

Supplementary Information

Plasmon Enabled Claisen Rearrangement with Sunlight

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Materials and reagents:

Tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), tetramethylammonium hydroxide (TMAOH) 25% wt. in water, 11-mercaptoundecanoic acid (MUA), hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ 50-60%), and tetrabutylammonium borohydride (TBAB) were purchased from Sigma-Aldrich. (Di-n-dodecyl) dimethylammonium bromide (DDAB) and dodecylamine (DDA) were purchased from Alfa Aesar. Allyl phenyl ether was purchased from Tokyo Chemical Industry (TCI). All the reagents were used as received without any further purification. All the stock solutions of metal ions were prepared in Milli-Q water.

UV-visible absorption spectroscopy:

UV-vis absorbance data for AuNPs was recorded on a Shimadzu 3600 UV-VIS-NIR spectrophotometer, over the wavelength range of 200-1000 nm.

Transmission electron microscopy studies:

The AuNPs were characterized using high resolution transmission electron microscopy (HR-TEM) studies on a JEOL JEM2200FS (200 kV) HRTEM instrument. AuNPs were drop-cast on a 400-mesh carbon-coated copper grid (Tedpella Inc.) and dried overnight under vacuum to prepare the TEM sample.

Synthesis of AuNPs:

Spherical gold nanoparticles (AuNPs) were synthesized following a modified literature procedure.^{1,2} Hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) was used as the reducing agent. In a typical experiment, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (12 mg), DDA (140 mg), and DDAB (140 mg) were mixed in toluene (4 mL) and sonicated for ~10 min for complete solubilization of Au (III) ions. This was followed by a rapid injection of another toluene solution containing 30 mg of TBAB and 46 mg of DDAB. The resulting solution was left stirring overnight to ensure the complete reduction of Au (III) ions. The seed particles were then grown to ~5.5 nm DDA-AuNPs. For this, a growth solution was prepared by adding 460 mg of DDAB, 1.4 g of DDA, 120 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and seed solution

in 30 mL toluene. The growth solution was further reduced with a dropwise addition of another toluene solution containing 160 μL of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and 560 mg of DDAB. The solution was stirred overnight for complete growth of the particles yielding monodisperse 5.5 ± 0.7 nm of DDA-AuNPs. The particles were further grown to ~ 12 nm DDA-AuNPs. A growth solution was prepared by adding 8 g of DDAB, 13.0 g of DDA, 1.1 g of $\text{HAuCl}_4\cdot 3\text{H}_2\text{O}$ and seed solution in 200 mL toluene. The growth solution was further reduced with a dropwise addition of another toluene solution containing 650 μL of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and 4.4 g of DDAB. The solution was stirred overnight for complete growth of the particles yielding monodisperse 12.09 ± 0.48 nm of DDA-AuNPs, as confirmed through TEM analysis.

Place exchange of AuNPs with 11-mercaptoundecanoic acid (MUA) ligands:

In a typical place exchange reaction, 12.09 ± 0.48 nm DDA-AuNPs (15 mL) were first precipitated by adding 50 mL of methanol which yielded a black precipitate. The supernatant was carefully removed, and the precipitate was then re-dispersed in 20 mL toluene. MUA ligand (equal to the moles of Au (III) in solution) dissolved in 10 mL dichloromethane (DCM) was added. The solution was left overnight to ensure a complete ligand exchange. Next, the supernatant was decanted, and the precipitate was washed with DCM (3×50 mL) and acetone (50 mL), respectively. The precipitate was then dried and redispersed in Milli Q water by adding ~ 20 μL of TMAOH base (25 % wt. in water), to deprotonate the carboxylic acid group for further studies.

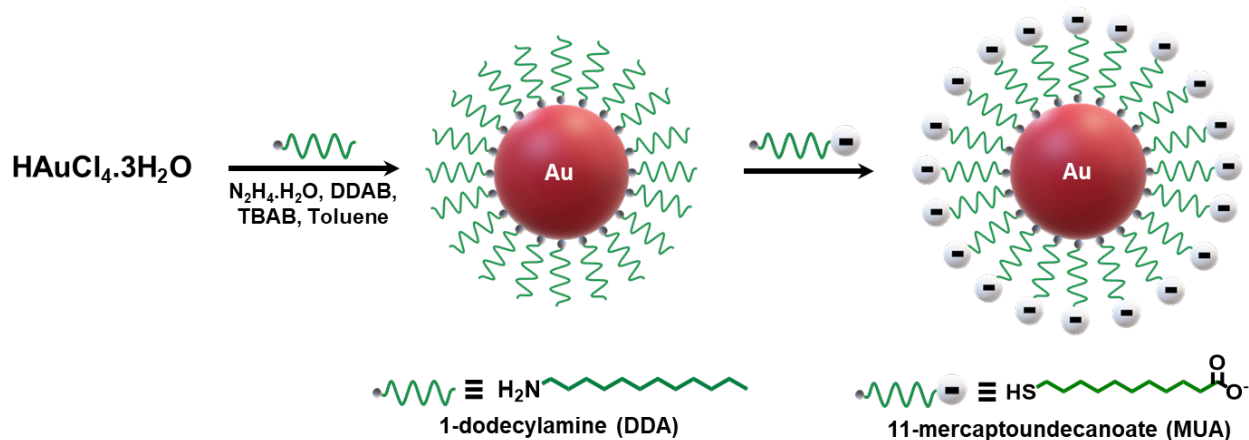


Fig. S1 General scheme for AuNPs synthesis and ligand exchange to obtain MUA-functionalized AuNPs in aqueous medium.

