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Highly enantioselective asymmetric autocatalysis induced by chiral ionic crystals of sodium chlorate and sodium bromate

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Abstract

Chiral crystals of sodium chlorate and sodium bromate induced highly enantioselective organic synthesis in combination with asymmetric autocatalysis. (*S*)-5-Pyrimidyl alkanols with up to 98% ee were obtained in the enantioselective addition of diisopropylzinc to pyrimidine-5-carbaldehydes in the presence of *d*-sodium chlorate. On the other hand, (*R*)-5-pyrimidyl alkanols with up to 98% ee were obtained for the corresponding reaction in the presence of *l*-sodium chlorate. Chiral crystals of *d*- and *l*-sodium bromate were also found to work as chiral initiators.

Keywords: Asymmetric synthesis; Asymmetric autocatalysis; Crystals; Enantiomorphism; Surface

1. Introduction

The origin of significant enantiomeric enrichment of organic compounds such as L-amino acids on the earth has been an intriguing puzzle [1]. One of the proposed mechanisms for the enantiomeric enrichment of organic compounds is asymmetric synthesis and asymmetric adsorption on the surface of inorganic enantiomorphic crystals [2] and chiral metal surface [3]. We recently reported enantioselective synthesis of pyrimidyl alkanols promoted by *d*- and *l*-quartz [4], which are enantiomorphic inorganic molecular (SiO_2) crystals with covalent bonds between silicon and oxygen atoms.

In contrast, sodium chlorate ($NaClO_3$) and sodium bromate ($NaBrO_3$) are enantiomorphic inorganic ionic crystals [5]. Achiral sodium cations and chlorate (and bromate) anions form either *d*- or *l*-crystals with a chiral cubic space group ($P2_13$), whose chirality is easily determined by a polarimeter. Recently, Kondepudi et al. reported that almost all of the $NaClO_3$ crystals precipitated from a particular stirred solution have the same chirality [6]. However, the relevance of the chirality of $NaClO_3$ to that of an organic compound has not been established. Since the interaction between chiral ionic crystals such as $NaClO_3$ and organic molecules is expected to be small, the degree of chiral induction in organic compounds induced on the surface of chiral inorganic crystals is expected to be possibly below the detection level. An earlier report [7] on the enantioselective adsorption of racemic compounds by $NaClO_3$ was disproved by the later examination by Gillard and da Luz de Jesus [8]. Thus, the question remains whether a significantly enantiomerically enriched organic compound can be formed using chiral inorganic ionic crystals of $NaClO_3$ and $NaBrO_3$ as chiral initiator(s).

During our continuing study on asymmetric autocatalysis, it was found that asymmetric autocatalysis of 5-pyrimidyl alkanol in the enantioselective addition of diisopropylzinc (*i*-Pr_2Zn) to pyrimidine-5-carbaldehyde proceeds with amplification of ee [9–13]. Thus, 5-pyrimidyl alkanols with as low as ca. 0.00005% ee act as asymmetric autocatalysts to produce themselves. During three consecutive asymmetric autocatalyses, the amount of pyrimidyl alkanol was multiplied by a factor of ca. 630,000, and the ee of alkanol enhanced to >99.5% ee [11f]. Moreover, when *i*-Pr_2Zn was reacted with pyrimidine-5-carbaldehyde in the presence of chiral initiators such as amino acids, amines, carboxylic acids, deuterated primary alcohols, helicenes, allenes, and [2,2]paracyclophanes, highly enantiomerically enriched pyrimidyl alkanols having the corresponding absolute configurations with those of the chiral initiators were

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formed [13]. A tiny enantiomeric imbalance was formed in the initially formed pyrimidyl alkanol, and the subsequent asymmetric autocatalysis of pyrimidyl alkanol with amplification of ee produced the highly enantiomerically enriched product.

We thought that, when pyrimidine-5-carbaldehyde was reacted with *i*-Pr_2Zn in the presence of *d*- or *l*-sodium chlorate, the resulting initial imbalance of chirality of (zinc alkoxide of) pyrimidyl alkanol would be amplified during the subsequent asymmetric autocatalysis and that 5-pyrimidyl alkanol with high ee could be formed having an absolute configuration depending on the enantiomorph of the chiral ionic crystal.

