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A rapid and green approach to chiral α-hydroxy esters: asymmetric transfer hydrogenation (ATH) of α-keto esters in water by use of surfactants

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ABSTRACT

A series of α-hydroxy esters were rapidly prepared (1.5 h) from α-keto esters via asymmetric transfer hydrogenation (ATH) in water by the use of surfactants for the first time. This green method, catalyzed by a water-soluble and recyclable Ru(II) complex, gave moderate to high enantioselectivities (up to 99.7% ee) with DTAB as an additive and HCOONa as the hydrogen source.

1. Introduction

Asymmetric transfer hydrogenation (ATH) of ketones plays an important role in asymmetric synthesis as it affords chiral secondary alcohols which are valuable intermediates in organic and pharmaceutical syntheses. Great efforts have been made to achieve this reaction, especially transfer hydrogenation of prochiral ketones[1] in aqueous media, which has been the focus of research over the past few years as a result of increasing requirements for environmentally friendly methods. Because of the insolubility of organic substrates in water, phase-transfer catalysts or surfactants were usually added to the reaction mixture. For example, Chung et al.[2a] found that introducing surfactants to the water-soluble Ru(II)-catalyzed ATH of ketones led to an increase in the catalytic activity and enantioselectivity. Deng et al.[2b] performed ATH of ketones in aqueous media containing micelles and vesicles formed by the surfactant cetyltrimethylammonium bromide (CTAB) and obtained a significant enhancement of activity, chemoselectivity, and enantioselectivity with the hydrophobic transition metal-amido complexes (TsDPEN-M) as the catalyst.

On the other hand, chiral α-hydroxy esters are important pharmaceutical intermediates and useful building blocks in asymmetric synthesis.[3] Although tremendous endeavors have been devoted to the preparation of these compounds including chemical and biological transformations,[4] there are very few examples concerning ATH. Lemaire et al.[5a] afforded two cases of α-keto ester in their Rh-catalyzed asymmetric reduction of prochiral ketones with (1*S*,2*S*)-*N*,*N*′-dimethyl-DPEN as the chiral ligand. Mohar et al.[5b] reported Ru(II)-catalyzed transfer hydrogenation of several α-keto esters and α,α,α-trifluoromethyl ketones using HCO_2H/Et_3N azeotrope as the hydrogen donor. Deng et al.[5c] introduced tunable dendritic *N*-mono-sulfonyl ligands to the ATH of ketones, olefins, and a few examples of keto esters.

In contrast, to the best of our knowledge, no work involving the rapid preparation of chiral α-hydroxy esters by ATH in water has been reported up to now. From practical and green chemistry standpoints, it is significant to study the enantioselective synthesis of chiral α-hydroxy esters by ATH of α-keto esters in aqueous media. We have recently disclosed a Ru-catalyzed enantioselective preparation of methyl (*R*)-*o*-chloromandelate and its application in the synthesis of (*S*)-clopidogrel (Fig. 1) by using Ru-(*R*,*R*)-2,4,6-triisopropyl $C_6H_2SO_2$-DPEN as the catalyst and HCOOH–Et_3N azeotrope as the hydrogen donor.[6] Herein, we report the first ATH of a series of α-keto esters catalyzed by Ru(II) complex in aqueous media in the presence of surfactants.

2. Results and discussion

In our previous work,[6] we have attempted the enantioselective preparation of methyl (*R*)-*o*-chloromandelate with PEG 400 or PEG 2000 as an additive to overcome the insolubility of the substrate in water. However, analytical experiments showed that the ee values decreased compared with that of HCO_2H/Et_3N system. Inspired by Chung[2a] and Deng's work,[2b] we attempted to perform ATH of a series of α-keto esters in water by using surfactants. We chose methyl benzoylformate **4a** as the model substrate, (*S*,*S*)-Ts-DPEN **1**, (*S*,*S*)-*o*-NO_2–$C_6H_4SO_2$-DPEN **2,** and (*S*,*S*)-2,4,6-triisopropyl $C_6H_2SO_2$-DPEN **3** as chiral ligands (Fig. 2) for the Ru-catalyzed ATH reaction of α-keto esters. The screening test including variant surfactants, metal complexes, different loads of surfactants, and reaction temperatures was carried out and the results are listed in Table 1.

