Electronic Supplemental Information

Tandem Semi-hydrogenation/Isomerization of Propargyl Alcohols to Saturated Carbonyl Analogues by Dodecanthiolate-Capped Palladium Nanoparticle Catalysts

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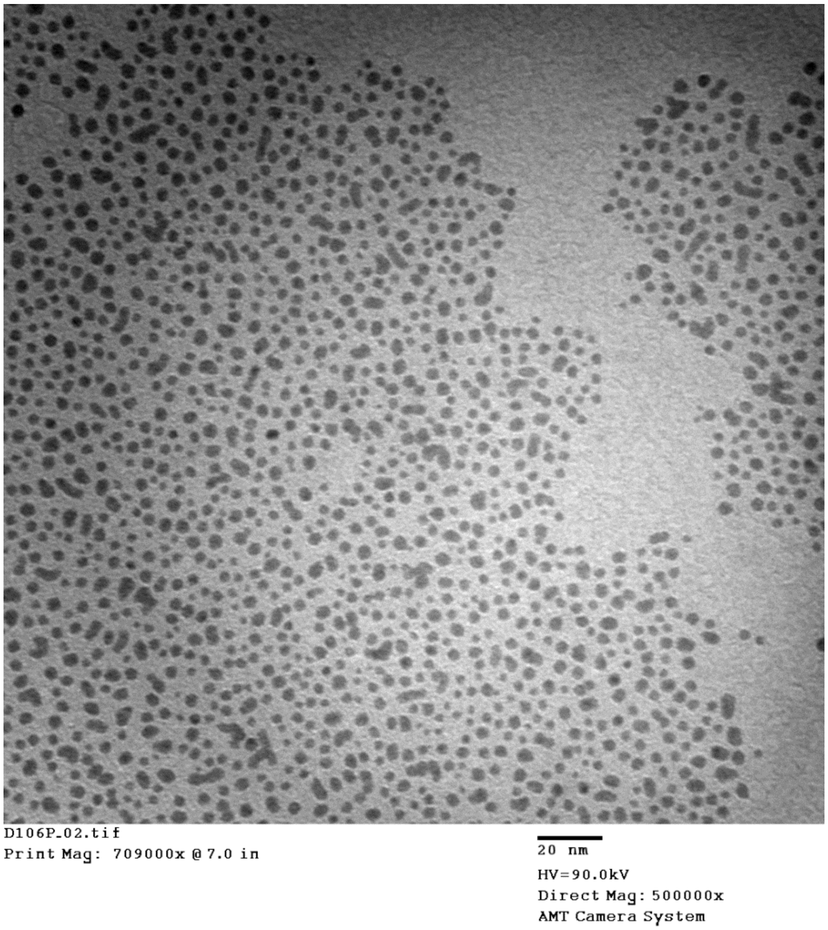
Materials and General Information. Propargyl alcohol (99%), 2-butyn-1-ol (97%), and 3-phenyl-2-propyn-1-ol (98%) were purchased from Acros Organics. $CDCl_3$ (99.8%) NMR solvent was purchased from Cambridge Isotope Laboratories. ^1H NMR spectra was recorded on a Bruker AC400 FT-NMR spectrometer operating at 400 MHz in $CDCl_3$ solutions and internally referenced to δ 7.26 ppm. Transmission electron microscopy (TEM) images were acquired by employing a JEOL 1200 EX II electron microscope operating a 90 keV. Samples were prepared by placing 10 μL of a PdNP dissolved in dry THF (~1 mg/mL) on a 200 mesh copper grid obtained from Ted Pella, Inc. Thermogravimetric Analysis was performed on a TA instruments SDT Q600 with a flow rate of 100 mL/min of N_2 gas and heating from 20 °C to 600 °C by 10°C/min. Alkanethiolate ligands were anticipated to volatilize past a temperature of 150 °C, anything prior was assumed moisture or trace solvent impurities.

