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Asymmetric Strecker reactions catalyzed by thiourea phosphonium and ammonium salts

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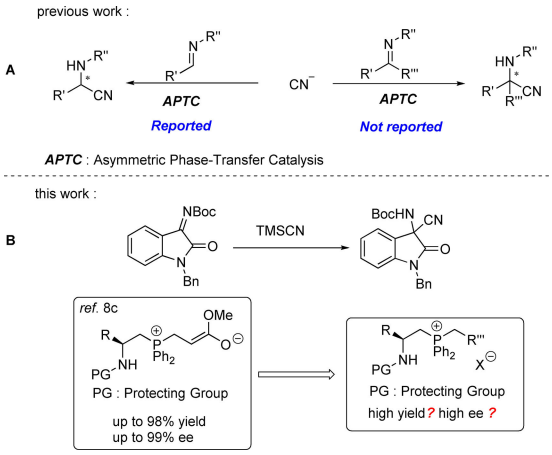
Abstract: The application of asymmetric phase-transfer catalysis to the Strecker reaction of ketimines was realized utilizing bifunctional thiourea-phosphonium salts. The asymmetric Strecker reaction of aldimines was also realized utilizing quaternary ammonium salts derived from amino acids.

Keywords: Thiourea-phosphonium salt; Thiourea-ammonium salt; Strecker reaction; Asymmetric catalysis; Phase-transfer catalysis

Since its discovery in 1850, the Strecker reaction has become an important method for building new C–C bonds, which is especially useful for synthesizing natural and unnatural amino acids.[1] In the realm of the asymmetric Strecker reaction, compared to aldimines,[2] ketimines are less electrophilic than aldimines. Therefore, it is more challenging to achieve excellent enantiocontrol in catalyzing the addition of cyanide reagents to ketimines, which involves the construction of chiral quaternary stereocenters.

Recently, some impressive advances have been accomplished in the asymmetric Strecker reaction with ketimines catalyzed by both metal catalysts[3] and organocatalysts.[4] However, asymmetric phase-transfer catalysis (APTC), which is an important catalytic strategy that has been largely applied to various fields of organic reactions because of its mild reaction conditions and environmentally benign experimental procedures,[5] has only been successfully applied to catalyze the Strecker reaction of aldimines with great efficiency.[6] To the best of our knowledge, there has been no report on the application of asymmetric phase-transfer catalysis to the reaction of ketimines(-Scheme 1A).



Scheme 1. Asymmetric cyanation of imines.

Chiral betaine catalysts have evolved as effective organocatalysts,[7] which have been demonstrated to be efficient in a series of asymmetric organic reactions. In addition, our group has successfully applied chiral phosphonium betaine catalysts to asymmetric Mannich, aza-Henry and Strecker reactions with excellent enantioselectivities and yields, in particular, this family of catalysts was shown toefficiently catalyze the asymmetric cyanation of the ketimines derived from isatins (Scheme 1B).[8] Inspired by these works, we

wondered if the highly modular structures of the bifunctional phosphonium salts as phase-transfer catalysts derived from amino acids could catalyze asymmetric Strecker reactions with ketimines. Although there are some structural similarities between the chiral phosphonium betaine and the phosphonium salt, they have displayed completely different catalytic effects in our previous work,[8a] which gives us a challenging topic for this ongoing project.

Notably, since the first work with thiourea containing ammonium salts was reported by Fernandez and Lassaletta,[9] a new series of (thio)urea(or squaramide)-phosphonium (ammonium) salts as highly efficient catalysts for various asymmetric organic reactions have been realized.[10] Herein, we describe the first application of chiral phase-transfer catalysts derived from amino acids to the Strecker reaction of ketimines.

Oxindole is an important skeleton occurring in numerous natural and biologically active compounds.-Therefore, asymmetric catalysis centered on this structure has received much attention, with many impressive accomplishments.[11] Moreover, the asymmetric addition reactions of ketimines derived from isatins conveniently allow for the preparation of various synthetically useful chiral quaternary stereocenters on the oxindole.[12] Therefore, we report that chiral amino acid-based thiourea-phosphonium salts (Figure 1) are highly efficient catalysts for the asymmetric Strecker reaction of isatin-derived ketimines.

