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Dual Pathway for the Asymmetric Transfer Hydrogenation of α-Ketoimides to Chiral α-Hydroxy Imides or Chiral α-Hydroxy Esters

Qiankun Zhao, Yuxi Zhao, Hang Liao, Tanyu Cheng, and Guohua Liu*[a]

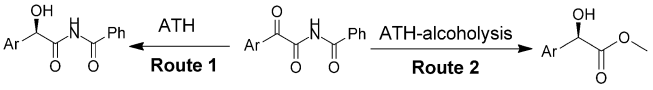
In an enantioselective reaction, we expect to obtain two types of chiral products through a controllable strategy in asymmetric catalysis. Herein, we develop Ru-catalysed asymmetric transfer hydrogenation of α-ketoimides to realise an enantioselective construction of chiral α-hydroxy imides or chiral α-hydroxy esters. The transformation of α-ketoimides catalysed by (*S*,*S*)-[RuCl(η^6-mesitylene)diamine] can afford various chiral α-hydroxy imides with high yields and enantioselectivities, whereas that catalysed by (*S*,*S*)-[RuCl(η^6-hexamethylbenzene)diamine] gives the desirable chiral α-hydroxy esters through a slight adjustment of the reaction conditions. The method described here is a controllable organic transformation with sodium formate as a hydrogen source under mild reaction conditions, and the benefit of this transformation is that various chiral α-hydroxy imides or α-hydroxy esters can be obtained selectively from α-ketoimides.

Introduction

Chiral η^5-Cp*-M complexes (η^5-Cp* = pentamethyl cyclopentadiene series, M = Ru, Rh and Ir) and η^6-arene-M complexes (η^6-arene = aromatic ring series) based on N-sulfonylated diamines have been well documented as efficient catalysts in various asymmetric reactions[1] and some have exhibited excellent catalytic activity and high enantioselectivity in asymmetric transfer hydrogenation (ATH).[2] In particular, developments in enantioselective divergence[3] to construct chiral product diversity have stimulated the further exploration of these organometallic complexes based on N-sulfonylated diamine greatly. Recently, Johnson et al. found that the chiral η^6-*p*-cymene-Ru complex based on N-sulfonylated diamine could produce chiral product diversity in the dynamic kinetic resolution of α-keto esters by asymmetric hydrogen transfer.[3c–e] These findings offer new opportunities to explore enantioselective divergence in ATH through the screening of chiral organometallic complexes based on N-sulfonylated diamines in asymmetric reactions.

Optically active α-hydroxy amides/imides and α-hydroxy esters, as important chiral motifs, are well known in the construction of various biologically active compounds, such as bradykinin B1 selective antagonists and inverse agonists.[4] Generally, an economical and efficient route for the simultaneous construction of α-hydroxy amides/imides and α-hydroxy esters is from α-ketoamides/imides, in which the direct reduction of a carbonyl group gives α-hydroxy amides/imides, whereas reduction followed by alcoholysis affords α-hydroxy esters. This route offers a potentially organic transformation for the construction of chiral α-hydroxy imides and α-hydroxy esters from α-ketoimides through the use of an asymmetric hydrogen transfer method (Scheme 1).

To date, chiral α-hydroxy amides/imides have been obtained through many well-established methodologies, which include



Scheme 1. Enantioselective transformation of α-ketoimides to chiral α-hydroxy imides and chiral α-hydroxy esters.

the asymmetric oxidation of racemic α-hydroxy amides,[5] the ring opening of chiral α-epoxy amides,[6] the enantioselective Passerini-type reaction[7] and the asymmetric addition of enamides to ketones.[8] However, the direct enantioselective reduction of α-ketoamides/imides to chiral α-hydroxy amides/imides only involves in chiral induction,[9] asymmetric hydrosilylation[10] and asymmetric hydrogenation.[11] Among these three direct reduction routes, the reduction of α-keto amides/imides through chiral induction needs a stoichiometric chiral auxiliary ligand and that through asymmetric hydrosilylation has a poor enantioselectivity. Although enantioselective reduction through asymmetric hydrogenation has a high enantioselectivity, sensitive chiral diphosphine ligands and high pressures of hydrogen are still a problem for its practical application.[11] Therefore, the development of an ATH strategy for the organic transformation of α-ketoimides to chiral α-hydroxy imides and the simultaneous realisation of an enantioselective transformation from α-ketoimides to chiral α-hydroxy esters is highly desirable.