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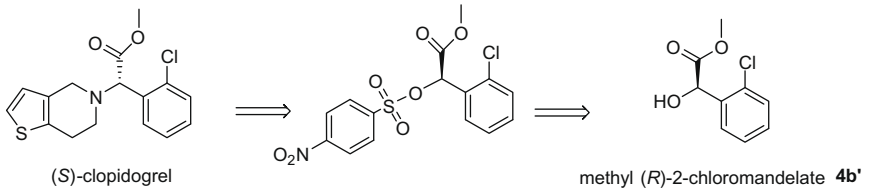


Figure 1. Asymmetric synthesis of (*S*)-clopidogrel.

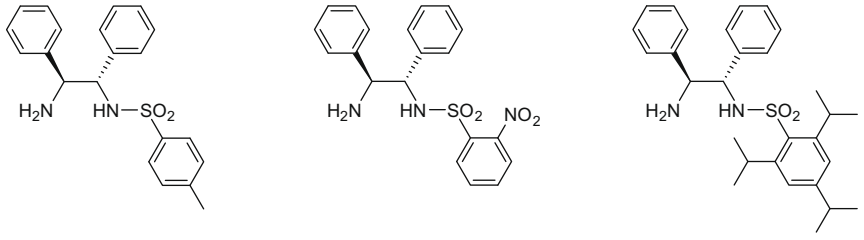
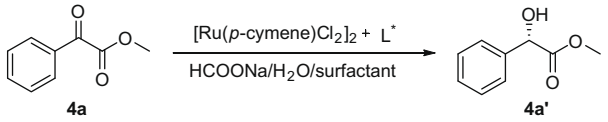


Figure 2. Chiral ligands used for ATH of α-keto esters in water.

Table 1
ATH of methyl benzoylformate **4a** in water[a] (screening test for optimal conditions)



Entry	Metal complex	Ligand	Surfactant	*T* (h)	Conv.[b] (%)	ee[b] (%)
1	$[RuCl_2(p\text{-cymene})]_2$	**1**	—	1.5	48	57.7
2	$[RuCl_2(p\text{-cymene})]_2$	**1**	CTAB	1.5	100	55.3
3	$[RuCl_2(p\text{-cymene})]_2$	**2**	CTAB	1.5	53	29.6
4	$[RuCl_2(p\text{-cymene})]_2$	**3**	CTAB	1.5	100	67.0
5	$[RuCl_2(p\text{-cymene})]_2$	**3**	SDS	1.5	51	67.7
6	$[RuCl_2(p\text{-cymene})]_2$	**3**	DTAB	1.5	100	90.9
7	$[RuCl_2(p\text{-cymene})]_2$	**3**	Triton X-100	1.5	100	81.6
8	$[RuCl_2(p\text{-cymene})]_2$	**3**	STAB	1.5	100	81.0
9	$[RuCl_2(p\text{-cymene})]_2$	**3**	DTAB/triton X-100 = 2:1	1.5	100	90.7
10	$[RuCl_2(p\text{-cymene})]_2$	**3**	STAB/Triton X-100 = 2:1	1.5	100	77.7
11	$[RuCl_2(p\text{-cymene})]_2$	**3**	SDS/DTAB = 2:1	13.5	100	84.4
12[c]	$[RuCl_2(p\text{-cymene})]_2$	**3**	DTAB	1.0	51	83.7
13[d]	$[RuCl_2(p\text{-cymene})]_2$	**3**	DTAB	22	100	85.6
14[e]	$[RuCl_2(p\text{-cymene})]_2$	**3**	DTAB	1.5	100	85.4
15	$[RuCl_2(\text{benzene})]_2$	**3**	DTAB	1.5	100	72.5
16[f]	$[RuCl_2(p\text{-cymene})]_2$	**3**	DTAB	20	98	85.1
17	$[RhCl_2Cp^*]_2$	**3**	DTAB	1.5	100	86.1
18	$[IrCl_2Cp^*]_2$	**3**	DTAB	1.5	100	48.9

