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Highly Atroposelective Synthesis of Arylpyrroles by Catalytic Asymmetric Paal–Knorr Reaction

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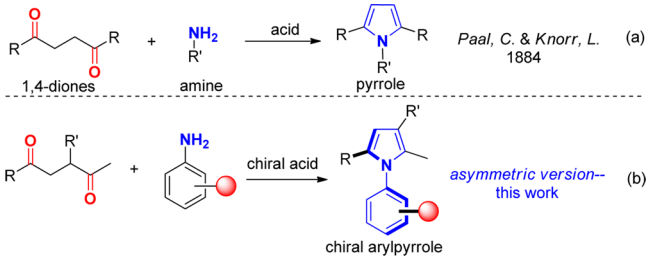
Supporting Information

ABSTRACT: A general and efficient method for accessing enantiomerically pure arylpyrroles by utilizing the catalytic asymmetric Paal-Knorr reaction has been developed for the first time. A wide range of axially chiral arylpyrroles were obtained in high yields with good to excellent enantioselectivities. The key to success is the use of the combined-acid catalytic system involving a Lewis acid and a chiral phosphoric acid for achieving effective enantiocontrol. Noteworthy is that an unexpected solvent-dependent inversion of the enantioselectivity was observed in the above-mentioned asymmetric reaction.

As one of the most prominent classes of heterocyclic compounds, pyrroles are key structural motifs in biologically active compounds and useful building blocks in the synthesis of natural products, as well as in material sciences.[1,2] Accordingly, their synthesis has always been among the most important research areas in synthetic chemistry and numerous methods have been widely developed.[2] One of the most common approaches for the construction of pyrroles is the Paal–Knorr reaction in which 1,4-diketones are converted into pyrroles from the reaction with primary amine or ammonia by acid-mediated dehydrative cyclization.[3] Remarkably, this reaction was first reported in 1884 (Scheme 1a); however, catalytic asymmetric

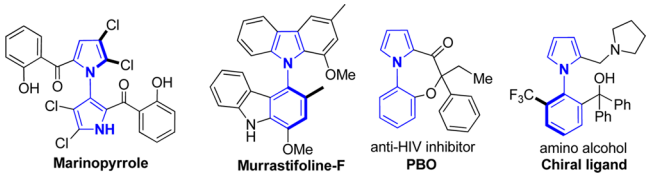
Scheme 1. Paal–Knorr Reaction for Pyrrole Synthesis



Paal–Knorr pyrrole synthesis still remained elusive to date. One of the easily missing reasons is the absence of intrinsic chirality at the pyrrole, revealing no obvious handle for asymmetric induction. We questioned whether the formation of chiral pyrroles in the course of the reaction would be feasible. Here we report an acid-catalyzed asymmetric Paal–Knorr reaction for atroposelective synthesis of axially chiral arylpyrroles (Scheme 1b).

Axially chiral biaryl compounds are prevalent in biologically active compounds, natural products as well as materials, and also play a significant role in acting as chiral ligands or organocatalysts.[4] Owing to the importance of this structural motif, the catalytic atroposelective construction of biaryl scaffolds has been intensively investigated and great progress has been accomplished in recent years.[4,5] In sharp contrast, the asymmetric synthesis of axially chiral arylpyrroles remains largely unexplored, although it exists in natural products (Marinopyrrole, Murrastifoline-F),[6] anti-HIV inhibitor (PBO)[7] and recently as chiral ligands[8] for asymmetric addition reactions (Scheme 2). However,

Scheme 2. Biologically Active Compounds and Ligand with Arylpyrrole Skeleton



the effective synthesis of optically pure arylpyrroles relies on conventional resolution,[9] which requires the stoichiometric amounts of chiral reagents. Therefore, the development of a catalytic asymmetric synthesis of axially chiral arylpyrroles is very challenging and highly appealing.

