

Supporting information:

Highly efficient Tsuji-Trost allylation in water catalyzed by Pd-nanoparticles

1. Material and methods

a) Material

All technical solvents and commercially available chemicals were used without further purification: dimethylcarbonate (99%, Sigma Aldrich), triazabicyclodecene (98%, Sigma Aldrich), allyl alcohol (>98.5%, Sigma Aldrich), allyl acetate (99%, Sigma Aldrich), ethyl aceto acetate (99%, Sigma Aldrich), dimethylmalonate (98%, Sigma Aldrich), acetylacetone (99%, Sigma Aldrich), Na₂PdCl₄ (98%, Sigma Aldrich), poly(vinylpyrrolidone) (K30, average MW 40,000, Sigma Aldrich), ethylene glycol (p.a., Fluka), poly(vinylpyridine) (5% cross-linked, Sigma Aldrich), pyridine (98%, Sigma Aldrich), 3-aminopropyl functionalized silica gel (0.9 mmol/g, Fluka), 3-aminopropyltriethoxysilane (>98%, Sigma Aldrich), 3-mercaptopropyltriethoxysilane (95%, ABCR), pyridine (99.8%, Sigma-Aldrich), chromium(III) acetylacetonate (99.99%, Sigma-Aldrich), 2-chloro-4,4,5,5-tetra-methyl-1,2,3-dioxaphospholane (95%, Sigma-Aldrich), palladium acetate (99.9%, Acros Chemicals), guaiacol (oxidation indicator, Sigma Aldrich), eugenol (99%, Acros Organic), 2,6-dimethoxy phenol (99%, Sigma Aldrich), vanillyl alcohol (>98%, Sigma Aldrich).

b) Characterization of the palladium nanoparticles

The palladium nanoparticles were characterized by transmission electron microscopy (TEM) with a FEI Tecnai F20 ST TEM (operating voltage 200 kV), which was equipped with a field emission gun and energy dispersive X-ray spectrometer. For TEM analysis, a small droplet of the nanoparticle dispersion was deposited on a carbon-coated, 400 mesh Cu grid and eventually air-dried. The particles size and the particle size distribution were statistically determined from TEM images based on at least 250 particles. The hydrodynamic diameter of the palladium nanoparticles stabilized by poly(vinylpyrrolidone) was determined by dynamic light scattering (DLS) using a Zetasizer Nano ZS equipped with a 633 nm laser (Malvern Instruments, non-invasive backscatter detection). The palladium content was analyzed by atomic emission spectroscopy with inductively coupled plasma (AES-ICP) using an Agilent 725 ICP-OES Spectrometer (Agilent Technologies).

c) Characterization of the products and conversion determination

The conversion was determined by ¹H NMR for ethyl aceto acetate **1a** and verified by GC. Both methods were in good agreement. The conversion of acetylacetone **1b** and dimethylmalonate **1c** was determined by GC.

NMR spectra were recorded on a Bruker AVANCE DPX spectrometer operating at 300 MHz for ^1H NMR and at 75 MHz for ^{13}C NMR measurements. CDCl_3 was used as solvent and all measurements took place at room temperature.

GC-MS (electron impact (EI)) measurements were performed on the following system: a Varian 431 GC instrument with a capillary column FactorFour VF-5 ms (30 m \times 0.25 mm \times 0.25 mm) and a Varian 210 ion trap mass detector. Scans were performed from 40 to 650 m/z at rate of 1.0 scans/s. The oven temperature program was: initial temperature 95 $^\circ\text{C}$, hold for 1 min, ramp at 15 $^\circ\text{C}/\text{min}$ to 220 $^\circ\text{C}$, hold for 4 min, ramp at 15 $^\circ\text{C}/\text{min}$ to 300 $^\circ\text{C}$, hold for 2 min. The injector transfer line temperature was set to 250 $^\circ\text{C}$. Measurements were performed in the split-split mode (split ratio 50:1) using helium as carrier gas (flow rate 1.0 mL/min).