[a] Reactions were carried out in 1 mmol scale at 28 °C with 50 mol % surfactants and S/C = 100 unless otherwise noted.
[b] The conversions were estimated by TLC or ^{1}H NMR analysis of the crude products and the ees were determined by HPLC on chiral OD-H column (hex: IPA = 90:10, 0.5 mL/min).
[c] Reaction temperature was 40 °C.
[d] Reaction was performed at 0 °C.
[e] With 10 mol % DTAB.
[f] S/C = 500.

The catalytic activity increased when cetyltrimethylammonium bromide (CTAB) was introduced to the catalytic system **1**-$[RuCl_2(p\text{-cymene})]_2$ (Table 1, entries 1 and 2). Catalytic system **2**-$[RuCl_2(p\text{-cymene})]_2$, with a nitro group on the sulfonyl part, presented both lower catalytic activity and enantioselectivity even in the presence of CTAB (Table 1, entry 3). On the other hand, catalytic system **3**-$[RuCl_2(p\text{-cymene})]_2$, which has three isopropyls on the sulfonyl part, gave full conversion and 67.0% ee for the modal substrate (Table 1, entry 4).

Based on the above elementary results, variant surfactants were subsequently screened (Table 1, entries 5–11) with **3**-$[RuCl_2(p\text{-cymene})]_2$ as the catalyst. The addition of sodium dodecyl sulfate (SDS, an anionic surfactant) slightly enhanced enantioselectivity (from 67.0% ee to 67.7% ee, Table 1, entry 5) but caused a decrease in catalytic activity. Poly (ethylene glycol) mono 4-(1,1,3,3-tetramethylbutylphenyl) ether (Triton X-100, a nonionic surfactant) and steartrimonium bromide (STAB, a cationic surfactant) further raised the ee values (81.6% ee for Triton X-100 and 81.0% ee for

STAB, Table 1, entries 7 and 8), while another cationic surfactant dodecyl trimethyl ammonium bromide (DTAB) gave the best result (90.9% ee, Table 1, entry 6) comparable to that of the HCOOH/Et_3N system. A further study on the influence of different types of surfactants was performed (DTAB and Triton X-100 (2:1, molar ratio), STAB and Triton X-100 (2:1, molar ratio), and SDS and DTAB (2:1, molar ratio), but no greater effect on improving conversions as well as enantioselectivities was observed (Table 1, entries 9–11).

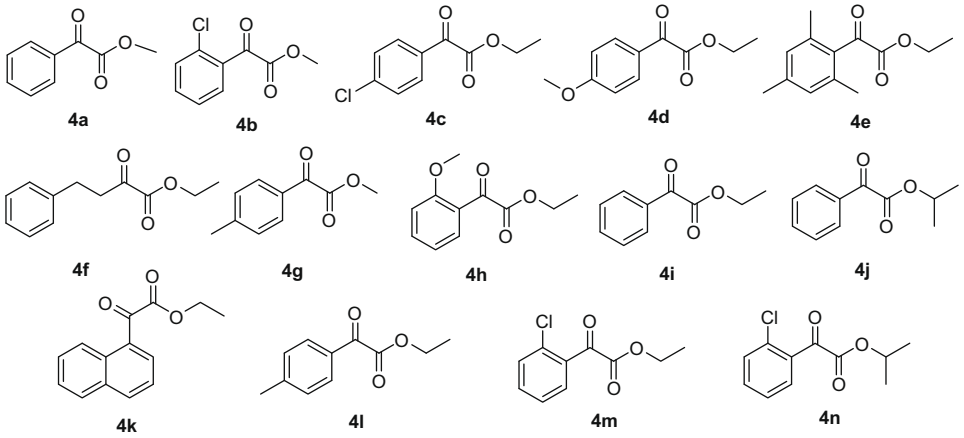
A temperature effect was also investigated and results showed that lower or higher reaction temperature was not favorable for the enantioselectivity. When the reaction was carried out at 0 °C, 85.6% ee with full conversion was obtained with a little prolonged reaction time (Table 1, entry 13). When the reaction was carried out at 40 °C, the ee value decreased to 83.7% and no enhancement in catalytic activity was observed (51% conversion for 1 h, Table 1, entry 12).

