Supporting Information

Mechanochemical Solid-State Synthesis of Pd-Based Catalysts with Tunable Size Effects for Suzuki–Miyaura Coupling Reaction

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Preparation of pure support

Preparation of bare supports (Al_2O_3, SiO_2, or TiO_2) followed the procedure reported by Poyraz et al [1]. 10 g of pluronic P-123 and 20 g of titania or silica or alumina precursor (titanium isopropoxide or tetraethyl orthosilicate or aluminum hydroxide) was dissolved into butanol (0.66 moles). The solution was stirred until fully dissolved, HNO3 (0.15 moles) was added to the solution and stirred overnight. The solvent was removed by heating the resulting gel at 120 ℃ for 4 hours. The obtained precipitate was washed with ethanol 4 times and dried at 80 ℃ overnight. The resulting powder was calcined at 450 ℃ for 4 hours.

Catalyst characterization techniques

The amount of palladium in the overall catalysts was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using the Thermo iCAP 6500 ICP-OES and Shimadzu ICPE-9820. The crystal structures of the catalysts were determined by powder X-ray diffraction (p-XRD) collected using a Rigaku MiniFlex 600 diffractometer with a Cu Kα X-ray source (λ = 0.154 nm). The diffractometer's operating conditions were 40 mA and 40 kV. Analysis of the catalyst's surface area, pore sizes, and pore volumes was carried out in a Micromeritics Tristar Porosimeter by analyzing N2 adsorption-desorption isotherms at -196.15 °C using the BET and BJH models. Fourier-transform infrared spectroscopy (FTIR) was used to monitor the support integrity upon deposition of different metal loadings. The analysis was performed in transmission mode with 32 scans at a resolution of 4 cm-1 in an ambient range of 400 to 4000 cm-1. RAMAN spectroscopy was used to verify the interaction between the support and Pd. Raman spectra were collected using Raman Micro200 (Perkin Elmer, USA)

with a laser wavelength of 750 nm. Thermo-gravimetric analysis (TGA) was used to evaluate the thermal stability of the catalysts, and the thermal profiles were analysed from 25 to 1000 °C, at a 10 ℃/min ramping rate in an air flow system. The Ultraviolet and Visible Diffuse Reflectance Spectrophotometry (UV–Vis DRS) was scanned with Shimadzu UV-2450 between 250 and 800 nm with a speed of 0.5 nm/s using BaSO4 as a reference. A scanning electron microscope (SEM) was used to determine the surface morphology, TESCAN with Vega TC software was utilized for the analysis. From the same instrument, energy-dispersive X-ray spectroscopy (EDX) was obtained to determine the percentages of the metal components in the overall catalysts. High-resolution transmission electron microscopy (HR-TEM) images were obtained to determine the distribution of particles for the measurement of the particle sizes of the nanoparticles and for defining the surface morphology. The synthesized catalysts were analysed using a Joel-Jem 2100F HR-TEM operating at a voltage of 200 kV. The 1H NMR spectra of the product(s) of the Suzuki−Miyaura coupling reaction were obtained using Bruker Topspin 500 MHz spectroscopy.

Zeta potential, 10 - 15 mg of a sample was dispersed in 400-500 mL deionised water to determine the surface charge properties and point of zero charge (PZC) on a Zetasizer Ver. 7.03 Nano ZS adapted from Malvern Instruments. The measurements were conducted with different pH adjusted with 0.1 M KCl and 0.1 M HCl solutions. Pyridine adsorption FTIR-Prior to recording FTIR spectra, the samples were exposed to pyridine for an hour. Pyridine adsorbed samples were heated under vacuum at 150 °C to eliminate the physiosorbed pyridine for 0.5 h.

