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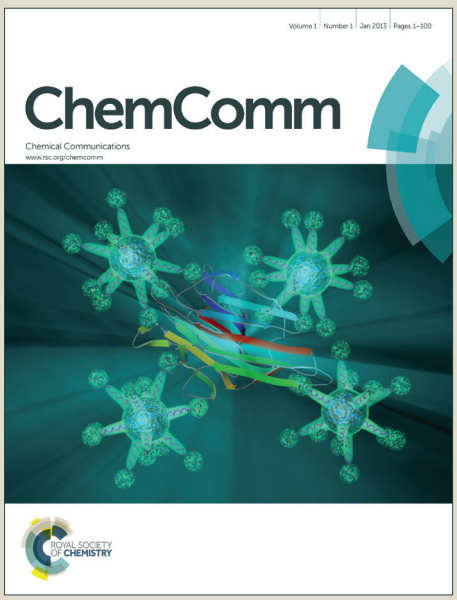

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H_8-BINOL Chiral Imidodiphosphoric Acids Catalyzed Highly Enantioselective Aza-Friedel–Crafts Reactions of Pyrroles and Enamides/Imines

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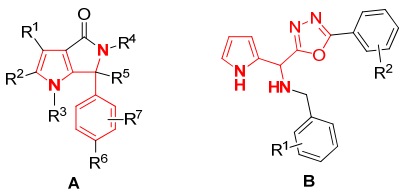
Kun Wu, Ming-Hua Zhuo, Di Sha, Yan-Sen Fan, Dong An, Yi-Jun Jiang* and Suoqi Zhang* [a]

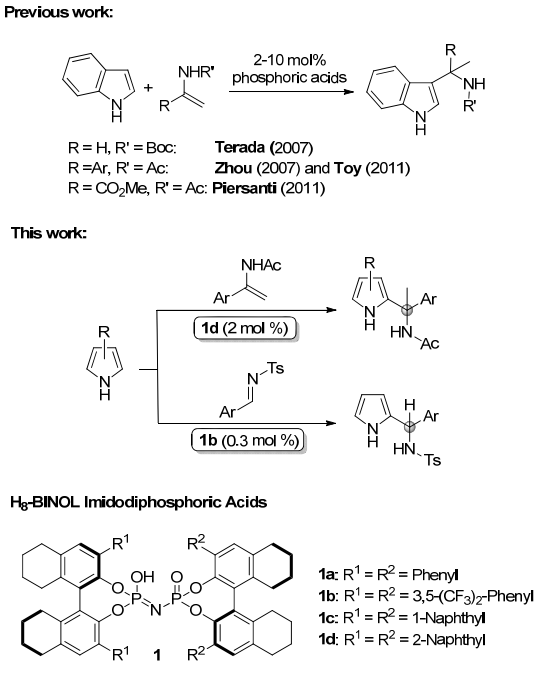
The first enantioselective aza-Friedel–Crafts reaction between pyrroles and enamides has been achieved by using novel H_8-BINOL type imidodiphosphoric acid catalyst. This methodology was also applied to the highly enantioselective aza-Friedel–Crafts reaction between pyrroles and imines. The catalyst loadings in these two reactions are low (0.3 -2 mol %). Both of these two processes are amenable to gram scales.

Aryl-(2-pyrrolyl)methanamine scaffold, which bears a stereocenter at the benzylic carbon, has been an attractive synthetic target because it is a privileged core structural motif in many pharmaceutically relevant compounds (Scheme 1).[1] The most direct way to achieve aryl-(2-pyrrolyl)methanamine is by using the aza-Friedel–Crafts reaction.[2] During the past decade, significant progress was made on the organocatalytic enantioselective aza-Friedel–Crafts reactions.[3] However, in these examples, whereas indoles are widely used as nucleophiles, attempts on the utilization of pyrroles are limited.[4,5] This is because pyrroles have several competitive nucleophilic sites[6] and more difficult enantiofacial discrimination. Although a few elegent enantioselective aza-Friedel–Crafts reactions using functionalized pyrroles with more fixed reaction sites and larger sizes have been reported,[4] the highly chemo-, regio- and stereoselective aza-Friedel–Crafts reaction of unmodified pyrrole has still been a challenging goal.[5]



Scheme 1. Aryl-(2-pyrrolyl)methanamine scaffolds in pharmaceutically compounds.

