

Asymmetric Catalysis

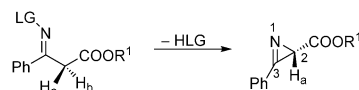
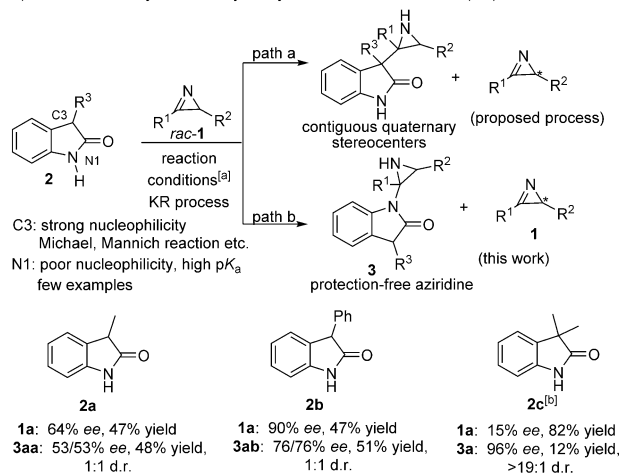
Deutsche Ausgabe: DOI: 10.1002/ange.201605251
Internationale Ausgabe: DOI: 10.1002/anie.201605251Kinetic Resolution of 2*H*-Azirines by Asymmetric Imine Amidation

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Abstract: Highly efficient kinetic resolution of 2*H*-azirines by an asymmetric imine amidation was achieved in the presence of a chiral *N,N'*-dioxide/Sc^{III} complex, thus providing a promising method to obtain the enantioenriched 2*H*-azirine derivatives and protecting-group free aziridines at the same time. It is rare to find an example of N1 of an oxindole participating in a reaction over C3. Moreover, chiral 2*H*-azirines were stereospecifically transformed into an unprotected aziridine and α -amino ketone.

Chiral 2*H*-azirine frameworks are key intermediates in organic synthesis and privileged structural units in a number of natural products and biological compounds.^[1,2] The interest in synthetic methodologies for the preparation of the smallest unsaturated nitrogen-containing heterocyclic compounds has increased in the last decades. So far, 2*H*-azirine can be synthesized by various methods,^[3,4] but their preparation in a catalytic way is lacking. Besides asymmetric Neber reactions,^[4a,d] which are only applicable for the synthesis of 2*H*-azirines bearing an ester at the 2-position (Scheme 1 a), other asymmetric strategies are limited. The ester group is indispensable for the enantiodifferentiation during the abstraction of the methylene protons. And the asymmetric synthesis of 2*H*-azirines with either aryl or alkyl substituents at the 2/3-position, without the ester substituent, remains a challenge. Additionally, aziridines are important building blocks and widely distributed in many natural products.^[5] Despite the many efficient approaches to aziridines, almost all of the reported research to date apply to aziridines which do not always have easily removable N-Ts or N-Boc groups.^[5d] Thus, it is meaningful to develop a catalytic method to atom-economically deliver protecting-group free chiral aziridines.

We envisioned that the possibility for kinetic resolution (KR)^[6,7] of 2*H*-azirines by an enantioselective nucleophilic addition reaction. This strategy could achieve chiral 2*H*-azirines and aziridines simultaneously (Scheme 1 b, path a). The idea was investigated by using oxindole derivatives^[8] as nucleophiles in the presence of *N,N'*-dioxide/scandium(III) complexes.^[9] Surprisingly, we found that the unpredicted imine amidation^[10] product was exclusively obtained rather

a) Asymmetric Neber reaction to deliver 2*H*-azirineb) Chemoselectivity in the catalytic asymmetric kinetic resolution (KR) of 2*H*-azirine

Scheme 1. Methods for the synthesis of chiral 2*H*-azirines. a) Reactions were performed with Sc(OTf)₃/L-RaPr₂ (1:1, 5 mol%), **1a** (0.10 mmol), and **2** (0.10 mmol) in CH₂Cl₂ (1 mL) at 35 °C for 6 h. b) Used 0.5 mL CH₂Cl₂. (**1a**: R¹, R² = Ph). LG = leaving group.