Characterization results

-FTIR

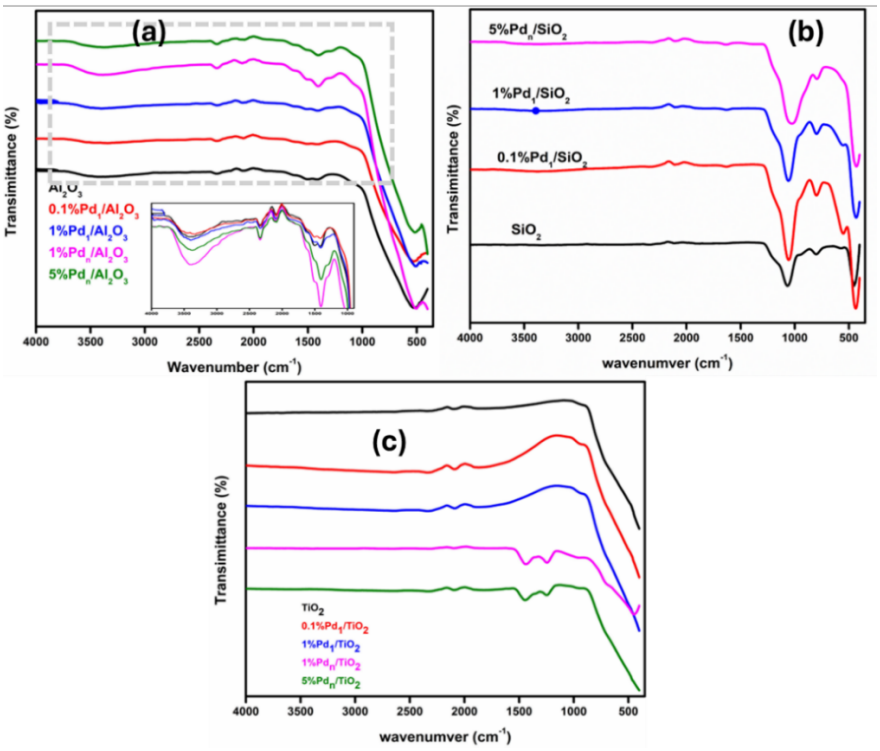

Figure S1: Shows the FTIR spectra of Al_2O_3 with different Pd loading. (a) Al_2O_3, (b) 0.1% Pd_1/Al_2O_3, (c) 1%Pd_1/Al_2O_3, (d) 1% Pd_n/Al_2O_3, and (e) 5% Pd_n/Al_2O_3

-TGA

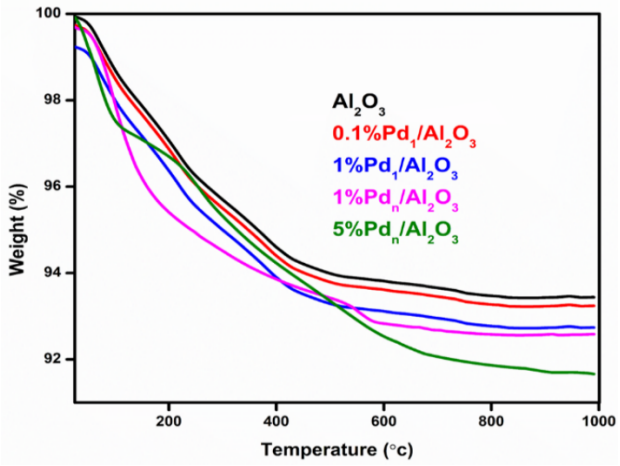

Figure S2. TGA thermograms of the prepared catalysts.