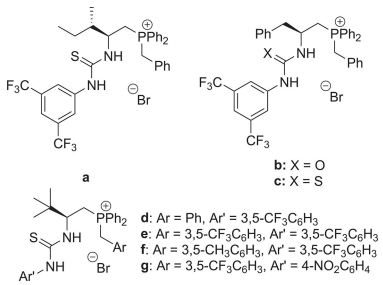
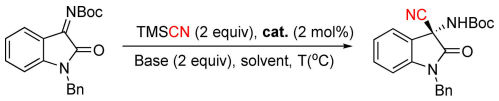


Figure 1. Chiral thiourea-phosphonium salts used in this study.

Initially, the reaction between N-Boc ketimine **1a** and TMSCN was selected as the model reaction for optimizing reaction conditions (Table 1). First, catalysts **a**–**d** based on different amino acid skeletons were examined in CH_2Cl_2 at 20 °C, and it was found that catalyst **d** derived from *tert*-butyl *L*-leucine was the most promising, giving 54% ee (Table 1, entry 4). Of note is the exceptionally short reaction time (1 min) required for this PTC system, which is in sharp contrast to the cinchona-thiourea system that usually requires 2–4 days.[13] Further modification of the structure of **d**, including varying the substituents on both the thiourea and phosphonium center, furnished a superior catalyst **e** (67% ee, Table 1, entry 5). Subsequent investigation of the effects of solvent and base with this catalyst revealed that a higher enantiocontrol could be obtained in $CHCl_3$ using NaOAc as the base (Table 1, entry 8). Pleasingly, lowering the reaction temperature to −40 °C improved the enantioselectivity significantly to give the highest ee of 91% with almost quantitative yield, albeit with a prolonged reaction time of 1 h (Table 1, entry 17).

Table 1. Optimization of the asymmetric Strecker reaction of ketimine **1a** under phase-transfer conditions.[a]



1a 2a

Entry	cat.	Solvent	Base	T(°C)	Yield[b] (%)	ee[c] (%)
1	**a**	CH_2Cl_2	NaOAc	20	98	38
2	**b**	CH_2Cl_2	NaOAc	–	98	20
3	**c**	CH_2Cl_2	NaOAc	–	99	22
4	**d**	CH_2Cl_2	NaOAc	–	98	54
5	**e**	CH_2Cl_2	NaOAc	–	98	67
6	**f**	CH_2Cl_2	NaOAc	–	99	49
7	**g**	CH_2Cl_2	NaOAc	–	98	62
8	**e**	$CHCl_3$	NaOAc	–	99	75
9	**e**	DCE	NaOAc	–	98	57
10	**e**	Toluene	NaOAc	–	98	55
11	**e**	TBME	NaOAc	–	97	39
12	**e**	$CHCl_3$	KOAc	–	99	72
13	**e**	$CHCl_3$	Na_2CO_3	–	99	71
14	**e**	$CHCl_3$	K_2CO_3	–	99	71
15[d]	**e**	$CHCl_3$	NaOAc	−10	98	85
16[e]	**e**	$CHCl_3$	NaOAc	−20	99	89
17[f]	**e**	$CHCl_3$	NaOAc	−40	98	91
18[g]	**e**	$CHCl_3$	NaOAc	−40	97	90

