

SUPPLEMENTARY INFORMATION

Co-generation of palladium nanoparticle and phosphate inside a metal-organic framework for hydrogenation catalyst

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Supporting data

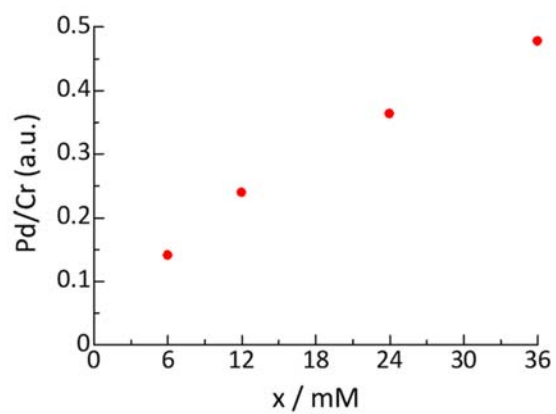


Figure S1. Pd/Cr atomic ratios of MOF composites after treating with Pd(OAc)₂ solution (in acetone) with different concentrations.

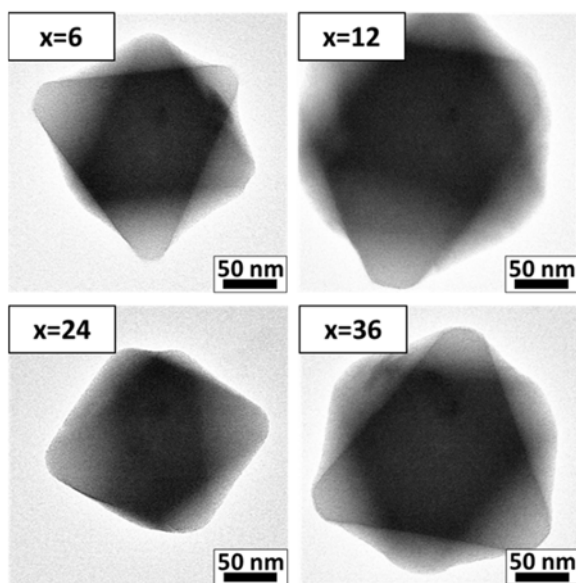


Figure S2. TEM images of MOF composites after treating with the acetone solution of Pd(OAc)₂ with different concentrations (x mM).

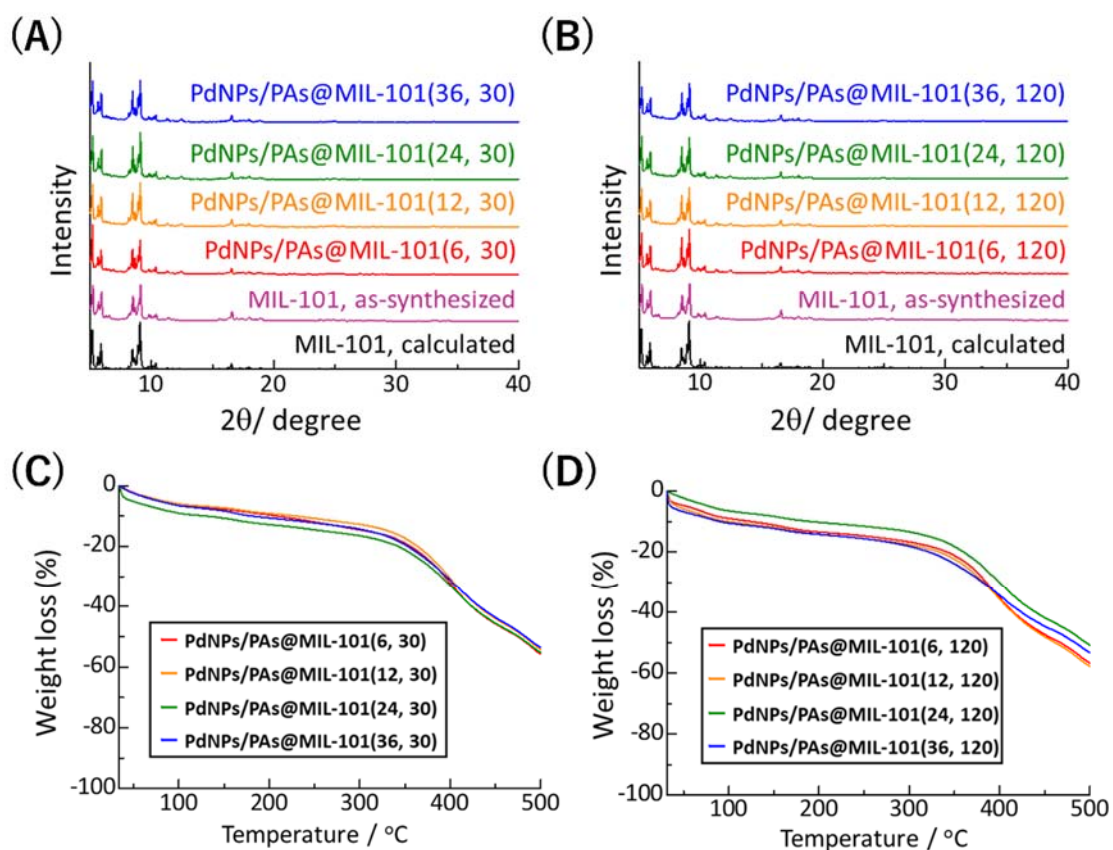


Figure S3. XRD diffraction data of (A) PdNPs/PAs@MIL-101(x, 30) and (B) PdNPs/PAs@MIL-101(x, 120)(x = 6, 12, 24 and 36). TG profiles of (C) PdNPs/PAs@MIL-101(x, 30) and (D) PdNPs/PAs@MIL-101(x, 120)(x = 6, 12, 24 and 36).

