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Asymmetric synthesis of chiral Roche ester and its derivatives via Rh-catalyzed enantioselective hydrogenation with chiral phosphine-phosphoramidite ligands

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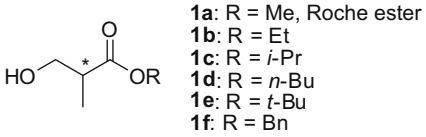
ABSTRACT

Methyl 3-hydroxy-2-methylpropionate, known as the Roche ester, was prepared with high enantioselectivity (up to 96.7% ee) via the Rh-catalyzed asymmetric hydrogenation of methyl 2-hydroxymethylacrylate with a chiral 1,2,3,4-tetrahydro-1-naphthylamine-derived phosphine-phosphoramidite ligand (THNAPhos **5a**) even at a low catalyst loading (0.1 mol %). An investigation on the substrate scope revealed that the ester group present in the substrate has a significant effect on the enantioselectivity, and the substrate with the bulkier ester group tended to give lower enantioselectivity.

1. Introduction

Chiral methyl 3-hydroxy-2-methylpropionate (Roche ester, **1a**, Fig. 1) is a very important building block for the enantioselective synthesis of many natural products and pharmaceutical compounds.[1] The enantioselective access to this compound is therefore of great interest.



1a: R = Me, Roche ester
1b: R = Et
1c: R = *i*-Pr
1d: R = *n*-Bu
1e: R = *t*-Bu
1f: R = Bn

Figure 1. Roche ester and its derivatives **1a–f**.

The present methods for the asymmetric synthesis of **1a** include the aldol reaction of formaldehyde;[2] the oxidative degradation of a chiral homoallylic acetate;[3] diastereoselective addition of chiral alcohols to arylketenes;[4] and bacterial or microbial enzyme-mediated transformations.[5] To the best of our knowledge, there are only a few reports on the catalytic asymmetric synthesis of the Roche ester and its derivatives except for some recent examples on the catalytic asymmetric hydrogenation of 2-hydroxymethylacrylates. In 2003, Saito et al. reported the enantioselective synthesis of the Roche ester **1a** via the first Rh-catalyzed asymmetric hydrogenation of methyl 2-hydroxymethylacrylate with BeePHOS and DuPHOS, affording an ee-value of up to 90%.[6] Genêt and Ratovelomanana–Vidal found that the Roche ester derivatives with bulky ester groups could be obtained in high enantioselectivity (up to 94% ee) in the first Ru-catalyzed asymmetric hydrogenation of the corresponding 2-hydroxymethylacrylates, although the parent Roche ester **1a** was obtained in only 88% ee.[7] Reek et al. reported that the Roche ester can be obtained with an ee-value of up to 98% ee using a Rh-INDOLPHOS catalyst.[8] However, the hydrogenation needed to be performed at −40 °C. When the hydrogenation temperature rose to room temperature, the enantioselectivity dropped to 93% ee. Very recently, Holz and Börner showed that the Rh-catalyzed asymmetric hydrogenation of 2-hydroxymethylacrylates with cat*A*Sium M ligands gave rise to the Roche ester and its derivatives in excellent enantioselectivities (up to 99% ee), which represent the best results so far.[9] Since the Roche ester is a liquid and the enantiomeric purity cannot be increased by crystallization,[8] the development of a new catalytic system with properties superior to its predecessors, for example, high enantioselectivity (more than 95% ee) and mild reaction conditions for the asymmetric synthesis of this building block, is therefore still highly desirable.

Over the past few years, we have developed a series of unsymmetrical hybrid chiral phosphine-phosphoramidite ligands (Fig. 2), which showed excellent enantioselectivities and catalytic activities in the Rh-catalyzed asymmetric hydrogenation of a variety of functionalized olefins including α-dehydroamino acid esters, β-dehydroamino acid esters, enamides, dimethyl itaconate, α-enamido phosphonates, and α-enol ester phosphonates.[10] Due to the easy accessibility, modularity, and high efficiency in

