Supplementary Material (ESI) for Green Chemistry

Highly-Selective and High-Speed Claisen Rearrangement induced with Subcritical Water Microreaction in the Absence of Catalyst

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1.Additional information of temperature and pressure effects

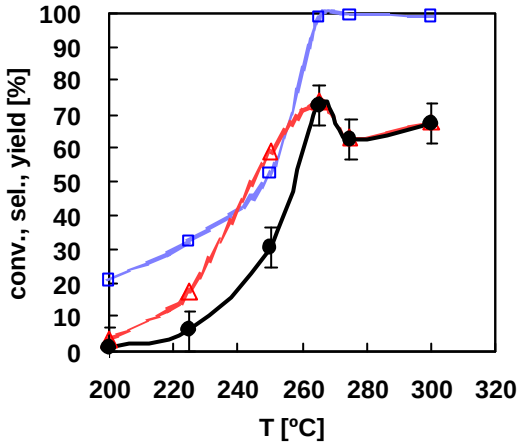

Fig. S1 Conversion (square), selectivity (triangle) and yield (filled circle) as functions of temperature on Claisen rearrangement of allyl phenyl ether (**1**) with subH_2O at 5MPa and 81s.

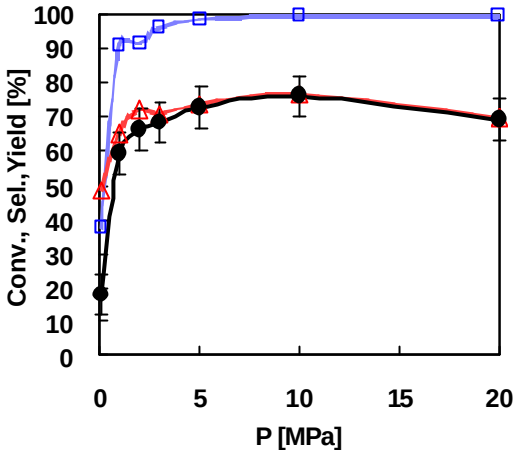

Fig. S2 Pressure vs. conversion (square), selectivity (triangle) and yield (filled circle) on Claisen rearrangement of allyl phenyl ether (**1**) with subH_2O at 265°C and 81s.

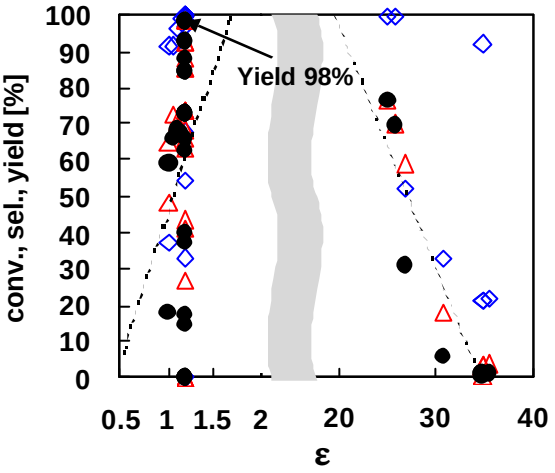

Fig. S3 Dielectric constant vs. conversion (square), selectivity (triangle) and yield (filled circle)on Claisen rearrangement of allyl phenyl ether(**1**) with subH_2O in various temperature and pressure.

2.Additional information of yield, energy consumption per production rate and E-factor

