Palladium(II) complex-catalysed enantioselective benzoylation of alcohols using carbon monoxide and an organobismuth(V) compound

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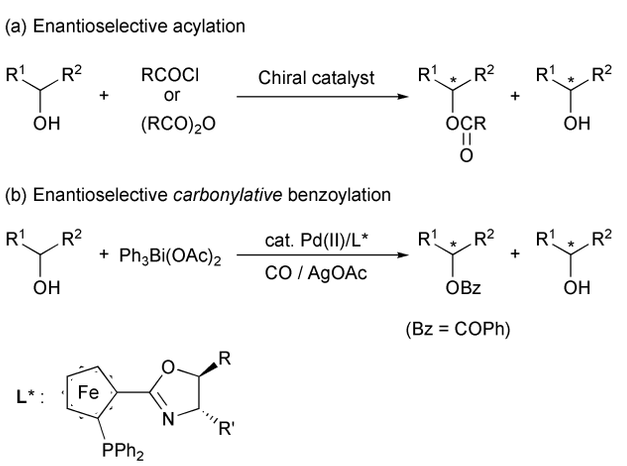
A novel method for the kinetic resolution of racemic secondary alcohols *via* their enantioselective benzoylation has been explored using CO, $Ph_3Bi(OAc)_2$, a catalytic amount of a chiral Pd(II) complex and AgOAc. In this catalytic system, $Ph_3Bi(OAc)_2$ has been revealed to work better than any other phenylating reagents such as $PhB(OH)_2$ or $PhSnMe_3$. It has also been disclosed that the planar chirality of optically active oxazolinylferrocenylphosphine (**3e**) has some positive effect on the enantioselectivity. Satisfactory enantioselectivity has not yet been obtained (up to 48% ee), but this reaction system seems to be interesting from the viewpoint of both asymmetric synthesis and organobismuth chemistry.

Introduction

Enantioselective acylation of alcohols is one of the most useful methods for obtaining optically active alcohols and their derivatives in organic chemistry. In this field, enzymatic methods have been used widely to synthesize natural products and bio-active compounds over many years.[1] To evaluate the efficiency of a method of resolution, it is convenient to use the selectivity factor (*s* value),[2] and many enzymatic methods give high selectivities with $s > 100$, but structural variations are limited because of the high substrate specificity in enzymatic reactions. Recently, non-enzymatic methods using chiral nucleophilic catalysts and acylating reagents such as acyl chlorides and acid anhydrides have been intensively studied [Scheme 1, (a)]. For example, Oriyama and co-workers reported the kinetic resolution of secondary alcohols and the desymmetrization of *meso*-diols catalysed by a chiral 1,2-diamine derived from (*S*)-proline,[3] which provides a high selectivity for the conversion of various alcohols. Fu and co-workers demonstrated the efficacy of planar-chiral derivatives of the 4-(dimethylamino)pyridine catalyst for the kinetic resolution of alcohols,[4] including allylic[4b] or propargylic[4c] substrates. There are also other successful methods in addition to those mentioned above.[5]



Scheme 1 Kinetic resolution of secondary alcohols.

The carbonylative acylation of alcohols using carbon monoxide (CO) is known to be an alternative tool for the preparation of esters and various transition metal-catalysed reaction systems have been reported.[6] We have previously reported the transition metal-catalysed carbonylative benzoylation of methanol with various aryl-heteroatom compounds (represented as PhM when aryl is phenyl) such as $ArB(OH)_2$,[7a] Ar_3Sb[7b] and Ar_3Bi[7c] under an atmospheric pressure of CO.[7] However, the application of carbonylative benzoylation to the kinetic resolution of racemic alcohols has not yet been reported.[8]

