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Enantioselective synthesis of pyrazolone α-aminonitrile derivatives via an organocatalytic Strecker reaction

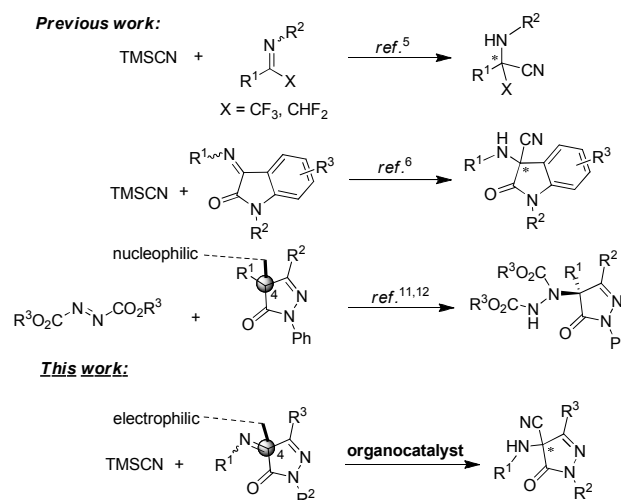Suruchi Mahajan,[†a] Pankaj Chauhan,[† a] Uğur Kaya,[a] Kristina Deckers,[a] Kari Rissanen[b] and Dieter Enders*[a]

A new organocatalytic enantioselective Strecker reaction of pyrazolone-derived ketimine electrophiles has been developed. Using pseudo-enantiomeric squaramide catalysts the nucleophilic 1,2-addition of trimethylsilyl cyanide to the ketimines efficiently provides a direct entry to both enantiomers of pyrazolone α-aminonitrile derivatives at will in good yields and high enantioselectivities for a wide variety of substrates.

The Strecker reaction is the oldest known method for the synthesis of α-amino nitriles, which are eventually utilized for the synthesis of natural and synthetic α-amino acids as well as other bioactive compounds including natural products.[1] The first example of a catalytic asymmetric Strecker reaction was published around two decades ago in 1996,[2] and since then a number of enantioselective methods employing chiral transition metal and organo-catalysts have been developed. Due to their high reactivity, a special emphasis was laid on the nucleophilic cyanation of aldimines to afford highly enantiomerically enriched α-amino nitriles.[3] Despite the significant progress in catalytic asymmetric Strecker reactions, the corresponding processes that utilize the ketimines as substrates are considered comparably more difficult and hence are less explored.[4] Therefore, the design and development of more reactive ketimines is of high interest. In this context, the ketimines derived from fluoromethylated ketones and isatin derivatives have been recently developed and also utilized in the catalytic asymmetric Strecker reaction (Scheme 1). These transformations lead to the formation of tetrasubstituted fluorinated[5] and oxindole-based amino nitriles[6]. In general, the ketimines derived from oxindoles have been widely explored in various asymmetric transformations.[7] Hence, we anticipated that the design of new ketimine substrates with a heterocyclic core will open new possibilities in asymmetric synthesis.

Like oxindoles, the pyrazolones are very important and interesting heterocyclic scaffolds for chemical modifications and biological evaluations. These 1,2-azoles have been known for more than a century and possess a broad spectrum of applications in dyes, analytical and pharmaceutical chemistry.[8] Due to the synthetic and biological significance of pyrazolones, a rapid progress has been noticed in the last few years, especially in catalytic asymmetric synthesis to obtain new potentially bioactive and virtually enantiopure pyrazolone derivatives.[9] Most of these methods utilized the known reactivity of pyrazolin-5-one derivatives, especially the C-4 nucleophilicity.[9,10] In this context, the groups of Feng[11] and Rios[12] reported the enantioselective α-amination of 4-substituted pyrazolones to afford the amino-pyrazolone derivatives using a chiral transition metal complex and an organocatalyst. To the best of our knowledge, the enantioselective nucleophilic addition to the C-4 position of pyrazolones is not known, hence we envisaged that the imines derived from the pyrazolin-5-ones can undergo a 1,2-addition reaction to afford the amino-pyrazolones bearing a tetra-substituted stereocenter.