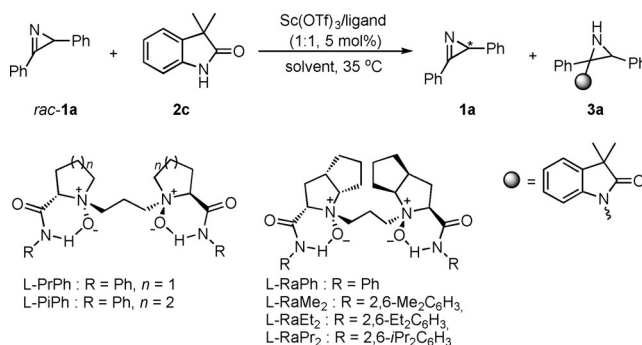
than the expected product arising from reaction at C3 of the oxindole (Scheme 1 b, path b). In general, the C3-position exhibits stronger nucleophilicity compared to the N1 position which has been verified by reactions such as Michael, Mannich, and aldol reactions. For the oxindoles **2a–c**, the nitrogen addition products were exclusively obtained. This phenomenon could be rationalized by the fact potential formation of two contiguous quaternary stereocenters through directly addition at C3 is difficult because of the steric repulsion between the substituents on the carbon center. The diastereoselectivity for the products **3aa** and **3ab** was 1:1 because the C3-position of the oxindole is easily racemized via an enolate intermediate. Therefore, 3,3-dimethylindolin-2-one (**2c**) was selected as the nucleophile to realize the KR process.

Initially, the reaction of 2,3-diphenyl-2*H*-azirine (**1a**) and 3,3-dimethylindolin-2-one (**2c**) were employed in the model reaction to optimize the reaction conditions. Several metal salts coordinating to the chiral *N,N'*-dioxide L-RaPh were tested in CH₂Cl₂ at 35 °C for 6 hours. Only the scandium(III) complex could promote the reaction, though the desired product was obtained with poor results (Table 1, entry 1). Then, a series of ligands were tested (entries 2–6). It was found that the steric hindrance at the amide of the ligand

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Table 1: Optimization of reaction conditions.^[a]

Entry	Ligand	Solvent	1a		3a		<i>s</i> ^[d]
			Yield [%] ^[b]	<i>ee</i> [%] ^[c]	Yield [%] ^[b]	<i>ee</i> [%] ^[c]	
1	L-RaPh	CH ₂ Cl ₂	67	< 5	31	45	–
2	L-RaMe ₂	CH ₂ Cl ₂	83	7	16	37	2
3	L-RaEt ₂	CH ₂ Cl ₂	77	17	20	65	6
4	L-RaPr ₂	CH ₂ Cl ₂	82	15	12	96	57
5	L-PiPr ₂	CH ₂ Cl ₂	90	6	5	70	6
6	L-PrPr ₂	CH ₂ Cl ₂	29	77	62	33	4
7	L-RaPr ₂	Et ₂ O	95	< 5	trace	73	–
8	L-RaPr ₂	THF	15	98	83	20	5
9	L-RaPr ₂	toluene	32	90	67	40	7
10	L-RaPr ₂	toluene/Et ₂ O (v/v, 4:1)	46	95	49	93	103
11 ^[e]	L-RaPr ₂	toluene/Et ₂ O (v/v, 4:1)	49	98	49	94	149
12 ^[f]	L-RaPr ₂	toluene/Et ₂ O (v/v, 4:1)	49	98	50	94	149
13 ^[g]	<i>ent</i> -L-RaPr ₂	toluene/Et ₂ O (v/v, 4:1)	50	–98	50	–94	149

[a] Unless otherwise noted, all reactions were performed with Sc(OTf)₃/ligand (1:1, 5 mol %), **1a** (0.10 mmol), and **2c** (0.10 mmol) in solvent (0.5 mL) at 35 °C for 6 h. [b] Yield of isolated product. [c] Determined by chiral-phase HPLC analysis. [d] Selectivity factors *s*, calculated according to the following equations: $s = \ln[(1-C)(1-ee_1)] / \ln[(1-C)(1+ee_1)]$, $C = (ee_1)/(ee_1 + ee_2)$. [e] The reaction was carried out with **2c** (0.10 mmol), metal/ligand (1:1.2, 5 mol %), **1a** (0.10 mmol), toluene (0.4 mL), Et₂O (0.1 mL) at 35 °C for 5.5 hours. [f] The reaction was performed with 0.5 mol % catalyst for 23 hours. [g] The reaction was run for 5.5 hours. The d.r. value of **3a** was over 19:1 as detected by ¹H NMR spectroscopy. THF = tetrahydrofuran.

