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Asymmetric synthesis of 2-substituted chroman-4-ones using lipase-catalyzed kinetic resolutions

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Abstract—2-Methylchroman-4-one and 2-phenylchroman-4-one were synthesized in optically active form. Their chiral intermediates were obtained via lipase-catalyzed enantioselective reactions.

1. Introduction

The 2-substituted chroman-4-one (2-substituted 2,3-dihydro-4*H*-1-benzopyran-4-one) skeleton can be found in many natural products, which often show biological activity such as anthelmintic activity and plant growth inhibition activity.[1,2] Furthermore, it has recently been reported that naringenin, one of the representatives of the 2-substituted chroman-4-ones, surprisingly enhanced the enantioselectivity in the kinetic resolution of alcohols with an enzyme.[3] Despite this interesting potential of the 2-substituted chroman-4-ones, there are few reports on their asymmetric synthesis. Amongst chemical methods, coupling of phenols and chiral alcohols[4,5] (or epoxides[6]), and conjugated addition of Me_2CuLi to chiral 3-substituted chromones[7] have been reported. It has also been reported that non-racemic chiral flavanone (2-phenylchroman-4-one) was obtained by recrystallization of flavanone derivatives,[8,9] enzymatic resolution of flavanone oxime,[10] and baker's yeast-mediated asymmetric reduction of flavanone.[11] In this paper, we describe the novel and facile asymmetric synthesis of 2-methylchroman-4-one **5** and 2-phenylchroman-4-one **10** from non-racemic chiral intermediates prepared by lipase-catalyzed reactions.[12]

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2. Results and discussion

2.1. Synthesis of enantiomers 2-methychroman-4-ones

The reaction of commercially available 4-penten-2-ol (±)-**1** and phenol with diethyl azodicarboxylate (DEAD) and triphenylphosphine in THF[13] gave the corresponding phenyl ether (±)-**2** (Scheme 1). The oxidation of the double bond of (±)-**2** with $KMnO_4$ in water–benzene containing tetrabutylammonium bromide[14] afforded 3-phenoxybutanoic acid (±)-**3**. (*R*)-3-Phenoxybutanoic acid (*R*)-**3** (>99% e.e.) and the butyl ester (*S*)-**4** (>99% e.e.) were obtained by the lipase (Roche Chirazyme® L-1 from *Burkholderia cepacia*)-catalyzed enantioselective esterification of (±)-**3** with 1-butanol in hexane containing anhydrous sodium sulfate to remove the water produced during the reaction from the reaction mixture. Although we also tried THF as an organic solvent instead of hexane, the reaction hardly proceeded. The intramolecular cyclization of (*R*)-**3** using trifluoroacetic acid and trifluoroacetic anhydride in CH_2Cl_2[15] afforded (*R*)-2-methylchroman-4-one (*R*)-**5** in >99% e.e. {$[\alpha]_D^{27}$ +46.6 (*c* 1.0, $CHCl_3$); lit.[4] $[\alpha]^D$ +51 (*c* 1, $CHCl_3$) (*R*)}. According to the same methods, (*S*)-2-methylchroman-4-one (*S*)-**5** was also synthesized in the optically active form {>99% e.e., $[\alpha]_D^{24}$ −48.1 (*c* 1.1, $CHCl_3$)} from (*S*)-**3** (>99% e.e.) which was obtained by the lipase (Amano PS from *Pseudomonas*