To address this issue, we envisioned that chiral phosphoric acids (CPA),[10] which have emerged as powerful organocatalysts for various reactions within the past 12 years, may be capable of facilitating this transformation enantioselectively by accelerating the intramolecular nucleophilic addition to form hemiaminal on the basis of previous mechanistic investigation on Paal–Knorr reaction. Motivated by the previous elegant work involving asymmetric Fischer indolization,[11] and as part of our ongoing interest in asymmetric construction of axially chiral compounds[12] and phosphoric acid catalysis,[13] we describe herein the results of the investigation, leading to the first phosphoric acid-catalyzed atroposelective synthesis of axially chiral arylpyrroles via asymmetric Paal–Knorr pyrrole synthesis.

To validate the feasibility of the hypothesis, we initially conducted the Paal–Knorr reaction of 1,4-dione **1a** with 2-(*tert*-butyl)aniline **2a** in CCl_4 at room temperature in the presence of

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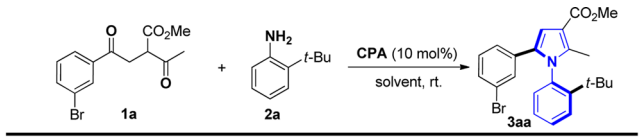
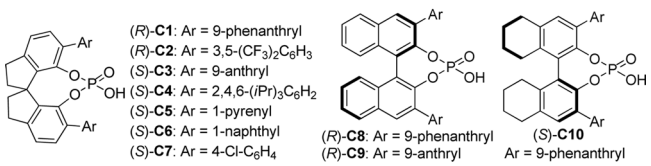
10 mol % of spinol-derived phosphoric acid[14] (*R*)-**C1** (Table 1, entry 1). Encouragingly, despite its high steric hindrance, the reaction proceeded smoothly to give the axially chiral arylpyrrole **3aa** in 94% yield with 68% ee. This proof-of-principle result obviously indicates that the control of axial chirality of arylpyrroles by using the chiral phosphoric acid-catalyzed asymmetric Paal–Knorr pyrrole synthesis was feasible. Having thus proven the efficiency of the chiral phosphoric acid in the current system, we next turned our attention to investigate the substituent effects and the axially chiral backbone on the catalysts (Table 1, entries 2–10). As shown in Table 1, the electron property and steric bulk on the aromatic ring, as well as backbone have very strong influences on enantioselectivity. We were glad to find catalyst (*S*)-**C3** gave the best result in terms of the enantioselectivity (72% ee) (Table 1, entry 3). The remarkable solvent effects were observed in this transformation (Table 1, entries 11–14 and Table S1 in Supporting Information (SI)). It is noteworthy that the absolute configuration of the obtained product was reversed by only changing the solvent from CCl_4 to methanol (entry 14). The enantioselectivity was also affected by the reaction temperature and reagents (Table 1, entries 15–16 and Table S1 in SI). Inspired by Yamamoto's combined-acid catalysis principle[15] and Luo's binary-acid catalysis,[16] in which the phosphoric acid could be activated by a Lewis acid to promote many challenging transformations, we imagined that the combined-acid system may prove a good opportunity to improve the enantioselectivity of the model reaction via synergistic interaction between the substrates and the catalysts. Therefore, we further optimized the reaction conditions by adding Lewis acids to the reaction system. To our delight, 10 mol % of $Fe(OTf)_3$ promoted the reactions very well and the enantioselectivity was improved to 88% ee (Table 1, entries 17–18 and Table S2 in SI). Finally, we identified the following protocol as optimal: When **1a** was treated with **2a** in the presence of catalyst (*S*)-**C3** (10 mol %) and $Fe(OTf)_3$ (10 mol %) in the mixture of CCl_4 (0.3 mL) and cyclohexane (1.2 mL) at 0 °C for 4 days, the axially chiral **3aa** was obtained in 95% isolated yield with 96% ee (Table 1, entry 18).

With the optimized conditions in hand, we next examined the substrate scope of various substituted 1,4-diketones. As shown in Table 2, different substituents and substitution patterns on the aromatic ring of the substrates (**1a–1m**) were all tolerated to give the corresponding products **3aa–3am** in 85–95% yields with 86–97% ee. Moreover, the substituted phenyl group could be replaced with naphthyl (**1n**) or heteroaryl (**1o**) group without obviously affecting the reaction results (**3an** and **3ao**). Encouraged by these results, we expanded the generality of the reaction with regard to variation of ester functional groups. The desired products (Table 2, **3ap–3as**) were formed with good axial chirality control and the transformation proceeded almost equally well with different groups, demonstrating the broad generality of this approach for the synthesis of axially chiral arylpyrrole derivatives.

