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Copper-Catalyzed Enantioselective Intramolecular *N*-Arylation, an Efficient Method for Kinetic Resolutions

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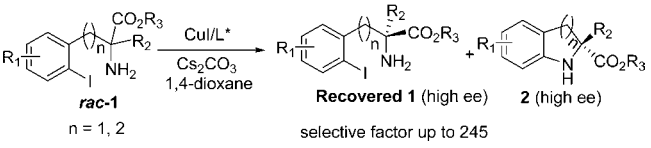
ABSTRACT



For the first time, copper-catalyzed intramolecular *N*-arylation was successfully applied to the kinetic resolution strategy. Under the catalysis of CuI−BINOL derived ligands, the kinetic resolution of *rac*-2-amino-3-(2-iodoaryl)propionates and *rac*-2-amino-4-(2-iodoaryl)butanoates afforded chiral intramolecular coupling products and recovered the starting materials in high enantioselectivity (*s* factors up to 245).

Functionalized aromatic and heteroaromatic amines have found extensive applications as key players in the synthesis of bioactive natural products, important pharmaceuticals, and materials.[1] Because of their widespread importance, many methods have been developed for the formation of the aryl C−N bond, in which transition metals, such as Pd,[2] Cu,[3] Ni,[4] etc., catalyzed coupling reactions of aryl halides with amines may be the most powerful methods. However, enantioselective *N*-arylation remains a remarkable challenge. In such reactions, the bond formation is between a sp^2 planar geometric carbon and a nitrogen atom which is usually not a configurationally stable chiral center, although N−C axially chiral compounds may be formed through Pd-catalyzed *N*-arylation reactions, as has been successfully achieved by the prominent work of Kitagawa and Taguchi since 2005.[5] Besides, for substrates bearing prochiral or achiral carbon centers which did not directly participate in the bond

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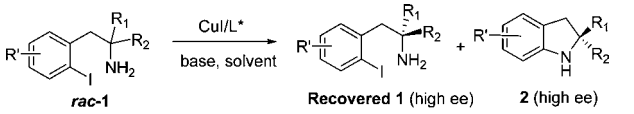
formation at the reactive site, little attention has been focused on asymmetric *N*-arylation reactions. So far, only sporadic examples have been reported in this field. Generally, two strategies may be utilized to achieve enantioselectivity: asymmetric desymmetrization[6] and kinetic resolution,[7] both of which have been successfully implemented in Pd-catalyzed asymmetric *N*-arylation reactions,[8,9] albeit only low to moderate enantioselectivity was obtained in most cases.

Based on the asymmetric desymmetrization strategy, our laboratory has developed the first copper-catalyzed highly enantioselective intramolecular *N*-arylation reaction, which afforded chiral indolines and 1,2,3,4-tetrahydroquinolines in high yields and excellent enantioselectivity.[10] However, such desymmetrization reactions have some disadvantages: the substrate scope is limited and the products bear two aryl rings with similar substituents, which may cause problems in later selective transformations. To overcome such problems and increase the applicability of asymmetric *N*-arylation reactions, we envisioned that the kinetic resolution strategy may be a good choice for achieving enantioselectivity through copper-catalyzed intramolecular aryl C−N coupling. According to this strategy, the kinetic resolution of racemic 2-(2-iodophenyl)ethanamine derivative (**1**) by copper-catalyzed intramolecular *N*-arylation reaction, would deliver indolines (**2**) and recover the starting material **1** in high enantioselectivities (Scheme 1). The kinetic resolutions of amines have been extensively studied,[11,12] however, mainly through acylations. The reported examples for resolutions of amines by enantioselective *N*-arylation are rare and the selectivities are poor to modest in most cases.[9] To the best of our knowledge, it is the first time for the kinetic resolution of amines to be achieved through copper-catalyzed coupling reactions. Herein we report the details of this research.