Synthesis of Pd Nanoparticles. The following synthesis is a standard procedure for $Pd_{1289}L_{164}$ syntheses. Reaction conditions which were systematically varied for $Pd_{116}L_{59}$ were: (1) the mole ratio of sodium *S*-dodecylthiosulfate (0.8 mmol for $Pd_{116}L_{59}$); (2) the mole ratio of $NaBH_4$ (8.0 mmol for $Pd_{116}L_{59}$); (3) the reaction temperature (60 °C for $Pd_{116}L_{59}$). Potassium tetrachloropalladate (K_2PdCl_4; 0.4 mmol) was dissolved in 12 mL of nanopure water. TOAB (2.0 mmol) was dissolved in 25 mL of toluene. Both solutions were mixed and continuously stirred until the organic layer turned dark orange and the aqueous layer cleared indicating the completion of the phase transfer of $PdCl_4^{2-}$. The aqueous layer was discarded and the organic layer was placed in a 250 mL round-bottom flask. Sodium *S*-dodecylthiosulfate (0.4 mmol) dissolved in 10 mL of 25% methanol was added to the organic layer. Additionally, TOAB (2.0 mmol) was added to the reaction flask. The reaction mixture was continuously stirred for 15 minutes. Afterwards, sodium borohydride ($NaBH_4$; 2.0 mmol) fully dissolved in 7 mL of nanopure water was rapidly delivered to the vigorously stirred reaction mixture. Consequently, a rapid color change (black) was observed indicating the formation of nanoparticles. Upon the completion of 3 hours of continuous stirring, the aqueous layer was removed by using a separatory funnel and the toluene was removed by vacuum. The resulting crude nanoparticles were suspended by using 25 mL of ethanol and poured down on a coarse funnel frit (F). The Pd nanoparticles were then further washed with ethanol, acetonitrile, and acetone. The resulting nanoparticles were dried in vacuum overnight at a pressure of 25 Psi.

Characterization of Pd Nanoparticles. Characterization of obtained PdNPs with proton NMR and UV-Vis spectroscopy can be found in our previous publication. Transmission electron microscope (TEM) images (Figure S1 and S2) were obtained with a JEOL 1200 EX II electron microscope operating a 90 keV. Samples were prepared by placing 25 μL of a Pd nanoparticle THF solution (~1 mg/ml) on a 200 mesh copper grid with formmvar film. Size distribution analysis of Pd nanoparticle core microscope images was executed with Scion Image Beta Release 2^{TM}. Background subtraction was done by Rolling Ball at a set radius of 25. Measurements options were done by Ellipse Major Axis. Thermo gravimetric analysis (TGA) was conducted using a TA instruments SDT Q600 with a flow rate of 100 mL/min of N_2 with heating from room temperature to 600 °C (Figure S3).