To explore further the generality of this transformation, we then evaluated the use of various aromatic amines (**2a–2l**). Most reactions reached completion within 4 days and gave axially chiral arylpyrroles (Table 3, **3aa–3la**) in high yields (83–95%) with good enantioselectivities (85–98% ee). The electronic and position properties of the aromatic ring substituents did not have significant effects on the enantioselectivity of the asymmetric Paal–Knorr reactions. It is noteworthy to point out that the *ortho*

Table 1. Optimization of the Reaction Conditions[a]

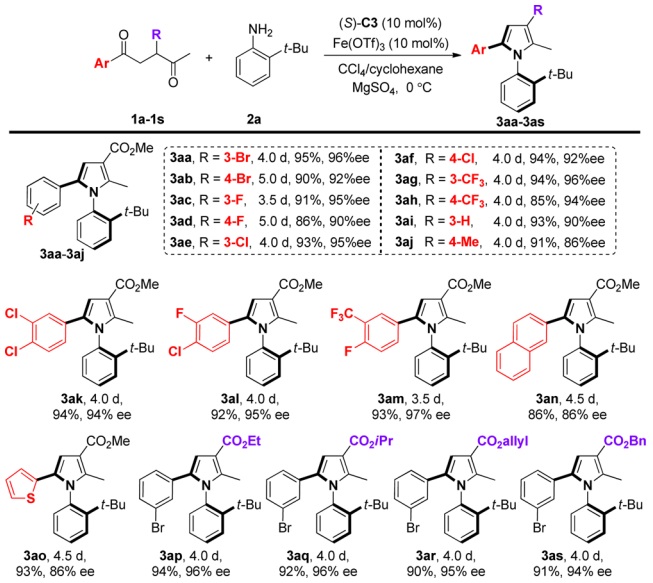




entry	catalyst	*T* (°C)	solvent	yield (%)[b]	ee (%)[c]
1	(*R*)-**C1**	rt	CCl_4	94	−68
2	(*R*)-**C2**	rt	CCl_4	90	−13
3	(*S*)-**C3**	rt	CCl_4	94	72
4	(*S*)-**C4**	rt	CCl_4	91	70
5	(*S*)-**C5**	rt	CCl_4	93	66
6	(*S*)-**C6**	rt	CCl_4	92	53
7	(*S*)-**C7**	rt	CCl_4	90	14
8	(*R*)-**C8**	rt	CCl_4	92	<5
9	(*R*)-**C9**	rt	CCl_4	91	6
10	(*S*)-**C10**	rt	CCl_4	92	−9
11	(*S*)-**C3**	rt	DCM	71	43
12	(*S*)-**C3**	rt	toluene	89	61
13	(*S*)-**C3**	rt	cyclohexane	92	61
14	(*S*)-**C3**	rt	MeOH	57	−52
15	(*S*)-**C3**	0	CCl_4	82	75
16[d]	(*S*)-**C3**	0	CCl_4	84	78
17[e]	(*S*)-**C3**	0	CCl_4	85	88
18[e]	(*S*)-**C3**	0	–[f]	95	96

[a]Unless otherwise stated, all reactions were carried out with **1a** (0.15 mmol), **2a** (0.1 mmol), **CPA** (0.01 mmol) in CCl_4 (1 mL) at rt or 0 °C. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]$MgSO_4$ (100 mg) was added. [e]$MgSO_4$ (100 mg) and $Fe(OTf)_3$ (10 mol %) were added. [f]CCl_4/cyclohexane (0.3 mL/1.2 mL) as solvents.

Table 2. Substrate Scope with Respect to 1,4-Diketones[a]



[a]All reactions were carried out with **1** (0.3 mmol), **2a** (0.2 mmol), $MgSO_4$ (200 mg), (*S*)-**C3** (0.02 mmol) and $Fe(OTf)_3$ (0.02 mmol) in CCl_4/cyclohexane (0.6 mL/2.4 mL) at 0 °C.

