Supporting information

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1. General

HPLC analysis were performed with a Shimadzu SCL-6A or SCL-10A chromatograph using chiral column (Chiralpak IB); the peak areas were obtained with a Shimadzu SPD-M10AVP diode array detector / Shimadzu Class-VP or Shimadzu SPD-6A UV detector / JASCO ChromNAV. Column chromatography was conducted on silica gel (Kanto 60 N). The dehydrated CH_2Cl_2 (No. 11338-85) was purchased from Kanto Chemical Co., Inc., and used without further purification. $Cu(OTf)_2$ was purchased from Kanto Chemical Co., Inc., and used after purification of drying by heating. (-)-2,2'-Isopropylidenebis[(4S)-4-phenyl-2-oxaoline] was purchased from Sigma-Aldrich Co. LLC.. The enolphosphonates (**1a**-**1f**) were prepared according to the literature procedure[#]. The corresponding α-ketophosphonates (**2a**-**2f**) were also known compounds[#].

2. General procedure and Supporting Results.

General conditions and procedure in Table 1 and Table 2

Both reactions were performed under nitrogen gas with the same size pyrex-glassware by the same glass workers. Both reactions were monitored by TLC analysis to confirm complete consumption of the starting material. The ee was determined by HPLC analysis.

2-1. Multi-mode microwave irradiation conditions

The EYELA Wave Magic MWO-1000S was used as a multi-mode apparatus attached by a thermocouple sensor for the temperature regulation. The specifications of EYELA Wave Magic MWO-1000S for this reaction were referred to our previous paper[#]. The internal temperature was monitored by a fiber optic thermometer (thermometer: AMOTH FL-2000 and probe: FS100-2M), which is the most standard tool for temperature monitoring in microwave chemistry. The stirring rate was set in sufficient rate (600 rpm).

2-1-1 Reaction procedure under the microwave conditions

After the glass vessel charged with a solution of Cu(OTf)$_2$ (5.4 mg, 0.015 mmol) and (3.(-)-2,2'-Isopropylidenebis[(4S)-4-phenyl-2-oxaoline] (6.0 mg, 0.018 mmol) in CH_2Cl_2 (2.7 mL) and was stirred at room temperature. After 2 hours, enolphosphonates **1** (0.30 mmol) in CH_2Cl_2 (3.0 mL) was slowly added at room temperature, and then reaction vessel was placed in MWO-1000S with cooling at –10 °C (external cooling system). The PID values were set using the controller installed in the microwave reactor for the reaction. Microwave irradiation was started with a temperature control mode. After the enolphosphonates **1** was completely consumed, the reaction mixture was purified by column chromatography (SiO_2, charged with $CHCl_3$, eluent: Hexane : EtOAc = 4/1) to afford the corresponding chiral biaryl α-ketophosphontes **2**.

2-2. Heat block conditions

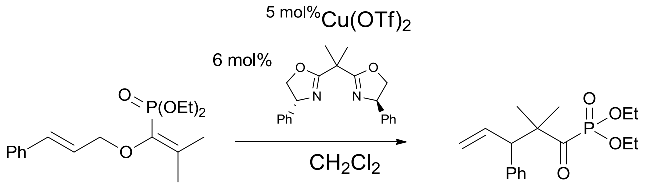
The external heating and stirring apparatus EYELA ChemiStation (PPS-5510 and/or PPS-5511) was used as an external heating block with temperature control. The internal temperature was monitored by a thermocouple sensor (thermometer: AM 8000K and probe: K type). The stirring rate was set in sufficient rate (600 rpm).

2-2-1. Reaction procedure under heat block conditions

After the glass vessel charged with a solution of $Cu(OTf)_2$ (5.4 mg, 0.015 mmol) and (3.(-)-2,2'-Isopropylidenebis[(4S)-4-phenyl-2-oxaoline] (6.0 mg, 0.018 mmol) in CH_2Cl_2 (2.7 mL) and was stirred at room temperature. After 2 hours, enolphosphonate **1** (0.30 mmol) in CH_2Cl_2 (3.0 mL) was slowly added at room temperature, and then reaction vessel was placed After the same reaction time as that of microwave conditions or the lactone **1** was completely consumed, After the enolphosphonates **1** was completely consumed, the reaction mixture was purified by column chromatography (SiO_2, charged with $CHCl_3$, eluent: Hexane : EtOAc = 4/1) to afford the corresponding chiral biaryl α-ketophosphontes **2**.

