Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

Inversion of Axial Chirality in Coordinated Bis-β-diketonato Ligands

Hisako Sato,[a*] Yukie Mori,[b] Takafumi Kitazawa[c] and Akihiko Yamagishi[c]

[a] *Graduated School of Science and Engineering, Ehime University, Matsuyama, Ehime 790-8577, Japan. Fax: +81-89-927-9599; Tel: +81-89-927-9590; E-mail: sato.hisako.my@ehime-u.ac.jp*
[b] *Faculty of Science, Ochanomizu University, Tokyo, 112-8610, Japan*
[c] *Department of Chemistry, Toho University, Funabashi, Chiba 274-8510, Japan .*

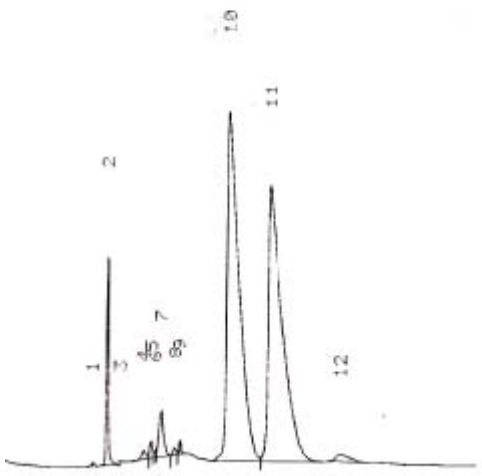


Figure S1. The HPLC chromatogram for the fraction containing [Ru(acac)$_2$(baetH)]. The mixture was eluted on a silica gel column (Inertsil, GL Science Inc., (Japan)) with a solvent of 95:5 (v/v) benzene-acetonitrile at a flow rate of 1.0 ml/min. The absorbance of the eluate was monitored at 600 nm. Peaks F_{10} at 9.8 min and F_{11} at 10.5 min (as denoted in the figure) were assigned to the two diastereomers (see text). The other small peaks were impurities.

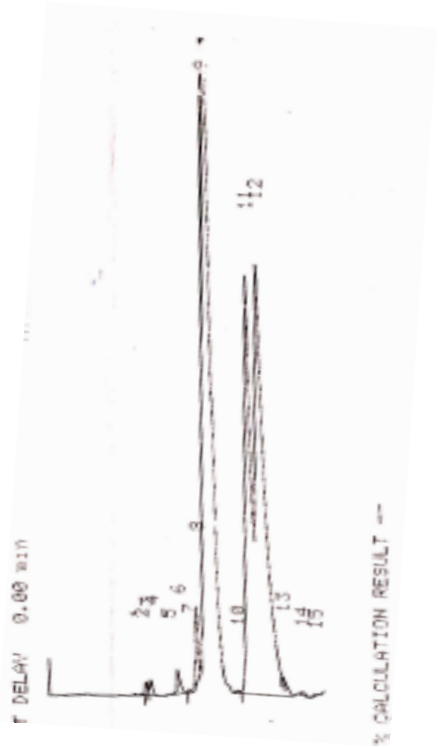


Figure S2. The HPLC chromatogram for the fraction containing $[Ru(acac)_2(baet)Ru(acac)_2]$. The mixture was eluted on a silica gel column (Inertsil, GL Science Inc. (Japan)) with a solvent of 8:2 (v/v) benzene-acetonitrile at a flow rate of 0.5 ml/min. The absorbance of the eluate was monitored at 600 nm. Peaks F_9 at 27.4 min, F_{11} at 34.9 min and F_{12} at 36.7 min (as denoted in the figure) were assigned to the meso-type, a racemic and the other racemic dinuclear complexes, respectively (see text).

The ^{1}H NMR spectra (400 MHz, $CDCl_3$) and mass analyses of free ligands and fractions B_{11}, B_{12}, B_{31}, B_{32} and B_{33}.

$dabeH_2$ as HL-LH

dabeH$_2$: δ = 2.0 (s, 6H, CH_3), 5.9 (s, 2H, CH), 7.0−8.0 (m, 10H, arom.); *m/z* = 322 (calc. 322).