-Nitrogen -Physorption

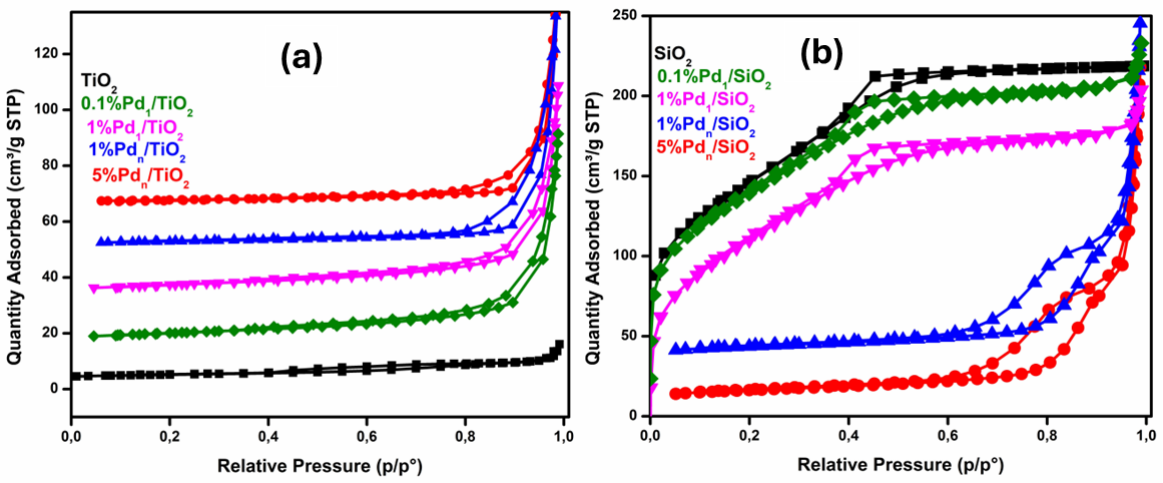

Figure S3: (a&b)- Shows N_2 adsorption-desorption isotherms of Pd-loaded TiO_2 and SiO_2 supports supported Catalysts as the loading size is reduced.