[a] *Q. Zhao, Y. Zhao, H. Liao, T. Cheng, Prof. G. Liu*
Key Laboratory of Resource Chemistry of Ministry of Education
Shanghai Key Laboratory of Rare Earth Functional Materials
Shanghai Normal University
No.100 Guilin Rd. (P.R. China)
E-mail: ghliu@shnu.edu.cn

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In an effort to develop various ATH methods,[12] we found that the chiral η^6-mesitylene-Ru complex based on *N*-(2-amino-1,2-diphenylethyl)-4-methylbenzenesulfonamide (TsDPEN) was highly efficient in the ATH of imines and ketones.[12a,b] In this contribution, we realise the dual transformation of α-ketoimides by ATH. As expected, the transformation of α-ketoimides catalysed by (*S*,*S*)-[RuCl(η^6-mesitylene)TsDPEN] affords various chiral α-hydroxy imides with high yields and enantioselectivities, whereas that catalysed by (*S*,*S*)-[RuCl(η^6-hexamethylbenzene)TsDPEN] gives the desirable chiral α-hydroxy esters through a slight adjustment of reaction conditions. Such a strategy makes this asymmetric reaction an attractive feature in the selective preparation of chiral α-hydroxy imides or α-hydroxy esters from α-ketoimides in a controllable manner.

Results and Discussion

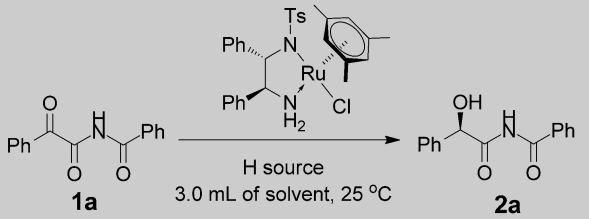
Optimisation of reaction conditions in the ATH of *N*-(2-oxo-2-phenylacetyl)benzamide to (*R*)-*N*-(2-hydroxy-2-phenylacetyl)benzamide

We chose the ATH of *N*-(2-oxo-2-phenylacetyl)benzamide as a model reaction. The asymmetric reaction was optimised through the use of 2.0 mol% (*S*,*S*)-[RuCl(η^6-mesitylene)TsDPEN] as a catalyst to determine the optimal hydrogen source, solvent and additive to obtain the highly efficient transformation of *N*-(2-oxo-2-phenylacetyl)benzamide to (*R*)-*N*-(2-hydroxy-2-phenylacetyl)benzamide.

First, we used four common hydrogen sources that are often used in ATH reactions, formic acid/triethylamine, formic acid, 2-propanol and sodium formate (HCOONa), to compare the catalytic performance systemically. In the case of HCOONa as a hydrogen source, the ATH of *N*-(2-oxo-2-phenylacetyl)-benzamide afforded (*R*)-*N*-(2-hydroxy-2-phenylacetyl)benzamide with a medium yield and *ee* value, which was clearly better than that obtained with the other hydrogen sources (Table 1, entry 4 vs. 1–3), which suggests that HCOONa was the best hydrogen source.

Next, because of the poor solubility of the substrate in water, a series of polar solvents was screened. As shown in entries 6–10, it was found that in all cases that yields increased relative to that in water within 2 h, even with the use of PEG-400 as a phase-transfer catalyst (Table 1, entry 5 vs. 6–10). However, their *ee* values were not affected clearly. To our surprise, if MeOH was used as the solvent, the enantioselectivity was enhanced greatly although the yield only increased slightly (Table 1, entry 5 vs. 11). A detailed analysis of this reaction found that the transformation of *N*-(2-oxo-2-phenylacetyl)benzamide is quantitative (more than 99% conversion), which suggests the formation of byproducts in this catalytic reaction. The byproduct was determined as (*R*)-methyl 2-hydroxy-2-phenylacetate, which demonstrates that the reaction goes through an alcoholysis process. This behaviour indicates an adjustable process that will be discussed below. To confirm the role of alcohols in this reaction system, two alcohols (EtOH and *i*PrOH) were further investigated as solvents. In both cases, the *ee* value of the target chiral products was enhanced steadily

Table 1. Optimisation of reaction conditions in the ATH of *N*-(2-oxo-2-phenylacetyl)benzamide to (*R*)-*N*-(2-hydroxy-2-phenylacetyl)benzamide.[a]