affected the enantioselectivities of recovered **1a** and product **3aa**. Improving the steric hindrance from a 2,6-dimethyl to 2,6-diisopropyl group resulted in an increase of the *s* factors from 2 to 57 (entries 2–4). Subsequently, L-pipecolic-acid-derivative L-PiPr₂ and L-proline-derived L-PrPr₂ were investigated (entries 5 and 6), but no better result was obtained. To further improve the reaction results, various solvents were screened. When Et₂O was used (entry 7), the recovered **1a** was obtained in 95 % yield with less than 5 % *ee*. Fortunately, the reaction rate was improved in both THF and toluene in spite of the decrease in the *s* factors (entries 8 and 9). Additionally, when the mixed solvent of Et₂O and toluene (v/v, 1:4) was added, both the *s* value and reactivity were greatly improved (entry 10). Finally, by adjusting the ratio of metal to ligand to 1:1.2, and the *s* factors increased up to 149. The unreacted **1a** was recovered in 49 % yield with 98 % *ee*, and **3a** was formed in 49 % yield with 94 % *ee* (entry 11). Gratifyingly, the catalyst loading could be reduced to 0.5 mol % without affecting the results (entry 12). As expected, *ent*-**1a** and *ent*-**3a** were formed enantioselectively

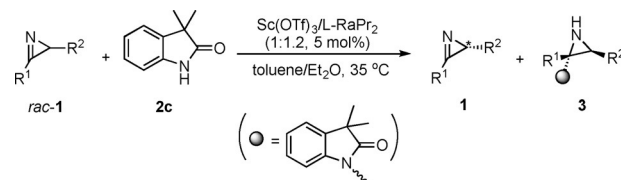
by using *ent*-L-RaPr₂ (entry 13). In all cases, the d.r. value of **3a** was over 19:1.

With the optimized reaction conditions established, various racemic 2*H*-azirines were tested (Table 2). Satisfyingly, 2*H*-azirines containing either electron-withdrawing or electron-donating substituents on the 4-position of the phenyl ring (R¹) were smoothly converted into the corresponding products **3b–h** in good yields and excellent enantioselectivities (entries 2–8). Meanwhile, the unreacted **1b–h** were recovered in yields of 43–52 % with 94–99 % *ee*. Although substituents on the 3/2-position of the phenyl group **1i/1j** and disubstituted **1k** exhibited lower reactivities (entries 9–11), the results were still satisfying after prolonging the reaction time and increasing the catalyst loading to 10 mol %. The compounds **1l** and **1m**, having a fused ring and naphthyl substituent, respectively, also underwent the KR process with the corresponding *s* factors of 354 and 100 (entries 12 and 13). Although alkyl groups on the 3-position of the 2*H*-azirine were compatible (entries 14 and 15), the substrate **1n**, having a methyl group gave low *s* factor. In comparison, **1o**, having a more bulky benzyl substituent resulted in an improved *s* factor of 41. Next, R² was varied (entries 16–20), and the reaction was unbiased

toward electronic properties, as excellent enantioselectivities were obtained for both the desired products **3p–s** (92–95 % *ee*) and the recovered **1p–s** (93–96 % *ee*). The reaction of *rac*-**1t**, having an alkyl group in the 2-position of the 2*H*-azirine, gave the recovered **1t** in 78 % *ee* with 20 % yield. The absolute configuration of the product **3q** was determined to be (2*S*, 3*S*) by X-ray crystallography analysis.^[11]

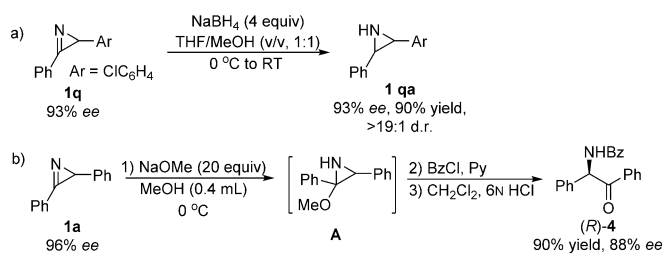
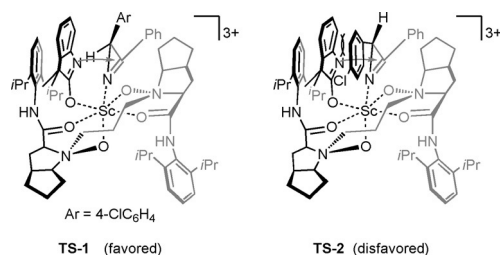
Next, the synthetic potential of the recovered 2*H*-azirines was investigated. In the presence of NaBH₄, **1q** was converted to into the unprotected aziridine **1qa** in 90 % yield with excellent diastereo- and enantioselectivity (Scheme 2a). Additionally, when **1a** was treated with NaOMe, the nucleophilic imine addition delivered the intermediate **A**, which was sequentially protected by BzCl and hydrolyzed with HCl (6*N*, aq.) to give the α-amino ketone **4** (Scheme 2b).