Scheme 1. Copper-Catalyzed Enantioselective Intramolecualr *N*-Arylation via Kinetic Resolution Strategy



In our previous work, we have realized that an ester group in the prochiral center is beneficial to the enantioselectivity of copper-catalyzed desymmetric *N*-arylation reactions, and it is also an important group for further functionalization.[10] Thus, in this work, we keep the ester group as an important directing group in the substrates and our investigation was started with the kinetic resolution of racemic methyl 2-amino-2-benzyl-3-(2-iodophenyl)-propanoate **1a** under the catalysis of 5 mol % of CuI and 6 mol % of BINOL-derived ligands and with 100 mol % of Cs_2CO_3 as the base.[13,14] As shown in Table 1, by using (*R*)-BINOL (L1) as the ligand, **1a** was recovered in 32% ee and **2a** was isolated in 57% ee (36% conversion, *s*-factor = 4.9)[15] after 0.5 h in 1,4-dioxane at room temperature (Table 1, entry 1). Next, several 3,3′-biaryl-substituted (*R*)-BINOL ligands were examined, and better selectivities were obtained with bulkier aryl substituents in the 3,3′-positions of the BINOL backbone (Table 1, entries 2−5), which is consistent with our previous results in copper/BINOL-catalyzed asymmetric desymmetric *N*-arylation reactions. As observed, the CuI−L5-catalyzed reaction showed the best result, which afforded the coupling product **2a** in 89% ee and recovered **1a** in 94% ee (51% conversion, $s = 70.0$) in 4 h (Table 1, entry 5). Further, a variety of solvents such as THF, MeCN, DMF, and toluene were screened and all gave inferior results under the similar reaction conditions (Table 1, entries 6−9).

With the optimized conditions in hand, we then investigated the scope of substrates for kinetic resolution by copper-catalyzed coupling reactions and the results are shown in Table 2. First, the substrates bearing different

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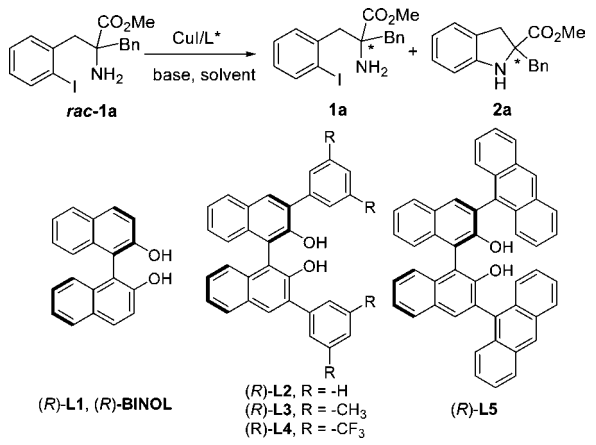
Table 1. Screening Reaction Conditions[a]



entry	L*	solvent	time (h)	conv[b] (%)	ee[c] (%) 1a	ee[c] (%) 2a	s
1	L1	dioxane	0.5	36	32	57	4.9
2	L2	dioxane	2	38	37	60	5.8
3	L3	dioxane	1.5	34	40	77	11.7
4	L4	dioxane	1	44	63	74	16.8
5	L5	dioxane	4	51	94	89	70.0
6	L5	THF	2	37	50	87	20.4
7	L5	MeCN	2	23	15	52	3.5
8	L5	DMF	2	37	24	42	3.0
9	L5	toluene	4	8	7	89	9.9

[a] Reagents and reaction conditions: **1a** (0.20 mmol, 1.0 equiv), CuI (0.01 mmol, 5 mol %), ligand (0.012 mmol, 6 mol %), base, (0.2 mmol, 1.0 equiv), solvent (1.5 mL), rt. [b] Calculated conversion. [c] Determined by HPLC analysis (Chirapak AD-H column).

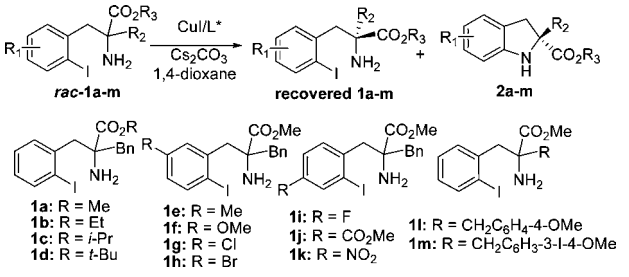
ester groups at the quaternary chiral carbon center were tested and all gave excellent enantioselectivities with *s*-factors from 57.2 to 70.0, well above the threshold for practical utility (Table 2, entries 1−4). Next, by controlling the conversion ratios between 45 and 55%, a variety of substrates bearing electron-withdrawing or electron-donating substituents on the 2-iodophenyl ring were tested and excellent enantioselectivities (s = 38−91) were also obtained in all cases tested (Table 2, entries 5−11). As an example to elucidate the applicability of such a kinetic resolution process, the recovered enriched enantiomer **1a** was transformed into **2a** under the catalysis of CuI/*rac*-BINOL[14] (97% yield, −94% ee).

