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Ru-catalyzed enantioselective preparation of methyl (*R*)-*o*-chloromandelate and its application in the synthesis of (*S*)-Clopidogrel

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ABSTRACT

The preparation of methyl (*R*)-*o*-chloromandelate via Ru-catalyzed asymmetric hydrogenation and transfer hydrogenation was investigated. With Ru-(*R*,*R*)-2,4,6-triisopropyl $C_6H_2SO_2$-DPEN as the catalyst and HCOOH–Et_3N azeotrope as the hydrogen donor, up to 92% ee was obtained in an optional condition. The synthesis of (*S*)-Clopidogrel was also studied.

1. Introduction

(*S*)-Clopidogrel, commercialized as a brand name, Plavix, is a potent oral antiplatelet agent often used in the treatment of coronary artery, peripheral vascular and cerebrovascular disease. Plavix (clopidogrel bisulfate), is the second best-selling drug in the world, with global sales of $6.4 billion in 2006 and $7.3 billion in 2007 [1,2]. It is marketed by Sanofi-Aventis and Bristol-Myers Squibb. Many of the early methods proposed for preparing enantiomerically pure clopidogrel involved separation of the desired enantiomerically pure compound from a racemic mixture. The asymmetric synthetic methods of preparing (*S*)-Clopidogrel with chiral building blocks were also developed in recent years. Among them, the most preferred one for industrial synthesis of this useful compound was with (*R*)-*o*-chloromandelic acid as starting material (Scheme 1). A number of approaches have been reported in the synthesis of (*R*)-*o*-chloromandelic acid or its methyl ester. Hyoda and Balint et al. described the preparation of (*R*)-*o*-chloromandelic acid by diastereomeric crystallization [3,4]. Zhu et al. disclosed their investigations on the enantioselective insertion reaction of α-diazoesters with water catalyzed by Cu/spirobox complexes, however, only 36% ee was obtained for (*R*)-(−)-methyl 2-hydroxy-2-(2-chlorophenyl)acetate [5]. Other groups also developed the methods of enantioselective enzymatic hydrolysis of the corresponding nitrile compounds [6–8] and ester compounds [9–12]. Recently, Ema et al. developed an asymmetric reduction of methyl *o*-chlorobenzoylformate with recombinant *Escherichia coli* over producing a versatile carbonyl reductase [13]. Lee et al. used a solvent-free enzymatic process for methyl (*R*)-*o*-chloromandelate through the CAL-A-catalyzed transesterification reaction using vinyl propionate as an acyl donor. Under the optimized condition, 41% yield with more than 99% ee was obtained [14]. On the other hand, the direct asymmetric reduction of *a*-keto esters has also been approached in recent years. Genet et al. developed the Ru-catalyzed asymmetric hydrogenation of *a*-keto ester to afford (*R*)-*o*-chloromandelate with 50% ee [15]. Zhang et al. reported the asymmetric hydrogenation of the corresponding ethyl ester with enantioselectivity of up to 78.2% ee [16,17]. In our previous study, we reported a total synthesis of (*R*)-Salmeterol, a selective long-acting β_2-adrenoreceptor agonist, via asymmetric transfer hydrogenation for preparing the chiral secondary alcohol which is the key intermediate in the synthesis. Herein, we report our study of ruthenium-catalyzed enantioselective preparation of methyl (*R*)-*o*-chloromandelate and its application in the synthesis of (*S*)-Clopidogrel.

2. Results and discussion

We first investigated the preparation of methyl (*R*)-*o*-chloromandelate by asymmetric hydrogenation with Ru-BINAP as the catalyst (Scheme 2). Nearly quantitative conversion with 41.6% ee was obtained when the reaction was carried out at 50 °C for 20 h with [Ru(*R*)-BINAP(*p*-cymene)Cl]Cl (Cat. **1a**) as the catalyst. Sparked by Zhang group's work [17], we introduced cerium