B$_{11}$: [Ru(acac)$_2$(dabeH)]. δ = -12.18 (3H, CH_3), -10.88 (3H, CH_3), -8.69 (3H, CH_3), 1.19 (3H, CH_3), 1.31 (3H, CH_3), 3.95 (3H, CH_3), 4.55 (2H, arom.), 5.49 (2H, arom.), 6.34 (1H, arom.), 6.65 (2H, arom.), 9.03 (1H, arom.), 9.98 (2H, arom.), 15.66 (1H, OH); *m/z*= 620 (calc. for ^{102}Ru: 621).

B$_{12}$: [Ru(acac)$_2$(dabeH)]. δ = -10.48 (3H, CH_3), -8.85 (3H, CH_3), -5.87 (3H, CH_3), -2.07 (3H, CH_3), 0.71 (3H, CH_3), 0.77 (3H, CH_3), 4.65 (2H, arom.), 5.77 (2H, arom.), 6.23 (1H, arom.), 6.74 (2H, arom.), 8.91 (1H, arom.), 9.64 (2H, arom.), 15.49 (1H OH); *m/z* = 620 (calc. for ^{102}Ru: 621).

B$_{31}$: ΔΛ-[Ru(acac)$_2$(dabe)Ru(acac)$_2$]. δ = -34.20 (2H, CH), -17.61 (2H, CH), -14.30 (3H, CH_3), -12.70 (3H, CH_3), -11.59 (3H, CH_3), -11.03 (3H, CH_3), -9.70 (3H, CH_3), -6.52 (3H, CH_3), 0.12 (3H, CH_3), 2.28 (3H, CH_3), 3.77 (3H, CH_3), 4.52 (2H, arom.), 4.67 (2H, arom.), 5.47 (3H, CH_3), 8.02 (2H, arom.), 8.34 (4H, arom.); *m/z* = 918 (calc. for ^{102}Ru: 920).

B$_{32}$: ΔΔ- (or ΛΛ) -[Ru(acac)$_2$(dabe)Ru(acac)$_2$]. δ = -35.10 (2H, CH), -16.10 (2H, CH), -15.3 (6H, CH_3), -10.13 (6H, CH_3), -6.90 (6H, CH_3), 0.77 (6H, CH_3), 4.01 (4H, arom.), 4.70 (6H, CH_3), 6.26 (4H, arom.), 7.58 (2H, arom.); *m/z* = 918 (calc. for ^{102}Ru: 920).

B$_{33}$: ΔΔ- (or ΛΛ) -[Ru(acac)$_2$(dabe)Ru(acac)$_2$]. δ = < -40 (2H, CH), -13.81 (6H, CH_3), -12.86 (6H, CH_3), -10.00 (2H, CH), -9.31 (6H, CH_3), 3.37 (6H, CH_3), 4.13 (4H, arom.), 6.65 (6H, CH_3), 7.89 (2H, arom.), 8.92 (4H, arom.); *m/z* = 918 (calc. for ^{102}Ru: 920).

$baetH_2$ as HL-LH

baetH$_2$: δ = 0.91 (d, 12H, CH_3), 1.98 (s, 6H, $COCH_3$), 2.11 (d, 4H, CH_2), 2.1−2.2 (m, 2H, CH), 17.05 (s, 2H, OH); *m/z* = 282 (calc. 282).

B$_{11}$: [Ru(acac)$_2$(baetH)]. δ = -33.7 (1H, CH), -23.3 (1H, CH), -12.40 (1H, $COCH_2$), -10.92 (1H, $COCH_2$), -10.36 (3H, CH_3), -9.86 (3H, CH_3), -5.59 (3H, CH_3), -2.96 (3H, CH_3), -0.32 (3H, CH_3), 0.34 (3H, $CH(C\underline{H}_3)_2$), 0.46 (3H, $CH(C\underline{H}_3)_2$), 0.85 (3H, $CH(C\underline{H}_3)_2$), 1.75 (3H, $CH(C\underline{H}_3)_2$), 2.1 (1H, $C\underline{H}Me_2$), 2.40 (3H, $COCH_3$), 2.45 (2H, $COCH_2$), 9.68 (1H, $C\underline{H}Me_2$), 15.66 (1H, OH); *m/z* = 580 (calc. for ^{102}Ru: 581).