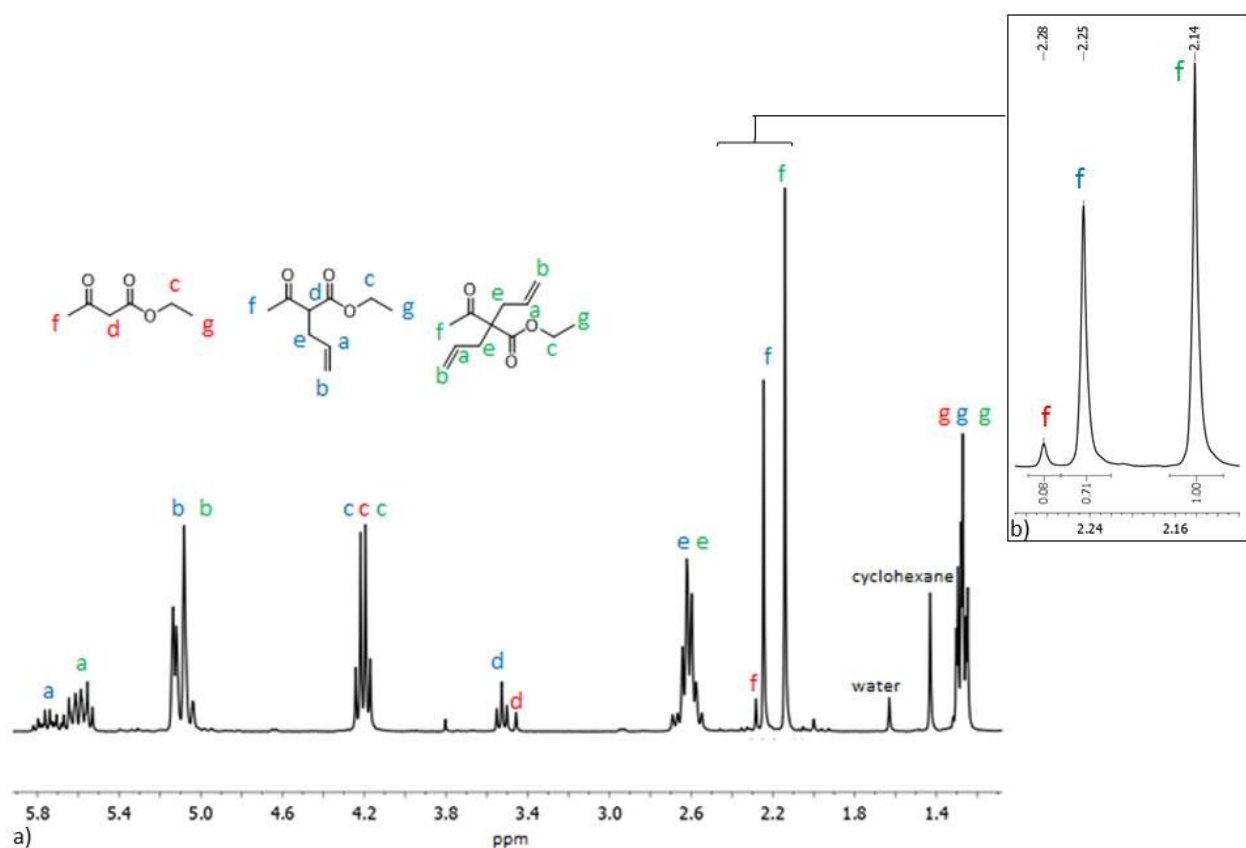


Figure S1. a) ^1H NMR spectrum of a mixture of ethyl aceto acetate, mono-allylated product and di-allylated product; b) Zoom on the methyl group between 2.10 ppm and 2.30 ppm in order to determine the conversion (here: 4% ethyl aceto acetate, 40% mono-allylated product, 56% di-allylated product).

Additionally, the pure products were analyzed with an Alpha Bruker FTIR spectrometer equipped with a Platinum ATR and high resolution mass spectra (HRMS) with electron impact ionization (EI) were recorded on a Finnigan MAT 95 mass spectrometer, or on a LTQ Orbitrap XL Q Exactive mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA) equipped with an HESI II probe.

d) Characterization of lignin

Size exclusion chromatography (SEC)

Molecular weight distributions of polymers were determined using a SEC system LC-20A from SHIMADZU equipped with a SIL-20A autosampler, precolumn PSS SDV (5 μm , 8 x 50 mm), main-column PSS DDV analytical 10000 \AA (5 μm , 8 x 300 mm) and a RID-10A refractive index detector in THF (flow rate 1.0 mL/min) at 50 $^{\circ}\text{C}$. The calibration was performed relative to PMMA standards (Polymer Standards Service, M_p 1100 - 981.000 Da)

Quantitative ^{31}P NMR

For ^{31}P NMR studies, an exact amount of 28 – 32 mg of the lignin sample was diluted in 400 μL CDCl_3 /pyridine (1 : 1.6, 150 μL :250 μL).

150 μL of a solution of chromium(III) acetylacetonate (0.54 mg, 3.6 $\text{mg}\cdot\text{mL}^{-1}$) as relaxation agent and cyclohexanol (0.6 mg, 4.0 $\text{mg}\cdot\text{mL}^{-1}$) as internal standard in CDCl_3 /pyridine (1:1.6, 560 μL :940 μL) were added and the solution was stirred for 5 minutes. 2-Chloro-4,4,5,5-tetra-methyl-1,2,3-dioxaphospholane (70 μL) was added and the solution was transferred into a NMR tube for subsequent measurement in a Bruker Ascend $^{\text{TM}}$ 400 MHz spectrometer with 512 scans, a delay time d1 of 5 seconds and a spectral width of 50 ppm (165 – 115 ppm).

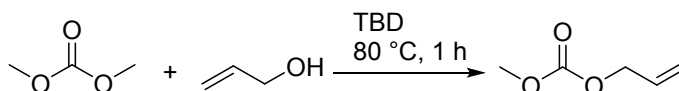
The chemical shifts are reported relative to the reaction product of 2-chloro-4,4,5,5-tetramethyl-1,2,3-dioxaphospholane with water at 132.2 ppm. Integrals are assigned to the functional groups as followed: $\delta = 150.0 - 145.5$ (aliphatic hydroxyl groups), 145.5 – 144.7 (cyclo-hexanol), 144.7 – 136.6 (phenolic hydroxyl groups)

2. Experimental procedures:

a) Synthesis of the palladium nanoparticles

In a typical synthesis, Na_2PdCl_4 (6.4 mmol, 1.870 g) and poly(vinylpyrrolidone) (PVP) (1.2497 g) were dissolved in 50 mL water. 10 mL of the solution and 10 mL ethylene glycol were loaded in a synthesis autoclave (Teflon, 100 mL). The total of five autoclaves was heated in a microwave oven (MARS $^{\text{TM}}$ synthesis, CEM) to 150 $^{\circ}\text{C}$ (2 min, 800 W) and kept for 10 min at 150 $^{\circ}\text{C}$. The palladium nanoparticles were precipitated stepwise by adding 30 mL acetone to 10 mL of the reaction mixture, followed by centrifugation and successive washing with acetone. The precipitates were collected and dissolved in 100 mL water to yield a homogenous, brown-black colloidal solution of palladium nanoparticles (palladium concentration 0.051 mol/L).

b) Synthesis of allyl methyl carbonate 2

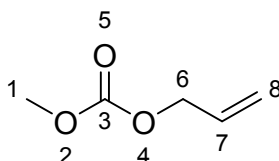


Scheme S1. Synthesis of allyl methyl carbonate from dimethyl carbonate and allyl alcohol.

A mixture of allyl alcohol (40 mL, 588 mmol) and dimethyl carbonate (372 mL, 4.40 mol) was stirred at 80 $^{\circ}\text{C}$ in a round bottom flask for a couple of minutes. Triazabicyclodecene (TBD,

816 mg, 5.88 mmol) was added to the flask. The reaction runs for 1h. A mixture of dimethyl carbonate, allyl methyl carbonate and diallyl carbonate is obtained and separated by distillation. Most of the dimethyl carbonate is removed using a rotary evaporator at 40 °C and about 150 mbar. The remaining product was purified by vacuum distillation at 100 mbar. The first fraction collected at 30 °C contains the remaining dimethyl carbonate and the second fraction at around 50 °C the allyl methyl carbonate.

Yield: 50%

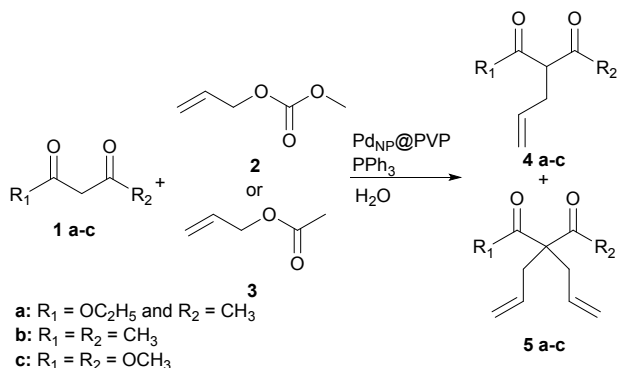


^1H NMR (300 MHz, CDCl_3 , δ in ppm): 6.06–5.77 (m, 1H, CH^7), 5.38–5.21 (m, 2H, CH_2^8), 4.60 (dd, 2H, CH_2^6), 3.68 (s, 3H, CH_3^1).