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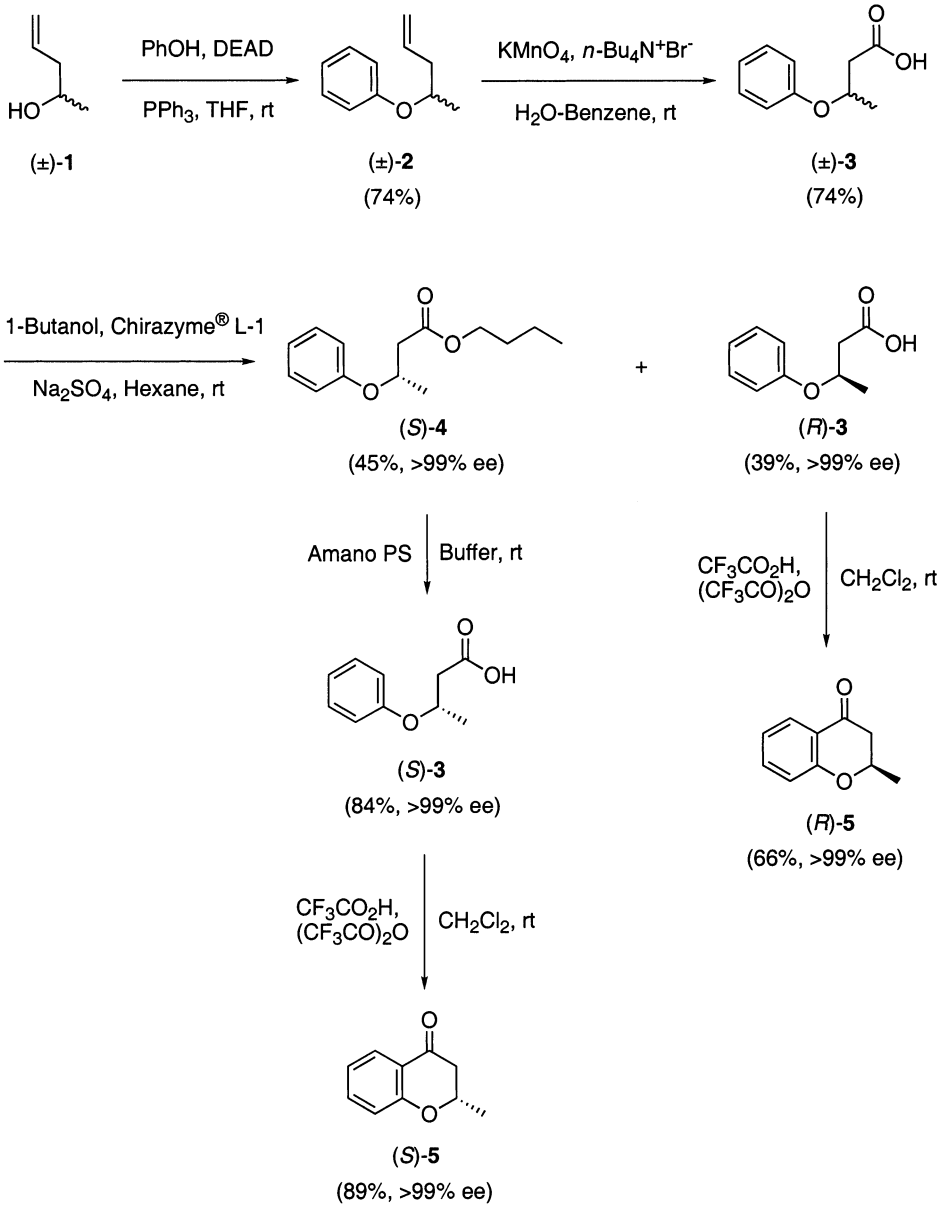
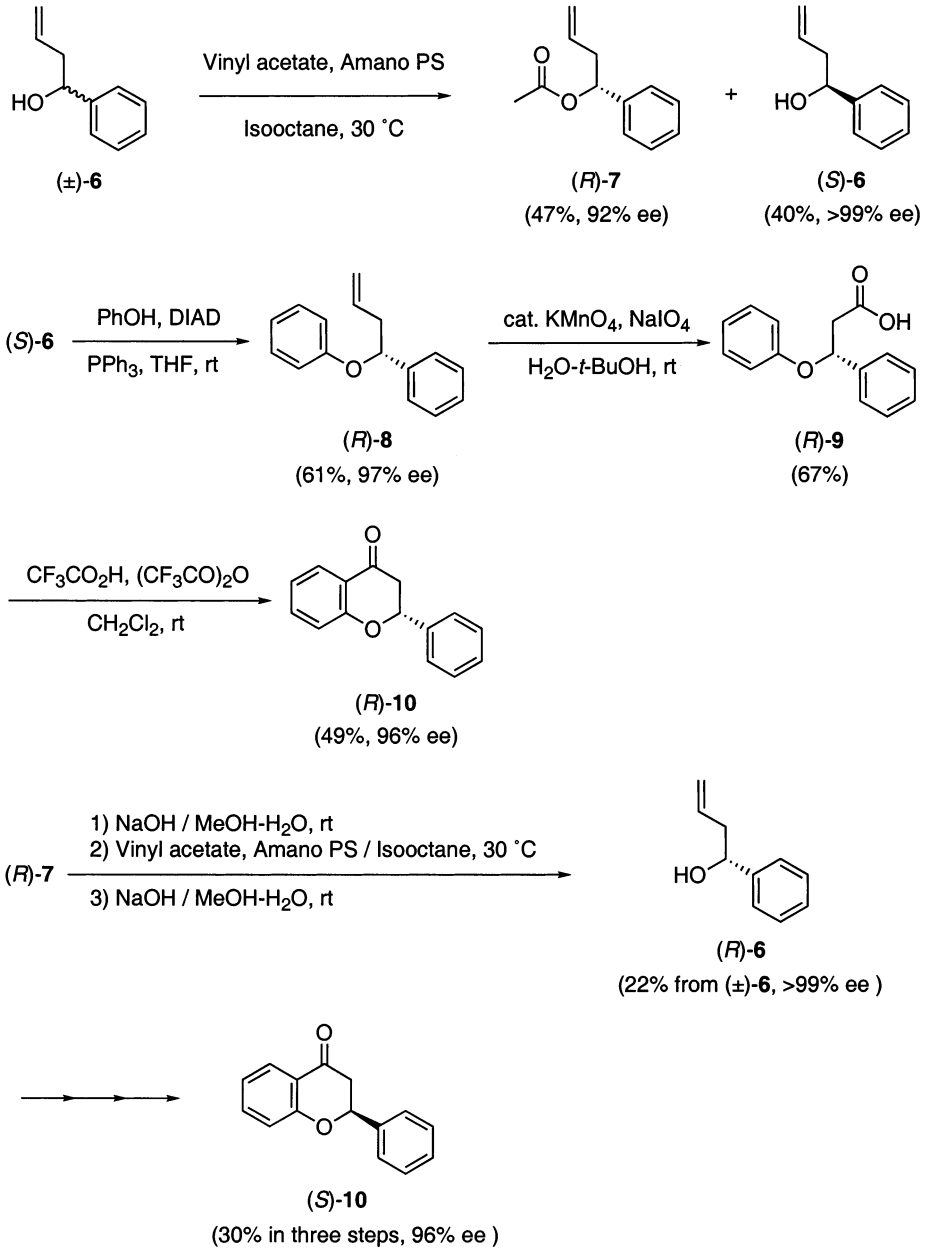
cepacia)-catalyzed hydrolysis of (*S*)-**4** in 0.07 M phosphate buffer (pH 7). When (*S*)-**4** was subjected to hydrolysis with NaOH in water-methanol, the elimination of phenol mainly resulted. Although the specific rotations of the (*R*)- and (*S*)-2-methylchroman 4-ones prepared by us are lower than those in the literature,[4] our e.e.s exceed 99%.