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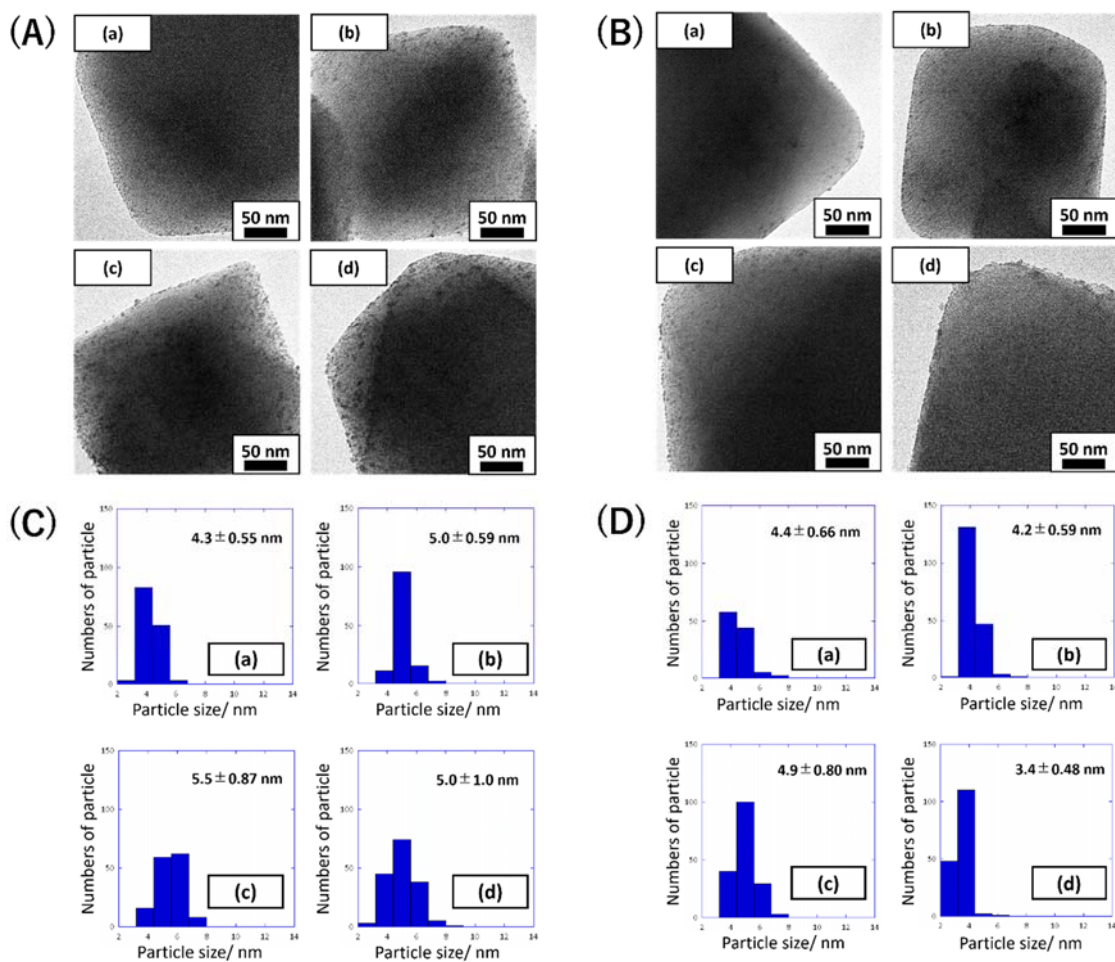


Figure S4. TEM images of (A) PdNPs/PAs@MIL-101(x, 30) and (B) PdNPs/PAs@MIL-101(x, 120): (a) x=6, (b) x=12, (c) x=24, (d) x=36. PdNP size distribution diagrams of (C) PdNPs/PAs@MIL-101(x, 30) and (D) PdNPs/PAs@MIL-101(x, 120) : (a) x=6, (b) x=12, (c) x=24, (d) x=36.

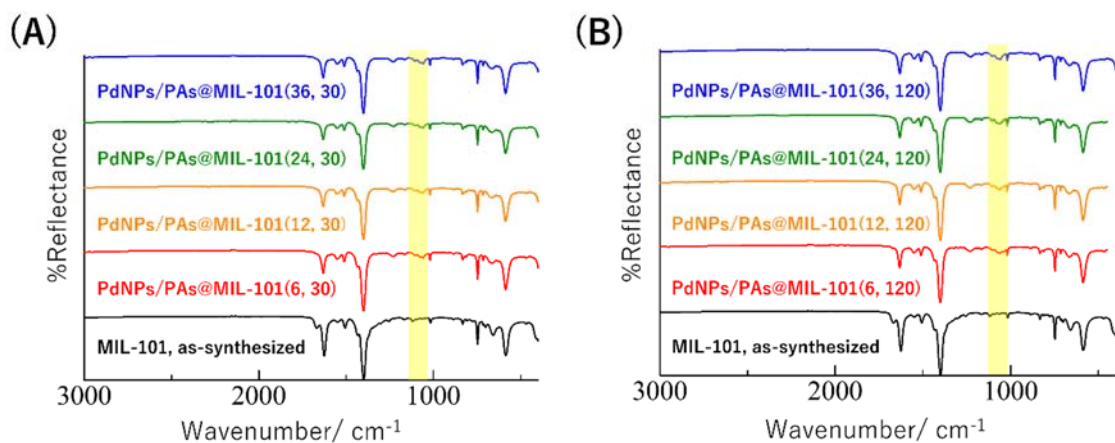


Figure S5. IR spectra of (A) PdNPs/PAs@MIL-101(x, 30)(x = 6, 12, 24 and 36) and (B) PdNPs/PAs@MIL-101(x, 120)(x = 6, 12, 24 and 36). The peaks corresponding to P=O stretching vibration were highlighted with yellow.

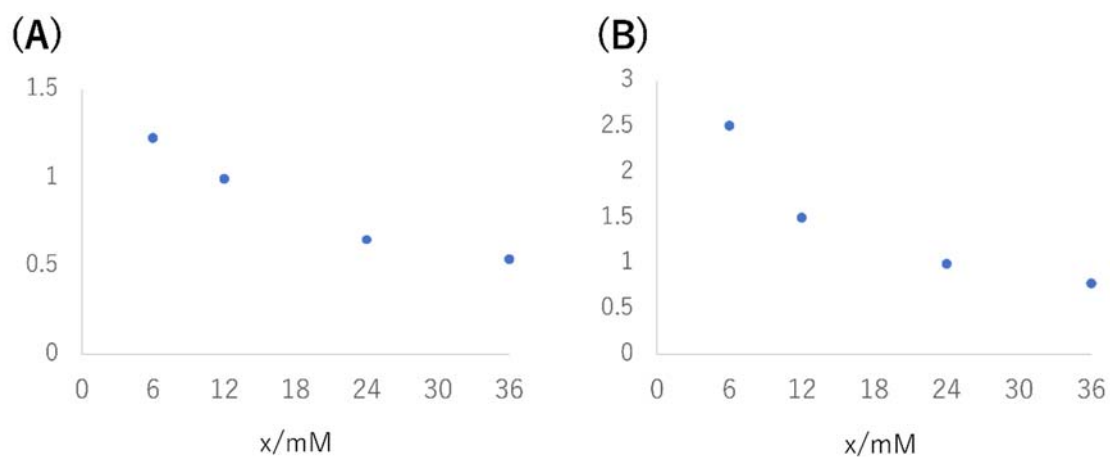


Figure S6. Atomic ratio of P/Pd in (A) PdNPs/PAs@MIL-101(x, 30)(x = 6, 12, 24 and 36) and (B) PdNPs/PAs@MIL-101(x, 120)(x = 6, 12, 24 and 36).