Entry	Solvent/hydrogen source	Acid	Time [h]	Yield [%][b]	*ee* [%][c]
1	HCOOH+NEt_3	–	8	40	70
2	*i*PrOH	–	24	n.d.[d]	n.d.[d]
3	HCOOH	–	24	5	n.d.[d]
4	H_2O/HCOONa	–	8	83	71
5	H_2O/HCOONa	–	2	62	70
6	PEG400/H_2O/HCOONa	–	2	86	63
7	THF/HCOONa	–	2	10	53
8	Acetone/HCOONa	–	2	80	78
9	DMF/HCOONa	–	2	80	72
10	DMSO/HCOONa	–	2	90	64
11	MeOH/HCOONa	–	2	68	96
12	EtOH/HCOONa	–	2	68	94
13	*i*PrOH/HCOONa	–	2	70	93
14	MeOH/HCOONa	HCOOH	1	95	95[e]
15	MeOH/HCOONa	HCOOH	1	86	91[f]
16	MeOH/HCOONa	HCOOH	3	89	86[g]
17	MeOH/HCOONa	AcOH	1	95	91
18	MeOH/HCOONa	TsOH	1	97	82

[a] Reactions were performed with 2.0 μmol of catalyst, 0.10 mmol of *N*-(2-oxo-2-phenylacetyl)benzamide and 10 equiv. of the hydrogen source in 3.0 mL of solvent at 25 °C. [b] Isolated yield. [c] Determined by HPLC. [d] Not detected. [e] Data were obtained with 5.0 equiv. of HCOOH as an additive. [f] Data were obtained with 2.5 equiv. of HCOOH as an additive. [g] Data were obtained with 7.5 equiv. of HCOOH as an additive.

(Table 1, entries 12–13). Similarly, their yields did not change significantly because of the same alcoholysis process.

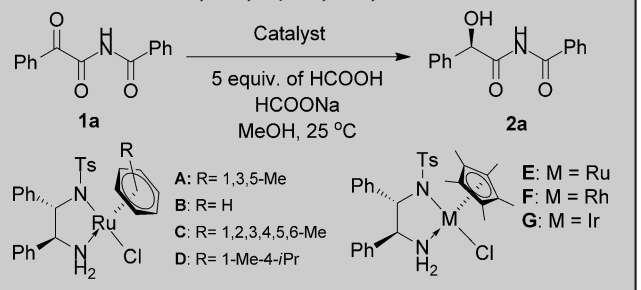
To suppress the alcoholysis of chiral products and to enhance the yield of (*R*)-*N*-(2-hydroxy-2-phenylacetyl)benzamide, HCOOH was introduced as an additive to this catalytic system, which was inspired by its suppressing role in the alcoholysis of α-ketoimides.[13] The result showed the yield of (*R*)-*N*-(2-hydroxy-2-phenylacetyl)benzamide could be enhanced significantly and the *ee* value had no clear decrease. Further optimisation of the molar amounts of HCOOH showed that 5.0 equivalents of HCOOH was optimal (Table 1, entry 14 vs. 15–16), with which the yield of (*R*)-*N*-(2-hydroxy-2-phenylacetyl)benzamide could be enhanced from 68 to 95% and the *ee* value reached 95%. Such a result was better than that of CH_3COOH or TsOH as additives (Table 1, entry 14 vs. 17–18).

Therefore, in the presence of 2.0 mol% of (*S*,*S*)-[RuCl(η^6-mesitylene)TsDPEN], the optimal reaction conditions for the transformation of α-ketoimides to chiral α-hydroxy imides were the use of HCOONa as the hydrogen source, MeOH as the solvent and HCOOH as the additive at a reaction temperature of 25 °C.

After we had determined the best reaction conditions in the case of 2.0 mol% of (*S*,*S*)-[RuCl(η^6-mesitylene)TsDPEN] as a catalyst, the analogues of chiral η^5-Cp*-M complexes **B–D** and η^6-

arene-M complexes **E–G** based on N-sulfonylated diamines were further examined in the ATH of *N*-(2-oxo-2-phenylacetyl)-benzamide under these reaction conditions. Although most of these complexes enabled efficient ATH, with the exception of **E**, the yields and enantioselectivities were worse than those with (*S*,*S*)-[RuCl(η^6-mesitylene)TsDPEN] (**A**) (Table 2, entry 1 vs. 2–7). Comprehensively, (*S*,*S*)-[RuCl(η^6-mesitylene)TsDPEN] was determined as the best catalyst in the ATH of *N*-(2-oxo-2-phenylacetyl)benzamide to (*R*)-*N*-(2-hydroxy-2-phenylacetyl)benzamide.