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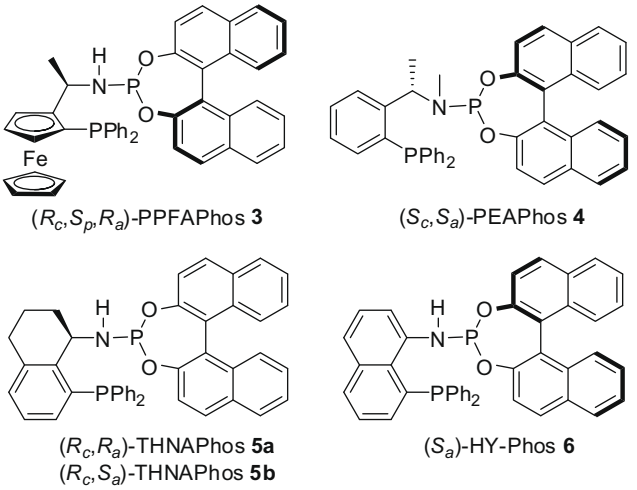
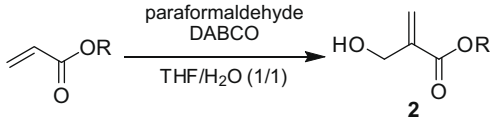


Figure 2. Chiral phosphine-phosphoramidite ligands developed within our group.

catalytic hydrogenation, we therefore surmised that this class of ligand may be also effective for the catalytic asymmetric hydrogenation of 2-hydroxymethylacrylates. As a result, we herein report our studies on the catalytic asymmetric synthesis of the Roche ester and its derivatives via the Rh-catalyzed asymmetric hydrogenation using a readily accessible, chiral 1,2,3,4-tetrahydro-1-naphthylamine-derived phosphine-phosphoramidite ligand, in which the Roche ester was prepared in 96.7% ee under mild conditions.

2. Results and discussion

Substrates **2a**–**f** for the hydrogenation reaction can be easily prepared from acrylates and paraformaldehyde via the Baylis–Hillman reaction via the reported procedures (Scheme 1).[11]

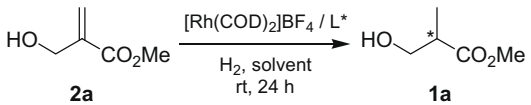


Scheme 1. Synthesis of substrates **2**.

With these substrates in hand, we first investigated the ligand effect in the Rh-catalyzed asymmetric hydrogenation of methyl 2-hydroxymethylacrylates **2a**. Hydrogenation was performed at room temperature under a H_2 pressure of 10 bar in the presence of 1 mol % of catalyst prepared in situ from $[Rh(COD)_2]BF_4$ and 1.1 equiv of phosphine-phosphoramidite ligand. The results are summarized in Table 1.

Initially, ferrocene-based phosphine-phosphoramidite ligand, (R_c,S_p,R_a)-PPFAPhos **3**,[10c] was examined, and full conversion was observed. However, the Roche ester **1a** was obtained in only low enantioselectivity (entry 1). Gratifyingly, the hydrogenation with α-phenylethylamine-derived (S_c,S_a)-PEAPhos **4**[10d] afforded the Roche ester with (*S*)-configuration and in up to 93.8% ee (entry 2). When (S_c,S_a)-PEAPhos **4** was replaced with 1,2,3,4-tetrahydro-1-naphthylamine-derived (R_c,R_a)-THNAPhos **5a**,[10e] the enantioselectivity was further increased (up to 96.7% ee, entry 3). The improved enantioselectivity is presumably due to the increased rigidity conferred by a cyclohexyl fragment in (R_c,R_a)-THNAPhos **5a**. However, further increasing the rigidity by replacing the 1,2,3,4-tetrahydro-1-naphthylamino moiety in (R_c,R_a)-THNAPhos **5a** with a 1-naphthylamino fragment[10g] resulted in a decreased enantioselectivity to 94.1% ee (entry 5). For the sake of comparison, ligand (R_c,S_a)-THNAPhos **5b** with an (S_a)-binaphthyl fragment was

Table 1
Rh-catalyzed asymmetric hydrogenation of methyl 2-hydroxymethylacrylate **2a**[a]



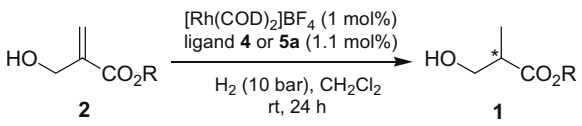
Entry	Ligand	H_2 (bar)	Solvent	Conv.[b] (%)	ee[c] (%)
1	(R_c,S_p,R_a)-**3**	10	CH_2Cl_2	100	36.3 (*S*)
2	(S_c,S_a)-**4**	10	CH_2Cl_2	100	93.8 (*S*)
3	(R_c,R_a)-**5a**	10	CH_2Cl_2	100	96.7 (*R*)
4	(R_c,S_a)-**5b**	10	CH_2Cl_2	100	7.0 (*S*)
5	(S_a)-**6**	10	CH_2Cl_2	100	94.1 (*S*)
6	(R_c,R_a)-**5a**	10	THF	100	3.4
7	(R_c,R_a)-**5a**	10	Toluene	100	19.3
8	(R_c,R_a)-**5a**	10	MeOH	100	73.8
9	(R_c,R_a)-**5a**	10	*i*-PrOH	100	14.9
10	(R_c,R_a)-**5a**	20	CH_2Cl_2	100	95.1
11	(R_c,R_a)-**5a**	5	CH_2Cl_2	100	95.5
12	(R_c,R_a)-**5a**	10	CH_2Cl_2	100	86.2[d]
13	(R_c,R_a)-**5a**	10	CH_2Cl_2	100	90.9[e]