Further efforts to increase the variations on the phenyl ring of benzyl also successfully afforded the coupling products and recovered the starting materials in excellent selectivities, as in the case of compounds **1l** and **1m** (Table 2, entries 12 and 13). Noticeably, in the case of **1m**, an iodo atom was introduced on the phenyl ring of the benzyl group, which could be a good reactive site for further transformations.

(16) For the assignment of absolute configuration of the products and recovered starting materials, see the Supporting Information.

Furthermore, the absolute configuration of the coupling product **2b** was assigned to be *R* by comparing with our reported compound through one-step chemical transformation.[16] Correspondingly, the absolute configurations of the recovered starting material **1b** were assigned to be *S*. The absolute configurations of other coupling products and recovered starting materials were assigned by analogue to that of **2b** and **1b**, respectively.

Table 2. Substrate Scope for the Kinetic Resolution of *rac*-2-Amino-3-(2-iodoaryl)propionates[a]



entry	*rac*-1	time (h)	conv[b] (%)	ee of 1 (yield,%)[c]	ee of 2 (yield, %)[c]	s
1	**1a**	4	51	94 (49)	89 (51)	70.0
2	**1b**	8	48	85 (51)	93 (46)	65.9
3	**1c**	2.5	49	87 (50)	90 (49)	57.2
4	**1d**	2.5	50	90 (49)	91 (50)	58.5
5	**1e**	4	50	86[d] (48)	87 (49)	40.7
6	**1f**	3.5	52	98 (46)	92 (51)	91.3
7	**1g**	1.5	51	92 (49)	90 (50)	53.1
8	**1h**	1.5	48	86 (46)	93 (46)	78.7
9	**1i**	2	47	80 (52)	91 (45)	47.7
10	**1j**	3	54	96 (46)	83 (50)	38.6
11	**1k**	2	47	80 (53)	91 (46)	47.7
12	**1l**	1.5	49	86 (50)	90 (49)	50.0
13	**1m**	2	53	96 (46)	86 (52)	48.4

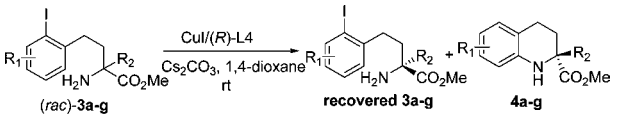
[a] Reagents and reaction conditions: **1** (0.2 mmol, 1.0 equiv), CuI (0.01 mmol, 5 mol %), L5 (0.012 mmol, 6 mol %), Cs_2CO_3, (0.2 mmol, 1.0 equiv), 1,4-dioxane (1.5 mL), rt. [b] Calculated conversion. [c] Isolated yields are given in parentheses; the enantiomeric excesses were determined by HPLC analysis (Chirapak AD-H or OD-H column). [d] The ee of **1e** was determined after one-step reaction.

Encouraged by the above success, we then explored the kinetic resolution of racemic 2-amino-4-(2-iodophenyl)-butanoates. As shown in Table 3, although they were less reactive than the corresponding 2-amino-3-(2-iodoaryl)-propionates, the reactions of 2-amino-4-(2-iodoaryl)-butanoates proceeded well under the catalysis of CuI and ligand (*R*)-L4,[17] affording the 1,2,3,4-tetrahydroquinoline coupling products and recovering the starting materials in even better enantioselectivities than their one-carbon-shorter couterparts (*s* factors up to 245, Table 3, entries 1−7).[18] It is noteworthy that, in these reactions, the size of R_2 group showed important influence to the efficiency of

(17) The electron-withdrawing $-CF_3$ groups on the aryl rings of the ligand L4 have obvious accelerating effect to the reactions; see ref 10.

(18) The absolute configuration of recovered **3d** was determined by X-ray experiments; see the Supporting Information.