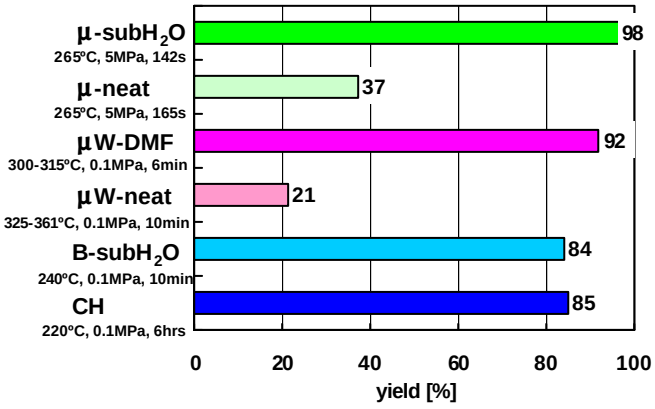

Fig. S4

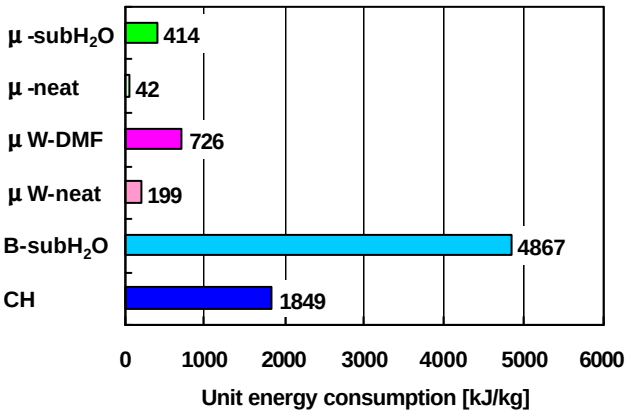

Fig. S5

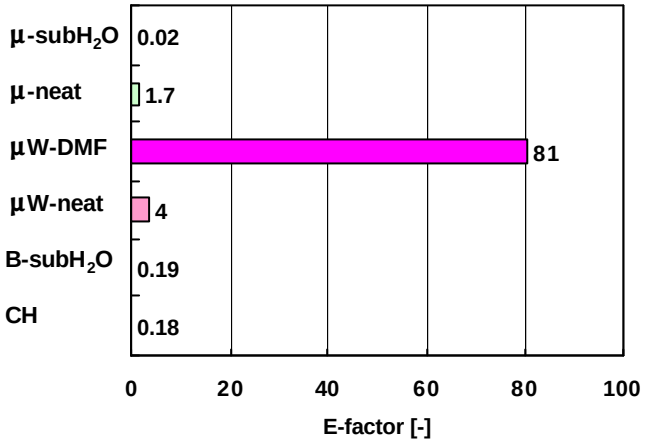

Fig. S6

2.. Experimental procedure

2-1. Claisen rearrangement of allyl phenyl ether to o-allyl phenol with subH$_2$O microreaction system

The subH$_2$O acylation was carried out by a flow-type of microreaction system equipped with a high-pressure and high-temperature infrared spectroscopy (JASCO FTIR/620) as shown in Fig. S7. The mixture of allylphenyl ether 90.0g (0.671mol) and toluene 3.09g (0.0335mol, 0.05 equiv.) was charged into a pump (JASCO PU-2086).

As shown in Fig. S9, a 49 μL tube-microreactor 316 (i.d. 0.50mm, length 247mm) made of SUS316 was installed into a furnace (Fig. S8) in place of the high-pressure and high-temperature IR flow cell except for the purpose of IR analysis. The subH$_2$O microreaction system can heat up momentarily at high temperatures above 300°C with ambient substrate solution and then can quench to sufficiently low temperatures within 10 s after the reaction, by passing through a cooling flange and cooling coil (i.d. 0.50mm, length 460cm). A stream of the alcohol-anhydride mixture at a linear velocity of 4.2 cm s^{-1} at ambient temperature and a pressure of 5 MPa was struck against subH$_2$O at a linear velocity of 42 cm s^{-1} at 265°C and 5MPa in a tee, followed by the introduction to the microreactor (placed in a furnace; maximum electric power 0.5kW), in which the temperature was realized to raise up to subcritical temperatures around 270°C within 0.06 s. In order to effect the rapid heating and to prevent temperature changes upon the addition of substrate, the interior space of this furnace was vacuumed at the pressure of 400-600 Pa, leading to the radiation heating without convection. The reaction time (=residence time) was adjusted to be shorter than 10 min to depress the consecutive hydrolysis of substrate and product. Pressure was controlled by a back-pressure regulator (JASCO back-pressure regulator 880-81). The fluctuations in temperature and pressure were controlled within ±0.2 °C and 0.1 MPa, respectively, within experimental error.