2.2. Synthesis of enantiomers 2-phenychroman-4-ones

Although we planned the synthesis of the (*R*)- and (*S*)-2-phenylchroman-4-ones, (*R*)- and (*S*) **10**, respectively, according to Scheme 1, our report that secondary alcohols similar to 1-phenyl 3-buten-2-ol (±)-**6** could be resolved with high enantioselectivity via lipase-catalyzed transesterification[16] led us to adopt the alternative route shown in Scheme 2. (*S*)-1-Phenyl-3 buten-2-ol (*S*)-**6** (>99% e.e.) and the acetate (*R*)-**7** (92% e.e.) were obtained by the lipase (Amano PS from *Pseudomonas cepacia*)-catalyzed transesterification of (±)-**6** with vinyl acetate as an acylating reagent in isooctane. (*S*)-**6** and phenol were treated with triphenylphosphine and diisopropyl azodicarboxylate (DIAD) to give the phenyl ether (*R*)-**8** (97% e.e.) with inversion of configuration (Mitsunobu inversion).[13] Racemization occurred slightly during the reaction. (*R*)-**8** was converted into (*R*)-2-phenylchroman-4-one (*R*)-**10** in 96% e.e., $[\alpha]_D^{24}$ +61.6 (*c* 1.0, $CHCl_3$) via oxidation[17] and subsequent cyclization.[15] Because (*R*)-**7** obtained through the resolution mentioned above did not have an enantiomeric excess high enough for use, (*R*)-**7** was hydrolyzed to (*R*)-**6** and the alcohol was again subjected to the Amano PS-catalyzed transesterification to raise its e.e. The obtained acetate (*R*)-**7** was then hydrolyzed in a similar manner to give (*R*)-**6** in >99% e.e. and (*R*)-**6** was converted to (*S*)-2-