Based on the X-ray structure of the *N,N'*-dioxide/Sc^{III} complex^[9a] and the absolute configuration of the product **3q**, a transition state for the KR process was proposed (Figure 1). In **TS-1**, the oxindole preferentially attacked (*S*)-**1** from the *Re* face of the 2*H*-azirine via imine formation

Table 2: Substrate scope for kinetic resolution of 2*H*-azirines.^[a]


Entry	R ¹	R ²	t [h]	Conv [%] ^[d]	Yield [%] ^[b]	1 a	ee [%] ^[c]	Yield [%] ^[b]	3 a	ee [%] ^[c]	s ^[d]
1	Ph	Ph	5.5	51	49 (1 a)		98	50 (3 a)		94	149
2	4-FC ₆ H ₄	Ph	7.0	52	47 (1 b)		99	53 (3 b)		93	145
3	4-ClC ₆ H ₄	Ph	4.5	52	45 (1 c)		97	53 (3 c)		90	80
4	4-BrC ₆ H ₄	Ph	3.0	52	43 (1 d)		97	52 (3 d)		91	89
5	4-CF ₃ C ₆ H ₄	Ph	2.5	54	50 (1 e)		94	47 (3 e)		81	33
6	4-C ₆ H ₅ C ₆ H ₄	Ph	4.5	52	50 (1 f)		96	47 (3 f)		90	74
7	4-MeOC ₆ H ₄	Ph	5.5	49	52 (1 g)		96	46 (3 g)		99	790
8	4-MeC ₆ H ₄	Ph	7.0	51	50 (1 h)		97	48 (3 h)		95	165
9	3-MeC ₆ H ₄	Ph	12.0	51	47 (1 i)		98	51 (3 i)		96	226
10 ^[e]	2-MeC ₆ H ₄	Ph	168.0	37	65 (1 j)		57	30 (3 j)		99	355
11 ^[e]	3,5-Me ₂ C ₆ H ₃	Ph	72.0	55	47 (1 k)		93	49 (3 k)		76	24
12		Ph	7.0	49	43 (1 l)		94	47 (3 l)		98	354
13	2-naphthyl	Ph	9.0	51	44 (1 m)		97	56 (3 m)		92	100
14 ^[f]	Me	Ph	1.0	71	19 (1 n)		64	60 (3 n)		30	3
15	C ₆ H ₅ CH ₂	Ph	0.6	56	44 (1 o)		> 99	55 (3 o)		78	41
16	Ph	4-FC ₆ H ₄	5.0	49	55 (1 p)		93	40 (3 p)		95	133
17 ^[g]	Ph	4-ClC ₆ H ₄	5.5	49	54 (1 q)		92	44 (3 q)		94 (<i>S,S</i>)	106
18	Ph	4-MeC ₆ H ₄	9.5	50	50 (1 r)		95	47 (3 r)		95	146
19	Ph	4-MeO ₂ C ₆ H ₄	5.5	51	48 (1 s)		96	52 (3 s)		92	94
20	Ph	C ₆ H ₄ CH ₂ CH ₂	17.0	76	20 (1 t)		78	67 (3 t)		25	4

[a] The reactions were carried out with **2** (0.10 mmol), metal/ligand (1:1.2, 5 mol%) in CH₂Cl₂ (0.5 mL) at 35 °C for 0.5 h, then CH₂Cl₂ was removed. And **1** (0.10 mmol) and solvent (0.5 mL) were added. [b] Yield of isolated product. [c] Determined by chiral-phase HPLC analysis. [d] Selectivity factors *s*, calculated according to the following equations: $s = \ln[(1-C)(1-ee_1)] / \ln[(1-C)(1+ee_1)]$, $C = (ee_1)/(ee_1 + ee_2)$. [e] 10 mol% catalyst was used. [f] The reaction was carried out at 0 °C. [g] The configuration of **3 q** was determined by X-ray crystallography analysis. The d.r. values of **3** were all over 19:1 as detected by ¹H NMR spectroscopy.

**Scheme 2.** Transformations of 2*H*-azirines. Bz = benzoyl.**Figure 1.** Proposed transition state.

because of the reduced steric bulk, thus delivering the corresponding *S,S*-configured product **3**, and is in accordance with the observed experiment result. The (*R*)-**1** is disfavored since there is steric repulsion between the phenyl group of the 2*H*-azirine and oxindole.

In summary, we have presented the first kinetic resolution of 2*H*-azirines by an asymmetric imine amidation under mild reaction conditions, thus achieving selectivity factors of up to 790. A series of chiral 2*H*-azirines and protecting-group free aziridines were formed with excellent results (up to > 99% *ee* and 99% *ee*, > 19:1 d.r.). Meanwhile, this is the first example of N1 of oxindole participating in a reaction instead of C3. Further studies on 2*H*-azirines and aziridines are under way.

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Keywords: asymmetric catalysis · enantioselectivity · heterocycles · kinetic resolution · scandium

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- [11] CCDC 1480937 (**3q**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. For more data see the Supporting Information.

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