A New Enantioselective Catalytic Route to Florhydral®

Sara Bovo, Alberto Scrivanti, Matteo Bertoldini, Valentina Beghetto, Ugo Matteoli*

Dipartimento di Chimica, Università di Venezia, Calle Larga S. Marta 2137, 30123 Venezia, Italy
Fax +39(041)2348967; E-mail: matteoli@unive.it

Received 15 April 2008; revised 29 April 2008

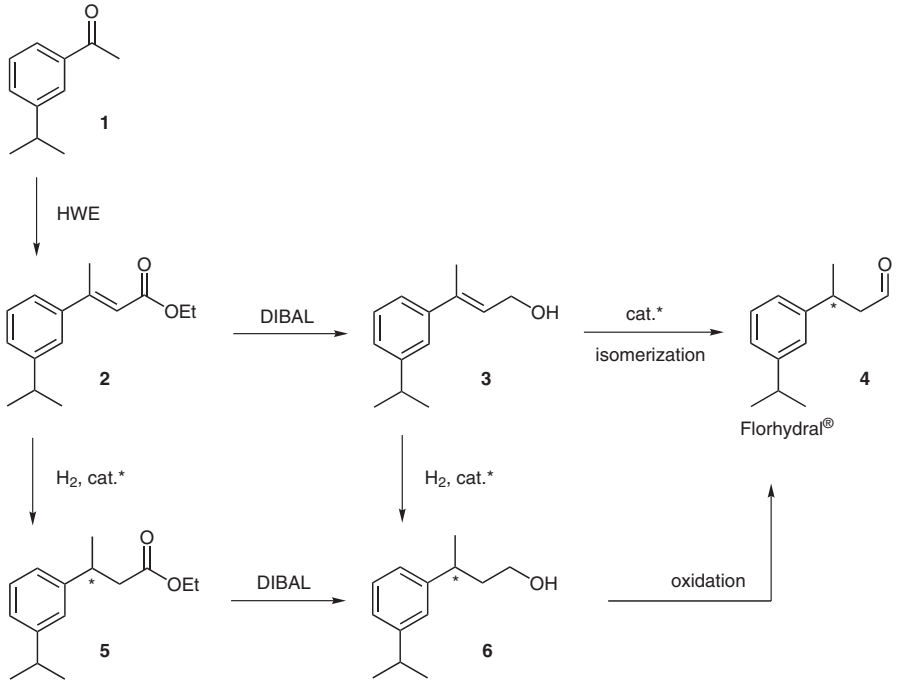
Abstract: The valuable fragrance Florhydral® [3-(3-isopropylphenyl)butanal] has been synthesized in almost enantiomerically pure form by a new catalytic route. The key step of the process is the enantioselective hydrogenation of (*E*)-3-(3-isopropylphenyl)but-2-en-1-ol, which is carried out with asymmetric inductions of up to 97% using an iridium-phosphinooxazoline chiral catalyst.

Key words: enantioselective hydrogenation, asymmetric catalysis, iridium, fragrance asymmetric synthesis, chiral fragrances

Nowadays flavors and fragrances are increasingly synthesized as enantiomerically pure compounds.[1,2] Different motivations stimulate chemists to devise stereoselective syntheses for fragrances. Most importantly, the use of a single stereoisomer of already known odorants until now used as racemic or diastereomeric mixtures may be an answer to the continuing quest of new odorants by perfurmers.[3–7] Impetus to develop stereoselective syntheses of odorants also comes from commercial considerations since stereoselective processes may be protected by new patents. Furthermore, many odorants are hardly biodegraded and have been found to accumulate in the ecosystem,[8] so that in the future also environmental concerns will prompt to use stereochemically enriched fragrances.[9] Manufacture and use of only the most olfactorily active stereoisomer of a perfumery raw material, instead of the racemate, could lead to a lower consumption and dispersion of these compounds in the environment.