Owing to the wide array of applications of pyrazolones and in view of the synthetic importance of the asymmetric Strecker

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Scheme 1 Organocatalytic enantioselective Strecker reactions with ketimines and the synthesis of tetrasubstituted α-amino pyrazolone derivatives.
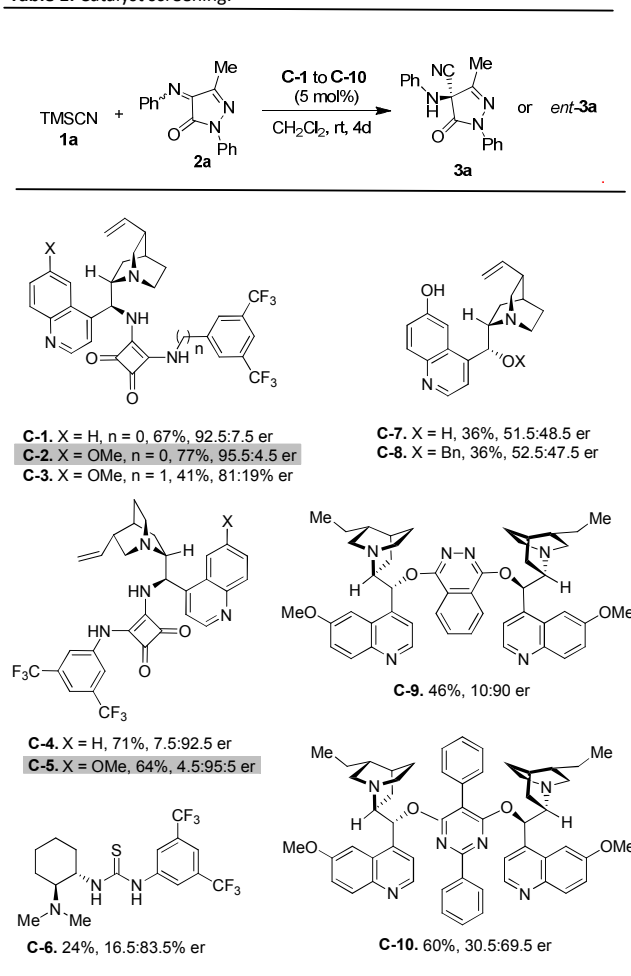
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reaction, we herein report a new organocatalytic enantioselective Strecker synthesis of pyrazolone α-amino nitrile derivatives employing pyrazolone derived ketimines as electrophiles.

In order to achieve this goal, we started the optimization studies by screening various bifunctional organocatalysts for the reaction of TMSCN (**1a**) with a pyrazolone-derived ketimine **2a** in dichloromethane as solvent at room temperature. Initially the reactions were carried out with 5 mol% of squarmides[13] (**C-1** to **C-5**) derived from cinchona alkaloids. The squaramides **C-1** and **C-2** where the squaramide unit is directly attached to an aryl group provided better yields and enantioselectivities of the desired product **3a** than the catalyst **C-3** bearing a benzylic group. The squaramide catalysts derived from the quinine **C-2** and quinidine **C-5** resulted in good yields and best er-values of **3a** and its enantiomer *ent*-**3a**, respectively. The other bifunctional hydrogen bonding catalysts, such as thiourea **C-6** and cupreine derivatives **C-7** and **C-8**, failed to provide better yields and enantioselectivities of **3a** than the squaramide catalysts. The cinchona alkaloid dimers **C-9** and **C-10** were also tested, but these catalysts only provide moderate yields and lower er-values.

Table 1. Catalyst screening.