It was found that lowering the load of surfactants was unfavorable for high enantioselectivity. When the amount of DTAB was reduced from 50 mol % to 10 mol %, 85.4% ee was afforded (Table 1, entry 14).

Last but not the least, the metal precursor also influenced the enantioselectivity of the reaction. When $[RuCl_2(benzene)]_2$ was employed instead of $[RuCl_2(p\text{-cymene})]_2$, only 72.5% ee was obtained (Table 1, entry 15). A higher ratio of substrate to catalyst (S/C = 500, with **3**-$[RuCl_2(p\text{-cymene})]_2$ as the catalyst) was also tested (Table 1, entry 16), 98% conversion with 85.1% ee was obtained when the reaction was quenched after 20 h. In addition, Rh and Ir complexes were also used for the reaction, but did not give better enantioselectivity, as expected (Table 1, entries 17 and 18, 86.1% ee for $[RhCl_2Cp^*]_2$ and 48.9% ee for $[IrCl_2Cp^*]_2$).

The results of the hydrogen-transfer reaction of a series of α-keto esters catalyzed by (*S*,*S*)-2,4,6-triisopropyl $C_6H_2SO_2$-DPEN **3** under the optimal conditions are listed in Table 2. It appeared that electron-withdrawing substituted aryl α-keto esters were unfavorable for high enantioselectivities. For example, methyl *ortho*- and *para*-chloro benzoylformate gave lower ee values (Table 2, entries 2 and 3, 75.5% and 69.9% ee, respectively). In contrast, an electron-donating group, methoxy at the *para*-position **4d** seemed favorable for the enantioselectivity (Table 2, entry 4, 90.1% ee). However, *ortho*-substitution by the same group **4h** dramatically reduced enantioselectivity (33.0% ee, Table 2, entry 8), which may indicate that steric hindrance played an important role in the enantioselectivity of the reaction. This hypothesis was further proved by the ATH of ethyl 2,4,6-trimethylphenylglyoxalate **4e**, which has two methyls at *ortho*-positions of the substrate, only 34.5% ee was provided with 50% conversion over 20 h (Table 2, entry 5). The highest enantioselectivity was obtained by 4-methylbenzoic acid methyl ester **4g**, which has an electron-donating group at the *para*-position of the phenyl group (99.2% ee, Table 2, entry 7).

Table 2
Asymmetric transfer hydrogenation of α-keto esters under optimal conditions[a]



Entry	Substrate	Product	*T* (h)	Conversion[b] (%)	ee[b] (%)
1	**4a**	**4a′**	1.5	100	90.9
2[c,d]	**4b**	**4b′**	1.5	100	75.5
3	**4c**	**4c′**	1.5	100	69.9
4	**4d**	**4d′**	2	100	90.1
5[e]	**4e**	**4e′**	20	50	34.5
6[d]	**4f**	**4f′**	1.5	100	55.5 (63.2[f])
7	**4g**	**4g′**	1.5	100	99.2
8	**4h**	**4h′**	2	100	33.0
9	**4i**	**4i′**	1.5	100	88.5
10	**4j**	**4j′**	1.5	100	90.0
11	**4k**	**4k′**	1.5	100	83.7
12	**4l**	**4l′**	1.5	100	91.1
13[c]	**4m**	**4m′**	1.5	100	78.6
14[g]	**4n**	**4n′**	1.5	100	77.0

