Supporting Information.

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Experimental:

General. All reactions and manipulations were performed under argon using standard Schlenk techniques. Toluene was distilled from sodium benzophenone ketyl under argon. Ethyl acetate was distilled from CaH_2. Hydrogen gas of 99.99 % purity was used without purification. Complex **4** ($((C_6H_5)_4C_4CO)_2H(\mu\text{-}H)(CO)_4Ru_2$) was prepared according to literature procedure.[1] The immobilized lipase from *Candida antarctica* (trade name: Novozym 435) was a generous gift from Novo Nordisk, Korea. Enol acetates **5a-i** and ketones **1f** and **1i** were prepared according to literature procedures.[2, 3]

A typical procedure for the transformation of ketones to chiral acetates: In a 100 mL flask equipped with a grease-free high-vacuum stopcock, acetophenone (**1a**) (120 mg, 1.00 mmol), $(Ph_4C_4CO)_2H(\mu\text{-}H)(CO)_4Ru_2$ (**4**) (22 mg, 0.020 mmol), and Novozym 435 (84 mg) were mixed in ethyl acetate (3.0 mL). The mixture was degassed with sonication under vacuum, and the flask was filled with hydrogen gas (1 atm). The resulting suspension was heated at 70 ^oC for 96 h. The reaction mixture was filtered and concentrated, the resulting residue was chromatographed on silica gel (ethyl acetate/hexane 1:8) to give chiral acetate **3a** (133 mg, 81 % yield). The optical purity (96% ee) was determined by HPLC equipped with a chiral column ((R,R)

Whelk-O1).

A typical procedure for the transformation of enol acetates to chiral acetates: In a 100 mL flask equipped with a grease-free high-vacuum stopcock, 1-phenylethenyl acetate (**5a**) (162 mg, 1.00 mmol), $(Ph_4C_4CO)_2H(\mu\text{-}H)(CO)_4Ru_2$ (**4**) (22 mg, 0.020 mmol), and Novozym 435 (30 mg) were mixed in toluene (3.0 mL). The resulting suspension was degassed with sonication under vacuum, and the flask was filled with hydrogen gas (1 atm). The suspension was heated at 70 ^{o}C for 50 h. The reaction mixture was filtered and concentrated, and the resulting residue was chromatographed on silica gel (ethyl acetate/hexane 1:8) to give chiral acetate **3a** (141 mg, 86 % yield). The optical purity (96% ee) was determined by HPLC equipped with a chiral column ((R,R) Whelk-O1).

1. Shvo, Y.; Menashe, N. *Organometallics* **1991**, *10*, 3885.
2. Larock, R. C. *Comprehensive Organic Transformations*; VCH: New York, 1989, p. 743.
3. Almeda, M. L. S.; Beller, M.; Wang, G.-Z.; Bäckvall, J.-E. *Chem. Eur. J.* **1996**, *2*, 1533.

Table 1. HPLC enantiomer assays for acetates

Compounds	Column	Eluent (Hexane/*i*PrOH)	Flow rate (mL/min)	Retention time (R)/(S) (min)
3a	(R,R)-Whelk-O1[(a)]	95:5	1.0	4.80 / 3.33
3b	(R,R)-Whelk-O1	95:5	1.0	6.22 / 3.60
3c	(R,R)-Whelk-O1	95:5	1.0	9.95 / 4.70
3d	(R,R)-Whelk-O1	99:1	1.0	4.86 / 5.00
3e-OH[(c)]	CHRALCEL OD[(b)]	99:1	1.0	30.01 / 25.57
3h-OH[(c)]	CHRALCEL OD	95:5	1.0	10.86 / 15.38
3i-OH[(c)]	CHRALCEL OD	98:2	1.0	12.82 / 11.62

[(a)] Merck. [(b)] Daicel chemical Ind. LTD. [(c)] The analysis was performed after hydrolysis to corresponding alcohol.

Table 2. Capillary GC enantiomer assays for acetates

Compounds	Column	Carrier gas	Thermal condition [Initial temp.(time) / Increase temp. rate / Final temp.]	Retention time (R)/(S) (min)
3f	Chiraldex B-PH[(a)]	N_2	60 ^{o}C (10 min) / 2 ^{o}C/min / 85 ^{o}C	24.63 / 24.45
3g	Chiraldex B-PH	N_2	60 ^{o}C (10 min) / 2 ^{o}C/min / 85 ^{o}C	16.07 / 15.55

[(a)] Alltech Associates, Inc.