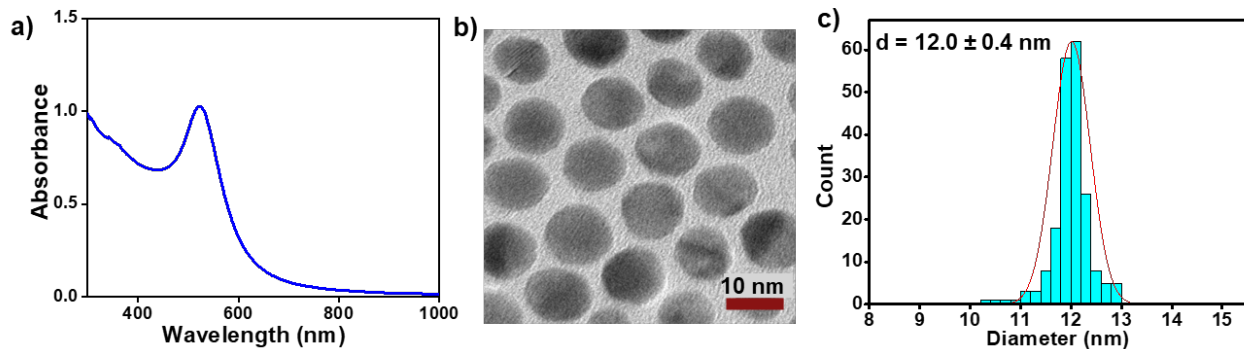


Fig. S2 Spectroscopic and microscopic characterization of AuNPs. (a) UV-vis absorption spectrum of MUA-functionalized AuNPs, with the SPR band centered at 522 nm. (b) A representative TEM image and (c) histogram showing the size distribution of MUA-functionalized AuNPs.

Calculation of NP concentration

The concentration of AuNPs in stock solution was calculated using Beer-Lambert's law:

$$A = \epsilon \cdot c \cdot l$$

where,

A is the absorbance

ϵ is the molar extinction coefficient ($M^{-1}cm^{-1}$)

c is the concentration of the solution (M)

l is the optical path length (cm).

Molar extinction coefficient (ϵ) for AuNP was taken to be $2.7 \times 10^8 M^{-1} cm^{-1}$ for ~ 12 nm diameter particles.³

The concentration of AuNP stock solution was estimated to be $\sim 0.38 \mu M$ (in terms of AuNPs).

Solar-driven Claisen rearrangement

Photothermal experiments were performed in a thermodynamically closed reactor system (**Fig. S3**). Briefly, a 15 mL glass test tube was wrapped with an Al-foil. A film of AuNP (25 μ L from 0.38 μ M stock solution; 9.5 pmol) was coated onto the Al-foil and dried at room temp. Next, 1 mL of allyl phenyl ether was taken in this reactor followed by irradiating the AuNP film with focused sunlight (**Fig. S3**). A Fresnel lens (28.5 cm \times 19.5 cm) was used to focus the sunlight at the AuNP film. The solar beam diameter was measured to be \sim 1 cm after focusing and the optical power illuminated at AuNP film was noted to be \sim 9 W.cm⁻². A thermopile optical power detector (Model LM-10 HTD; Coherent, Santa Clara, CA 95054 USA) was used for measuring the power of sunlight falling on the AuNP film, after focussing. The colorless reactant turned to reddish yellow within 2 h of solar irradiation, indicating the thermal conversion of allyl phenyl ether to 2-allylphenol. The reaction mixture was purified by column chromatography (silica column, 5 % ethyl acetate in hexane), and the product was characterized using proton-NMR and HRMS techniques (**Fig. S4** and **S5**). Control experiments were performed under focused sunlight without the AuNP film, under similar experimental conditions. Briefly, 1 mL of allyl phenyl ether in an Al-foil wrapped test tube *without AuNP film* (**Fig. S3c**) was irradiated with focused sunlight for 2 h. The thermal experiment was performed in the laboratory at 250 $^{\circ}$ C with normal electrical heater.

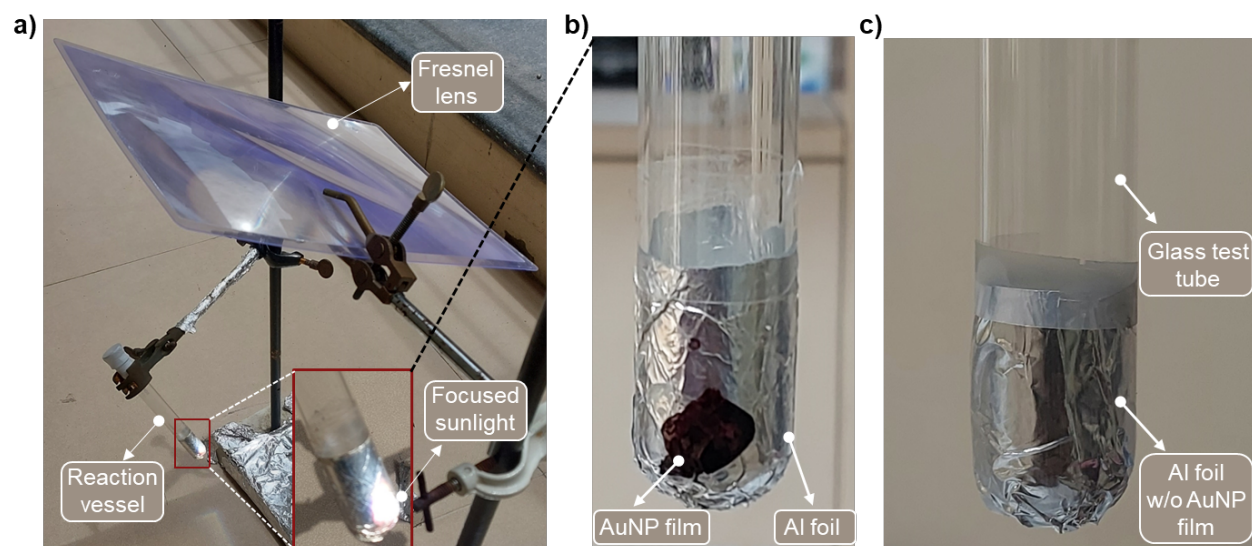


Fig. S3 (a) and (b) Experimental setup for the plasmonic-heat driven Claisen rearrangement. A film of AuNPs was coated on the Al-foil wrapped test tube. The sunlight was focused on the AuNPs film using a Fresnel lens (28.5 cm \times 19.5 cm). (c) The reactor setup for the control experiment where allyl phenyl ether reactant in an Al-foil wrapped test tube without AuNP film was irradiated with focused sunlight.