Enamides have become an increasingly exploited class of valuable intermediates in a wide range of nitrogen-containing synthetic targets.[7] However, the majority of catalytic enantioselective



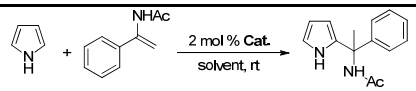
Scheme 2. Chiral imidodiphosphoric acids catalyzed high enantioselective aza-Friedel–Crafts reactions.

approaches of enamides have focused on their nucleophilicity. Although it is known that enamides can also be considered masked imines and be converted to chiral iminium ion electrophile in the presence of chiral Brønsted acids,[8] there are only a few corresponding reports so far.[9] Most of them were enantioselective aza-Friedel–Crafts reactions between enamides and indoles (Scheme 2).[9a,9b,9d,9e] To the best of our knowledge, the enantioselective aza-Friedel–Crafts reaction between enamides and pyrroles has not been reported. Here we report the first example of such a process, in which α–aryl substituted enamides are used and chiral quaternary carbon centered aryl-(2-pyrrolyl)methanamines are synthesized. To date, reports on the enantioselective aza-Friedel–Crafts reactions th

could fabricate the chiral quaternary carbon centered pyrroles are rare.[4b,5d] In addition to the enantioselective aza-Friedel–Crafts reactions of pyrroles and enamides, the corresponding reaction with imines will also be described.[4a,5a-c]

Chiral imidodiphosphoric acid catalyst have firstly been reported by List and co-workers in 2012.[10] We have developed several types of chiral imidodiphosphoric acids from 2012 and applied them to a range of enantioselective aza-Friedel–Crafts reactions of pyrroles/indoles successfully.[11] In particular, the H_8-BINOL type chiral imidodiphosphoric acid catalysts we developed very recently (Scheme 2) is believed to have more rigid and stereoselective chiral environment due to the slightly larger dihedral angle of H_8-BINOL scaffold compared with the BINOL scaffold in previous imidodiphosphoric acid catalysts.[10,11a-d]

Table 1 Optimization of the reaction conditions for the enantioselective aza-Friedel–Crafts reaction of pyrrole and enamide[a]



2a **3a** **4a**

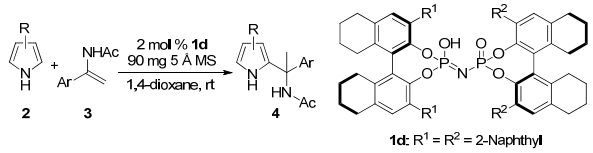
Entry	Cat.	Solvent	Molecular Sieves	Time [h]	Yield [%][b]	*ee* [%][c]
1	**1a**	toluene	none	1	58	85
2	**1b**	toluene	none	1	20	72
3	**1c**	toluene	none	1	60	87
4	**1d**	toluene	none	1	65	93
5	**1d**	1,4-dioxane	none	1	64	96
6	**1d**	1,4-dioxane	45 mg 5 Å	2	76	96
7	**1d**	1,4-dioxane	90 mg 5 Å	2	90	96

[a] Reaction conditions: **3a** (0.1 mmol), **2a** (0.11 mmol), solvent (1 mL). [b] Isolated yield. [c] Determined by HPLC analysis on Chiralpak AS-H column.