Our group, in addition to some other groups, has designed and prepared new optically active oxazolinylferrocenylphosphines **L*** having both planar and central chiralities.[9] By using **L*** as chiral ligands, a variety of catalytic asymmetric reactions have been developed such as hydrosilylation of ketones, imines and oximes, transfer hydrogenation of ketones and allylic arylation.[10] We envisaged the application of these chiral ligands **L*** to the transition metal-catalysed enantioselective carbonylative acylation of racemic alcohols. In this report, we describe the results of the enantioselective benzoylation of alcohols catalysed by a Pd(II) complex using CO, an organobismuth(V) compound and the oxidant AgOAc in the presence of **L*** [Scheme 1, (b)].[11,12]

Results and discussion

Effect of phenylating reagent and chiral ligand

At first, we examined several phenylating reagents (PhM) in this catalytic system using 1-phenylethanol (**1a**) as a model substrate. We attempted the reaction of **1a** (0.5 mmol) with PhM (0.6 mmol) in the presence of AgOAc (1.5 mmol) and a catalytic amount of a Pd(II) complex (5 mol%), including an achiral ligand (**3f**), in tetrahydrofuran (THF) under a CO atmosphere at room temperature. Typical results are shown in Table 1. As shown in the table, the reaction proceeded only slightly with Ph_3Sb and Ph_4Sn. The reaction using $PhSnMe_3$ and $PhB(OH)_2$, which have been used in some asymmetric reactions by other groups,[13] also did not give satisfactory results here. On the other hand, the treatment of **1a** with $Ph_3Bi(OAc)_2$ under CO (1 atm) gave the corresponding ester (**2a**) in 43%

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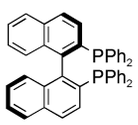
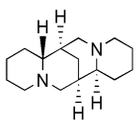
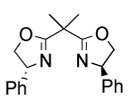
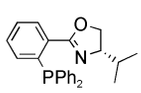
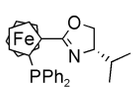
Table 1 Effect of phenylating reagent[a]

PhM	Pd complex (mol%)	CO (atm)	GLC yield (%)
Ph_3Sb	5	1	3
Ph_4Sn	5	1	7
$PhSnMe_3$	5	1	12
$PhB(OH)_2$	5	1	13
Ph_3Bi	5	1	14
$Ph_3Bi(OAc)_2$	5	1	43
$Ph_3Bi(OAc)_2$	5	5	71
$Ph_3Bi(OAc)_2$	10	5	82

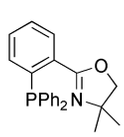
[a] Reaction conditions: **1a** (0.5 mmol), PhM (0.3 mmol), [$PdCl_2$(**3f**)], AgOAc (1.5 mmol), THF (2.5 ml) at room temperature under a CO atmosphere (5 atm) for 48 h.

Table 2 Effect of chiral ligand[a]

L*		Benzoate (**2a**)	
		Isolated yield (%)	Ee (%)[b]
	**3a**	0	—
	**3b**	9	3 (*S*)
	**3c**	8	13 (*S*)
	**3d**	31	6 (*S*)
	**3e**	34	19 (*R*)

[a] Reaction conditions: **1a** (0.5 mmol), $Ph_3Bi(OAc)_2$ (0.3 mmol), [$PdCl_2$**L***] (10 mol%), AgOAc (1.5 mmol), THF (25 ml) at 30 °C under a CO atmosphere (5 atm) for 48 h. [b] Determined by HPLC analysis using a suitable chiral column.

yield. Moreover, when the reaction was carried out in the presence of 10 mol% of Pd catalyst under CO (5 atm), the yield of **2a** improved to 82%. The reason why $Ph_3Bi(OAc)_2$ works well in this system is not yet clear, but it may be conceivable that the transmetallation between the organobismuth(V) compound and Pd(II) proceeds smoothly in this case because of the relatively longer C–Bi bond length compared to that in the organobismuth(III) compound.



3f

We then applied this carbonylative acylation to the kinetic resolution of alcohols using a variety of chiral ligands (**L***). The results are summarised in Table 2. Benzoylation of **1a** using a bidentate phosphine ligand such as (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP, **3a**) did not give **2a** at all. The bidentate nitrogen ligands (−)-sparteine (**3b**) and bisoxazoline compound (**3c**) were also examined, but the yield of **2a** was very poor. When a hybrid phosphine–nitrogen ligand **3d** (developed independently by Pfaltz and Helmchen[14]) was used, the reaction proceeded smoothly and **2a** was obtained in 31% yield. This result indicates that a hybrid phosphine–nitrogen ligand is superior to the bidentate diphosphine or dinitrogen ligands in this reaction system, but the enantiomeric excess obtained was still unsatisfactory (6% ee).