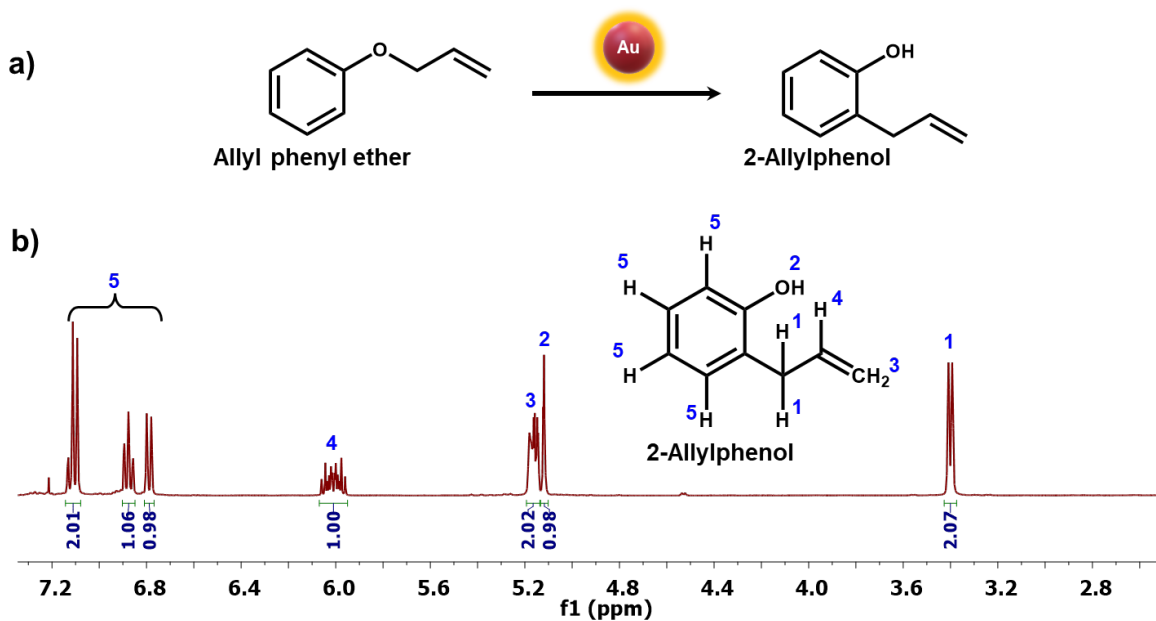


Fig. S4 (a) Reaction scheme and (b) ^1H -NMR spectrum of the purified product obtained from the plasmonic-heat driven Claisen rearrangement. Presence of all the characteristic NMR peaks of the product, 2-allylphenol, confirms the successful chemical transformation using plasmonic-heat.

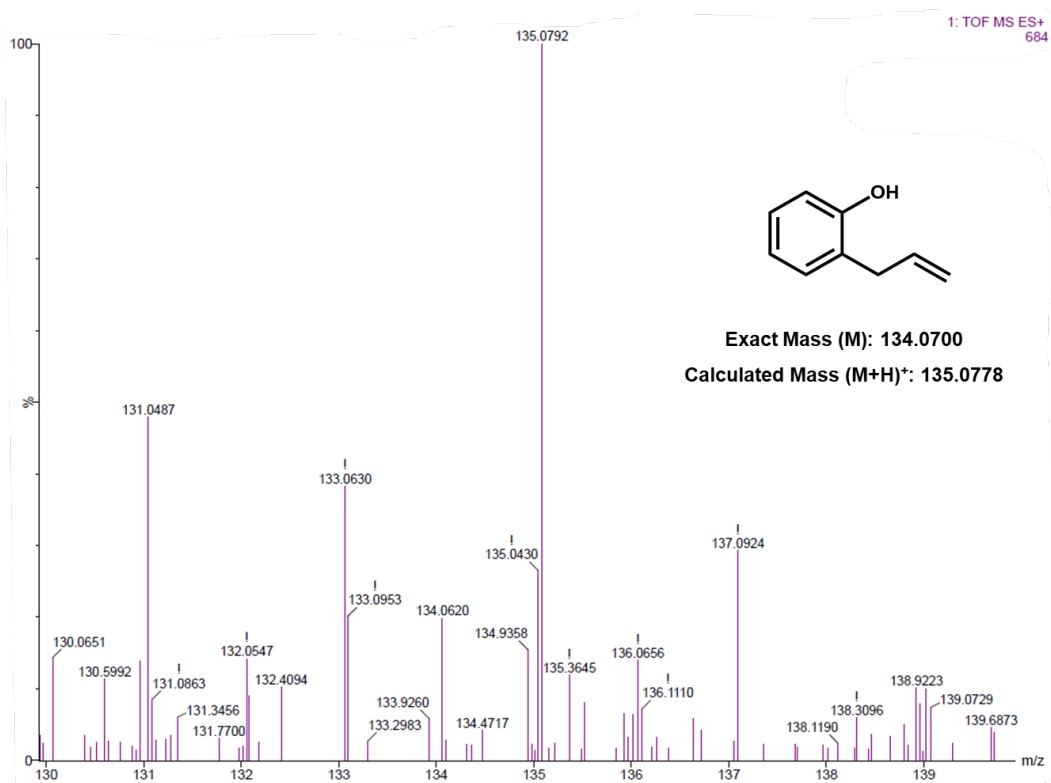


Fig. S5 HRMS spectrum of the purified product, 2-allylphenol, obtained from plasmonic-heat driven Claisen rearrangement.