Table 2. Optimisation of catalysts in the ATH of *N*-(2-oxo-2-phenylacetyl)-benzamide to (*R*)-*N*-(2-hydroxy-2-phenylacetyl)benzamide.[a]



Entry	Catalyst	Time [h]	Yield [%][b]	*ee* [%][c]
1	**A**	1	95	95
2	**B**	1	94	85
3	**C**	12	20	93
4	**D**	2	94	89
5	**E**	12	n.d.[d]	–
6	**F**	2	85	86
7	**G**	2	85	87

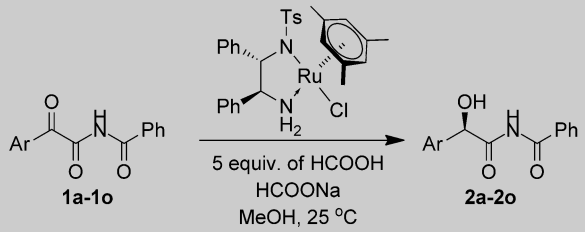
[a] Reactions were performed with 2.0 μmol of catalyst, 0.10 mmol of *N*-(2-oxo-2-phenylacetyl)benzamide and 10 equiv. of hydrogen source in 3.0 mL of solvent at 25 °C. [b] Isolated yield. [c] Determined by HPLC. [d] Not detected.

ATH of α-ketoimides to α-hydroxy imides

Based on the optimised catalyst and reaction conditions in the ATH of *N*-(2-oxo-2-phenylacetyl)benzamide to (*R*)-*N*-(2-hydroxy-2-phenylacetyl)benzamide, we further investigated the applicability of the reaction with a series of aryl-substituted α-ketoimides. In general, asymmetric reactions with high yields and medium to high enantioselectivities could be obtained under the optimal reaction conditions (Table 3). If we take the ATH of *N*-(2-oxo-2-phenylacetyl)benzamide as an example, we found that the 95% *ee* value was higher than that obtained by other methods reported,[9–11] which suggests the benefit of this ATH because of the use of air-stable (*S*,*S*)-[RuCl(η^6-mesitylene)TsDPEN] as a catalyst under mild reaction conditions.

The electronic properties of the substituents at the Ar group did not affect their enantioselectivities significantly, and various electron-withdrawing and -donating substituents on the Ar group were equally efficient. However, the steric effect was clear, and substituents at the 2-position of the Ar group, which included 1-naphthyl, decreased their enantioselectivities greatly (Table 3, entries 3, 10 and 14). Such a result suggests that the asymmetric reaction described here was suitable for the construction of a wide range of α-hydroxy imides through a facile ATH strategy.

Table 3. ATH of α-ketoimides to convert α-hydroxy imides.[a]



Entry	Ar	2	Time [h]	Yield [%][b]	*ee* [%][c]
1	Ph (**1a**)	**2a**	1	95	95
2	4-FPh (**1b**)	**2b**	1	94	88
3	2-FPh (**1c**)	**2c**	3	91	81
4	4-ClPh (**1d**)	**2d**	1	94	91
5	4-BrPh (**1e**)	**2e**	1	93	94
6	3-BrPh (**1f**)	**2f**	1	84	91
7	4-I Ph (**1g**)	**2g**	2	93	86
8	4-MePh (**1h**)	**2h**	2	94	91
9	3-MePh (**1i**)	**2i**	2	94	95
10	2-MePh (**1j**)	**2j**	6	90	62
11	4-*i*PrPh (**1k**)	**2k**	2	94	81
12	4-MeOPh (**1l**)	**2l**	2	90	92
13	3-MeOPh (**1m**)	**2m**	1	93	91
14	1-naphthyl (**1n**)	**2n**	4	88	73
15	2-naphthyl (**1o**)	**2o**	2	93	93

[a] Reactions were performed with 2.0 μmol of catalyst, 0.10 mmol of α-ketoimide, 5 equiv. of HCOOH and 10 equiv. of HOOONa in 3.0 mL of MeOH at 25 °C. [b] Isolated yield. [c] Determined by HPLC.