Next, we investigated the hybrid phosphine–nitrogen ligand **3e**, which has both planar and central chiralities. This ligand has been developed by our group[9] as well as by some other groups and has so far been applied to various asymmetric reactions.[10] When **3e** was used as a chiral ligand, benzoylation of **1a** proceeded smoothly, as expected, and more interestingly, the enantiomeric selectivity for **2a** rose (19% ee). Comparing the results using **3d** with those using **3e**, it is clear that the planar chirality of **3e** has some effect on the enantioselectivity. Other ligands were also examined that have a different substituent group on the oxazoline ring or a different aryl group on the phosphine atom of **3e**, but these ligands were less effective than **3e**. In addition, other solvents such as CH_2Cl_2, Et_2O and CH_3CN, and other reoxidants such as $CuCl_2$, $Cu(OAc)_2$ and ammonium cerium(IV) nitrate were not effective. So, we chose the reaction conditions shown in Table 2 using **3e** as the optimum ligand and applied them to the kinetic resolution of other secondary alcohols.

Kinetic resolution of secondary alcohols

We attempted the kinetic resolution of benzylic alcohols. Typical results are shown in Table 3. Benzoylation of **1a** gave the corresponding ester **2a** in 34% yield with 19% ee, together with unreacted **1a** in 52% yield with 8% ee. A slightly increased selectivity was observed in the reaction of 1-phenylpropan-1-ol (**1b**). The alcohols bearing 1- or 2-naphthyl group (**1d** and **1e**) gave enantioselectivities similar to that for **1a**.

Substituents such as chloro (**1f**) and a methoxy group (**1g**) at the *para* position were not effective in improving the enantioselectivity (Table 4). In contrast, the presence of a sterically bulky substituent at the *ortho* position, such as in **1h** and **1i**, improved the enantioselectivity of the corresponding ester up to 38% ee.

The results of the kinetic resolution of cyclic secondary alcohols, such as 2-substituted cyclopentanol and cyclohexanol, are shown in Table 5. Benzoylation of *cis*-2-phenyl alcohols gave the corresponding products in a higher selectivity than that of the *trans* substrates. Thus, the treatment of **1j** and **1k** in this reaction system afforded the corresponding esters with 28 and 38% ee, respectively. In particular, *cis*-2-phenylcyclohexan-1-ol (**1n**) was converted to **2n** in 21% yield with 48% ee (s = 3.2)[2] in this system. The ligand **3e** was revealed to be more effective than **3d**, as shown in Table 5, in the case of the benzoylation of **1l** and **1n**. No satisfactory enantioselectivity was observed in the reaction of cyclic alcohols containing a C–C double bond, such as **1m**, **1o** and **1p**.

Plausible reaction pathway

A plausible reaction pathway is shown in Scheme 2. The reaction of Pd(II) complex (**I**) with $Ph_3Bi(OAc)_2$ (PhM) gave a phenylpalladium species (**II**) *via* transmetallation followed by migratory insertion of CO to give an acylpalladium species (**III**). The attack of the alcohol **1** on **III** results in the formation of the enantio-enriched benzoate **2** together with the Pd(0) species. The Pd(0) species is reoxidised to **I** by AgOAc. The enantioselectivity of this catalytic reaction is governed by the step involving the attack of alcohol **1** on the acylpalladium species **III**, which bears the chiral phosphine–nitrogen ligand.