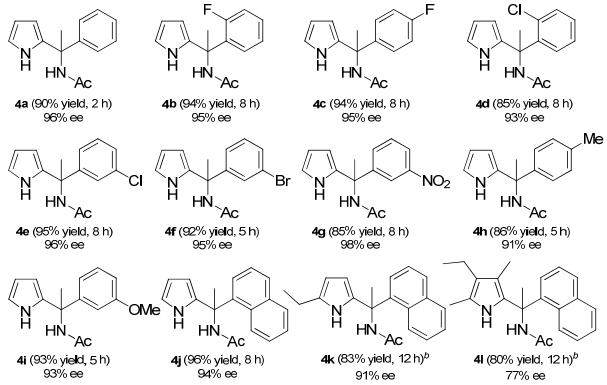
With the goal of applying the novel H_8-BINOL type chiral imidodiphosphoric acid catalysts **1** to the aza-Friedel–Crafts reactions between pyrroles and enamides, we initiated our studies by using α–phenyl substituted enamide **3a** as a model substrate. Initially, a catalyst screen was conducted utilizing 2 mol % imidodiphosphoric acid catalysts **1a-d** in toluene at room temperature. Fortunately, this catalytic system was effective and selective to produce the quaternary carbon centered product **4a** with moderate to good enantioselectivities generally.[5d] Among the catalysts **1a-d**, 2-naphthyl substituted H_8-BINOL catalyst **1d** was more stereoselective and provided the product **4a** with high enantioselectivity (Table 1, entry 4). Catalyst **1b** only gave poor yield and moderate ee value (Table 1, entry 2). This might be because the 3,5-$(CF_3)_2$-phenyl substitutions in catalyst **1b** were overcrowded for the formation of the sterically hindered quaternary chiral carbon center in product **4a**. In addition, 2-naphthyl substituted BINOL type imidodiphosphoric acid and 2-naphthyl substituted H_8-BINOL type phosphoric acid were also tested and found to be less stereoselective compare with H_8-BINOL catalyst **1d** (See Supporting Information). An improvement to 96% ee was observed when the solvent was changed from toluene to 1,4-dioxane (Table 1, entry 5). However, the chemoselectivity was still low. To our delight, the yield was increased dramatically by adding 45 mg of 5 Å molecular sieves (Table 1, entry 6). Increasing the amount of molecular sieves further improved the yield of **4a** and resulted the best conditions in Table 1 (Table 1, entry 7).

With the optimized conditions in hand (Table 1, entry 7), we investigated the range of the substrates. α–Phenyl substituted enamides **3** with electron-withdrawing or -donating groups at the ortho, meta and para position of the phenyl rings gave rise to the quaternary carbon centered products **4a-i** in high yields with excellent enantioselectivities (Table 2, 85−96% yield, 91−98% ee). The aza-Friedel–Crafts reaction of 1-naphthyl enamide **3j** and pyrrole **2a** also give the corresponding product **4j** with excellent yield and ee (Table 2, 96% yield, 94% ee). Variation of the pyrrole substituents was also tested in toluene (Table 2, **4k** and **4l**). 2-Ethyl pyrrole **2b** was employed and reacted smoothly with 1-naphthyl enamide **3j** to give the product **4k** with high yield and excellent ee (Table 2, 83% yield, 91% ee). When multi-substituted pyrrole **2c** was selected as the substrate, the corresponding product **4l** was obtained with high yield and good ee value (Table 2, 80% yield, 77% ee). It is noteworthy that although the process of producing the quaternary carbon center in product **4** is crowded, the ortho-substituted enamides are still well tolerated and afforded the corresponding products with high efficiency and selectivity (Table 2, **4b**, **4d**, **4j** and **4k**). However, in Zhou's report of the aza-Friedel–Crafts reaction of indoles and enamides, both the reactivity and enantioselectivity of the products were strongly diminished when ortho-substituted enamides were used.[9b]

Table 2 Enantioselective aza-Friedel–Crafts reaction of pyrroles and enamides[a]



2 **3** **4**

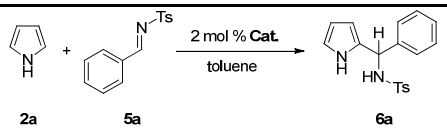


[a] Reaction conditions: **3** (0.1 mmol), **2** (0.11 mmol), **1d** (2 mol %), 5 Å M.S. (90 mg), 1,4-dioxane (1 mL), RT. Isolated yield. The ee value was determined by HPLC analysis on Chiralpak AS-H column. [b] Reactions were run in toluene.

Encouraged by the successful enantioselective aza-Friedel– Crafts reaction of unmodified pyrrole and enamides, we next turned our attention to imines. To date, there are only a few related reports.[5a] In addition, the chemo-, stereoselectivity and substrate scope of imines in these reports are still limited and high catalyst loadings were always required (5-10 mol %). Thus, the highly efficient chemo- and enantioseletive aza-Friedel–Crafts reactions between pyrroles and imines are still in great demand. We initiated our studies by using imine **5a** as a model substrate and the reaction conditions were reoptimized (Table 3). To our delight, H_8-BINOL type imidodiphosphoric acid catalyst **1** were still found to be effective for the aza-Friedel–Crafts reaction of pyrrole and imine. C

