

## ***Supplementary Information***

# **Combination of near-infrared spectroscopy and transient flow method for efficient kinetic analysis of Claisen rearrangement**

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**S1. NIR spectrum of solvent NMP**

**S2. Steady-state experiment at 280°C**

**S3. HPLC chromatogram of the effluent**

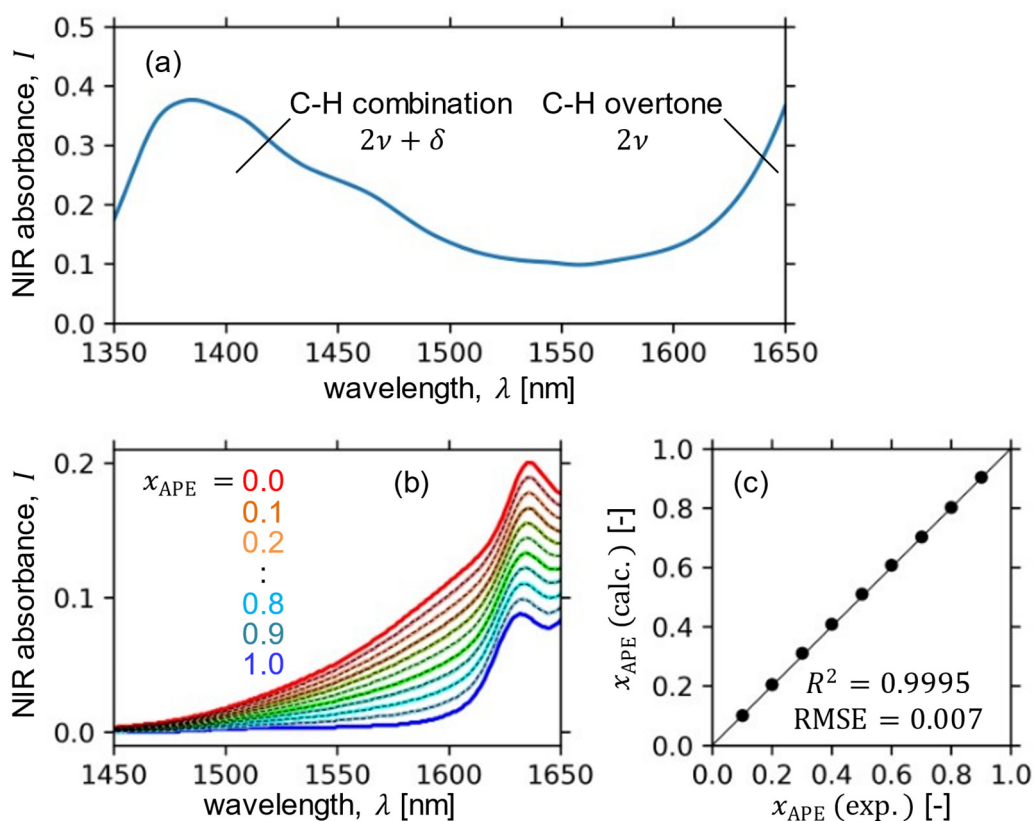
**S4. Residence time measurement by pulse injection method**

**S5. Eyring plot**

## S1. NIR spectrum of solvent NMP

NIR spectrum of solvent *N*-methylpyrrolidone (NMP) shown in Fig. S1a was used as a reference. The NMP spectrum consists of the first overtone band  $2\nu$  of the C-H stretching vibration and the combination band  $2\nu + \delta$  of the first overtone with the bending vibration. NMP was slightly colored brown after heating above 250°C probably due to the thermal degradation of impurity, but the coloring had no influence on the NIR spectrum.