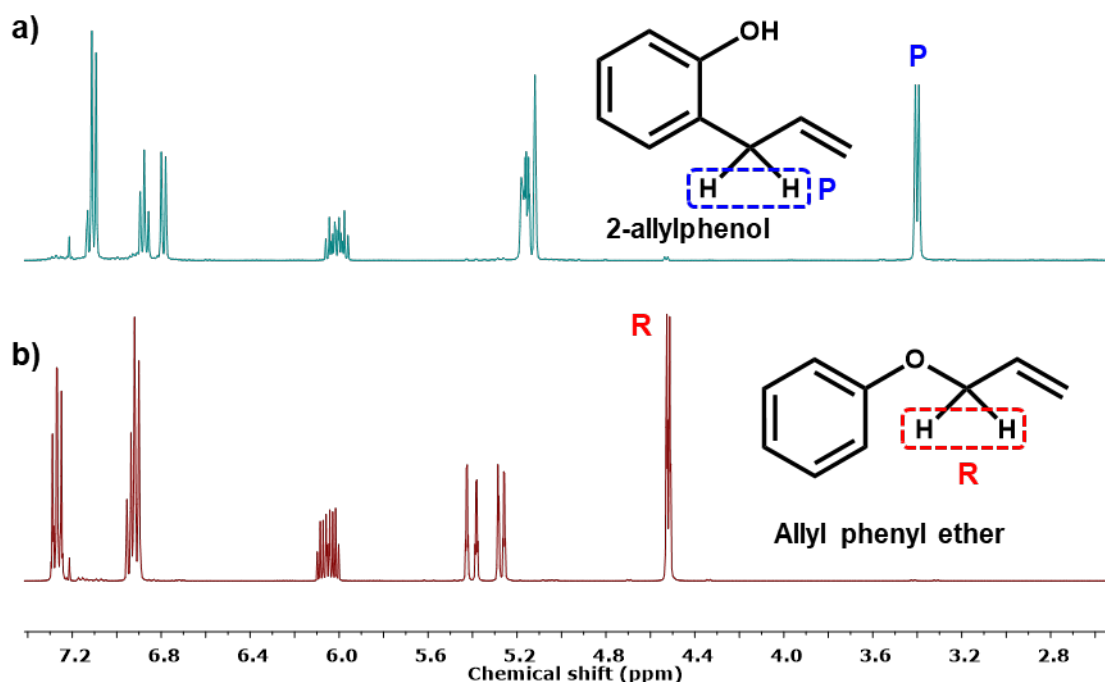


Fig. S6. ¹H-NMR spectra of (a) product (2-allylphenol) and (b) reactant (allyl phenyl ether). The main characteristic peaks in product and reactant are marked as P and R, respectively.

Reaction yield calculation using NMR spectroscopy:

The yield of the reaction was determined from ¹H-NMR of the crude reaction mixture. The ¹H-NMR spectrum of the reaction mixture contains the signals of the following organic molecules: allyl phenyl ether (the unreacted reactant), 2-allylphenol (the major product), and other possible side products.

In order to find the number of moles of product formed, a known amount of the internal standard (1,1,2,2-tetrachloroethane, 1 μ L, 9.47 μ mol) was added to the reaction mixture in CDCl₃. The signal for two equivalent protons of the internal standard appears as a singlet at δ 5.95 ppm. This peak does not overlap with the NMR peaks of any other compounds in the reaction mixture. For more clarity, a representative ¹H-NMR spectrum and yield calculation are given below (**Fig. S6**).

The reaction under consideration here is a 1:1 reaction, in which for every one mole of reactant reacted, an equivalent mole of product is expected to form. Thus, the yield (in percentage) was calculated as follows:

$$\text{Yield} = \frac{\text{number of moles of product formed}}{\text{number of moles of reactant used}} \times 100$$

Here, the number of moles of reactant used was 34.0 μ mol, and the number of moles of product formed was determined from the NMR spectrum with known amount of the internal standard (9.47 μ mol).

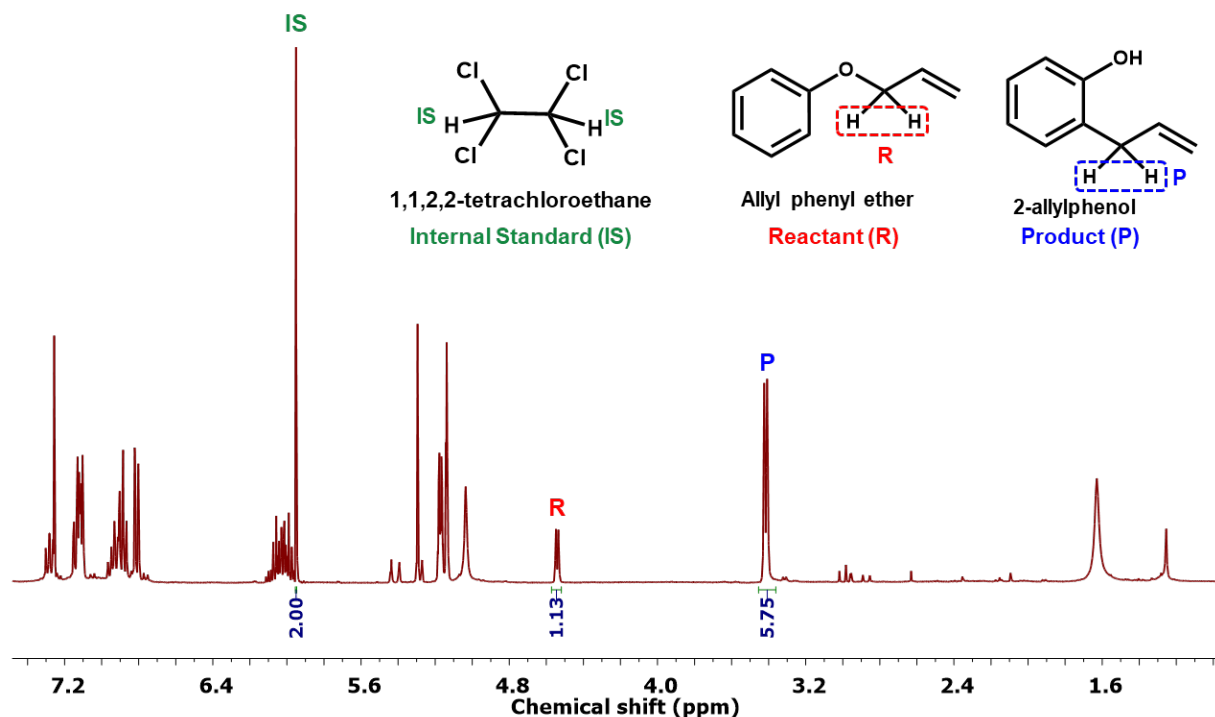


Fig. S7. Representative ^1H -NMR spectrum of the crude reaction mixture with 1,1,2,2-tetrachloroethane as internal standard (IS). The characteristic peaks are marked with P, R and IS for product, reactant, and internal standard, respectively.

