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Research on the pig liver esterase (PLE)-catalyzed kinetic resolution of half-esters derived from prochiral diesters

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ABSTRACT

The pig liver esterase (PLE)-catalyzed kinetic resolution of half-esters derived from prochiral diesters is described. Generally, the PLE-catalyzed enantioselective hydrolysis of prochiral diesters affords the corresponding half-esters in high yield, because further hydrolysis of the half-esters does not typically occur. However, we found that some half-esters undergo PLE-catalyzed hydrolysis when they are gradually added to a PLE suspension in a potassium phosphate buffer at pH 8.0 via a syringe pump, leading to the kinetic resolution of the half-esters.

1. Introduction

The preparation of new chiral compounds is important for enantioselective synthesis, because it sometimes requires many steps if a chiral compound suitable for the synthesis is not readily available. Thus, the preparation of a new chiral compound involves reducing the number of steps in enantioselective synthesis, thereby improving its efficiency.

Various methods have been reported to prepare chiral compounds; for example, preparation from the chiral pool, asymmetric synthesis from prochiral compounds, and resolution of racemic mixtures.[1] Among these methods, asymmetric synthesis, in particular catalytic asymmetric synthesis from prochiral compounds, is an area of growing interest because of its efficiency. However, enzymatic transformations have the advantages of employing mild reaction conditions that do not require anhydrous or toxic reagents, organic solvents, or an inert atmosphere. They also do not produce toxic effluents and by-products.[2] Thus, enzyme-catalyzed transformations can be easily carried out on a large scale, have been considered as environmentally benign processes, and have also been utilized in industrial-scale syntheses.

Generally, the enzyme catalyzes the reaction of a specific substrate, that is, it exhibits substrate specificity. However, some enzymes catalyze a broad range of substrates and have, therefore, been utilized to prepare many new chiral compounds. For example, lipase and PLE have been extensively used in the preparation of chiral compounds.[3] Baker's yeast is a whole cell and yet shows broad applicability.[4]

PLE is known to show low substrate specificity and has been utilized in the catalytic asymmetric hydrolysis of prochiral diesters, as well as in the kinetic resolution of racemic esters.[5] In addition, PLE has been utilized for the conversion of diesters to half-esters in high yield.[6]

In addition to its wide applicability, another notable feature of PLE is that it does not catalyze the hydrolysis of half-esters produced through PLE-mediated hydrolysis of prochiral diesters[7] except for one special case.[8] That is, in general, the PLE-catalyzed hydrolysis of prochiral diesters typically affords the corresponding half-esters almost quantitatively, and does not yield di-carboxylic acids. Therefore, chiral half-esters suitable for the total synthesis of natural products have been prepared via PLE-catalyzed hydrolysis in high yield.

We investigated the PLE-catalyzed hydrolysis of dialkyl α,α-disubstituted malonates and found that in some cases the corresponding half-esters were obtained in high yield and enantiomeric excess (ee).[9] During our studies, the PLE-catalyzed kinetic resolution of a half-ester (89% ee) was observed, which resulted in the half-ester being recovered in an enantioenriched form (96% ee) (Scheme 1).[10] To the best of our knowledge, this is the first example of the PLE-catalyzed kinetic resolution of a half-ester.

This successful result encouraged us to conduct further studies on the PLE-catalyzed kinetic resolution of half-esters which were derived from prochiral diesters, and we report the results herein.

2. Results and discussion

We found that the PLE-catalyzed hydrolysis of the prochiral dimethyl malonate derivative **1a** quantitatively afforded the corresponding half-ester **2a** in 89% ee (Scheme 1). The PLE-catalyzed hydrolysis of isolated **2a** was found to afford enantioenriched **2a** (96% ee, 88% recovery),[10] which was successfully used in the total synthesis of (+)-ophiobolin A.[11]

