## **Supplementary information**

Toluene was dried over CaH<sub>2</sub> overnight, distilled under argon, and stored over 4-Å molecular sieves. Isopropenyl acetate was washed with saturated K<sub>2</sub>CO<sub>3</sub>, dried with CaCl<sub>2</sub>, and distilled under argon. IR spectra were recorded on a Shimadzu IR-440 spectrometer. EI mass spectra (MS) were run on a HP-5989A massspectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker AM 330 (300 MHz) or Bruker AM-400 (400 MHZ) spectrometer in CDCl3 and chemical shifts were reported in ppm downfield relative to TMS (internal standard); <sup>31</sup>P NMR was reported on a Bruker AM-400 (400 MHZ) spectrometer with CDCl<sub>3</sub> as the solvent and H<sub>3</sub>PO<sub>4</sub> as the external standard. Elemental analysis values were detected on Heraeus Rapid-CHNO apparatus. The enantiomeric excess values of products were determined by GC (HP 6890) with chiral columns (RT BDEXM and J-W CYCLOSIL-B) or HPLC (Waters) with chiral columns (CHIRALPAK AD-H and CHIRALPAK OD). The optical rotation values were determined by polarimeter (J-S P-1030).

### Synthesis of ruthenium complex 3

Ru<sub>3</sub>(CO)<sub>12</sub> (213 mg, 0.3 m mol) and 1,2,3,4,5-pentaphenyl-cyclopenta-2,4-dienol (462mg 1m mol) were placed in a schlenk tube, toluene (5 ml) was added and the mixture was flushed with argon 5 min before the system was closed. The reaction was stirred at 150°C (bath temperature) during 24h, then cooled down and removed the carbon monoxide in solution. The system was closed and stirred at the same temperature for additional 48h. The reaction was cooled down once more, the resulting solution was concentrated and chromatographed on aluminium oxide column to give a pale yellow solid 260 mg, yield: 41%, (when molecular sieve was added to this reaction, 360 mg ruthenium complex **3** was obtained, chemical yield was increased to 57% )mp: 285°C (decomposed); (found: C, 72.32; H, 4.08; C<sub>38</sub>H<sub>24</sub>O<sub>3</sub>Ru requires C, 72.48; H, 3.84);  $v_{max}$  /cm<sup>-1</sup> 3054, 2922, 2022, 1966, 1630, 1586, 1502, 1172, 857, 695, 637, 569;  $\delta_{\rm H}$ (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.60 (1H, d, *J*=7Hz), 7.43 (1H, d, *J*=7Hz ), 7.27 (1H, t, *J*=7Hz ), 6.99-7.17 (21H, m );  $\delta_{\rm C}$ (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 229.56, 198.91, 164.35, 136.30, 132.08, 131.88, 131.05, 130.81, 130.39, 129.24, 128.19, 127.79, 127.74, 127.64, 127.39, 121.05, 113.31, 109.45; m/z (EI) 630 (M).

X-ray quality crystal was grown in toluene; suitable single crystal of as-synthesized compound with the dimensions of  $0.447 \times 0.368 \times 0.221$ mm3 was carefully selected under an optical microscope and glued to a thin glass fiber with epoxy resin. Crystal structure determination by X-ray diffraction was carried out on a Siemens SMART CCD diffractometer with graphite-monochromated Mo-*Ka*( $\lambda$ =0.71073 Å) radiation at 293 K. An empirical absorption correction was applied using the SDAABS program. <sup>[1]</sup> A total of 18300 reflections were collected in the range of 1.69  $<\theta$ <26.00° at 293 K, of which 6797(R<sub>int</sub>= 0.1004) were independent and 3636 were observed with  $I > 2\sigma(I)$ . All of the collected reflections were used in the structure analysis. Heavy atoms were solved by direct methods, and other non-hydrogen atoms were determined with successive difference Fourier syntheses. The hydrogen atoms