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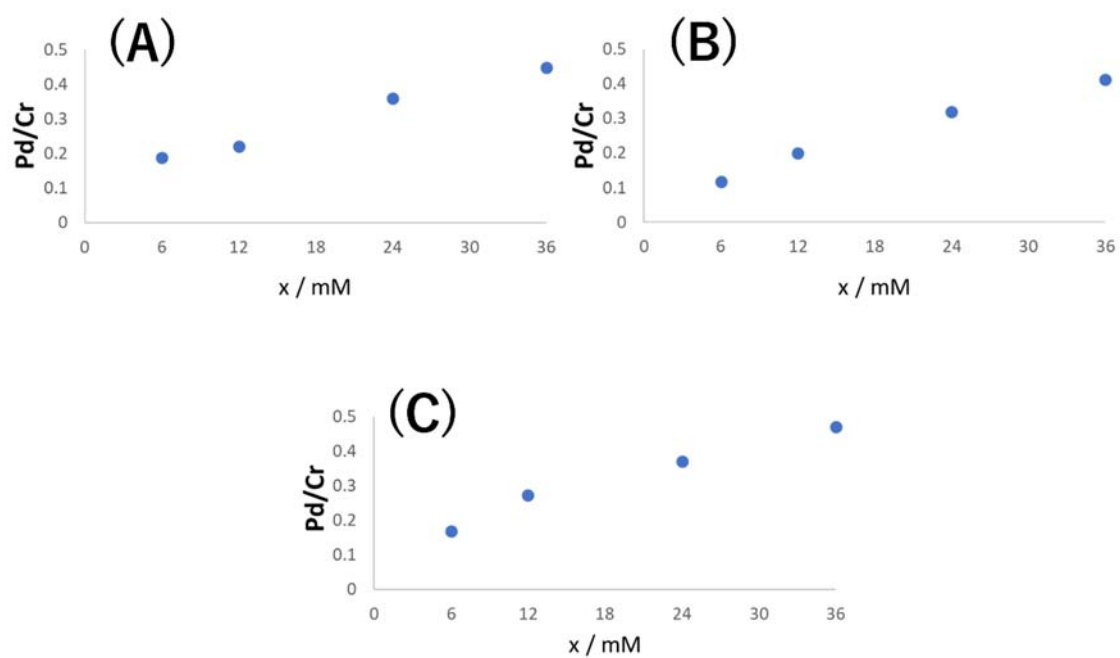


Figure S7. Atomic ratio of Pd/Cr in (A) PdNPs/PAs@MIL-101(x, 30)(x = 6, 12, 24 and 36), (B) PdNPs/PAs@MIL-101(x, 120)(x = 6, 12, 24 and 36) and (C) PdNPs/PAs@MIL-101(x, 480)(x = 6, 12, 24 and 36)

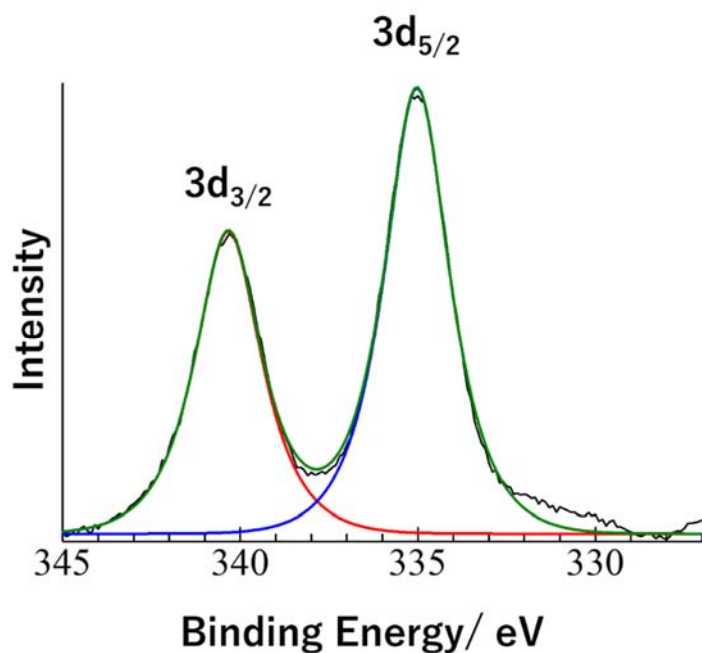


Figure S8. Pd 3d peaks in XPS spectra of PdNPs/PAs@MIL-101 (24, 480). Fitted curves to $3d_{3/2}$, $3d_{5/2}$ and $3d_{3/2}+3d_{5/2}$ were colored with red, blue and green, respectively.

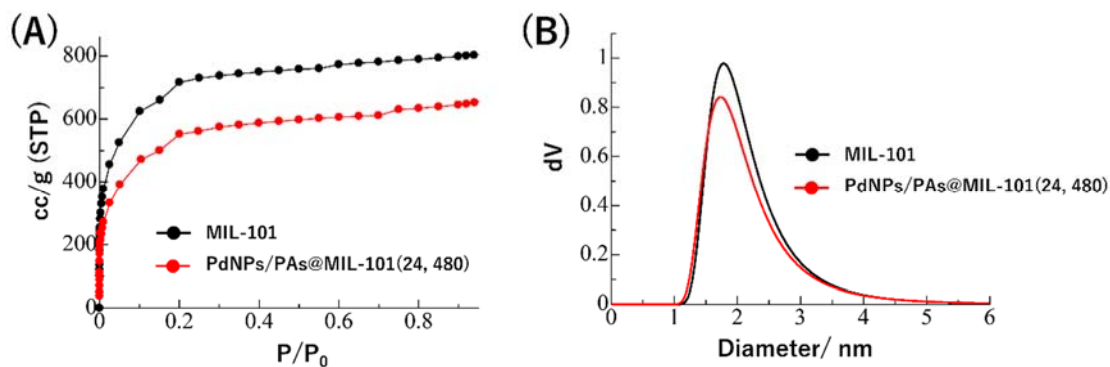
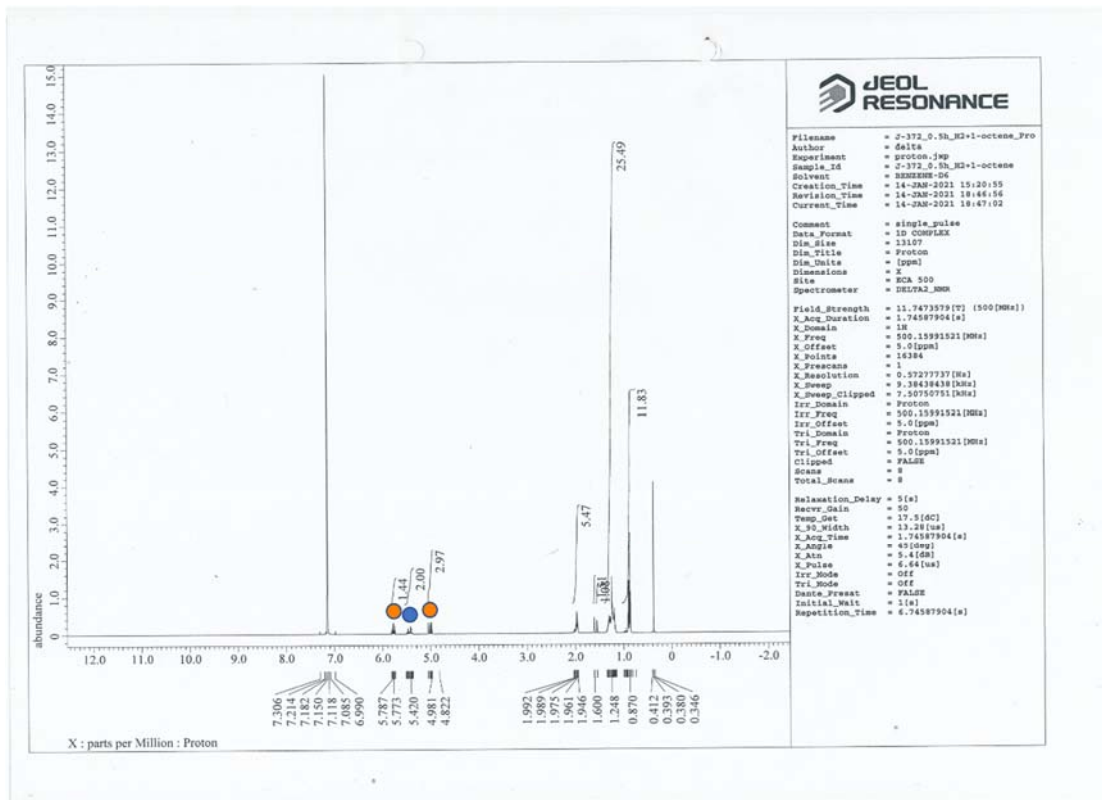


