Kinetic Resolution

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Highly Enantioselective Kinetic Resolution of Axially Chiral BINAM Derivatives Catalyzed by a Brønsted Acid**

Dao-Juan Cheng, Liang Yan, Shi-Kai Tian, Ming-Yue Wu, Lu-Xin Wang, Zi-Li Fan, Sheng-Cai Zheng, Xin-Yuan Liu,* and Bin Tan**

Abstract: *A highly efficient strategy for the kinetic resolution of axially chiral BINAM derivatives involving a chiral Brønsted acid-catalyzed imine formation and transfer hydrogenation cascade process was developed. The kinetic resolution provides a convenient route to chiral BINAM derivatives in high yields with excellent enantioselectivities.*

The axially chiral BINAP, BINOL, and their derivatives are among the most successful chiral ligands/catalysts in asymmetric catalysis, with extensive applications in various catalytic enantioselective transformations.[1] As a result, the construction of these scaffolds has attracted considerable attention and the relatively practical methods have already been achieved.[2] In contrast, 1,1′-binaphthyl-2,2′-diamine (BINAM), with a similar axially chiral skeleton, remains largely unexplored with respect to the application in asymmetric synthesis, which is probably due to the rather expensive production cost resulting from the lack of reliable synthetic routes.[3] Noteworthy is that several well-established BINAM-based compounds[4] have recently been developed as effective chiral organocatalysts (Figure 1).[5] For example, the Barbas research group[4a] has discovered a highly efficient organocatalytic domino approach for the direct construction of bispirooxindole derivatives with three quaternary chiral centers with excellent stereocontrol by employing a multifunctional organocatalyst containing an axially chiral BINAM skeleton. In this context, a more reliable and straightforward approach to optically pure BINAM derivatives would greatly widen the application scope of this particular class of axially chiral catalyst in asymmetric catalysis.

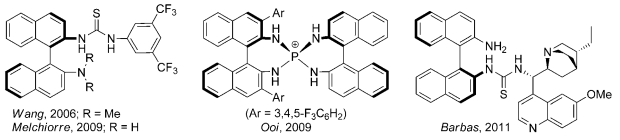
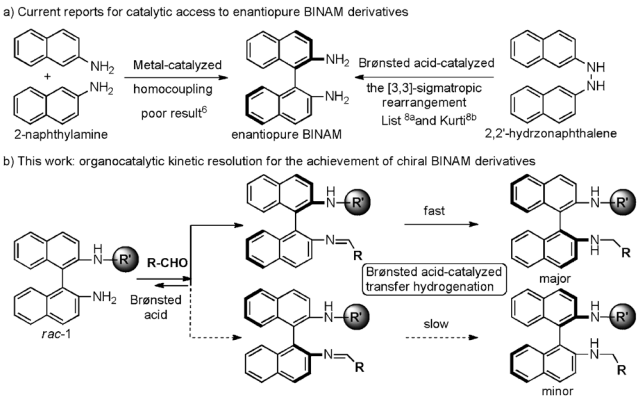


Figure 1. Examples of BINAM-based organocatalysts.

There have only been a few synthetic attempts toward enantiopure BINAM derivatives, including a direct catalytic enantioselective oxidative homocoupling of 2-naphthylamines with modest results[6] and [3,3]-sigmatropic rearrangement promoted by a camphor sulfonic acid with poor enantioselectivity.[7] Quite recently, with Brønsted acids as efficient organocatalysts, the [3,3]-sigmatropic rearrangement strategy was further improved by the groups of List[8a] and Kürti,[8b] respectively (Scheme 1a). Over the past several decades, the kinetic resolution[9] of racemic starting materials has been one of the most powerful and reliable strategies for the synthesis of enantiopure compounds in both academia and industry, which would serve as a valuable complementary approach to the traditional synthetic methods, such as asymmetric synthesis and classic resolution. However, examples of catalytic kinetic resolution of axially chiral BINAM derivatives, to the best of our knowledge, have not been reported. Although during the preparation of this manuscript, an efficient method for the kinetic resolution of 2-amino-1,1′-biaryl compounds by phase-transfer-catalyzed *N*-allylation was reported by Maruoka and co-workers,[10] only one BINAM derivative was utilized as the substrate with fairly good results. Therefore, it still remains a challenging undertaking for the catalytic kinetic resolution of these axially chiral compounds.



