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## Chiral *N,N'*-dioxide–FeCl<sub>3</sub> complex-catalyzed asymmetric intramolecular Cannizzaro reaction†

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**An environmentally benign catalyst, the *N,N'*-dioxide–FeCl<sub>3</sub> complex, has been developed for the asymmetric intramolecular Cannizzaro reaction. Aryl and alkyl glyoxal monohydrates were applied to obtain  $\alpha$ -hydroxy acid esters with excellent results. Deuterium-label and control experiments shed light on the reaction mechanism.**

Iron is becoming a rising star in sustainable metal catalysis, given its advantages of earth-abundance, cheapness and low toxicity.<sup>1</sup> Nonetheless, iron salts scarcely perform better than other transition metals in asymmetric catalysis.<sup>2</sup> Until recent years, significant achievements have been made in iron-based asymmetric transformations with high enantioselectivities.<sup>1–3</sup> In most cases, nitrogen-, nitrogen/oxygen-, or nitrogen/phosphorus-containing chiral ligand sets have been used. FeCl<sub>3</sub>, being the most common of the iron salts that are commercially accessible on a large scale, is a much more interesting and viable choice for asymmetric catalysis. According to Pearson's HSAB principle,<sup>4</sup> FeCl<sub>3</sub> is usually classified as a hard Lewis acid. Consequently, after the combination with proper hard chiral Lewis bases, FeCl<sub>3</sub> complexes can function as good chiral Lewis acid catalysts. Therefore, the development of tailor-made chiral ligands for the FeCl<sub>3</sub> catalysis is highly desirable.

The asymmetric intramolecular Cannizzaro reaction of  $\alpha$ -keto aldehydes is an efficient method to optically active  $\alpha$ -hydroxy carboxylic acids and derivatives.<sup>5</sup> Nishinaga and co-workers firstly used Co(III)–Schiff base complexes in the selective conversion of arylglyoxals to mandelic esters.<sup>6</sup> After that, chiral Cu(II)-complexes of oxazoline-type ligands were used independently in this reaction by the groups of Morken,<sup>7</sup> Ishihara,<sup>8</sup> and Tang.<sup>9</sup> Notably, Tang's TOX ligand exhibited an

extremely high efficiency, receiving up to 99% yield and up to 98% ee for both aryl and alkyl glyoxal substrates. The enantioselectivity was promoted by means of a slow substrate-release strategy with an unusual and bulky alcohol (*i*-Pr<sub>2</sub>CHOH). As a part of our ongoing efforts to develop chiral *N,N'*-dioxides as ligands, we have realized a variety of asymmetric catalytic processes using a chiral platform of *N,N'*-dioxide–metal complexes.<sup>10</sup> We considered that the hard acid of the Fe(III) salt had affinities for the hard O-based *N,N'*-dioxides, thus performing as efficient chiral Fe(III) Lewis acids to activate heteroatoms *via*  $\sigma$ -complexes in asymmetric catalysis.<sup>4</sup> Herein, we report an *N,N'*-dioxide–FeCl<sub>3</sub>-catalyzed asymmetric intramolecular Cannizzaro reaction. Excellent yields and enantioselectivities were obtained for both aryl and alkyl glyoxals with several alcohols in air atmosphere.

