

Kinetic Resolution

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Chiral Phosphoric Acid Catalyzed Kinetic Resolution of Indolines Based on a Self-Redox Reaction

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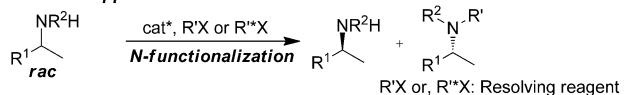
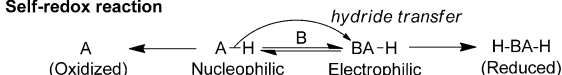
Abstract: A strategy for oxidative kinetic resolution of racemic indolines was developed, employing salicylaldehyde derivative as the pre-resolving reagent and chiral phosphoric acid as the catalyst. The iminium intermediate, formed by the condensation reaction of an enantiomer of indoline with salicylaldehyde derivative, was hydrogenated by the same enantiomer of indoline to afford another enantiomer of indoline by a self-redox mechanism. The oxidative kinetic resolution of 2-aryl-substituted indolines proceeded to give enantiomers in good yields with excellent enantioselectivities.

The development of new methods for the asymmetric synthesis of chiral skeletons has captured the attention of synthetic organic chemists.^[1] Kinetic resolution (KR) of racemic substrates is one of the most important methods for obtaining chiral compounds.^[2] Although efficient KR of alcohol derivatives has been achieved by many research groups using catalytic nonenzymatic methods, KR of amines is little investigated because of the high reactivity and coordinating ability of amines. KR of amines and alcohols is generally carried out in the presence of a chiral catalyst using more than half an equivalent of resolving reagent R'X or chiral resolving reagent R*X (Scheme 1, *N*-functionalization).

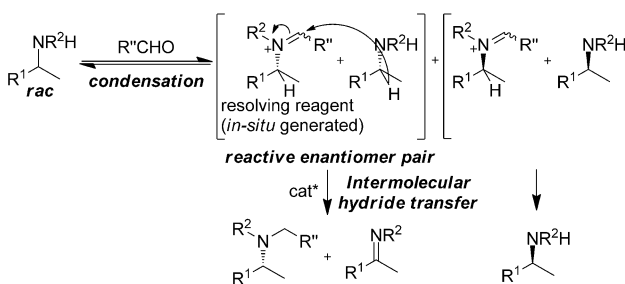
Over the last decades, indolines have attracted considerable attention in the pharmaceutical as well as agrochemical sciences.^[3] Nevertheless, there are few reports on the catalytic synthesis of indolines that use KR to achieve high enantioselectivity. Fu and Hou independently developed KR of indolines derived from functionalization of the nitrogen atom of indoline.^[4,5] On the other hand, we recently reported oxidative KR of indolines based on an asymmetric hydrogen transfer reaction to aromatic ketimine by means of chiral phosphoric acid.^[6] Although that was the first report on KR of secondary amines that employed a dehydrogenation reaction without oxidation of the nitrogen atom,^[7,8] we still had to synthesize, isolate, and use an excess of the resolving reagent (ketimine).

The redox amination reaction has received much attention as a powerful tool for C–N bond formation.^[9] Recently,

Standard approach for KR of racemic amine

This work
Self-redox reaction

KR based on self-redox reaction



Scheme 1. Approaches for kinetic resolution of racemic amines.