[a] Reactions were performed in 2 mL of solvent, Rh/L* = 1: 1.1, Rh/**2a** = 1: 100, 10 bar of H_2, at room temperature for 24 h using 0.25 mmol of **2a** and $[Rh(COD)_2]BF_4$ as a metal precursor unless otherwise specified.
[b] Conversion was determined by GC.
[c] Enantiomeric excesses were determined by GC using a capillary chiral column [cyclodex-β,2,3,6-methylated, 30 m × 0.25 mm (i.d.)]. The absolute configuration was determined by comparing the specific rotations with the reported data or the GC retention times with GC data in the literature.
[d] Using $[Rh(COD)_2]SbF_6$ as a metal precursor.
[e] Rh/**2a** = 1:1000.

employed in this hydrogenation, displaying very low enantioselectivity and favoring a hydrogenation product with a configuration opposite to that obtained with (R_c,R_a)-THNAPhos **5a** (entry 4). Having found that (R_c,R_a)-THNAPhos **5a** is the best ligand, we set out to determine the optimal conditions for this asymmetric hydrogenation. The effect of solvents on this hydrogenation was first investigated, and in all cases, full conversions were achieved. However, the results disclosed that the enantioselectivity of this hydrogenation was strongly dependent on the nature of the solvent used. The best result was obtained in aprotic CH_2Cl_2, whereas all other aprotic solvents, such as THF and toluene led to lower selectivities (entries 3, 6, and 7). Alcoholic solvents proved to be less efficient for this hydrogenation, and gave lower enantioselectivities in comparison with those obtained in CH_2Cl_2 (entries 8 and 9). The hydrogen pressure has a slight impact on the enantioselectivity. Lowering the hydrogen pressure to 5 bar or elevating the hydrogen pressure to 20 bar led to a slight decrease in enantioselectivity (entries 10 and 11). Using $[Rh(COD)_2]SbF_6$ instead of $[Rh(COD)_2]BF_4$ as the catalyst precursor also resulted in decreased enantioselectivity (entry 12). Reducing the catalyst loadings from 1 mol % to 0.1 mol % also gave rise to the Roche ester **1a** with a good enantioselectivity of 90.9% ee, thus demonstrating the high efficiency of the present catalytic system in this hydrogenation (entry 13). This result represents the highest substrate/catalyst ratio successfully used in this hydrogenation reported so far.[6–9]

Having established the optimized conditions {1 mol % of catalyst loading prepared in situ from $[Rh(COD)_2]BF_4$ and ligand, performed under 10 bar of H_2 pressure in CH_2Cl_2 at room temperature for 24 h}, we subsequently evaluated the effect of the ester function of 2-hydroxymethylacrylate substrates on this hydrogenation. A series of 2-hydroxymethylacrylate substrates **2a**–**f** with different ester groups were submitted to this hydrogenation by using Rh/(S_c,S_a)-PEAPhos and Rh/(R_c,R_a)-THNAPhos catalysts under the optimized conditions, and the results are shown in Table 2. In all cases, full conversions were obtained, and (S_c,S_a)-PEAPhos displayed the opposite stereo-induction to (R_c,R_a)-THNAPhos. The

Table 2
Catalytic asymmetric hydrogenation of substrates **2** with Rh-(S_c,S_a)-PEAPhos and Rh-(R_c,R_a)-THNAPhos catalyst[a]



Entry	Substrate	Ligand	Conv.[b] (%)	ee[c] (%)
1	**2a**: R = Me	**4**	100	93.8
2	**2a**: R = Me	**5a**	100	96.7
3	**2b**: R = Et	**4**	100	87.8
4	**2b**: R = Et	**5a**	100	95.7
5	**2c**: R = *i*-Pr	**4**	100	86.0
6	**2c**: R = *i*-Pr	**5a**	100	90.5
7	**2d**: R = *n*-Bu	**4**	100	91.6
8	**2d**: R = *n*-Bu	**5a**	100	95.3
9	**2e**: R = *t*-Bu	**4**	100	49.8
10	**2e**: R = *t*-Bu	**5a**	100	79.1
11	**2f**: R = Bn	**4**	100	90.1
12	**2f**: R = Bn	**5a**	100	90.1