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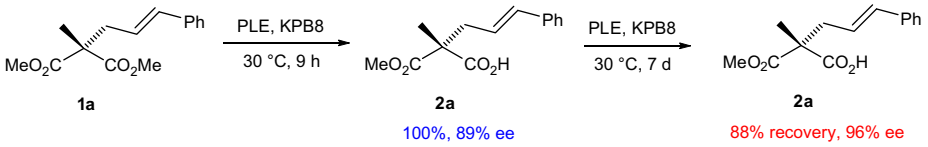
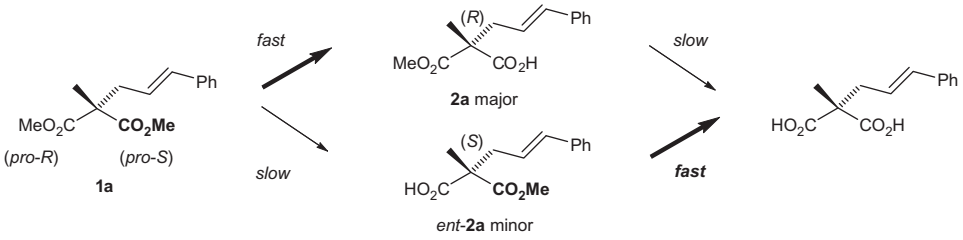


Scheme 1. PLE-catalyzed asymmetric hydrolysis of **1a** and kinetic resolution of **2a**.



Scheme 2. A rationale for the kinetic resolution of **2a**.

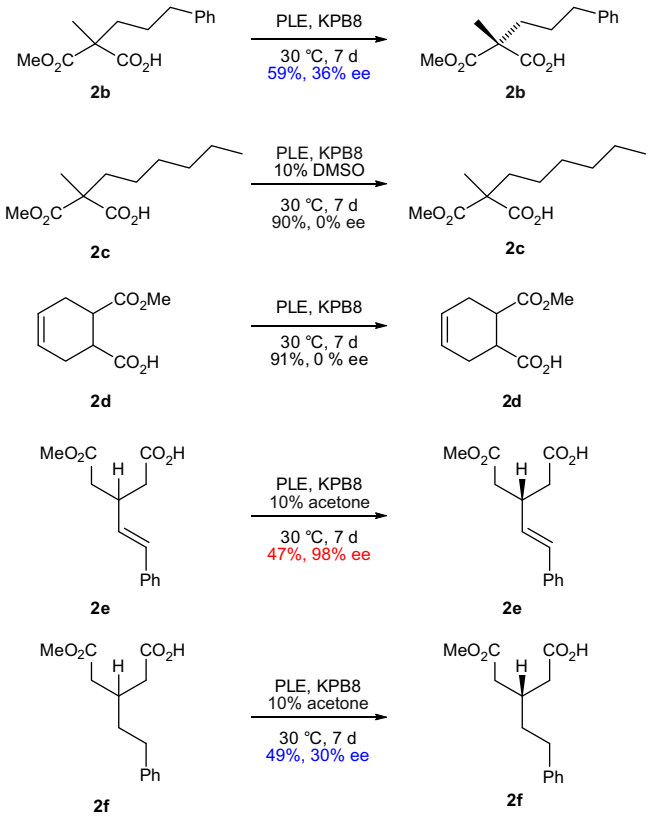
The PLE-catalyzed hydrolysis of **2a** in Scheme 1 suggests that the PLE-catalyzed kinetic resolution of a half-ester occurred as shown in Scheme 2, that is, the PLE-catalyzed hydrolysis of the *pro*-(*S*) methyl ester of **1a** proceeded faster than that of the *pro*-(*R*) methyl ester of **1a**. Therefore, the PLE-catalyzed hydrolysis of the half-ester *ent*-**2a** that affords the corresponding di-carboxylic acid would be faster than that of the half-ester **2a**, thus leading to an increase of the ee of the half-ester **2a**.

We were surprised to find the kinetic resolution of **2a** since the PLE-catalyzed kinetic resolution of half-esters has not been reported. Therefore, we conducted the PLE-catalyzed hydrolysis of **2a** repeatedly, and found that the hydrolysis of 3.7 mg of **2a** using 15 units of PLE in a 0.1 M potassium phosphate buffer (pH 8.0, KPB8) at room temperature for 7 d afforded **2a** of 96% ee. On the other hand, we also found that the hydrolysis of 791.0 mg of **2a** using 350 units of PLE in 0.1 M KPB8 for 7 d afforded **2a** of 91% ee (95% recovery). These results suggested that the ratio of the amount of PLE to **2a** might be important in its kinetic resolution. Therefore, we investigated the use of a syringe pump to add **2a** gradually to the suspension of PLE in 0.1 M KPB8 over 3 d, and found that the kinetic resolution of **2a** occurred reproducibly, to afford **2a** of 96% ee.