Scheme 1. General strategies for creating axially chiral BINAM derivatives.

[*] Dr. D.-J. Cheng, M.-Y. Wu, L.-X. Wang, Z.-L. Fan, Dr. S.-C. Zheng, Prof. Dr. X.-Y. Liu, Prof. Dr. B. Tan
Department of Chemistry, South University of Science and Technology of China, Shenzhen, 518055 (China)
E-mail: liuxy3@sustc.edu.cn
tanb@sustc.edu.cn
L. Yan, Prof. Dr. S.-K. Tian
Department of Chemistry, University of Science and Technology of China, Hefei, Anhui, 230026 (China)
E-mail: tiansk@ustc.edu.cn

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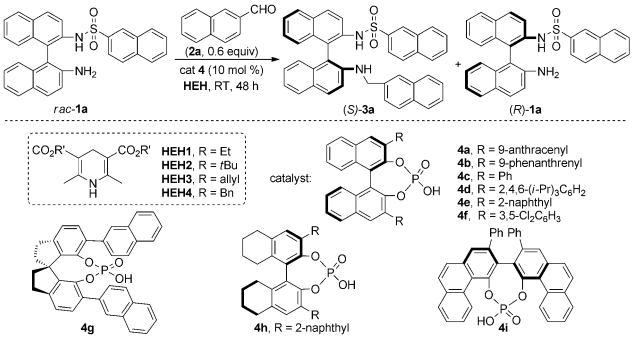
Recently, organocatalytic asymmetric transfer hydrogenation with organic hydride donors[11] has emerged as a powerful method for the construction of diverse cyclic and acyclic amines by reduction of imines in the presence of Brønsted acids. Based on the "three-point contact model" for asymmetric transfer hydrogenation reported recently by Goodman and co-workers,[12] we envisioned that an organocatalytic kinetic resolution through a phosphoric acid catalyzed[13] imine formation and transfer hydrogenation cascade process could potentially be a powerful and general approach toward chiral BINAM derivatives. This strategy consists of consecutive asymmetric kinetic resolution process by means of chiral phosphoric acid catalysis, in which installing a bulky group in one of amines of racemic BINAM was presumed to increase the rotation energy barrier and effective steric interaction for improved enantioselectivity (Scheme 1b). Herein, we present the details of our studies with this strategy.

To validate the feasibility of the proposed process, we selected *N*-[2′-amino(1,1′-binaphthalen)-2-yl]naphthalene-2-sulfonamide *rac*-**1a** with a bulky naphthalenesulfonamide group as the model substrate for the optimization of reaction conditions. We initiated our studies by evaluating the reaction between *rac*-**1a** and 0.6 equiv of 2-naphthaldehyde **2a** using 10 mol% of chiral phosphoric acid **4a** as the Brønsted acid catalyst and diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**HEH1**) as the hydride source in ethyl acetate (EA) at room temperature for 48 h. To our delight, the reaction proceeded smoothly and afforded the desired product **3a** in 43% yield with 93% *ee*, albeit with only moderate *ee* (53%) of the recovered starting material (*R*)-**1a**[14] (Table 1, entry 1). After calculation, a selectivity factor[9a] ($S = k_{fast}/k_{slow}$) of 47 was obtained (entry 1). Encouraged by this, a detailed optimization study was first done with different phosphoric acid catalysts. Several BINOL, H_8-BINOL, SPINOL, and VAPOL-derived catalysts were investigated, which displayed remarkable effects on the outcome of the reaction. It should be noted that the yield and *ee* of product **3a** was always excellent with different BINOL-derived catalysts (Table 1, entries 2–6), even in the presence of the catalyst with phenyl group on the 3,3′-positions (Table 1, entry 3), while *ee* of the recovered **1a** varied. It is interesting to find that the kinetic resolution reaction did not proceed with VAPOL **4i** as catalyst, which is most likely due to the steric hindrance with the bulky starting material (Table 1, entry 9). Considering catalyst **4e** with the best results ($S = 354$) for both the transfer hydrogenation product **3a** (50% yield, 98% *ee*) and the recovered starting material (*R*)-**1a** (41% yield, 94% *ee*) (Table 1, entry 5), this catalyst was selected for further optimization. Predictably, the solvent played an important role in this transformation, especially as to the enantioselectivity of the recovered starting material, and EA was proved to be the best choice (Table 1, entries 10–14). Inspired by a recent review on Hantzsch esters as the hydride sources for transfer hydrogenations,[16] we screened different Hantzsch esters (Table 1, entries 15–17) and found that **HEH3** gave rise to a better result ($S = 303$) with 98% *ee* of the recovered **1a** and 97% *ee* of the product (Table 1, entry 16). Finally, we investigated the effects of the reaction temperature and 3 Å molecular sieves as the additive without significant improvement (Table 1, entries 18–20).