Florhydral® [3-(3-isopropylphenyl)butanal, **4**] marketed by Givaudan, is a floral odorant widely used to convey at once fresh and marine long lasting notes. Fuganti and coworkers have been successful in synthesizing a single enantiomer of Florhydral® by an enzymatic approach. Evaluation of the odor profiles of the two enantiomers showed that, even if they have similar olfactory notes, the *S*-enantiomer is much more powerful as its odor threshold is 25 times lower than that of the opposite enantiomer.[10] Spurred by our interest in developing practical synthetic routes to enantiomerically enriched fragrances,[11,12] we were interested to develop an enantioselective catalytic route to this valuable fragrance.

The three different routes outlined in Scheme 1 were recognized as the most promising. They all have the ketone **1**



Scheme 1

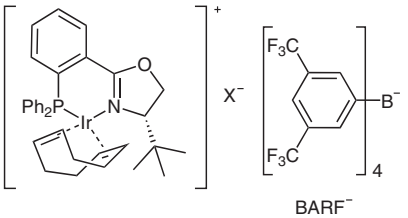
SYNTHESIS 2008, No. 16, pp 2547–2550
Advanced online publication: 08.07.2008
DOI: 10.1055/s-2008-1067167; Art ID: Z08908SS

as the common precursor,[13] which can be converted into the unsaturated ester **2** (*E*/*Z* ratio >12:1 by ^{1}H NMR spectroscopy) using a Horner–Wadsworth–Emmons olefination.

The first devised synthetic pathway entails the reduction of **2** with diisobutylaluminum hydride (DIBAL) followed by the catalytic asymmetric isomerization of the allyl alcohol **3**, which is the key step of the process. Asymmetric isomerization of olefins has been widely studied;[14] in particular, excellent results have been obtained with allylamines so that the process is applied in the industrial production of (–)-menthol.[14] It seems more difficult to achieve high asymmetric inductions in the isomerization of allylic alcohols.[15] As a matter of fact, high enantioselectivities have been obtained only in few cases: very good results (ee values up to 92%) were obtained by Fu[16] using rhodium/phosphaferrocene catalysts, and interesting results were obtained also by Crévisy[17] with a rhodium/phosphoramidite catalyst (ee values up to 64%) and by Ikariya[18] with ruthenium catalysts (62–74% ee).

The most used catalysts for C=C isomerization are cationic rhodium complexes containing chiral diphosphines;[15,16,19] accordingly we carried out some exploratory experiments on the isomerization of **3** in the presence of [Rh(COD)(*R*)-BINAP]ClO_4.[20] At 70 °C in THF, an allyl alcohol conversion of 35% is attained after 24 hours; unfortunately, the chemoselectivity of the reaction is poor and the yield in the sought fragrance is only 13%, because under these conditions the formed aldehyde further reacts to give aldol condensation by-products. Chiral GC shows that the asymmetric induction is also only quite modest, (*R*)-Florhydral® (**4**) being formed only in 17% ee. Aiming to improve both the chemo- and the enantioselectivity, a second experiment was carried out at 50 °C using a longer reaction time (72 h). Indeed, the lower reaction temperature favorably affects the asymmetric induction and (*R*)-Florhydral® (**4**) is obtained in 37% ee; however, both the reaction rate (substrate conversion: 22%) and the chemoselectivity (24%) remain low, so that this elegant and atom efficient synthetic scheme was not further explored.

As an alternative synthetic approach we investigated the asymmetric hydrogenation of **2** followed by the transformation of the ester moiety of **5** into the aldehydic group in two steps: i) reduction of the ester group to give **6**, and ii) oxidation to aldehyde of the methylol moiety. The key reaction is the enantioselective hydrogenation of **2**. The asymmetric hydrogenation of β-substituted cinnamic acids and their derivatives has been relatively unexplored,[21,22] nevertheless, very good results have been obtained in the asymmetric hydrogenation of β-methylcinnamates using iridium cationic catalysts containing P–N ligands.[23–25] To assess the practical feasibility of this synthetic scheme, the asymmetric hydrogenation of **2** was carried out in the presence of [Ir-(*S*)-PHOX]-1[23] (Figure 1), which is easily accessible owing to the commercial availability of the chiral ligand.