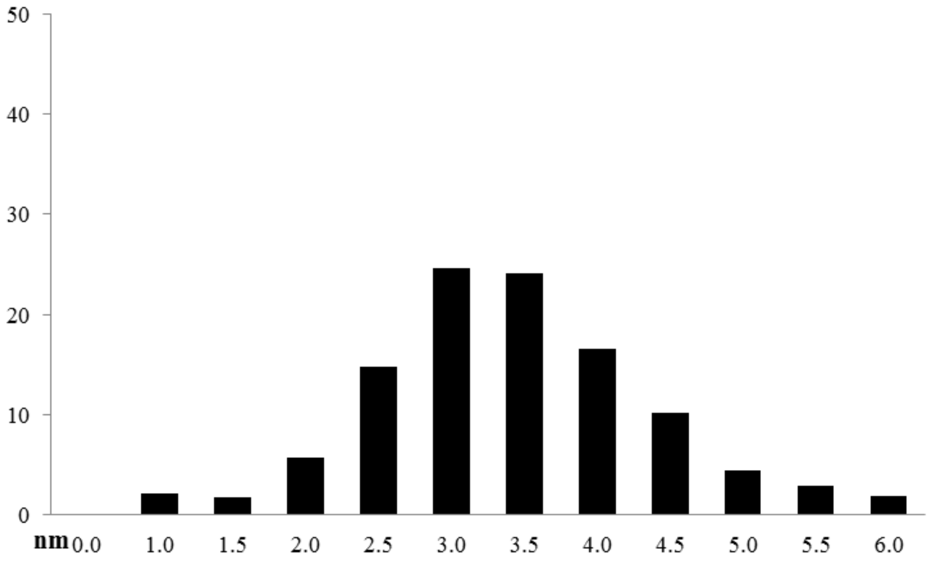
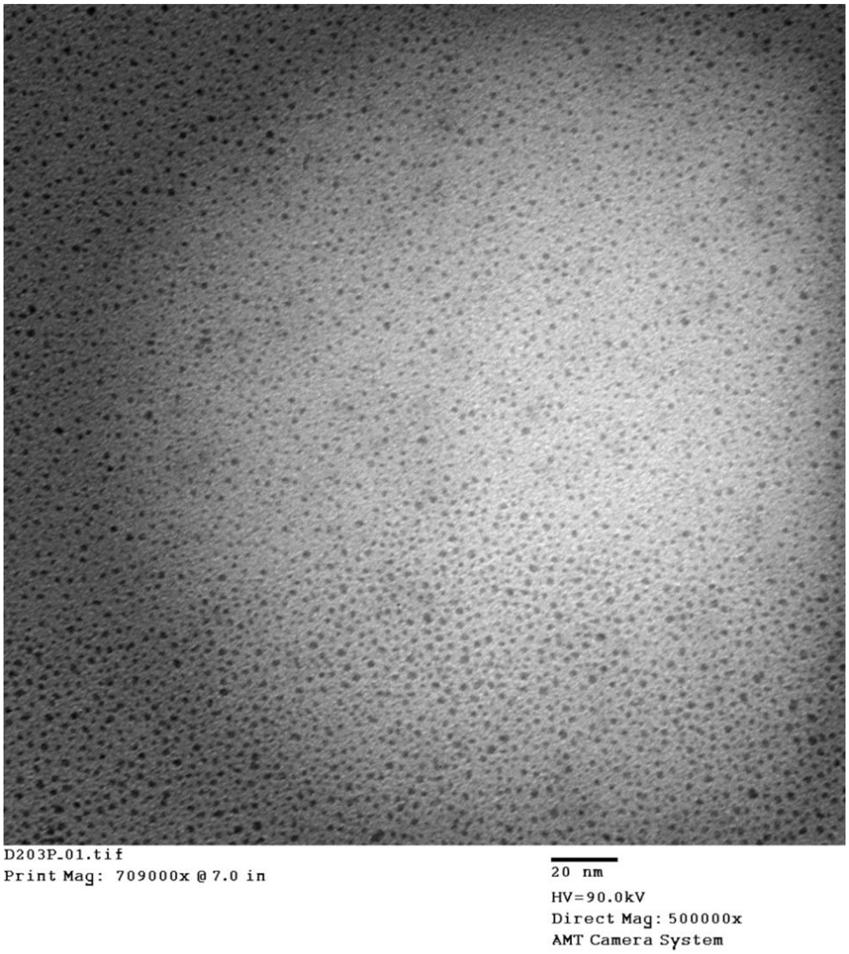


Figure S1. TEM image and histogram of $Pd_{1289}L_{164}$ showing an average core size of 3.38 ± 0.95 nm.