the Brønsted acid catalyzed redox amination reaction of cyclic amines with aldehyde (operating via an intramolecular hydride transfer step) has undergone extensive study by many research groups. The organocatalyzed asymmetric intermolecular redox amination (reductive amination) is also well-known,^[10] but requires addition of terminal reductants, such as Hantzsch ester. As an interesting example, the groups of Pan and Seidel independently reported the benzoic acid catalyzed self-redox amination reaction of indolines.^[9i,j] Their reports describe efficient intermolecular hydride transfer from starting material (A–H) to iminium intermediate (BA–H), which is generated by reacting starting material with aldehyde (B), to give oxidized (A) and reduced (H–BA–H) products (Scheme 1). Zhou and Fan et al. reported an asymmetric disproportionation reaction of achiral dihydroquinoxaline using chiral phosphoric acid, wherein two molecules of dihydroquinoxaline reacted to afford quinoxaline and tetrahydroquinoxaline with excellent enantioselectivity by a self-transfer hydrogenation reaction.^[11] Nevertheless, to the best of our knowledge the asymmetric self-redox reaction of racemic substrates has not been reported. Our strategy for KR of amines is based on the self-redox reaction of a chiral starting material to form a chiral iminium intermediate, which is generated by condensation of the racemic starting amine and aldehyde. Two working hypotheses were required to realize the proposed KR: 1) the reduction of one enantiomer of racemic iminium intermediates (enantiomers are in equilibrium) is faster than that of the other enantiomer (in situ generated chiral resolving reagent is required); 2) one

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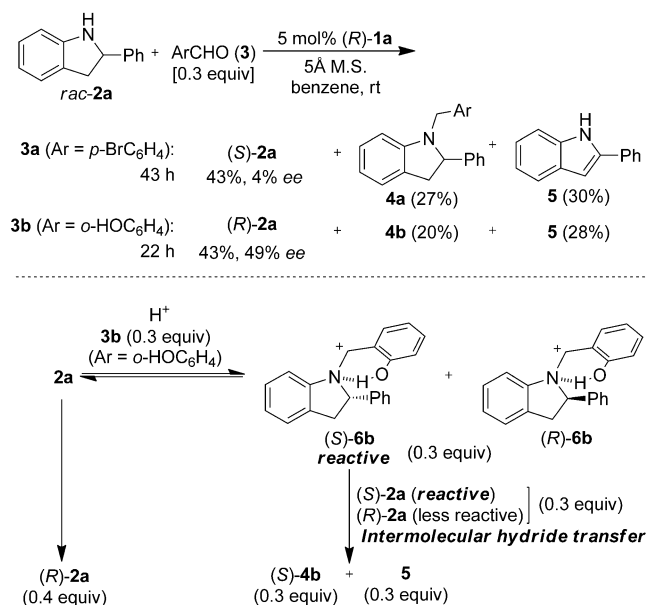
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enantiomer of the racemic starting material preferentially donates a hydride to the iminium intermediate, thereby resulting in an enantiomerically enriched starting material and a chiral reductive amination product.

At the outset, we chose racemic 2-phenylindoline (*rac*-**2a**) as the model substrate and treated it with 0.3 equiv of 4-bromobenzaldehyde (**3a**) in the presence of a catalytic amount of phosphoric acid (*R*)-**1a** at room temperature (Scheme 2). An intermolecular hydride transfer reaction



proceeded to give (*S*)-**2a** in 43% yield with 4% *ee*, **4a** (27% yield), and **5** (30% yield). On the other hand, use of 0.3 equiv of salicylaldehyde (**3b**) resulted in the formation of (*R*)-**2a** in 43% yield with 49% *ee* accompanied by **4b** and **5**.^[14] A plausible reaction mechanism for describing the phosphoric acid catalyzed KR is proposed in Scheme 2. When **3b** was employed, intermolecular hydride transfer from (*S*)-**2a** to iminium intermediate **6b** occurred with moderate *ee*.^[9b,15] Importantly, to achieve a highly enantioselective KR by the self-redox method, equivalent enantiomers of **2a** have to cooperate to form an iminium intermediate **6b** and preferentially supply a hydride to **6b**.

We examined the effect of the 3,3'-substituents of phosphoric acid on selectivity (Table 1). The connection of the substituents at the *ortho* and *para* positions of the aromatic ring to the 3,3'-positions of the BINOL backbone played an important role in the enantiocontrol of KR. Introduction of the 9-anthryl group ((*R*)-**1b**) gave the highest *ee* of 91% (entry 2), and the loading of (*R*)-**1b** could be reduced to 2 mol% without any deleterious effect on enantioselectivity (entry 3). Subsequently, we tried to optimize the resolving reagent for KR using (*R*)-**1b**. Resolving reagents bearing a substituent at the position *ortho* to the hydroxyl and formyl groups induced no conversion (entry 4)

Table 1: Screening of aldehydes for catalytic kinetic resolution.