Conclusion

In summary, we have demonstrated the Pd(II)-catalysed kinetic resolution of racemic secondary alcohols using CO and an

Table 3 Kinetic resolution of benzylic alcohols

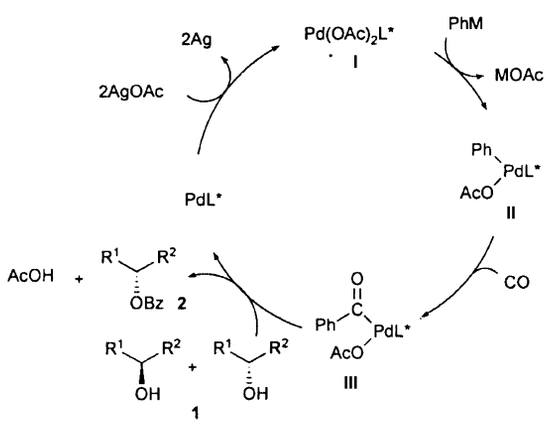
Alcohol (**1**)		Benzoate (**2**)		Unreacted alcohol (**1**)	
		Yield (%)[b]	Ee (%)[c]	Yield (%)[b]	Ee (%)[c]
Ph, Me, OH	**1a**	34	19 (*R*)	52	8 (*S*)
Ph, Et, OH	**1b**[d]	34	22	52	8
Ph, ^{i}Pr, OH	**1c**[d]	38	13	59	14
(1-Naph), Me, OH	**1d**	30	18	70	11
(2-Naph), Me, OH	**1e**	20	19	67	13

[a] Reaction conditions: **1** (0.5 mmol), $Ph_3Bi(OAc)_2$ (0.3 mmol), [$PdCl_2$(**3e**)] (10 mol%), AgOAc (1.5 mmol), THF (25 ml) at 30 °C under a CO atmosphere (5 atm) for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis using a suitable chiral column. [d] THF (5 ml).

Table 4 Kinetic resolution of benzylic alcohols

Ar in Ar, Me, OH		Benzoate (**2**)		Unreacted alcohol (**1**)	
		Yield (%)[b]	Ee (%)[c]	Yield (%)[b]	Ee (%)[c]
Cl–Ar–	**1f**	31	12	33	3
MeO–Ar–	**1g**	32	18	48	17
Me, Ar	**1h**	29	25	43	13[d]
^{i}Pr, Pr^i, ^{i}Pr, Ar	**1i**[e]	24	38	48	14[d]

[a] Reaction conditions: **1** (0.5 mmol), $Ph_3Bi(OAc)_2$ (0.3 mmol), [$PdCl_2$(**3e**)] (10 mol%), AgOAc (1.5 mmol), THF (25 ml) at 30 °C under a CO atmosphere (5 atm) for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis using a suitable chiral column. [d] Determined after conversion to the corresponding benzoate. [e] THF (5 ml).



Scheme 2 Plausible reaction pathway.

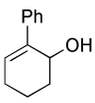
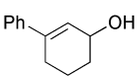
organobismuth(v) compound in the presence of AgOAc as reoxidant. It was also disclosed that the planar chirality of **3e** is important for obtaining high enantioselectivity in this catalytic system. Although the enantiomeric excess obtained has not yet been satisfactory (up to 48% ee; s = 3.2), this catalytic system should provide a novel methodology for the kinetic resolution of racemic alcohols. Moreover, as there is only one known example of the use of organobismuth compounds in asymmetric reactions,[15] the reaction presented here should be interesting from the viewpoint of organobismuth chemistry.

Experimental

General

^{1}H and ^{13}C NMR spectra were measured on JEOL EX-400, JEOL JNM-AL300, and JEOL JNM-GSX270 spectrometers for solutions in $CDCl_3$ with Me_4Si as an internal standard. ^{31}P NMR spectra were recorded on a JEOL EX-400 spectrometer for solutions in $CDCl_3$ with $P(OMe)_3$ as an external standard. Chemical shifts are reported in ppm relative to Me_4Si or $P(OMe)_3$ in the solvents specified. ^{1}H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, sept = septet, m = multiplet), coupling constant (Hz), relative intensity. GLC analyses were carried out with a Shimadzu GC-14A instrument equipped with a CPB

Table 5 Kinetic resolution of cyclic alcohols[a]