^{13}C NMR (75 MHz, CDCl_3 , δ in ppm): 155.7 (C^3), 131.7 (CH^7), 118.8 (CH_2^8), 68.5 (CH_2^6), 54.8 (CH_3^1).

IR (neat): ν [cm^{-1}]: 3088.4, 2959.2, 1745.4, 1650.5, 1443.8, 1382.7, 1249.4, 964.9, 926.3.

c) Tsuji Trost reaction of methylene activated compounds



Scheme S2. Tsuji-Trost reaction of different methylene activated compounds with allyl methyl carbonate and allyl acetate, leading to mono or/and di-allylated products.

General procedure

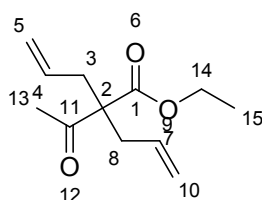
In a typical procedure, nucleophile **1(a-c)**, allylmethylcarbonate **2** or allylacetate **3** and triphenylphosphine were dissolved in 1.5 mL of water in a carousel reactor tube (carousel 12 Plus reaction station from Radleys Discovery Technologies, UK). Palladium nanoparticles stabilized by poly(vinylpyrrolidone) in water were added to the mixture. The reaction was stirred at a temperature between 80 °C and 120 °C in a carousel reactor. After the reaction, the tube was removed from the carousel. The product was extracted with ethylacetate. The organic phase was washed two times with water and one time with brine, dried by adding magnesium sulfate and after filtration, the filtrate was evaporated under vacuum (minimum 70 mbar) to recover the products. The sample was dried under vacuum. If traces of triphenylphosphine

remained, the sample was purified by flash chromatography with a cyclohexane ethylacetate mixture (95/5) to recover the pure product.

The reaction performed with 0.001 mol% catalyst was carried out in a round bottom flask (because the carousel tubes were too small) employing the following conditions: ethyl aceto acetate (20 mmol, 2.60 g), allyl methyl carbonate (50 mmol, 5.8 g), triphenylphosphine (1 mmol, 272 mg), water (30 mL) and Pd_{NP}@PVP (0.2 μmol, 4 μL).

The reaction performed with 0.0004 mol% catalyst was carried out in a round bottom flask (because the carousel tubes were too small) employing the following conditions: ethyl aceto acetate (53.7 mmol, 7.00 g), allyl methyl carbonate (134 mmol, 15.6 g), triphenylphosphine (2.69 mmol, 705 mg), water (80 mL) and Pd_{NP}@PVP (0.2 μmol, 4 μL).

Ethyl 2-acetyl-2-allylpent-4-enoate 5a



Ethyl aceto acetate **1a** (1 mmol, 130 mg), allyl methyl carbonate **2** (2.5 mmol, 290 mg) and triphenylphosphine (0.05 mmol, 13.6 mg) were dissolved in 1.5 mL of water in a carousel tube. Palladium nanoparticles stabilized by poly(vinylpyrrolidone) in water (0.001 mmol, 20 μL) were added to the mixture. The reaction is stirred at 80 °C for 10 min in the carousel. The work up is carried out as mentioned in the general procedure.

Yield: 98%

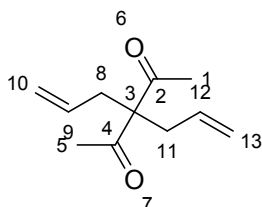
¹H NMR (300 MHz, CDCl₃, δ in ppm): 5.66–5.52 (m, 2H, CH^{4,7}), 5.12–5.07 (m, 4H, CH₂^{5,10}), 4.23–4.16 (q, 2H, CH₂¹⁴), 2.68–2.53 (m, 4H, CH₂^{3,8}), 2.13 (s, 3H, CH₃¹³), 1.25 (t, 3H, CH₃¹⁵)

¹³C NMR (75 MHz, CDCl₃, δ in ppm): 203.6 (C¹¹), 171.6 (C¹), 131.8 (CH^{4,7}), 118.8 (CH₂^{5,10}), 58.9 (C²), 61.0 (CH₂¹⁴), 35.6 (CH₂^{3,8}), 27.3 (CH₃¹³), 13.7 (CH₃¹⁵).

IR (neat): ν [cm⁻¹]: 3079.1, 2981, 1710.0, 1640.9, 1438.1, 1356.6, 1278.3, 1206.9, 1139.4, 1049.4 996.1, 918.9.

HRMS (EI): *m/z* calculated for C₁₂H₈O₃: 210.1250; found: 210.1250

3,3-Diallylpentane-2,4-dione 5b



Acetylacetone **1b** (1 mmol, 100 mg), allyl methyl carbonate **2** (2.5 mmol, 290 mg) and triphenylphosphine (0.2 mmol, 52.4 mg) were dissolved in 1.5 mL of water in a carousel tube.

Palladium nanoparticles stabilized by poly(vinylpyrrolidone) in water (0.001 mmol, 20 μ L) were added to the mixture. The reaction was stirred at 120 $^{\circ}$ C for 60 min in the carousel. The work up was carried out as mentioned in the general procedure.

Yield: 91%

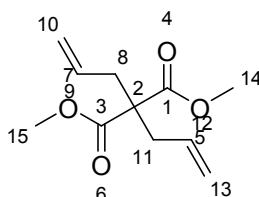
^1H NMR (300 MHz, CDCl_3 , δ in ppm): 5.48–5.45 (m, 2H, $\text{CH}^{9,12}$), 5.14–5.08 (m, 4H, $\text{CH}_2^{10,13}$), 2.66 (d, 4H, $\text{CH}_2^{8,11}$), 2.10 (s, 3H, $\text{CH}_3^{1,5}$).

^{13}C NMR (75 MHz, CDCl_3 , δ in ppm): 205.8 (C^4), 132.1 ($\text{CH}^{9,12}$), 119.4 ($\text{CH}_2^{13,10}$), 70.4 (C^3), 35.1 ($\text{CH}_2^{8,12}$), 27.3 ($\text{CH}_3^{1,5}$)

IR (neat): ν [cm^{-1}]: 3079.0, 2980.0, 1696.3, 1640.9, 1437.2, 1357.8, 1271.5, 1242.1, 1191.1, 1120.1, 995.5, 919.1.

HRMS (EI): m/z calculated for $\text{C}_{11}\text{H}_{16}\text{O}_2$: 180.1145; found: 180.1146

Dimethyl 2,2-diallylmalonate **5c**



Dimethylmalonate **1c** (1 mmol, 132 mg), allyl methyl carbonate **2** (2.5 mmol, 290 mg) and triphenylphosphine (0.2 mmol, 52.4 mg) were dissolved in 1.5 mL of water in a carousel tube. Palladium nanoparticles stabilized by poly(vinylpyrrolidone) in water (0,001 mmol, 20 μ L) were added to the mixture. The reaction was stirred at 120 $^{\circ}$ C for 60 min in the carousel. The work up was carried out as mentioned in the general procedure.