Initially, we conducted the model reaction of phenylglyoxal monohydrate **1a** with *tert*-butanol **2a** in the presence of 3 Å molecular sieves (MS)<sup>9</sup> by employing a chiral *N,N'*-dioxide–metal complex as the catalyst (Table 1, entries 1–5). The ligand **L-RaPr<sub>2</sub>**, when used in combination with Sc(OTf)<sub>3</sub>, Yb(OTf)<sub>3</sub>, and Fe(OTf)<sub>3</sub>, facilitated the formation of the product **3aa** in good enantioselectivity albeit with 24–41% yield (entries 1–3). Surprisingly, Cu(OTf)<sub>2</sub>, a good metal precursor in previous reports,<sup>7,9</sup> showed no reactivity (entry 4). Although FeCl<sub>3</sub> has a strong affinity for Cl<sup>–</sup>, the multidentate *N,N'*-dioxide and the substrates lower the  $\eta$  value (the absolute hardness) of the ionic Fe(III). The complex of **L-RaPr<sub>2</sub>**–FeCl<sub>3</sub> produced **3aa** in 38% yield with 93% ee, indicating that the counterion Cl<sup>–</sup> can be replaced by the substrate (Table 1, entry 5). Evaluation of the chiral amino acid backbone and the amide units of *N,N'*-dioxide, such as in the ligands **L-PrPr<sub>2</sub>** and **L-PiPr<sub>2</sub>**, resulted in less improved results (entries 5–7). We deduced that the yield of the reaction might be promoted using additional solvent. Gratifyingly, after a series of screenings (see the ESI† for details), a yield of 94% was obtained by employing a mixed solvent of *tert*-butanol and CH<sub>2</sub>Cl<sub>2</sub> at a volume ratio of 6/1 (93% ee, Table 1, entry 8). To our delight, the catalyst loading could be reduced to 5 mol% without loss of efficiency. Further reducing the catalyst

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Table 1 Optimization of the reaction conditions

$\text{1a} + t\text{-BuOH} \xrightarrow[\text{3 \AA MS, additions}]{\text{L-Metal (1-10 mol\%)}} \text{3aa}$

**L-RaPr<sub>2</sub>**: R = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>  
**L-PrPr<sub>2</sub>**: R = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, n = 1  
**L-PiPr<sub>2</sub>**: R = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, n = 2

Entry <sup>a</sup>	Metal (x mol%)	Ligand	Yield <sup>b</sup> (%)	ee <sup>c</sup> (%)
1	Sc(OTf) <sub>3</sub> (10)	<b>L-RaPr<sub>2</sub></b>	41	87
2	Yb(OTf) <sub>3</sub> (10)	<b>L-RaPr<sub>2</sub></b>	24	74
3	Fe(OTf) <sub>3</sub> (10)	<b>L-RaPr<sub>2</sub></b>	39	91
4	Cu(OTf) <sub>2</sub> (10)	<b>L-RaPr<sub>2</sub></b>	0	—
5	FeCl <sub>3</sub> (10)	<b>L-RaPr<sub>2</sub></b>	38	93
6	FeCl <sub>3</sub> (10)	<b>L-PrPr<sub>2</sub></b>	30	86
7	FeCl <sub>3</sub> (10)	<b>L-PiPr<sub>2</sub></b>	51	82
8 <sup>d</sup>	FeCl <sub>3</sub> (10)	<b>L-RaPr<sub>2</sub></b>	94	93
9 <sup>d,e</sup>	FeCl <sub>3</sub> (5)	<b>L-RaPr<sub>2</sub></b>	93	93
10 <sup>d,f</sup>	FeCl <sub>3</sub> (1)	<b>L-RaPr<sub>2</sub></b>	95	93
11 <sup>d,g</sup>	FeCl <sub>3</sub> (5)	<b>L-RaPr<sub>2</sub></b>	81	91
12 <sup>d,h</sup>	FeCl <sub>3</sub> (5)	<b>L-RaPr<sub>2</sub></b>	92	93
13 <sup>d</sup>	FeCl <sub>2</sub> (5)	<b>L-RaPr<sub>2</sub></b>	93	93
14 <sup>d,g</sup>	FeCl <sub>2</sub> (5)	<b>L-RaPr<sub>2</sub></b>	65	92

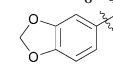
<sup>a</sup> Unless specified, the reactions were performed with L-metal (1.2:1, 10 mol%), **1a** (0.25 mmol), 3 Å MS (100 mg) in *t*-BuOH (1.0 mL) at 30 °C for 12 h in air. <sup>b</sup> Yields of the isolated products. <sup>c</sup> Determined by HPLC analysis using a chiral stationary phase. <sup>d</sup> With L-metal (1.1:1) in *t*-BuOH/CH<sub>2</sub>Cl<sub>2</sub> (v/v = 6/1, 0.4 mL) at 30 °C for 12 h in air. <sup>e</sup> L-metal (1.1:1, 5 mol%). <sup>f</sup> L-metal (1.1:1, 1 mol%) for 51 h. <sup>g</sup> In N<sub>2</sub> atmosphere. <sup>h</sup> In O<sub>2</sub> atmosphere.