Since the peak of internal standard (IS) corresponds to 2 protons and peak of product (P) corresponds to 2 protons, the number of moles of product formed can be calculated using the following equation:

$$\text{number of moles of product} = \frac{\left(\frac{I_P}{2}\right)}{\left(\frac{I_{IS}}{2}\right)} \times \frac{w_{IS}}{M_{IS}} = \frac{I_P}{I_{IS}} \times n_{IS}$$

Where,

I_P = integration value for NMR peak of *product* marked 'P' (5.75)

I_{IS} = integration value for NMR peak of *internal standard* marked 'IS' (2.00)

w_{IS} = weight of *internal standard* added after reaction (volume \times density)

M_{IS} = molar mass of *Internal standard*

n_{IS} = number of moles of *Internal standard* used (9.47 μ mol)

Substituting these values and relevant values from the NMR spectrum, we get:

$$\text{number of moles of product} = \frac{5.75}{2.00} \times 9.47 = 27.2262 \mu\text{mol}$$

The number of moles of reactant used was 34.0 μ mol. Therefore, percentage yield in this case is:

$$\text{Yield} = \frac{27.2262}{34.0} \times 100 = \mathbf{80.07\%}$$

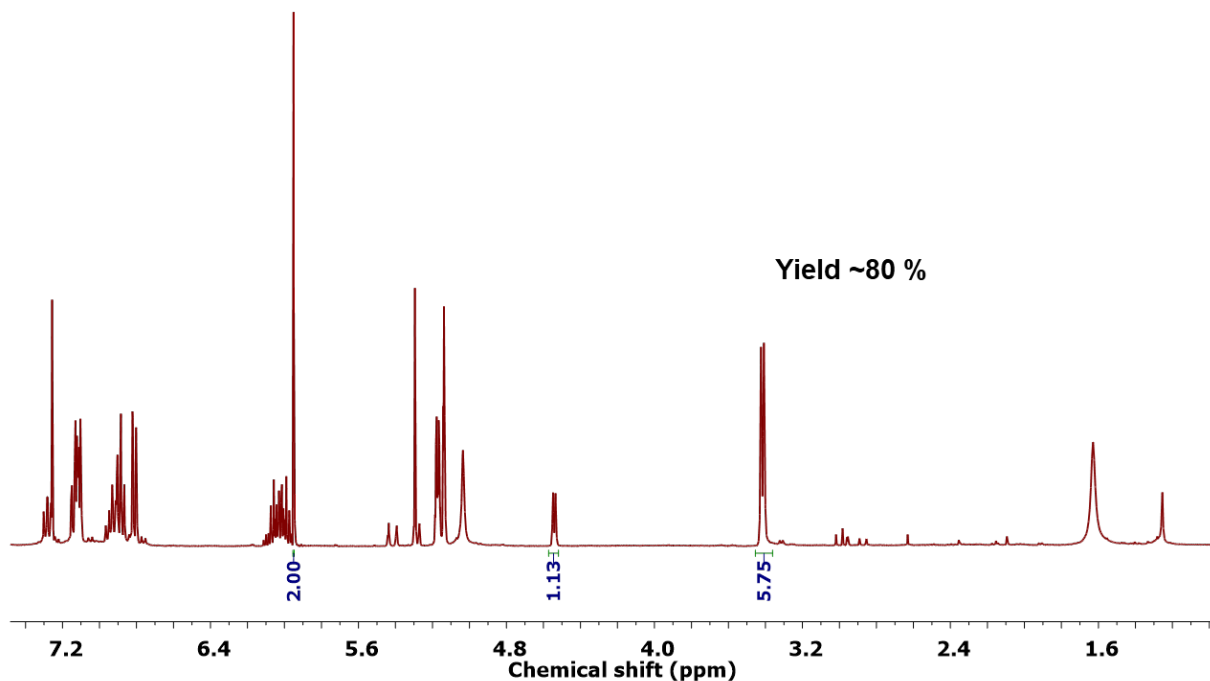


Fig. S8 ¹H-NMR spectrum of the crude reaction mixture after 2 h sunlight irradiation of the reactant in a AuNP coated Al-foil wrapped test-tube (plasmonic-heat driven Claisen rearrangement).