B$_{12}$: [Ru(acac)$_2$(baetH)]. δ = -32.6 (1H, CH), -22.6 (1H, CH), -11.32 (1H, $COCH_2$), -10.72 (3H, CH_3), -10.08 (1H, $COCH_2$), -9.34 (3H, CH_3), -4.48 (3H, CH_3), -2.90 (3H, CH_3), -1.16 (3H, CH_3), -0.32 (d, 3H, $CH(C\underline{H}_3)_2$,), 0.60 (d, 3H, $CH(C\underline{H}_3)_2$), 1.14 (d, 3H, $CH(C\underline{H}_3)_2$), 1.20 (d, 3H, $CH(C\underline{H}_3)_2$), 1.20 (3H, $COCH_3$), 1.57 (2H, $COCH_2$), 8.36 (1H, $C\underline{H}Me_2$), 15.47 (1H, OH); *m/z* = 580 (calc. for ^{102}Ru: 581).

B$_{31}$: ΔΛ-[Ru(acac)$_2$(baet)Ru(acac)$_2$]. δ = -29.8 (1H, CH), -28.5 (1H, CH), -22.7 (1H, CH), -22.1 (1H, CH), -19.59 (1H, $COCH_2$), -18.29 (1H, $COCH_2$), -15.67 (1H, $COCH_2$), -14.96 (1H, $COCH_2$), -13.73 (3H), -13.01 (3H), -7.88 (3H), -7.37 (3H), -3.87 (3H), -3.46 (3H), -2.84 (3H), -2.83 (3H), -1.07 (3H), -0.62 (3H), 0.08 (3H), 0.44 (3H), 0.93 (3H), 0.94 (3H), 9.67 (2H); *m/z* = 879 (calc. for ^{102}Ru: 880).

B_{32}: ΔΔ- (or ΛΛ) -[$Ru(acac)_2(baet)Ru(acac)_2$]. δ = -28.3 (2H, CH), -24.4 (2H, CH), -16.91 (2H, $COCH_2$), -16.44 (2H, $COCH_2$), -13.07 (6H), -7.27 (6H), -3.95 (6H), -3.02 (6H), -1.09 (6H), -0.63 (6H), 1.59 (6H), 10.05 (2H, C<u>H</u>Me_2); *m/z* = 879 (calc. for ^{102}Ru: 880).

B_{33}: ΔΔ- (or ΛΛ) -[$Ru(acac)_2(baet)Ru(acac)_2$]. δ = -31.9 (2H, CH), -20.2 (2H, CH), -15.16 (2H, $COCH_2$), -14.73 (2H, $COCH_2$), -11.85 (6H), -8.37 (6H), -5.08 (6H), -2.93 (6H), -1.81 (6H), 1.53 (12H), 7.37 (2H, C<u>H</u>Me_2); *m/z* = 879 (calc. for ^{102}Ru: 880).

<u>$dpeH_2$ as HL-LH</u>

$dpeH_2$: δ = 1.12 (t, 6H, CH_3), 2.01 (s, 6H, $COCH_3$), 2.30 (q, 4H, CH_2), 16.87 (s, 2H, OH); *m/z* = 226 (calc. 226).