loading to 1 mol% led to 95% yield and 93% ee after a prolonged reaction time (entries 9 and 10). It is worth noting that the reaction performed better in air or under O<sub>2</sub> than under N<sub>2</sub> (entries 9, 11 and 12), leading to a facile procedure without extrusion of air. The counter anion of Fe(III) in the optimized solvent was then examined, and Cl<sup>-</sup> was chosen due to a better result as well as a consideration of atom economy and the prices of the metal salts (see the ESI† for details). In addition, the reaction promoted by **L-RaPr<sub>2</sub>**-FeCl<sub>2</sub> in air gave a higher yield than that under N<sub>2</sub> (93% yield vs. 65% yield; entries 13 and 14), whereas the enantioselectivity was unaffected. A by-product of the  $\alpha$ -ketoester was clearly detected using both FeCl<sub>3</sub> and FeCl<sub>2</sub> as the metal precursors in N<sub>2</sub> atmosphere. The results indicate that Fe(III) works as an active species, which is more stable in the presence of O<sub>2</sub>.

With the optimized reaction conditions in hand (Table 1, entry 9), we examined the reaction scope using a variety of  $\alpha$ -keto aldehyde monohydrates. As listed in Table 2, these substrates underwent the asymmetric Cannizzaro reaction smoothly. In general, the reaction displayed good reactivity and enantioselectivity for both aryl and alkyl substituted glyoxals (49–99% yields, 81–95% ee). *Meta*- and *para*-substituted aryl glyoxals gave higher enantioselectivities than those of *ortho*-substituted ones

Table 2 Substrate scope of glyoxal monohydrates for the catalytic asymmetric intermolecular Cannizzaro reaction

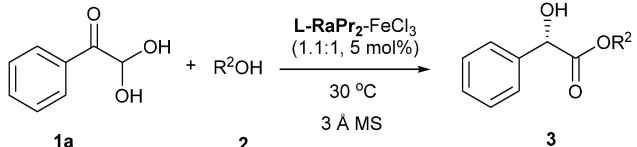
$\text{1} + t\text{-BuOH} \xrightarrow[\text{3 \AA MS}]{\text{L-RaPr}_2\text{-FeCl}_3 \text{ (1.1:1, 5 mol\%)}} \text{3}$

