Electronic Supplementary Information for

A New Hierarchically Porous Pd@HSQ Monolithic Catalyst for Mizoroki-Heck Cross-Coupling Reaction

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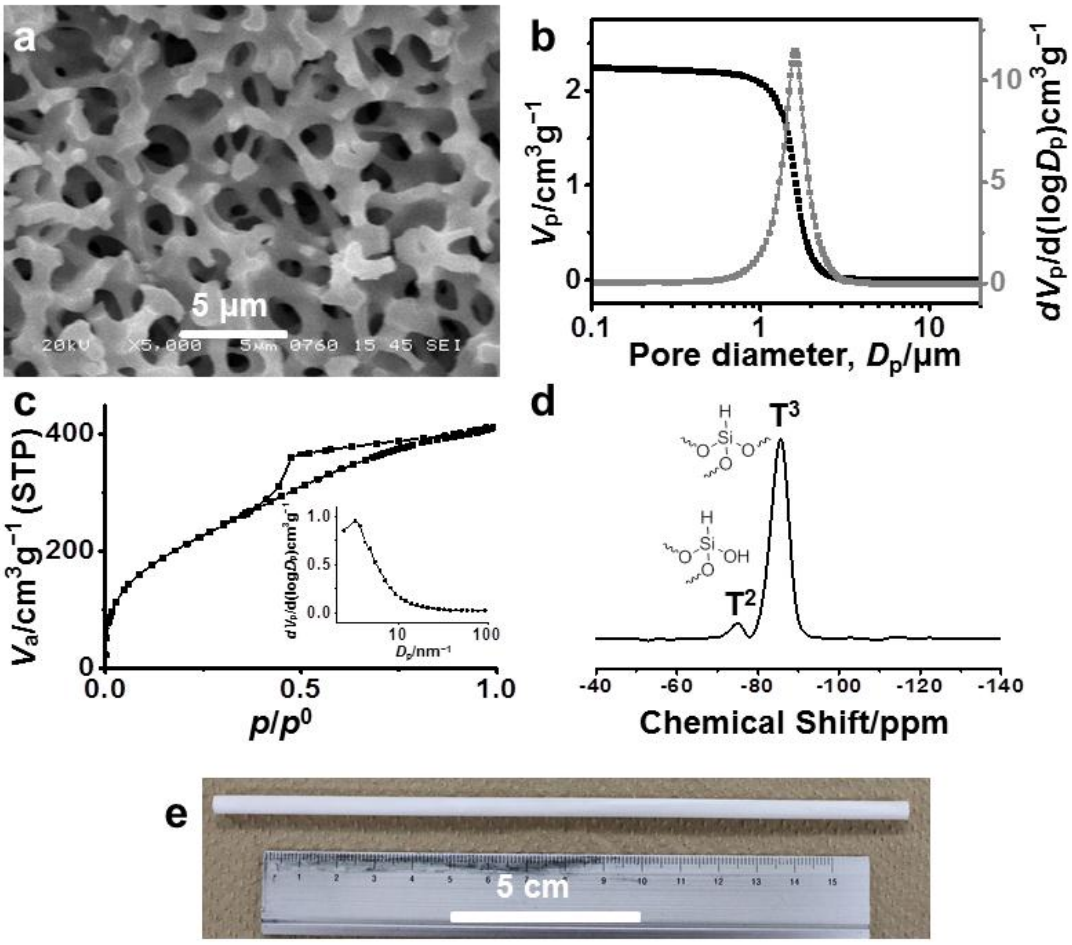


Fig. S1. Characterizations of the HSQ support. (a) SEM image of as-dried HSQ monolith, showing the presence of well-defined co-continuous macroporous structure. (b) Mercury porosimetry result, showing a sharp distribution of macropore size. (c) High specific surface area (800 m^2/g) due to the presence of small meso- and micropores was confirmed by nitrogen adsorption desorption measurement and the BJH pore size distribution curve (inset). (d) Total preservation of highly reactive Si-H bond and high condensation degree was confirmed by ^{29}Si solid-state NMR. (e) Digital camera image of the as-prepared HSQ monolith.