The reaction products were first obtained as a suspension in water, but were separated completely from the aqueous solution within the collection of 40 min. Detailed analysis of the reaction mixture was performed by GC-MS/MS (Varian CP-3800-1200L) for qualitative analysis and GC-FID (Agilent Technologies Inc., GC 6890N) for quantitative analysis using calibration curve of an authentic sample based on the internal standard of toluene.

In the Claisen rearrangement of allylphenyl ether (**1**), o-allylphenol (**2**) was obtained as a colored liquid of 3.57g (isolated yield 93%) at the bottom of aqueous solution as shown in Fig. S11, which was confirmed to be nearly pure. Reaction time (residence time) is calculated by the following equation (1-1) as below,

$$t = 60p\left(\frac{r}{20}\right)^2 \times \left(\frac{L_0 r_A}{F_A} + \frac{L_1 r_{265} + L_2 r_{100}}{F_A + F_B}\right) \quad (1\text{-}1)$$

where t : reaction time[sec], F_A: flow rate of pump A(=6.96g/min), F_B: flow rate of pump B(=0.245g/min), r: inner diameter of SUS316 tube (=0.50mm), L_0: the length of substrate preheating tube(=300cm), L_1: the length of microreactor tube(=24.7cm), L_2: the tubular length of cooling coil (=460cm), ρ_A :density of allylphenyl ether(=0.978g/cm^3), ρ_{265}:density of water at 265°C,5MPa (=0.025g/cm^3), ρ_{100} :density of water at 100°C,5MPa (=0.961g/cm^3) . Density and volume were determined with the software of the NIST/ASME Steam properties. [8b] Reaction time t=149 s was obtained in this example.

After 30min, 1ml of GC sample solution was collected and diluted with 1ml of acetone to prevent from producing biphasic solution. Thus initial molality of 0.27 mol/kg was decreased to 0.15mol/kg. Molality of reactant (allyl phenyl ether) and product (o-allyl phenol) in the sample solution were estimated from the ratio of GC peak area based on toluene with calibration. Then conversion, selectivity and yield were determined by the equation as bellow,

$$conv.[\%] = 100 - reactant\ [\%] \quad (1\text{-}2)$$

$$sel.[\%] = \frac{product(s)[\%]}{conv.} \times 100 \quad (1\text{-}3)$$

$$yield[\%] = \frac{conv. \times sel.}{100} \quad (1\text{-}4)$$

The results of conv.=100%, sel.=98% and yield=98.0% was derived from the GC analysis.