-SEM &EDX

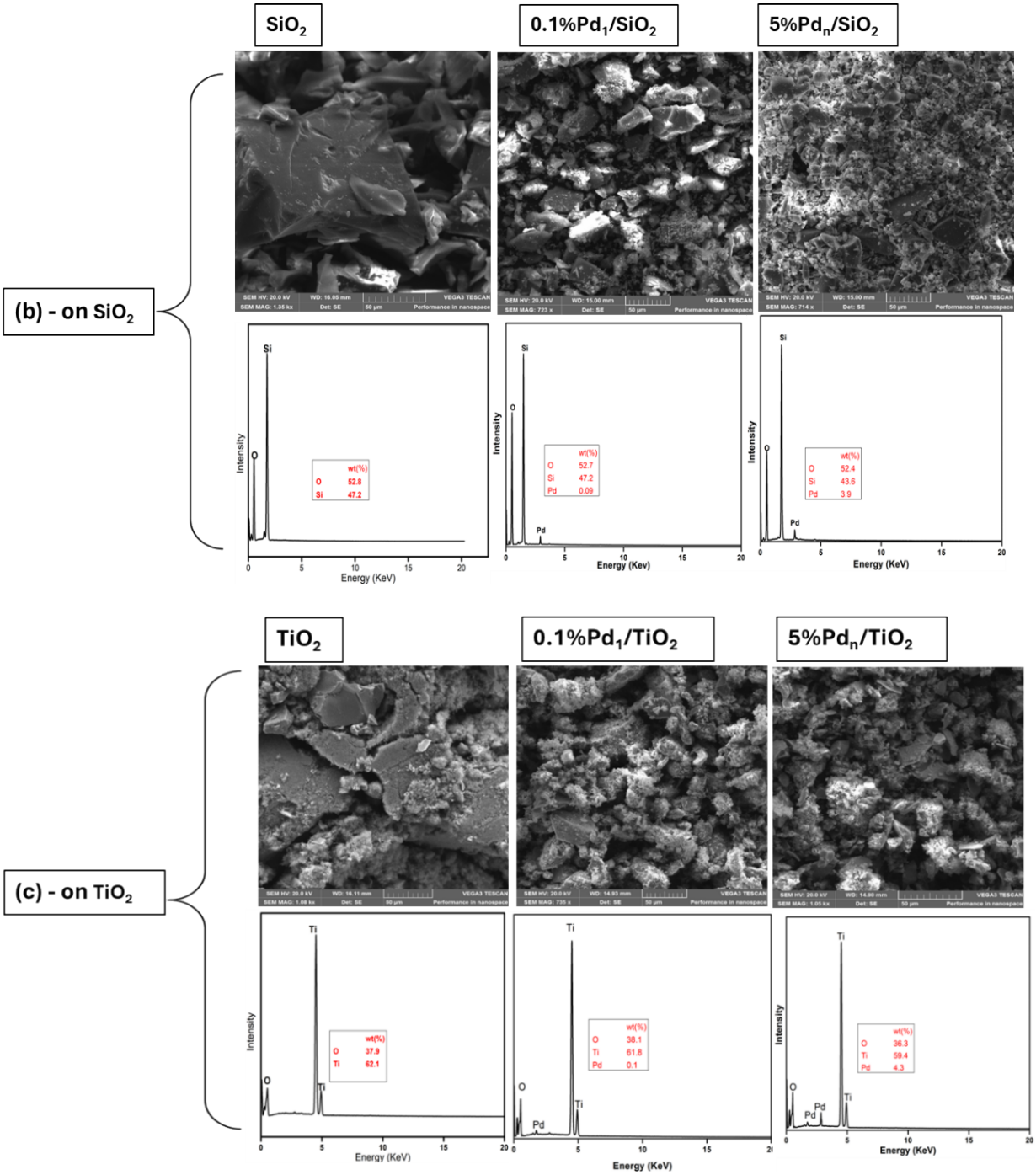

Figure S4: Shows the SEM and EDX for the prepared catalysts, (b) Pd/SiO_2 and (c) Pd/TiO_2.

-HRTEM and Elemental Mapping

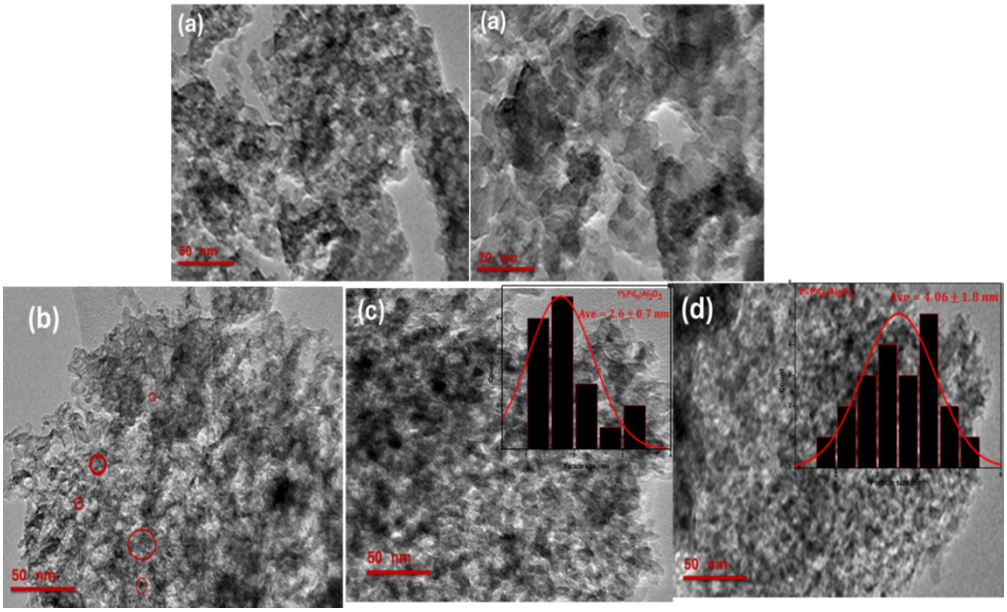

Figure S5: Shows the TEM picture with the size distribution histogram of Pd. (a) 0.1% Pd_1/Al_2O_3 in different magnification, (b) 1% Pd_1/Al_2O_3, (c) 1% Pd_n/Al_2O_3, and (d) 5% Pd_n/Al_2O_3