Yield: 82%

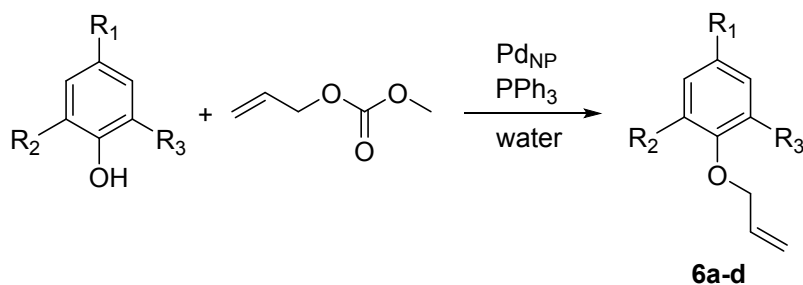
^1H NMR (300 MHz, CDCl_3 , δ in ppm): 5.70–5.57 (m, 2H, $\text{CH}^{7,5}$), 5.12–5.07 (m, 4H, $\text{CH}_2^{10,13}$), 3.70 (s, 6H, $\text{CH}_3^{14,15}$), 2.64 (d, 4H, $\text{CH}_2^{11,8}$).

^{13}C NMR (75 MHz, CDCl_3 , δ in ppm): 171.1 ($\text{C}^{1,3}$), 132.2 ($\text{CH}^{7,5}$), 119.4 ($\text{CH}_2^{10,13}$), 57.6 (C^2), 52.6 ($\text{CH}_3^{14,15}$), 36.9 ($\text{CH}_2^{8,11}$).

IR (neat): ν [cm^{-1}]: 3079.0, 2955.0, 1731.8, 1642.4, 1436.0, 1373.4, 1328.3, 1287.5, 1200.9, 1148.2, 1045.5, 995.7, 920.5.

HRMS (EI): m/z calculated for $\text{C}_{11}\text{H}_{16}\text{O}_4$: 212.1043; found: 212.1042

d) Tsuji Trost reaction of bio-based phenolic compounds

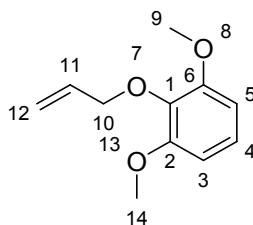


- a:** R₁ = H, R₂ = R₃ = OCH₃
b: R₁ = H, R₂ = OCH₃ and R₃ = H
c: R₁ = CH₂-CH=CH₂, R₂ = OCH₃ and R₃ = H
d: R₁ = CH₂-OH, R₂ = OCH₃ and R₃ = H

Scheme S2. Tsuji-Trost reaction of different bio-based phenolic compounds with allyl methyl carbonate.

In a typical procedure, phenolic compounds (1.00 eq.), allyl methyl carbonate **2** (2.50 eq.) and triphenylphosphine (0.05 eq.) were mixed with water (concentration = 0.67 mol/L) in a carousel tube. Palladium nanoparticles stabilized by poly(vinylpyrrolidone) in water (0.001 eq., palladium concentration: 0.051 mol/L) were added and the reaction was stirred at 80-90°C for 2-16 hours. The reaction mixture was poured in a separation funnel and extracted with ethyl acetate. The combined organic phase was dried with sodium sulfate, filtrated and the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography (SiO₂, cyclohexane: ethyl acetate gradient 98:2 -> 60:40).

2-(allyloxy)-1,3-dimethoxybenzene **6a**



Syringol (1.94 mmol, 300 mg), allyl methyl carbonate **2** (4.86 mmol, 565 mg) and triphenylphosphine (97.3 μmol, 25.5 mg) were mixed in 2.7 mL of water in a carousel tube. Palladium nanoparticles stabilized by poly(vinylpyrrolidone) in water (1.94 μmol, 38 μL) were added to the mixture and the reaction was stirred at 90 °C for 16 hours in the carousel. The work up was carried out as mentioned in the general procedure.

Yield: 96 %

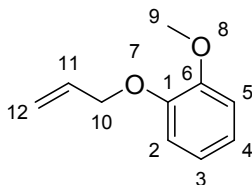
¹H NMR (300 MHz, CDCl₃, δ in ppm) 6.98 (t, 1H, CH⁴), 6.57 (d, 2H, CH^{3,5}), 6.22 – 5.95 (m, 1H, CH¹¹), 5.27 (ddd, 2H, CH₂¹²), 4.52 (d, 2H, CH₂¹⁰), 3.85 (s, 6H, CH₃^{9,14}).

¹³C NMR (75 MHz, CDCl₃, δ in ppm) 153.73 (C^{2,6}), 136.76 (C¹), 134.58 (CH¹¹), 123.65 (CH⁴), 117.63 (CH₂¹⁰), 105.25 (CH^{3,5}), 74.12 (CH₂¹⁰), 56.07 (CH₃^{9,14}).

IR (neat) ν [cm^{-1}] : 3079.9, 2938.3, 2837.2, 1594.9, 1492.5, 1475.7, 1435.4, 1421.1, 1295.3, 1250.7, 1184.9, 1106.3, 1034.5, 985.8, 922.2.

HRMS (ESI-Orbitrap) m/z : $[\text{M}+\text{Na}]^+$ Calculated for $\text{C}_{11}\text{H}_{14}\text{O}_3\text{Na}$: 217.08406; found: 217.08308.

1-(allyloxy)-2-methoxybenzene **6b**



Guaiacol (2.41 mmol, 300 mg), allyl methyl carbonate **2** (6.04 mmol, 702 mg) and triphenylphosphine (0.12 mmol, 31.7 mg) were mixed in 2.7 mL of water in a carousel tube. Palladium nanoparticles stabilized by poly(vinylpyrrolidone) in water (2.41 μmol , 47 μL) were added to the mixture and the reaction was stirred at 80 $^\circ\text{C}$ for 2 hours in the carousel. The work up was carried out as mentioned in the general procedure.

Yield: 92 %

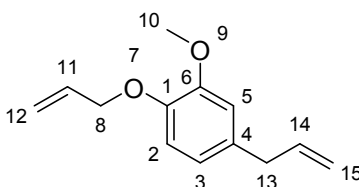
^1H NMR (300 MHz, CDCl_3 , δ in ppm) 6.90 (s, 4H, CH^{2-5}), 6.09 (ddd, 1H, CH^{11}), 5.35 (dd, 2H, CH_2^{12}), 4.61 (d, 2H, CH_2^{10}), 3.87 (s, 3H, CH_3^9).