Alcohol (**1**)		THF/ml	Benzoate (**2**)		Unreacted alcohol (**1**)		
			Yield (%)[b]	Ee (%)[c]	Yield (%)[b]	Ee (%)[c,d]	*s* value[e]
	**1j**	10	37	28	36	11	2.1
	**1k**	5	29	38	32	18	2.6
	**1l**	10 10[g]	32 38	39[f] 16	46 41	23 7	2.7 1.5
	**1m**	10	32	22	49	13	1.7
	**1n**	5 5[g]	21 27	48 4	45 35	5 6	3.2 1.1
	**1o**	10	28	27	65	18	1.9
	**1p**	10	55	3	35	2	1.1

[a] Reaction conditions: **1** (0.5 mmol), $Ph_3Bi(OAc)_2$ (0.3 mmol), [$PdCl_2$(**3e**)] (10 mol%), AgOAc (1.5 mmol), THF (25 ml) at 30 °C under a CO atmosphere (5 atm) for 48 h. [b] Isolated yield. [c] Determined by HPLC analysis using a suitable chiral column. [d] Determined after conversion to the corresponding benzoate. [e] See ref. 2. [f] Absolute configuration is 1*R*, 2*S*. [g] **3d** was used instead of **3e**.

10-S25-050 (Shimadzu, fused silica capillary) column for determination of the GLC yields using bibenzyl as an internal standard, and with a GC-14B instrument equipped with a CHIRALDEX G-TA (30 m) (Tokyo Kasei Kogyo) column for determination of the ee values, both using He as the carrier gas. HPLC analyses were carried out on an L-7300 instrument with an L-7400 detector (HITACHI) using Daicel Chiralpak AD and AS, and Daicel Chiralcel OD and OJ columns. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. Analytical thin layer chromatography (TLC) was performed with silica gel 60 Merck F-254 plates. Column chromatography was performed with Merck silica gel 60 using hexane and ethyl acetate as eluents.

Materials

Solvents were obtained commercially and purified by standard procedures. $Ph_3Bi(OAc)_2$ [16] and ligands (**3d**,[14] **3e**[10] and **3f**[17]) were prepared by reported methods. 2-Methyl-1-phenylpropan-1-ol (**1c**), 1-(1-naphthyl)ethanol (**1d**), 1-(2-naphthyl)ethanol (**1e**), 1-(4-methoxyphenyl)ethanol (**1g**), 1-(2-methylphenyl)ethanol (**1h**) and 3-phenylcyclohex-2-en-1-ol (**1p**)[18] were prepared by the reduction of the corresponding ketone using $NaBH_4$. 1-(2,4,6-Triisopropylphenyl)ethanol (**1i**) was prepared by lithiation of 2-bromo-1,3,5-triisopropylbenzene followed by the addition of acetaldehyde. *trans*-2-Phenylcyclopentan-1-ol (**1j**) and *trans*-6-phenylcyclohex-3-en-1-ol (**1m**) were prepared by the reaction of the corresponding epoxide with $Ph_2Cu(CN)Li_2$.[19] 2-Phenylcyclohex-2-en-1-ol (**1o**) was prepared by the reported method.[20] *cis*-2-Phenylcyclopentan-1-ol (**1k**) and *cis*-2-phenylcyclohexan-1-ol (**1n**) were prepared from **1j** and **1l**, respectively, by the Mitsunobu reaction[21] followed by hydrolysis. Other commercially available organic and inorganic compounds were used without further purification. All new organic compounds (**2d**, **2i**, **2k**, **2m**, **2o** and **2p**) were characterised by ^1H and ^{13}C NMR and by elemental analysis or HRMS. New palladium complexes ([$PdCl_2$(**3c**)] and [$PdCl_2$(**3f**)]) were characterised by ^1H NMR and HRMS.