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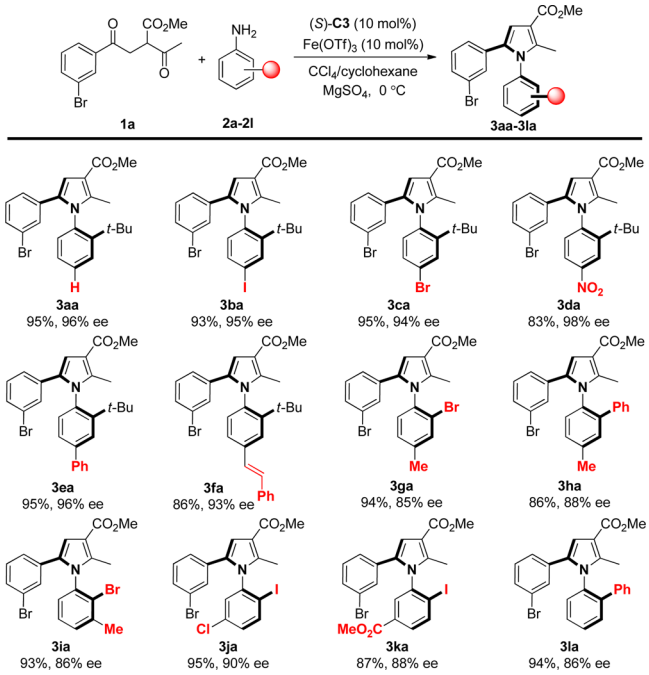
Table 3. Substrate Scope with Respect to Aromatic Amines[a]

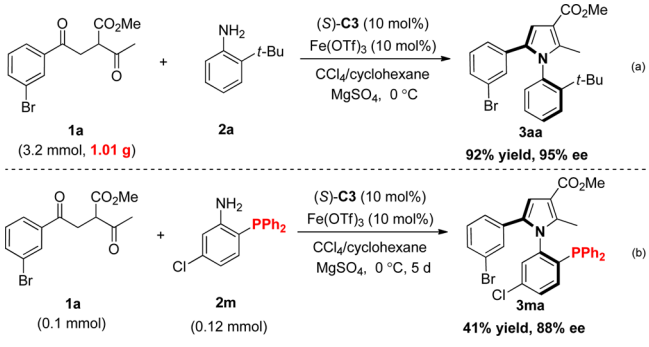


[a]Unless otherwise stated, reactions carried out with **1a** (0.15 mmol), **2** (0.1 mmol), $MgSO_4$ (100 mg), (*S*)-**C3** (0.01 mmol) and $Fe(OTf)_3$ (0.01 mmol) in CCl_4/cyclohexane (0.3 mL/1.2 mL) at 0 °C for 4 d.

group was not only restricted to *tert*-butyl group, and the bromo, iodo or phenyl group at this position could also be tolerant to give the expected products with good to excellent enantiocontrol (**3ga**–**3la**). The absolute configuration of **3fa** was determined as being (*aR*) by X-ray diffraction analysis (See SI) and those of other products were assigned by analogy.

To demonstrate the utility of this transformation, we carried out a preparative scale synthesis of product **3aa** (Scheme 3a). The

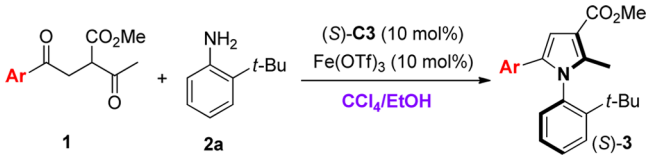
Scheme 3. Preparative Synthesis of 3aa and Synthesis of Axially Chiral Phosphine 3ma



reaction performed efficiently and there was almost no change in chemical yield (92%) and enantioselectivity (95% ee), thus suggesting that large-scale chemical production of axially chiral arylpyrroles may be possible. Motivated by the wide application of chiral monophosphorus ligand[17] and phosphine organocatalyst in asymmetric catalysis,[18] we has attempted to synthesize the axially chiral phosphine **3ma**. To our delight, the expected product was obtained with good enantioselectivity (88% ee), albeit with a relatively low yield (Scheme 3b).