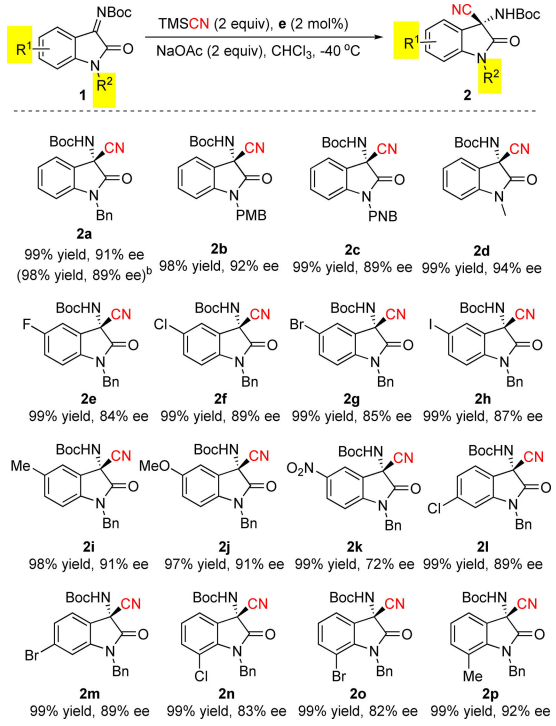
[a] Unless otherwise noted, all the reactions were carried out with **1a** (0.1 mmol), TMSCN (0.2 mmol) and base (0.2 mmol) in solvent (1 mL) in the presence of a catalyst (2 mol%) for 1 min.
[b] Isolated yield.
[c] Determined by HPLC analysis.
[d] The reaction was carried out for 5 min.
[e] The reaction was carried out for 10 min.
[f] The reaction was carried out for 1 h.
[g] The reaction was carried out with **1a**(0.1 mmol), TMSCN (0.2 mmol) and NaOAc (0.2 mmol) in $CHCl_3$(5 mL) in the presence of **e**(2 mol%) for 1 h.

The effect of dilution on this reaction was also explored, which exhibited a strong effect on the enantioselectivity in previous work reported by Waser and co-workers,[10k] however, no palpable difference was observed in the diluted solution (Table 1, entry 18). We also meticulously explored the influences of

the conditions of the reaction, such as TMSCN concentration, NaOAc concentration, catalyst loading and temperature (see *Supporting Information* for more details). From these tables, we found that lowering the temperature improved the enantioselectivity, while increasing the NaOAc concentration decreased the enantiocontrol. When we surveyed the concentration of the reagent TMSCN, no influence was detected. To our delight, we were able to lower the catalyst loading to 2 mol% to achieve the same enantioselectivity, but a modest enantioselectivity (75% ee) was found when 0.5 mol% **e** was loaded.

Under the optimized conditions, the substrate scope of the reaction was investigated with different ketimines (Table 2). Changing the N-protecting group benzyl in **1a** to substituted-benzyl groups bearing electron-withdrawing or electron-donating groups or a methyl group did not show any apparentchanges in either the yield or ee value. To our delight, various substituents on the benzene ring of the isatin skeleton of the ketimines were well tolerated in the reaction to

Table 2. Scope of the reaction of ketimines.[a]



[a] The reactions were carried out with **1**(0.1 mmol), TMSCN (0.2 mmol) and NaOAc(0.2 mmol) in $CHCl_3$(1 mL) catalyzed by **e** (2 mol%) at −40 °C for 1 h, the absolute configurations of **2** were determined by comparison of the optical rotation values with literature data[13a].

[b] The reaction was performed with **1a**(30 mmol), TMSCN (60 mmol) and NaOAc (60 mmol) in $CHCl_3$(100 mL) catalyzed by **e** (2 mol%) at −40 °C for 12 h.PMB:*p*-$MeOC_6H_4$, PNB:*p*-$NO_2C_6H_4$.

achieve comparable results irrespective of their electronic nature or positions, except for substrate **1k** with a strongly electron-withdrawing NO_2 group that likely resulted in better reactivity of this substrate enabling more non-catalytic background cyanation. Notably, this reaction was also performed on a gram scale in the presence of 2 mol% of the bifunctional catalyst **e** to provide almost quantitative yield, however, a slightly decreased enantioselectivity was obtained (89% ee) together with prolonged reaction time (12 h).

