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ROYAL SOCIETY OF CHEMISTRY

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DOI: 10.1039/D0CC02380A

Journal Name

COMMUNICATION

Chiral Brønsted Acid-Catalyzed Dynamic Kinetic Resolution of Atropisomeric ortho-Formyl Naphthamides

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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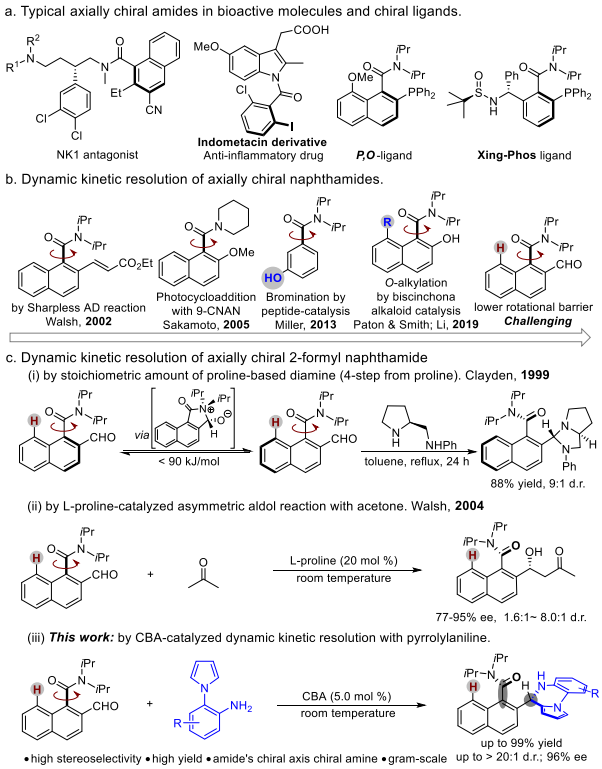
Despite the widespread use of naphthamide atropisomers in the biologically active compounds and asymmetric catalysis, few catalytic methods have succeeded in the enantioselective synthesis of these compounds. Herein, a chiral Brønsted acid (CBA) catalysis strategy was developed for readily scalable dynamic kinetic resolution of challenging ortho-formyl naphthamides with pyrrolylanilines. The atropisomeric amide's chiral axis and a stereogenic center were simultaneously established for a new family of potential biologically active pyrrolopyrazine compounds with high enantio- and diastereoselectivities (up to >20:1 d.r. and 98:2 e.r.). Epimerization experiments of its derivatives reveal that the N-substitution of nearby stereogenic center could affect the configurational stability of axially chiral aromatic amides. These results might be useful for the construction of other kinds of novel axially chiral molecules with a low rotational barrier.

Axially chiral aromatic amide is one of the most important scaffold in numerous in biologically active skeletons and asymmetric catalysis (Scheme 1, a).[1,2] Nevertheless, in a sharp contrast with the blossoming of axially chiral biaryls,[3,4] the catalytic enantioselective construction of these compounds is more challenging due to the lower barrier to amide atropisomerization and difficult structural modification. Compared with the elegant asymmetric cycloaddition to construct aromatic rings although that always suffers from unavoidable multistep synthetic dilemmas of starting materials,[5] directly and efficiently catalytic dynamic kinetic resolution (DKR) of atropisomeric amides might represent the cutting-edge technologies from the point of atom/step economy since a pair of racemic compounds could be converted into a single enantiomer in quantitative yield theoretically, although success in the case of direct DKR are very sparse (Scheme 1, b). In 2002, Walsh realized the first kinetic resolution of atropisomeric 2-vinyl-1-aryl amides in moderate results by Sharpless asymmetric dihydroxylation.[6] After that, Sakamoto reported a conglomerate crystallization process for DKR of (2-methoxynaphthalen-1-yl)(piperidin-1-yl)methanone by asymmetric photocycloaddition with 9-cyanoanthracene (9-CNAN).[7] Breakthrough came from Miller's group in 2013. They exploited an interesting peptide-based catalysis for effective



Scheme 1. Representative axially chiral amides and the dynamic kinetic resolution synthesis.