Preparation of palladium complexes

A typical experimental procedure for the preparation of [$PdCl_2$(**3e**)][22] is as follows. To a solution of $PdCl_2(CH_3CN)_2$ (259 mg, 1.00 mmol) in benzene (10 ml) was added a solution of **3e** (491 mg, 1.02 mmol) in benzene (10 ml) in a dropwise fashion at room temperature. After stirring for 2 h, an orange solid was obtained by filtration. Drying of this solid under reduced pressure gave pure palladium complex [$PdCl_2$(**3e**)] (593 mg, 90% yield) as an orange solid; mp (decomp.) 220–221 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (d, J = 6.8 Hz, 3H), 1.06 (d, J = 6.8 Hz, 3H), 3.00–3.16 (m, 1H), 3.80 (s, 5H), 4.35–4.53 (m, 3H), 4.75–4.85 (m, 1H), 5.02–5.13 (m, 1H), 7.22–7.70 (m, 8H), 8.25–8.40 (m, 2H); ^{31}P NMR (160 MHz, $CDCl_3$) δ 12.

Other palladium complexes were also prepared according to the same procedure. Spectroscopic data are as follows.

[$PdCl_2$(3a)].[23] Prepared from $PdCl_2(CH_3CN)_2$ and (*R*)-BINAP: a yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 6.68–7.87 (m).

[$PdCl_2$(3b)].[12a] Prepared from $PdCl_2(CH_3CN)_2$ and (−)-sparteine: a brown solid; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31–4.18 (m).

[$PdCl_2$(3c)]. Prepared from $PdCl_2(CH_3CN)_2$ and **3c**: a yellow solid; mp (decomp.) 169–170 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.89 (s, 3H), 2.00 (s, 3H), 4.52–4.71 (m, 4H), 5.91–5.95 (m, 2H) [Found (M^+ − Cl) 475.0419. $C_{21}H_{22}ClN_2O_2Pd$ requires M^+ − Cl, 475.0410].

[$PdCl_2$(3d)].[24] Prepared from $PdCl_2(CH_3CN)_2$ and **3d**: a pale yellow solid; ^1H NMR (400 MHz, $CDCl_3$) δ 0.27 (d, J = 6.8 Hz,

3H), 0.81 (d, J = 6.8 Hz, 3H), 2.60–2.72 (m, 1H), 4.36–4.52 (m, 2H), 6.98 (t, J = 7.8 Hz, 1H), 7.27–8.15 (m, 14H).

[$PdCl_2$(3f)]. Prepared from $PdCl_2(CH_3CN)_2$ and **3f**: a yellow solid; mp (decomp.) 245–246 °C (Found: C, 52.65; H, 4.12; Cl, 12.40; N, 2.34; $C_{23}H_{22}Cl_2NOPPd$ requires C, 51.47; H, 4.13; Cl, 13.21; N, 2.61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 6H), 3.95 (s, 2H), 7.27–7.92 (m, 14H) [Found ($M^+ - Cl$) 502.0160. $C_{23}H_{22}ClNOPPd$ requires $M^+ - Cl$, 502.0161].

Typical procedure for the enantioselective acylation of secondary alcohols

To a solution of $PdCl_2$**L*** (0.05 mmol) and AgOAc (250.4 mg, 1.50 mmol) in THF were added a secondary alcohol **1** (0.5 mmol) and $Ph_3Bi(OAc)_2$ (167.5 mg, 0.30 mmol), and then the mixture was transferred into a 50 ml stainless-steel autoclave. The autoclave was charged with carbon monoxide (5 atm) and the solution was stirred at 30 °C for 48 h. The resulting mixture was filtered through Florisil and Celite, and the filtrate was concentrated under reduced pressure. Purification of the residue by column chromatography gave the benzoyl ester **2** and the unreacted **1**. Enantiomeric excess was determined by GLC or HPLC analysis using a suitable chiral column.

1-Phenylethanol (1a). The ee value was determined by GLC analysis with a Tokyo Kasei Kogyo CHIRALDEX G-TA (30 m) column (carrier gas: N_2 = 20 kPa, He = 80 kPa, column temperature: 100 °C, retention time: 22.28 and 22.95 min).

