **2a**. In all cases, excellent yields and ee values were obtained for the desired alkylation products (87−93% yield, 81−94% ee, entries 2−5, Table 3). The reaction also proceeded well with substituted nitroolefins **3f**−**i**, containing an electron-withdrawing group, affording their corresponding alkylation products in 90−92% yield with 90−92% ee (entries 6−9, Table 3). 2-Naphthyl- and heteroaryl-substituted nitroolefins **3j**−**l** were well tolerated under the optimized reaction conditions (89−91% yield, 89−93% ee, entries 10−12, Table 3). Unfortunately, the reaction gave low enantioselectivity for

(12) For recent examples, see: (a) Chen, X.-H.; Zhang, W.-Q.; Gong, L.-Z. *J. Am. Chem. Soc.* **2008**, *130*, 5652. (b) Wang, X.-W.; Reisinger, C. M.; List, B. *J. Am. Chem. Soc.* **2008**, *130*, 6070. (c) Hu, W.; Xu, X.; Zhou, J.; Liu, W.-J.; Huang, H.; Hu, J.; Yang, L.; Gong, L.-Z. *J. Am. Chem. Soc.* **2008**, *130*, 7782. (d) Li, G.; Fronczek, F. R.; Antilla, J. C. *J. Am. Chem. Soc.* **2008**, *130*, 12216. (e) Cheng, X.; Vellalath, S.; Goddard, R.; List, B. *J. Am. Chem. Soc.* **2008**, *130*, 15786. (f) Guo, Q.-S.; Du, D.-M.; Xu, J.-X. *Angew. Chem., Int. Ed.* **2008**, *47*, 759. (g) Wang, X.-W.; List, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 1119. (h) Jiang, J.; Yu, J.; Sun, X.-X.; Rao, Q.-Q.; Gong, L.-Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 2458. (i) Xu, S.; Wang, Z.; Zhang, X.; Zhang, X.; Ding, K. *Angew. Chem., Int. Ed.* **2008**, *47*, 2840. (j) Sickert, M.; Schneider, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3631. (k) Terada, M.; Soga, K.; Momiyama, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 4122. (l) Cheng, X.; Goddard, R.; Buth, G.; List, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 5079. (m) Rueping, M.; Antonchick, A. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 5836. (n) Rueping, M.; Antonchick, A. P.; Sugiono, E.; Grenader, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 908. (o) Schrader, W.; Handayani, P. P.; Zhou, J.; List, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 1463. (p) Terada, M.; Tanaka, H.; Sorimachi, K. *J. Am. Chem. Soc.* **2009**, *131*, 3430. (q) Lu, M.; Zhu, D.; Lu, Y.; Zeng, X.; Tan, B.; Xu, Z.; Zhong, G. *J. Am. Chem. Soc.* **2009**, *131*, 4562. (r) Liu, H.; Dagousset, G.; Masson, G.; Retailleau, P.; Zhu, J. *J. Am. Chem. Soc.* **2009**, *131*, 4598. (s) Terada, M.; Machioka, K.; Sorimachi, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 2553. (t) Terada, M.; Toda, Y. *J. Am. Chem. Soc.* **2009**, *131*, 6354.

TABLE 3. Enantioselective Friedel–Crafts Reaction of Pyrroles with Nitroolefins[a]



entry	2	3, R	time (h)	4, yield (%)	ee (%)[b]
1	**2a**	**3a**, C_6H_5	3	**4aa**, 93	88
2	**2a**	**3b**, 4-CH_3-C_6H_4	6	**4ab**, 93	87
3	**2a**	**3c**, 4-MeO-C_6H_4	6	**4ac**, 91	94
4	**2a**	**3d**, 3-CH_3-C_6H_4	6	**4ad**, 90	81
5	**2a**	**3e**, 3,4,5-MeO-C_6H_2	24	**4ae**, 87	92
6	**2a**	**3f**, 4-Br-C_6H_4	6	**4af**, 91	91
7	**2a**	**3g**, 4-Cl-C_6H_4	6	**4ag**, 90	92
8	**2a**	**3h,** 4-F-C_6H_4	5	**4ah**, 92	92
9	**2a**	**3i,** 4-CF_3-C_6H_4	5	**4ai,** 92	90
10	**2a**	**3j,** 2-furyl	5	**4aj**, 90	92
11	**2a**	**3k,** 2-thienyl	5	**4ak,** 91	93
12	**2a**	**3l,** 2-naphthyl	6	**4al,** 89	89
13	**2a**	**3m**, 2-Br-C_6H_4	12	**4am**, 81	11
14	**2a**	**3n**, cyclohexyl	24	< 5%	
15	**2b**	**3j**, 2-furyl	6	**4bj**, 94	93
16	**2c**	**3a**, C_6H_5	2	**4ca**, 91	86

[a]Reaction conditions: 3 equiv of **2**, 5 mol % of (*S*)-**1k**, rt, 0.25 mol/L of **3** in CH_2Cl_2/benzene. [b]Determined by chiral HPLC analysis.