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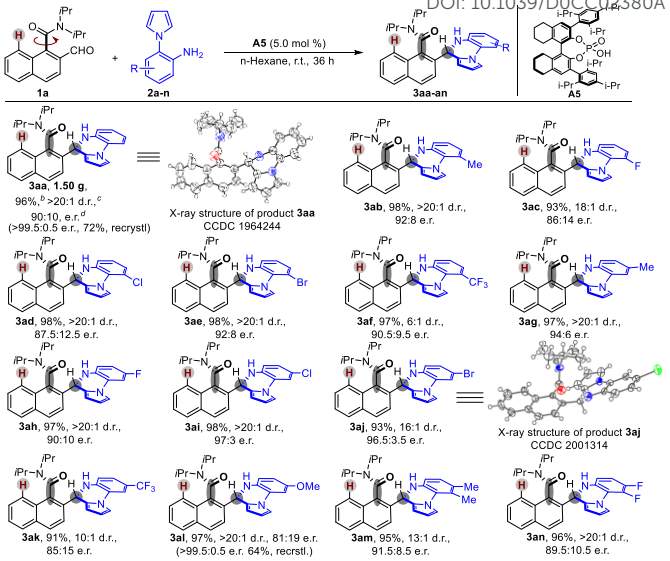
† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

atropisomer-selective tribromination of simple atropisomeric benzamides although the substrates have strong dependence of *meta*-phenolic hydroxyl group.[8a] Recently, Smith[9] and Li[10] groups developed independently an asymmetric DKR of amide naphthols by bulky biscinchona alkaloid-based catalysts via atroposelective *O*-benzylation and allylation. For the former reaction, the substituent at *peri*-position of the substrate was very essential.[9] Despite these impressive advances, the DKR of simple atropisomeric *ortho*-formyl naphthamides is still challenging due to its finite reaction modes and lower rotational barrier.[11] Compared with other naphthamide counterparts, its intrinsic trigonal CHO group might be unfavourable for barrier to rotation about the Aryl-CO bond.[11a] The interaction of the transient pyramidalised nitrogen's lone pair with π*(C=O) could decrease the barrier energy via a five-membered ring transition state.[11a] Two decades ago, Clayden and Lai achieved the first DKR of atropisomeric *ortho*-formyl naphthamides by using stoichiometric amount of four-step proline-based diamine (Scheme 1, c-(i)).[12a-b] The pioneering work on catalytic DKR of amide aldehyde with acetone was reported by Walsh group in the presence of L-proline, giving products ranged from 77% to 95% with the diastereoselectivities from 1.6:1 to 8.0:1 (Scheme 1, c-(ii)).[12c] Herein, we reported an efficient CBA strategy for its catalytic DKR with pyrrolylanilines in high enantio- and diastereoselectivities (up to >20:1 d.r. and 98:2 e.r.), which established a new reaction model to assemble potentially biological active molecules bearing chiral axis, stereogenic center and heterocycle (Scheme 1, c-(iii)).

Nitrogen-containing heterocycles like pyrrole and indole are ubiquitous and privileged motifs in myriad of natural products and pharmaceuticals.[13] By considering the formation of new potential bioactive molecules containing axially chiral aromatic amide and another microstructure of centers and heterocyclic rings, the catalytic DKR of naphthamides with a reactive heterocycle should be an efficient and practical methodology through only one step. As contrasted with indole, the nucleophilicity of inert N-substituted pyrrole is much weaker leading to its immanent low reactivity and the huge difficulties to control the stereoselectivity. In our recent efforts, (1H-pyrrol-1-yl)anilines have been proved efficient and successful for asymmetric cascade cyclization reaction by CBA catalysis.[14] Such compounds possess two reaction sites, similar to the (S)-N-(pyrrolidin-2-ylmethyl)aniline,[12] but it is more rigid. We anticipate that the kind of substrates should be more favourable control of enantio- and diastereoselectivities for catalytic DKR of challenging *ortho*-formyl naphthamides.

After careful optimization of the reaction conditions (for details, see ESI), the reaction between amide naphthaldehyde **1a** (0.1 mmol) and 2-(1H-pyrrol-1-yl)aniline **2a** (0.15 mmol) with a 5.0 mol % of CBA catalyst **A5** at room temperature in n-hexane provided the desired product 3aa in 98% yield with >20:1 d.r. and 93:7 e.r. Upon the result, we first amplified the reaction up to gram-scale to evaluate the practicability of the catalytic DKR process. Gratifyingly, 1.50 g of **3aa** was smoothly isolated in 96% yield with >20:1 diastereoselectivity and 90:10 e.r. (Scheme 2). The enantioselectivity could be increased up to >99.5:0.5 after once recrystallization. The structure of **3aa** was determined by X-ray crystal analysis. And according to the X-ray single crystal structure of **3aj**, its absolute configuration was assigned as *aS,S*.