We report an unprecedented highly enantioselective synthesis of organic compounds induced by chiral ionic crystals [14]. The enantioselective addition of *i*-Pr_2Zn to pyrimidine-5-carbaldehydes in the presence of $NaClO_3$ or $NaBrO_3$, in combination with asymmetric autocatalysis, gave pyrimidyl alkanols with high ee (up to 98% ee) in high yields.

2. Results and discussion

2.1. Sodium chlorate mediated asymmetric autocatalysis

First, we examined the addition reaction of *i*-Pr_2Zn to 2-alkynylpyrimidine-5-carbaldehyde **1** in the presence of sodium chlorate (Scheme 1). A toluene solution of *i*-Pr_2Zn was slowly added to an ice cooled suspension of finely powdered sodium chlorate crystals (222 mg, particle size: ca. 5–2 μm) and pyrimidine-5-carbaldehyde **1** (9.4 mg, 0.05 mmol) in toluene (0.2 ml). After the mixture was stirred for 12 h, a toluene solution of *i*-Pr_2Zn and pyrimidine-5-carbaldehyde **1** was added in two portions for further asymmetric autocatalysis. The results are shown in Table 1. When *d*-$NaClO_3$ was used, (*S*)-5-pyrimidyl alkanol **2** with 98% ee was obtained in 93% yield (entry 1). The reaction is reproducible. Thus, (*S*)-5-pyrimidyl alkanol **2** with 97−98% ee was obtained in the presence of *d*-$NaClO_3$ (entries 2 and 3). On the other hand, in the presence of *l*-$NaClO_3$ instead of *d*-$NaClO_3$, reactions between pyrimidine-5-carbaldehyde **1** and *i*-Pr_2Zn gave (*R*)-5-pyrimidyl alkanol with 98% ee in yields of 91−98% (entries 4−6).

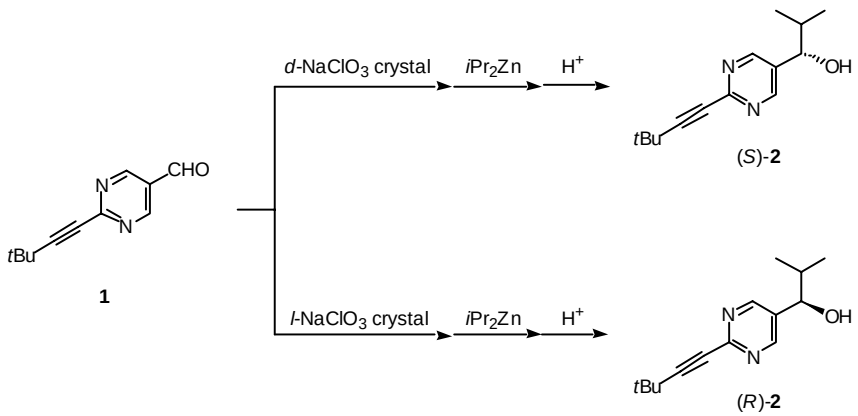
Table 1
Enantioselective synthesis of 5-pyrimidyl alkanol **2** in the presence of *d*- or *l*-$NaClO_3$[a]

Entry	$NaClO_3$	5-Pyrimidyl alkanol **2**		
		Yield (%)	ee[b] (%)	Configuration
1	*d*	93	98	*S*
2	*d*	99	98	*S*
3	*d*	90	97	*S*
4	*l*	91	98	*R*
5	*l*	95	98	*R*
6	*l*	98	98	*R*
7	*d*/*l* (3/1)	92	97	*S*
8	*l*/*d* (3/1)	90	97	*R*

[a] Molar ratio. $NaClO_3$: pyrimidine-5-aldehyde **1**: *i*-Pr_2Zn = 1.9; 1.0; 2.0. See also Section 4.
[b] ee was determined by HPLC analysis using a chiral column (Chiralcel OD).