^{13}C NMR (75 MHz, CDCl_3 , δ in ppm) 149.53 ($\text{C}_q^{\text{aromatic}}$), 148.04 ($\text{C}_q^{\text{aromatic}}$), 133.46 (CH^{11}), 121.26 ($\text{C}^{\text{aromatic}}$), 120.75 ($\text{C}^{\text{aromatic}}$), 117.84 (CH_2^{12}), 113.63 ($\text{C}^{\text{aromatic}}$), 111.80 ($\text{C}^{\text{aromatic}}$), 69.83 (CH_2^{10}), 55.86 (CH_3^9).

IR (neat) ν [cm^{-1}] : 3065.4, 2936.1, 2835.5, 1591.5, 1501.2, 1454.0, 1423.3, 1287.6, 1247.9, 1222.0, 1177.9, 1122.4, 1051.7, 1022.4, 994.1, 924.3.

HRMS (ESI-Orbitrap) m/z $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{10}\text{H}_{12}\text{O}_2\text{Na}$: 187.07350; found: 187.07264.

4-allyl-1-(allyloxy)-2-methoxybenzene **6c**



Eugenol (122 mmol, 20.00 g), allyl methyl carbonate **2** (244 mmol, 28.3 g, 2.00 eq) and triphenylphosphine (6.09 mmol, 1.60 g) were mixed in 100 mL of water in a round-bottom flask. Palladium nanoparticles stabilized by poly(vinylpyrrolidone) in water (121 μmol , 2.38 mL) were added to the mixture and the reaction was stirred at 80 $^\circ\text{C}$ for 4 hours. The extraction of the reaction mixture was carried out as indicated in the general procedure. The crude was then purified by high-vacuum distillation (0.05 mbar, 120 $^\circ\text{C}$) to give the pure product.

Yield: 89 %

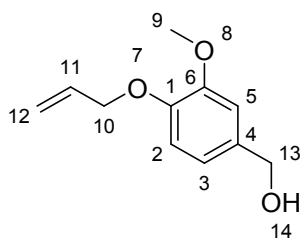
^1H NMR (300 MHz, CDCl_3 , δ in ppm) 6.89 – 6.62 (m, 3H, $\text{CH}^{2,3,5}$), 6.20 – 5.84 (m, 2H, $\text{CH}^{11,14}$), 5.33 (ddd, 2H, CH_2^{12}), 5.18 – 4.99 (m, 2H, CH_2^{15}), 4.59 (d, 2H, CH_2^8), 3.87 (s, 3H, CH_3^{10}), 3.34 (d, 2H, CH_2^{13}).

^{13}C NMR (75 MHz, CDCl_3 , δ in ppm) 137.66 (s, $\text{CH}^{\text{olefinic}}$), 133.58 (s, $\text{CH}^{\text{olefinic}}$), 120.35 (s, $\text{CH}^{\text{aromatic}}$), 117.79 (s, CH_2^{12}), 115.64 (s, CH_2^{15}), 113.62 (s, $\text{CH}^{\text{aromatic}}$), 112.25 (s, $\text{CH}^{\text{aromatic}}$), 70.02 (s, CH_2^8), 55.86 (s, CH_3^{10}), 39.83 (s, CH_2^{13}).

IR (neat): ν [cm^{-1}]: 3078.0, 3001.8, 2977.8, 2906.5, 1638.3, 1589.7, 1508.6, 1463.1, 1419.4, 1257.5, 1227.6, 1139.2, 1023.2, 992.9, 913.5.

HRMS (ESI-Orbitrap) m/z [$\text{M}+\text{Na}$] $^+$ calculated for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Na}$: 227.10480; found: 227.10399.

(4-(allyloxy)-3-methoxyphenyl)methanol 6d



Vanillyl alcohol (1.94 mmol, 300 mg), allyl methyl carbonate **2** (4.86 mmol, 565 mg) and triphenylphosphine (97.3 μmol , 25.5 mg) were mixed in 2.7 mL of water in a carousel tube. Palladium nanoparticles stabilized by poly(vinylpyrrolidone) in water (1.94 μmol , 38 μL) were added to the mixture and the reaction was stirred at 90 $^\circ\text{C}$ for 16 hours in the carousel. The work up was carried out as mentioned in the general procedure.

Yield: 85 %

^1H NMR (300 MHz, CDCl_3 , δ in ppm) 6.89 – 6.54 (m, 3H, $\text{CH}^{2,3,5}$), 6.00 (dtd, 1H, CH^{11}), 5.26 (dd, 2H, CH_2^{12}), 4.66 – 4.25 (m, 4H, $\text{CH}_2^{10,13}$), 3.76 (s, 3H, CH_3^9), 1.97 (s, 1H, OH^{14}).

^{13}C NMR (75 MHz, CDCl_3 , δ in ppm) 149.54 (C^6), 147.46 (C^1), 134.02 (C_q^4), 133.30 (CH^{11}), 119.26 ($\text{CH}^{\text{aromatic}}$), 117.97 (CH^{12}), 113.33 ($\text{CH}^{\text{aromatic}}$), 110.81 ($\text{CH}^{\text{aromatic}}$), 69.93 (CH_2^{10}), 65.18 (CH_2^{13}), 55.87 (CH_3^9).

IR (neat) ν [cm^{-1}]: 3400.3, 2935.8, 2870.2, 1591.5, 1509.7, 1462.4, 1418.9, 1364.3, 1257.5, 1224.4, 1156.2, 1135.7, 1017.6, 993.4, 923.0, 854.7, 802.4, 735.2, 550.1.

HRMS (ESI-Orbitrap) m/z : [$\text{M}+\text{Na}$] $^+$ Calculated for $\text{C}_{11}\text{H}_{14}\text{O}_3\text{Na}$: 217.08406; found: 217.08337

e) Extraction of Organosolv lignin

Oven dried beech wood chips (50.0 g) were placed in a 500 mL pressure reactor and suspended in a 65% mixture of ethanol/water (195:105 mL). Concentrated sulfuric acid (1.5 % w/w, 0.75 g) was added and the mixture was mechanically stirred at 195 °C for 90 minutes.

The mixture was filtered and the solid was washed with a warm solution of ethanol/water (65%). The filtrate was poured into a large volume of water (1.50 L) to precipitate lignin. The precipitated brown solid was filtrated, washed with water and dried overnight under vacuum.