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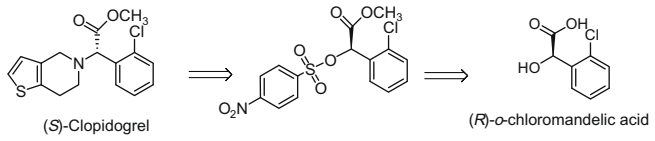
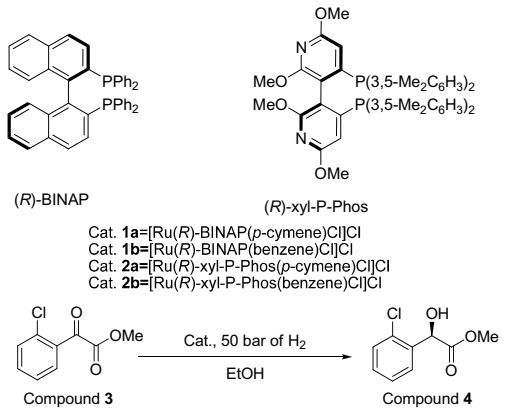


Scheme 1. Asymmetric synthesis of (*S*)-Clopidogrel.



Scheme 2. Ruthenium-catalyzed asymmetric hydrogenation of compound **3**.

chloride hydrate as the additive to the reaction system, the ee increased from 41.6% to 58.4% (Table 1, entries 1 and 2). [Ru(*R*)-BINAP(benzene)Cl]Cl complex (Cat. **1b**) as the catalyst seemed slightly favorable for the enantioselectivity, which gave 64.8% ee at the same reaction conditions. We then used (*R*)-xyl-P-Phos as the chiral ligand for the hydrogenation. Comparison experiments, made between [Ru(*R*)-xyl-P-Phos(*p*-cymene)Cl]Cl (Cat. **2a**) and [Ru(*R*)-xyl-P-Phos(benzene)Cl]Cl (Cat. **2b**) with or without additive, turned out that the addition of cerium chloride hydrate did enhance the enantioselectivities. (The ee values increased from 31.1% to 50.4% for Cat. **2a** and 29.8–64.8% for Cat. **2b**, respectively. Table 1, entries 4–7.)

It is well known that asymmetric transfer hydrogenation (ATH) is an alternative to asymmetric hydrogenation (AH) because this method does not need either pressure vessels or hydrogen gas and can be carried out in ordinary laboratories, however, to the best of our knowledge, there are no reports about the preparation of methyl (*R*)-*o*-chloromandelate via asymmetric transfer hydrogenation (ATH). For exploring the possibility of ATH as a key strategy in asymmetric synthesis of (*S*)-Clopidogrel, we first chose Ts-DPEN (**5a**), a widely used chiral ligand in the catalytic asymmetric transfer hydrogenation of ketones, for the Ru-catalyzed ATH of methyl *o*-chlorobenzoylformate (compound **3**) (Scheme 3). With HCOOH–Et_3N azeotrope as the hydrogen donor, the reaction proceeded smoothly in a short time and gave the desired product with good enantioselectivity and conversion (Table 2, entry 1, 100% conversion with 91% ee; the ratio of substrate to catalyst: 200). We then screened other ligands for the reaction under the same reaction conditions. The results indicated that electronic-drawing groups on the sulfonyl part of the ligands seemed unfavorable to the enantioselectivity of the reaction. When (*R*,*R*)-*o*-NO_2-$C_6H_4SO_2$-DPEN (**5b**) was chosen as the chiral ligand, only 78% ee was obtained. On the other hand, ligand (**5c**), which has three isopropyl groups on the sulfonyl part, gave full conversion with 92.6% ee. The conversions and the enantioselectivities were almost consistent when the S/C ratio was increased to 500, though increasing reaction time was required (Table 2, entries 4 and 5). Compared with that of HCOOH–Et_3N azeotrope, there was not much difference in conversion and the reaction time when water was used as the reaction media (with PEG 2000 or PEG 400 as additive) and HCOONa as the hydrogen donor. However, the ee values debased obviously, especially with **5a** and **5c** as chiral ligands (Table 2, entries 6–11). The temperature effect was not much significant for the reaction; when reaction temperature was droped to 0 °C, the ee values remained nearly the same (Table 2, entries 12–14).