[Ir-(*S*)-PHOX]-1 : X$^-$ = BARF$^-$

[Ir-(*S*)-PHOX]-2 : X$^-$ = PF_6^-

Figure 1 Chiral catalysts used in the asymmetric hydrogenation

The hydrogenation of **2** in the presence of [Ir-(*S*)-PHOX]-1 under 10 atm of H_2 at 23 °C in CH_2Cl_2 furnishes (*R*)-**5** with 27% ee (Table 1, entry 1). This modest but promising asymmetric induction is accompanied by an unsatisfactory reaction rate, thus, with the aim of increase both the rate and the enantioselectivity, the hydrogen pressure was raised to 50 atm. Favorably, the enantioselectivity increases to 75%, but the reaction rate still remains unsatisfactory; a further increase of the hydrogen pressure to 100 atm does not lead to better results since both the olefin conversion and the asymmetric induction are practically unaffected. Also an increase of the temperature does not significantly improve the reaction rate and adversely affects the asymmetric induction. Finally, it should be mentioned that at 0 °C the reaction rate becomes unacceptable without significant variation of the asymmetric induction.

Table 1 Asymmetric Hydrogenation of **2** in the Presence of [Ir-(*S*)-PHOX]-1

Entry	Temp (°C)	*P* (H_2) (atm)	Time (h)	Conv (%)	ee (%)[a,b]
1	23	10	24	38	27 (*R*)
2	23	50	24	47	75 (*R*)
3	23	100	24	54	72 (*R*)
4	50	50	24	52	66 (*R*)
5	0	50	72	33	77 (*R*)

Reaction conditions: substrate: 0.30 mmol, cat.: 0.012 mmol, substrate/cat. = 25:1, solvent: CH_2Cl_2 (10 mL).

[a] The ee values were determined by chiral HPLC.

[b] The configuration of the prevailing enantiomer was attributed by transforming **5** into **6** whose chiroptical properties are known.[10]

These results prompted us to investigate a different synthetic approach since, even if the enantioselectivity obtained might be regarded as suitable for the production of a chiral fragrance, the reaction rates are so poor that the process does not appear to be of practical interest.

We focused our studies on the **2** → **3** → **6** → **4** alternative route in which the stereogenic centre is formed by the asymmetric hydrogenation of the allylic alcohol **3**. Among the catalysts which have been successfully used in the asymmetric hydrogenation of substituted allylic alcohols, the iridium-phosphinooxazoline cationic complexes

[Ir-(*S*)-PHOX]-1 and [Ir-(*S*)-PHOX]-2 (Figure 1) emerge as particularly efficient being able to furnish high reaction rates and enantiomeric excesses higher than 90%.[23] Serendipitously, at 23 °C under 50 atm of H_2 the hydrogenation of **3** in the presence of 1.0 mol% of [Ir-(*S*)-PHOX]-1 furnished (*R*)-**6** in quantitative yield and 97% ee (chiral GC, see below) confirming the great efficiency of this Pfaltz's catalyst in asymmetric hydrogenation of allylic alcohols. For the sake of comparison, the hydrogenation of **3** was carried out under the same reaction conditions using [Ir-(*S*)-PHOX]-2; with this catalyst the reaction rate (38% substrate conversion after 20 h) and the enantioselectivity (90%) turned out to be significantly lower.

The strong influence of the nature of the counter ion when using iridium hydrogenation catalysts has been investigated by Pfaltz and co-workers.[23] The higher reaction rates and the higher asymmetric inductions are attributed to the fact that $BARF^-$ is a weaker coordinating ion than PF_6^-, moreover $BARF^-$ also appears to be more stable under the reaction conditions.

Oxidation of alcohol (*R*)-**6** with pyridinium chlorochromate affords in almost quantitative yield (*R*)-**4**. We used this reaction also to evaluate the enantiomeric purity of **6**; in fact, while it was not possible to separate the enantiomers of **6** in GC on a Chiraldex G TA column, the same column resolves very well the enantiomers of **4**.