[a] Reactions were carried out in 1 mmol scale at 28 °C with 50 mol % DTAB and S/C = 100.
[b] The conversions and ees were determined by HPLC on chiral OD-H column unless otherwise noted. Configurations were assigned by comparison with the retention times in published literature.
[c] Chiral OJ-H column (hex: IPA = 92:8, 1.0 mL/min).
[d] (*R*,*R*)-2,4,6-Triisopropyl $C_6H_2SO_2$-DPEN as the chiral ligand.
[e] Chiral AD-H column (hex: IPA = 90:10, 0.5 mL/min).
[f] S/C = 40.
[g] Chiral OD-H column (hex: IPA = 95:5, 1.0 mL/min).

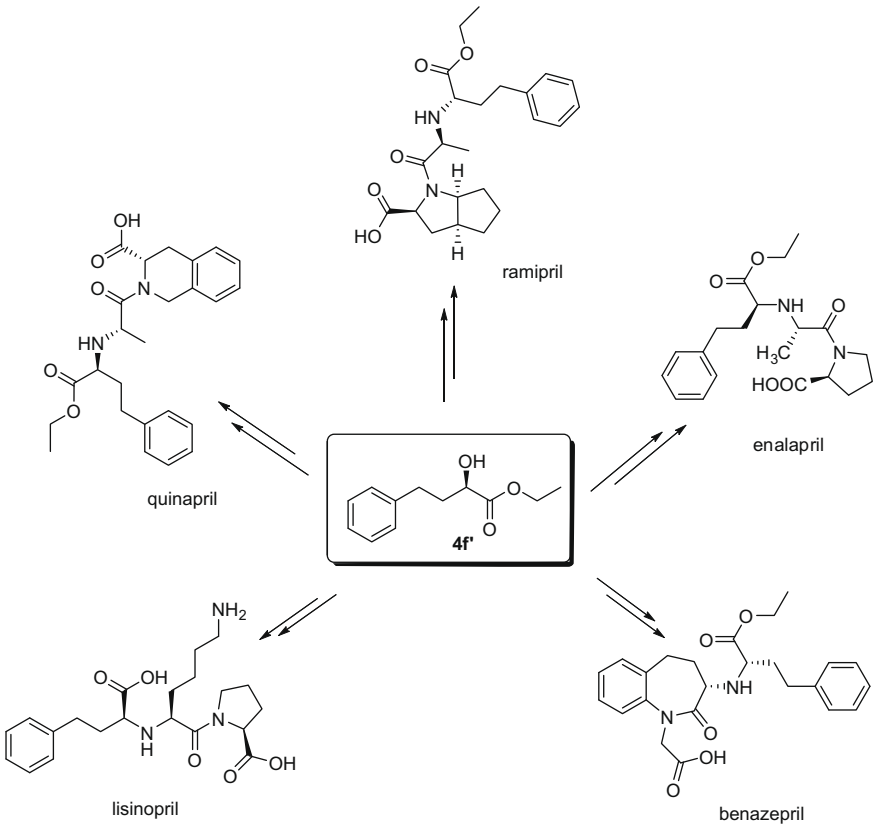


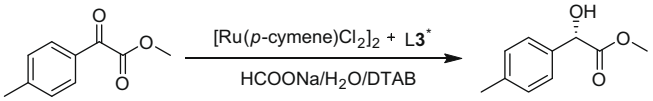
Figure 3. ACE inhibitors derived from chiral ethyl 2-hydroxy-phenylbutyrate.