3. Arrhenius plot

We investigated the temperature dependence on the enantioselectivity in the reaction of the enolphosphonate **1a** under heat block conditions



1a **2a**

Entry[a]	Temp./°C[b,c]	Time/h	Yield/% [d]	Ee/% [e]
1	10.2±0.4	72	76	94.9
2	15.0±0.1	40	86	91.8
3	20.1±0.3	16	84	90.5
4	25.2±0.4	8	91	87.4
5	30.2±0.4	4	83	84.3
6	35.2±0.3	2	86	81.2
7	38.6±0.2	1	92	78.6

[a] Reactions were carried out on a 0.30 mmol scale under microwave conditions and heat block conditions. [b] The accurate internal reaction temperature was monitored by a thermocouple sensor. [c] Temperature refers to the average temperature±2σ (σ: Standard deviation). [d] Yield is that of the isolated product. [e] Ee was determined by HPLC analysis.

Based on the result we made Arrhenius plot of ln[(100+%ee)/(100–%ee)] versus reaction temperature, both the observed results and theoretical values of the enantioselectivities were plotted.

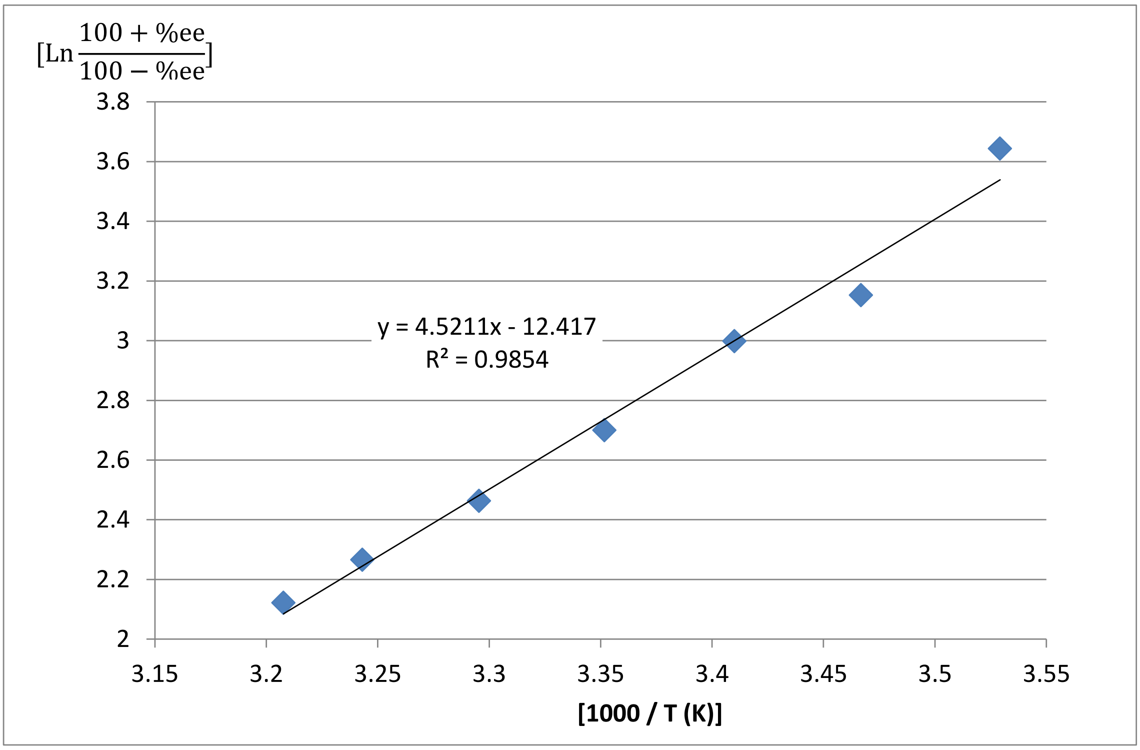


Figure S1. Arrhenius plot over the temperature range from 10 to 40 °C (Preset temperature of Heatblock). Enthalpy and entropy values extracted from this plot are $\Delta\Delta H^{\ddagger} = -37.59$ kJmol^{-1} and $\Delta\Delta S^{\ddagger} = -0.10$ kJmol^{-1}K^{-1}, respectively.