In conclusion, we have developed a new strategy for the synthesis of almost enantiomerically pure Florhydral® (**4**); the process might be of practical feasibility provided that a more economical and sustainable synthesis of **3** shall be developed.

All compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy and mass spectrometry. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance AC 300 spectrometer operating at 300.213 and 75.44 MHz, respectively. GC-MS analyses were performed on a Hewlett-Packard 5890 SERIES II gas chromatograph interfaced with an HP 5971 quadrupole mass detector. GC analyses were performed on an Agilent 6850 gas chromatograph with a FID detector. The enantiomeric excesses were determined either by chiral GC using a Chiraldex G-TA column (50 m × 0.25 mm i.d.) installed on an Agilent 6850 gas chromatograph with a FID detector or by chiral HPLC using a CHIRALCEL OD-H column (250 × 4.6 mm i.d.) installed on an Agilent 1100 chromatograph equipped with an UV detector. Optical rotations were determined using a PerkinElmer 241 polarimeter (Na lamp at 20 °C).

(*S*)-2-(*o*-Diphenylphosphinophenyl)-3-*tert*-butyloxazoline was purchased from Strem; all other reagents were available from commercial sources and were used without further purification. 1-(3-Isopropylphenyl)ethanone,[13] {Ir[(*S*)-2-(*o*-diphenylphosphinophenyl)-3-*tert*-butyloxazoline]COD}(BARF),[23a] {Ir[(*S*)-2-(*o*-diphenylphosphinophenyl)-3-*tert*-butyloxazoline]COD}(PF_6)[23a] and {Rh[(*R*)-BINAP](COD)}ClO_4[20] were prepared as described in the literature.

(*E*)-3-(3-Isopropylphenyl)but-2-enoic Acid Ethyl Ester (2)

Under N_2, to a chilled (0 °C) solution of BuLi in *n*-hexane (12.5 mL of a 2.5 M solution in hexanes, 31 mmol) were sequentially added: anhyd THF (10 mL), triethyl phosphonoacetate (6 mL, 30 mmol diluted in 10 mL of THF), anhyd LiBr (8.07 g, 93 mmol, dissolved in 20 mL of THF) and finally 1-(3-isopropylphenyl)ethanone (**1**; 5.0 g, 31 mmol) diluted with THF (12 mL). The resulting orange solution was kept under stirring for 24 h, then treated with H_2O (15 mL), and extracted with Et_2O (3 × 60 mL). The combined organic phases were washed with brine (30 mL) and dried ($MgSO_4$). The solvents were removed in vacuo to give **2** as a pale yellow oil (*E*/*Z* = 12:1), which was purified by chromatography (silica gel, eluent: hexane–EtOAc, 9:1); yield: 5.0 g (70%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.20–7.35 (m, 4 H_{arom}), 6.13 (q, *J* = 1.2 Hz, 1 H, HC=), 4.22 (q, *J* = 7.1 Hz, 2 H, CH_2O), 2.93 (sept, *J* = 6.8 Hz, 1 H, CH), 2.58 (d, *J* = 1.2 Hz, 3 H, CH_3), 1.32 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.27 (d, *J* = 6.8 Hz, 6 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3, 18.0, 23.8, 34.2, 59.8, 116.9, 123.9, 124.4, 127.1, 128.4, 142.3, 149.1, 156.0, 166.9.

MS (EI): *m*/*z* (%) = 232 ([M]$^+$, 50), 217 (11), 187 (22), 171 (40), 144 (100), 128 (41), 115 (35), 91 (16).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.38; H, 8.84.

