Integrated Catalysis-Surface Science-Theory Approach to Understand Selectivity in the Hydrogenation of 1-Hexyne to 1-Hexene on PdAu Single-Atom Alloy Catalysts

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Table 1. Metal loading of the samples

Sample	Total metal loading	Pd/Au ratio
$Pd_{0.004}Au/SiO_2$	3.8 wt%	1/250
$Pd_{0.01}Au/SiO_2$	3.9 wt%	1/85
$Pd_{0.2}Au/SiO_2$	4.5 wt%	1/5

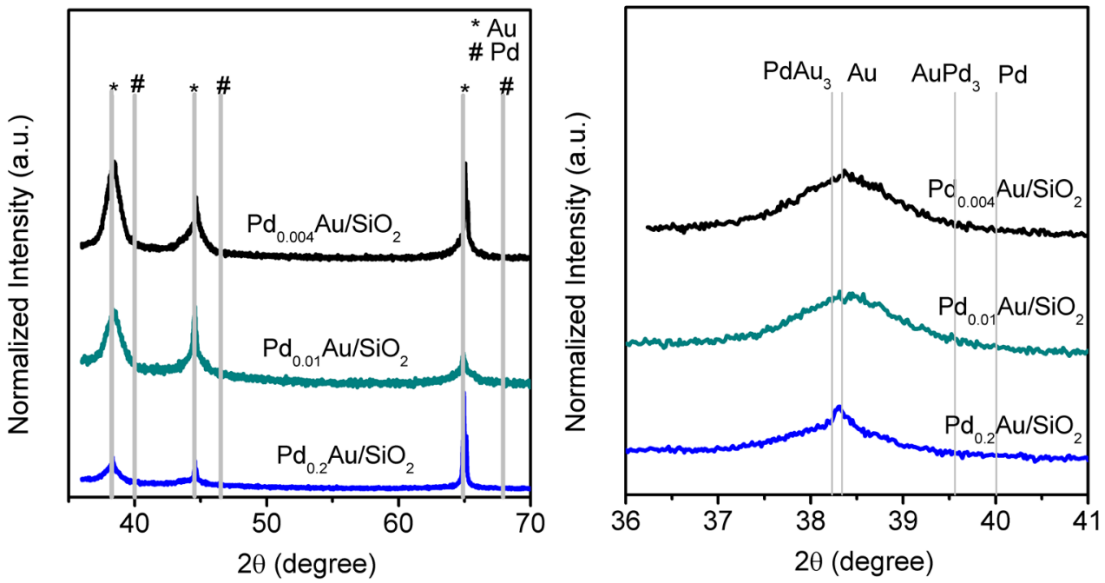

Figure S1. Powder XRD of PdAu samples with different Pd/Au ratios. The $Pd_{0.004}Au/SiO_2$ is the single-atom alloy (SAA) sample investigated in this paper.

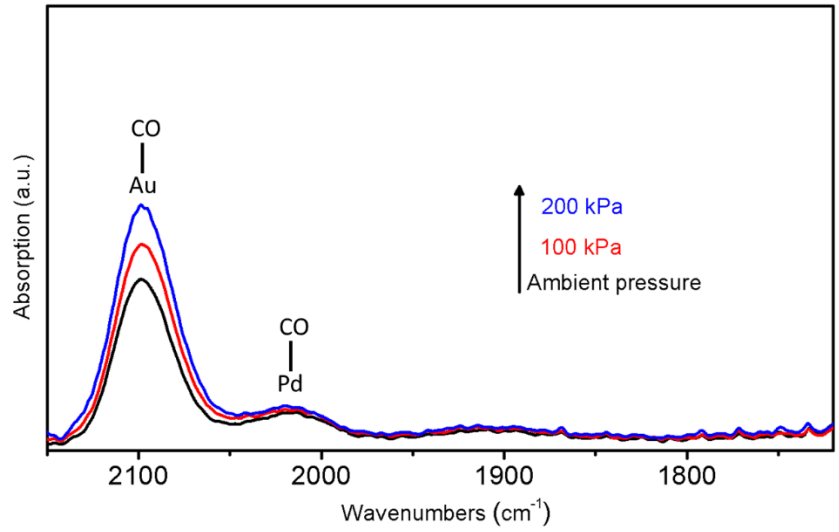

Figure S2. ATR-IR spectra of the CO stretch on unsupported $Pd_{0.004}Au$-SAA samples. Spectra were collected at 30 °C with different CO partial pressure in the gas phase. The bridge adsorbed CO typically appears at 1920 cm^{-1}, which is not observed on the PdAu-SAA sample.