this occasion, 3,5-$(CF_3)_2$-phenyl substituted H_8-BINOL catalyst **1b** afforded the mono-alkylated product **6a**[12] more chemo- and stereoselective at -20°C (Table 3, entry 2) while catalyst **1d** only gave moderate yield and ee value (Table 3, entry 4). The use of 3,5-$(CF_3)_2$-phenyl-substituted BINOL type imidodiphosphoric acid and 3,5-$(CF_3)_2$-phenyl-substituted BINOL type phosphoric acid led to apparent decreases of stereochemical induction (See Supporting Information). Lowering the reaction temperature to −60°C improved the yield and ee value significantly (Table 3, entry 5). Gratifyingly, excellent enantioselectivity was achieved when only a small amount of 5Å molecular sieves were added to this reaction (5mg, Table 3, entry 6). In addition, the molecular sieves accelerate the reaction rate dramatically and the reaction time was reduced from 24 hours to 3 hours (Table 3, entries 5 and 6). It might

Table 3 Optimization of the reaction conditions for the enantioselective aza-Friedel–Crafts reaction of pyrrole and imine[a]



2a 5a 6a

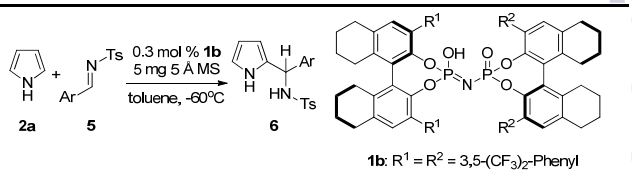
Entry	Cat. (mol %)	Temp	Molecular Sieves	Time [h]	Yield [%][b]	*ee* [%][c]
1	**1a**(2)	-20 °C	none	32	58	57
2	**1b**(2)	-20 °C	none	11	82	82
3	**1c**(2)	-20 °C	none	20	45	81
4	**1d**(2)	-20 °C	none	17	60	57
5	**1b**(2)	-60 °C	none	24	90	93
6	**1b**(2)	-60 °C	5 mg 5 Å	3	90	98
7	**1b**(0.3)	-60 °C	5 mg 5 Å	9	92	98
8	**1b**(0.3)	-60 °C	5 mg 5 Å	9	92	99[d]

[a] Reaction conditions: **5a** (0.1 mmol), **2a** (0.11 mmol), solvent (1 mL). [b] Isolated yield. [c] Determined by HPLC analysis on Chiralpak AD-H column. [d] The volume of the solvent was 0.3 mL.

be because the molecular sieves could act as a weak base,[13] which can accelerate the deprotonation of the hydrogen on 2-position of pyrrole **2a** (the hydrogen on 1-position of pyrrole is captured by the Brønsted basic site[10a] of the chiral imidodiphosphoric acid catalyst) and promote the 2-position addition of pyrrole to imine **5a**. It was exciting to note that the catalyst loading of **1b** could be reduced to 0.3 mol % and did not affect the catalytic profile or stereochemical outcome (Table 3, entry 7). Finally, the enantioselectivity was improved to 99% ee when the volume of toluene reduced from 1mL to 0.3 mL (Table 1, entry 8).