In addition, reactions in the presence of a mixture of *d*- and *l*-$NaClO_3$ were also examined. When a 3:1 mixture of *d*- and *l*-$NaClO_3$ was used, (*S*)-5-pyrimidyl alkanol **2** with 97% ee was obtained in 92% yield (entry 7). In contrast, by using a 1:3 mixture of *d*- and *l*-$NaClO_3$, (*R*)-5-pyrimidyl alkanol **2** with 97% ee was formed (entry 8). Thus, the configurations of 5-pyrimidyl alkanol **2** formed were dependent on the major enantiomorphs in the mixture of *d*- and *l*-$NaClO_3$. The high ee's of 5-pyrimidyl alkanol suggest that asymmetric autocatalysis with amplification of ee is critically important in this reaction system.

When the reactions were run in the presence of *d*-, *l*-, *d*- and *l*-$NaClO_3$, alternatively, using exactly the same reaction equipment (Table 2), (*S*)-, (*R*)-, (*S*)- and (*R*)-5-pyrimidyl alkanol **2** with 96% ee were obtained in 93−94% yields, respectively (runs 1−4). These results clearly show that the



Scheme 1. Highly enantioselective synthesis of 5-pyrimidyl alkanol **2** using *d*- or *l*-$NaClO_3$.

Table 2
Consecutive reaction in the presence of $NaClO_3$ using same equipments[a]

Run	$NaClO_3$	5-Pyrimidyl alkanol **2**		
		Yield (%)	ee (%)	Configuration
1	*d*	93	96	*S*
2	*l*	94	96	*R*
3	*d*	93	96	*S*
4	*l*	94	96	*R*

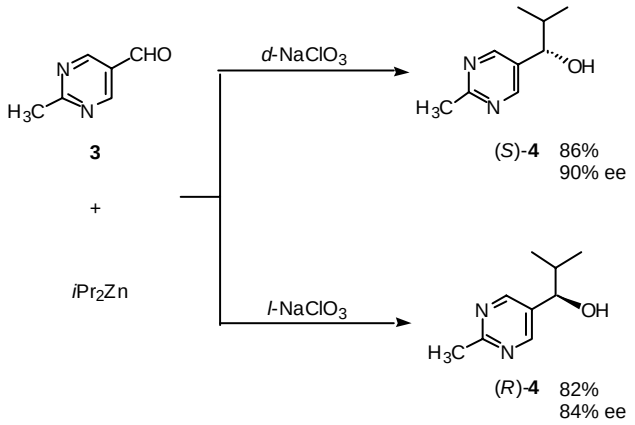
[a] Reactions were carried out in the order of run numbers using the same equipment.

chirality of $NaClO_3$ controls the absolute configuration of the 5-pyrimidyl alkanol **2** formed.

When the reaction was run at −73 °C for 1 h in the presence of *l*-$NaClO_3$, (*R*)-5-pyrimidyl alkanol **2** with 2% ee was obtained in 4% yield. On the other hand, for the corresponding reaction in the absence of $NaClO_3$, 5-pyrimidyl alkanol **2** (ee was below the detection level) was obtained in 5% yield. Thus, acceleration in the reaction rate by $NaClO_3$ crystals is not significant, and the present asymmetric reaction scheme may be described as follows: chiral $NaClO_3$ induces a very small enantiomeric enrichment in the initially formed isopropylzinc alkoxide of 5-pyrimidyl alkanol. The formed isopropylzinc alkoxide of 5-pyrimidyl alkanol acts as an asymmetric autocatalyst with amplification of ee. After working up, 5-pyrimidyl alkanol **2** with high ee is obtained in high yield, possessing the absolute configuration corresponding to the chirality of the $NaClO_3$ used.

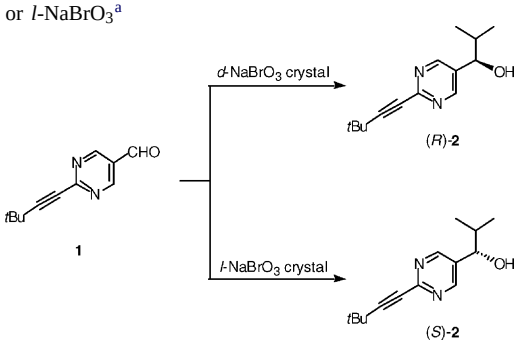
Studying the effect of the substituent at the 2-position of pyrimidine-5-carbaldehyde, enantioselective addition of *i*-Pr_2Zn to 2-methylpyrimidine-5-carbaldehyde **3** in the presence of *d*-$NaClO_3$ gave (*S*)-2-methyl-5-pyrimidyl alkanol **4** with 90% ee, while reaction in the presence of *l*-$NaClO_3$ gave (*R*)-5-pyrimidyl alkanol **4** (Scheme 2).