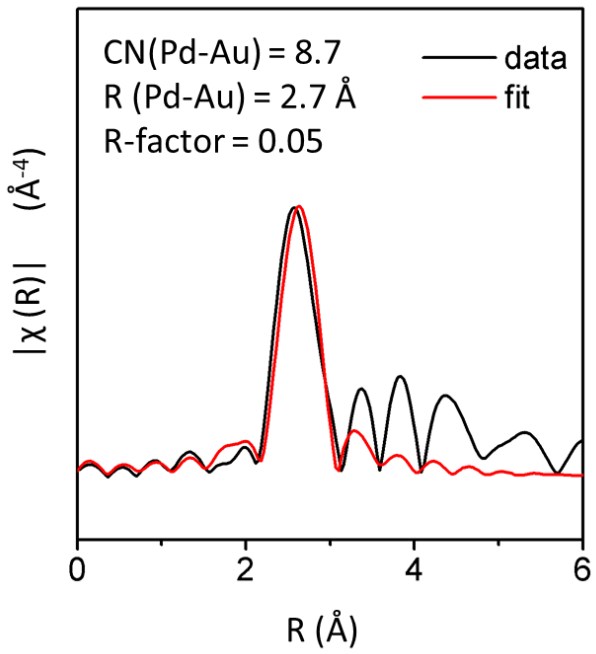

Figure S3. Fourier transform of EXAFS spectra of Pd K edge for the $Pd_{0.004}Au$-SAA/SiO_2 and the EXAFS modeling fitting results.

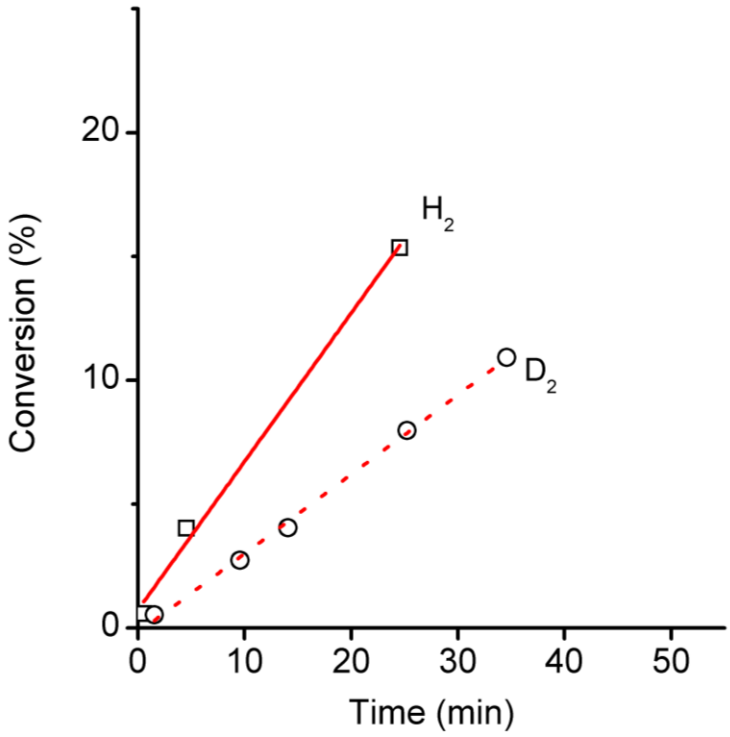

Figure S4. Kinetic Isotope Effect (KIE) measurements. Conversion vs. reaction time for 1-hexyne hydrogenation on $Pd_{0.004}Au/SiO_2$ catalysts. The initial rate is calculated from the slope of the conversion-time curve. Reaction conditions: 1% hexyne-ethanol solution, 5 bar H_2 or D_2, 600 rpm, 25 ^oC.