Scheme 1.



Scheme 2.

phenylchroman-4 one (*S*)-**10** in 96% e.e. $[\alpha]_D^{26}$ −58.6 (*c* 1.0, $CHCl_3$); lit.[4] $[\alpha]_D$ −67 (*c* 1, $CHCl_3$) (*S*) according to the same route which we followed to prepare (*R*)-**10**. Exploratory experiments to depress the racemization during the Mitsunobu reaction are underway.

3. Conclusion

We have been able to synthesize in optically active form 2-methylchroman-4-one and 2-phenylchroman-4-one. We believe that the methods described herein are general enough to synthesize optically active 2-substituted chroman-4-ones, because a variety of derivatives of (±)-**1** and (±) **6**, which are starting materials in our methods, can be easily prepared from aldehydes and allyl bromide[18] and the lipase-catalyzed resolution can be successfully applied to a wide variety of substrates.[12] Furthermore, severe reaction conditions and complicated handling are not required. We are now synthesizing novel optically active 2-substituted chroman-4-ones and testing their biological activity.

4. Experimental

4.1. General

Lipase Chirazyme® L-1 was purchased from Roche Ltd. Lipase PS was supplied by Amano Enzyme Inc. All commercially available reagent chemicals were obtained from Aldrich, Nacalai Tesque, Tokyo Kasei and Wako Chemicals, and generally used without further purification. ^1H NMR spectra were recorded on a

Jeol JNM-LA 400 spectrometer for solutions in $CDCl_3$ with TMS as an internal standard and J values are given in Hertz (Hz). IR spectra were obtained using a Jasco FT/IR-410 spectrometer. Mass spectra (MS) were obtained using a JEOL JMS-GCmate spectrometer. High-resolution mass spectra (HRMS) were obtained using a JEOL JMS-AX505HAD spectrometer. Optical rotations were measured with a Horiba SEPA-300 polarimeter. Melting points were measured with a Yanaco MP-S3 melting point apparatus. Gas chromatograms were recorded on a Shimadzu GC-14B with GAMMA DEX™ 120 capillary column (Supelco), 30 m×0.25 mm. HPLC analyses were carried out on a Hitachi L-6250 intelligent pump with a Hitachi L-4000 UV detector using CHIRALCEL OB-H (Daicel), 250 mm×4.6 mm or CHIRALCEL OJ (Daicel), 250 mm× 4.6 mm chiral columns.

Conditions for the determination of the e.e.s of the following compounds are as follows. (*R*)-**3** and (*S*)-**3**: GC (GAMMA DEX™ 120), 140°C; (*R*)-**5** and (*S*)-**5**: HPLC (CHIRALCEL OB-H), hexane:2-propanol= 10:1 (v/v); (*R*)-**6** and (*S*)-**6**: HPLC (CHIRALCEL OB-H), hexane:2-propanol=9:1 (v/v); (*R*)-**8** and (*S*)-**8**: HPLC (CHIRALCEL OJ), hexane:2-propanol=10:1 (v/v); (*R*)-**10** and (*S*)-**10:** HPLC (CHIRALCEL OJ), hexane:2-propanol=1:1 (v/v).