Table 1
Asymmetric hydrogenation of compound **3**.[a]

Entry	Catalyst	Additive	Conversion [b] (%)	Ee [b] (%)
1	Cat. **1a**	None	100	41.6
2	Cat. **1a**	$CeCl_3 \cdot 7H_2O$	100	58.4
3	Cat. **1b**	$CeCl_3 \cdot 7H_2O$	100	64.8
4	Cat. **2a**	None	100	31.1
5	Cat. **2b**	None	100	29.8
6	Cat. **2a**	$CeCl_3 \cdot 7H_2O$	100	50.4
7	Cat. **2b**	$CeCl_3 \cdot 7H_2O$	100	64.8

[a] Reactions were carried out in 1 mmol scale, at 50 °C for 20 h.
[b] The conversion and ee values were determined by HPLC on chiral OJ-H column (Hexane: *i*-PrOH = 92:8, 1.0 mL/min); (*R*)-configuration was assigned by comparing the retention time with that reported in the literature [5].

The synthesis of (*S*)-Clopidogrel was also carried out according to the literature reported procedure [18] with methyl (*R*)-*o*-chloromandelate as the starting material (Scheme 4). The ee of the product (*S*)-Clopidogrel free base was almost the same as that of compound **4**, which was determined by HPLC analysis.

3. Conclusions

In summary, we have developed an asymmetric transfer hydrogenation process for the preparation of methyl (*R*)-*o*-chloromandelate, which could be carried out in a very mild condition with high conversion and good ee, and the strategy was successfully applied to the synthesis of (*S*)-Clopidogrel.

4. Experimental

4.1. General

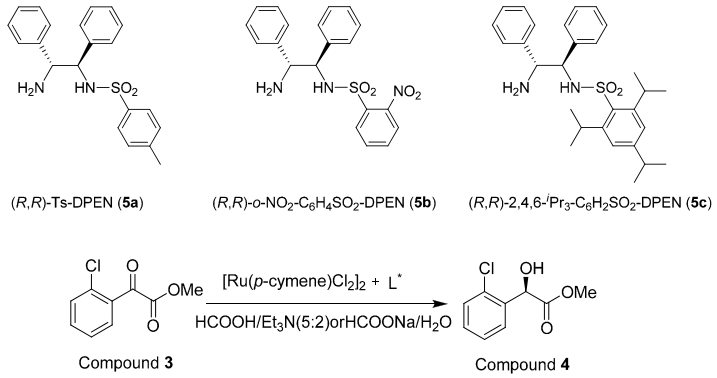
^1H NMR spectra were recorded with TMS as the internal standard on a Bruker AV400 in $CDCl_3$. Chiral HPLC analysis was performed on a SHIMADZU LC-20AT chromatography using Daicel Chiralcel OJ-H column. (*R*)-BINAP and (*R*)-xyl-P-Phos were purchased from Alfa Aesar Company. DMF and dichloromethane were distilled over calcium hydride. Ethanol used for asymmetric hydrogenation was obtained by distillation from magnesium under nitrogen.

4.2. Methyl 2-hydroxy-2-(2-chlorophenyl)acetate [18]

To a solution of racemic 2-hydroxy-2-(2-chlorophenyl)acetic acid (1.2 g, 6.43 mmol) in methanol (4.8 mL) was added 98% sulfuric acid (0.048 g, 0.4894 mmol) with stirring and the mixture was heated to reflux. After stirring for 2 h, the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (6.5 mL), washed with 10% potassium carbonate and then water. The solvent was removed in vaccum to afford methyl 2-hydroxy-2-(2-chlorophenyl)acetate as colorless oil (1.24 g, 94% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.4–7.2 (m, 4H), 5.58 (s, 1H), 3.66 (s, 3H), 4.22 (brs, 1H).