Entry <sup>a</sup>	R <sup>1</sup>	t (h)	Yield <sup>b</sup> (%)	ee <sup>c</sup> (%)
1	Ph ( <b>1a</b> )	12	93 ( <b>3aa</b> )	93
2 <sup>d</sup>	2-MeC <sub>6</sub> H <sub>4</sub> ( <b>1b</b> )	72	97 ( <b>3ab</b> )	81
3	3-MeC <sub>6</sub> H <sub>4</sub> ( <b>1c</b> )	24	94 ( <b>3ac</b> )	92
4	4-MeC <sub>6</sub> H <sub>4</sub> ( <b>1d</b> )	12	94 ( <b>3ad</b> )	94
5	4- <i>t</i> -BuC <sub>6</sub> H <sub>4</sub> ( <b>1e</b> )	24	91 ( <b>3ae</b> )	91
6	3-MeOC <sub>6</sub> H <sub>4</sub> ( <b>1f</b> )	24	97 ( <b>3af</b> )	92
7	4-MeOC <sub>6</sub> H <sub>4</sub> ( <b>1g</b> )	24	90 ( <b>3ag</b> )	95
8	 ( <b>1h</b> )	24	96 ( <b>3ah</b> )	95
9	4-FC <sub>6</sub> H <sub>4</sub> ( <b>1i</b> )	12	90 ( <b>3ai</b> )	92
10	3-ClC <sub>6</sub> H <sub>4</sub> ( <b>1j</b> )	24	95 ( <b>3aj</b> )	93
11	4-ClC <sub>6</sub> H <sub>4</sub> ( <b>1k</b> )	12	95 ( <b>3ak</b> )	91
12 <sup>d</sup>	2,3,4-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> ( <b>1l</b> )	24	92 ( <b>3al</b> )	81
13	4-BrC <sub>6</sub> H <sub>4</sub> ( <b>1m</b> )	24	93 ( <b>3am</b> )	91
14	4-NCC <sub>6</sub> H <sub>4</sub> ( <b>1n</b> )	24	91 ( <b>3an</b> )	92
15	4-F <sub>3</sub> CC <sub>6</sub> H <sub>4</sub> ( <b>1o</b> )	24	99 ( <b>3ao</b> )	91
16	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ( <b>1p</b> )	12	63 ( <b>3ap</b> )	91
17	2-Naphthyl ( <b>1q</b> )	12	99 ( <b>3aq</b> )	92
18	2-Furyl ( <b>1r</b> )	24	49 ( <b>3ar</b> )	97
19	2-Thienyl ( <b>1s</b> )	24	89 ( <b>3as</b> )	95
20	3-Thienyl ( <b>1t</b> )	24	92 ( <b>3at</b> )	94
21 <sup>e</sup>	<i>n</i> -Nonyl ( <b>1u</b> )	48	90 ( <b>3au</b> )	89
22 <sup>e</sup>	<i>c</i> -Pentyl ( <b>1v</b> )	48	89 ( <b>3av</b> )	89
23 <sup>e</sup>	<i>c</i> -Hexyl ( <b>1w</b> )	48	97 ( <b>3aw</b> )	91
24 <sup>e</sup>	<i>t</i> -Bu ( <b>1x</b> )	48	99 ( <b>3ax</b> )	81
25 <sup>e</sup>	1-Adamantyl ( <b>1y</b> )	48	87 ( <b>3ay</b> )	95

<sup>a</sup> Unless specified, the reactions were performed with **L-RaPr<sub>2</sub>**-FeCl<sub>3</sub> (1.1:1, 5 mol%), **1** (0.25 mmol), 3 Å MS (100 mg) in *t*-BuOH/CH<sub>2</sub>Cl<sub>2</sub> (v/v = 6/1, 0.4 mL) at 30 °C in air. <sup>b</sup> Yields of the isolated products. <sup>c</sup> Determined by HPLC analysis using a chiral stationary phase. <sup>d</sup> At 0 °C. <sup>e</sup> 10 mol% catalyst loading.

(Table 2, entries 1–16). Functional groups such as -CN, -CF<sub>3</sub>, and -NO<sub>2</sub> were tolerated, although 4-NO<sub>2</sub>-substituted **1p** turned the reaction color black and the yield was moderate, while the enantioselectivity was maintained (Table 2, entry 16). The reaction also worked well with fused-ring and heteroaromatic substrates, giving excellent enantioselectivities (92–97% ee, Table 2, entries 18–20). 2-Furyl substituted glyoxal monohydrate **1r** gave a moderate yield as a result of the instability of the furan ring, but the enantioselectivity was excellent (49% yield, 97% ee; Table 2, entry 18). Notably, linear, branched, as well as cyclic alkyl glyoxal monohydrates **1u–1y** all performed well with high yields and good to excellent enantioselectivities (81–95% ee; Table 2, entries 21–25). When the reaction of **1a** was performed on a gram scale in the presence of 5 mol% or even 1 mol% of the catalyst, excellent enantioselectivities (94% and 92% ee) were achieved with satisfying yields (92% and 80%, respectively) (see the ESI† for details).

It was also found that the reaction was amenable to various alcohols. The catalyst had good enantiocontrol for the small-sized ethanol and the ee value was 75% (Table 3, entry 1). For larger hindered alcohols, such as iso-propanol, cyclopentanol, cyclohexanol, and adamantan-1-ol, the corresponding mandelic