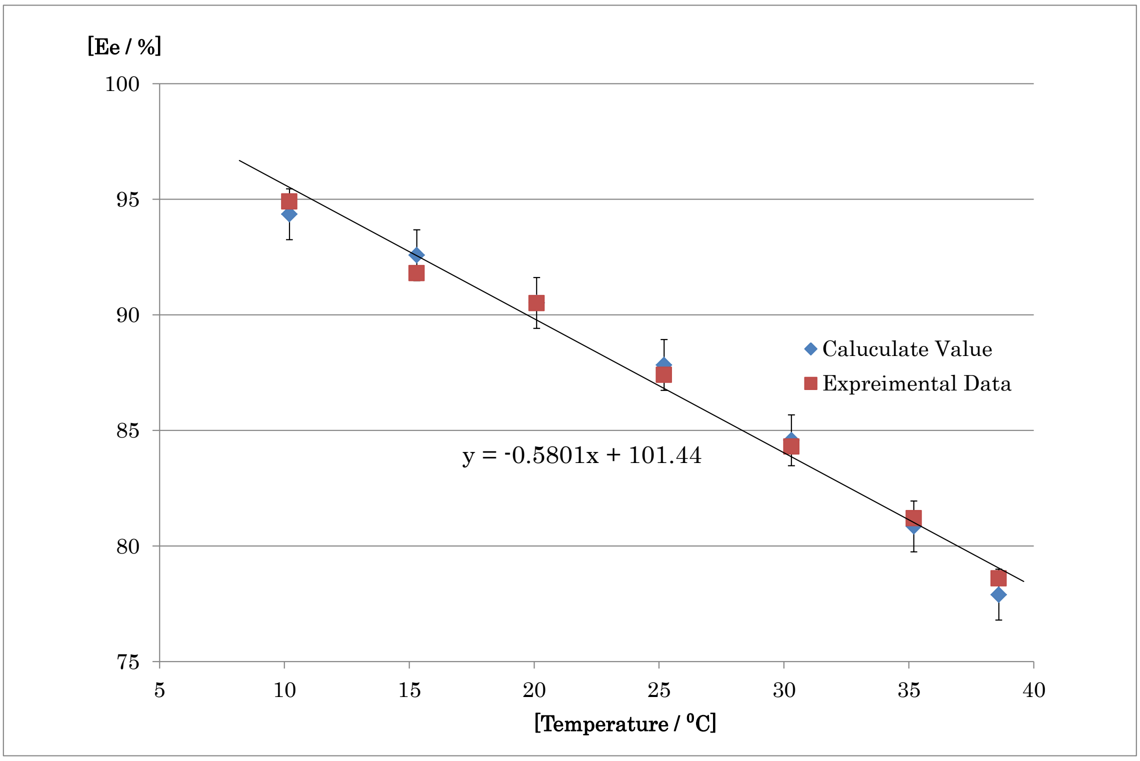
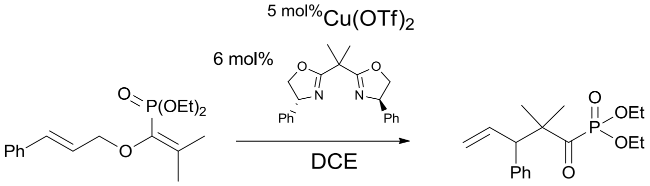


Figure S2. Plots of calculated values and experimental data of temperature dependence on the enantioselectivity and error value (2σ) for the calculated values (2σ = 1.1).