In order to explore the scope and limitations of the PLE-catalyzed kinetic resolution via this protocol, we examined the PLE-catalyzed hydrolysis of some racemic mono-esters (Scheme 3). In the hydrolysis of **2b**, a half-ester of a malonate derivative, 59% of **2b** was recovered and the ee was 36%. In the hydrolysis of **2c**,[12] also a half-ester of a malonate derivative, the starting material remained almost unchanged and the recovered half-ester was a racemic mixture. In the hydrolysis of the non-malonate half-ester **2d**,[13] virtually no hydrolysis occurred, and racemic **2d** was recovered. The hydrolysis of half-ester **2e**[14] afforded enantio-enriched **2e** (47% recovery, 98% ee). Considering that the maximum recovery yield of kinetic resolution is 50%, 47% is an excellent recovery yield. In the case of its saturated form **2f**,[14] the ee of the recovered **2f** was 30% (49% recovery).

The results in Schemes 1 and 3 indicate that the PLE-catalyzed hydrolysis of half-esters occurs depending on the structure of substrate. It is premature to discuss the relationships between the structures of half-esters and their hydrolysis before accumulating further examples. However, among the substrates shown in Schemes 1 and 3, half-esters containing a phenyl group **2a**, **2b**, **2e**, and **2f** were hydrolyzed by PLE, whereas other substrates, such as **2c** and **2d**, remained almost unchanged.

As aforementioned, the PLE-catalyzed hydrolysis of half-esters depends on the ratio of the amount of PLE to that of half-ester;



Scheme 3. PLE-catalyzed kinetic resolution of racemic half-esters **2b–f**.

the use of a syringe pump is also required for the efficient kinetic resolution on a large scale. The reason for the substrate/PLE ratio problem and the necessity for use of a syringe pump have not yet been explained. Therefore, further studies including kinetic studies are under investigation and will be reported in due course.

3. Conclusion

In conclusion, we found in some cases that the PLE-catalyzed hydrolysis of half-esters results in their kinetic resolution and is dependent on the structure of substrates. The kinetic resolution required a slow addition of the half-esters using a syringe pump,

and converted some racemic half-esters into enantioenriched ones. Therefore, the developed protocol could be used to improve the ee of half-esters prepared via PLE-catalyzed hydrolysis of prochiral diesters, although it depends on the structure of substrates.

4. Experimental

4.1. General procedures

^{1}H and ^{13}C NMR spectra were recorded on JEOL AL-400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; band, several overlapping signals; br, broad. IR spectra were recorded on a JASCO FT/IR-8300. Optical rotations were measured using a 2 ml cell with a 1 dm path length on a JASCO DIP-1000. Chiral HPLC analysis was performed on a JASCO PU-980 and UV-970. Mass spectra and elemental analyses were provided at the Materials Characterization Central Laboratory, Waseda University. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and phosphomolybdic acid and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on self-made 0.3 mm E. Merck silica gel plates (60F-254). Pig liver esterase was purchased from Sigma–Aldrich, and all the other reagents were purchased from Aldrich, TCI, or Kanto Chemical Co. Ltd.

4.2. Preparation of (*R*,*E*)-2-methoxycarbonyl-2-methyl-5-phenylpent-4-enoic acid 2a by the PLE-catalyzed hydrolysis

To a suspension of diester **1a** (30.0 mg, 0.114 mmol) in a pH 8 phosphate buffer (3 mL) was added PLE (15 units), and the reaction mixture was stirred at 30 °C. After **1a** had disappeared, 2 M HCl was added to the reaction mixture to adjust the solution to pH 3. The aqueous layer was extracted with EtOAc (1.5 mL × 2), dried over Na_2SO_4, filtered and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate = 4:1) to afford **2a** (28.3 mg, 100%, 89% ee. Ee was determined by the HPLC analysis of **3a**) as a colorless liquid: R_f = 0.33 (dichloromethane/methanol = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.20 (5H, m), 6.47 (1H, d, J = 15.6 Hz), 6.10 (1H, dt, J = 15.6, 7.6 Hz), 3.75 (3H, s), 2.82 (1H, dd, J = 13.9, 7.6 Hz), 2.76 (1H, dd, J = 13.9, 7.6 Hz), 1.49 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 172.1, 136.9, 134.4, 128.4, 127.4, 126.2, 123.6, 54.0, 52.8, 39.5, 20.1; IR (neat) ν_{max} 2956, 2360, 1736, 1112 cm^{-1}; HRMS (FAB) [M+H]$^+$ Calcd for $C_{14}H_{17}NO_4$: 249.1127. Found: 249.1127; $[\alpha]_D^{28} = +4.9$ (*c* 0.9, MeOH).