Yield: 7.82 g, 15.6 %

Lignin composition: aromatic-OH 2.93 mmol/g, aliphatic-OH 0.76 mmol/g (determined by ³¹P NMR).

f) Tsuji Trost allylation of lignin

General procedure

In a pressure tube, organosolv lignin (210 mg), triphenylphosphine (0.5 eq. per OH, 245 μmol, 64.3 mg), allyl methyl carbonate (5.00 eq. per OH, 2.45 mmol, 285 mg) were dissolved in 4.00 mL of a mixture of water:cosolvent (1:3). Palladium nanoparticles stabilized by poly(vinylpyrrolidone) in water (0.01 eq., palladium concentration: 0.051 M) were added and the reaction was stirred at 80-95 °C for 120-144 hours). Monophasic solvent systems were purified by method A and biphasic solvent systems were purified by method B. The conversion was calculated by ³¹P NMR after derivatization with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.

Work-up A: the crude reaction mixture was poured in a large amount of water and filtrated using a fritted glass. The precipitate was dissolved in THF, re-precipitated in cyclohexane, filtrated using a fritted glass and dried under vacuum.

Work-up B: the reaction mixture was poured in a separation funnel and extracted with ethyl acetate. The combined organic phase was poured in a large amount of cyclohexane, filtrated using a fritted glass and dried under vacuum.

Table S 1. Conversion of the hydroxyl groups in the Tsuji Trost reaction of lignin with allyl methyl carbonate depending on the experimental conditions.

Solvent system	Time [hours]	Temp. [°C]	% of Aromatic-OH converted	% of Aliphatic-OH converted
H ₂ O / DMAC	120	95	66 %	26 %
H ₂ O / DMC	120	95	75 %	41 %
H ₂ O/ EtOAc	144	80	82 %	1 %
H ₂ O / DMAC	144	80	36 %	7 %

g) Poisoning experiments

The experiments were performed as described in the general procedure with 0.05 mol% of Pd_{NP}@PVP and ethyl aceto acetate **1a** as nucleophile. Before the introduction of allyl methyl carbonate **2**, 400 equivalents of poisons to palladium catalyst (3-aminopropyltriethoxysilane (100 eq.), pyridine, 3-mercaptopropyltriethoxysilane, polyvinylpyridine, 3-aminopropyl functionalized silica gel) were added to the reaction flask and stirred for few minutes.

3. Characterization and complementary data

a) Nanoparticle characterization

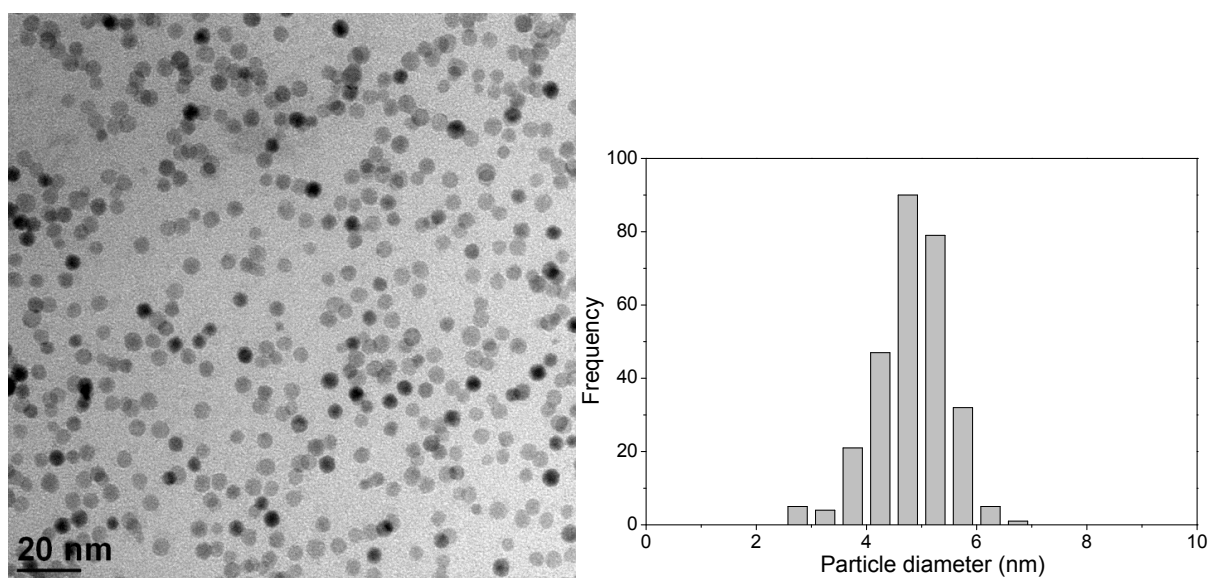


Figure S2. TEM image of the Pd_{NP}@PVP with particle size histogram (mean particle size 4.8 (±0.7) nm).

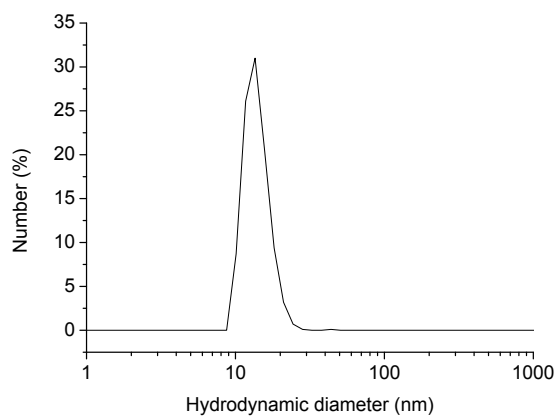
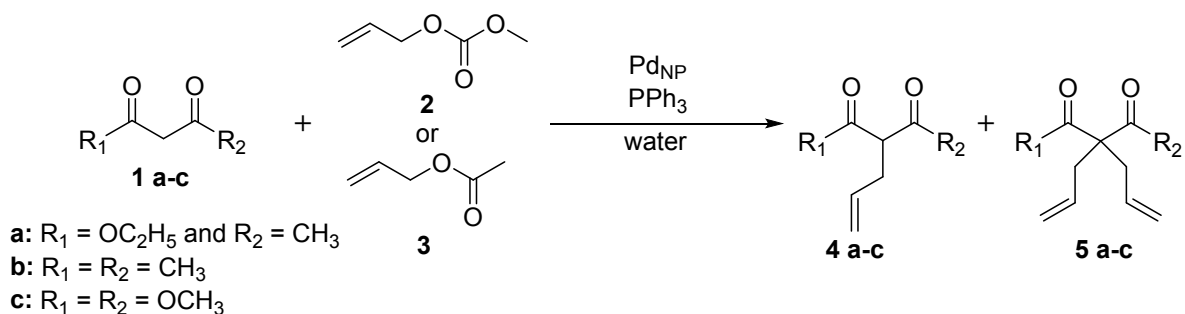


Figure S3. DLS analysis (hydrodynamic diameter 13 nm) of the Pd_{NP}@PVP

b) Tsuji-Trost reaction of ethyl aceto acetate 1a: condition screening



Scheme S3. Tsuji-Trost reaction of different nucleophiles **1** with allyl methyl carbonate **2** and allyl acetate **3** yielding to mono or di-allylated product.