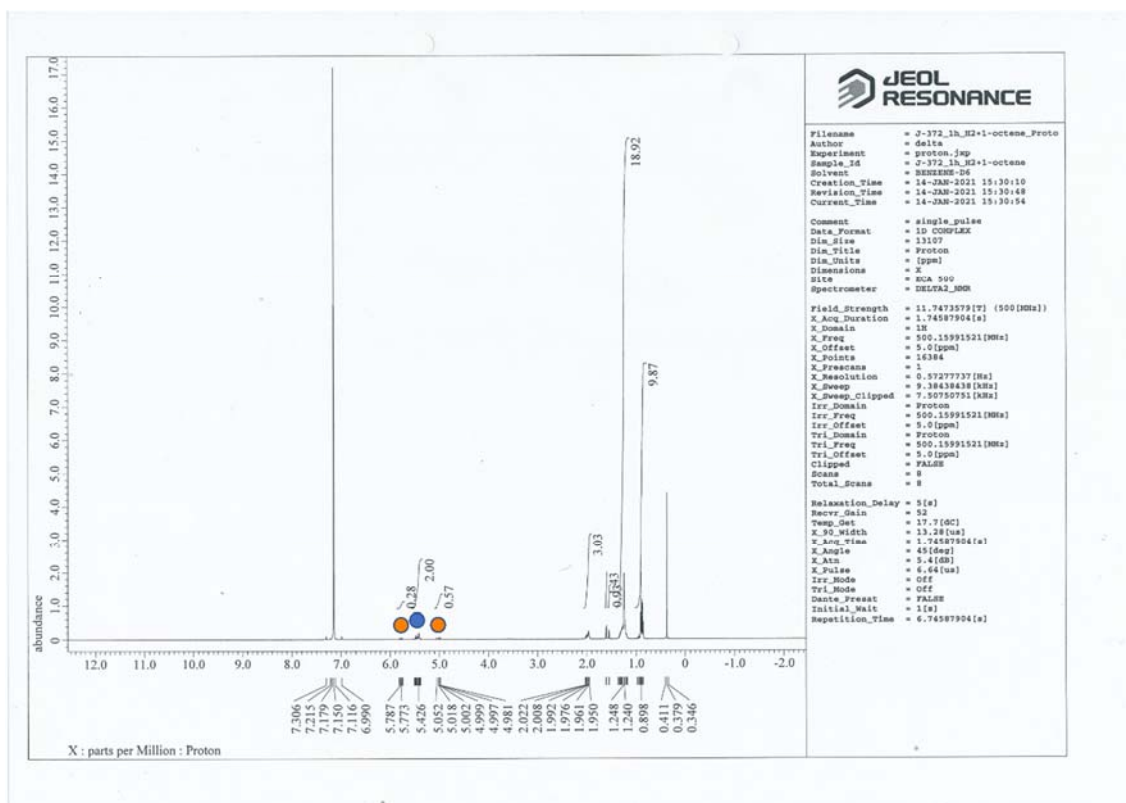
Figure S9. (A) N_2 gas adsorption of MIL-101 and PdNPs/PAs@MIL-101(24, 480) at 77 K. BET surface areas for MIL-101 and PdNPs/PAs@MIL-101(24, 480) were $2082 \text{ m}^2/\text{g}$ and $1872 \text{ m}^2/\text{g}$, respectively. (B) Pore size distributions of MIL-101 and PdNPs/PAs@MIL-101(24, 480) based on DA method.

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(A)