(*E*)-3-(3-Isopropylphenyl)-2-but-2-enol (3)

To a chilled (0 °C) solution of **2** (960 mg, 4.14 mmol) in Et_2O (30 mL) was slowly added diisobutylaluminum hydride (8.3 mL of a 1.0 M solution in hexanes, 8.3 mmol). The resulting yellow solution was kept overnight under stirring, diluted with Et_2O (50 mL), and then cautiously treated with 4 N HCl (30 mL) at 0 °C. The organic phase was separated and the aqueous phase extracted with Et_2O (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, and taken to dryness. The resulting pale yellow oil was purified by chromatography (silica gel, eluent: hexane–EtOAc, 9:1); yield: 630 mg (80%); colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.14–7.35 (m, 4 H_{arom}), 5.99 (tq, *J* = 1.3, 6.6 Hz, 1 H, CH), 4.39 (d, *J* = 6.6 Hz, 2 H, CH_2), 2.94 (sept, *J* = 6.9 Hz, 1 H, CH), 2.11 (d, *J* = 1.3 Hz, 3 H, CH_3), 1.50 (br s, 1 H, OH), 1.28 (d, *J* = 6.9 Hz, 6 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.1, 24.0, 34.2, 60.0, 123.7, 124.9, 125.4, 126.3, 128.2, 138.3, 142.9, 148.8.

MS (EI): *m*/*z* (%) = 190 ([M]$^+$, 27), 175 (10), 147 (100), 129 (48), 115 (47), 105 (42), 91 (34), 77 (18).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.21; H, 9.77.

Asymmetric Isomerization of 3

In a typical experiment, under N_2 in a Schlenk-flask were introduced a THF solution (6 mL) of **3** (200 mg, 1.05 mmol) and {Rh[(*R*)-BINAP](COD)}ClO_4 (4.9 mg, 0.0052 mmol). The reactor was heated at 70 °C with a thermostatic bath and the mixture stirred for 24 h. After cooling to r.t., the mixture was evaporated, diluted with Et_2O (10 mL) and filtered on a short silica column (eluent: Et_2O). GC-MS and GC analyses showed that the substrate conversion was 35% and that the crude reaction product was composed of 38% of **4**, 12% of a dehydration product, and about 50% of aldol condensation by-products. Chiral GC (Chiraldex GT-A column, T = 100 °C, N_2: 3.5 mL/min; *S*-enantiomer: t_R = 61.35 min, *R*-enantiomer: t_R = 61.94 min) showed that (*R*)-**4** was present in 17% ee; the configuration of the prevailing isomer was determined by polarimetry comparing the optical rotation data with the value reported in the literature.[10]

Asymmetric Hydrogenation of 2 in the Presence of [Ir-(*S*)-PHOX]-1

In a typical experiment (Table 1, entry 2), a magnetically stirred 150 mL stainless steel autoclave was charged with a CH_2Cl_2 solution (10 mL) containing **2** (70 mg, 0.30 mmol) and [Ir-(*S*)-PHOX]-1 (18.7 mg, 0.012 mmol) under an inert atmosphere The reactor was then pressurized with H_2 (50 atm) and kept under stirring at 23 °C. After

24 h, the crude product was concentrated and the residue filtered on a short silica column (eluent: Et_2O–hexane, 1:1). GC-MS and GC analyses showed that the crude material was a mixture of unreacted **2** (53%) and (*R*)-**5** (47%) (75% ee by chiral HPLC: CHIRALCEL OD-H column (250 × 4.6 mm i.d.) with *n*-hexane as eluent (1.0 mL/min), UV detector, λ = 266 nm; *S*-enantiomer: t_R = 11.17, *R*-enantiomer: t_R = 27.7 min). The configuration of the prevailing enantiomer was inferred by polarimetry. The mixture of **2** and **5** obtained in the asymmetric hydrogenation was treated with DIBAL to give a mixture of **3** and **6**, shown to be levorotatory. Since Fuganti[10] has reported an $[\alpha]_D^{20}$ +16.6 (*c* = 1.25, $CHCl_3$) for (*S*)-**6**, we concluded that the prevailing enantiomer formed by asymmetric hydrogenation of **2** is (*R*)-**5**. A sample of racemic **5** for the chiral HPLC analyses was obtained by hydrogenation of **2** in the presence of 5% Pd/C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.05–7.30 (m, 4 H_{arom}), 4.10 (q, *J* = 7.1 Hz, 2 H, CH_2O), 3.28 (m, 1 H, CH), 2.89 (sept, *J* = 6.9 Hz, 1 H, CH), 2.59 (m, 2 H, CH_2), 1.32 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.27 (d, *J* = 6.9 Hz, 6 H, CH_3), 1.21 (t, *J* = 7.1 Hz, CH_3).