4.3. Methyl o-chlorobenzoylformate (compound 3) [19]

To a solution of methyl 2-hydroxy-2-(2-chlorophenyl)acetate (3.73 g, 20 mmol) in CH_2Cl_2 (20 mL) at room temperature was

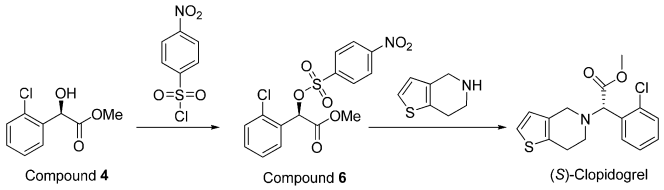


Scheme 3. Ruthenium-catalyzed asymmetric transfer hydrogenation of compound **3**.

Table 2
Asymmetric transfer hydrogenation of compound **3**.[a]

Entry	Ligand	Hydrogen source	S/C	Time (h)	Conversion [b] (%)	Ee[b] (%)
1	**5a**	$HCOOH/Et_3N(5:2)$	200	40 (min)	100	91.4
2	**5b**	$HCOOH/Et_3N(5:2)$	200	40 (min)	100	77.5
3	**5c**	$HCOOH/Et_3N(5:2)$	200	40 (min)	100	92.6
4	**5b**	$HCOOH/Et_3N(5:2)$	500	20	100	78.9
5	**5c**	$HCOOH/Et_3N(5:2)$	500	1.5	100	92.1
6[c]	**5a**	$HCOONa/H_2O$	200	1	100	78.4
7[c]	**5b**	$HCOONa/H_2O$	200	1	100	76.4
8[c]	**5c**	$HCOONa/H_2O$	200	1	100	72.1
9[d]	**5a**	$HCOONa/H_2O$	200	1	100	75.8
10[d]	**5b**	$HCOONa/H_2O$	200	1	100	74.6
11[d]	**5c**	$HCOONa/H_2O$	200	1	100	77.5
12[e]	**5a**	$HCOOH/Et_3N(5:2)$	200	5	100	89.2
13[e]	**5b**	$HCOOH/Et_3N(5:2)$	200	5	100	80.7
14[e]	**5c**	$HCOOH/Et_3N(5:2)$	200	5	100	90.3

[a] Reactions were carried out in 1 mmol scale; for reaction details, see Section 4.
[b] The conversion and ee values were determined by HPLC on chiral OJ-H column (Hexane: *i*-PrOH = 92:8, 1.0 mL/min); (*R*)-configuration was assigned by comparing the retention time with that reported in the literature [5].
[c] PEG 2000 (PEG 2000/H_2O = 3:1, v/v) was added.
[d] PEG 400 (PEG 400/H_2O = 3:1, v/v) was added.
[e] Reactions were carried out at 0 °C.



Scheme 4. Synthesis of (*S*)-Clopidogrel from compound **4**.

added $KMnO_4$ (3.17 g, 20 mmol) followed by $Al_2(SO_4)_3 \cdot 18H_2O$ (4.84 g, 20 mmol). The resulting mixture was stirred vigorously for 2 h. After this time the reaction mixture was filtered and the filtrate was concentrated under reduced pressure to provide methyl *o*-chlorobenzoylformate (compound **3**) as light yellow oil (3.53 g, 88% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.7–7.4 (m, 4H), 3.95 (s, 3H).

4.4. Typical procedure for asymmetric hydrogenation [17]

A solution of $[Ru(benzene)Cl_2]_2$ (2.5 mg, 0.005 mmol) and (*R*)-xyl-P-Phos (8.51 mg, 0.011 mmol) was heated at 50 °C in degassed EtOH and CH_2Cl_2 (0.75 mL/0.75 mL) for 1 h under argon atmosphere. After the mixture was cooled to ambient temperature and vacuumed to give the catalyst, $CeCl_3 \cdot 7H_2O$ (18.75 mg, 0.05 mmol) in degassed EtOH (2 mL) and compound **3** (0.198 g, 1.0 mmol) were added. The reactor was purged three times with hydrogen before the pressure was set to 50 bar. The autoclave was stirred at 50 °C for 20 h and cooled, and then hydrogen was released carefully. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel to give the desired product.