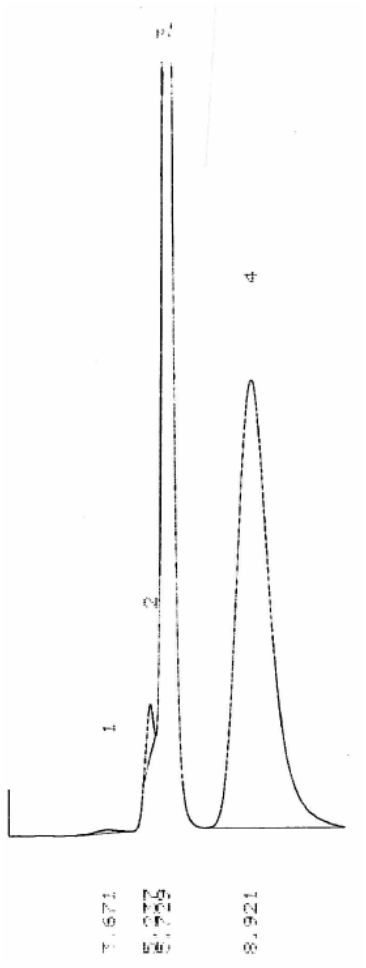
B_{11}: [$Ru(acac)_2(dpeH)$]. δ = -12.57 (1H, $COCH_2$), -10.78 (3H, CH_3), -9.95 (3H, CH_3), -8.48 (1H, $COCH_2$), -6.43 (3H, CH_3), -3.31 (3H, CH_3), 0.68 (3H, CH_3), 2.37 (3H), 3.58 (2H, CH_2), 16.01 (1H, OH). Some signals in 1.0-1.8 ppm were obscured due to overlap with the signal of residual water in the solvent; *m/z* = 524 (calc. for ^{102}Ru: 525).

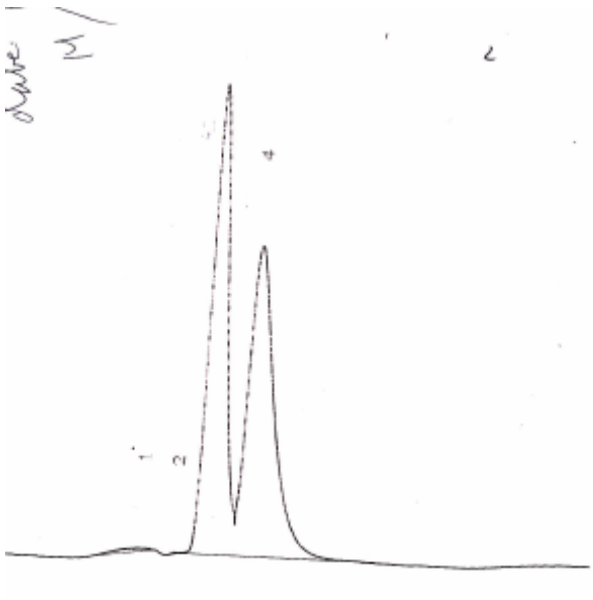
B_{12}: [$Ru(acac)_2(dpeH)$]. δ = -12.46 (3H, CH_3), -9.85 (3H, CH_3), -8.41 (1H, $COCH_2$), -8.05 (3H, CH_3), -5.44 (1H, $COCH_2$), -1.56 (3H, CH_3), 1.89 (3H), 3.90 (2H, CH_2), 16.08 (1H, OH). Some signals in 1.0-1.8 ppm were obscured due to overlap with the signal of residual water in the solvent; *m/z* = 524 (calc. for ^{102}Ru: 525).

B_{31}: ΔΛ-[$Ru(acac)_2(dpe)Ru(acac)_2$]. δ = -12.07 (3H, CH_3), -11.40 (3H, CH_3), -11.02 (2H, $COCH_2$), -10.95 (3H, CH_3), -10.23 (2H, $COCH_2$), -8.95 (3H, CH_3), -7.29 (3H, CH_3), -5.00 (3H, CH_3), -2.81 (3H, CH_3), -0.47 (3H, CH_3), 0.59 (3H, CH_3), 2.72 (3H, CH_3), 3.69 (3H, CH_3), 4.41 (3H, CH_3); *m/z* = 822 (calc. for ^{102}Ru: 824).

B_{32}: ΔΔ- (or ΛΛ) -[$Ru(acac)_2(dpe)Ru(acac)_2$]. δ = -11.51 (12H, CH_3), -11.16 (2H, $COCH_2$), -10.19 (2H, $COCH_2$), -7.31 (6H, CH_3), -0.99 (6H, CH_3), 2.40 (6H, CH_3), 4.01 (6H, CH_3); *m/z* = 822 (calc. for ^{102}Ru : 824).

