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# **Enantioselective Synthesis of** *cis*-4-Formyl-β-lactams *via* Chiral N-Heterocyclic Carbene-Catalyzed Kinetic Resolution

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**Abstract:** An efficient synthesis of optically pure *cis*-4-formyl- $\beta$ -lactams (up to 99% *ee*) by a chiral NHC-catalyzed ring expansion reaction has been realized, featuring the ready availability of both the substrate and the catalyst, and the mild reaction conditions. The current method is also suitable for the synthesis of enantioenriched 4-formyl- $\beta$ -lactams and succinimides containing quaternary carbon centers.

**Keywords:** asymmetric catalysis; 4-formyl-β-lactams; kinetic resolution; N-heterocyclic carbene; organocatalysis

The  $\beta$ -lactam skeleton is the key structural unit responsible for the antibacterial properties of the most widely employed antibacterial agents to date.<sup>[1]</sup> Particularly, the cis-4-formyl-\beta-lactams are versatile building blocks for the synthesis of many biologically important targets such as monobactams, isocephams, carbapenems, β-hydroxyaspartates, hydroxybutanoic acids, biotin, and sphingolipids.<sup>[2]</sup> As a consequence, numerous methods for the synthesis of *cis*-4-formyl-βlactams were developed, which also accelerated the rapid development of versatile transformations based on this material.<sup>[3]</sup> The most convenient synthesis of *cis*-4-formyl- $\beta$ -lactams is the [2+2] cyclocondensation of ketenes with diimines, namely the Staudinger reaction,<sup>[4]</sup> mainly due to the ready availability of both starting materials. Over the past several decades, the asymmetric Staudinger reaction has been extensively studied to deliver optically pure β-lactams.<sup>[5]</sup> However, only limited methods are useful for the direct synthesis of optically pure cis-4-formyl-β-lactams. Most of the current synthesis of optically pure cis-4-formylβ-lactams still use chiral starting materials such as aldehydes, acids/acid halides and amines,<sup>[6]</sup> most of which were derived from chiral auxiliaries in multiple steps. A direct catalytic asymmetric synthesis of *cis*-4-formyl- $\beta$ -lactam remains rare and highly desirable.

Recently, N-heterocyclic carbenes (NHCs) have been utilized for a variety of transformations by the means of umpolung,<sup>[7]</sup> reversing of the reactivity of aldehydes, providing an unconventional access to some important target molecules.<sup>[8,9]</sup> We recently found that in the presence of an NHC catalyst *cis*-4-formyl- $\beta$ -lactams could undergo the ring expansion reaction to afford succinimide derivatives [Eq. (1)].<sup>[10]</sup>

In addition, the kinetic resolution version of this transformation was attempted with a chiral NHC (Scheme 1), and the *cis*-4-formyl- $\beta$ -lactam could be recovered with a moderate *ee* of 64%. It should be noted that the aldehyde was further reduced by NaBH<sub>4</sub> to its corresponding alcohol **3a** for the ease of handling. To the best of our knowledge, this is the first report for the catalytic asymmetric synthesis of *cis*-4-formyl- $\beta$ -lactams. Encouraged by these results, we further explored readily available chiral NHCs and realized a highly efficient kinetic resolution to deliver optically pure *cis*-4-formyl- $\beta$ -lactams. In this paper, we report our preliminary results.

Initially, several chiral NHC precursors (Figure 1) were examined for the kinetic resolution of *cis*-4-formyl- $\beta$ -lactam **1a**. The results are summarized in Table 1.

In the presence of 5 mol% of chiral NHC precursor **4** and DBU at room temperature, the ring expansion



Scheme 1. Chiral NHC-catalyzed kinetic resolution of  $(\pm)$ -1a.