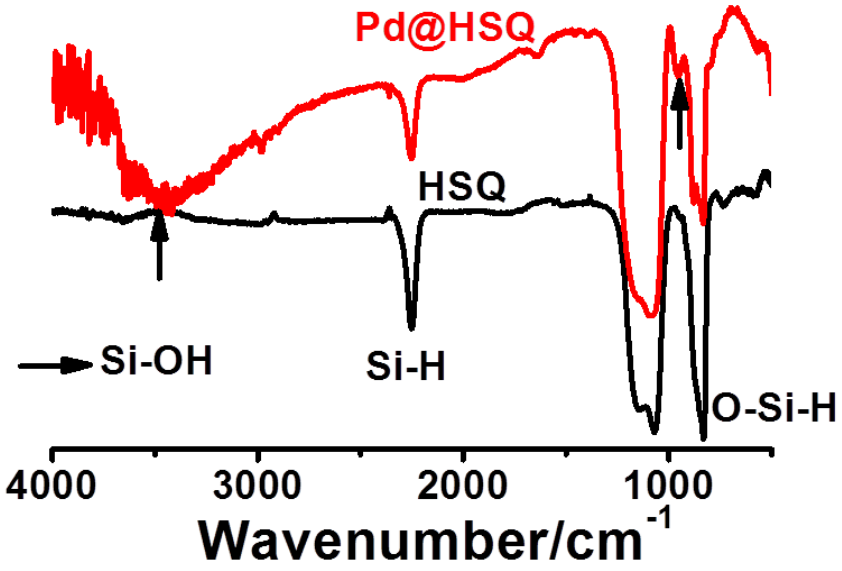


Fig. S2. FT-IR spectra showing the decreased absorption peaks of Si-H and O-Si-H and increased absorption peaks of the Si-OH stretching vibration.

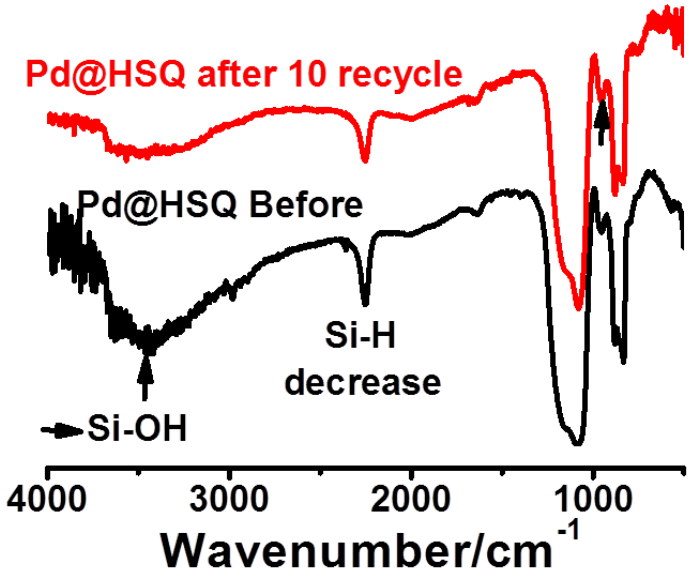
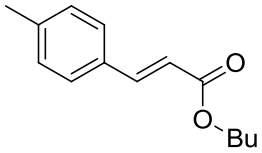


Fig. S3. FT-IR spectra of the Pd@HSQ monolith before and after 10-time reuses. The decrease in absorption by Si-H and O-Si-H stretching vibrations suggests slight decomposition of Si-H in the course of reuse.

^{1}H and ^{13}C NMR of the Products

Entry 4:



^{1}H NMR ($CDCl_3$); δ = 7.66 (d, J = 16 Hz, 1H) , 7.43 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 6.40 (d, J = 16 Hz, 1H), 4.20 (t, J = 6.4 Hz, 2H), 2.37 (s, 3H), 1.64-1.74 (m, 2H), 1.38-1.50 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$); δ= 13.70, 19.24, 21.39, 30.72, 64.27, 117.19, 127.97, 129.53, 131.65, 140.54, 144.50, 167.25.

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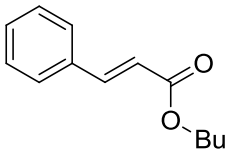
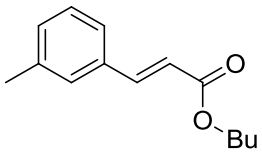


^{1}H NMR ($CDCl_3$); δ = 7.69 (d, J = 16.4 Hz, 1H), 7.50-7.57 (m, 2H), 7.36-7.43 (m, 3H), 6.45 (d, J = 16 Hz, 1H), 4.21 (t, J = 6.4 Hz, 2H), 1.65-1.75 (m, 2H), 1.38-1.50 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$); δ = 13.70, 19.26, 30.72, 64.25, 116.91, 127.94, 128.41, 128.52, 135.19, 144.95, 167.18.

Entry 6:



^{1}H NMR ($CDCl_3$); δ = 7.65 (d, J = 16 Hz, 1H), 7.16-7.38 (m, 4H), 6.43 (d, J = 15.6 Hz, 1H), 4.21 (t, J = 6.8 Hz, 2H), 2.37 (s, 3H), 1.65-1.75 (m, 2H), 1.38-1.50 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$); δ = 13.70, 19.14, 21.24, 30.59, 64.32, 117.96, 125.18, 128.64, 128.68, 130.38, 130.99, 134.34, 138.43, 144.67, 167.12.

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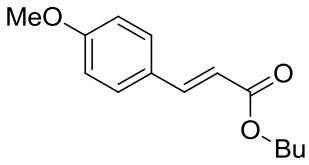
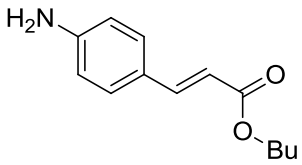


^{1}H NMR ($CDCl_3$); δ = 7.64 (d, J = 16 Hz, 1H), 7.48 (d, J = 7.2 Hz, 2H), 6.91 (d, J = 6.8 Hz, 2H), 6.31 (m, J = 16 Hz, 1H), 4.20 (t, J = 6.8 Hz, 2H), 3.84 (s, 3H), 1.64-1.74 (m, 2H), 1.38-1.50 (m, 2H), 0.97 (t, J = 7.6 Hz, 3H).