Scheme 2. Substrate Scope of 2-(1H-pyrrol-1-yl)aniline.[a]



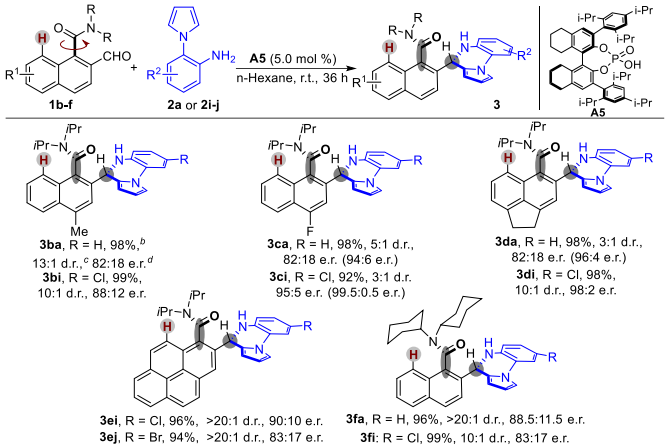
Unless indicated otherwise, the reaction was carried out on 0.1 mmol under the reaction conditions of entry 16 in Table 1. [a] Amide naphthaldehyde **1a** (0.1 mmol), 2-(1H-pyrrol-1-yl)aniline **2** (0.15 mmol, 1.5 equiv.) and chiral acid catalyst **A5** (5.0 mol %) were stirred in n-hexane (1.0 mL, 0.1 M) at room temperature under N_2 for 36 h. [b] Yield of isolated product. [c] d.r. value was determined by ^{1}H NMR spectroscopy. [d] ee value was determined by chiral HPLC analysis.

The investigation of 2-(1H-pyrrol-1-yl)aniline scope reveals that the approach proceeded readily to deliver the corresponding compounds **3ab**-**an** in good outcomes no matter with electron-deficient or electron-rich groups on the aromatic rings (Scheme 2). Substituents at the 2-position of the aryl rings near with the pyrrole were well compatible with current reaction conditions to furnish the desired products **3ab**-**3af** in high enantioselectivities and diastereoselectivities ranging from 6:1 to >20:1 d.r. Substrates with a substituent at the 3-position were also tolerated to produce adducts **3ag**-**ak** with excellent results in terms of both conversion and chirality control. Fortunately, the e.r. value of the methoxyl substituted 2-(1H-pyrrol-1-yl)aniline **2l** could be increased to more than 99.5:0.5 via a simple recrystallization although original enantioselectivity of the product **3an** is moderate. Then, multi-substituted reactants **2m**-**n** were employed into this reaction system and resulted in products **3am**-**an** in good results, respectively.

We then investigated the scope of amide naphthaldehydes **1** with 2-(1H-pyrrol-1-yl)anilines **2a** and **2i**-**j**. As demonstrated in Scheme 3, axially chiral products **3ba** and **3bi** were easily synthesized with high enantiomeric excess and excellent diastereoselectivities from 4-Me substituted naphthaldehyde **1b**. High yields and acceptable e.r. values were detected for **3ca** and **3ci** from naphthamide **1c** having a fluorine atom at the4-position, respectively. Delightedly, dihydroacenaphthylene (**1d**) and pyrene aldehydes (**1e**) were also amenable to the reaction conditions, providing **3da**, **3di**, **3ei** and **3ej** in 94-98% yields with good enantio- and diastereoselectivities. Finally, the dicyclohexylamide **1f** was subject to the reaction. The desired product **3fa** and **3fi** were generated readily with high yields and diastereoselectivities.

To highlight the synthetic potential of this asymmetric catalytic DKR strategy, further transformations of the axially

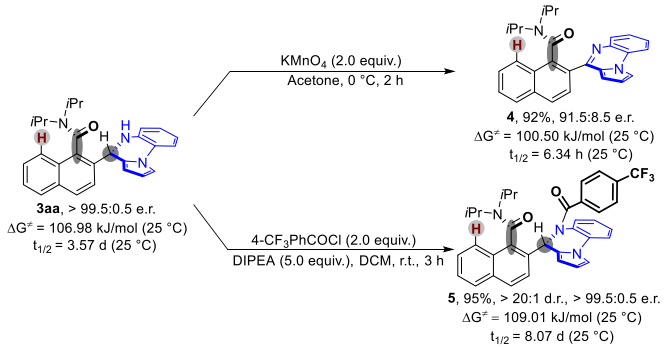
Scheme 3. Scope of the amide naphthaldehydes.[a]



[a] Amide naphthaldehyde **1** (0.1 mmol), 2-(1H-pyrrol-1-yl)aniline **2** (0.15 mmol, 1.5 equiv.) and chiral phosphoric acid catalyst **A5** (5.0 mol %) were stirred in n-hexane (1.0 mL, 0.1 M) at room temperature under N_2 for 36 h. [b] Yield of isolated product. [c] d.r. value was determined by ^{1}H NMR spectroscopy. [d] ee value was determined by chiral HPLC analysis.