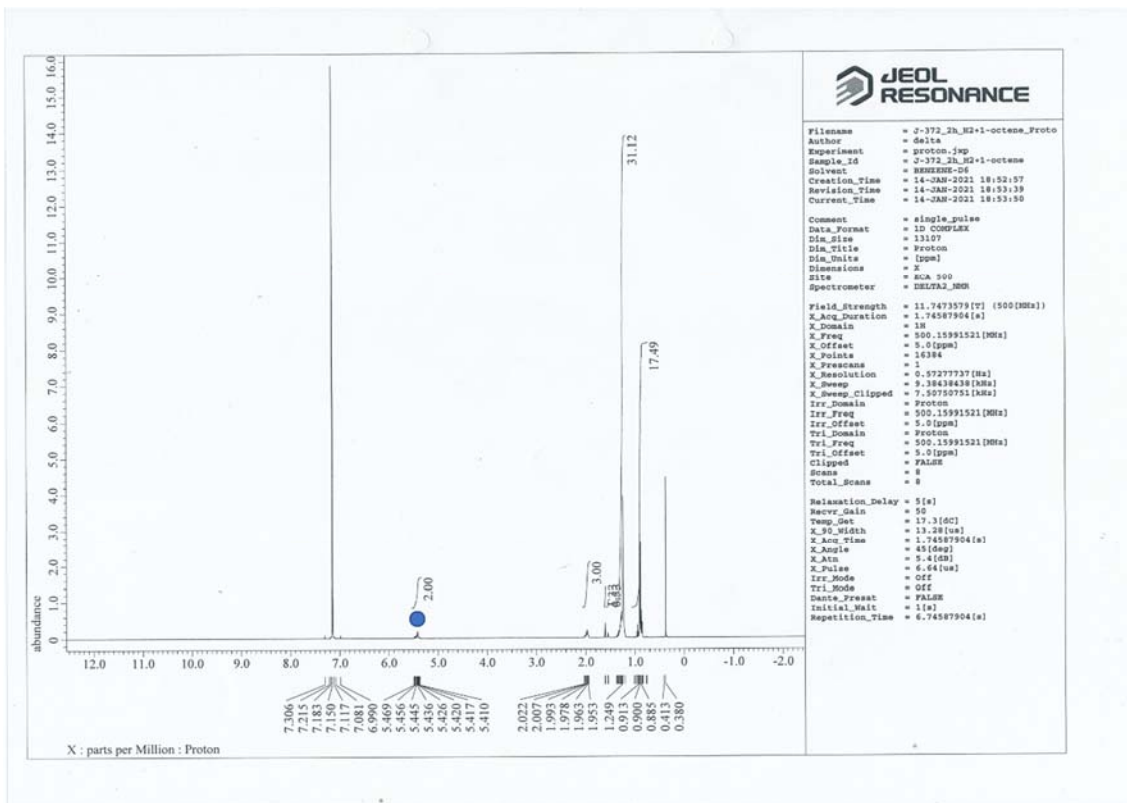


(B)

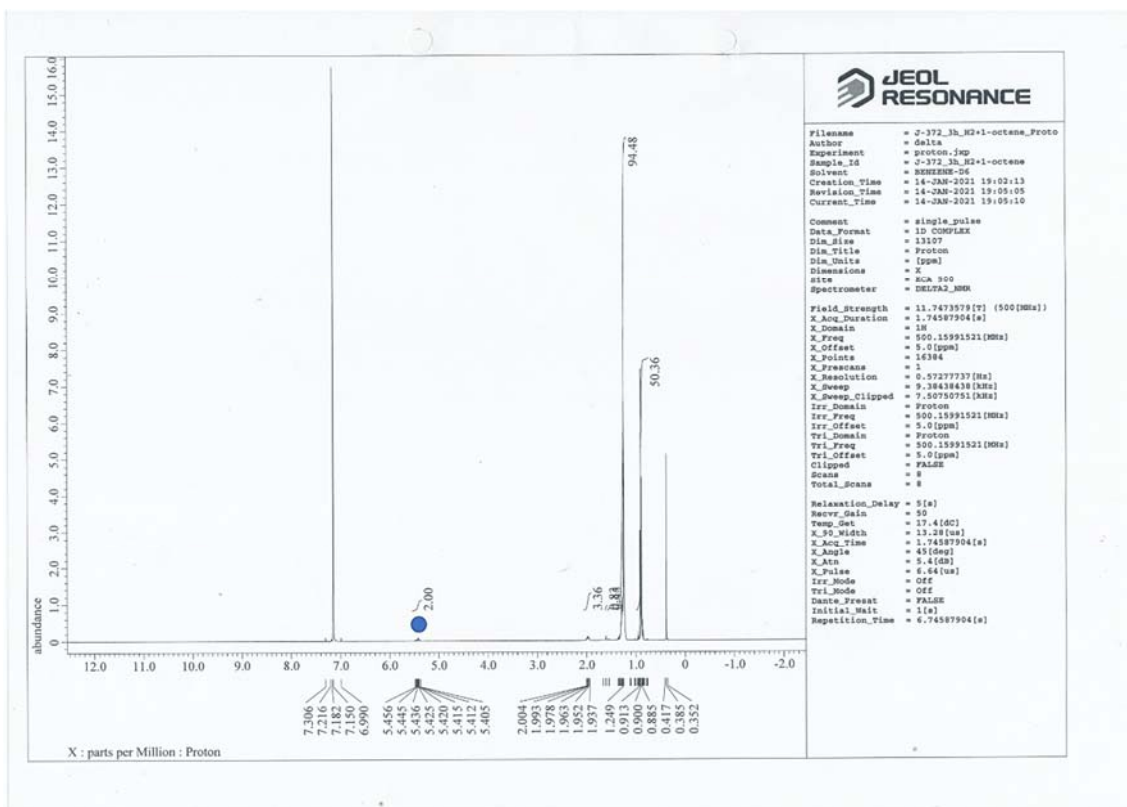


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(C)



(D)



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(E)