MS (EI): *m*/*z* (%) = 234 ([M]$^+$, 33), 160 (100), 147 (68), 131 (37), 117 (14), 105 (17), 91 (21).

Asymmetric Hydrogenation of 3 in the Presence of [Ir-(*S*)-PHOX]-1

In a typical experiment, a magnetically-stirred 150 mL stainless steel autoclave was charged, under an inert atmosphere, with a CH_2Cl_2 solution of **3** (100 mg, 0.53 mmol) and [Ir-(*S*)-PHOX]-1 (9.8 mg, 0.0063 mmol). The reactor was pressurized with H_2 (50 atm) and kept under stirring at 23 °C. After 20 h, the residual gas was vented off, GC analysis of the crude mixture showed complete conversion of the substrate. The mixture was concentrated and the residue filtered on a short silica gel column (eluent: Et_2O–hexane, 1:1) to afford (*R*)-**6** (97% ee, as determined by chiral GC after oxidation to **4**: Chiraldex GT-A column, T = 100 °C, N_2: 3.5 mL/min; *S*-enantiomer: t_R = 61.35 min, *R*-enantiomer: t_R = 61.94 min); yield: 90 mg (90%); colorless oil; $[\alpha]_D^{20}$ –16.5 (*c* 1.20, $CHCl_3$). The spectroscopic data and the $[\alpha]_D$ value agree with the literature.[10]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.01 – 7.25 (m, 4 H_{arom}), 3.58 (td, *J* = 3.0, 6.6 Hz, 2 H, CH_2O), 2.81–2.296 (m, 2 H, CH + CH), 1.86 (q, *J* = 7.1 Hz, 2 H, CH_2), 1.28 (d, *J* = 7.1 Hz, 3 H, CH_3), 1.25 (d, *J* = 7.1 Hz, 6 H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.3, 24.0, 34.1, 36.5, 41.0, 61.3, 124.0, 124.3, 125.2, 128.4, 146.8, 149.0.

MS (EI): *m*/*z* (%) = 192 ([M]$^+$, 40), 159 (16), 147 (70), 131 (53), 117 (26), 105 (100), 91 (42).

Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 8.42; H, 10.36.

(*R*)-3-(3-Isopropylphenyl)butanal (4)

To a solution of (*R*)-**6** (168 mg, 0.88 mmol) in CH_2Cl_2 (3 mL) was added pyridinium chlorochromate (750 mg, 3.5 mmol), the resulting suspension was stirred for 6 h, and then diluted with Et_2O (10 mL). The mixture was filtered on a short silica gel column (eluent: Et_2O). Concentration of the filtrate afforded (*R*)-**4** (97% ee as determined by chiral GC: Chiraldex GT-A column, T = 100 °C, N_2: 3.5 mL/min; *S*-enantiomer: t_R = 61.35 min, *R*-enantiomer: t_R = 61.94 min); yield: 141 mg (85%); colorless oil; $[\alpha]_D^{20}$ –27.5 (*c* 1.35, $CHCl_3$). The spectroscopic data and the $[\alpha]_D$ value agree with the literature.[10]

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.75 (t, *J* = 2.0 Hz, 1 H, CHO), 7.06–7.31 (m, 4 H_{arom}), 3.38 (m, *J* = 6.8 Hz, 1 H, CH), 2.93 (sept, *J* = 6.9 Hz, 1 H, CH), 2.64–2.83 (m, 2 H, CH_2), 1.36 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.28 (d, *J* = 6.9 Hz, 6 H, CH_3).

MS (EI): *m*/*z* (%) = 190 ([M]$^+$, 25), 175 (5), 147 (100), 133 (30), 105 (76), 91 (47), 77 (13).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.33; H, 9.70.

Acknowledgment

This work has been performed with the Financial Support from the MIUR (Cofin 2004).