Entry	Aldehyde	Yield [%]	<i>ee</i> [%]	Yield [%]	<i>ee</i> [%]
1 ^[a]	3b	43	49	20	31
2 ^[b]	3b	36	91		
3	3b	41	90	27	51
4	3c	no reaction			
5	3d	45	40		
6	3e	53	83	20	58
7	3f	36	86	29	50
8	3g	45	96	24	78

Ar =

1a: R = R' = *i*-Pr
1b: R = *i*-Pr, R' = 9-anthryl

Yields of isolated products reported, *ee* determined by chiral phase HPLC analysis. [a] (*R*)-**1a** (5 mol%) was used. [b] (*R*)-**1b** (5 mol%) was used.

and lowered the enantioselectivity (entry 5). Introduction of a substituent *para* with respect to the hydroxy group had a significant impact on enantioselectivity; in particular, an electron-donating group had a positive effect on enantioselectivity (entries 6–8). Finally, we found that commercially available 5-methoxysalicylaldehyde (**3g**) was the aldehyde of choice for this reaction (entry 8).

To examine the scope of the KR method, a series of 2-substituted indolines **2a–2u** were subjected to the optimized reaction conditions (Table 2). All of the racemic indolines reacted smoothly to give the corresponding chiral indolines in high yields with good to excellent enantioselectivities. Indolines **2m–2t** bearing electron-donating or -withdrawing groups at the 4-, 5-, and 6-positions were also suitable substrates, affording the corresponding chiral indolines in high yields with excellent enantioselectivities. Substrate **2u** bearing a 7-methyl group participated in oxidative KR with a high selectivity factor (*s* = 49). It is noted that the 2-aryl-substituted indolines bearing no protecting group on the nitrogen atom are inaccessible by the previously reported asymmetric hydrogenation approaches.^[5,16] Moreover, it should also be noted that the recovered **2a** had an opposite absolute configuration compared to the previous oxidative kinetic resolution (OKR) product when ketimine **7** was used

Table 2: Scope of catalytic kinetic resolution of indolines.

Entry	Indoline	Yield [%]	<i>ee</i> [%]	
1	2a	45	96	
2	2b	49	98	
3	2c	44	93	
4	2d	41	98	
5	2e	44	97	
6	2f	42	97	
7	2g	40	97	
8	2h	41	96	
9	2i	50	87	
10	2j	38	89	
11	2k	46	93	
12	2l	43	94	
13	2m	40	95	
14	2n	41	95	
15	2o	39	96	
16	2p	41	99	
17	2q	43	97	
18	2r	40	98	
19	2s	47	92	

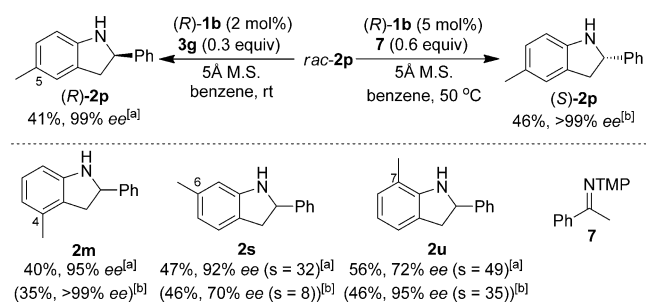
Table 2: (Continued)

Entry	Indoline	Yield [%]	<i>ee</i> [%]
20	2t	52	93
21	2u	77 (56 ^[a])	33 (72 ^[a])

Yields of isolated products reported, *ee* determined by chiral phase HPLC analysis. [a] **3g** (0.05 mmol) was used.