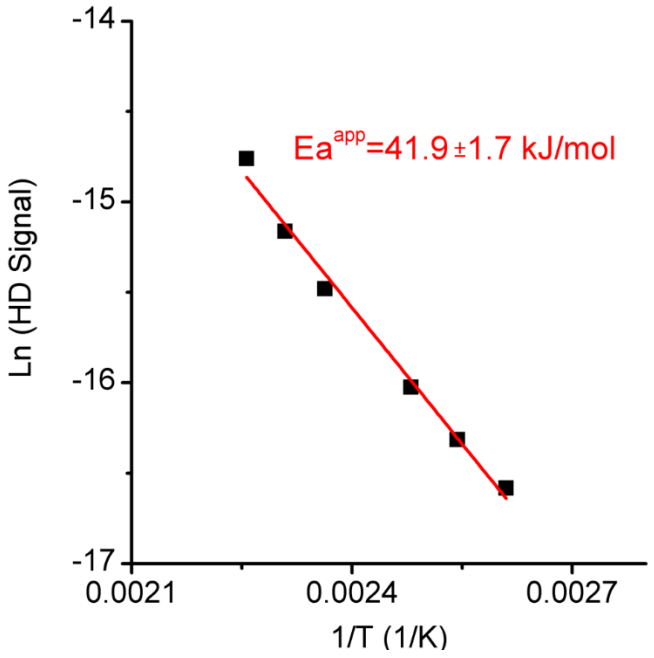

Figure S5. Arrhenius-type plot for H_2-D_2 exchange over $Pd_{0.004}Au$-SAA/SiO_2 catalyst.

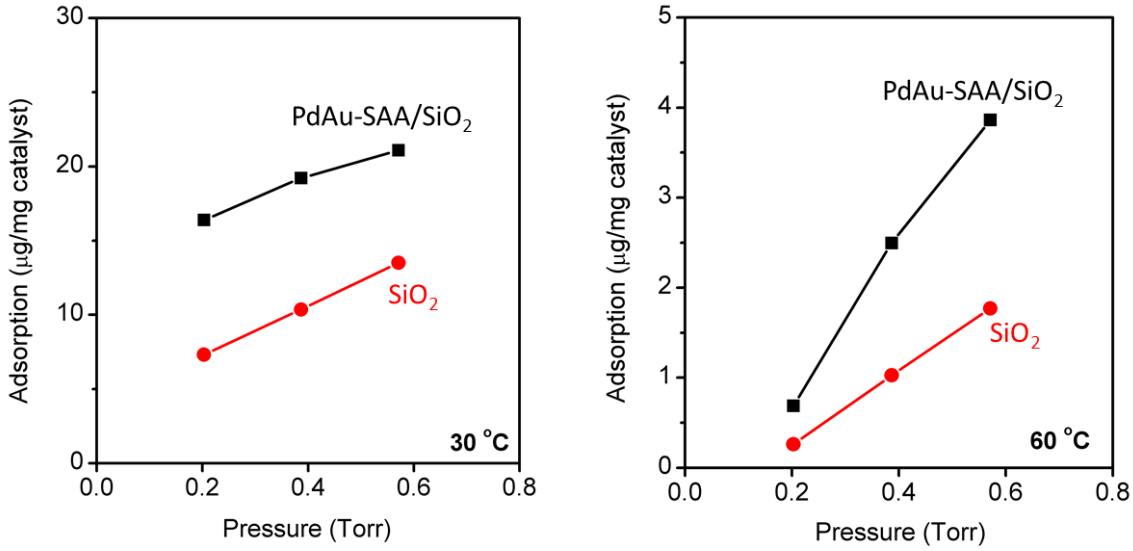

Figure S6. 1-hexyne adsorption isotherm at 30° and 60 °C with $Pd_{0.004}Au$-SAA/SiO_2.