4.2. 1-Methyl-3-butenyl phenyl ether (±)-2

A solution of DEAD (11.33 g, 65.04 mmol) in dry THF (30 ml) was added dropwise to a mixture of (±)-**1** (5.34 g, 62.0 mmol), phenol (6.49 g, 69.0 mmol), and triphenylphosphine (17.90 g, 68.24 mmol) in dry THF (90 ml) at 0°C under Ar. The mixture was stirred overnight at rt. After evaporation of the THF, a mixture of hexane and diethyl ether (1:1, 150 ml) was added to the viscous residue. Suspended solid was filtered with suction, and the filtrate was concentrated. Chromatography (silica gel, hexane–ethyl acetate 20:1 (v/v)) of the crude product provided (±)-**2** (7.42 g, 74%) as a colorless oil; ^{1}H NMR: δ 7.25–7.29 (2H, m), 6.89–6.95 (3H, m), 5.82–5.92 (1H, m), 5.08–5.14 (2H, m), 4.38–4.46 (1H, m), 2.47–2.54 (1H, m), 2.31–2.38 (1H, m), 1.31 (3H, d, J=6.1); IR (neat): 1243, 1642 cm^{-1}; MS (m/z) 162 (M^+). HRMS calcd for $C_{11}H_{14}O$ (M^+), 162.1045. Found: 162.1072.

4.3. 3-Phenoxybutanoic acid (±)-3

To a stirred solution of $KMnO_4$ (16.50 g, 104.4 mmol) in water (350 ml) were added benzene (100 ml), tetrabutylammonium bromide (1.06 g), and (±)-**2** (5.50 g, 33.9 mmol) at 0°C. The mixture was stirred for 20 h at ambient temperature. A solution of $KMnO_4$ (14.83 g, 93.84 mmol) in water (650 ml), benzene (100 ml), and tetrabutylammonium bromide (0.71 g) were added to the mixture to consume (±)-**2** completely and the resulting mixture was stirred for 24 h at ambient temperature. $NaHSO_3$ (60.00 g) was added to the cooled reaction mixture followed by the addition of 6 M HCl (300 ml). The mixture was extracted three times with benzene. The organic layer was washed with brine, then dried over $NaSO_4$ and concentrated under reduced pressure. The residue was chromatographed (silica gel, hexane–ethyl acetate 1:1 (v/v)) to give (±)-**3** (4.49 g, 74%) as a colorless oil; ^{1}H NMR: δ 7.26–7.30 (2H, m), 6.92 6.98 (3H, m), 4.79–4.86 (1H, m), 2.86 (1H, dd, J=15.6, J=6.8), 2.60 (1H, dd, J=15.9, J=6.1), 1.39 (3H, d, J=6.1); IR (neat): 1238, 1712 cm^{-1}; MS (m/z) 180 (M^+). HRMS calcd for $C_{10}H_{12}O_3$ (M^+), 180.0786. Found: 180.0793.

4.4. Lipase-catalyzed esterification of (±)-3

(±)-**3** (2.83 g, 15.7 mmol) and 1-butanol (3.52 g, 47.5 mmol) were dissolved in dry hexane (290 ml). Then Na_2SO_4 (3.10 g) and Chirazyme® L-1 (3.00 g) were added, and the mixture was stirred for 12 h at rt. The reaction was quenched by filtration, and the filtrate was concentrated under reduced pressure. The residue was chromatographed (silica gel, hexane–ethyl acetate 1:1 (v/v)) to give (*R*)-3-phenoxybutanoic acid (*R*)-**3** (1.09 g, 39%, >99% e.e.) as a colorless oil and (*S*)-butyl 3-phenoxybutanoate (*S*)-**4** as a colorless oil. The ester (*S*)-**4** was subjected to chromatography (silica gel, hexane–ethyl acetate 5:1 (v/v)) again (1.65 g, 45%, >99% e.e.). To determine the e.e. of (*S*)-**4**, a drop of (*S*)-**4** was hydrolyzed (6 M NaOH, MeOH) to the corresponding alcohol (*S*)-**3**.

(*R*)-**3**: ^{1}H NMR spectral date of this sample were identical with those of (±)-**3**.

(*S*)-**4**: ^{1}H NMR: 7.19–7.22 (2H, m), 6.84–6.90 (3H, m), 4.74–4.78 (1H, m), 4.02 (2H, t, J=6.7), 2.73 (1H, dd, J=15.3, J=7.0), 2.46 (1H, dd, J=15.1, J=6.3), 1.48–1.55 (2H, m), 1.37 (3H, d, J=6.1), 1.30–1.40 (2H, m), 0.83 (3H, t, J=7.4); IR (neat): 1186, 1241, 1736 cm^{-1}; MS (m/z) 236 (M^+). HRMS calcd for $C_{14}H_{20}O_3$ (M^+), 236.1412. Found: 236.1396.