C-1. X = H, n = 0, 67%, 92.5:7.5 er
C-2. X = OMe, n = 0, 77%, 95.5:4.5 er
C-3. X = OMe, n = 1, 41%, 81:19% er

C-7. X = H, 36%, 51.5:48.5 er
C-8. X = Bn, 36%, 52.5:47.5 er

C-4. X = H, 71%, 7.5:92.5 er
C-5. X = OMe, 64%, 4.5:95:5 er

C-9. 46%, 10:90 er

C-6. 24%, 16.5:83.5% er

C-10. 60%, 30.5:69.5 er

Reaction conditions: 0.3 mmol of **1a**, 0.2 mmol **2a**, 5 mol% of **C-1** to **C-10** in 1.0 mL of dichloromethane.

In order to further improve the yield and enantioselectivity of α-amino nitrile **3a**, further optimizations were carried out by screening different solvents (Table 2, entries 1-9). The solvent

screening revealed that the dichloroethane provided the best yield of 83% with an er-value of 96:4 (entry 2). It is well established in the literature that protic solvents as an additive lead to the improvement of the yield and enantioselectivity in the enantioselective Strecker reaction.[6b,7a-b,14] Hence, different protic solvents such as isopropanol, trifluoroethanol, hexafluoroisopropanol and water were tested as additives (entries 10-13), however, no improvement in enantioselectivity was observed. Furthermore, varying the catalyst loading did not lead to any improvement of yield and er-value of **3a** (entries 14-15). However, a lowering of the reaction concentration gave a better yield of 88% without affecting the enantioselectivity of **3a** (entry 16).

Table 2. Optimization of the reaction conditions.[a]

Entry	1	Solvent	Yield (%)[b]	er[c]
1	**1a**	CH_2Cl_2	77	95.4.5
2	**1a**	$ClCH_2CH_2Cl$	83	96:4
3	**1a**	$CHCl_3$	71	96:4
4	**1a**	Toluene	59	90.5:9.5
5	**1a**	Xylene	60	90:10
6	**1a**	Et_2O	46	76:24
7	**1a**	THF	55	84.5:15.5
8	**1a**	EtOH	40	64.5:35.5
9	**1a**	*i*-PrOH	28	69:31
10[d]	**1a**	$ClCH_2CH_2Cl$	77	95.5:4.5
11[e]	**1a**	$ClCH_2CH_2Cl$	79	96:4
12[f]	**1a**	$ClCH_2CH_2Cl$	83	96:4
13[g]	**1a**	$ClCH_2CH_2Cl$	69	95.4.5
14[h]	**1a**	$ClCH_2CH_2Cl$	84	93.5:6.5
15[i]	**1a**	$ClCH_2CH_2Cl$	88	90.5:9.5
16[j]	**1a**	$ClCH_2CH_2Cl$	88	95.4.5
17	**1b**	$ClCH_2CH_2Cl$	60	93:7
18	**1c**	$ClCH_2CH_2Cl$	traces	ND
19	**1d**	$ClCH_2CH_2Cl$	traces	ND
20[k]	**1a**	$ClCH_2CH_2Cl$	83	55:45

[a] Reaction conditions: 0.3 mmol of **1**, 0.2 mmol **2a**, 5 mol% of **C-2** in 1.0 mL of solvent. [b] Yield of isolated product **3a** after column chromatography. [c] The enantioselectivity was determined by HPLC analysis on a chiral stationary phase. [d] 0.2 mmol of *i*-PrOH was used. [e] 0.2 mmol of trifluoroethanol was used. [f] 0.2 mmol of hexafluoroisopropanol was used. [g] 0.2 mmol of water was used. [h] 2.5 mol% of catalyst was used. [i] 10 mol% of catalyst was used. [j] 3 mL of solvent was used. [k] An *N*-Boc ketimine **2b** was used and the reaction was carried out for 3 days.