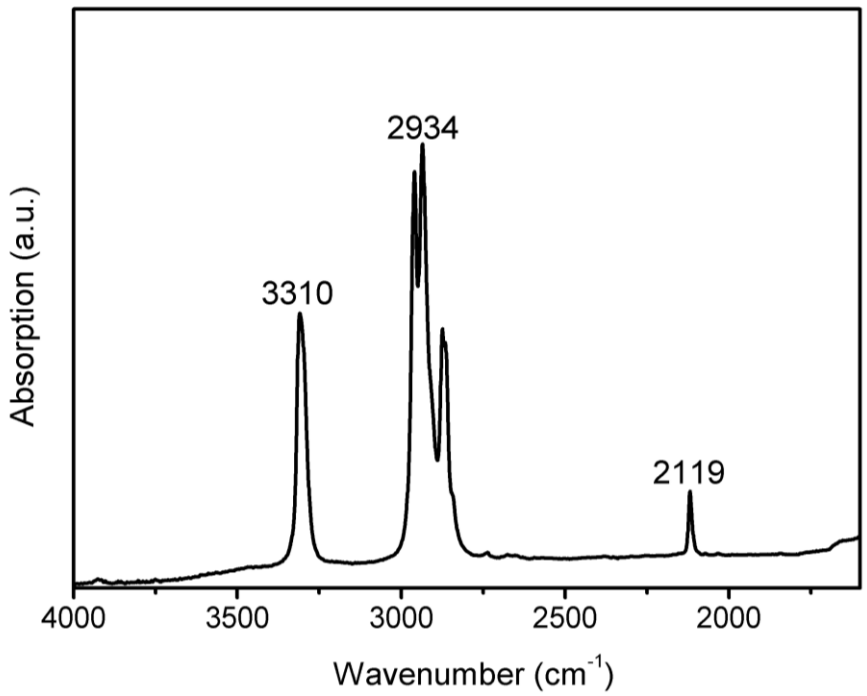

Figure S7. ATR-IR spectra of liquid 1-hexyne in ATR cell without catalyst.

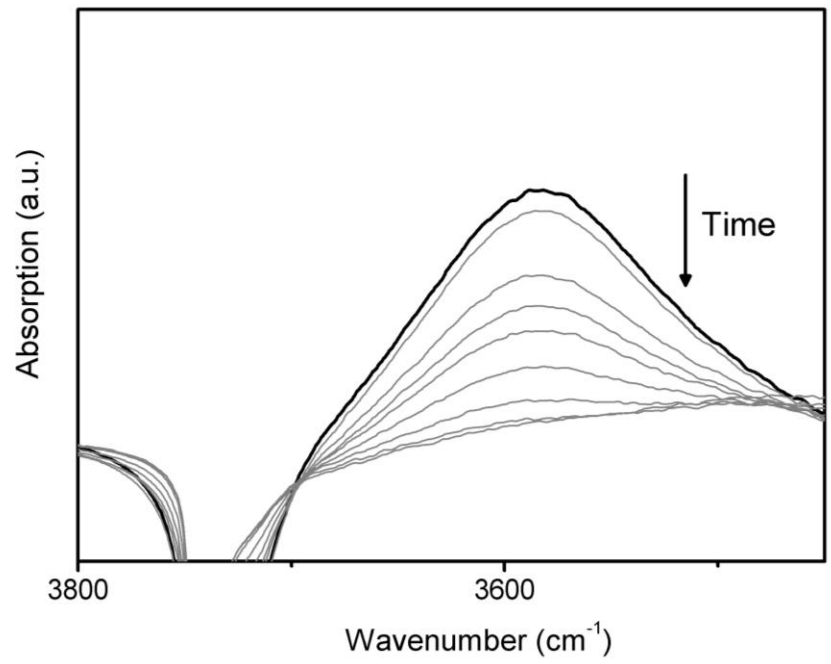

Figure S8. DRIFT spectra between 3800 and 3450 cm^{-1} recorded when 1-hexyne and H_2 are carried over $Pd_{0.004}Au$-SAA/SiO_2 at room temperature.