On the other hand, the influence of the ester group on enantioselectivity was also investigated. Substrates **4a**, **4i,** and **4j**, with increased steric bulk gave almost the same level of enantioselectivities (Table 2, entries 1, 9, and 10, 90.9% ee for **4a**, 88.5% ee for **4i,** and 90.0% ee for **4j**). While **4b**, **4m,** and **4n**, the *ortho*-Cl substituted keto esters bearing an increased bulkiness of ester substitutions, presented similar potency in enantioselectivities (Table 2, entries 2, 13, and 14, 75.5% ee for **4b**, 78.6% ee for **4m,** and 77.0% ee for **4n**). Furthermore, 4-methyl-benzoic acid ethyl ester **4l**, which has merely a slight change at the ester part of **4g**, afforded only 91.1% ee (Table 2, entry 12).

Ethyl 2-hydroxy-4-phenylbutanoate **4f'** (Table 2, entry 6), an important ACE inhibitor intermediate (Fig. 3), was also prepared by this method. It is interesting to note that the reaction processed smoothly in only 1.5 h with full conversion, much more rapidly than that of HCOOH/Et_3N system which required 24 h for the same conversion.[5b]

Finally, the recycling of catalyst Ru-2,4,6-triisopropyl $C_6H_2SO_2$-DPEN **3** was tested with 4-methyl-benzoic acid methyl ester **4g** as the substrate and HCOONa as the hydrogen donor in water (Table 3). After each catalytic cycle, hexane was added to extract the product and the residue containing the catalyst was reused by adding pure formic acid to regenerate sodium formate for the next run. As shown in Table 3, enantioselectivities remained high until the 4th run; however, conversion decreased to 50% with prolonged reaction time (10 h). At the end of the 5th run, 50% conversion was provided with only 89.9% ee over 24 h, which demonstrated a loss in activity of the catalyst. The loss of catalyst during each extraction process may be partly attributed to the hydrophobic nature of the three isopropyls on the sulfonyl.

Table 3
The recycling test of catalyst[a]



Run	1	2	3	4	5
T (h)	2.5	3.0	6	10.0	24
Conv.[b] (%)	100	>95	85	50	50
ee[b] (%)	99.2	98.6	99.7	98.6	89.9

[a] Reaction conditions were the same as those used in Table 2, and 1.1 equiv of HCOOH was added to regenerate HCOONa after each run.
[b] The conversions and ees were determined by HPLC on chiral OD-H column (Hex: IPA = 90:10, 0.5 mL/min, t_1 = 17.85 min, t_2 = 19.34 min).

3. Conclusion

In conclusion, we have developed a practical method for rapid preparation of a series of α-hydroxy esters in water by use of Ru(II) complex-catalyzed asymmetric transfer hydrogenation and surfactants as additives. The reactions in water were much faster than that in HCOOH/Et_3N azeotrope in organic solvent[5b] and high enantioselectivities (up to 99.7% ee) were obtained. In addition, the catalyst Ru-2,4,6-triisopropyl $C_6H_2SO_2$-DPEN **3**) could be reused until the 4th run without any loss in enantioselectivity. Further study on the improved enantioselective preparation of the important ACE inhibitor intermediate—ethyl 2-hydroxy-4-phenylbutanoate **4f'** is in progress.

4. Experimental

4.1. General

The ^{1}H NMR spectra were recorded with TMS as an internal standard on a Bruker AV400 spectrometer. Ee values were determined on a SHIMADZU LC-20AT chromatography using Daicel Chiralcel columns (OD-H, AD-H and OJ-H). The optical rotation was measured with a Perkin–Elmer Model 341 polarimeter at 589 nm and 20 °C, using a 1 dm path length. Pure water was used in ATH of α-keto esters. Chiral ligands, substrates **4b, 4m, and 4n** were prepared as the procedure described in our previous work.[6] Compounds **4a** and **4c–4f** were purchased from Lancaster Chemicals and used without further purification.