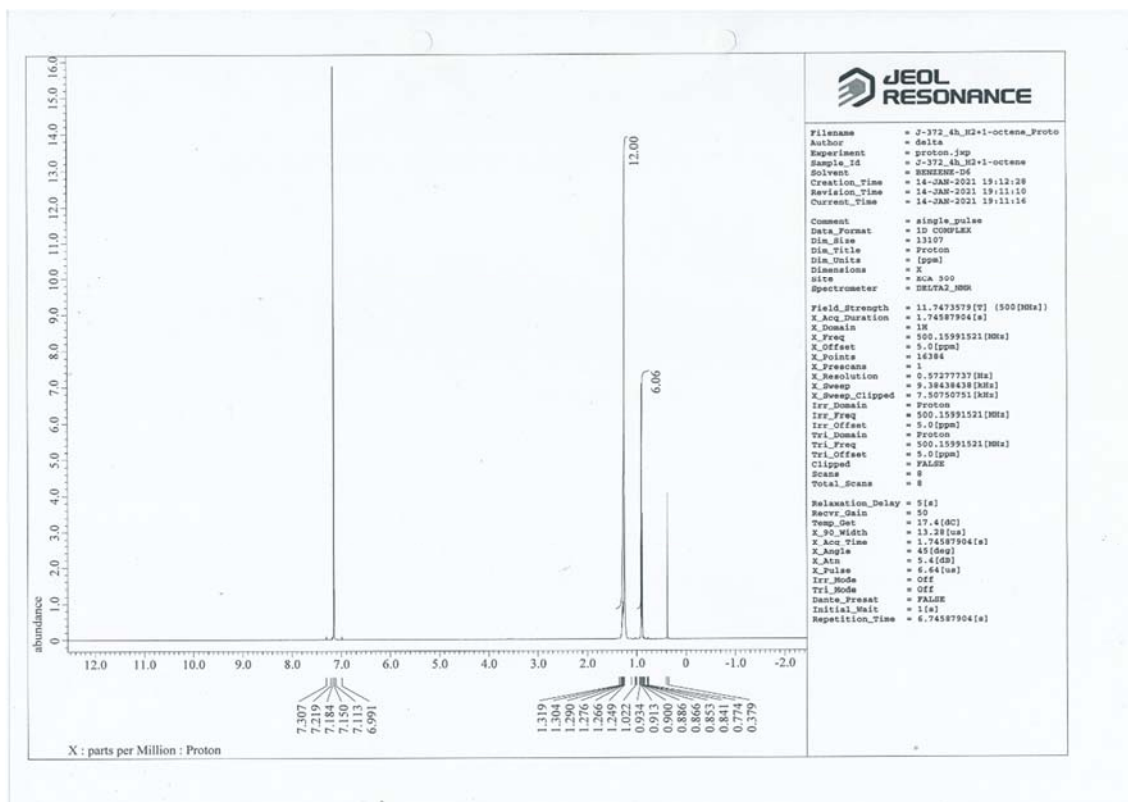
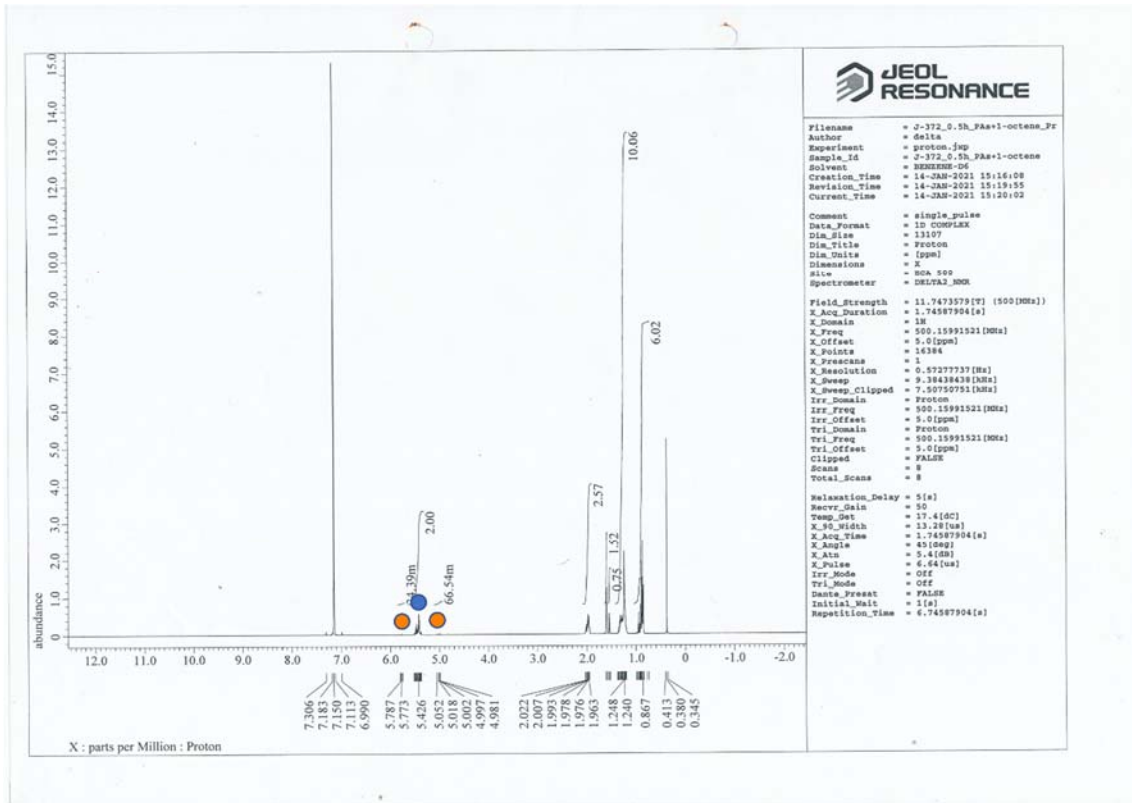


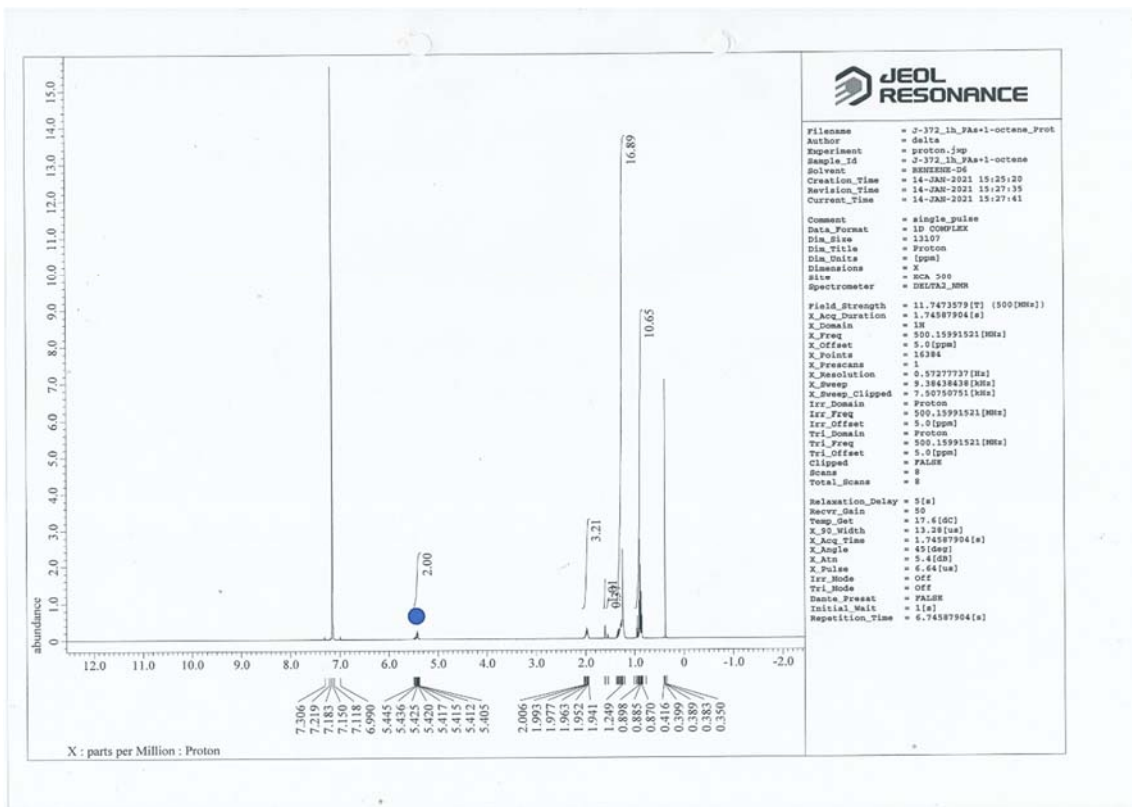
Figure S10. ¹H NMR charts of the reaction solutions after (A) 30 mins, (B) 1 hour, (C) 2 hours, (D) 3 hours and (E) 4 hours for the hydrogenation of 1-octene in the presence of PdNPs@MIL-101([Pd] 0.04 mol%). The peaks corresponding to the alkene protons of 1-octene and 2-octene were marked with orange and blue circles, respectively.