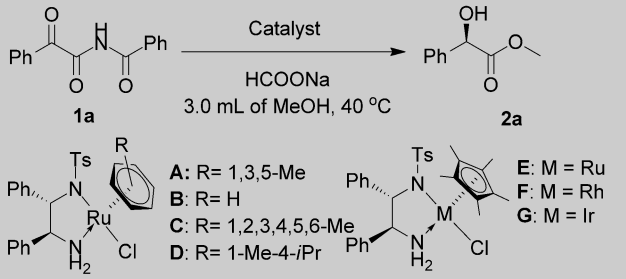
ATH of α-ketoimides to α-hydroxy esters

Notably, this ATH of α-ketoimides can be used for the construction of chiral α-hydroxy esters as mentioned above during the optimisation process. Although many well-established methods for the construction of chiral α-hydroxy esters have appeared in the literature,[3c–e,14] direct transformations of aryl-substituted α-ketoimides to chiral aryl-substituted α-hydroxy esters have not been explored through the use of an ATH method. In this case, through a controlled organic transformation, aryl-substituted α-ketoimides could also be converted to chiral α-hydroxy esters through the slight adjustment of the reaction conditions.

During the optimisation of alcohol solvents (Table 1, entries 11–13) to determine the structure of the byproduct of (*R*)-methyl 2-hydroxy-2-phenylacetate in the ATH of *N*-(2-oxo-2-phenylacetyl)benzamide to (*R*)-*N*-(2-hydroxy-2-phenylacetyl)-benzamide, we found that the nearly quantitative conversion of (*R*)-methyl 2-hydroxy-2-phenylacetate could be obtained if the reaction temperature was increased to 40 °C without a change of the other reaction conditions, which included no acid as an additive. This finding indicates that through only the increase of the reaction temperature, the ATH of aryl-substituted α-ketoimides could form chiral α-hydroxy esters con-

trollably. Although the ATH of *N*-(2-oxo-2-phenylacetyl)benzamide catalysed by (*S*,*S*)-[RuCl(η⁶-mesitylene)TsDPEN] afforded the corresponding (*R*)-methyl 2-hydroxy-2-phenylacetate with 86% *ee*, this offered another possibility to optimise the best catalysts suitable for this chiral organic transformation. Catalyst **C** in the ATH of *N*-(2-oxo-2-phenylacetyl)benzamide could produce (*R*)-methyl 2-hydroxy-2-phenylacetate with 95% yield and 95% *ee*, which was better than the other catalysts (Table 4, entry 3 vs. 1–2 and 4–7). This behaviour demonstrated

Table 4. Optimisation of catalysts in the ATH of *N*-(2-oxo-2-phenylacetyl)-benzamide to (*R*)-methyl 2-hydroxy-2-phenylacetate.[a]



Entry	Catalyst	Solvent/hydrogen source	Time [h]	Yield [%][b]	*ee* [%][c]
1	**A**	MeOH/HCOONa	3	94	86
2	**B**	MeOH/HCOONa	3	94	80
3	**C**	MeOH/HCOONa	3	95	95
4	**D**	MeOH/HCOONa	3	93	73
5	**E**	MeOH/HCOONa	8	n.d.[d]	–
6	**F**	MeOH/HCOONa	3	93	82
7	**G**	MeOH/HCOONa	3	93	88

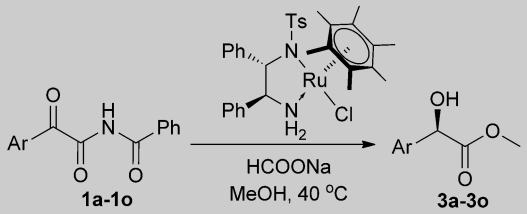
[a] Reactions were performed with 2.0 μmol of catalyst, 0.10 mmol of *N*-(2-oxo-2-phenylacetyl)benzamide and 10 equiv. of hydrogen source in 3.0 mL of solvent at 40 °C. [b] Isolated yield. [c] Determined by HPLC. [d] Not detected.

that the ATH of *N*-(2-oxo-2-phenylacetyl)benzamide was a controllable process, which not only enabled the efficient transformation of α-ketoimides to chiral α-hydroxy imides but also produced chiral α-hydroxy esters.

Based on this highly efficient organic transformation, the use of (*S*,*S*)-[RuCl(η⁶-hexamethylbenzene)TsDPEN] (**C**) as a catalyst was further investigated to test its general applicability for the above aryl-substituted α-ketoimides. In the presence of 2.0 mol% of **C**, the use of HCOONa as a hydrogen source and MeOH as a solvent at a reaction temperature of 40 °C, the ATH of these α-ketoimides could afford various chiral α-hydroxy esters with high yields and desirable enantioselectivities (Table 5), which suggests the benefit of the dual pathway in the construction of various chiral α-hydroxy esters.