chiral product were performed. As shown in Scheme 4, **3aa** was oxidized into the derivative **4** by $KMnO_4$ at 0 °C in acetone for 2 h with a slightly decreased e.r. value of 91.5:8.5. By acylation with 4-(trifluoromethyl)benzoyl chloride at the presence of N-ethyl-N-isopropylpropan-2-amine (DIPEA) at room temperature, adduct **5** was isolated in almost quantitative yield without any loss of chirality. In order to investigate the rotational stability of these novel compounds, racemization experiments by Eyring equation[15] were carried out. To the free rotation around the Ar-CO axially chiral bond, the higher shield effect of stereogenic tetrahedral Csp^3 amine

Scheme 4. Further transformation and epimerization investigation.[a]

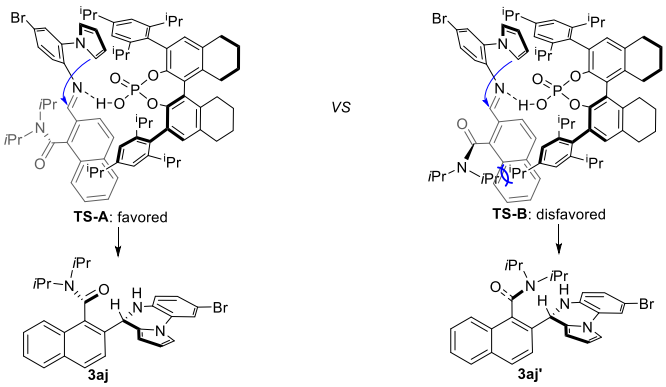


[a] About 1.0 mg of an enantioenriched sample was dissolved in 0.1 mL toluene and heated at a specified temperature. The change in enantiomeric excess over time was monitored by chiral HPLC. **3aa** at 50 °C, 4 at 30 °C, 5 at 60 °C. For details, please see the ESI.

in **3aa** than that of the planar Csp^2 imine in **4** was affirmed by an energy gap of about 6.5 kJ/mol, and the half-time dropped from 3.57 days to 6.34 hours. As expected, the configurational stability could be improved by increase the steric hindrance through installing a bulky substituent group at the nitrogen site. As a result, compound **5** has a longer half-time of 8 days than that of **3aa**. The free rotation of an axis would be prevented by a chiral center with large steric hindrance, which should be a useful principle to the asymmetric synthesis of novel axially chiral molecules with feeble rotational barriers.

Based on the previous reports,[14,16] above DKR transformation should undergo the imine formation with a sequential nucleophilic addition to the pyrrole unit in the presence of CBA. By using the imine intermediate as the starting material under the standard reaction conditions, **3aa** was obtained in 26.4:73.6 e.r., lower than that of one-pot reaction. The preliminary results imply that CPA catalyst might have chiral recognition for each step in the cascade reaction and the synergistic effect would benefit the final enantioselectivity (for the detail, please see the ESI). We postulated the catalytic transition state to reasonably explain the stereoselectivity (Scheme 5). Theoretically, the **TS-A** should be more favourable than the **TS-B** in which the larger steric impulsion is existed between the N-isopropyl groups and the catalyst skeleton. On the other hand, the addition of the pyrrole to the intermediate imine would take place from the anti-face of the isopropyl groups with lower steric hindrance, leading to the desired product **3aj** with the absolute configuration as *aS,S*.

Scheme 5. Postulated reaction models rationalizing the observed enantioselectivity



In conclusion, we developed the first readily scalable CBA-catalyzed enantioselective DKR between naphthamides and pyrrolylanilines with high enantio- and diastereoselectivities (up to >20:1 d.r. and 98:2 e.r.). This strategy can install easily and simultaneously an atropisomeric amide's chiral axis, a stereogenic center and nitrogen-containing heterocycle into a new family of valuable potential biologically active pyrrolopyrazine compounds. Importantly, obvious barrier effect of the chiral center with larger substituent was confirmed and might be benefit to prepare other new kinds of axially chiral compounds with lower rotational barrier. Examination of biological activities of this kind of molecules was ongoing in our lab.

Financial support from the National Natural Science Foundation of China (21602231), the Natural Science Foundation of Jiangsu Province (BK20191197, BK20181373) and Major Program of Natural Science Research of Jiangsu Higher Education Institutions of China (No. 18KJA150005) is gratefully acknowledged.

Conflicts of interest

There are no conflicts to declare.

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