Table 1: Screening results of reaction conditions.[a]



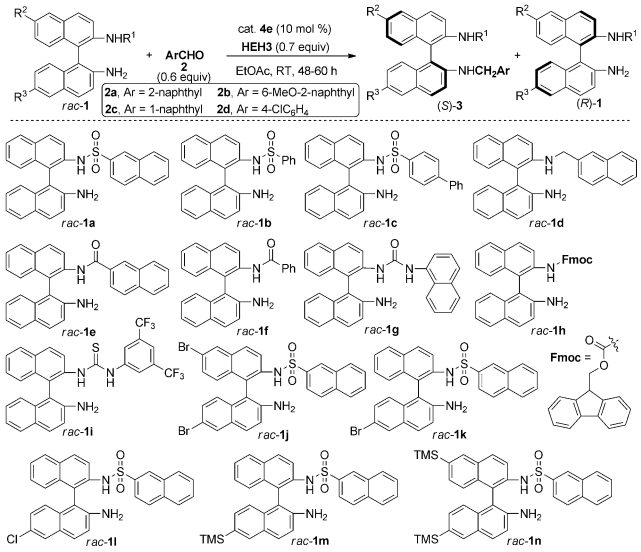
Entry	cat.	HEH	Solvent	3a		1a		S[d]
				yield [%][b]	*ee* [%][c]	yield [%][b]	*ee* [%][c]	
1	**4a**	**1**	EtOAc	43	93	50	53	47
2	**4b**	**1**	EtOAc	48	94	46	73	71
3	**4c**	**1**	EtOAc	42	98	49	87	283
4	**4d**	**1**	EtOAc	52	95	37	48	63
5	**4e**	**1**	EtOAc	50	98	41	94	354
6	**4f**	**1**	EtOAc	44	98	46	83	259
7	**4g**	**1**	EtOAc	42	−97	50	−74	146
8	**4h**	**1**	EtOAc	46	98	45	88	290
9	**4i**	**1**	EtOAc	NR	ND	NR	ND	–
10	**4e**	**1**	DCE	27	73	69	24	8
11	**4e**	**1**	toluene	40	90	39	73	42
12	**4e**	**1**	MTBE	36	91	44	75	48
13	**4e**	**1**	CH_3CN	25	90	50	38	28
14	**4e**	**1**	*i*PrOAc	41	98	49	86	276
15	**4e**	**2**	EtOAc	48	98	47	80	244
16	**4e**	**3**	EtOAc	47	97	44	98	303
17	**4e**	**4**	EtOAc	45	99	43	97	844
18[e]	**4e**	**3**	EtOAc	50	98	46	92	328
19[f]	**4e**	**3**	EtOAc	46	98	44	64	192
20[g]	**4e**	**3**	EtOAc	47	97	46	99	327

[a] Reaction conditions: *rac*-**1a** (0.050 mmol), Hantzsch ester (0.70 equiv), catalyst **4** (10 mol%), EtOAc (0.6 mL). [b] Determined by chiral stationary phase HPLC analysis. [c] Yield of isolated product. [d] The selectivity factor was calculated as $S = \ln[(1-C)(1-ee(\mathbf{1a}))]/\ln[(1-C)(1+ee(\mathbf{1a}))]$, $C = ee(\mathbf{1a})/(ee(\mathbf{3a}) + ee(\mathbf{1a}))$. [e] 10 mg of 3 Å MS was added. [f] The reaction was run at 50°C. [g] The reaction was performed at 10°C for 72 h.