Table S2. Screening of experimental conditions for Tsuji-Trost reaction of ethyl acetoacetate **1a** and allyl methyl carbonate **2**.

1a (mmol)	2 (mmol)	Pd _{NP} @PV P (mmol)	Water (mL)	PPh ₃ (mmol)	Time (min)	Temperature (°C)	Conversion (%) ^[a]	Product ^[a]	
								% 4a	% 5a
1.0	2.5	0	1.5	0	360	120	0	0	0
1.0	2.5	0.05	1.5	0	360	120	10	2	0
1.0	2.5	0.05	1.5	0.2	60	120	100	0	100
1.0	2.5	0.001	1.5	0.05	10	80	100	0	100
1.0	2.5	0.001	1.5	0.01	10	80	96	39	57
1.0	2.5	0.001	1.5	0.05	10	60	56	43	13
1.0	1.0	0.001	1.5	0.05	10	80	80	37	43
1.0	1.0	0.001	1.5	0.05	30	60	60	37	23

[a] Conversion determined by ¹H NMR

Table S3. Screening of experimental conditions for Tsuji-Trost reaction of ethyl acetoacetate **1a** and allylacetate **3**.

1a (mmol)	3 (mmol)	Pd _{NP} @PVP (mmol)	Water (mL)	PPh ₃ (mmol)	Time (min)	Temperature (°C)	Conversion (%) ^[a]	Product ^[a]	
								% 4a	% 5a
1.0	2.5	0.001	1.5	0.05	10	80	12	10	2
1.0	2.5	0.001	1.5	0.2	10	120	25	24	1
1.0	2.5	0.01	1.5	0.2	10	120	24	22	2
1.0	2.5	0.001	0.75	0.2	10	120	77	17	10
1.0	2.5	0.001	1.5	0.2	360	120	34	26	5
1.0	2.5	0.001	1.5	0.05	10	80	12	10	2
1.0	2.5	0.001	1.5	0.2	10	120	25	24	1
1.0	2.5	0.01	1.5	0.2	10	120	24	22	2

[a] Conversion determined by ¹H NMR

c) Tsuji-Trost reaction of acetylacetone **1b**: condition screening

Table S4. Screening of experimental conditions for Tsuji-Trost reaction of acetylacetone **1b** and allyl methyl carbonate **2**.

1b (mmol)	2 (mmol)	Pd _{NP} @PVP (mmol)	Water (mL)	PPh ₃ (mmol)	Time (min)	Temperature (°C)	Conversion (%) ^[a]	Product ^[a]	
								% 4b	% 5b
1.0	2.5	0.001	1.5	0.05	10	80	90	8	82
1.0	2.5	0.01	1.5	0.2	10	120	100	0	100
1.0	2.5	0.001	1.5	0.2	10	120	100	0	100

[a] Conversion determined by GC

Table S5. Screening of experimental conditions for Tsuji-Trost reaction of acetylacetone **1b** and allyl acetate **3**.

1b (mmol)	3 (mmol)	Pd _{NP} @PVP (mmol)	Water (mL)	PPh ₃ (mmol)	Time (min)	Temperature (°C)	Conversion (%) ^[a]	Product ^[a]	
							% 4b	% 5b	
1.0	2.5	0.01	1.5	0.2	60	120	58	24	34
1.0	2.5	0.001	1.5	0.2	360	120	57	28	29

[a] Conversion determined by GC

d) Tsuji-Trost reaction of dimethylmalonate 1c: condition screening**Table S6.** Screening of experimental conditions for Tsuji-Trost reaction of dimethylmalonate **1c** and allyl methyl carbonate **2**.

1c (mmol)	2 (mmol)	Pd _{NP} @PVP (mmol)	Water (mL)	PPh ₃ (mmol)	Time (min)	Temperature (°C)	Conversion (%) ^[a]	Product ^[a]	
							% 4c	% 5c	
1.0	2.5	0.001	1.5	0.05	10	80	37	37	0
1.0	2.5	0.01	1.5	0.2	10	120	100	15	85
1.0	2.5	0.001	1.5	0.2	60	120	100	0	100

[a] Conversion determined by GC

Table S7. Screening of experimental conditions for Tsuji-Trost reaction of dimethylmalonate **1c** and allyl acetate **3**.

1c (mmol)	3 (mmol)	Pd _{NP} @PVP (mmol)	Water (mL)	PPh ₃ (mmol)	Time (min)	Temperature (°C)	Conversion (%) ^[a]	Product ^[a]	
							% 4c	% 5c	
1.0	2.5	0.001	1.5	0.05	10	80	2	2	0
1.0	2.5	0.001	1.5	0.2	10	120	2	2	0
1.0	2.5	0.001	1.5	0.2	60	120	5	5	0
1.0	2.5	0.01	1.5	0.2	60	120	10	10	0
1.0	2.5	0.001	0.5	0.2	60	120	7	7	0

[a] Conversion determined by GC

e) Summary

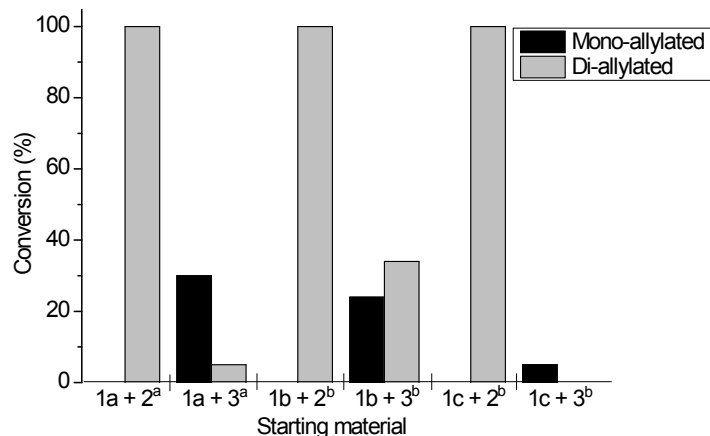


Figure S4. Conversion of different nucleophiles under optimized reaction conditions (a: 1.0 mmol nucleophile, 2.5 mmol allyl compound, 0.05 mmol PPh₃, 1.5 mL water, 0.1 mol% Pd_{NP}@PVP, T = 80 °C, t = 10 min ; b: 1.0 mmol nucleophile, 2.5 mmol allyl compound, 0.2 mmol PPh₃, 1.5 mL water, 0.1 mol% Pd_{NP}@PVP, T = 120 °C, t = 60 min).

f) Poisoning experiments

Table S8. Results on the poisoning experiments on the Tsuji-Trost reaction of ethyl aceto acetate **1a** with allyl methyl carbonate **2**.