Figure 1. Several readily available chiral NHC precursors.

reaction was stopped at 50% conversion of the starting material (by <sup>1</sup>H NMR). Succinimide **2a** was obtained in 38% yield with 9% *ee*, and *cis*-4-formyl- $\beta$ lactam **1a** was recovered and reduced to its corresponding alcohol **3a** in 34% yield with 64% *ee* (entry 1, Table 1). Triazolium salt **5**, with a bulky 2,4,6-trimethylphenyl substituent was found to be a better catalyst for the kinetic resolution, affording succinimide **2a** in 39% yield with 27% *ee* and **3a** in 40% yield with 99% *ee*, respectively. N-Heterocyclic carbene catalysts derived from precursors **6** and **7** proved unable to catalyze the ring expansion reaction (entries 3 and 4, Table 1). By utilizing triazolium salt **5**, different bases were examined in order to minimize the racemization of ring expansion product **2a**. In the presence of 5 mol% of **5**, with 5 mol% of Cs<sub>2</sub>CO<sub>3</sub> or DIPEA as a base, partial racemization of **2a** was also observed, and **2a** was obtained with 24% *ee* and 17% *ee*, respectively. In both cases, **3a** can still be obtained with excellent *ees* (98% *ee* and 99% *ee*, respectively). Unfortunately, no reaction occurred when 5 mol% of K<sub>3</sub>PO<sub>4</sub> or *t*-BuOK were used as the base.

To understand further the mechanism of racemization of **2a**, enantiopure (–)-**1a** was subjected to the ring expansion reaction with the imidazolium chloride (1 mol%) and DBU (1 mol%) in CH<sub>2</sub>Cl<sub>2</sub> [Eq. (2)].<sup>[10a]</sup> After refluxing for 5 h, the succinimide **2a** was almost

Table 1. Screening different chiral NHC catalysts and bases.<sup>[a]</sup>

| Ph, CHO<br>N<br>O Mes<br>(cis) | 1) <b>cat.</b> (5 mol%)<br>base (5 mol%), CH <sub>2</sub> Cl <sub>2</sub><br>25 °C (50% conv.)<br>2) NaBH <sub>4</sub> | Ph<br>ONO<br>Mes | Ph,,CH <sub>2</sub> OH |
|--------------------------------|--|------------------|------------------------|
| (+/–) <b>-1a</b>               |  | (+) <b>-2</b> a  | (–)- <b>3a</b>         |

| Entry            | Catalyst (cat.) | Base       | 2a                       |                       | <b>3</b> a               |                       |
|------------------|-----------------|------------|--------------------------|-----------------------|--------------------------|-----------------------|
|                  |                 |            | Yield [%] <sup>[b]</sup> | ee [%] <sup>[c]</sup> | Yield [%] <sup>[b]</sup> | ee [%] <sup>[c]</sup> |
| 1                | 4               | DBU        | 38                       | 9                     | 34                       | 64                    |
| 2                | 5               | DBU        | 39                       | 27                    | 40                       | 99                    |
| 3 <sup>[d]</sup> | 6               | DBU        | /                        | /                     | /                        | /                     |
| 4 <sup>[d]</sup> | 7               | DBU        | /                        | /                     | /                        | /                     |
| 5 <sup>[d]</sup> | 5               | $K_3PO_4$  | /                        | /                     | /                        | /                     |
| 6                | 5               | $Cs_2CO_3$ | 32                       | 24                    | 34                       | 98                    |
| 7 <sup>[d]</sup> | 5               | KÕ-t-Bu    | /                        | /                     | /                        | /                     |
| 8                | 5               | DIPEA      | 30                       | 17                    | 35                       | 99                    |

<sup>[a]</sup> Reaction conditions: 5 mol% of cat., 5 mol% of base, 0.25 mmol of  $(\pm)$ -1a in 1.0 mL CH<sub>2</sub>Cl<sub>2</sub> at 25 °C. The reaction mixture was quenched and charged with NaBH<sub>4</sub> when the conversion of  $(\pm)$ -1a was 50% (by <sup>1</sup>H NMR).

<sup>[b]</sup> Isolated yields.

<sup>[c]</sup> Determined by chiral HPLC analysis.