1-Phenylethyl benzoate (2a). The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 9.82 and 11.74 min).

1-Phenylpropan-1-ol (1b). The ee value was determined by GLC analysis with a Tokyo Kasei Kogyo CHIRALDEX G-TA column (carrier gas: N_2 = 20 kPa, He = 80 kPa, column temperature: 100 °C, retention time: 31.21 and 33.25 min).

1-Phenyl-1-propyl benzoate (2b). The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 9.90 and 12.16 min).

2-Methyl-1-phenylpropan-1-ol (1c). The ee value was determined after conversion to **2c**.

2-Methyl-1-phenyl-1-propyl benzoate (2c). The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 10.77 and 13.38 min).

1-(1-Naphthyl)ethanol (1d). The ee value was determined by HPLC analysis with a Daicel Chiralcel AS column (eluent: hexane–propan-2-ol = 98 : 2, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 28.72 and 30.56 min).

1-(1-Naphthyl)ethyl benzoate (2d). A white solid; mp 65–66 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.87 (d, J = 6.4 Hz, 3H), 6.93 (q, J = 6.4 Hz, 1H), 7.43–8.24 (m, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.8, 70.2, 123.2, 125.3, 125.6, 126.3, 128.3, 128.4, 128.9, 129.6, 130.2, 130.4, 132.9, 133.8, 137.5, 165.8 [Found (M^+) 276.1151. $C_{19}H_{16}O_2$ requires M^+, 276.1150]. The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 12.84 and 16.37 min).

1-(2-Naphthyl)ethanol (1e). The ee value was determined by HPLC analysis with a Daicel Chiralpak OD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 25 °C, retention time: 40.80 and 71.24 min).

1-(2-Naphthyl)ethyl benzoate (2e). The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 11.36 and 13.09 min).

1-(4-Chlorophenyl)ethanol (1f). The ee value was determined by GLC analysis with a Tokyo Kasei Kogyo CHIRALDEX G-TA (30 m) column (carrier gas: N_2 = 20 kPa, He = 80 kPa, column temperature: 120 °C, retention time: 28.49 and 30.55 min).

1-(4-Chlorophenyl)ethyl benzoate (2f). The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 10.08 and 12.74 min).

1-(4-Methoxyphenyl)ethanol (1g). The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 12.39 and 17.11 min).

1-(4-Methoxyphenyl)ethyl benzoate (2g). The ee value was determined by HPLC analysis with a Daicel Chiralpak OD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 29.74 and 32.94 min).

1-(2-Methylphenyl)ethanol (1h). The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 15.85 and 17.58 min).

1-(2-Methylphenyl)ethyl benzoate (2h). The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 8.65 and 9.62 min).

1-(2,4,6-Triisopropylphenyl)ethanol (1i). The ee value was determined after conversion to **2i**.

1-(2,4,6-Triisopropylphenyl)ethyl benzoate (2i). A white solid; mp 111–112 °C (Found: C, 81.50; H, 9.17; $C_{24}H_{32}O_2$ requires C, 81.77; H, 9.15%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.24 (d, J = 6.8 Hz, 12H), 1.34 (d, J = 6.8 Hz, 6H), 1.75 (d, J = 6.8 Hz, 3H), 2.86 (sept, J = 6.8 Hz, 1H), 3.45–4.00 (m, 2H), 6.80 (q, J = 6.8 Hz, 1H), 6.90–8.10 (m, 7H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 22.4, 23.87, 23.92, 24.4, 25.0, 29.4, 34.1, 68.9, 128.2, 129.6, 130.6, 132.1, 132.8, 148.1, 166.0. The ee value was determined by HPLC analysis with a Daicel Chiralpak OD column (eluent: hexane–MeOH = 200 : 1, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 6.72 and 7.67 min).

***trans*-2-Phenylcyclopentan-1-ol (1j).** The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 23.96 and 26.65 min).

***trans*-2-Phenyl-1-cyclopentyl benzoate (2j).** The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 97 : 3, flow rate: 0.5 ml

min^{-1}, column temperature: 30 °C, retention time: 13.50 and 14.30 min).