B_{33}: ΔΔ- (or ΛΛ) -[$Ru(acac)_2(dpe)Ru(acac)_2$]. δ = -11.66 (4H, $COCH_2$), -10.46 (6H, CH_3), -9.70 (6H, CH_3), -5.53 (6H, CH_3), -2.78 (6H, CH_3), 0.50 (6H, CH_3), 3.07 (6H, CH_3); *m/z* = 822 (calc. for ^{102}Ru: 824).





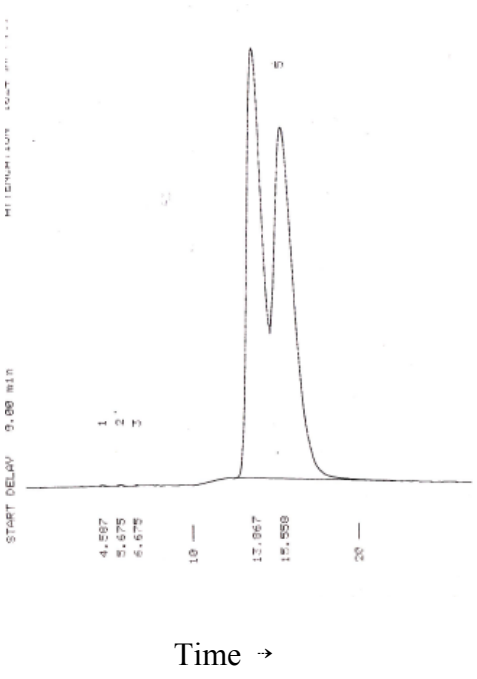


Figure S3. The HPLC chromatograms for ΔΛ-[Ru(acac)$_2$(dabe)Ru(acac)$_2$] (top), ΔΛ-[Ru(acac)$_2$(baet)Ru(acac)$_2$] (middle) and ΔΛ-[Ru(acac)$_2$(dpe)Ru(acac)$_2$] (bottom). Each racemate was eluted on a chiral column (4 mm (i.d.) × 25 cm) packed with an ion-exchange adduct of Δ-[Ru(phen)$_3$]$^{2+}$ (phen = 1,10-phenanthroline) and synthetic hectorite at a flow rate of 0.5 ml/min. The eluting solvent was a mixture of methanol and chloroform. The absorbance of the eluate was monitored at 600 nm.

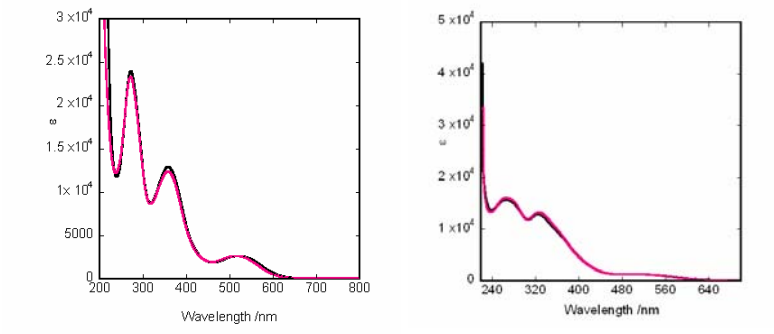


Figure S4. (left) The electronic spectra of methanol solutions of ΔΛ-[Ru(acac)$_2$(baet)Ru(acac)$_2$] (black line) and ΔΛ-[Ru(acac)$_2$(dpe)Ru(acac)$_2$] (red line).

(right) The electronic spectra of methanol solutions of the two diastereomers of [Ru(acac)$_2$(dabeH)], **B$_{11}$** (red line) and **B$_{12}$** (black line).