A similar effect of the electronic properties and sterics was observed, in which various electron-withdrawing and -donating substituents on the Ar group were equally efficient, whereas substituents at the 2-position of the Ar group, which included 1-naphthyl, decreased their enantioselectivities (Table 5, entries 3, 10 and 14). In addition to the construction of (*R*)-methyl 2-hydroxy-2-phenylacetate, reactions with ethanol and isopropanol could also afford the chiral products (*R*)-ethyl 2-hydroxy-

Table 5. ATH of α-ketoimides to convert α-hydroxy esters.[a]



Entry	Ar	**3**	Time [h]	Yield [%][b]	*ee* [%][c]
1	Ph (**1a**)	**3a**	3	95	95
2	4-FPh (**1b**)	**3b**	3	94	90
3	2-FPh (**1c**)	**3c**	5	90	70
4	4-ClPh (**1d**)	**3d**	3	95	85
5	4-BrPh (**1e**)	**3e**	3	95	84
6	3-BrPh (**1f**)	**3f**	3	95	75
7	4-IPh (**1g**)	**3g**	3	93	83
8	4-CH_3Ph (**1h**)	**3h**	3	95	95
9	3-MePh (**1i**)	**3i**	3	95	95
10	2-CH_3Ph (**1j**)	**3j**	5	78	27
11	4-*i*PrPh (**1k**)	**3k**	4	93	96
12	4-MeOPh (**1l**)	**3l**	3	95	96
13	3-MeOPh (**1m**)	**3m**	3	94	94
14	1-naphthyl (**1n**)	**3n**	5	81	36
15	2-naphthyl (**1o**)	**3o**	5	89	90
16	EtOH (**1p**)	**3p**	4	92	93[d]
17	*i*PrOH (**1q**)	**3q**	5	80	80[e]

[a] Reactions were performed with 2.0 μmol of catalyst, 0.10 mmol of α-ketoimides and 10 equiv. of HOOONa in 3.0 mL of MeOH at 40 °C. [b] Isolated yield. [c] Determined by HPLC. [d] Data were obtained with EtOH as the solvent and reagent. [e] Data were obtained with *i*PrOH as the solvent and reagent at 60 °C.

2-phenylacetate and (*R*)-isopropyl 2-hydroxy-2-phenylacetate with desirable enantioselectivities (Table 5, entries 16–17).

Conclusions

By the exploration of the asymmetric transfer hydrogenation of α-ketoimides, we found that this asymmetric reaction can convert various chiral α-hydroxy imides or α-hydroxy esters through a slight adjustment of the reaction conditions. Furthermore, the mild reaction conditions make this asymmetric reaction attractive in practical organic transformations.

Experimental Section

General procedure for the ATH of α-ketoimides to chiral α-hydroxy imides

Catalyst **A** (2.0 μmol, S/C = 50), α-ketoimide (0.10 mmol), HCOOH (0.50 mmol), HCOONa (1.0 mmol, 68.0 mg) and MeOH (3.0 mL) were added to a 5 mL round-bottomed flask sequentially. The mixture was allowed to react at 25 °C, and the reaction was monitored constantly by TLC. After completion of the reaction, the solvent was removed by evaporation. The residue was dissolved in water (2 mL), and the aqueous solution was extracted by ethyl acetate (3 × 3.0 mL). The combined ethyl acetate solution was washed with brine twice and dehydrated with Na_2SO_4. After the evaporation of ethyl acetate, the residue was purified by silica gel flash column

chromatography to afford the desired products. The yields were determined by ^{1}H NMR spectroscopy. The *ee* values were determined by a Daicel Chiralcel column AD-H, OD-H or OJ-H.

General procedure for the ATH of α-ketoimides to chiral α-hydroxy esters

Catalyst **C** (2.0 μmol, S/C = 50), α-ketoimides (0.10 mmol), HCOONa (1.0 mmol, 68.0 mg) and MeOH (3.0 mL) were added to a 5 mL round-bottomed flask sequentially. The mixture was allowed to react at 40 °C, and the reaction was monitored constantly by TLC. After the completion of the reaction, the solvent was removed by evaporation. The residue was dissolved in water (2 mL), and then the aqueous solution was extracted by ethyl acetate (3 × 3.0 mL). The combined ethyl acetate solution was washed with brine twice and dehydrated with Na_2SO_4. After the evaporation of ethyl acetate, the residue was purified by silica gel flash column chromatography to afford the desired products. The yields were determined by ^{1}H NMR spectroscopy. The *ee* values were determined by a Daicel Chiralcel column AD-H, OJ-H or AS-H.

Acknowledgements

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