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(A)

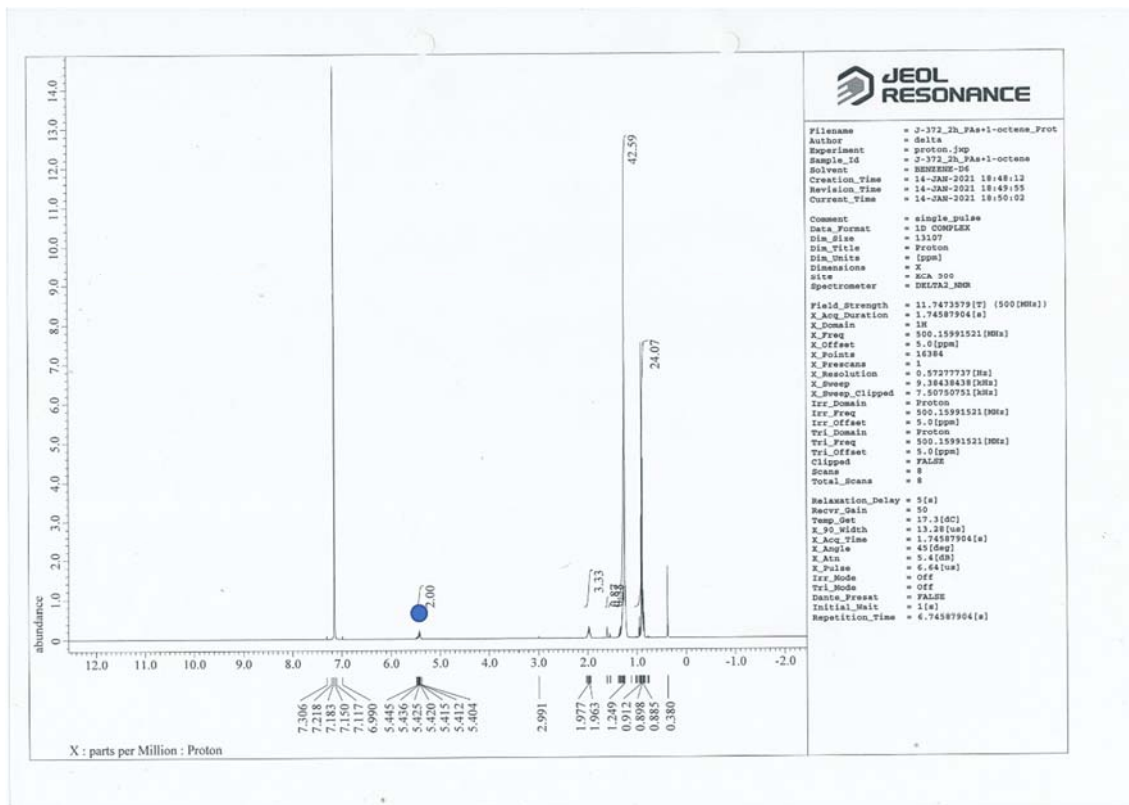


(B)

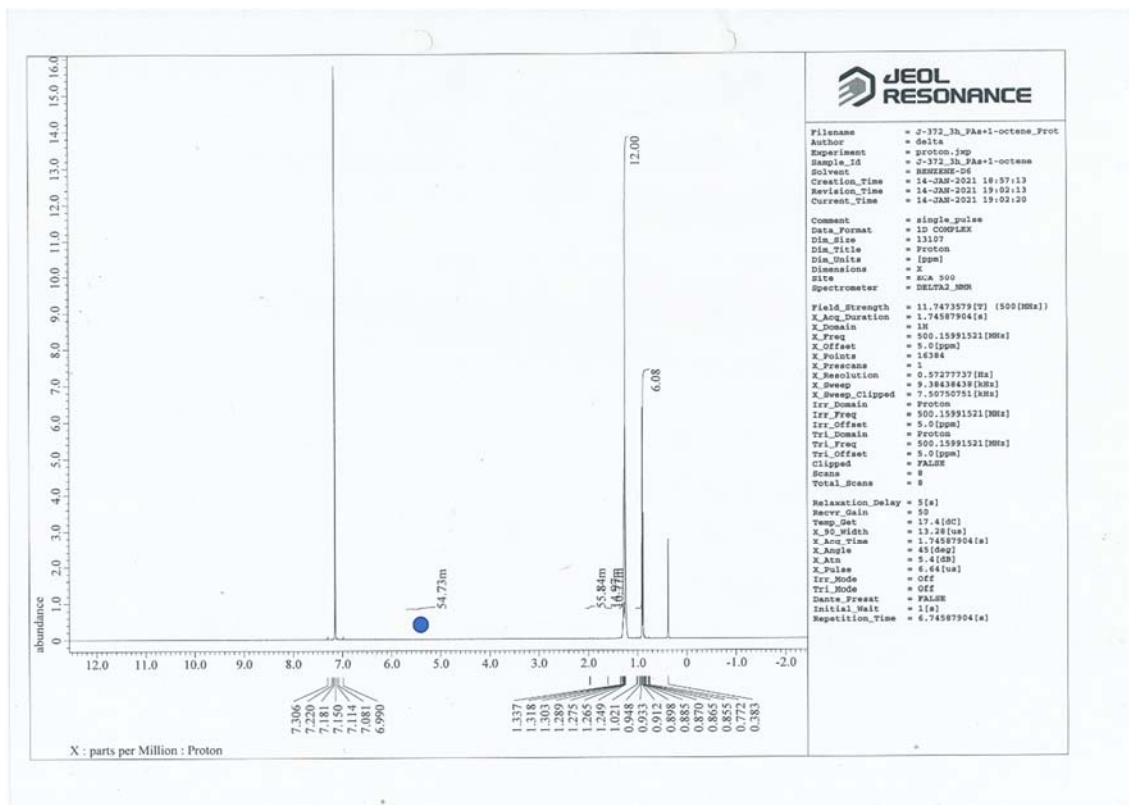


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(C)



(D)



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(E)