With the optimal reaction conditions in hand, we set out to explore the substrate generality of this procedure. As shown in Table 2, the functional groups on aldehydes, such as 1-naphthyl, 2- naphthyl, 6-OMe-2-naphthyl, and 4-chlorobenzyl groups, were well-tolerated, giving the corresponding products **3a**-**3d** in good to excellent enantioselectivities with good yields ($S = 15$–303, Table 2, entries 1–4). Notably, the 2-naphthaldehyde exhibited the best performance in terms of stereoselectivity and yield for both of the product **3a** and recovered starting material **1a**, indicating an aromatic stacking interaction during the transfer hydrogenation step.

Based on this observation, we next examined other bulky protecting groups for this process. This reaction shows excellent compatibility with different types of protecting groups, such as sulfonyl, benzoyl, 2-naphthylmethyl, Fmoc, amido and thioamido groups ($S = 7$-340, Table 2, entries 5–

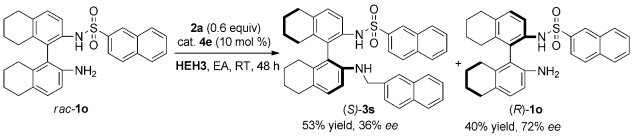
Table 2: Reaction scope for the kinetic resolution of BINAM derivatives.[a]



Entry	*rac*-**1**	**2**	**3**		**1**		*S*[d]
			Yield [%][b]	*ee* [%][c]	Yield [%][b]	*ee* [%][c]	
1	*rac*-**1a**	**2a**	47 (**3a**)	97	44 (**1a**)	98	303
2	*rac*-**1a**	**2b**	43 (**3b**)	98	47 (**1a**)	80	246
3	*rac*-**1a**	**2c**	51 (**3c**)	75	43 (**1a**)	90	21
4[e]	*rac*-**1a**	**2d**	58 (**3d**)	64	40 (**1a**)	94	15
5	*rac*-**1b**	**2a**	52 (**3e**)	80	41 (**1b**)	94	31
6	*rac*-**1c**	**2a**	47 (**3f**)	98	46 (**1c**)	93	340
7	*rac*-**1d**	**2a**	49 (**3g**)	92	43 (**1d**)	96	94
8	*rac*-**1e**	**2a**	44 (**3h**)	88	45 (**1e**)	99	82
9	*rac*-**1f**	**2a**	55 (**3i**)	80	41 (**1f**)	82	23
10[e]	*rac*-**1f**	**2d**	59 (**3j**)	62	38 (**1f**)	97	17
11[e]	*rac*-**1g**	**2d**	59 (**3k**)	40	35 (**1g**)	92	7
12[e]	*rac*-**1h**	**2d**	58 (**3l**)	52	40 (**1h**)	93	10
13	*rac*-**1i**	**2a**	55 (**3m**)	44	42 (**1i**)	92	8
14	*rac*-**1j**	**2a**	50 (**3n**)	85	43 (**1j**)	90	38
15	*rac*-**1k**	**2a**	46 (**3o**)	98	45 (**1k**)	90	307
16	*rac*-**1l**	**2a**	45 (**3p**)	96	47 (**1l**)	96	194
17	*rac*-**1m**	**2a**	47 (**3q**)	93	43 (**1m**)	96	108
18	*rac*-**1n**	**2a**	55 (**3r**)	47	40 (**1n**)	98	11