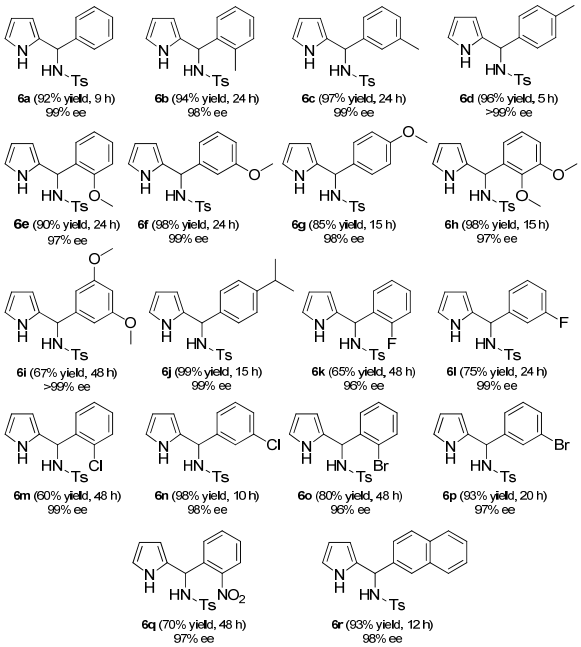
The scope of the aza-Friedel–Crafts reaction was explored under the optimized reaction conditions (Table 3, entry 8). Imines **5** bearing electron-donating and electron-withdrawing groups on the phenyl ring could all gave excellent ee values and good to excellent yields for the products **6a-q** under only 0.3 mol% of catalyst loading (60−99% yield, 96−>99% ee). Aryl imines derived from 2-naphthalenecarbaldehyde were also examined and the reaction proceeded smoothly to afford the product **6r** with excellent enantioselectivity and yield (93% yield, 98% ee). Notably, ortho-substituted substrates were still well tolerated in this system and excellent enantioselectivities were achieved for all the corresponding products (96-98% ee, Table 4, compounds **6b**, **6e**, **6h**, **6k**, **6m**, **6o** and **6q**). For the systems in previous report,[5a-c] however, only one ortho-substituted aldimine substrate was tested by Antilla and lower ee value (88%) were obtained for the product.[5a] More importantly, the catalyst loading (0.3 mol %) in our system is much lower than the reported processes (5-10 mol %).[5a-c]

Table 4 Enantioselective aza-Friedel–Crafts reaction of pyrrole and imines[a]



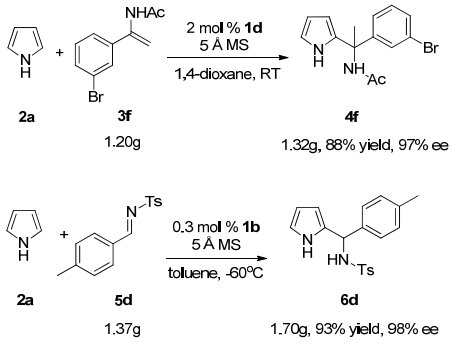
2a 5 6

1b: $R^1 = R^2 = 3,5\text{-}(CF_3)_2\text{-Phenyl}$



[a] Reaction conditions: **5** (0.1 mmol), **2a** (0.11 mmol), **1b** (0.3 mol %), toluene(0.3 mL), 5 Å M.S. (5 mg), -60 °C. Isolated yield. The ee value was determined by HPLC analysis on Chiralpak AD-H or OD-H column.

To further demonstrate the practicality and efficiency of our highly enantioselective aza-Friedel–Crafts reaction in the scale-up synthesis of aryl-(2-pyrrolyl)methanamine scaffolds, two gramscale reactions were performed under the standard conditions (Table 1, entry 7 and Table 3, entry 8). To our delight, when 1.20g enamide **3f** was applied to the aza-Friedel–Crafts reaction, increased



2a 3f 4f
1.20g 1.32g, 88% yield, 97% ee
2a 5d 6d
1.37g 1.70g, 93% yield, 98% ee

Scheme 3. Gram-scale reactions

enantioselectivity was observed from 95% ee to 97% ee for the product **4f** in spite of the slightly decreased yield. When imine 1.37g **5d** was used as the substrate, 1.70g product **6d** could be obtained with slightly decreased chemo- and enantioselectivity.

In conclusion, we have developed the first enantioselective aza-Friedel–Crafts reaction of pyrroles and enamides by using novel H_8-BINOL-type chiral imidodiphosphoric acids. In addition, we applied this efficient catalytic system to the highly chemo-, regio- and enantioselective aza-Friedel–Crafts reaction of pyrrole and imines. During these two processes, a range of enantioenriched quaternary or tertiary carbon centered aryl-(2-pyrrolyl)methanamine scaffolds were synthesized in high yields (up to 99%) with excellent enantioselectivities (up to >99%) with low catalyst loadings (as low as 0.3 mol %) unprecedentedly. In addition, both of these two process could be extended to the gramscale reactions, which suggested their great potential for providing opportunities for further study on enantiopure bioactive aryl-(2-pyrrolyl)methanamine scaffold containing molecules in the future.

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Notes and references

College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012 (P.R. China).

E-mail: jiangyijun@jlu.edu.cn, suoqin@jlu.edu.cn

† Electronic Supplementary Information (ESI) available: Experimental procedures and characterization data for all new compounds. See DOI: 10.1039/c000000x/

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