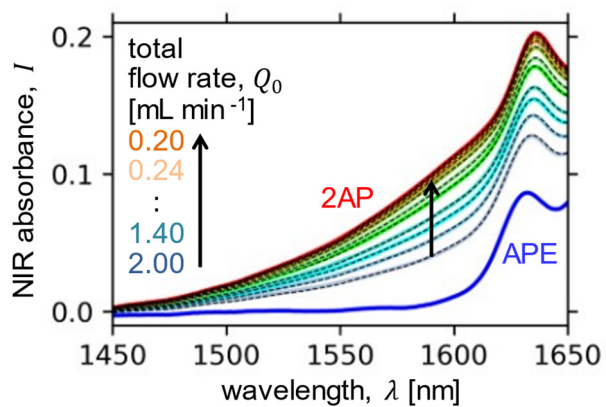
The NIR absorption of NMP was weak enough (absorbance  $< 0.4$ ) to measure the spectrum of solutes dissolved therein. Fig. S1b shows the spectrum of the mixture of allyl phenyl ether (APE) and 2-allylphenol (2AP) in NMP as a function of the APE mole fraction  $x_{\text{APE}}$ . Fig. S1c shows the correlation between the  $x_{\text{APE}}$  calculated from the spectrum by Eq. (1) and the experimental  $x_{\text{APE}}$ .



**Figure S1.** (a) NIR spectrum of NMP. (b) Spectrum of APE + 2AP mixture in NMP as a function of the APE mole fraction  $x_{\text{APE}}$ . (c) Correlation between the experimental and calculated  $x_{\text{APE}}$ .

## S2. Steady-state experiment at 280°C

Fig. S2 shows the NIR spectra measured by a series of steady-state experiments for various total flow rates at 280°C.

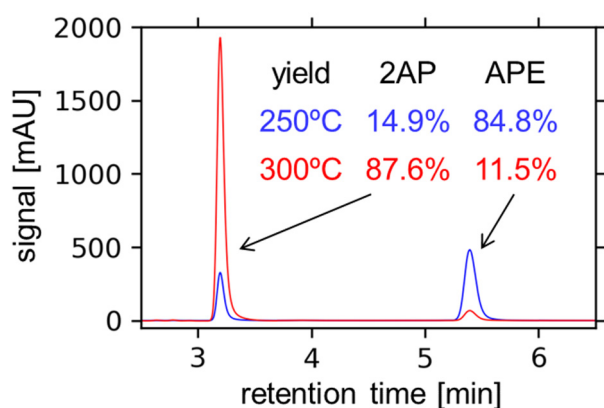


**Figure S2.** NIR spectrum of APE reacted at 280°C as a function of the total flow rate  $Q_0$  in comparison with those of unreacted APE and 2AP.

### S3. HPLC chromatogram of the effluent

Fig. S3 shows HPLC chromatograms of the effluents reacted at temperatures of 250 and 300°C and a total flow rate of 1.0 mL min<sup>-1</sup>. No peaks other than 2AP (3.2 min) and APE (5.3 min) were observed, and the total yield of 2AP and APE almost satisfied the mass balance, indicating that APE was selectively reacted into 2AP with negligible byproducts.

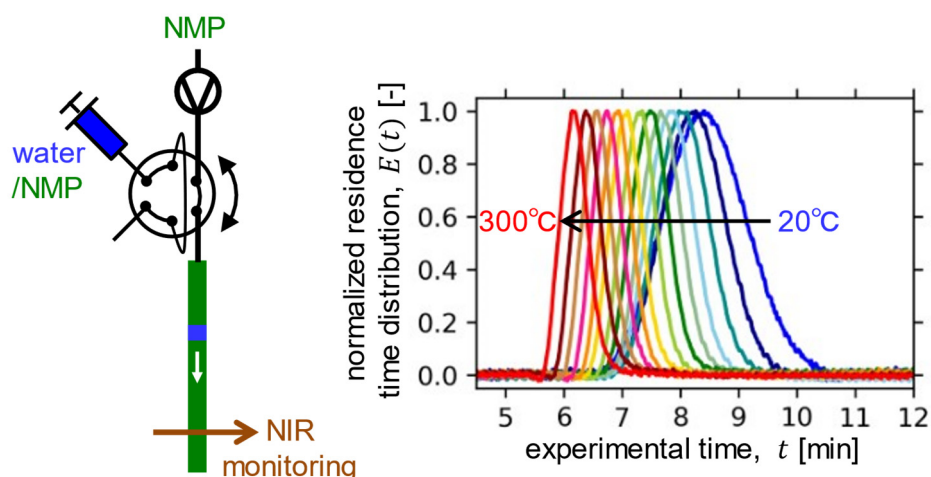
Measurement condition: HPLC system was Agilent LC1100. Mobile phase was a mixture of 60 vol% acetonitrile and 40 vol% water containing 0.1 vol% phosphoric acid. The mobile phase was supplied at a constant flow rate of 1.0 mL min<sup>-1</sup>. Chromatographic separation was carried out with a ZORBAX Eclipse XDB-C18 column (4.6 mm inner diameter, 15 cm length, and 5 µm particle size) thermostated at 40°C. Injection volume of the sample was 0.4 µL. Detection was made with a diode-array detector (Agilent G1315A) at the wavelength of 281 nm.