2-Br-phenyl substituted nitroolefin **3m** and very low conversion for cyclohexyl-substituted nitroolefin **3n** (entries 13 and 14, Table 3). Substituted pyrroles were also tested. The pyrroles bearing either an alkyl or aryl substituent at the 2-position were well tolerated (entries 15 and 16, Table 3). As seen from above, the current methodology is suitable for a wide range of substrates for both pyrroles and aryl-substituted nitroolefins. With this protocol, highly enantioenriched 2-substituted or 2,5-disubstituted pyrroles could be easily obtained.

The absolute stereochemistry of the products was determined by comparison of the optical rotations with those reported by Du and co-workers.[9b] The absolute configuration of the products was determined to be *R*.

As shown in Figure 1, a similar working model to that previously reported is proposed.[10d] Chiral phosphoric acid acts as a bifunctional catalyst, and the acidic proton and phosphoryl oxygen of the catalyst form the hydrogen bond with nitroolefin and pyrrole nitrogen proton, respectively. This proposed working model can be partially supported by the fact that the NH of pyrrole is critical for the reaction. When the *N*-methylpyrrole was used under the optimal reaction conditions, a significant decrease of reaction rate and ee was observed compared to pyrrole itself (eq eq 1).

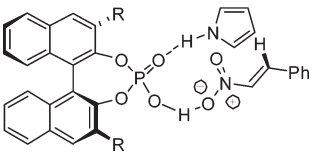
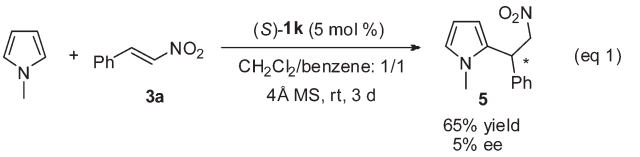


FIGURE 1. Proposed catalyst working model.



In conclusion, we have developed the enantioselective Friedel–Crafts alkylation reaction of pyrroles with nitroolefins by utilizing chiral phosphoric acid as an efficient catalyst. This metal-free process, together with mild reaction conditions and excellent yields and enantioselectivities, provides a practical method to synthesize highly enantioenriched 2-substitued and 2,5-disubstituted pyrroles.

Experimental Section

General Procedure for the Catalytic Asymmetric Friedel–Crafts Reaction. In a dry Schlenk tube, pyrrole **2** (0.9 mmol), chiral phosphoric acid (*S*)-**1k** (11 mg, 0.015 mmol), 4 Å molecular sieves (powder, activated, 50 mg), and CH_2Cl_2/benzene (0.6 mL, 1:1) were added under argon. The reaction mixture was stirred at room temperature, and then a solution of nitroolefin **3** (0.3 mmol) in CH_2Cl_2/benzene (0.6 mL, 1:1) was added by syringe pump over 2 h. When the reaction was complete, the reaction mixture was concentrated, and the residue was purified by flash chromatography (dichloromethane /petroleum ether = 1/10 to 1/1) to afford the product. **4aa** was obtained as a brown crystal (60 mg, 93% yield, 88% ee) following silica gel chromatography (dichloromethane/petroleum ether = 1/4, v/v). Analytical data for **4aa**: $[\alpha]^{20}_D$ +61.7 (*c* 0.48, MeOH). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.74–4.99 (m, 3H), 6.07 (s, 1H), 6.15 (s, 1H), 6.66 (s, 1H), 7.20–7.37 (m, 5H), 7.85 (br s, 1H). The enantiomeric ratio was determined by Daicel Chiralcel OD-H (25 cm), hexanes/IPA = 80/20, 1.0 mL·min^{-1}, λ = 254 nm, *t*(major) = 13.3 min, *t*(minor) = 15.9 min.

Acknowledgment. We thank the National Natural Science Foundation of China (20732006, 20821002), the National Basic Research Program of China (973 Program 2009CB825300), and the Science and Technology Commission of Shanghai Municipality (07pj14106, 07JC14063) for generous financial support. We thank Professor Christian A. Sandoval (SIOC) for help with the manuscript preparation.

Supporting Information Available: Experimental procedures and analysis data for **4**. This material is available free of charge via the Internet at http://pubs.acs.org.