4.5. Lipase-catalyzed hydrolysis of (*S*)-4

To a suspension of (*S*)-**4** (1.47 g, 6.22 mmol) in 0.07 M phosphate buffer (KH_2PO_4 and Na_2HPO_4, pH 7, 150 ml) was added Amano PS (1.00 g). The mixture was stirred for 23 h at rt. Suspended solid was filtered with suction. The filtrate was extracted three times with ethyl acetate. The organic layer was washed with brine, then dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was chromatographed (silica gel, hexane–ethyl acetate 1:1 (v/v)) to give (*S*)-3-phenoxybutanoic acid (*S*)-**3** (0.94 g, 84%, >99% e.e.) as a colorless oil. ^{1}H NMR spectral date of this sample were identical with those of (±)-**3**.

4.6. (*R*)-2-Methylchroman-4-one (*R*)-5

To a solution of (*R*)-**3** (1.00 g, 5.55 mmol) in CH_2Cl_2 (20 ml) were added slowly trifluoroacetic acid (7 ml) and trifluoroacetic anhydride (7 ml). The mixture was stirred for 30 min at rt. The reaction mixture was poured onto ice and the CH_2Cl_2 layer was separated.

The organic phase was washed with water, saturated sodium hydrogen carbonate, brine and dried over sodium sulfate. After removal of the solvent, the residue was chromatographed (silica gel, hexane–ethyl acetate 5:1 (v/v)) to give (*R*)-**5** (0.59 g, 66%, >99% e.e.) as a white solid; mp 42.8–44.5°C; $[\alpha]_D^{27}$ +46.6 (*c* 1.0, $CHCl_3$) (lit.[4] $[\alpha]_D$ +51 (*c* 1, $CHCl_3$) (*R*)); ^1H NMR: δ 7.87–7.90 (1H, m), 7.45–7.50 (1H, m), 6.96–7.03 (2H, m), 4.56–4.64 (1H, m), 2.69 (2H, d, $J=7.6$), 1.53 (3H, d, $J=6.1$); IR (CCl_4): 1229, 1695 cm^{-1}; MS (*m*/*z*) 162 (M^+). HRMS calcd for $C_{10}H_{10}O_2$ (M^+), 162.0681. Found: 162.0651.

4.7. (*S*)-2-Methylchroman-4-one (*S*)-5

(*S*)-**5** was prepared from (*S*)-**5** according procedure described above in 89% yield and >99% e.e.; mp 44.0–44.5°C (lit.[7] 39–40°C); $[\alpha]_D^{24}$ −48.1 (*c* 1.1, $CHCl_3$) (lit.[4] $[\alpha]_D$ +51 (*c* 1, $CHCl_3$) (*R*)); ^1H NMR: δ 7.87–7.89 (1H, m), 7.46–7.49 (1H, m), 6.96–7.03 (2H, m), 4.57–4.63 (1H, m), 2.69 (2H, d, $J=8.3$), 1.52 (3H, d, $J=6.4$); IR (CCl_4): 1229, 1696 cm^{-1}; MS (*m*/*z*) 162 (M^+). HRMS calcd for $C_{10}H_{10}O_2$ (M^+), 162.0681. Found: 162.0689.