**Figure S3.** HPLC chromatograms of the effluents reacted at temperatures of 250°C (blue line) and 300°C (red line) and a total flow rate of 1.0 mL min<sup>-1</sup>.

#### S4. Residence time measurement by pulse injection method

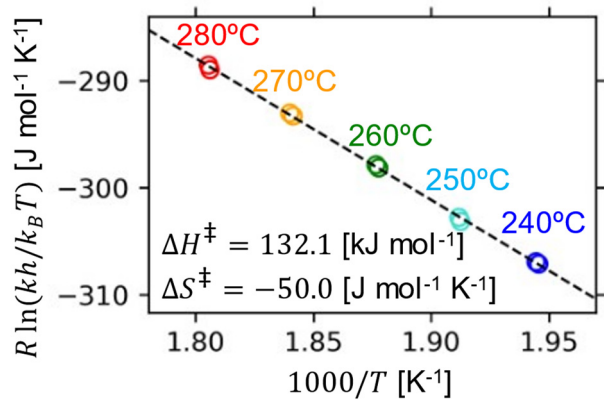
Fig. S4 shows a residence time distribution (RTD) measured by a pulse injection method as a function of the temperature from 20 to 300°C at a constant flow rate of 0.25 mL min<sup>-1</sup>, where the residence time in the injecting, cooling, and monitoring regions was excluded from the experimental time  $t$ . Water was chosen as a tracer because of its strong NIR absorption and thermal stability. Water + NMP mixture was injected using an automatic switching valve (FLOM VA-21-602, 0.25 mm path diameter, PEEK) equipped with a 5  $\mu$ L PEEK sample loop (Rheodyne 9055-020). Water : NMP volume ratio was 1 : 2 at 20 to 75 °C, 1 : 3 at 100 to 175 °C, and 1 : 5 at 200 to 300°C. NIR absorption of water was monitored at 1435 nm, which is assigned to the combination mode of the symmetric and anti-symmetric O-H stretching vibrations  $\nu_1 + \nu_3$  of water. The RTD obtained by the water injection method at 20°C was significantly narrower than that by the step change method shown in Fig. 3b using 2AP as a tracer. This is probably because the diffusion coefficient  $D_{AB}$  of water is larger than that of 2AP due to the smaller molecular size, leading to the smaller axial dispersion coefficient  $D_{ax}$  according to Eq. (7).



**Figure S4.** Residence time distribution measured by the pulse injection method.

### S5. Eyring plot

The activation enthalpy  $\Delta H^\ddagger$  and entropy  $\Delta S^\ddagger$  were determined to be  $132 \pm 1 \text{ kJ mol}^{-1}$  and  $-50 \pm 2 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively, from the slope and intercept of the Eyring plot shown in Fig. S5.



**Figure S5.** The Eyring plot of the first-order rate constant  $k$  of the Claisen rearrangement of APE to 2AP in NMP.  $R$  is the gas constant,  $h$  is the Planck constant,  $k_B$  is the Boltzmann constant, and  $T$  is the reaction temperature.