4.5. General procedure for the preparation of ligands [20]

4.5.1. (R,R)-Ts-DPEN (**5a**)

To a solution of (*R*,*R*)-diphenylethylene-diamine (0.5 g, 2.36 mmol) in CH_2Cl_2 (4 mL) was added 1 M NaOH solution (4 mL) at 0 °C, followed by a cold solution of *p*-toluenesulphonyl chloride (0.45 g, 2.36 mmol) in CH_2Cl_2 (8 mL) at the same temperature in 10 min. After stirring for 1 h, the reaction mixture was washed with brine and water. The organic phase was concentrated under reduced pressure and the residue was purified by crystallization (toluene:hexane; v/v 3:1) to afford (*R*,*R*)-Ts-DPEN as a white crystal solid (0.27 g, 31% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8 Hz, 2H), 7.15 (m, 10H), 6.96 (d, J = 7.6 Hz, 2H), 4.38 (d, J = 5.2 Hz, 1H), 4.13 (d, J = 5.2 Hz, 1H), 2.31 (s, 3H), 1.42 (brs, 2H).

4.5.2. (R,R)-o-NO_2-$C_6H_4SO_2$-DPEN (**5b**) and (R,R)-2, 4, 6-^{i}Pr$_3$-$C_6H_2SO_2$-DPEN (**5c**)

To a solution of (*R*,*R*)-diphenylethylene-diamine (0.5 g, 2.36 mmol) and 2,4,6-triisopropylbenzenesulfonyl chloride

(0.713 g, 2.36 mmol) in CH_2Cl_2 (8 mL) was added 1 M NaOH solution (4 mL) at 0 °C. With the same procedure as that of (*R*,*R*)-Ts-DPEN, crude (*R*,*R*)-2,4,6-$^{i}Pr_3$-$C_6H_2SO_2$-DPEN was obtained, which was purified by flash column chromatography on silica gel to give an off-white powder (1.0 g, 89% yield); Similarly, (*R*,*R*)-*o*-NO_2-$C_6H_4SO_2$-DPEN as a yellow powder (0.83 g, 88% yield) was obtained by reaction of (*R*,*R*)-diphenylethylene-diamine (0.5 g, 2.36 mmol) with 2-nitro-benzenesulfonyl chloride (0.523 g, 2.36 mmol) in CH_2Cl_2 (8 mL).

(R,R)-2,4,6-$^{i}Pr_3$-$C_6H_2SO_2$-DPEN. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-6.98 (m, 10H), 6.82 (d, J = 7.2 Hz, 2H), 4.51 (d, J = 7.6 Hz, 1H), 4.06 (d, J = 7.6 Hz, 1H), 3.98 (m, 2H), 2.82 (m, 1H), 1.21 (d, J = 7.2 Hz, 6H), 1.17 (d, J = 6.8 Hz, 6H), 1.09 (d, J = 6.4 Hz, 6H).

(R,R)-o-NO_2-$C_6H_4SO_2$-DPEN. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, J = 7.6 Hz, 1H), 7.45 (t, J = 8.4 Hz, 2H), 7.30 (m, 1H), 7.25–6.98 (m, 10H), 4.69 (d, J = 3.6 Hz, 1H), 4.30 (d, J = 3.6 Hz, 1H).

4.6. General procedure for asymmetric transfer hydrogenation

4.6.1. HCOOH/Et_3N (5:2) as hydrogen source [21]

To a Schlenk tube were added [Ru(*p*-cymene)Cl_2]$_2$ (1.53 mg, 0.005 mmol) and the chiral ligand (1.2 equiv., to the metal atom) under argon atmosphere, followed by the addition of DMF (0.5 mL). The system was allowed to stir at 80 °C for 20 min before cooling to room temperature. Methyl *o*-chlorobenzoylformate (0.198 g, 1.0 mmol) and HCOOH/Et_3N azeotrope (0.44 g, 5 mmol HCOOH) were subsequently added. The resulting mixture was stirred at 25 °C for the time shown in Table 2 and then concentrated in vacuum. The residue was purified by silica gel chromatography to give pure methyl (*R*)-*o*-chloromandelate (compound **4**).