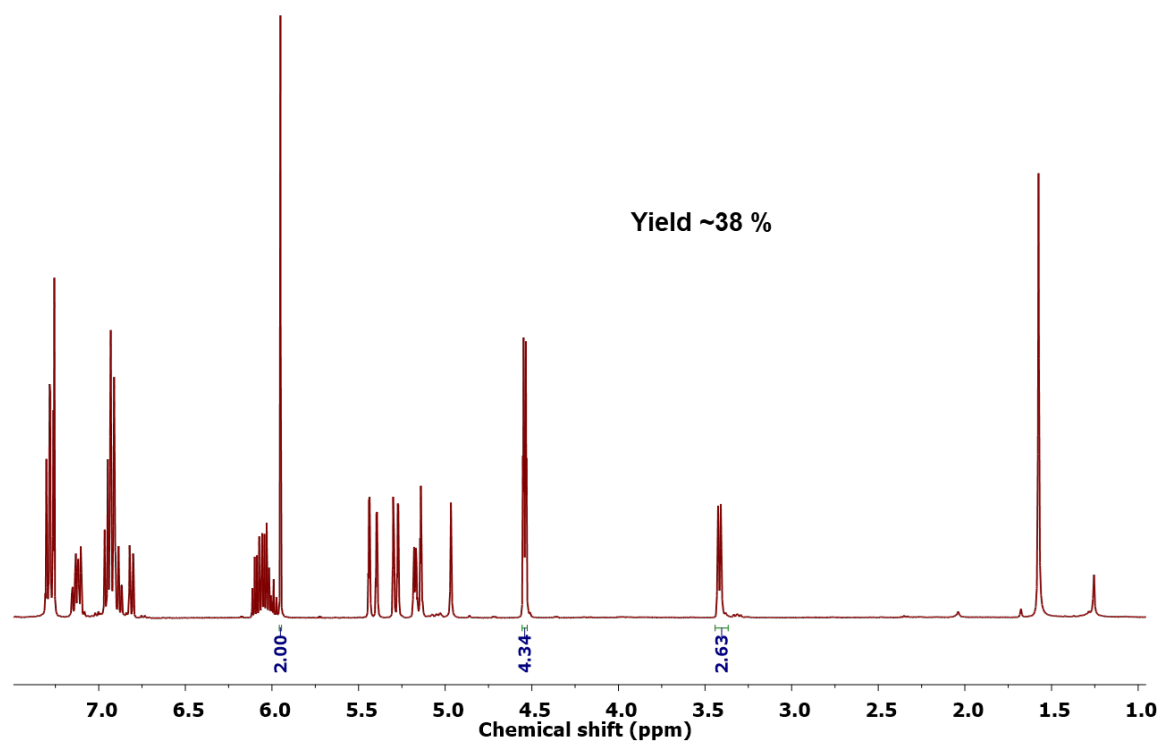


Fig. S9 ^1H -NMR spectrum of the crude reaction mixture after 2 h under thermal condition at 250 °C with electrical heating.

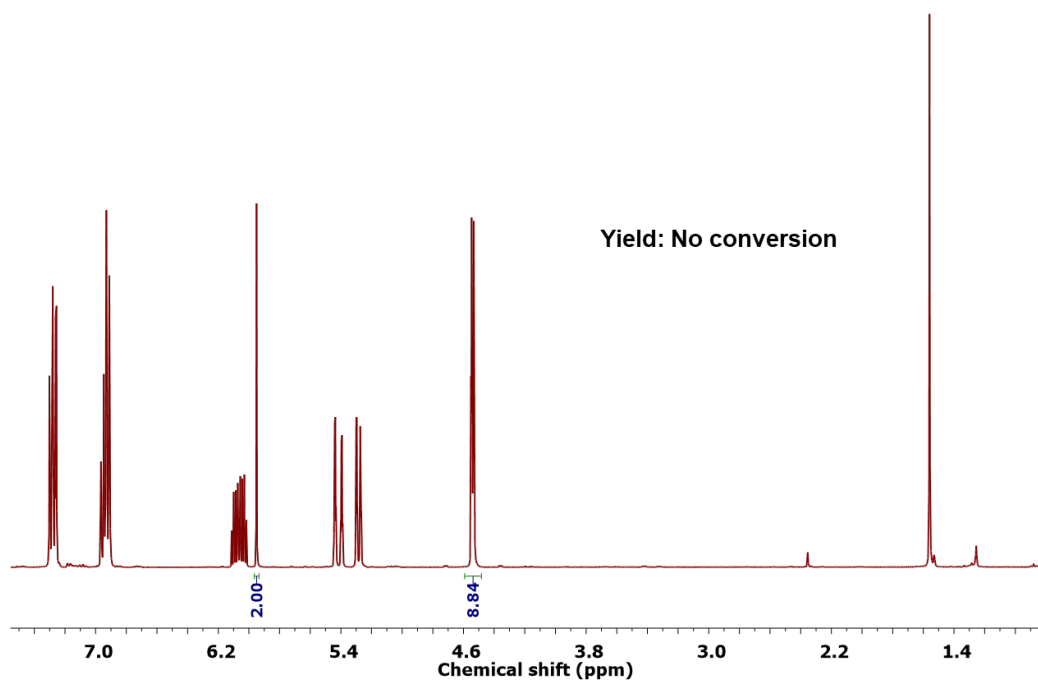


Fig. S10 ^1H -NMR spectrum of the crude reaction mixture after 2 h in dark in a AuNP coated Al-foil wrapped test-tube.

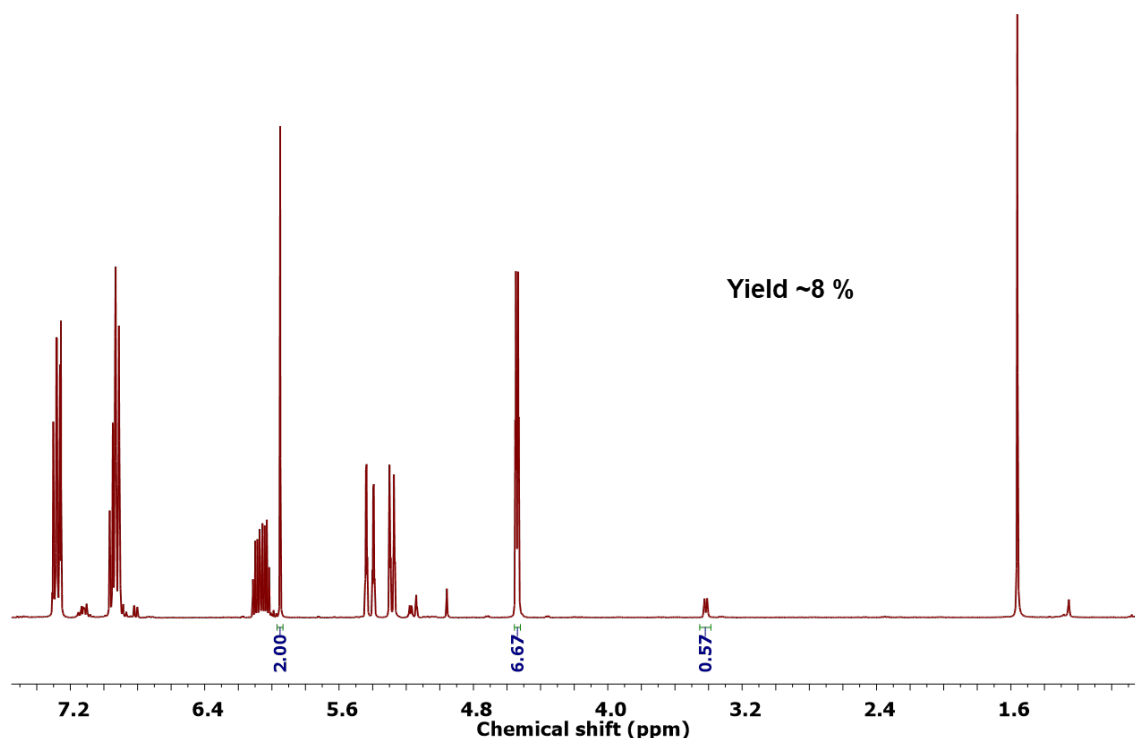


Fig. S11 ^1H -NMR spectrum of the crude reaction mixture obtained after 2 h sunlight irradiation of the reactant in an Al-foil wrapped test-tube (please note that the Al-foil doesn't contain any AuNP coating).