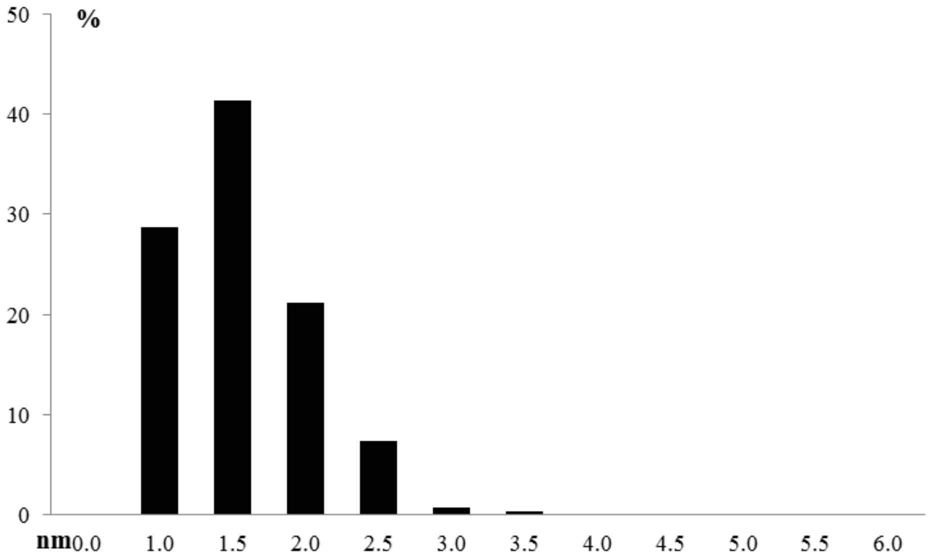


Figure S2. TEM image and histogram of $Pd_{116}L_{59}$ showing an average core size of 1.51 ± 0.46 nm.

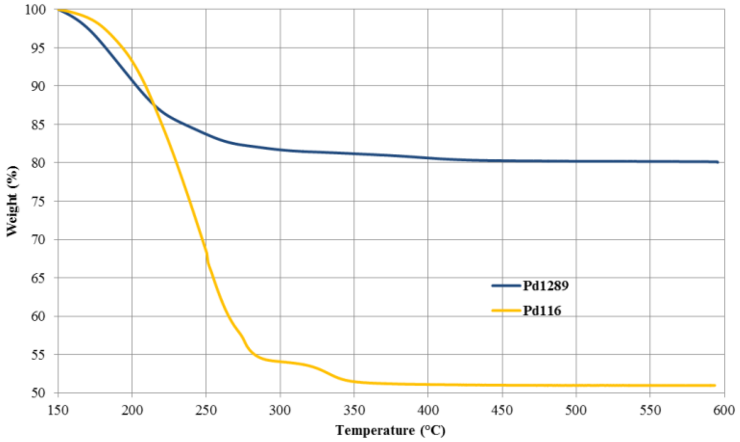
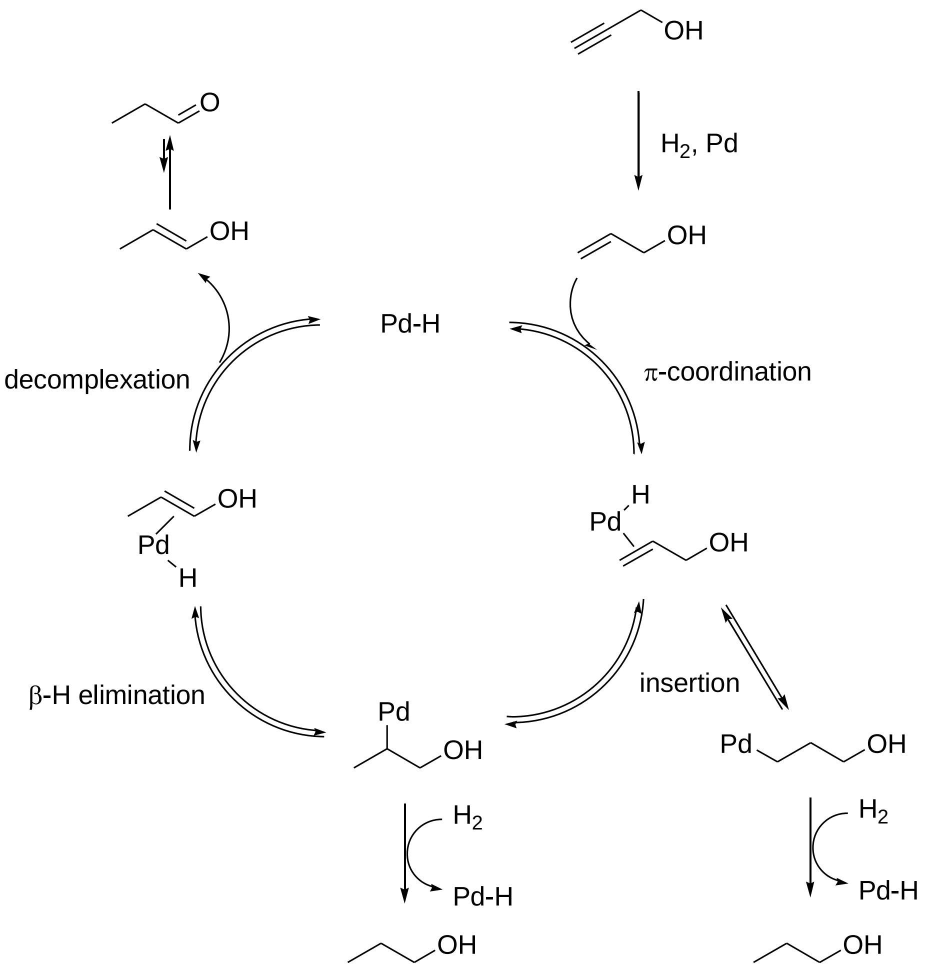