4.2.1. (*R*)-Methyl 2-methyl-5-phenyl-2-phenylcarbamoyl-4-pentenoate 3a

Compound **3a** was prepared from **2a** in 54% yield by a standard procedure (EDC·HCl and aniline were used.): R_f = 0.48 (hexane/ethyl acetate = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (1H, s), 7.54 (2H, d, J = 8.5 Hz), 7.34–7.18 (7H, m), 7.11 (1H, t, J = 7.6 Hz), 6.48 (1H, d, J = 15.9 Hz), 6.10 (1H, dt, J = 15.9, 7.6 Hz), 3.79 (3H, s), 2.96 (1H, ddd, J = 13.9, 7.3, 1.2 Hz), 2.79 (1H, ddd, J = 13.9, 7.6, 1.2 Hz), 1.58 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 168.6, 137.5, 136.8, 134.2, 128.9, 128.4, 127.4, 126.2, 124.4, 124.0, 120.1, 54.6, 52.9, 41.8, 21.1; IR (neat) ν_{max} 3352, 2956, 1738, 1674, 1542, 1248 cm^{-1}; HRMS (FAB) [M+H]$^+$ Calcd for $C_{20}H_{22}NO_3$: 324.1600. Found: 324.1603; $[\alpha]_D^{27} = +42.0$ (*c* 0.3, $CHCl_3$); 89% ee. Ee was determined by the HPLC analysis; DICEL CHIRALPAK AS-H 0.46 cm ϕ × 25 cm; hexane/isopropanol = 9/1; flow rate = 0.5 mL/min; retention time: 16.8 min for *ent*-**3a**, 17.9 min for **3a**.

4.3. PLE-catalyzed kinetic resolution of 2a

To a suspension of PLE (350 units) in a pH 8 potassium phosphate buffer (250 mL) was added half-ester **2a** (791 mg, 3.19 mmol, 89% ee) via a syringe pump over 72 h at 30 °C. One week after the addition of **2a**, 2 M HCl was added to the reaction mixture to adjust the solution to pH 3. The aqueous layer was extracted with EtOAc (200 mL × 3), dried over Na_2SO_4, filtered and evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate = 4/1) to recover **2a** (508 mg, 88%, 96% ee) as a colorless liquid. The ee of the recovered half-esters was determined by the HPLC analysis of the corresponding anilides, which were prepared by a standard method (EDC·HCl, aniline).

4.3.1. Racemic 2-methoxycarbonyl-2-methyl-5-phenylpentanoic acid 2b

To a stirred solution of (*E*)-2-methoxycarbonyl-2-methyl-5-phenylpent-4-enoic acid (13.8 mg, 0.056 mmol) in EtOH (1.0 mL) was added a catalytic amount of 10% Pd/C under an atmosphere of Ar, and the reaction mixture was stirred under an atmosphere of hydrogen. After the reaction was complete, the mixture was filtered and concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (dichloromethane/methanol = 10/1) to afford racemic **2b** (8.3 mg, 60%): R_f = 0.33 (dichloromethane/methanol = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.26 (2H, m), 7.20–7.16 (3H, m), 3.73 (3H, s), 2.63 (2H, t, J=7.3 Hz), 2.00–1.86 (2H, m), 1.68–1.55 (2H, m), 1.44 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 172.6, 141.5, 128.3, 125.8, 53.6, 52.7, 36.0, 35.5, 26.3, 20.2; IR (neat) ν_{max} 3028, 2996, 2956, 1736, 1718, 1454, 1268 cm^{-1}; FAB-MS [M+H]$^+$ Calcd for $C_{14}H_{19}O_4$: 251.1283. Found: 251.1288.