Poison ^[a]	Equivalent of poison/ Pd _{NP} @PVP	Conversion (%) ^[b]	Product ^[b]	
			% 4a	% 5a
No	-	100	0	100
3-Aminopropyltriethoxysilane	100	100	0	100
Pyridine	400	100	0	100
3-mercaptopropyltriethoxysilane	400	81	55	26
PVP	400	100	0	100

[a] 1.0 mmol ethyl aceto acetate **1a**, 2.5 mmol allyl methyl carbonate **2**, 0.05 mmol PPh₃, 1.5 mL water, 0.05 mol% Pd_{NP}@PVP, T = 80 °C, t = 30 min

[b] Conversion determined by ¹H NMR

g) TEM images after reaction

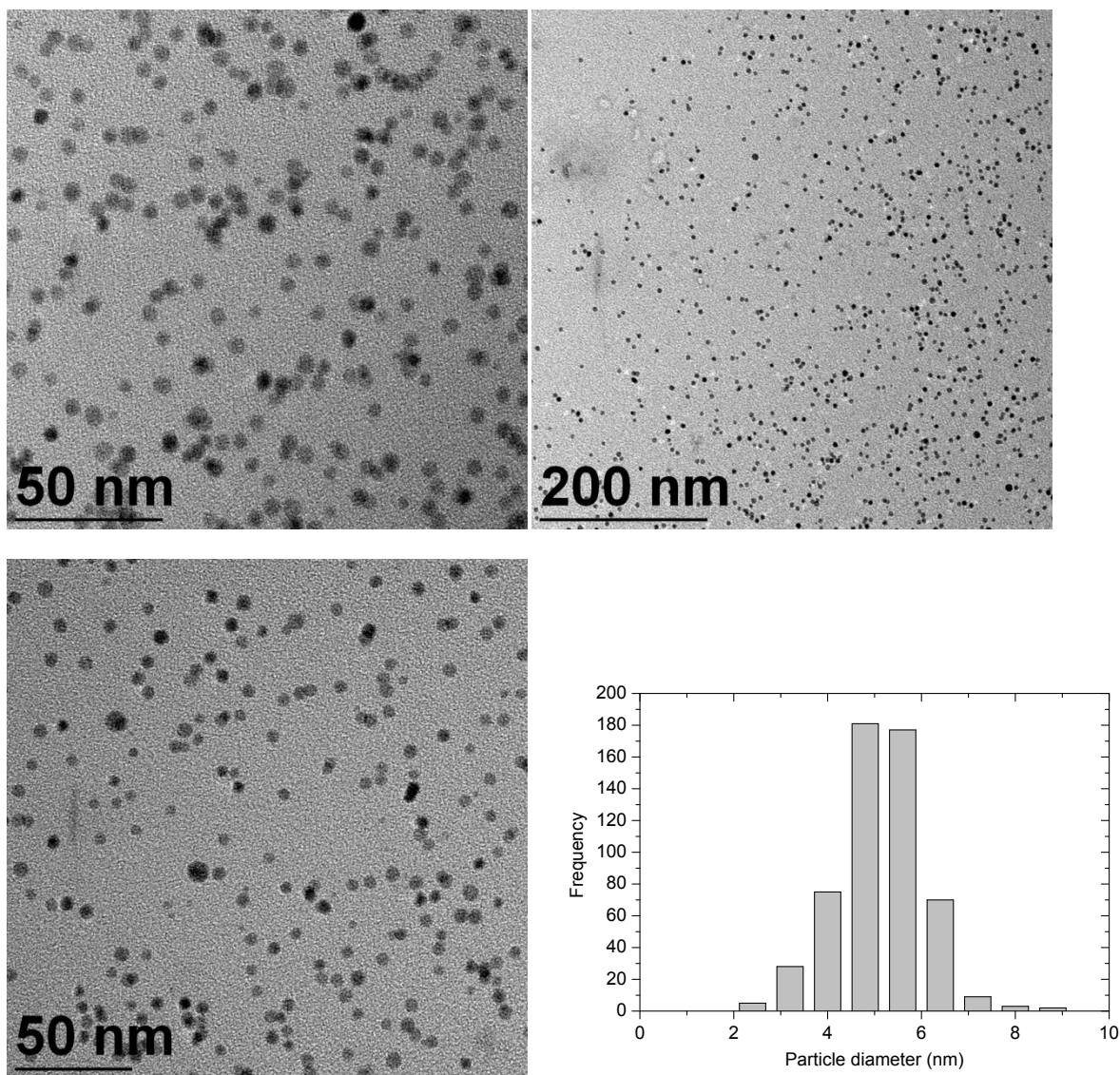


Figure S5. TEM image of the Pd_{NP}@PVP, which were recovered around/inside the organic droplets after catalytic testing, with particle size histogram (mean particle size 5.1 (\pm 0.9) nm).

h) SEC analyses of lignin and allylated lignin

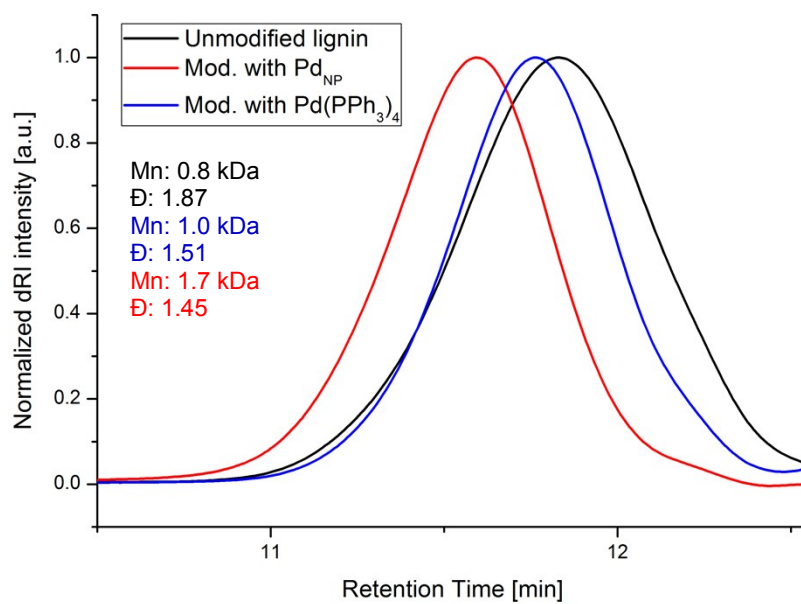


Figure S6. SEC traces of unmodified lignin (black), allylated lignin employing the Pd_{NP}@PVP (red), allylated lignin employing palladium acetate (blue).