Thus, the corresponding 2-alkynyl- and 2-methylpyrimidyl alkanols with the same configuration were obtained from the reaction of *i*-Pr_2Zn with 2-alkynyl- and 2-methylpyrimidine-5-carbaldehyde in the presence of $NaClO_3$.



Scheme 2. Enantioselective synthesis of (*S*)- and (*R*)-5-pyrimidyl alkanol **4** in the presence of *d*- and *l*-$NaClO_3$, respectively.

Table 3
Enantioselective synthesis of 5-pyrimidyl alkanol **2** in the presence of *d*- or *l*-$NaBrO_3$[a]



Entry[b]	$NaBrO_3$	5-Pyrimidyl alkanol **2**		
		Yield (%)	ee (%)	Configuration
1	*d*	88	97	*R*
2	*d*	92	98	*R*
3	*d*	86	97	*R*
4	*l*	90	97	*S*
5	*l*	88	96	*S*
6	*l*	87	92	*S*
7	*l*	89	94	*S*
8	*d*	93	98	*R*
9	*d*	92	98	*R*
10	*l*	92	96	*S*
11	*l*	93	98	*S*
12	*l*	93	95	*S*

[a] Molar ratio. $NaBrO_3$: pyrimidine-5-aldehyde **1**: *i*-Pr_2Zn = 3.8; 1.0; 2.0. See also Section 4.

[b] For entries 1–7, sodium bromate was suspended in 0.1 ml of toluene. For entries 8–12, sodium bromate was suspended in 0.2 ml of toluene.

2.2. Sodium bromate mediated asymmetric autocatalysis

Sodium bromate exhibits enantiomorphism. We examined the reaction between 2-alkynylpyrimidine-5-carbaldehyde **1** and *i*-Pr_2Zn in the presence of $NaBrO_3$ crystals (Table 3). Initially, we were surprised to observe that, when *d*-$NaBrO_3$ was used for the reaction, (*S*)-pyrimidyl alkanol **2** was not formed, rather (*R*)-5-pyrimidyl alkanol **2** with 97% ee was obtained in 88% (entry 1). Repeated reaction using *d*-$NaBrO_3$ also produced (*R*)-5-pyrimidyl alkanol **2** with 97–8% ee (entries 2 and 3). Thus, the reproducibility of the absolute configuration of 5-pyrimidyl alkanol **2** was confirmed. Note that *l*-$NaClO_3$, not *d*-$NaClO_3$, gives (*R*)-5-pyrimidyl alkanol **2**, as described in the preceding section. However, the observations that both *d*-$NaBrO_3$ and *l*-$NaClO_3$ gave the same (*R*)-5-pyrimidyl alkanol **2** is explained by the fact that *d*-$NaBrO_3$ has the opposite absolute configuration of the crystal structure to that of *d*-$NaClO_3$. In other words, *d*-$NaBrO_3$ and *l*-$NaClO_3$ have the same absolute configuration of the crystal structure [15].

On the other hand, in the presence of *l*-$NaBrO_3$ instead of *d*-$NaBrO_3$, the reaction between pyrimidine-5-carbaldehyde **1** and *i*-Pr_2Zn gave (*S*)-5-pyrimidyl alkanol **2** with 92–7% ee (entries 5−7). The reactions under dilute conditions (entries

8−12) gave (*S*)-5-pyrimidyl alkanol **2** with up to 98% ee in yields of 92−93%.

We postulate that the chiral surfaces of $NaClO_3$ and $NaBrO_3$ discriminate the *re* and *si* enantiofaces of pyrimidine-5-carbaldehydes **1** to a very small extent in the interaction between pyrimidine-5-carbaldehyde **1** and the surfaces of chiral inorganic crystals. Then the initial addition of *i*-Pr_2Zn to pyrimidine-5-carbaldehyde **1** produces very slightly enantioenriched isopropylzinc alkoxide of pyrimidyl alkanol with the absolute configuration correlated to that of the chiral inorganic crystals. The subsequent asymmetric autocatalysis with amplification of ee finally gives the pyrimidyl alkanol with very high ee. Thus, $NaClO_3$ and $NaBrO_3$ as chiral initiators are considered to tip the balance of the chirality of pyrimidyl alkanol in the initial stage of the reaction.