[a] Reactions were performed in 2 mL of CH_2Cl_2, Rh/L* = 1: 1.1, Rh/**2** = 1:100, 10 bar of H_2, at room temperature for 24 h using 0.25 mmol of **2** and $[Rh(COD)_2]BF_4$ as a metal precursor.
[b] Conversion was determined by GC or ^{1}H NMR.
[c] Enantiomeric excesses were determined by capillary GC analysis with a chiral β-120 column (0.25 mm × 30 m) for **1a**–**b**, **1e**, and by HPLC analysis with a chiral column (Chiralcel OD-H, 0.46 mm × 25 cm) for **1c**–**d** and **1f**.

results in Table 2 indicated that the introduction of a bulky ester function into the substrates has a deleterious influence on the enantioselectivity. With the increase of the steric demand of the ester moiety from methyl **2a** to the bulkier ester groups **2b**–**f**, a significant decrease in enantioselectivity was observed. Thus, ethyl ester **2b** led to a slight drop in enantioselectivity when compared to the methyl ester **2a** (entry 4 vs entry 2), while substrate **2e** with a bulky *tert*-butyl group led to a drastic drop in the enantioselectivity [49.8% ee with (S_c,S_a)-PEAPhos **4** and 79.1% ee with (R_c,R_a)-THNAPhos **5a**] (entries 9 and 10). The results also disclosed that in most cases, the Rh/(R_c,R_a)-THNAPhos catalyst showed a better enantioselectivity than Rh/(S_c,S_a)-PEAPhos. One exception is in the hydrogenation of substrate **2f** with a benzyl ester function, in which similar enantioselectivities were achieved by the use of PEAPhos **4** and THNAPhos **5a** (entries 11 and 12).

3. Conclusion

In conclusion, we have developed an efficient Rh-catalyzed asymmetric hydrogenation of 2-hydroxymethylacrylate ester compounds **2** with a chiral 1,2,3,4-tetrahydro-1-naphthylamine-derived phosphine-phosphoramidite ligand [(R_c,R_a)-THNAPhos **5a**], which provides a direct way to synthetically important Roche ester derivatives in high enantioselectivities (up to 96.7% ee). In particular, even at low catalyst loadings (0.1 mol %), the hydrogenation also gave good results (full conversion and 90.9% ee), which represents the highest substrate/catalyst ratio successfully used in this hydrogenation reported so far. Further investigations on the substrate scope revealed that the ester function present on the substrate has a significant effect in the enantioselectivity, while the substrate with a bulkier ester group tended to give lower enantioselectivity.

4. Experimental

4.1. General

All synthetic reactions and manipulations were performed in a nitrogen or argon atmosphere using standard Schlenk techniques. Hydrogenations were carried out in a stainless steel autoclave. Solvents were reagent grade, dried, and distilled before use following the standard procedures. 2-Hydroxymethylacrylates **2a**–**f**[11] are known compounds, which were prepared according to the literature methods. All other chemicals were obtained commercially.

^{1}H NMR spectra were recorded on BRUKER DEX-400 spectrometer. Chemical shift values (δ) are denoted in ppm, and are referenced to residue protons in deuterated solvents for ^{1}H NMR ($CDCl_3$: 7.27 ppm). Mass spectra (MS) were measured on a Agilent 6890-5973N instrument. Optical rotation was recorded using a JASCO P-1020 high sensitive polarimeter. Enantiomeric excesses were determined by capillary GC analysis with a chiral β-120 column (0.25 mm × 30 m) for **1a**–**b** and **1e**, and by HPLC analysis with a chiral column (Chiralcel OD-H, 0.46 mm × 25 cm) for **1c**–**d** and **1f**.

4.2. General procedure for asymmetric hydrogenation

In a nitrogen-filled glovebox, a stainless steel autoclave was charged with $[Rh(COD)_2]BF_4$ (1.0 mg, 0.25×10^{-2} mmol) and (R_c,R_a)-THNAPhos **5a** (1.8 mg, 0.28×10^{-2} mmol) in 1 mL of a degassed CH_2Cl_2. After stirring at room temperature for 10 min, a substrate (0.25 mmol) in 1 mL of the same solvents was added to the reaction mixture. The hydrogenation was performed at room temperature under an H_2 pressure of 10 bar for 24 h. The reaction mixture was then passed through a short silica gel column to remove the catalyst. After evaporating the solvent, the crude product was subjected to determine the conversion by GC or ^{1}H NMR and the enantiomeric excesses by GC or HPLC.