Table 3. Kinetic Resolution of *rac*-2-Amino-4-(2-iodoaryl)-butanoates[a]



3a: R_1 = H, R_2 = -CH_2Ph; **3b:** R_1 = 5-Me, R_2 = -CH_2Ph; **3c:** R_1 = 4-Cl, R_2 = -CH_2Ph
3d: R_1 = H, R_2 = -$CH_2C_6H_4$-4-OMe; **3e:** R_1 = H, R_2 = Me;
3f: R_1 = H, R_2 = *i*-Pr; **3g:** R_1 = H, R_2 = -CH_2CH_2Ph

entry	*rac*-**1**	time (h)	conv[b] (%)	ee of **3** (yield, %)[c]	ee of **4** (yield, %)[c]	*s*
1	**3a**	5	48	89 (50)	95 (45)	165
2	**3b**	36	48	86 (50)	95 (47)	79
3	**3c**	17	48	88 (51)	96 (46)	122
4	**3d**	10	47	85 (49)	97 (50)	129
5	**3e**	27	52	88 (47)	80 (47)	28
6	**3f**	29	53	98 (46)	85 (48)	65
7	**3g**	24	48	90 (50)	96 (46)	245

[a] Reagents and reaction conditions: **3** (0.2 mmol, 1.0 equiv), CuI (0.02 mmol, 10 mol %), L4 (0.024 mmol, 12 mol %), Cs_2CO_3, (0.2 mmol, 1.0 equiv), 1,4-dioxane (1.5 mL), rt. [b] Calculated conversion. [c] Isolated yields are given in parentheses; the enantiomeric excesses were determined by HPLC analysis (Chirapak AD-H or OD-H column).

the kinetic resolutions. As observed, better selectivities were obtained with bulkier R_2 groups (Table 3, entries 1 and 5−7).

Although the mechanistic details are not clear at this point, based on the literature reports[19] and our experimental results, a plausible transition-state model was proposed for the excellent enantioselectivity achieved in our reaction system. As shown in Figure 1, the CuI may coordinate with the racemic substrate and the chiral ligand to form two different tetrahedral Cu^I complexes. Obviously, the aryl C−I bond in the *R* enantiomer of **1** can preferentially interact with the Cu center (TS-1), while the aryl C−I bond in the *S* enantiomer of **1** may suffer with the steric hindrance from the aryl moiety of the chiral ligand (TS-2). Thus, the *R* enantiomer of **1** would react faster than the *S* enantiomer to produce enantiomerically enriched *R* indoline products and recover enantiomerically enriched *S* starting materials in excellent selectivity.

In summary, for the first time, copper-catalyzed *N*-arylation has been successfully applied in the kinetic resolution of the *rac*-2-amino-3-(2-iodoaryl)propionates and *rac*-2-amino-4-(2-iodoaryl)butanoates. Excellent enantioselectivities have been achieved in such a process. The reactions led

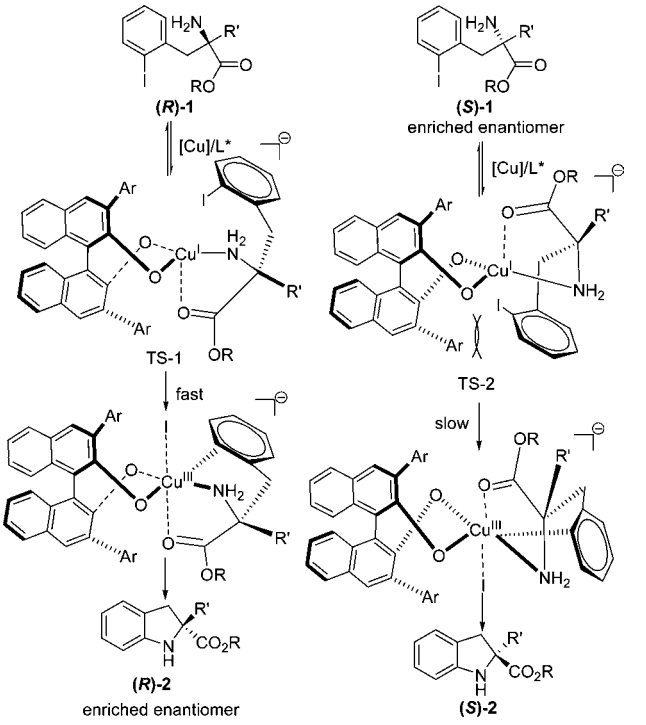


Figure 1. Proposed mechanism for kinetic resolution.

to the formation of the coupled chiral indoline and 1,2,3,4-tetrahydroquinoline products in good yields and high ee values and recovered the starting materials in high ee values. Such a method overcomes some shortcomings in our previous research of asymmetric desymmetric *N*-arylation and provides a more general tool for asymmetric *N*-arylation. Further exploration and applications of this reaction in organic synthesis is underway in our laboratory.

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Supporting Information Available. Full experimental procedures, characterization data for all the compounds, and crystal structure (CIF) of **3d**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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