4.8. Lipase-catalyzed transesterification of (±)-6 with vinyl acetate

Amano PS (20 g) was added to a solution of (±)-**6** (5.00 g, 33.7 mmol) and vinyl acetate (11.60 g, 134.7 mmol) in isooctane (300 ml). The mixture was stirred for 48 h at 30°C. The reaction was quenched by filtration and the filtrate was concentrated under reduced pressure. The residue was chromatographed (silica gel, hexane–ethyl acetate 99:1–9:1 (v/v)) to give (*S*)-**6** (2.00 g, 40%, >99% e.e.) as a colorless oil and the acetate (*R*)-**7** (3.01 g, 47%, 92% e.e.) as a colorless oil. 6 M NaOH (5 ml) was added to a solution of the (*R*)-**7** (3.01 g, 15.8 mmol) in methanol (30 ml). The mixture was stirred for 6 h at rt. After removal of the solvent, the residue was extracted with ethyl acetate. The organic layer was washed with brine, then dried over Na_2SO_4 and concentrated under reduced pressure to give (*R*)-**6**. According to the procedures described above, the crude alcohol (*R*)-**6** obtained here was again subjected to the lipase-catalyzed transesterification, and the resultant ester (*R*)-**7** was again hydrolyzed with NaOH to give (*R*)-**6** (1.10 g, 22% from (±)-**6**, >99% e.e.). ^1H NMR spectral date of (*R*)-**6** and (*S*)-**6** were identical with those of (±)-**6**.

4.9. (*R*)-Phenyl 1-phenyl-3-butenyl ether (*R*)-8

(*R*)-**8** was prepared from (*S*)-**6** and phenol using triphenylphosphine and DIAD (diisopropyl azodicarboxylate) in 61% yield and 97% e.e. according to the procedure for preparation of (±)-**2**. Chromatography (silica gel, hexane–ethyl acetate 20:1 (v/v)) of the crude product afforded (*R*)-**8** as a colorless oil; ^1H NMR: δ 7.16–7.37 (7H, m), 6.83–6.88 (3H, m), 5.81–5.92 (1H, m), 5.06–5.16 (4H, m), 2.73–2.80 (1H, m), 2.55–2.62 (1H, m); IR (neat): 1238, 1642 cm^{-1}; MS (*m*/*z*) 224 (M^+). HRMS calcd for $C_{16}H_{16}O$ (M^+), 224.1201. Found: 224.1239.

4.10. (*S*)-Phenyl 1-phenyl-3-butenyl ether (*S*)-8

(*S*)-**8** was prepared in 62% yield and 95% e.e. from (*R*)-**6** by the above method. ^1H NMR spectral date of this sample were identical with those of (*R*)-**8**.

4.11. (*R*)-3-Phenoxy-3-phenylpropanoic acid (*R*)-9

A solution of $NaIO_4$ (15.56 g, 72.75 mmol) in water (330 ml) was treated with $KMnO_4$ (0.23 g, 1.46 mmol), K_2CO_3 (1.17 g, 8.47 mmol) and *tert*-butyl alcohol (85 ml). To the mixture, a solution of (*R*)-**8** (1.78 g, 7.94 mmol) in *tert*-butyl alcohol (80 ml) was slowly added. The resulting brown suspension was stirred for 3 h at rt. A solution of $KMnO_4$ (0.30 g, 1.90 mmol) in water (20 ml) was added to the mixture to consume (*R*)-**8** completely, and the resulting mixture was stirred for 1 h at ambient temperature. The mixture was treated with ethylene glycol (3 ml), stirred for 2 h, and acidified to pH 4 with 1 M HCl. The resulting brown solid was filtrated with suction, and the filtrate was extracted three times with ethyl acetate. The organic layer was washed with brine, then dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was chromatographed (silica gel, hexane–ethyl acetate 1:2 (v/v)) to give (*R*)-**9** (1.28 g, 67%) as a colorless viscous oil; ^1H NMR: δ 7.16–7.41 (7H, m), 6.85–6.91 (3H, m), 5.62 (1H, dd, $J=9.2$, $J=4.3$), 3.09 (1H, dd, $J=16.0$, $J=9.2$) 2.83 (1H, dd, $J=20.1$, $J=4.4$); IR (CCl_4): 1236, 1704 cm^{-1}; MS (*m*/*z*) 242 (M^+). HRMS calcd for $C_{15}H_{14}O_3$ (M^+), 242.0943. Found: 242.0945.

4.12. (*S*)-3-Phenoxy-3-phenylpropanoic acid (*S*)-9

(*S*)-**9** was prepared in 80% yield from (*S*)-**8** by the above method. ^1H NMR spectral date of this sample were identical with those of (*R*)-**9**.