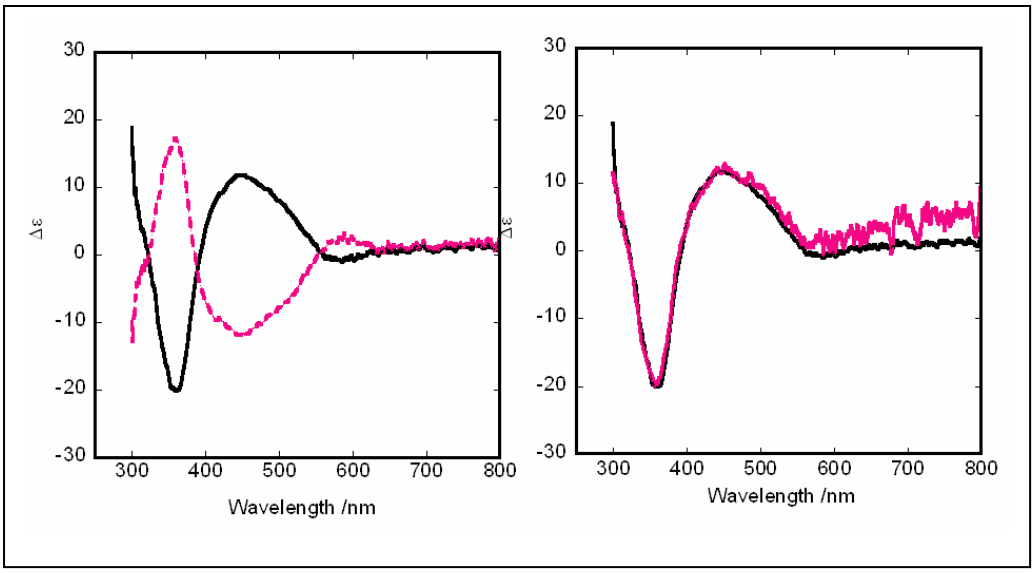


Figure S5. (left) The ECD spectra of methanol/chloroform solutions of the first (black) and the second (red) fractions when the diastereomer of [Ru(acac)$_2$(dabeH)] (**B$_{12}$**) was eluted on the chiral column;

(right) The ECD spectrum of a methanol solution of the first fraction when the diastereomer of [Ru(acac)$_2$(dabeH)], **B$_{11}$**, was eluted on the chiral column (red). For comparison, the ECD spectrum of the first fraction for **B$_{12}$** is also included (black).

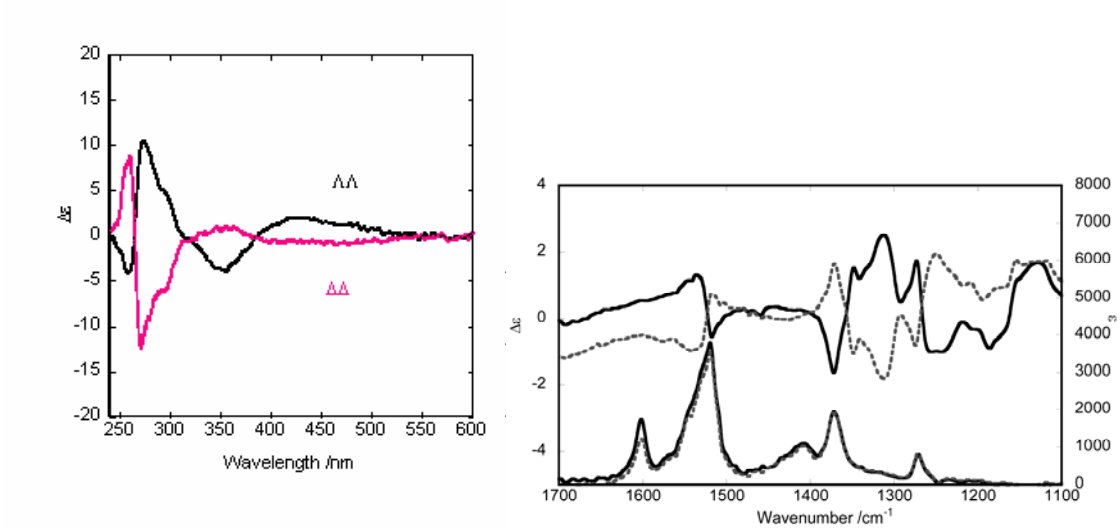


Figure S6. The ECD (left) and VCD (right) spectra of ΔΔ- (dotted line) or ΛΛ- (solid line) [Ru(acac)$_2$(baet)Ru(acac)$_2$].