To obtain some insight into the mechanism, we explored the influences of the bifunctional catalyst on control experiments (Table 3). When we performed the asymmetric reaction catalyzed by **h**, which lacks the quaternary phosphonium center, we obtained a low yield, long reaction time and racemic product. Similarly, the use of catalyst **j**, with one blocked H-bonding site, also gave inferior results with low yield and long reaction time, but with a 50% ee, which suggested that the H-bond is not crucial for the enantioselectivity. However, the bifunctional catalyst **i** gave 55% ee and 99% yield in 1 h at the same conditions. We also performed some NMR experiments as a mechanistic study (see *SI*, Figure S1).The acidic hydrogen could be extracted by the basic NaOAc. If KCN as cyanide source was added to the reaction system under the optimized conditions, almost no product was obtained, even when stirring for a long time, which all illustrated the importance of TMSCN as the cyanide source. Therefore, according to the experimental results and previous work,[14] we propose a plausible reaction pathway as shown in Scheme 2. Firstly the catalyst reacts with the basic NaOAc, then the newly generated betain **i′** will activate TMSCN to form the actual catalyst **i**“, which then induces the asymmetric Strecker reaction. We also propose a possible transition state according to the results. The hydrogen-bonding interaction between the N–H and the ketimine strengthens the electrophilic capacity of the ketimine.The CN^-anion and the quaternary phosphonium center constitutes a nucleophile-phosphonium ion pair.The backbone of the catalyst blocks the *Si* face and makes the approach of the nucleophile from the *Re* face more favorable.

Next, in order to expand the scope of the application of the phase-transfer catalysts derived from amino acids, we continued to explore the asymmetric Strecker reaction of aldimines.[6] Based on our previous and above work, we speculated that the novel phase-transfer catalysts derived from amino acids may be applicable for N-Boc protected aldimines. However, when the thiourea-phosphonium salt was used, poor results were obtained. To our delight, we found that the N-Boc protected aldimines could be efficiently catalyzed by the quaternary ammonium salt **k** (for more details, see *SI*).

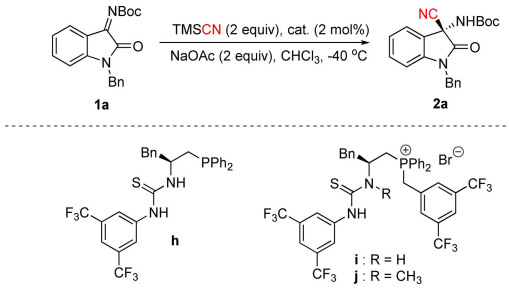
According to previous work and our work,[10j,15] we supposed that the narrower space around the ammonium center than around the phosphonium center may be beneficial to control the stereoselectivity of the asymmetric cyanation of aldimine. In addition, the scope of the reaction is shown in Table 4. N-Boc imines with electron-donating and sterically different aromatic groups, except for the aliphatic group, were all well tolerated to provide the products in excellent yields and enantioselectivities. The imines with electron-withdrawing groups also gave good enantioselectivities and excellent yields.

In summary, we have realized the first application of asymmetric phase-transfer catalysis to the enantioselective addition of TMSCN to ketimines derived from isatins.The asymmetric Strecker reaction of the aldimines was also realized for the first time utilizing a quaternary ammonium salt derived from an amino acid. The novel thiourea-phosphonium (ammonium) salts demonstrated high efficiency in catalyzing the asymmetric reactions in excellent yields and high enantioselectivities within short reaction times. Further investigation of the mechanism of the asymmetric reaction andextension of the application scope of these thiourea-phosphonium(ammonium) salts are underway in our laboratory.

Experimental Section

General procedure for the asymmetric reactions of TMSCN to ketimines: To a vial containing catalyst **e** (2 mol%), a solution of ketimine (0.1 mmol) and NaOAc (5 equiv) in CH_2Cl_2 (1 mL) was added, and TMSCN (0.2 mmol) was added at −40 °C. The mixture was stirred until the reaction was completed (monitored by TLC), and then, the crude product was purified by column chromatography on silica gel to afford product **2**.

Table 3. Control experiments for the mechanistic study.[a]



Entry	cat.	Time	Yield(%)[b]	ee(%)[c]
1	**h**	24 h	40	2
2	**i**	1 h	99	55
3	**j**	24 h	20	50

[a] The reactions were carried out with **1a** (0.1 mmol), TMSCN (0.2 mmol), NaOAc (0.2 mmol) and the catalyst (2 mol%) in $CHCl_3$ at −40 °C. [b] Isolated yield. [c] Determined by HPLC.