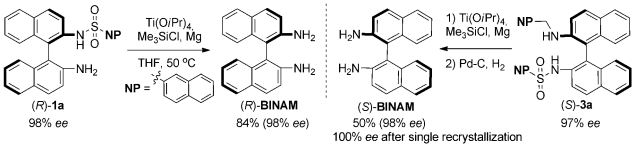
[a] Reaction conditions: *rac*-**1** (0.050 mmol), **2** (0.030 mmol), Hantzsch ester (0.035 mmol), catalyst **4e** (10 mol%), EtOAc (0.6 mL), RT. [b] Yield of isolated product. [c] Determined by chiral stationary phase HPLC analysis. [d] The selectivity factor was calculated as $S = \ln[(1-C)(1-ee(\mathbf{1}))]/\ln[(1-C)(1+ee(\mathbf{1}))]$, $C = ee(\mathbf{1})/(ee(\mathbf{3}) + ee(\mathbf{1}))$. [e] **HEH1** was used instead of **HEH3**.

13). Furthermore, investigations into the effect of substituents on the BINAM skeleton of the substrates revealed that the reaction was also efficient for substrates with functional groups (R^3 = Br, Cl, TMS) at the 6-position or 6,6′-positions ($R^2 = R^3$ = Br or TMS) with good yields and good to excellent enantioselectivity (S = 11–307, Table 2, entries 14–18). The resultant halogen-containing (Br, Cl) products can be easily transformed into other substituted compounds by cross-coupling reactions,[16] providing opportunities for the efficient construction of more complicated BINAM derivatives. To further probe the substrate scope, under the similar reaction conditions described above, the current reaction system was extended to *rac*-H_8-BINAM **1o** with moderate results (Scheme 2), which further demonstrated that aromatic stacking interaction may play an important role in achieving good stereocontrol.



Scheme 2. Kinetic resolution of H_8-BINAM derivative.

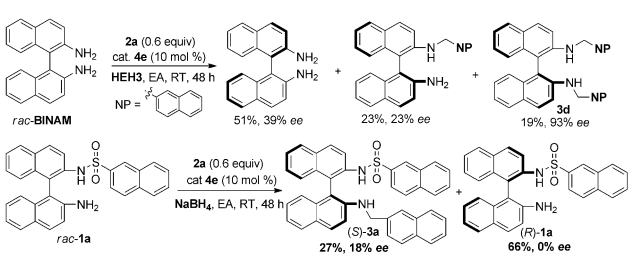
To demonstrate the utility of the current procedure, the bulky protecting groups of the resulting optically pure transfer hydrogenation product (*S*)-**3a** and recovered starting material (*R*)-**1a**[17] could be readily removed to produce (*S*)-BINAM and (*R*)-BINAM with moderate to high yields, and the enantiopurity can be completely retained (Scheme 3), which has been suggested to have wide applications as the effective asymmetric organocatalysis.[4,5] The optically pure product (up to 100% *ee*) can be obtained after a single recrystallization process of the enantiomerically enriched (*S*)-BINAM from toluene.[8b]



Scheme 3. Access to enantiopure BINAM.

Furthermore, the unsatisfactory results obtained in the kinetic resolution of simple non-protected BINAM under the standard conditions demonstrated that the bulky protecting group is necessary for good interaction between the catalyst and the substrate. In this case, the isolation of product **3d** with 93% *ee* further indicated the importance of the presence of a bulky group (Scheme 4). To better understand this cascade kinetic resolution process, we also tested the reductive step with the use of sodium borohydride ($NaBH_4$) as hydrogen source. The poor enantioselectivity of the product might not only suggest that the first imine formation step was not the determining process of the kinetic resolution, but also indicate that the cooperation of Hantzsch ester and phosphoric acid for the transfer hydrogenation should be crucial for the kinetic resolution process, which is in accordance with previous reports.[15]

In conclusion, we have developed a highly efficient and practical strategy for the kinetic resolution of axially chiral



Scheme 4. Control experiments by using simple reagents.

BINAM derivatives in high yields with excellent enantioselectivities, involving a chiral Brønsted acid-catalyzed imine formation and transfer hydrogenation cascade process. This method features a general strategy by employing the well-known reactions for the kinetic resolution of structurally useful compounds with a high level of enantioselectivity. Further applications of this strategy toward the kinetic resolution of similar axially chiral compounds are currently under active investigation.

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