were located at the theoretical positions. The anisotropic thermal parameters for all non-hydrogen atoms were refined by full-matrix least-squares on  $F^2$  for 443 parameters. All calculations were performed on a computer with SHELX-97 program package. <sup>[2, 3]</sup> The final R = 0.0714 and wR = 0.1738 ( $w = 1/[\sigma^2(F_o^2) + (0.1032P)^2 + 0.0000P$ ], where  $P = (F_o^2 + 2F_c^2)/3$ ).  $(\Delta/\sigma)_{max} = 0.000$ , S = 0.950,  $(\Delta\rho)_{max} = 2.271$  and  $(\Delta\rho)_{min} = -0.754$  e/Å<sup>3</sup>. CCDC 682225 contains the supplementary crystallographic data for ruthenium complex **3**. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

# Procedure for racemization of (S)-1-phenylethanol

In a 25ml dry schlenk flask, 220 mg potassium phosphate and Ru catalyst **3** (30 mg 0.05 m mol) were placed in. The Schlenk flask was evacuated and filled with argon, then toluene (3 mL) and (S)-1-Phenylethanol (120  $\mu$ L, 1 mmol) were added, this reaction was stirred at argon atmosphere. Six hours later, the resulting solution was concentrated and chromatographed on aluminium oxide column; (S)-1-Phenylethanol was completely racemized, 27 mg catalyst **3** was recovered with 90% yield. (S)-1-Phenylethanol also can be completely racemized by using this recovered catalyst within six hours.

# General procedure for dynamic kinetic resolution of secondary alcohols

Dynamic kinetic resolution of 1-phenylethanol: In a 25ml dry schlenk flask, 220 mg potassium phosphate and 170 mg molecular sieve 4Å were placed in. The Schlenk flask was evacuated and filled with argon, CALB 10mg and Ru catalyst **3** (32 mg 0.05 m mol) were quickly added, then toluene (3 mL) was added, and the mixture was stirred for 5 min, 1-Phenylethanol **1a** (120 µL, 1 mmol) was then added, and after 5 min isopropenyl acetate (200 µL, 1.8 mmol) was added. Argon atmosphere was maintained throughout the reaction. Yield and Ee value were determined by GC: Samples of 20 µL were withdrawn from the reaction mixture by means of a syringe, diluted to 1ml with  $CH_2Cl_2/MeOH$  (1:1), and filtered through a pad of cotton. The solution was filtered and washed with EtOAc, and the solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel with petroleum ether/ $CH_2Cl_2$  (1:1-1:10). The product **1b** was obtained as a colorless liquid (151 mg, yield: 94%, ee: 99%).



**1b** (*R*)-acetic acid 1-phenyl-ethyl ester, obtained as a colorless liquid, 151 mg, yield: 94%, 97% (GC), ee: 99% (Using RT BDEXM column),  $[\alpha]_D^{27}$ =+104 (*c* 0.60, CHCl<sub>3</sub>); Lit. <sup>[4]</sup>:  $[\alpha]_D^{25}$ = +106 (*c* 1.00, Et<sub>2</sub>O);  $\delta_H$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.25-7.36 (5H, m), 5.85-5.92 (1H, m), 2.07 (3H, s), 1.53 (3H, d, *J*=6Hz).

**2b** (R)-acetic acid 1-*p*-tolyl-ethyl ester, obtained as a colorless liquid, 161mg, yield: 92%, 96% (GC), ee: 98% (Using RT BDEXM column),  $[\alpha]_D^{26}$ =+113 (*c* 0.87, CHCl<sub>3</sub>); Lit<sup>[5]</sup>:  $[\alpha]_D^{25}$ = +94.6 (*c* 5.20, CHCl<sub>3</sub>);  $\delta_H$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.25 (2H, d, *J*=8Hz), 7.15 (2H, d, *J*=8Hz), 5.82-5.89 (1H, m), 2.33 (3H, s), 2.05 (3H, s), 1.52 (3H, d, *J*=6Hz).