4.6.2. HCOONa as hydrogen source [22]

A mixture of [Ru(*p*-cymene)Cl_2]$_2$ (1.53 mg, 0.005 mmol), (*R*,*R*)-Ts-DPEN (2.2 mg, 0.006 mmol) in water (0.5 mL) was heated at 40 °C for 1 h under argon atmosphere. After cooling to room temperature, a mixture of methyl *o*-chlorobenzoylformate (0.198 g, 1.0 mmol), 2.5 M HCOONa (2 mL, 5.0 mmol) and PEG 2000 (or PEG 400) (1.5 mL) was introduced. The resulting solution was stirred at 40 °C for a certain period of time. Then the mixture was extracted with *n*-hexane, dried over anhydrous sodium sulfate, filtered and concentrated in vacuum to give the crude product which was purified by silica gel chromatography.

4.7. Preparation of (S)-Clopidogrel from compound **4**

4.7.1. 4,5,6,7-Tetrahydrothieno[3,2-c]pyridine hydrochloride [23]

A solution of 2-thienylethylamine (5 g, 39.3 mmol) in dichloroethane (30 mL) was stirred for 5 min in a vessel equipped with a dean stark assembly for azeotropic removal of water formed in the reaction. Paraformaldehyde (1.32 g) was added and the resulting mixture was heated to reflux for 4 h. After this period the reaction mixture was cooled to ambient temperature, 6.6 N hydrochloric acid solution (6.65 mL) in dimethylformamide was added. The reaction mass was heated to 70 °C for 4 h. After cooling to room temperature, the mixture was filtered under vacuum and washed with dichloroethane. The filter cake was dried in oven at 50 °C to provide the title compound as a white solid (4.8 g, 70% yield).

4.7.2. (R)-4-nitrobenzenesulfonyloxy-2-(2-chlorophenyl)acetate (compound 6) [18]

To a stirred mixture of DMAP (0.073 g, 0.6 mmol), (*R*)-2-hydroxy-2-(2-chlorophenyl)acetate (1.2 g, 6.0 mmol) and Et_3N (0.78 g, 7.8 mmol) in CH_2Cl_2 (2 mL) at 0 °C was slowly added an ice-cold solution of 4-nitrobenzenesulfonyl chloride (1.33 g, 6.0 mmol) in CH_2Cl_2 (3 mL). After stirring for 3 h at the same temperature, the mixture was quenched with water. The organic layer was separated, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the title compound as a light yellow solid (1.8 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, J = 8.8 Hz, 2H), 8.08 (d, J = 8.8 Hz, 2H), 7.39–7.24 (m, 4H), 6.39 (s, 1H), 7.35 (s, 3H).

4.7.3. (S)-Clopidogrel free base [18]

To a stirred mixture of 4,5,6,7-tetrahydrothieno [3,2-c] pyridine (0.168 g, 1.2 mmol) and 30% aqueous solution of potassium carbonate (0.57 g) in CH_2Cl_2 (1.5 mL) was added a solution of compound **6** (0.385 g, 1.0 mmol) in CH_2Cl_2 (0.5 mL). The two-phase mixture was refluxed for 2.5 h. The mixture was cooled to room temperature and filtered under vaccum then washed with a small amount of CH_2Cl_2 to give the (*S*)-Clopidogrel or methyl (*S*)-2-(2-chlorophenyl)-2-(4,5,6,7-tetrahydrothieno[3,2-c]pyridyl)acetate (0.23 g, 70% yield, 90% ee, determined by HPLC analysis). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (m, 1H), 7.41 (m, 1H), 7.33–7.22 (m, 2H), 7.06 (d, J = 5.2 Hz, 1H), 6.67 (d, J = 5.2 Hz, 1H), 4.92 (s, 1H), 3.74 (s, 2H), 3.73 (s, 3H), 2.88 (s, 4H).

Acknowledgements

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