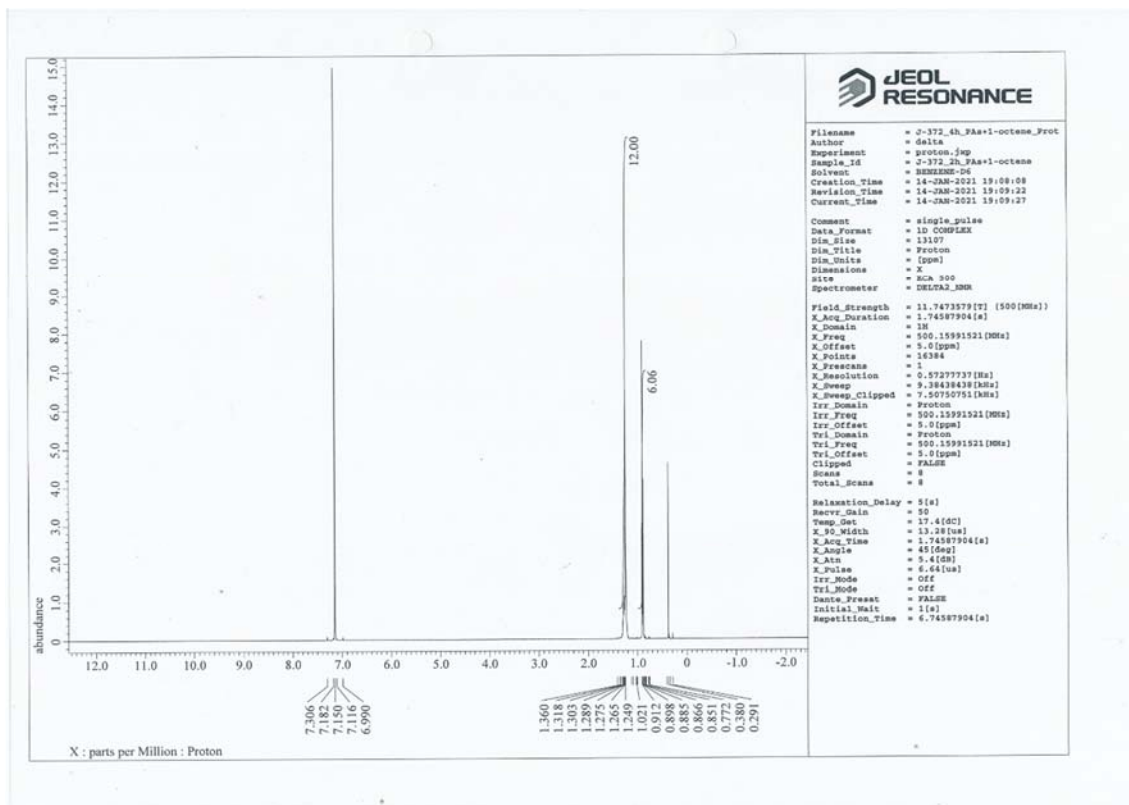


Figure S11. ¹H NMR charts of the reaction solutions after (A) 30 mins, (B) 1 hour, (C) 2 hours, (D) 3 hours and (E) 4 hours for the hydrogenation of 1-octene in the presence of PdNPs/PAs@MIL-101(24, 480) ([Pd] 0.04 mol%). The peaks corresponding to the alkene protons of 1-octene and 2-octene were marked with orange and blue circles, respectively.

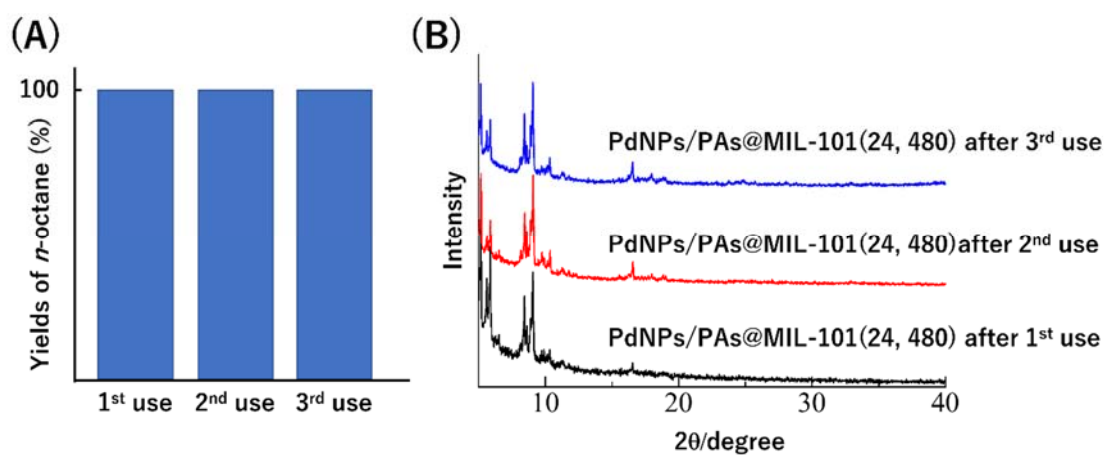


Figure S12. (A) Recycling of PdNPs/PAs@MIL-101(24, 480) in the hydrogenation reaction of 1-octene. (B) XRD patterns of PdNPs/PAs@MIL-101(24, 480) after recycling.

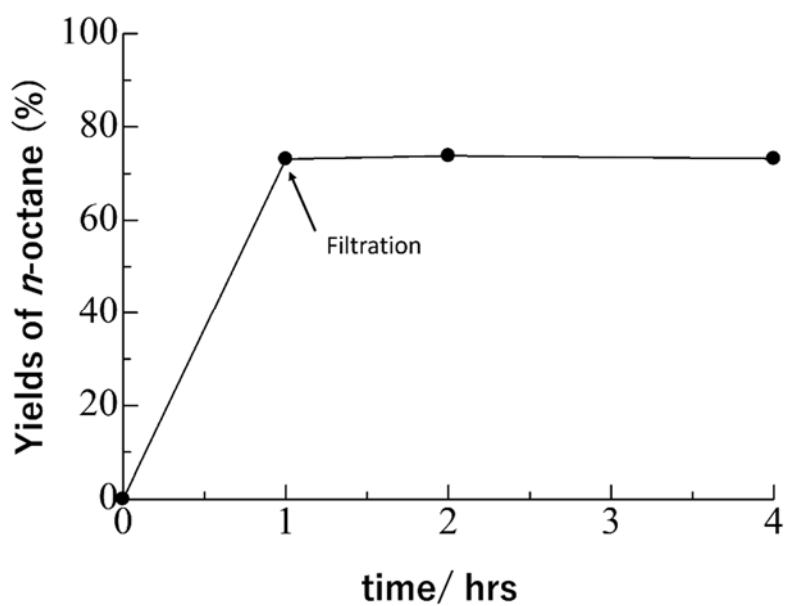


Figure S13. Filtration test in the hydration reaction with 1-octene with PdNPs/PAs@MIL-101(24, 480).

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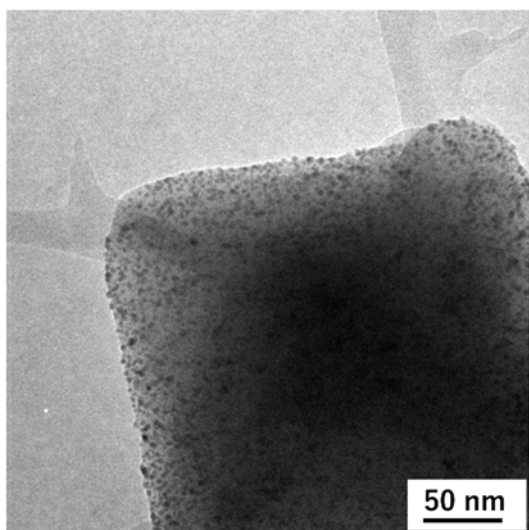


Figure S14. TEM image of PdNPs/PAs@MIL-101(24, 480) after use as catalyst.