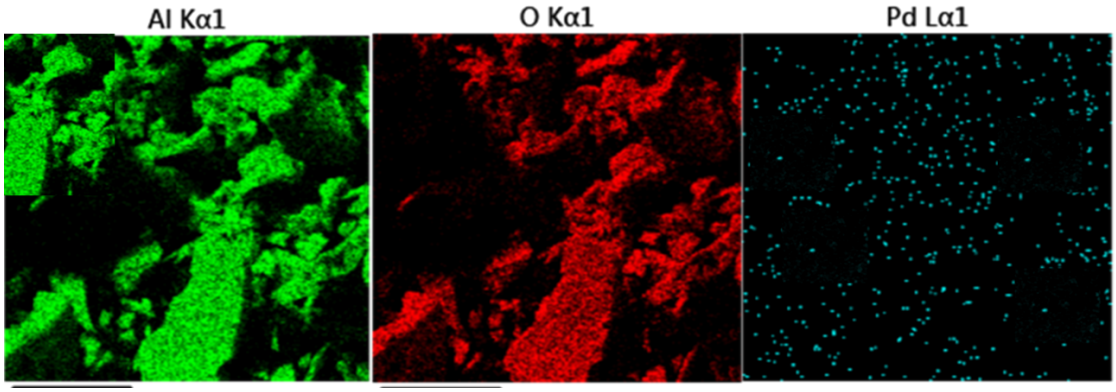

Figure S6: Shows the corresponding elemental mapping distribution of each element for 0.1% Pd_1/ Al_2O_3

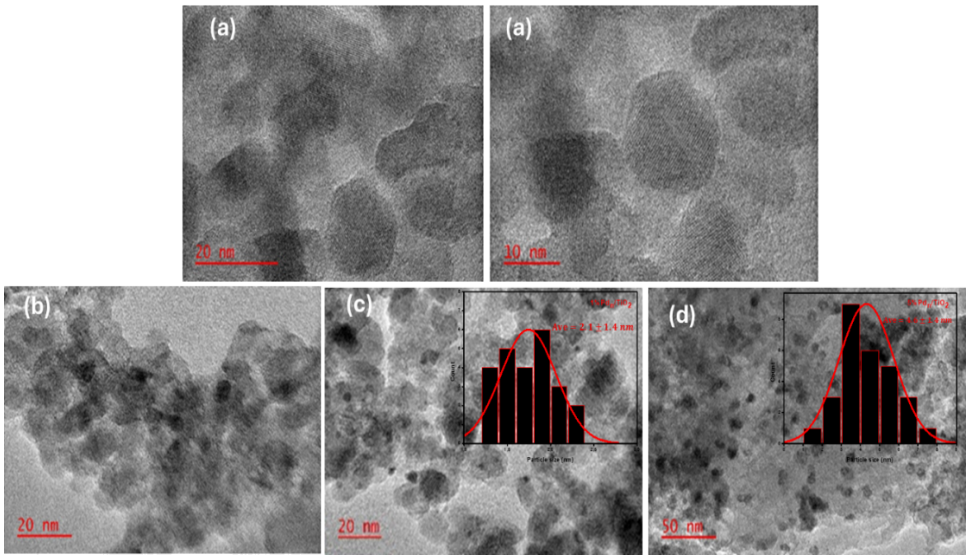

Figure S7: Shows the TEM picture with the size distribution histogram of Pd. (a) 0.1% Pd_1/ TiO_2 on different magnification, (b) 1% Pd_1/ TiO_2, (c) 1% Pd_n/ TiO_2, and (d) 5% Pd_n/ TiO_2

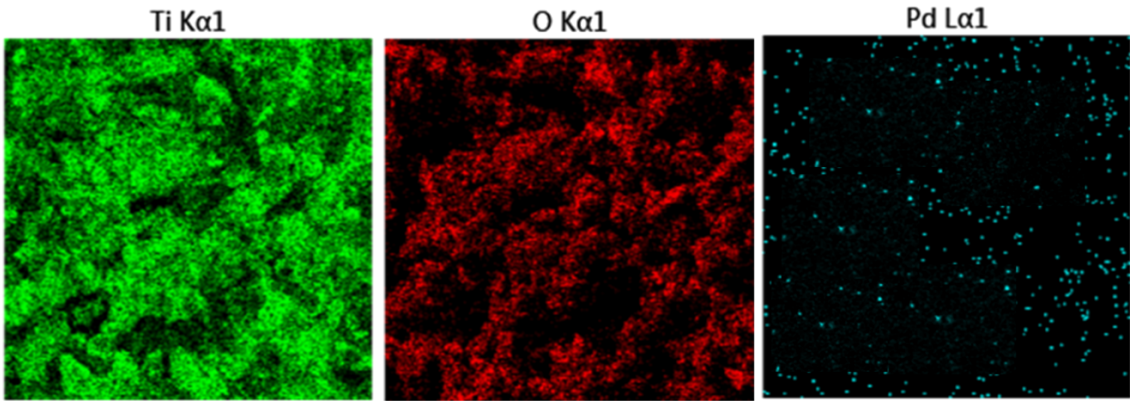

Figure S8: Shows the corresponding elemental mapping distribution of each element for 0.1% Pd_1/ TiO_2