References

(1) Abate, A.; Brenna, E.; Dei Negri, C.; Fuganti, C.; Gatti, F. G.; Serra, S. *J. Mol. Catal. B: Enzym.* **2004**, *32*, 33.
(2) Blaser, H. U.; Spindler, F.; Studer, M. *Appl. Catal., A. Gen.* **2001**, *221*, 119.
(3) Bentley, R. *Chem. Rev.* **2006**, *106*, 4099.
(4) Sell, C. S. In *Perspectives in Flavor and Fragrance Research*; Kraft, P.; Swift, K. A. D., Eds.; Verlag Helvetica Chimica Acta: Zurich, **2005**, 67.
(5) Chapuis, C.; Jacoby, D. *Appl. Catal., A: Gen.* **2001**, *221*, 93.
(6) Abate, A.; Brenna, E.; Fuganti, C.; Gatti, F. G.; Serra, S. In *Perspectives in Flavor and Fragrance Research*; Kraft, P.; Swift, K. A. D., Eds.; Verlag Helvetica Chimica Acta: Zurich, **2005**, 55.
(7) Brenna, E.; Fuganti, C.; Serra, S. *Tetrahedron: Asymmetry* **2003**, *14*, 1.
(8) Peck, A. M.; Hornbuckle, K. C. *Atmos. Environ.* **2006**, *40*, 6101.
(9) Niederer, M.; Bollhalder, R.; Hohl, C. *J. Chromatogr., A* **2006**, *1132*, 109.
(10) Abate, A.; Brenna, E.; Dei Negri, C.; Fuganti, C.; Serra, S. *Tetrahedron: Asymmetry* **2002**, *13*, 899.
(11) Matteoli, U.; Ciappa, A.; Bovo, S.; Bertoldini, M.; Scrivanti, A. *Tetrahedron: Asymmetry* **2007**, *18*, 797.
(12) Scrivanti, A.; Bovo, S.; Ciappa, A.; Matteoli, U. *Tetrahedron Lett.* **2006**, *47*, 9261.
(13) Paganelli, S.; Ciappa, A.; Marchetti, M.; Scrivanti, A.; Matteoli, U. *J. Mol. Catal. A: Chem.* **2006**, *247*, 138.
(14) (a) Akutagawa, S.; Tani, K. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: Weinheim, **2000**, 145. (b) Akutagawa, S. In *Chirality in Industry*; Collins, A. N.; Sheldrake, G. N.; Crosby, J., Eds.; Wiley: New York, **1992**, Chap. 16, 325.
(15) van der Drift, R. C.; Bouwman, E.; Drent, E. *J. Organomet. Chem.* **2002**, *650*, 1.
(16) Tanaka, K.; Fu, G. C. *J. Org. Chem.* **2001**, *66*, 8177.
(17) Boeda, F.; Mosset, P.; Crévisy, C. *Tetrahedron Lett.* **2006**, *47*, 5021.
(18) Ito, M.; Kitahara, S.; Ikariya, T. *J. Am. Chem. Soc.* **2005**, *127*, 6172.
(19) Tani, K. *Pure Appl. Chem.* **1985**, *57*, 1845.
(20) Tani, K.; Yamagata, T.; Otsuka, S.; Kumobayashi, H.; Akutagawa, S. *Org. Synth.* **1989**, *67*, 33.
(21) Ohkuma, T.; Kitamura, M.; Noyori, R. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; Wiley-VCH: Weinheim, **2000**, 25.
(22) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029.
(23) (a) Lightfoot, A.; Schnider, P.; Pfaltz, A. *Angew. Chem. Int. Ed.* **1998**, *37*, 2897. (b) Roseblade, S. J.; Pfaltz, A. *Acc. Chem. Res.* **2007**, *40*, 1402. (c) Wuestenberg, B.; Pfaltz, A. *Adv. Synth. Catal.* **2008**, *350*, 174.
(24) Tang, W.; Wang, W.; Zhang, X. *Angew. Chem. Int. Ed.* **2003**, *42*, 943.
(25) Li, X.; Kong, L.; Gao, Y.; Wang, X. *Tetrahedron Lett.* **2007**, *48*, 3915.