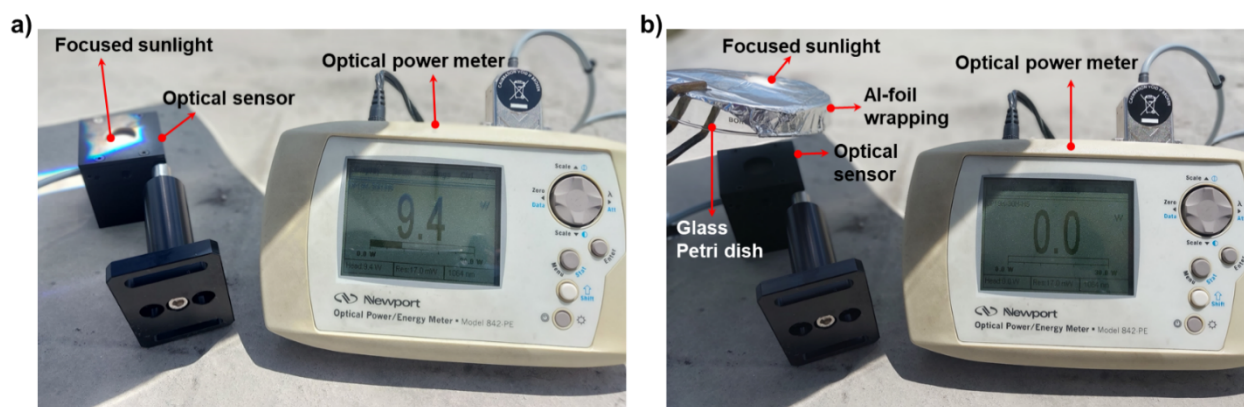


Fig. S12. Focused solar power measured in the (a) absence and (b) presence of Al-foil wrapped glass Petri dish. The Al-foil completely blocks the focused sunlight.

In-situ visualization of photothermal Claisen rearrangement (Supplementary Movie S1):

In a typical experiment, film of AuNPs (25 μL from 0.38 μM stock solution) at the inner wall of a 15 ml glass test tube was made by drying its aqueous suspension at room temperature. Next, 1 mL of allyl phenyl ether (reactant) was added into the test tube. Finally, the AuNP film which was in physical contact with the reactant was irradiated with focused sunlight. Fresnel lens (19.5 cm X 28.5 cm) was used to focus the sunlight onto the AuNP film, the spot diameter was measured to

be ~ 1 cm. A thermopile optical power detector (Model LM-10 HTD; Coherent, Santa Clara, CA 95054 USA) was used for measuring the power of sunlight falling on the AuNP film, after focusing. The solar power measured under our experimental conditions was ~ 9 W.cm⁻². Supplementary movie S1 clearly shows the vigorous boiling of the reactant (b.p. = 191.7 °C), along with a distinct color change to reddish yellow (indicating the successful chemical transformation).

The control experiment in the absence of AuNP keeping other experimental parameter constant failed to show any boiling of the reactant as well as color change reaffirming the negligible chemical transformation.

Reusability study:

The reusability was performed using the same AuNP coated Al-foil wrapped test-tube set-up for five cycles. In each cycle, 1 mL of the allyl phenyl ether was taken in the test-tube and the same AuNP coated Al-foil was irradiated with focused sunlight for 90 min. The next cycle was performed after carefully washing and drying the inside of the test-tube. All the experimental parameters were kept identical in all cycles. The yield of the reaction was similar till five cycles, which can be attributed to the excellent photostability of AuNPs.

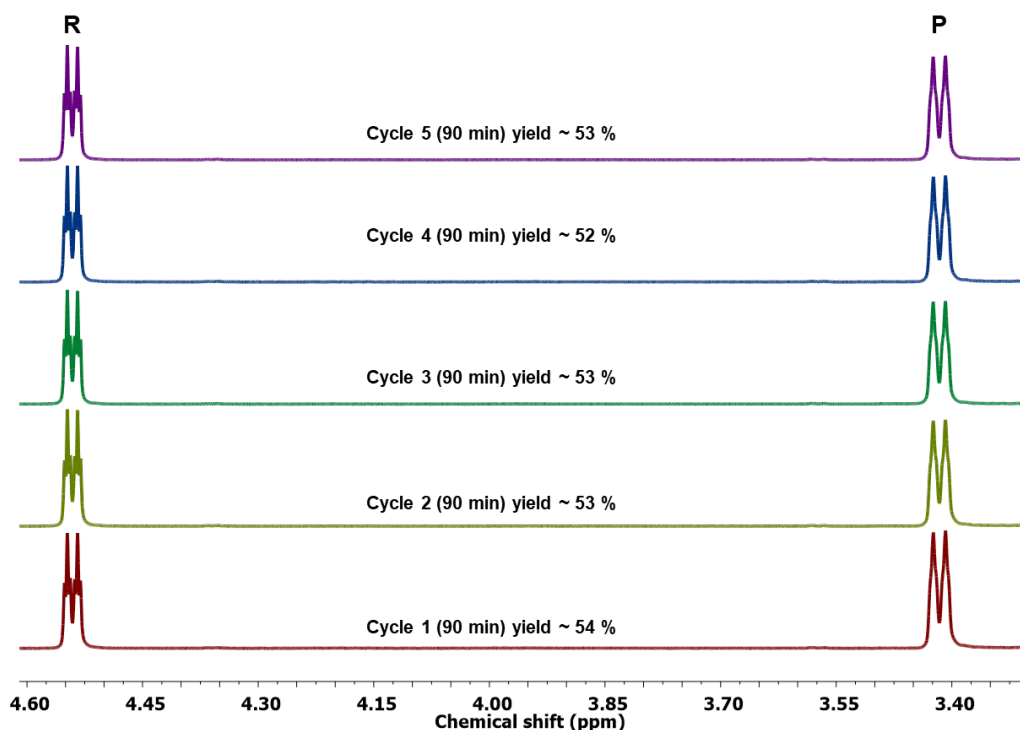


Fig. S13 ¹H-NMR spectra of the reaction mixture obtained in each cycle during the reusability study are stacked together. R and P corresponds to the characteristic peaks of reactant and product, respectively.