**Table 3** Substrate scope of alcohols for the catalytic asymmetric intermolecular Cannizzaro reaction


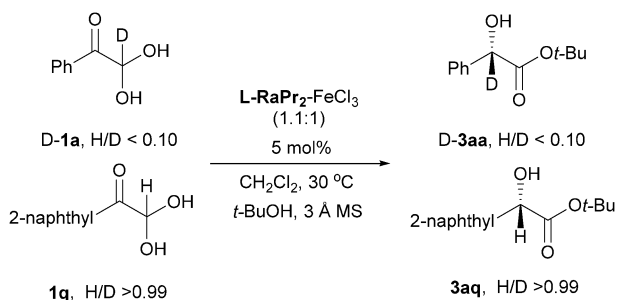
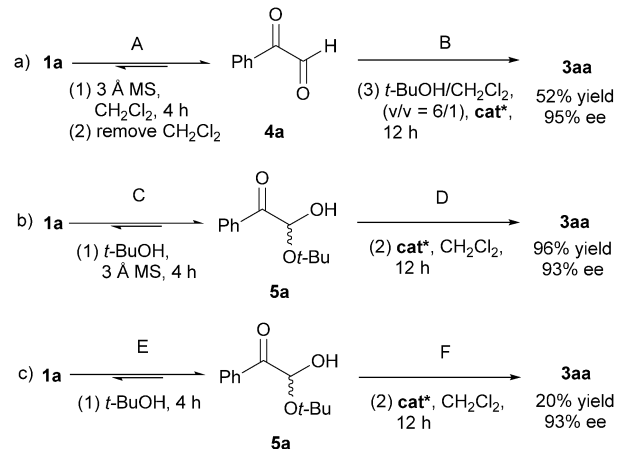
Entry <sup>a</sup>	R <sup>2</sup>	t (h)	Yield <sup>b</sup> (%)	ee <sup>c</sup> (%)
1	Et ( <b>2b</b> )	48	71 ( <b>3ba</b> )	75
2	i-Pr ( <b>2c</b> )	48	66 ( <b>3ca</b> )	81
3	c-Pentyl ( <b>2d</b> )	48	88 ( <b>3da</b> )	86
4	c-Hexyl ( <b>2e</b> )	48	62 ( <b>3ea</b> )	84
5 <sup>d</sup>	1-Adamantyl ( <b>2f</b> )	48	52 ( <b>3fa</b> )	96

<sup>a</sup> Unless specified, the reactions were performed with **L-RaPr**<sub>2</sub>/FeCl<sub>3</sub> (1.1 : 1, 5 mol%), **1a** (0.25 mmol), 3 Å MS (100 mg) in R<sup>2</sup>OH (1.0 mL) at 30 °C in air. <sup>b</sup> Yields of the isolated products. <sup>c</sup> Determined by HPLC analysis using a chiral stationary phase. <sup>d</sup> **2f** (1.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL).

esters were obtained in good to excellent yields and enantioselectivities (81–96% ee, Table 3, entries 2–5). The enantioselectivity increased as the alkyl group of the alcohols enlarged.

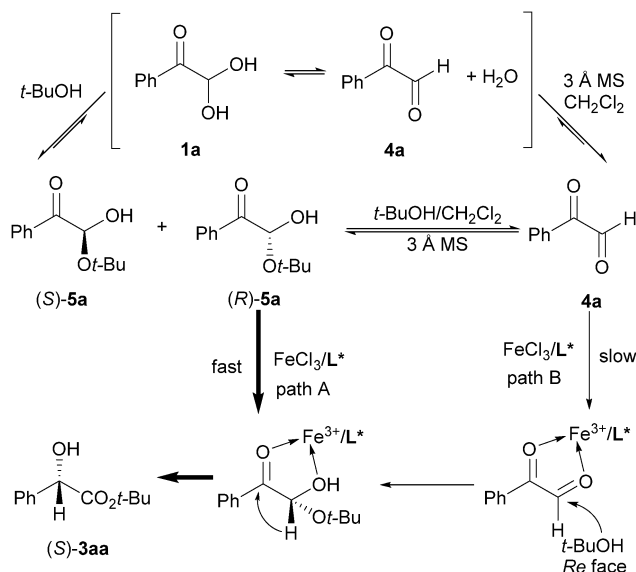
To study the hydride transfer process in this reaction, we chose the crossover reaction of 1-deuterated phenylglyoxal monohydrate **D-1a** and 2-naphthylglyoxal monohydrate **1q** (Scheme 1). There was no incorporation of deuterium into the 2-naphthyl product **3aq**, indicating an intramolecular 1,2-hydride shift as described in previous reports.<sup>5f,g,7</sup>