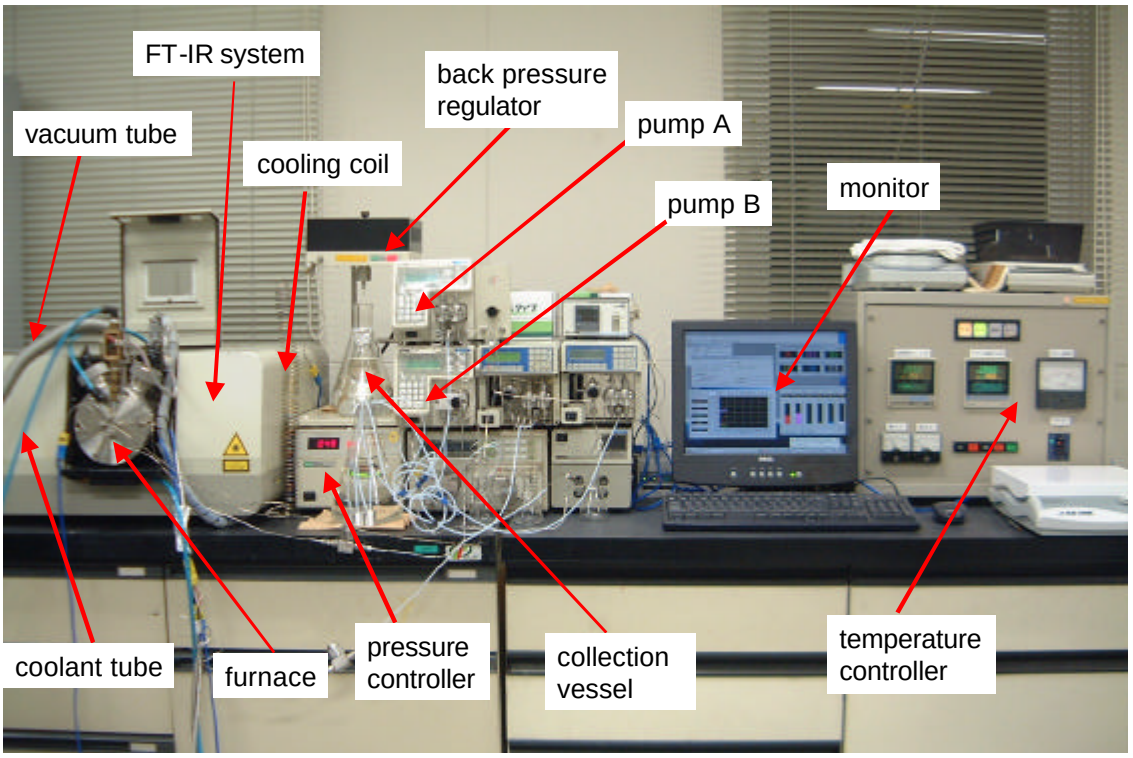

Fig. S7 Total-view of subH_2O microreaction system

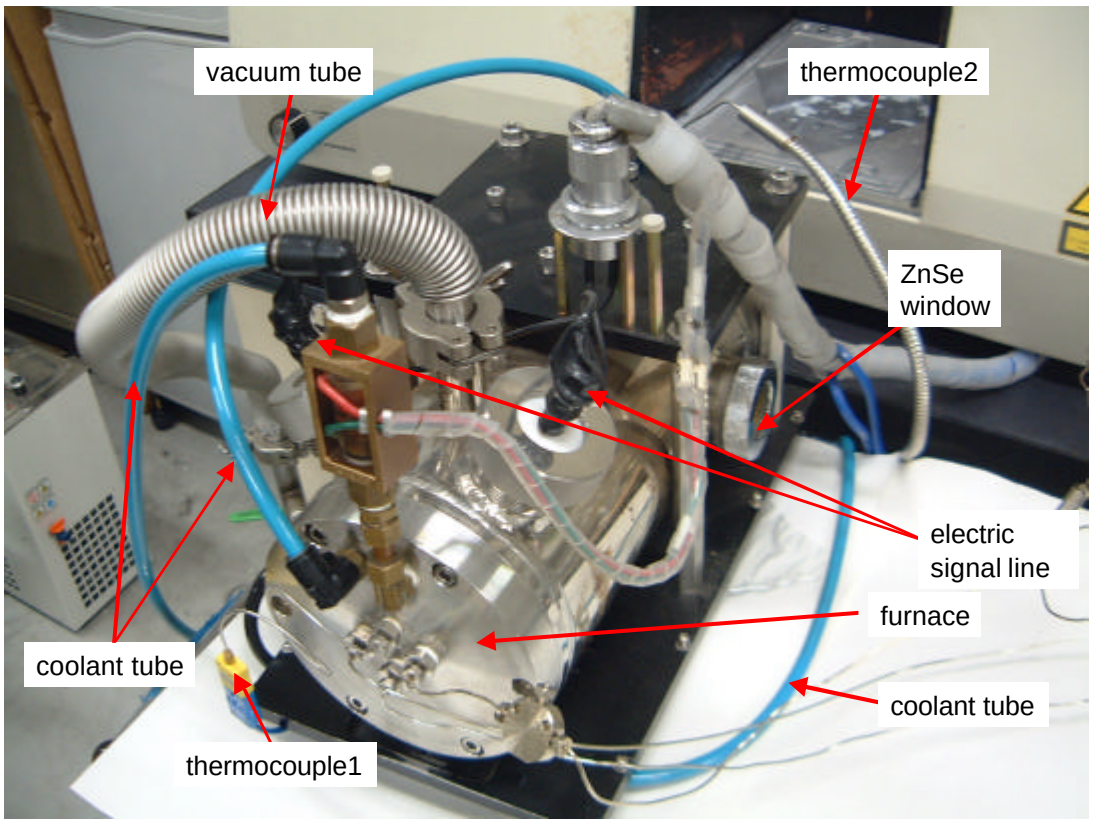

Fig. S8 Total-view of furnace in subH_2O microreaction system

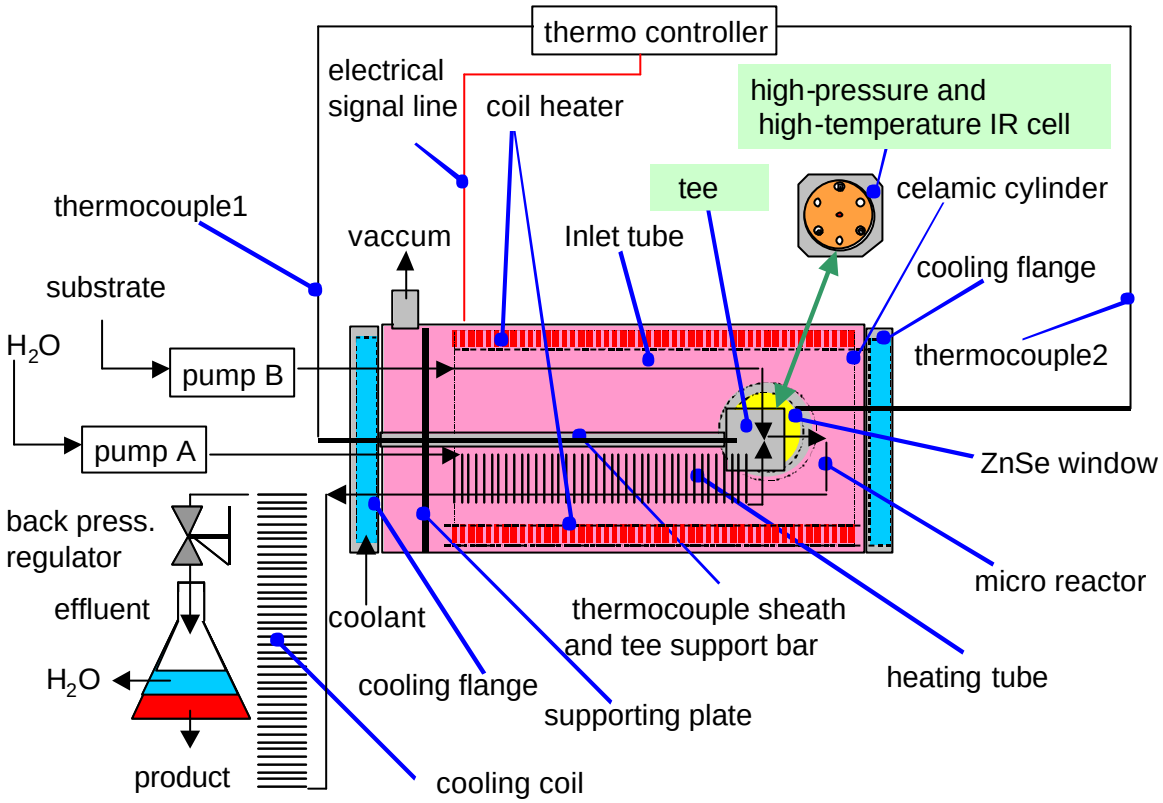

Fig.S9 Schematic diagram around furnace in subH_2O microreaction system

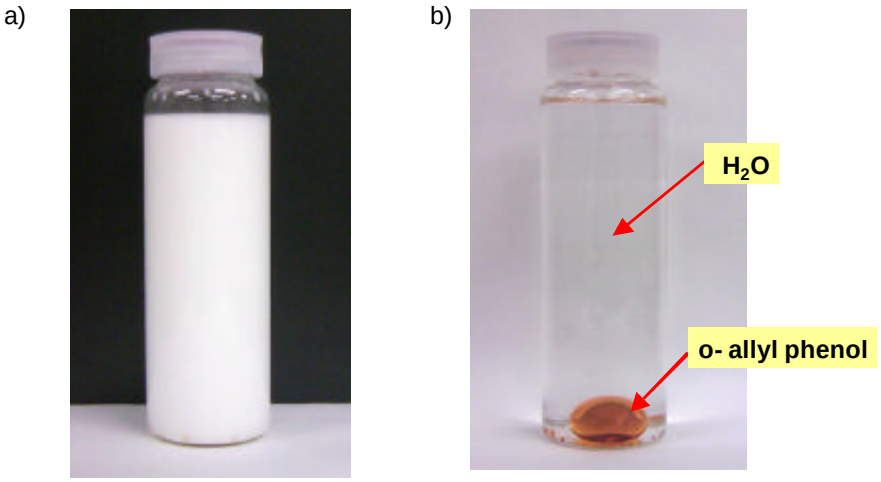

Fig. S10 Collected solution by Claisen rearrangement of allyl phenyl ether (1) to o-allyl phenol (1a) at 265℃, 5MPa and 149s in subH_2O micro-reaction system. a) suspended solution after reaction, b) biphasic solution after 1day.

3. Calculation of dielectric constant of water