^{13}C NMR ($CDCl_3$); δ = 13.70, 19.14, 30.74, 55.27, 64.19, 114.21, 115.65, 127.10, 129.61, 144.14, 161.24, 167.38.

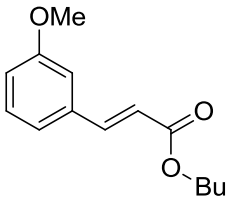
Entry 8:



^{1}H NMR ($CDCl_3$); δ = 7.59 (d, J = 16 Hz, 1H), 7.35 (m, J = 8.8 Hz, 2H), 6.65 (d, J = 8 Hz, 2H), 6.24 (m, J = 15.6 Hz, 1H), 4.18 (t, J = 7.2 Hz, 2H), 3.94 (br, 2H), 1.62-1.72 (m, 2H), 1.38-1.49 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$); δ = 13.65, 19.08, 30.70, 63.99, 113.35, 114.64, 124.34, 129.73, 144.79, 148.74, 167.77.

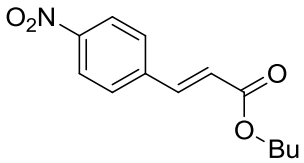
Entry 9:



^{1}H NMR ($CDCl_3$); δ = 7.65 (d, J = 16 Hz, 1H) ,7.30 (t, J = 8.4 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.05 (s, 1H), 6.94 (d, J = 8 Hz, 1H), 6.43 (d, J = 16 Hz, 1H), 4.21 (t, J = 6.8 Hz, 2H), 3.83 (s, 3H), 1.65-1.75 (m, 2H), 1.38-1.50 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$); δ = 13.69, 19.14, 30.69, 55.20, 64.39, 112.77, 116.03, 118.47, 120.69, 129.78, 135.73, 144.41, 159.79, 166.99.

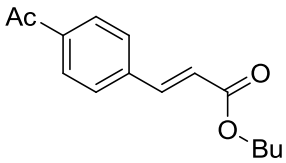
Entry 10:



^{1}H NMR ($CDCl_3$); δ = 8.25 (d, J = 8.8 Hz, 1H), 7.75-7.65 (m, 3H), 6.57 (m, J = 16.4 Hz, 1H), 4.24 (t, J = 6.8 Hz, 2H), 1.65-1.75 (m, 2H), 1.38-1.50 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$); δ = 13.67, 19.10, 30.61, 64.84, 122.52, 124.09, 128.56, 140.53, 141.37, 166.07.

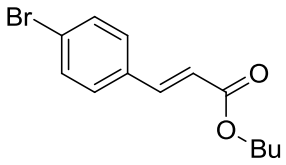
Entry 11:



^{1}H NMR ($CDCl_3$); δ = 7.97 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.4 Hz, 1H), 7.61 (d, J = 8 Hz, 2H), 6.53 (d, J = 16 Hz, 1H), 4.23 (t, J = 6.8 Hz, 2H), 2.61 (s, 2H), 1.65-1.75 (m, 2H), 1.38-1.50 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$); δ = 13.62, 19.05, 26.56, 30.77, 67.53, 120.68, 128.00, 130.31, 137.80, 138.66, 142.83, 166.45, 197.19.

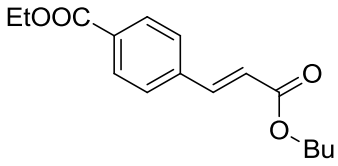
Entry 12:



^{1}H NMR($CDCl_3$); δ = 7.61 (d, J = 16 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 6.43 (m, J = 16 Hz, 1H), 4.21 (t, J = 6.8 Hz, 2H), 1.64-1.74 (m, 2H), 1.37-1.49 (m, 2H), 0.97 (t, J = 7.6 Hz, 3H).

^{13}C NMR ($CDCl_3$); δ = 13.68, 19.11, 30.67, 64.47, 118.90, 119.26, 124.35, 129.34, 132.02, 133.29, 143.05, 166.72.

Entry 13:



^{1}H NMR ($CDCl_3$); δ = 8.06 (d, J = 8 Hz, 1H), 7.70 (d, J = 16 Hz, 1H), 7.58 (d, J = 8 Hz, 1H), 6.52 (m, J = 16 Hz, 1H), 4.39 (d, J = 6.8 Hz, 2H), 4.23 (t, J = 6.8 Hz, 2H), 1.65-1.75 (m, 2H), 1.38-1.50 (m, 5H), 0.97 (t, J = 7.6 Hz, 3H).

^{13}C NMR ($CDCl_3$); δ = 13.57, 14.13, 19.03, 30.57, 61.00, 64.43, 120.42, 127.67, 129.60, 129.87, 131.50, 138.41, 142.98, 166.41.