<sup>[d]</sup> No reaction.



completely racemized  $(1\% \ ee)$ . In addition, when the succinimide **2a** (27% ee) was refluxed under the same conditions, the succinimide was recovered with only 3% ee [Eq. (3)]. When (-)-**1a** (99% ee) was tested with 5 mol% thiazolium bromide and 5 mol% DBU, as reported by Alcaide et al.,<sup>[10b]</sup> severe racemization was also observed (2% ee). Therefore, the low ee of **2a** might be due to the acidic nature of the chiral center in the succinimide derivative.

In the presence of 5 mol% of **5** and DBU, various structurally diversified  $(\pm)$ -*cis*-4-formyl- $\beta$ -lactams have been tested to investigate the generality of the

reaction. The reaction time varied from 4.5 to 72 h. As summarized in Table 2, either N-(2,4,6-trimethylphenyl)- or N-(4-methoxyphenyl)-substituted substrates afford the chiral *cis*-4-formyl- $\beta$ -lactams **1** with high enantioselectivities (entries 1–7). Substrates bearing either electron-donating groups (4-OMe, entries 2 and 5) or electron-withdrawing groups (2-Br, 4-Br, 4-Cl, entries 3, 6, and 7) were well tolerated in the reaction, affording their accordant alcohols 3 in 30-47% yield with 80->99% ee. The substrate having a heterocyclic substituent such as a 2-thienyl group occurred with 56% ee (entry 8). Notably, the cis-4-formyl- $\beta$ -lactams 1j and 1k containing quaternary carbon centers underwent the kinetic resolution giving their corresponding succinimides 2 and *cis*-4-formyl- $\beta$ -lactams in excellent yields with moderate ees (entries 10 and 11). *trans*-4-Formyl-β-lactam **1i** bearing a quaternary carbon center has also been tested and relatively lower *ees* of both ring expansion product and starting material were obtained (entry 9). Unfortunately, substrates bearing alkyl groups such as *n*-pentyl and isopropyl afforded their corresponding *cis*-4-formyl-βlactams with 36% and 19% ee, respectively (entries 12 and 13).

To determine the absolute stereochemistry of the product **3**, a single crystal of **3f** was obtained. An X-ray analysis disclosed that the absolute configuration of **3f** is (3R,4R) (Figure 2).<sup>[11]</sup>