as the resolving reagent in conjunction with catalyst (*R*)-**1b**.^[6] In this manner, an enantiodivergent synthesis of 2-substituted indoline could be achieved with identical catalyst simply by changing the resolving reagent. To confirm the utility of this method, we compared the reactivity and selectivity of the present KR procedure with that of the previous method (Scheme 3).^[6] Both enantiomers of **2p** and **2m** were obtained with excellent enantioselectivity after an appropriate choice of resolving agent was made. The present method proved to be superior for **2s**, whereas the previous OKR approach was superior for **2u** in terms of conversion.^[17]

In conclusion, we have developed a highly efficient method for kinetic resolution of indoline derivatives, which involves an asymmetric intermolecular hydride transfer from indoline to iminium intermediate, which is generated by reacting aldehyde with indoline. KR enabled synthesis of 2-aryl-substituted indolines in high yields with excellent enantioselectivities. The method features mild OKR using a hydride transfer reaction and a small amount of resolving reagent. Investigations into mechanistic function, and applications that extend to the synthesis of more complex molecules, are under way.



Scheme 3. Enantiodivergent synthesis of 2-substituted indolines. Yields of isolated products reported, *ee* determined by chiral phase HPLC analysis. [a] Resolutions were carried out on a 0.1 mmol scale with racemic **2** (0.1 mmol), **3g** (0.03 mmol), (*R*)-**1b** (2 mol%), and 5 Å M.S. (50 mg) in benzene (0.1 M) at room temperature for 22 h. [b] Resolutions were carried out on a 0.1 mmol scale with racemic **2** (0.1 mmol), **7** (0.06 mmol), (*R*)-**1b** (5 mol%), and 5 Å M.S. (50 mg) in benzene (0.1 M) at 50 °C for 19 h.

Experimental Section

A typical procedure for the reaction of *rac*-**2a**: A magnetic stirrer bar and 5 Å M.S. (50 mg) were placed in a test tube (10 mL) under a nitrogen atmosphere. The 5 Å M.S. were then dried with a heat gun

under reduced pressure and the test-tube refilled with nitrogen. *rac*-**2a** (19.6 mg, 0.100 mmol), phosphoric acid (*R*)-**1b** (2.0 mg, 2 μ mol), and aldehyde **3g** (4.5 mg, 0.030 mmol) were added to the test tube successively, under nitrogen atmosphere, and at room temperature. Benzene degassed by sonication under reduced pressure (1 mL) was added to the test tube. After stirring for 22 h at room temperature, the mixture was filtered through a Celite pad (previously washed with CH₂Cl₂), the filtrate concentrated under reduced pressure, and the residue purified by preparative thin layer chromatography on silica gel (AcOEt/hexanes = 1:5) to give 8.8 mg (0.045 mmol, 45 %) of (*R*)-**2a** as an amorphous solid.

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Keywords: asymmetric synthesis · heterocycles · hydrogen transfer · kinetic resolution · organocatalyst

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- [14] The absolute configuration of the recovered enantio-enriched **2a** was determined by comparison of retention times using chiral phase HPLC analysis and the sign of optical rotation derived from our previous report (ref. [6]).
- [15] The reaction of (*S*)-**2a** (> 99% *ee*) and **3b** in the presence of a catalytic amount of (*R*)-**1b** gave (*S*)-**2a** (40%, > 99% *ee*) and (*S*)-**4b** (28%, > 99% *ee*). This result indicates that racemization of the 2-position of **2a** by intramolecular 1,3-hydrogen shift did not occur during this process.
- [16] The reaction of 2-alkyl substituted indolines resulted in lower conversions and selectivities (in the case of racemic 2-methylindoline, 62% yield with 24% *ee*). Additionally, 2,3-disubstituted indolines were not converted efficiently. These substrates were successfully kinetically resolved by our previous method (Ref. [6]).
- [17] In our previous report (Ref. [6]), the effect of substituents on the aromatic ring of indoline was not fully examined.

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