3. Conclusions

We have demonstrated that chiral crystals of sodium chlorate and sodium bromate, i.e. inorganic ionic enantiomorphs, act as chiral initiators to tip the balance of the addition reaction of diisopropylzinc to pyrimidine-5-carbaldehydes to produce, in combination with asymmetric autocatalysis, highly enantioenriched pyrimidyl alkanols having the corresponding absolute configurations of those of $NaClO_3$ and $NaBrO_3$. The present results, as well as our preceding report on chiral quartz promoted highly enantioselective synthesis, correlate the chirality of inorganic crystals with highly enantioenriched organic molecules.

4. Experimental

4.1. General details

Optical rotation was measured by Jasco DIP-1000 polarimeter. Compounds **1**–**4** are known in [11c,13a]. Toluene was distilled from lithium aluminum hydride. All other reagents and solvents were purchased from commercial sources and used as received.

4.2. Preparation of crystals and powders of $NaClO_3$ and $NaBrO_3$

Crystallization of $NaClO_3$ from purified water gave small crystals. A small crystal was put in an aqueous solution of $NaClO_3$ at room temperature, and the mixture was kept standing until the size of the crystal reached over 5 mm. Absolute configuration of the crystal was determined by polarimeter [16]. Crystals were ground into powder using a pestle and mortar (microscopic analysis of *d*-$NaClO_3$ showed the particle size: 5–12 μm), washed with ether, and dried in vacuo before use. Crystallization, determination of absolute configuration [16] and preparation of powders of $NaBrO_3$ were performed in a similar manner.

4.3. Typical experimental procedure of $NaClO_3$-induced enantioselective addition of diisopropylzinc to 2-(3,3-dimethy-1-butynyl)pyrimidine-5-carbaldehyde **1**

To a suspension of pyrimidine-5-carbaldehyde **1** (9.4 mg, 0.05 mmol) and *d*-$NaClO_3$ (222 mg, 2.09 mmol) in toluene (0.2 ml), a 1 M toluene solution (0.15 ml) of *i*-Pr_2Zn was added dropwise with stirring (60–70 rpm) over a period of 30 min at 0 °C. After the mixture was stirred for 12 h, toluene (4.8 ml), a 1 M toluene solution (0.4 ml) of *i*-Pr_2Zn, and pyrimidine-5-carbaldehyde **1** (37.6 mg, 0.2 mmol) in toluene (1.5 ml) were added successively. After 3 h, toluene (14 ml), a 1 M toluene solution (1.6 ml) of *i*-Pr_2Zn, and pyrimidine-5-carbaldehyde **1** (151 mg, 0.8 mmol) in toluene (4 ml) were added and the mixture was stirred for further 3 h. The reaction was quenched by adding 1 M hydrochloric acid (4 ml), made alkaline by saturated aqueous sodium bicarbonate (12 ml). The mixture was filtered through Celite, and the separated aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over sodium sulfate and concentrated. Purification of the residue by silica gel thin layer chromatography (developing solvent, hexane: ethyl acetate = 2:1) gave 5-pyrimidyl alkanol **2** (242 mg, 1.04 mmol) in 99%. Ee was determined as 98% by HPLC analysis on a column with a chiral stationary phase (Chiralcel OD) (Table 1, entry 2).

4.4. Reaction of 2-(3,3-dimethy-1-butynyl)pyrimidine-5-carbaldehyde **1** and diisopropylzinc in the presence of $NaClO_3$ at −72 °C

A suspension of pyrimidine-5-carbaldehyde **1** (9.4 mg, 0.05 mmol) and *d*-$NaClO_3$ (216 mg, 2.03 mmol) in toluene (0.5 ml) was cooled to −78 °C. A 1 M toluene solution (0.15 ml) of *i*-Pr_2Zn was added to the mixture in one portion, and the mixture was stirred for 1 h at −72 °C. The reaction was quenched by adding 1 M hydrochloric acid (2 ml), made alkaline by saturated aqueous sodium bicarbonate (6 ml). The mixture was filtered through Celite, and the separated aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over sodium sulfate and concentrated. Purification of the residue by silica gel thin layer chromatography (developing solvent, hexane: ethyl acetate = 2: 1) gave 5-pyrimidyl alkanol **2** (0.5 mg, 0.002 mmol) in 4% together with the recovery of pyrimidine-5-carbaldehyde **1** (7.0 mg, 0.030 mmol). An ee value of (*R*)-5-pyrimidyl alkanol **2** was determined as 2% by HPLC analysis using a chiral column (Chiralcel OD).