It was confirmed that less enantioselectivity was observed at higher reaction temperatures and the experimental results fell within ca. 2σ error area of the predicted values. If the present reaction enhancement would be caused by high temperature of reaction media, the resulting enantioselectivity should be remarkably damaged. Whereas, the enantioselectivity was maintained with microwave acceleration (91.7% ee versus 91.3% ee, Entries 1 and 3 in Table 1). The reaction was accelerated about 1.52 times 84% yield versus 55% yield)) and if the reaction acceleration was caused by only thermal effect, temperature should rise 6.1 °C. Because the reaction rate become about twice as fast as that of original data as the temperature rises every 10 °C. But if the temperature increased 6.1 °C from 21.1 °C, ee was calculated as 89.2% ee based on the approximate equation in Figure S2. The obtained result (91.7% ee) was better than the error area (88.1-90.3% ee). Therefore, it was concluded that the enantioselectivity obtained with the remarkable reaction enhancement by microwave irradiation was not caused by a simple thermal effect.

And We investigated temperature dependence of enantioselectivity the ranges of 15 to 80 degrees 1,2-dichloroethane as solvent conditions. As a result, we confirmed that the enantioselectivity decrease at higher temperatures such as 80 degrees.



1a **2a**

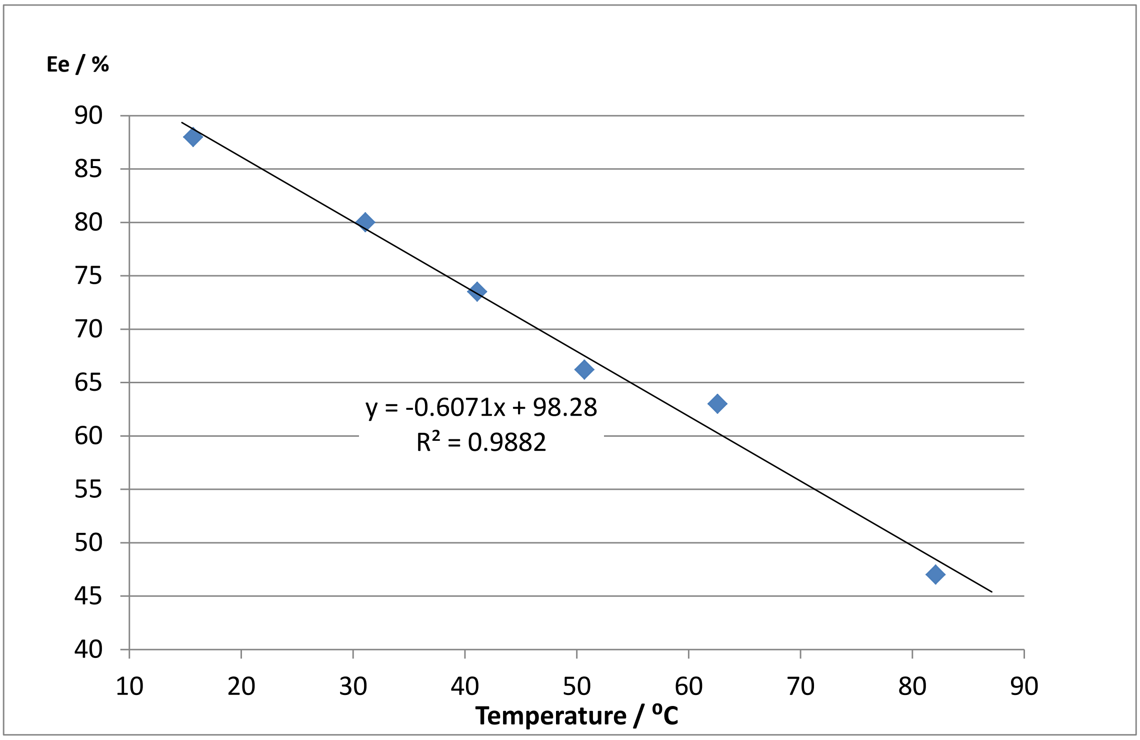


Figure S3. Arrhenius plot of catalytic enantioselective Claisen rearrangement at high temerature.