|                     |            | R              | <sup>2</sup> R <sup>3</sup> H CHO 1) 5 (<br>CH | 5 mol%), DE<br><sub>2</sub> Cl <sub>2</sub> , 25 °C ( | DI%), DBU (5 mol%) R <sup>3</sup> R <sup>2</sup><br>25 °C (50% conv.) |                             | R <sup>2</sup> R <sup>3</sup> H<br>CH <sub>2</sub> OH |                             |                                |
|---------------------|------------|----------------|--|---|---|-----------------------------|---|-----------------------------|--------------------------------|
|                     |            |                | 0 R <sup>1</sup> 2) NaBH₄, Me                  |   | , <b>r</b> .t.  | 0 N 0<br>R <sup>1</sup>     | O R <sup>1</sup>                                      |                             |                                |
|                     |            |                | (+/-)-1  |   |   | (+) <b>-2</b>               | (-)-3   |                             |                                |
| Entry               | 1          | $\mathbf{R}^1$ | $\mathbb{R}^2$                                 | <b>R</b> <sup>3</sup>                                 | <i>t</i> [h]  | <b>2</b> [%] <sup>[b]</sup> | <b>2</b> ee [%] <sup>[c]</sup>                        | <b>3</b> [%] <sup>[b]</sup> | <b>3</b> ee [%] <sup>[c]</sup> |
| 1                   | <b>1</b> a | Mes            | Ph   | Н   | 40  | 39                          | 27  | 40                          | 99                             |
| 2                   | 1b         | Mes            | PMP  | Н   | 36  | 36                          | 0   | 30                          | >99                            |
| 3                   | 1c         | Mes            | $2-Br-C_6H_4$                                  | Н   | 55  | 35                          | 0   | 46                          | 84                             |
| 4                   | 1d         | PMP            | Ph   | Н   | 14  | 50                          | 26  | 47                          | 80                             |
| 5 <sup>[d]</sup>    | 1e         | PMP            | PMP  | Н   | 4.5   | 40                          | 0   | 45                          | 95                             |
| 6                   | 1f         | PMP            | $4-Br-C_6H_4$                                  | Н   | 8   | 37                          | 0   | 32                          | 99                             |
| 7 <sup>[d,e]</sup>  | 1g         | PMP            | $4-Cl-C_6H_4$                                  | Н   | 72  | 38                          | 0   | 37                          | 97                             |
| 8 <sup>[d]</sup>    | 1h         | PMP            | 2-thienyl                                      | Н   | 7   | 26                          | 0   | 30                          | 56                             |
| 9                   | 1i         | PMP            | Et   | Ph  | 12  | 48                          | 29  | 49                          | 30                             |
| 10 <sup>[d,f]</sup> | 1j         | PMP            | Ph   | Et  | 45  | 47                          | -44   | 44                          | 58                             |
| 11 <sup>[d]</sup>   | 1k         | PMP            | Ph   | Me  | 24  | 41                          | 44  | 35                          | 54                             |
| 12                  | 11         | Mes            | $n - C_5 H_{11}$                               | Н   | 48  | 28                          | 0   | 30                          | 36                             |
| 13                  | 1m         | Mes            | <i>i</i> -Pr                                   | Η   | 40  | 34                          | 10  | 37                          | 19                             |

Table 2. Kinetic resolution of  $(\pm)$ -cis-4-formyl- $\beta$ -lactam 1 by chiral NHC 5.<sup>[a]</sup>

<sup>[a]</sup> Reaction conditions: see the Experimental Section.

<sup>[b]</sup> Isolated yields.

<sup>[c]</sup> Determined by chiral HPLC analysis.

<sup>[d]</sup> The reaction was run at 20 °C.

<sup>[e]</sup> The concentration of  $(\pm)$ -1g was 0.08 mol/L.

<sup>[f]</sup> The conversion of  $(\pm)$ -1j was 58%.



Figure 2. X-Ray structure of the compound (3R, 4R)-3f.

In summary, we have reported a novel efficient synthesis of optically pure *cis*-4-formyl- $\beta$ -lactams by a chiral NHC-catalyzed ring expansion reaction. This reaction features the ready availability of both the substrate and the catalyst, and mild reaction conditions. Notably, with the current method, enantioenriched 4-formyl- $\beta$ -lactams and succinimides containing quaternary carbon centers can be obtained in excellent yields with mild enantioselectivities. Further exploration of the reaction's scope and applications of the methodology in organic synthesis are currently underway.

### **Experimental Section**

## General Procedure for the Kinetic Resolution Ring Expansion of $(\pm)$ -1

To a solution of the pre-catalyst 5 (5.2 mg, 0.013 mmol) in  $CH_2Cl_2$  (1.0 mL) was added DBU (1.8  $\mu$ L, 0.013 mmol). After stirring for 5 min,  $(\pm)$ -1 (0.25 mmol) was added. The reaction mixture was stirred at 25 °C. When the conversion of  $(\pm)$ -1 was about 50% (by <sup>1</sup>H NMR), the reaction was quenched with saturated aqueous NaHCO<sub>3</sub>. The organic layer was isolated and the solvent was removed under vacuum. To the residue, MeOH (2.0 mL) and NaBH<sub>4</sub> powder (9.5 mg, 0.25 mmol) were added. After stirring for 30 min, the solvent was removed under vacuum and water (2.0 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 mL×2). The organic layer was washed with brine (10 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then purified by column chromatography (silica gel, PE/EtOAc = 8/1-3/1) to afford the corresponding alcohol 3 and succinimide derivative 2.

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