When the corresponding reaction (−72 °C, 1 h) in the absence of $NaClO_3$ was performed, racemic 5-pyrimidyl alkanol **2** (0.6 mg, 0.003 mmol) and pyrimidine-5-carbaldehyde **1** (5.0 mg, 0.022 mmol) were obtained. The ee value is below the detection level in HPLC analysis using a chiral stationary phase.

4.5. $NaClO_3$-induced enantioselective addition of diisopropylzinc to 2-methylpyrimidine-5-carbaldehyde **3**

To a suspension of 2-methylpyrimidine-5-aldehyde **3** (12.2 mg, 0.1 mmol) and *d*-$NaClO_3$ (423.2 mg, 3.98 mmol) in toluene (0.5 ml), a 1 M toluene solution (0.3 ml) of *i*-Pr_2Zn was added dropwise over a period of 30 min at 0 °C. After the mixture was stirred for 17 h, toluene (2.3 ml), a 1 M toluene solution (0.96 ml) of *i*-Pr_2Zn, and 2-methylpyrimidine-5-aldehyde **3** (48.8 mg, 0.4 mmol) in toluene (1.0 ml) were added successively. After 6 h, toluene (9.4 ml), a 1 M toluene solution (3.8 ml) of *i*-Pr_2Zn, and 2-methylpyrimidine-5-aldehyde **3** (195.4 mg, 1.6 mmol) in toluene (2.5 ml) were added and the mixture was stirred for further 14 h. The reaction was quenched by adding 1 M hydrochloric acid (5 ml), made alkaline by saturated aqueous sodium bicarbonate (15 ml). The mixture was filtered through Celite, and the separated aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over sodium sulfate and concentrated. Purification of the residue by silica gel thin layer chromatography (developing solvent, hexane: acetone = 3:2) gave 5-pyrimidyl alkanol **4** (302 mg, 1.82 mmol) in 86%. The ee value was determined as 90% by HPLC analysis on a column with a chiral stationary phase (Chiralcel OD).

4.6. Typical experimental procedure of $NaBrO_3$-induced enantioselective addition of diisopropylzinc to 2-(3,3-dimethy-1-butynyl)pyrimidine-5-carbaldehyde **1**

To a suspension of pyrimidine-5-aldehyde **1** (4.7 mg, 0.025 mmol) and *d*-$NaBrO_3$ (302 mg, 2.0 mmol) in toluene (0.2 ml), a 1 M toluene solution (0.075 ml) of *i*-Pr_2Zn was added dropwise over a period of 30 min at 0 °C. After the mixture was stirred for 15 h, toluene (2.0 ml), a 1 M toluene solution (0.2 ml) of *i*-Pr_2Zn, and pyrimidine-5-aldehyde **1** (18.8 mg, 0.1 mmol) in toluene (1.0 ml) were added successively. After 4 h, toluene (7 ml), a 1 M toluene solution (0.8 ml) of *i*-Pr_2Zn, and pyrimidine-5-aldehyde **1** (75.3 mg, 0.4 mmol) in toluene (2 ml) were added and the mixture was stirred for further 3 h. The reaction was quenched by adding 1 M hydrochloric acid (4 ml), made alkaline by saturated aqueous sodium bicarbonate (12 ml). The mixture was filtered through Celite, and the separated aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over sodium sulfate and concentrated. Purification of the residue by silica gel thin layer chromatography (developing solvent, hexane: ethyl acetate = 2:1) gave 5-pyrimidyl alkanol **2** (112 mg, 0.48 mmol) in 92%. Ee was determined as 98% by HPLC analysis on a column with a chiral stationary phase (Chiralcel OD) (Table 3, entry 9).

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