-H-NMR

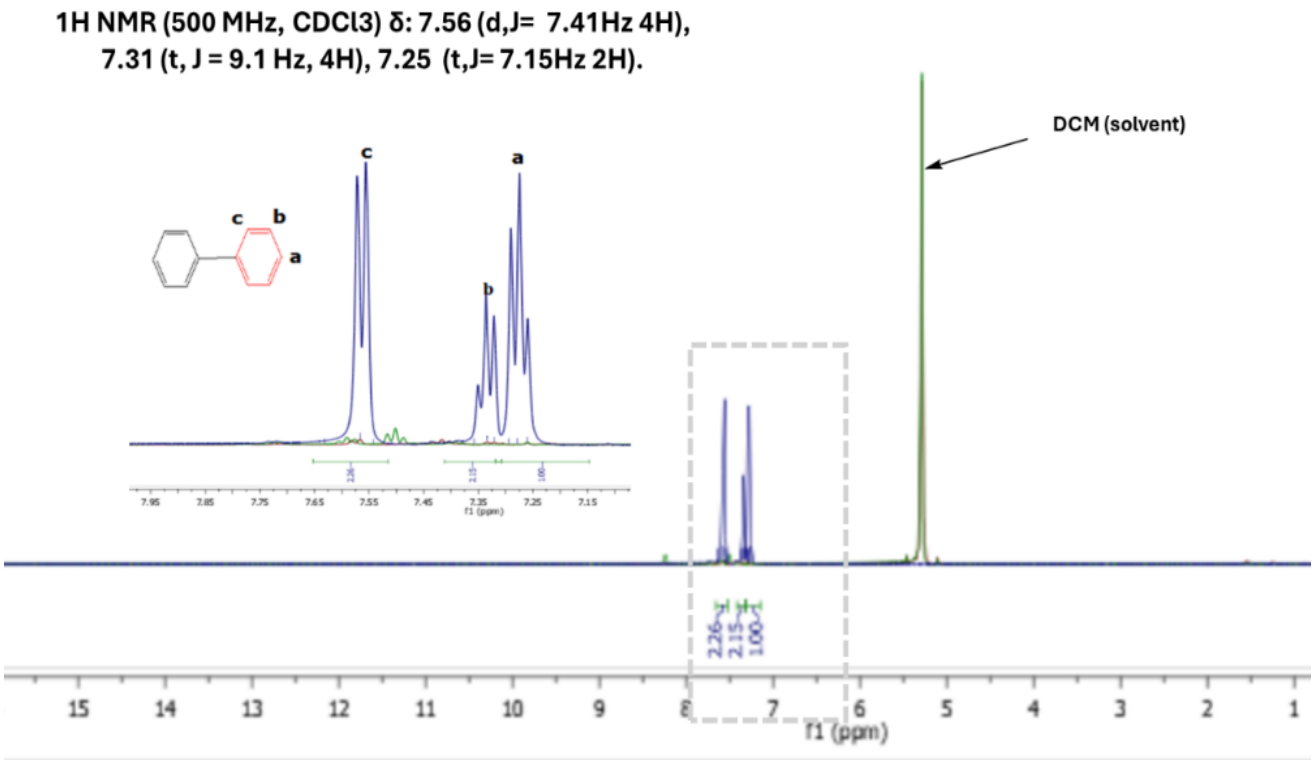

Figure S9: The 1H NMR spectrum of the biphenyl product

References

[1] A.S. Poyraz, C. Kuo, S. Biswas, S.L. Suib, pore size mesoporous materials, (2013) 1–10. https://doi.org/10.1038/ncomms3952.