***cis*-2-Phenylcyclopentan-1-ol (1k).** The ee value was determined by HPLC analysis with a Daicel Chiralpak OD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 11.68 and 12.94 min).

***cis*-2-Phenyl-1-cyclopentyl benzoate (2k).** A colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.67–2.20 (m, 6H), 3.16–3.22 (m, 1H), 5.50–5.53 (m, 1H), 7.03–7.39 (m, 8H), 7.68–7.71 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.5, 29.2, 32.8, 49.9, 78.8, 126.2, 127.9, 128.0, 128.4, 129.2, 130.6, 132.4, 139.5, 165.8 [Found (M^+ + H) 267.1385. $C_{18}H_{19}O_2$ requires M^+ + H, 267.1385]. The ee value was determined by HPLC analysis with a Daicel Chiralpak OJ column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 13.58 and 25.38 min).

***trans*-2-Phenylcyclohexan-1-ol (1l).** The ee value was determined by HPLC analysis with a Daicel Chiralpak OD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 13.96 and 15.11 min).

***trans*-2-Phenyl-1-cyclohexyl benzoate (2l).** The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 11.59 and 13.64 min).

***trans*-6-Phenylcyclohex-3-en-1-ol (1m).** The ee value was determined after conversion to **2m**.

***trans*-6-Phenylcyclohex-3-en-1-yl benzoate (2m).** A white solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.30–2.70 (m, 4H), 3.16–3.33 (m, 1H), 5.42–5.51 (m, 1H), 5.64–5.73 (m, 1H), 5.79–5.84 (m, 1H), 7.12–7.80 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 31.1, 32.8, 44.9, 73.5, 124.1, 126.4, 126.6, 127.6, 128.1, 128.4, 129.4, 130.5, 132.6, 142.3, 166.0 [Found (M^+ + H) 279.1387. $C_{19}H_{19}O_2$ requires M^+ + H, 279.1385]. The ee value was determined by HPLC analysis with a Daicel Chiralpak OJ column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 13.12 and 17.84 min).

***cis*-2-Phenylcyclohexan-1-ol (1n).** The ee value was determined after conversion to **2n**.

***cis*-2-Phenyl-1-cyclohexyl benzoate (2n).** The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 97 : 3, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 14.60 and 15.31 min).

2-Phenylcyclohex-2-en-1-ol (1o). The ee value was determined after conversion to **2o**.

2-Phenylcyclohex-2-en-1-yl benzoate (2o). A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.72–2.45 (m, 6H), 6.15 (t, J = 3.9 Hz, 1H), 6.40 (t, J = 3.9 Hz, 1H), 7.15–8.05 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.6, 25.7, 29.1, 68.3, 125.6, 127.0, 128.2, 128.4, 129.6, 130.6, 131.2, 132.7, 135.5, 139.8, 166.2 [Found (M^+) 278.1303. $C_{19}H_{18}O_2$ requires M^+, 278.1307]. The ee value was determined by HPLC analysis with a Daicel Chiralpak OJ column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 14.66 and 24.34 min).

3-Phenylcyclohex-2-en-1-ol (1p). The ee value was determined after conversion to **2p**.

3-Phenylcyclohex-2-en-1-yl benzoate (2p). A colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.42–2.10 (m, 5H), 2.06–2.62 (m, 1H), 5.68–5.76 (m, 1H), 6.22 (t, J = 1.8 Hz, 1H), 7.22–8.08 (m, 10H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.5, 27.4, 28.1, 69.5, 122.3, 124.5, 127.7, 128.27, 128.31, 129.6, 130.7, 132.8, 141.1, 142.3, 166.3 [Found (M^+) 278.1308. $C_{19}H_{18}O_2$ requires M^+, 278.1307]. The ee value was determined by HPLC analysis with a Daicel Chiralcel AD column (eluent: hexane–propan-2-ol = 95 : 5, flow rate: 0.5 ml min^{-1}, column temperature: 30 °C, retention time: 10.41 and 11.30 min).

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