With regard to the enantiocontrol profile, two controversial processes are suggested in literature: one is the dynamic kinetic resolution of the hemiacetals<sup>5</sup>;<sup>7,8</sup> the other is the enantioselective addition of alcohols to the glyoxals.<sup>9</sup> To elucidate the reaction process in this case, we further conducted control experiments. As mentioned above, the reaction of phenylglyoxal monohydrate **1a** in *t*-BuOH afforded the product in 38% yield and 93% ee (Table 1, entry 5). Upon reaction of **1a** with a mixture of *t*-BuOH/CH<sub>2</sub>Cl<sub>2</sub> (v/v = 6/1), a significant improvement in the yield (94%) occurred (Table 1, entry 8), revealing that CH<sub>2</sub>Cl<sub>2</sub> might accelerate the dehydration process of **1a** toward anhydrous glyoxal **4a**. Different intervals of treating phenylglyoxal monohydrate **1a** with *t*-BuOH or CH<sub>2</sub>Cl<sub>2</sub> were tested (Scheme 2). When treating **1a** with 3 Å MS in CH<sub>2</sub>Cl<sub>2</sub> beforehand, the reaction (a) gave a decreased yield, whilst an ee of up to 95% was obtained (Scheme 2a). Alternatively, the

**Scheme 1** Deuterium-label crossover experiment.**Scheme 2** Control experiments for the intramolecular Cannizzaro reaction.

reaction (b), dissolving **1a** in *t*-BuOH with 3 Å MS, afforded the product in 96% yield (Scheme 2b). When the reaction was performed without 3 Å MS, the yield dropped drastically (20% yield; Scheme 2c). In all cases, the enantioselectivities were nearly unaffected. Such results were different from those with Tang's TOX-Cu(OTf)<sub>2</sub> catalytic system.<sup>9</sup> It is reasonable to speculate that the dynamic kinetic resolution of the hemiacetals might dominate in this case,<sup>7,8</sup> although the enantioselective addition pathway could not be completely excluded.

On the basis of our observations, we proposed the reaction mechanism shown in Scheme 3. Glyoxal **4a**, which formed from glyoxal monohydrate **1a** assisted by 3 Å MS and CH<sub>2</sub>Cl<sub>2</sub>, reacted with *t*-BuOH to give the racemic hemiacetal **5a**. Subsequently, (*R*)-**5a** preferably coordinates to the chiral *N,N'*-dioxide-FeCl<sub>3</sub> complex. As a result of an intramolecular hydride transfer, the (*S*)-product **3aa** is generated with a newly formed stereocenter. Mismatched (*S*)-**5a** underwent racemization assisted

**Scheme 3** Proposed catalytic processes for the asymmetric intramolecular Cannizzaro reaction.

by 3 Å MS, and then continued to undergo the chiral Fe(III)-catalyzed enantiomer selective hydride transfer. Additionally, glyoxal **4a** could also coordinate to the chiral Fe(III) complex, enabling the asymmetric addition of *t*-BuOH from the *Re*-face to give (*R*)-**5a**. The perfect chiral environment created by the *N,N*-dioxide-FeCl<sub>3</sub> complex benefited both the dynamic kinetic resolution and the enantioselective addition processes. Therefore, excellent enantioselectivities were obtained regardless of the reaction procedure.

In summary, we have developed a highly efficient FeCl<sub>3</sub> complex of chiral *N,N*-dioxide for the asymmetric intramolecular Cannizzaro reaction, with advantages such as being environmentally benign and air-insensitive. The reactions of aryl and alkyl glyoxals with various alcohols gave the  $\alpha$ -hydroxy acid esters in high yields (up to 99%) and high enantioselectivities (up to 97% ee). A mechanistic study revealed the perfect enantioselective environment for the catalyst which accounts for either the dynamic kinetic resolution process or the asymmetric addition process. The outcomes accomplished using the iron catalyst show the potential of earth-abundant iron for asymmetric reactions.

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