4.3.2. (*R*)-2-Methoxycarbonyl-2-methyl-5-phenylpentanoic acid 2b

Compound **2b** (36% ee. Ee was determined by HPLC of **3b**) was obtained in 59% yield according to the procedure for the PLE-catalyzed kinetic resolution of **2a**: R_f = 0.33 (dichloromethane/methanol = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.26 (2H, m), 7.20–7.16 (3H, m), 3.73 (3H, s), 2.63 (2H, t, J = 7.3 Hz), 2.00–1.86 (2H, m), 1.68–1.55 (2H, m), 1.44 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 172.6, 141.5, 128.3, 125.8, 53.6, 52.7, 36.0, 35.5, 26.3, 20.2; IR (neat) ν_{max} 3028, 2996, 2956, 1736, 1718, 1454, 1268 cm^{-1}; HRMS (FAB) [M+H]$^+$ Calcd for $C_{14}H_{19}O_4$: 251.1283. Found: 251.1288; $[\alpha]_D^{26} = +0.7$ (*c* 0.8, $CHCl_3$).

4.3.3. (*R*)-Methyl 2-methyl-2-phenylcarbamoyl-5-phenylpentanoate (3b)

$[\alpha]_D^{36} = +11.9$ (*c* 0.5, $CHCl_3$); 36% ee. Ee was determined by HPLC analysis; DICEL CHIRALCEL OD-H 0.46 cm ϕ × 25 cm; hexane/isopropanol = 9/1; flow rate = 0.3 mL/min; retention time: 27.2 min for *ent*-**3b**, 29.1 min for **3b**. The absolute configuration of the product was determined by the comparison of the sign of the specific rotation with that of compound **3b** {$[\alpha]_D^{28} = +23.3$ (*c* 0.4, $CHCl_3$), 89% ee}, which was prepared by the hydrogenation of **3a**.

4.3.4. Methyl 2-(4-methoxyphenylcarbamoyl)-2-methyloctanoate 3c

The ee of **2c** was determined by HPLC of **3c**: R_f = 0.57 (hexane/ethyl acetate = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (1H, s), 7.45 (2H, AA′XX′ pattern, J = 9.0 Hz), 6.85 (2H, AA′XX′ pattern,

J = 9.0 Hz), 3.78 (6H, s), 2.03 (1H, dt, J = 15.4, 7.6 Hz), 1.86 (1H, dt, J = 15.4, 7.6 Hz), 1.51 (3H, s), 1.26–1.19 (8H, m), 0.86 (3H, t, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 169.0, 156.2, 130.9, 121.6, 114.0, 55.4, 54.1, 52.7, 38.9, 31.5, 29.4, 25.1, 22.5, 21.1, 14.0; IR (neat) ν_{max} 3336, 2932, 1714, 1666, 1602, 1516, 1246 cm^{-1}; HRMS (FAB) $[M+H]^+$ Calcd for $C_{18}H_{28}NO_4$: 322.2018. Found: 322.2005; racemic mixture; ee was determined by HPLC; DICEL CHIRALCEL OD-H 0.46 cm $\phi \times 25$ cm; hexane/isopropanol = 19/1; flow rate = 0.4 mL/min; retention time: 20.0, 22.0 min.

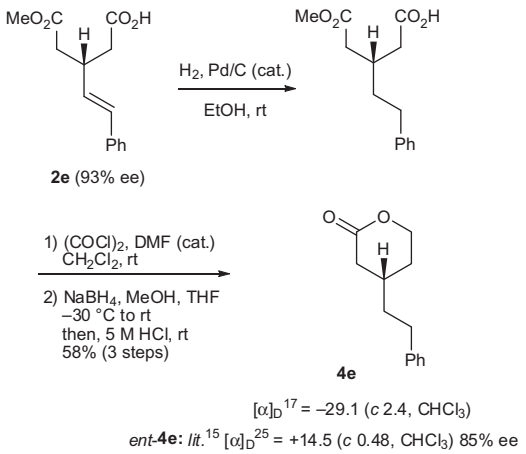
4.3.5. Methyl 6-phenylcarbamoyl-3-cyclohexenecarboxylate 3d