High-pressure and high-temperature water has an important feature to be able to continuously change physico-chemical properties such as dielectric constant along with temperature and pressure. Especially dielectric constant of pure water is correlated as a function of temperature and density (NIST/ASME Steam properties), which can estimate with the International Association for the Properties of Water and Steam(IAPWS) standard formula and available from NIST (U.S. Department of Commerce, National Institute of Standards and Technology). [8b] * Thus at a given temperature and pressure it is easily possible to calculate some physicochemical properties such as dielectric constant. Dielectric constants calculated from temperature sets of Fig. 3 at a constant pressure (5MPa) were correlated with the yield in Fig. S3. The dielectric constant is 1.1 at 265oC, 5MPa.

For the sake of convenience, temperature and pressure dependence of dielectric constant was shown in Fig. S11 at θ265ºC and 0.1-40MPa.

*In reference [8b], reference therein with regard to calculation of dielectric constant at high-pressure and high-temperature water as shown below.

D. P. Fernandez, A. R. H. Good win, E.W. Lemmon, J. M. H. L. Sengers and R. C. Williams, "A Formulation for the static Permittivity of Water and Steam at Temperature from 238 to 873K at Pressures up to 1200MPa, Including Derivatives And Debye-Hückel Coefficients", *J.Phys.Chem Ref. Data*, 1997, **26**, 1125.

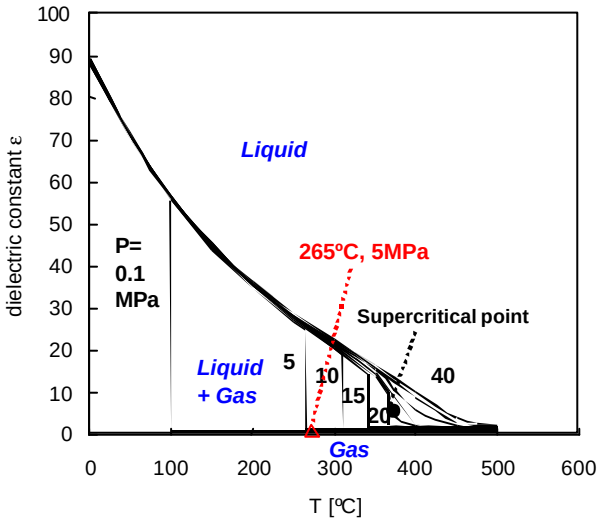

Fig. S11 dielectric constant of water