Reaction kinetics

Aliquots were taken from the reaction mixture at different time intervals, and the product yield was estimated. Briefly: for plasmonic-heat driven Claisen rearrangement, the aliquots were analyzed at 30, 45, 75, 90 and 120 mins. A continuous rise in the product peak (marked P) was observed along with simultaneous decrease in the reactant peak (marked R) upon increase in the reaction time. ~80% yield was obtained after 2 h of irradiation.

Likewise, kinetic studies for thermal reaction were performed. Here, the aliquots were taken out till 6 h as the reaction, so as to obtain a yield of ~80%. The amount of reaction mixture analyzed in each aliquot was same.

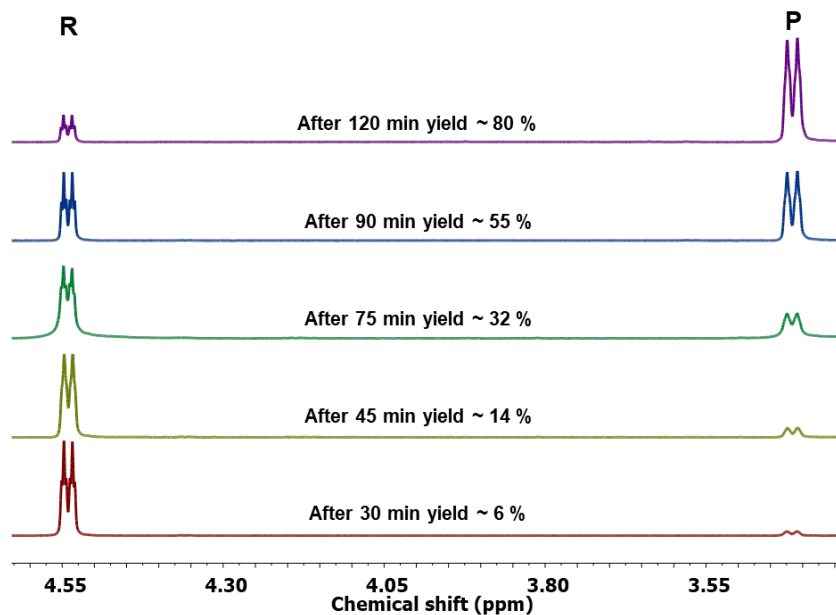


Fig. S14 A plot showing the variation in $^1\text{H-NMR}$ signals with respect to time for plasmonic-heat driven Claisen rearrangement (only the region covering the reactant and product is shown for clarity). A gradual increase in the product peak (marked P), along with a decrease in the reactant peak (marked R), was observed with time.

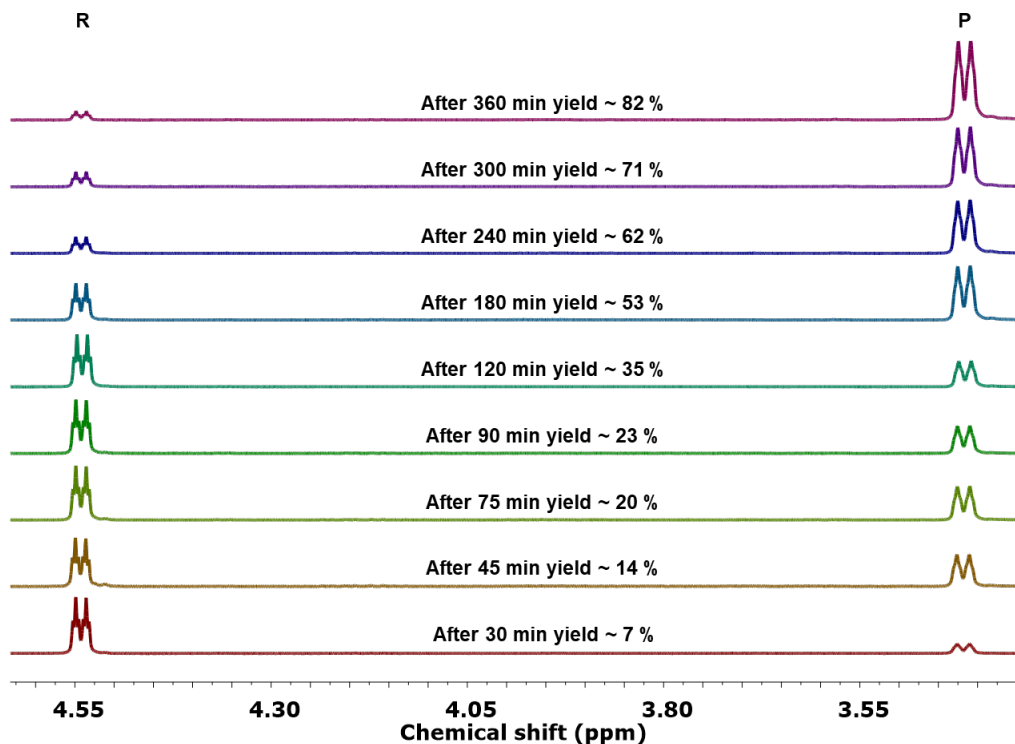


Fig. S15 A plot showing the variation in $^1\text{H-NMR}$ signals with respect to time for thermal Claisen rearrangement performed at 250 °C with electrical heating (only the region covering the reactant and product is shown for clarity). A gradual increase in the product peak (marked P), along with a decrease in the reactant peak (marked R), was observed with time.

References:

- (1) N. R. Jana and X. Peng, *J. Am. Chem. Soc.*, 2003, **125**, 14280–14281.
- (2) S. Roy, S. Roy, A. Rao, G. Devatha, and P. P. Pillai, *Chem. Mater.*, 2018, **30**, 8415–8419.
- (3) Y. Kim, J. G. Smith, and P. K. Jain, *Nat. Chem.*, 2018, **10**, 763–769.