4.2. Preparation of substrates

4.2.1. Preparation of 4g, 4h, and 4l (method A)[6,7] (modified procedure)

To a solution of *p*-tolualdehyde (8.04 g, 67 mmol) and tetrabutyl ammonium bromide (TBAB) (1.6 g, 5 mmol) in chloroform (12 mL) at 55 °C was dropwise added 50% NaOH solution (13 g of NaOH dissolved in 13 mL of water) over 1.5–2 h. After stirring at the same temperature for another 2 h, the reaction mixture was cooled and diluted with water. The organic phase was separated, acidified to pH 1 with 3 M HCl, and then extracted with ethyl acetate. The combined organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated in vacuo to afford crude α-hydroxy acid.

The α-hydroxy ester was prepared by esterifying the crude α-hydroxy acid in alcohol catalyzed by conc H_2SO_4 and purified through column chromatography. Oxidation with $KMnO_4$ and $Al_2(SO_4)_3{\cdot}18H_2O$ in CH_2Cl_2 at room temperature gave the pure α-keto ester with quantitative conversion (monitored by TLC).

4.2.2. Preparation of 4i and 4j (method B)[8]

Sodium (0.115 g, 5 mmol) was placed in a flask with absolute alcohol (10 mL) and the two-phase mixture was stirred until a homogeneous solution was formed. The resulting mixture was refluxed for 15 min after addition of $ZnBr_2$ (1.125 g, 5 mmol). Then methyl benzoylformate (0.164 g, 1 mmol) in alcohol (2 mL) was added and the mixture was heated at reflux until the reaction was completed. Excess alcohol was evaporated and the residue was extracted with diethyl ether (2 × 10 mL). The combined extracts were washed with water (2 × 10 mL) and dried over anhydrous Na_2SO_4. Pure title compounds were obtained by flash silica gel column chromatography.

4.3. Typical procedure for ATH of α-keto esters in water by use of surfactants

A mixture of $[Ru(p\text{-cymene})Cl_2]_2$ (3.06 mg, 0.005 mmol), (*S*,*S*)-2,4,6-triisopropyl $C_6H_2SO_2$-DPEN (5.74 mg, 0.012 mmol), and DTAB (0.1542 g, 0.5 mmol) in degassed water (0.5 mL) was stirred and heated at 40 °C for 1 h under argon atmosphere. After cooling to room temperature, methyl benzoylformate **4a** (0.1641 g, 1.0 mmol) and 2.5 M HCOONa (2 mL, 5.0 mmol) were subsequently introduced. After the reaction was complete (monitored by TLC), the reaction mixture was extracted with *n*-hexane for two times. The combined extracts were dried over anhydrous sodium sulfate, filtered, and concentrated in vacuum to afford the crude product which was purified by silica gel chromatography for determining the enantioselective excess.

The analytical data of ATH products of keto esters **4a**,[9] **4b**,[6] **4c**,[10] **4d**,[11] **4e**,[12] **4f**,[13] **4g**,[14] **4h**,[12] **4i**,[15] **4j**,[16] **4k**,[9] **4l**,[10] and **4m**[17] were in agreement with those reported in the literature. ATH product of **4n**, (*S*)-isopropyl 2-(2-chlorophenyl)-2-hydroxyacetate. $[\alpha]_D^{20} = +56.7$ (*c* 0.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.35 (m, 2H), 7.29–7.22 (m, 2H), 5.51 (s, 1H), 5.12–5.03 (h, J = 6.4 Hz, 1H), 3.74 (br s, 1H), 1.26–1.25 (d, J = 6.4 Hz, 3H), 1.11–1.10 (d, J = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 172.3, 136.2, 133.1, 129.4, 129.2, 128.3, 126.7, 70.1, 69.8, 21.2, 21.0. The enantiomeric excess was determined by chiral HPLC, using a chiral OD-H column, hex: IPA = 95:5, 1.0 mL/min, 254 nm; t_1 (major) = 6.88 min, t_2 (minor) = 7.99 min.

Acknowledgments

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