**F 3b** (R)-acetic acid 1-(4-fluoro-phenyl)-ethyl ester, obtained as a colorless liquid, 160mg, yield: 90%, 90% (GC), ee: 99% (Using RT BDEXM column),  $[\alpha]_D^{26}$ =+89 (*c* 0.98, CHCl<sub>3</sub>);  $[\alpha]_D^{26}$ =+113 (*c* 0.87, CHCl<sub>3</sub>); Lit.<sup>[6]</sup>:  $[\alpha]_D^{32}$ = +92.8 (*c* 3.36, CHCl<sub>3</sub>);  $\delta_H$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.26-7.35 (2H, m), 6.99-7.05 (2H, m), 5.82-5.89 (1H, m), 2.06 (3H, s), 1.52 (3H, d, *J*=6Hz).



**4b** (R)-acetic acid 1-naphthalen-2-yl-ethyl ester, obtained as a colorless liquid, 200mg, yield: 95%, 99% (HPLC), ee: 99% (Using OD column, hexane/<sup>i</sup>PrOH=95/5, 0.8mL/min),  $[\alpha]_D^{29}$ =+46 (*c* 0.88, CHCl<sub>3</sub>); Lit<sup>[7]</sup>:  $[\alpha]_D^{20}$ = +33 (*c* 1.00, CHCl<sub>3</sub>);  $\delta_H$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 8.08 (1H, d, *J*=8Hz), 7.84-7.88 (1H, m), 7.79 (1H, d, *J*=8Hz), 7.43-7.61 (4H, m), 6.65 (1H, t, *J*=6Hz ), 2.11 (3H, s), 1.70 (3H, d, *J*=6Hz).

**5b** (R)-acetic acid 1-cyclohexyl-ethyl ester, obtained as a colorless liquid, 150mg, yield: 90%, 92% (GC) ee: 99% (Using RT BDEXM column),  $[\alpha]_D^{27}$ =+7.2 (*c* 0.77, CHCl<sub>3</sub>); Lit. <sup>[8]</sup>:  $[\alpha]_D^{24}$ =+6.6 (*c* 2.6, CHCl<sub>3</sub>);  $\delta_H$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.69-4.74 (1H, m), 2.02 (3H, s), 1.65-1.76 (5H, m), 1.12-1.43 (4H, m), 1.16 (3H, d, *J*=6Hz), 0.93-1.01 (2H, m).

**6b** (R)-acetic acid 1-methyl-heptyl ester, obtained as a colorless

liquid, 155mg, yield: 92%, 95% (GC), ee: 96% (Using RT BDEXM column),  $[\alpha]_D^{27}$ =-2.3 (*c* 0.73, CHCl<sub>3</sub>); Lit. <sup>[9]</sup>:  $[\alpha]_D^{25}$ = -1.9 (*c* 1.50, EtOH);  $\delta_H$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 4.86-4.92 (1H, m), 2.03 (3H, s), 1.45-1.59 (2H, m), 1.28-1.33 (8H, m), 1.20 (3H, m), 0.88 (3H, t, *J*=6Hz).



**7b** (R)-acetic acid 1-methyl-3-phenyl-allyl ester, obtained as a colorless liquid, 174mg, yield: 92%, 95% (GC) ee: 92% (Using RT BDEXM column),  $[\alpha]_D^{27}$ =+130 (*c* 0.73, CHCl<sub>3</sub>); Lit. <sup>[10]</sup>:  $[\alpha]_D^{20}$ = +80 (neat);  $\delta_H$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.24-7.39 (5H, m), 6.60 (1H, d, *J*=11Hz), 6.15-6.22 (1H, m), 5.51-5.55 (1H, m), 2.07 (3H, s), 1.41 (3H, d, *J*=6Hz).