Stimulated by the dramatic solvent effect as mentioned above, we expected to get the opposite enantiomer with the same configurational chiral catalyst by just changing the solvent system.[19] After further optimizing the reaction conditions (for details, see Table S3 in SI), we established the acceptable reaction condition for the generality investigation of the solvent-dependence in this reaction. As shown in Table 4, the solvent-

Table 4. Generality of the Solvent-Dependence[a,b,c]



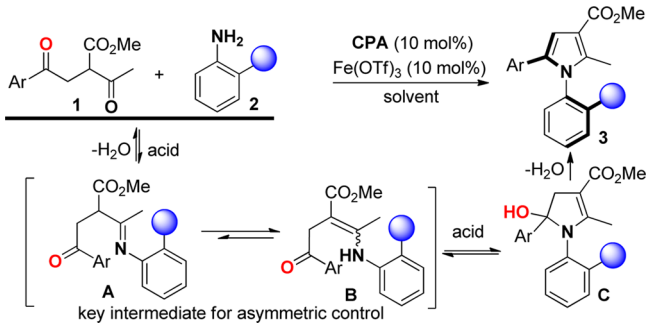
entry	Ar	(*S*)-3	yield[b] (%)	ee[c] (%)
1	3-Br-C_6H_4 (**1a**)	(*S*)-**3aa**	83	−75
2	3-F-C_6H_4 (**1c**)	(*S*)-**3ac**	82	−76
3	3-Cl-C_6H_4 (**1e**)	(*S*)-**3ae**	83	−76
4	4-Cl-C_6H_4 (**1f**)	(*S*)-**3af**	80	−73
5	2-naphthyl (**1n**)	(*S*)-**3an**	77	−73
6	2-thienyl (**1o**)	(*S*)-**3ao**	83	−74

[a]All reactions carried out with **1** (0.15 mmol), **2a** (0.1 mmol), (*S*)-**C3** (0.01 mmol) and $Fe(OTf)_3$ (0.01 mmol) in **CCl_4 /EtOH** (0.5 mL/1.5 mL) at rt. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

dependent inversion of the enantioselectivity took place in all reactions when treating several 1,4-diketones with 2-(*tert*-butyl) aniline **2a**, albeit with relatively low ee values. Further investigations are necessary to elucidate the solvent-dependent results.[19]

To gain further insight into the reaction mechanism, we performed extensive control experiments for trapping the intermediate. Fortunately, the key intermediate **B** could be isolated and the enamine structure was confirmed by the analysis of NMR and HRMS (For details to the corresponding discussion of the detailed mechanism, see SI). These observations suggested that the desired pyrrole formation might involve an enamine intermediate **B** followed by acid-catalyzed dehydrative cyclization, which is not completely in agreement with the widely accepted pathway[20] of the Paal–Knorr reaction (Scheme 4).

Scheme 4. Proposed Reaction Process



Additionally, we found that the ester group is essential for asymmetric induction (for details, see SI). As such, we proposed that combined catalysts play an important role in promoting the cyclization step and creating a suitable chiral environment for stereoinduction.[15,16]

In summary, we have developed a general and efficient method for accessing enantiomerically pure arylpyrroles by utilizing the

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first catalytic asymmetric Paal−Knorr reaction. A wide range of axially chiral arylpyrroles were obtained in high yields with good to excellent enantioselectivities. The combined-acid catalytic system involving a Lewis acid and a chiral phosphoric acid was the key point to improve the enantioselectivity. Interestingly, an unexpected solvent-dependent inversion of the enantioselectivity was observed. We anticipate that this strategy will be applied to natural product synthesis and the axially chiral arylpyrroles will have potential application in asymmetric catalysis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b09634.

Experimental procedures and characterizations (PDF)
Data for $C_{31}H_{30}BrNO_2$ (CIF)

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Notes

The authors declare no competing financial interest.

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