Other nitrile donors were also tested for the organocatalytic Strecker reaction of pyrazolone imines (entries 17-19). It turned out that ethyl cyanoformate (**1b**) resulted in the formation of 60% of α-amino nitrile **3a** with 93:7 er-value (entry 17), however, acetyl cyanide (**1c**) and diethyl cyanophosphonate (**1d**) turned out to be

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unreactive under the standard reaction conditions (entries 18-19). Under the optimized reaction conditions an N-Boc ketimine **2b** resulted in very good yield of **3b** with a faster reaction rate, albeit with a poor er-value (entry 20).

In the next stage, the substrate scope and limitations of the optimized Strecker reaction have been evaluated at 0.3 mmol scale (Table 3). Initially, the effect of the N-aryl groups (R^1) was tested. It was observed that the aryl groups bearing electron-withdrawing and electron-donating substituents at different positions led to the formation of the desired products **3c-g** with high er-values, except in the case of 4-CF_3 substituent, where only a moderate er was observed. The electron-donating aryl groups showed lower reactivity, and hence gave a lower yield of the corresponding products. A reason of the lower yield of **3g** as compared to **3f** may be steric hindrance caused by the *ortho*-methyl substituent to the

incoming cyanide nucleophile. The ketimines with different N-aryl groups (R^2) on the pyrazolone nitrogen were also well tolerated to provide very good yields and enantioselectivities of the pyrazolone products **3h-j**. An N-alkyl pyrazolone imine was also used under the standard reaction conditions and it was found out that the reaction was faster than the imines bearing aryl substituents, thus leading to the formation of amino nitrile **3k** in good yield after 3 days with high enantioselectivity. At last, the variation of the substituents (R^3) at the C-3 position of the pyrazolone imines has been evaluated. It turned out that with an increase in the steric bulk of the R^3 alkyl group, an improvement in the enantioselectivity of **3l-n** was observed with a gradual decline in the product yield. A t-Bu at this position, however didn't provide any product whereas a phenyl group was found to be less reactive to give **3p** in good enantioselectivity, albeit in a poor yield.
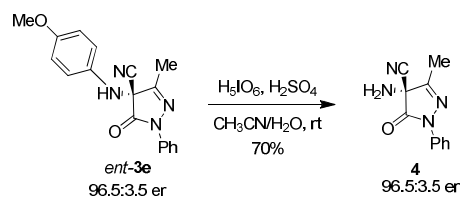
The substrate scope and the limitation were also evaluated with the *pseudo*-enantiomeric squaramide catalyst **C-5** (Table 3). The enantiomeric products *ent-***3** were synthesized without much effect on the yield and stereochemical outcome of the transformation.

Deprotection of the N-aryl group (4-$MeOC_6H_4$) was also carried with periodic acid and sulfuric acid to afford free amino nitrile product **4** without affecting the er-value (Scheme 2).

Table 3. Substrate scope with catalyst **C-2** and **C-5**.[a]