OAc O O<sup>t</sup>Bu **8b** (R)- 3-acetoxy-butyric acid *tert*-butyl ester, obtained as colorless liquid, 195mg, yield: 99%, ee: 97% (Using RT BDEXM column),  $[\alpha]_D^{27}$ =+5.5 (*c* 1.06, CHCl<sub>3</sub>); Lit. <sup>[11]</sup>:  $[\alpha]_D^{25}$ = +7.59 (*c* 1.00, CHCl<sub>3</sub>);  $\delta_H$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 5.15-5.32 (1H, m), 2.35-2.55 (2H, m), 1.99 (3H, s), 1.41 (9H, s), 1.24 (3H, d, *J*=6Hz).



9b (R)-acetic acid 2-(4-chlorophenyl)sulfonyl-1-methyl-ethyl

ester, obtained a as colorless liquid, 250mg, yield: 94%, ee: 94% (Using AD-H column, hexane/<sup>i</sup>PrOH=95/5, 0.7mL/min, retention time: (S)-enantiomer, 45.61 min, (R)-enantiomer, 51.79 min),  $[\alpha]_D^{26}$ =+1.4 (*c* 1.00, CHCl<sub>3</sub>); (Found C, 47.48; H, 4.67; C<sub>11</sub>H<sub>13</sub>ClO<sub>4</sub>S requires C, 47.74; H, 4.73);  $v_{max}$  /cm<sup>-1</sup> 3093, 2984, 2937, 1742, 1584, 1478, 1347, 1316, 1238, 1154, 1129,1090, 1044, 1014, 834, 783, 573;  $\delta_{H}$ (300 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 7.85 (2H,d, *J*=9Hz), 7.56 (2H, d, *J*=9Hz), 5.27-5.30 (1H, m), 3.46-3.54 (1H, m), 3.20-3.27 (1H,m), 1.82 (3H,s), 1.34 (3H, d, *J*=6Hz);  $\delta_{C}$ (100 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 212.41, 169.64, 140.70, 138.01, 129.71, 65.04, 60.79, 20.79, 20.23; m/z (ESI) 294 (M<sup>+</sup>+NH<sub>4</sub><sup>+</sup>), 331 (M<sup>+</sup>+Na<sup>+</sup>+MeOH).

O O P O O Et 1

OEt 10b (R)-acetic acid 2-(diethoxy-phosphoryl)-1-methyl-ethyl ester, a

pale yellow transparent liquid, 180mg, yield: 80%, ee: 92% (Using J-W CYCLOSIL-B column),  $[\alpha]_D^{26}$ =+8.92 (*c* 1.00, CHCl<sub>3</sub>); Lit. <sup>[12]</sup>:  $[\alpha]_D^{25}$ =+9.7 (*c* 0.50, CHCl<sub>3</sub>);  $\delta_H$ (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 5.17-5.21 (1H, m), 4.08-4.15 (4H, m), 1.99-2.21 (5H, m), 1.32-1.39 (9H, m);  $\delta_P$ (121.5 MHz, CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>) 27.07.

AcO P-O<sup>i</sup>Pr

<sup>OiPr</sup> **11b** (R)-acetic acid 1-(diisopropxy-phosphoryl)-ethyl ester, obtained as a pale yellow transparent liquid, 215mg, yield: 88%, ee: >95% (Determined by <sup>31</sup>P NMR <sup>[9]</sup>),  $[\alpha]_D^{27}$ =+17.4 (*c* 0.92, CHCl<sub>3</sub>); Lit. <sup>[12]</sup>:  $[\alpha]_D^{25}$ = +20.1 (*c* 1.70, CHCl<sub>3</sub>);  $\delta_H$ (400 MHz, CDCl<sub>3</sub>, Me<sub>4</sub>Si) 5.13-5.21 (1H, m), 4.69-4.79 (2H, m), 2.09 (3H, s), 1.38-1.45 (3H, m), 1.23-1.33 (12H, m);  $\delta_P$ (121.5 MHz, CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>) 20.28.

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