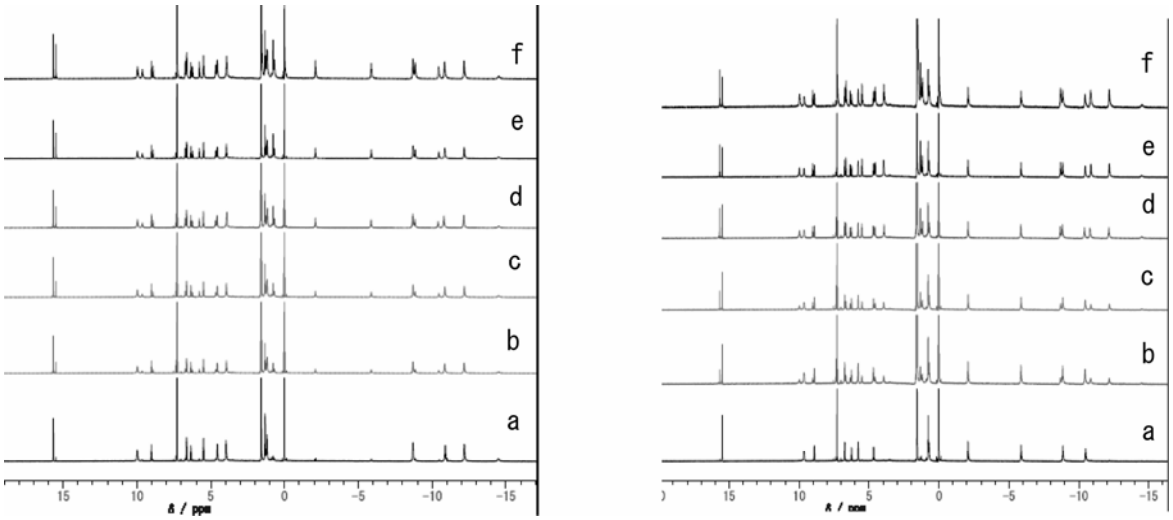
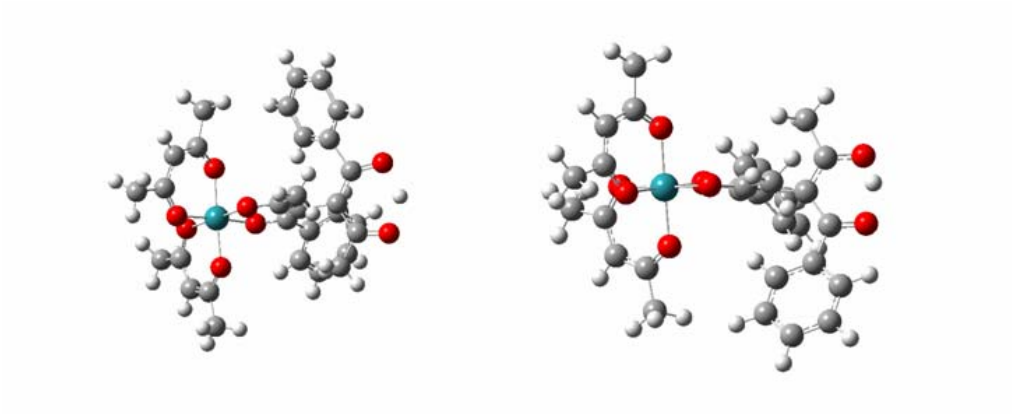


Figure S7. The change of the ^{1}H NMR spectra of the two diastereomers of [Ru(acac)$_2$(dabeH)] with time. The reactions started from B_{11} (left) and B_{12} (right), respectively; (a) 0, (b) 2, (c) 5, (d) 8, (e) 16 and (f) 25 hours. The solvents were $CDCl_3$.



Δ-[Ru(acac)$_2$(*S*-dabeH)] Δ-[Ru(acac)$_2$(*R*-dabeH)]

Figure S8. The optimized structures of Δ-[Ru(acac)$_2$(*S*-dabeH)] (left) and Δ-[Ru(acac)$_2$(*R*-dabeH)] (right) by the DFT calculation (see text). The total energy of each diastereomer is calculated as below:

diastereomer	Total Energy (a.u.)
Δ-[Ru(acac)$_2$(*S*-dabeH)]	-1858.67319667
Δ-[Ru(acac)$_2$(*R*-dabeH)]	-1858.67459518