4.13. (*R*)-2-Phenylchroman-4-one (*R*)-10

(*R*)-**10** was prepared from (*R*)-**9** according to the procedure for preparation of (*R*)-**5**. Chromatography (silica gel, hexane–ethyl acetate 5:1 (v/v)) of the crude product and subsequent recrystallization from hexane afforded (*R*)-**10** (49%, 96% e.e.) as a white solid; $[\alpha]_D^{24}$ +61.6 (*c* 1.0, $CHCl_3$) (lit.[4] $[\alpha]_D$ −67 (*c* 1, $CHCl_3$) (*S*)); mp 77.8–79.0°C (lit.[11] mp 74.5–75°C); ^1H NMR: δ 7.94–7.95 (2H, m), 7.40–7.54 (6H, m), 7.06–7.09 (2H, m), 5.50 (1H, dd, $J=13.3$, $J=2.8$), 3.07–3.14 (1H, m) 2.88–2.93 (1H, m); IR (CCl_4): 1228, 1697 cm^{-1}; MS (*m*/*z*) 224 (M^+). HRMS calcd for $C_{15}H_{12}O_2$ (M^+), 224.0837. Found: 224.0833.

4.14. (*S*)-2-Phenylchroman-4-one (*S*)-10

(*S*)-**10** was prepared in 60% yield and 96% e.e. from (*S*)-**9** according to the procedure for preparation of (*R*)-**5**; $[\alpha]_D^{26}$ −58.6 (*c* 1.0, CHCl3) (lit.[4] $[\alpha]_D$ −67 (*c* 1, $CHCl_3$) (*S*)); mp 77.4–78.2°C (lit.[11] mp 75–77°C); ^1H NMR: δ 7.93–7.96 (2H, m), 7.38–7.54 (6H, m), 7.05–7.08 (2H, m), 5.50 (1H, dd, $J=13.4$, $J=2.9$), 3.07–3.14 (1H, m) 2.88–2.93 (1H, m); IR (CCl_4): 1228, 1697 cm^{-1};

MS (m/z) 224 (M^+). HRMS calcd for $C_{15}H_{12}O_2$ (M^+), 224.0837. Found: 224.0824.

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References

1. Saengchantara, S. T.; Wallace, T. W. *Nat. Prod. Rep.* **1986**, 465–475.
2. Ellis, G. P. *Chromenes, Chromanones and Chromones*; John Wiley & Sons: New York, 1977.
3. Nakamura, K.; Takenaka, K. *Tetrahedron: Asymmetry* **2002**, *13*, 415–422.
4. Hodgetts, K. J. *Tetrahedron Lett.* **2001**, *42*, 3763–3766.
5. Rama Rao, A. V.; Gaitonde, A. S.; Prakash, K. R. C.; Prahlada Rao, S. *Tetrahedron Lett.* **1994**, *35*, 6347–6350.
6. Noda, Y. (Nihon University, Japan). Jpn. Kokai Tokkyo Koho 2002 332,282, 2002; *Chem. Abstr.* **2002**, *137*, 384748.
7. Saengchantara, S. T.; Wallace, T. W. *Tetrahedron* **1990**, *46*, 6553–6564.
8. Rákosi, M.; Tökés, A. L.; Bognár, R. *Acta Chim. Acad. Sci. Hung.* **1975**, *87*, 161–164.
9. Corey, E. J.; Mitra, R. B. *J. Am. Chem. Soc.* **1962**, *84*, 2938–2941.
10. Izumi, T.; Suenaga, K. *J. Heterocyclic Chem.* **1997**, *34*, 1535–1538.
11. Izumi, T.; Hino, T.; Kasahara, A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1265–1267.
12. For a review, see: Roberts, S. M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1–21.
13. Heumann, A.; Faure, R. *J. Org. Chem.* **1993**, *58*, 1276–1279.
14. Herriott, A. W.; Picker, D. *Tetrahedron Lett.* **1974**, *15*, 1511–1514.
15. Katagiri, N.; Kato, T.; Nakano, J. *Chem. Pharm. Bull.* **1982**, *30*, 2440–2446.
16. Nakamura, K.; Kawasaki, M.; Ohno, A. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1079–1085.
17. Aristoff, P. A.; Johnson, P. D.; Harrison, A. W. *J. Am. Chem. Soc.* **1985**, *107*, 7967–7974.
18. Li, C. J.; Chan, T. H. *Tetrahedron Lett.* **1991**, *32*, 7017–7020.