The ee of **2d** was determined by HPLC of **3d**: R_f = 0.14 (hexane/ethyl acetate = 4/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (1H, s), 7.50 (2H, d, J = 8.3 Hz), 7.29 (2H, dd, J = 8.3, 7.3 Hz), 7.08 (1H, t, J = 7.3 Hz), 5.77 (2H, s), 3.72 (3H, s), 3.14–3.05 (2H, m), 2.76–2.27 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 170.9, 137.9, 128.8, 125.6, 124.8, 124.0, 119.8, 52.1, 41.6, 40.6, 26.9, 26.0; IR (neat) ν_{max} 3324, 3032, 2952, 1730, 1666, 1602, 1538, 1442, 1250, 1206 cm^{-1}; HRMS (FAB) $[M+H]^+$ Calcd for $C_{15}H_{18}NO_3$: 260.1287. Found: 260.1279; Ee was determined by the HPLC analysis and found to be 0% ee: DICEL CHIRALPAK AS-H 0.46 cm $\phi \times 25$ cm; hexane/isopropanol = 3/1; flow rate = 0.3 mL/min; retention time: 31.5, 36.6 min.

4.3.6. (*S*,*E*)-Methyl 3-phenylcarbamoylmethyl-5-phenylpent-4-enoate 3e

The ee of **2e** was determined by HPLC of **3e**: R_f = 0.22 (hexane/ethyl acetate = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (1H, s), 7.49 (2H, d, J = 7.8 Hz), 7.33–7.19 (7H, m), 7.08 (1H, t, J = 7.3 Hz), 6.50 (1H, d, J = 15.9 Hz), 6.18 (1H, dd, J = 15.9, 8.1 Hz), 3.67 (3H, s), 3.28 (1H, dtt, J = 8.1, 7.1, 6.8 Hz), 2.67–2.51 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 169.2, 137.7, 136.7, 131.1, 130.5, 128.9, 128.4, 127.4, 126.2, 124.2, 119.8, 51.8, 42.3, 38.8, 36.7; IR (KBr) ν_{max} 3345, 1736, 1655, 1600, 1527, 1256 cm^{-1}; mp 98.1–98.6 °C; HRMS (FAB) $[M+H]^+$ Calcd for $C_{20}H_{22}NO_3$: 324.1600. Found: 324.1591; $[\alpha]_D^{27} = -27.4$ (c 0.3, $CHCl_3$); 98% ee. Ee was determined by the HPLC analysis; DICEL CHIRALPAK AS-H 0.46 cm $\phi \times 25$ cm; hexane/isopropanol = 3/1; flow rate = 0.4 mL/min; retention time: 42.8 min for *ent*-**3e**, 47.2 min for **3e**. The absolute configuration of the product was determined to be the same as that of compound **3e** {$[\alpha]_D^{20} = -40.8$ (c 1.3, $CHCl_3$), 93% ee}, which was prepared from **2e**[14] (93% ee), by the comparison of their specific rotation.

The absolute configuration of **2e** was determined by comparison of the specific rotation of its derivative **4e** with the reported data.[15] Compound **2e** was converted into **4e** as follows:



4.3.7. (*S*,*E*)-Methyl 3-phenylcarbamoylmethyl-5-phenylpentanoate 3f

The ee of **2f** was determined by HPLC of **3f**: R_f = 0.16 (hexane/ethyl acetate = 4/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (1H, s), 7.52 (2H, d, J = 7.8 Hz), 7.33–7.17 (7H, m), 7.09 (1H, t, J = 7.6 Hz), 3.71 (3H, s), 2.71 (2H, t, J = 7.3 Hz), 2.56–2.38 (5H, m), 1.84–1.64 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 169.9, 141.5, 137.9, 128.9, 128.4, 128.3, 125.9, 124.1, 119.6, 51.8, 41.9, 37.7, 36.2, 33.3, 33.1; IR (KBr) ν_{max} 3312, 3023, 2944, 2856, 1730, 1659, 1598, 1523, 1441, 1207, 1153 cm^{-1}; HRMS (FAB) $[M+H]^+$ Calcd for $C_{20}H_{24}NO_3$: 326.1756. Found: 326.1751; $[\alpha]_D^{28} = +4.0$ (c 0.5, $CHCl_3$); 30% ee; ee was determined by HPLC; DICEL CHIRALCEL OD-H 0.46 cm $\phi \times 25$ cm; hexane/isopropanol = 3/1; flow rate = 0.3 mL/min; retention time: 26.2 min for **3f**, 29.4 min for *ent*-**3f**. The absolute configuration of the product was determined to be the same as that of compound **3f** {$[\alpha]_D^{21} = +8.1$ (c 4.7, $CHCl_3$), 93% ee}, which was prepared by the hydrogenation of **3e** (93% ee), by comparison of their specific rotation.

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