Figure S3. Thermogravimetric analysis of both $Pd_{1289}L_{164}$ and $Pd_{116}L_{59}$ indicating the volatilization of dodecanethiol ligands from 150 °C to 600 °C.



Scheme 1. The proposed mechanism of the tandem semi-hydrogenation/isomerization reaction.

Catalytic Semi-Hydrogenation/Isomerization Reactions. Pd nanoparticle catalyst (5 mol % Pd) was placed in a round-bottom flask of appropriate size to control the amount of H_2 gas. The nanoparticle was dissolved with 2.00 mL of $CDCl_3$ NMR solvent and the vessel was capped with a rubber septum. The solution was conditioned with H_2 gas for 10 minutes. After the source of H_2 gas was removed, 50 μL of the corresponding propargyl alcohol was injected into the stoppered flask. The reaction was placed into a water bath at the temperature indicated by the methods for continuous temperature and stirred continuously. Yields determined by NMR were calculated by the integration of distinguishable pairs of protons. TEM image of Pd nanoparticles after the catalytic reaction is obtained and shown in Figure S4. The results of catalytic reactions of 3-butyn-2-ol under various H_2 molar equivalents are shown in Figure S5.

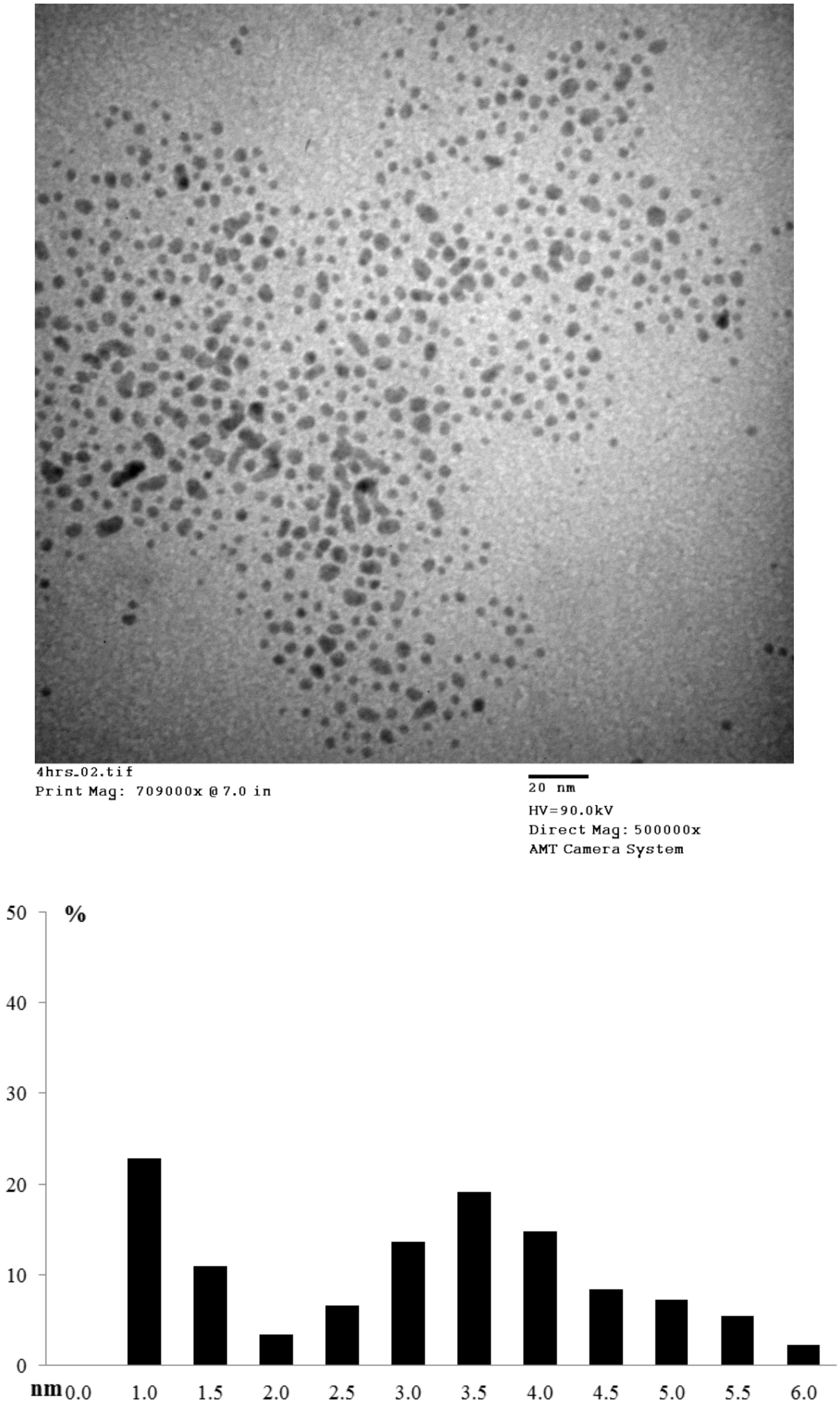


Figure S4. TEM image and histogram of $Pd_{1289}L_{164}$ after the 4 hour reaction time of entry 1 in Table 2.

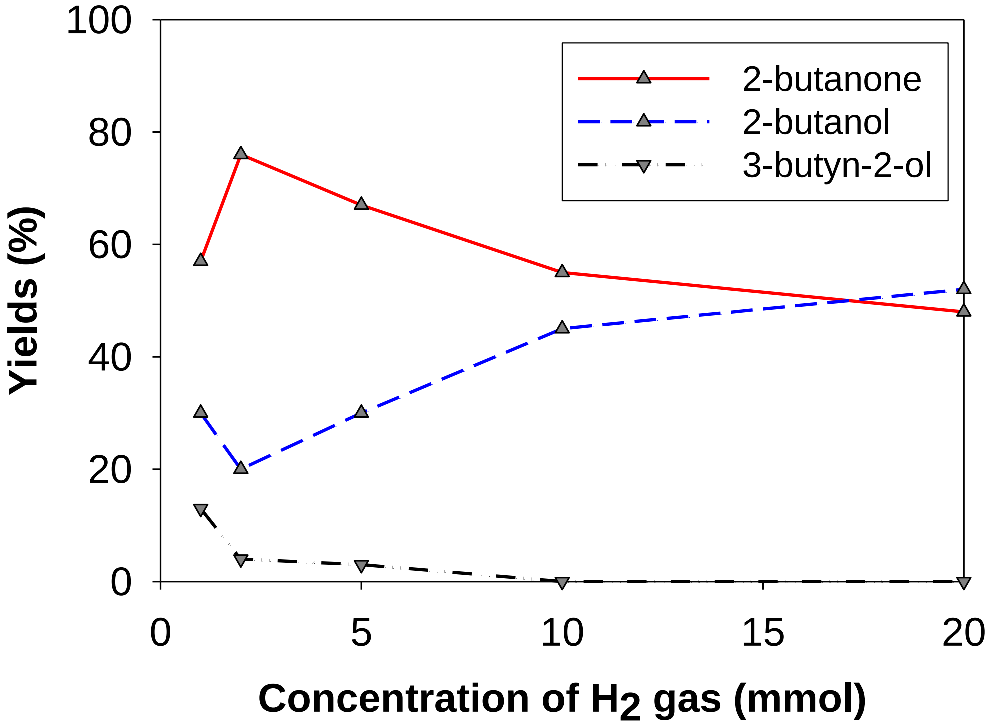


Figure S5. Effects of H_2 molar equivalents for the conversion of 3-butyn-2-ol.