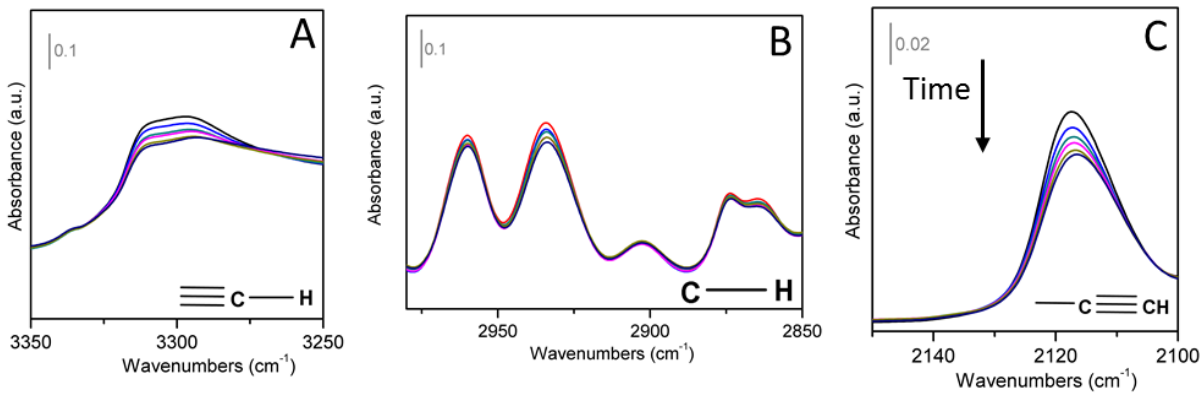

Figure S9. ATR-IR collected with 1-hexyne and 120 psi H_2 applied on $Pd_{0.004}Au$-SAA in the batch mode at room temperature.

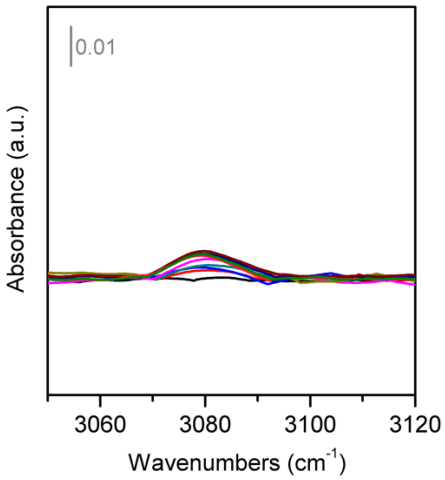

Figure S10. Peak between 3070 and 3100 cm^{-1}. ATR-IR spectra were collected with 1-hexyne and 120 psi H_2 applied on $Pd_{0.004}Au$-SAA catalysts in the batch mode at room temperature.