3	2	Yield (%)[b]	er[c]
a	R^1 = Ph, R^2 = Ph, R^3 = Me (**2a**)	90	95.5:4.5
ent-a		86	94:4
c	R^1 = 4-FC_6H_4, R^2 = Ph, R^3 = Me (**2c**)	75	97:3
ent-c		69	97:3
d	R^1 = 4-ClC_6H_4, R^2 = Ph, R^3 = Me (**2d**)	80	94.5:5.5
ent-d		79	94.5:5.5
e	R^1 = 4-$CF_3C_6H_4$, R^2 = Ph, R^3 = Me (**2e**)	82	84.5:15.5
ent-e		80	89:11
f	R^1 = 4-$MeOC_6H_4$, R^2 = Ph, R^3 = Me (**2f**)	60	97.5:2.5
ent-f		59	96.5:3.5
g	R^1 = 2-MeC_6H_4, R^2 = Ph, R^3 = Me (**2g**)	38	93.5:6.5
ent-g		37	92:8
h	R^1 = Ph, R^2 = 4-ClC_6H_4, R^3 = Me (**2h**)	78	95.7:2.5
ent-h		78	97:3
i	R^1 = Ph, R^2 = 2-ClC_6H_4, R^3 = Me (**2i**)	87	97:3
ent-i		87	95.5:4.5
j	R^1 = Ph, R^2 = 4-MeC_6H_4, R^3 = Me (**2j**)	79	97:3
ent-j		75	96:4
k	R^1 = Ph, R^2 = Me, R^3 = Me (**2k**)	92[d]	96.5:3.5
ent-k		92[d]	97.5:2.5
l	R^1 = Ph, R^2 = Ph, R^3 = Et (**2l**)	81	96.5:3.5
ent-l		79	95.5:4.5
m	R^1 = Ph, R^2 = Ph, R^3 = n-Pr (**2m**)	75	98:2
ent-m		74	98:2
n	R^1 = Ph, R^2 = Ph, R^3 = i-Pr (**2n**)	56	98.5:1.5
ent-n		54	98.5:1.5
o	R^1 = Ph, R^2 = Ph, R^3 = t-Bu (**2o**)	-	-
ent-o		-	-
p	R^1 = Ph, R^2 = Ph, R^3 = Ph (**2p**)	14	95.5:4.5
ent-p		13	95.5:4.5

[a] Reaction conditions: 0.3 mmol of **1a**, 0.45 mmol of pyrazolone imines **2**, 5 mol% of catalyst **C-2** or **C-5** in 4.5 mL of dichloroethane. [b] Yield of isolated products **3** after column chromatography. [c] Enantioselectivity was determined by HPLC analysis on a chiral stationary phase. [d] Yield after 3 days.

Scheme 2. Synthesis of α-amino nitrile product **4**.

The absolute configuration of the products **3a-p** synthesized with catalyst **C-2** could be assigned to be (R) in analogy with the X-ray crystal structure of the product **3h** (Figure 1).[15]
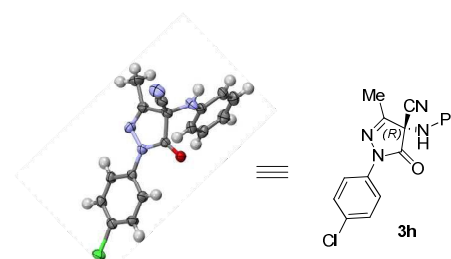
Fig. 1 Determination of the absolute configuration by X-ray crystal structure analysis of **3h**.

By knowing the absolute configuration, we could also propose the possible transition state for the enantioselective Strecker reaction of the pyrazolone ketimine (Scheme 3). It is postulated that HCN (generated from TMSCN and traces of water present in the solvent), gets deprotonated by the tertiary amine of the catalyst.[5c] Simultaneously, the imine is activated by H-bonding with the squaramide moiety to undergo a *Re*-face attack of the cyanide anion to afford the (R)-enantiomer of the product.

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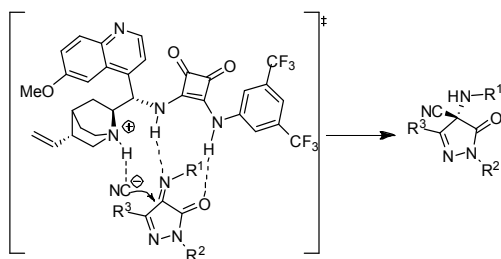
Scheme 3 Proposed transition state for the enantioselective Strecker reaction of pyrazolone-derived ketimines.

In summary, we have developed an organocatalytic enantioselective Strecker reaction employing a series of new pyrazolone ketimines as substrates. In the presence of pseudo-enantiomeric squaramide organocatalysts, both enantiomers of the corresponding α-amino nitrile pyrazolone derivatives bearing a tetrasubstituted stereocenter have been synthesized in moderate to good yields and good to excellent level of enantioselectivities. Further applications of pyrazolone ketimines in asymmetric transformation are currently under investigation in our laboratory.

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15   CCDC 1542055 (**3h**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.