General procedure for the asymmetric reactions of TMSCN to aldimines: To a vial containing catalyst **k** (3 mol%), a solution of aldimine (0.1 mmol) and NaOAc (5 equiv) in CH_2Cl_2 (1 mL) was added, and TMSCN (0.2 mmol) was added at −45 °C. The mixture was stirred until the reaction was completed (monitored by TLC), and then, the crude product was purified by column chromatography on silica gel to afford product **4**.

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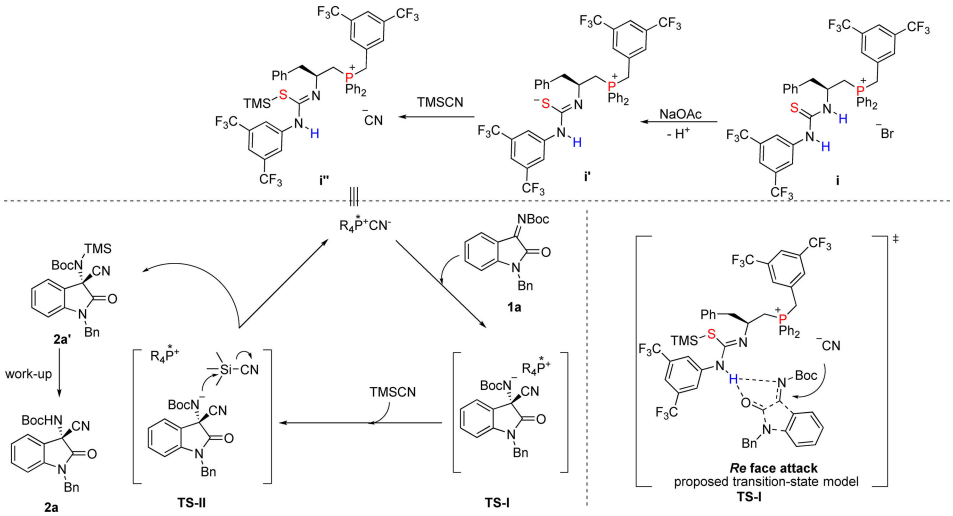
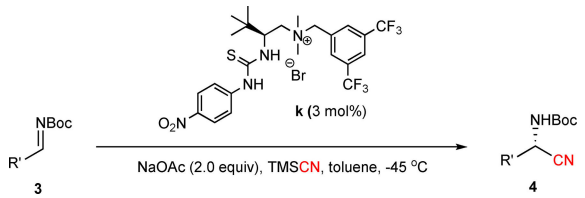


Scheme 2. Plausible reaction pathway.

Table 4. Asymmetric Strecker reactions of aldimines catalyzed by the quaternary ammonium salt.[a]



Entry	4	Ar	Yield (%)[b]	ee (%)[c]
1	**4a**	C_6H_5	90	85
2	**4b**	*p*-$MeOC_6H_4$	90	85
3	**4c**	*p*-FC_6H_4	93	75
4	**4d**	*m*-MeC_6H_4	90	87
5	**4e**	*m*-$MeOC_6H_4$	86	87
6	**4f**	*o*-$MeOC_6H_4$	89	82
7	**4g**	2-thiophyl	92	87
8	**4h**	α-naphthyl	90	92
9	**4i**	cyclohexyl	92	53[d]

[a] Unless other noted, the reactions were carried out with **3** (0.1 mmol), NaOAc (0.2 mmol) and TMSCN (0.2 mmol) catalyzed by **k** (3 mol%) in toluene (1 mL) at −45 °C for 24 h, the absolute configurations of **4** were determined by comparison of the optical rotation values with literature data.[6d]
[b] The isolated yield.
[c] Determined by HPLC analysis.
[d] Determined by the derivatization of **4i**, see *SI*.

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COMMUNICATIONS

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