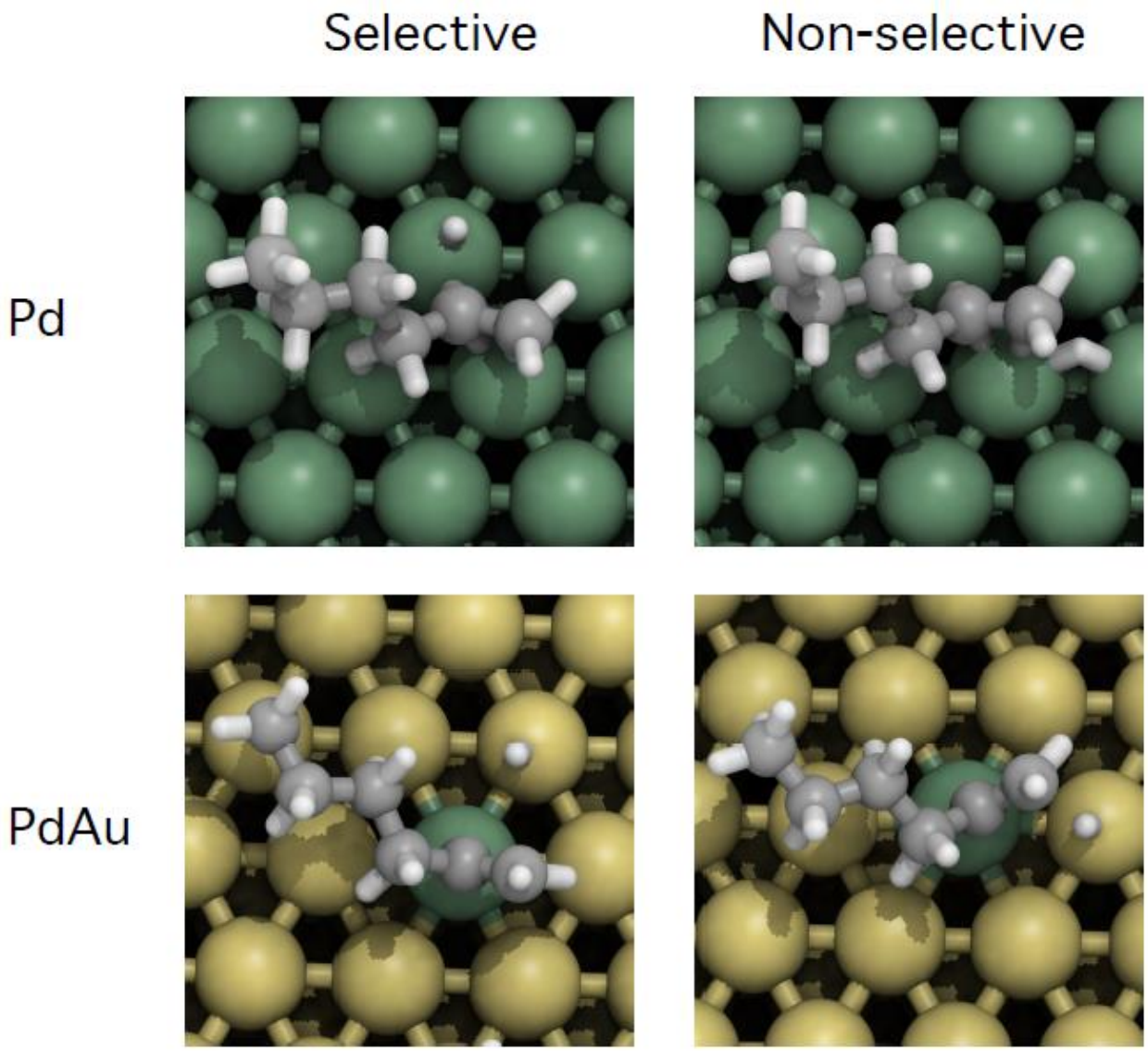

Figure S11. Transition state geometries for the selective (formation of hexene) and non-selective (over-hydrogenation of the terminal C) pathways on Pd(111) and PdAu(111) SAA.

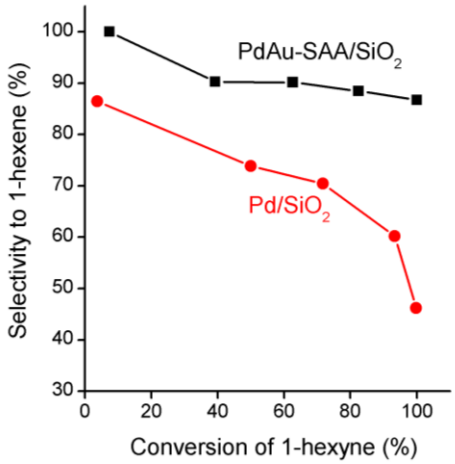

Figure S12. Time-resolved batch reactor data for the hydrogenation of 1-hexyne over $Pd_{0.004}Au$ - SAA catalysts vs Pd.

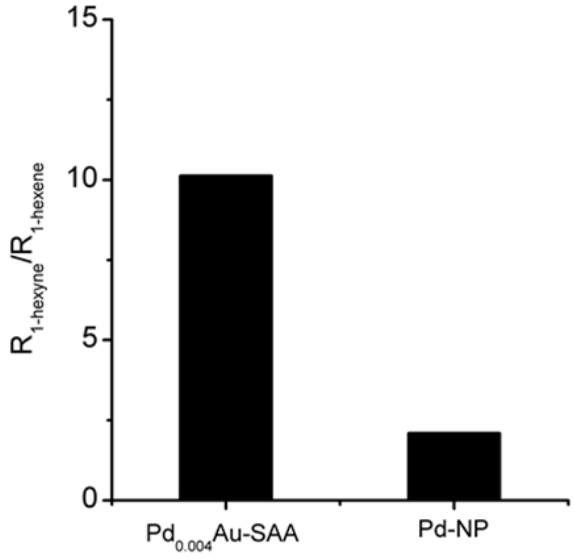

Figure S13. Ratio between the conversion rate of 1-hexyne and 1-hexene in hydrogenation reaction conditions. Reaction conditions: 1% hexyne-ethanol or hexene-ethanol solution, 5 bar H_2, 25 ^oC.