4.2.1. (*R*)-3-Hydroxy-2-methylpropionic acid methyl ester 1a

$[\alpha]_D^{20} = -22.8$ (*c* 0.85, MeOH) {lit. $[\alpha]_D^{20} = -28.2$ (*c* 1.34, MeOH); ee >99% commercially available from Aldrich}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 7.2 Hz, 3H), 2.65–2.72 (m+br, 2H), 3.67–3.76 (m, 5H). GC analysis: chiral β-120 column (0.25 mm × 30 m); t_R = 6.32 min, (*R*)-isomer; t_R = 6.59 min, (*S*)-isomer; ee = 96.7%.

4.2.2. (*R*)-3-Hydroxy-2-methylpropionic acid ethyl ester 1b

$[\alpha]_D^{20} = -22.2$ (*c* 1.0, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 2.50 (br, 1H), 2.66 (ddq, *J* = 4.8, 6.8, 7.2 Hz, 1H), 3.68 (dd, *J* = 4.8, 11.2 Hz, 1H), 3.74 (dd, *J* = 6.8, 11.2 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H). GC analysis: chiral β-120 column (0.25 mm × 30 m); t_R = 8.08 min, (*R*)-isomer; t_R = 8.37 min, (*S*)-isomer; ee = 95.7%.

4.2.3. (*R*)-3-Hydroxy-2-methylpropionic acid *i*-propyl ester 1c

$[\alpha]_D^{20} = -16.0$ (*c* 1.2, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 7.2 Hz, 3H), 1.23–1.26 (m, 6H), 2.60–2.66 (m, 1H), 2.70 (br, 1H), 3.65–3.75 (m, 2H), 5.01–5.08 (m, 1H). HPLC analysis: chiralcel OD-H column; flow rate: 1.0 mL/min; eluent: *n*-hexane/propan-2-ol (99/1); detection at 215 nm; t_R = 10.8 min, (*R*)-isomer; t_R = 11.7 min, (*S*)-isomer; ee = 90.5%.

4.2.4. (*R*)-3-Hydroxy-2-methylpropionic acid *n*-butyl ester 1d

$[\alpha]_D^{20} = -14.8$ (*c* 0.9, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.6 Hz, 3H), 1.18 (d, *J* = 7.2 Hz, 3H), 1.36–1.42 (m, 2H), 1.60–1.65 (m, 2H), 2.64–2.69 (m, 1H), 2.80 (br, 1H), 3.67–3.76 (m, 2H), 4.10–4.13 (t, *J* = 6.6 Hz, 2H). HPLC analysis: chiralcel OD-H column; flow rate: 1.0 mL/min; eluent: *n*-hexane/propan-2-ol (99/1); detection at 215 nm; t_R = 11.8 min, (*R*)-isomer; t_R = 13.3 min, (*S*)-isomer; ee = 95.3%.

4.2.5. (*R*)-3-Hydroxy-2-methylpropionic acid *t*-butyl ester 1e

$[\alpha]_D^{20} = -11.6$ (*c* 1.15, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (dd, *J* = 2.0, 7.2 Hz, 3H), 1.46 (s, 9H), 2.53–2.58 (m, 1H), 2.73 (br, 1H), 3.64–3.71 (m, 2H). GC analysis: chiral β-120 column

(0.25 mm × 30 m); t_R = 9.57 min, (*S*)-isomer; t_R = 9.78 min, (*R*)-isomer; ee = 79.1%.

4.2.6. (*R*)-3-Hydroxy-2-methylpropionic acid benzyl ester 1f

$[\alpha]_D^{20} = -24.2$ (*c* 0.85, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (d, *J* = 7.2 Hz, 3H), 2.68–2.73 (m, 1H), 2.87 (br, 1H), 3.65–3.76 (ddd, *J* = 2.4, 4.8, 6.6 Hz, 2H), 5.13 (s, 2H), 7.30–7.37 (m, 5H). MS (EI) *m/z* 194 ([M]$^+$). HPLC analysis: chiralcel OD-H column; flow rate: 1.0 mL/min; eluent: *n*-hexane/propan-2-ol (98/2); detection at 215 nm; t_R = 23.0 min, (*R*)-isomer; t_R = 25.8 min, (*S*)-isomer; ee = 90.1%.

Acknowledgments

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